Institute of Crop Science
University of Hohenheim

Fertilisation and Soil Matter Dynamics

Prof. Dr. Torsten Müller

Removal of organic and inorganic pollutants from aqueous solutions by organically modified clayey sediments

Dissertation
Submitted in fulfillment of the requirements for the degree
“Doktor der Agrarwissenschaften”

(Dr. sc. agr. / Ph.D. in Agricultural Sciences)

to the

Faculty of Agricultural Sciences

Presented by

Dalia Mohamed Fahmy Mubarak

from Egypt

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Table of contents

SUMMARY **1**

ZUSAMMENFASSUNG **4**

1. GENERAL INTRODUCTION **8**

1.1 WATER SCARCITY 8
1.2 SITUATION IN EGYPT 9
1.2.1 Using of non-conventional water resources to overcome water scarcity.... 9
1.2.2 Impact of the reutilization of non-conventional water resources 11
1.3 POLLUTANTS OF INTEREST 13
1.3.1 Priorities of pollutants' selection 13
1.3.2 Inorganic cationic pollutants 13
1.3.2.1 Cadmium 13
1.3.2.2 Lead 14
1.3.3 Inorganic anionic pollutant 14
1.3.3.1 Chromate (VI) 14
1.3.4 Organic pollutants 15
1.3.4.1 Metalaxyl-m 15
1.4 REMEDIATION OF LOW QUALITY WATER 16
1.4.1 General remediation techniques 16
1.4.2 Clay minerals and natural clays as potential adsorbents 17
1.5 DISTRIBUTION OF CLAY SEDIMENTS IN EGYPT 19
1.5.1 Kaolinitic sediments 19
1.5.2 Bentonitic sediments 22
1.6 OBJECTIVES OF THE THESIS 24

2. PREPARATION AND CHARACTERIZATION OF ORGANICALLY MODIFIED CLAYEY SEDIMENTS (OMCS). **27**

2.1 ABSTRACT 27
2.2 INTRODUCTION 28
2.3 MATERIALS AND METHODS 30
2.3.1 Materials 30
2.3.1.1 Clayey sediments 30
2.3.1.2 Organic modifiers 31
2.3.2 Methods 31
2.3.2.1 Preparation of organically modified clayey sediments 31
2.3.2.2 Characterization of natural and organically modified clayey sediments 32
2.3.2.3 Screening experiments with cadmium, lead and dichromate ions 34
2.4 RESULTS 34
2.4.1 Characteristics of natural and organically modified clayey sediments..... 34
2.4.1.1 Mineralogical and chemical characteristics of natural clayey sediments 34

2.4.1.2 Content of organic modifiers in the organically modified clayey sediments (OMCs) 37
2.4.1.3 X-ray diffraction of organically modified clayey sediments compared with the original sediments 39
2.4.1.4 Mid infrared spectroscopy (MIRS) 40
2.4.2 Screening experiments with cadmium, lead and dichromate ions 44
2.5 DISCUSSION 48
2.5.1 Characteristics of natural clayey sediments 48
2.5.2 Characteristics of OMCs 48
2.5.3 Removal of heavy metals by OMCs 51
2.6 CONCLUSIONS 54

3. SORPTION AND DESORPTION OF CADMIUM, LEAD AND DICHROMATE FROM AQUEOUS SOLUTIONS BY ORGANICALLY MODIFIED BENTONITIC SEDIMENTS 55

3.1 ABSTRACT 55
3.2 INTRODUCTION 56
3.3 MATERIALS AND METHODS 59
3.3.1 Synthesis of organically modified bentonitic sediments 59
3.3.2 Sorption and desorption experiments of cadmium, lead and dichromate . 60
3.3.2.1 Sorption isotherm experiments 60
3.3.2.2 Desorption experiments 61
3.3.3 Factors affecting sorption 61
3.3.3.1 Sorption time 61
3.3.3.2 pH of initial solution 62
3.3.3.3 Electrolyte concentration 62
3.3.4 Sorption experiments with combinations of cadmium and dichromate.... 62
3.4 MODELS CALCULATION 63
3.5 RESULTS 66
3.5.1 Speciation of heavy metals 66
3.5.2 Sorption of cadmium, lead and dichromate 67
3.5.3 Desorption experiments 72
3.5.4 Factors affecting sorption 74
3.5.4.1 Sorption time 74
3.5.4.2 pH of the initial solution 77
3.5.4.3 Electrolyte concentration 79
3.5.5 Sorption experiments with combinations of cadmium and dichromate.... 81
3.6 DISCUSSION 84
3.6.1 Sorption and desorption characteristics of cadmium, lead and dichromate 84
3.6.2 Competition effect of cadmium and dichromate sorption 90
3.7 CONCLUSIONS 90

4. **SIMULTANEOUS SORPTION OF ORGANIC AND INORGANIC POLLUTANTS ON ORGANICALLY MODIFIED BENTONITIC SEDIMENTS 92**
4.1 ABSTRACT 92
4.2 INTRODUCTION 93
4.3 MATERIALS AND METHODS 95
4.3.1 The sorbent materials 95
4.3.2 The pollutants tested 95
4.3.3 Screening experiment with metalaxyl-m 96
4.3.4 Sorption isotherm experiment with metalaxyl-m 96
4.3.5 Sorption of metalaxyl-m, cadmium and dichromate from single and ternary component systems 96
4.4 MODELS CALCULATION 97
4.5 RESULTS 98
4.5.1 Screening experiment 98
4.5.2 Sorption isotherms of metalaxyl-m from single component systems 99
4.5.3 Simultaneous sorption of cadmium, chromate and metalaxyl-m from ternary component systems 101
4.6 DISCUSSION 105
4.6.1 Sorption of metalaxyl-m from single component systems 105
4.6.2 Simultaneous sorption of cadmium, chromate and metalaxyl-m from the ternary component systems 107
4.7 CONCLUSIONS 109

5. **GENERAL DISCUSSION AND OUTLOOK 110**
5.1 CHARACTERIZATION OF THE SORBENTS AND SELECTION OF THE PROMISING ORGANICALLY MODIFIED CLAYEY SEDIMENTS (OMCS) 110
5.2 SORPTION CHARACTERISTICS OF THE SELECTED OMCS 112
5.3 REMOVAL OF POLLUTANTS FROM BINARY AND TERNARY COMPONENT SYSTEMS 114

6. **REFERENCES 117**

7. **ACKNOWLEDGEMENTS 134**

8. **CURRICULUM VITAE 136**

9. **ARABIC SUMMARY 1**

List of Tables

Table 1-1 Water supplies and demands in Egypt [10^9 m^3yr^{-1}] (Abdel-Shafy and Aly, 2002) 11
Table 2-1 Organic modifiers used in this study 31
Table 2-2 Mineralogical and chemical characteristics of natural clayey sediments 35
Table 2-3 Total elemental oxides distribution of the natural clayey sediments measured by XRF 37
Table 2-4 Contents of organic modifiers (%) in the OMCs and the loading ratios as percentages of CEC of the natural clayey sediments 38
Table 3-1 Acronyms, type of organic modifier, initial modifier concentration, chemical structure of modifiers, concentration of total organic carbon (TOC) and cation exchange capacity (CEC) of the natural clayey sediment (bent) and the organically modified bentonitic sediments used in the current study 65
Table 3-2 Sorption isotherm parameters and coefficient of determinations (R^2) of Cd^{2+} and Pb^{2+} 70
Table 3-3 Sorption isotherm parameters and coefficient of determinations (R^2) of $Cr_2O_7^{2-}$ .. 71
Table 3-4 Parameters of the pseudo-second-order kinetics models for Cd^{2+}, Pb^{2+} and $Cr_2O_7^{2-}$ 76
Table 3-5 Mean amount of sorbed Cd^{2+} (mmol kg^{-1}) under different electrolytes oncentrations of $Ca(NO_3)_2$ and $NaNO_3$ 80
Table 3-6 Mean amount of sorbed Pb^{2+} (mmol kg^{-1}) under different electrolytes concentrations of $Ca(NO_3)_2$ and $NaNO_3$ 80
Table 3-7 Mean amount of sorbed $Cr_2O_7^{2-}$ (mmol kg^{-1}) under different electrolytes concentrations of $Ca(NO_3)_2$ and $NaNO_3$ 81
Table 4-1 Freundlich equation parameters and coefficients of determination (R^2) for metalaxyl-m sorption 100

List of Figures

Fig. 1-1 Water scarcity in the world 9

Fig. 1-2 Water resources in Egypt 11

Fig. 1-3 Localities of kaolin in peninsula of Sinai 20

Fig. 1-4 Deposits of kaolinite and bentonite of Egypt 21

Fig. 1-5 Distribution of bentonite shale in EL-Fayoum Governorate 23

Fig. 2-1 XRD patterns of natural clayey sediments as powder.. 36

Fig. 2-2 XRD patterns of organically modified bent sediments compared with the natural bent sediment.. 39

Fig. 2-3 MIRS spectra of the clayey sediment collected from Sinai before (kao sediment) and after treatment with different organic modifiers. 42

Fig. 2-4 MIRS spectra of the clayey sediment collected from Qaser el-Sagha before (bent sediment) and after treatment with different organic modifiers.. 43

Fig. 2-5 Sorption of Cd^{2+}, Pb^{2+} and $Cr_2O_7^{2-}$ (mmol kg^{-1}) to the organically modified kao sediments prepared from different concentrations of the added modifiers. 46

Fig. 2-6 Sorption of Cd^{2+}, Pb^{2+} and $Cr_2O_7^{2}$ (mmol kg^{-1}) to the organically modified bent sediments prepared with different concentrations of the added modifiers. 47

Fig. 3-1 Sorption isotherms of Cd^{2+}, Pb^{2+} and $Cr_2O_7^{2-}$ by the natural clayey sediment (Na-bent) and organically modified bentonitic sediment (OMCs). 69

Fig. 3-2 The separation factor (F) versus the initial metal ion concentrations (Ci) for Cd^{2+}, Pb^{2+} and $Cr_2O_7^{2-}$. 71

Fig. 3-3 Two desorption steps (I, II each 24 h) of Cd^{2+} and Pb^{2+} as percentage of the element sorbed to different organically modified bentonitic sediments (OMCs) by using 0.1 M HCl, H_2O and 0.1 M NaOH as desorbing agents. 73

Fig. 3-4 Two desorption steps (I, II each 24 h) of $Cr_2O_7^{2-}$as percentage of the element sorbed to the natural clayey sediment modified with Cys_ester by using 0.1 M HCl, H_2O and 0.1 M NaOH as desorbing agents. 74

Fig. 3-5 Time course (t) of sorption of Cd^{2+} and Pb^{2+} by organically modified bentonitic sediments (OMCs). 75

Fig. 3-6 Time course of the sorption of $Cr_2O_7^{2-}$ by the organically modified bentonitic sediments (OMCs). 76

Fig. 3-7 Effect of initial solution pH on Cd^{2+}, Pb^{2+} and $Cr_2O_7^{2-}$ sorption by the natural clayey sediment (Na-bent) and the organically modified bentonitic sediments (OMCs). 78

Fig. 3-8 Sorption of Cd^{2+} alone and in combination with $Cr_2O_7^{2-}$ by natural clayey sediment and selected organically modified bentonitic sediments from aqueous solutions. 82

Fig. 3-9 Sorption of $Cr_2O_7^{2-}$ alone and in combination with Cd^{2+} by natural clayey sediment and selected organically modified bentonitic sediments from aqueous solutions. 83

Fig. 4-1 Chemical structure of the organic modifiers and metalaxyl-m (fungicide). 97

Fig. 4-2 Sorption of metalaxyl-m (MM) on natural clayey sediment and organically modified bentonitic sediments. 98

Fig. 4-3 Sorption isotherms of metalaxyl-m (MM) on natural clayey sediment and organically modified bentonitic sediments from single component systems.... 100
Fig. 4-4 Sorption of Cd^{2+} alone and in combination with metalaxyl-m and $Cr_2O_7^{2-}$ by the natural clayey sediment and organically modified bentonitic sediments (OMCs). . 102
Fig. 4-5 Sorption of $Cr_2O_7^{2-}$ alone and in combination with metalaxyl-m and Cd^{2+} by the natural clayey sediment and organically modified bentonitic sediments 103
Fig. 4-6 Sorption of metalaxyl-m alone and in presence of Cd^{2+} and $Cr_2O_7^{2-}$ on natural clayey sediment and organically modified bentonitic sediments (OMCs) 104

List of Abbreviation

AAS:	atomic absorption spectroscopy
bent sediment:	clayey sediment collected from Qaser el-Sagha, El Fayoum, Egypt
Carnitin:	L-Carnitine
Carnitin-bent:	bent sediment modified with Carnitin
Carnitin-kao:	kao sediment modified with Carnitin
Cd^{2+}:	cadmium
Ce:	the end concentration of the pollutant in the solution
CEC	cation exchange capacity
Ci:	the initial concentration of the pollutant in the solution
$Cr_2O_7^{2-}$:	dichromate
Cs:	sorbed amount of the pollutant per unit mass
Cys_ester:	L Cystine dimethyl ester
Cys_ester-bent:	bent sediment modified with Cys_ester
Cys_ester-kao:	kao sediment modified with Cys_ester
F:	separation factor
HA:	Humic acid
HA-bent:	bent sediment modified with HA
HDTM:	Hexadecyltrimethylammonium
HDTM-bent:	bent sediment modified with HDTM
HDTM-kao :	kao sediment modified with HDTM
IC:	inorganic carbon content (%)
K and b:	parameters of Langmuir equation
kao sediment :	clayey sediment collected from Sinai, Egypt
Kf and 1/n:	parameters of Freundlich equation
mg kg^{-1}:	milligram sorbate per kilogram sorbent
mg l^{-1}:	milligram per liter
MIRS:	mid infrared spectroscopy
mM:	millimol per liter
MM:	Fungicide metalaxyl-m

mmol kg^{-1}:	millimoles sorbate per kilogram sorbent
MTP	Methyltriphenyl-phosphonium
MTP-bent	bent sediment modified with MTP
MTP-kao	kao sediment modified with MTP
Na-bent	sodium form of bent sediment
Na-clay	sodium exchanged clayey sediment
OC:	organic carbon content of the natural clayey sediments(%)
OMCs	organically modified clayey sediments
Pb^{2+}:	lead
qe and qt	amounts of the metal ions sorbed at equilibrium and at time (t),respectively
R^2:	coefficient of determination
t	Time course
TC	total carbon content (%)
TOC	total organic carbon (%)
XRD	X-ray diffraction
XRF	X-ray fluorescence

Summary

Re-use of agricultural drainage water and industrial wastewater is one of the adopted strategies in different countries to close the gap between water resources and water demands. Drainage and industrial wastewater contain varieties of toxic pollutants that can potentially cause hazard on humans and environment. Although adsorption techniques are considered one of the proper methods for the wastewater treatments, economic aspect is a crucial factor for the broad application of such technique.

Addressing this, the thesis concerns on proposing sorbents having the potential to remove heterogeneous pollutants simultaneously, particularly taken in consideration the limited resources in developing and emerging countries, in this study exemplified for Egypt. For this purpose, natural clayey sediments as cheap and environmentally friendly materials were used in combination with various organic modifiers to produce of organically modified clayey sediments (OMCs). In contrast to the natural clayey sediments, OMCs are expected to have the ability to remove heterogeneous pollutants including anionic and cationic as well as organic and inorganic pollutants. The sorbability and desorbability characteristics of OMCs were investigated for Cd^{2+} and Pb^{2+} (cationic-), $Cr_2O_7^{2-}$ (anionic-) and metalaxyl-m (MM; organic-pollutants).

The basic clay materials in OMCs were naturally occurring kaolinitic (kao sediment) and bentonitic (bent sediment) clayey sediments distributed widely in Egypt. Different concentrations of the organic modifiers L-Carnitine (Carnitin), L-Cystine dimethyl ester (Cys_ester), Methyltriphenyl-phosphonium (MTP) or Hexadecyltrimethyl-ammonium (HDTM) were employed. The modification of natural clayey sediments with organic modifiers increased the organic carbon contents of OMCs following the order Carnitin < Cys_ester < MTP < HDTM. OMCs based on bent sediments had a higher loading of the organic modifiers than those based on kao sediments and the loading increased with increasing the used concentrations of the organic modifiers. To characterize and confirm the modification of OMCs, the prepared materials were analyzed by mid infrared spectroscopy (MIRS). The obtained spectra showed shifting of the vibration bands of the natural clayey sediments, and depicted the characteristic vibrations bands of the organic modifiers, indicating the interaction between the natural clayey sediments with the organic modifiers and the

successful loading. Further analysis by X-ray diffraction showed that the modification of OMCs based bent sediments with MTP or HDTM caused an expansion of the interlayer spacing of the clay from 14.5 Å to 17.1 or 19.7 Å, respectively; reflecting a bilayer or pseudo-trimolecular arrangements of MTP or HDTM, respectively, in the clays interlayer. The loading ratios of the organic modifiers on OMCs as a percentage of the CEC of the natural clayey sediments were also calculated.

Following the characterization of OMCs, screening experiments were conducted to select the suitable concentration of each organic modifier to be loaded in order to achieve the highest removal of heavy metals. The results showed that loading of OMCs based on kao sediments by HDTM and Carnitin at concentrations equal to or higher than 71and 8 % of the CEC of the natural kao sediment, respectively, caused no relevant differences in the sorption of Cd^{2+} and Pb^{2+} compared to natural kao sediment. However, the loading of Cys_ester and MTP at concentrations equal to 38 and 21 % of the CEC or higher increased the sorption of those metal ions. Remarkable enhancements in the sorption of $Cr_2O_7^{2-}$ were obtained by the modification of OMCs based kao sediments with HDTM and Cys_ester. The outcome from these screening experiments with OMCs based bent sediments can be concluded as follow: HDTM and MTP at loading concentrations > 50 % of the CEC of the natural bent sediments were able to remove all Cd^{2+} and Pb^{2+} from the solutions. However, increasing the loading concentration of Cys_ester decreased the sorption of those metal ions as compared to natural bent sediment. OMC modified with Carnitin at loading concentration up to 21 % of the CEC was able to remove 84 % of Cd^{2+} and 100 % of Pb^{2+} from the solutions but a further increase of Carnitin loading decreased the sorption of the metal ions. The OMCs modified with HDTM and Cys_ester were very efficient in removing $Cr_2O_7^{2-}$ from the solutions and the removal increased with increasing loading concentrations of the organic modifiers.

The OMCs based on bent sediments loaded with HDTM, MTP, Carnitin and Cys_ester at loading concentrations equal to 102, 79, 18 and 66 % of CEC of the natural bent sediments, respectively, and in addition OMC loaded with Humic acid (HA), were selected as promising sorbents to test the sorbability and desorbability of OMCs with respect to the pollutants. The sorption processes were investigated as function of the metal concentration, sorption time, the initial solution pH and the electrolyte concentration. OMCs modified with HDTM, MTP, HA and Carnitin showed high sorbability for Cd^{2+} and Pb^{2+}. However, OMCs modified with Cys_ester displayed the best sorbent for $Cr_2O_7^{2-}$. OMCs were successful to remove almost all Cd^{2+}, Pb^{2+} from the solutions at wide ranges of pH; 4-8 and 4-6, respectively, while the optimum for the sorption of $Cr_2O_7^{2-}$ was pH 4. The Langmuir model described adequately the observed sorption data of Cd^{2+} and Pb^{2+} on all sorbents and $Cr_2O_7^{2-}$ on OMC modified with Cys_ester better than the Freundlich model. The sorption followed the pseudo second order kinetics with the rate constants demonstrating faster sorption on OMCs with Carnitin and HA for Cd^{2+} and Pb^{2+} and faster sorption on OMCs with MTP and Cys_ester for $Cr_2O_7^{2-}$. Sorption of Cd^{2+} and Pb^{2+}, particularly on OMCs with Carnitin and HA, were decreased with increasing electrolyte concentrations. Whereas, increasing the electrolyte concentrations enhanced the sorption of $Cr_2O_7^{2-}$ to OMC with Cys_ester. OMCs showed ability to release the sorbed heavy metals, which shows the potential for re-using.

The presence of other solutes in the binary and ternary component systems strengthened the sorption of $Cr_2O_7^{2-}$ on OMCs based bent sediments with HDTM and MTP and enhanced the sorption of MM on OMCs with Cys_ester and MTP. Competition phenomena were recorded for the sorption of Cd^{2+} and MM on OMC with HDTM. No competition behaviours were observed in the sorption of the tested pollutants on OMC with Cys_ester. OMCs with HDTM, MTP and Cys_ester were able to remove Cd^{2+}, $Cr_2O_7^{2-}$ and MM simultaneously from the binary and ternary component systems. The results indicate the prospective application of the OMCs in the treatments of natural agricultural drainage water and industrial wastewater.

Zusammenfassung

In verschiedenen Ländern ist die Nutzung landwirtschaftlichen Dränagewassers und industriellem Abwasser eine etablierte Methode um die Diskrepanz zwischen Wasserressourcen und -verbrauch zu überbrücken. Diese Wasserquellen enthalten eine Vielzahl toxischer Schadstoffe die die menschliche Gesundheit sowie die Umwelt beeinträchtigen können. Auch wenn Sorptionsverfahren als für die Aufbereitung dieser Wasserquellen geeignet betrachtet werden, ist der ökonomische Faktor ausschlaggebend für den Einsatz dieser Verfahren. Die vorgelegte Arbeit beschreibt, unter Berücksichtigung der begrenzten Ressourcen in Entwicklungs- und Schwellenländern, Sorptionsmittel, die die Fähigkeit aufweisen verschiedene Schadstoffe gleichzeitig dem Wasser zu entziehen.

Zur Herstellung der Sorptionsmittel wurden natürliche tonige Sedimente, als kostengünstige und umweltfreundliche Materialien, in Kombination mit verschiedenen organischen Modifikatoren verwendet um "organisch modifizierte tonige Sedimente" (organically modified clayey sediments: OMCs) zu erzeugen.

Im Vergleich zu natürlichen tonigen Sedimenten sollen OMCs die Eigenschaft aufweisen verschiedenartige organische Schadstoffe, einschließlich anionischer, kationischer, organischer und anorganischer Schadstoffe zu sorbieren. Die Sorptions- und Desorptionseigenschaften der OMCs wurden für Cd^{2+}, Pb^{2+} (kationisch-), $Cr_2O_7^{2-}$ (anionisch) and Metalaxyl--m (MM; organisch) untersucht.

Die tonigen Sedimente, die zur Herstellung der OMCs verwendet wurden, sind in Ägypten natürlich vorkommende kaolinitische (kao sediment) und bentonitische (bent sediment) tonige Sedimente. Verschiedene Konzentrationen der organischen Modifikatoren L-Carnitine (Carnitin), L-Cystine dimethyl ester (Cys_ester), Methyltriphenyl-phosphonium (MTP) oder Hexadecyltrimethyl-ammonium (HDTM) wurden verwendet. Die organische Modifikation der natürlichen tonigen Sedimente führte zu einem ansteigendem Gehalt an organischem Kohlenstoff, der folgenden Reihenfolge entsprechend: Carnitin < Cys_ester < MTP < HDTM.

Die auf bentonitischen Sedimenten basierenden OMCS wiesen höhere Gehalte an organischem Kohlenstoff auf als die auf kaolinitischen Sedimenten basierenden

OMCs. Ebenso stiegen die Gehalte an organischem Kohlenstoff mit steigenden Konzentrationen der organischen Modifikatoren.

Zur Charakterisierung und Bestätigung der Modifikation der OMCs wurden die Proben mittels Mittlerer Infrarot Spektroskopy (MIRS) untersucht. Die Spektralanalyse zeigte eine Verschiebung der der Schwingungsspektren natürlicher toniger Sedimente, und wies charakteristische Schwingungsspektren der organischen Modifikatoren auf. Dies weist auf eine Interaktion zwischen den natürlichen tonigen Sedimenten und den organischen Modifikatoren, sowie auf eine erfolgreiche Beladung der tonigen Sedimente hin. Die Analyse mittles Röntgendiffraktion zeigte dass die Modifikation bentonitischer Sedimente mit MTP oder HDTM den Abstand der Tonzwischenschichten von 14.5 Å auf 17.1, bzw. 19.7 Å vergrößerte; dies deutet auf eine Doppelschicht, bzw. Pseudo-trimolekulare Anordnung von MTP, bzw. HDTM in den Tonzwischenschichten hin. Des weiteren wurden die Beladungskonzentrationen der organischen Modifikatoren als Prozentanteil der Kationen Austausch Kapazität der natürlichen tonigen Sedimente berechnet.

Im Anschluss an die Charakterisierung der OMCs wurden Screening-Experimente durchgeführt um die geignete Konzentration der einzelnen organischen Modifikatoren mit Hinblick auf die Entfernung von Schwermetallen auszuwählen. Die Ergebnisse zeigen dass, im Vergleich zu natürlichen kaolinitischen Sedimenten, die Beladung von auf kaolinitischen Sedimenten basierenden OMCs mit HDTM und Carnitin in Konzentrationen größer gleich 71 % und 8 % der natürlichen KAK der kaolinitischen Sedimente keine Unterschiede in der Sorption von Cd^{2+} und Pb^{2+} bewirkte. Allerdings bewirkte die Beladung mit Cys_ester und MTP mit Konzentrationen größer gleich 38 und 21 % der KAK eine erhöhte Sorption dieser Schwermetalle. Eine beachtlich erhöhte Sorption von $Cr_2O_7^{2-}$ wurde durch die Modifikation der af kaolinitischen Sedimenten basierenden OMCs mit HDTM und Cys_ester beobachtet. Das Ergebnis der Screening-Experimente mit auf bentonitischen Sedimenten basierenden OMCs kann wie folgt zusammengefasst werden: Bei Konzentrationen > 50 % der KAK natürlicher bentonitischer Sedimente bewirkten HDTM und MTP die vollständige Entfernung von Cd^{2+} and Pb^{2+} aus der Lösung; allerdings führte eine erhöhte Beladung mit Cys_ester zu einer verringerten Sorption dieser Schwermetalle, verglichen mit natürlichen bentonitischen Sedimenten. OMC, welches mit einer

Konzentration von bis zu 21 % Carnitin modifiziert wurde, entfernte 84 % des Cd^{2+} und 100 % des Pb^{2+} aus der Lösung, allerdings führte die weitere Erhöhung der Carnitin-Konzentration zu einer verringerten Sorption der Metalle. OMCs die mit HDTM und Cys_ester modifiziert wurden entfernten effektiv $Cr_2O_7^{2-}$ aus der Lösung, und die Sorptionsrate nahm mit steigender Konzentration der Modifikatoren zu.

Auf bentonitischen Sedimenten basierende OMCs, die mit HDTM-, MTP-, Carnitin- und Cys_esterkonzentrationen gleich jeweils 102, 79, 18 and 66 % der KAK natürlicher bentonitischer Sedimente beladen waren, sowie mit Huminsäure (HA) beladenes OMC, wurden als geignete Sorbenten ausgewählt um die Sorption und Desorption von Schadstoffen zu untersuchen. Die Sorptionsprozesse wurden als Funktion der Metallkonzentration, der Sorptionszeit, des Ausgangs-pH der Lösung sowie der Elektrolyt-konzentration untersucht. OMCs die mit HDTM, MTP, HA und Carnitin modifiziert wurden, wiesen eine hohe Sorption von Cd^{2+} and Pb^{2+} auf. Jedoch zeigte mit Cys_ester modifiziertes OMC die höchste Sorption von $Cr_2O_7^{2-}$. OMCs entfernten Cd^{2+} und Pb^{2+} fast vollständig von Lösungen mit einem pH-Bereich von 4-8, bzw. 4-6. Das Sorptionsmaxima von $Cr_2O_7^{2-}$ lag bei pH 4. Das Langmuir-Model eignete sich besser als das Freundlich-Model zur Beschreibung der Sorptionsrate aller Sorbenten für Cd^{2+} und $Pb^{2+,}$ sowie für die Sorption von $Cr_2O_7^{2-}$ durch mit Cys_ester modifiziertes OMC. Die Sorption folgte einer Kinetik pseudo-zweiter Ordnung; die Absorptionskonstanten weisen auf eine schnellere Sorption von Cd^{2+} und Pb^{2+} durch OMCs mit Carnitin und HA, sowie auf eine schnellere Sorption von $Cr_2O_7^{2-}$ durch OMCs mit MTP und Cys_ester hin. Die Sorption von Cd^{2+} und Pb^{2+} wurde durch höhere Elektrolyt-Konzentrationen beeinträchtigt, insbesondere für OMC mit Carnitin und HA, während eine eine Erhöhung der Elektrolyt-Konzentration zu einer erhöhten Sorption von $Cr_2O_7^{2-}$ durch OMC mit Cys_ester führte. Des weiteren können OMCs die sorbierten Schwermetalle desorbieren, wodurch die Wiedervertbarkeit der Materialen möglich wird.

Die Präsenz anderer gelöster Stoffe in Systemen mit zwei oder drei Komponenten verstärkt die Sorption von $Cr_2O_7^{2-}$ durch mit HDTM und MTP modifizierten OMCs die auf bentonitischen Sedimenten basieren, und führt zu einer größeren Sorption von MM durch mit Cys_ester und MTP modifizierten OMCs. Es wurde eine Konkurrenz für die Sorption von Cd^{2+} and MM durch OMC mit HDTM beobachtet, allerdings wurde keine Konkurrenz zwischen den untersuchten Schadstoffen für mit Cys_ester modifizierten OMCs beobachtet. Mit HDTM, MTP und Cys_ester modifzierte OMCs konnten simulatan Cd^{2+}, $Cr_2O_7^{2-}$ und MM von den Systemen mit zwei und drei Komponenten sorbieren.

Die Ergebnisse deuten auf die Möglichkeit eines erfolgreichen Einsatzes organisch modifizierter toniger Sedimente für die Aufbereitung landwirtschaftlichen Dränagewassers, sowie industrieller Abwassers hin.

1. General Introduction

1.1 Water scarcity

Water scarcity is one of the global challenges accompanied with the climatic changes. Middle Europe as example for countries haveing sufficient water resources is also exposed to water scarcity and drought, where the situation is expected to worsen with increasing temperature due to climatic changes (Anonymous[1], 2007). Furthermore, escalating water demand as result of growing population and urbanization is aggravating the global water scarce. There are two types of water scarcity: economic scarcity with unequal distribution of water supplies beside the lower economy that limit utilization of some water resources. Most of sub-Saharan Africa is an example for a region associated with this type of scarcity (Fig. 1-1). The second type is physical scarcity by which the water resources are limited to meet the increasing water demand. Dried and arid regions such as Mediterranean countries are most affected by the physical scarcity (Anonymous[2], 2006). According to the World Health Organization (WHO, 2009), 1.2 billion people counted as one fifth of the world's population are living under physical water scarce.

The agricultural sector is consuming 50 -80 % of the available water supply in the northern and the southern of Mediterranean countries, respectively (Hamdy and Monti, 2005). In the past, irrigated agriculture generally played an important role in improvement the rural economies and helped against poverty alleviation; however, with growing population in arid and semiarid areas as in the Near East and North Africa, as well as in Mexico, Pakistan, South Africa, China and India the increase of irrigated agriculture lead to the aggravation of water scarcity. Meanwhile, agriculture is the first activity suffering from the problem of water deficiency that ultimately affects food security and obstructs poverty reduction (FAO, 2007a). Therefore, the situation of global water shortage calls for efficient management of water resources by finding different approaches for the efficient utilization of available ground and surface water supplies, and, in addition, developing technologies that help for providing other non-conventional water resources such as desalination and wastewater treatment techniques (Drever, 2011; Oelkers et al., 2011).

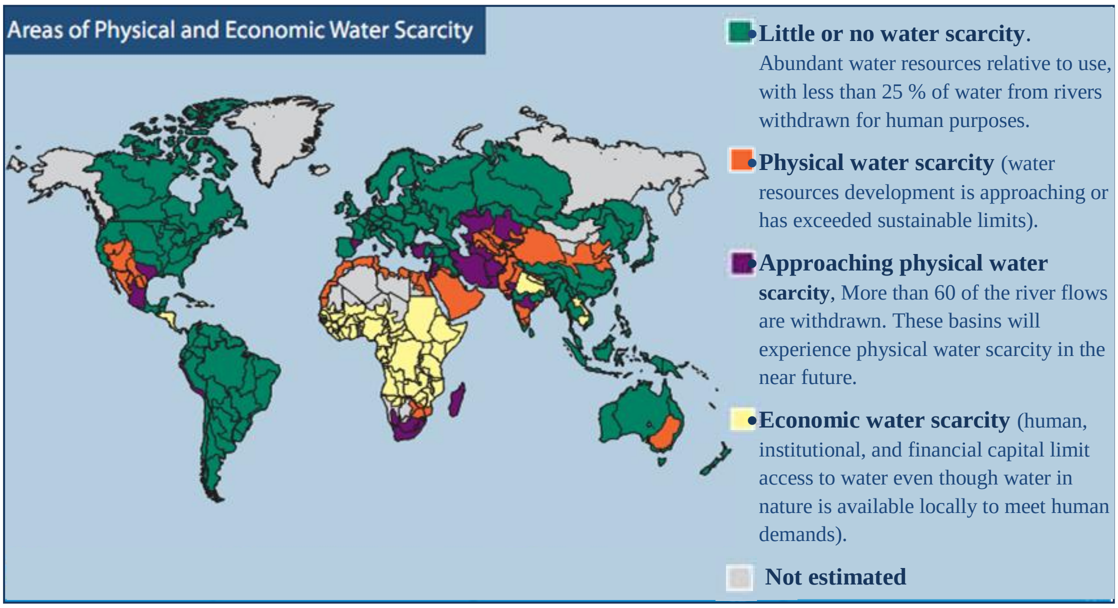


Fig. 1-1 Water scarcity in the world (FAO, 2007b)

1.2 Situation in Egypt

1.2.1 Using of non-conventional water resources to overcome water scarcity

Egypt is one of the southern Mediterranean countries under hyper-arid and arid climatic regional conditions (Hussein, 2008). Precipitation is scarce and occurs as scattered showers along a narrow band of the Mediterranean coasts in the winter season and sometime as sparse floods in Sinai Peninsula and in South Egypt. Most of the fresh water resources is obtained from Nile River by fixed amounts of 55.5 billion cubic meter (BCM) as well as from groundwater including renewable and non-renewable aquifers (Fig 1-2; Biswas et al. , 2008; Alnaggar, 2003). Almost 78 % of the water supplies are allocated to agricultural activity. The water share per capita is lower than 1000 CM /year which is equal to the international “water poverty limit” and more decline is expected (500 CM/capita/ year) in 2025 (Assaf et al., 2004). In general, the total water needs for different sectors are 75 BCM/year which are expected to increase by 20 % in 2020 (MWRI, 2010).

Growing population is the great challenge facing any improvement in the country reaching 79 million at 2007 with a growth rate of 1.9 %. Population is expected to be 120-150 million in 2050 (MWRI, 2010). Therefore the government is forced to intensify the horizontal and vertical agricultural production to feed the growing population, thus consequently the water demand increased. In addition, contamination of surface and ground water is worsening the situation.

To cope with the limitation of water resources, planners are imposed to consider any economically feasible and useful source of water which might be able to promote further development. In this situation of water scarcity, recycling of drainage water as well as wastewater and desalination of salty water have high importance in the adopted national water resource plan. However, desalination of salty water is constrained and produced only for drinking purpose in some areas due to economic aspects. The use of drainage water is done through public stations that push drainage water to the irrigation canals and through illegal use by the farmer at the tail ends of irrigation canals when they have shortage in irrigation water (Abdel-Shafy and Aly, 2002). Reuse of drainage water has been implemented in Nile Delta area via pushing it directly or after mixing it with the fresh water in the irrigation canals. El-Salam canal, one of the largest irrigation projects, is fed with Nile water mixed with agricultural drainage water to irrigate large areas in northern Sinai, Sahl El-Tina and the surroundings till El-Arish (Abdel-Shafy and Aly, 2002). In addition, about 1.0 BCM of primary treated domestic wastewater have been already used as irrigation water in outside Greater Cairo area (Assaf et al., 2004; Abdel-Azim and Allam, 2004). As implementation of the national plan, further increase in utilization of drainage and wastewater in the future is intended (Table 1-1). On the other hand, deterioration of water quality and charging drainage canal by pollutants due to extravagant use of agrochemicals (fertilizer and pesticides), moreover the seepage of untreated municipal and wastewater into the water bodies are threatening the water safety utilization (Elassiouti and Khalifa, 2009). In this sense removing pollutants from these water bodies before the utilization is an essential task.

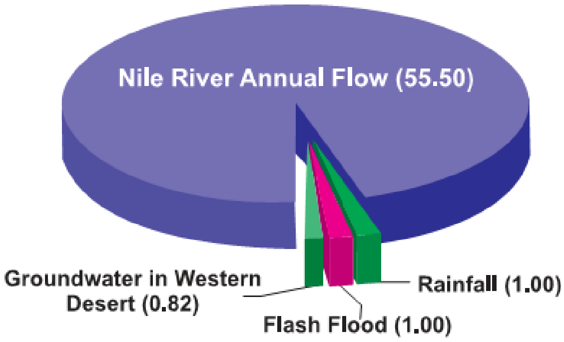


Fig. 1-2 Water resources in Egypt (ICID 2005)

Table 1-1 Water supplies and demands in Egypt [10^9 m^3yr^{-1}] (Abdel-Shafy and Aly, 2002)

I. Water supplies	**1990**	**2000**	**2025**
Nile water	55.5	57.5*	55.5
Groundwater:			
In the Delta and New Valley	2.6	5.1	6.3
In the desert	0.5		
Reuse of agricultural drainage water	4.7	7.0	8.0
Treated sewage water	0.2	1.1	2.4
Management and saving wasted water	-	1.0	-
Total	63.5	71.7	72.2
II. Water demands			
Agriculture	49.7	59.9	61.5
Households	3.1	3.1	5.1
Industry	4.6	6.1	8.6
Navigation	1.8	0.3	0.4
Total	59.2	69.4	75.6

* After the Gungli Canal.

1.2.2 Impact of the reutilization of non-conventional water resources

Industrial wastewater effluents and drainage water contain various pollutants that cause serious environmental problems. Pollutants (such as heavy metals, petroleum hydrocarbons, solvents, pesticides) can easily be transported from industrial wastewater and agricultural drainage water through the agricultural system and altering the quality of water, soil and food crops ending up with a potentially hazardous impact on human health and environment.

Higher Cd and Pb concentrations than the permissible limits allowed by the European Commission were detected in some drains at the point of its discharge to the Nile water and irrigation water (non- or mixed with drainage water) (Badr et al., 2006; Mohamed, 2007; Abd El-Wahed, 2007). In their study on water quality of Ismailia irrigation canal, Stahl and Ramadan (2008) collected and evaluated water samples along the canal as well as discharging points of the industrial effluents. They reported that Pb was detected in high concentrations at the discharging points.

Some studies pointed out major environmental impacts on Lake Manzala, one of the largest Delta lakes and important source for fish in Egypt, which were caused by the direct discharging of agricultural drainage and industrial wastewater into the lake, resulting in a significant deterioration of water quality and disappearance of several important species of fish (Abbassy et al., 2003; Badawy and Wahaab, 1997). Previous studies investigated the influence of Nile water, drainage water and mixed water (50 % Nile water + 50 % drainage water) on Pb, Cd and Ni concentrations in sugar beet plants. It was shown that heavy metals accumulation were higher in sugar beet roots than in leaves, especially when irrigated with drainage water was mixed (Zein et al., 2002). Generally, concentrations of heavy metals (Cd, Cr, Pb and Ni) in plants grown in farms irrigated with wastewater for many years were higher than those in plants grown in farms irrigated with well water (Badawy and Helal, 1997; El-Motaium and Badawy, 2000). Other studies have shown that concentrations of heavy metals in sugar beet, canola, sunflower, soybean, cotton, wheat and maize plants were augmented with increasing the irrigation periods with industrial or mixed sewage and agricultural wastewater (Abd El-Wahed 2007). Mohamed (1998) found that total Cr in sandy soil irrigated by Cairo sewage effluent for 23 and 75 years increased between 1.3 and 15.6 times as compared to the soils irrigated by high quality water (see Abdel-Sabour, 2007). According to WHO, poor environmental quality is a main cause of one fourth of the avoidable ill health in the world (Anwar, 2003).

A significant challenge facing Egypt is to keep appropriate balance between the sustainable re-use of agricultural drainage and wastewater for food security and environmental safety and health. Thereby, adequate wastewater treatment through inexpensive and simple technologies is needed and important to accomplish the future governmental plan under water management and pollution control.

1.3 Pollutants of interest

1.3.1 Priorities of pollutants' selection

In many cases, drainage and wastewater effluents contain mixture rather than mono type of pollutants (Max Roundhill, 2001; Oyanedel-Craver and Smith, 2006). Therefore the priority of the pollutants selection was done on the base that they possess the following items:

- They are commonly present in all drainage and wastewater worldwide and particularly in Egypt.
- They represent two general types organic and inorganic pollutants
- They have different chemical properties and structures: cationic, anionic and neutral pollutants.
- They are classified as hazards for environment and human health.

1.3.2 Inorganic cationic pollutants

1.3.2.1 Cadmium

Cadmium is known as an extremely toxic metal even in low concentrations. It is recorded as number seventh of the priority list of hazardous substances (ATSDR, 2011), which include most significant potential threat to human health, that listed by "The Comprehensive Environmental Response, Compensation and Liability Act" (CERCLA). According to WHO, cadmium is mainly absorbed in the human body through ingestion of contaminated food. It accumulates mainly in kidney and liver with long biological half-life causing renal cortex disorder and kidney damage (Mahvi et al., 2008; WHO, 2010). Moreover, the high accumulation could lead to interrupt calcium metabolism and causes osteoporosis and kidney stone (WHO, 2010). Cadmium is brought to the water canals through the discharge of sewage effluent and industrial wastewater effluent, e.g. paint pigments for electroplating or plastic industry, smelting and mining processes, battery manufacturing and oil, soap and fertilizers factories. World Bureau of Metal Statistics has reported an enhancement in the industrial use of cadmium from 18400 tons in 2003 to 20400 tons in 2007 (Moulis and Thévenod, 2010). Cadmium was detected in different water bodies in Egypt including most of the agricultural drains and mixed water canals for irrigation purposes (Abd El-Wahed, 2007; Mansour and Sidky, 2003; Abdel-Azeem et al., 2007; Abdel-Sabour et al., 2001; Sharaf, 2002; El-Sharawy et al., 2004). According to the Egyptian law 48/1982, levels of cadmium in the mentioned canals are higher than the permissible limit (0.01 mg l^{-1}).

1.3.2.2 Lead

Lead and lead containing compounds are very toxic for human health and the environment. It causes inhibition of some enzymes activity and disruption in the nervous system resulting in severe health problems, ending up by death. Further, it accumulates in bones, brain and muscles and leads to axonal degeneration, demyelination, cerebral oedema and congestion. Beside that it causes lower IQs, behavioural changes and concentration disorder in children (Gupta et al., 2001; Lenntech, 2011). CERCLA has listed lead as No. 2 out of 783 materials in its priority list of hazardous substances. Generally, lead exists as organic and inorganic compounds. The organic form converts quickly to inorganic ones when it is brought into water bodies. It is detected in significant amounts in plants where accumulates and limits chlorophyll synthesis. Half of the human lead exposure is caused by food (Lenntech, 2011).

Discharging effluents of the industrial activities, such as mining industry, petroleum production, battery, computer and TV screens manufactories, and paint and electroplating process, are important pathways of lead to irrigation water. Lead was detected in many drain canals in Egypt. It was detected in high amounts in Baher El-Bakar, Umoum, Mosturud drains as well as in Elgabal-Elasfar drain with concentrations exceeding the permissible limit reported in the 48/1982 law of Egypt (Abd El-Wahed, 2007; El-Sharawy and Elbordiny, 2001; Abdel-Sabour et al., 1996; Elewa, 2010).

1.3.3 Inorganic anionic pollutant

1.3.3.1 Chromate (VI)

Chromate is the anionic form of chromium (VI), soluble in water, bioavailable to organisms, and strongly affected by the media pH and redox conditions (Leung, 2010). Chromate receives a special environmental concern because it induces oxidative stress that leads to cell damage and toxicity for both plants and animals even in low concentrations (Panda and Choudhury, 2005). It is considered as No.17 out of 783, according to the priority list of hazardous substances for human and environment reported by CERCLA (ATSDR, 2011) and is classified as human carcinogen by WHO (Tashauoei et al., 2010). Ingestion of chromate causes stomach pain, ulceration and haemorrhage and may lead to cardiovascular shock. It may cause necrosis and damage of kidney or liver (WHO, 2000). Anthropogenic activities such as stainless steel production, electroplating, tanning, wood preserving, bleaches and detergents production, textiles and corrosion inhibitors in cooling water are sources releasing chromate to the environment (Abdel-Sabour, 2007). In assessment of the effect of industrial waste discharges on water bodies quality, chromate was detected in Nile water near Assiut in Upper Egypt (Abdel-Shafy and Aly, 2002). Abdulla et al. (2010) found chromate (III) and chromate (VI) in high concentrations in tannery effluents while Abou-Elela et al. (2008) detected 38.9 mg l^{-1} of chromate in the final effluent of one of the largest metal plating company located in El-Sadat City, North of Cairo, Egypt.

1.3.4 Organic pollutants

1.3.4.1 Metalaxyl-m

Metalaxyl-m, N-(2,6-Dimethylphenyl)-N-(methoxyacetyl)-D-alanine methyl ester, belongs to the phenylamide chemical group and is known by the trade name “Ridomil plus”, is a widely used systemic fungicide that has a broad activity spectrum. The isomeric mixture of this substance has the common ISO name metalaxyl, and the fate of metalaxyl can be accepted to depict the metabolism and the fate of metalaxyl-M (Anonymous[3], 2011; Hamilton, 2004). It is used for disease control in different crops, ornamentals, horticultural plants and vegetables such as potato, tomato, cotton, lettuce, peppers, avocado, citrus and vines, also for seedling treatments like maize, peas, sorghum and sunflowers through foliar and soil application (Anonymous[4], 2011). It is stable to hydrolysis up to pH 7 even at 50°C, not degradable by light, and has a high stability in wide range of pH and temperature. Therefore, its use increased worldwide as well as in Egypt (FAO, 2004). However, due to its high mobility in soils, especially that contain low organic matter, it has a great tendency to leach and contaminate the ground water as well as the drainage water particularly after extensive fungicide application (Sukul and Spiteller, 2000). Furthermore, it has a high residual level particularly in green house cultivated plants (Massoud et al., 2008; Ismail and Badr, 2004; Nikologianni et al., 2010). In metabolism studies in plants after fungicide application, metalaxyl-m alone/and its residual ingredients were detected in lettuce, potato, grapes and grape juice (FAO, 2004; Dasgupta et al., 2011). Moreover, metalaxyl is accounted as one of the major hazardous pesticides in cotton (Anonymous[5], 2007). Animals' livers are the main target of metalaxyl. In an investigation on the toxicity effect of fungicide on mammals, Lamfon (2011) reported that metalaxyl and its metabolites caused blood vessels congestion, necrosis and adipose degeneration, strong reduction of the activity of antioxidant enzymes and superoxide dismutase in the liver of treated albino mice. Other studies stated the co-carcinogenic potential of metalaxyl in Swiss albino mice (Paolini et al., 1996). Ahmed et al. (2010) found a high resistance of metalaxyl degradation in Egyptian soils particularly in soils with low microbial activity.

1.4 Remediation of low quality water

1.4.1 General remediation techniques

Mainly there are two remediation techniques of wastewater, biotic and abiotic. The biotic technique depends on microorganisms and/or plants via bioremediation and phytoremediation processes. Bioremediation includes microorganisms, called bioremediators, which have the ability to break down contaminants or to assimilate them in their bodies. This technique is effective to remove organic substances from water and minimizing the toxicity of ammonia, nitrite, hydrogen sulfide and methane (Reynolds, 2002). Wetland is an example for the phytoremediation process, in which the plants have the ability to bio-concentrate pollutants in high amounts from the contaminated water via sequestering them in the vacuoles or by the binding of metal-proteins and metallothioneins, (Aiyen et al., 2002; Lasat, 2000; Liao and Chang, 2004; Olguín and Sánchez-Galván, 2010). Those types of plants belong to group called hyperaccumulators. Although the biotic technology showed a remarkably removal of pollutants due to the availability of the materials (plants and microorganisms) and the decomposition of the pollutants to the harmless substances, it has disadvantages that led to the need for other methods to clarify polluted water. Biotic technologies depend on climatic conditions and might need long times to get a significant remediation. The consumption of the harvested plants might be a threat to human health and the deleterious effect of the contaminated plant residuals remain in the long run (Singer, 2003).

Abiotic is an alternative expeditious technique that is used largely in remediation of industrial wastewater. It is based mainly on chemical and physical processes such as ion exchange, electrochemical, electrocoagulation, oxidation/reduction, filtration, reverse osmosis, membrane and adsorption technologies (O'Connell et al., 2006; Dermentzis et al., 2011). Owing to their application possibility and simplicity, ion exchange and adsorption are the most applied techniques in wastewater treatments (Simonović et al., 2009). Activated carbon is one of the extensively used adsorbents in this application since it showed significant removal of organic and inorganic contaminants from different origins of polluted water (Weber, 1974; Marzal et al., 1996; Khan et al., 1997; Singh and Yenkie, 2004; Ahn et al., 2009; Zhang et al., 2011). Despite the efficiency of this adsorbent, the cost and the less availability of the material are major obstacles that limit its application, especially in small scale fields (O'Connell et al., 2006). Clay minerals (Sanchez et al., 1999; Auboiroux et al., 1996; Zhao et al., 2011) activated alumina (Luisa et al., 2003) and oxide and hydroxide minerals (Lazaridis et al., 2005) were also used as effective adsorbents for heavy metals. Recently, several researchers developed natural and cheaper adsorbents for heavy metal removal such as natural zeolite (Erdem et al., 2004), polysaccharide derivatives (Crini, 2005), natural clay (Bedelean et al., 2009), biosorbent materials (Dhabab, 2011; Senthilkumar et al., 2010), chitosan (Nomanbhay and Palanisamy, 2005; An and Dultz, 2007), cellulose, industrial and agricultural wastes (Sud et al., 2008). The use of the these raw and natural materials is still limited due to the lake of knowledge about their availability, dosage, quality and behavior and also the opportunity to be regenerated after using (Bedelean et al., 2009).

1.4.2 Clay minerals and natural clays as potential adsorbents

Utilisation of clay and clay minerals have been defined in different environmental issues since a long time. They were used for radioactive waste disposal and water purification, particularly as flocculants and adsorbents for the turbidity and disease-bearing organisms (Bergaya et al., 2006). Because of their availability in soil components and their wide physical and chemical characteristics, clay and clay minerals were used widely as barriers in landfills to immobilize pollutants in the leachate from going deeper through subsoil to groundwater (Barbier et al., 2000). In addition, several studies showed the capability of clay minerals; i.e. kaolinite (Srivastava et al., 2005), vermiculite (Malandrino et al., 2006), illite, beidellite and montmorillonite (Rybicka et al., 1995) as adsorbents of cationic pollutants from aqueous medium. Owing to its large specific area and higher cation exchange capacity, montmorillonite among different clay minerals has a wide application in the removal of heavy metals from wastewater (Bhattacharyya and Gupta, 2008).

As natural adsorbents, clay sediments and natural occurring clays have a significant role to immobilize different types of contaminants such as nuclear elements (Abd-Allah et al., 2007) and cationic pollutants (Shama and Gad, 2010; Kamel et al., 2004; Zahra et al., 2008).

In general, heavy metals are adsorbed on the clay minerals by two main mechanisms, ion exchange and specific adsorption, whereas they form inner-sphere and outer-sphere complexes on the layer edges and interlamellar surfaces of the clays (Schlegel et al., 1999; Farrah et al., 1980).

In soils, clay and organic matter are main components, which play an important role in retaining contaminants (Sheng et al., 2001; Sharma and Awasthi, 1997; Monkiedje and Spiteller, 2002). This urged the attention for the modification of clay minerals by organic compounds to enhance their removal capacity of organic pollutants from wastewater. There have been considerable efforts in developing modified clay minerals based sorbents for the removal of those pollutants. A common method to increase the removal efficiency of clay is replacing the clay’s natural inorganic exchangeable cations by organic cations with alternative surface properties (Yariv and Cross, 2002)

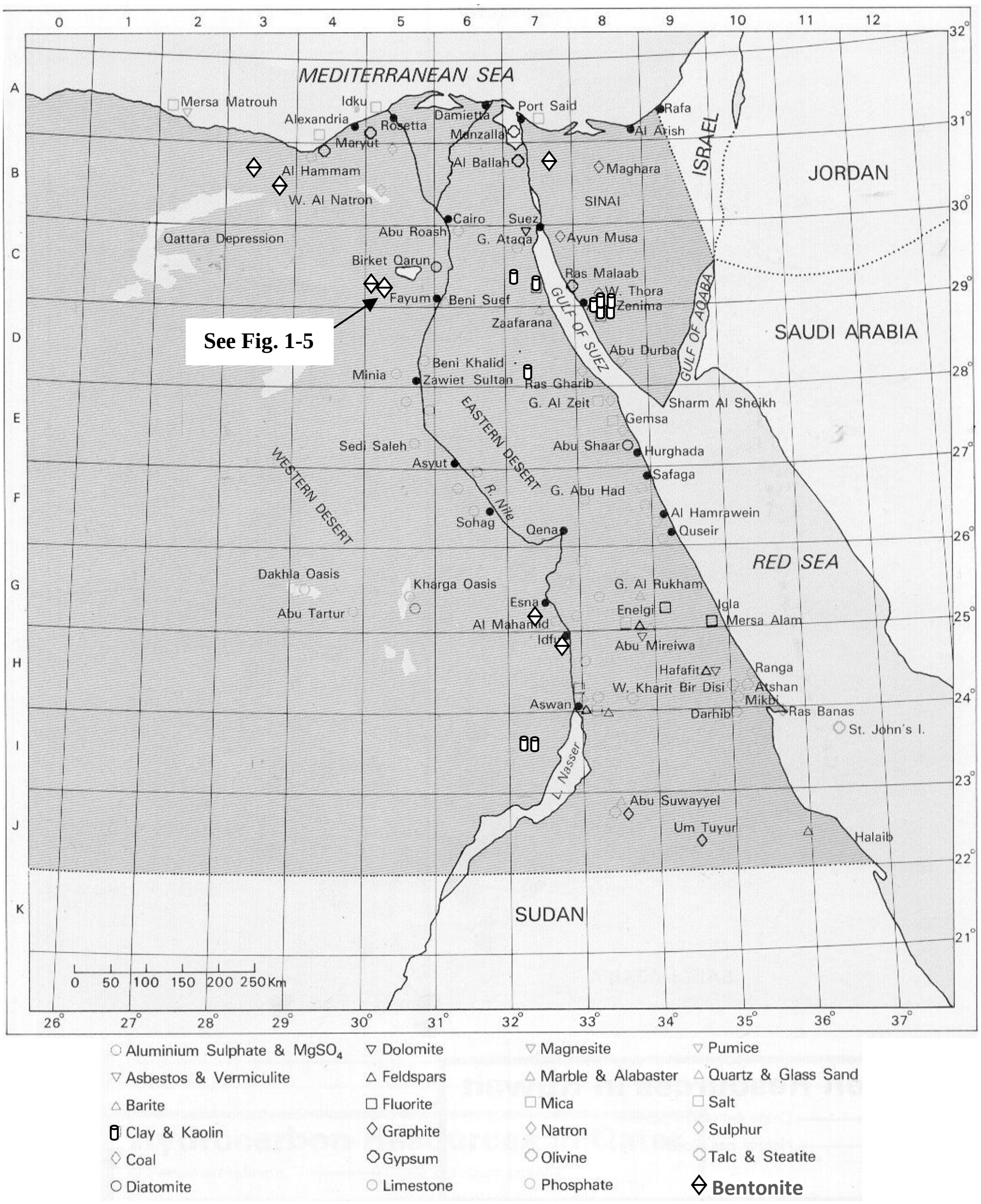
Removal of organic and inorganic contaminants from aqueous origins are affected by several factors. Abollino et al. (2003) reported that Na-montmorillonite is an efficient adsorbent for Cd, Pb, Cr, Cu, Mn, Ni and Zn, with the solution pH being one of the important factors affecting the adsorption process. In addition to solution pH, two other factors, different initial heavy metal concentrations and the existence of major elements (Ca, Mg, Al and Fe), affect the adsorption process. This was shown by Zhu et al. (2011) in their investigation on the competitive sorption among Cu, Pb and Cr simultaneously on Na-montmorillonite. Sheng et al. (2002) demonstrated that hydration energies of interlayer cations played a strong role on the adsorption of dinitrophenol herbicide (4,6-dinitro-o-cresol) on reference smectite clay. The weakly hydrated cations (e.g. K^+ and Cs^+) led to a higher adsorption than the strongly hydrated cations (e.g. Na^+ or Ca^{2+}).

1.5 Distribution of clay sediments in Egypt

1.5.1 Kaolinitic sediments

Kaolinitic deposits are clays composed essentially of kaolinite minerals, which are non-expandable layer silicate minerals of 1:1 types, consisting of one octahedral and one tetrahedral layer. These deposits have a white colour, which may change due to existence of impurities. The shale might contain quartz, feldspars and/or muscovite minerals in small amounts (see El Nahry, 2007). Kaolinite is used for many industries such as ceramic, paper, rubber and textiles fabrics. In medical preparation, kaolin may be used as basis for different disinfectant powders and as an adsorbent to bind gastrointestinal toxins (Naser and Chukri, 1954). The ore spreads in many localities in peninsula of Sinai. The reserves are presented in Fig. 1-3. It is found as alternating beds with thick sandstone beds in El Teeh and Abu Zeneima (including Khbboba, Mossabba Salama, Gabal Hazbar, Abu Anskar, El Eseila, Farsh el Ghuzlan, El Deheesa, El Shallal, Naqb Budra and Umm Algan sites). The reserve estimates in these two sites are 100 million tons (Fawzy and Naim, 1993). The Gabal El Gunna area is another important reserve in Sinai. Further, Kaolinite shale is discovered (Fig. 1-4) in Abu El Reesh and Kalabsha areas, southern Egypt (El Gundy et al., 1994).

Fig. 1-3 Localities of kaolin in peninsula of Sinai. (Fawzy and Naim 1993)



See Fig. 1-5

Fig. 1-4 Deposits of kaolinite and bentonite of Egypt (Habashi and Bassyouni, 1982 updated with data obtained from the Egyptian Mineral Resources Authority)

1.5.2 Bentonitic sediments

Bentonites are types of shale largely composed of montmorillonites, which are 2:1 phyllosilicate mineral types consisting of one octahedral layer in the centre between two tetrahedral layers. Bentonite deposits may contain some gangue minerals like calcite, gypsum and/or kaolinite as well as quartz, illite or feldspar as minor components. The quality of the ore is defined by the percentage of montmorillonite which differs by location. Bentonite is characterized by several features, such as swelling ability as result of water adsorption and de-colorization, which led to its utilization in many fields. Bentonitic shale exist as horizontal layers either outcrop or subsurface with a thickness of 2 – 20 meters. The outcrop bentonites have a yellowish-green, greenish or reddish grey or grey color and at depth it is bluish-green and lighter colored after drying. The age of the Egyptian bentonite extended from the upper to lower Eocene as in El-Fayoum and from lower to medium Miocene as in Abu-Zeneima and Alexandrea desert road areas. The reserve of this material in Egypt is estimated by 63 million tons (Kandeel, 1989). Egyptian bentonite deposits Fig. (1-4) are distributed in several localities (Hassan and Abdel-Khalek, 1998; Kandeel, 1989; Tahoun et al., 2005; Abdel-Motelib et al., 2011). Qasr El-Sagha, Kom Osheim and Tamya Shaloufa, kaser El-Basein, wadi Rayan in El-Fayoum governorate are the important reserves (Fig. 1-5). In addition, Alexandria desert road, Al-Suez desert road (Katameia), Aun-Musa, Gabal Hamdal of Abu-Zeneima in Sinai, Maadi, Helwan, south and southwest Alameen, south of El Hammam city in Western Desert, New Valley, As-Sibaiyyah, Edfu and El Minia governorate areas have been utilized to quarry bentonites.

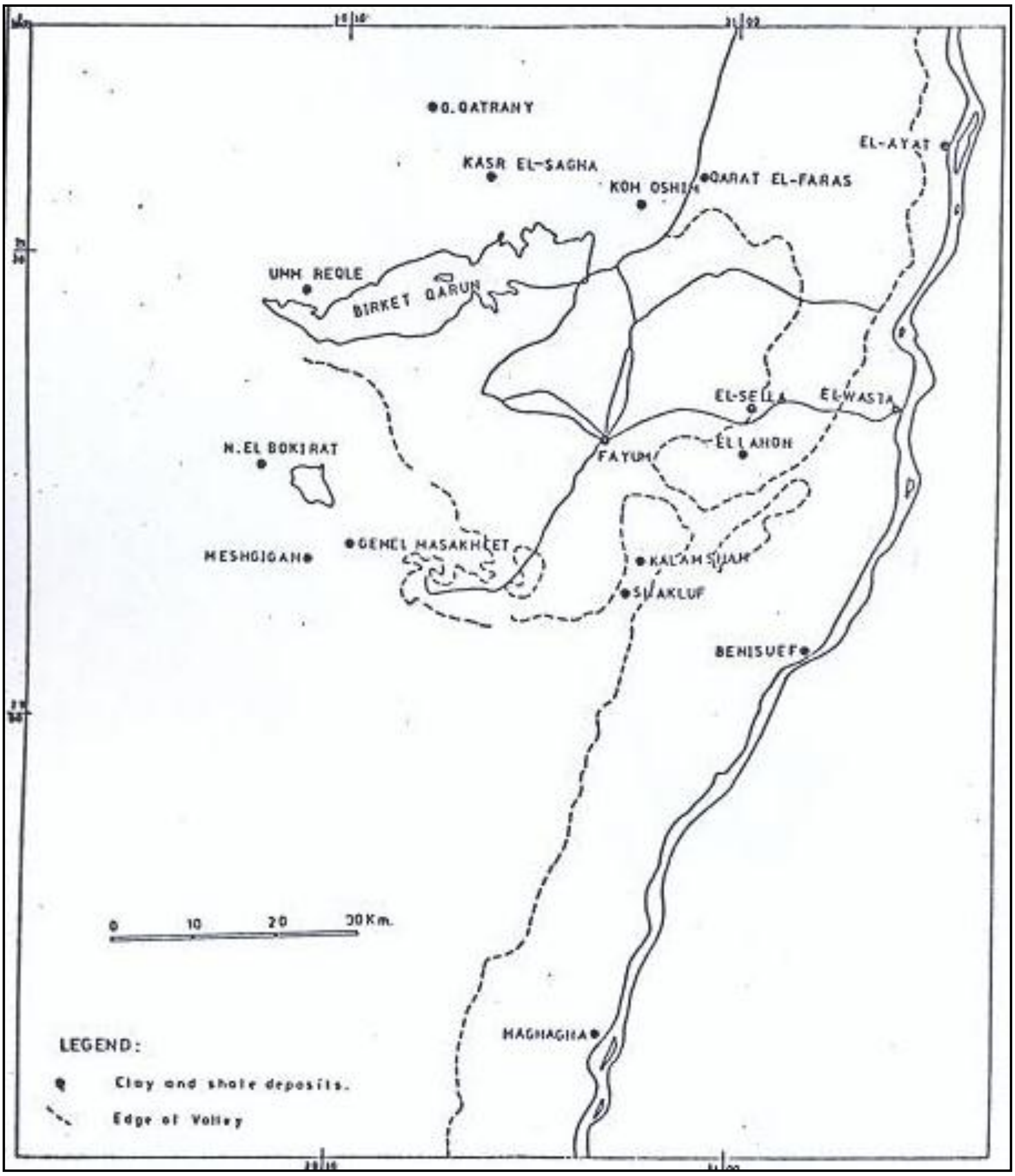


Fig. 1-5 Distribution of bentonite shale in EL-Fayoum Governorate, [see indication in Fig. 1-4] (kandeel 1989)

1.6 Objectives of the thesis

With the shortage of water especially in developing countries, the development of proper methods for low quality water treatment techniques, taking into account environmental and the economical aspects, is a key goal to maintain the sustainable use of the non-conventional water resources. The previous mentioned literature demonstrated that clays may be considered as remarkable adsorbents for heavy metals. However, they have lower capability to remove anions as well as hydrophobic or neutral pollutants, giving attention to the importance of clay modification to enhance their adsorption. In two studies the ability of organo clays prepared from three natural organic substances were investigated (Cruz-Guzmán et al. 2004 and 2006). L-carnitine (Carnitin), L-cystine dimethyl ester (Cys_ester) and thiamine, in combination with a reference montmorillonite clay mineral were used to remove the herbicide Simazine, as well as Hg^{2+} and Pb^{2+}, individually, from aqueous solution. The authors reported that all adsorbents were effective to remove simazine and Hg^{2+}, while only montmorillonite treated with Carnitin was able to take up Pb^{2+} as compared with the untreated montmorillonite. Nevertheless, up to the knowledge of the author of this study, no investigation was done so far on optimizing the adsorption conditions by studying the needed contact time or the effect of changing pH and electrolyte ionic strength on the adsorption efficiency. No other heavy metals except Pb^{2+} and Hg removals were investigated by clay mineral modified with those natural organic substances. Furthermore, the usage of these organic substances to modify any other types of clay minerals or clay sediments (as cost effective source of clay minerals) to produce adsorbents was not reported before. Wastewater is commonly contaminated by different varieties of pollutants (Oyanedel-Craver and Smith 2006). In developing countries it is crucial to use adsorbents which are prepared from available materials and which have the ability to remove heterogeneous pollutants simultaneously. Only limited information is available on the removal of heterogeneous pollutants simultaneously from wastewater, in particular on the removal of cationic and anionic inorganic as well as organic pollutants by clay sediments modified with organic substances. To maintain the synthesis simplicity, economic feasibility and the environmental quality, adsorbents based on naturally occurring Egyptian clayey sediments differ in their mineralogical composition have been prepared and used in the current study. The clayey sediments in combination with L-Carnitine, L-Cystine dimethyl ester or humic acid as natural organic modifiers or Methyltriphenyl-phosphonium or Hexadecyltrimethyl-ammonium as synthetic organic modifiers were used for the synthesis of organically modified clayey sediments (OMCs). After preparation of OMCs their efficacy to remove cationic and anionic inorganic pollutants as well as organic pollutants simultaneously from aqueous solution was evaluated. The thesis is subdivided into five chapters and the objectives are to:

- Select the prospective OMCs in which the loading ratio of each organic modifier to clayey sediments will achieve a high potential of pollutants sorption.
- Evaluate the sorption capacities of the prospective OMCs to take up Cd^{2+}, Pb^{2+} as cationic pollutants, $Cr_2O_7^{2-}$ as anionic pollutant and Metalaxyl-m (MM) as organic pollutant, individually, in comparison to those of the natural clayey sediments.
- Test the regeneration ability of the loaded prospective OMCs with pollutants.
- Figure out to which extend the sorption of Cd^{2+}, Pb^{2+} and $Cr_2O_7^{2-}$, individually, can be enhanced by changing the sorption conditions such as pH, contact time and electrolyte type and concentrations.
- Quantify the potential removal of Cd^{2+}, $Cr_2O_7^{2-}$ and MM by the prospective OMCs from their binary and ternary component systems and relative to those achieved from the single component systems with low and high initial pollutants concentrations.
- Investigate the sorptive selectivity of the prospective OMCs to the pollutants under study.

The thesis outlines are as follow: Chapter 1 is a general introduction including the water scarcity problem in the world and in Egypt particularly, the pollutants of interest (their environmental hazard, existence and influences in Egyptian water bodies), distribution of the clay sediments in Egypt as suggested sorbents.

Chapter 2 is concerning mainly on the preparation and characterization of OMCs.

In chapter 3, adsorption isotherm and desorption experiments were conducted to quantify the capacity of the prospective OMCs to take up Cd^{2+}, Pb^{2+} and $Cr_2O_7^{2-}$ from aqueous solutions. Further, several sorption experiments were carried out to study the effect of different factors such as heavy metal concentrations, pH, electrolytes concentrations and contact time on the sorption process. Moreover, the removals of

Cd^{2+} and $Cr_2O_7^{2-}$ from their binary component systems were performed to study the competitive effects.

Chapter 4 is mainly investigating the sorption isotherm of MM fungicide by the prospective OMCs. In addition to that, the simultaneous sorption of organic and inorganic pollutants were studied, taken in consideration the effect of different initial pollutants concentrations. Chapter 5 is general discussion and outlook.

2. Preparation and Characterization of Organically Modified Clayey Sediments (OMCs).

2.1 Abstract

Naturally occurring clayey sediments instead of defined clay minerals were proposed as basic materials for the syntheses of organically modified clayey sediments (OMCs). The basic materials were loaded by different concentrations of organic modifiers: L-Cystine dimethyl ester (Cys_ester), L-Carnitine (Carnitin), Methyltriphenyl-phosphonium (MTP) and Hexadecyltrimethylammonium (HDTM). The OMCs are produced to be used for the removal of pollutants from aqueous solutions.

The characteristics of OMCs were studied by X-ray diffraction (XRD) and mid infrared spectroscopy (MIRS) techniques. Contents of the organic carbon (%) and the loading of the organic modifiers as ratio of the cation exchange capacity (CEC) of the natural clayey sediments were also determined. Screening experiments were designed for the sorption of Cd^{2+}, Pb^{2+} and $Cr_2O_7^{2-}$ on the synthesized OMCs as function of the added concentrations of the organic modifiers. The screening experiments were conducted to find out the optimal loading of each organic modifier by which the highest removal of pollutants could be achieved.

The characterization of the two natural clayey sediments confirmed that as a main component one material consist of smectite [bentinitic (bent) sediment] and the other of kaolinite [kaolinitic (kao) sediment]. MIRS spectra of OMCs depicted the absorption bands corresponded to the natural clayey sediments as well as to the organic modifiers, indicating the successful preparation of the OMCs. Changes in the basal spacing were indicated by the XRD patterns scanned for the OMCs based bent sediments compared with the natural bent sediment, suggesting different arrangements of the organic modifiers in the interlayer. Increasing the added concentrations of the organic modifiers induced an increase of the content of organic modifiers on OMCs based kao or bent sediments relative to the natural clayey sediments. The loading of organic modifiers on the OMCs based bent sediments were higher than those for the OMCs based kao sediments. The content of the organic modifiers on the OMCs followed the order HDTM- > MTP- > Cys_ester- > Carnitin-OMC.

The results obtained from the screening experiments with OMCs based kao sediment showed that increasing loading of MTP and Cys_ester on OMCs improved the sorption of Cd^{2+}, Pb^{2+} and of $Cr_2O_7^{2-}$ relative to the natural kao sediment. OMCs with Carnitin and HDTM achieved sorption of Cd^{2+} and Pb^{2+} similar to that of the natural kao sediment. Among all treatments, the modification with HDTM improved the sorption of $Cr_2O_7^{2-}$ by eleven fold compared with the natural kao sediment. The results from the screening experiments with OMCs based bent sediments demonstrated that the OMCs with HDTM and MTP at any loading concentrations were efficient to remove almost all Cd^{2+} and Pb^{2+} ions provided in the sorption experiments. OMCs with Carnitin up to loading ratio equal to 21 % of the CEC of bent sediment had the ability to remove all Pb^{2+} and 84 % of Cd^{2+} ions from the tested aqueous solutions. The sorption of Cd^{2+} and Pb^{2+} by OMC decreased with increasing loading of Cys_ester. In contrast, increasing modifiers concentrations on the OMCs with HDTM, MTP and Cys_ester improved significantly the sorption of $Cr_2O_7^{2-}$ as compared with the natural bent sediment.

The results showed great influence of the modifier type and loading concentrations on the sorptive properties of the OMCs

2.2 Introduction

Clay minerals and clayey sediments are generally considered as the most important soil components retaining soil pollutants. They represent natural barriers due to their small grain size, their high chemical and mechanical stability, their large specific surface area, their surface charge and their chemical reactivity permitting them to immobilize contaminants like heavy metals. In addition, clayey sediments contain different percentages of other reactive compounds that fix or immobilize heavy metals such as Fe- and Mn-oxides and -hydroxides and carbonates (Mahdy, 2004).

The sorption capacity of clay is generally determined by its chemical nature and pore structure. The pore structure, such as the nature and volume of pores, is a predominant factor for gas-phase sorption. In contrast, the chemical properties of the surface groups affect the sorption from the liquid phase (Lin and Juang, 2002).

Because of the surface characteristics and the net negative charge of clay minerals, they are capable of adsorbing cationic inorganic pollutants but have limitations in removing anionic and organic pollutants from polluted water. To overcome these limitations, acid activation and/or loading of the clay with organic cations have been used to modify the surface properties of clay minerals. This modification changes the sorption affinity of clays towards organic and inorganic pollutants (Krishna et al., 2001; Arfaoui et al., 2008).

Several authors reported changes in chemical properties after loading clay minerals with organic modifiers. Jiang et al. (2002) studied the development of modified montmorillonites by loading them with polymeric Al/Fe species in the absence and presence of Hexadecyltrimethylammonium (HDTMA). They found that intercalating montmorillonites with polymeric Al/Fe species increased the clay’s surface area. On the other hand, loss of surface area was observed for montmorillonites, when intercalated with HDTMA, polymeric Fe/HDTMA, polymeric Al/HDTMA and polymeric Fe/Al/HDTMA. Oyanedel-Craver and Smith (2006) found that quaternary ammonium cations (QAC) loaded at different percentages of the clay’s cation exchange capacity (CEC) affected the surface charge of the clays. Loading of benzyltrimethylammonium cations (BTEA) increased the negative charge on the surface of BTEA-bentonite relative to the untreated clay, whereas a higher portion of QAC loading on HDTMA-bentonite caused an increase of positive charge. In addition, Lee et al. (2004) and Rytwo et al. (2005) demonstrated that the sorption properties of organo-clays for organic contaminants significantly depend on the amount and size of the organic compounds used for the production of organo-clays.

The type and the concentration of the organic modifiers is a key factor to produce effective modified clays in removing heavy metals. Oyanedel-Craver and Smith (2006) studied the sorption of Pb, Cd, Zn and Hg to HDTMA-bentonites as a function of HDTMA loading at 25, 50 and 100 % of the clay's CEC. They reported that sorption of Cd, Pb, and Zn metal ions to 25 % HDTMA bentonite was similar to or greater than sorption to untreated Ca-bentonite. The adsorption decreased with increasing loading of the HDTMA. In contrast, the loading percentage of the organic cation had no effect on Hg adsorption. Erdemoĝlu et al. (2004) investigated the removal of Pb^{2+} ions from aqueous solutions using pyrophyllite modified by coating with 3-(2-aminoethylamino) propyl-methyldimethoxysilane (APMDS-modified pyrophyllite). The APMDS-modified pyrophyllite adsorbed about 93 % of Pb^{2+} ions at an initial concentration of 20 mg l^{-1}, while natural pyrophyllite adsorbs only 35 % under the same conditions. In their study on the removal of Pb^{2+} and Hg^{2+} by organo-clays, Cruz-Guzmán et al. (2006) concluded that organo-clays prepared from reference montmorillonite in combination with functionalized organic materials adsorbed Hg^{2+} very effectively. In contrast, most of the organo-clay complexes were not effective to adsorb Pb^{2+}, except the montmorillonite treated with organic materials which possessed carboxyl groups.

Clayey sediments as natural and economical sources of clay minerals have been suggested as effective sorbents for heavy metals, whereby the adsorption efficiency was greatly affected by the source of clay sediments (Abd-Allah et al., 2005, 2007, 2009a and 2009b; Bahgeet et al., 2005). Studies were proposed for thermal transformation and acid washing treatments to increase the affinity of natural Egyptian clays for the removal of heavy metals (Abdallah, 2006; Talaat et al., 2011). However, little information is available on the characteristic changes of clay sediments that occur after the modification with organic substances and the importance of these changes on the increases of sorption of anionic and organic pollutants.

In this study, two locally available clayey sediments representing two groups of clay minerals, kaolinitic and bentonitic clays, which are distributed widely in Egypt instead of defined purified and/or processed clay minerals were investigated. The clayey sediments were loaded with L-Carnitine, L-Cystine dimethyl ester, Methyltriphenyl-phosphonium or Hexadecyltrimethylammonium organic modifiers to prepare organically modified clayey sediments, which were later used for removing organic and inorganic pollutants from wastewater. The study is divided into a series of papers from which this first one focuses on the preparation and the property change of the clayey sediments after modification. The following hypotheses were tested: I) Modification of the clayey sediments by organic modifiers changes the mineralogical and chemical characteristics of clays and II) the sorption of cadmium, lead and dichromate to the clayey sediments is affected by the type and the concentration of the organic modifiers.

2.3 Materials and Methods

2.3.1 Materials

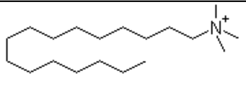
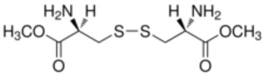
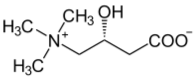
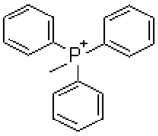
2.3.1.1 Clayey sediments

Two natural clayey sediments were collected from different localities in Egypt. The first sediment was collected from Sinai, Egypt (29^{o} 13′ 10″ N and 33^{o} 20′ 18″ E) and is referred to as kao sediment. The second was collected from Qaser el-Sagha (29^{o} 34′ 06″ N and 30^{o} 49′ 52″ E), El-Fayoum, Egypt and is referred to as bent sediment.

2.3.1.2 Organic modifiers

The four organic modifiers used in the study are described in table 2-1.

Table 2-1 Organic modifiers used in this study

Organic modifier type	Acronym	Structure*	MW**
Hexadecyltrimethylammonium chloride[1]	HDTM		320.01
L-Cystine dimethyl ester dihydro-chloride[2]	Cys_ester		341.28
L-Carnitin[2]	Carnitin		197.66
Methyltriphenyl-phosphonium chloride[2]	MTP		312.78

* Provided by online Database of Chemicals from Around the World (http://www.chemblink.com, 04 – 04 - 2011).
** Molecular weight
[1] Analytical grade, provided by Fluka
[2] Analytical grades, provided by Sigma & Aldrich, Germany

2.3.2 Methods

2.3.2.1 Preparation of organically modified clayey sediments

The collected clayey sediments were pulverized to pass through a 63 µm sieve. The materials were analyzed for their chemical and mineralogical properties (see 2.3.2.2.). In order to eliminate the effect of the different natural exchangeable inorganic cations on the modifier sorption process, sodium exchanged clayey (Na-clay) sediments were prepared by saturating and centrifuging the materials three times with 1 M NaCl, followed by washing three times with ultrapure deionized water. The resulting suspensions were transferred into dialysis tubes (Servapor dialysis tubing, MWCO 12000 - 14000) inserted into an aerated water bath with daily changing of the water until this water was free of Cl^- (Photo 2-1).

Photo 2-1. Dialysis tubes system for washing Na-clay suspensions free of Cl^-

Afterwards, the clayey sediments were oven dried at 70 °C, ground again with an agate ball-mill (Retsch MM 30, Germany) for 3.5 min and then used for the preparation of the organically modified clayey sediments (OMCs). The OMCs were prepared by modification of the Na-clays with solutions of the four organic modifiers, described in Table 2-1, in five different concentrations (see next paragraph) using 1 % w/v ratio.

The solutions were prepared by dissolving 3, 5, 8, 10 and 14 mmol of the organic modifiers in 1 L of 1 mM HNO_3. The diluted acid was used to obtain the protonated form of the organic modifiers as reported by Cruz-Guzmán et al. (2004). The solutions were then added to the Na-clay suspensions and shaken at room temperature for 72 h. Control samples (H-clay) were prepared by suspending the Na-clays in HNO_3 with no organic modifier. Afterwards, the suspensions were centrifuged, washed with ultrapure deionized water several times and freeze dried. Before using the OMCs for the following sorption experiments, the samples were ground for 1.5 – 2.3 min using agate ball-mill and kept in plastic vials under dry conditions.

2.3.2.2 Characterization of natural and organically modified clayey sediments

Elemental composition of the natural clayey sediments was done by X-ray fluorescence (XRF) using Siemens SRS 200 instrument. To prepare XRF tablets, four C_{10}-tablets (≈ 1.333 g) were mixed with double weight (≈ 2.666 g) of clayey sediments (dried at 105°C) in a micro mill for 5 min. The ground materials were pressed with $3x10^4$ kg for 5 min. Afterwards, tablets were measured and data were processed using the software spectra 3000 v2.0, 1986-1995.

X-ray diffraction (XRD) patterns were recorded for the natural clayey sediments as powder preparations in the scanning range of 2 - 60° 2θ and as oriented clay preparation in the scanning range of 2 - 36° 2θ using a Bruker-AXS D-500 Siemens diffractometer with a Cu-Kα radiation (50 mA and 33 kV) source. For distinguishing the diagnostic d-spacing in the natural clayey sediments, oriented preparations of the clay fraction (< 2µm) were analyzed after various pretreatments: magnesium saturation (Mg-air dried), Mg–glycerol- salvation (Mg+Gly), potassium saturation (K-air dried) and potassium saturation heated to 600 °C (K+600°C). The minerals identification was done by data processing using the software Diffrac At ver 3.3 socabim 1986-93 and Seifert Analytical X-ray Autoquan.

OMCs based bent sediments in combination with 10 mM Cys_ester, 5 mM Carnitin, 5 mM MTP or 5 mM HDTM were subjected to XRD analyses and denoted as Cys_ester-, Carnitin-, MTP- or HDTM-bent, respectively. XRD analyses of OMCs were performed as oriented preparation in scanning range of 2 - 36° 2θ. Whereby, OMCs suspensions (1:50 w/v) were deposited after sonification without previous treatment onto porous ceramic tiles, followed by drying at ambient temperature.

Mid infrared spectroscopy (MIRS) spectra were obtained on the natural kao and bent sediments, organic modifiers (pure substances) and OMCs using the diffuse reflectance method. OMCs were prepared from both sediments in combination with the organic modifiers at concentrations similar to those used for the XRD analyses. Samples for MIRS analysis were dried overnight at 32 °C. Spectra were recorded on a Tensor-27 (Bruker Optik GmbH, Ettlingen, Germany) Fourier transform spectrometer with a potassium bromide (KBr) beam splitter and a liquid nitrogen cooled mid-band mercury-cadmium-telluride detector. The spectrometer was mounted with a Praying Mantis diffuse reflectance chamber (Harrick Scientific Products, New York, USA) purged with dry air via a compressor (Jun-Air International, Nørresundby, Denmark) at 200 l hr^{-1}. Wavenumbers from 4000 to 600 cm^{-1} were recorded at a resolution of 4 cm^{-1}. A single spectrum was produced from 16 co-added scans. Three separate spectra were measured for each sample by measuring, returning the sample to the sample container, mixing, and again placing in the measurement cup. Figures of MIRS spectra represent an average of the three replicate analyses. Spectral pre-processing included atmospheric correction for carbon dioxide (CO_2) and water, normalization and baseline correction via the rubber band correction method excluding CO_2 bands using the spectral processing software OPUS version 6.5 (Bruker Optik GmbH).

Chemical properties of the natural clayey sediments were analyzed according to Hoffmann (1991). pH was determined in sediment-water suspension 1:2.5 w/v using a glass electrode pH meter (digital-pH-meter E532, Metrohm Herisau, Switzerland). Cation exchange capacities (CEC) were determined by both barium chloride and ammonium acetate (Chapman, 1965) methods.

Total carbon (TC) and organic carbon (OC) were determined by dry combustion in a stream of oxygen combined with IR-spectrometry (elementary analysis) using an elemental analyzer (Vario EL, Elementar, Germany). Carbonates were removed by treating the samples with 6 M HCl prior to analysis of organic carbon (DIN ISO [10694], 1996a). Inorganic carbon (IC) is calculated as the difference of total minus organic carbon.

2.3.2.3 Screening experiments with cadmium, lead and dichromate ions

To investigate the effect of loading the organic modifiers on the removal of heavy metals from aqueous solutions, Cd^{2+}, Pb^{2+} and $Cr_2O_7^{2-}$ were interacted with OMCs containing different concentrations of organic modifiers. H-clays or OMCs were shaken with 0.01 M NaCl (pH 5.4 ± 0.2) aqueous solution containing $0.3x10^{-3}$, $0.2x10^{-3}$ or $0.6x10^{-3}$ M of $Cd(NO_3)_2{\cdot}4H_2O$, $Pb(NO_3)_2$ or $K_2Cr_2O_7$, respectively, for 24 h at ambient temperature. The solid concentration was 1 %. Afterwards, the slurries were centrifuged and Cd^{2+}, Pb^{2+} and $Cr_2O_7^{2-}$ were measured in the supernatant by AAS (Unicam 939 AA Spectrometer). The sorbed ion was calculated from the difference between the initial concentration and that remaining after equilibration.

2.4 Results

2.4.1 Characteristics of natural and organically modified clayey sediments

2.4.1.1 Mineralogical and chemical characteristics of natural clayey sediments

The XRD patterns of the natural clayey sediments are shown in Fig. 2-1. The resulting mineralogical composition and the chemical analyses are represented in table 2-2. The XRD pattern of clayey sediment collected from Sinai (kao sediment) obtained from the powder preparation showed that kaolinite was the only clay mineral in the clay fraction and the rest was quartz (12 %). An intense and sharp peak at 7.2 Å was obtained from the oriented preparation patterns scanned after K or Mg saturation

(K- or Mg-air dried) treatments and remained unaffected after the Mg-glycerol-salvation (Mg+Gly) treatment. This peak was destroyed after the heating treatment (K+600 °C).

According to the XRD-pattern of the powder preparation, the clayey sediment collected from Qaser el-Sagha (bent sediment) was composed of smectite, kaolinite, calcite, feldspar and quartz. The smectite is characterized by the reflected peaks observed after the saturation by Mg followed by Mg+Gly treatments, in which a shifting of the peak from 14 Å to 18 Å was occurred, indicating expansion in the interlayer space. In addition to that, reflected peak at 12.1 Å obtained after the K-air dried treatment shifted to 10 Å after the heating treatment (K+600°C), indicating collapse of interlayer space (Fig. 2-1). Interestingly, the reflected peak at 7.1 Å was also observed in the XRD oriented preparation patterns of bent sediment. This peak reflection was unaffected by K- and Mg-air dried and Mg+Gly pretreatments but disappeared after the heating treatment (K+600°C).

Total elemental oxides values of the natural clayey sediments in Table 2-3 shows high percentages of SiO_2 in all materials. The kao sediment is characterized by a higher percentage of alumina (44.3 %) as compared with bent sediment. The Fe_2O_3 amount was high in bent sediment (7.81 %) which is interpreted by presence of a small amount of goethite, according to the identification by the Diffrac software. Furthermore, bent sediment had higher contents of alkali oxides namely Na_2O (1.44 %), K_2O (1.27 %), CaO (5.15 %) and MgO (1.53 %) compared to kao sediment (0.03 %, 0.09 %, 0.3 % and 0.26 %, respectively). kao sediment showed a low CEC value (7.3 cmol kg^{-1}) as compared with bent sediment (48.1 cmol kg^{-1}). Higher contents of inorganic and organic carbons were recorded for bent sediment relative to kao sediment (Table 2-2).

Table 2-2 Mineralogical and chemical characteristics of natural clayey sediments

Clayey sediment	Clay minerals	Calcite	Feldspar	Quartz	Clay fraction (%)		TC	OC	IC	CEC* cmol kg^{-1}		pH
	(%)				Kaolinite	Smectite	(%)			$BaCl_2$	NH_4OAC	Suspension 1:2.5
kao [1]	88	-	-	12	100	-	0.09	0.08	0.01	7.3	7.3	7.8
bent [2]	40	12	16	32	13	87	0.97	0.27	0.70	29.7	48.1	9.1

1: clayey sediment collected from Sinai, 2: clayey sediments collected from Qaser el-Sagha. * Cation exchange capacity. TC: total carbon content. OC and IC: organic and inorganic carbon contents.

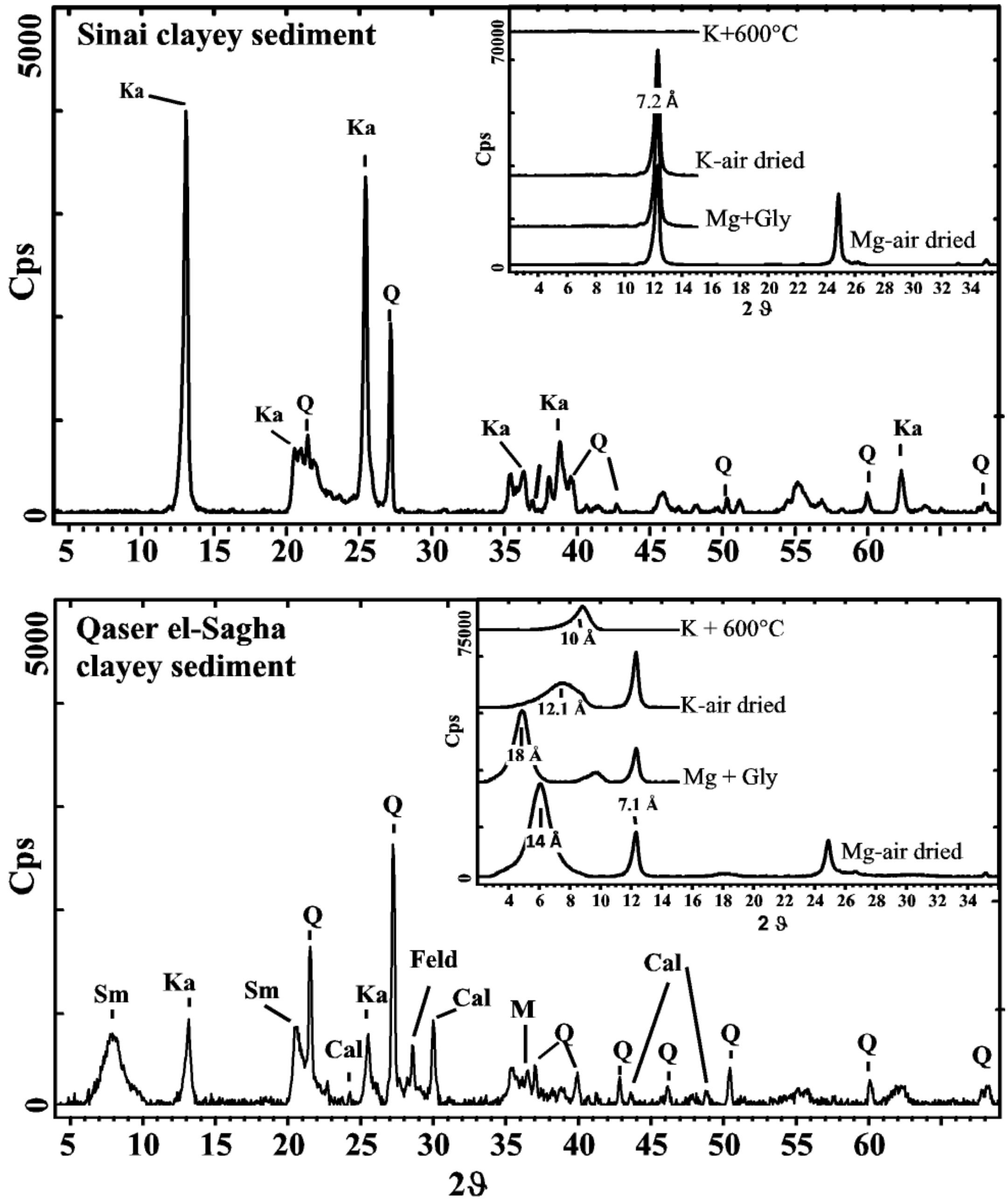


Fig. 2-1 XRD patterns of natural clayey sediments as powder. The inset shows XRD patterns of the pre treatments of the clay fractions. CPS: count per second, 2ϑ: two theta. Q = Quartz, Feld = feldspar, Cal = Calcite, Sm = Smectite and Ka = Kaolinite.

Table 2-3 Total elemental oxides distribution of the natural clayey sediments measured by XRF

Clayey sediments	Al_2O_3	SiO_2	Na_2O	K_2O	CaO	MgO	Fe_2O_3	P_2O_5	TiO_2	ZrO_2	Ignition loss
	%										
kao sediment[1]	44.3	50.0	0.03	0.09	0.30	0.26	1.41	0.14	3.34	0.13	-
bent sediment[2]	20.7	56.3	1.44	1.27	5.15	1.53	7.81	0.10	1.45	0.04	4.21

1: clayey sediments collected from Sinai. 2: clayey sediments collected from Qaser el-Sagha. XRF: X-ray fluorescence

2.4.1.2 Content of organic modifiers in the organically modified clayey sediments (OMCs)

Contents of organic modifiers (%) in the OMCs were calculated from the carbon contents of the samples by subtracting the carbon contents of the H-clay samples. Content of the organic modifiers were used to compute the loading ratio as percentage of the CEC of the natural clayey sediments obtained by using different concentrations of the organic modifiers.

Irrespective of the clayey sediment type, the contents of organic modifiers in the OMCs followed the descending order HDTM- > MTP- > Cys_ester- > Carnitin-OMC (Table 2-4). In general, the contents of the organic modifiers in the OMCs based kao sediment were much lower than those in the OMCs based bent sediments. The values increased with increasing modifiers concentrations in the solution from 0 – 3 mM, while further increases of the modifier concentrations did not reflect any changes of the modifiers loading. However, the loading of the organic modifiers on OMCs based bent sediments increased with increasing modifiers concentrations in the solutions from 0 to 14 mM except for MTP and HDTM-OMC. Their loading reached the plateau at 5 and 10 mM initial modifiers concentrations, respectively.

Table 2-4 Contents of organic modifiers (%) in the OMCs and the loading ratios as percentages of CEC of the natural clayey sediments.

Clayey sediment	Modifier	%	Initial concentration of organic modifiers in the solution (mM)				
			3	5	8	10	14
bent sediment [2]	Carnitin	organic modifier content	0.50	1.39	1.21	1.64	1.81
		loading ratio	6	18	16	21	23
	Cys_ester	organic modifier content	0.00	1.36	4.37	4.28	5.04
		loading ratio	0	21	67	66	78
	MTP	organic modifier content	6.89	10.6	10.9	10.9	11.3
		loading ratio	52	79	81	82	84
	HDTM	organic modifier content	7.66	14.0	17.5	19.7	19.3
		loading ratio	56	102	128	144	141
kao sediment [1]	Carnitin	organic modifier content	0.10	0.11	mv.	mv.	0.09
		loading ratio	8	10	-	-	8
	Cys_ester	organic modifier content	0.38	0.41	0.41	0.32	0.39
		loading ratio	38	42	41	33	39
	MTP	organic modifier content	0.42	0.59	0.53	0.58	0.53
		loading ratio	21	29	26	28	26
	HDTM	organic modifier content	1.48	1.46	1.46	1.46	1.42
		loading ratio	71	70	70	71	68

1: clayey sediments collected from Sinai. 2: clayey sediments collected from Qaser el-Sagha.

Carnitin, Cys_ester, MTP and HDTM are the organic modifiers described in Table 2-1. mv.: missing value due to technical problems.

2.4.1.3 X-ray diffraction of organically modified clayey sediments compared with the original sediments

Fig. 2-2 displays the XRD patterns of bent sediments after loading with different organic modifiers. The changes of bent sediments after modification were recorded according to the shifting that occurred to the reflected peaks at 14.5 Å indicating the changes in the clay's basal space after modification. For comparison reasons, the sodium exchanged bent sediment (Na-clay) was also subjected to XRD analysis and the obtained results showed reflected peak at 15.3 Å (not shown). The basal spacing of the original bent sediments after modification depicted the following order: Cys_ester- < natural- < Carnitin- < Na- < MTP- < HDTM-bent, recorded by the reflected peaks at 13.9, 14.5, 15.2, 15.3, 17.1 and 19.7 Å, respectively.

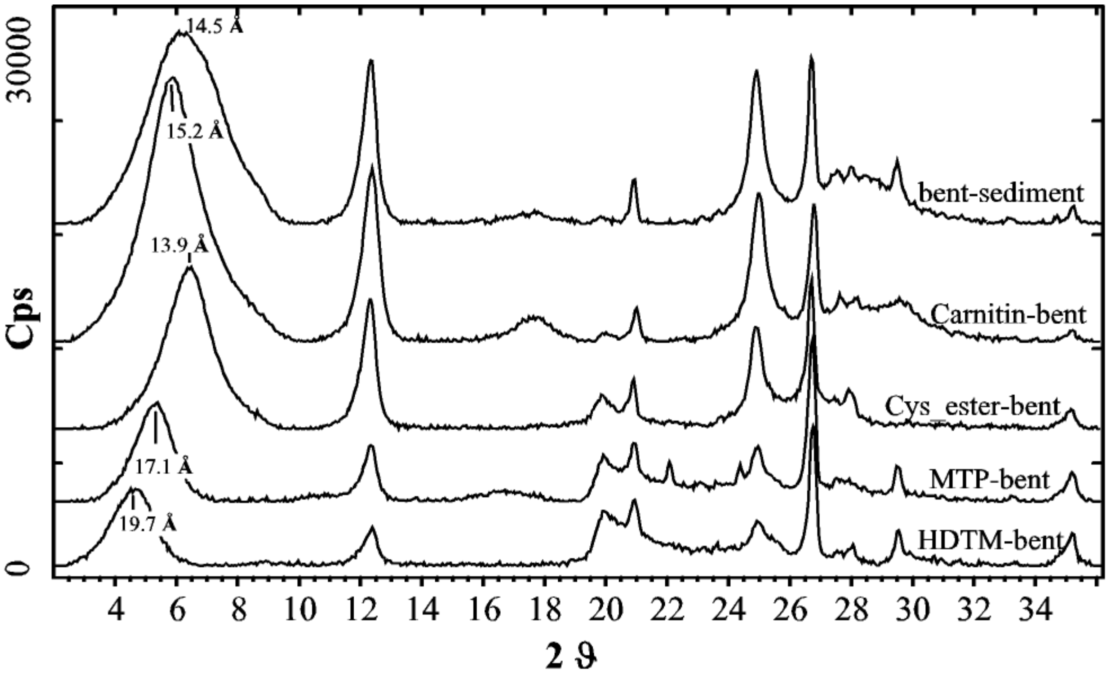


Fig. 2-2 XRD patterns of organically modified bent sediments compared with the natural bent sediment. Carnitin, Cys_ester, MTP and HDTM are the organic modifiers described in Table 2-1.

2.4.1.4 Mid infrared spectroscopy (MIRS)

MIRS spectra of the natural clayey sediments and OMCs are displayed in Fig. 2-3 for OMCs based kao sediments and in Fig. 2-4 for OMCs based bent sediments. In both sediments, bands in the region of 669- 800 cm^{-1} (not shown) corresponded to Si-O stretching vibrations, indicating the presence of quartz (Nayak and Singh, 2007). For kao sediment, the observed bands at 1111, 1020, 945, 685 and 644 cm^{-1} and the four bands in the region of 3697-3622 cm^{-1} are characteristic of kaolinite. The 3697 and 3622 cm^{-1} peaks are assigned to stretching vibrations of OH groups (Ravisankar et al., 2010; Johnston et al., 1985). The bands in region of 1100-1000 cm^{-1} refer to Si-O and Si-O-Al stretching vibrations (Volkmann, 1972). Spectrum of bent sediment (Fig. 2-4) showed bands in the regions of 3622, 1100-1000, 920, 878, 799 and 697 cm^{-1}. Those bands along with the characteristic broad band in the range of 3455-3400 cm^{-1}, assigned to H-O-H stretching vibrations of H-bonded water (Madejová, 2003), indicates the presence of smectite (Farmer, 1974). Additional vibrations at 3697, 3657, 669 and 650 cm^{-1} were observed, which might be attributed to kaolinite. No changes were observed in MIRS spectra of the Na-clays or H-clays as compared with those for the natural clayey sediments (not shown).

MIRS spectra of the OMCs show the characteristic bands of the natural clayey sediments in addition to specific characteristic bands of the organic modifiers. The bands recorded on OMCs spectra are those obtained after subtracting the spectra of the natural clayey sediments from the spectra of OMCs. In general, the MIRS peaks were much more pronounced with higher absorbance for modified bent sediments than for those for the modified kao sediments. The HDTM organic modifier was characterized by the bands at 2924 and 2851 cm^{-1}, which correspondence to asymmetric and symmetric vibrations of CH_2 stretching, respectively, and 1489 and 1464 cm^{-1} which assigned for CH deformation of the alkyl chain (Navrátilová et al., 2007; Li and Gallus, 2007). MIRS spectrum of kao sediment scanned after the modification with HDTM (HDTM-kao) shows the CH_2 stretching vibration at 2924 and 2853 cm^{-1} and the CH deformation bands at 1481 and 1469 cm^{-1}. MIRS spectrum of bent sediment modified with HDTM (HDTM-bent) shows the CH_2 stretching vibration at 2928 and 2851 cm^{-1} and the CH deformation bands at 1474 and 1448 cm^{-1}.

The characteristic bands of MTP were displayed at 1438 cm^{-1} (C-C stretching), 1487 and 1586 cm^{-1} (C=C stetching) and 2899 – 3021 cm^{-1} (C-H aromatic stretching), which are assigned to attached phenyl rings to the phosphonium ion (see structure in Table 2-1) (Avalos et al., 2009). Those characteristic bands were visible in the spectra of kao (MTP-kao) and bent (MTP-bent) sediments modified with MTP around 1441, 1486, 1588 and 2924 – 3066 cm^{-1}. However, the bands were relatively weak in the MTP-kao spectrum. In case of Carnitin, characteristic vibrations were found at 1733 and 1577 cm^{-1} (C=O and symmetric C-O stretching of carboxylic groups, respectively; Hardie et al., 2007), 2929 – 3046 cm^{-1} (O-H stretching of carboxylic groups; Socrates, 2001), 3418 cm^{-1} (OH of alcoholic group), 1477 - 1489 cm^{-1} (CH deformation and/or CN stretching of tertiary amine; Cruz-Guzmán et al., 2004) and 1223 - 1361 cm^{-1} (C-O stretching and bending vibrations of carboxylic groups; Hardie et al., 2007). Those characteristic bands have been observed at 2929, 1726 and as broad band around 1262 cm^{-1} in the MIRS of modified bent sediment (Carnitin-bent) and at 1586 and 1475 cm^{-1} in the modified kao sediment (Carnitin-kao). The MIRS spectrum of Cys_ester assigned the following wavenumbers: vibration around 2930 – 2981 cm^{-1} (CH stretching vibration), 1737 – 1745 cm^{-1} (C=O stretching vibration of ester group), 1600 – 1583 cm^{-1} (NH_2 deformation), 1511–1496 cm^{-1} (probably for –NH deformation), 1245 cm^{-1} (CH or CNH vibration; Pinazo et al., 1993) and four bands at 678- 607 cm^{-1} (C-S streching; Girija et al., 1995). The bands of Cys_ester were gained in the MIRS spectra of the modified kao (Cys_ester-kao) at 652 (not shown), 1748, 1738, 1510 and 1491 and of modified bent (Cys_ester-bent) at 618 (not shown), 1742, 1595, 1443, 1411 and 1270 cm^{-1}.

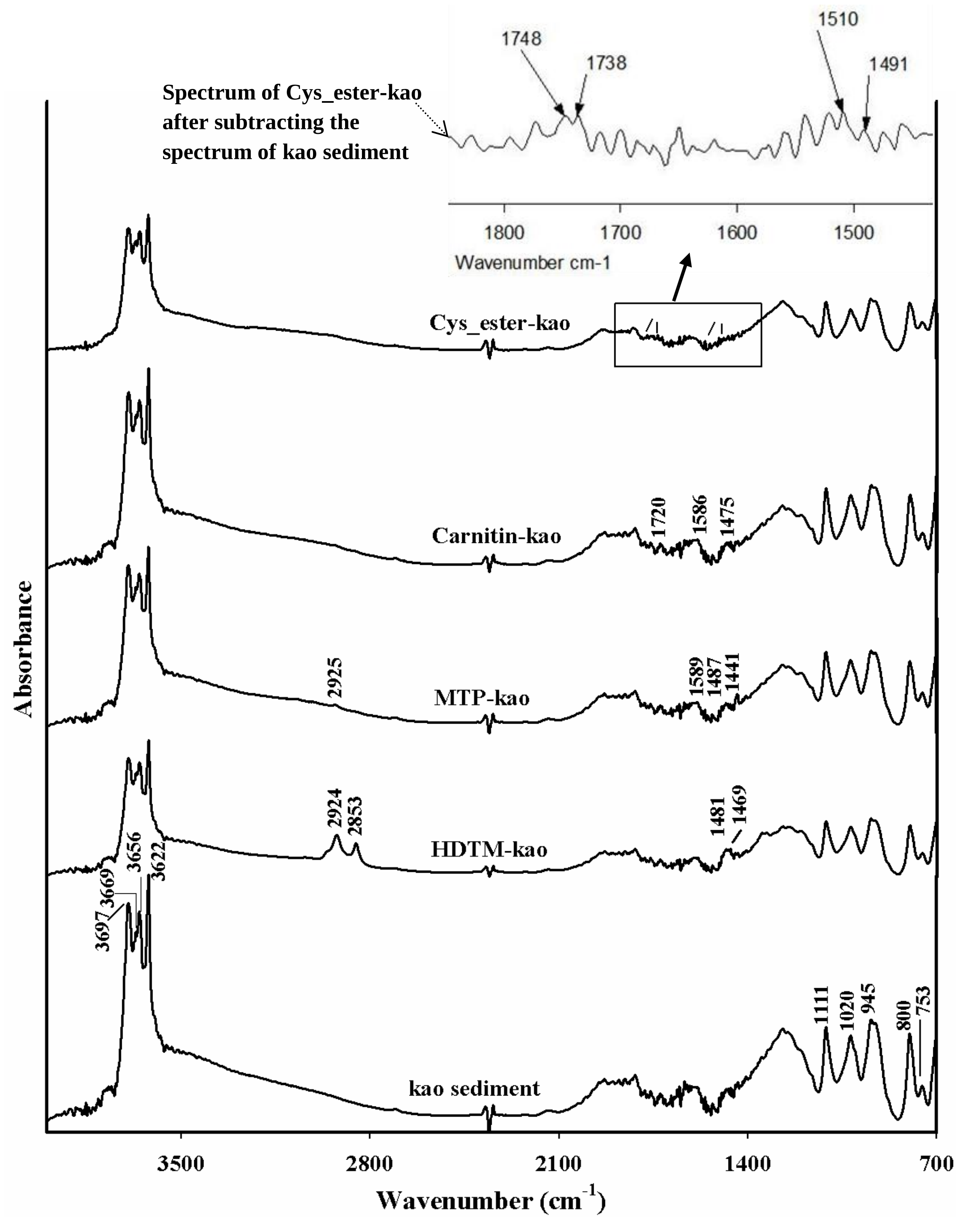


Fig. 2-3 MIRS spectra of the clayey sediment collected from Sinai before (kao sediment) and after treatment with different organic modifiers. Cys_ester, Carnitin, MTP and HDTM are the organic modifiers described in Table 2-1.

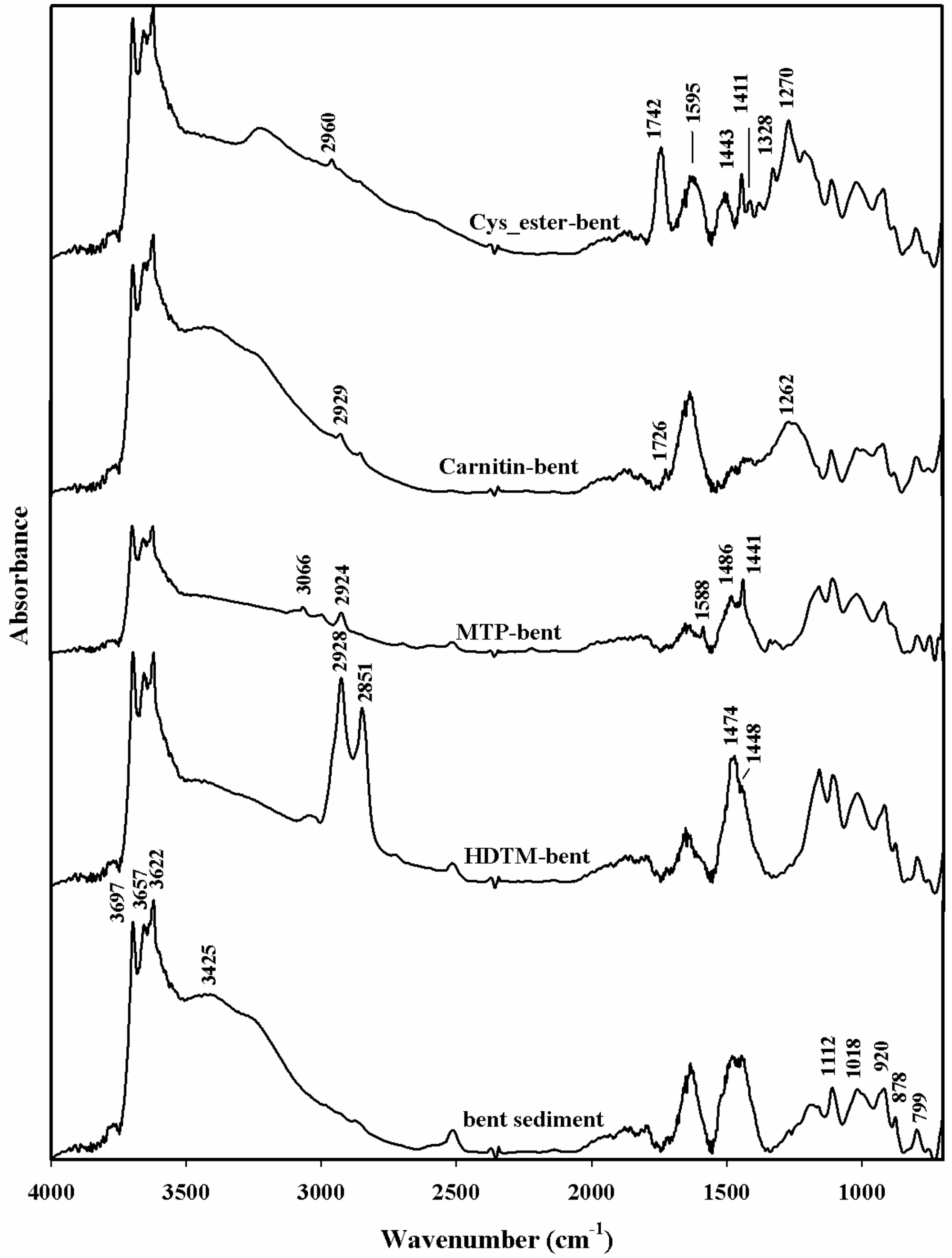


Fig. 2-4 MIRS spectra of the clayey sediment collected from Qaser el-Sagha before (bent sediment) and after treatment with different organic modifiers. Cys_ester, Carnitin, MTP and HDTM are the organic modifiers described in Table 2-1.

2.4.2 Screening experiments with cadmium, lead and dichromate ions

Natural and OMCs based kao sediments had low heavy metals removals relative to the natural and OMCs based bent sediments. Sorption of Cd^{2+}, Pb^{2+} and $Cr_2O_7^{2-}$ by OMCs based kao sediments, loaded with different concentrations of the organic modifiers are presented in Fig 2-5. Loading kao sediments with MTP and Cys_ester organic modifiers increased significantly the sorption of Cd^{2+} (by 2.4 and 2.5 fold, respectively), Pb^{2+} (by 1.4 and 1.4 fold, respectively) and of $Cr_2O_7^{2-}$ (by 2.2 and 4.4 fold, respectively) compared to the original kao sediments. Modification of kao by Carnitin at any concentration does not show any significant differences in the sorption of Cd^{2+} and $Cr_2O_7^{2-}$ as compared with the natural kao sediments. However, the high initial concentration of Carnitin increased significantly Pb^{2+} sorption by 1.4 fold. Higher sorption of $Cr_2O_7^{2-}$ relative to the natural clayey sediments, increased by eleven times, were achieved by kao modified with HDTM, while similar or reduced amounts of Cd^{2+} and Pb^{2+} were sorbed to kao loaded with HDTM compared to the natural kao sediment.

The sorption of Cd^{2+}, Pb^{2+} and $Cr_2O_7^{2-}$ to the OMCs based bent sediments loaded with different concentrations of organic modifiers are presented in Fig. 2-6. Sorption of Cd^{2+} to bent sediments modified with HDTM and MTP increased significantly with increasing initial modifiers concentrations from 0 to 5 mM, where 99 % of the metal ion concentrations in the solution were sorbed (29.3 mmol kg^{-1}). Further increase in the initial modifiers concentrations (5 to 14 mM) had no effect on the sorption. Sorption of Pb^{2+} by bent modified with HDTM and MTP at any initial concentration were similar to that obtained by the natural bent sediment, whereby 99 % of the metal ions concentrations in the solution were sorbed due to the modification by both modifiers. $Cr_2O_7^{2-}$ sorption increased in proportion to HDTM and MTP loading on bent sediment and reached to the 385 and 30 fold (46.1 and 3.6 mmol $Cr_2O_7^{2-}$ kg^{-1}), compared to the natural clayey sediment (0.1 mmol kg^{-1}).

Modification of bent sediments with Cys_ester and Carnitin modifiers decreased the sorption of Cd^{2+} by 60 % and 30 %, respectively, relative to the original bent sediment. At low initial concentrations of those modifiers, 83 and 88 %, respectively, of Cd^{2+} concentration in the solutions were removed, whereas these percentages were reduced to 38 and 63 %, respectively, at high initial modifiers concentrations.

Natural and Carnitin-modified bent sediments showed the capability to remove all the Pb^{2+} ions from the solution at all modifier concentrations except at the highest loading, which reduced the sorption of Pb^{2+} by 10 % of the metal ions concentration in the solution. Conversely, those sorbents showed negligible sorption of $Cr_2O_7^{2-}$ from the aqueous solutions.

Compared with the natural clayey sediments, a reduction in the sorption of Pb^{2+}, which reached only 30 % of the total ion concentration, was observed with increasing modifier loading on the Cys_ester-modified bent sediments. At the same time increase the modifier loading considerably enhanced the removal of $Cr_2O_7^{2-}$ up to 265 times (31.8 mmol ions kg^{-1}) higher than the original bent sediment (0.1 mmol ions kg^{-1}).

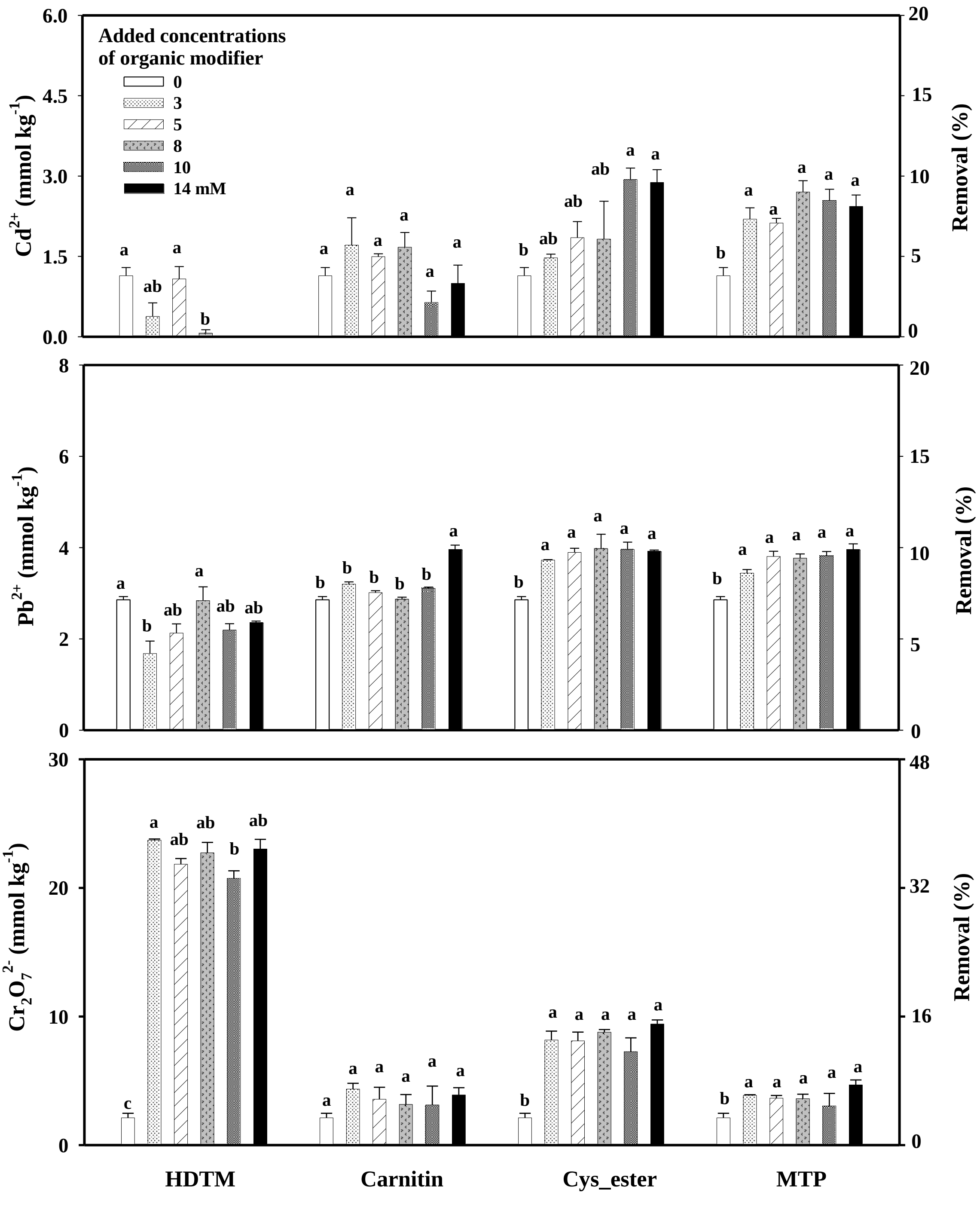


Fig. 2-5 Sorption of Cd^{2+}, Pb^{2+} and $Cr_2O_7^{2-}$ (mmol kg^{-1}) to the organically modified kao sediments prepared from different concentrations of the added modifiers.

HDTM, Carnitin, Cys_ester and MTP are the organic modifiers described in Table 2-1. The initial concentrations of Cd^{2+}, Pb^{2+} and $Cr_2O_7^{2-}$ were 0.3×10^{-3}, 0.2×10^{-3} and 0.6×10^{-3} M, respectively. Data present means and standard errors of three replicates. Different letters indicate significant differences of the sorbed metal ions ($P < 0.05$) between the different concentrations of organic modifier within one sorbent

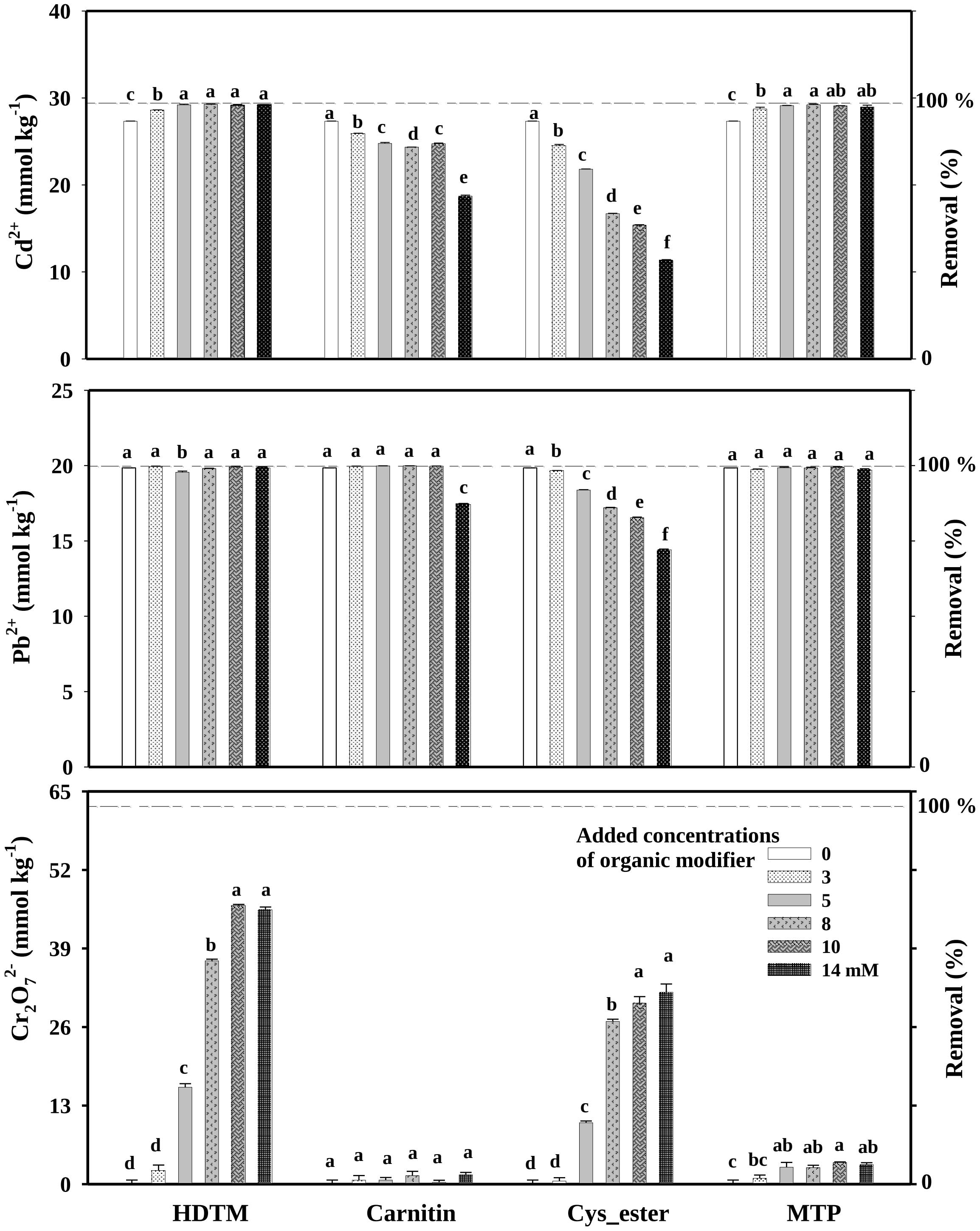


Fig. 2-6 Sorption of Cd^{2+}, Pb^{2+} and $Cr_2O_7^{2}$ (mmol kg^{-1}) to the organically modified bent sediments prepared with different concentrations of the added modifiers.

HDTM, Carnitin, Cys_ester and MTP are organic modifiers described in Table 2-1. The initial concentrations of Cd^{2+}, Pb^{2+} and $Cr_2O_7^{2-}$ were $0.3x10^{-3}$, $0.2x10^{-3}$ and $0.6x10^{-3}$ M , respectively. Data present means and standard errors of three replicates. Dashed lines indicate the removal of all metal ions (100 %) from the solution. Different letters indicate significant differences of the sorbed metal ions ($P < 0.05$) between the different concentrations of organic modifier within one sorbent

2.5 Discussion

2.5.1 Characteristics of natural clayey sediments

The XRD patterns of the natural kao sediment scanned after Mg-air dried treatment followed by Mg + Gly were not different from that of K-air dried, indicating the absence of expanded minerals. Furthermore, the disappearing of the diagnostic reflection at 7.2 Å in the scanned sample after the K-air dried treatment followed by the heating at 600C° was attributed to dehydroxylation and indicated the presence of kaolinite (Harris and White, 2007). The high content of Al-oxide and the low CEC of the natural kao sediment confirms the presence of kaolinite minerals and the absence of expanded minerals (Mahdy, 2004; Sparks, 2003).

The XRD patterns of the natural bent sediment showed the diagnostic d-spacing of smectite group minerals which is consistence with that observed by Brindley (1955). The detected reflection at 7.1 Å in the clay fraction of the natural bent sediment, which was destroyed after K+600°C treatment, might indicate the presence of kaolinite as minor mineral. In addition, the high content of CaO and relatively high contents of K_2O and Na_2O suggest the presence of calcite and feldspar in the natural bent sediment as well (Stahr et al., 2000), which supports the obtained XRD results. The measured CEC value of natural bent sediment was higher than that of natural kao sediment due to the presence of expanded smectitic minerals. However, CEC was lower than reported in published data for pure smectitic minerals, (70-120 cmol kg^{-1}; Jasmund and Lagaly, 1993), which was probably due to the presence of other components in bent sediment besides smectites.

The obtained results of MIRS analyses depicted the diagnostic vibrations of kaolinite and quartz in the natural kao sediment and the diagnostic vibrations of quartz, smectite and kaolinite minerals in the natural bent sediment (van der Marel and Beutelspacher, 1976; Farmer, 1974). Results of MIRS spectra were in agreement with the sediments composition suggested from the results of XRD and chemical analyses of the natural clayey sediments.

2.5.2 Characteristics of OMCs

In general, all prepared OMCs from the different sediments showed increased organic carbon contents (OC) as compared with the natural clayey sediments indicating a successful loading of the organic modifiers on the sediments.

Smaller CEC of kao sediment compared to bent sediment is the reason for the low loading of organic modifiers on OMCs based on kao sediments as compared with those based on bent sediments.

Low organic modifier contents and low loading ratio (%) of the bent sediment after modification with Carnitin (Carntin-bent) even at the highest initial modifier concentration (14 mM) indicated that Carnitin has a low affinity to the clay’s surface and low ability to replace the hydrated inorganic ions (Na^+) on the exchanged sites of the natural clayey sediments. A similar case was also found with the modified kao sediment. The results were in agreement with those found by Cruz-Guzmán et al. (2004), who demonstrated that Carnitin, a monovalent cation, has low affinity to the negative charge on the clay surface due to the presence of carboxylic functional groups with negative charge in its molecular structure (Table 2-1). However, Cys_ester is a divalent cation, therefore, it showed a better capability to satisfy the surface charges and to replace the exchanged Na^+ ions on the natural clayey sediments, in which two exchangeable sites can be satisfied by one Cys_ester cation. Consequently, the clayey sediments modified by different concentrations of Cys_ester achieved higher loading ratio as percentage of CEC as compared by those modified by different concentrations of Carnitin.

Higher loading ratios (%) of CEC of the natural clayey sediments were achieved by the treatment with MTP and HDTM as compared with loading by Carnitin and Cys_ester, referred to the effective replacement of the hydrated Na^+ ions by the large molecules of MTP and HDTM (with 19 carbons) as compared with Carnitin (7 carbons) and Cys_ester (8 carbons). Zhang et al. (1993) and Shen (2004) pointed out that organic cations with large alkyl chain can effectively replace inorganic ions on the clay’s exchange sites more effectively than those with short alkyl chain. Most of the organic modifiers may loaded via saturating the surface charges and the exchangeable sites on clays and thus the loading ratios (%) were within the CEC values of the clayey sediments. However, increasing HDTM concentration by more than 5 mM increased the modifier loading beyond the CEC of bent sediment (128 - 144 % of CEC). The excess of the loading percentages indicted that other mechanisms in addition to the saturation of the exchangeable sites were involved. Shen (2004) and Jaynes and Vance (1996) reported that adsorption of organic cation on clay occurred mainly via electrostatic force, while the role of van der Walls forces and hydrophobic bonding took place with the excess loading of the organic cations.

Whereby, interaction between the nonpolar moiety (alkyl chain) of the exchanged HDTM and that of the excess HDTM occurred.

The appearance of characteristic vibrations of the pure organic modifiers in the MIRS of OMCs indicated the successful formation of the OMCs. However, the weak absorbance of the bands observed in MIRS spectra of OMCs based kao sediments relative to those of OMCs based bent sediments are attributed to the low mass of the organic modifiers loaded on kao sediments. This explanation was in agreement with the obtained results of organic modifier contents of the modified kao sediments.

In preliminary measurements, Kao sediment was scanned by XRD before and after the modification with HDTM (HDTM-kao). The obtained pattern of HDTM-kao remained unchanged as compared with that obtained for the natural kao sediment (not shown). The similarity of the obtained XRD patterns may indicate that adsorption of the organic modifier was on the external surface of the clay (Rangsriwatananon and Khumbudda, 2007). That result was expected since kaolinite is the predominant clay mineral in kao sediment. Jaynes and Boyd (1991) concluded that HDTM did not change the XRD patterns of the non-expandable clays. Under the conditions of this study, XRD technique did not help to characterize the OMCs based kao sediments. Nevertheless, the loading of the different organic modifiers on kao sediments were confirmed by increasing OC contents after the modification as compared with the natural kao sediments. In addition, the obtained MIRS spectra of OMCs based kao sediment depicted the diagnostic vibrations of the natural kao sediment as well as those of the organic modifiers. Thus, MIRS results are a further evidence of a successful modification.

The basal spacing of the natural bent sediment at 14.5 Å was shifted to 15.3 Å in Na-clay due to the exchange by the hydrated Na^+ ions. After the modification by Cys_ester, the basal spacing collapsed to 13.9 Å. Cys_ester is a low hydrated divalent cation (Cruz-Guzmán et al., 2004), and thus the replacement of the hydrated Na^+ ions by the low hydrated Cys_ester led to an exclusion of the interlayer water resulting in reduction of the basal spacing. A previous study (Yariv and Cross, 2002) reported that basal spacing of untreated montmorillonite of 15 Å is a sum of the clay's layer thickness 9.5 Å and two layers of water. When a divalent organic cation was adsorbed, the basal spacing reduced to 13 Å due to the desorption of the interlayer water proposing monolayer arrangement of the organic ion in the clay's interlayer, showing similarities to the results obtained with Cys_ester. The exclusion of the interlayer water after the modification with Cys_ester was demonstrated by the obtained results from MIRS spectrum of Cys_ester-bent, in which a decrease in absorbance of bands in the region 3455-3400 cm^{-1} relative to that of the bent sediment were observed.

Unlike Cys_ester, the modification by Carnitin (15.2 Å) caused a little change in the basal spacing compared with the Na-clay (15.3 Å), which might indicate partial replacement of hydrated Na^+ ions and partial desorption of interlayer water. These results were in consistence with those obtained from the MIRS spectrum of Carnitin-bent, whereby, the remaining of the broad band in the region of 3455-3400 cm^{-1}, corresponding to the interlayer water as compared with bent sediment spectrum, was depicted. Nonetheless, the observed characteristic vibrations of the Canitin modifier on MIRS spectrum of Carnitin-bent as well as the increases obtained of the organic modifier content compared to that of the natural bent sediment confirmed the loading of Carnitin modifier on the bent sediment. According to Bergaya et al. (2006), Carnitin-bent with d-spacing 15.2 Å might suggest a monolayer arrangement of the organic modifier in the interlayer space of the clay.

The obtained XRD and MIRS results for Cys_ester- and Carnitin-bent were in agreement with those found by Cruz-Guzmán et al. (2004).

Modification of bent sediments by MTP or HDTM led to expand basal spacings due to the adsorption of these modifiers in the clays' interlayer space, proposing bilayer arrangement for MTP and pseudo-trimolecular arrangement for HDTM in the interlayer of clay (Bergaya et al., 2006; He et al., 2007). The adsorption of these modifiers resulted in a dehydration of the interlayer water due to the replacement of the hydrated Na^+ ions. The dehydration was confirmed by the decreasing in the absorbance bands of water vibrations in the MIRS spectra of MTP- and HDTM-bent as compared to the natural bent sediment. The obtained basal spacing were similar to those recorded by He et al. (2007) and Patel et al. (2007) for adsorbed HDTM and MTP on purified montmorillonite.

2.5.3 Removal of heavy metals by OMCs

Removal of heavy metals by clays occurs via ion exchanging and / or complexing with the surface functional groups (silanol and aluminol groups) at the clay edges. With increasing loading of organic modifiers in the clay's interlayer surfaces, the removal of heavy metals might attribute mainly to the complexation with the edge sites (Oyanedel-Craver and Smith, 2006).

The kao sediment composed mainly of kaolinite minerals with low CEC, whereas smectitic minerals with higher CEC were the main component in bent sediment. Therefore, sorption of heavy metal by OMCs based kao sediments were lower compared with OMCs based bent sediments. A significant effect of the modification on kao sediment was observed with Cys_ester, MTP and HDTM, but not with Carnitin. However, increasing initial modifier concentrations (> 3 mM) showed no further increase in the sorption of metals. These results were in consistence with those obtained from the organic modifier contents, showing that the increase of the initial modifiers concentration from 0 to 3 mM increased the loading ratios of Cys_ester, MTP and HDTM, while lowest loading ratio obtained with Carnitin. Thus the sorption of heavy metals by kao sediment were similar to those by Carnitin modified kao sediment. Moreover, changing the initial modifiers concentration from 3 to 14 mM did not cause any changes in the organic modifier contents on kao sediments indicating no increase of the modifiers loading, and did not reflect any relevant differences in the sorption of metal ions.

It can be concluded from the results that HDTM-, Cys_ester- and MTP-modified kao sediment had the capability to remove $Cr_2O_7^{2-}$ with greater efficacy than the other metal ions. The efficient removal of inorganic anionic ions by kaolinite mineral modified with HDTM was reported in a previous study by Li and Bowman (2001).

The lower sorption of Pb^{2+} and Cd^{2+} on Cys_ester-modified bents than those on Carnitin-modified bents indicate that the modification with Cys_ester caused a larger reduction in the available sorption sites on the clay surfaces compared with the modification with Carnitin and led to a competition with the inorganic ions on these sites. This behavior of Cys_ester and Carnititn are compatible with the calculated values of the loading ratios (%) obtained after exchanging with different concentrations of both modifiers, in which Cys_ester showed higher values indicating higher occupation than Carnitin. Furthermore, exchanging the natural bent sediment with Cys_ester reduced the basal spacing of the clay (see XRD results obtained after the modification). This collapse of the clay’s interlayer surface, thereby, could limit the access of the metal ions to the sorption sites.

The greater sorption of Pb^{2+} achieved by Carnitin-modified bents compared with Cd^{2+} could be attributed to the affinity between the carboxyl group in the Carnitin structure and Pb^{2+} ions. This affinity phenomenon was mentioned previously by Sheng et al. (1999) and Cruz-Guzmán et al. (2006).

Sorption characteristics of Cd^{2+} and Pb^{2+} on HDTM and MTP modified bent sediments were in accordance with the results on sorption of Cd^{2+} and contradict the results on sorption of Pb^{2+} to HDTM-modified bentonite obtained by Yoo et al. (2004). They observed that the sorption of Cd^{2+} on the HDTM-modified bentonite was similar to that on the untreated clay, while the sorption of Pb^{2+} on the modified bentonit was lower than the untreated.

Impacts of different modifiers concentrations were pronounced with the sorption of $Cr_2O_7^{2-}$ to Cys_ester and HDTM-modified bent sediments. HDTM with quaternary ammonium and Cys_ester with two amino positive functional groups in their structures (Table 2-1) play important roles in neutralizing the negative charges predominated on the clays' surfaces. They reduce the repulsion forces between the clays' predominant surface charges and $Cr_2O_7^{2-}$ ions, resulting in a possible access of $Cr_2O_7^{2-}$ to suitable binding sites. In a previous study Majdan et al. (2005) suggested that the sorption of chromate on HDTM-modified-bentonite occurred via alkylammonium- chromates and dichromates formation.

Independent of the sediment type, sorption of $Cr_2O_7^{2-}$ to sediments exchanged with HDTM (a monovalent cation) was remarkably higher than that exchanged with Cys_ester (a divalent cation), indicating a higher neutralization of the surface charge by HDTM. This is attributed to an increase in the mass of HDTM loaded on the clay, achieving a higher loading ratio as compared with the Cys_ester at the same initial modifier concentration. Moreover, increasing the loading of HDTM beyond the CEC of bent sediment could reverse the charges on the clays' surfaces providing more adsorption sites for $Cr_2O_7^{2-}$ ions. Zhang et al. (1993) stated that the quaternary amine cations keep their cationic form when the loading ratio of the large quaternary alkyl ammonium ion is over the clay's CEC, resulting in charge reversal. In our study, increasing the modifier initial concentration from 3 to 14 mM led to an increase of the loading ratio of Cys_ester form 0.2 to 77.6 % of the bent's CEC and the loading ratio of HDTM from 56.0 to 144 %. Hence, development of positive charge probably occurred and caused extra sorption of $Cr_2O_7^{2-}$ to the bent exchanged with HDTM. The development of the positive charge on the montmorillonite surface after the modification with HDTM was also suggested by Wang et al. (2004). Nevertheless, this later interpretation (reverse surface's charge) needs more specific analyses to be confirmed.

2.6 Conclusions

This study focuses on the production and characterization of organically modified clayey sediments (OMCs) prepared from natural clayey sediments. One of the selected sediments composed mainly of kaolinite clay mineral (kao sediment); whereas in the other sediments smectite and kaolinite were the main clay minerals (bent sediment). Bent sediment had a higher pH and total carbon content (%) compared with the kao sediment. Contents of organic carbon (%) of the OMCs were increased by the modification compared with the natural clayey sediments. HDTM achieved the highest loading on both clayey sediments among the modifiers, while Carnitin had the lowest loading. MIRS spectra of the OMCs prepared from both sediments showed the characteristic absorbance of natural clayey sediments as well as that of the organic modifiers. Increasing organic carbon contents of OMCs relative to the natural clayey sediments and the results obtained from MIRS analyses of OMCs confirmed the successful loading of the organic modifiers on the sediments. OMCs based on bent sediments showed changes in the basal spacing than that recorded for the natural bent sediments. The basal spacing changed from 14.5 Å to 13.9, 15.2, 17.1 and 19.7 Å after the modification with Cys_ester, Carnitin, MTP and HDTM, respectively. Increasing loading of Cys_ester and MTP on OMCs prepared from kao sediments enhanced the sorption of the tested metal ions compared with their sorption on the natural clayey sediment. Similar trend was obtained with increasing loading of MTP on OMC based bent sediment. However, increasing the loading of Cys_ester on the OMCs based bent sediments inhibited the sorption of Cd^{2+} and Pb^{2+} but improved significantly the sorption of $Cr_2O_7^{2-}$ relative to the sorption on natural bent sediment. The modification with HDTM improved the tendency of the natural clayey sediments toward the removal of $Cr_2O_7^{2-}$. Increasing loading of HDTM had no relevant effect on the sorption of Cd^{2+} and Pb^{2+} by OMCs. OMC with Carnitin showed similar sorption of the tested metal ions as that by the kao sediment. The high loading ratio of Carnitin (= 23.2 % of the CEC of clay) on OMC based bent sediment decreased the sorption of Cd^{2+} and Pb^{2+} compared to the natural clayey sediments but had no effect on the sorption of $Cr_2O_7^{2-}$.

3. Sorption and Desorption of Cadmium, Lead and Dichromate from Aqueous Solutions by Organically Modified Bentonitic Sediments

3.1 Abstract

Sorption characteristics of Cd^{2+}, Pb^{2+} and $Cr_2O_7^{2-}$ from single and binary component systems using organically modified bentonitic sediments (OMCs) were studied. OMCs were synthesized from the sodium form of a natural clayey sediment (Na-bent) from Qaser el-Sagha, El Fayoum, Egypt, in combination with Humic acid (HA), L-Cystine dimethyl ester (Cys_ester), L-Carnitine (Carnitin), Methyltriphenylphosphonium (MTP) and Hexadecyltrimethyl-ammonium (HDTM) as organic modifiers. The characteristics of the sorption of metal ions on OMCs were investigated under different conditions such as pH, solutes concentrations, sorption time and electrolyte concentration. Desorbabilities of the metal ions from the loaded OMCs were also tested.

Overall, Na-bent and OMCs were effective in sorbing of the cationic metal ions. However, the removal of $Cr_2O_7^{2-}$ form aqueous solutions was only possible by OMCs modified with MTP, HDTM, HA and Cys_ester. Langmuir isotherm model fits the experimental data better than Freundlich model and the sorbed amounts of the metal ions were different according to modifier type. The maximum sorption capacities of the OMCs decreased in the order MTP-bent > Carnitin-bent > HDTM-bent > HA-bent > Cys_ester-bent for the sorption of Cd^{2+} and in the order of MTP-bent > HDTM-bent > Carnitin-bent > HA-bent > Cys_ester-bent for the sorption of Pb^{2+}. Among the sorbents, OMC modified with Cys_ester exhibited the highest sorption of $Cr_2O_7^{2-}$.

The sorption processes followed pseudo-second-order kinetic models and the optimal sorption of the metal ions were approached at pH ranging from 4 to 8 for Cd^{2+}, from 4 to 6 for Pb^{2+} and at pH 4 for $Cr_2O_7^{2-}$. Increasing concentration of electrolytes reduced significantly the removals of Cd^{2+} and Pb^{2+}. The removals of $Cr_2O_7^{2-}$ by the OMC modified with Cys_ester were enhanced by increasing concentrations of $Ca(NO_3)_2$ and $NaNO_3$.

Competitive behavior was observed with sorption of the metal ions from the binary component system by selective OMCs except the one modified with Cys_ester.

Sorption of Cd^{2+} in the presence of $Cr_2O_7^{2-}$ was lower than that obtained when it is the only solute in solutions. Presence of Cd^{2+} displayed synergetic effects on the sorption of $Cr_2O_7^{2-}$.

The results demonstrated that the proposed OMCs have potential to remove heavy metals from low quality water under different conditions and the successful desorbabilities of the metal ions enhance the economic aspect of using OMCs as cost effective sorbents.

3.2 Introduction

Cadmium, lead as cationic and chromate as anionic pollutants are commonly occurring heavy metals in wastewater. These pollutants are released into the environment from human activities, such as agricultural practices, lead containing pesticides, transport, industrial activities and waste disposal such as pigments and stabilizers in plastic, electroplating, metal plating, wood preserving, anodizing, ink manufacture, glass, ceramics, battery manufacturing (Anonymous[6], 2002). They are known as hazardous materials for human and animal health and the environment. The "Comprehensive Environmental Response, Compensation and liability Act" recorded lead, cadmium and chromate as No. 2, 7 and 17, respectively, in its list of priorities concerning hazard substances (ATSDR 2011). In general, lead causes kidney damage, influences the central nervous system, slowing down nerval response particularly in children influencing learning abilities and behavior. Cadmium accumulates in the kidney and causes its dysfunction; moreover, it is classified according to the "International Agency for Research on Cancer" (IARC, 1993) in Class 1 (carcinogenic to humans). Chromium can exist in multiple valence states, among which the hexavalent form, Cr (VI), has the highest environmental hazard (Abdel-Sabour, 2007). It has a number of adverse effects ranging from causing irritation to cancer for human and causing inhibition of growth and various metabolic processes of microorganisms. IARC (1990) has classified Cr (VI) in Group 1 (human carcinogen). Because of the above-mentioned hazards, the removal of heavy metals has a high priority in environmental remediation and cleaning up.

Many papers have been published on the potential use of clay minerals to remove cationic heavy metals from wastewater (e.g. Zahra et al., 2008; Gupta and Bhattacharyya, 2008; Eba et al., 2011). In contrast, clays without previous modification, showed very limited affinity for anions (Bois et al., 2003). Some studies pointed out the possible sorption capabilities of clay minerals for anionic pollutants after modification with organic compounds producing organo-clay complexes (Kaufhold et al., 2007). Krishna et al. (2000), and Li and Bowman (2001) reported that the adsorption of Cr (VI) significantly increased on clay modified with hexadecyltrimethylammonium (HDTM) compared with the unmodified clay, which had no sorption affinity for Cr (VI) ions.

Modification of the clay minerals also affects the adsorption of cationic pollutants. Using organic modifiers containing certain functional groups in producing of organo-clays could enhance adsorption of cationic heavy metals. Oyanedel-Craver and Smith (2006) reported that the adsorption of Pb, Cd, Zn and Hg to bentonite loaded with the organic cations HDTM and benzyltriethyl-ammonium at 25% of its cation exchange capacity were similar to or greater than that of the sorption to the untreated bentonite. Lagadic et al. (2001) used thiol-functionalized layered magnesium phyllosilicate material (Mg-MTMS) prepared artificially from mixing magnesium chloride with mercaptopropyltrimethoxy-silane in methanol-aqua solution to adsorb Pb, Cd and Hg. Mg-MTMS exhibited strong adsorption for each heavy metal. Additionally, Mg-MTMS showed an equivalent sorption for the heavy metals in mixed solutions. The results are in agreement with those of Stathi et al. (2007), who used ammonium and organic cations containing functional groups (-NH_2, -COOH, -SH or -CS_2) with montmorillonite clay to prepare organo-clay complexes for the adsorption of Pb, Cd and Zn from aqueous solutions as a function of pH. They concluded that the loaded organic cations behaved as specific binding site on the clay which led to a significant enhancement of sorption selectivity and capacity as compared with the untreated montmorillonite.

Relatively few studies have been done on removal of heavy metal by using natural adsorbents. Hizal and Apak (2006) investigated the adsorption of copper and lead ions on kaolinite-based clay minerals individually and in the presence of humic acid. The authors suggested that humic acid coated kaolinite worked most likely as chelating ion-exchanger sorbent for heavy metals rather than inorganic ion-exchanger. Cruz-Guzmán et al. (2006) prepared organo-clay complexes from natural organic cations L-Carnitine, L-Cysteine ethyl ester, L-Cystine dimethyl ester, and thiamine cations with two montmorillonite clay minerals and compared them with the clay loaded with a non functionalized organic cation (HDTM). They investigated the sorption of Pb^{2+}

and Hg^{2+} by the prepared complexes. The results showed that the functionalized organo-clays containing sulfur adsorbed Hg^{2+} very effectively. In contrast, as compared with the untreated montmorillonite, most of the organo-clay complexes were not effective in adsorbing Pb^{2+}, except the montmorillonite treated with L-carnitine, which possesses carboxyl groups. Assaad et al. (2007) studied the removal of Co^{2+}, Ni^{2+} and Cu^{2+} from water by coagulation–flocculation in the chitosan-montmorillonite systems. They found that coagulation–flocculation depends on pH and the composition of the liquid medium. Both chitosan and montmorillonite exhibited great efficiency in metal ion removal when used separately and displayed a synergy effect when used simultaneously. The removals of the studied cations were significantly affected by the ratio of chitosan/montmorillonite, solution pH and concentration of the metal cations. Abou Hussien et al. (2002) found that the adsorbed amounts of Fe and Zn increased with increasing amount of humic acid on the clay.

Studying kinetic properties and factors that affect the adsorption process could help to improve the ability of modified clays to retain pollutants. Say et al. (2006) incorporated dithiocarbamate functional groups into the nanolayer of organo-clays and used it in the adsorption of heavy metals. They reported a maximum adsorption of Cr^{3+} at pH 4 and of Cd^{2+} and Pb^{2+} at pH 6.0; adsorption equilibria were reached within 15-20 min. The authors showed that the desorption of the metal ions were effective by using 0.5 M NaCl, which indicated the possibility to use the sorbents in repeated adsorption–desorption cycles. Erdemoğlu et al. (2004) found that maximum adsorption of Pb ions on modified pyrophyllite was at pH about 6.5 and adsorption time was found to be 90 min. Brum et al. (2010) used a cationic surfactant cetylpyridinium bromide (CPB) to prepare organo-clay based montmorillonite clay minerals in order to remove Cr(VI) from aqueous solutions. CPB-montmorillonite effectively adsorbed Cr(VI) anions over a wide pH range from 3.0 to 6.0. The pH of the suspension had a significant influence on the adsorption of Cr(VI), as the adsorption decreases with the increase of pH above 6. The pH-dependence is related to the surface charge of the adsorbent.

More work is needed to characterize the sorption of different heavy metals on naturally occurring sediments modified with natural organic materials, containing certain functional groups. Studying the potential removal and/or the competition effect of the metal ions on the organically modified clayey sediments is an important step for the application of those prospective sorbents in wastewater treatment.

In the current study, naturally occurring clayey sediment in combination with a variety of organic modifiers, containing different functional groups (-NH_2, -COOH, -CO, -CS_2, -OH, P^+ or –Phenol) were used for the preparation of organically modified bentonitic sediments (OMCs). OMCs were evaluated with respect to their abilities to sequester Cd^{2+} and Pb^{2+} (cationic pollutants) and $Cr_2O_7^{2-}$ (anionic pollutants) from single and binary aqueous solutions, considering the following hypotheses: i) the presence of functional groups in the organic modifiers increase the tendency of organically modified bentonitic sediments to retain Cd^{2+}, Pb^{2+} and $Cr_2O_7^{2-}$ ions. ii) The efficiency of heavy metal sorption depends on the concentration of metal ions, the initial solution pH, the electrolyte concentration and the sorption time.

3.3 Materials and methods

3.3.1 Synthesis of organically modified bentonitic sediments

The basic material used for preparation of organically modified bentonitic sediments (OMCs) is a natural clayey sediment (bent) collected from El-Fayoum, Egypt (Qaser el-Sagha, 29^o 34’ 06” N and 30^o 49‘ 52“ E). Smectite clay mineral is the main component in the sediment with a cation exchange capacity (CEC) of 48.1 cmol kg^{-1} (Chapter 2). The material was converted to the sodium form and denoted as Na-bent. The procedure used for the preparation of Na-bent was similar to that outlined in Chapter 2, which comprises the following steps: grinding, sieving, exchanging with Na^+, washing free of Cl^-, drying and grinding again with a ball-mill for 3.5 min. Suspension of Na-bent in 1 mM HNO_3 was prepared and used for the producing of OMCs.

OMCs were prepared by dissolving the organic modifiers mentioned in Table 3-1 in 1 mM HNO_3 and mixing each solution with Na-bent suspension to obtain a solid concentration of 10 g l^{-1}. The final concentrations of modifiers in the suspensions are shown in Table 3-1. The mixtures were then shaken at room temperature for 72 h at 175 rpm. Afterwards, suspensions were centrifuged (using Hermile Z513 Centrifuge, Germany), washed with ultrapure deionized water and freeze dried.

Before using the OMCs for the following sorption experiments, the materials were ground for 1.5 – 2.3 min using a ball-mill and kept in plastic vials under dry conditions. The acronyms, content of total organic carbon (TOC) and cation exchange capacities (CEC) of the different sorbents prepared are summarized in Table 3-1. CEC were determined by the ammonium acetate method (Chapman, 1965). TOC were determined by dry combustion in a stream of He/oxygen (oxidation/reduction) (elementary analysis; DIN ISO [45014], 1996b) using NA 2500 elemental analysis (EC Instruments, Germany). Characterization of OMCs and the natural clayey sediments were described in chapter 2.

3.3.2 Sorption and desorption experiments of cadmium, lead and dichromate

3.3.2.1 Sorption isotherm experiments

All metal sorption studies were performed in batch experiments. The tested concentrations of heavy metals were ranging from 0.00 to 1.24x10^{-3} M of Cd^{2+}, from 0.00 to 3.44x10^{-3} M of Pb^{2+} and 0.00 to 9.49x10^{-3} M of $Cr_2O_7^{2-}$ as $Cd(NO_3)_2 \cdot 4H_2O$, $Pb(NO_3)_2$ and $K_2Cr_2O_7$ salts, respectively. The sorption isotherm experiments were performed by equilibrate of 5 ml of 0.01 M NaCl aliquot, whose initial pH value was 4.7 ± 0.3, containing the desired concentration of heavy metal with 50 mg of Na-bent or OMCs in 10 ml polypropylene centrifuge tubes in triplicates. Equilibration was reached after 24 hours shaking at 175 rpm at room temperature (23±2 °C). Changes in the initial pH of the solution after the contact with sorbents were recorded. To simulate natural conditions of polluted water, the author did not correct the changes in the pH of the suspension (the initial solution pH after contacting with the sorbents in the presence of heavy metals), which is different than the approach in literature. Thus it favours an easier handling in the application of the proposed sorbents in the remediation of natural wastewater. The pH of the samples at zero concentration of heavy metals were measured to test the effect of the sorbents on the initial pH after equilibration for 24 h and were denoted as pH_{est}. The pH_{est} changed to 9.3 with Na-bent, 8.9 with HDTM-bent, 8.8 with MTP-bent, 8.0 with Carnitin-bent, 4.4 with Cys_ester-bent and 5.9 with HA-bent. Those changes in the initial pH are assumed to occur also with the presence of heavy metals. According to this assumption, pH_{est} were used as the equilibration pH to estimate the speciation of the Cd^{2+} and Pb^{2+} by "visual Minteq program version3.0" (Gustafsson, 2011). This program is built based on USEPA's "MINTEQA2" software. The database of visual Minteq program includes Cr^{3+} speciation but does not include the speciation of Cr^{6+}. Therefore, the $Cr_2O_7^{2-}$ speciation was done according to Baes and Mesmer (1976) and Dionex (1998).

3.3.2.2 Desorption experiments

Three desorbing agents, 0.1 M HCl, 0.1 M NaOH solutions and tap water, were used separately to estimate metal desorbability from OMCs after interaction with aqueous metal solutions have initial concentrations of 1.36×10^{-3} M and 1.2×10^{-3} M for Cd^{2+} and Pb^{2+}, respectively. For $Cr_2O_7^{2-}$, desorption experiments were performed only for the Cys_ester-bent with 2.9×10^{-3} M $Cr_2O_7^{2-}$ initial concentration. Solid residues remaining in the centrifuge tubes after the sorption experiments were treated with 5 ml of each desorbing agents. Suspensions were shaken on a mechanical shaker at 175 rpm for 24 h at room temperature followed by centrifugation at 4500 rpm for 30 min and subsequent filtration of the supernatants using blue band filter paper. Heavy metal concentrations in supernatants were analysed by AAS (Unicam 939 AA Spectrometer). Two sequential desorption steps were performed (Desorption I and II). All desorption studies were conducted in triplicates. Relative desorption was calculated by Eq. 3-1:

$$Desorption\,\% = \frac{C_{des}}{C_{load}} \times 100 \quad \text{----------------------------------} \quad \text{Eq. 3-1}$$

where C_{des} is the concentration of metal ions in the desorbing solution and C_{load} is the loaded amount of this element on the OMCs.

3.3.3 Factors affecting sorption

3.3.3.1 Sorption time

For kinetic studies, sorption experiments were performed at time intervals between 30 and 1440 minutes. The initial concentrations of the metal ions were 3×10^{-3}, 3.44×10^{-3} or 11.2×10^{-3} M of Cd^{2+}, Pb^{2+} or $Cr_2O_7^{2-}$, respectively. The experiments were conducted in triplicates under constant conditions of pH (5) and ionic strength (0.01 M NaCl) at ambient conditions and a sorbent concentration of 10 g l^{-1}.

3.3.3.2 pH of initial solution

Sorption experiments were carried out by shaking the desired amount of OMCs with aqueous solutions containing $0.3x10^{-3}$ M Cd^{2+}, $0.2x10^{-3}$ M Pb^{2+} or $0.6x10^{-3}$ M $Cr_2O_7^{2-}$. The tested pH values ranged from 2 to 8, from 2 to 6 and from 2 to 10, respectively, for Cd^{2+}, Pb^{2+} and $Cr_2O_7^{2-}$,and were adjusted either by NaOH or HCl (0.1-0.01 M) using a digital pH meter E532, Metrohm Herisau, Switzerland. Solutions without sorbents were prepared by identical procedures to determine the initial concentrations. The results obtained at pH values higher than the mentioned limits were discarded due to the reduction of metal concentrations recorded by measuring the initial solutions. The experiments were done in triplicates at constant conditions such as ionic strength (0.01 M), sorbent concentration (10 g l^{-1}) and shaking time (24 h).

3.3.3.3 Electrolyte concentration

Sorption of heavy metals by OMCs in two electrolytes were studied by suspending of 10 g l^{-1} OMCs in $Ca(NO_3)_2$ or $NaNO_3$ solutions at three concentrations (0.001, 0.01, 0.1 M). The suspensions were shaken at 175 rpm for 24 h at ambient conditions.

3.3.4 Sorption experiments with combinations of cadmium and dichromate

According to the results obtained from the sorption isotherm experiments of single heavy metals (see section 3.5.2.), Cys_ester-, MTP- and HDTM-bent were selected as the most promising OMCs for the removal of Cd^{2+} and $Cr_2O_7^{2-}$ from aqueous solutions. Sorption experiments of Cd^{2+} and $Cr_2O_7^{2-}$ from their single and binary component systems with the selected OMCs or Na-bent were conducted at pH 4 in 0.01 M $NaNO_3$ as background solution. The initial concentrations of the sorbates were 0 - 3 and 0 - 6 mM of Cd^{2+} and $Cr_2O_7^{2-}$, respectively, and the solid concentration was 10 g l^{-1}. The suspensions were shaken at 175 rpm for 24h at ambient conditions.

In all sorption experiments, solutions without sorbents were prepared by identical procedures to determine the initial metal ion concentrations. After reaching the desired shaking time, the suspensions and solutions were centrifuged at 4500 rpm for 30 min. The concentrations of heavy metals in the supernatants or solutions were determined by atomic absorption spectroscopy (AAS). The sorbed amounts of the metal ions per unit mass (Cs) were calculated by Eq 3-2:

$$C_s = \frac{C_i - C_e}{SR} \quad \text{----------------------------------} \quad \text{Eq 3-2}$$

where Ci and Ce are the initial and the end concentration of the metal ions in the solution, respectively. SR is the solid concentration.

3.4 Models calculation

The data from the sorption isotherms of Cd^{2+}, Pb^{2+} and $Cr_2O_7^{2-}$ were analyzed using two commonly applied isothermal models: Freundlich (Eq. 3-3; Sparks, 2003) and Langmuir (Eq. 3-4; Langmuir, 1918). In addition, a simple linear model was used for analysing $Cr_2O_7^{2-}$ sorption data.

$$C_s = K_f C_e^{\frac{1}{n}} \quad \text{----------------------------------} \quad \text{Eq. 3-3}$$

where C_s is the sorbed amount of metal ions per unit mass, C_e is the concentration of metal ions at equilibrium in the solution and K_f and 1/n are the adsorption capacity and the adsorption intensity, respectively.

$$C_s = \frac{bKC_e}{1+KC_e} \quad \text{----------------------------------} \quad \text{Eq. 3-4}$$

where K and b are the theoretical Langmuir affinity constant and the maximum adsorption capacity, respectively.

The constants of Freundlich and Langmuir were calculated from the intercept and slope of the linear equation form of each.

According to Hall et al. (1966), Langmuir affinity constant is used to obtain a dimensionless parameter expressed as separation factor (F) defined by Eq. 3-5.

The F value describes the favourability of the sorption process, in which the value between 0 and 1 indicates favourable sorption and the value of more than 1 indicates unfavourable sorption (Gupta and Bhattacharyya, 2008).

$$F = \frac{1}{1+K\,C_i} \quad \text{----------------------------------} \quad \text{Eq. 3-5}$$

Two kinetic models were used to describe the sorption of Pb^{2+} and Cd^{2+} ions on HA-, Carnitin-, MTP- and HDTM-bent and sorption of $Cr_2O_7^{2-}$ ions on Cys_ester-bent. Those sorbents were selected because of their high removal capacities (see 3.5.2). Lagergren pseudo-first order and pseudo second order kinetic models are expressed by Eq. 3-6 and Eq. 3-7, respectively, (Ho and McKay, 1999).

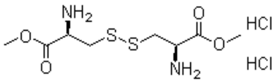
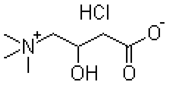
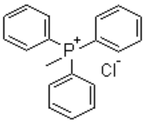
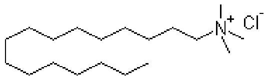
$$\log\left(q_e - q_t\right) = \log(q_e) - \frac{K_s}{2.303}t \quad \text{----------------------------------} \quad \text{Eq. 3-6}$$

where q_e and q_t are the amount of the metal ions sorbed at equilibrium and at time (t), respectively. K_s is the rate constant of the first order sorption, The rate constant was determined experimentally from the slope of a plot of $\log(q_e - q_t)$ versus t.

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e}t \quad \text{----------------------------------} \quad \text{Eq. 3-7}$$

where K_2 is the pseudo-second order rate constant for the adsorption process. The constants, q_e^2 and K_2 were calculated from the plot of $\frac{t}{q_t}$ versus t.

Table 3-1 Acronyms, type of organic modifier, initial modifier concentration, chemical structure of modifiers, concentration of total organic carbon (TOC) and cation exchange capacity (CEC) of the natural clayey sediment (bent) and the organically modified bentonitic sediments used in the current study

Acronym	Organic modifier	Initial modifier concentration**	Chemical structure of modifiers***	TOC (%)	CEC $cmolkg^{-1}$
bent*	-	-	-	0.27	48.1
Cys_ester-bent	L-Cystine dimethyl ester[2]	10 mM		2.0	45.9
Carnitin-bent	L-Carnitine[2]	5 mM		0.9	51.7
MTP-bent	Methyltriphenylphosphonium[2]	5 mM		8.1	15.7
HDTM-bent	Hexadecyltrimethylammonium[1]	5 mM		9.4	32.0
HA-bent	Humic acid[1]	0.5 g l^{-1}		1.5	54.7

1 analytical grade, supplied by Fluka. 2 analytical grade, supplied by Sigma & Aldrich

* clayey sediment collected from Qaser el-Sagha locality.

* *initial concentration in the suspension

***Molecular structure provided by online Database of Chemicals from Around the World (http://www.chemblink.com, 04 – 04 - 2011).

3.5 Results

3.5.1 Speciation of heavy metals

As recorded by the speciation program, the free metal ions are the estimated species in the initial solutions of heavy metals at any concentration before contacting with the sorbents. The predicted speciation of Cd^{2+} and Pb^{2+} were highly affected by the sorbent type, the pH and the initial concentration of the metal ions.

At low to medium concentrations of Cd^{2+} up to $0.3x10^{-3}$ M with MTP-bent and up to $0.2x10^{-3}$ M with HDTM-bent, free metal cations were the only metal species in the solutions, whereby Cd^{2+} and $CdCl^+$ species represent 96 % and $Cd(OH)^+$ represents 2 - 4 % of the total concentrations. With increasing initial concentration, $Cd(OH)_2$ is precipitated in addition to the mentioned soluble free metal cations. The percentages of each species are differing with increasing solute concentration, whereby the percentages of cationic species are decreased relative to increasing hydroxide forms. In Na-bent systems, free metal cations are the predominant species at low initial concentration (87 %), while $Cd(OH)_2$ forms 96 % of the total solute at the high concentration. On the other hand, Cd^{2+} and $CdCl^+$ are the most common species in the solution after an equilibration of 24 h at all solute concentrations with HA-, Carnitin- and Cys_ester-bent sorbents.

At any concentration of Pb^{2+}, $Pb(OH)_2$ precipitation is the only form predicted with Na-bent, HDTM-, MTP- and Carnitin-bent systems. In the case of HA-bent, free metal cations are the only expected species up to $0.34x10^{-3}$ M of Pb^{2+}, whereby Pb^{2+}, $PbCl^+$ and $PbOH^+$ represent 80 %, 18 % and 1.2 % of the total concentration, respectively. The precipitated form of Pb^{2+} started to appear with increasing initial concentration and reached to 85 % of the total concentration at $3.4x10^{-3}$ M Pb^{2+}. In Cys_ester-bent system, the free metal cations are only the expected species at any initial concentration and distributed as follow: 80 % of the solute is Pb^{2+}, 15 % is $PbCl^+$ and 5 % is $PbNO_3^+$.

The anionic species dichromate and chromate could be the predominant species of chromate in all systems and at any concentration according to Dionex (1998) and Ganjali et al. (2012).

3.5.2 Sorption of cadmium, lead and dichromate

The amount of ions removed from the solutions increased with increasing initial ion concentrations to different extent. OMCs modified with Carnitin, MTP and HDTM showed higher Cd^{2+} sorption than the Na-bent. The highest sorption was achieved by MTP-bent (88.5 mmol kg^{-1} at an initial concentration of $1.24x10^{-3}$ M). HA-bent showed the same or a little lower sorption of Cd^{2+} relative to the Na-bent.

The OMCs showed Pb^{2+} sorption characteristics similar to Na-bent at low initial concentrations up to $0.2x10^{-3}$ M. When the initial concentration of Pb^{2+} was increased to $2.3x10^{-3}$ M, Carnitin-, HA- and Cys_ester-bent exhibited a lower sorption (10, 27 and 73 % reduction, respectively) compared with Na-bent, while MTP- and HDTM-bent displayed a similar sorption. Further increases of the initial concentrations reduced the sorption of Pb^{2+} to MTP- and HDTM-bent by 9 or 13 %, respectively, compared to the sorption by Na-bent.

All OMCs under study were more effective in removing $Cr_2O_7^{2-}$ from solutions than Na-bent, except the one treated with Carnitin as organic modifier. Dichromate sorption by Na-bent was very low. The highest $Cr_2O_7^{2-}$ sorption was 187 mmol kg^{-1} for Cys_ester-bent at an initial concentration of $9.49x10^{-3}$ M.

The experimental data and fitting curves of the sorption behaviours of Cd^{2+}, Pb^{2+} and $Cr_2O_7^{2-}$ on Na-bent and OMCs as a function of the added concentrations of metal ion after an equilibration for 24 h are shown in Fig. 3-1. The sorption isotherm parameters and the coefficient of determination (R^2) are presented in Table 3-2 and 3-3. As it is revealed by R^2, Langmuir model describes the sorption data of Cd^{2+} and Pb^{2+} better than the Freundlich model. The maximum Cd^{2+} sorption capacities (b) of the different sorbents varied in a range from 36.9 to 90.1 mmol kg^{-1} and decreased in the order MTP-bent > Carnitin-bent > HDTM-bent > HA-bent > Na-bent > Cys_ester-bent (Table 3-2). The maximum sorption capacities of Pb^{2+} ranged from 59.6 – 372 mmol kg^{-1} and ordered as follows: Na-bent > MTP-bent > HDTM-bent > Carnitin-bent > HA-bent > Cys_ester-bent. The order of b values were the same as that of the sorbed amounts at equilibrium of Cd^{2+} and Pb^{2+} by the different sorbents and completely coincided with the trends observed for the isotherms in Fig. 3-1, which indicates that the Langmuir model is suitable to represent the sorption data of both metal ions.

The low R^2 values of Langmuir (range: 0.03-0.42) and Freundlich (range: 0.15 - 0.82) models for $Cr_2O_7^{2-}$ sorption indicated limitations of these two models to describe the experimental data (Table 3-3). The simple linear model, however, resulted in higher R^2 values in the range 0.73 – 0.92. That was true for all OMCs used in the current study except for Cys_ester-bent, where, Langmuir and Freundlich models had higher R^2 values up to 0.99 (Table 3-3). K_f parameter of Freundlich model may consider a theoretic measure of the adsorption capacity (Chiban et al., 2011). In comparison, the obtained value of K_f parameter was lower than the value of the sorption capacity of $Cr_2O_7^{2-}$ achieved experimentally at the high initial $Cr_2O_7^{2-}$ concentration, whereas the calculated sorption capacity from Langmuir model (b) was close to the experimental value. Thus, Langmuir is the best adequate model fitting with the observed data from the Cys_ester-bent system.

The relationship between the Separation factor (F) versus C_i for Cd^{2+}, Pb^{2+} and $Cr_2O_7^{2-}$ are shown in Fig 3-2. The F values were less than 1 for all sorbents with all metal ions. Sorption of Pb^{2+} by HDTM-, MTP-, Carnitin- and Na-bent were more favourable (close to zero) for all initial ion concentrations. F values for Pb^{2+} and Cd^{2+} sorption by Cys_ester- and HA-bent, Cd^{2+} by Carnitin-bent and $Cr_2O_7^{2-}$ by Cys_ester-bent were more favourable for the higher initial metal ion concentration than for the lower ones. The sorption was very favourable (close to zero) for Pb^{2+} and favourable for Cd^{2+} and $Cr_2O_7^{2-}$.

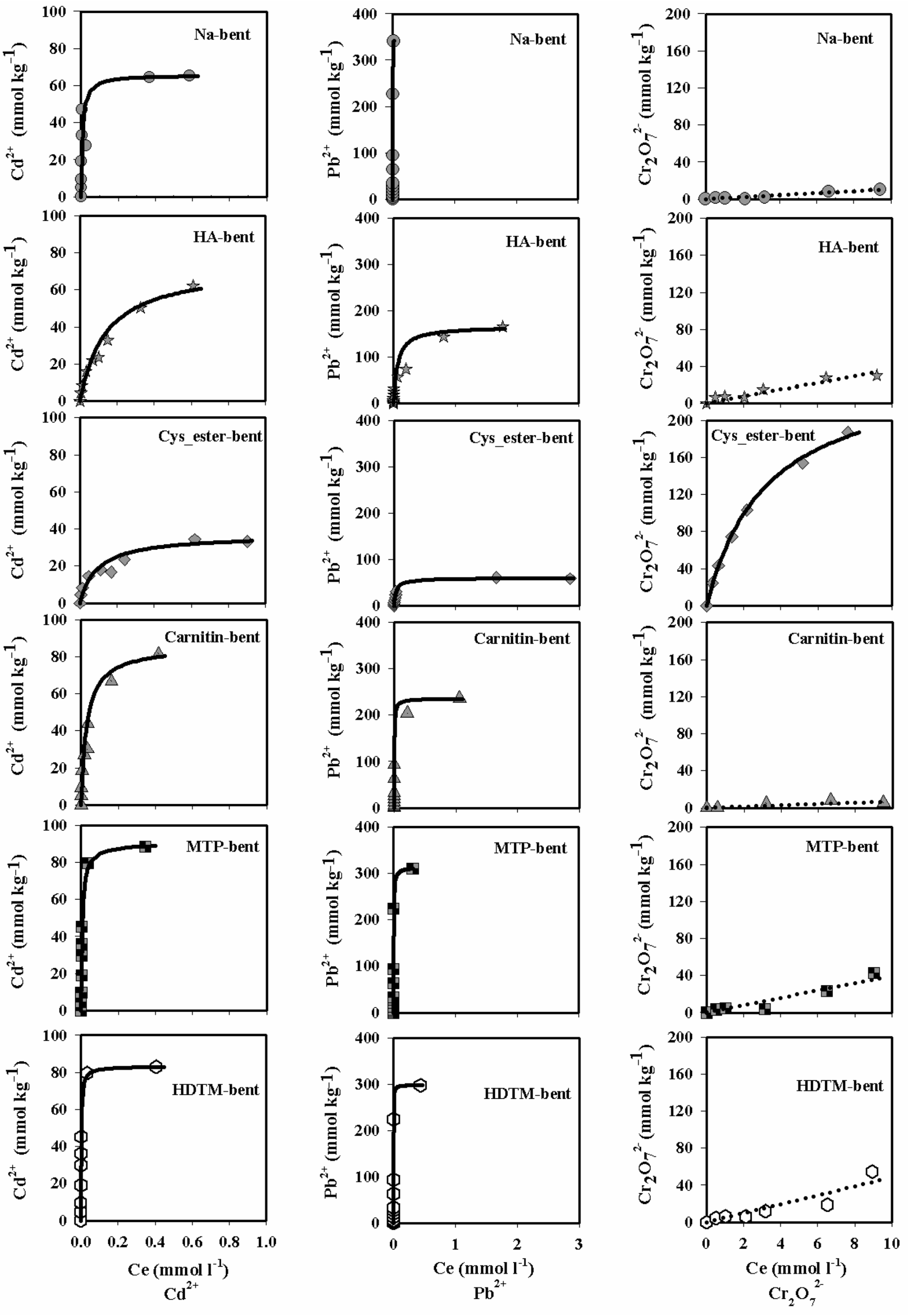


Fig. 3-1 Sorption isotherms of Cd^{2+}, Pb^{2+} and $Cr_2O_7^{2-}$ by the natural clayey sediment (Na-bent) and organically modified bentonitic sediment (OMCs).

Solid lines represent Langmuir and dotted lines represent linear model. Symbols show the mean of measured data of three replicates. HA-, Cys_ester-, Carnitin-, MTP- and HDTM-bent are the OMCs prepared from the organic modifiers described in Table 3-1. Ce: concentration of the metal ions at equilibrium

Table 3-2 Sorption isotherm parameters and coefficient of determinations (R^2) of Cd^{2+} and Pb^{2+}

Adsorbent	**Freundlich constants**			**Langmuir constants**		
	K_f (1) (mmol kg^{-1})	**1/n** (2)	**R^2**	**k** (3) (l $mmol^{-1}$)	**b** (4) (mmol kg^{-1})	**R^2**
Cd^{2+}						
Na-bent	91.8	0.25	0.846	132	65.7	0.997
HA-bent	90.5	0.55	0.987	7.18	73.5	0.955
Cys_ester-bent	38.9	0.38	0.967	10.5	36.9	0.971
Carnitin-bent	134	0.41	0.983	32.3	85.7	0.983
MTP-bent	245	0.42	0.797	158	90.1	1.00
HDTM-bent	187	0.32	0.690	436	83.3	1.00
Pb^{2+}						
Na-bent	6628	0.61	0.876	600	372	0.939
HA-bent	166	0.42	0.921	15.6	167	0.982
Cys_ester-bent	56.3	0.38	0.861	25.7	59.6	0.999
Carnitin-bent	282	0.26	0.933	249	236	0.999
MTP-bent	1164	0.47	0.726	298	314	0.999
HDTM-bent	927	0.38	0.708	1098	298	1.00

(1) & (2) are Freundlich empirical constants related to sorption capacity and sorption intensity, respectively.

(3) Langmuir affinity constant, related to the energy of adsorption. (4) Maximum adsorption capacity. Na-bent: the natural clayey sediment. HA-, Cys_ester-, Carnitin-, MTP- and HDTM-bent are the organically modified bentonitic sediments prepared from the organic modifiers described in Table 3-1.

Table 3-3 Sorption isotherm parameters and coefficient of determinations (R^2) of $Cr_2O_7^{2-}$

Adsorbent	Linear equation	R^2	Freundlich constants			Langmiur constants		
			K_f [(1)] (mmol kg^{-1})	1/n [(2)]	R^2	k [(3)] (l mmol^{-1})	b [(4)] (mmol kg^{-1})	R^2
Na-bent	y = 1.0518x	0.92	0.837	0.85	0.38	-	-	-
HA-bent	y = 3.7522x	0.90	7.62	0.58	0.82	0.125	55.8	0.42
Cys_ester-bent	y = 28.122x	0.83	56.2	0.63	0.987	0.304	262	0.99
Carnitin-bent	y = 0.7895x	0.73	-	-	-	-	-	-
MTP-bent	y = 3.9727x	0.87	0.00006	14.6	0.72	-	-	-
HDTM-bent	y = 4.5992x	0.79	5.61	0.78	0.82	0.025	185	0.03

(1) & (2) are Freundlich empirical constants related to sorption capacity and sorption intensity, respectively.

(3) Langmuir affinity constant, related to the energy of adsorption. (4) Maximum sorption capacity.

Na-bent: the natural clayey sediment. HA-, Cys_ester-, Carnitin-, MTP- and HDTM-bent are the organically modified bentonitic sediment prepared from the organic modifiers described in Table 3-1.

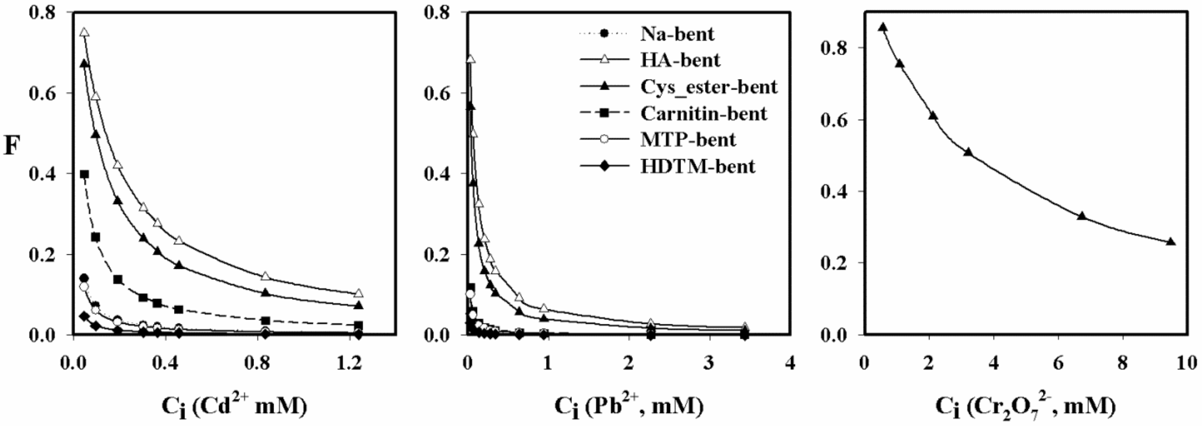


Fig. 3-2 The separation factor (F) versus the initial metal ion concentrations (Ci) for Cd^{2+}, Pb^{2+} and $Cr_2O_7^{2-}$.

Na-bent is the sodium form of the natural clayey sediment. HA-, Carnititn-, Cys_ester-, MTP- and HDTM-bent are the organically modified bentonitic sediments prepared from the organic modifiers described in Table 3-1.

3.5.3 Desorption experiments

Cd^{2+}, Pb^{2+} and $Cr_2O_7^{2-}$ desorption data are presented in Fig. 3-3 and 3-4. Cd^{2+} and Pb^{2+} showed high desorption from all metal loaded OMCs by using 0.1 M HCl as desorbing agent. Differences in the sorption reversibility were very small in the range of less than 10 % following the order Cys_ester- > HA- > Carnitin- > MTP- > HDTM-bent for Cd^{2+} and Cys_ester- > MTP- > HA- > Carnitin- ≥ HDTM-bent for Pb^{2+} (Fig. 3-3).

The sorbed Cd^{2+} ions showed no or very limited (Cys_ester- and HA-bent) desorption when using NaOH and H_2O as desorbing agents. In contrast, 67, 60, 88.7, 37.8 and 38.9 % of sorbed Pb^{2+} ions could be desorbed from Cys_ester-, Carnitin-, HA-, MTP- and HDTM-bent, respectively, by using tap water as desorbing agent and around 28.5 to 37.8 % could be desorbed when using 0.1 M NaOH as desorbing agent.

The degree of $Cr_2O_7^{2-}$ desorption by the used desorbing agents followed the order HCl > H_2O > NaOH representing 42.3, 27.9, 14.2 % of the sorbed amount (Fig. 3-4).

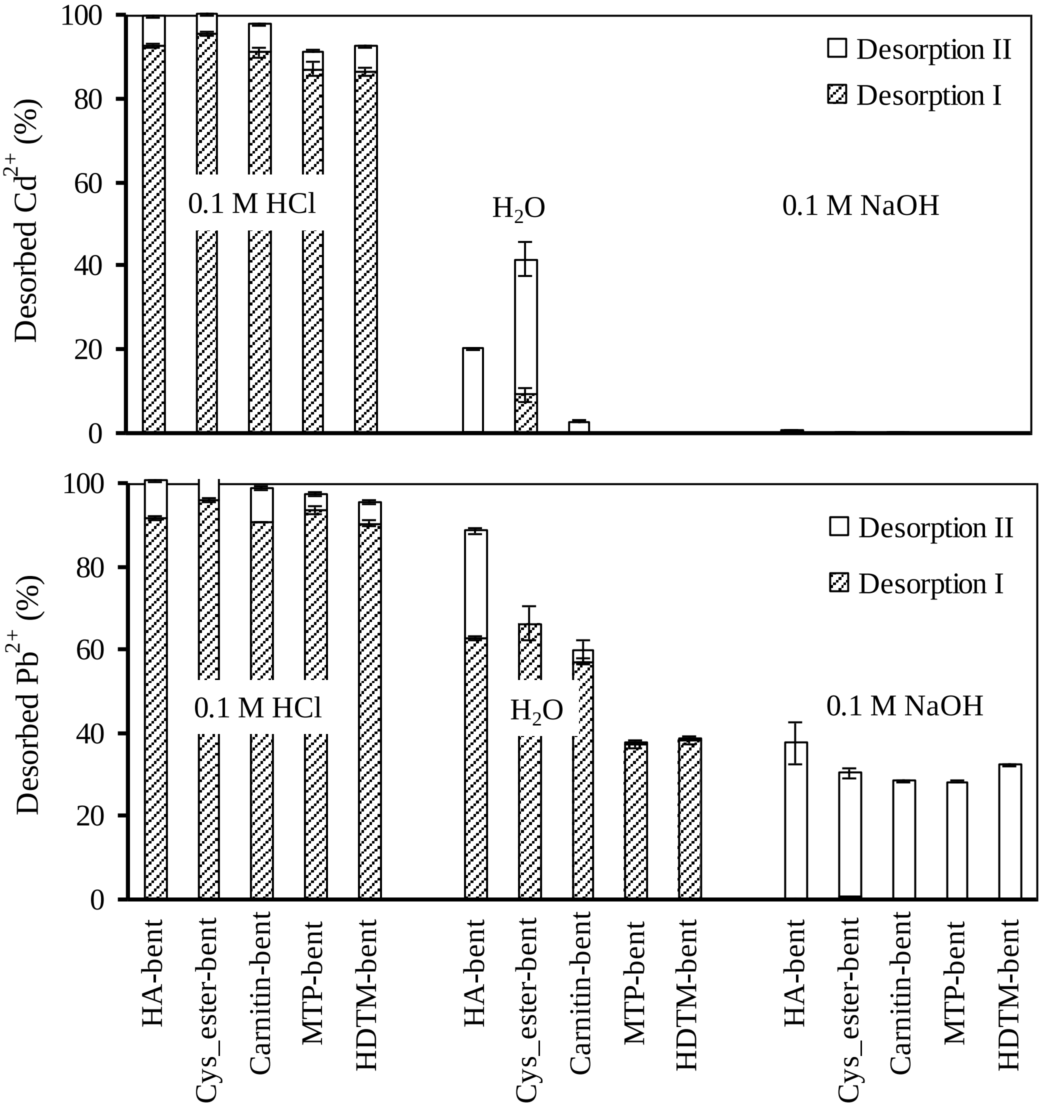


Fig. 3-3 Two desorption steps (I, II each 24 h) of Cd^{2+} and Pb^{2+} as percentage of the element sorbed to different organically modified bentonitic sediments (OMCs) by using 0.1 M HCl, H_2O and 0.1 M NaOH as desorbing agents.

Cys_ester-, Carnitin-, HA-, MTP- and HDTM-bent are the OMCs prepared from the organic modifiers described in Table 3-1. n.d. noted second desorption step is not determined. Bars represent means ± standard errors; n =3.

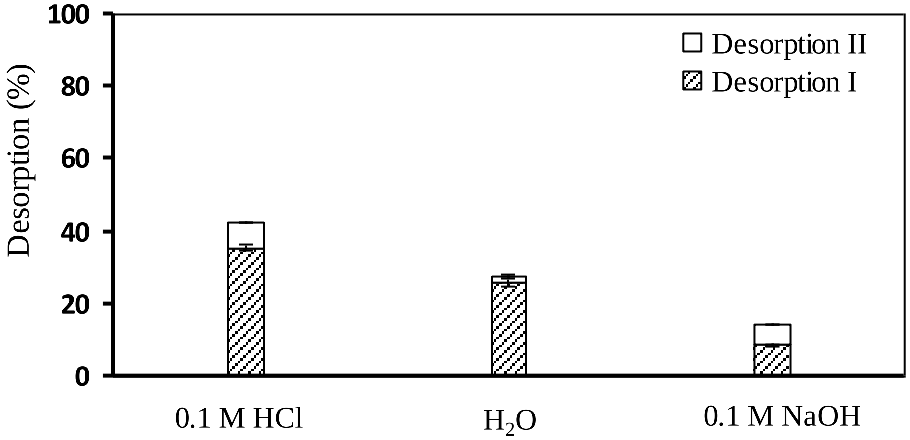


Fig. 3-4 Two desorption steps (I, II each 24 h) of $Cr_2O_7^{2-}$as percentage of the element sorbed to the natural clayey sediment modified with Cys_ester (Cys_ester-bent, see Table 3-1) by using 0.1 M HCl, H_2O and 0.1 M NaOH as desorbing agents.
Bars represent means ± standard errors; n =3.

3.5.4 Factors affecting sorption

3.5.4.1 Sorption time

The relationships between time (t) and Pb^{2+}or Cd^{2+} ions sorbed by HA-, Carnitin-, MTP- and HDTM-bent or $Cr_2O_7^{2-}$ ions sorbed by Cys_ester-, MTP- and HDTM-bent are shown in Fig. 3-5 and 3-6.

It is shown that the sorption of the metal ions increased with time. The sorbed amounts of Cd^{2+} approached an equilibrium after 8 h with HDTM- and MTP-bent. However, only 73 and 81 % of the total sorption of Pb^{2+} ions by MTP- and HDTM-bent, respectively, were achieved after 12 hours and an equilibrium is not reached even after 24 h. For Carnitin- and HA-bent, the highest sorbed amount of both metal ions, 93 - 100 % of Cd^{2+} and 79 – 96 % of Pb^{2+}, respectively, were reached after 30 min. Nevertheless, after 24 the sorption of Pb^{2+} by HDTM- and MTP-bent was substantially higher than that by Carnitin- and HA-bent (Fig. 3-5).

$Cr_2O_7^{2-}$ sorption reached the equilibrium state after 2 and 4 hours for MTP- and Cys_ester-bent, respectively. However, for HDTM-bent an equilibrium is not visible after 24 h (Fig. 3-6).

The obtained R^2 from Lagergren pseudo-first order kinetic model showed lower values compared with that of the pseudo second order model (not shown data). The calculated constants of the pseudo second order kinetic model and their corresponding coefficient of determination (R^2) are given in Table 3-4. Since the obtained R^2 for the pseudo-second-order kinetics model were close to one, except for the MTP- and HDTM-bent sorbents, the pseudo-second-order kinetics model was found to represent appropriately the experimental data. Besides, the values of $q_{e\ calculated}$ obtained from the model were consistent with those of $q_{e\ measured}$ achieved experimentally.

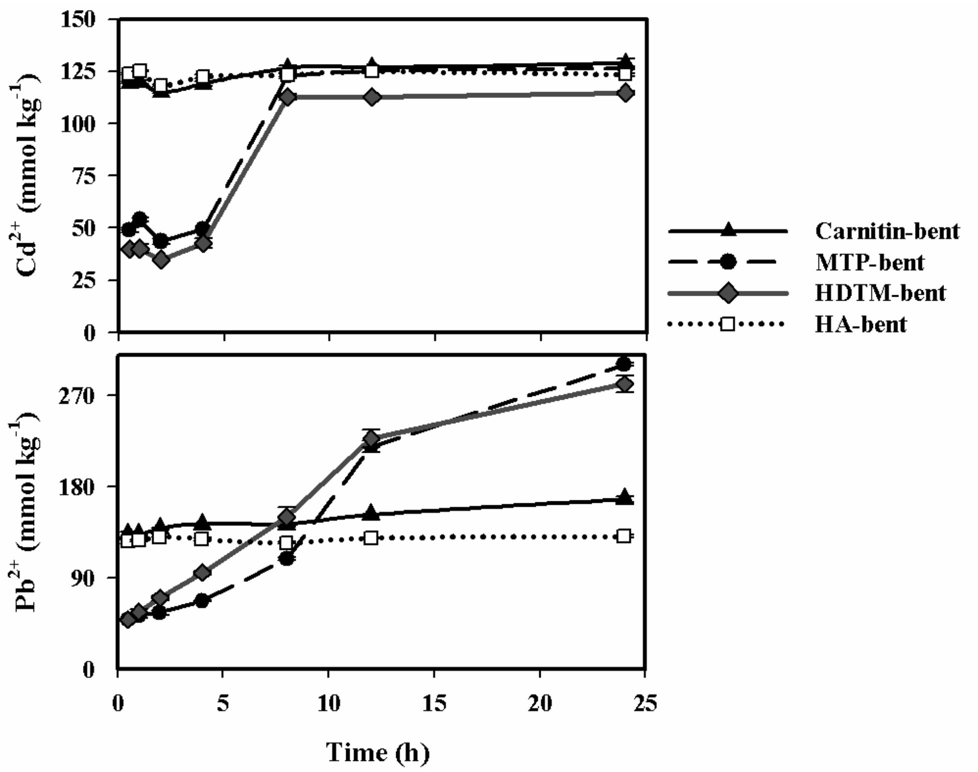


Fig. 3-5 Time course (t) of sorption of Cd^{2+} and Pb^{2+} by organically modified bentonitic sediments (OMCs).

Carnitin-, MTP-, HDTM- and HA-bent are the OMCs prepared from the organic modifiers described in Table 3-1. The initial metal concentrations of Pb^{2+} and Cd^{2+} were $3x10^{-3}$ M and $3.44x10^{-3}$ M, respectively. Bars represent means ± standard errors; n =3

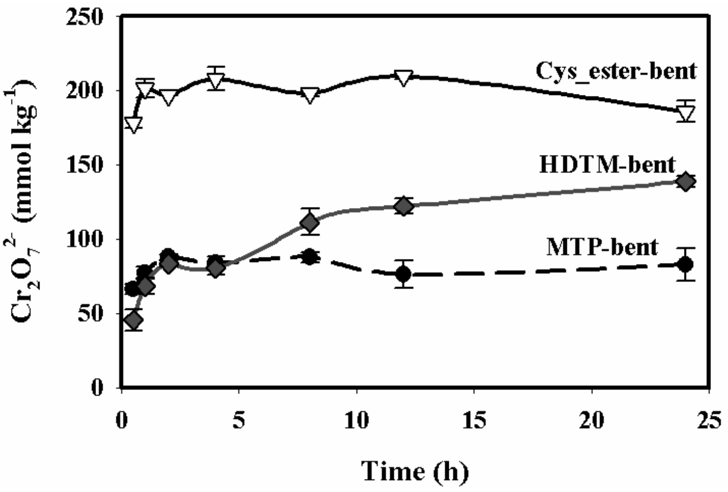


Fig. 3-6 Time course of the sorption of $Cr_2O_7^{2-}$ by the organically modified bentonitic sediments (OMCs).

Cys_ester-, HDTM- and MTP-bent are the OMCs prepared from the organic modifiers described in Table 3-1. Initial concentration of $Cr_2O_7^{2-}$ was 11.2×10^{-3} M. Bars represent means ± standard errors; n =3.

Table 3-4 Parameters of the pseudo-second-order kinetics models for Cd^{2+}, Pb^{2+} and $Cr_2O_7^{2-}$

Sorbent	$^1q_{e,\ measured}$ (mmol kg^{-1})	$q_{e,\ calculated}$ (mmol kg^{-1})	k_2 (kg mmol^{-1} min^{-1})	R^2
		Cd^{2+}		
HA-bent	123	124	0.00755	1.00
Carnitin-bent	129	129	0.00072	0.9998
MTP-bent	126	145	0.00004	0.92
HDTM-bent	115	135	0.00003	0.91
		Pb^{2+}		
HA-bent	131	131	0.001368	1.000
Carnitin-bent	168	168	0.000167	0.996
MTP-bent	301	408	0.000003	0.60
HDTM-bent	282	350	0.000007	0.90
		$Cr_2O_7^{2-}$		
Cys_ester-bent	186	187	-0.0003	0.997
MTP-bent	83	82	0.0092	0.997
HDTM-bent	139	146	0.0001	0.99

[1] is the measured sorbed amount of ion at equilibrium. k_2 and R^2 are the pseudo-second order rate constant and coefficient of determinations, respectively.

bent is the natural clayey sediment. HA, Cys_ester, Carnitin, MTP and HDTM are the organic modifiers described in Table 3-1.

3.5.4.2 pH of the initial solution

The influence of the initial solution pH on the sorption of the metal cations and anion by Na-bent and OMCs are shown in Fig. 3-7.

OMCs showed minimal sorption of Cd^{2+} and Pb^{2+} at pH 2. The sorption was increased with rising the initial pH from 2 to 4. At pH 4, all Cd^{2+} and Pb^{2+} ions were removed from the solutions by Na-bent, MTP- and HDTM-bent, while at the similar pH, 82, 94 and 67 % of Cd^{2+} and 99, 100 and 88 % of Pb^{2+} ions are removed by HA-, Carnitin- and Cys_ester-bent, respectively. Further increase of the initial pH has no or only small effect on the sorption of these ions.

The highest sorption of $Cr_2O_7^{2-}$ ions was obtained by MTP-bent at initial pH 2 and 4. With further increases of pH, the sorption was reduced. In contrast, HDTM- and Cys_ester-bent exhibited a clear maximum at pH 4.

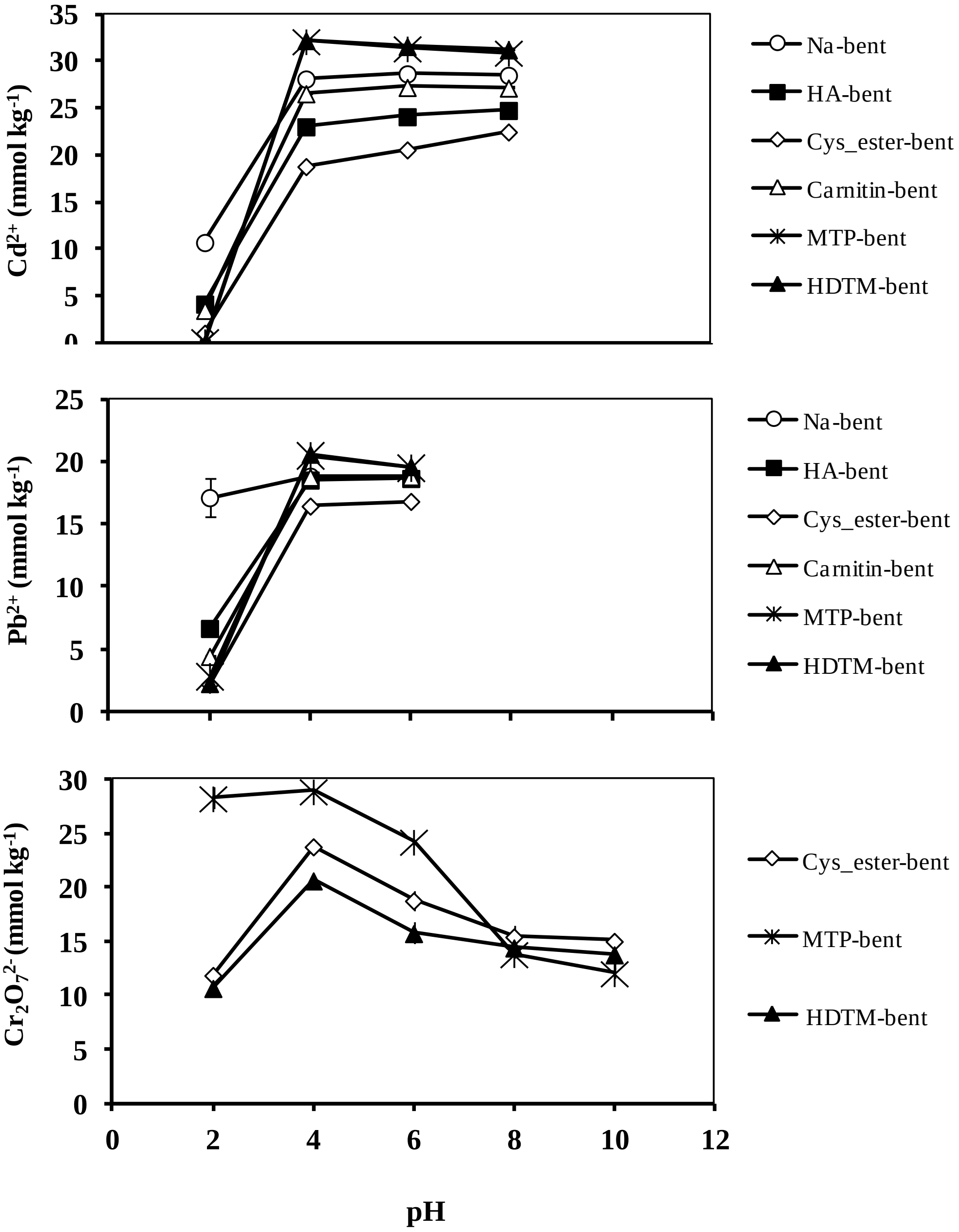


Fig. 3-7 Effect of initial solution pH on Cd^{2+}, Pb^{2+} and $Cr_2O_7^{2-}$ sorption by the natural clayey sediment (Na-bent) and the organically modified bentonitic sediments (OMCs). HDTM-, MTP-, Carnitin-, HA- and Cys_ester-bent are the OMCs prepared from the organic modifiers described in Table 3-1. Initial metal concentration was $0.3x10^{-3}$ M, $0.2x10^{-3}$ M and $0.6x10^{-3}$ M of Cd^{2+}, $Pb^{2+}$and $Cr_2O_7^{2-}$, respectively.

3.5.4.3 Electrolyte concentration

Increasing the electrolyte concentration from 0.001 M to 0.01 M and further to 0.1 M by using $Ca(NO_3)_2$ decreased significantly the sorption of Cd^{2+} to OMCs by 24 to 80 %. The lowest reductions were obtained with HDTM- and MTP-bent. In contrast, increasing the electrolyte concentration from 0.001 to 0.01 M had no significant effect on the sorbed Cd^{2+} when $NaNO_3$ was used as background solution. Nevertheless, increasing the background concentration up to 0.1 M $NaNO_3$ reduced the sorption significantly by 3 - 37 %, where the lowest reductions were obtained with MTP- and HDTM-bent (Table 3-5).

At an initial Pb^{2+} concentration of $2.3x10^{-3}$ M, MTP- and HDTM-bent were efficient to remove all Pb^{2+} from the media (not shown data) hiding any effect of the electrolyte type and concentration. Therefore, the initial Pb^{2+} concentration was increased to $3.5x10^{-3}$ M.

When the concentration of $Ca(NO_3)_2$ or $NaNO_3$ electrolytes were increased from 0.001 M to 0.1 M, no or only very limited changes (less than 10 %) in the sorption of Pb^{2+} by Carnitin-, MTP- and HDTM-bent are observed. For HA-bent, however, Pb^{2+} sorption decreased significantly by 47 or 25 % with increasing $Ca(NO_3)_2$ or $NaNO_3$ concentration, respectively, from 0.001 M to 0.1 M (Table 3-6).

Rising the background concentration of $Ca(NO_3)_2$ from 0.001 to 0.01 M enhanced significantly the sorption of $Cr_2O_7^{2-}$ by the tested OMCs, in case of MTP-bent by 1250 % (Table 3-7). A further increase of the $Ca(NO_3)_2$ concentrations did not lead to significant changes with Cys_ester- and MTP-bent but it decreased the sorption on HDTM-bent. Increasing the $NaNO_3$ concentration from 0.001 to 0.01 M did not affect significantly the sorption of $Cr_2O_7^{2-}$. A further increase of the $NaNO_3$ concentration to 0.1 M increased or decreased the $Cr_2O_7^{2-}$ sorption on Cys_ester-bent or HDTM-bent, respectively. $Cr_2O_7^{2-}$ sorption on MTP-bent remained unaffected by increasing $NaNO_3$ concentrations (Table 3-7).

Table 3-5 Mean amount of sorbed Cd^{2+} (mmol kg^{-1}) under different electrolytes concentrations of $Ca(NO_3)_2$ and $NaNO_3$

Sorbent	$Ca(NO_3)_2$			$NaNO_3$		
	0.001 M	0.01 M	0.1 M	0.001 M	0.01 M	0.1 M
HA-bent	111^a	66^b	22^c	146^a	143^a	93^b
Carnitin- bent	161^a	115^b	62^c	164^a	167^a	128^b
MTP- bent	141^a	127^b	104^c	145^a	148^a	138^b
HDTM- bent	138^a	128^b	105^c	141^{ab}	142^a	137^b

Initial Cd^{2+} concentration was 3.4×10^{-3} M. bent is the natural clayey sediment. HA, Carnitin, MTP and HDTM are the organic modifiers described in Table 3-1. Different small letters in the same row indicate significant differences (Tukey, $p < 0.05$) between concentrations within one electrolyte and one sorbent.

Table 3-6 Mean amount of sorbed Pb^{2+} (mmol kg^{-1}) under different electrolytes concentrations of $Ca(NO_3)_2$ and $NaNO_3$

Sorbent	$Ca(NO_3)_2$			$NaNO_3$		
	0.001 M	0.01 M	0.1 M	0.001 M	0.01 M	0.1 M
HA- bent*	127^a	88^b	69^b	134^a	129^b	100^c
Carnitin- bent*	199^a	187^b	186^b	200^a	201^a	193^b
MTP- bent **	303^b	310^a	296^b	311^a	300^a	306^a
HDTM- bent **	293^a	302^a	300^a	314^a	290^b	298^b

* initial Pb^{2+} concentration was 2.3×10^{-3} M

** initial Pb^{2+} concentration was 3.5×10^{-3} M

bent is the natural clayey sediment. HA, Carnitin, MTP and HDTM are the organic modifiers described in Table 3-1. Different small letters in the same row indicate significant differences (Tukey, $p < 0.05$) between concentrations within one electrolyte and one sorbent.

Table 3-7 Mean amount of sorbed $Cr_2O_7^{2-}$ (mmol kg^{-1}) under different electrolytes concentrations of $Ca(NO_3)_2$ and $NaNO_3$

Sorbent	$Ca(NO_3)_2$			$NaNO_3$		
	0.001 M	0.01 M	0.1 M	0.001 M	0.01 M	0.1 M
Cys_ester- bent	103^b	125^a	113^{ba}	103^b	99^b	112^a
MTP- bent	2^b	27^a	21^a	21^a	18^a	11^a
HDTM- bent	17^b	31^a	17^b	33^a	28^a	13^b

Initial $Cr_2O_7^{2-}$ concentration was $3x10^{-3}$ M. bent is the natural clayey sediment. Cys_ester, MTP and HDTM are the organic modifiers described in Table 3-1. Different small letters in the same row indicate significant differences (Tukey, $p < 0.05$) between concentrations within one electrolyte and one sorbent.

3.5.5 Sorption experiments with combinations of cadmium and dichromate

A general decline in Cd^{2+} sorption by all sorbents with differences in the amounts are observed in the binary component systems as compared with the single component systems (Fig. 3-8). This phenomenon was most pronounced by HDTM- and MTP-bent. However, at low initial concentrations of Cd^{2+} and $Cr_2O_7^{2-}$ (0.5 and 1.0 mM, respectively), the differences between the sorbed amounts of Cd^{2+} from the binary component system and those from the single component system were not relevant (2 - 5 %).

Among the sorbents, Cys_ester-bent showed the lowest Cd^{2+} sorption, which is in agreement with the isotherm experiment reported in Fig. 3-1. At the same time, the sorption of Cd^{2+} to Cys_ester-bent was not affected significantly by the existence of $Cr_2O_7^{2-}$.

As shown on Fig. 3-9, the presence of Cd^{2+} increased significantly sorption of $Cr_2O_7^{2-}$ in the binary component systems, reaching 5.2, 373 and 1.3 fold when using HDTM-, MTP- and Cys_ester-bent, respectively. In general, sorption of $Cr_2O_7^{2-}$ on Na-bent was very low reaching only 1.5 and 15.0 mmol kg^{-1} in single and binary component systems, respectively. In the single component systems, the sorption of $Cr_2O_7^{2-}$ decreased in the order Cys_ester- > HDTM- > MTP- > Na-bent. However, this order changed to HDTM- > Cys_ester- > MTP- > Na-bent for $Cr_2O_7^{2-}$ sorption from the binary component systems. The enhancement in $Cr_2O_7^{2-}$ sorption with the presence of Cd^{2+} was most pronounced for HDTM-bent at the higher initial concentrations of the two metal ions.

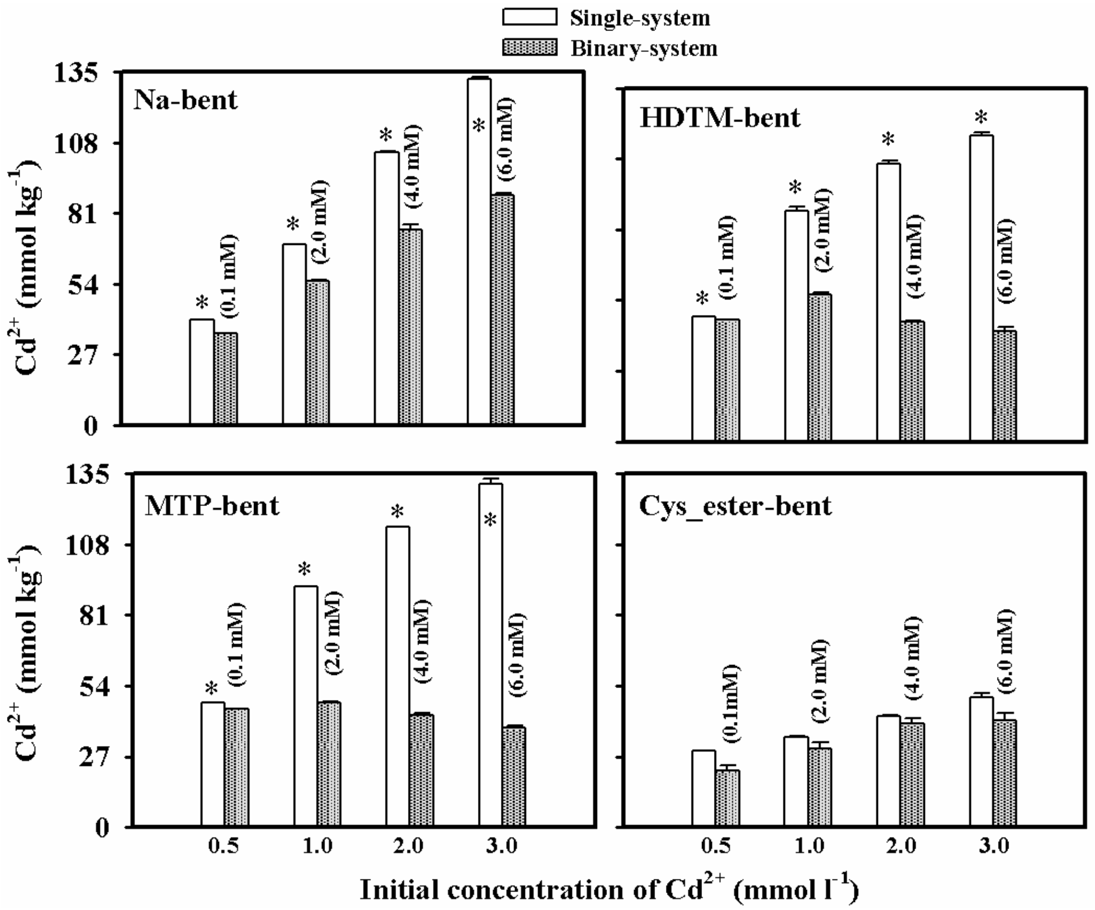


Fig. 3-8 Sorption of Cd^{2+} alone and in combination with $Cr_2O_7^{2-}$ by natural clayey sediment (Na bent) and selected organically modified bentonitic sediments (OMCs) from aqueous solutions.

Brackets show the initial concentration of $Cr_2O_7^{2-}$. HDTM-, MTP- and Cys_ester-bent are the OMCs prepared from the organic modifiers described in Table 3-1. Bars represent means ± standard errors; n =3. Stars indicate statistically significant differences (Tukey test, $P < 0.05$) between the sorbed Cd^{2+} from single and binary component systems within one initial concentration of the pollutants and one sorbent

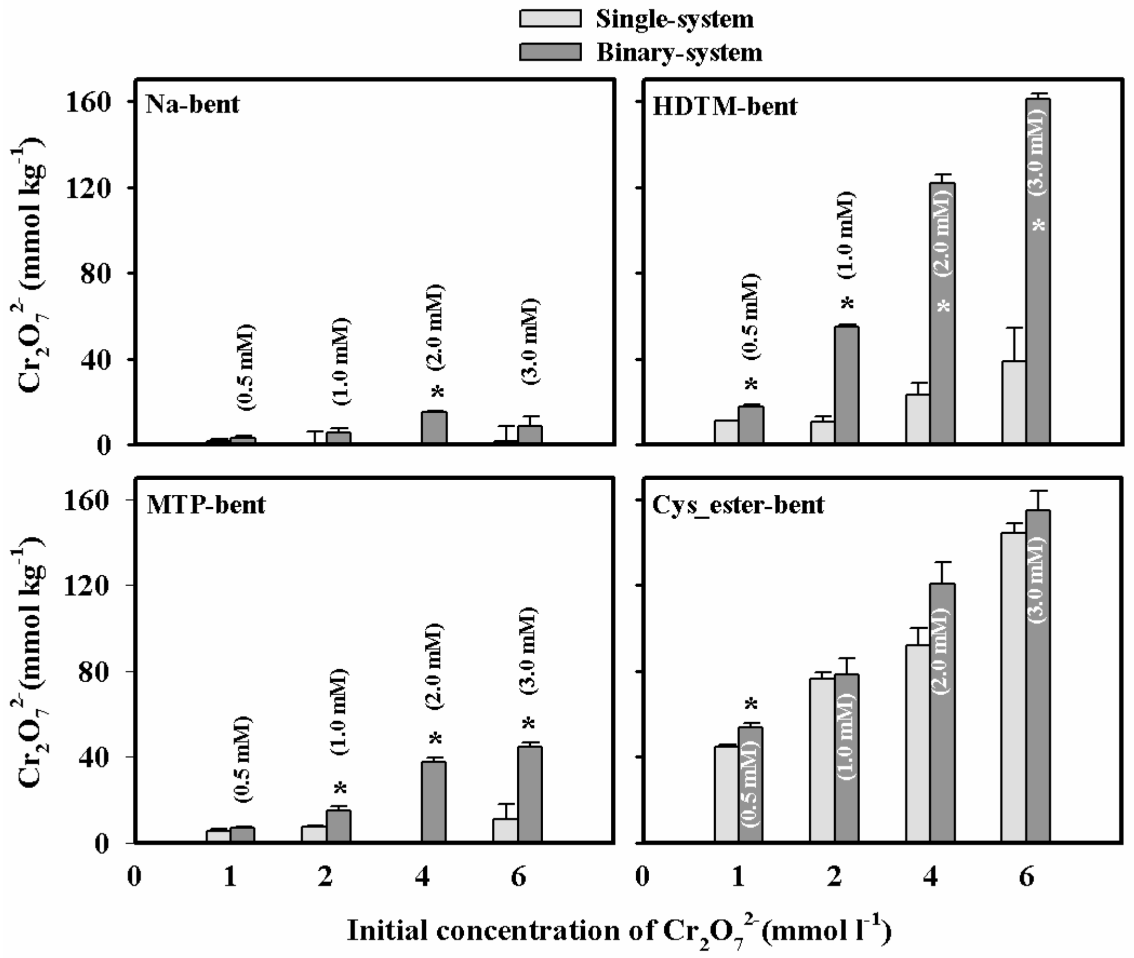


Fig. 3-9 Sorption of $Cr_2O_7^{2-}$ alone and in combination with Cd^{2+} by natural clayey sediment (Na bent) and selected organically modified bentonitic sediments (OMCs) from aqueous solutions.

Brackets show the initial concentration of Cd^{2+}. HDTM-, MTP- and Cys_ester-bent are the OMCs prepared from the organic modifiers described in Table 3-1. Bars represent means ± standard errors; $n = 3$. Stars indicate statistically significant differences (Tukey test, $P < 0.05$) between the sorbed $Cr_2O_7^{2-}$ from single and binary component systems within one initial concentration of the pollutants and one sorbent.

3.6 Discussion

3.6.1 Sorption and desorption characteristics of cadmium, lead and dichromate

Although the Langmuir model is the best model which fits to the isotherm data, adsorption cannot be defined as the sole predominant mechanism playing a role in the removal of heavy metals under the employed study conditions. This was confirmed by Sparks (2003), who stated that Langmuir model can represent well the adsorption or precipitation systems. Further, it is stated in literature that several processes are included in the removal of heavy metals by clay minerals (Bergaya et al. 2006).

It can be implied from the predicted speciation of the metal ions that adsorption is the main mechanism which controls the removal of Cd^{2+} by Na-bent, MTP- and HDTM-bent at the low initial solute concentration, Cd^{2+}, $Cd(Cl)^{+}$ and $Cd(OH)^{+}$ being the predominant species. Adsorption together with hydroxide nucleation and precipitation at the sorbents surfaces seem to be processes which contribute in the removal of Cd^{2+} by the mentioned sorbents with increasing the solute concentration, where cationic species as well as hydroxide precipitation are the estimated forms of Cd^{2+}. The free metal cations are the prevalent Cd^{2+} species in Carnitin-bent systems at any solute concentration. Therefore, ion exchange and surface complexation are the proposed mechanisms explaining the removal of Cd^{2+} by Carnitin-bent. In addition, Carnitin possess carboxylic groups in its structure that gives Carnitin-bent additional specific active sites on the surface as compared with Na-bent. These sites play an important role in the removal of cationic heavy metals. Higher CEC value of Carnitin-bent as compared to Na-bent may support the latter explanation concerning the role of carboxylic groups (Table 3-1).

At the same initial concentration, sorption of Pb^{2+} was higher than of Cd^{2+} to all sorbents, which is consistent with the favorabilities depicted by F values. This finding is in agreement with the observed data by Barbier et al. (2000). Surface precipitation is the suggested process playing the main role in the removal of Pb^{2+} by Na-bent, MTP-, HDTM- and Carnitin-bent, since $Pb(OH)_2$ is the expected form of Pb^{2+} at any initial solute concentration.

The formation of polynuclear complex and hydroxide precipitation of metal ions on the clay and silicate surfaces at high concentrations of ions and at neutral or high pH was previously proposed by several studies (Parker and Rae, 1998; Huang and Fuerstenau, 2001; Agrawal and Sahu, 2006). Compared with Na-bent systems, enhancement in the sorption of Cd^{2+} and reduction in the sorption of Pb^{2+} are observed in HDTM-, MTP- and Carnitin-bent systems. Those phenomena probably are due to the smaller ionic radius of Cd^{2+} compared to Pb^{2+}, enabling Cd^{2+} to penetrate more easily into the interlamellar of the sorbents. Further, loading the clayey sediments with MTP and HDTM led to expand the interlayer space of the clay (Chapter 2) providing more interaction surfaces for the metals ions, which enhances the sorption of Cd^{2+} to MTP- and HDTM-bent compared to Na-bent. Stathi et al. (2007) concluded that the intercalated organic substances in the modified montmorillonite strongly bind with the first hydroxide species of the metal ions, resulting in an increase of the removal of heavy metals compared with the untreated clay.

The speciation of heavy metals showed that the metal cations and the mono hydroxide and mono chloride forms are the predominant species of Cd^{2+} and Pb^{2+} in Cys_ester-bent systems. In other words, the precipitation of the metals ions is not expected in the presence of that sorbent, explaining probably the lower removal of these pollutants by Cys_ester-bent than Na-bent. Further, our previous work elucidated a reducing in the basal spacing of the clayey sediment after the loading with Cys_ester (Chapter 2). The produced collapse may partially reduce the accessibility of the metal ions to the interlayer spacing, resulting in a reduction of the sorption of Cd^{2+} and Pb^{2+} by Cys_ester-bent compared with other sorbents. Nevertheless, Cys_ester-bent showed the ability to remove 90 % of Pb^{2+} or 54 % of Cd^{2+} at the low initial solution concentration ($0.35x10^{-3}$ M of Pb^{2+} or Cd^{2+}). The removed amounts of these metal ions are reduced with increasing their initial concentrations in the solutions. Cys_ester is a small molecule and is loaded on the clay with percentage less than the CEC of the natural clayey sediment (Chapter 2). Cruz-Guzman et al. (2005) reported that the small organic cations are loaded on the modified smectite as separated ions in the interlayer spacing, providing occupied areas with organophilic characteristics and non-occupied areas have the adsorptive properties of the natural smectite. Moreover, Cys_ester has different types of functional groups, such as disulfide and carbonyl groups. Hence, the sorption of Cd^{2+} and Pb^{2+} by Cys_ester-bent can be attributed to different processes: (i) surface complexation on the non-occupied surface, (ii) binding with the functional groups provided by the Cys_ester and (iii) ion exchange mechanisms. The occupation of the suitable adsorption sites on Cys_ester-bent increases with increasing initial solution concentration and thus reduces the removal of metal ions at high concentrations. Jr and Spiff (2005) observed that the functional groups on the sulfur-modified biosorbent bind quickly with the available metal ions at the low initial concentration.

It is well known in literature that HA is an organic macromolecule that contains varieties of functional groups like alcohol, amide, amine, carboxylic, carbonyl, phenolic, hydroxyl and quinone groups (Adekunle et al., 2007; Leita et al., 2009). The presence of oxygen-containing functional groups such as carboxyl and phenol on HA structure enables HA-bent to bind Cd^{2+} and Pb^{2+} ions. The maximum sorption of Cd^{2+} by HA-bent was higher than by Na-bent which in a contrast with the observed data by Levy and Francis (1978), who found that the coating of Ca- or Na-montmorillonite with HA, which was extracted from soils, has no influence on their removal capacities of Cd^{2+}. Sorption of Cd^{2+} on HA-bent may mainly refers to adsorption and surface complexation mechanisms, since the free metal cations are the predominant species in the system at any initial metal concentration. These mechanisms played also the main role in the sorption of Pb^{2+} at low initial concentration, whereas surface precipitation might be involved with increasing initial Pb^{2+} concentration.

The negligible sorption of $Cr_2O_7^{2-}$ by Na-bent and Carnitin-bent is attributed to the predominant negative charges on the clay's surface of both sorbents in addition to the deprotonated carboxylic group on Carnitin-bent, which repulses the similar charged free ions in the solution.

Sorption of $Cr_2O_7^{2-}$ by the other sorbents could mainly be due to the binding between $Cr_2O_7^{2-}$ ions and the protonated amino groups in the structures of HDTM- and Cys_ester-bent or the phosphonium ion in MTP-bent. Anion exchange might be another interpretation for the removal of $Cr_2O_7^{2-}$ by these sorbents, whereby the $Cr_2O_7^{2-}$ anions in the solution are exchanging with the counter anions associated with the sorbents. Similar explanations were reported by Sarkar et al. (2010) in their study on the usage of commercial type of alkyl ammonium material to remove $Cr_2O_7^{2-}$ at lower concentrations than those employed in the herein study. Further assumptions to explain the sorption of $Cr_2O_7^{2-}$ were reported by Majdan et al. (2005). They assumed that $Cr_2O_7^{2-}$ ions are bound with HDTM which was loaded on the hydrophobic surface of the clay via Van der Waals forces, forming HDTMHCrO4-----HDTM-clay.

Moreover, Cys_ester is a divalent organic cation, which is bound with the clay surface probably via one of its amino groups, providing more positive charge on the clay surface by the non bound amino group. That, consequently, increases the sorptivity of $Cr_2O_7^{2-}$ to Cys_ester-bent more than HDTM- and MTP-bent. An interaction between anions and standard HAs was studied by Pacheco et al. (2003) and Leita et al. (2009). This interaction was related to the zweitterionic character of HAs and the formation of anion-humic micelles. Leita et al. (2009) added that the persistence of Cr(VI) in the soil might be interpreted by the formation of Cr(VI)-HA micelles. Hence, the removal of $Cr_2O_7^{2-}$ by HA-bent from the solution under our study conditions could be attributed to the binding of free metal anions with the positively charged sites and the formation of $Cr_2O_7^{2-}$-HA micelles on the sorbent surface.

Sorption of metal ions by all sorbents can be expressed by the pseudo second order kinetic model. That model was also selected as an appropriate kinetic model to describe the sorption of heavy metals on modified bentonite by Huang et al. (2011). The model may indicate chemical sorption as noted by Rao et al. (2006).

The low sorption of metal ions by OMCs at initial pH 2 may refer to the competition between the H^+ and the metal cations on active sorption sites. In addition, protonation of the functional groups, like surface hydroxyl, carboxyl or amino groups, on the sorbents might take place, producing repulsive forces to positively charged ions in the solution (Malakul et al., 1998; Al-Jlil, 2010). These results are in agreement with that obtained by Oyanedel-Craver and Smith (2006) in their study on the sorption of Cd^{2+} and Pb^{2+} by HDTM-bentonite at different pH. With increasing initial pH deprotonation of the functional groups may occur. Consequently, the metal ions species react with the sorbent surfaces via electrostatic forces, surface complexation and precipitation thus enhancing the sorption of Cd^{2+} and Pb^{2+}. Agrawal and Sahu (2006) and Papelis and Hayes (1996) demonstrated that sorption of metal ions on clay minerals may take place on the permanent charge and surface hydroxyl sites at pH higher than 6.5 at low electrolyte concentration. The effect of pH on the sorption of Cd^{2+} and Pb^{2+} by OMCs recorded a similar trend as that reported on the sorption of these metal ions by activated carbon from industrial wastewater, whereby the highest sorption was recorded at pH 4 and remained constant up to pH 10 (Kadirvelu et al., 2001).

Optimal sorption of $Cr_2O_7^{2-}$ was recorded at pH 4. At this pH, amino or phosphonium groups on the sorbents are protonated, providing positive charges on the surfaces and increasing the sorption of anions. A similar trend was shown by Pandey et al. (2010) and Hong et al. (2008). Increasing pH reduces the sorption of $Cr_2O_7^{2-}$. The reason can be referred to the partial deprotonation of the silanol and aluminol groups on the sorbents producing net negative charges on the surface which led to a repulsion with anions in the solution. The described effect could be also due to the deprotonation of the amino groups reducing the ability of the sorbents to bind with $Cr_2O_7^{2-}$ ions. In addition, an increase in the pH increases the concentration of OH^- ions in the medium which compete with $Cr_2O_7^{2-}$ on the sorption sites (Majdan et al., 2005).

The reduction in the sorption of Cd^{2+} obtained with increasing the $Ca(NO_3)_2$ concentration can be attributed to the competition between Ca^{2+} and Cd^{2+} on the sorption sites. These competition phenomena may confirm the assumption that adsorption mechanisms are involved in the removal of Cd^{2+} by OMCs. The competition was less pronounced with MTP- and HDTM-bent, indicating that other mechanisms such as surface precipitation or poly-nucleation are involved in the sorption of Cd^{2+} by these sorbents. However, the presence of $NaNO_3$ up to 0.01 M had no significant effect on the sorption of Cd^{2+}, which might be refered to the low ability of monovalent cations (Na^+) of the electrolyte to compete with the divalent metal cations (Cd^{2+}), particularly at low concentrations of Na^+ ions. If the electrolyte concentration increased, the competition phenomenon becomes more important, leading to a reduction of Cd^{2+} sorption. No relevant differences in the sorption of Pb^{2+} by Carnitin-, MTP- and HDTM-bent were observed with changing of the electrolyte concentration. This may indicate that other mechanisms rather than adsorption were playing the main role in the sorption of Pb^{2+}. The obtained behavior of Pb^{2+} in this study was in accordance with that obtained for the sorption of metal ions to montmorillonite by Chen and Hayes (1999) under similar electrolyte concentration. The authors confirmed the sorption via forming surface co-precipitates by X-ray absorption spectroscopy investigations. Moreover, the higher affinity constant (K) recorded for MTP- and HDTM-bent with Cd^{2+} or Pb^{2+} among all OMCs, could be another explanation for the low or none influence of the electrolyte concentration on the sorption of metal ions by both sorbents (see section 3.5.2).

In contrast, the sorption of Pb^{2+} ions by HA-bent was significantly influenced by increasing concentrations of different electrolytes due to the competition between Pb^{2+} ions and Ca^{2+}or Na^{+} ions on the active sorption sites on HA-bent. In an investigation on the sorption of Cd^{2+} and Pb^{2+} on particulate organic matter in soils, the influence of electrolyte concentration on the sorption of metal ions were attributed to the nature of the binding sites on the sorbent (Guo et al., 2006). The ability of electrolyte ions to replace the metal ions was increased with the availability of outer-sphere adsorption sites and was reduced with the inner-sphere adsorption. Comparing that finding with the results of this study, the formation of outer-sphere complexes could be suggested as a mechanism of the sorption of Cd^{2+} and Pb^{2+} to HA-bent.

The obtained results support the predicted speciation of the metal ions and the proposed sorption mechanisms reported above.

Slight decrease in the sorption of $Cr_2O_7^{2-}$ was recorded when $NaNO_3$ was used as background electrolyte (Table 3-7). This trend could support the assumption that inner-sphere complexes are prevalent processes in the sorption of $Cr_2O_7^{2-}$ by OMCs (Goh et al., 2010). However the enhancement of the sorption of $Cr_2O_7^{2-}$ observed in case of $Ca(NO_3)_2$ was unexpected. This finding may be referred to the role of Ca, whereby the Ca ions of the electrolyte may form a ternary complex with the $Cr_2O_7^{2-}$ ions at the sorbents surface (OMC-Ca-$Cr_2O_7^{-}$), providing additional sorption sites for $Cr_2O_7^{2-}$. Elzinga et al. (2001) stated that the formation of Pb-SO_4 ternary complexes at the goethite surface promoted the sorption of SO_4^{2-}.

The high recovery of Cd^{2+} and Pb^{2+} achieved by HCl may be attributed to increasing protons (H^{+}) concentrations, which replaces the sorbed metal cations on the sorption sites. Further, acidic conditions provided by HCl led to a protonation of the functional groups on the OMCs, reducing the binding with metal cations and displacing the bound cations by H^{+}. On the other hand, deprotonation of the functional groups may occur due to the usage of NaOH as desorbing agent, inhibiting the desorbability of the metal ions. Similar explanations were reported by Wankasi et al. (2005). Approximately, half of the sorbed $Cr_2O_7^{2-}$ ions were retained on the OMCs, indicating partial irreversibility of these ions by Cys_ester-bent. Incomplete reversibility of the sorbed $Cr_2O_7^{2-}$ ions on HDTM-modified clinoptilolite was obtained previously by Haggerty and Bowman (1994). Desorbability of the metal ions give the potential for the sorbents to be regenerated and reused in the pollutants removals, increasing the economic feasibility of OMCs.

3.6.2 Competition effect of cadmium and dichromate sorption

Sorption of Cd^{2+} ions neutralizes the negative charges on the sorbent surface, which reduces the surface repulsion with the anions in the solutions and promotes the sorption of $Cr_2O_7^{2-}$. On the other hand, sorption of $Cr_2O_7^{2-}$ probably causes a steric hindrance for Cd^{2+} ions, limiting the access of Cd^{2+} ions to the active sites on the OMCs. In case of a Cys_ester-bent system, no significant differences between the sorption of Cd^{2+} and $Cr_2O_7^{2-}$ from their single and binary component systems were observed. Such behavior indicates that each of these ions adsorbed on different sorption sites of Cys_ester-bent.

It can be concluded from the results that MTP-, HDTM- and Cys_ester-bent have the potential to remove anions and cations pollutants at all initial concentrations. That indicates the prospective application of the proposed OMCs in wastewater treatment.

3.7 Conclusions

Natural bentonitic sediments loaded with organic modifiers possesses different functional groups (OMCs) were used in the removal of cationic (Cd^{2+} and Pb^{2+}) and anionic ($Cr_2O_7^{2-}$) pollutants from aqueous solutions. Successful removal of the metal ions by the prepared sorbents was shown, whereby the maximum sorption capacities were different according to the modifier type. The sorption of Cd^{2+} and Pb^{2+} at the low initial ions concentrations probably occurred via adsorption mechanisms, whereas ion exchange as well as surface complexations and precipitation is probably involved in the sorption of the metal ions at high initial concentration. Sorption of $Cr_2O_7^{2-}$ was mainly controlled by adsorption mechanisms. In addition, the presence of functional groups with oxygen, i.e. phenol, carbonyl and carboxylic groups, as well as disulfide and amino groups on the structure of the organic modifiers increased the abilities of the modified bentonitic sediments towards an effective depletion of the studied metal ions from aqueous solutions.

Highest removals of the metal ions Cd^{2+} and Pb^{2+} were obtained at pH ranging from 4 to 8 and from 4 to 6, respectively. Optimum sorption of $Cr_2O_7^{2-}$ exhibited at pH 4. The sorption data were expressed by Langmuir isotherm model and followed the pseudo second order kinetics. Desobability of the studied heavy metals were achieved by 0.01 M HCl as desorbing agent, indicating a possibility for the reuse of the OMCs. It can be concluded from the sorption of metal ions from the binary systems that the OMCs have the potential to remove both cationic and anionic pollutants from their binary component systems.

4. Simultaneous Sorption of Organic and Inorganic Pollutants on Organically Modified Bentonitic Sediments

4.1 Abstract

Natural clayey sediments initially treated with various organic modifiers with different functional groups (OMCs) were tested to remove heterogeneous pollutants from aqueous solutions. Metalaxyl-m (MM) as organic pollutant, Cd^{2+} and $Cr_2O_7^{2-}$ as cationic and anionic inorganic pollutants, respectively, were selected as common pollutants frequently detected in drainage and wastewater. Sorption experiments with OMCs were conducted as function of the initial concentrations of all pollutants.

The results from the single component systems showed a higher sorption of MM by OMCs as compared with the natural clayey sediment (bentonitic sediment). Freundlich model properly described the sorption data. The highest soption constants (K_f) were displayed by OMCs with the organic modifiers Hexadecyltrimethyl-ammonium (HDTM-bent) and L-Cystine dimethyl ester (Cys_ester-bent). The sorption of MM can be explained via adsorption mechanisms and hydrophobic interaction with the organic modifiers located in the interlaminar of clay.

Competitive phenomena were recorded between the pollutants when their sorption from the ternary component systems was investigated. Compared with their sorption from the single component systems, in the ternary component systems a reduction in the sorption of Cd^{2+} to OMCs with Methyltriphenyl-phosphonium organic modifier (MTP-bent) and HDTM-bent as well as in the sorption of MM to HDTM-bent was observed. Concomitantly, remarkable enhancements in the sorption of $Cr_2O_7^{2-}$ to the mentioned OMCs were obtained from the ternary component systems.

The presence of Cd^{2+} and $Cr_2O_7^{2-}$ in the ternary component systems promoted the sorption of MM to Cys_ester-bent as compared to the sorption of MM when it was the only solute in the system. However, no appreciable changes in the sorption of Cd^{2+} and $Cr_2O_7^{2-}$ to Cys_ester-bent from the ternary component systems compared with the single component systems were found.

The results illustrated that the natural clayey sediment had no potential to remove heterogeneous pollutants from an aqueous solution. However, OMCs exhibited high efficiencies in the removal of both cationic and anionic inorganic as well as organic pollutants from aqueous solutions.

4.2 Introduction

Metalaxyl-m (MM) is a fungicide widely used in Egypt and worldwide to control plant diseases in field crops and vegetables as well as in green houses as soil or foliar application. Owing to its properties as a stable and resistance substance at day light at a broad range of pH (Andrades et al., 2001), it was detected in high concentrations in agricultural drainage water (Müller and Busser, 1995). Cadmium and chromate are inorganic pollutants often found in the wastewater. Since metals and organic compounds have different behavior and transport characteristics in soil and water, remediation of both contaminants simultaneously is generally more difficult than of a single contaminant (Oyanedel-Craver and Smith, 2006). The development of an adsorbent, which removes heavy metals and organic pollutants at the same time in heterogeneous combinations is thus rather challenging. There have been considerable efforts in developing modified clay based adsorbents for the removal of these pollutants.

The efficacy of using organo-clay complexes for the adsorption of organic pollutants was reported in literature (Sheng et al., 2001; Shakir et al., 2008; Suciu and Capri, 2009). A common method to produce organo-clay complexes is replacing (partly) the clay's natural inorganic exchangeable cations by organic cations. The type of these organic ions plays an important role in the adsorptive properties of the modified clay. Azejjel et al. (2009) investigated the sorption of terbutryn (basic), dicamba (anionic) and paraquat (cationic) herbicides by natural and modified Moroccan clay. They concluded that modifying the clay with long chain organic compounds was effective to remove anionic and basic herbicides, while the original clay was effective to remove the cationic ones. The significance of using long-chain organic ions in the modification of clay minerals toward the adsorption of hydrophobic fungicides was also reported by Rodríguez-Cruz et al. (2007). They concluded that the modification of montmorillonite clay by two-chain organic cations increased the Freundlich constant 4 to 112 fold for metalaxyl as compared to the unmodified clay. Further, Cruz-Guzmán et al. (2004) used natural organic cations with low charge montmorillonite to prepare organo-clay complexes with different functional groups (such as NH_2, COOH, CS_2 or pyrimidine ring). The organo-clay complexes were used to adsorb the herbicide si4.4mazine. The authors demonstrated that the presence of the functional groups afforded a suitable interlayer environment which increased the adsorption efficiency of the modified clay to simazine.

Consistent with the above idea, the simultaneous sorption of lead and chlorobenzene was investigated by Sheng et al. (1999) using organo-clay complexes with carboxylic functional groups and montmorillonite as clay material. As stated from their results, Pb^{2+} was efficiently bonded to the carboxylic group and the organo clay was effectively capable to remove both pollutants Pb^{2+} and chlorobenzene from their binary component system.

The simultaneous adsorption of pollutants by organo-clay complexes is affected by the presence of other solutes in the medium, which might cause a competition on the adsorption sites of the clay. Separate adsorption of Pb, Cd, Zn and Hg on benzyltriethylammonium bentonite clay (BTEA-clay) and hexadecyltrimethyl-ammonium bentonite clay (HDTMA-clay) in the presence or absence of benzene was studied by Oyanedel-Craver et al. (2007). The authors observed competitive behaviors between the organic pollutant and the metal ions. These behaviors were indicated by a decline in the adsorption of metal ions in presence of benzene as compared with those in absence of benzene. The competitive effects were pronounced with all the metal ions studied except for Hg, which showed no difference in the adsorption. They also reported that the presence of heavy metals decreased the adsorption of benzene on BTEA-clay relative to that from the single solution system.

In an investigation aiming to stabilize wastes by using modified bentonite with benzyldimethyl octadecyl-ammonium in cement-based processes, a strong competitive effect was found when the modified bentonite was used for the adsorption of 2-chlorophenol (CP) simultaneously with Cd or Pb from aqueous solutions (Andini et al., 2006). As compared with the sorption of a pollutant as sole contaminant, the competition between both inorganic and organic contaminants reduced the adsorption of CP to the half, whereas no or only a slight adsorption of Cd and Pb were obtained.

More work is needed to study the adsorption of different type of pollutants (anionic, cationic, organic and inorganic) by organically modified clayey sediments.

In our previous studies the effectiveness of organically modified bentonitic sediments (OMCs) as environmentally friendly and cost effective sorbents in the removal of Cd^{2+}, Pb^{2+} and $Cr_2O_7^{2-}$in single and binary component systems were investigated. In this study, OMCs, which were synthesized from natural clayey sediments by loading with various types of organic modifiers (Humic acid, L-Carnitine, L-Cystine dimethyl ester, Methyltriphenyl-phosphonium and Hexadecyltri-methylammonium) are evaluated with respect to their potential to remove different pollutants ($Cr_2O_7^{2-}$, Cd^{2+} and MM) simultaneously from aqueous solution. Hereby, the following hypotheses were tested: i) Modification of natural clayey sediments with different organic modifiers increase the sorption of MM. ii) the presence of dichromate (anionic) and cadmium (cationic) affect the sorption of MM by OMCs.

4.3 Materials and Methods

4.3.1 The sorbent materials

The materials used in this study were organically modified bentonitic sediments (OMCs) synthesized from natural clayey sediments treated with different organic modifiers (see structure in Fig. 4-1) according to the procedure described in chapter 3. The natural clayey sediment was collected from Qaser el-Sagha, El-Fayoum, Egypt. Smectite clay minerals are the predominant component in this sediment and cation exchange capacity is 48.1 cmol kg^{-1} (Chapter 2). The clayey sediment was used as sodium clay (Na-bent). In brief, the organic modifiers were dissolved in 1 mM HNO_3 and mixed with Na-bent to obtain a solid concentration of 10 g l^{-1}. The concentrations of the organic modifiers in the suspensions were $5x10^{-3}$ M of L-Carnitine (Carnitin), Hexadecyltri-methylammonium (HDTM) or Methyltriphenyl-phosphonium (MTP), $10x10^{-3}$ M of L-Cystine dimethyl ester (Cys_ester) or 0.5 g l^{-1} of Humic acid (HA). The suspensions were shaken for 27 h under dark conditions at room temperature. Afterwards, they were centrifuged and the solid materials were washed with ultrapure deionized water and freeze dried. The exact procedure and the characteristics of all prepared materials are described in chapter 2 and 3. The obtained materials denoted as Carnitin-bent, Cys_ester-bent, MTP-bent, HDTM-bent and HA-bent for the OMCs modified with Carnitin, Cys_ester, MTP, HDTM and HA, respectively.

4.3.2 The pollutants tested

High purity $Cd(NO_3)_2 \cdot 3H_2O$ (Fluka, 99 %) and $K_2Cr_2O_7$ (Sigma-Aldrich, 99 %) were used in the preparation of heavy metal solutions. Metalaxyl-m pestanal, HPLC analytical standard, 99 % (N-(2,6-Dimethylphenyl)-N-(methoxyacetyl)-D-alanine methyl ester) was supplied from Sigma-Aldrich Chemie GmbH in liquid form (see structure in Fig. 4-1).

4.3.3 Screening experiment with metalaxyl-m

To test the sorbability of OMCs for MM, screening experiments were performed by mixing 2 mg l^{-1} MM, prepared in 0.01 M NaCl at pH 4, with Na-bent or OMCs in centrifuge tubes. The solid concentration was 10 g l^{-1}. The samples were shaken for 24 h with 175 rpm at ambient conditions. To exclude the sorption of fungicide by the tubes, control samples without sorbent were prepared by identical procedures to determine the initial concentration of MM. The experiments were performed in duplicates.

4.3.4 Sorption isotherm experiment with metalaxyl-m

To study the sorption isotherms of MM, batch sorption experiments were conducted by using Na-, Cys_ester-, MTP-, and HDTM-bent with different concentrations of MM ranging from 0 to 2 mg l^{-1}. The samples were prepared in 0.01 M $NaNO_3$ at pH 4 in triplicates. Samples were shaken for 24 h at ambient conditions.

4.3.5 Sorption of metalaxyl-m, cadmium and dichromate from single and ternary component systems

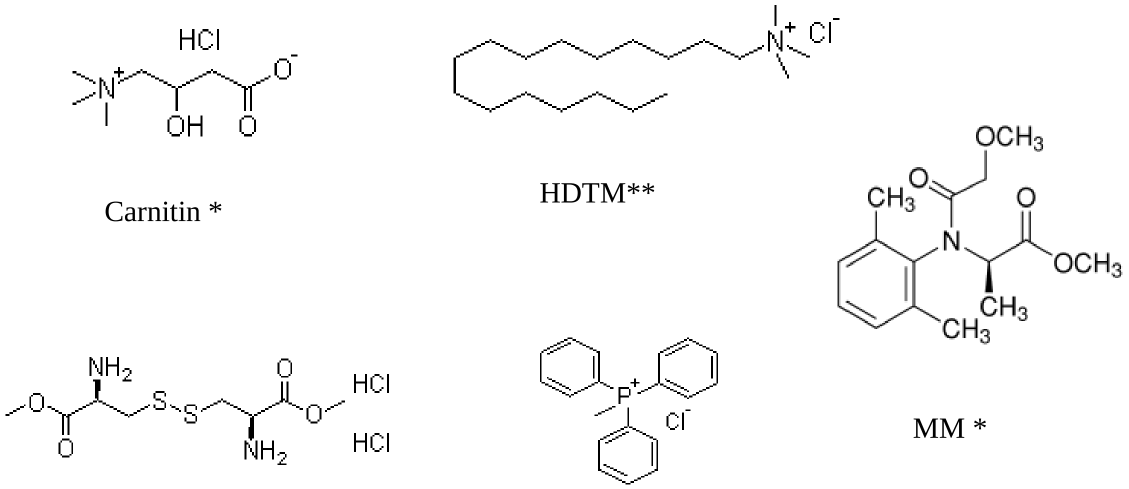
Sorption isotherm experiments were carried out to study the competitive effects of organic and inorganic pollutants on their sorption by Na-bent and OMCs from ternary component systems compared with single component systems. Each sorbent was equilibrated with 0.01 M $NaNO_3$ (pH 4) containing concentrations of 0 - 2 mg l^{-1} MM, 0 - 3 mM Cd^{2+} and 0 - 6 mM $Cr_2O_7^{2-}$ individually or mixed (ternary component systems) in triplicates. The solid : liquid ratio was 10 g l^{-1}. The samples were shaken for 24 h at room temperature.

In all sorption experiments, solutions without sorbents were prepared by identical procedures to determine the initial concentration of pollutants. Afterwards, the suspensions and solutions were centrifuged and the supernatants were removed for analyses.

The concentrations of MM in the supernatants and solutions were determined by high-performance liquid chromatography LC-MS/MS (HPLC; Sil-20, Shimadzu, Germany). The following conditions were used: Column: Gemini-NX C18, 150 x 3 mm, 3 µm core size, Phenomenex; flow rate: 0.3 ml min^{-1}; injection volume: 5 µl; eluent system: ammonium acetate in methanol; Temperature: 30°C.

External calibration was used for quantification. The concentrations of heavy metals in the supernatants or solutions were determined by atomic absorption spectroscopy (AAS) using an Unicam 939 AA spectrometer.

The sorbed amount of each pollutant was calculated by the difference between the initial and the final sorbate concentration.



Carnitin *

HDTM**

MM *

Cys_ester *

MTP *

Fig. 4-1 Chemical structure of the organic modifiers and metalaxyl-m (fungicide).
The Molecular structure provided by online Database of Chemicals from Around the World (http://www.chemblink.com, 04 – 04 - 2011). * Analytical grade, provided by Sigma & Aldrich, Germany, ** Analytical grade, supplied by Fluka.

4.4 Models calculation

Sorption isotherms data of MM from the single component system were analyzed using Freundlich isotherme (Eq. 4-1; Sparks, 2003).

$$C_s = K_f C_e^{\frac{1}{n}} \quad \text{----------------------------------} \quad \text{Eq. 4-1}$$

$$\log C_s = \log K_f + \frac{1}{n} \log C_e \quad \text{--------------} \quad \text{Eq. 4-2}$$

Where C_s is the sorbed amount of MM per unit mass, C_e is the concentration of MM at equilibrium in the solution; K_f and $\frac{1}{n}$ are the constant parameters indicated the relative sorption capacity (when C_e =1; Carrizosa et al., 2000) and the sorption intensity, respectively. The constants of Freundlich were calculated from the intercept and slope of the linear form (Eq. 4-2).

In order to determine the competitive effect on the sorption of the organic (MM) and inorganic (Cd^{2+}; $Cr_2O_7^{2-}$) pollutants, the sorption data of each pollutant from each single and ternary component system were compared statistically by using Tukey test ($p < 0.05$).

4.5 Results

4.5.1 Screening experiment

Sorption of MM by the different OMCs and Na-bent are presented in Fig. 4-2. Among all sorbents, the lowest sorption of MM was recorded for Na-bent. OMCs showed increasing sorption of MM in the following order: Carnitin- < HA- < MTP- < Cys_ester- < HDTM-bent.

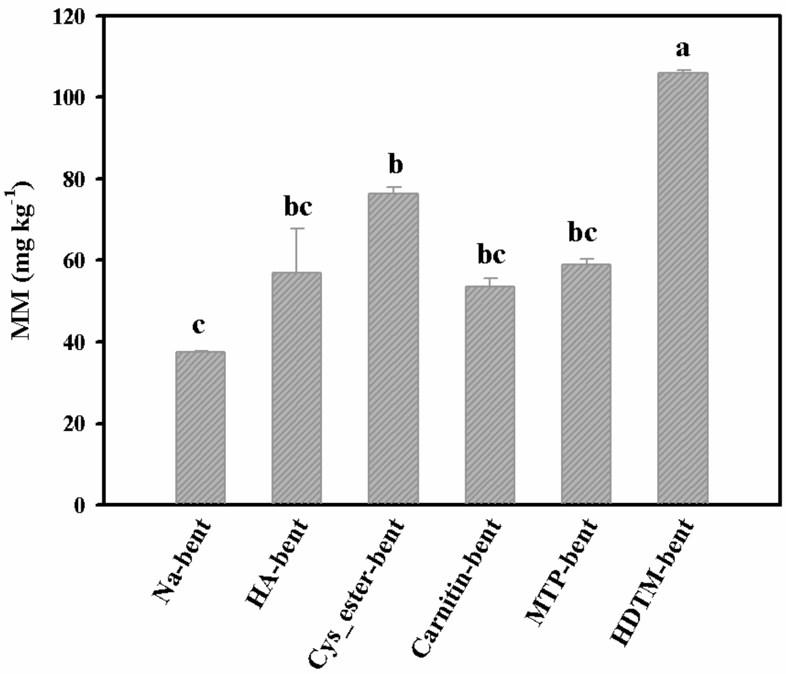


Fig. 4-2 Sorption of metalaxyl-m (MM) on natural clayey sediment (Na-bent) and organically modified bentonitic sediments (OMCs).

HA-, Carnitin-, Cys_ester-, MTP- and HDTM-bent are the OMCs with the organic modifiers described in Fig. 4-1. Initial concentration of metalaxyl-m was 2 mg l^{-1}, prepared in 0.01 M NaCl at pH 4. Bars indicate standard errors of the means (n=2). Columns with different letters are statistically significant different in the sorbed MM between the different sorbents (Tukey test, $p \leq 0.05$).

4.5.2 Sorption isotherms of metalaxyl-m from single component systems

Fig. 4-3 shows the sorption isotherms of MM by Na-bent and OMCs and Table 4-1 presents the parameters and coefficients of determination (R^2) of the Freundlich isotherm. Na-bent showed very low sorption of MM (0.7 – 7.6 mg kg^{-1}) at low to the middle initial MM concentrations, which increased to 20 mg kg^{-1} at the highest initial concentration. A similar trend was exhibited by the sorption of MM to MTP-bent. The results indicated that the sorption of MM by OMCs increased with increasing initial concentration and did not reach the plateau even with the highest initial concentration (2 mg l^{-1}). Modifying the clayey sediment with HDTM and Cys_ester increased the sorption of MM by 11 fold at the low initial concentrations and 2.3 fold at the highest initial MM concentrations compared with Na-bent. Freundlich model were found to appropriately represent the observed sorption data indicated by the high R^2 (Fig. 4-3 and Table 4-1). Cys_ester- and HDTM-bent achieved the highest sorption coefficient (K_f) among the tested sorbents (Table 4-1).

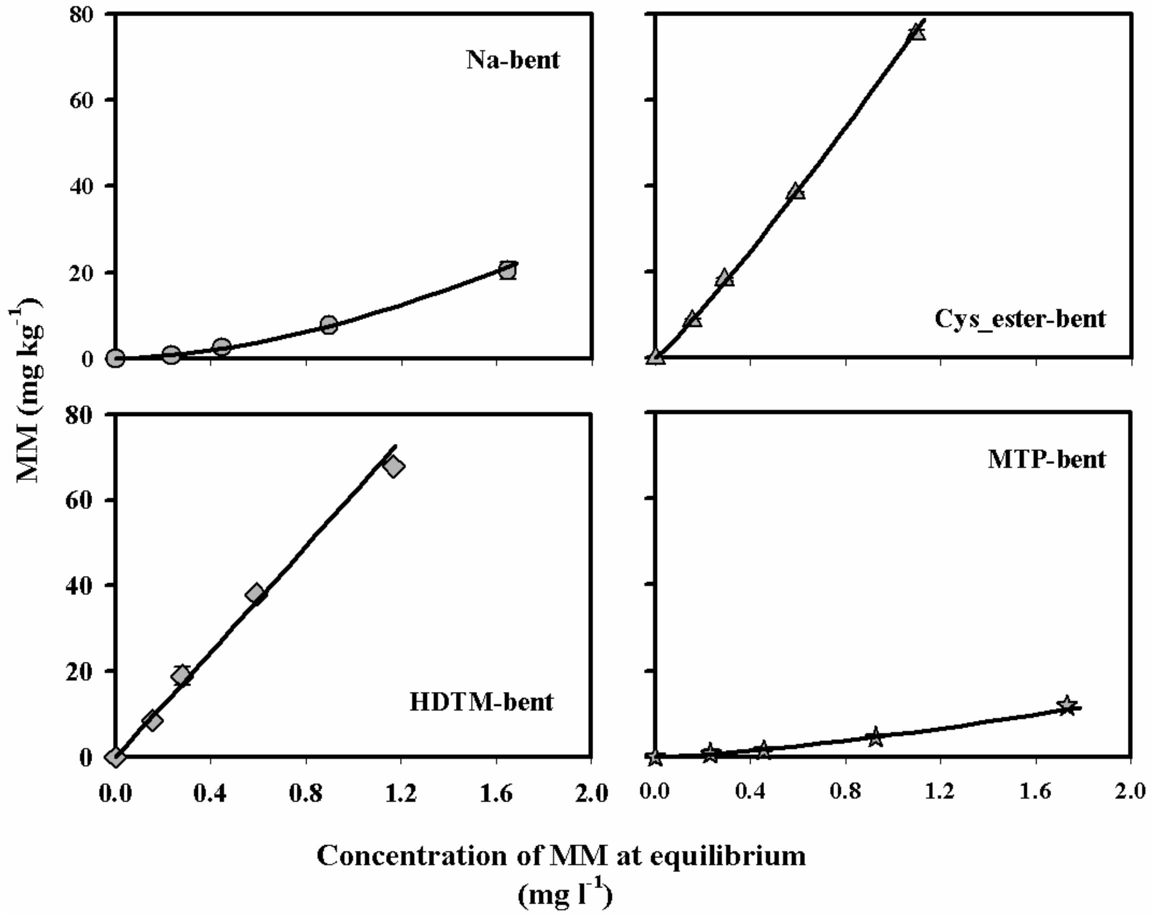


Fig. 4-3 Sorption isotherms of metalaxyl-m (MM) on natural clayey sediment (Na-bent) and organically modified bentonitic sediments (OMCs) from single component systems Lines show Freundlich model fiting to the measured data. Cys_ester-, HDTM- and MTP-bent are the OMCs with the organic modifiers described in Fig. 4-1. Initial concentrations of metalaxyl-m ranged from 0 to 2 mg l^{-1}, prepared in 0.01 M $NaNO_3$ at pH 4. Standard errors are hidden by the data points (n=3).

Table 4-1 Freundlich equation parameters and coefficients of determination (R^2) for metalaxyl-m sorption

Adsorbent	log K_f	K_f*	1/n**	R^2
Na-bent	0.96	9.09	1.71	0.997
Cys_ester-bent	1.84	68.7	1.11	0.999
MTP-bent	0.71	5.11	1.39	0.987
HDTM-bent	1.79	61.6	1.01	0.99

*Freundlich sorption constant. ** Freundlich exponent (intensity).

Na-bent is sodium form of the natural clayey sediment, Cys_ester-, HDTM- and MTP-bent are the OMCs with the organic modifiers described in Fig. 4-1.

4.5.3 Simultaneous sorption of cadmium, chromate and metalaxyl-m from ternary component systems

The results obtained for Cd^{2+}, $Cr_2O_7^{2-}$ and MM sorption from single and ternary component systems on Na-bent and OMCs as function of the initial solutes concentrations are presented in Figs. 4-4, 4-5 and 4-6, respectively. The ternary combination of MM, Cd^{2+} and $Cr_2O_7^{2-}$ decreased significantly the sorption of Cd^{2+} to the different sorbents compared with the single component system, except for Cys_ester-bent, particularly when initial pollutant concentrations increased. These reductions of the sorbed Cd^{2+} were highly pronounced by HDTM- and MTP-bent, especially at high initial concentrations of the tested pollutants. The sorption of Cd^{2+} to MTP- and HDTM-bent were declined by 30 and 3 %, respectively, with the presence of MM and $Cr_2O_7^{2-}$ at low initial concentration, whereas the diminution reached 71 and 63 %, respectively, at high initial concentrations (Fig. 4-4).

In comparison with the sorption from single component systems, the presence of Cd^{2+} and MM in the media increased significantly the sorption of $Cr_2O_7^{2-}$ to HDTM- and MTP-bent (Fig. 4-6), whereby the observed effect was increased with increasing initial solutes concentrations. In case of Cys_ester-bent, no appreciable differences in the sorption of $Cr_2O_7^{2-}$ were noticed in absence or presence of other solutes in the media at any of the initial pollutant concentrations (Fig. 4-5).

The presence of Cd^{2+} and $Cr_2O_7^{2-}$ in the solution inhibited the sorption of MM by Na-bent to negligible amounts at low to the middle initial solutes concentrations. At high initial solutes concentrations, the sorption was reduced from 20 to 6.9 mg kg^{-1}. Only little changes of the sorption of MM on MTP-bent were observed when comparing single with ternary component systems. Significant increases in the sorption of MM by Cys_ester-bent from ternary component systems compared with single component systems were obtained at all initial solutes concentrations.

Differences in the sorbed MM by HDTM-bent between single and ternary component systems were observed with increasing initial solutes concentrations and these differences were significant at the two highest levels of initial concentrations (Fig. 4-6).

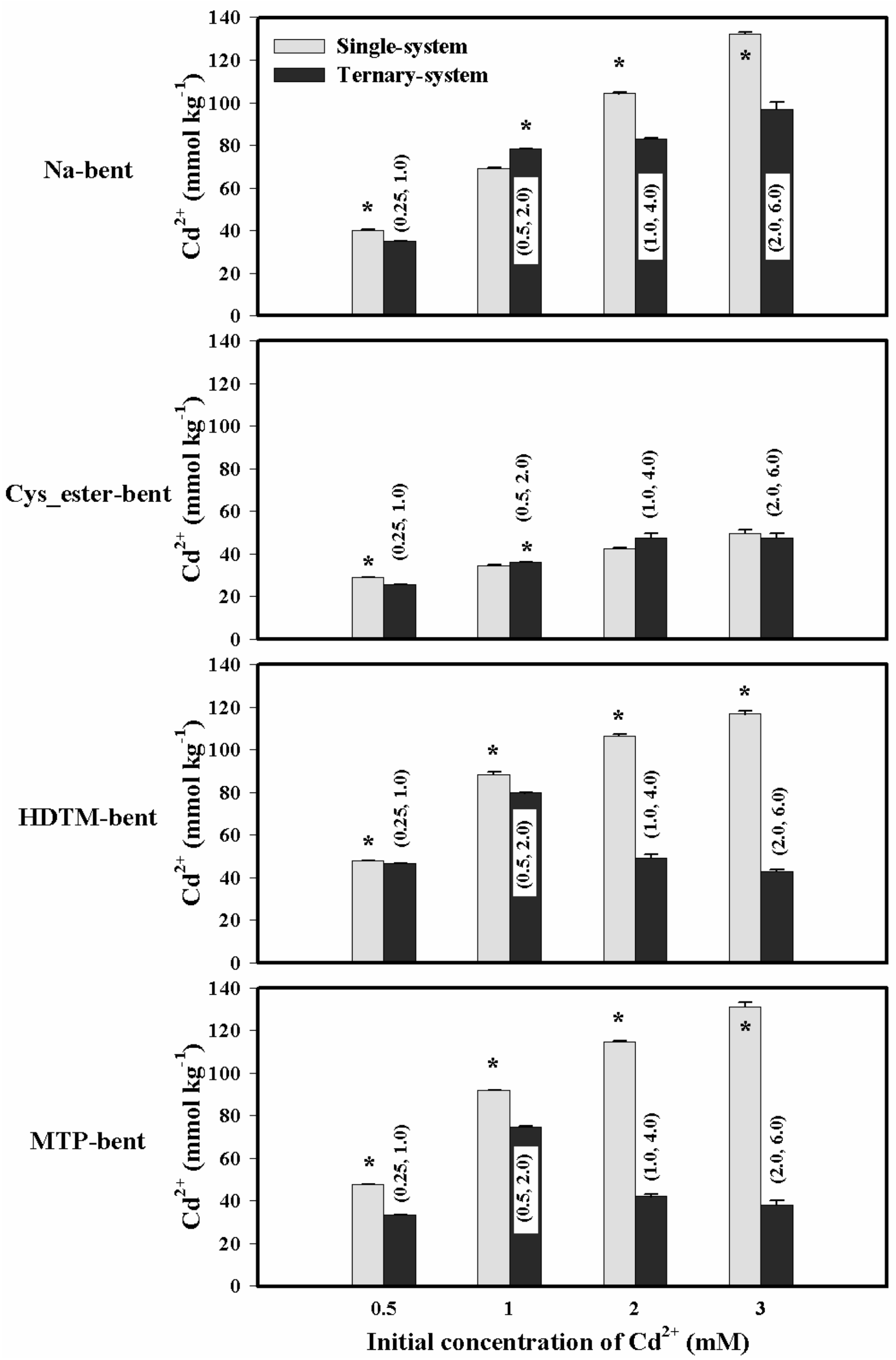


Fig. 4-4 Sorption of Cd^{2+} alone (single-systems) and in combination with metalaxyl-m and $Cr_2O_7^{2-}$ (ternary-systems) by the natural clayey sediment (Na-bent) and organically modified bentonitic sediments (OMCs).

In brackets the initial concentrations of metalaxyl-m (mg l^{-1}) and $Cr_2O_7^{2-}$ (mM), respectively, in the ternary component systems are shown. Cys_ester-, HDTM- and MTP-bent are OMCs with the organic modifiers described in Fig. 4-1. Bars indicate standard errors of the means (n=3). Asterisks indicate statistically significant differences (Tukey test, P<0.05) between the sorbed Cd^{2+} from single and ternary component systems within one initial concentration of the pollutants and one sorbent.

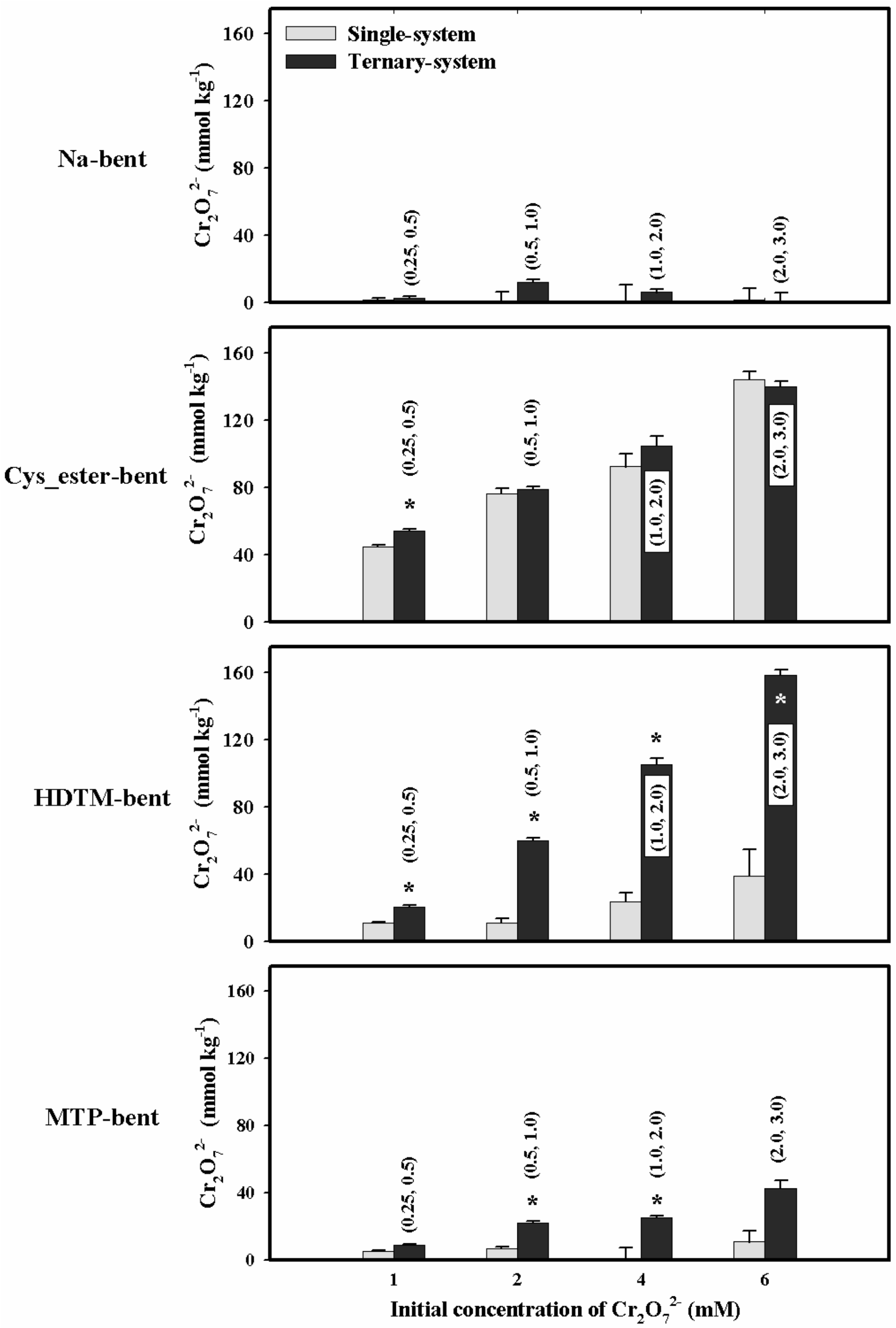


Fig. 4-5 Sorption of $Cr_2O_7^{2-}$ alone (single-systems) and in combination (ternary-systems) with metalaxyl-m and Cd^{2+} by the natural clayey sediment (Na-bent) and organically modified bentonitic sediments (OMCs).

In brackets, the initial concentrations of metalaxyl-m (mg l^{-1}) and Cd^{2+} (mM), respectively, in the ternary component systems are shown. Cys_ester-, HDTM- and MTP-bent are OMCs with the organic modifiers described in Fig. 4-1. Bars indicate standard errors of the means (n=3). Asterisks indicate statistically significant differences (Tukey test, P<0.05) between the sorbed $Cr_2O_7^{2-}$ from single and ternary component systems within one initial concentration of the pollutants and one sorbent.

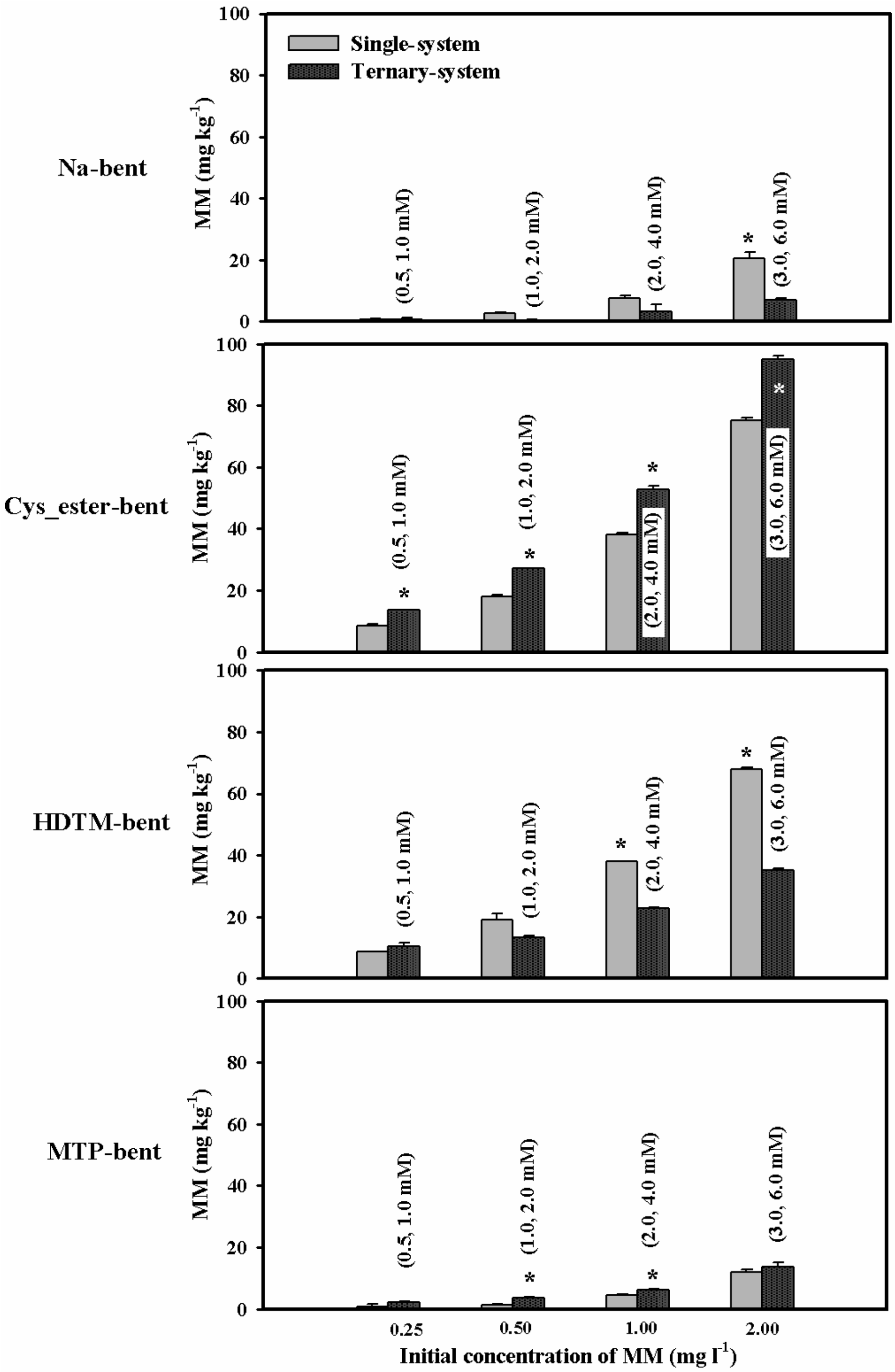


Fig. 4-6 Sorption of metalaxyl-m (MM, mg kg-1) alone (single-systems) and in presence of Cd^{2+} and $Cr_2O_7^{2-}$ (ternary-systems) on natural clayey sediment (Na-bent) and organically modified bentonitic sediments (OMCs)

In brackets, the initial concentrations of Cd^{2+} and $Cr_2O_7^{2-}$ (mM), respectively, in the ternary component systems are shown. Cys_ester-, HDTM- and MTP-bent are OMCs with the organic modifiers described in Fig. 4-1. Bars indicate standard errors of the means (n=3). Asterisks indicate statistically significant differences (Tukey test, P<0.05) between the sorbed MM from single and ternary component systems within one initial concentration of the pollutants and one sorbent.

4.6 Discussion

4.6.1 Sorption of metalaxyl-m from single component systems

Sorption of MM on Na-bent was negligible at the low initial MM concentration, while with increasing initial concentration the sorption increased to 20 mg MM kg^{-1} clay. Low sorption of MM by Na-bent might be due to the presence of hydration shells of the initial inorganic ions (Na^+) exchanged on the clay surface, hampering the sorption of MM especially at low initial concentration. The later increase may be attributed to the adsorption in the interlayer space as reported by Andrades et al., (2001). Above explanation for low sorption was previously stated by Fernandes et al. (2003) from their investigation on the sorption of metalaxyl on soil components.

MM sorption on MTP- and Na-bent displayed S-type, indicating the low affinity of the sorbents to the sorbate at low initial concentrations (Essington, 2004). Andrades et al. (2001) reported that at low fungicide concentrations, the isotherms depicted S-type with 1/n values higher than one denoting competition on the sorption sites between water molecule and fungicide, which is in agreement with the reported results herein (Fig. 4-3, Table 4-1).

Higher sorption of MM on HDTM- and Cys_ester-bent was confirmed by the higher relative sorption capacity (K_f) values compared to those for Na- and MTP-bent (Table 4-1). The sorption isotherm curves of MM on the former two sorbents were almost linear and depicted a C-type, which displays a constant partitioning of the sorbate between the sorbent and the aqueous media (Essington, 2004). Since the linearity of the curves did not change until the highest initial MM concentration (2 mg l^{-1}), the maximum sorption capacity was not reached and more sorption is possible.

Replacement of the inorganic cations, initially on the clay surface, with organic cations give hydrophobic and organophilic properties to the clay surface, consequently increasing the sorption of MM. Our previous studies on the characterization of OMCs stated that exchanging of the clayey sediments with Cys_ester and Carnitin organic modifiers reduced the basal spacing of the clay and minimized the intensities of the vibration bands of water molecules, which were displayed by the XRD patterns and MIRS spectra of Cys_ester- and Carnitin-bent as compared with the natural clayey sediments (chapter 2). Thus, hydrophobic environments are formed on these OMCs, allowing the sorption of MM. However, the differences in the sorbed concentrations of MM to the mentioned sorbents could be referred to structure variations of the organic modifiers. Thereby, the bivalency of Cys_ester may afford a better neutralization of the charges on the clay surface (Cruz-Guzmán et al., 2004) and/or provide more interaction sites between the sorbent surface and the polar group of MM as compared with the mono valence Carnitin.

In case of HDTM-bent, alkyl chains are known as water structure breakers (Yariv and Cross, 2002). Substitution of the large molecule HDTM on the clayey sediment produced a sufficient interlayer separation (d-spacing increased to 19.68 Å, chapter 2), thereby promoting the access of MM to the interlayer spacing. Besides, it reduces the amount of water molecules in the interlayer (Chapter 2), providing a hydrophobic and organophilic environment. This led to an increased sorption of MM to HDTM-bent compared with Na-bent and the other OMCs. Similar mechanismns were reported to explain the sorption of partially polar organic contaminants (i.e. bentazone) on organoclays (Carrizosa et al., 2000).

Although the exchanged MTP on the clayey sediment produced interlayer separation of the clay indicated by an increase of the basal spacing to 17.06 Å (Chapter 2), the sorption of MM by MTP-bent was lower than that on Cys_ester- and HDTM-bent. The low sorption of MM might be attributed to the geometry and the large molecular size of MTP with three phenol groups, causing a non-suitable environment to the interaction with MM. Similar interpretation was deduced by El-Nahhal (2003) in his study on the sorption of acetochlor to montmorillonite modified by phosphonium cations compared with those modified by alkyl ammonium cations.

It is reported that sorption of organic pollutants to montmorillonite loaded with straight alkyl chain organic modifiers is relatively higher than that to montmorillonite loaded with aromatic chain organic modifiers (Jaynes and Vance, 1996), whereby the straight alkyl chain organic modifier in the clay’s interlayer redistributes around the organic pollutant and pretend a solvent behavior for it, suggesting the partitioning into the organic modifier in clay’s interlamellar as a sorption mechanism. On the other hand, the structure of aromatic organic modifier located inside the interlayer space causes a steric hindrance, which partially limited the interacting between the organic pollutant and the sorbent surface, resulting in low sorption. Above assumption may explain the higher sorption of MM to HDTM-bent, which possess a straight alkyl chain, compared with MTP-bent with an aromatic chain, proposing partitioning as a sorption mechanism of MM to HDTM-bent.

The MM molecule has a hydrophobic and polar structural nature, which is shown by dimethylphenyl and methoxyacetyl moieties, respectively (Andrades et al., 2001). This structural nature indicates that binding with adsorption sites and hydrophobic interaction between sorbate and organic modifier loaded in the interlamellar of the clay are evolved in the sorption mechanism of MM by OMCs.

It is obvious from the screening and the results of the sorption isotherms that structure and different chemical properties of the organic modifiers played an important role on MM sorption. Previous work confirmed a significant correlation between soil organic matter and relative sorption capacity values (K_f) of metalaxy (Andrades et al., 2001). Further, in their study on sorption of penconazole by soil with different OM contents, Andrades et al. (2004) stated that content as well as nature of OM were implicated in the sorption process.

4.6.2 Simultaneous sorption of cadmium, chromate and metalaxyl-m from the ternary component systems

One explanation for the decreasing Cd^{2+} sorption from the ternary component systems compared to the single component systems by MTP- and HDTM-bent is presumably due to a steric hindrance caused by the sorbed MM, which reduces the possible contact to the sorption sites on the sorbent surface. This explanation was mentioned before in other cases for the competition between benzene and heavy metals sorption by HDTM- and benzyltriethyl-ammonium-bentonite clay (Oyanedel-Craver et al., 2007). Another possible explanation for the reduction in Cd^{2+} sorption is the formation of an OMC-Cd-Cr_2O_7 ternary complex, whereas the sorption of Cd^{2+} on montmorillonite from the single component system might take place via the formation of Cd-Cd and Cd-O molecules in the interlayers and on the surface of clay minerals (Malferrari et al., 2007). The existence of $Cr_2O_7^{2-}$ may prevent Cd-Cd formation by constructing monodentate bonds with Cd (OMC-Cd^+) on the clay surface, resulting in the ternary complex (OMC-Cd-Cr_2O_7), thus limiting Cd^{2+} sorption. Our previous investigation showed similar competition behavior between the sorption of Cd^{2+} and $Cr_2O_7^{2-}$ by HDTM- and MTP-bent from a binary component system (Chapter 3). Therefore, the decline of Cd^{2+} sorption from the ternary component system may mainly refer to the presence of $Cr_2O_7^{2-}$.

In contrast, the decline in Cd^{2+} sorption was concomitantly with increasing $Cr_2O_7^{2-}$ sorption. This observation may confirm the formation of the ternary complexes OMC-Cd-Cr_2O_7, wherein new sorption sites are provided for $Cr_2O_7^{2-}$ via the formed surface-monodentate-mononuclear-Cd^+ (OMC-Cd^+). The ternary complexes formation was previously suggested for Pb^{2+} and sulfate co-sorption on goethite surface by Tabatabai and Sparks (2005) and Elzinga et al. (2001). They concluded that the sorption of cationic heavy metals alters the surface charge of the clay, resulting in enhanced sulfate sorption.

The reduction in the sorption of MM by Na-bent from ternary component system (Cd^{2+}, $Cr_2O_7^{2-}$, MM) at the high initial concentration was probably caused by the sorbed Cd^{2+}. Sorption of Cd^{2+} might have two effects, from which the first is that Cd^{2+} might block the available surface sites on the clay and the second effect may be caused by the hydration shell formation of Cd^{2+}, which possibly led to a competition between water molecule and MM on the sorption sites of the clay surface.

The effect of hydration shell formation of Cd^{2+} may also explain the diminution of MM sorption to HDTM- and MTP-bent from the ternary component systems compared to the single component systems. Sun and Zhou (2010) observed reduction in the sorption of 1,4-dichlorobenzene accompanied with Cd and Cu on soils. They demonstrated that heavy metals with hydration shell of high density of water competed with the organic pollutant for the adsorption sites on soils. The observed phenomena were in agreement with those reported by Arias et al. (2006). They recorded a slight decline of MM sorption by soils with high OC content (4.4 and 4.9 % C) with the existence of copper relative to the sorption in the absence of copper.

It can be implied from the non-competitive sorption behavior of Cd^{2+} and $Cr_2O_7^{2-}$ from ternary component systems obtained with Cys_ester-bent that the sorption of each pollutant mainly occurred on different active sites on the sorbent. Cys_ester has a small molecular size, thereby distributed as separate molecules in the interlamellar, leaving some surfaces not occupied (Cruz-Guzmán et al., 2004). Those not occupied areas have the sorptive characteristics of the original clay, whereas the occupied areas have a organophilic characteristic, promoting the sorption of both Cd^{2+} and MM. Besides, the zwitterionic properties of Cys_ester afford different active sites on the Cys_ester-bent to bind with different pollutants types (Berthon, 1995). Cys_ester possess disulfide and carbonyl, which bind with the cationic pollutants, and amino groups, which bind with anionic pollutants. Similarity in the behavior of Cd^{2+} and

$Cr_2O_7^{2-}$ sorption on Cys_ester-bent was obtained from the binary (Chapter 3) and ternary component systems, which supports the suggested interpretations. Moreover, the coexistence of Cd^{2+} and $Cr_2O_7^{2-}$ increased the neutralization of the Cys_ester-bent surface, consequently inducing the dissolving of MM in the organic phase. The latest probably explains the enhancement of MM sorption to Cys_ester-bent recorded from the ternary component systems as compared with the single ones. In general, Cys_ester-bent had the lowest Cd^{2+} sorption among the OMCs, which might be another reason for the reduced competition of sorbates. The obtained results show the potential for using the proposed OMCs in the treatment of agricultural drainage water as well as industrial wastewater.

4.7 Conclusions

Negligible or low sorption of MM was shown by the natural clayey sediment, whereas loading the clays with different organic modifiers increased the removal of MM from aqueous solutions. MM was efficiently sorbed to Cys_ester- and HDTM-bent, wherein the sorption was based on binding to the available adsorption surface sites and partitioning between the hydrophobic organic phase (formed by the modifiers located on the clay surface) and the aqueous phase.

No competitive effects were observed for the Cd^{2+} sorption by Cys_ester-bent in the presence of other solutes in the medium, while a reduction in Cd^{2+} sorption was pronounced, when HDTM-, MTP- and Na-bent were used as sorbents, indicating the competitive effect among Cd^{2+}, $Cr_2O_7^{2-}$ and MM.

On the other hand, synergistic effects on sorption of $Cr_2O_7^{2-}$ by OMCs were obtained with the coexistence of Cd^{2+} and MM in the solution. The enhancement in $Cr_2O_7^{2-}$ sorption could be attributed to the formation of ternary complexes between Cd^{2+} sorbed on the OMC surface and $Cr_2O_7^{2-}$ ions (OMC-Cd-Cr_2O_7).

A decline in the sorption of MM by HDTM-bent was observed, however, an enhancement in its sorption was obtained by Cys_ester-bent from the ternary component systems compared to the single component systems.

Cys_ester- and HDTM-bent showed the capability to remove Cd^{2+}, $Cr_2O_7^{2-}$ and MM simultaneously from their ternary component systems.

The obtained results pointed out that type and the structure properties of the organic modifier are important factors to increase the efficacy of the clayey sediment to retain pollutants.

5. General Discussion and Outlook

5.1 Characterization of the sorbents and selection of the promising organically modified clayey sediments (OMCs)

Wastewater effluents are commonly contaminated by organic as well as inorganic pollutants. With the shortage of water especially in developing and emerging countries, an establishment of proper methods to remediate these waste waters is a main goal in sustaining the limited water resources, e.g. for irrigation purposes. The development of a sorbent, which removes heavy metals (cationic and anionic bonding forms) and organic pollutants at the same time, may be consider to efficiently clean up heterogeneous contaminations. Clays are considered as efficient sorbents for cationic heavy metals but they have a very limited ability to remove anionic or organic pollutants (Gonen and Rytwo, 2006).

Under this study conditions, the clayey sediment collected from Qaser el-Sagha (bent sediment) as natural source of smectite clay mineral showed high ability to remove Cd^{2+} and Pb^{2+} from aqueous solutions (Figs. 2-6 and 3-1). However, the clayey sediments collected from Sinai (Kao sediment) representing a natural source of kaolinite clay mineral had low removal of those metal ions (Fig. 2-5). Comparable results were reported by Chaves and Tito (2011) on the sorption of Cd^{2+} on the bentonite clay from Brazil and Talaat et al. (2011) on the sorption of Cd^{2+} and Pb^{2+} on Egyptian clay. On the other hand, both clayey sediments showed low or negligible sorption of $Cr_2O_7^{2-}$ (Figs. 2-5, 2-6 and 3-1). In addition bent sediment showed low ability to remove metalaxyl-m (MM) from aqueous solution (Fig. 4-3).

Modification of clay mineral with organic modifiers changes the characteristics of clay mineral and influences the sorption efficiencies of pollutants (Shen, 2004; He et al., 2006). The natural clayey sediments were used as basic materials in the preparation of organically modified clayey sediments (OMCs) to enhance the sorbability of clayey sediments toward the heterogeneous pollutants. kao and bent sediments were treated with organic modifiers L-Cystine dimethyl ester (Cys_ester), L-Carnitine (Carnitin), methyltriphenylphosphonium (MTP), hexadecyltrimethylammonium (HDTM) and humic acid (HA) to produce the OMCs. The results obtained from the X-ray diffraction (XRD) and mid infrared spectroscopy (MIRS) analyses of OMCS indicated that the organic modifiers are successfully loaded on the clayey sediments and the loading occurred in the interlamellar of OMCs based bent sediments and on the clay surfaces of OMCs based kao sediments. Similar results were reported by Rangsriwatananon and Khumbudda (2007) from their study on the sorption of HDTM on kaolinite and bentonite clay.

As stated in the literature, the modification of clay minerals with organic modifiers could enhance or reduce their sorption tendencies to retain pollutants depending on the loading ratio of the organic modifier to the clay (Lee and Kim, 2003; Oyanedel-Craver and smith, 2006). Therefore, one of the objectives of this study was to select the prospective OMCs, in which the loading concentrations of the organic modifiers on the clay will achieve high sorption of heavy metals both in cationic and anionic bonding forms. To achieve this aim, sorption of Cd^{2+}, Pb^{2+} and $Cr_2O_7^{2-}$ were tested as function of the added concentrations of the organic modifiers HDTM, MTP, Carnitin and Cys_ester (screening experiments in chapter 2). Discussing the results of the screening experiments in parallel with that obtained for the loading ratios achieved by the organic modifiers (see Table 2-4) as function of the added concentrations of the organic modifier, it can be concluded for the sorption on OMCs based on kao sediment (Fig. 2-5) that

- increasing the loading of the organic modifier enhanced the sorption of Cd^{2+}, Pb^{2+} on the OMC with MTP and Cys_ester, however it let to similar or a little lower sorption of those metal ions on OMC with HDTM compared with the natural kao sediment. Increase the added concentration of the modifier on the OMC with Carnitin reflected low loading ratio (8 % of the CEC of kao sediment) on the clay, resulting in similar sorption of Cd^{2+} and Pb^{2+} compared with the natural kao sediment. In fact, low removals % of Cd^{2+} or Pb^{2+} concentrations in the solutions were obtained by the OMCs based on kao sediments. However, remarkable enhancements in the sorption of $Cr_2O_7^{2-}$ on OMCs with HDTM and Cys_ester were observed and increasing modifier concentrations did not affect the sorption (Fig. 2-5). The successful removal of $Cr_2O_7^{2-}$ by kaolinite clay minerals modified with HDTM was stated earlier by Li and Bowman (2001).

Additional studies are needed including changing the sorption conditions, i.e. solid : liquid ratio, to enhance the sorption on the modified kao sediments. The sorbtivity of organic pollutants on the modified kao sediments also need to be tested.

The following were obtained for the sorption on OMCs based bent sediments:

- Loading of OMCs with any concentration of HDTM and MTP (up to 141 and 84 % of the CEC of bent sediment, respectively) were able to remove all Cd^{2+} and Pb^{2+} applied in the test solutions (Fig. 2-6 and Table 2-4). Contradicting results were reported by Lee and Kim (2003) and Cruz-Guzmán et al. (2006). Whereby the sorption of Cd^{2+} or Pb^{2+} was diminished with increasing loading of HDTM and the lowest sorption was recorded at HDTM loading equal to the CEC of smectite.
- All Pb^{2+} and 84 % of Cd^{2+} concentrations applied in the solutions were sorbed on OMC modified with Carnitin at loading concentration up to 21 % of CEC of the natural bent sediment. Further increase of Carnitin loading ratio the sorption of the metal ions decreased (Fig. 2-6 and Table 2-4). Cruz-Guzmán et al. (2006) studied the sorption of Pb^{2+} on modified Wyoming montmorillonite and observed increasing sorption of Pb^{2+} with increasing loading of Carnitin.
- Among all sorbents, the highest removals of $Cr_2O_7^{2-}$ were achieved by the OMCs modified with Cys_ester and HDTM at organic modifier contents equal to 66 % and 144 %, respectively, of the CEC of bent sediment (Fig. 2-6 and Table 2-4). The sorption behaviours of $Cr_2O_7^{2-}$ on HDTM were in agreement with that obtained by Majdan et al. (2005).

Due to the higher sorption of the metal ions obtained by the modified bent sediments than that by the modified kao sediments, the prospective sorbents were selected from the OMCs based on bent sediments.

To minimize cost for an effective removal of pollutants, natural bent sediments with the added concentrations of HDTM, MTP, Carnitin and Cys_ester which achieved loading modifier contents equal to 102, 79, 18 and 66 % of the CEC of bent sediment were selected to produce the promising OMCs and are referred to in the study as HDTM-bent, MTP-bent, Carnitin-bent and Cys_ester-bent, respectively.

5.2 Sorption characteristics of the selected OMCs

Bent sediment treated with HA (HA-bent) and the above mentioned promising OMCs were used for the sorption of Cd^{2+}, Pb^{2+}, $Cr_2O_7^{2-}$ and metalaxyl-m (MM). The maximum sorption capacities on the OMCs followed the order MTP- > Carnitin- > HDTM- > HA- > Cys_ester-bent for Cd^{2+}, MTP- > HDTM- > Carnitin- > HA- > Cys_ester-bent for Pb^{2+} and HDTM- > Cys_ester- > MTP- > HA- > Carnitin-bent for MM. Cys_ester-bent was the most efficient sorbent for $Cr_2O_7^{2-}$ followed by HDTM-, MTP- and HA-bent.

The separation factors (F) indicated that the sorption processes were favorable for the high initial pollutants concentrations than the low concentrations. The sorption was very favorable for Pb^{2+} (F value close to zero) and favorable for Cd^{2+} and $Cr_2O_7^{2-}$ as indicated by the separation factors (Fig. 3-2). Comparable trends were obtained by Polcaro et al. (2003) from their investigation on the sorption of Pb^{2+}, Zn^{2+}, Cd^{2+} on soils.

Optimum sorption of the heavy metals was observed at pH 4. The sorption keeps constant with an further increases of the pH for Cd^{2+} and Pb^{2+} but it decreased for $Cr_2O_7^{2-}$.

Those results indicated the potential application of OMCs in remediation of a wide range of wastewaters differing in properties (i.e. pH or pollutants concentrations)

The enhancement of the sorption on the clayey sediments by use of organic modifiers might be explained by different means. Exchanging the clayey sediments (bent sediment) with MTP and HDTM organic modifiers caused separation of the clay platelets, allowing and increasing the interaction between the surfaces of OMCs and the metal ions in the solutions, consequently, increased the sorption. This mechanism was stated previously by Stathi et al. (2007). They added that the intercalated organic substances in the modified montmorillonite strongly bind with the first hydroxide species of the metal ions, resulting in an increase of the removal of heavy metals compared with the untreated clay. HA, Carnitin and Cys_ester include different functional groups in their structures, i.e. COO-, CS_2, NH_2, -OH, -phenol. Loading of clays with these organic modifiers increased the number and the varieties of the active sorption sites on the clayey sediments, enhancing the sorption of ionic pollutants (Cruz-Guzmán et al., 2006). In addition, the organic modifiers increased the hydrophobic characteristics of the clay surface and, thus, enhanced organophilic properties, facilitating the sorption of organic pollutants. He et al., (2006) investigated the sorption characteristics of organic pollutants on montmorillonite modified with HDTM. They concluded that adsorption and partitioning mechanisms are responsible for sorption of organic pollutants when HDTM was loaded up to 1.0 CEC. However, partitioning is the only mechanism controlling the removal of the pollutants with increase the loading of HDTM higher than the CEC of montmorillonite.

Mechanisms controlling the retention of pollutants under the study conditions might have been adsorption of $Cr_2O_7^{2-}$ and adsorption as well as surface precipitation of Cd^{2+} and Pb^{2+}. In case of MM, partitioning mechanism, controlling the distribution of the pollutant between the organic modifier located in the interlayer of clay and in the aqueous phase, in addition to the adsorption process may contribute in the sorption of MM on OMCs.

Specific analyses are needed to prove the suggested mechanisms such as the analysis by X-ray absorption spectroscopy. Identifying the mechanisms may help to increase the sorption efficiency or help to predict the behavior of other pollutants with the proposed OMCs, which increase the applicability of these sorbents for wastewater remediation.

High recovery of Cd^{2+} and Pb^{2+} and about 40 % of $Cr_2O_7^{2-}$ were obtained by using 0.1 M HCl as desorbing agent. However, OMCs were able to release, partially, the sorbed Cd^{2+} and $Cr_2O_7^{2-}$ when tap water was used. Wankasi et al. (2005) stated that the discharges of the metal ions are faster with the acidic reagents than with basic or neutral ones. The regeneration abilities of the OMCs by the desorbing agents increase the potential for re-using those sorbents in subsequent sorption desorption cycles. Nevertheless, specific studies should be carried out to investigate possible changes in the structure and the activity of those sorbents after the recovery steps.

It can be concluded from the results that HDTM- and MTP-bent are effective sorbents for Cd^{2+}, Pb^{2+} and MM, individually. Cys_ester-bent is an effective sorbent for $Cr_2O_7^{2-}$ and MM.

5.3 Removal of pollutants from binary and ternary component systems

The OMCs modified with HDTM, MTP and Cys_ester were used for the sorption of Cd^{2+} and $Cr_2O_7^{2-}$ from binary component systems and the sorption of Cd^{2+}, $Cr_2O_7^{2-}$ and MM from ternary component systems. Competition phenomena were recorded in both systems. Obvious reductions in the sorption of Cd^{2+} on HDTM and MTP-bent were observed from binary and ternary component systems compared with the single ones. However, synergic effects on both sorbents were obtained with the sorption of $Cr_2O_7^{2-}$. Binding between the sorbed Cd^{2+} on the OMC surfaces (monodentate; $OMC\text{-}Cd^{+}$) with the $Cr_2O_7^{2-}$ ions in the solutions to form ternary complexes ($2(OMC\text{-}Cd)\text{-}Cr_2O_7$ or $OMC\text{-}Cd\text{-}Cr_2O_7^{-}$) may explain the increasing sorption of $Cr_2O_7^{2-}$ when other solutes are present in the solutions. Elzinga et al. (2001) investigated the co-sorption of Pb^{2+} and SO_4^{2-} on a goethite surface. They demonstrated that the sorbed Pb^{2+} enhanced the sorption of SO_4^{2-} through two ways:

one by the formation of Pb-SO_4 ternary complexes and the second by changing the charges on the goethite surface. Changing the surface charges permits more bindings between the surface and SO_4^{2-}, thus, increasing the sorption.

The inhibition obtained with the sorption of Cd^{2+} could be interpreted by the steric hindrance occurring due to the presence of $Cr_2O_7^{2-}$ on the interlayer of the sorbents in case of the binary component systems or the presence of $Cr_2O_7^{2-}$ and MM in case of the ternary component systems, limiting the accessability of Cd^{2+} to the active sorption sites on the sorbents surfaces. The suggested interpretation was stated previously in other cases with the sorption of benzene and Pb^{2+} or Cd^{2+} to clay minerals modified with HDTM (Oyanedel-Craver et al., 2007).

Declining in the adsorbed amounts of MM on HDTM-bent were detected for the ternary component systems compared to the single component systems, particularly at high concentrations of the solutes. The declining of MM sorption were concurrent with increasing $Cr_2O_7^{2-}$ sorption. This may imply that sorption of $Cr_2O_7^{2-}$ on HDTM-bent inhibits the sorption of MM. In other words, the sorbed $Cr_2O_7^{2-}$ on the HDTM-bent may limit partially the interaction between the MM and the sorbent surface or compete with MM on the active sorption sites. The hydration shells of the sorbed metal ions could be another reason explaining the reduction of the adsorbed MM to HDTM-bent in presence of Cd^{2+} and $Cr_2O_7^{2-}$. Here, the hydration shells of the metal ions may compete with MM on the sorption sites of the clay. The competitive effect on the sorption sites between organic pollutants and hydration shells of the sorbed metal ions were stated by Sun and Zhou (2010) in their study on the sorption behavior of 1,4-dichlorobenzene on soils in presence of Cd^{2+} and Cu^{2+}.

Enhancements in the sorption of MM and similar sorption of $Cr_2O_7^{2-}$ and Cd^{2+} were observed on Cys_ester-bent for the ternary component systems if compared to the single component systems. These noncompetitive effects for Cys_ester-bent were also observed for the binary component systems, indicating that each pollutant is adsorbed at different active sites of the sorbent. When the cationic and anionic pollutants are adsorbed on Cys_ester-bent, they help to neutralize the different surface charges of the sorbent. The obtained neutralization permits the hydrophobic binding between MM and the organic phase located in the interlayer, thus, enhancing the sorption of MM on Cys_ester-bent.

It is obvious from the results that the structure and the chemical properties of the organic modifiers played an important role in the selection of the pollutants. That was shown for example by the high efficiencies of OMCs with Cys_ester for $Cr_2O_7^{2-}$ and MM sorption and OMCs with Carnitin for Cd^{2+} and Pb^{2+} sorption.

Cys_ester-, HDTM- and MTP-bent showed the efficacy to remove Cd^{2+}, $Cr_2O_7^{2-}$ and MM simultaneously from the aqueous solution. The results indicated potential application of OMCs as sorbents for heterogeneous pollutants from natural polluted water.

Further investigations are required to test the stability of OMCs under different conditions (i.e. temperature and time).

To achieve a higher application of OMCs in the wastewater treatments, the chemical composition of the contaminated water is needed to select the best organically modified clayey sediment suitable for each source of contaminants.

Toward more environmental friendly and cost effective adsorbent, compost extract is other natural organic material could be used in the modification of the natural clayey sediments in order to enhance the efficiency of the sediment to remove pollutants from aqueous media.

6. References

Abbassy M S, H Z Ibrahim and H M Abdel-Kader. 2003. Persistent organochlorine pollutants in the aquatic ecosystem of Lake Manzala, Egypt. Bull. Environ. Contam. Toxicol., 70:1158-1164.

Abdallah S M. 2006. Towards a more safe environment: (1) A New modified clay for removing heavy metals from low quality water. J. Appl. Sci. Res., 2:391-396

Abd-Allah S M, O M El Hussaini and R M Mahdy. 2005. Towards a more safe environment: (4) Sorpability of vanadium as a nuclear constructing material by some clay sediments in Egypt. J. App. Sci. Res., 1: 168-175.

Abd-Allah S M, O M El Hussaini and R M Mahdy. 2007. Towards a more safe environment: (2) characterization of some clay sediments in Egypt for safe environmental applications. Aust. J. Basic Appl. Sci., 1:813-823.

Abd-Allah S M, O M El Hussaini and R M Mahdy. 2009a. Towards a more safe environment: (5) Disposability of Uranium by some clay sediments in Egypt. Aust. J. Basic Appl. Sci., 3: 1476-1488.

Abd-Allah S M, O M El Hussaini and R M Mahdy. 2009b. Towards a more safe environment: (6) Monitoring the recovery of boron adsorbed by some clay sediments in Egypt by FTIR spectroscopy. Aust. J. Basic Appl. Sci., 3:1450-1460.

Abd El-Wahed S. 2007. Impact of use of treated wastewater on some eco-agricultural characteristics in Bahr El-Bakar area. M.Sc., Faculty of Agriculture, Ain Shams University.

Abdel Azim R and M N Allam. 2004. Agricultural drainage water reuse in Egypt: Strategic issue and mitigation measures. Non convential water use workshop, Cairo, Egypt. Available at: http://ressources.ciheam.org/om/pdf/b53/00800755.pdf

Abdel-Azeem M, T S Abdel-Moneim, M E Ibrahim, M A A Hassan and M Y Saleh. 2007. Effects of long-term heavy metal contamination on diversity of terricolous fungi and nematodes in Egypt - A Case study. Water, Air, Soil Pollut., 186:233-254.

Abdel-Motelib A, Z A Kader, Y A Ragab and M Mosalamy. 2011. Suitability of a Miocene bentonite from North Western Desert of Egypt for pharmaceutical use. Appl. Clay Sci., 52:140-144.

Abdel-Sabour M F. 2007. Chromium in receiving environment in Egypt (an overview). Elec. J. Env. Agric. Food Chem., 6:2178-2198

Abdel-Sabour M F, A S Ismail and H H Abou Naga. 1996. Environmental impact of Cairo sewage effluent on El-Gabal El-Asfar farm. Egypt. J. Soil Sci., 36:329-342

Abdel-Sabour M F, F H Rabie, T Mostafa and S A Hassan. 2001. Impact of industrial wastewater disposal on surface water bodies in Mostord area, North Greater Cairo. J. Environ. Sci., 13:485-490

Abdel-Shafy H I and R O Aly. 2002. Water issue in Egypt: Resources, pollution and protection endeavors. CEJOEM, 8:3-21

Abdulla H M, E M Kamal, A H Mohamed and A D El-Bassuony. 2010. Chromium removal from tannery wastewater using chemical and biological techniques aiming zero discharge of pollution. Proceeding of Fifth Scientific Environmental Conference, Zagazig Uni., 171-183.

Abollino O, M Aceto, M Malandrino, C Sarzanini and E Mentasti. 2003. Adsorption of heavy metals on Na-montmorillonite: effect of pH and organic substances. Water Res., 37:1619-1627.

Abou Hussien E A, R A Khalil and A A Aki. 2002. Adsorption of Fe and Zn by clay-humic complexes. Egypt J. Soil Sci., 42:127-138

Abou-Elela S I, H S Ibrahim and E Abou-Taleb. 2008. Heavy metal removal and cyanide destruction in the metal plating industry: an integrated approach from Egypt. Environmentalist, 28:223–229.

Adekunle I M, T A Arowolo, N P Ndahi, B Bello and D A Owolabi. 2007. Chemical characteristics of humic acids in relation to lead, copper and cadmium levels in contaminated soils from south west Nigeria. Ann. Environ. Sci., 1:23-34.

Agrawal A and K K Sahu. 2006. Kinetic and isotherm studies of cadmium adsorption on manganese nodule residue. J. Hazard. Mater., 137:915-924

Ahmed S M, A A Ismail and A A Houusien. 2010. Dissipation and persistence of fungicides, carbendazim and metalaxyl in Egyptian soil under biotic and abiotic conditions. J. Appl. Sci. Res., 6:1240-1246

Ahn C K, D Park, S H Woo and J M Park. 2009. Removal of cationic heavy metal from aqueous solution by activated carbon impregnated with anionic surfactants. J. Hazard. Mater., 164:1130-1136.

Aiyen, R Schulz and V Römheld. 2002. Acquisition of Cd and Zn by the hyperaccumulator plant Thlaspi caerulescens: role of chemical and spatial availability. In: 9th New Phytologist Symposium “Heavy metals in plants - from ecosystems to biomolecules” Proceeding, Philadelphia, USA, Proceeding. 41. Available at: http://www.newphytologist.org/ heavymetals/posters1.htm#Aiyen

Al-Jlil S A. 2010. Removal of heavy metals from industrial wastewater by adsorption using local bentonite clay and toasted date pits in Saudi Arabia. Trends Appl. Sci. Res., 5:138-145.

Alnaggar D. 2003. Water resources management and policies for Egypt. Presented at the workshop on policies and strategies options for water management in Islamic countries

(Tehran), Ministry of Water Resources & Irrigation. Available at: http://www.rcuwm.org.ir/events/workshop/03/files/Dalal-AlNaggar.pdf

An J and S Dultz. 2007. Adsorption of tannic acid on chitosan-montmorillonite as a function of pH and surface charge properties. Appl. Clay Sci., 36:256-264.

Andini S, R Cioffi, F Montagnaro, F Pisciotta and L Santoro. 2006. Simultaneous adsorption of chlorophenol and heavy metal ions on organophilic bentonite. Appl. Clay Sci., 31:126-133.

Andrades M S, M J Sánchez-Martín and M Sánchez-Camazano. 2001. Significance of soil properties in the adsorption and mobility of the fungicide metalaxyl in vineyard soils. J. Agric. Food. Chem., 49:2363-2369

Andrades M S, M S Rodriguez-Cruz, M J Sánchez-Martín and M Sánchez-Camazano. 2004. Effect of the addition of wine distillery wastes to vineyard soils on the adsorption and mobility of fungicides. J. Agric. Food. Chem., 52:3022-3029

Anonymous[1]. 2007. Communication from the commission to the European parliament and the council: Addressing the challenge of water scarcity and droughts in the European Union. COM/2007/0414 final) published in July 2007. Available at: http://ec.europa.eu/environment/ water/quantity/eu_action.htm#2007_com

Anonymous[2]. 2006. Insights from the comprehensive assessment of water management in agriculture. Stockholm World Water Week. Available at: http://thewaterproject.org/ world_water_week.pdf

Anonymous[3]. 2011. Metalaxyl-m data sheet. Available at: http://www.alanwood.net/ pesticides/sitemap.html.

Anonymous[4]. 2011. Zhejiang Heben Pesticide & Chemicals Co.,Ltd. Available at: http:// www.chinaheben.com/showprd-38696/Metalaxyl-M.html

Anonymous[5]. 2007. The deadly chemicals in cotton. Environmental Justice Foundation in collaboration with Pesticide Action Network UK. Available at: http:// www.ejfoundation.org/ pdf/the_deadly_chemicals_in_cotton.pdf

Anonymous[6]. 2002. Heavy metal report. Available at: http://ec.europa.eu/environment/waste/studies/pdf/heavy_metalsreport.pdf

Anwar W A. 2003. Environmental health in Egypt. Int. J. Hyg. Environ. Health, 206:339-350

Arfaoui S, N Frini-Srasraa and E Srasraa. 2008. Modelling of the adsorption of the chromium ion by modified clays. Desalination., 222:474-481.

Arias M, M Paradelo, E López and J Simal-Gándara. 2006. Influence of pH and soil copper on adsorption of metalaxyl and penconazole by the surface layer of vineyard soils. J. Agric. Food. Chem., 54:8155-8162

Assaad E, A Azzouz, D Nistor, A V Ursu, T Sajin, D N Miron, F Monette, P Niquette and R Hausler. 2007. Metal removal through synergic coagulation-flocculation using an optimized chitosan-montmorillonite system. Appl. Clay Sci., 37:258-274

Assaf K, B Attia, A Darwish, B Wardam and S Klawitter. 2004. Water as a human right: The understanding of water in the Arab countries of the Middle East – A four country analysis. Heinrich Böll Foundation, Palestine.

ATSDR. 2011. Priority list of hazardous substances. Agency for Toxic Substances and Disease Registry, Division of Toxicology and Environmental Medicine, Atlanta. Available at: http://www.atsdr.cdc.gov/spl/resources/index.html.

Auboiroux M, P Baillif, J C Touray and F Bergaya. 1996. Fixation of Zn 2+ and Pb2+ by a Ca-montmorillonite in brines and dilute solutions: Preliminary results. Applied Clay Science, 11:117-126

Avalos F, J C Ortiz, R Zitzumbo, M A López-Manchado, R Verdejo and M Arroyo. 2009. Phosphonium salt intercalated montmorillonites. Appl. Clay Sci., 43:27-32.

Azejjel H, C Del Hoyo, K Draoui, M S Rodríguez-Cruz and M J Sánchez-Martín. 2009. Natural and modified clays from Morocco as sorbents of ionisable herbicides in aqueous medium. Desalination, 249:1151-1158.

Badawy M I and R A. Wahaab. 1997. Environmental impact of some chemical pollutants on Lake of Manzala. J. Environ. Health Res., 7:161-170.

Badawy S H and M I D Helal. 1997. Impacts of heavy metals of sewage effluent on soils and plants of Helwan area. J. Agric. Sci., 22:4737-4754.

Badr M H, A Elewa, M B Shehata, L F Mohamed and G S Abdelaziz. 2006. Studies on the effect of el rahaway drain on the river Nile water pollution by trace metals and major cations at El Kanater El khyria area under the effect of seasonal variation. Ass. Univ. Bull. Environ. Res., 9:35-54

Baes C F and R E Mesmer. 1976. The hydrolysis of cations: John Wiley & Sons, US

Bahgeet A K, S M Abdallah and M A Harith. 2005. Laser monitoring of remediation of some heavy metals from low quality water by natural sediments. Proc. Int. Conference on Laser Appl., January 10-14, 2005, National Institute of Laser Enhanced Science, Cairo, Egypt

Barbier F, G Duc and M Petit-Ramel. 2000. Adsorption of lead and cadmium ions from aqueous solution to the montmorillonite/water interface. Colloids Surf. A, 166:153-159.

Bedelean H, A Măicăneanu, M Stanca and S Burcă. 2009. Removal of heavy metal ions from wastewaters using natural materials. Geologia, 16:179-180

Bergaya F, B K G Theng and G Lagaly. 2006. Handbook of clay science. Elsevier science Ltd., Netherlands. pp. 309-377, 625-675.

Berthon G. 1995. Critical evaluation of the stability constants of metal complexes of amino acids with polar side chains. Pure Appl. Chem., 67:1117-1240

Bhattacharyya K G and S S Gupta. 2008. Adsorption of a few heavy metals on natural and modified kaolinite and montmorillonite: A review. Adv. Colloid Interface Sci., 140:114-131

Biswas A K, E Rached and C Tortajada. 2008. Water as a human right for the Middle East and North Africa. Routledge Pub. Oxon pp 133-148. Available at: http://web.idrc.ca/openebooks/380-5/

Bois L, A Ribes, M Petit-Ramel and M F Grenier-Loustalot. 2003. Experimental study of chromium adsorption on minerals in the presence of phthalic and humic acids. Chem. Ecol., 19:263-273

Brindley G W. 1955. Identification of clay minerals by x-ray diffraction analysis. Clays Clay Technol., 169:119-129.

Brum M C, J L Capitaneo and J F Oliveira. 2010. Removal of hexavalent chromium from water by adsorption onto surfactant modified montmorillonite. Miner. Eng., 23:270-272.

Carrizosa M J, M J Calderón, M C Hermosín and J Cornejo. 2000. Organosmectites as sorbent and carrier of the herbicide bentazone. Sci. Total Environ., 247:285-293.

Chapman H D. 1965. Cation-exchange capacity. In: C. A. Black (ed.) Methods of soil analysis - Chemical and microbiological properties. Agronomy, 9:891-901.

Chaves L H G and e G A Tito. 2011. Cadmium and copper adsorption on bentonite: effects of pH and particle size. Rev. Ciênc. Agron., 42:278-284.

Chen C-C and K F Hayes. 1999. X-ray absorption spectroscopy investigation of aqueous Co(II) and Sr(II) sorption at clay–water interfaces. Geochim. Cosmochim. Acta, 63:3205-3215.

Chiban M, A Soudani, F Sinan and M Persin. 2011. Single, binary and multi-component adsorption of some anions and heavy metals on environmentally friendly Carpobrotus edulis plant. Colloids Surf. B, 82:267-276

Crini, G. 2005. Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment. Prog. Polym. Sci., 30:38-70

Cruz-Guzmán M, R Celis, M C Hermosín and J Cornejo. 2004. Adsorption of the herbicide simazine by montmorillonite modified with natural organic cations. Environ. Sci. Technol., 38:180-186

Cruz-Guzmán M, R Celis, M. C Hermosín, W C Koskinen and J Cornejo. 2005. Adsorption of pesticides from water by functionalized organobentonites. J. Agric. Food Chem., 53:7502-7511

Cruz-Guzmán M, R Celis, M C Hermosin, W C Koskinen, E A Nater and J Cornejo. 2006. Heavy metal adsorption by montmorillonites modified with natural organic cations. Soil Sci. Soc. Am. J., 70:215–221.

Dasgupta S, K Banerjee, KN Dhumal and PG Adsule. 2011. Optimization of detection conditions and single-laboratory validation of a multiresidue method for the determination of 135 pesticides and 25 organic pollutants in grapes and wine by gas chromatography time-of-flight mass spectrometry. J AOAC Int., 94:273-85

Dermentzis K, A Christoforidis and E Valsamidou. 2011. Removal of nickel, copper, zinc and chromium from synthetic and Industrial wastewater by electrocoagulation. Int. J. Environ. Sci., 1:697-710.

Dhabab J M. 2011. Removal of Fe(II), Cu(II), Zn(II), and Pb(II) ions from aqueous solutions by duckweed. J. Oceanogr. Mar. Sci., 2:17-22.

DIN ISO [10694]. 1996a. Bodenbeschaffenheit - Bestimmung von organischem Kohlenstoff und Gesamtkohlenstoff nach trockener Verbrennung (Elementaranalyse)

DIN ISO [45014] 1996b. Bodenbeschaffenheit - Bestimmung von total Stickstoff und Gesamtkohlenstoff nach trockener oxidation/reduktion (Elementaranalyse)

Dionex 1998. Determination of Cr(VI) in water, waste water, and solid waste extracts. Technical Note26, Available at: http://www.dionex.com/en-us/webdocs/4428-TN26_LPN034398-02.pdf

Eba F, J A Ondo, S Gueu, J N Nlo, R K Biboutou and B K Yao. 2011. Treatment of aqueous solution of lead content by using natural mixture of kaolinite-albite-montmorillonite-illite clay. J. Appl. Sci., 11:2536-2545.

El Gundy M M, H H Hassana, M F Abdel Sabour and R A S Zalalu. 1994. Zinc sorption and desorption of some Egyptian shales. Egypt. J. Soil Sci., 34:389-401.

El Nahry A H. 2007. Using geostatistical analysis and spectral signature for identifying shale distribution and type in El-Salhia project, Ismaillia, Egypt. Int. J. Geol., 1:22-26.

Elassiouti I M and E A Khalifa. 2009. Integrated water resource management II. Training needs assessment of the ministry of water resources & irrigation. Report No. 8. Available at: http://www.iwrm2eg.org/report/IWRMII/report8.pdf

Elewa H H. 2010. Potentialities of water resources pollution of the Nile River Delta, Egypt. The Open Hydrol. J., 4:1-13

El-Motaium R A and S H Badawy. 2000. Effect of irrigation using sewage water on distribution of some heavy metals in bulk and rhizosphere soils and different plant species: Cabbge plants (Brassica oleracea L.) and orange trees (Citrus sinensis L.). Egypt. J. Soil Sci., 40:285-303

El-Nahhal Y. 2003. Adsorptive behavior of acetochlor on organoclay complexes. Bull. Environ. Contam. Toxicol., 70:1104-1111.

El-Sharawy M A O, M M Elbordiny. 2001. Evaluating the suitability of certain drainage water irrigation with regards to heavy metal content in Qalubia governorate. Minufiya J. Agric., Res., 26:1759-1772.

El-Sharawy M A O, M M Elbordiny and H E Abu Hussin. 2004. Phytoremediation of wastewater for irrigation purpose using Azolla. Egypt. J. Soil Sci., 44:73-84.

Elzinga E J, D Peak, and D L Sparks. 2001. Spectroscopic studies of Pb(II)-sulfate interactions at the goethite-water interface. Geochim. Cosmochim. Ac., 65: 2219-2230

Erdem E, N Karapinar and R Donat. 2004. The removal of heavy metal cations by natural zeolites. J. Colloid Interface Sci., 280:309-314

Erdemoğlu M, S Erdemoğlu, F Sayılkan, M Akarsu, Ş Şener and H Sayılkanc. 2004. Organo-functional modified pyrophyllite: Preparation, characterisation and Pb(II) ion adsorption property. Appl. Clay Sci., 27:41-52.

Essington M E. 2004. Soil and water chemistry: An integrative approach. CRC Press LLC, US.

FAO. 2004. Pesticide residues in food, evaluations Part I-Residues, FAO plant production and protection paper 182/1, Rome, Italy. Available at: http://www.fao.org/ag/AGP/AGPP/Pesticid/JMPR/Download/2004_eva/JMPR2004eva.pdf.

FAO, 2007a. Coping with water scarcity - Challenge of the twenty-first century. World Water Day 2007. Available at: http://www.fao.org/nr/water/docs/escarcity.pdf

FAO, 2007b. Comprehensive assessment of water management in agriculture. Available at: http://www.fao.org/nr/water/docs/wwd07brochure.pdf

Farmer V C. 1974. The infra spectra of minerals. Mineralogical Soc., London.

Farrah H, D Hatton and W F Pickering. 1980. The affinity of metal ions for clay surfaces. Chem. Geol., 28:55-68.

Fawzy I and G M Naim.1993. Kaolin. Egyptian Geological Survey and Mining Authority.

Fernandes M C, L Cox, M C Hermosin and J Cornejo. 2003. Adsorption-desorption of metalaxyl as affecting dissipation and leaching in soils: Role of mineral and organic components. Pest Manage. Sci., 59:545-552.

Ganjali M R, Z Rafiei-Sarmazdeh, T Poursaberi, S J Shahtaheri and P Norouzi. 2012. Dichromate ion-selective sensor based on functionalized SBA-15/ ionic liquid/MWCNTs/graphite. Int. J. Electrochem. Sci., 7:1908 -1916.

Girija E K, S Narayana Kalkura and P Ramasamy. 1995. Crystallization of cystine. J. Mater. Sci.: Mater. In Med., 6:617-619

Goh K, T Lim, A Banas and Z Dong. 2010. Sorption characteristics and mechanisms of oxyanions and oxyhalides having different molecular properties on Mg/Al layered double hydroxide nanoparticles. J. Hazard. Materials, 179:818-827.

Gonen Y and G Rytwo. 2006. Using the dual-mode model to describe adsorption of organic pollutants onto an organoclay. J. Colloid Interface Sci., 299: 95-101

Guo X, S Zhang, X Shan, L Luo, Z Pei, Y Zhu, T liu, Y Xie and A Gault. 2006. Characterization of Pb, Cu, and Cd adsorption on particulate organic matter in soil Environ. Toxicol. Chem., 25:2366-2373.

Gupta S S and K G Bhattacharyya. 2008. Immobilization of Pb(II), Cd(II) and Ni(II) ions on kaolinite and montmorillonite surfaces from aqueous medium. J. Environ. Manage., 87:46-58

Gupta V, M Gupta and S Sharma. 2001. Process development for the removal of lead and chromium from aqueous solutions using red mud an aluminum industry waste. Water Res.., 35:1125-1134.

Gustafsson J P. 2011. Chemical equilibrium model for metal speciation build on MINTEQA2/PRODEFA2, a Geochemical Assessment Model for Environmental Systems, Version 3.0, EPA/600/3-91/021, U.S. Environmental Protection Agency. KTH., Sweden.

Habashi F and F A Bassyouni. 1982. Mineral resources of the Arab countries, 2nd Edit., Chemecon Pub. Limited, London. Pp. map3-5.

Haggerty G M and R S Bowman. 1994. Sorption of chromate and other inorganic anions by organo-zeolite. Environ. Sci. Technol., 28:452-458.

Hall K R, L C Eagleton, A Acrivos and T Vermeulen. 1966. Pore- and solid-diffusion kinetics in fixed-bed adsorption under constant-pattern conditions. Ind. Eng. Chem. Fundam., 5:212-223.

Hamdy A and R Monti. 2005. Food security under water scarcity in the Middle East: Problems and solutions. Options Méditerranéennes, Série A n. 65:29-48. Available at: http://www.iamb.it/ download/options/options_A65.pdf

Hamilton D. 2004. Metalaxyl-M (212). Available at: http://www.fao.org/ag/AGP/ AGPP/Pesticid/JMPR/Download/2004_eva/MetalaxylM.pdf

Hardie A G, J J Dynes, L M Kozak and P M Huang. 2007. Influence of polyphenols on the integrated polyphenol-maillard reaction humification pathway as catalyzed by birnessite, Ann. Environ. Sci., 1:91-110

Harris W and N White. 2007. X-ray diffraction techniques for soil mineral identification. Available at: (http://wgharris.ifas.ufl.edu/SEED/6464/4%20XRD%20Galley%20 Willie%20 Harris.pdf).

Hassan M S and N A Abdel-Khalek. 1998. Beneficiation and applications of an Egyptian bentonite. Appl. Clay Sci., 13: 99-115.

He H, Q Zhou, R L Frost, B J Wood, L V Duong and J T Kloprogge. 2007. A X-ray photoelectron spectroscopy study of HDTMAB distribution within organoclays. Spectrochim. Acta A., 66:1180-1188.

He H, Q Zhou, W N Martens, T J Kloprogge, P Yuan, Y Xi, J Zhu and R L Frost. 2006. Microstructure of HDTMA+-modified montmorillonite and its influence on sorption characteristics. Clay Clay Miner., 54:689-696

Hizal J and R. Apak. 2006. Modeling of copper(II) and lead(II) adsorption on kaolinite-based clay minerals individually and in the presence of humic acid. J. Colloid Interface Sci., 295:1-13.

Ho Y S, G McKay. 1999. Pseudo-second order model for sorption processes. Process Biochem., 34:451-465.

Hoffmann G. 1991. Die Untersuchung der Böden. VDLUFA-Methodenbuch Bd. I, VDLUFA-Verlag, Germany.

Hong H, W Jiang, X Zhang, L Tie and Z Li. 2008. Adsorption of Cr(VI) on STAC-modified rectorite. Appl. Clay Sci., 42:292-299

Huang P and D W Fuerstenau. 2001. The effect of the adsorption of lead and cadmium ions on the interfacial behavior of quartz and talc. Colloids Surf. A, 177:147-156

Huang R, B Wang, B Yang, D Zheng and Z Zhang. 2011. Equilibrium, kinetic and thermodynamic studies of adsorption of Cd(II) from aqueous solution onto HACC–bentonite. Desalination, 280:297-304.

Hussein I A. 2008. Desertification challenge in Egypt. Beijing International Conference on Combating Desertification, 22-24 January 2008, Beijing, China. Available at: http://www.un.org/esa/sustdev/sdissues/desertification/beijing2008/

IARC. 1990. Chromium and chromium compounds. Chromium[VI] (Group1). Metallic chromium and chromium[III] compounds (Group 3). Available at http://www.inchem.org/documents/ iarc/vol49/chromium.html.

IARC. 1993. Beryllium, cadmium, mercury, and exposures in the glass manufacturing industry. IARC Monogr. Eval. Carcinog. Risks Hum., 58:1-415.

ICID 2005. Water policy issues of Egypt. Country policy support programme (CPSP) report 7. International Commission on Irrigation and Drainage (ICID). New Delhi. Available at: http://www.icid.org/cpsp_report7_web.pdf

Ismail A A and S E Badr. 2004. Effect of some applicator types on metalaxyl residue in cucumber with special reference to its toxicological effects. Minufiya J. Agric. Res., 29:557-567

Jasmund K and G Lagaly. 1993.Tonminerale und Tone: Strukture, Eigenschaften, Anwendung und Einsatz in Inddustrie und Umwelt. Steinkopff Verlag, Darmstadt, Germany.

Jaynes W F and S A Boyd. 1991. Clay mineral type and organic compound sorption by hexadecyl-trimethlyammonium-exchanged clays. Soil Sci. Soc. Am. J., 55:43-48.

Jaynes W F and G F Vance. 1996. BTEX Sorption by organo-clays: Cosorptive enhancement and equivalence of interlayer complexes. Soil Sci. Soc. Am. J., 60:1742-1749.

Jiang J Q , C Cooper and S Ouki. 2002. Comparison of modified montmorillonite adsorbents. Part I: preparation, characterization and phenol adsorption. Chemosphere, 47:711-716.

Johnston C T, G Sposito and R R Birge. 1985. Raman spectroscopic study of kaolinite in aqueous suspension. Clays Clay Miner., 33:483-489.

Jr M H and A I Spiff. 2005. Sorption of lead, cadmium and zinc in sulfur containing chemically modified wastes of fuited pumpkin (*Telfairia occidentalis Hook f.*). Chem. Biodiversity, 2:373-385.

Kadirvelu K, K Thamaraiselvi and C Namasivayam. 2001. Removal of heavy metals from industrial wastewaters by adsorption onto activated carbon prepared from an agricultural solid waste. Bioresour. Technol., 76:63-65

Kamel M M, M A Ibrahm, A M Ismael, and M A El-Motaleeb. 2004. Adsorption of some heavy metal ions from aqueous solutions by using kaolinite clay. Ass. Univ. Bull. Environ. Res., 7:101-110.

kandeel S H. 1989. Bentonite in Arab republic of Egypt. Public Authority of industrialization, Egypt.

Kaufhold S, M Pohlmann-Lortz, R Dohrmann and R Nüesch. 2007. About the possible upgrade of bentonite with respect to iodide retention capacity. Appl. Clay Sci., 35:39-46.

khan A R, T A Al-Bahri and A Al-Haddad. 1997. Adsorption of phenol based organic pollutants on activated carbon from multi-component dilute aqueous solutions. Water Res., 31: 2102-2112

Krishna B S, D S R Murty and B S Jai Prakash. 2000. Thermodynamics of chromium(VI) anionic species sorption onto surfactant-modified montmorillonite clay. J. Colloid Interface Sci., 229:230-236.

Krishna B S, D S R Murty and B S Jai Prakash. 2001. Surfactant-modified clay as adsorbent for chromate. Appl. Clay Sci., 20:65-71.

Lagadic I L, M K Mitchell and B D Payne. 2001. Highly effective adsorption of heavy metal ions by a thiol-functionalized magnesium phyllosilicate clay. Environ. Sci. Technol., 35:984-990.

Lamfon H A. 2011. Protective effect of ginger (Zingiber officinale) against metalaxyl induced hepatotoxicity in albino mice. J. Am. Sci., 7:1093-1100.

Langmuir I. 1918. The adsorption of gases on plane surfaces of glass, mica and platinum. J. Am. Chem. Soc., 40:1361-1403

Lasat M M. 2000. The use of plants for the removal of toxic metals from contaminated soil. Available at: http://nepis.epa.gov/Exe/ZyPURL.cgi?Dockey=9100FZE1.txt

Lazaridis N K, D N Bakoyannakis and E A Deliyanni. 2005. Chromium(VI) sorptive removal from aqueous solutions by nanocrystalline akaganèite. Chemosphere, 58:65-73.

Lee S Y and S J Kim. 2003. A study on the sorption characteristics of polycyclic aromatic hydrocarbons (PAHs) and cadmium by organoclays. Econ. Environ. Geol., 36:171-176.

Lee S Y, S J Kim, S Y Chung and C H Jeong. 2004. Sorption of hydrophobic organic compounds onto organoclays. Chemosphere., 55:781-785.

Leita L, A Margon, A Pastrello, I Arčon, M Contin and D Mosetti. 2009. Soil humic acids may favour the persistence of hexavalent chromium in soil. Environ. Poll., 157:1862-1866

Lenntech B V. 2011. Lead and water. Water Treatment Solutions. Available at: http://www.lenntech.com/periodic/water/lead/lead-and-water.htm

Leung K L. 2010. Ecological risk analysis of polycyclic aromatic hydrocarbons, black carbon and heavy metals on soils and plants from coal factories in Jiyuan city, China. MSc. The University of Hong Kong. Available at: http://hdl.handle.net/10722/132294

Levy R and C W Francis. 1978. Adsorption and desorption of cadmium by synthetic and natural organo--clay complexes. Geoderma, 15:361-370.

Li Z and R S Bowman. 2001. Retention of inorganic oxyanions by organo-kaolinite. Water Res., 35:3771-3776.

Li Z and L Gallus. 2007. Adsorption of dodecyl trimethylammonium and hexadecyltrimethyl ammonium onto kaolinite - Competitive adsorption and chain length effect. Appl. Clay Sci., 35:250-257.

Liao S and W Chang. 2004. Heavy metal phytoremediation by water hyacinth at constructed wetlands in Taiwan. J. Aquat. Plant Manage., 42:60-68

Lin S H and R S Juang. 2002. Heavy metal removal from water by sorption using surfactant-modified montmorillonite. J. Hazard. Mater. B, 92:315-326

Luisa C M, A M Carmen and M de la Guardia. 2003. Removal of heavy metals by using adsorption on alumina or chitosan. Anal. Bioanal. Chem., 375 : 820–825

Madejová J. 2003. FTIR techniques in clay mineral studies. Vib. Spectrosc., 31:1-10.

Mahdy R M A H. 2004. Potentiality of clay minerals to adsorb some elements from nuclear waste materials. MSc. Ain Shams University.

Mahvi A H, F Gholami and S Nazmara. 2008. Cadmium biosorption from wastewater by Ulmus leaves and their ash. Eur J. Sci. Res., 23:197-203

Majdan M, O Maryuk, S Pikus, E Olszewska, R Kwiatkowski and H Skrzypek. 2005. Equilibrium, FTIR, scanning electron microscopy and small wide angle X-ray scattering studies of chromates adsorption on modified bentonite. J. Mol. Struct., 740:203-211.

Malakul P, K R Srinivasan and H Y Wang. 1998. Metal adsorption and desorption characteristics of surfactant-modified clay complexes. Ind. Eng. Chem. Res., 37:4296-4301

Malandrino M, O Abollino, A Giacomino, M Aceto and E Mentasti. 2006. Adsorption of heavy metals on vermiculite: Influence of pH and organic ligands. J. Colloid Interface Sci., 299:537-546

Malferrari D, M F Brigatti, A Laurora, S Pini and L Medici. 2007. Sorption kinetics and chemical forms of Cd (II) sorbed by thiol-functionalized 2:1 clay minerals. J. Hazard. Mater., 143:73-81.

Mansour S A and M M Sidky. 2003. Ecotoxicological studies. 6. The first comparative study between Lake Qarun and Wadi El-Rayan wetland (Egypt), with respect to contamination of their major components. Food. Chem., 82:181–189

Marzal P, A Seco and C Gabaldon. 1996. Cadmium and Zinc adsorption onto activated carbon: Influence of temperature, pH and metal/carbon ratio. J. Chem. Tech. Biotechnol., 66:279-285

Massoud A H, A S Derbalah and E B Belal. 2008. Microbial detoxification of metalaxyl in aquatic system. J. Environ. Sci., 20:262-267

Max Roundhill D. 2001. Extraction of metals from soils and waters. Kluwer Academic/Plenum Puplishers, US.

Mohamed H A A. 2007. Status of some heavy metals and nitrate in some soils and water resources in El-Fayoum governorat. M.Sc., Faculty of Agriculture, El-Fayoum University.

Mohamed N A A. 1998. A study on some trace metals as related to soil environment. Ph.D thesis, Agriculture Faculty, Ain Shams University.

Monkiedje A and M Spiteller. 2002. Sorptive behavior of the phenylamide fungicides, mefenoxam and metalaxyl, and their acid metabolite in typical Cameroonian and German soils. Chemosphere, 49:659-668.

Moulis J and F Thévenod. 2010. New perspective in cadmium toxicity: An introduction. Biometals, 23:763-768.

Müller M D and H R Busser. 1995. Environmental behaviour of acetamide pesticide stereoisomers. 2. Stereo- and enantioselective degradation in sewage sludge and soil. Environ. Sci. Technol., 29:2031-2037.

MWRI. 2010. Water challenges in Egypt. Water Communication Unit Brochure. Ministry of Water Resources and Irrigation. Available at: http://www.mwri.gov.eg/En/pdf_files%20english/Brochure%20%20Eng.pdf

Naser S A and B E Chukri. 1954. Sinai prospecting expedition: prospecting and exploration in South Sinai, 1953-1954. Imprimerie française, Paris. Pp. 33

Navrátilová Z, P Wojtowicz, L Vaculíková and V Šugárková. 2007. Sorption of alkylammonium cations on montmorillonite. Acta Geodyn. Geomater., 4:59-65.

Nayak P S and B K Singh. 2007. Instrumental characterization of clay by XRF, XRD and FTIR. Bull. Mater. Sci., 30:235-238.

Nikologianni A, P Andreou, P A Nektarios and A N Markoglou. 2010. Metalaxyl-m leaching from different substrates and drainage systems in intensive green roofs. Acta Hort., 881:725-728

Nomanbhay S M and K Palanisamy. 2005. Removal of heavy metal from industrial wastewater using chitosan coated oil palm shell charcoal. J. Biotechnol., 8:43-53.

O'Connell D W, C Birkinshaw and T F O'Dwyer. 2006. Design of a novel cellulose-based adsorbent for use in heavy metal recovery from aqueous waste streams. Trans. Ecol. Environ., 95:490-498

Oelkers E H, J G Hering and C Zhu. 2011. Water: Is there a global crisis?. Elem., 7:157-162.

Olguín E J and G Sánchez-Galván. 2010. Aquatic phytoremediation: Novel insights in tropical and subtropical regions. Pure Appl. Chem., 82:27-38

Oyanedel-Craver V A and J A Smith. 2006. Effect of quaternary ammonium cation loading and pH on heavy metal sorption to Ca bentonite and two organobentonites. J. Hazard. Mater., 137:1102-1114.

Oyanedel-Craver VA, M Fuller and JA Smith. 2007. Simultaneous sorption of benzene and heavy metals onto two organoclays. J. Colloid Interface Sci., 309:485-492.

Pacheco M L, E M Peña-Méndez and J Havel. 2003. Supramolecular interactions of humic acids with organic and inorganic xenobiotics studied by capillary electrophoresis. Chemosphere, 51:95-108.

Panda S K and S Choudhury. 2005. Chromium stress in plants. Braz. J. Plant Physiol., 17:95-102.

Pandey P K, S K Sharma and S S Sambi. 2010. Kinetics and equilibrium study of chromium adsorption on zeolite NaX. Int. J. Environ. Sci. Tech., 7:395-404.

Paolini M, R Mesirca, L Pozzetti, A Sapone and G Cantelli-Forti. 1996. Biomarkers of effect in evaluating metalaxyl cocarcinogenesis. Selective induction of murine CYP 3A isoform. Mutat. Res., 361:157-164.

Papelis C and K F Hayes. 1996. Distinguishing between interlayer and external sorption sites of clay minerals using X-ray absorption spectroscopy. Colloids Surf. A, 107:89-96.

Parker A, and J E Rae. 1998. Environmental interactions of clays. Springer-Verlag, Germany. Pp. 96

Patel H A, R S Somani, H C Bajah and R V Jasra. 2007. Preparation and characterization of phosphonium montmorillonite with enhanced thermal stability. Appl. Clay Sci., 35:194-200.

Pinazo A, M Diz, C Solans, M A Pes, P Erra and M R Infante. 1993. Synthesis and properties of cationic surfactants containing a disulfide bond. J. Am. Oil Chem. Soc., 70:37-42.

Polcaro A M, M Mascia, S Palmas, A Vacca and G Tola. 2003. Competitive sorption of heavy metal ions by soils. Environ. Eng. Sci., 20: 607-616

Rangsriwatananon K and T Khumbudda. 2007. Characteristics of organoclays modified with hexadecyltrimethylammonium chloride prepared by convention and microwave. Available at: http://hdl.handle.net/123456789/2727.

Rao M M, A Ramesh, G P C Rao and K Seshaiah. 2006. Removal of copper and cadmium from the aqueous solutions by activated carbon derived from Ceiba pentandra hulls. J. Hazard. Mater., 129:123-129

Ravisankar R, G Senthilkumar, S Kiruba, A Chandrasekaran and P P Jebakumar. 2010. Mineral analysis of coastal sediment samples of Tuna, Gujarat, India. Indian J. Sci. Technol., 3:774-780.

Reynolds K A. 2002. Bioremediation: Using microbes to clean up hazardous waste. WCPM. Available at: http://www.wcponline.com/column.cfm?T=T&ID=1725&AT=T

Rodríguez-Cruz M S, M S Andrades and M J Sánchez-Martín. 2007. Significance of the long-chain organic cation structure in the sorption of the penconazole and metalaxyl fungicides by organo clays. J. Hazard. Mater., 160:200-207.

Rybicka E H, W Calmano and A Breeger. 1995. Heavy metals sorption/desorption on competing clay minerals; an experimental study. Appl. Clay Sci., 9:369-381

Rytwo G, Y Gonen, S Afuta and S Dultz. 2005. Interactions of pendimethalin with organo-montmorillonite complexes. Appl. Clay Sci., 28:67-77.

Sanchez A G, E A Ayuso and O J de Blas. 1999. Sorption of heavy metals from industrial waste water by low-cost mineral silicates. Clay Miner., 34:469-477.

Sarkar B, Y Xi, M Megharaj, G S R Krishnamurti, D Rajarathnam and R Naidu. 2010. Remediation of hexavalent chromium through adsorption by bentonite based Arquad® 2HT-75 organoclays. J. Hazard. Mater., 183:87-97.

Say R, E Birlik, A Denizli and A Ersöz. 2006. Removal of heavy metal ions by dithiocarbamate-anchored polymer/organosmectite composites. Appl. Clay Sci., 31:298-305.

Schlegel M L, L Charlet and A Manceau. 1999. Sorption of metal ions on clay minerals: II. Mechanism of Co sorption on hectorite at high and low ionic strength and impact on the sorbent stability. J. Colloid Interface Sci., 220:392-405.

Senthilkumar R, K Vijayaraghavan, J Jegan and M Velan. 2010. Batch and column removal of total chromium from aqueous solution using Sargassum polycystum. Environ. Prog. Sustainable Energy, 29:334-341.

Shakir K, H F Ghoneimy, A F Elkafrawy, S G Beheir and M Refaat. 2008. Removal of catechol from aqueous solutions by adsorption onto organophilic-bentonite. J. Hazard. Mater., 150:765-773.

Shama S A and M A Gad. 2010. Removal of heavy metals (Fe3+, Cu2+, Zn2+, Pb2+, Cr3+ and Cd2+) from aqueous solutions by using hebba clay and activated carbon. Portugaliae Electrochim. Acta, 28:231-239.

Sharaf E F. 2002. Impact of industrial wastewater effluents on mycoflora of the shore sediments of the 3rd oxidation pond, with reference to biosorption of heavy metals. Acta Microbiol Pol., 51:293-306.

Sharma D and M D Awasthi. 1997. Adsorption and movement of metalaxyl in soils under unsaturated flow conditions. Plant Soil, 195:293-298.

Shen Y H. 2004. Phenol sorption by organoclays having different charge characteristics. Colloids Surf. A, 232:143-149.

Sheng G, C T Johnston, B J Teppen and S A Boyd. 2001. Potential contributions of smectite clays and organic matter to pesticide retention in soils. J. Agric. Food Chem., 49:2899-2907.

Sheng G, C T Johnston, B J Teppen and S A Boyd. 2002. Adsorption of dinitrophenol herbicides from water by montmorillonites. Clays Clay Miner., 50:25-34.

Sheng G, S Xu and S A Boyd. 1999. A Dual function organoclay sorbent for lead and chlorobenzene. Soil Sci. Soc. Am. J., 63:73-78.

Simonović B R, D Aranđelović, M Jovanović, B Kovačević, L Pezo and A Jovanović. 2009. Removal of mineral oil and wastewater pollutants using hard coal. Chem. Ind. Chem. Eng. Q., 15:57-62.

Singer D M. 2003. Applied phytoremediation. Available at: http://pangea.stanford.edu/~dmsinger/Applied_Phytoremediation.pdf

Singh S and M K N Yenkie. 2004. Competitive adsorption of some hazardous organic pollutants from their binary and ternary solutions onto granular activated carbon columns. Water, Air, Soil Pollut., 156:275-286.

Socrates G. 2001. Infrared and raman characteristic group frequencies: tables and charts. Wiley and Sons Ltd, England. [available at: http://books.google.de/books?id=LDoAAjMnwEIC&pg=PA94&lpg=PA94&dq=OH+vibration+of+alcoholic&source=bl&ots=Cn13UZNqcE&sig=aIIezsnZM1X3TGXI1v-6DCu9EWY&hl=de&sa=X&ei=qj08T_eKONH4sgbwutSXBw&sqi=2&ved=0CD4Q6AEwAQ#v=onepage&q=OH%20vibration%20of%20alcoholic&f=false]

Sparks D L. 2003. Environmental soil chemistry. (2nd ed.) Academic press: An Imprint of Elsevier, printed in USA . pp. 43, 151, 152.

Srivastava P, B Singh and M Angove. 2005. Competitive adsorption behavior of heavy metals on kaolinite. J. Colloid Interface Sci., 290:28-38

Stahl R and A Ramadan. 2008. Environmental studies on water quality of the Ismailia canal / Egypt. Forschungszentrum Karlsruhe in der Helmholtz-Gemeinschaft Wissenschaftliche Berichte (GmbH) FZKA 7427.

Stahr K, J Kühn, J Trommler, KH Papenfuß, M Zarei and A Singer. 2000. Palygorskite-cemented crusts (palycretes) in Southern Portugal. Aust. J. Soil Res., 38:169-188.

Stathi P, K Litina, D Gournis, T S Giannopoulos and Y Deligiannakis. 2007. Physicochemical study of novel organoclays as heavy metal ion adsorbents for environmental remediation. J. Colloid Interface Sci., 316:298-309.

Suciu N A and E Capri. 2009. Adsorption of chlorpyrifos, penconazole and metalaxyl from aqueous solution by modified clays. J. Environ. Sci. Health. B, 44:525-532.

Sud D, G Mahajan and M P Kaur. 2008. Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions – A review. Bioresour. Technol., 99:6017-6027

Sukul P and M Spiteller. 2000. Metalaxyl: Persistence, degradation, metabolism, and analytical methods. Rev. Environ. Contam. Toxicol., 164:1-26

Sun F and Q Zhou. 2010. Interactive effects of 1,4-dichlorobenzene and heavy metals on their sorption behaviors in two chinese soils. Arch. Environ. Contam. Toxicol., 58:33-41

Tabatabai M A and D L Sparks. 2005. Chemical processes in soils. SSSA, Inc. USA. pp.619.

Tahoun S A, E A El-Naka, M El-Tohamy and M El-Fahham. 2005. El-Fayoum bentonite: from brick and ceramic industry to agricultural production. The 3rd International Conference Soils of Urban Industrial, Traffic, Mining and Military Areas. Available at: http://193.227.1.53/suitma/index.php

Talaat H A, N M El Defrawy, A G Abulnour, H A Hani and A Tawfik. 2011. Evaluation of heavy metals removal using some Egyptian clays. 2nd Int. Conference on Environ. Sci. Technol. (IPCBEE) IACSIT Press, Singapore.

Tashauoei H R, H Movahedian Attar, M Kamali, M M Amin and M Nikaeen. 2010. Removal of hexavalent chromium (VI) from aqueous solutions using surface modified nanozeolite A. Int. J. Environ. Res., 4:491-500

van der Marel H W and H Beutelspacher. 1976. Atlas of infrared spectroscopy of clay minerals and their admixtures. Elsevier scientific publishing company, Amsterdam, Netherlands. PP. 65-116

Volkmann H. 1972. Handbuch der Infrarot-Spektroskopie. Verlag chemie, Germany. Pp. 302.

Wang C, L Juang, C Lee, T Hsu, J Lee and H Chao. 2004. Effects of exchanged surfactant cations on the pore structure and adsorption characteristics of montmorillonite. J Colloid Interface Sci., 280:27-35.

Wankasi D, H M Jnr and A I Spiff. 2005. Desorption of Pb^{2+} and Cu^{2+} from Nipa palm (Nypa fruticans Wurmb) biomass. Afr. J. Biotechnol., 4:923-927

Weber W. J., Jr. 1974. Adsorption processes. Pure Appl. Chem., 37: 375-392

WHO. 2000. Chromium chapter 6.4. Air quality guidelines – 2ndEd WHO Regional Office for Europe, Copenhagen, Denmark. Available at: http://www.euro.who.int/-data/assets/pdf_file/0017/123074/aqg2nded_6_4chromium.pdf

WHO. 2009. 10 facts about water scarcity. Available at: http://www.who.int/ features/factfiles/water/en/.

WHO. 2010. Exposure to cadmium: A major public health concern. Preventing disease through healthy environments. Available at: http://www.who.int/ipcs/features/ cadmium.pdf

Yariv S and H Cross. 2002. Organo-Clay complexes and interactions. Marcel Dekker Inc. USA. pp. 193-222.

Yoo J, J Choi, T Lee and J Park. 2004. Organobentonite for sorption and degradation of phenol in the presence of heavy metals. Water Air Soil Pollut., 154:225-237.

Zahra N, S T Sheikh and K Javed. 2008. Batch adsorption studies of cadmium in wastewater on bentonites. J. Chem. Soc. Pak., 30:797-799.

Zein F I, M S El-Yammani, A A El-Leithy and A T A Moustafa. 2002. Effect of polluted irrigation water on some crops and their contents of heavy metals. 2. Sugar beet. Egypt. J. Soil Sci., 42:307-318.

Zhang C, D Guo, J Guo, R Yuan, J Gu, D Wang and B Zhou. 2011. Competitive adsorption amongst several organic pollutants on activated carbon. International Conference on Electric Technology and Civil Engineering (ICETCE).

Zhang Z Z, D L Sparks and N C Scrivner. 1993. Sorptlon and desorption of quaternary amine cations on clays. Environ. Sci. Technol, 27:1625-1631.

Zhao G, X Wu, X Tan and X Wang. 2011. Sorption of heavy metal ions from aqueous solutions: a review. Open Colloid Sci. J., 4:19-31.

Zhu J, V Cozzolino, M Pigna, Q Huang, A G Caporale and A Violante. 2011. Sorption of Cu, Pb and Cr on Na-montmorillonite: Competition and effect of major elements. Chemosphere, 84:484-489

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كل الحب والعرفان بالجميل

I dedicate this work to my Father and my sister Heba, I wish God bless you in Heaven

يرحمكم الله ويسكنكم فسيح جناته

8. Curriculum vitae

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Education

2001	M.Sc. in Agric. Sci. (Soil Sci.), Faculty of Agriculture, Ain Shams University, Cairo, Egypt. Thesis title is `` Effect of Land Use Periods on The Status of Some Nutrients in New Reclaimed Lands``
1995	B.Sc. in Agric. Sci. (Soil Sci.), Faculty of Agriculture, Ain Shams University, Cairo, Egypt.

Professional experiences

2008 - present	PhD student Fertilisation and Soil Matter Dynamics, Institute of Crop Science, University of Hohenheim, Stuttgart, Germany.
2004 - 2007	Assistant researcher in Soil & Water Use Department, National Research Centre, Dokki, Cairo, Egypt

Scientific contributions

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Mubarak D, R Schulz, D Martens, M Zarei, T Müller. 2011. Removal of metalaxyl-m by organically modified sediment from aqueous solution. Development on The Margin, Tropentag, Bonn, Germany (Poster presentation).

Other experiences and skill

2010	ETS Toefl
2008	Participated the ELLS Summer University ´´Rhizotechnology for enhancing efficiency in low-input farming`` organised by Universität für Bodenkultur Wien (BOKU).
2007	PC Skill (ICDL certificate)
2007	Deutsch Course (level B1) by Goethe Institut.
2003	Attendance the “ Pilot Distance Learning Course on Sustainable Agriculture from April 28th to Mai 27th, 2003. The organizer is International Centre for Advanced Mediterranean Agronomic Studies.
1996- 2001	Member in Central Laboratory for Soil, Water and Plant Analysis., Fac. Agric., Ain Shams University

Membership

2011	Membership of the Mineralogical Society
2005	Member of Egyptian National Soil Science Committee
2005	Founded member of Researcher Youth Association (NGO), Egypt

- أوضحت النتائج أن رواسب البنتونيت المُعَدلة عضوياً لها القدرة على إزالة الملوثات الكاتيونية من المحاليل ذات مدى واسع من درجة الحموضة (pH)، حيث تحقق أعلى إمتصاص في مدى pH ٤ - ٨ للكادميوم و ٤ - ٦ للرصاص. بينما درجة الحموضة pH = ٤ كانت الأمثل لإمتصاص الداى كرومات.
- أجريت دراسة السعة الامتصاصية لرواسب البنتونيت المُعَدلة عضوياً باستخدام النماذج الرياضية لانجموير و فروندليش، حيث كانت معادلة لانجموير الأمثل للتعبير عن نتائج الامتصاص. كما أختيرت معادلة الحركية من الدرجة الثانية pseudo second order kinetics في دراسة حركية عملية الامتصاص و التي دلت على معدل إمتصاص سريع للكادميوم و الرصاص بواسطة رواسب البنتونيت المُعَدلة بإستخدام Carnitin و HA. بينما معدل الامتصاص السريع للداى كرومات تمثل برواسب البنتونيت المُعَدلة بإستخدام Cys_ester.
- دلت النتائج على إمكانية إطلاق الملوثات بعد إمتصاصها بواسطة رواسب البنتونيت المُعَدلة عضوياً، بما يوحى بإمكانية إعادة إستخدام هذه المواد الماصه فى دورة إمتصاص أخرى.

أما عن دراسة إمتصاص الملوثات من المحاليل ذات النظم الثنائية و الثلاثية المكون، فقد أوضحت النتائج ما يلي:

- وجود ملوث آخر في المحلول عزز إمتصاص الداى كرومات بواسطة رواسب البنتونيت المُعَدلة بإستخدام HDTM وMTP , كما أدى إلى زيادة إمتصاص ميتالاكسيل بواسطة رواسب البنتونيت المُعَدلة بإستخدام Cys_ester وMTP.
- لوحظ تأثير التنافس بين الملوثات على إمتصاص الكادميوم و المبيد الفطرى ميتالاكسيل بواسطة رواسب البنتونيت المُعَدلة بإستخدام HDTM. بينما لم يكن هناك أي سلوك تنافسي بين الملوثات الممتصة بواسطة رواسب البنتونيت المُعَدلة عضوياً بإستخدام Cys_ester.
- مما سبق ممكن الإستدلال على أن رواسب البنتونيت المُعَدلة باستخدام MTP, HDTM Cys_ester, لها القدرة على الإزالة المتزامنة للكادميوم وداى كرومات و ميتالاكسيل من المحاليل ذات النظم الثنائية و الثلاثية المكون.

النتائج المتحصل عليها تشير لإمكانيه إستخدام رواسب البنتونيت المُعَدلة عضوياً في معالجة مياة الصرف الزراعي و الصناعى.

XRD لرواسب البنتونيت المُعَدلة عضوياً بإستخدام MTP و HDTM زيادة المسافة البينية لطبقات الطين من ١٤,٥أنجستروم إلى ١٧,١ و ١٩,٧ أنجستروم على الترتيب.

بعد توصيف الرواسب الطينية المُعَدلة عضوياً، أُجريت دراسة لتحديد التحميل المناسب من المُعَدِّل العضوي على OMCs الذي يحقق أعلى إزالة للملوث المعدنى.

أظهرت نتائج الدراسة التى أجريت على رواسب الكاؤلينيت أن التعديل العضوى باستخدام HDTM , Carnitin بنسبة تحميل ≤ ٧١ % و ٨ % من السعة التبادلية الكاتيونية للرواسب الغير معاملة , على التوالى , لم يؤدى إلى تغير ملحوظ فى إمتصاص الكادميوم و الرصاص مقارنة بالرواسب الغير معاملة. بينما أدى تحميل رواسب الكاؤلينيت باستخدام Cys_ester , MTP بتركيزات ≤ ٣٨ % و ٢١ % من السعة التبادلية الكاتيونية, على التوالى , إلى زيادة إمتصاص هذيين الملوثين. تم الحصول على زيادة ملحوظة فى امتصاص داى كرومات من قبل رواسب الكاؤلينيت المعدلة عضويا باستخدام Cys_ester , HDTM .

يمكن تلخيص النتائج المتحصل عليها باستخدام رواسب البنتونيت المُعَدلة عضوياً على النحو التالي:

- رواسب البنتونيت لها القدرة على إزالة كل التركيزات الموجودة من الكادميوم و الرصاص من المحاليل عندما كانت نسبة تحميلها بالمُعَدِّلات العضوية HDTM , MTP ≤ ٥٠ % من السعة التبادلية الكاتيونية للرواسب. بينما زيادة تحميل المُعَدِّل العضوى Cys_ester أدت إلى خفض إمتصاص تلك الملوثين بالمقارنة مع رواسب البنتوبيت الطبيعية. كما أظهرت رواسب البنتونيت المُعَدلة عضوياً باستخدام Carnitin بنسبة تحميل حتي ٢١ % من السعة التبادلية الكاتيونية القدرة على إزالة ٨٤ % من الكادميوم و ١٠٠ % من الرصاص الموجودين في المحاليل، بينما أدى زيادة تحميل العضوى بمعدل أكبر إلى نقص الامتصاص.
- بالمقارنة مع رواسب البنتونيت الطبيعية، أظهرت الرواسب المعدلة بإستخدام HDTM و Cys_ester كفاءة لإزالة الداى كرومات و إزدادت هذه الكفاءة مع زيادة تحميل المُعَدِّل العضوى على الرواسب.

بناءاً على ما سبق، تم إختيار رواسب البنتونيت المُعَدلة عضوياً بإستخدام HDTM, MTP, Carnitin, Cys_ester بنسب تحميل تكافئ ١٠٢، ٧٩، ١٨، ٦٦ % من السعة التبادلية الكيتونية ،على الترتيب، بالإضافة إلى رواسب البنتونيت المُعَدلة بحامض الهوميك (Humic acid, HA) كمواد ماصة فعالة لإزالة الملوثات المعدنية.

بعد ذلك تم دراسة القدرات الامتصاصية للمواد الماصه المختاره (OMCs) لإزالة الملوثات تحت الدراسة و كذلك تم بحث العوامل المؤثرة على عملية الامتصاص وشملت تأثير درجة حموضة المحلول (pH)، زمن التماس، تركيز الملوثات، تأثير وجود إلكتروليت في المحلول.

تتلخص النتائج المتحصل فيما يلي:

- أظهرت رواسب البنتونيت المعدلة عضويا باستخدام HDTM, MTP, Carnitin, HA قدرة امتصاصية عاليه للكادميوم و الرصاص. بينما تلك المعدلة باستخدام Cys_ester كانت الأعلى قدرة امتصاصية للداى كرومات.

9. Arabic Summary

الملخص العربى

إعادة إستخدام مياة الصرف الزراعي و الصناعي هى واحدة من الإستراتيجيات المتبعة فى العديد من البلاد لسد الفجوة القائمة بين الموارد المائية المتاحة و الحاجات المستقبلية. هذه المصادر المائية تحتوى على العديد من الملوثات التى تضر بصحة الإنسان و البيئة. بالرغم من أن الإدمصاص يعتبر من إحدى الأساليب المناسبة لإزالة الملوثات من مياة الصرف، فإن الجانب الاقتصادى هو العامل الحاسم للتطبيق الواسع لهذه التقنية.

أجريت هذه الدراسة بهدف إقتراح مواد لها القدرة على إمتصاص العديد من الملوثات الغير متجانسة، آخذة في الاعتبار محدودية الموارد في البلاد النامية و الناشئة مثل مصر. لهذا الغرض تم إختيار رواسب طينية طبيعية كمواد رخيصه و صديقه للبيئة و تحميلها بمواد عضوية مختلفة لإنتاج رواسب طينية معدله عضويا (OMCs). مقارنةً مع الرواسب الطينية الطبيعية، تمتلك الرواسب الطينية المعدله عضويا القدرة على إزالة الملوثات الغير متجانسة بما في ذلك الكاتيونية و الأنيونية وكذلك العضوية و الغير عضوية.

و من ثم فقد ركزت الدراسة على بحث خواص الامتصاص و الانطلاق بواسطة الرواسب الطينية المُعدله عضويا لكلا من الكادميوم (Cd^{2+}) و الرصاص (Pb^{2+}) (مثالان من الملوثات الغير عضوية الكاتيونية) و داى كرومات ($Cr_2O_7^{2-}$, ملوث غير عضوي انيونى)، والمبيد الفطرى ميتالاكسيل (MM , ملوث عضوى).

بدأت الدراسة العملية بتحضير الرواسب الطينية المعدلة عضويا باستخدام رواسب طينية طبيعية تم تجميعها من مناطق مختلفة بجمهورية مصر العربية. حيث تم إختيار رواسب طينية من سيناء لتمثل رواسب الكاؤلينيت (kao sediment) و رواسب طينية من منطقة قصر الصاغة بمحافظة الفيوم لتمثل رواسب البنتونيت (bent sediment). كما تم إستخدام تركيزات مختلفة من المُعَدِّلات العضوية :

L-Carnitine (Carnitin), L-Cystine dimethyl ester (Cys_ester), Methyltriphenyl-phosphonium (MTP) or Hexadecyltrimethyl-ammonium (HDTM)

المعالجة العضوية للرواسب الطينية أدت إلى زيادة محتوى الكربون العضوى متخذا الترتيب التالى:

Carnitin < Cys_ester < MTP < HDTM

كما ان محتوى الكربون العضوي كان أعلى في رواسب البنتونيت المعدله عضوياً عنه في رواسب الكاؤلينيت المعدلة.

لتوصيف الرواسب وإثبات التحميل العضوى عليها ، تم تحليل الرواسب الطينية المُعَدلة عضوياً باستخدام أجهزة التحليل الطيفي XRD، MIRS. كما تم تقدير السعه التبادلية الكاتيونيه لها. أظهرت مخططات MIRS الاهتزازات الخاصة بالرواسب الطينية الطبيعية بالإضافة إلى تلك المميزة للمُعَدِّل العضوى. حيث دل ذلك على نجاح تحميل هذه المركبات العضوية على الطين. كما أظهرت مخططات