



HELLENIC REPUBLIC
National and Kapodistrian
University of Athens
— EST. 1837 —

SCHOOL OF SCIENCES
DEPARTMENT OF GEOLOGY AND GEOENVIRONMENT

MSc Program "Geology and Geoenvironment"

**Assessment of Fe- rich smectite clays in adsorbing Pb and Cu from
aqueous solutions: A batch experiment approach**

THESIS for the MSc Diploma in the Specialization

"ENVIRONMENTAL MANAGEMENT AND MINERAL RESOURCES"

by

Athanasia N. Kazantzoglou

Supervisor:

Ariadne Argyraki

Associate Professor of Geochemistry

ATHENS

2019

**Assessment of Fe- rich smectite clays in adsorbing Pb
and Cu from aqueous solutions: A batch experiment
approach**

Athanasia Kazantzoglou

R.N.: 21528

Supervisor:

Ariadne Argyraki, Associate Professor

Examining board: Michael Stamatakis, Professor

Ioannis Mitsis, Assistant Professor

ATHENS

2019

**Αξιολόγηση σιδηρούχου σμεκτιτικής αργίλου για την προσρόφηση μολύβδου και χαλκού
σε υδατικά διαλύματα**

***When you are enthusiastic about what you do,
you feel this positive energy. It's simple!***

Paolo Coelho

To my family

Abstract

The Fe-rich smectite clay mined in the area of Grevena, Greece, is a natural material, environmentally friendly, readily available with efficiency in environmental remediation of soil contaminated by heavy metals. The main propose of this thesis was to study the interaction between Fe-rich smectite clays quarried at Knidi, Grevena by Geohellas S.A., and Copper (Cu) and Lead (Pb) cations in monometallic aqueous solutions by comparing the adsorption capacity of raw and thermally modified clay material.

Adequate quantity of powdered clay material was supplied by Geoellas S.A.. Separate samples were heat treated at temperatures of 130, 330, 500 and 800 °C for 4 hours in a muffle. The raw material studied is a mixture mainly of Fe-rich dioctahedral and trioctahedral smectite and palygorskite and its properties are a combination of the properties of the contained minerals. Mineralogical analysis by X-ray diffraction (XRD) before and after heat treatment showed that the crystal lattice of Fe-smectite gets destructed at temperatures higher than 130°C. The comparative study of Cu and Pb adsorption efficiently of heat treated and non-treated material, was subsequently performed by using an adsorbent dose from 2 to 15 g/L, initial metal concentration of 50mg/L, shaking time between 5 minutes to 2 hours and pH 2-8. The effect of ionic strength was studied by adding NaNO₃ at concentrations from 0 to 0.5 mole/L. All experiments were carried out in a thermostatic chamber set at 22°C. Metal concentrations before and after interaction, were measured by Flame Atomic Absorption Spectroscopy (F-AAS).

A decrease in the concentration of the metals in the aqueous solution was observed with increasing adsorbent dose. A clay dose of 10 g/L in the suspension was the most effective, as 90-100% of Cu and Pb was retained in the clay after interaction with all raw and heat treated materials, except the sample heated at 800 °C. The optimum pH of the standard aqueous solution was between 4 and 6 for thermally modified and raw material. In general, equilibrium was achieved after the first 30 minutes of interaction, however, a significant decrease of metal concentration was observed within the first 5 minutes indicating that adsorption is a fast process. A decrease in adsorption was observed as the concentration of NaNO₃ was raised, probably due to competition between Na⁺ and metal ions for the available adsorption sites. The adsorption isotherm is of L-type, indicating high relation between the studied metals and the surface of the adsorbent. The samples treated at different temperatures present different adsorption capacity because of differences in their mineralogy. A difference in the physical and mechanical parameters of the material is also noticed for different temperatures of treatment. Finally, the results compared with different studies from the bibliography about materials of the same clay group like smectite, palygorskite etc. The raw as the thermally modified material was effective in the adsorption of the two metals (with small differences in their adsorption capacity)

except the sample heated at 800 °C. Overall, the clay material has the potential to act as a binding agent of heavy metals from aqueous solutions in either raw or heat treated condition.

Key words: Fe-smectite, palygorskite, clay, heat treatment, adsorption, copper (Cu), lead (Pb)

Περίληψη

Η σμεκτιτική άργιλος πλούσια σε Fe η οποία εξορύσσεται στην περιοχή των Γρεβενών, είναι ένα φυσικό υλικό, φιλικό προς το περιβάλλον και άμεσα διαθέσιμο με αποτελεσματικότητα στην περιβαλλοντική αποκατάσταση εδαφών τα οποία έχουν μολυνθεί από βαρέα μέταλλα. Βασικός σκοπός της εργασίας αυτής ήταν να μελετηθεί η αλληλεπίδραση μεταξύ της Fe-πλούσιας σμεκτιτικής άργιλου, που εξορύσσεται στην περιοχή Κνίδη, Γρεβενών από την εταιρεία ΓΕΩΕΛΛΑΣ, και κατιόντων Χαλκού (Cu) και Μολύβδου (Pb) σε μονομεταλλικά υδατικά διαλύματα, συγκρίνοντας την ικανότητα προσρόφησης του ακατέργαστου και του θερμικά τροποποιημένου αργιλικού υλικού.

Επαρκής ποσότητα αργιλικού υλικού σε μορφή πούδρας δόθηκε από την εταιρεία ΓΕΩΕΛΛΑΣ. Διαφορετικά δείγματα τροποποιήθηκαν θερμικά σε θερμοκρασίες 130,330,500 και 800°C για 4 ώρες σε κατάλληλο φούρνο. Το ακατέργαστο υλικό που μελετάται είναι ένα μίγμα που αποτελείται κυρίως από Fe-πλούσιο διοκταεδρικό και τριοκταεδρικό σμεκτίτη και παλυγορσκήτη και οι ιδιότητες του είναι ένας συνδυασμός των ιδιοτήτων των επιμέρους ορυκτών. Η ορυκτολογική ανάλυση με τη μέθοδο XRD πριν και μετά τη θερμική τροποποίηση έδειξε ότι το κρυσταλλικό πλέγμα του Fe-πλούσιου σμεκτίτη καταστρεφεται σε θερμοκρασίες υψηλότερες των 130°C. Η μελέτη για την αποτελεσματικότητα της προσρόφησης του Cu και του Pb από ακατέργαστο και θερμικά τροποποιημένο υλικό πραγματοποιήθηκε σε ευρύς συγκέντρωσης του προσροφητικού υλικού από 2 έως 15 g/L, αρχική συγκέντρωση μετάλλου 50mg/L, χρόνο ανατάραξης 5 λεπτά ως 2 ώρες και σε ευρύς pH 2-8. Η επίδραση της ιοντικής ισχύς μελετήθηκε με την προσθήκη NaNO₃ σε συγκέντρωση από 0 έως 0,55mole/L. Όλα τα πειράματα διεξήχθησαν σε θερμοθάλαμο ρυθμισμένο στους 22°C. Οι συγκεντρώσεις των μετάλλων πριν και μετά την αλληλεπίδραση μετρήθηκαν με τη μέθοδο της Φασματομετρίας Ατομικής Απορρόφησης με φλογα (F-AAS).

Μείωση της συγκέντρωσης των μετάλλων στο υδατικό διάλυμα παρατηρήθηκε με την αύξηση της δόσης του προσροφητικού υλικού. Δόση αργίλου 10 g/L ήταν η καταλληλότερη, καθώς 90-100% του Cu και του Pb συγκρατήθηκαν στο αργιλικό υλικό μετά την αλληλεπίδραση με το ακατέργαστο και το θερμικά τροποποιημένο υλικό, εκτός από το δείγμα που θερμάνθηκε στους 800°C. Το βέλτιστο pH του πρότυπου υδατικού διαλύματος ήταν μεταξύ 4 και 6 για το θερμικά τροποποιημένο υλικό και για το ακατέργαστο. Γενικά, η ισορροπία επιτεύχθηκε μετά τα πρώτα 30 λεπτά αλληλεπίδρασης, ωστόσο παρατηρήθηκε σημαντική μείωση της συγκέντρωσης μετάλλου μέσα στα πρώτα 5 λεπτά, υποδεικνύοντας ότι η προσρόφηση είναι μια γρήγορη διαδικασία. Μείωση στην προσρόφηση παρατηρήθηκε με την αύξηση της συγκέντρωσης NaNO₃, πιθανά λόγω του ανταγωνισμού που αναπτύσσεται ανάμεσα στο Na⁺ και τα μεταλλικά ιόντα για τις διαθέσιμες θέσεις προσρόφησης. Οι ισόθερμες καμπύλες είναι τύπου-L, αυτό δηλώνει ισχυρή σχέση ανάμεσα στα μέταλλα που μελετώνται και την επιφάνεια του προσροφητικού υλικού. Τα δείγματα που υπεστήσαν θερμική επεξεργασία σε διαφορετικές θερμοκρασίες παρουσιάζουν διαφορετική ικανότητα προσρόφησης λόγω διαφορών στην ορυκτολογική τους σύσταση. Διαφορά στις φυσικές και

μηχανικές παραμέτρους του υλικού παρατηρήθηκε επίσης για τις διαφορετικές θερμοκρασίες επεξεργασίας. Τέλος, έγινε σύγκριση των αποτελέσματος με άλλες εργασίες από τη βιβλιογραφία που αφορούν αργιλικά υλικά όπως σμεκτίτη, παλυγορσκήτη κτλ. Το ακατέργαστο όσο και το θερμικά τροποποιημένο υλικό ήταν αποτελεσματικό στην προσρόφηση Cu και Pb (με μικρές διαφορές στην ικανότητα προσρόφησης) εκτός από το δείγμα που θερμάνθηκε στους 800°C. Σύμφωνα με όλα τα παραπάνω, το αργιλικό υλικό έχει τη δυνατότητα να δρα ως δεσμευτικός παράγοντας βαρέων μετάλλων από υδατικά διαλύματα τόσο σε ακατέργαστη όσο και σε θερμικά τροποποιημένη κατάσταση.

Λέξεις κλειδιά: Fe-σμεκτίτης, παλυγορσκήτης, άργιλος, θερμική επεξεργασία, προσρόφηση, χαλκός (Cu), μόλυβδος (Pb)

Acknowledgments

The writing of a master thesis is for the student a source of knowledge, experience and inspiration around the scientific subject, which he has voluntarily and conveniently chosen to deal with.

I would like to thank all those who supported me and helped me carry out this study.

First of all, I would like to thank my supervisor Dr.Ariadne Argyraki, Associate Professor of Geochemistry, Section of Economic Geology and Geochemistry (NKUA), for the confidence that she has shown me and has instructed me to draw up this specific work, for her guidance and for her overall cooperation.

I would also like to thank the members of the examining board of my thesis Dr.Michael Stamatakis, Professor (NKUA) and Dr.Ioanni Mitsi, Associate Professor (NKUA) for the critical study of the text and for their comments. A further thank you to Dr.Eustratios Kelepertzis and PhD candidate Zaxarenia Kypridou for their help during the laboratory experiments. In addition, Dr.Vasili Zotiadi and Chari Tsavo for the diligence of the tests for the determination of the physical and mechanical properties of the clay material in the laboratory of Edafomichaniki S.A., as well as for the useful discussions on the topic of the study, as well as the company Geoellas S.A. for the supply of the material. Moreover I have to thank the TITAN Group for the XRF results.

Finally, I appreciate the help from all those who I have not mentioned but from their own position, they contributed to the successful completion of this master thesis.

CONTENTS

1. INTRODUCTION	1
1.1 Research purpose and specific objects.....	1
2. LITERATURE REVIEW	4
2.1 Pollution of aqueous solutions by PTEs.....	4
2.2 Characteristics of the studied metals.....	5
2.2.1 Copper.....	5
2.2.2 Lead.....	7
2.3 Clay minerals.....	8
2.4 Smectite clay minerals as adsorbents.....	12
2.5 Attapulgite clay as adsorbent.....	13
2.6 Environmental uses of clay minerals.	15
2.7 Clay deposits of the Ventzia basin, north Greece	18
2.8 Batch tests and adsorption isotherms.....	19
3.METHODOLOGY	23
3.1 Heat treatment.....	23
3.2 Determination of mineralogical composition (X-ray diffraction, XRD).....	23
3.3 Determination of the microstructure (Scanning Electron Microscope, SEM).....	24
3.4 The preparation of the standard solutions.....	24
3.5 Batch tests.....	25
3.6 Measurement of pH and temperature.....	26
3.7 Measurement of metal ion concentrations by Flame Atomic Adsorption Spectrometry (F-AAS).....	27
3.8 Determination of natural parameters of adsorbent material.....	28
4. RESULTS AND DISCUSSION	30
4.1 Minerology of clay material and effect of heat treatment.....	30
4.1.1 X-Ray Diffraction (XRD) mineralogical analyses.....	30

4.1.2 Micromorphology and composition of grains of raw and heat-treated clay material.....	32
4.2 Adsorption experiment results.....	35
4.2.1 Quality control.....	35
4.2.2 Effect of the clay dose.....	35
4.2.3 Effect of pH.....	38
4.2.4 Effect of contact time.....	40
4.2.5 Effect of the ionic strength.....	42
4.2.6 Adsorption isotherms.....	44
4.3 Physical parameters of raw and heat treated clay material.....	47
4.3.1 Permeability tests.....	47
4.3.2 Plasticity and Liquid limit.....	51
4.4 Comparison of results with previous studies and potential uses of the studied clay material.....	51
5. CONCLUSIONS AND SUGGESTIONS FOR FURTHER STUDY.....	53
5.1 Conclusions.....	53
5.2 Suggestions for further research.....	55
REFERENCES.....	56
APPENTICES.....	60

APPENDICES

Appendix 1: Heat treatment.....	60
Appendix 2: Preparation of standard solutions.....	61
Appendix 3: Effect of the clay dose.....	63
Appendix 4: Effect of pH.....	65
Appendix 5: Effect of time contact.....	67
Appendix 6: Effect of ionic strength.....	71
Appendix 7: Adsorption isotherms.....	74
Appendix 8: Adsorption isotherm models.....	77
Appendix 9: XRD patterns.....	79

LIST OF FIGURES

Figure 2.2.1: Eh-ph diagram for the system Cu-O-H-S-Cl in seawater at 25 °C (after Hannington, 1993). Stability fields are shown for the principal aqueous copper species, basic copper salts, copper oxides, native copper and chalcocite.....	6
Figure 2.2.2: Eh-pH diagram for the system Pb-O ₂ -PO ₄ -S-H ₂ O, assuming that EPb = 10 ⁻⁸ , 10 ⁻⁷ , and 10 ⁻⁶ mol/kg at solid/liquid boundaries; ES = 10 ⁻⁵ mol/kg; and EPO ₄ = 10 ⁻⁶ mol/kg. Diagram shows the stability fields of the lead phosphate, pyromorphite, and galena (PbS). After Barnes and Langmuir, 1978.....	8
Figure 2.3.1: Single silica tetrahedron (shared) and the sheet structure of silica tetrahedrons arranged in a hexagonal network.....	9
Figure 2.3.2: (A) Ideal hexagonal tetrahedral sheet. (B) Contracted sheet of ditrigonal symmetry owing to the reduction of mesh size of the tetrahedral sheet by rotation of the tetrahedrons.....	9
Figure 2.3.3: Single octahedron (shaded) and the sheet structure of octahedral units.....	9
Figure 2.3.4: Structure of 1:1 layer silicate (kaolinite) illustrating the connection between tetrahedral and octahedral sheets.....	10
Figure 2.3.5: Schematic presentation of (A) 1:1 layer structures and (B) 2:1 layer structures.....	11
Figure 2.4.1: (a) 2:1 structure of clay minerals., (b) 1:1 structure of clay minerals.	12
Figure 2.5: Structural arrangement of attapulgite and sepiolite. (a,b) tetrahedral sheet of attapulgite and sepiolite, (001), the black and grey color correspond to tetrahedrons with extreme oxygen presenting in opposite directions, (c,d) tetrahedral sheet of attapulgite and sepiolite, (100), the grey color corresponds to the octahedral sheet, (e,f) octahedral sheet of attapulgite and sepiolite, (001), (g, h) schematic view of a 1_1_2 alveolar of attapulgite and sepiolite.....	14
Figure 2.7: Simplified map of the Vourinos ofiolite complex.....	18
Figure 2.8: The four main types of adsorption isotherms.....	21
Figure 3.2: X-ray diffraction instrument at the laboratory of Economic Geology and Geochemistry, NKUA.....	24
Figure 3.6: The pH meter at the laboratory of Economic Geology and Geochemistry, NKUA.....	27
Figure 3.7: Flame Atomic Adsorption Spectrometry instrument at the laboratory of Economic Geology and Geochemistry, NKUA.....	28
Figure 3.8.1: The oedometer device, at the laboratory of Edafomichaniki S.A	28
Figure 3.8.2: Applying the method to measure the liquid limit	29

Figure 4.1.1.: XRD pattern before and after glycolating the XLS0 sample, showing the move of smectite basal reflection peak from 6° to 5°.....	31
Figure 4.1.2: Mineral grains of raw and heat-treated material observed by SEM....	34
Figure 4.2.2a: Effect of the clay dose on the adsorption of Cu from an aqueous solution.....	37
Figure 4.2.2b: Effect of the clay dose on the adsorption of Pb from an aqueous solution.....	37
Figure 4.2.3a: Effect of the pH on the removal of Cu from an aqueous solution.....	39
Figure 4.2.3b: Effect of the pH on the removal of Pb from an aqueous solution	39
Figure 4.2.4a: Effect of the contact time on the adsorption of Cu from an aqueous solution.....	41
Figure 4.2.4b: Effect of the contact time on the adsorption of Pb from an aqueous solution.....	42
Figure 4.2.5a: Effect of the ionic strength on the adsorption of Cu from an aqueous solution.....	43
Figure 4.2.5b: Effect of the ionic strength on the adsorption of Pb from an aqueous solution.....	43
Figure 4.2.6a: Adsorption isotherms (Cu).....	45
Figure 4.2.6b: Adsorption isotherms (Pb).....	45
Figure 4.3.1.1a,b: Results of the permeability tests (XLS0).....	48
Figure 4.3.1.2a,b: Results of the permeability tests (XLS130).....	48
Figure 4.3.1.3a,b: Results of the permeability tests (XLS330).....	49
Figure 4.3.1.4a,b: Results of the permeability tests (XLS500).....	50
Figure 4.3.1.5a,b: Results of the permeability tests (XLS800).....	50

LIST OF TABLES

Table 2.1: Sources and health effects of some widely used heavy metals (Mooms et al.2008).....	4
Table 4.1.1: Mineralogical phases in raw and heat treated samples, identified by XRD method.....	30
Table 4.1.2.1: Total chemical analyses of the clay material XLS.....	32
Table 4.1.2.2: EDS measurements for XLS samples.....	34
Table 4.2.2: Results from AAS method-Effect of the clay dose.....	36
Table 4.2.3: Results from AAS method-Effect of the pH.....	38
Table 4.2.4: Results from AAS method-Effect of contact time.....	41
Table 4.2.5: Results from the AAS method-Effect of the ionic strength.....	42
Table 4.2.6.1: Results from AAS method-Adsorption isotherms.....	44
Table 4.2.6.2: Parameters K and n for Cu and Pb (Freundlich).....	46
Table 4.2.6.3: Parameters K and Q_0 for Cu and Pb (Langmuir).....	46
Table 4.3.1: Results of permeability testes on clay samples in oedometer device....	47
Table 4.3.2: Plastic and liquid limits for samples XLS130 and XLS330.....	51

1. INTRODUCTION

1.1 Research purpose and specific objects

Contamination of water or soils by potentially toxic elements (PTEs) has been a major environmental problem. Elevated or toxic concentrations of these elements are noticed in areas of mining and metallurgical activities, of rural activities (with the use of herbicides, pesticides etc), at the industrial zones etc. The mobility of each element is different and it depends on a number of factors, affecting its bioaccessibility and toxicity. A lot of natural (e.g. clay minerals, zeolite and iron oxides) or synthetic materials have been researched for their ability to adsorb toxic elements, for the protection of the environment and consequently that of human health.

The use of natural substances as adsorbents is a widely used modern method of removing toxic metals from natural systems and has numerous benefits including low cost, rapid kinetics, environmental friendliness etc. This is the reason why many scientists have studied the effectiveness of clay materials in adsorption of PTEs. Bourliva (2013) in her doctoral thesis studied the effect of bentonite addition in chemical flocculants for the adsorption of PTEs (Cr, Cu, Ni, Mn, Zn) during treatment of urban waste water. The adsorption of Pb (II) ions onto Tunisian smectite-rich clay in aqueous solution was studied by Chaari et al., (2008). They concluded that the type of smectitic clay could adsorb Pb (II) via two different mechanisms: cation exchange and inner sphere complex formations. Ghobel-Adid and Trabelsi-Avadi (2011) have investigated the interaction of Cr(III) and Cd(II) ions in solution with the local landfill clay of Jebel Chakir located in the northwest of Tunis (Tunisia, North Africa). The adsorption properties of natural clay and the Na-purified clay in a chromium and cadmium rich aqueous solution have been studied by batch technique. This study indicates that the smectic clay JCK could be used as an efficient low-cost adsorbent. The effect of a new method of adsorption using membrane filtration to determine the maximum amount of lead adsorbed by smectite clay was studied by Mhamdi et al. (2013). It was concluded that clay has a strong adsorption capacity for Pb (II) as the maximum interaction occurring with purified clay treated at a high concentration of lead. These are only some examples of the studies which have been carried out to investigate the potential use of clay materials as adsorbents.

Previous research in the Laboratory of Economic Geology and Geochemistry has investigated extensively the potential of using natural materials quarried in Greece for environmental purposes. Kypridou and Argyraki (2018) in their study present a methodological approach of combining batch experiment data and geochemical modeling for the characterization of the interaction of Mg-Fe-rich clay materials with monometallic solutions of Pb and Cu. For this purpose, a palygorskite clay (PCM), an

Fe-smectite clay (SCM) and a natural palygorskite-Fe-smectite mixed clay (MCM) were assessed for their effectiveness as metal ion sorbents. They suggest that a combination of sorption mechanisms occurs during the interaction of clay materials with metal solutions. These involve surface complexation, ion exchange and precipitation of solid compounds onto the solid surface.

Argyraki et al., (2017) in their study tested, diasporic bauxite in raw form as well as after heat treatment at different temperatures (105 °C, 350 °C and 450° C) for its effectiveness in reducing the mobility of potentially harmful elements (PHEs) in contaminated soil. A pot experiment was set up where raw and calcined bauxite was mixed at different proportions with contaminated soil from the sulfide ore mining village of Stratoni, north Greece. Both raw and calcined bauxite in a mixing proportion of 7% reduced leachable concentrations of the elements in comparison to the original soil.

Messini (2014) in her thesis, presented results of laboratory experiments on the adsorption of Pb^{2+} and Cu^{2+} from standard aqueous solutions by comparing the adsorption capacity of raw and thermally modified attapulgite, mined in the area of Grevena, Greece. Outer sphere complexation and ion exchange are probably the main adsorption mechanisms at the studied pH. This data implies that significant changes in the adsorption capacity of the used attapulgite clay occur after calcination in temperatures, due to destruction of the crystal lattice of the material and nanoporosity change. Zotiadis et al., (2012) tested an in situ pilot-scale application of attapulgitic clay for stabilization of toxic metals and metalloids in contaminated soil. On the basis of the site-specific soil geochemical properties, an appropriate proportion of specific grain-size attapulgitic clay was added and mixed in situ with simultaneous adjustment of soil moisture content to reach saturation. Analytical data showed a significant reduction of water leachable metal fraction. In addition, soil pH was stabilized at slightly alkaline conditions and remained constant during a 7-month monitoring period after amending the soil. Overall, the use of attapulgitic clay as a binder for immobilizing metals in contaminated land is a promising stabilization method at a competitive cost under present market conditions.

The rich attapulgite- smectite clay deposits of the Ventzia Basin in north Greece have been exploited for more than 15 years by Geohellas S.A., a Greek mining company. As a part of its Research and Development, the company has been collaborating with universities and research institutions in exploring new environmental applications among other uses of its products (Geohellas.com). Specifically, Geohellas natural and enhanced porous clay products can be used in a variety of important environmental applications which take advantage of the products' ability to adsorb and immobilize PTEs and other toxic chemicals from liquids and gases. The quarried Fe-Mg rich clays own there chemical composition to their parent material - the serpentinised

ultramafic rocks of South Vourinos Complex and include attapulgite rich and smectite rich clays.

Within this framework, the main propose of this research was to study the interaction between Fe-rich smectite clays quarried at Knidi, Grevena by Geohellas S.A., and Copper (Cu) and Lead (Pb) cations in monometallic aqueous solutions by comparing the adsorption capacity of raw and thermally modified clay material.

The specific objectives of this research were:

1. To characterize the clay material with respect to its mineralogical and chemical composition and physical parameters
2. To determine the distribution of cations Cu and Pb between the aqueous solutions and the clay material by conducting batch experiments.
3. To explore the effect of various factors in the adsorption performance, such as the dose of the absorptive medium, the pH of the aqueous solution, the time of interaction, the ionic strength of the solution and the concentration of each metal in the solution.
4. To compare the adsorption capacity of the raw and thermally modified clay material at 130, 330, 500 and 800 °C.

2. LITERATURE REVIEW

2.1 Pollution of aqueous solutions by PTEs

Water pollution is any chemical, physical or biological change in the quality of water that has a harmful effect of any living being that drinks, uses or lives in it. The pollutant is every soluble or insoluble physical, chemical or biological substance which becomes harmful for organisms when it enters the environment by anthropogenic activities due to its unfavorable environmental effects. The most significant pollutants on the water are the trace metals (Cu, Pb, Cd etc.), metalloids (As, Se etc.), organic compounds (detergents, pesticides, petroleum products etc.), radioactive substances and pathogenic microorganisms (bacteria and viruses).

The term heavy metal has been used until recently in the literature and refers to any metallic chemical element that has a relatively high density and is toxic or poisonous at low concentrations (Pb, Cu, Ni, Cd, Pt, Zn, Hg, As, Sb) (Kelepertzis, 2000). Recently it has been suggested to replace this term by others, such as Potentially Toxic Elements (which is adopted in this research) or trace metals or trace elements (Duffus, 2002). PTEs are natural components of the Earth's crust. They cannot be degraded or destroyed and to a small extent they enter the body via food, drinking water and air. They occur in elemental, anionic, or cationic form, as complexes and solid phases.

The causes of water pollution by PTEs could be natural, such as disintegration and erosion of rocks, or anthropogenic, such as the mining and metallurgical activity, the fuel consumption, intensive agriculture, chemical industry etc.. In general, PTEs are environmentally dangerous due to their wide uses, their toxicity and their wide dispersion (Table 2.1).

Table 2.1: Sources and health effects of some widely used PTEs (Mooms et al.2008).

Metal	Sources	Health effects
Cadmium	Coal combustion, metal plating, phosphatic fertilizers, water pipe, tobacco smoke, zinc mining etc.	Cardiovascular diseases, hyretations, cancer, kidney damage.
Chromium	Anodizing, cooling towers, dyes, electroplating, inks, paints, tanning etc.	Cancer.
Copper	Pulp and paper, electrical goods, utensil, electronics chemicals etc.	Severe mucosal irritation, cancer.
Iron	Steel, machinery, dye, textile, medicine etc.	Cancer (suspected).
Lead	Battery industry, auto exhausts, paints etc.	Affects nervous and renal systems causes weakness headache, brain damage, convulsions, constipation and cancer.

Mercury	Chlor-alkali industry, coal combustion electrical batteries.	Nerve damage, death kidney and brain damage.
Nickel	Coal, diesel oil, metal plating, steel and non-ferrous alloys, tobacco smoke etc.	Lug cancer, respiratory problems.
Zinc	Galvanizing alloys, rayon paper etc.	Cancer

2.2 Characteristics of the studied metals

2.2.1 Copper

Copper (Cu) has atomic number 29. It has standard atomic weight 63.546, melting point 1084.6 °C and boiling point 2562 °C. It is a soft, malleable, and ductile metal with very high thermal and electrical conductivity. A freshly exposed surface of pure copper has a reddish-orange color. The copper has 2 oxidation numbers (+1 and +2) and it is not a particularly active metal and therefore does not react easily with other elements. It occurs as native copper, in the copper sulfides (chalcopyrite and chalcocite), in the copper carbonates (azurite and malachite), and in the copper(I) oxide mineral cuprite. In Figure 2.2.1, the pH-Eh diagram for copper phases is presented (Zhongwei et al, 2016). Copper can be released into the environment from both natural sources and human activities. Examples of natural sources are wind-blown dust, decaying vegetation, forest fires and sea spray. A few examples of human activities that contribute to copper release are industries, agriculture, mining, metal production, wood production and phosphate fertilizer production. Copper is often found near mines, industrial settings, landfills and waste disposal sites.

The production of copper has been on a rise over the last decades. Due to this, copper quantities released in the environment have increased. This basically means that more and more copper ends up in the environment. Rivers are depositing sludge on their banks that is contaminated with copper, due to the disposal of copper-containing wastewater. Copper also enters the air, mainly through release during the combustion of fossil fuels and remains in the air for an eminent period of time, before it settles due to rain. As a result soils may also contain large quantities of copper. Most copper compounds will settle and be bound to either water sediment or soil particles.

Copper can be found in many kinds of food, in drinking water and in air. Because of that we adsorb eminent quantities of copper each day by eating, drinking and breathing (www.lennotech.com). The adsorption of copper is necessary, because copper is a trace element that is essential for human health. Although humans can handle proportionally large concentrations of copper, too much copper can still cause eminent health problems. Copper concentrations in air are usually quite low, so that exposure to copper through breathing is negligible. But people that live near smelters that process copper ore into metal, do experience this kind of exposure. People that live in houses that still have copper plumbing are exposed to higher levels of copper than most people, because copper is released into their drinking

water through corrosion of pipes. Occupational exposure to copper often occurs. In the working environment, copper contagion can lead to a flu-like condition known as metal fever. This condition will pass after two days and is caused by over sensitivity (www.lenntech.com).

Long-term exposure to copper can cause irritation of the nose, mouth and eyes and it causes headaches, stomachaches, dizziness, vomiting and diarrhea. Intentionally high uptakes of copper may cause liver and kidney damage and even death. Whether copper is carcinogenic has not been determined yet. There are scientific articles that indicate a link between long-term exposure to high concentrations of copper and a decline in intelligence with young adolescents. Whether this should be of concern is a topic for further investigation. Industrial exposure to copper fumes, dusts, or mists may result in metal fume fever with atrophic changes in nasal mucous membranes. Chronic copper poisoning results in Wilson's Disease, characterized by a hepatic cirrhosis, brain damage, demyelization, renal disease, and copper deposition in the cornea (www.lenntech.com).

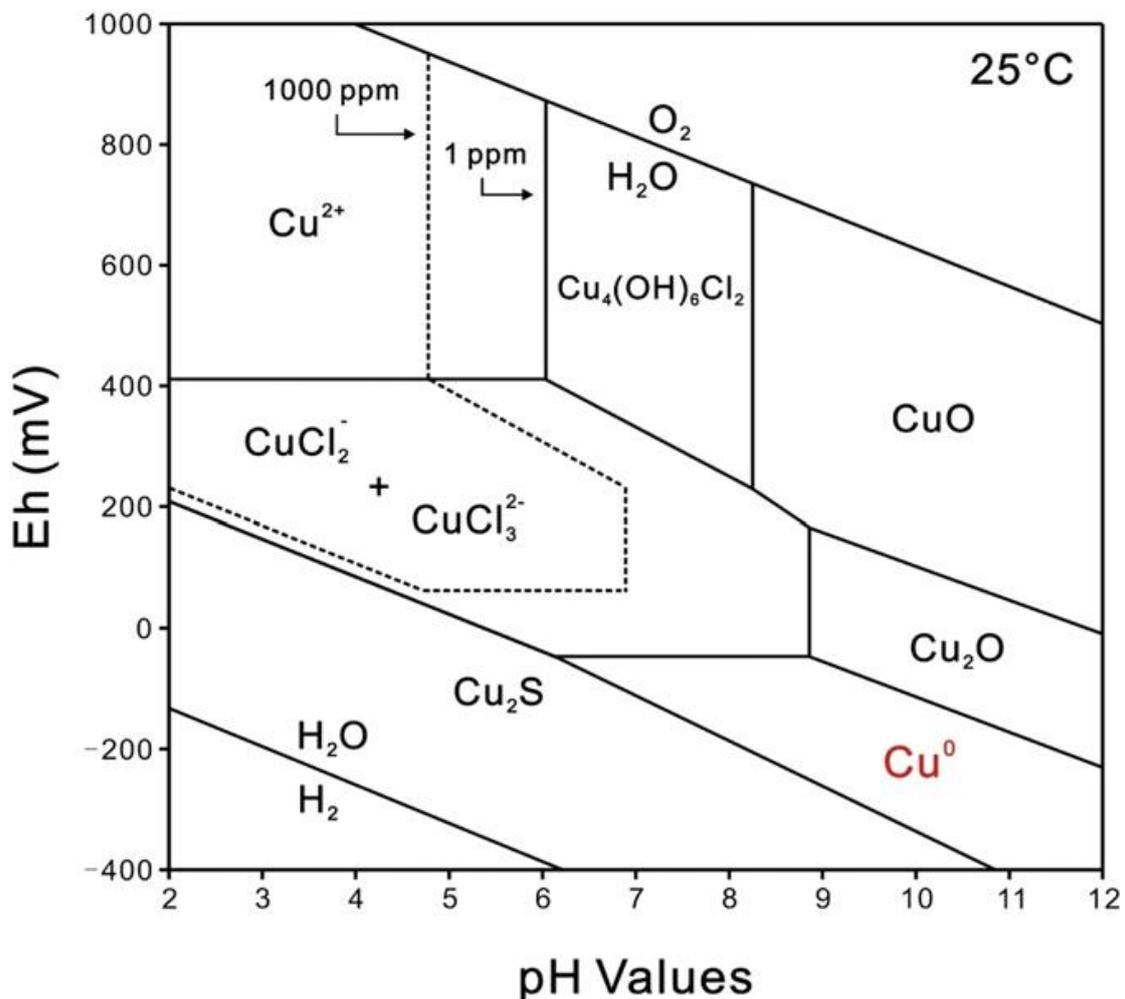


Figure 2.2.1: Eh-pH diagram for the system Cu-O-H-S-Cl in seawater at 25 °C (after Hannington, 1993). Stability fields are shown for the principal aqueous copper species, basic copper salts, copper oxides, native copper and chalcocite (Zhongwei et al, 2016).

2.2.2 Lead

Lead (Pb) is a chemical element with atomic number 82. It is a heavy metal with a density exceeding that of most common materials; it is soft, malleable, and melts at a relatively low temperature. When freshly cut, it has a bluish-white tint; it tarnishes to a dull gray upon exposure to air. It has standard atomic weight 207.2, melting point 327.46°C and boiling point 1749°C. Lead shows two main oxidation states: +4 and +2.

Lead is classified as a chalcophile under the Goldschmidt classification, meaning it is generally found combined with sulfur. It rarely occurs in its native, metallic form. Many lead minerals are relatively light and, over the course of the Earth's history, have remained in the crust instead of sinking deeper into the Earth's interior. This accounts for lead's relatively high crustal abundance of 14 mg/kg; it is the 38th most abundant element in the crust. The main lead-bearing mineral is galena (PbS), which is mostly found with zinc ores. Other lead minerals are boulangerite, (Pb₅Sb₄S₁₁), anglesite (PbSO₄) and cerussite (PbCO₃). In Figure 2.2.2 the pH-Eh diagram for Pb is presented. Arsenic, tin, antimony, silver, gold, copper, and bismuth are common impurities in lead minerals (*Langmuir et al, 2005*).

Lead occurs naturally in the environment. However, most lead concentrations that are found in the environment are a result of human activities. In car engines lead is burned, forming lead salts (chlorines, bromines, oxides), which enter the environment through the car exhausts. The larger particles are dropped to the ground immediately and pollute soils or surface waters, whereas the smaller particles may travel long distances through air, remain in the atmosphere and fall on the earth surface when it rains. This lead-cycle caused by human activities is much more extended than the natural lead-cycle, and has caused lead pollution to be a worldwide issue (www.lenntech.com).

Food such as fruit, vegetables, meats, grains, seafood, soft drinks and wine may contain significant amounts of lead. Cigarette smoke also contains small amounts of lead. Lead can enter (drinking) water through corrosion of pipes. This is more likely to happen when the water is slightly acidic. That is why public water treatment systems are now required to carry out pH-adjustments in water that will serve drinking purposes. For as far as we know, lead fulfils no essential function in the human body, it can merely do harm after uptake from food, air or water.

Lead can cause several unwanted effects, such as: Disruption of the biosynthesis of haemoglobin and anaemia, a rise in blood pressure, kidney damage, miscarriages and subtle abortions, disruption of the nervous system, brain damage, declined fertility of men through sperm damage, diminished learning abilities of children and behavioral disruptions of children, such as aggression, impulsive behavior and hyperactivity ([Table 2.1](#)). Lead can enter a fetus through the placenta of the mother. Because of this it can cause serious damage to the nervous system and the brains of unborn children (www.lenntech.com).

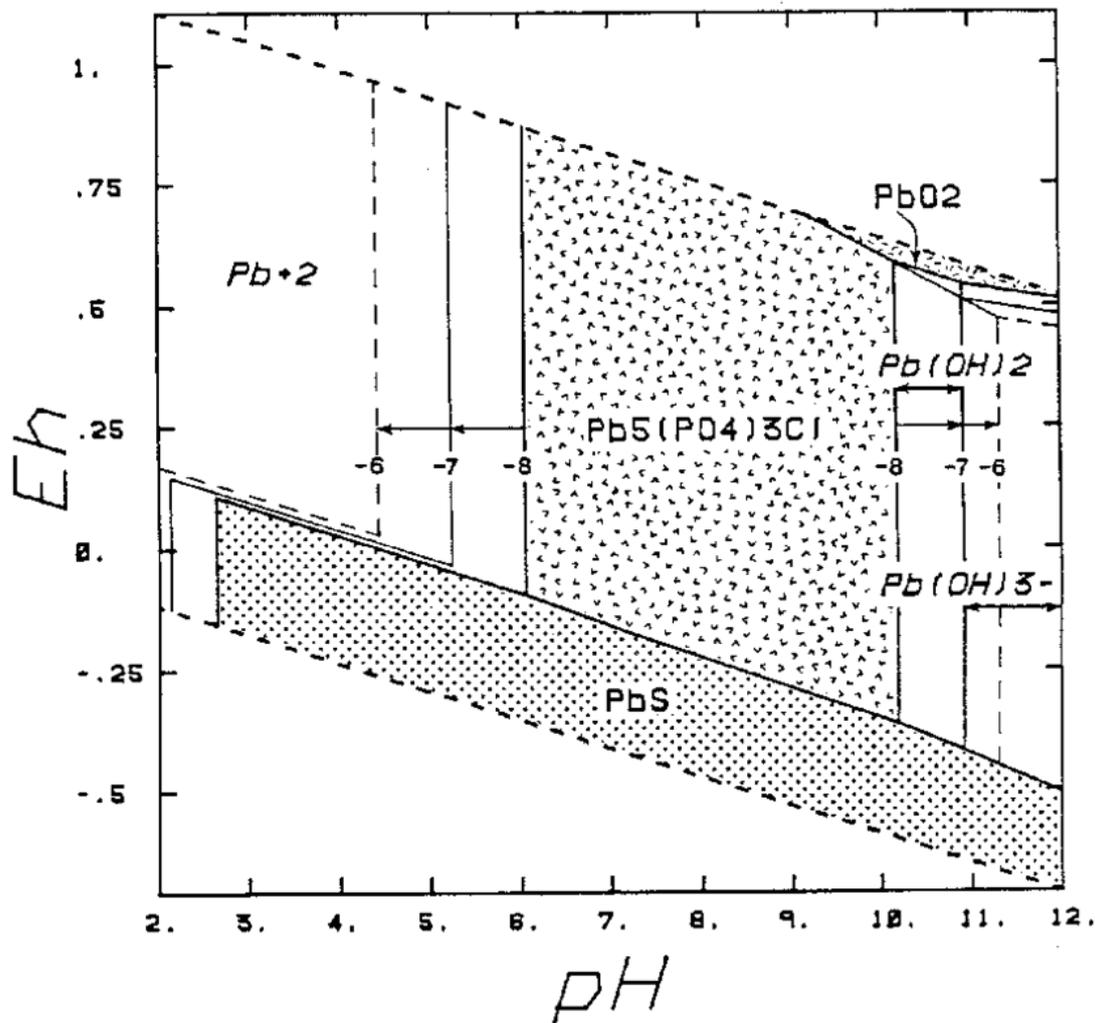


Figure 2.2.2: Eh-pH diagram for the system Pb-O₂-PO₄-S-H₂O, assuming that EPb = 10⁻⁸, 10⁻⁷, and 10⁻⁶ mol/kg at solid/liquid boundaries; ES = 10⁻⁵ mol/kg; and EPO₄ = 10⁻⁶ mol/kg. Diagram shows the stability fields of the lead phosphate, pyromorphite, and galena (PbS). After Barnes and Langmuir, 1978 (Langmuir et al, 2005).

2.3 Clay minerals

Clay minerals belong to the phyllosilicate group (from the Greek “phyllo”: leaf, and from the Latin “silic”: flint). They are very small (<2mm) and they prefer to be formed under surface (laterites, soils, sediments) or subsurface (diagenesis, hydrothermal alterations) conditions. They are distinguished by layered structures composed of polymeric sheets of SiO₄ tetrahedron linked into sheets of (Al, Mg, Fe)(O,OH)₆ octahedron (Ismadji et al, 2015).

The essential features of hydrous layer silicates are continuous two-dimensional tetrahedral sheets which are composed by Si₂O₅, with SiO₄ tetrahedrons (Fig.2.3.1) linked by the sharing of three corners of each tetrahedron to form a hexagonal mesh pattern (Fig.2.3.2A).

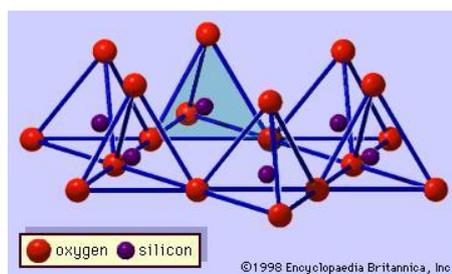


Figure 2.3.1: Single silica tetrahedron (shared) and the sheet structure of silica tetrahedrons arranged in a hexagonal network (*Grim and Kodama, 2014-Retrieved from www.britannica.com*).

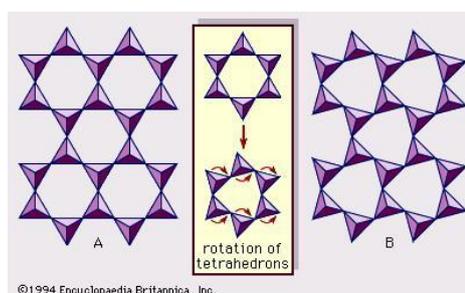


Figure 2.3.2: (A) Ideal hexagonal tetrahedral sheet. (B) Contracted sheet of ditrigonal symmetry owing to the reduction of mesh size of the tetrahedral sheet by rotation of the tetrahedrons (*Grim and Kodama, 2014-Retrieved from www.britannica.com*).

Frequently, aluminum and, to a lesser extent, ferric iron partially substitute the silicon atoms of the tetrahedrons. The apical oxygen at the fourth corner of the tetrahedrons, which is usually directed normal to the sheet, forms part of an adjacent octahedral sheet in which octahedrons are linked by sharing edges (*Fig.2.3.3*).

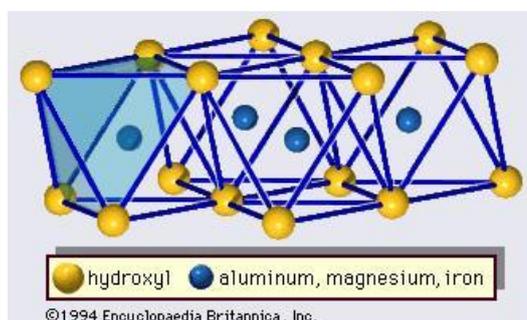


Figure 2.3.3: Single octahedron (shaded) and the sheet structure of octahedral units (*Grim and Kodama, 2014-Retrieved from www.britannica.com*).

The junction plane between tetrahedral and octahedral sheets consists of the shared apical oxygen atoms of the tetrahedrons and unshared hydroxyls that lie at the center of each hexagonal ring of tetrahedrons and at the same level as the shared apical oxygen atoms (*Fig.2.3.4*).

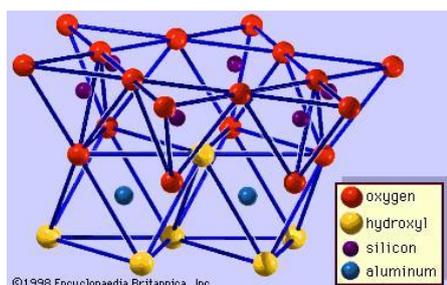


Figure 2.3.4: Structure of 1:1 layer silicate (kaolinite) illustrating the connection between tetrahedral and octahedral sheets (*Grim and Kodama, 2014-Retrieved from www.britannica.com*).

Common cations that coordinate the octahedral sheets are Al, Mg, Fe³⁺, and Fe²⁺; and more rarely Li, V, Cr, Mn, Ni, Cu, and Zn substitute in considerable amounts. If divalent cations (M²⁺) are in the octahedral sheets, the composition is M²⁺/₃ (OH)₂O₄ and all the octahedrons are occupied (trioctahedral). If there are trivalent cations (M³⁺), the composition is M³⁺/₂ (OH)₂O₄ and two-thirds of the octahedrons are occupied, with the absence of the third octahedron (dioctahedral). If all the anion groups are hydroxyl ions in the compositions of octahedral sheets, the resulting sheets may be expressed by M²⁺(OH)₂ and M³⁺(OH)₃, respectively. Such sheets, called hydroxide sheets, occur singly, alternating with silicate layers in some clay minerals. Brucite, Mg(OH)₂, and gibbsite, Al(OH)₃, are typical examples of minerals having similar structures.

There are two major types for the structural “backbones” of clay minerals called silicate layers:

- The unit silicate layer formed by aligning one octahedral sheet to one tetrahedral sheet is referred to as a 1:1 silicate layer, and the exposed surface of the octahedral sheet consists of hydroxyls.
- In another type, the unit silicate layer consists of one octahedral sheet sandwiched by two tetrahedral sheets that are oriented in opposite directions and is termed a 2:1 silicate layer ([Fig.2.3.5](#)).

These structural features, however, are limited to idealized geometric arrangements. Real structures of clay minerals contain substantial crystal strains and distortions, which produce irregularities (a) deformed octahedrons and tetrahedrons rather than polyhedrons with equilateral triangle faces, b) ditrigonal symmetry modified from the ideal hexagonal surface symmetry, and c) puckered surfaces instead of the flat planes made up by the basal oxygen atoms of the tetrahedral sheet) (*Grim and Kodama, 2014-Retrieved from www.britannica.com*).

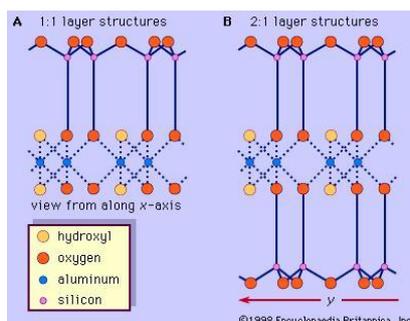


Figure 2.3.5: Schematic presentation of (A) 1:1 layer structures and (B) 2:1 layer structures (*Grim and Kodama, 2014-Retrieved from www.britannica.com*).

The existence of charge in clay minerals is the basis for cation exchange and the swelling properties of the minerals. The tetrahedral and octahedral sheets of clay minerals usually possess a charge. The charge in the clay minerals exists in two forms: structural and surface charge. The structural charge is permanent and exists due to ion substitutions while the surface charges, usually depends on the value of pH. The structural charge originates within the interior of the layers. In clay minerals with 2:1 layer, the surface charge originates on the basal surface of tetrahedral sheets, while for clay with 1:1 layer type the surface charge come from both of tetrahedral and octahedral sheets. The edges of the sheets of both 1:1 and 2:1 clay also contribute the surface charge (*Eslinger and Pevear, 1988*).

Cation exchange capacity (CEC) is one of the important properties in clay minerals. CEC is a measure of the capacity of clay minerals to exchange cations from the solution. CEC is also a measure of the concentration of unfixed cations in the interlayers and surface layers, which depends on the magnitude of the total layer charge. Since the surface layer charge is the function of pH, thus, CEC also varies with pH. The common metallic cations found in exchange positions in clay minerals are Ca^{2+} , Mg^{2+} , Na^+ , and K^+ . Clay minerals have also been explored as the adsorbents for the removal of heavy metals from aqueous solution.

Clay and clay minerals have been explored as adsorbents for the removal of PTEs from aqueous solutions. The advantages of using clay minerals as alternative adsorbents for the removal are the high ion sorption/exchange capacity, the low permeability, the swelling ability, the chemical and mechanical stability, and the large specific surface area (*Wang et al, 2007*). The adsorption of PTEs from aqueous solution using clay minerals are influenced by several factors such as pH, temperature, the presence of other compounds, initial concentration, etc. The pH value significantly influences the chemistry of PTEs (precipitation, hydrolysis, complexation, redox reaction, etc.). In certain range of pH, the uptake of PTEs by the clay minerals increases with the increase of pH to certain value and then followed by reduction of the amount uptake on a further increase of pH (*Ismadji et al., 2015*).

2.4 Smectite clay minerals as adsorbents

The smectites are the main clay minerals of bentonites. The structure of the smectite minerals consists essentially of layers made up of two inwardly pointing sheets of silica tetrahedral sandwiching a sheet where various trivalent and divalent cations are octahedrally coordinated by oxygen and hydroxyl ions. The structure is therefore referred to as a 2:1 structure and closely resembles that of mica. Smectites are important in industry because of their ion exchange capacity, surface area, absorptive capacity and catalytic action.

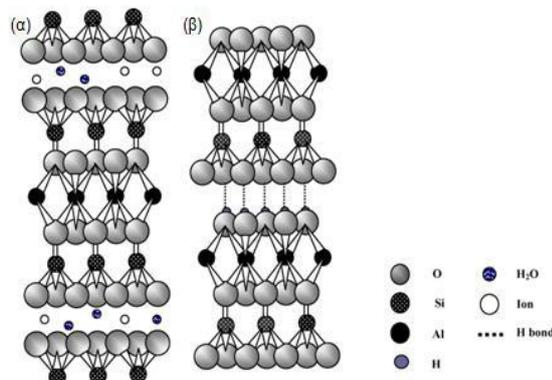


Figure 2.4.1: (a) 2:1 structure of clay minerals., (b) 1:1 structure of clay minerals (Vimonses *et al*, 2009).

A large number of different mineral species belonging to the smectite group have been recognized, depending on the composition of the octahedral and tetrahedral sheets, but only a limited number of these can be described as rock-forming minerals. These include the dioctahedral smectites montmorillonite, beidellite and nontronite and the trioctahedral smectites saponite, hectorite and stevensite (Wilson, 2013). Below there is information about saponite and nontronite because these two clay minerals exist in the clay material of the present study.

Saponite derives its name from “sapo”, meaning soap, and was first analyzed in Sweden in 1842 by Svanberg, who showed it to be a hydrous magnesium silicate. Saponite has the same general smectite structure as a modmorillonite and nontronite, but its trioctahedral with all cationic sites in the octahedral sheet being filled. Its chemical type is:

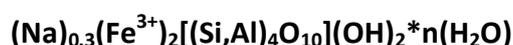


In the ideal structure of saponite, the octahedral sheet contains only Mg ions and the layer charge arises from the substitution of Al^{+3} for Si^{+4} in the tetrahedral sheet. Some saponites approach this ideal composition, but usually there is some substitution of Fe^{+2} and Fe^{+3} for Mg^{+2} in the octahedral sheet. The surface area of saponite as measured by nitrogen adsorption isotherms (BET surface area) is rather variable ranging from 30 to 160 m^2g^{-1} . The BET surface areas of synthetic saponites are usually much higher than those found for natural samples.

The genesis of saponites may be due to different ways, for which, data are available and which are listed below.

- a) There are few examples of saponite forming as a pedogenic mineral as this would require an unusual Mg-rich environment.
- b) Authigenic saponite is found in both lacustrine and oceanic sediments. In lacustrine environment it forms in particular association with other Mg-rich minerals such as sepiolite, palygorskite, kerolite and stevensite. In oceanic sediments, saponite for the most part is related to the alteration of volcanic detritus rather than to precipitation from interstitial solutions. Further, the saponite occurring in oceanic sediments is often of an iron-rich variety, where Fe^{+2} exceed Mg^{+2} in the octahedral sheet.
- c) Also, there is evidence that saponite formation is due to interactions of basalt and seawater.
- d) Finally, there is some evidence that smectites in general, and saponite in particular, are not necessarily unstable under more extreme temperature conditions than those described above. There are examples that relate its genesis with high temperature formation in the igneous and metamorphic rocks. (*Wilson, 2013*)

Nontronite is the iron(III) rich member of the smectite group of clay minerals. A general view of the nontronite structure reveals its dioctahedral nature and its overall similarity to the structure of montmorillonite. Its general type is:



With regard to configuration of exchangeable cations and water molecules in the interlayer space of nontronite, this would not be expected to differ significantly from beidellite, as long as there is no reduction of structural iron. Thus, as the most of the layer charge in nontronite in the natural state comes from substitution of Si^{4+} in the tetrahedral sheet by Al^{3+} and Fe^{3+} it would be anticipated that the layer charge is localized on those oxygens bound to the substituted sites and that the interlayer cations are placed close to these oxygens.

Nontronite occurs in a variety of geological environments including weathered rocks, soils, oceanic sediments and as a result of hydrothermal activity (*Wilson, 2013*).

2.5 Attapulgitic clay as adsorbent

The attapulgitic (palygorskite) is a hydrated aluminosilicate mineral with theoretical chemical type:



where magnesium has been partially replaced by aluminum or ferrous iron (*Fan et al, 2008*). It belongs to the phyllosilicate minerals (2:1) and it presents an intermediary dioctahedral and trioctahedral structure (*Galan, 1996*), its grid consists of continuous chains of tetrahedrons SiO_4 which extend parallel to the x-axis (fibrous structure) and are joined by inverse bonds Si-O-Si, creating a continuous tetrahedral

and a discontinuous octahedral sheet (Fig.2.5). The octahedral positions are predominantly filled with Mg^{2+} ions, which can be partially replaced by Al^{3+} and Fe^{3+} . This discontinuous octahedral structure creates free channels, which are filled with zeolitic water molecules (Galan, 1996).

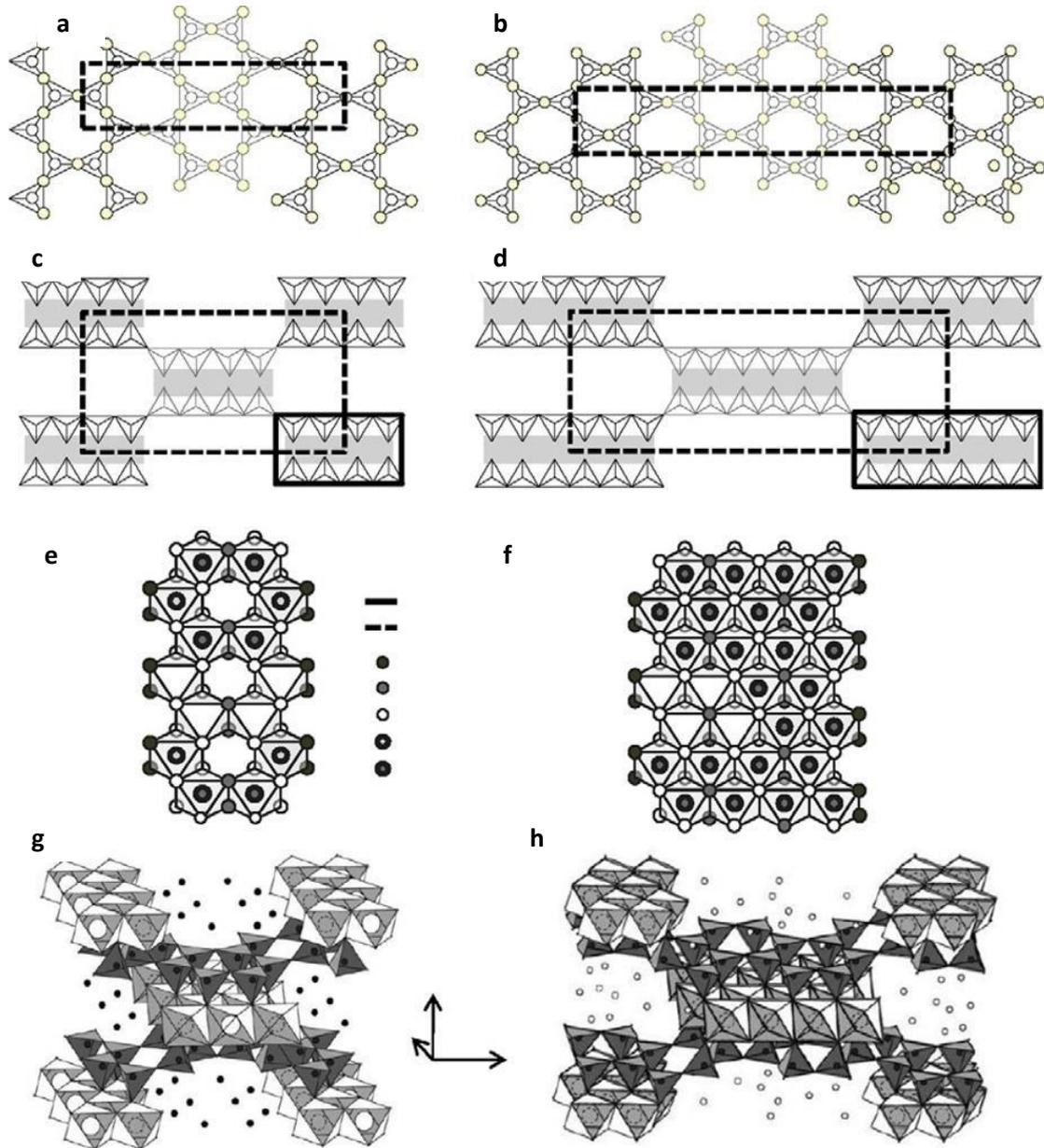


Figure 2.5: Structural arrangement of attapulgite and sepiolite. (a,b) tetrahedral sheet of attapulgite and sepiolite, (001), the black and grey color correspond to tetrahedrons with extreme oxygen presenting in opposite directions, (c,d) tetrahedral sheet of attapulgite and sepiolite, (100), the grey color corresponds to the octahedral sheet, (e,f) octahedral sheet of attapulgite and sepiolite, (001), (g, h) schematic view of a 1_1_2 alveolar of attapulgite and sepiolite (Sanchez del Rio et al, 2005, Suarez and Garcia Romero, 2011).

The genesis of attapulgite may be due to different ways, which are listed below (Tsirampidis, 2006):

- a) its formation in soils, lakes and shallow seas is related to a Mediterranean climate type.
- b) it can be formed under specific conditions in the presence of solutions rich in Mg due to chemical precipitation in lakes or restricted seas.
- c) by hydrothermal erosion of volcanic glass or volcanic sediments.
- d) in environments which are dominated by turbid currents.

The attapulgite has an excellent porous structure and its loose retaining water can be removed through heating procedure, thereby increasing its adsorption capacity. It has the potential to adsorb from 80-100% (Galan, 1996) to 200% of its weight in water (El-Mofty et al, 2008).

2.6 Environmental uses of clay minerals

Adsorption is a widely used modern method of removing PTEs and it belongs to the best available processes (Best Available Techniques). The adsorption, which continues to be a challenge to research so far, it excels compared to other processes, due to its cost, flexibility, simplicity of the design, the ease of design, the ease of operation, and the fact that it leads to formation of non-harmful substances.

Bourliva in her doctoral thesis (2013) studied the effect of bentonite addition to chemical flocculants for the adsorption of trace metals (Cr, Cu, Ni, Mn, Zn) during the treatment of urban waste water. The samples were selected from the Biological Wastewater Treatment Unit at Kilkis city, North Greece. This study shows that when the amount of the trace metals is <1mg/L the addition of bentonite seems to be useful, and notably for the removal of Cu and Cr. The addition of bentonite results to the reduction of the mobility of toxic substances and this explains the fixation of the harmful substances in the bentonite. She also studied the treatment of metallurgical wastewater with natural clays and especially with bentonite. The results show that after the treatment of the pH there is greater removal of trace metals. In addition, an important role in the remove process plays the amount of the clay and the presence of other competing metals.

Guerra et al., (2010), studied the adsorption of Cr⁺⁶ in smectites from the Amazon region, Brazil, and in particular the effect on them of contact time, pH and concentration. The indicative pH for Cr⁺⁶ adsorption ranges from 4 to 5 and the minimum contact time to achieve equilibrium is 10 and 20 minutes for synthetic and natural saponites, respectively.

Parthasarathy et al., (2003), for the first time demonstrated the usefulness of iron-rich saponite in the reduction of hexavalent chromium. The results showed that the Ferrous saponite has the ability to adsorb and reduce the valence of Cr from +6 to +3. Results from the work of Parthasarathy et al., (2007), show the ability of Fe-rich saponite to adsorb Cr and contribute to the reduction of valence from Cr⁺⁶ to Cr⁺³. It should be noted that the ferrous saponite from the Killari region in India, used in the given work, could be a useful mineral that would help to manage contaminated areas with Cr⁺⁶.

The adsorption capacity of saponite for triazine herbicides from water was found to be greater than that of the beidellite, irrespective of the exchangeable

cation (Aqqarwal et al., 2006). This was thought to be due to the lower CEC of saponite in this instance, resulting in a less-crowded interlayer and with more available surface for adsorption.

Brigitti et al., (1999), studied the rate of dissolution of a iron-rich saponite from Prinzerza, Italy, with respect to pH and the reaction time at 25 ° C. Furthermore, Cr adsorption capacity was studied in a series of concentrations and with different competing anions (CH_3OO^- , Cl^- , NO_3^-). The results showed that the Cr adsorption is related both to the amount of the initial concentration and to the type of the competitive anions (the order is $\text{CH}_3\text{OO}^- < \text{Cl}^- < \text{NO}_3^-$).

Awadh et al., (2013) studied the use of a palygorskite from Iraq as an adsorbent for the removal of Pb from aqueous solution by the means of batch technique. A series of adsorption tests were conducted to analyze the sorption mechanism and capacity of palygorskite. Standard solutions of Pb were prepared with known clay doses (10, 25, 50, 75, 100, 125, 150, 175, 200, 225, and 250 ppm). Each solution was mixed with 1g of palygorskite, and treated with total volume up to 100 ml for 1h with stirring at temperature of 25°C. The treated palygorskite was then separated by filter paper. Each filtrate solution was subjected to physical and chemical measurements. Adsorption equilibrium reaction time, pH and Pb ion concentration were determined. The sorption capacity was recorded as 99.5% of 10 ppm solution, whereas it was 22.22% of 250 ppm solution.

Zotiadis et al., (2012), conducted an in situ pilot-scale application of attapulgitic clay for stabilization of toxic metals and metalloids in contaminated soil. The selected field for the pilot-scale experiment was heavily contaminated with toxic metals and metalloids in total (Cu: 122 mg/Kg, Pb: 6,610 mg/Kg, Zn: 3,630 mg/Kg, Cd: 26.3 mg/Kg, Ag: 9.4 mg/Kg, As: 802 mg/Kg, Mn: 1,435 mg/Kg, Ba: 304 mg/Kg, Sb: 95.3 mg/Kg) and leachable concentrations. On the basis of the site-specific soil geochemical properties, an appropriate proportion of specific grain-size attapulgitic clay was added and mixed in situ with simultaneous adjustment of soil moisture content to reach saturation. Analytical data of amended soil samples collected 1 month after the application showed a significant reduction of water leachable metal fraction (Cu: 17%, Pb: 50%, Zn: 45%, Cd: 41%, Ag: 46%, As: 18%, Mn: 47%, Ba: 45%, Sb: 29%).

The potential of activated palygorskite was assessed for sorption of phosphate from aqueous solution by Gan et al., (2009). The natural palygorskite used was treated by thermal activation over 100-1000°C for 2h. The thermal activation increased the phosphate sorption capacity and the highest phosphate sorption capacity occurred at 700°C. The dependence of the phosphate sorption capacity in the heating samples on thermal activation appears to be related to major changes in the crystal structure of palygorskite.

The sorption behaviour of palygorskite has been studied with respect to lead, copper, zinc and cadmium by Alvarez Ayuso et al, (2003), in order to consider its application to remediate soils polluted with these metals. The maximum sorption values were 37.2 mg/g for lead, 17.4 mg/g for copper, 7.11 mg/g for zinc and 5.83 mg/g for cadmium at pH 5-6. In addition the effect of palygorskite amendment in a highly polluted mining soil has been studied by means of batch extractions and leaching column studies. The soluble metal concentrations as well as the readily-extractable metal concentrations were substantially decreased at any dose of

palygorskite applied to soil (1, 2, 4%), although the highest decrease is obtained at the 4% dose. The column studies also showed a high reduction in the metal leaching (50% for lead, 59% for copper, 52% for zinc and 66% for cadmium) when a palygorskite dose of 4% was applied.

Purpose of heat treatment and effect on adsorption:

Over the last few decades natural clays are acquiring prominence as low-cost adsorbents due to their local and abundant availability and the capability to undergo modification to enhance the surface area, adsorption capacity, and range of applicability (Monvisade and Siriphannon, 2009). Nonetheless, the effective application of these materials is limited due to small surface area and presence of net negative surface charge, leading to low adsorption capacity. All these factors have led to the need for research and development in the field of modification of clay surfaces to enhance their adsorptive properties. Therefore, in order to ameliorate the adsorption properties and range of applicability, a number of physical and chemical methods have been investigated to modify the clays, including heat treatment (Chaisena et al, 2004, Al-Asheh et al 2003). Thermal activation of clay mineral is a physical treatment which involves calcination of clays at high temperatures (Al-Asheh et al 2003) and it is done in order to remove any impurities or moisture attached to the clay particles (Steudel et al, 2009) and induce structural changes.

On heating, all clay minerals pass through a temperature range in which they dehydrate to various degrees. They lose adsorbed, pore and interlayer water. Loss of adsorbed water alters the macro- and microporosity of the clay mineral as well as its plasticity. Interlayer spaces of TOT minerals collapse and their CEC is reduced. The tenacity with which interlayer water is retained in smectites depends on various factors including the hydration energy of the exchangeable cations, the magnitude and location of the layer charge, and the size and morphology of the samples. These effects were investigated in a series of recent studies based on modelling of experimental X-ray diffraction patterns (Ferrage et al, 2007). Kaufhold and Dohrmann (2010) concluded that the layer charge distribution within adjacent layers was an important factor. Partial loss of adsorbed and hydration water increases hydrophilicity and surface acidity. (Heller-Kallai, 2006)

Changes in specific surface area (SSA) and pore size distribution of sepiolite and palygorskite on heating were extensively investigated. Three temperature regions were distinguished in which loss of hydration water and concomitant changes in porosity occurred. In the first stage, adsorbed and zeolitic water was lost; in the second, two of the four molecules of coordination water were driven off, causing the structure to fold; and in the third, the remaining two water molecules were eliminated (Nagata et al, 1974, Van Scoyoc et al, 1979). The actual temperature ranges in which these changes occurred were found to depend on the sample, the pre-treatment and the thermal regime.

2.7 Clay deposits of the Ventzia basin, north Greece

The clay material tested in the present study originates from the sedimentary ore deposits of clays, in Western Macedonia, NE of Grevena city. The deposit is characterized by high quality and economic significance. The deposit consists of attapulgite, smectite and mixtures of them. In the course of quarry development activity, Geohellas S.A. has developed quarries in the area of the Aianis Municipality, Kozani, Macedonia, North Greece. The company except from the mining activity has established a modern unit for the processing of the clays in Knidi, Grevena, Greece. Processing of the material includes natural drying, milling, drying and thermal activation, grinding, sifting and granulometric grading and standardization.

The deposit belongs to Ventzia continental basin, east of Grevena in Western Macedonia, Greece. This basin represents a small section of a much larger continental basin that developed in western Macedonia during the Late Pliocene/Early Pleistocene. The Ventzia basin, as we define it here, is found northeast of the city of Grevena. It has a maximum width of 6 km, a length of 22 km, and area of $\sim 70 \text{ km}^2$. The basement of the Ventzia basin consists mainly of ultramafic rocks of the Vourinos ophiolite complex and molassic sediments of the Mesohellenic Trench. According to Kastritis et al., (2003), geological data indicate that the smectite clays formed by transformation of pre-existing smectitic material that was transported into the basin from two different sources: the altered ultramafic rocks of the Vourinos complex and the smectite-bearing sands of the Mesohellenic trench. The palygorskite clays appear to have formed diagenetically by in-situ reaction of smectite with silica rich solutions. Smectite beds have a greenish, green-yellowish, brownish or red-brownish color and a waxy appearance. Smectite content in these beds ranges from approximately 60-95%. The most common minor phases in these beds are: platy serpentine, quartz, plagioclase, palygorskite and dolomite.

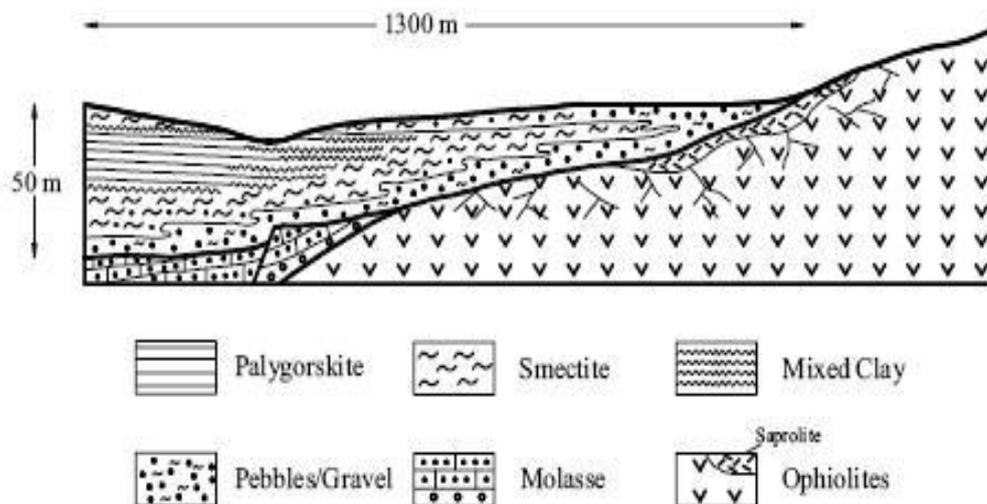


Figure 2.7: Schematic cross section from Piori palygorskite and smectite deposits (Kastritis et al, 2003).

2.8 Batch tests and adsorption isotherms

The phenomenon of retention of substances on the surface of liquids and solids is called adsorption. The phase on the surface of which the adsorption occurs is called adsorbent while the substance being retained is called adsorbed substance. Adsorption is a superficial phenomenon in which there is a concentration of one component on a surface or on an interface between two phases. Depending on the type of the phases which are found in contact, the following adsorption systems can be discriminated: gas-liquid, liquid-liquid, gas-solid and liquid-solid. It is very important to distinguish between the terminologies of adsorption, absorption, sorption and ionic exchange. Absorption is the process in which a substance accumulates internally in another phase. The adsorption and the ion exchange, due to common features can be grouped under the term sorption. The ion exchange as opposed to adsorption is a stoichiometric process (*Essington, 2004*).

Adsorption depends on certain factors associated with the characteristics of the adsorbed substance and the adsorbent as well as with the properties of the solution. The three main factors are (*Bourliva, 2013*):

- The nature of the adsorbent: The chemical and physical properties of the adsorbent affect significantly the adsorption of a substance from an aqueous solution.
- The nature of the adsorbed substance: the solubility, size and shape of the particles, and the polarity.
- The properties of the solution: pH, temperature and presence of competitive components.

The most common way to describe the distribution of the substance's concentration is the adsorption isotherms; expressing the change of quantity q_e (mg/g) with the C_e (mg/L) concentration at a certain temperature.

Batch tests

By this method the adsorbent is mixed with a solution of known concentration of a particular cation. The pH is adjusted and the mixture is shaken for a specific time until equilibrium is reached. Then, the concentration of the cation in the solution is measured and the cation distribution between the solution and the adsorbent is calculated from the change in concentration. The experiments are repeated at different cation concentrations, ionic strengths and pH values of the solution in order to calculate the effect of these parameters on the studied adsorption process. At the end, the experimental results are compared with adsorption isotherms (*Eslinger and Pevear, 1988*).

Adsorption isotherms

The adsorption isotherms present the distribution of an ingredient between an aqueous phase and solid particles. For very low concentrations, this distribution may be linear, but generally more complex relationships are observed and the distribution of components varies as a function of concentration. For very low concentrations the system behaves ideally and the distribution between the aqueous phase and the adsorbent is stable. Under these circumstances, we can calculate an allocation coefficient (k_d) that describes the distribution pattern between the two phases. With increasing concentration, the behavior diverges from the ideal. In very high concentrations we may have precipitation so that no change in the concentration of the solution is observed, so there is saturation of the solution. (Eby, 2012)

Adsorption can be described in four general types (L, H, S and C) as shown in the Figure 2.8 (Sparks, 1995).

- The L-type isotherm is characterized by a decrease in the slope of the isotherm with increasing concentration of the substance, as available positions are initially gradually completed. It reflects the strong adsorption of the substance from the surface at low concentrations; which decreases as the concentration of the substance in the solution increases.
- The type-H isotherm (strong relationship) is characterized by strong reactions between the surface and the adsorbed substance.
- The S-type isotherm is characterized by an increase in slope with increase of the concentration of the substance in the solution, which gradually decreases and finally reaches zero as the adsorption sites are filled. At low concentrations the surface adsorption expresses a weak preference for the adsorbed substance, which increases at higher concentrations.
- The C-type isotherm is characterized by individual mechanisms, through which ions or molecules are adsorbed on the surface without any particular ties between them.

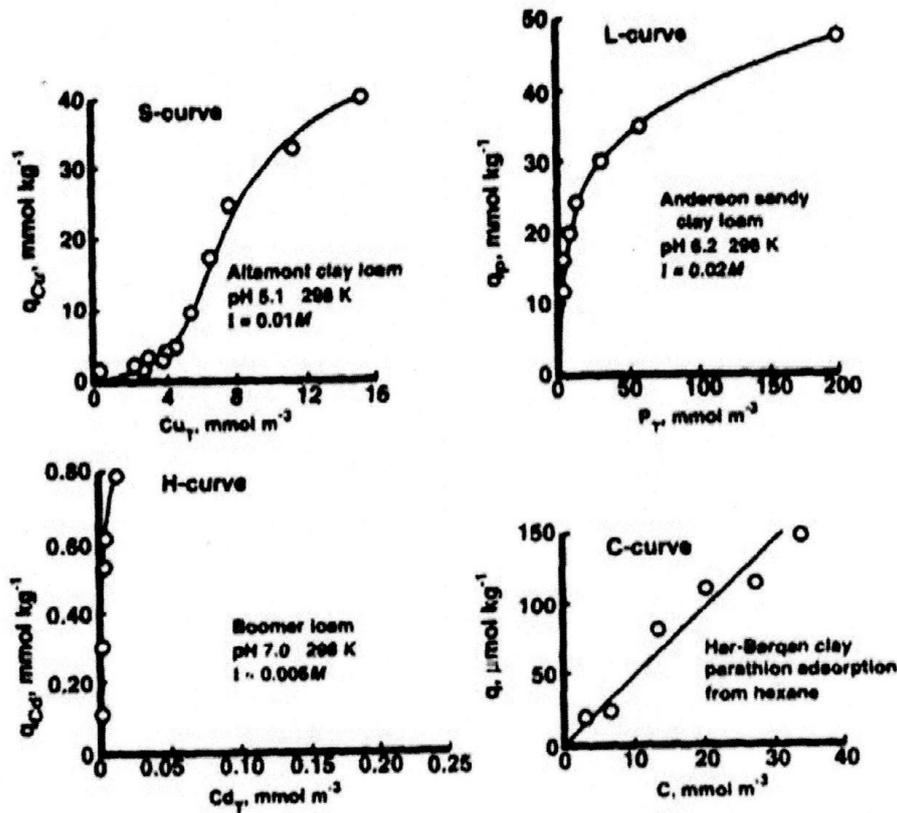


Figure 2.8: The four main types of adsorption isotherms. (Sparks, 1995)

The data of adsorption may be consistent with one or more mathematical models. The two most commonly used models are the Langmuir isotherms and the Freundlich isotherms.

The **Freundlich** equation is:

$$q_{ads} = KC_{soln}^n$$

Where:

q_{ads} = the weight of the ingredient adsorbed by the adsorbent (mg/g)

K = a constant

C_{soln} = the concentration of the ion in the solution (mg/L)

n = a constant

When $n=1$, $K=K_d$. In order to determine if experimental data conform to the model K_d or Freundlich isotherm, we normalize the isotherm exhausting the logarithms

$$\log q_{ads} = \log K + n \log C_{soln}$$

If the graphical representation is linear then the data obey the Freundlich model and the point of incision with axon y corresponds to the value of K and the slope is calculated the value of n. If n=1, the data obey the K_d model. These models assume that there are infinite positions of adsorption to the solvent.

The **Langmuir** equation is:

$$q_{ads} = \frac{Q^0 K C_{soln}}{1 + K C_{soln}}$$

Where:

q_{ads} =the weight of the adsorbed substance/ the weight of the adsorbent (mg/L)

Q^0 =the maximum adsorption capacity of the surface (mg/g)

K=an allocation factor that reflects the extent of the adsorption

C_{soln} = the concentration of the ion in the solution

The Langmuir equation, assumes that there is finite number of adsorption positions. The linear form of the Langmuir equation is:

$$\frac{1}{q_{ads}} = \frac{1}{Q^0} + \frac{1}{KQ^0} \times \frac{1}{C_{soln}}$$

If the experimental results can be described by the Langmuir equation, the graphical representation of $(1/q_{ads}) / (1/C_{soln})$ is a straight line. The incision point with y axe is the $1/Q^0$ and the slope is $1/KQ^0$.

3. METHODOLOGY

3.1 Heat treatment

The prolonged exposure to high temperatures is a simple method of modifying clay minerals. The increase of the specific surface, as the effect of heat treatment, has the consequence of improving the adsorption capacity of the mineral. Layered clay minerals such as saponite in room temperature have three types of water:

- Adsorbent water on the surface of the mineral (it is removed at 130°C)
- Zeolitic water that exists between the layers of tetrahedrons and octahedrons (it is removed at 330°C).
- Crystalline water which is a component of crystalline mineral matrix and it is strongly bound (it is removed at temperatures >500°C).

The modified clay material samples, of the present study were prepared after heat treatment, as follows: 100g of the clay stayed for four hours in appropriate oven at 130, 330, 500, 800°C. After that, they remained in the oven with the heating off, so that they gradually returned to room temperature and then, they were placed in a desiccator until their use. The analytical procedure of the clay's heat treatment is presented at the Appendix 1.

3.2 Determination of mineralogical composition (X-ray diffraction, XRD).

In this study the qualitative determination of the mineral phases has been achieved by X-ray diffraction (XRD). An X-ray diffractometer consists of a high-voltage generator, an X-ray tube, a goniometer, an X-ray counter and a computer unit. The specimen is placed on special sample holder from a non-crystalline material, not affecting the measurement, in a special chamber and it starts to rotate with a constant rate of a goniometer. During the rotation of the sample, a new X-ray incidence angle is continually created. The beam of sputtered rays is collected through the detector and analyzed, giving the final diffraction pattern, which is imprinted on a computer screen. From the diffraction patterns, the crystalline form of the solid material is extracted. The essential condition for the appearance of the diffraction phenomenon was expressed by Bragg, and its mathematical expression is given by the following relationship, also known as Bragg's law: $2d\sin\theta = n\lambda$, where n is a positive integer and λ is the wavelength of incident wave, d is the distance between the lattice levels in the examined crystalline direction and θ the angle of incidence.



Figure 3.2: X-ray diffraction instrument (SIEMENS D5005 X-RAY DIFFRACTIONMETER) at the laboratory of Economic Geology and Geochemistry, NKUA.

3.3 Determination of the microstructure (Scanning Electron Microscope, SEM)

A scanning electron microscope (SEM) is a type of electron microscope that produces images of a sample by scanning the surface with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that contain information about the sample's surface topography and composition. The electron beam is scanned in a raster scan pattern, and the beam's position is combined with the detected signal to produce an image. SEM can achieve resolution better than 1 nanometer. Specimens can be observed in high vacuum in conventional SEM, or in low vacuum or wet conditions in variable pressure or environmental SEM, and at a wide range of cryogenic or elevated temperatures with specialized instruments.

In the study we used a SEM JEOL JSM-5400 equipped with a X-ray elemental microanalysis system with dispersive energy (EDS, Oxford Energy Dispersive X-ray), Laboratory of Economic Geology and Geochemistry, NKUA.

3.4 The preparation of the standard solutions

During the experiment and the sorption tests, prepared solutions of copper and lead were used. Standard solutions with known Cu and Pb concentration, were prepared by dissolving specific amounts of copper nitrate [$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$] and lead nitrate [$\text{Pb}(\text{NO}_3)_2$] in deionized water. The analytical procedure of the preparation of the standard solutions is presented in Appendix 2.

3.5 Batch tests

Effect of the dose of the adsorbent material

The purpose of this experimental process is to examine the effect of the different clay doses on the mineral adsorption capacity.

The process

Copper: Clay material at doses of 0, 2, 5, 10, 15 g/L is added to 25 ml of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ solution with estimated Cu^{2+} concentration of 50 mg/L. After stirring for two hours, the samples are centrifuged, their pH and temperature are measured and finally they are analyzed by the AAS method for Cu. The analytical procedure is presented in Appendix 3.

Lead: Clay doses of 0, 2, 5, 10, 15 g/L is added to 25 ml of $\text{Pb}(\text{NO}_3)_2$ solution with estimated Pb^{2+} concentration of 50 mg/L. After stirring for two hours, the samples are centrifuged, their pH and temperature are measured and finally they are analyzed by the AAS method for Pb. The analytical procedure is presented in Appendix 3.

Effect of the pH

The purpose of this experimental process is to examine the effect of changing the pH of the solution on the mineral adsorption capacity.

Copper: In 25 ml of standard solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, a known clay dose is added. The pH of the solution is adjusted by the use of HNO_3 0.1 M and NaOH 0.1 M at values from 2 to 8. After stirring for two hours, the samples are centrifuged, their pH and temperature are measured and finally they are analyzed by the AAS method for Cu. The analytical procedure is presented in Appendix 4.

Lead: In 25 ml of standard solution of $\text{Pb}(\text{NO}_3)_2$, a known clay dose is added. The pH of the solution is adjusted by the use of HNO_3 0.1M and NaOH 0.1M at values from 2 to 8. After stirring for two hours, the samples are centrifuged, their pH and temperature are measured and finally they are analyzed by the AAS method for Pb. The analytical procedure is presented in Appendix 4.

Effect of the contact time

The purpose of this experimental process is to examine the time which is required to adsorb the maximum amount of metal cations that are found in the solution.

Copper: In 25 ml of standard solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ with estimated Cu^{2+} concentration of 50 mg/L and fixed pH, a known clay dose is added. After stirring at different times of 5,30,60,90,120 minutes the samples are centrifuged, their pH and

temperature are measured and finally they are analyzed by the AAS method for Cu. The analytical procedure is presented in Appendix 5.

Lead: In 25 ml of standard solution of $\text{Pb}(\text{NO}_3)_2$ with estimated Pb^{2+} concentration of 50mg/L and fixed pH, a known clay dose is added. After stirring at different times of 5,30,60,90,120 minutes the samples are centrifuged, their pH and temperature are measured and finally they are analyzed by the AAS method for Pb. The analytical procedure is presented in Appendix 5.

Effect of ionic strength

The purpose of this experimental process is to examine the effect of the ionic strength on the metal cation adsorption capacity.

Copper: In 25 ml of standard solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ with metal concentration of 50mg/L and fixed pH, a known clay dose and NaOH 0.01/0.1/0.5 M are added. After stirring for two hours the samples are centrifuged, their pH and temperature are measured and finally they are analyzed by the AAS method for Cu. The analytical procedure is presented in Appendix 6.

Lead: In 25 ml of standard solution of $\text{Pb}(\text{NO}_3)_2$ with metal concentration of 50mg/L and fixed pH, a known clay dose and NaOH 0.01/0.1/0.5 M are added. After stirring for two hours the samples are centrifuged, their pH and temperature are measured and finally they are analyzed by the AAS method for Pb. The analytical procedure is presented in Appendix 6.

Adsorption isotherms.

Copper: In 25 ml of standard solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ with metal concentration of 25,50,75,100 mg/L and fixed pH, a known clay dose is added. After stirring for two hours the samples are centrifuged, their pH and temperature are measured and finally they are analyzed by the AAS method for Cu. The analytical procedure is presented in Appendix 7.

Lead: In 25 ml of standard solution of $\text{Pb}(\text{NO}_3)_2$ with metal concentration of 25,50,75,100 mg/L and fixed pH, a known clay dose is added. After stirring for two hours the samples are centrifuged, their pH and temperature are measured and finally they are analyzed by the AAS method for Pb. The analytical procedure is presented in Appendix 7.

3.6 Measurement of pH and temperature

The pH is a measure of how acidic or alkaline a solution is: $\text{pH} = -\log[\text{H}_3\text{O}^+]$. The pH scale goes from 0 to 14 with 7 being neutral and anything below 7 is considered

acidic and anything above considered basic or alkaline. It is a measurement of the concentration of hydrogen ions. The value of pH in water:

- Is directly related to the type of chemicals that are contained in it.
- It regulates the mechanisms of the reactions.
- Accelerates or prevents the biochemical processes that are taking place.

The pH and the temperature of the solutions were measured by a specific instrument which is called pH-meter (JENWAY 3040 Ion Analyser) (Fig.3.6), in order to examine how the value of the pH of the samples changes with respect to the various changes in the conditions of the experiments.



Figure 3.6: The pH meter (JENWAY 3040 Ion Analyser) at the laboratory of Economic Geology and Geochemistry, NKUA.

The TDS values have been measured with the use of a portable TDS-meter (Multi parameter analyzer Consort C561).

3.7 Measurement of metal ion concentrations by Flame Atomic Adsorption Spectrometry (F-AAS)

The AAS analytical technique is now widely used to measure concentrations of trace metals in solutions, based on the adsorption by free atoms of radiated energy. The solution to be analyzed is first converted into aerosol, into the spray system so as to increase its specific surface and facilitate its evaporation. Then, it is led to the flame, where it is atomized, passes through a beam of light of appropriate wavelength, and excites the atoms of the determined element during the adsorption by them. The measured light-ray adsorption is compared to the adsorption resulting from a calibration standard of known concentration and thus determines the element concentration in the sample .



Figure 3.7: Flame Atomic Adsorption Spectrometry instrument (Perkin Elmer 1100B) at the Laboratory of Economic Geology and Geochemistry, NKUA.

3.8 Determination of natural parameters of adsorbent material

The determination of the physical characteristics of the studied adsorbent clay sample was carried out at the Certified Laboratory of Edafomichaniki S.A.

Permeability test

Each test is performed according to the standard loading schedule given, which is proposed in the relevant specification ASTM D2435-1: 12.5kPa-25.0kPa-50.0kPa-100.0kPa-200.0kPa-400.0kPa-25.0kPa.

At the beginning of each loading stage a small seating pressure is applied (12.5kPa) on the specimen in order to adjust the deformation indicator. The duration of each loading increment is 24 hours. After this period the deformation is recorded and the permeability measurements are initiated.



Figure 3.8.1: The oedometer device, at the laboratory of Edafomichaniki S.A.

Plasticity limit

The plasticity limit (PL) is determined by rolling out a thread of the fine portion of the material on a flat, non-porous surface. If the sample is at a moisture content where its behavior is plastic, this thread will retain its shape down to a very narrow diameter. The sample can then be remolded and the test repeated. As the moisture content falls due to evaporation, the thread will begin to break apart at larger diameters. The plasticity limit is defined as the moisture content where the thread breaks apart at a diameter of 3 mm. Then the weight of the sample is measured, the sample is placed in the oven and then its weight is measured again. A sample is considered non-plastic if a thread cannot be rolled out down to 3 mm at any moisture possible.

Liquid limit

The liquid limit (LL) is conceptually defined as the water content at which the behavior of a clay soil changes from plastic to liquid. The precise definition of the liquid limit is based on standard test procedures described below.

The liquid limit test involved mixing a part of clay with water in the Cassagrande device. A groove was cut through the clay with a spatula, and the bowl was then struck many times against the palm of one hand. The procedure is repeated until 20 to 30 blows are required to close the groove. Then the weight of the sample is measured, the sample is placed in the oven and then its weight is measured again.



Figure 3.8.2: Applying the method to measure the liquid limit.

4. RESULTS AND DISCUSSION

4.1 Mineralogy of clay material and effect of heat treatment

4.1.1 X-Ray Diffraction (XRD) mineralogical analysis

The material which is studied in this research is a laboratory sample of Geohellas S.A. and it is encoded as XLS. The XLS sample is not a pure phase, but it is a mixture of mineral phases.

The mineralogical analysis was performed in 9 samples:

- Raw material (XLS0), with no heat treatment.
- Heat treated material at temperatures of 130, 230, 330, 400, 500, 600, 700, 800°C (respective codes: XLS130, XLS230, XLS330, XLS400, XLS500, XLS600, XLS700, XLS800).

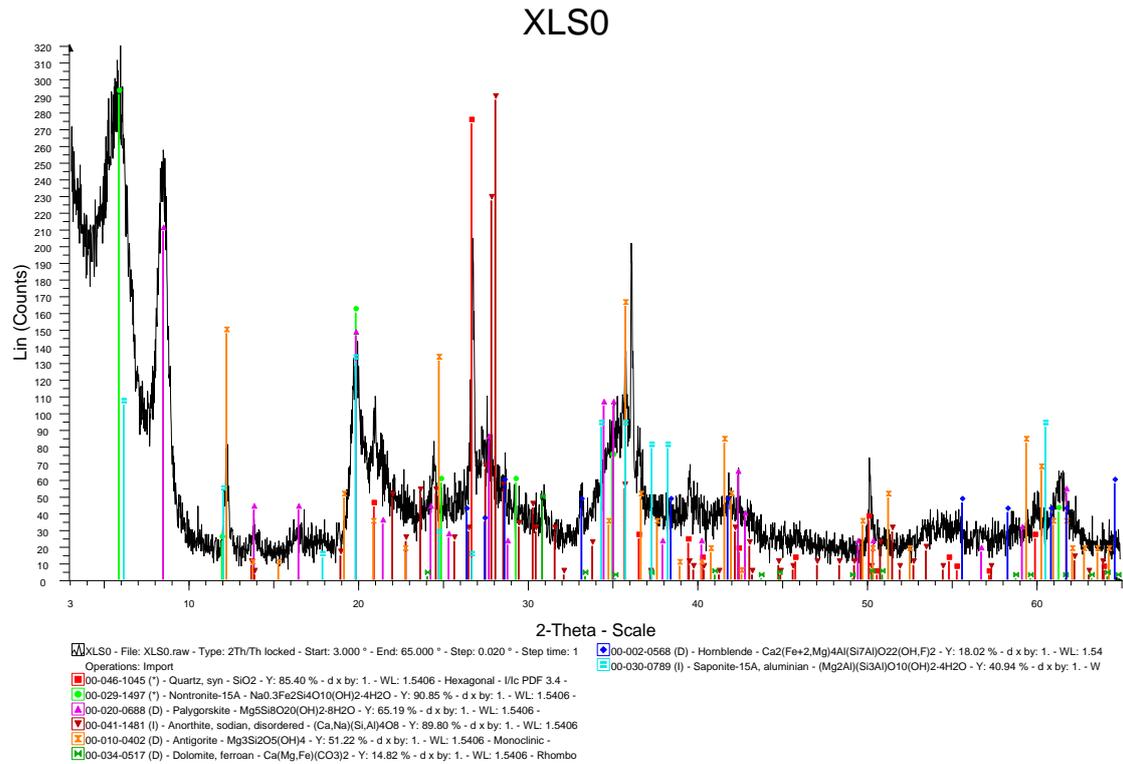
X-ray diffraction analysis was also carried out in oriented mounts using the glass slide method (*Moore and Reynolds, 1989, Poppe et al, 2001*). The oriented mounts were prepared by dispersing a small amount of clay material in deionized water. The clay suspension was then used to make a thin film onto the surface of a glass slide. The sample was air-dried and glycoliated by placing it in a desiccator which contained ethylene glycol in the oven at 60° C for 24hrs. The oriented samples were scanned from 3 to 20° with time step 0.01°/3 min. The corresponding XRD pattern diagram is presented in Figure 4.1.1. All the other samples scanned from 3 to 65° with step time 1°/1 min.

The mineralogical phases which were identified in the samples are presented in Table 4.1.1.

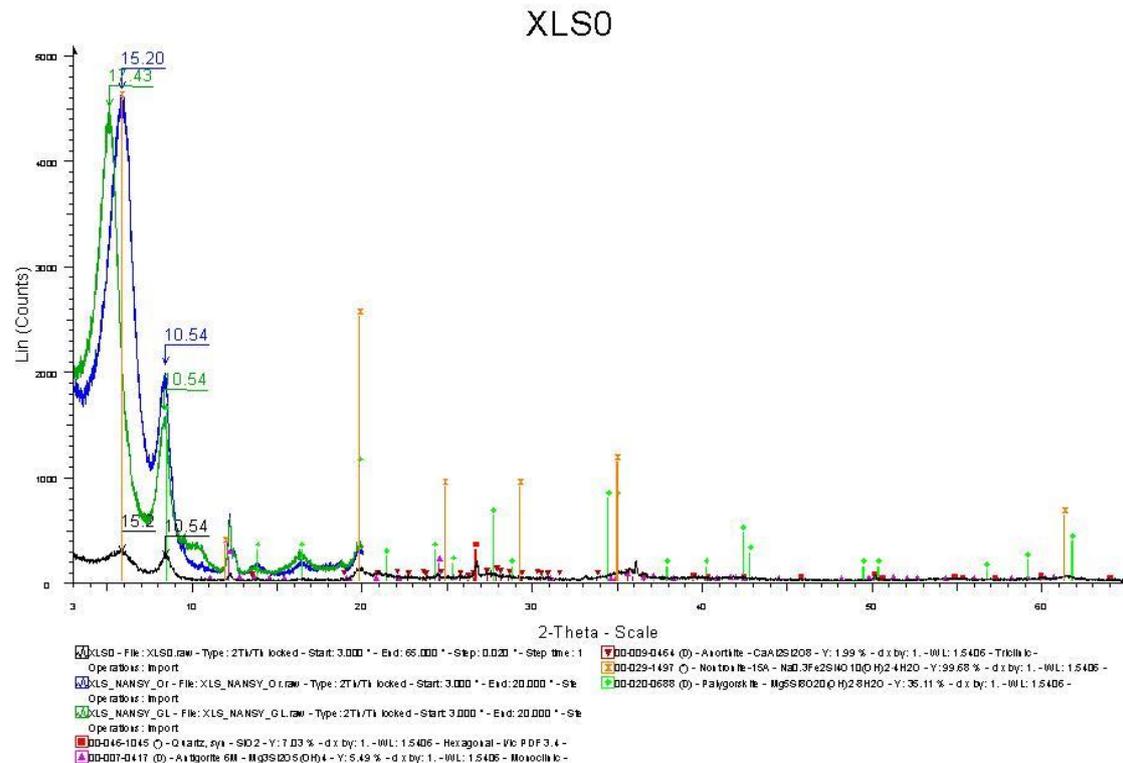
Table 4.1.1: Mineralogical phases in raw and heat treated samples, identified by XRD method.

	XLS0	XLS130	XLS230	XLS330	XLS400	XLS500	XLS600	XLS700	XLS800
QUARTZ	X	X	X	X	X	X	X	X	X
SAPONITE	X	X							
NONTRONITE	X	X	X						
PALYGORSKITE	X	X	X	X	X	X	X	X	X
DOLOMITE	X	X							
ANTIGORITE (SERPENTINE)	X	X		X	X	X	X		
ANORTHITE	X		X	X		X	X		
CALCITE		X	X	X			X		
HORNBLLENDE	X			X					
FORSTERITE					X				X
GOETHITE					X				
ENSTATITE				X			X	X	X
ORTHOCLAST								X	

Assessment of Fe- rich smectite clays in adsorbing Pb and Cu from aqueous solutions:
A batch experiment approach



a) XRD pattern of the raw XLS0 sample.



b) XRD pattern of the raw XLS0 sample after glycoliation.

Figure 4.1.1.: XRD pattern before and after glycolating the XLS0 sample, showing the move of smectite basal reflection peak from ~15d to ~17d.

The raw XLS sample is a mixed clay sample consisting of smectite and palygorskite (attapulgite) and subordinate mineralogical phases including quartz, dolomite, antigorite and plagioclase (Fig.4.1.1a). Attapulgite exhibits the main (001) reflection at $2\theta = 8.5^\circ$ which remains unchanged during the orientation and glycoliation treatment. Smectite basal reflection however was moved from $\sim 15d$ to $\sim 17d$ upon glycoliation and the (060) reflection at $1.5d$ indicates that it is a dioctahedral smectite (Poppe et al, 2001 Harris and White, 2008, Chipera and Bish, 2001).

The most resistant minerals upon heat treatment are quartz, palygorskite and serpentine (antigorite). The smectite is easily destroyed after heat treatment (saponite and nontronite crystals begin to collapse from 130°C). The palygorskite is more resistant to heat treatment. The XRD patterns in different temperatures are presented in Appendix 9.

4.1.2 Micromorphology and composition of grains of raw and heat-treated clay material

SEM images of material grains observed in back scatter electron mode (BSE) are presented in Figure 4.1.2. The grains appear porous with granular or platy morphology. No substantial differences in the grain morphology were identified between raw and heat-treated material at the scale of observation.

Several different minerals comprise the material, a common feature in their chemistry being the Mg-Fe enrichment due to their origin from ultramafic rocks. Some typical microanalysis results of the selected grains are presented in Table 4.1.2.2. The main elements for all samples are O, Si, Mg, Fe, and Al. Although it is difficult to identify specific mineral phases based on the stichiometry of these results, assessment of the data in combination with the XRD findings verify that the samples are rich in secondary Si-Al minerals rich in Mg and Fe. These include minerals of the serpentine group (e.g. antigorite), Fe-rich smectite, and attapulgite.

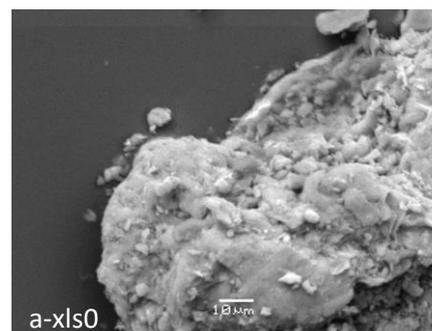
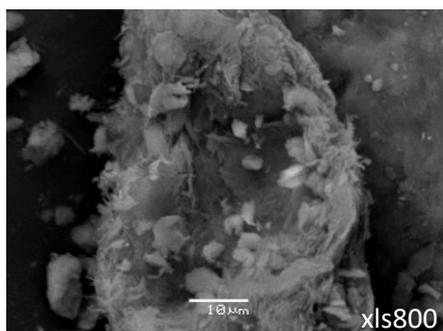
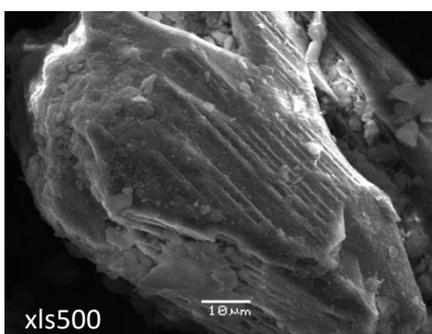
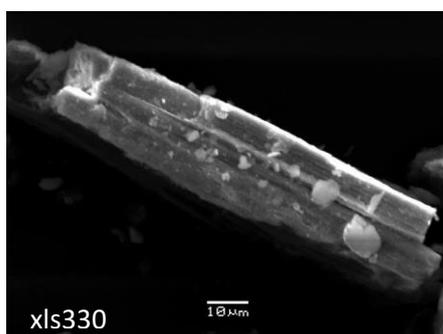
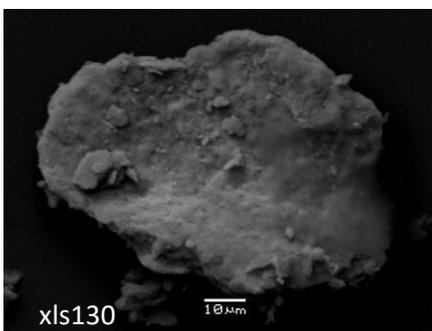
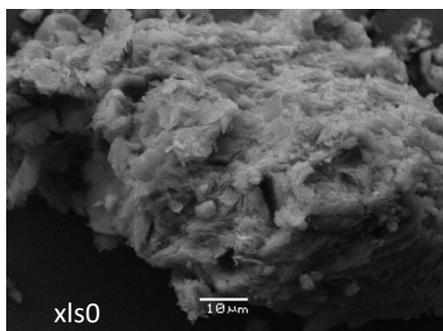
These results are also in agreement with the total bulk chemical analysis of the clay sample. The total chemical analysis of the clay material was performed at the laboratory of Titan S.A with the XRF method, for the determination of the main compounds and elements. The results are presented in Table 4.1.2.1.

Table 4.1.2.1: Total chemical analyses by XRF of the clay material XLS.

Compound	Concentration	Unit
<i>SiO2</i>	58.00	%
<i>TiO2</i>	0.33	%
<i>Al2O3</i>	3.60	%
<i>Fe2O3</i>	8.26	%

Assessment of Fe- rich smectite clays in adsorbing Pb and Cu from aqueous solutions:
A batch experiment approach

MnO	0.13	%
MgO	20.39	%
CaO	0.85	%
Na2O	0	%
K2O	0.41	%
P2O5	0.02	%
SO3	0.01	%
Pb	20.5	mg/kg
Zn	132.9	mg/kg
Cu	91.1	mg/kg
Cr	3882	mg/kg
Ni	2543.9	mg/kg
Co	577	mg/kg
V	63.4	mg/kg



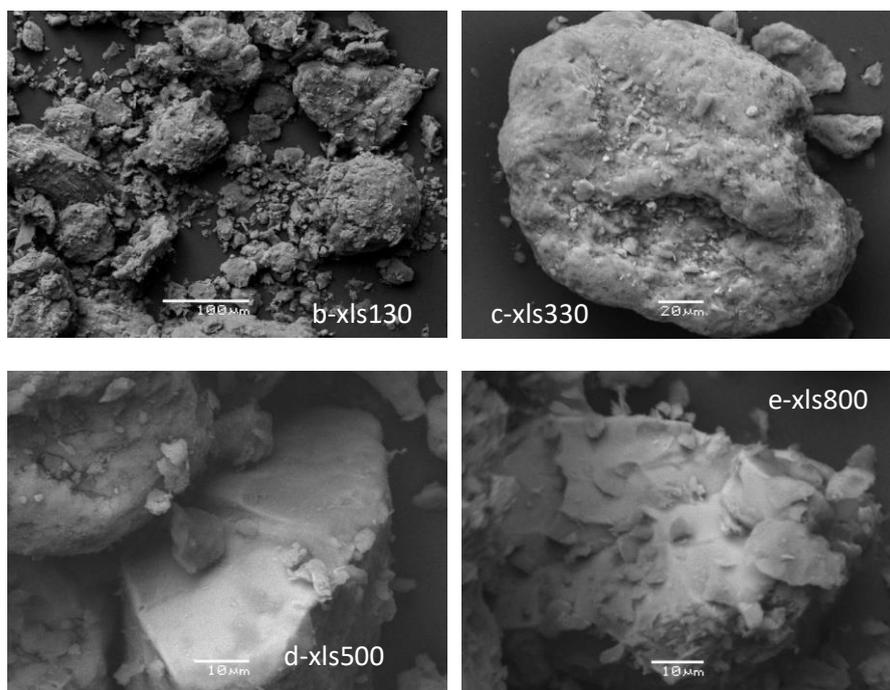


Figure 4.1.2: Mineral grains of raw and heat-treated material observed by SEM.

Table 4.1.2.2: EDS measurements for XLS samples

Element %	XLS0	XLS130	XLS330	XLS500
Mg	7.0	8.3	19.0	8.2
Al	5.5	5.2	0.8	10.9
Si	29.6	29.1	24.5	3.4
K	0.4	X	X	X
Fe	7.7	7.1	4.1	12.3
Cu	0.8	0.7	X	X
O	46.8	46.9	42.9	36.7
Ti	X	0.5	X	X
Ca	X	0.2	X	X
Cr	X	X	X	27.1
total	97.9	98.1	91.4	98.6

The EDS measurements are indicativelies-qualitatives and we do not have SEM images. By noticing these measurements the samples XLS0 and XLS130 are probably clay minerals, the sample XLS330 may be antigorte and the sample XLS500 is probably a chromatite granule.

4.2 Adsorption experiment results

4.2.1 Quality control

The quality control of the chemical analysis for this study, was carried out by determining the repeatability of the measurements, which is a quantification of random analytical errors and is expressed by the Standard Deviation of the triplicate experimental determinations. The values of the standard deviation of the measurements are presented in each table of results for the determined parameters in the following paragraphs.

4.2.2 Effect of the clay dose

The experimental results for raw and heat treated material are presented in Table 4.2.2. The analytical results from the AAS method are presented in Appendix 3.

From the experimental data (Table 4.2.2) and the corresponding charts (Fig.4.2.2 a,b), it is noticed that when the dose of the adsorbent material in the solution is higher, there is a decrease in the concentration of the metals in the final suspension. This result may be due to the fact that the increase of the solid particles leads to more available positions for the adsorption of the metals. All the samples follow the same pattern except from sample XLS800 on the adsorption of Cu.

The value q is the adsorption capacity which is expressed as:

$$q = (C_B - C) \cdot (V/m) \text{ [mg/g]}$$

where:

C_B = the concentration of the metal in the initial solution (mg/L)

C = the concentration of the metal in the solution after mixing with the adsorbent material (mg/L)

V = the volume of the solution (L)

m = the mass of the adsorbent material (g)

Table 4.2.2: Results from AAS method-Effect of the clay dose.

	Clay material g/L	Cu q (mg/g)	Cu q-SD	Pb q (mg/g)	Pb q-SD
XLS0	0	0.0	0.0	0.0	0.0
	2	7.2	0.3	13.6	0.4
	5	5.3	0.0	6.2	0.2
	10	3.4	0.0	3.2	0.0
	15	2.5	0.0	2.2	0.0
XLS130	0	0.0	0.0	0.0	0.0
	2	6.7	3.5	14.4	0.2
	5	5.7	0.1	6.4	0.0
	10	3.6	0.0	3.3	0.0
	15	2.6	0.0	2.2	0.0
XLS330	0	0.0	0.0	0.0	0.0
	2	6.5	0.2	12.4	3.1
	5	5.5	0.1	6.2	0.0
	10	3.7	0.0	3.1	0.0
	15	2.7	0.0	2.1	0.0
XLS500	0	0.0	0.0	0.0	0.0
	2	5.9	0.4	14.4	0.4
	5	5.7	0.3	6.4	0.0
	10	3.7	0.0	3.2	0.0
	15	2.6	0.0	2.2	0.0
XLS800	0	0.0	0.0	0.0	0.0
	2	2.5	0.5	11.8	0.2
	5	3.5	0.4	6.4	0.0
	10	3.4	0.1	3.2	0.0
	15	2.6	0.0	2.1	0.0

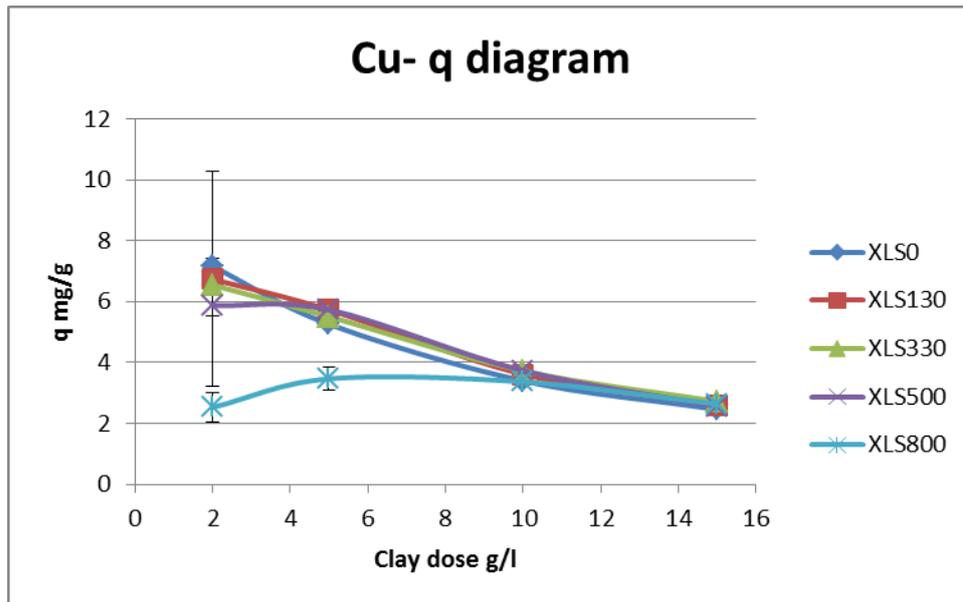


Figure 4.2.2a: Effect of the clay dose on the adsorption of Cu from an aqueous solution.

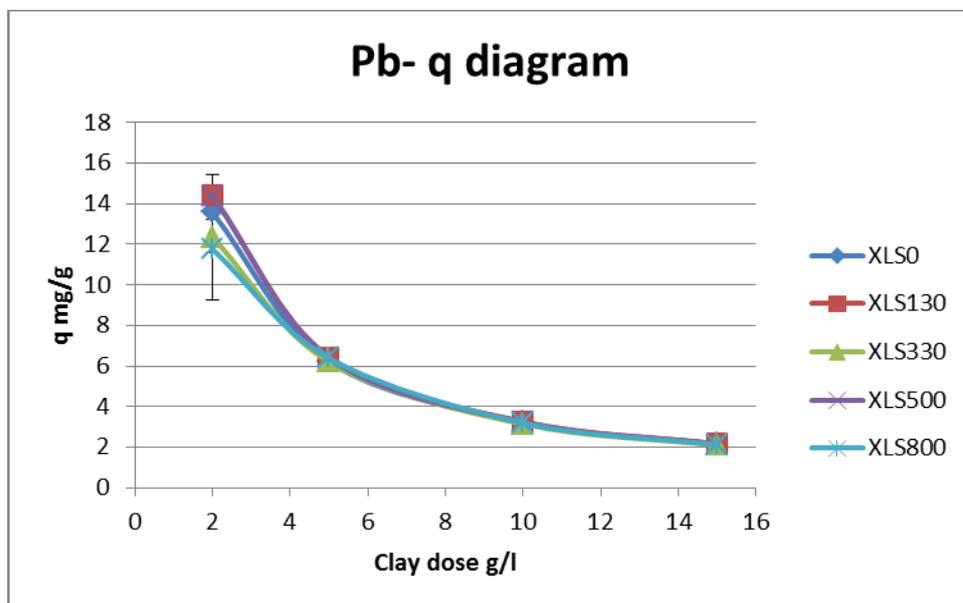


Figure 4.2.2b: Effect of the clay dose on the adsorption of Pb from an aqueous solution.

The sorption capacity of the samples decreases with mass, either because of agglomeration, or because there too many available sorption sites compared to the metal ions present in the solution.

In the following adsorption experiments of Cu and Pb the clay was chosen to be added to a dose of 10mg/L, because as it appears from the above results and charts, a significant metal removal associates with this amount.

4.2.3 Effect of pH

Experimental results are presented in Table 4.2.3. The analytical results from the AAS method are presented in Appendix 4.

From the experimental data (Table 4.2.3) and the corresponding charts (Fig.4.2.3 a,b), it is noticed that the removal of metals by an adsorbent depends on the effect of the pH of the metallic aqueous solution.

Table 4.2.3: Results from AAS method-Effect of the pH. Final solution pH is measured after a two-hour interaction with clay.

	Initial solution pH	Final solution Cu pH	Cu q (mg/g)	Cu q-SD	Final solution Pb pH	Pb q (mg/g)	Pb q-SD
XISO	2	2.3	1.5	0.1	2.4	2.4	0.2
	4	5.6	4.2	0.0	6.7	4.0	0.0
	6	5.9	4.3	0.0	7.1	3.7	0.0
	8	8.5	2.2	0.0	7.8	1.5	0.0
XLS130	2	2.3	1.6	0.0	2.5	2.3	0.1
	4	5.8	4.4	0.0	6.7	4.0	0.0
	6	5.8	4.5	0.0	7.2	3.7	0.0
	8	8.4	3.6	0.0	7.9	1.5	0.0
XLS330	2	2.3	1.3	0.1	2.5	1.3	0.2
	4	5.8	4.4	0.0	6.5	4.0	0.0
	6	5.8	4.0	0.0	7.0	3.7	0.0
	8	7.9	3.6	0.0	7.5	1.5	0.0
XLS500	2	2.5	0.8	0.1	2.9	1.9	0.0
	4	6.1	4.6	0.0	7.2	4.0	0.0
	6	6.1	4.7	0.0	7.2	3.7	0.0
	8	7.9	3.6	0.0	7.8	1.5	0.0
XLS800	2	2.2	0.6	0.2	2.5	0.7	0.0
	4	5.8	3.6	0,1	9.3	4.0	0.0
	6	5.9	3.8	0.3	9.4	3.8	0.0
	8	9.8	3.6	0.0	9.6	1.5	0.0

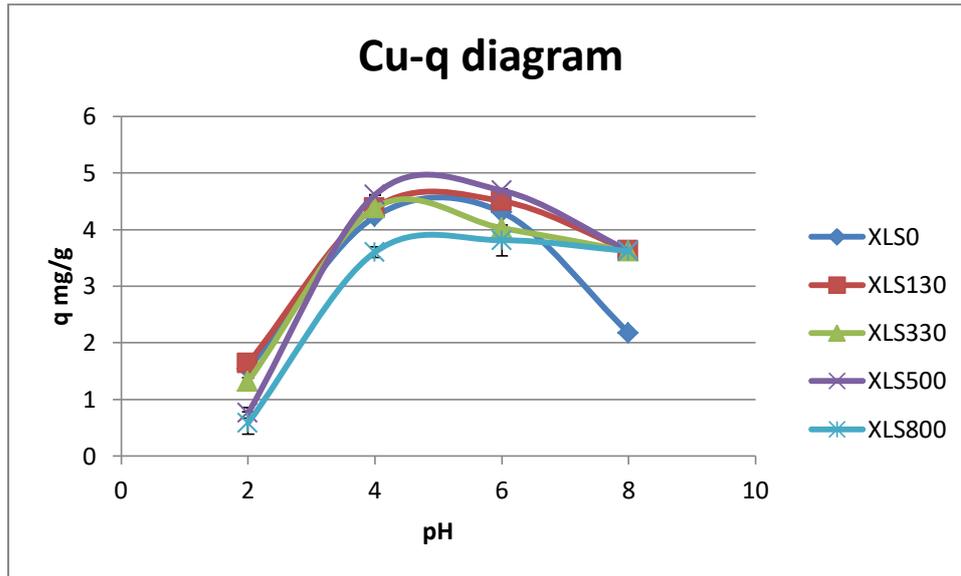


Figure 4.2.3a: Effect of the pH on the removal of Cu from an aqueous solution.

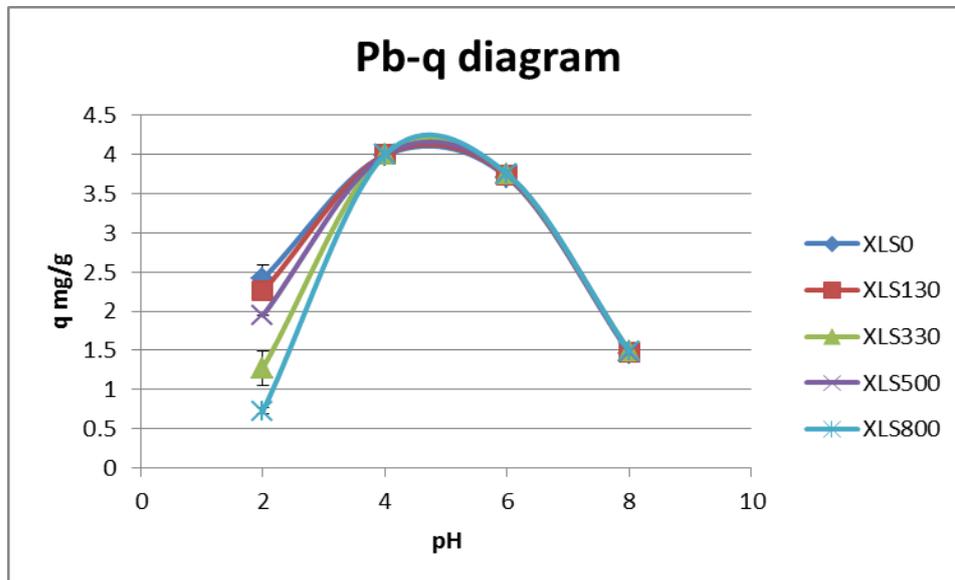


Figure 4.2.3b: Effect of the pH on the removal of Pb from an aqueous solution.

The pH influences the form of the metals (metal speciation) and their association with ligands such as OH^- , by creating complexes (Messini, 2014). For pH values <4 we find that the removal of metals from the aqueous solution is small and this may be due to the competition between H^+ and the metallic ions for the same active adsorption sites. In general, the minimal metal adsorption at low pH values may be due to the presence of high concentrations and mobility of H^+ which have an advantage in adsorption as compared to metallic ions. That means that at low pH the adsorption surface is encompassed by H^+ and thus prevents the adsorption of trace metals by the clay material. On the other hand, when the pH increases, the charge of the adsorbent surface becomes less positive due to the OH^- increase. As a result, there is an increase in the electrostatic attraction between the metal ions and the

surface of the adsorbent. The removal of metals is maximized when the pH values of solution take values 4-6. It is very important to note that when aqueous solutions are made basic (pH>7), precipitation of the metals which are presented in the solution is observed. The metal ions precipitate in the form of hydroxides [Pb(OH)₂ & Cu(OH)₂]. In conclusion, the greater adsorption capacity of the clay material tested in this research is noticed at pH=4-6, while when the pH of the solution has values >6 there is precipitation of the metals and not adsorption by the clay.

Similar results are reported in the literature. According to Potgieter et al., (2005), the influence of the pH on adsorption of Pb²⁺ and Cu²⁺ onto palygorskite was investigated in the pH range 3-10. The adsorption of Pb ion increases with an increase in pH of the solution to a maximum around neutral pH or slightly basic pH, and then decreases as the pH becomes more basic. The removal of Cu by palygorskite adsorption increases very slightly with increasing pH from its minimum at pH=3 to its maximum at a pH about 8.5. After that the percentage adsorption decreases slightly in pH range of 8.5-10. According to Bourliva (2013), in the case of application of the attapulgite sample, removal of Pb (II) shows a continuous increase. The removal of metal by attapulgite is very low especially for pH 2, while for pH range 3-6 there is a significant increase. Also, Bourliva (2013) noticed that the amount of copper (qe) removed per unit mass (g) increases with the increase of pH. The minimum removal was at pH=2. For pH range 3-6 there is a significant increase.

During all the experiments, the TDS values have been measured and no differences have been noticed in their values during the progress of each experiment. The only occasion when discrepancies have been noticed is at the experiment of the effect of the pH. When the pH values were low the TDS values that have been measured were higher, maybe due to the dissolution of the material that caused additional release of elements such as Ca, Mg, Al, Fe.

4.2.4 Effect of contact time

Experimental results are presented in Table 4.2.4. The analytical results from the AAS method are presented in Appendix 5.

From the experimental data (Table 4.2.4) and the corresponding charts (Fig.4.2.4 a,b), it is noticed that there is an intense Cu and Pb adsorption in the first 5 minutes for all tested materials. After the first 30 minutes it seems that the system attains equilibrium. This fact is due to the active adsorption sites on the surface of the mineral. The sample with heat treatment at 800°C, is observed to have a slightly slower adsorption capacity.

Table 4.2.4: Results from AAS method-Effect of contact time.

	Time (min)	Cu q (mg/g)	Cu q-SD	Pb q (mg/g)	Pb q-SD
XLS0	5	3.8	0.0	3.7	0.0
	30	4.2	0.0	4.1	0.0
	60	3.9	0.0	4.4	0.0
	90	4.2	0.0	4.0	0.0
	120	4.2	0.0	4.2	0.0
XLS130	5	4.0	0.0	4.1	0.0
	30	4.3	0.0	4.1	0.0
	60	4.0	0.0	4.4	0.0
	90	4.4	0.0	4.0	0.0
	120	4.3	0.0	4.2	0.0
XLS330	5	3.5	0.1	3.7	0.0
	30	4.1	0.0	4.1	0.0
	60	4.0	0.0	4.4	0.0
	90	4.3	0.0	4.0	0.0
	120	4.3	0.0	4.2	0.0
XLS500	5	3.4	0.1	3.7	0.0
	30	4.3	0.0	4.1	0.0
	60	4.1	0.0	4.4	0.0
	90	4.6	0.0	4.0	0.0
	120	4.5	0.0	4.2	0.0
XLS800	5	2.4	0.2	3.7	0.0
	30	3.5	0.0	4.1	0.0
	60	4.2	0.0	4.4	0.0
	90	3.7	0.0	4.0	0.0
	120	3.8	0.0	4.2	0.0

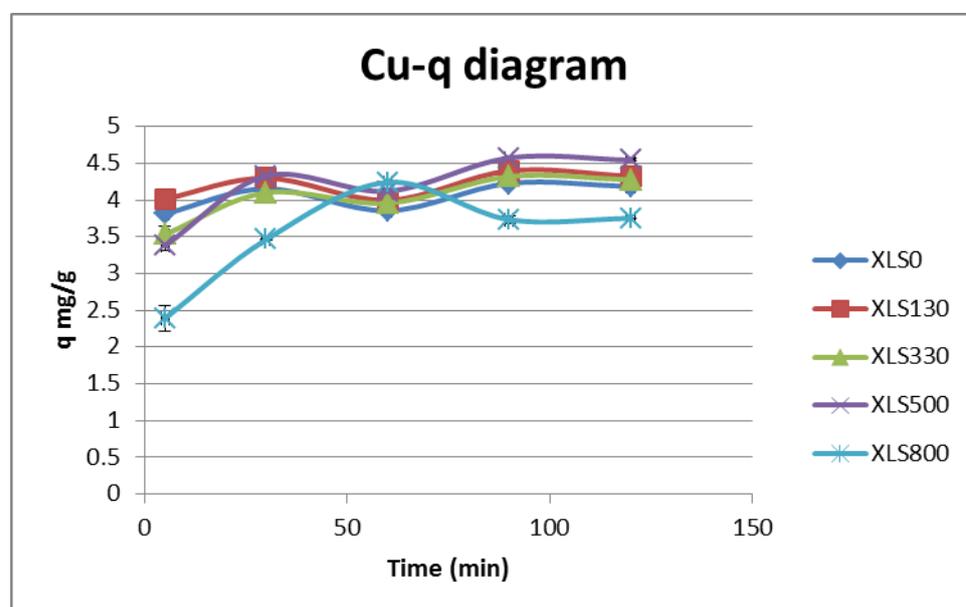


Figure 4.2.4a: Effect of the contact time on the adsorption of Cu from an aqueous solution.

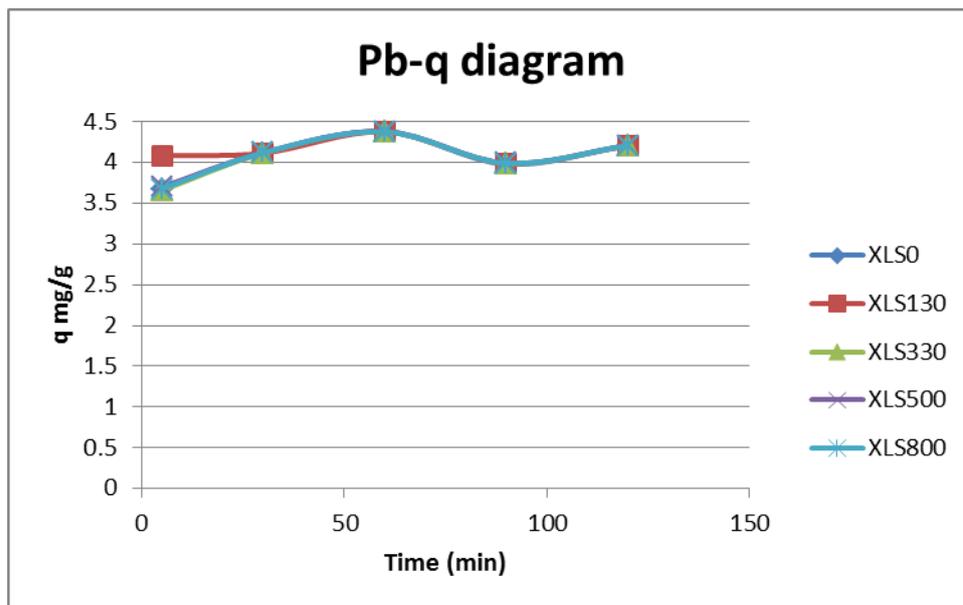


Figure 4.2.4b: Effect of the contact time on the adsorption of Pb from an aqueous solution.

4.2.5 Effect of the ionic strength

Experimental results are presented in Table 4.2.5. The analytical results from the AAS method are presented in Appendix 6.

Table 4.2.5: Results from the AAS method-Effect of the ionic strength.

	C (NaNO ₃) [mol/L]	Cu (mg/g)	q	Cu q-SD	Pb (mg/g)	q	Pb q-SD
XLS0	0.0	3.6		0.0	4.0		0.0
	0.1	2.7		0.0	4.0		0.0
	0.5	2.3		0.0	3.5		0.1
XLS130	0.0	3.8		0.0	4.0		0.0
	0.1	3.1		0.0	4.0		0.0
	0.1	2.8		0.0	3.7		0.0
XLS330	0.0	3.7		0.0	4.0		0.0
	0.1	3.1		0.0	3.9		0.1
	0.5	2.9		0.1	3.5		0.1
XLS500	0.0	4.0		0.0	4.0		0.0
	0.1	3.4		0.0	4.1		0.0
	0.5	3.0		0.1	3.8		0.0
XLS800	0.0	3.0		0.1	4.0		0.0

	0.1	3.7	0.0	4.1	0.0
	0.5	2.6	0.3	3.9	0.0

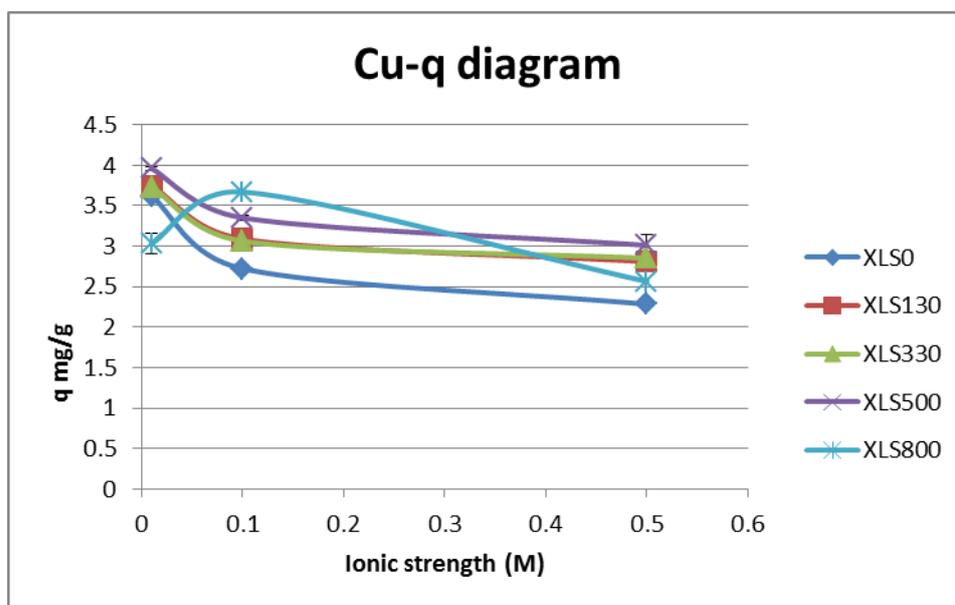


Figure 4.2.5a: Effect of the ionic strength on the adsorption of Cu from an aqueous solution.

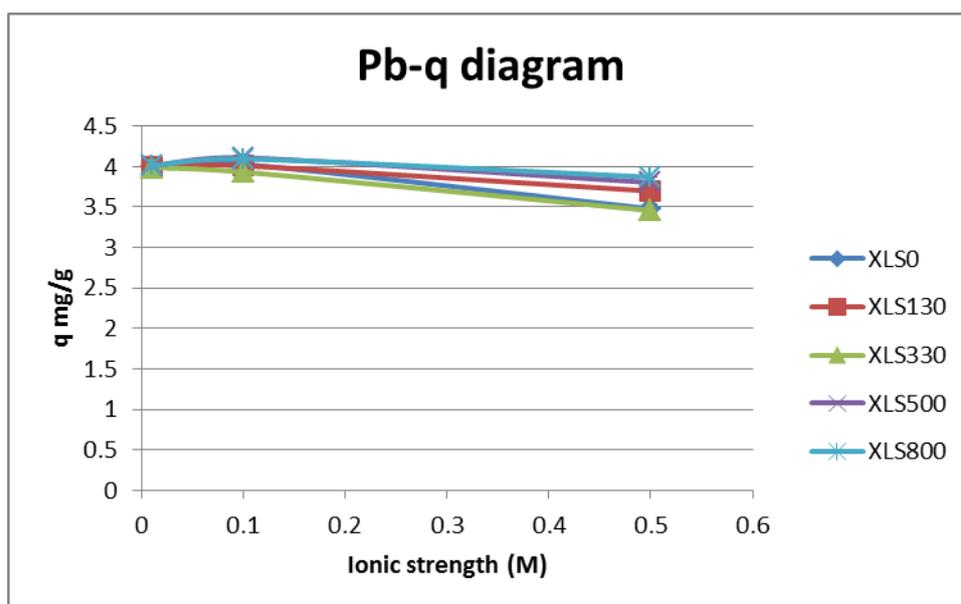


Figure 4.2.5b: Effect of the ionic strength on the adsorption of Pb from an aqueous solution.

The ionic strength of the aqueous phase affects greatly the adsorption of a metal (Fig.4.2.5 a,b) (Table 4.2.5). In particular, the increase in ionic strength has a negative effect on the adsorption phenomenon of Cu and Pb, it inhibits and blocks the metals from binding due to the competitive relationship developed between them and the

Na⁺ cation, for the active positions. Consequently, as the concentration of salt in the aqueous solution increases, the adsorption of metallic minerals from the clay decreases due to the competition between the Na⁺ and the metals.

4.2.6 Adsorption isotherms

Experimental results are presented in Table 4.2.6. The analytical results from the AAS method are presented in Appendix 7.

The increase in the concentration of the heavy metals in aqueous solutions under constant temperature and pH conditions results in an increase in the amount of the metal which are retained per unit mass of the adsorbent material (Table 4.2.6) (Fig.4.2.6 a,b).

Table 4.2.6.1: Results from AAS method-Adsorption isotherms.

	C (mg/L)	Cu Sorption%	Cu Sorption%- SD	Pb Sorption%	Pb Sorption%- SD
XLS0	25	99.0	0.1	99.7	0.1
	50	87.0	0.3	99.7	0.0
	75	77.9	1.1	99.5	0.0
	100	67.2	1.6	97.8	1.3
XLS130	25	99.3	0.2	99.9	0.0
	50	90.4	0.1	99.9	0.0
	75	80.8	1.6	99.8	0.0
	100	67.5	4.7	98.3	0.9
XLS330	25	99.7	0.0	99.6	0.1
	50	88.8	0.2	99.9	0.0
	75	76.7	0.9	99.7	0.1
	100	62.3	6.2	98.6	0.3
XLS500	25	99.8	0.1	99.8	0.1
	50	94.2	0.1	99.9	0.1
	75	79.4	2.4	99.8	0.0
	100	62.3	8.7	99.4	0.1
XLS800	25	99.7	0.1	99.6	0.1
	50	78.0	1.7	99.9	0.0
	75	61.8	1.5	99.9	0.0
	100	38.7	8.4	97.8	0.0

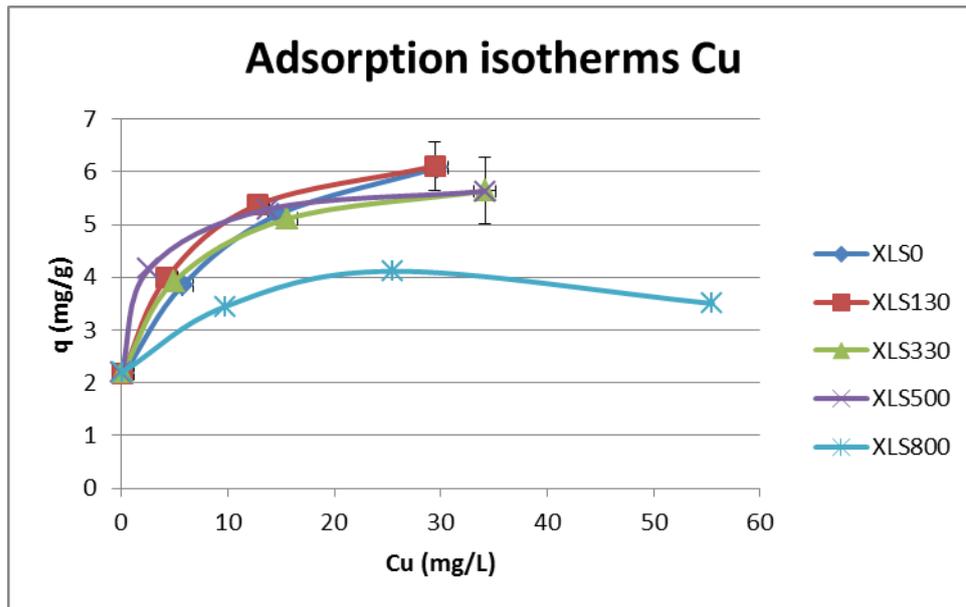


Figure 4.2.6a: Adsorption isotherms (Cu).

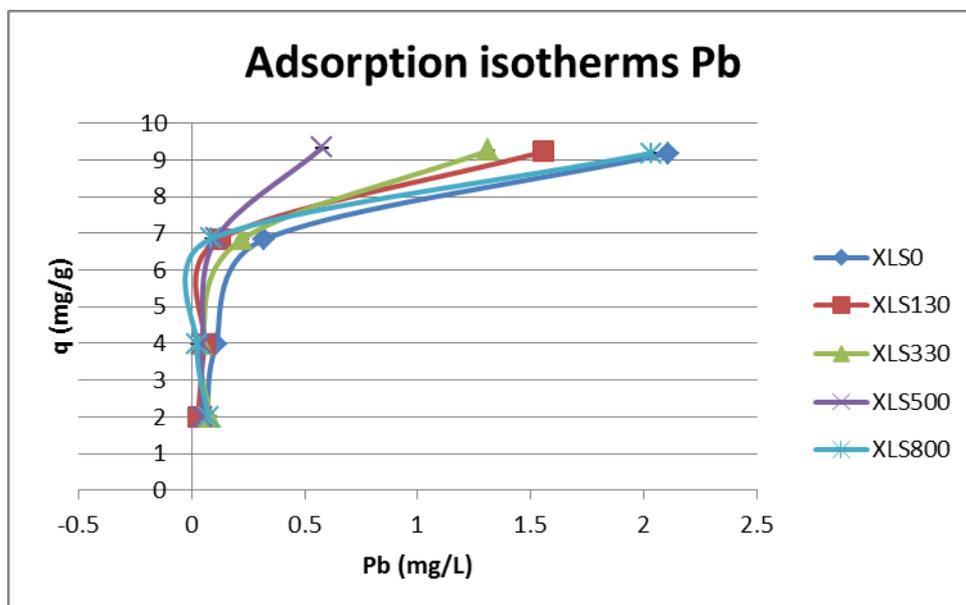


Figure 4.2.6b: Adsorption isotherms (Pb).

From the Figures 4.2.6a,b, it is observed that the diagrams of the adsorption isotherms of Cu and Pb correspond to an L-type isotherm. The L-type isotherm is characterized by a decrease in the slope of the isotherm with the increase of the concentration of the substance, as available positions are gradually completed. It reflects the strong adsorption of the substance from the surface at low concentrations; which decreases as the concentration of the substance in the solution increases.

Also, the Freundlich and Langmuir models have been tested for fitting to the experimental data (the diagrams are in appendix 8.)

Freundlich

A favorable adsorption tends to have Freundlich parameter n between 1 and 10 (Febriano et al, 2009). When the parameter is equal to 1, the adsorption is linear, and identical adsorption energies for all adsorption active sites are observed. In table 4.2.6.2 there are the results for parameters n and K for Cu and Pb.

Table 4.2.6.2: Parameters K and n for Cu and Pb.

Cu	K	n	R ²	Pb	K	n	R ²
XLS0	2.89	1.62	0.99	XLS0	8.03	2.48	0.83
XLS130	3.15	1.57	0.99	XLS130	9.39	2.18	0.79
XLS330	3.25	1.42	0.99	XLS330	8.79	2.31	0.63
XLS500	3.53	1.39	0.99	XLS500	1.,70	2.99	0.69
XLS800	2.82	1.21	0.88	XLS800	7.45	1.68	0.41

In both metals, with the increase of the temperature, the parameter n is close to 1 and the adsorption tends to be linear. This is due to the destruction of the structure and as a result the presence of less available sites. From the R^2 factor that has been measured for each sample, this model seems to be proper for Cu, but for Pb it is proper only in lower temperatures.

Langmuir

The parameter K measures how strong a molecule is attracted onto a surface (Do, 1998). Theoretically, when the value of parameter K is larger the interaction between the surface of the adsorbent and the solute molecules becomes stronger and the surface of adsorbent will be covered by the solute molecules. In tables 4.2.6.3 there are the results for parameters K and Q_0 for Cu and Pb.

Table 4.2.6.3: Parameters K and Q_0 for Cu and Pb.

Cu	Q ₀	K	R ²	Pb	Q ₀	K	R ²
XLS0	5.01	3.32	0.92	XLS0	14.10	2.81	0.95
XLS130	5.12	5.04	0.94	XLS130	13.00	6.99	0.99
XLS330	4.82	11.85	0.94	XLS330	6.51	15.22	0.27
XLS500	4.99	19.48	0.96	XLS500	18.55	3.67	0.64
XLS800	3.68	26.10	0.94	XLS800	4.64	102.67	0.05

The R^2 for Cu samples are high and that means that the calculated values are reliable. On the other hand, for Pb samples the factor R^2 is high only for 0 and 130°C. For higher temperature this model is not reliable for this set of calculations.

4.3 Physical parameters of raw and heat treated clay material

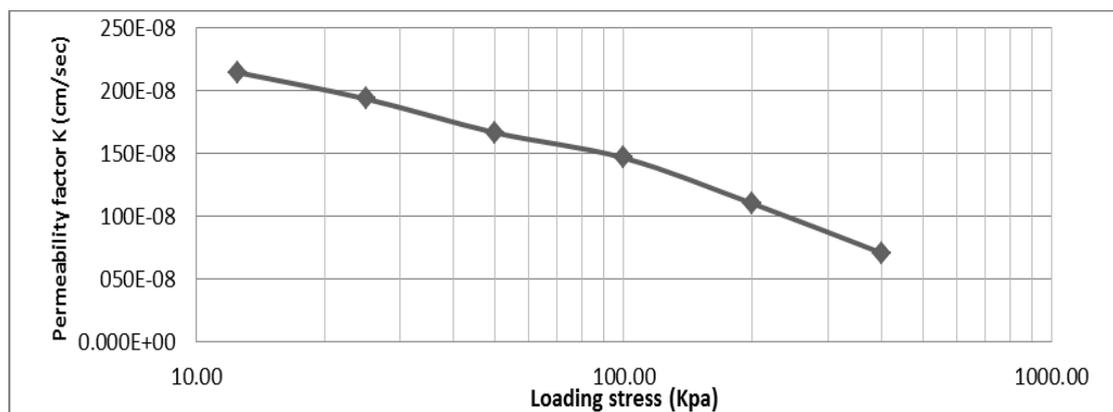
4.3.1 Permeability tests

The results of the permeability tests are presented in Table 4.3.1. The overall permeability of the samples decreases with the increase of the temperature.

Table 4.3.1: Results of permeability test on clay samples in oedometer device.

Loading stress	XLS0	XLS130	XLS330	XLS500	XLS800
12.5 kPa	2.15E-06	2.03E-07	1.85E-06	8.27E-07	3.73E-07
25.0 kPa	1.94E-06	2.32E-07	9.68E-07	5.22E-07	3.40E-07
50.0 kPa	1.67E-06	1.99E-07	6.41E-07	4.51E-07	3.38E-07
100.0 kPa	1.47E-06	1.32E-07	4.57E-07	4.02E-07	3.44E-07
200.0 kPa	1.10E-06	6.43E-08	4.65E-07	3.49E-07	3.90E-07
400.0 kPa	7.09E-07	9.73E-09	2.01E-07	2.42E-07	3.17E-07
25.0 kPa	8.43E-07	2.93E-08	6.20E-07	7.05E-07	3.67E-07

Below there are the diagrams (Fig.4.3.1.1-4.3.1.5.5) which present the results of the permeability tests. It is clear that initially there is swelling (negative values) and then deformation due to the pressure. After discharging there is swelling again but not up to the initial stage. With the increase of the temperature (130, 330°C) the sample is deformed more slowly because it has lower permeability (there is still smectite in the structure). At higher temperatures (500, 800°C) there is a direct deformation because the structure has been destroyed (there is not smectite any more).



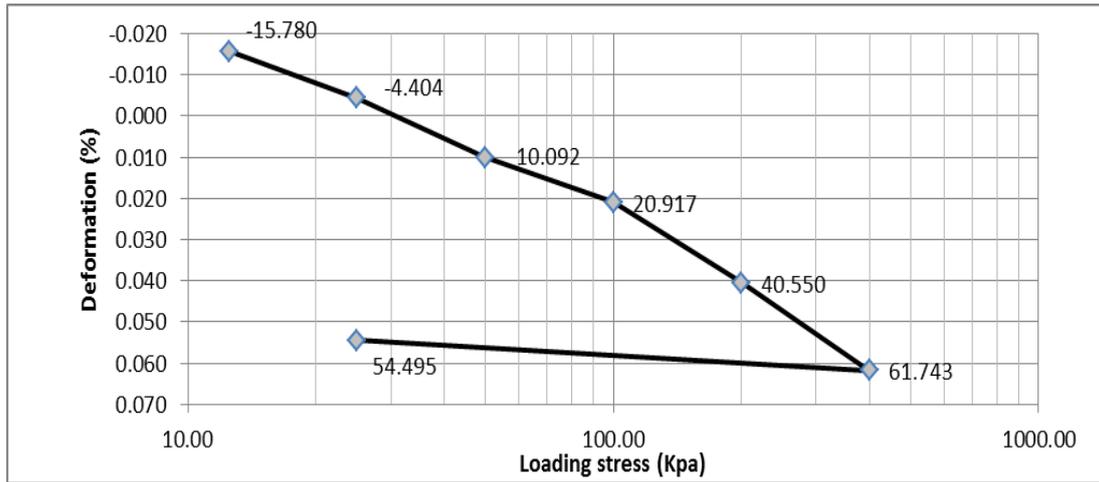


Figure 4.3.1.1a,b: Results of the permeability tests (XLS0).

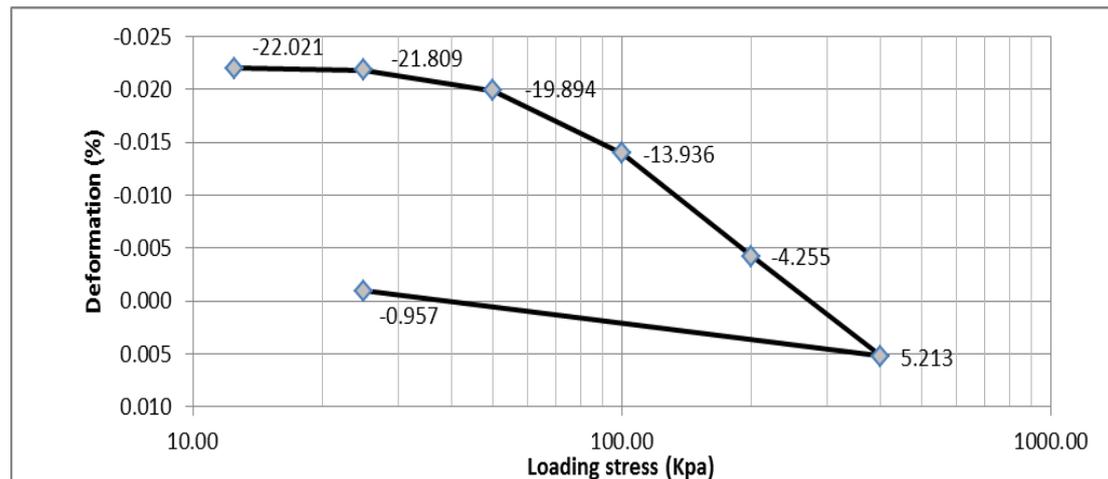
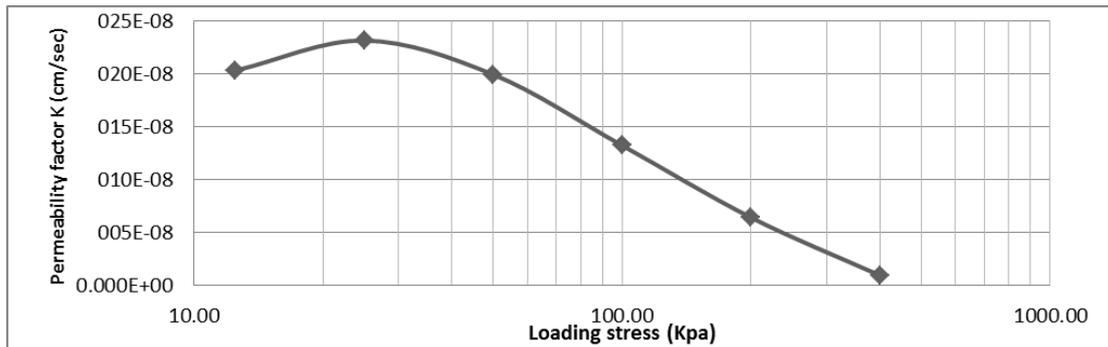


Figure 4.3.1.2a,b: Results of the permeability tests (XLS130).

Assessment of Fe- rich smectite clays in adsorbing Pb and Cu from aqueous solutions:
A batch experiment approach

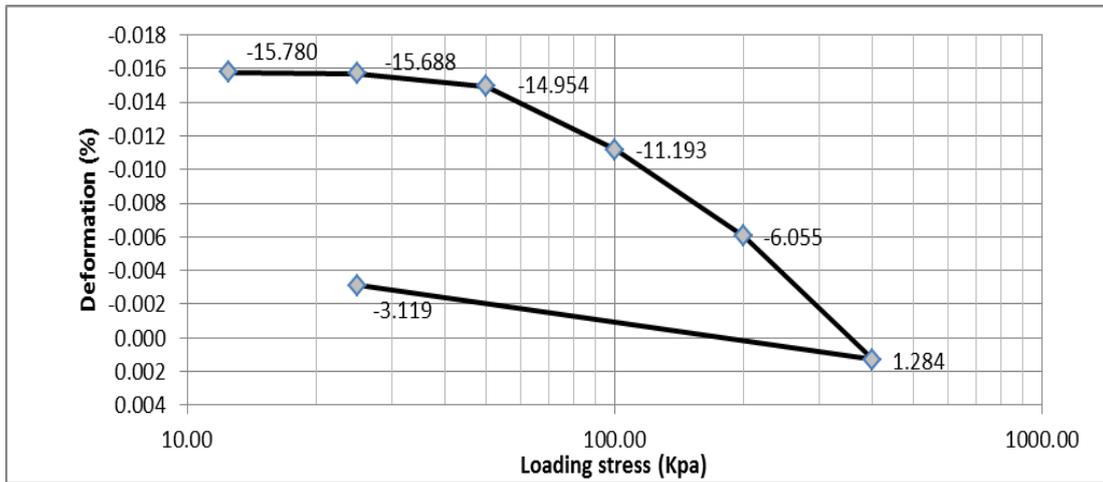
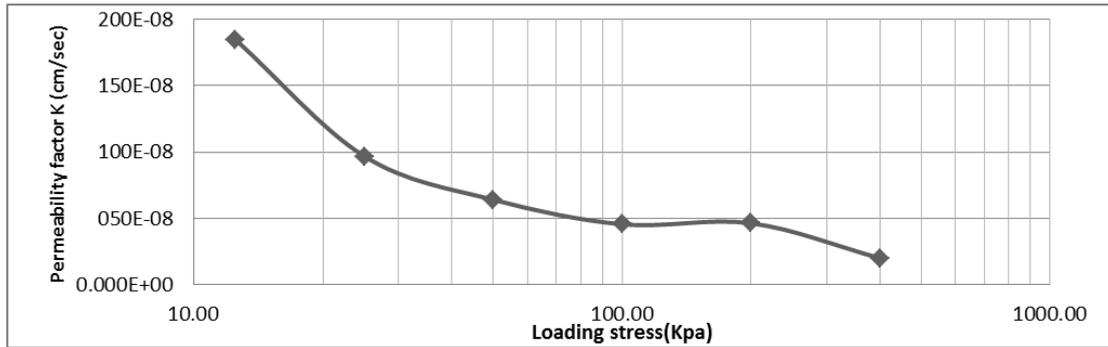
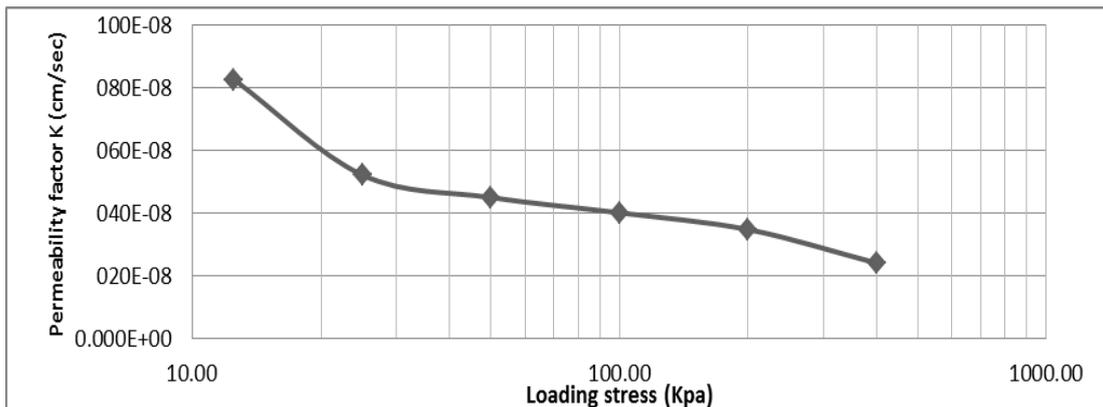


Figure 4.3.1.3a,b: Results of the permeability tests (XLS330).



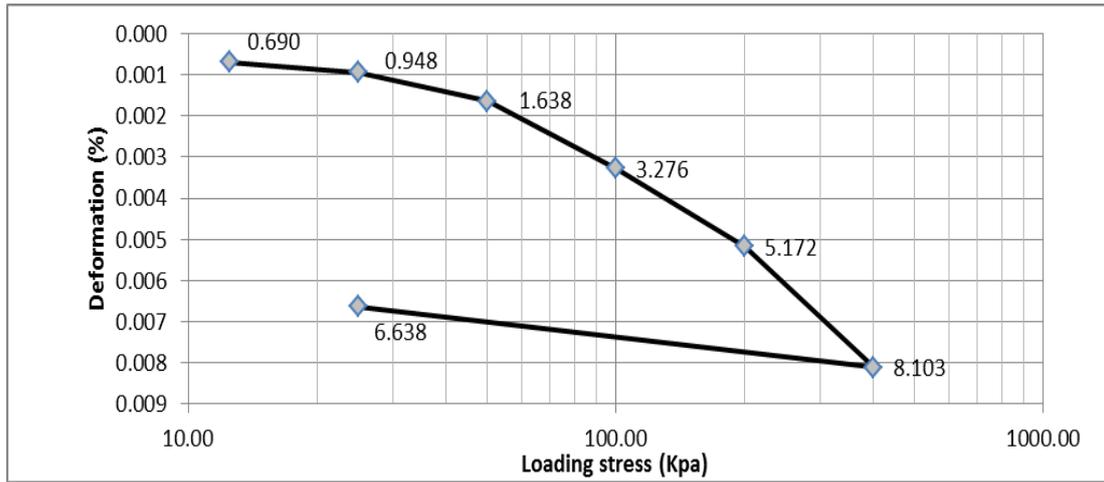


Figure 4.3.1.4a,b: Results of the permeability tests (XLS500).

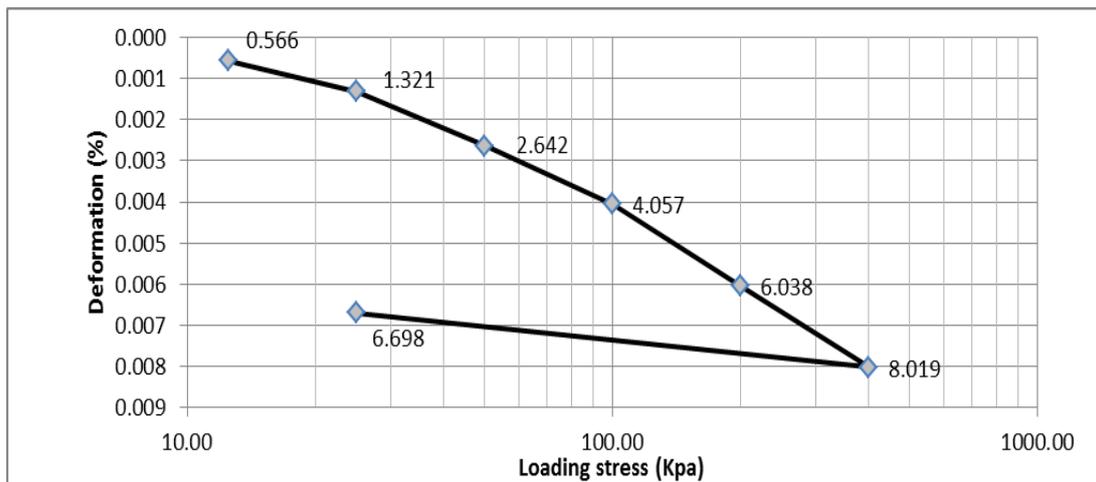
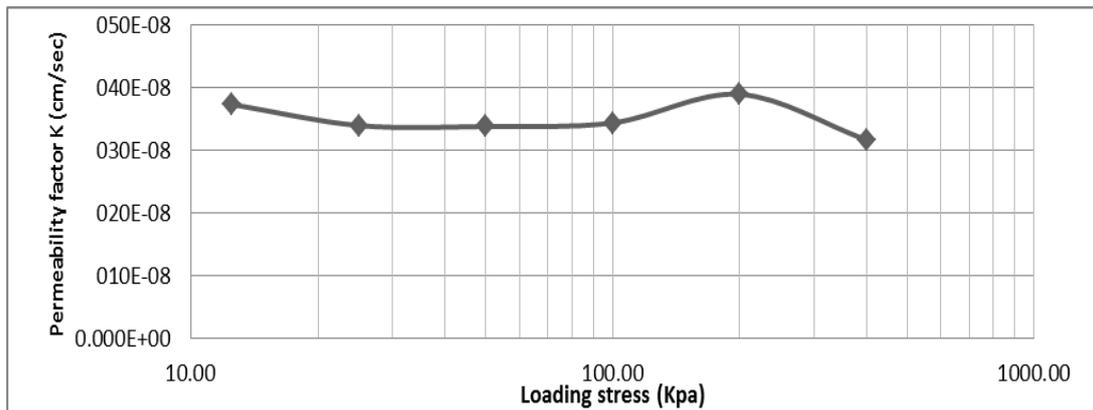


Figure 4.3.1.5a,b: Results of the permeability tests (XLS800).

From the permeability tests (Table 4.3.1 and Fig.4.3.1.1-4.3.1.1.5) it is clear that in the heat treated samples the permeability is lower, because the structure of the material is being distracted. This is noticeable for all the temperatures, even from the sample with heat treatment at 130°C (XLS130).

4.3.2 Plasticity and Liquid limit

In Table 4.4.2 are presented the results of the plastic and liquid limits for sample XLS130 and XLS330. The samples XLS500 and XLS800 have neither liquid nor plastic limit, because the material has been burned.

Table 4.3.2: Plastic and liquid limits for sample XLS130 and XLS330.

Sample	Liquid limit (W_L)	Plastic limit (W_P)	Plasticity index ($I_P=W_L-W_P$)
XLS130	151.4	69.8	81.6
XLS330	79.4	54.6	24.8

From these results it is noticed that with the increase of temperature the liquid limit is decreased significantly because the structure is destroyed. On the other hand the plastic limit does not seem to have a very noticeable reduction.

The results of these tests are in correlation with the results from XRD. In lower temperatures of heat treatment there are more minerals in the samples which can justify the plastic and liquid limits. In higher temperatures most of the minerals have been destroyed and thus the limits are significantly reduced.

4.4 Comparison of results with previous studies and potential uses of the studied clay material

Based on the results presented in the previous paragraphs a brief discussion on how the material could be used for environmental purposes follows.

The results from this study indicate that the clay material could be effective on the adsorption of Cu and Pb. The adsorption capacity of the material is influenced by different factors like pH, contact time etc. If these factors are determined in the right way the effectiveness of the material will be enlarged and the possibility for use too.

Messini (2014) in her master thesis, presented results of laboratory experiments on the adsorption of Pb^{2+} and Cu^{2+} from standard aqueous solutions by comparing the adsorption capacity of raw and thermally modified attapulgite, mined in the area of Grevena, Greece. It is useful to study her results in comparison with the result of the present study, since the same experimental procedure has been followed. Within this framework, it is noticeable that the two studies have similarities. First of all, in both studies when the clay dose in the solution is higher, there is a decrease in the concentration of the studied metal ions. The adsorption reaches the percentage of 90-100%. Secondly, in both studies the pH value plays an important role in the adsorption. In our study the removal of metals is greater when the pH values of

solutions are within the range 4 to 6, while in Messini's study the greater removal occurs in pH values 4-8. There is a difference between the two studies in the experiment of the effect of contact time: in our study after the first 30 minutes it seems that the system reaches equilibrium, while the results from Messini's study present that the equilibrium is reached after the first 5 minutes. This may be due to the fact that the Fe-rich smectite needs more time for ion exchange than attapulgite. Finally, in both studies the ionic strength of the aqueous phase affects greatly the adsorption of a metal, as the concentration of salt in the aqueous solution increases, the adsorption of metallic minerals from the clay decreases due to the competition between the Na^+ and the metals.

Through the bibliography there are several studies about the effectiveness of various clay minerals as adsorbents and the potential of uses in the environmental industry. Vega et al., (2005) for example studied the bentonites as adsorbents of heavy metals from mine waste leachates. The adsorption rates of this study indicate the suitability of these materials to be applied in the environmental industry for retention of heavy metals from mine waste leachates. Also the results show that these materials could be used as physical barriers as well as chemical barriers. It should be noticed that the results from Vega's et al., (2005) study for Cu are similar with the results from this study. This indicates that the use of Fe-rich smectite in the environmental industry is possible. Bourliva (2013) in her doctoral thesis studied the effect of bentonites addition in chemical flocculants for the adsorption of heavy metals (Cr, Cu, Ni, Mn, Zn) for the treatment of urban waste water. The results show that all the clay materials which were studied are effective on the removal of heavy metals from aqueous solutions. Also, this adsorption process could be proposed for the treatment of liquid wastes with low concentrations of heavy metals. The experimental design of Bourliva's study is close to this study, so the Fe-rich smectite could be also proposed for the same uses.

All in all, from the combination of the results presented in the previous paragraphs and the different studies from the bibliography, this research provides evidence that the Fe-rich smectite from Knidi, North Greece could be proposed as adsorbent of heavy metals and in general as effective material on the environmental industry (sealing material etc.).

5. CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER STUDY

5.1 Conclusions

This chapter summarizes the final conclusions of the experimental method with the application of the clay material to standard aqueous solutions. An attempt has been made to investigate the material's efficiency as an adsorption agent for two trace metals (Cu^{2+} and Pb^{2+}), and the effect of the heat treatment on the adsorption capacity of the material, and to compare the adsorption efficiency between the heat treated samples. Also, an attempt has been made to determine the effect of certain parameters as the dose of the absorptive material, the pH of the aqueous solution, the time contact, the ionic strength and the concentration of the heavy metal in the solution, at the adsorption capacity of the clay material.

From the experimental results it is clear that the material with or without heat treatment, can effectively remove metallic ions Cu^{2+} and Pb^{2+} .

More analytically we observed that:

- The XLS sample that we studied is a mixture mainly of Fe-rich dioctahedral and trioctahedral smectite and palygorskite and its properties are a combination of the properties of the contained minerals.
- When the clay dose in the solution is higher, there is a decrease in the concentration of the studied metal ions. This result, may be due to the fact that the increase of the solid particles leads to more available positions for the adsorption of the metals, thus eliminating metals from the aqueous solutions.
- The pH influences the form of the metals (metal speciation) and their association with inorganic ligands such as OH^- , by creating complexes. For pH values <4 we find that the removal of metals from the aqueous solution is low and this may be due to the competition between the protons and the metallic ions for the same active adsorption sites. The removal of metals is greater when the pH values of solutions are between 4-6. It is very important to note that when aqueous solutions are made basic ($\text{pH}>7$), sedimentation of the metallic elements which are presented in the solution is observed. The metallic elements precipitate in the form of hydroxides [$\text{Pb}(\text{OH})_2$ & $\text{Cu}(\text{OH})_2$].
- There is an intense Cu adsorption from the untreated vs heat treated material and from the material with heat treatment at 130, 330, 500°C in the first 5 minutes. After the first 30 minutes it seems that the system reaches equilibrium. This fact is due to the active adsorption sites on the surface of the mineral. For the heat treated sample at 800°C, a slower adsorption is observed, without reaching equilibrium at 120 minutes. However, the concentrations have decreased significantly. On the other hand Pb

adsorption is greater than Cu adsorption within the first 5 minutes. Also, high adsorption of Pb is observed after heat treatment at 800°C. In general, Pb adsorption appears to be smoother and more gradual.

- The ionic strength of the aqueous phase affects greatly the adsorption of a metal. In particular, the increase in ionic strength has a negative effect on the adsorption phenomenon of Cu and Pb, it inhibits and blocks the metals from binding due to the competitive relationship developed between them and the added cation. Consequently, as the concentration of salt in the aqueous solution increases, the adsorption of metallic minerals from the clay decreases due to the competition between the Na⁺ and the metals.
- The increase in the concentration of the heavy metals in aqueous solutions under constant temperature and pH conditions results in an increase of the amount of the retained metal per unit mass of adsorbent material.
- The samples with different temperature modification present similar adsorption capacity although there is different mineralogy.
- With the temperature modification the XLS material has been changed and different minerals are presented in each temperature. As a result different physical and mechanical parameters are noticed.
- The adsorption is a fast process, a sharp increase in the removal is observed at the beginning of the process, as a result the maximum removal of metals is achieved in the first 5-30 minutes, while it is followed by a less rapid stage with the system reaching equilibrium at 60-120 minutes. This happens due to the fact that, firstly, the rhythm of the removal on the bare surface is very high, but as the active positions are covered with metal ions, the rate is reduced.
- The reduction of the amount of metals adsorbed onto the surface of the studied adsorbents (q_e) by increasing the clay dose could be attributed to the fact that with high mineral ratios in the solution, a very quick superficial adsorption is carried out, this contributes to the reduction of the number of active positions adsorption per unit mass leading to a reduction in adsorption capacity with increasing dose of the adsorbent.
- The adsorption isotherm is of L-type, this means that there is high relation between the studied metals and the surface of the adsorbent.
- The results for Pb²⁺ are better than those of Cu²⁺ due to: (i) a lower hydrolysis constant, (ii) a higher atomic weight, and (iii) a larger ionic radius, making it a better candidate than copper for surface reactions.

From the results of the study, it is evident that the clay material has the potential to act as a binding agent of heavy metals from aqueous solutions due to its adsorption capacity in either raw or heat treated condition.

5.2 Recommendations for further research

To continue the research with the main object the adsorption of copper and lead from aqueous solutions by heat treated clay material, it is proposed:

- The investigation of possible desorption of the adsorbed elements from the clay material after a change in physicochemical conditions.
- Extension of the research by the study of adsorption capacity of other metals-elements, by the use of Fe-rich smectite or other clay minerals or of a mixture of clays.
- The application of the methodology in natural water solutions (multi-elemental) which have been contaminated by trace metals (e.g. industrial wastes).
- The extension of research beyond contaminated aqueous solutions by trace metals, to contaminated soil samples by trace metals.

REFERENCES

- Al-Asheh, S., F. Banat, F., Abu-Aitah, L. (2003):** Adsorption of phenol using different types of activated bentonites. *Sep. and Pur. Technol.* 33, 1-10.
- Alvarez-Ayuso, E. and García- Sánchez, A. (2003):** Palygorskite as a Feasible Amendment to Stabilize Metal Polluted Soils. *Environmental Pollution.* 125.
- Argyraki, A., Boutsis, Z., Zotiadis, V. (2017):** Towards sustainable remediation of contaminated soil by using diasporic bauxite: Laboratory experiments on soil from the sulfide mining village of Stratoni, Greece. *Journal of Geochemical Exploration.* 183, 214-222.
- Argyraki, A., (2013):** Analytical Geochemistry, NKUA, Athens.
- Aqqarwal, V., Li, H., Teppen, B.J., (2006):** Triazine absorption by saponite and beidellite clay minerals. *Environ. Toxicol. Chem.* 25, 392-399.
- Awadh, S. M. and Towfik, S. M. (2013):** Sorption mechanism and capacity evaluation of palygorskite from Iraq to remove Pb from aqueous solution. *Geology and Geosciences*, Vol. 2, Issue 3.
- Bourliva, A., (2013):** Use of natural clays in the removal of heavy metals from water solutions and urban and industrial wastes. (doctoral thesis)
- Briggati, M.F., Lugli, C., Poppi, L., (2000):** Kinetics of heavy-metal and recovery in sepiolite, Modena, Italy., *Clay Minerals.* 16, 45-57.
- Chaari, I., Fakhfakh, E., Chakroun, S., Bouzid, J., Boujelben, N., Feki, M., Rocha, F., Jamoussi, F., (2008):** Lead removal from aqueous solutions by a Tunisian smectitic clay. *J. Hazard. Mater.* 156, 545–551.
- Chaisena, A., Rangriwatananon, K., Suranaree. J., (2004):** Effects of thermal and acid treatments on some physic-chemical properties of Lampang diatomite. *Sci. Technol.* 11, 289-299.
- Chipera, S.J., Bish, D.L., (2001):** Baseline Studies of the Clay Minerals Society Source Clays: Powder X-Ray Diffraction Analysis. *Clay Clay Miner.* 49, 398–409.
- Do, D.D., (1998):** Adsorption Analysis: Equilibria and Kinetics. Imperial Collage Press, London.
- Duffus J., (2002):** “Heavy metals”- a meaningless term? (IUPAC Technical Report). *Pure and Applied Chemistry.* 74, 793-807.
- Eby , G.N., (2012):** Principles of Environmental Geochemistry. (book)
- El-mofty, S.E., Ashour, F.H., El-Shall, H., (2008):** Absorption mechanism of toxic metal ions by clay (attapulgitite). Twelfth international water technology conference, IWTC12 2008, Alexandria, Egypt.
- Eslinger, E., Pevear, D., (1988):** Clay Minerals for Petroleum Geologists and Engineers. SEPM Short Course Notes no. 22. Society of Economic Paleontologists and Mineralogists, Tulsa.
- Essington M.E., (2004):** Soil and water chemistry: An integrative approach. CRC Press LLC, Florida, U.S.A.

- Fan, Q.H., Shao, D.D., Hu, J., Wu, W.S., Wang, X.K., (2008):** Comparison of Ni²⁺ sorption to bare and ACT-graft attapulgites: Effect of pH, temperature and foreign ions. Lanzhou, China. Surface Science. 602, 778-785.
- Febriano, J., Kosasih, A.N., Sunarso, J., Ju, Y.H, Indraswati, N., Ismadji, S., (2009):** Equilibrium and kinetic studies in adsorption of heavy metals using biosorbent: a summary of recent studies. Journal of Hazard. 162, 616-645.
- Ferrage, E., Lanson, B., Sakharov, B.A., Geoffroy, N., Jacquot, E., Drits, V.A., (2007):** Investigation of dioctahedral smectite hydration properties by modeling of X-ray diffraction profiles: influence of layer charge and charge location. Am. Mineral. 92, 1731–1743.
- Galan, E., (1996):** Properties and applications of Palygorskite-Sepiolite clays. Clay minerals. 31.
- Gan, F., Zhou, J., Wang, H., Du, C., Chen, X., (2009):** Removal of phosphate from aqueous solution by thermally treated natural palygorskite. Water research. 43, 2907-2915.
- Grim, R.E., Kodama, H., (2014):** Clay minerals. Retrieved from: www.britannica.com/science/clay-mineral
- Guerra, D.L., Oliviera, H.C.P., Correa de Costa, P.C., Viana, R.R., Airoidi, C., (2010):** Absorption of chromium(VI) ions on Brazilian smectite: Effect of contact time, pH, concentration and calorimetric investigation., Elsevier. 82, 35-44.
- Ghorbel-Abid, I., Trabelsi-Ayadi, M., (2011):** Competitive adsorption of heavy metals on local landfill clay. Laboratoire des Applications de la Chimie aux Ressources et Substances Naturelles et à l'Environnement (LACReSNE), Faculty of Sciences of Bizerte, Zarzouna 7021, Tunisia.
- Harris, W., White, G.N., (2008):** X-ray diffraction techniques for soil mineral identification. Methods Soil Anal. Part 5 – Mineral. Methods. 81–115.
- Heller-Kallai, L. (2006):** Thermally modified clay minerals. In: Bergaya , Ed.n Handbook of clay Sciences. 168.
- Ismadji, S., Soetaredjo, F.E., Ayucitra, A., (2015):** Clay materials for environmental remediation, Springer briefs in molecular science, Green chemistry for sustainability. (book)
- Kastritis, I.D., Kacandes, G.H., Mposkos. E., (2003):** The palygorskite and Mg-Fe Smectite Clay Deposits of the Ventzia Basin, Western Macedonia, Greece., Mineral Exploration and Sustainable Development.
- Katsumata, H., Kaneco, S., Inomata, K., Itoh, K., Funasaka, K., Masuyama, K., Suzuki, T., Ohta K. (2003):** Removal of heavy metals in rinsing wastewater from plating factory by adsorption with economical viable materials. Journal of Environmental Management. 69, 187-191.
- Kaufhold, S., Dohrmann, R., (2010):** Effect of extensive drying on the cation exchange capacity of bentonites. Clay Miner. 45, 441–448.

- Kelepertzis, A., (2000):** Applied Geochemistry, Makedonikes Publishing Group, Athens.
- Kypridou, Z., Argyraki, A. (2018):** A multi-site mechanism model for studying Pb and Cu retention from aqueous solutions by Fe-Mg-rich clays. Clay Minerals. 1-42
- Langmuir, D., Chrostowski, P., Vinneault, B., Chaney, R., (2005):** Issue paper on the environmental chemistry of metals. U.S. Environmental Protection Agency Risk Assessment Forum. Retrieved from: https://www.researchgate.net/figure/237330649_fig22_Figure-23-Eh-pH-diagram-for-the-system-Pb-O-2-PO4-S-H-2-O-assuming-that-EPb-10-8
- Malamis, S., Katsou, E., (2013):** A review on zinc and nickel adsorption on natural and modified zeolite, bentonite and vermiculite: Examination of process parameters, kinetics and isotherms. Elsevier, Journal of Hazardous Materials. 252-253 428-461.
- Messini, P., (2014):** Adsorption of lead and copper from aqueous solution by heat treated attapulgite clay. (master thesis)
- Mhamdi, M., Galai, H., Mnasri, N., Elaloui, E., Trabelsi-Ayadi, M., (2013):** Adsorption of lead onto smectite from aqueous solution. Environ. Sci. Pollut. Res. Int. 20 1686–1697.
- Monvisade, P., Siriphannon, P., (2009):** Chitosan intercalated modmorillonite: Preparation, characterization and cationic dye adsorption. Appl. Clay Sci. 42, 427-431.
- Moonis Ali Khan, Rifaqat Ali Khan Rao and Mohammad Ajmal, (2008):** Heavy metal pollution and its control through nonconventional absorbents (1998-2007): a review. J. Int. Environmental Application & Science, Vol. 3 (2): 101-141.
- Moore, D.M., Reynolds, R.C.,J., (1989):** Sample Preparation Techniques for Clay Minerals. X-Ray Diffraction and the Identification and Analysis of Clay Minerals. 204-226.
- Nagata, H., Shimoda, S., Sudo, T., (1974):** On dehydration of bound water of sepiolite. Clays Clay Miner. 22, 285–293.
- Parthasarathy, G., Chundary, B.M., Sreedhar, B., Kunwar, a.c., (2007):** Environmental mineralogy: spectroscopic studies on ferrous saponite and the reduction of hexavalent chromium. Natural Hazards. 40, 647-655.
- Parthasarathy, G., Choundary, B.M., Sreedhar, B., Kunwar, A.C., Srinivasan, R., (2003):** Ferrous saponite from the Deccan Trap, India, and its application in absorption and reduction of hexavalent chromium. American Mineralogist. 88, 1983-1988.
- Poppe, L.J., Paskevich, V.F., Hathaway, J.C. &Blackwood, D.S., (2001):** A Laboratory Manual for X-Ray Powder Diffraction. U.S. Geological Survey Open-File Report. 01-041, 88
- Potgieter, J.H., Potgieter-Vrmaak, S.S., Kalibantonga, P.D., (2005):** Heavy metals removal from solution by palygorskite clay. Elsevier, Minerals Engineering. 19, 463-470.

- Sanchez del Rio, M., Suarez, M., Garcia Romero, E., Alianelli, L., Felici, R., Martinetto, P., Dooryhee, E., Reyes-Valerio, C., Borgatti, F., Doyle, B., Giglia, a., Mahne, N., Pedio, M., Nannarone S., (2005):** Mg K-edge XANES of sepiolite and palygorskite. Nuclear Instruments and Methods.
- Sparks, D.L., (1995):** Environmental soil chemistry. Academic Press, San Diego.
- Steudel A, Batenburg F, Fischer R., Weidler G, Emmerich K, (2009):** Alternation of swellable clays by acid treatment. Applied Clay Science. 44, 105-115.
- Suarez, M., and Garcia Romero, E., (2011):** Advancesn in the crystal chemistry of sepiolite and palygorskite. In: Developments in clay science – volume 3 Developments in palygorskite-sepiolite Research (E. Galan and A.Singer Eds.), Elsevier, Amsterdam. 35.
- Tsirampidis, A., (2006):** Petrographic sedimentary rocks, A.U.T.
- Van Scoyoc, G.E., Serna, C.J., Ahlrichs, J.L., (1979):** Structural changes in palygorskite during dehydration and dehydroxylation. Am. Mineral. 64, 215–223.
- Vega, J. L., Ayala, J., Loredó, J. & García Iglesias, J. (2005):** Bentonites as adsorbents of heavy metals ions from mine waste leachates – Experimental data. – In: Loredó, J. & Pendás, F.: Mine Water 2005 – Mine Closure. – p. 603-609, 3 fig., 8 tab.; Oviedo (University of Oviedo).
- Vimonses, V., Lei, S., Jin, B., Chow, C.W.K., Saint, C., (2009):** Kinetic study and equilibrium isotherm analysis of Congo Red absorption by clay materials. Chemical Engineering Journal. 148, 354-364.
- Wang, W., Chen, H., Wang, A., (2007):** Adsorption characteristics of Cd(II) from aqueous solutions onto activated palygorskite. Separation and Purification Technology. 55, 157-164.
- Wilson, M.J., (2013):** Rock-Forming Minerals , Sheet Silicates, Clay Minerals. Second edition, Published by the Geological Society, volume 3C. (book)
- Zhongwei, W., Xiaoming, S., Huifang, X., Hiromi, K., Yan W., Chi, W., Yingzhi, D., Xiguang D., Miao, Y., (2016):** Occurences and distribution of “invisible” precious metals in sulfide deposits from the Edmond hydrothermal field, Central Indian Ridge. Elsevier, Ore Geology Reviews, 79. Retrieved from: https://www.researchgate.net/figure/303094779_fig10_Fig-14-Eh-ph-diagram-for-the-system-Cu-O-H-S-Cl-in-seawater-at-25-C-after-Hannington
- Zotiadis, V., Argyraki, A., & Theologou, E. (2012):** A Pilot Scale Application of Attapulgitic Clay for Stabilization of Toxic Elements in Contaminated Soil. Journal of Geotechnical and Geoenvironmental Engineering, Vol. 138, No. 5, May 1, 2012, ©ASCE.
- <http://www.lenntech.com/periodic/elements/cu.htm>
<http://www.lenntech.com/periodic/elements/pb.htm>

APPENDICES

Appendix 1- Heat treatment.

Laboratory utensils:

- 1) refractory vessel
- 2) high temperature oven
- 3) dryer

Procedure:

- 1) weighing 10g of the clay and placing it in the refractory pot.
- 2) placing the clay material in the oven for 4 hours at 130, 330, 500, 800°C.
- 3) holding the material in the oven with closed thermostat for 24 hours to cool down gradually.
- 4) place the material in the dryer until the use, so that it does not regain moisture.

Appendix 2- Preparation of standard solutions.

For $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, concentration 50mg/L

Laboratory utensils:

- 1) 4L volumetric vessel
- 2) copper nitrate $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$
- 3) distilled water

Procedure:

- 1) weighing 0,761g of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$
- 2) placing 4L of distilled water in the vessel and adding the copper nitrate
- 3) thoroughly stirring the solution to completely dissolve the substance

For $\text{Pb}(\text{NO}_3)_2$, concentration 50mg/L

Laboratory utensils:

- 1) 4L volumetric vessel
- 2) lead nitrate $\text{Pb}(\text{NO}_3)_2$
- 3) distilled water

Procedure:

- 1) weighing 0,1590g of $\text{Pb}(\text{NO}_3)_2$
- 2) placing 4L of distilled water in the vessel and adding the copper nitrate
- 3) thoroughly stirring the solution to completely dissolve the substance

Appendix 3- Effect of the clay dose.

For the aqueous solution of Cu.

Laboratory utensils:

- 1) precision scale
- 2) plastic centrifusion test tubes
- 3) thermal shaker chamber
- 4) centrifugal
- 5) pH-meter
- 6) instrument to measure TDS and temperature

Procedure:

- 1) weighing 0,05 / 0,125 / 0,250 / 0,375g of clay saponite thermally modified at 0/130/330/500 / 800°C and placement on plastic test tubes
- 2) addition of 25ml of copper nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) at a concentration of 50g/L
- 3) place the samples in a thermal shaker chamber with a constant temperature of 22°C for 2 hours
- 4) centrifuge the samples for 15 minutes
- 5) measurement of pH, TDS and temperature
- 6) analysis of the samples using atomic adsorption spectrometry with flame (AAS)

For the aqueous solution of Pb.

Laboratory utensils:

- 1) precision scale
- 2) plastic centrifugal test tubes
- 3) thermal shaker chamber
- 4) centrifugal
- 5) pH-meter

6) instrument to measure TDS and temperature

Procedure:

- 1) weighing 0,05 / 0,125 / 0,250 / 0,375g of clay saponite thermally modified at 0/130/330/500 / 800°C and placement on plastic test tubes
- 2) addition of 25ml of copper nitrate ($\text{Pb}(\text{NO}_3)_2$) at a concentration of 50g/L
- 3) place the samples in a thermal shaker chamber with a constant temperature of 22°C for 2 hours
- 4) centrifuge the samples for 15 minutes
- 5) measurement of pH, TDS and temperature
- 6) analysis of the samples using atomic adsorption spectrometry with flame (AAS).

Experimental results:

Assessment of Fe- rich smectite clays in adsorbing Pb and Cu from aqueous solutions:
A batch experiment approach

Cu(NO ₃) ₂ *3H ₂ O	sample	g/L	weight (g)	ph	TDS (mg/L)	T (C)	AAS (mg/L)	Pb(NO ₃) ₂	sample	g/L	weight (g)	ph	TDS (mg/L)	T (C)	AAS (mg/L)
XLSO	1	0	0	5.2	89.6	21.9	38.95	XLSO	A	0	0	4.2	40.1	20	34.6
	2	0	0	5.1	86.6	22.1	37.75		B	0	0	3.9	39.8	19.9	29.95
	3	0	0	5.1	86.4	22.2	38.45		Γ	0	0	4.2	34.4	20	33.25
	4	2	0.05	5.2	92.1	24.3	24.25		Δ	2	0.0503	5.4	31.4	22.4	5.21
	5	2	0.0504	5.2	88.6	25.8	24.35		E	2	0.0506	5.2	33.7	22.4	5.91
	6	2	0.0504	5.3	80.4	24.8	23.3		Z	2	0.0504	5.7	27.7	21.9	4.55
	7	5	0.1251	5.6	84.9	23	12.05		H	5	0.1255	6.4	31.2	21.5	2.03
	8	5	0.1252	5.6	93.3	23.2	12.05		Θ	5	0.1254	6.2	34.9	22	0.5
	9	5	0.125	5.7	86.6	25.3	12.05		I	5	0.1255	6.3	33	21.3	1.47
	10	10	0.25	5.9	93.4	24.1	4.48		K	10	0.2506	6.9	30.7	23.3	0.06
	11	10	0.2501	5.9	96.7	24.7	4.55		Λ	10	0.2509	6.8	34.7	23.4	0.07
	12	10	0.2501	5.9	83.1	23.6	4.14		M	10	0.2508	7.2	35.6	22.4	0.05
	13	15	0.3754	6.2	84.5	23.3	1.45		N	15	0.3758	7.3	39.7	21.9	0.05
	14	15	0.3754	6.3	87.9	23.4	1.4		Ξ	15	0.375	7.2	41.3	22.4	0.01
	15	15	0.375	6.3	84.6	23.7	1.37		O	15	0.3754	7.3	37.2	21.3	0.03
XLS130	1	0	0	5.12	83.4	21.4	38	XLS130	A	0	0	4.8	34	18.2	29.45
	2	0	0	5.11	85.4	21.5	40.25		B	0	0	4.7	34.7	17.8	38
	3	0	0	5.09	86	20.9	40.45		Γ	0	0	5.0	30.6	18.3	30.85
	4	2	0.0504	5.2	87.4	21.5	25.7		Δ	2	0.05	5.9	29.9	18	3.62
	5	2	0.0501	5.3	80.3	21.4	26.05		E	2	0.0509	5.9	30.1	17.8	3.58
	6	2	0.5	5.2	82.2	22.9	26.15		Z	2	0.0503	5.9	30	17.7	4.07
	7	5	0.125	5.22	92.6	22.2	10.7		H	5	0.1252	6.4	27.4	17.7	0.6
	8	5	0.1251	5.53	94.2	24.2	10.55		Θ	5	0.125	6.6	29.1	17.9	0.45
	9	5	0.1252	5.65	91.6	23.4	11.2		I	5	0.1251	6.6	28.4	18	0.51
	10	10	0.2501	5.96	95.9	24.6	3.32		K	10	0.2503	6.8	32	18.7	0.05
	11	10	0.2502	6.05	90.9	24.1	3.36		Λ	10	0.25	7.2	33.5	19	0.05
	12	10	0.2503	6.09	90.3	22.6	3.33		M	10	0.2501	7.2	31.8	18.2	0.11
	13	15	0.3754	6.43	92.5	24	0.52	N	15	0.3752	7.2	38.7	18.7	0.06	
	14	15	0.3752	6.51	90	22.8	0.49	Ξ	15	0.3752	7.2	35.1	17.9	0.05	
	15	15	0.3752	6.55	90.2	23.6	0.44	O	15	0.375	7.5	35.9	17	0.06	
XLS330	1	0	0	5.11	88.3	19.7	42.25	XLS330	A	0	0	5.1	32.2	18.5	31.85
	2	0	0	4.91	90.3	19.5	41.55		B	0	0	4.6	31.5	18.8	31.3
	3	0	0	5.28	88.7	19.7	40.5		Γ	0	0	5.1	31.9	17.8	31.65
	4	2	0.0499	5.5	90.4	20.5	28.5		Δ	2	0.0505	5.5	28.2	18.7	5.74
	5	2	0.0505	5.44	91.9	20.5	28.45		E	2	0.0507	5.5	29.6	18.9	6.47
	6	2	0.0503	5.56	93	19.8	27.9		Z	2	0.0507	5.6	27.5	18.6	7.54
	7	5	0.1256	5.86	92.1	20.3	13.8		H	5	0.1253	5.9	27.3	18.9	0.56
	8	5	0.1253	5.79	93	19.8	14.2		Θ	5	0.1252	6.0	25.6	18.4	0.51
	9	5	0.1251	5.9	92.5	19.5	13.5		I	5	0.1253	6.1	28.3	18.1	0.47
	10	10	0.2502	6.09	96.7	21.3	4.36		K	10	0.2503	6.5	32.7	20	0.09
	11	10	0.2506	6.34	96	20.7	3.98		Λ	10	0.2501	6.6	31.5	20.1	0.1
	12	10	0.2504	6.05	93.8	20.8	4.02		M	10	0.2503	6.5	28.3	19	0.12
	13	15	0.3752	6.59	96	19.9	0.69		N	15	0.3753	6.6	33.5	20.1	0.06
	14	15	0.3755	6.65	97.6	21.7	0.43		Ξ	15	0.3755	6.7	36.5	18.9	0.04
	15	15	0.3753	6.53	97.1	21.6	0.48		O	15	0.3755	6.7	33.7	19.5	0.04
XLS500	1	0	0	5.01	92.2	19.6	38	XLS500	A	0	0	4.3	32	18.2	33.15
	2	0	0	5.14	90.6	20.1	40.75		B	0	0	4.6	29.3	18.3	31.5
	3	0	0	5.01	91.2	20.2	36.75		Γ	0	0	4.9	29.5	18.2	33
	4	2	0.0503	5.49	96.2	20.1	25.9		Δ	2	0.0501	5.7	30	20.1	2.78
	5	2	0.0502	5.27	92.6	21.9	26.8		E	2	0.0509	5.6	29.4	19.8	3.64
	6	2	0.05	5.64	92.2	22.2	27.4		Z	2	0.05	5.7	31.7	19.9	4.41
	7	5	0.125	5.73	94	22.2	10.05		H	5	0.1253	6.4	30.3	20.1	0.26
	8	5	0.1252	5.77	93	21.3	11.05		Θ	5	0.1255	6.5	32.4	19.2	0.28
	9	5	0.1254	5.92	93	21.6	8.3		I	5	0.1252	6.6	29.3	19.7	0.57
	10	10	0.2519	6.4	100.2	22.8	0.83		K	10	0.25	7.1	36.8	20.7	0.15
	11	10	0.2503	6.21	105.5	23.5	1.13		Λ	10	0.2509	6.8	34.6	20.3	0.24
	12	10	0.2509	6.42	102.5	22.8	1.08		M	10	0.25	7.1	35.6	21	0.1
	13	15	0.3751	6.76	101.5	22.8	0.06		N	15	0.375	7.2	36.7	20.4	0.14
	14	15	0.3755	7.01	101.6	21.8	0.06		Ξ	15	0.3753	7.3	37.4	20.1	0.21
	15	15	0.3751	7.13	101.5	22.1	0.06		O	15	0.3751	7.3	36.7	20.1	0.1
XLS800	1	0	0	4.98	93.2	18.5	42.1	XLS800	A	0	0	4.3	28.8	18	32.6
	2	0	0	5.25	90.4	18.5	40.5		B	0	0	4.8	29.3	17.7	31.8
	3	0	0	5.19	88.6	18.6	42.4		Γ	0	0	4.9	28.4	17.8	31.9
	4	2	0.05	5.48	91.5	18.9	35.65		Δ	2	0.0504	5.5	29.5	21	8.48
	5	2	0.0502	5.32	95	19.4	37.4		E	2	0.0507	5.6	28	21.5	7.9
	6	2	0.0509	5.64	90.9	19.3	35.7		Z	2	0.05	5.7	26.7	21.4	8.85
	7	5	0.1251	5.65	92.7	18.9	22.9		H	5	0.1252	7.1	29.5	21.2	0.07
	8	5	0.1252	5.85	87.5	18.8	23.55		Θ	5	0.1255	6.8	31.1	20.6	0.03
	9	5	0.1253	5.81	88.3	18.5	26.5		I	5	0.1251	7.2	30.6	21.1	0.12
	10	10	0.2503	6.07	100.3	17.9	8.99		K	10	0.2505	9.1	39.6	22.3	0.06
	11	10	0.2508	6.08	81.8	18.2	7.71		Λ	10	0.2508	8.9	38.4	23.1	0.03
	12	10	0.2502	6.15	80.1	18.5	7.18		M	10	0.2502	9.0	38.3	22.1	0.07
	13	15	0.3751	6.31	85.8	18.4	3.01		N	15	0.3752	9.3	44.9	22	0.2
	14	15	0.3753	6.43	83.1	18.5	1.55		Ξ	15	0.3753	9.3	45.9	21	0.1
	15	15	0.3754	6.4	82.8	18	1.91		O	15	0.3751	9.3	45.8	20.8	0.11

Appendix 4- Effect of pH.

For the aqueous solution of Cu.

Laboratory utensils:

- 1) precision scale
- 2) plastic droplets
- 3) NaOH solution and HNO₃ solution
- 4) plastic centrifugal test tubes
- 5) thermal shaker chamber
- 6) centrifugal
- 7) pH-meter
- 8) instrument to measure TDS and temperature

Procedure:

- 1) weighing 0,250g of clay saponite thermally modified at 0/130/330/500 / 800°C and placement on plastic test tubes
- 2) addition of 25 ml of copper nitrate (Cu(NO₃)₂* 3H₂O) of a concentration of 50g/L whose pH was adjusted to 2, 4, 6, 8 using 0.1 M NaOH and 0.1 M HNO₃ solutions
- 3) place the samples in a thermal shaker chamber with a constant temperature of 22°C for 2 hours
- 4) centrifuge the samples for 15 minutes
- 5) measurement of pH, TDS and temperature
- 6) analysis of the samples using atomic adsorption spectrometry with flame (AAS)

For the aqueous solution of Pb.

Laboratory utensils:

- 1) precision scale
- 2) plastic droplets
- 3) NaOH solution and HNO₃ solution
- 4) plastic centrifugal test tubes
- 5) thermal shaker chamber
- 6) centrifugal
- 7) pH-meter
- 8) instrument to measure TDS and temperature

Procedure:

- 1) weighing 0,250g of clay saponite thermally modified at 0/130/330/500 / 800°C and placement on plastic test tubes
- 2) addition of 25 ml of copper nitrate (Pb(NO₃)₂) of a concentration of 50g/L whose pH was adjusted to 2, 4, 6, 8 using 0.1 M NaOH and 0.1 M HNO₃ solutions
- 3) place the samples in a thermal shaker chamber with a constant temperature of 22°C for 2 hours
- 4) centrifuge the samples for 15 minutes
- 5) measurement of pH, TDS and temperature
- 6) analysis of the samples using atomic adsorption spectrometry with flame (AAS)

Experimental results:

Assessment of Fe- rich smectite clays in adsorbing Pb and Cu from aqueous solutions:
A batch experiment approach

	Cu(NO3)2*3H2O	sample	g/L	weight (g)	ph	TDS (g/L)	T (C)	AAS (mg/L)	Pb(NO3)2	sample	g/L	weight (g)	ph	TDS	T (C)	AAS (mg/L)
pH=2	Blank	1	0	0	2.1	2.44	17	46.05	Blank	1P	0	0	2.0	1.72	12.7	63.5
	Blank	2	0	0	2.1	2.41	17.5	44.1	Blank	2P	0	0	2.0	1.91	10.7	53.5
	Blank	3	0	0	2.1	2.4	17.5	44.4	Blank	3P	0	0	2.0	1.72	12.6	63
	XLS0	4	10	0.2505	2.3	1.58	17.1	29.5	XLS0	4P	10	0.2501	2.4	0.93	11.6	58
		5	10	0.2502	2.3	1.68	16.5	28.8		5P	10	0.2501	2.4	0.99	10.1	50.5
		6	10	0.25	2.3	1.61	17.5	30.1		6P	10	0.2506	2.4	0.94	11.1	55.5
	XLS130	7	10	0.2506	2.3	1.56	17.1	29	XLS130	7P	10	0.2503	2.5	0.88	11.7	58.5
		8	10	0.2502	2.3	1.55	16.8	28.2		8P	10	0.2501	2.5	0.86	11.9	59.5
		9	10	0.25	2.3	1.5	17.2	28.25		9P	10	0.2506	2.5	0.86	11.9	59.5
	XLS330	10	10	0.2505	2.3	1.56	17.7	32.35	XLS330	10P	10	0.25	2.5	0.86	11.8	59
		11	10	0.25	2.3	1.62	17.2	31.15		11P	10	0.2501	2.5	0.93	10.3	51.5
		12	10	0.25	2.3	1.55	17.3	31.5		12P	10	0.2502	2.4	0.87	12.4	62
	XLS500	13	10	0.2506	2.5	1.13	17.1	36.2	XLS500	13P	10	0.2505	2.8	0.6	12.3	61.5
		14	10	0.2501	2.5	1.15	17	37.75		14P	10	0.25	2.9	0.62	12.5	62.5
		15	10	0.2501	2.5	1.15	17.2	37.9		15P	10	0.2499	3.0	0.59	12.4	62
	XLS800	16	10	0.2509	2.3	1.52	18.8	40.95	XLS800	16P	10	0.2504	2.5	0.86	11.6	58
		17	10	0.2508	2.2	1.7	17.8	39.05		17P	10	0.2503	2.5	0.92	10.7	53.5
		18	10	0.25	2.2	1.67	18.9	37.05		18P	10	0.2502	2.5	0.87	12	60
pH=4	Blank	19	0	0	4.0	260	16.7	48	Blank	19P	0	0	3.9	52.5	14.3	71.5
	Blank	20	0	0	3.9	228	18.8	47.7	Blank	20P	0	0	3.9	52.8	13.3	66.5
	Blank	21	0	0	4.0	232	16.9	48.3	Blank	21P	0	0	3.9	50.8	14.6	73
	XLS0	22	10	0.2503	5.4	237	17.5	5.66	XLS0	22P	10	0.2506	6.7	48.4	12.8	0.48
		23	10	0.2505	5.6	240	17.3	5.75		23P	10	0.2503	6.7	49.7	12	0.34
		24	10	0.2502	5.7	236	18.9	5.53		24P	10	0.2502	6.7	43	12.8	0.21
	XLS130	25	10	0.2507	5.8	236	19	4.13	XLS130	25P	10	0.2503	6.7	43.3	13.1	0.41
		26	10	0.2505	5.9	238	18.2	3.92		26P	10	0.2505	6.6	42.9	13.2	0.26
		27	10	0.2504	5.9	238	19	4.07		27P	10	0.2504	6.7	62	13.4	0.18
	XLS330	28	10	0.25	5.8	236	17.7	4.28	XLS330	28P	10	0.2503	6.6	54	12.5	0.26
		29	10	0.2503	5.8	234	18.4	3.98		29P	10	0.2504	6.5	42.5	13.6	0.17
		30	10	0.25	5.8	232	18.7	4.11		30P	10	0.25	6.4	42.5	13.5	0.17
	XLS500	31	10	0.2508	6.1	238	19.1	1.67	XLS500	31P	10	0.2505	7.2	50.6	11.7	0.31
		32	10	0.2507	6.1	242	18.6	1.75		32P	10	0.2506	7.1	50.3	13.1	0.2
		33	10	0.2503	6.0	243	17.8	1.85		33P	10	0.2506	7.1	49.4	13.6	0.24
	XLS800	34	10	0.2509	5.8	236	18.4	10.8	XLS800	34P	10	0.2508	9.2	59	12.6	0.22
		35	10	0.2507	5.8	254	19.2	12.55		35P	10	0.2506	9.3	61	12.7	0.34
		36	10	0.2502	5.9	257	18	12.35		36P	10	0.2501	9.3	58	13	0.26
pH=6	Blank	37	0	0	5.4	102	16.1	49.8	Blank	37P	0	0	5.4	36.5	13.9	69.5
	Blank	38	0	0	5.4	109	14.9	49.4	Blank	38P	0	0	5.4	36.5	12.8	64
	Blank	39	0	0	5.4	105	16.7	48.15	Blank	39P	0	0	5.4	33.6	14.1	70.5
	XLS0	40	10	0.25	5.9	114	17.5	6.49	XLS0	40P	10	0.2502	6.8	37.1	14	0.44
		41	10	0.2503	5.9	112	16.9	5.8		41P	10	0.2504	7.2	37.8	14.3	0.45
		42	10	0.2503	5.9	107	17.5	5.73		42P	10	0.2503	7.3	37.3	14.4	0.47
	XLS130	43	10	0.2508	6.0	112	16.9	4.06	XLS130	43P	10	0.2505	7.2	42.1	13.4	0.33
		44	10	0.2505	6.0	114	18.3	4.3		44P	10	0.2502	7.3	40.5	14.6	0.22
		45	10	0.2502	6.0	114	17.2	3.59		45P	10	0.2501	7.3	40.2	15	0.32
	XLS330	46	10	0.2508	5.9	116	17.8	4.64	XLS330	46P	10	0.2504	7.1	37.5	15.4	0.04
		47	10	0.2504	5.9	110	18.3	4.54		47P	10	0.2505	7.0	37.6	15.4	0.07
		48	10	0.2507	5.9	112	18.1	4.41		48P	10	0.2506	6.9	38.2	15.5	0.03
	XLS500	49	10	0.2507	6.0	122	17.4	2.15	XLS500	49P	10	0.2503	7.1	44.2	15.7	0.04
		50	10	0.25	6.1	114	18.5	1.88		50P	10	0.2504	7.1	44.1	16.2	0.07
		51	10	0.25	6.0	115	18.9	2.43		51P	10	0.2506	7.5	44.4	14.6	0.06
	XLS800	52	10	0.2507	5.8	115	18.3	14	XLS800	52P	10	0.2503	9.3	47.4	16.3	0.03
		53	10	0.2502	5.9	118	17.3	9.05		53P	10	0.25	9.4	49.2	16.2	0.02
		54	10	0.2504	6.0	112	18.9	9.7		54P	10	0.2502	9.4	49.5	16.2	0.06
pH=8	Blank	55i	0	0	7.2	114	11.4	36.5	Blank	55P	0	0	6.3	35.3	14.4	72
	Blank	56i	0	0	7.2	117	11.7	6.6	Blank	56P	0	0	6.3	34.6	13.9	69.5
	Blank	57i	0	0	7.1	110	12.7	3.7	Blank	57P	0	0	6.2	34.7	14.5	72.5
	XLS0	58i	10	0.25	8.3	124	10.2	0.28	XLS0	58P	10	0.2502	7.8	42.1	14.6	0.81
		59i	10	0.2501	8.6	128	9.4	0.17		59P	10	0.2501	7.7	41.9	14.6	0.06
		60i	10	0.2503	8.6	126	9.9	0.16		60P	10	0.2506	7.9	40.1	14.6	0.06
	XLS130	61i	10	0.2504	8.5	122	10.3	0.12	XLS130	61P	10	0.2507	7.9	47.4	15.2	0.17
		62i	10	0.2506	8.4	123	10.2	0.1		62P	10	0.2503	7.9	44.6	13.7	0.13
		63i	10	0.2505	8.4	122	10.3	0.12		63P	10	0.2502	7.9	43.7	16	0.29
	XLS330	64i	10	0.2502	8.0	122	10.6	0.28	XLS330	64P	10	0.2502	7.6	41.6	16	0.07
		65i	10	0.2504	7.9	128	9.7	0.24		65P	10	0.2507	7.4	41.9	16	0.05
		66i	10	0.2505	7.7	123	10.8	0.21		66P	10	0.2505	7.3	41.6	15.9	0.11
	XLS500	67i	10	0.2506	7.9	124	10.7	0.16	XLS500	67P	10	0.2505	7.6	51.7	15.5	0.03
		68i	10	0.2505	7.9	125	10.9	0.12		68P	10	0.2502	7.8	50	14.7	0.05
		69i	10	0.25	7.8	129	10.7	0.13		69P	10	0.2507	7.9	50.3	16	0.35
	XLS800	70i	10	0.2502	9.7	136	10.9	0.28	XLS800	70P	10	0.2501	9.6	59	16.2	0.08
		71i	10	0.2507	9.8	136	10.5	0.17		71P	10	0.2502	9.7	59	16.1	0.11
		72i	10	0.2508	9.8	133	10.4	0.2		72P	10	0.2503	9.7	57	16.3	0.04

Appendix 5-Effect of time contact.

For aqueous solution of Cu.

Laboratory utensils:

- 1) precision scale
- 2) plastic droplets
- 3) NaOH solution and HNO₃ solution
- 4) plastic centrifugal test tubes
- 5) thermal shaker chamber
- 6) centrifugal
- 7) pH-meter
- 8) instrument to measure TDS and temperature

Procedure:

- 1) weighing 0,250g of clay saponite thermally modified at 0/130/330/500 / 800°C and placement on plastic test tubes
- 2) addition of 25 ml of copper nitrate (Cu(NO₃)₂* 3H₂O) of a concentration of 50g/L whose pH was adjusted 4 using 0.1 M NaOH and 0.1 M HNO₃ solutions
- 3) place the samples in a thermal shaker chamber with a constant temperature of 22°C for 5, 30, 60, 90, 120 minutes
- 4) centrifuge the samples for 15 minutes
- 5) measurement of pH, TDS and temperature
- 6) analysis of the samples using atomic adsorption spectrometry with flame (AAS)

For aqueous solution of Pb.

Laboratory utensils:

- 1) precision scale
- 2) plastic droplets
- 3) NaOH solution and HNO₃ solution
- 4) plastic centrifugal test tubes
- 5) thermal shaker chamber
- 6) centrifugal
- 7) pH-meter
- 8) instrument to measure TDS and temperature

Procedure:

- 1) weighing 0,250g of clay saponite thermally modified at 0/130/330/500 / 800°C and placement on plastic test tubes
- 2) addition of 25 ml of copper nitrate (Pb(NO₃)₂) of a concentration of 50g/L whose pH was adjusted 4 using 0.1 M NaOH and 0.1 M HNO₃ solutions
- 3) place the samples in a thermal shaker chamber with a constant temperature of 22°C for 5, 30, 60, 90, 120 minutes
- 4) centrifuge the samples for 15 minutes
- 5) measurement of pH, TDS and temperature
- 6) analysis of the samples using atomic adsorption spectrometry with flame (AAS)

Experimental results:

Assessment of Fe- rich smectite clays in adsorbing Pb and Cu from aqueous solutions:
A batch experiment approach

	Cu(NO3)2*3H2O	sample	g/L	weight (g)	ph	TDS (mg/L)	T (C)	AAS (mg/L)	Pb(NO3)2	sample	g/L	weight (g)	ph	TDS (mg/L)	T (C)	AAS (mg/L)
t=5min	Blank	5.1	0	0	4.0	118	11.7	48.25	Blank	5.1P	0	0	4.1	55	9.5	36.5
	Blank	5.2	0	0	4.1	117	11.4	46.8	Blank	5.2P	0	0	4.1	52.6	9.5	39
	Blank	5.3	0	0	4.0	112	11.8	46.5	Blank	5.3P	0	0	3.9	59	9.5	36.05
	XLS0	5.4	10	0.2506	5.3	104	11.9	8.89	XLS0	5.4P	10	0.25	6.4	40.6	9.8	0.44
		5.5	10	0.2501	5.5	104	12.8	8.71		5.5P	10	0.2504	6.5	39.3	8.9	0.45
		5.6	10	0.2502	5.5	110	11.8	9.19		5.6P	10	0.2504	6.4	39.7	9.7	0.34
	XLS130	5.7	10	0.2504	5.5	106	12.5	6.9	XLS130	5.7P	10	0.2504	6.3	36.9	9.8	0.33
		5.8	10	0.2501	5.6	105	12.8	7.05		5.8P	10	0.2506	6.6	40.1	11	0.45
		5.9	10	0.2507	5.6	110	13.2	6.74		5.9P	10	0.2505	6.5	38.1	10.4	0.34
	XLS330	5.10	10	0.2502	5.4	113	12.4	12.5	XLS330	5.10P	10	0.2503	6.0	39.3	8.6	0.54
		5.11	10	0.25	5.4	112	12.7	12.35		5.11P	10	0.2505	5.7	39.5	10.9	0.58
		5.12	10	0.2502	5.3	110	13.6	10.4		5.12P	10	0.2504	6.1	41.4	11.3	0.55
	XLS500	5.13	10	0.2502	5.5	111	13.4	12.85	XLS500	5.13P	10	0.2502	6.1	40.5	10.5	0.2
		5.14	10	0.2503	5.4	113	11.6	12.9		5.14P	10	0.2507	6.2	41.5	12.2	0.13
	XLS800	5.15	10	0.2505	5.4	110	12.8	14.05	XLS800	5.15P	10	0.25	6.2	39	12.3	0.17
		5.16	10	0.2502	5.4	112	13.5	24.75		5.16P	10	0.2508	6.4	42.3	12	0.24
		5.17	10	0.2502	5.6	112	13.3	21.4		5.17P	10	0.2505	6.3	58	9.8	0.6
		5.18	10	0.2502	5.6	115	12.9	23.45		5.18P	10	0.2502	6.6	43.2	11.7	0.22
t=30min	Blank	30.1	0	0	4.0	120	13.4	49.25	Blank	30.1P	0	0	3.8	370	12.6	43.95
	Blank	30.2	0	0	3.9	127	11.8	48.95	Blank	30.2P	0	0	3.7	62	10.1	38.7
	Blank	30.3	0	0	4.0	121	13.6	47.25	Blank	30.3P	0	0	3.9	52.1	12.3	41.15
	XLS0	30.4	10	0.2501	5.6	113	12.3	6.94	XLS0	30.4P	10	0.2505	6.5	43.1	10	0.1
		30.5	10	0.2507	5.6	115	11.1	6.86		30.5P	10	0.2503	6.5	41.4	9.2	0.1
		30.6	10	0.2503	5.6	109	12	6.91		30.6P	10	0.2502	6.6	40.3	10	0.09
	XLS130	30.7	10	0.2508	5.7	108	12.3	5.41	XLS130	30.7P	10	0.2504	6.6	40	10.9	0.09
		30.8	10	0.2503	5.7	110	12.1	5.47		30.8P	10	0.2505	6.6	40.8	11.1	0.09
		30.9	10	0.2503	5.8	107	12.4	5.42		30.9P	10	0.2502	6.6	40.5	11.5	0.09
	XLS330	30.10	10	0.2505	5.7	111	13.5	7.16	XLS330	30.10P	10	0.2506	6.5	43.7	9.7	0.04
		30.11	10	0.2504	5.6	118	11.7	7.73		30.11P	10	0.2502	6.4	40.5	11.3	0.08
		30.12	10	0.2507	5.6	110	12.8	7.34		30.12P	10	0.2508	6.3	40.5	10.8	0.12
	XLS500	30.13	10	0.2503	5.7	114	13.3	5.68	XLS500	30.13P	10	0.25	6.4	41.9	11.5	0.07
		30.14	10	0.2504	5.8	114	13.7	4.74		30.14P	10	0.25	6.4	43	12	0.05
		30.15	10	0.2503	5.8	113	13.1	5.04		30.15P	10	0.2504	6.5	43.8	12	0.05
	XLS800	30.16	10	0.2504	5.8	114	13.5	13.85	XLS800	30.16P	10	0.2506	7.9	49.5	10.5	0.03
		30.17	10	0.2503	###	121	11.6	13.9		30.17P	10	0.25	7.9	49.3	9.9	0.05
		30.18	10	0.2506	5.9	113	13.2	13.7		30.18P	10	0.2504	8.3	46.2	11.7	0.03
t=60min	Blank	60.1	0	0	4.0	117	12.7	45.2	Blank	60.1P	0	0	3.7	66	10.1	48.45
	Blank	60.2	0	0	3.9	130	11.5	45.9	Blank	60.2P	0	0	4.1	54	12.4	40.5
	Blank	60.3	0	0	4.0	117	13	44.85	Blank	60.3P	0	0	4.0	52.5	13.7	42.6
	XLS0	60.4	10	0.2503	5.5	110	13.6	6.73	XLS0	60.4P	10	0.25	6.4	45.3	12.6	0.11
		60.5	10	0.2506	5.5	118	11.9	6.7		60.5P	10	0.25	6.5	46.7	9.8	0.05
		60.6	10	0.2506	5.6	113	13.4	6.59		60.6P	10	0.2504	6.5	43.8	11.5	0.07
	XLS130	60.7	10	0.2505	5.7	112	14.3	5.03	XLS130	60.7P	10	0.2503	6.7	45.2	12.6	0.14
		60.8	10	0.2508	5.8	109	14.5	4.95		60.8P	10	0.25	6.7	44.2	12.6	0.06
		60.9	10	0.2508	5.7	113	14	5.64		60.9P	10	0.2507	6.6	44.9	12.6	0.04
	XLS330	60.10	10	0.2502	5.7	112	13.9	5.72	XLS330	60.10P	10	0.25	6.5	44.5	9.6	0.07
		60.11	10	0.2502	5.6	118	12	5.66		60.11P	10	0.2504	6.4	42.3	11.7	0.04
		60.12	10	0.2503	5.6	113	14	5.65		60.12P	10	0.2504	6.4	42.3	12.3	0.03
	XLS500	60.13	10	0.2502	5.7	111	14.3	4.33	XLS500	60.13P	10	0.2505	6.9	48.2	10.2	0.05
		60.14	10	0.2502	5.7	109	14.3	3.79		60.14P	10	0.2501	6.9	47	12.6	0.03
		60.15	10	0.2505	5.8	111	14.6	4.01		60.15P	10	0.25	6.9	46.7	12.8	0.03
	XLS800	60.16	10	0.2503	5.7	113	14.3	2.78	XLS800	60.16P	10	0.2505	8.6	50.4	10.7	0.05
		60.17	10	0.2501	5.7	122	12	2.86		60.17P	10	0.2505	9.0	51.1	10.7	0.02
		60.18	10	0.2502	5.7	115	14.1	2.9		60.18P	10	0.2505	8.9	48.6	12.4	0.03
t=90min	Blank	90.1	0	0	3.8	243	14.1	49.5	Blank	90.1P	0	0	4.0	51.9	16.3	38.45
	Blank	90.2	0	0	4.1	132	11.8	49.05	Blank	90.2P	0	0	4.0	54	16.1	39.45
	Blank	90.3	0	0	4.1	123	14.5	48.15	Blank	90.3P	0	0	3.8	62	16.5	40.75
	XLS0	90.4	10	0.2501	5.6	110	12.5	6.89	XLS0	90.4P	10	0.2504	6.4	52.2	15	0.22
		90.5	10	0.2504	5.7	115	10.9	6.42		90.5P	10	0.2503	6.6	18.5	14.4	0.16
		90.6	10	0.2501	5.7	112	11.9	6.47		90.6P	10	0.25	6.6	40.1	15.2	0.15
	XLS130	90.7	10	0.2506	5.8	107	12.4	4.8	XLS130	90.7P	10	0.2503	6.6	41.2	15.5	0.03
		90.8	10	0.2504	5.8	109	12.7	4.86		90.8P	10	0.2504	6.6	45.3	15.5	0.04
		90.9	10	0.2505	5.8	107	12.5	4.85		90.9P	10	0.25	6.6	40.8	15.7	0.1
	XLS330	90.10	10	0.2503	5.7	109	13.1	5.52	XLS330	90.10P	10	0.25	6.5	44.3	14.4	0.11
		90.11	10	0.2504	5.7	118	10.8	5.75		90.11P	10	0.2502	6.5	40.2	14.9	0.06
		90.12	10	0.2505	5.7	113	12.3	5.61		90.12P	10	0.2506	6.5	41	15.4	0.06
	XLS500	90.13	10	0.2506	5.8	112	12.7	3.18	XLS500	90.13P	10	0.2503	6.8	46.8	15.4	0.03
		90.14	10	0.2505	5.9	114	12.9	2.93		90.14P	10	0.25	6.8	51.8	16.1	0.03
		90.15	10	0.2504	5.9	114	13	3.08		90.15P	10	0.2503	6.8	44.2	16.3	0.04
	XLS800	90.16	10	0.2501	5.8	113	13.5	11.5	XLS800	90.16P	10	0.2505	9.1	60	15.7	0.01
		90.17	10	0.2504	5.8	118	11.3	11.05		90.17P	10	0.2506	9.4	56	15	0.01
		90.18	10	0.2506	5.9	111	13.8	12		90.18P	10	0.25	9.3	58	16.3	0.03
t=120min	Blank	120.1	0	0	4.1	122	14.3	49.75	Blank	120.1P	0	0	4.0	52.8	16.8	45.05
	Blank	120.2	0	0	4.1	130	12.6	46.7	Blank	120.2P	0	0	4.0	51.6	15	40.7
	Blank	120.3	0	0	4.1	118	14.4	45.95	Blank	120.3P	0	0	4.0	48.9	16.2	40.75
	XLS0	120.4	10	0.2503	5.7	111	13.7	5.66	XLS0	120.4P	10	0.2503	6.7	44.3	16	0.05
		120.5	10	0.2506	5.8	115	12.5	5.65		120.5P	10	0.2505	6.8	44	14.1	0.11
		120.6	10	0.2502	5.8	110	13.6	5.51		120.6P						

Appendix 6- Effect of ionic strength.

For the aqueous solution of Cu.

Laboratory utensils:

- 1) precision scale
- 2) plastic droplets
- 3) NaOH solution and HNO₃ solution
- 4) plastic centrifugal test tubes
- 5) thermal shaker chamber
- 6) centrifugal
- 7) pH-meter
- 8) instrument to measure TDS and temperature
- 9) NaNO₃

Procedure:

- 1) weighing 0,250g of clay saponite thermally modified at 0/130/330/500 / 800°C and placement on plastic test tubes
- 2) addition of 25 ml of copper nitrate (Cu(NO₃)₂* 3H₂O) of a concentration of 50g/L whose pH was adjusted 4 using 0,1 M NaOH and 0,1 M HNO₃ solutions
- 3) addition of 0,42505/4,2525/21,2525g NaNO₃
- 4) place the samples in a thermal shaker chamber with a constant temperature of 22°C for 120 minutes
- 5) centrifuge the samples for 15 minutes
- 6) measurement of pH, TDS and temperature
- 7) analysis of the samples using atomic adsorption spectrometry with flame (AAS)

For the aqueous solution of Pb.

Laboratory utensils:

- 1) precision scale
- 2) plastic droplets
- 3) NaOH solution and HNO₃ solution
- 4) plastic centrifugal test tubes
- 5) thermal shaker chamber
- 6) centrifugal
- 7) pH-meter
- 8) instrument to measure TDS and temperature
- 9) NaNO₃

Procedure:

- 1) weighing 0,250g of clay saponite thermally modified at 0/130/330/500 / 800°C and placement on plastic test tubes
- 2) addition of 25 ml of copper nitrate (Pb(NO₃)₂) of a concentration of 50g/L whose pH was adjusted 4 using 0,1 M NaOH and 0,1 M HNO₃ solutions
- 3) addition of 0,42505/4,2525/21,2525g NaNO₃
- 4) place the samples in a thermal shaker chamber with a constant temperature of 22°C for 120 minutes
- 5) centrifuge the samples for 15 minutes
- 6) measurement of pH, TDS and temperature
- 7) analysis of the samples using atomic adsorption spectrometry with flame (AAS)

Assessment of Fe- rich smectite clays in adsorbing Pb and Cu from aqueous solutions:
A batch experiment approach

Experimental results:

	Cu(NO3)2*3H2O	sample	g/L	weight (g)	ph	TDS (g/L)	T (C)	AAS (mg/L)	Pb(NO3)2	sample	g/L	weight (g)	ph	TDS (g/L)	T (C)	AAS (mg/L)	
0,01M	Blank	1	0	0	4.0	0.71	18.8	43.55	Blank	1P	0	0	3.9	0.63	17.8	40.1	
	Blank	2	0	0	4.0	0.73	17.7	42.2	Blank	2P	0	0	3.9	0.68	16.2	39.3	
	Blank	3	0	0	4.0	0.7	18.7	40.3	Blank	3P	0	0	4.0	0.66	17.7	41.15	
	XLS0	4	10	0.2501	5.7	0.69	19.1	5.72	XLS0	4P	10	0.2508	6.5	0.63	16.6	0.09	
			5	10	0.2505	5.7	0.71	18.3	5.81		5P	10	0.2506	6.5	0.67	15.3	0.18
			6	10	0.2503	5.8	0.69	18.7	5.81		6P	10	0.2505	6.5	0.63	16.3	0.16
	XLS130	7	10	0.2501	5.9	0.68	19.2	4.46	XLS130	7P	10	0.2502	6.6	0.62	16.7	0.18	
			8	10	0.2508	5.9	0.66	19	4.57		8P	10	0.2502	6.6	0.63	16.8	0.26
			9	10	0.2506	6.0	0.67	18.8	4.23		9P	10	0.2501	6.7	0.61	16.7	0.26
	XLS330	10	10	0.2505	5.8	0.68	19.3	4.35	XLS330	10P	10	0.2506	6.1	0.67	15.6	0.29	
			11	10	0.2504	5.8	0.71	19	4.58		11P	10	0.25	6.1	0.62	17.2	0.32
			12	10	0.2507	5.8	0.68	20	4.9		12P	10	0.2504	6.2	0.64	16.9	0.19
	XLS500	13	10	0.2507	6.0	0.67	20.3	2.18	XLS500	13P	10	0.2503	6.7	0.62	17.5	0.1	
			14	10	0.2502	6.0	0.67	20	2.22		14P	10	0.2501	6.7	0.62	17.6	0.09
			15	10	0.25	6.0	0.67	19.7	2.71		15P	10	0.2501	6.7	0.62	17.4	0.08
	XLS800	16	10	0.2501	5.8	0.68	20.3	11.1	XLS800	16P	10	0.2499	9.1	0.66	17.1	0.05	
		17	10	0.2504	6.0	0.71	19.3	13.1		17P	10	0.2504	9.2	0.69	15.4	0.03	
		18	10	0.2504	6.1	0.69	20.5	10.65		18P	10	0.2503	8.8	0.65	18.2	0.04	
0,1M	Blank	19	0	0	4.1	5.2	18.7	37.95	Blank	19P	0	0	3.9	5.4	17.7	42.75	
	Blank	20	0	0	4.1	5.4	17.8	40.75	Blank	20P	0	0	4.0	5.8	15.9	40.2	
	Blank	21	0	0	4.0	5.3	18.8	41.35	Blank	21P	0	0	3.9	5.6	17.2	41.1	
	XLS0	22	10	0.2502	5.5	5.3	16.7	12.5	XLS0	22P	10	0.2501	6.3	5.4	16.4	1	
			23	10	0.2502	5.6	5	17.9	13.2		23P	10	0.2505	6.3	5.7	14.7	1.02
			24	10	0.2506	5.6	5.1	18.6	12.5		24P	10	0.2501	6.4	5.5	16.1	0.92
	XLS130	25	10	0.25	5.8	5.3	18.5	9.08	XLS130	25P	10	0.2505	6.4	5.3	16.6	1	
			26	10	0.2506	5.8	5.2	18.6	9.25		26P	10	0.25	6.4	5.3	16.7	1.59
			27	10	0.25	5.8	5.1	18.5	8.9		27P	10	0.2507	6.4	5.4	16.7	0.81
	XLS330	28	10	0.2505	5.7	5.5	17.5	9.32	XLS330	28P	10	0.2503	5.9	5.5	16	1.61	
			29	10	0.2506	5.6	5.3	18.5	9.25		29P	10	0.2501	5.9	5.8	14.3	1.56
			30	10	0.2506	5.6	5.3	18.6	9.32		30P	10	0.25	5.9	5.5	16.7	2.71
	XLS500	31	10	0.2505	5.8	5.3	18.6	6.39	XLS500	31P	10	0.2501	6.6	5.5	16.8	0.24	
			32	10	0.2505	5.9	5.2	18.6	6.15		32P	10	0.2506	6.6	5.4	17	0.08
			33	10	0.2508	5.8	5.3	18.4	6.69		33P	10	0.2507	6.6	5.4	17.2	0.09
	XLS800	34	10	0.2504	5.7	5.2	20	3.15	XLS800	34P	10	0.25	8.8	5.6	15.7	0.18	
		35	10	0.2504	5.8	5.6	17.5	3.35		35P	10	0.2505	8.7	5.8	14.9	0.38	
		36	10	0.25	5.9	5.3	19.4	3.26		36P	10	0.2499	8.5	5.6	16.7	0.43	
0,5M	Blank	37	0	0	3.6	21.2	18.6	41.55	Blank	37P	0	0	3.9	21.2	16.5	38.35	
	Blank	38	0	0	3.5	21.8	17.1	40.85	Blank	38P	0	0	4.0	21.8	15.2	38.35	
	Blank	39	0	0	3.8	21.2	19	42.1	Blank	39P	0	0	4.1	21.2	16.8	39.55	
	XLS0	40	10	0.2502	5.6	20.6	18.5	18.85	XLS0	40P	10	0.2503	6.1	20.6	17.1	4.03	
			41	10	0.2505	5.7	21.7	17	18.55		41P	10	0.2504	6.1	22.2	15.2	4.57
			42	10	0.2504	5.8	21.1	17.8	18.5		42P	10	0.2505	6.1	21.2	16.4	3.54
	XLS130	43	10	0.25	5.9	20.6	18.6	13.7	XLS130	43P	10	0.25	6.4	20.9	16.8	2.09	
			44	10	0.2505	5.9	20	18.5	13.4		44P	10	0.25	6.4	20.2	17	1.71
			45	10	0.2508	5.9	20.3	18.3	13		45P	10	0.2502	6.4	20.5	17.1	1.92
	XLS330	46	10	0.2507	5.7	21.6	16.9	12.5	XLS330	46P	10	0.25	5.8	21.1	15.8	3.74	
			47	10	0.2404	5.6	20.6	18.7	15		47P	10	0.2503	5.8	22.4	15.6	4.54
			48	10	0.2503	5.6	21	18.3	12.4		48P	10	0.2504	5.8	21.1	17.1	4.63
	XLS500	49	10	0.2498	5.7	20.3	19	12.3	XLS500	49P	10	0.2501	6.4	20.8	18.4	1.02	
			50	10	0.2508	5.8	20.2	19.2	9.75		50P	10	0.2505	6.5	20.4	18.2	0.67
			51	10	0.2507	5.8	20.3	18.7	11.95		51P	10	0.25	6.5	20.5	17.9	0.8
	XLS800	52	10	0.25	5.8	20.9	18.6	15.35	XLS800	52P	10	0.2498	8.9	22	16.4	0.14	
		53	10	0.2503	5.8	22.4	16.3	13.25		53P	10	0.2503	9.0	22.6	15.2	0.18	
		54	10	0.2502	5.9	20.3	18.9			54P	10	0.2502	8.9	22	16.9	0.22	

Appendix 7- Adsorption isotherms.

For the aqueous solution of Cu.

Laboratory utensils:

- 1) precision scale
- 2) plastic droplets
- 3) NaOH solution and HNO₃ solution
- 4) plastic centrifugal test tubes
- 5) thermal shaker chamber
- 6) centrifugal
- 7) pH-meter
- 8) instrument to measure TDS and temperature

Procedure:

- 1) weighing 0,250g of clay saponite thermally modified at 0/130/330/500 / 800°C and placement on plastic test tubes
- 2) addition of 25 ml of copper nitrate (Cu(NO₃)₂* 3H₂O) of a concentration of 25, 50, 75, 100g/L whose pH was adjusted 4 using 0,1 M NaOH and 0,1 M HNO₃ solutions
- 3) place the samples in a thermal shaker chamber with a constant temperature of 22°C for 120 minutes
- 4) centrifuge the samples for 15 minutes
- 5) measurement of pH, TDS and temperature
- 6) analysis of the samples using atomic adsorption spectrometry with flame (AAS)

For the aqueous solution of Pb.

Laboratory utensils:

- 1) precision scale
- 2) plastic droplets
- 3) NaOH solution and HNO₃ solution
- 4) plastic centrifugal test tubes
- 5) thermal shaker chamber
- 6) centrifugal
- 7) pH-meter
- 8) instrument to measure TDS and temperature

Procedure:

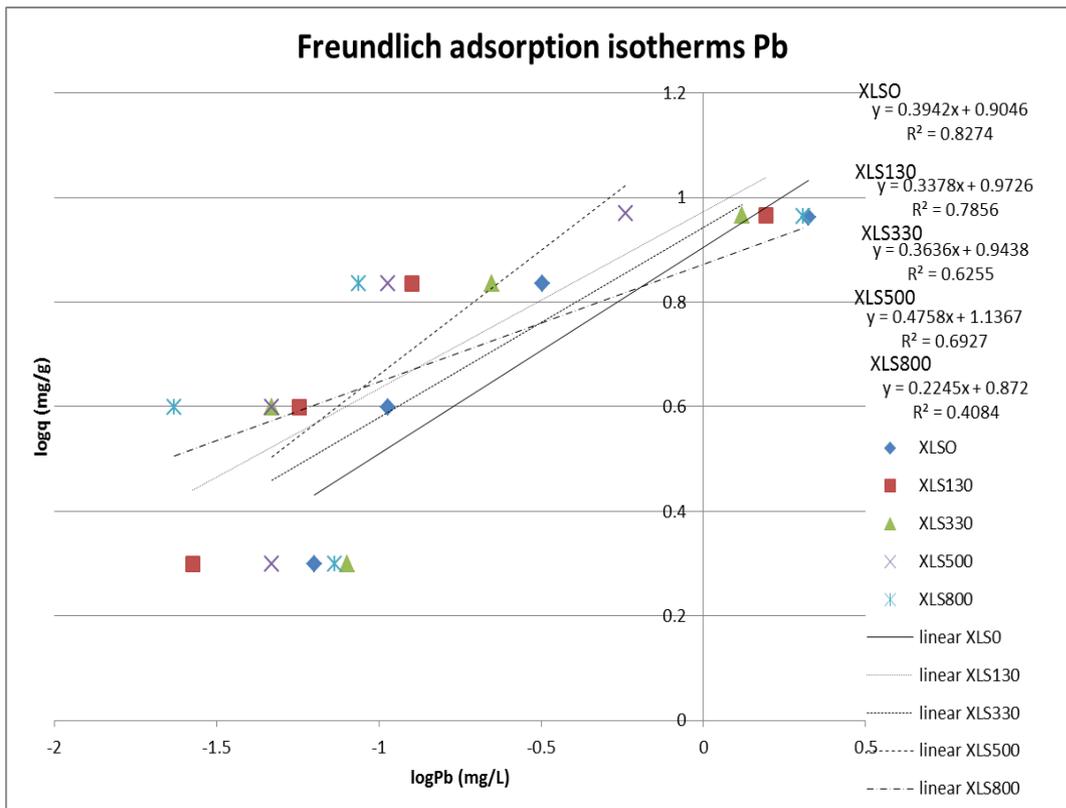
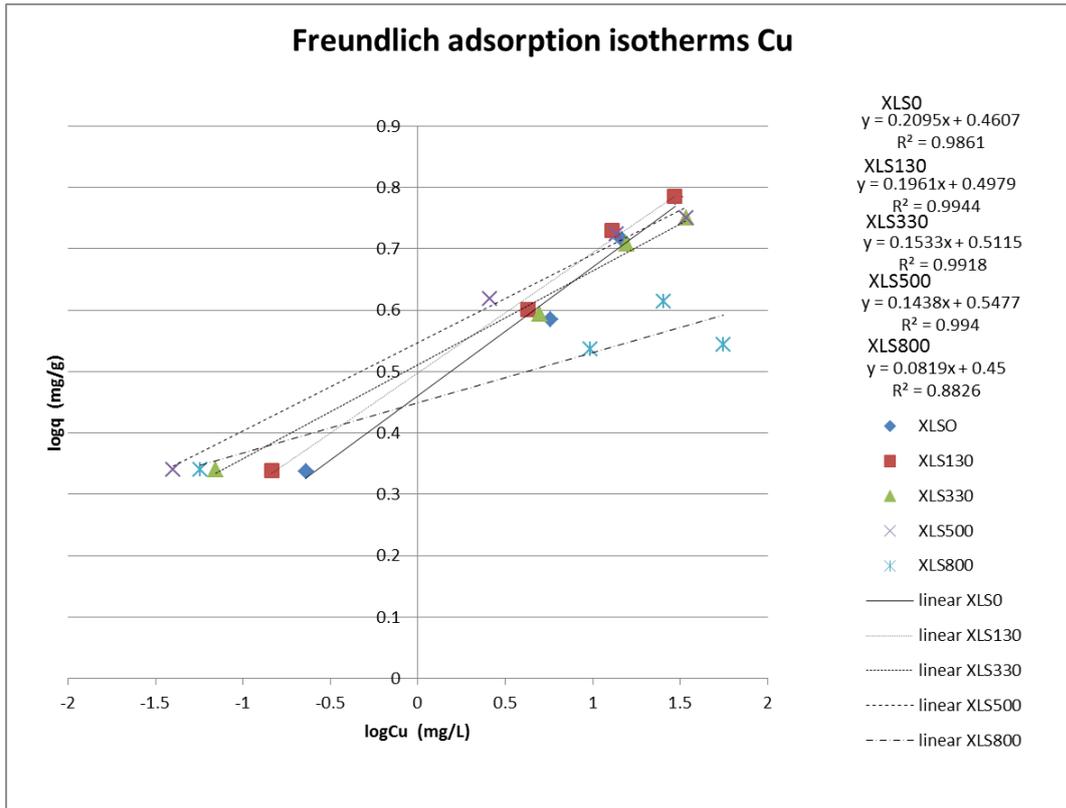
- 1) weighing 0,250g of clay saponite thermally modified at 0/130/330/500 / 800°C and placement on plastic test tubes
- 2) addition of 25 ml of copper nitrate (Pb(NO₃)₂) of a concentration of 25, 50, 75, 100g/L whose pH was adjusted 4 using 0,1 M NaOH and 0,1 M HNO₃ solutions
- 3) place the samples in a thermal shaker chamber with a constant temperature of 22°C for 120 minutes
- 4) centrifuge the samples for 15 minutes
- 5) measurement of pH, TDS and temperature
- 6) analysis of the samples using atomic adsorption spectrometry with flame (AAS)

Assessment of Fe- rich smectite clays in adsorbing Pb and Cu from aqueous solutions:
A batch experiment approach

Experimental results:

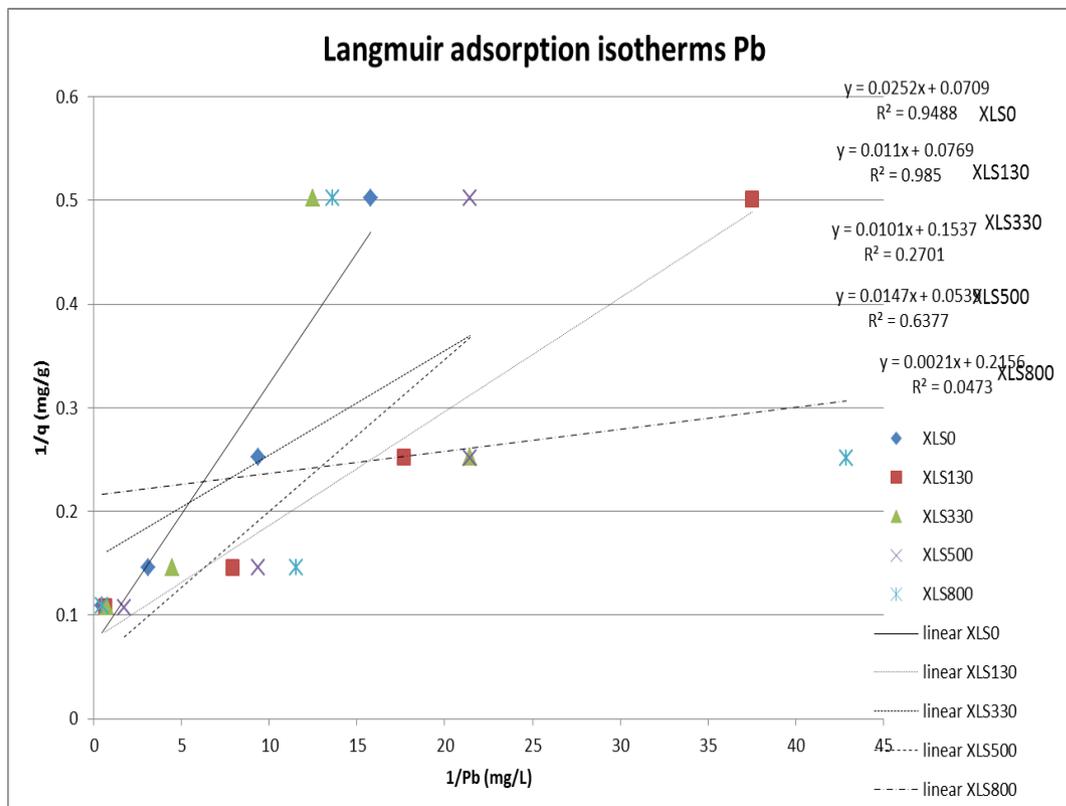
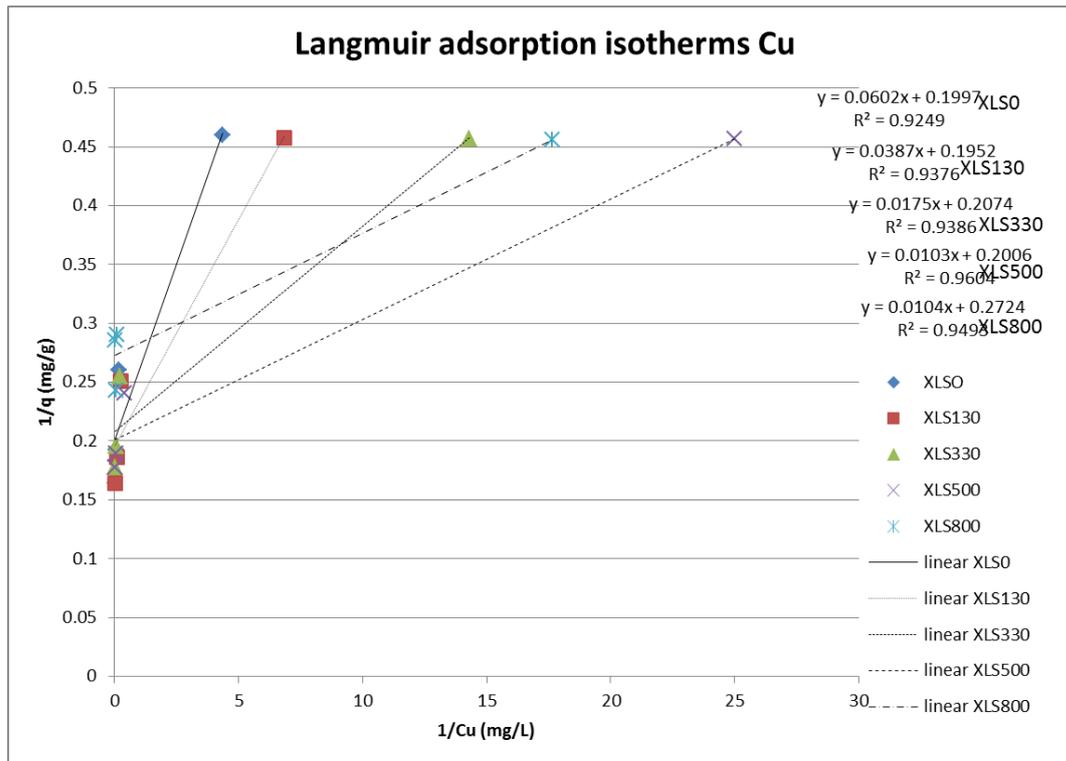
	Cu(NO3)2*3H2O	sample	g/L	weight (g)	ph	TDS (mg/L)	T (C)	AAS (mg/L)	Pb(NO3)2	sample	g/L	weight (g)	ph	TDS (mg/L)	T (C)	AAS (mg/L)
25mg/L	Blank	1	0	0	3.8	59	19.3	21.9	Blank	1P	0	0	3.9	36.6	23.3	20.3
	Blank	2	0	0	3.9	61	20.5	21.9	Blank	2P	0	0	4.4	22.9	24	20.15
	Blank	3	0	0	3.9	60	20.9	22.3	Blank	3P	0	0	4.3	24.3	23.3	19.45
	XLS0	4	10	0.2506	6.3	63	20.2	0.21	XLS0	4P	10	0.2505	7.4	27.9	24.4	0.08
		5	10	0.25	6.4	64	19.7	0.26		5P	10	0.2501	7.6	27.1	23.6	0.06
		6	10	0.2503	6.4	62	20.5	0.22		6P	10	0.25	7.5	27.6	24.3	0.05
	XLS130	7	10	0.2502	6.6	62	20.8	0.2	XLS130	7P	10	0.2501	7.5	28	24.9	0.03
		8	10	0.25	6.6	62	20.9	0.12		8P	10	0.2503	7.5	28.1	25	0.03
		9	10	0.2501	6.7	61	21.1	0.12		9P	10	0.2505	7.6	28.1	25	0.02
	XLS330	10	10	0.2502	6.3	66	19.3	0.06	XLS330	10P	10	0.2504	7.0	30.3	22.6	0.1
		11	10	0.2507	6.3	64	20.8	0.07		11P	10	0.2504	7.0	29.8	24.1	0.06
		12	10	0.2505	6.3	64	21.1	0.08		12P	10	0.2503	6.9	29.2	24.8	0.08
	XLS500	13	10	0.2506	6.8	67	21.3	0.02	XLS500	13P	10	0.2502	7.6	33.3	25.6	0.03
		14	10	0.2505	6.9	66	21.5	0.04		14P	10	0.2502	7.7	32.9	25.8	0.05
		15	10	0.2506	6.8	67	21.5	0.06		15P	10	0.2508	7.6	32.6	25.6	0.06
	XLS800	16	10	0.2503	7.3	67	20.3	0.04	XLS800	16P	10	0.2501	9.5	42.2	27.2	0.08
		17	10	0.2503	7.7	70	18.2	0.05		17P	10	0.2504	9.1	32.9	23.6	0.08
		18	10	0.2503	8.0	67	20.8	0.08		18P	10	0.2501	9.4	39.7	26.6	0.06
50mg/L	Blank	19	0	0	3.9	108	19	44.4	Blank	19P	0	0	4.0	40.5	22.7	39.5
	Blank	20	0	0	4.0	105	18.4	44	Blank	20P	0	0	4.1	37.8	23	39
	Blank	21	0	0	4.0	108	19.1	44.15	Blank	21P	0	0	3.9	39.2	22.7	40.8
	XLS0	22	10	0.25	5.6	109	18.8	5.61	XLS0	22P	10	0.25	6.6	40	24.1	0.1
		23	10	0.2502	5.6	108	18.3	5.87		23P	10	0.2504	6.8	40.8	22.7	0.12
		24	10	0.2499	5.7	108	19.1	5.73		24P	10	0.2501	6.9	40.2	23.7	0.1
	XLS130	25	10	0.25	5.7	106	19.4	4.31	XLS130	25P	10	0.2509	6.9	40.5	24	0.07
		26	10	0.2502	5.7	106	19.7	4.21		26P	10	0.25	6.9	39.7	24.1	0.05
		27	10	0.2501	5.7	104	19.7	4.27		27P	10	0.2504	6.9	39.3	24.2	0.05
	XLS330	28	10	0.25	5.3	108	19.3	5.04	XLS330	28P	10	0.2501	6.4	39.8	24	0.03
		29	10	0.2501	5.4	112	18.3	4.88		29P	10	0.2508	6.3	38.9	25.1	0.06
		30	10	0.25	5.5	109	19.7	4.93		30P	10	0.2508	6.3	38.7	25.5	0.05
	XLS500	31	10	0.2507	5.8	109	20.1	2.53	XLS500	31P	10	0.25	6.9	42	26	0.07
		32	10	0.2502	5.9	109	20.4	2.61		32P	10	0.2503	7.1	42.7	25.9	0.04
		33	10	0.2505	5.8	109	20.2	2.6		33P	10	0.2501	7.1	43.5	25.1	0.03
	XLS800	34	10	0.2505	5.7	112	20	8.9	XLS800	34P	10	0.2502	8.9	49.7	24.1	0.03
		35	10	0.25	5.8	115	18.3	10.35		35P	10	0.2506	8.9	49.6	23.2	0.01
		36	10	0.2503	5.9	112	19.3	9.95		36P	10	0.2502	9.0	49.3	24.6	0.03
75mg/L	Blank	37	0	0	4.0	156	20.5	64.4	Blank	37P	0	0	3.9	62	22.4	65.4
	Blank	38	0	0	4.0	157	19.3	63.7	Blank	38P	0	0	3.9	59	22.6	68.2
	Blank	39	0	0	4.1	156	20.1	72	Blank	39P	0	0	4.0	59	22.5	72.5
	XLS0	40	10	0.2506	5.4	159	19.6	14.3	XLS0	40P	10	0.2501	6.3	55	23.7	0.31
		41	10	0.2503	5.4	152	20.6	14.3		41P	10	0.2501	6.5	56	22.5	0.32
		42	10	0.2499	5.4	152	20.3	15.6		42P	10	0.25	6.5	52.7	23.4	0.33
	XLS130	43	10	0.2506	5.6	150	20.8	11.7	XLS130	43P	10	0.2501	6.5	54	23.7	0.12
		44	10	0.2501	5.5	149	20.9	13.8		44P	10	0.2502	6.5	57	23.8	0.13
		45	10	0.2507	5.6	149	21	13		45P	10	0.2503	6.6	53	23.9	0.13
	XLS330	46	10	0.2503	5.3	164	18.7	14.9	XLS330	46P	10	0.2505	6.0	52.8	24.1	0.18
		47	10	0.2503	5.3	157	20.8	15.9		47P	10	0.2501	5.8	56	22.2	0.3
		48	10	0.2502	5.3	154	21.2	15.9		48P	10	0.2501	5.9	58	23.4	0.19
	XLS500	49	10	0.2506	5.5	153	20.9	13.4	XLS500	49P	10	0.25	6.8	59	24.3	0.11
		50	10	0.2503	5.6	153	21.5	15.5		50P	10	0.2502	6.9	59	24.7	0.11
		51	10	0.25	5.5	151	21.5	12.3		51P	10	0.2502	6.9	58	24.4	0.1
	XLS800	52	10	0.2503	5.6	159	21.2	25	XLS800	52P	10	0.2502	8.3	64	22.5	0.09
		53	10	0.2508	5.7	166	29.8	26.6		53P	10	0.2502	8.6	62	24	0.08
		54	10	0.2501	5.8	158	21.8	24.8		54P	10	0.25	8.5	62	24.4	0.09
100mg/L	Blank	55	0	0	4.0	202	19.4	90.8	Blank	55P	0	0	4.1	79	21.1	91.9
	Blank	56	0	0	4.0	209	18.9	90.2	Blank	56P	0	0	4.0	75	22.3	97
	Blank	57	0	0	4.1	206	19.3	90.7	Blank	57P	0	0	4.0	74	22.9	93
	XLS0	58	10	0.2506	5.4	200	20	30.4	XLS0	58P	10	0.2501	6.2	71	21.7	3.36
		59	10	0.2505	5.5	205	18.7	30.7		59P	10	0.2507	6.1	72	21.3	2.02
		60	10	0.25	5.5	198	19.7	28		60P	10	0.25	6.2	70	22.3	0.94
	XLS130	61	10	0.25	5.6	196	20	31.4	XLS130	61P	10	0.2508	6.2	68	22.7	2.44
		62	10	0.2501	5.6	192	19.7	24.6		62P	10	0.2498	6.3	68	22.9	0.83
		63	10	0.2505	5.6	194	19.3	32.4		63P	10	0.2508	6.2	68	22.9	1.4
	XLS330	64	10	0.2507	5.3	198	20.8	27.9	XLS330	64P	10	0.2503	5.8	72	20.7	1.53
		65	10	0.25	5.3	210	18.9	38.8		65P	10	0.2501	5.8	68	23.9	1
		66	10	0.2499	5.3	201	20.5	35.8		66P	10	0.2505	5.8	70	22.4	1.41
	XLS500	67	10	0.2508	5.4	197	21	28	XLS500	67P	10	0.25	6.8	73	23.1	0.63
		68	10	0.2506	5.5	194	20.7	31.4		68P	10	0.2506	6.7	73	23.6	0.57
		69	10	0.2501	5.5	197	20.4	43.1		69P	10	0.2505	6.7	73	23.8	0.53
	XLS800	70	10	0.2505	5.6	201	21.2	58.6	XLS800	70P	10	0.25	8.4	76	22.1	2.08
		71	10	0.2502	5.8	207	19.8	61.1		71P	10	0.2503	8.5	75	22.9	2.02
		72	10	0.25	5.8	201	21.3	46.9		72P	10	0.2505	8.4	75	23.9	2

Appendix 8 – Adsorption isotherm models



Freundlich adsorption isotherms for Cu and Pb.

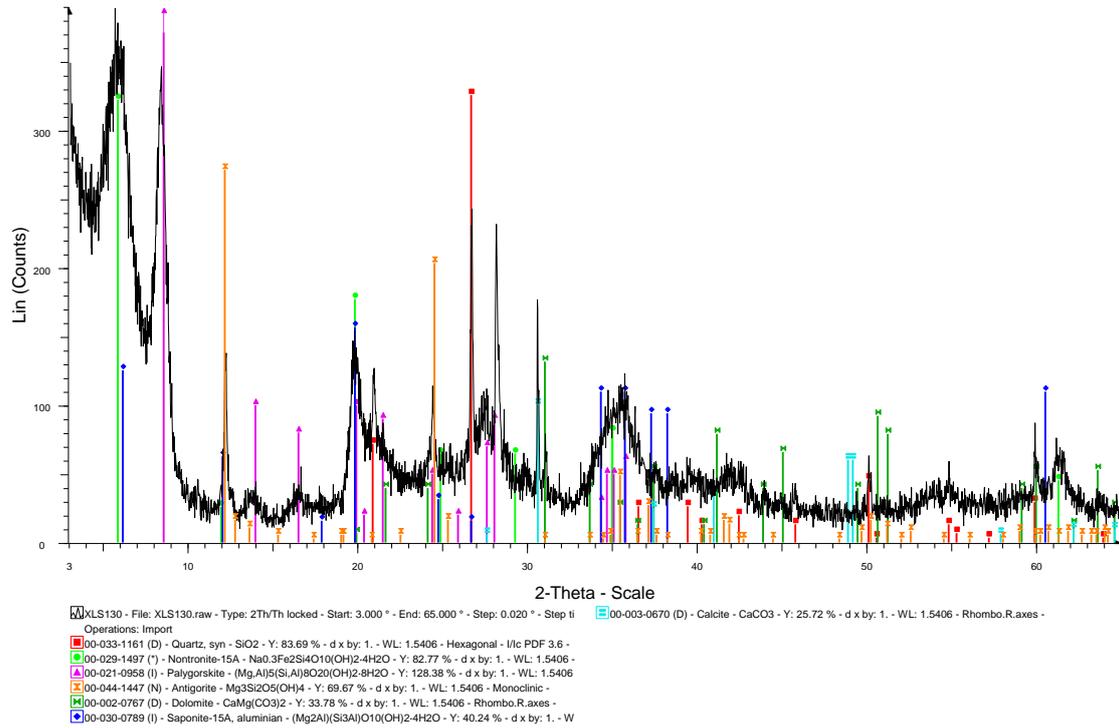
Assessment of Fe- rich smectite clays in adsorbing Pb and Cu from aqueous solutions:
A batch experiment approach



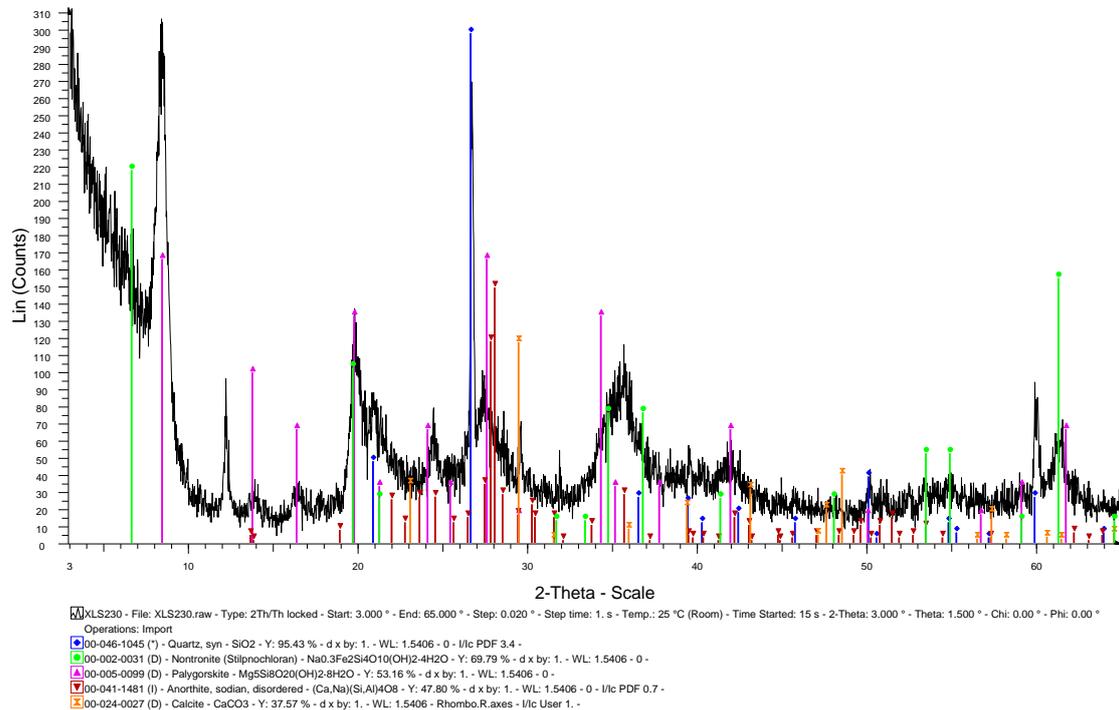
Langmuir adsorption isotherms for Cu and Pb.

Appendix 9 – XRD patterns

XLS130

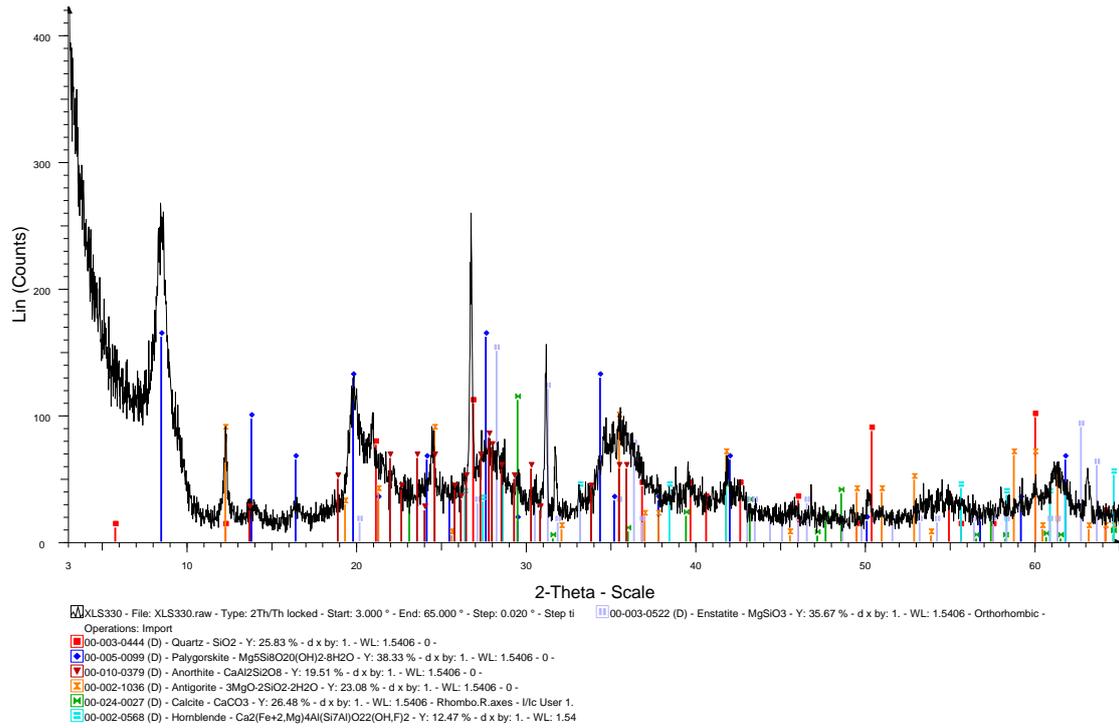


XLS230

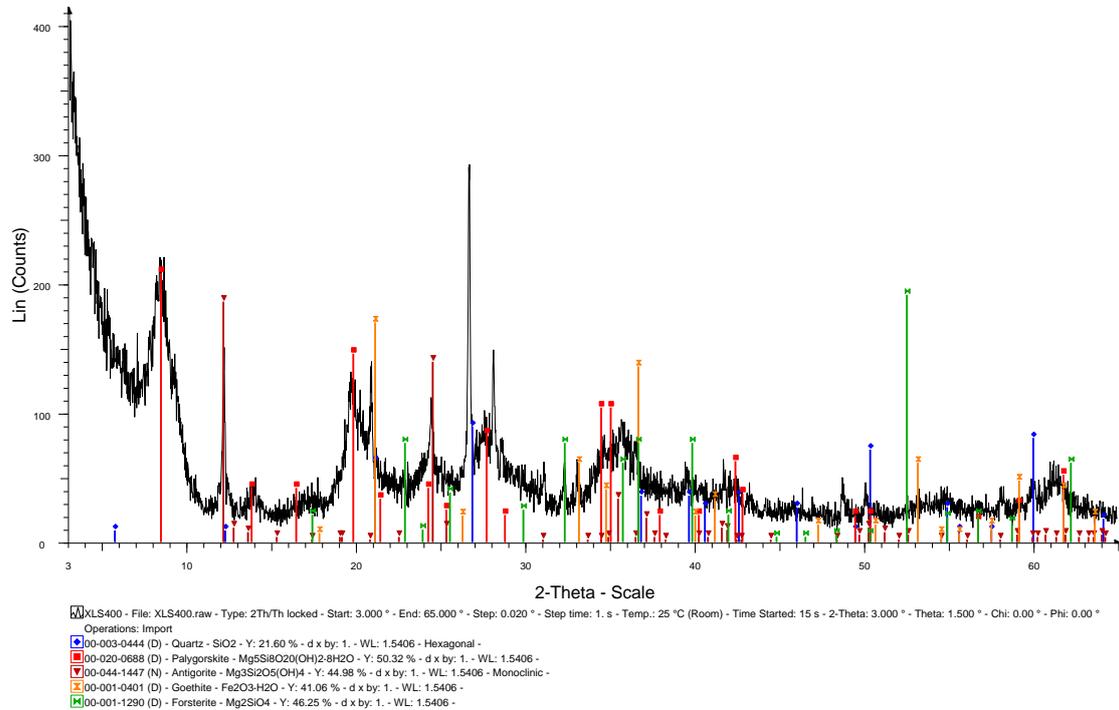


Assessment of Fe- rich smectite clays in adsorbing Pb and Cu from aqueous solutions:
A batch experiment approach

XLS330

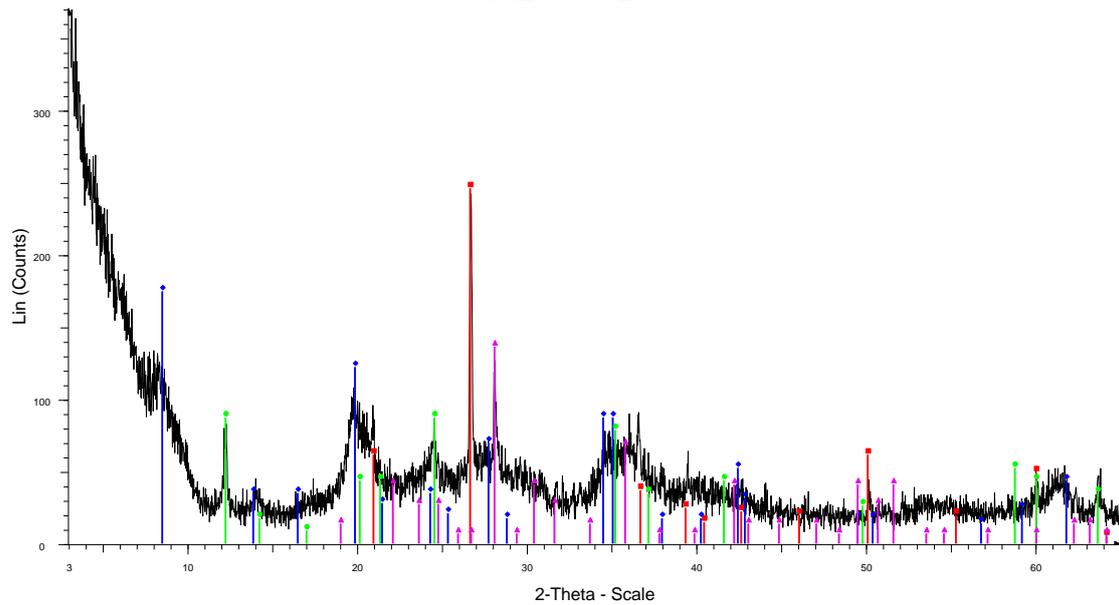


XLS400



Assessment of Fe- rich smectite clays in adsorbing Pb and Cu from aqueous solutions:
A batch experiment approach

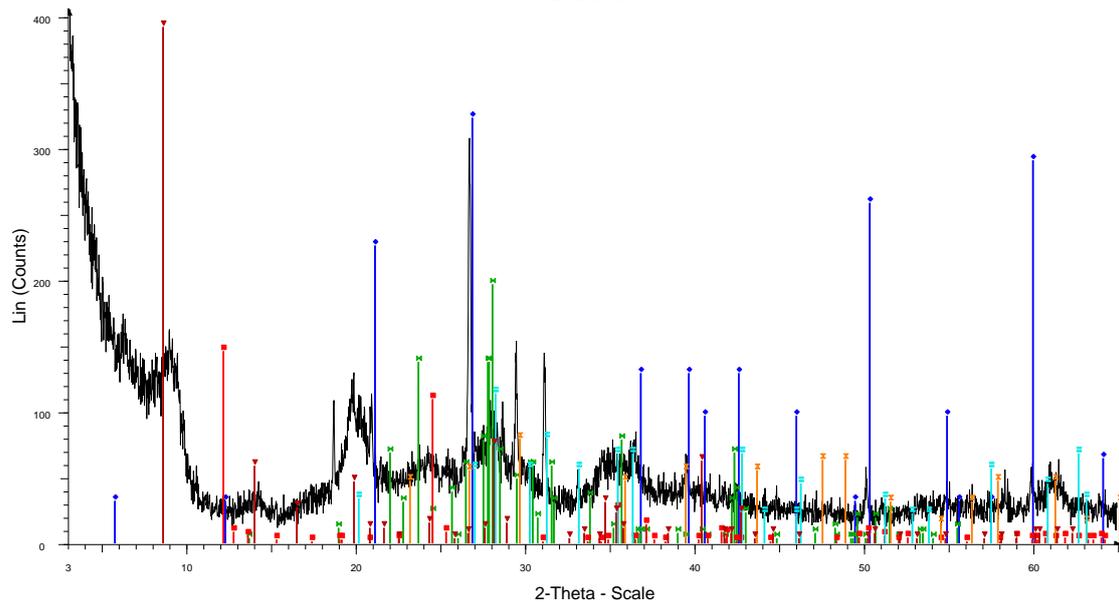
XLS500B



XLS500B - File: XLS500B.raw - Type: 2Th/Th locked - Start: 3.000 ° - End: 65.000 ° - Step: 0.020 ° - Step time: 1. s - Temp.: 25 °C (Room) - Time Started: 9 s - 2-Theta: 3.000 ° - Theta: 1.500 ° - Chi: 0.00 ° - Phi: 0.00 °
Operations: Import

- 00-001-0649 (D) - Quartz - SiO₂ - Y: 66.55 % - d x by: 1. - WL: 1.5406 - 0 -
- 00-020-0688 (D) - Palygorskite - Mg₅Si₈O₂₀(OH)₂·8H₂O - Y: 47.23 % - d x by: 1. - WL: 1.5406 - 0 -
- 00-002-0098 (D) - Antigorite - 3MgO·2SiO₂·2H₂O - Y: 23.61 % - d x by: 1. - WL: 1.5406 - 0 -
- 00-002-0537 (D) - Anorthite - Al₂Ca(SiO₄)₂/Al₂O₃·CaO·2SiO₂ - Y: 36.89 % - d x by: 1. - WL: 1.5406 - 0 -

XLS600

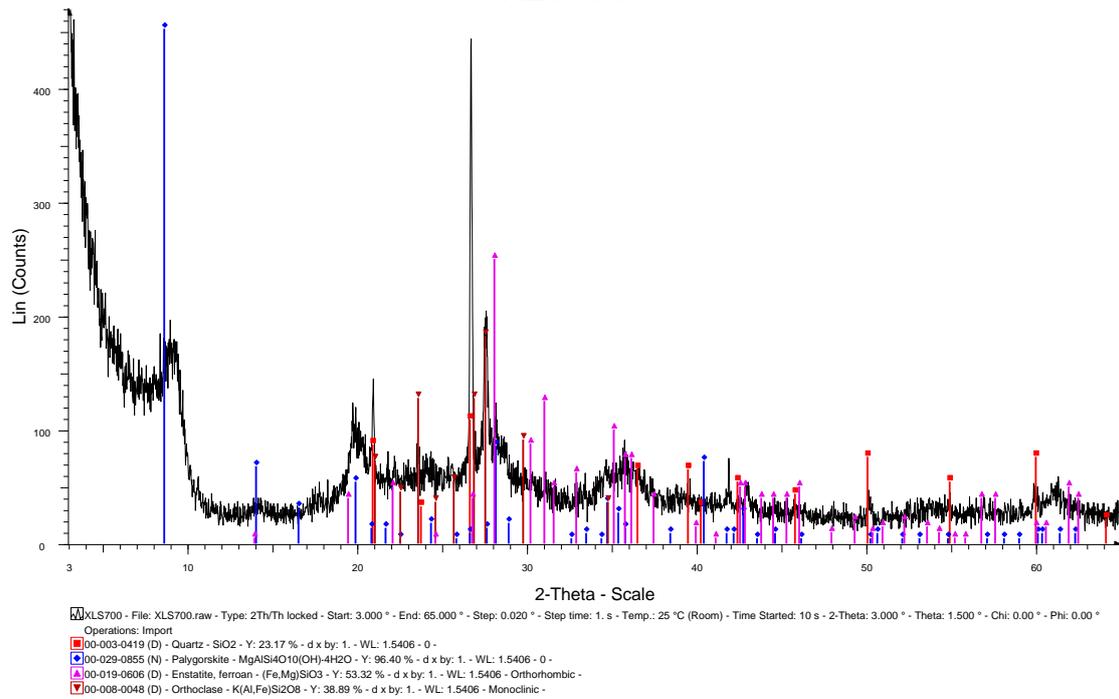


XLS600 - File: XLS600.raw - Type: 2Th/Th locked - Start: 3.000 ° - End: 65.000 ° - Step: 0.020 ° - Step time: 1. s - Temp.: 25 °C (Room) - Time Started: 16 s - 2-Theta: 3.000 ° - Theta: 1.500 ° - Chi: 0.00 ° - Phi: 0.00 °
Operations: Import

- 00-003-0444 (D) - Quartz - SiO₂ - Y: 79.76 % - d x by: 1. - WL: 1.5406 - Hexagonal -
- 00-029-0855 (N) - Palygorskite - Mg₅Si₈O₂₀(OH)₂·4H₂O - Y: 96.76 % - d x by: 1. - WL: 1.5406 - Monoclinic -
- 00-018-1202 (I) - Anorthite, sodian, intermediate - (Ca₂Na)(Si₄Al)₄O₈ - Y: 48.54 % - d x by: 1. - WL: 1.5406 - Triclinic -
- 00-044-1447 (N) - Antigorite - Mg₃Si₂O₅(OH)₄ - Y: 36.01 % - d x by: 1. - WL: 1.5406 - Monoclinic - ITC User 1 -
- 00-003-0612 (D) - Calcite - CaCO₃ - Y: 19.58 % - d x by: 1. - WL: 1.5406 - Rhombo.R axes -
- 00-002-0546 (D) - Enstatite - MgSiO₃/MgO·SiO₂ - Y: 28.10 % - d x by: 1. - WL: 1.5406 - Orthorhombic -

Assessment of Fe- rich smectite clays in adsorbing Pb and Cu from aqueous solutions:
A batch experiment approach

XLS700



XLS800

