

Towards a more safe environment: III. Phosphatic clays as solution for removing Pb²⁺ from wastewater

Samy Mohamed abd Allah

*Soils Dept., Fac. Agric., Ain Shams Univ. Cairo, Egypt. P.o.Box 68 hadayek shoubra 11241, Cairo, Egypt.
E-mail samyabdallah@hotmail.com*

Abstract

To immobilize the pollutants from wastewater in situ, two phosphatic clays collected from different areas in Egypt used to remove ions contaminant from industrial wastewater. Obtained results confirmed the strong relationship between phosphatic clay and Pb elimination from wastewater. As well as suggesting the sensitivity classification of phosphatic clay toward ion retained onto three categories, highly sensitive to retain Pb, Al and Cr, moderately sensitive for Mn and weak sensitive for B and Zn. Desorption data suggested that large fraction of Pb removed by phosphatic clays stayed intact under a wide variation in extracting solution pH.

In situ immobilizations consider a promising technique that has the potential to remove contaminant ions from wastewater. In that concern, two important factors need to consider when applying this technique: The first, is that the clay must be effective and selective under different composition of wastewater. The second is the immobilized ions should be stable and non-leachable under varying water conditions. Phosphatic clays with Pb²⁺ were suitable to achieve these two factors.

Possible mechanism for removal Pb²⁺ by phosphatic clays proves its formed fluoropyromorphite through the dissolution of fluoro and hydroxyl apatite by its precipitation from solution, beside, Pb complexation at phosphatic clay surface at P-OH sites.

Key words: Ion contaminants - Industrial wastewater - Phosphatic clays Pyromorphite – XRD.

Introduction

With growing population increasing living standards and growing concern for environmental issues, claims on water resources are intensifying. Competition between sectors is increasing and water allocation mechanisms currently in place- such as fixed allocations or rationing may no longer be adequate. At the World Water Forum 2000, a

Samy Mohamed abd Allah

large international conference and the majority of the international water community called for reforms in water allocation mechanisms. Reforms relate especially urgently to agriculture. Worldwide, 70-80% of all developed water resources is used for agricultural production. In arid countries, where rainfall is insufficient for rainfed agriculture this percentage reached to 90%. As such, reuse treated wastewater is necessary to utilize in different purposes.

The principal objective of wastewater treatment is generally to allow human and industrial effluents to be disposed of without danger to human health or unacceptable damage to the natural environment. Irrigation with wastewater is both disposal and utilization and indeed is an effective form of wastewater disposal. There are several methods to treat the ion contaminated effluent through precipitation, ion exchange and adsorption, etc., but the selection of the wastewater treatment methods is based on the concentration of waste and the cost of treatment, Yavuz et al.(2003) and mercier et al.(2002). In situ immobilization of metals using inexpensive sequestering agents, such as minerals (apatite or clay minerals) is an attractive alternative to many current remediation methods. The most common among these remediation minerals are apatite and zeolite. Phosphatic clay minerals form naturally and are stable across a wide range of geologic conditions Ma (1996). Phosphatic clay has been used primarily in association with remediation Pb-contaminated soils (Ma et al.(1995), singh et al.(2001), seaman et al.(2001) and Ryan et al.(2001). Therefore, the objectives of the current study are to:

- 1- Investigate the effectiveness of phosphatic clay in removing different contaminants from low quality water.
- 2- Evaluate the stability of formed solid phase under acidic and alkaline conditions.
- 3- Got the answer of the question, what is the specific relationship between phosphatic clay and lead?

Materials and Methods

1. Samples location, preparation and characterization:

1.1. Phosphatic clays

Two phosphatic clays taken from Egyptian Geological Survey and Mining Authority, their coordinates as follows:

Sample location	Latitude	Longitude
Aswan(eastern sebaia) (p1)	25° 15' 22" N	32° 38' 8" E
Aswan (western sebaia)(p2)	25° 14' 45" N	32° 38' 46" E

All the characteristics of used phosphatic clays are recorded in the Geological Survey and Mining Authority and continuously updating every four years.

Clay samples were prepared by grinding the raw clay to a fine powder to pass through a 400-mesh (38 μ m) standard sieve and rinsing with deionized water. According to Black et al.(1985) the different analyses were carried out as follows: pH and Ec were determined by glass electrode and electrical conductivity, respectively. Surface area of the clay determined by single point BET (N_2) adsorption procedure. Chemical analysis was done through preparation of two main solutions, an alkaline solution for SiO_2 determination and an acid solution for the determination of most of the other oxides like Al_2O_3 , CaO, total iron, Na_2O , K_2O , etc. Special sample portions were used for the determination of the anions CO_3^{--} HCO_3^- SO_4^{--} and Cl^- Proper ignition loss at various temperatures was also determined.

Mineralogical analyses:

Infra – red spectroscopy

Infra red absorption spectra in region of 400 cm^{-1} to 4000 cm^{-1} were recorded using KBr sample pellets. The samples prepared as pellet method according to Russell and Fraser (1994). In the present work, A Bruker Vector spectrophotometer model FT-IR-22 Germany, in the region of 4000-250 cm^{-1} was used.

X-ray diffraction analysis

XRD analysis was carried out prior to and after each treatment. Thin slurry of the clay suspension deposited on a glass slide, air dried at room temperature and subjected to X-ray diffraction analysis. XRD analysis was done using Philips pw 1140/90 x-ray apparatus, with Ni filter and Cu- $K\alpha$ radiation. Constant criteria for all samples X-rayed used were as follows: -

KV=40, MA=20, Gain=60, Range=1000, time constant were 2, chart drive 2cm /min. Scanning speed: driven shaft (24), motor shaft (96), its gives 2 $^\circ$ (20 per min.), therefore, according to chart drive and scanning speed 20/2cm/min.

1.2. wastewater source

Non-treated wastewater sample was collected from the 10TH of Ramadan city (one the old biggest industrial areas in Egypt), zone A-3 from Arab steel factory, fabrication pole unit (w).

Wastewater samples were prepared according to Greenberg et al.(1992) for both chemical analysis and heavy metals determination.

2. Contaminants removal experiment:

Four tenth grams from each phosphatic clay source was equilibrated with an aliquot of 40 ml from wastewater separately for different times 30, 60, 90,120,180,240 and 300min. intervals.

Thus generating a set of two separate experiments was established (two phosphatic clays and wastewater) (P1w) and P2w). All measurements run in triplicate. The slurries were discarded and acidified to pH=2 with concentrated nitric acid for metal determination by inductive coupled plasma, chen et al.(1997).The ion removed amount was taken as the difference between the initial concentration in wastewater and that remaining in solution after the equilibration. Solids residues remaining in the centrifuge tubes washed three times with deionized water for both leaching experiment and mineralogical analysis.

3. Recovery experiment:

In order to evaluate the reversibility of contaminants removed by phosphatic clays, their recovery characteristics were also determined. Four extracting solutions varied in pH values were prepared to estimate metal leachability from phosphatic clay after interaction with wastewater.

Two acidic solutions were prepared from acetic acid at pH ~3 and ~5 the other two extracting were alkaline solution pH ~ 9 and ~ 11 prepared by diluting concentrated NaOH solution with deionized water. Washed residues from the first experiment after five hours were treated with 40 ml from each leaching solution and the slurries were shaken on a reciprocating shaker for 24hrs. Also all measurements run in triplicate. Slurries were centrifuged and their supernatants were analyzed for different contaminants and pH while solid residues after each leaching solution washed again and subjected to XRD analysis.

Results and Discussions

1. system characterization:

1.1. phosphatic clays

Obtained data in table (1) show that clays were slightly alkaline, non-saline and their surface area reached 31 and 27 m² g⁻¹. Relatively high contents of Al, Si, Fe, Ca and P in the chemical composition were reflecting the presence of apatite and phyllosilicates as major constituents. From both I.R spectrum Figs.(1&2) and XRD patterns Figs.(6A), the mineralogical composition indicated that beside the apatite there are some differences between two phosphatic clays in eastern sebaia (P1) quartz was dominant beside minor kaolinite and smectite clay minerals while in western sebaia (P2) kaolinite was dominant clay mineral.

The I.R spectrum in Figs. (1&2) gave some detailed about the type of apatite, several diagnostic bands at 3570 and 632 cm⁻¹ arise, respectively, from the stretching and bending vibrations of OH groups in the apatite structure wilson, (1994). A weak band at 3535 cm⁻¹ in the spectra of apatite arise significant proportion of OH groups substituting for F. The fluor-apatite structure apparently can tolerate appreciable OH for F replacement without significant change in the spectrum, Wilson (1994).

1.2. wastewater

Chemical composition of used wastewater in table (2) showed a lot of contaminants i.e. Zn , Pb , Mn , Fe , Cr , B, and Al.

2. Phosphatic clays as contaminants removal:

After treated wastewater with phosphatic clays powder in the amount equivalent to clay: solution ratio 1:100, the different ion concentrations were

substantially decreased as shown in tables (3 and 4). Phosphatic clays were effective in removing all ions with differences in the amount removed. The percentage of the dissolved contaminant ions removed ranged from 95.3 to 95.28 for Pb, 65.43 to 58.93 for Al , 64.64 to 58.59 for Cr, 16.6 to 35.29 for Mn , 8.18 to 6.48 for Zn and 8.04 to 4.52 for B ,in both (P1) and (P2) , respectively.

Except Mn ions, phosphatic clay (P1) removed more amounts from ions than (P2), This may attributed to high surface area and presence some smectite clay mineral in (P1) as detected from both I.R and XRD patterns.

The presence of hydroxyl and fluoroapatite and other minerals in used phosphatic clays significantly enhanced its sorption capacity for different ions through dissolution and precipitation mechanism, particularly in the case of Pb.

Higher amount removed from Pb by phosphatic clays reached to 1.887 and 1.89 mg/g in (P1) and (P2) respectively, suggested its higher affinity for Pb compared with other ions. Comparing initial concentration of ions contaminant in wastewater with their removed amount percent by phosphatic clays , one can conclude, that the efficiency of phosphatic clays in retaining ions contaminant depend on the ion itself rather than its initial concentration. For example, initial concentration of Zn and Cr was 441.3 and 3.14 mg/l respectively, while their removed amount percent by (P1) reached to 8.18 and 64.64% while reached to 6.48 and 58.59% in (P2), respectively.

In all cases, obtained results confirmed the strong relationship between phosphatic clays and Pb elimination from wastewater, which resulted in over 95% removal by used phosphatic clays and reduced the concentration of dissolved Pb from 19mg/l (which consider a dangerous level) to nearly 1 mg/l.

From obtained results drawn in Figs.(3 and 4) one can summarize the sensitivity classification of phosphatic clays towards ions retained in three categories as follows:

Highly sensitivity for retaining Pb, Cr and Al, moderately sensitivity for retaining Mn and weak sensitivity for retaining B and Zn if all these ions present together in solution or wastewater. This point may need more researches to establish this classification and to agree or refuse it.

This sensitivity classification did not congruent with those of Singh and Harris (2001) and Cao et al.(2004) specially for Zn.

The previous authors used ternary mixture and pure solutions and carried sorption desorption experiment while this study deals with wastewater directly. As such, some deviation is likely, beside their experiment did not enter Al and Cr in their account.

During the sorption experiments, pH in the equilibrium solutions after each time recorded and drawn in Fig. (5). Interaction of phosphatic clays with wastewater caused a decrease in solution pH from 6.35 to 5 and 5.2 in P1 and P2, respectively as the amount of removed ions increased by the time. Decreasing solution pH indicated that these ions act as weak bronsted acids, however, it is indicates that in addition to the precipitation reaction the different ions retained onto phosphatic clays might be supplemented by the sorption of these ions in hydroxy complexes.

Similar results were observed by mavropoulos et al. (2002) and cao et al. (2004). The latter author gave serial reactions indicating that the H^+ consumed during dissolution of phosphatic clay and precipitation of fluoropyromorphite liberated an equal amount of H^+ as follows:



It means that Pb ions uptake via fluoromorphite precipitation should not cause a net pH change (mavropoulos et al.(2002). This not the case in current study, then other surface mechanisms beside phosphatic clay dissolution and fluoropyromorphite precipitation may have contributed to pH decrease. One possibility was Pb complexation at phosphatic clay surface as the following reaction:



So decreasing pH could be linked to the proton liberated by Pb complexation at P-OH sites. Visual MINTEQ modeling applied by cao et al (2004) and ma(1996) indicated that the solutions were undersaturated with respect to $Pb(OH)_2$ or $Cu(OH)_2$. Thus, the reduction in solution pH cannot contribute to hydrolysis of Pb or other ions. Clearly more metal disappearance (adsorbed by phosphatic clays) would release more H^+ resulting in a greater pH reduction.

3. Recovery experiment:

Recovery experiment carried out on the solid residues formed after equilibrated phosphatic clays with wastewater for three hours. Four leaching solutions were equilibrated with residues for 24 hours; the resulted supernatant did not contain a detectable concentration from most studied ions. Therefore could not calculate amount recovered.

4. Solid phase examination:

Figure (6) showed the XRD patterns of the used phosphatic clay minerals before and after treated with wastewater. These XRD patterns indicated the formation of pyromorphite as solid residue formed after the reaction between wastewater and clays, as indicated by diffraction pattern at 2.95Å, chen et al.(1997), singh et al.(2001) and cao et al.(2004). The dissolved Pb was removed from wastewater mainly through several retention processes such as precipitation; co-precipitation, diffusion and surface sorption contribute simultaneously toward metal removal from aqueous solutions because phosphatic clay is a heterogeneous mixture of several minerals. Singh et al.(2001), cao et al.(2004) and Ma et al.(1995) generally, confirmed the previous mechanism but the latter added that such dissolution- precipitation process was the primary mechanism in the immobilization of Pb in the presence of apatite minerals and resulted in the formation of carbonate fluoropyromorphite type phases. In the current study, different mineralogical and chemical analyses indicated the absence of carbonate from the crystal structure of used phosphatic clays. Moreover, the XRD maximum of the pyromorphite –type compound also suggests that carbonate ions did not occur in its crystal structure. As such, formation of carbonate pyromorphite is not likely under the study while hydroxyl fluoro pyromorphite very likely.

The members of pyromorphite family are the most stable environmental Pb compounds under a wide variety of conditions, the solubility products of pyromorphite are extremely low, i.e. $10^{-71.6}$ and $10^{-76.8}$ for fluoro and hydroxyl pyromorphite, respectively, chen et al.(1997). Thus, the formation of hydroxyl fluoro pyromorphite under the study should be able to resist the leaching with different PH solutions. XRD patterns drawn in Figs.(6 C,D,E,F) proved that after leaching experiment the formed hydroxyl fluoropyromorphite stayed intact as indicated by their respective XRD patterns. The intensities of XRD peaks after treatments remained, as it is supporting its stability under a wide range of PH.

It worthy to mention, that although phosphatic clay eliminate many contaminants from wastewater only one solid phase related to lead are formed, this finding reflects high selectivity and affinity of phosphatic clays with lead and achieves the third objective of this study.

In conclusion, phosphatic clays were effective to remediate Pb from wastewater because its achieves the following two factors;

- 1- Clay must be effective and selective under different composition of wastewater.
- 2- The second is the immobilized ions should be stable and non-leacheable under varying water conditions.

Conclusion

Phosphatic clay was extremely effective in removing Pb from wastewater. Approximately 95% of Pb was removed from wastewater representing capacity 1.9

mg/g. Obtained results suggested the sensitivity classification of phosphatic clay with ion removing into three main categories, highly sensitive to retain Pb, Al and Cr, moderately sensitive for Mn and weak sensitive for B and Zn. Although phosphatic clay eliminates many contaminants ion from wastewater, only one solid phase related to Pb formed. The hydroxy fluoropyromorphite formed through the dissolution of fluoro and hydroxyl apatite followed by its precipitation from solutions. Beside, Pb complexation at phosphatic clay surface at P-OH sites which proved via pH decreasing after ions removal. The immobilized Pb stayed stable and not remobilized under wide variety of pH conditions ranging from 3 to 11.

These results imply that phosphatic clay could be a cost-effective option in the remediation of Pb from water, wastes and soils.

References

- Black, C.A., Evans, D.D., Ensminger, L.E., White, J.L. and Clark, F.E.(1985).** Methods of Soil Analysis. American Society of Agronomy, Inc., Madison, Wisconsin, USA Library of Congress Catalog Card Number:65-15 8 00, Seventh printing.
- Cao, X.; Ma, L. Q.; Rhue, D.R. and Appel, C.S. (2004).** Mechanism of lead, copper and zinc retention by phosphate rock. Environ. Pollu. 131:435-444.
- Chen, X.; Wright, J.V.; Conca, J.L. and Peurrung, L.M.(1997).** Evaluation of heavy metal remediation using mineral apatite. Water, Air and Soil Pollution 98:57-78.
- Greenberg, A.E.; Clesceri, L.S. and Eaton, A.D. (1992).** Standard methods for the examination of water and wastewater. Published by American public health association 18th edition Washington, DC. Library congress ISBN 0-87553-207-1
- Ma, L.Q.(1996).** Factors influencing the effectiveness and stability of Aqueous lead immobilization by hydroxyapatite. J. Environ. Qual. 25:1420-1429.
- Ma, L.Q.; Logan, T.J.; and Traina, S.J.(1995).** Lead immobilization from aqueous solutions and contaminated soils using phosphate rocks. Environ. Sci. Technol. 29, 1118-1126.
- Mavropoulos, F.; Rossi, A.M.; Costa, A.M.; Peter, C.A.C.; Morena, J.C. and Saldanha, M.(2002).** Studies on the mechanisms of lead immobilization by hydroxyl apatite. Environ. Sci. Technol. 36:1625-1629.

- Mercier,G.:** **Duchesne,J. and Blackburn,D.(2002).** Removal of metals from contaminated soils by mineral processing techniques followed by chemical leaching. *Water, Air and Soil pollution* 135:105-130.
- Russell, J.D. and Fraser, A.R. (1994).** Infrared methods. Chapter (2),pp: 11-67. In: *Clay mineralogy : spectroscopic and chemical determinative methods.* Wilson,M.J.(ed)Chapman & Hall, London.UK. Congress Catalog card no. 93-74207.
- Ryan, J.A., P. Zhang, D. Hesterberg, L. Chou, and D.E. Sayers. (2001).** Formation of chloropyromorphite in a lead-contaminated soil amended with hydroxyapatite. *Environ. Sci. Technol.* 35:3798-3803.
- Seaman, C.J., Mehan, J. and Bertsch, P.M. (2001).** Immobilization of cesium-137 and uranium in contaminated sediments using soil amendments. *J. Environ. Qual.*, 30:1206-1213.
- Singh,S.P.:** **Ma,L.Q and Harris,W.G.(2001).** Heavy metal interactions with phosphatic clay: sorption and desorption behavior. *J.Environ.Qual.*30:1961-1968.
- Wilson, M.J., (editor) (1994),** *Clay Mineralogy Spectroscopic and Chemical Determinative Methods.* Chapman & Hall, London, New York, Tokyo, 300-327
- Yavuz,O.:****Alunkaynak,Y. and Uzel,F.G.(2003).** Removal of copper, Nickel , Cobalt and Manganese from aqueous solution by kaolinite.*Water research* 37:948-952.

Table (1) Some characteristics of used phosphatic clays

Sample	pH 1:2.5	EC (ds/m 1:5)	Surface (m ² /g)	Chemical composition (%)													
				LOI	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	MnO	ZnO	TiO ₂	P ₂ O ₅	SO ₃	Total
Eastern sbaia (P1)	8.1	0.81	31	10.32	21.16	1.07	2.12	33.6	0.48	0.12	0.24	0.15	3.89	0.08	21.29	5.24	99.76
Western sebaia (P2)	7.9	0.62	27	8.73	19.53	1.55	1.75	28.79	0.96	0.31	0.72	0.21	5.95	0.12	24.81	6.18	99.61

Table (2) Chemical composition of used wastewater (mg/l)

Sample	pH 1:2.5	EC (ds/ m 1:5)	Al	B	Cd	CO	Cr	Cu	Fe	Mn	Mo	Ni	Pb	V	Zn
wastewa ter(w)	6.3 5	32.5	11.1 4	4.35	<0.0 02	0.15 44	3.14	<0.0 2	254. 9	17.3 4	0.16 17	0.76 92	19.8 7	<0.0 2	441. 3

Table (3) Equilibrium concentration, percentage of amount removed and amount removed mg/g from ions contaminant after treated with (P1)

Time (min)	Al mg /l	Al %	Al mg/ g	B mg/l	B %	B mg/ g	Cr mg/l	Cr %	Cr mg/ g	Pb mg /l	Pb %	Pb mg/ g	Mn mg/ l	Mn %	Mn mg/ g	Zn mg/l	Zn %	Zn mg /g
30	5.17	53.59	0.597	4.16	4.36	0.019	1.52	51.59	0.162	1.81	90.89	1.806	14.99	13.55	0.235	413.5	6.29	2.78
60	4.88	56.19	0.626	4.12	5.69	0.023	1.48	52.86	0.166	1.75	91.19	1.812	14.57	15.97	0.277	412.5	6.52	2.88
90	4.71	57.71	0.643	4.06	6.66	0.029	1.35	57.00	0.179	1.47	92.60	1.8437	14.12	17.77	0.296	410.6	6.95	3.07
120	4.51	59.51	0.663	4.05	6.89	0.038	1.29	58.66	0.1842	1.43	92.804	1.84433	14.35	17.35	0.301	410.2	7.04	3.11
180	4.52	59.42	0.662	4.05	6.89	0.032	1.2	61.78	0.194	1.2	92.96	1.867	14.17	18.28	0.317	408.6	7.40	3.27
240	3.95	64.54	0.719	4.01	7.81	0.034	1.14	63.69	0.2	1.1	93.46	1.877	14.93	13.89	0.241	407.2	7.72	3.41
300	3.85	65.43	0.729	4.0	8.04	0.035	1.11	64.64	0.203	1.0	95.387	1.846	14.60	16.08	0.288	405.2	8.18	3.61

Table (4) Equilibrium concentration, percentage of amount removed and amount removed mg/g from ions contaminant after treated with (P2)

Time (min)	Al (mg/l)	Al (%)	Al (mg/g)	B (Mg/l)	B (%)	B (mg/g)	Cr (mg/l)	Cr (%)	Cr (mg/g)	Pb (mg/l)	Pb (%)	Pb (mg/g)	Mn (mg/l)	Mn (%)	Mn (mg/g)	Zn (mg/l)	Zn (%)	Zn (mg/g)
30	5.85	47.48	0.529	4.33	0.459	0.002	1.68	46.49	0.146	1.183	94.04	1.86	13.06	24.68	0.428	420.6	4.69	2.07
60	5.32	52.24	0.582	4.313	0.85	0.0037	1.6	49.04	0.154	1.084	94.54	1.87	12.85	25.89	0.449	418.2	5.23	2.31
90	4.95	55.56	0.619	4.311	0.89	0.0039	1.52	51.59	0.162	1.055	94.69	1.88	12.74	26.54	0.46	418	5.27	2.33
120	4.9	56.01	0.624	4.283	1.54	0.0067	1.47	53.18	0.167	1.045	94.74	1.88	12.31	29.00	0.503	417.3	5.43	2.4
180	4.876	56.22	0.6264	4.217	3.05	0.0133	1.41	55.09	0.173	1.035	94.79	1.88	13.62	31.08	0.539	415.4	5.86	2.59
240	4.699	57.81	0.6441	4.196	3.54	0.0154	1.33	57.64	0.181	1.006	94.93	1.88	11.95	35.23	0.611	415.4	5.86	2.59
300	4.575	58.93	0.6565	4.153	4.52	0.0197	1.3	58.59	0.184	0.937	95.28	1.89	11.22	35.29	0.612	412.7	6.48	2.86





