Journal of Novel Applied Sciences
Available online at www.jnasci.org
©2014 JNAS Journal-2014-3-1/5-13
ISSN 2322-5149 ©2014 JNAS

Towards a Safer Environment: (9) Remediation of heavy metals from low quality water in asir region southwestern of Saudi Arabia

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ABSTRACT: To evaluate the effectiveness of apatite mineral in removing different contaminants from low quality water in the industrial city of abha, Asir region, southwestern of Saudi Arabia two phosphatic clay dominated by apatite mineral were selected. In situ remediation experiment proved that apatite mineral has the highest affinity for Pb and removed more than 94% from initial Pb concentration. The rest of contaminants followed the descending order of: Zn **>** Mn **>**Cu **>** Co **>** Ni. The sorption of Pb, Zn and Mn onto apatite mineral was well characterized by the Langmuir model. Ternary-metal addition induced competitive sorption among the three metals, with the interfering effect of Pb **>** Zn **>** Mn. During metal retention by apatite mineral calcium and phosphate were determined in equilibrium solution. Calcium increased and phosphate decreased with increasing metal disappearance. The greatest increase of calcium and the largest phosphate reduction were found with Pb^{+2}sorption. This is suggested that Pb^{+2} retention by apatite was through the dissolution of apatite which mean release of Ca and P into solution and formation of pyromorphite (lead phosphate) as consuming of P. Obtained results suggested that there are two general mechanisms for the ability of apatite mineral to take up Pb^{2+}, Zn^{+2} and Mn^{+2}. The first is (ion – ion exchange mechanism) concerned with adsorption of ions on the solid surface followed by their diffusion into apatite mineral and the release of cations originally contained within apatite. The second is (dissolution – precipitation mechanism) concerned to the dissolution of apatite in the aqueous solution containing Pb^{2+}, Zn^{+2} and Mn^{+2} followed by the precipitation or coprecipitation. Pb^{+2} desorption responding to solution pH may indicate that not all the Pb^{+2} was chemisorbed and fraction of Pb^{+2} was weakly adsorbed or complexed on the surface of apatite mineral.

***Keywords*:** Abha industrial city, wastewater treatment, apatite minerals, heavy metals retention, in situ remediation.

INTRODUCTION

Abha is located in Asir region in the south-west of the Kingdom of Saudi Arabia. Abha is the administrative capital of the Asir region; it is the home of the headquarters of the regional Governorate. Abha's position, some 7,200 feet (2,200 meters) above sea-level, gives it a relatively moderate climate. Temperatures remain within a narrower band than is the case in many other parts of the Kingdom. The Abha region also enjoys the highest level of rainfall of any part of Saudi Arabia. The natural beauty of the region and its fertility has encouraged the Saudi Arabian Government to establish a number of industrial regions in both abha and Khamis Mushayt to avoid pollution in the cities. Abha industrial area lies in the eastern part of abha city on the main general road of abha - khamis mushayt. It contains a lot of small factories and many cars repair, smithery, turnery workshops. It releases huge quantities of wastewater daily, this study may be considers the first one in this area.

Increased use of metals and chemicals in process industries has resulted in generation of large quantities of effluent that contain high level of toxic heavy metals. Their presence poses environmental–disposal problems due to their bioaccumulation, non biodegradable properties and toxicity even at low concentrations Elouear et al. (2008), Dong et al. (2003), Trivedi , Abdallah (2010) and Axe (2000). Because of their high solubility in the aquatic environments; heavy metals can be absorbed by living organisms. Once they enter the food chain, large concentrations of heavy metals may accumulate in the human body. If the metals are ingested beyond the permitted concentration, they can cause serious health disorders. Therefore, it is necessary to treat metal-contaminated wastewater prior to its discharge to the environment. Different treatment techniques for wastewater laden with heavy metals have been developed in recent years both to decrease the amount of wastewater produced and to improve the quality of the treated effluent.

The conventional technologies for heavy metal ions removal from aqueous solution are chemical precipitation, ion exchange, reverse osmoses, electrochemical treatment and sorption. Among these, sorption is a promising technology for cleaning up contaminated soils and wastes. In the last decade, a great effort has been invested to develop new sorbents such as calcite, Trivedi and Axe, (2000), goethite, Buerge-Weirich et al. (2002), birnesite, Manning et al, (2002), phosphatic clay, Abdallah, (2004), kaolinite, bentonite and vermiculite, Abdallah et al, (2005) and (2007), modified kaolinite, Abdallah, (2006), and zeolite (clinoptilolite), Fred Jr et al, (2005).
Therefore, the objectives of the current study are to:

1- Evaluate the effectiveness of apatite mineral in removing different contaminants from low quality water in the industrial city of abha, Asir region, southwestern of Saudi Arabia.

Answer the question of how apatite mineral remediates Pb^{+2}, Zn^{+2} and Mn^{+2} from wastewater?

MATERIALS AND METHODS

2.1 Materials

2.1.1 Apatite minerals

Two phosphatic clays (P1 and P2) dominated by apatite mineral were taken from Egyptian Geological Survey and Mining Authority, their coordinates as follows:

Sample location	Latitude	Longitude
Aswan(rock phosphate) (P1)	25° 15- 22- N	32º 38- 8- E
Aswan (rock phosphate) (P2)	25° 14- 45- N	32º 38- 46- E

Both chemical and mineralogical characterization of the studied sediments and samples preparation were mentioned in the previous study by abdallah (2004).

2.1.2. Wastewater source

Non-treated wastewater sample was collected from the Abha industrial city, Asir district, southwestern of Saudi Arabia. Wastewater samples were prepared and analyzed according to Greenberg et al. (1992) for both chemical analysis and heavy metals determination.

2.2 Methods

2.2.1 In-situ remediation experiment:

Four tenth grams from each apatite minerals (P1 and P2) was equilibrated with an aliquot of 40 ml from wastewater separately for various times intervals 30, 60, 90,120,180 and 240 min. All measurements run in triplicate. According chen et al.(1997) the slurries were discarded and acidified to pH=2 with concentrated nitric acid for metal determination by inductive coupled plasma. The amount of ion removed was taken as the difference between the initial concentration in wastewater and that remaining in solution after the equilibration.

2.2.2 Mechanism of removing Pb, Mn and Zn by apatite mineral

To understand how apatite minerals retained and removed Pb^{+2}, Zn^{+2} and Mn^{+2} from wastewater and aqueous solution three experiments were carried out as follows:

1 - Sorption of mono- metal and ternary metals mixture in controlled pH system:

Two sets of experiments were designed including (mono and ternary metals). The adsorption of each lead, zinc and manganese by apatite mineral were examined as follows:

Mono experimental remediation:

Individual aqueous solution of Pb^{+2} Zn^{+2}, and Mn^{+2} were prepared at different concentrations (0- 0.15- 0.245- 0.35- 0.475- 0.575- 0.7 mM) from their nitrate salts. Solution ionic strength was controlled at 0.05M using a KNO_3 background electrolyte solution.

Ternary experimental remediation:

Deionized distilled water (DD-H_2O) was used to prepare the ternary heavy metals solution (Pb^{+2} Zn^{+2}, and Mn^{+2}) used in this study. The preparation carried out in the same different concentrations in mono- metal experiment from their nitrate salts according to (Xinde Cao et al., 2004).

Series of 30 mL of 0.05 M KNO_3 containing the above different concentrations of either one or an equal-molar mixture of Pb^{+2}, Zn^{+2} and Mn^{+2} were added to 0.1 g of apatite mineral. The suspensions were shaken at 350 rpm on a reciprocating shaker at room temperature for four hours equilibration. Solution pH was controlled at (6) with diluted HCl and NaOH. The supernatants were separated by centrifugation at 3000 rpm/ 30 min. The filtrate was retained for analysis of pH, P, Ca, Pb, Zn and Mn. Treatment blanks carrying 30 mL of 0.05 M KNO_3 with 0.1 g of apatite mineral were included. The amount of adsorbed metal was taken as the difference between the amount added initially and that remaining in solution after equilibration.

Sorption isotherm:

Heavy metals sorption data in two experiments of mono and ternary metals sorption isotherms onto apatite mineral have been analyzed using the Langmuir model to evaluate parameters associated with their sorption behaviors. The linear form of Langmuir equation is represented by:

$$C/q = C/Q_m + 1/K_L * Q_m$$

where (C) is the equilibrium concentration (mmol/L), (q) is the amount of heavy metals sorbed onto apatite mineral (mmol/100g apatite), (Q_m) is the maximum sorption capacity (mmol/100g apatite), and (K_L) is the sorption constant related to binding energy (L/ mmol). The sorption data were fit to a linear form of the Langmuir equation. Langmuir sorption parameters for each metal were calculated by using least squares fitting, R^2 is the correlation coefficients.

2 - pH- free control system experiments:

The previous mono experimental and ternary experimental remediation was carried out without controlling the pH. The reaction system was free of acidity control and the final pH was monitored at different initial metal concentrations.

3 – Desorption of ternary metal solution experiments:

To confirm and to validate the suggesting mechanism, desorption experiments were conducted. Four extracting solutions of varying pH prepared according to abdallah(2004). After ternary metal sorption experiments was carried out the remaining solid residues from apatite mineral reaction with 0.4 mM metals were chosen and washed twice with deionized water and supernatants were discarded immediately after 25-min of centrifugation. The washed residues were then treated with 30 mL of the extracting solutions of pH 3-9 and the slurries were shaken on a reciprocating shaker for 24 h. The slurries were centrifuged and their supernatants were filtered and analyzed for pH, Pb^{+2}, Zn^{+2} and Mn^{+2}.

RESULTS AND DISCUSSION

In situ remediation experiment:

According to Pescod (1992) the chemical characteristics of industrial wastewater used in table (1) showed several heavy metal contaminants i.e. Pb , Zn , Mn , Cu , Co , and Ni.

Both apatite minerals were effective to remediate all the six contaminant ions with differences amount as indicated from figure (1 A and B) for (P1) and (P2), respectively. Pb was superior on other all ions for remediation and apatite removed more than 94% from initial Pb concentration; the rest of contaminants followed the descending order of: Zn > Mn >Cu > Co > Ni. Because the phosphatic clay sample (P1) have higher surface area and presence of smectite clay mineral as proved in the previous study by Abdallah (2004) the amount of contaminants removed were high in (P1) compared with the second sample (P2). Except Mn, the percentage of decreasing in the amount of metal removed from (P1) to (P2) was not great differences as follows: less than (2%) for Pb, (3.1%) for Zn, (10.42%) for Mn, (4.99%) for Cu, (2.18%) for Co and (1.38%) for Ni.

The obtained data showed the importance of mineralogical composition of the sediment used in retaining the contaminants from wastewater. On other side, Mn decreased from 28.47% by (P1) to 18.05 % by (P2) appearing the greatest decrease percent between two sediments used among all the studied contaminants. The presence of smectite mineral in phosphatic clay (P1) may have high selectivity of Mn and responsible to remove this metal rather than apatite mineral.

The previous discussion proved that apatite mineral was effective to remediate heavy metals as contaminant ions from wastewater in Abha industrial city, Asir area, this is achieve the first aim of the current study.

In types of apatite mineral, the retaining Pb^{+2}, Zn^{+2} and Mn^{+2} were in higher amount, more efficient and more sensitive than from Cu^{+2}, Co^{+2} and Ni^{+2}. Thus, the study focused on these metals to put the mechanism of their remediation by apatite minerals.

Table 1. Chemical characteristics of industrial wastewater used

pH (1:2.5)	6.12	Ec ds/m(1:5)	22.4	Total dissolved solids (TDS) mg L^{-1}	520
Total Solids (TS) (mgL^{-1})	715	Chemical oxygen demand (COD)(mgL^{-1})	498	Biological oxygen demand (BOD)(mgL^{-1})	231
element	concentration (mgL^{-1})	element	concentration (mgL^{-1})	element	concentration (mgL^{-1})
Ca	18	Cl	71	Co	9.17
Mg	11	SO_4	32	Cr	0.4
Na	79	PO_4	17	Hg	0.1
K	16	NO_3	32	V	0.02
Fe	176	NO_2	18	Ba	1.1
Mn	14.4	pb	16.75	Li	0.01
Zn	28.79	Cd	0.08	Al	2.1
Cu	18.04	Ni	10.14	Sr	0.01

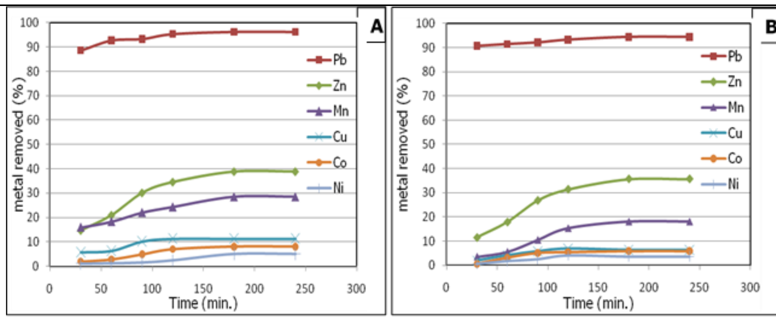

Figure 1. percentage of ions removed from wastewater by apatite mineral (A) (P1) and (B) (P2)

Mechanism of removing Pb, Zn and Mn by apatite mineral

To achieve the second aim of the current study, sorption of mono-metal and ternary mixture of Pb, Zn and Mn were carried out as following:

Suitable equilibrium time:

The amount adsorbed of Pb^{+2}, Zn^{+2} and Mn^{+2} after different times were drawn in figure (2). The adsorbed amount of pb^{+2} slightly increased in the first hour and stabilizes within two hours. The Adsorbed amount of Zn^{+2} jumps after the first hour from 1.5 to 8 mmol/ 100g clay where it is stabilized with increasing time intervals, in case of Mn^{+2} the adsorbed amount increase gradually and reach stability after two hours also. These results are in harmony with that obtained by Singh et al., (2001).

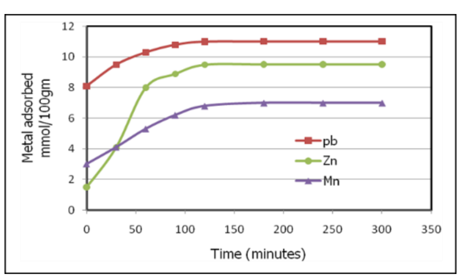

Figure 2. adsorbed amount of studied heavy metals as a function of time

1 - Sorption of mono- metal and ternary metals mixture in controlled pH system:

Sorption isotherm for Pb^{+2}, Zn^{+2} and Mn^{+2} at pH = 6 and room temperature (25°C) were drawn in figure (3). In both mono and ternary metal sorption exhibited two important things, first, the apatite minerals was effective in retaining all three metals by the same order in the remediation experiment. Second, there are differences between the studied metals in shape and in the amount of metal adsorbed.

Sorption behaviors of Zn^{+2} and Mn^{+2} in both mono-metal and ternary metal systems, were significantly different from that of Pb^{+2} as presented in figures (3A and B respectively). Zinc and manganese retention gradually increased with increasing initial concentration and then leveled off while lead retention increased rapidly; initial linear part of the isotherm was almost straight and then was constant. The obtained sorption patterns were similar to those observed by (Mavropoulos et al., (2002); Singh et al., (2001). According to Echeverria et al. (1998), isotherms that have similar equilibrium concentrations for different amounts of metal added was reflect a surface adsorption or precipitation mechanism.

The competition among metals in the Pb^{+2}, Zn^{+2} and Mn^{+2}ternary system, figure (3B) affected of all metals sorption. The initial linear part of the isotherms was shorter and knee was sharper when compared with mono-metal sorption figure (3A). Competitive metal retention by apatite mineral suggested that complexation mechanisms may have contributed partially to metal sorption by apatite mineral.

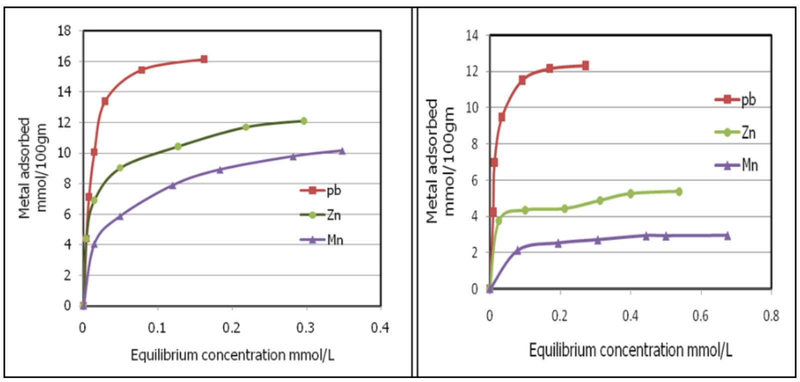

Figure 3. Adsorption isotherms of (A) mono-metal and (B) ternary-metal on apatite mineral at pH (6)

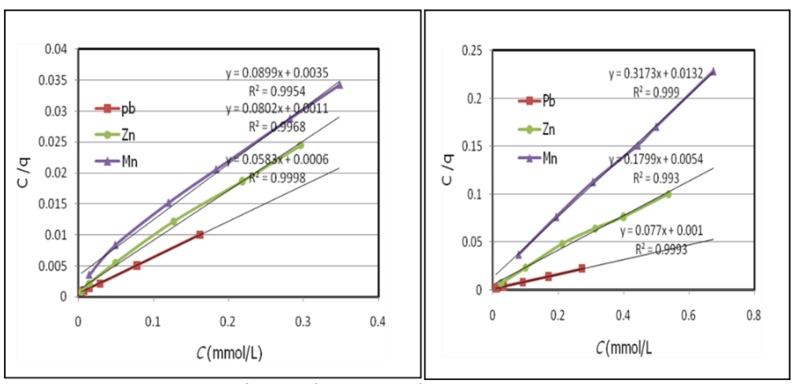

Figure 4. Langmuir adsorption isotherm of Pb^{2+}, Zn^{+2} and Mn^{+2} on apatite mineral (A) mono-metal and (B) ternary-metal

The characteristics of heavy metal sorption onto apatite mineral could be well described by the Langmuir model as clearly indicated from figure (4). The maximum adsorption capacity (Q_m) and binding energy (K_L) values were summarized in table (2) based on the application of the Langmuir model to mono-metal and ternary-metal competitive sorption.

Comparing between Langmuir parameters, in general, adsorption maxima (Qm) and binding energy (K_L) for each studied heavy metals in mono-metal was higher than the same metals in competitive experiment, of course, the competition between different ions on the exchange sites in apatite may be the reason. General trend in both (Qm) and (K_L) values of different heavy metals adsorption on apatite mineral was the same in two experiments following a descending order of Pb > Zn > Mn supported what happened in remediation experiment.

In the ternary system, the competition leads to reduce the maximum adsorbed amount of Pb only from 17.15 to 12.99 mmol/100g with percentage 24%., Zn from 12.47 in mono-metal system to 5.56 mmol/100g with percentage 55% and from 11.12 to 3.15 mmol/100g with percentage 72% for Mn. While the binding energy reduced by 20%, 54% and 7% for Pb, Zn and Mn, respectively. It means that there are high selectivity and priority of apatite to retain Pb either present alone or with other ions. The binding energy between apatite mineral and Mn did not change greatly as happened in other two heavy metals; it means that there is more than one mechanism involved in retaining studied heavy metals by apatite mineral or there are specific mechanism for certain metals.

The higher sorption of Pb^{+2} from aqueous solution may attributed to its high electro negativity 2.33 pauling scale and its very close of ionic radius (1.2A^o) with the Ca^{+2} ion (0.99A^o). Zn^{+2} with ionic radius 0.74A^o which is smaller than Ca^{+2} and less electro negativity 1.65 pauling scale than Pb^{+2} are exchanged to a lesser extent than Pb^{+2}. Moreover, Mn^{+2} with ionic radius 0.46 A^o and less electro negativity 1.55 pauling scale show also lesser extent than Pb^{+2} and Zn^{+2} behavior. It corroborates the observations of earlier investigators, LeGeros and LeGeros (1984) they mentioned that cations whose ionic radius were smaller than Ca^{+2}, may be incorporated in the apatite lattice to a much lesser extent than those of larger ionic radius. Therefore, coprecipitation of Zn^{+2} and Mn^{+2} with Ca^{+2} in the presence of apatite would be less likely to occur compared to Pb^{+2}. This may be the reason for the selectivity order of rock phosphate towards exanimated cation. The previous finding may interpret the descending order in adsorption maxima (Q_m) between the studied heavy metals.

In trial to put clear answer about the question of the third aim of the current study, calcium and phosphate were determined in equilibrium solution after adsorption carried out. Calcium was the main cation in apatite mineral, constituting 34.3% on a mass basis Singh et al., (2001). Calcium release appeared to be related to the amount of Pb^{+2}, Zn^{+2} and Mn^{+2} sorbed figure (*5*A). During metal retention by apatite mineral solution Ca^{+2} increased with increasing metal disappearance. The greatest increase was found with the Pb sorption. The largest P (phosphate) reduction was also found with Pb^{+2} sorption figure (*5*B). The fact that Pb^{+2} sorption by apatite induced the greatest increase in solution Ca^{+2} concentration as well as the largest decrease in P concentration is consistent with the hypothesis that Pb^{+2} retention by apatite was through the dissolution of apatite which mean release of Ca and P into solution and formation of pyromorphite (lead phosphate) as consuming of P. It appeared to be consistent with the hypothesis of the previous study Abdallah (2004) who proposed that Pb^{+2} retention by hydroxyapatite is controlled by hydroxyapatite dissolution followed by hydroxypyromorphite precipitation.

Table 2. Langmuir parameters for mono- metal and ternary-metal sorption on apatite mineral
Q_m maximum sorption capacity (mmol/100g apatite), K_L sorption constant related to binding energy (L/mmol)

Mono-metal system						Ternary –metal system					
Pb		Zn		Mn		Pb		Zn		Mn	
Q_m	K_L	Q_m	K_L	Q_m	K_L	Q_m	K_L	Q_m	K_L	Q_m	K_L
17.15	97.17	12.47	72.91	11.12	25.69	12.99	77	5.56	33.31	3.15	24.04

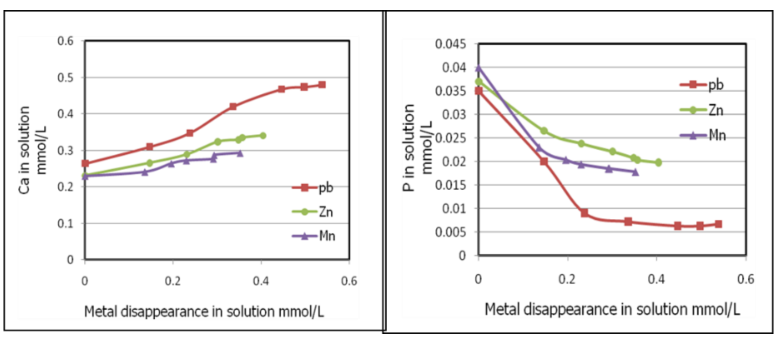

Figure 5. Calcium (A) and Phosphate (B) in equilibrium solution as a function of heavy metal disappearance

In addition, Ca levels increased and P levels decreased upon reaction of Zn^{+2} and Mn^{+2} with apatite mineral but to a lesser extent. So, it cannot exclude the possibility of Zn and Mn phosphate precipitation or coprecipitation of Zn^{+2} and Mn^{+2} with apatite mineral. In this respect, Xu et al., (1994) suggested possible coprecipitation of Zn^{+2} with Ca^{+2} to form solid phase when aqueous Zn^{+2} reacted with apatite. Ma et al. (1994) studied the hydroxyapatite with aqueous Zn^{+2} and speculated precipitation of amorphous to poorly crystalline Zn phosphate. These results are not the case in the previous study by Abdallah (2004) and (Xinde Cao et al., 2004).

To resolve this disagreement, there are two theories about the formation of solid phase between metal (Zn and Mn) and apatite as precipitation mechanism. Abdallah (2004), (Xinde Cao et al., 2004) and Wei Zheng et al. (2007) indicated that no solid phase formed but precipitation may be occurred, from other side, Xu et al., (1994) and Ma et al. (1994) indicated that the precipitation was occurred in poorly crystalline form. From figure (6) after Sona saxena and D’souza (2006), both theories are correct because the precipitation between metal ions (M) and apatite mineral occurred but may be did not complete exchange to represent solid phase and / or precipitation may occurred with different ions i.e Zn,Mn,Cu, Co and others. Moreover, Ca in apatite structure still presents in high amount and represented the finger print of apatite mineral. In the case of pb the structure of apatite mineral destructed and new mineral hydroxypyromorphite formed and tacked its finger print. This finding interpreted the absence of solid phase when apatite reacted with Zn and/ or Mn and did not appear in X-ray diffraction analysis of the results of Abdallah (2004) and Xinde cao et al. (2004), Otherwise; 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 fluro and hydroxyl pyromorphite, respectively, chen et al, (1997).

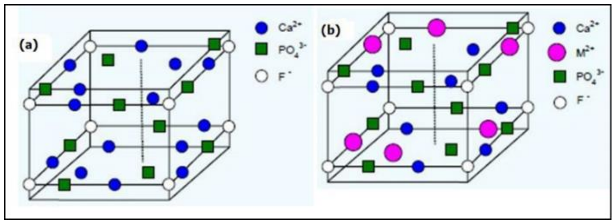

Figure 6. unit cell of apatite mineral (a) before and (b) after interaction with heavy metal ions (M^{+2})

2 - pH- free control system experiments:

To represent the clear picture about the effect of pH and in order to know what happened about the proton change during the metal adsorption, the reaction system was free of acidity control and the final pH was monitored at different initial metal concentrations. As shown in Figure (7 A and B) in mono-metal and for ternary competitive adsorption, respectively. The figures revealed that in all cases pH decreased when increasing the metal ion adsorbed with no differences between the presence of metal ion alone in solution and presence with some competitive ions. The figures revealed that the metal uptake caused a significant decrease of solution pH by up to 1.7 unit and 1.1 unit change in mono-metal and ternary -metal, respectively. Similar results were observed in previous studied, Abdallah (2004), Mavropbulos et al., (2002) and Wei Zheng et al. (2007). The addition of this study that both experiments showed the ion adsorption induced pH reduction to less than 6.87, in this range of pH the pOH is a dominant functional group for apatite mineral. Decreasing solution pH indicated that these ions act as weak bronsted acids. Thus, when Pb^{+2}, Mn^{+2} and Zn^{+2} were mixed with apatite, complexation occurred on the mineral surface partially displacing the H^+ ions and resulting in pH decline as described from the following equations:

$\equiv POH + Pb^{+2} = \equiv POPb^{+} + H^{+}$

$\equiv POH + Zn^{+2} = \equiv POZn^{+} + H^{+}$

$\equiv POH + Mn^{+2} = \equiv POMn^{+} + H^{+}$

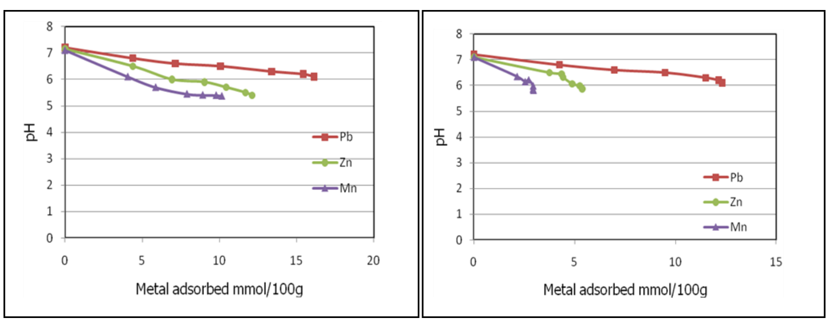

Figure 7. Final pH as a function of metal adsorbed mmol/100g free control system (A) mono-metal (B) ternary –metal

3 – Desorption of ternary metal solution experiments:

Effect of pH on the percentage of metal desorbed from apatite mineral after 0.4 mM metal reaction with apatite ternary-metal experiment was studied and drawn in figure (8). The studied heavy metal desorption depended on the pH of the extracting solutions. The percentage of Zn^{+2} and Mn^{+2} desorption significantly decreased with increasing pH reached to up to 30% and 50% of total adsorbed, respectively. However, the behavior of Pb^{+2} desorption was different from Zn^{+2} and Mn^{+2} from two sides. First, much less Pb^{+2} were desorbed i.e. less than 16% in the pH range of (3-9). Second, the Pb^{+2} desorption increased from 9.77% to 15.49% as pH increased from (3) to (5) though Pb^{+2} desorption decreased as pH increased from (5) to (9) like Zn^{+2} and Mn^{+2}. The reason of decreasing Pb desorption in pH (3) may referred to that in high acidity is likely to induce dissolution of both weakly-bound Pb^{+2} and apatite mineral, facilitating formation of hydroxypyromorphite and leading to reduction of Pb^{+2} desorption, this finding supported by Basta et al. (2001).

Zn^{+2} and Mn^{+2} was weakly bound by complexation with apatite mineral, (again it is may be another reason of why no solid phase formed between Zn and Mn with apatite minerals), thus pH reduction induced greater Zn^{+2} and Mn^{+2} solubility. In consistent Pb^{+2} desorption responding to solution pH may indicate that not all the Pb^{+2} was chemisorbed by precipitating as hydroxypyromorphite and fraction of Pb^{+2} was weakly adsorbed or complexed on the surface of apatite mineral. Comparing the total amount of immobilized Pb^{+2} with Pb^{+2} incorporated into the hydroxypyromorphite phase Mavropoulos et al. (2002) concluded that up to 30% of Pb^{+2} was immobilized by other surface mechanisms such as adsorption or complexation besides apatite dissolution and hydroxypyromorphite crystallization.

To achieve the third aim of the current study and based on the previous discussions, there are two general mechanisms for the ability of apatite mineral to take up Pb^{2+}, Zn^{+2} and Mn^{+2}. The first is (ion – ion exchange mechanism) concerned with adsorption of ions on the solid surface followed by their diffusion into apatite mineral and the release of cations originally contained within apatite, the second is (dissolution – precipitation mechanism) concerned to the dissolution of apatite in the aqueous solution containing Pb^{2+}, Zn^{+2} and Mn^{+2} followed by the precipitation or coprecipitation. Similarly, the current study propose, beyond pH (5) the sorption capacity is found to be almost constant. In this case, the removal of Pb can be attributed to surface sorption and / or complexation. Similar findings were reported by Elouear et al. (2008), Aklil et al. (2004), G´omez del R´ıo,et al. (2004) and Mouflih et al. (2006) the former author mentioned that the maximum sorption capacity for Cd^{+2}, Cu^{+2} and Zn^{+2+} were found to be at pH value between 4 and 6 for phosphate rock.

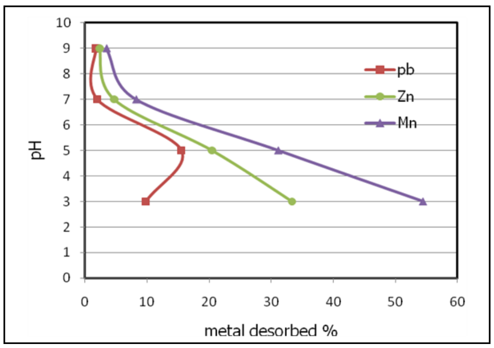

Figure 8. Percentage of metal desorption as a function of pH

CONCULSION

Apatite mineral was effective to remediate heavy metals as contaminant ions from wastewater in Abha industrial city, Asir region southwestern of Saudi Arabia. In situ remediation experiment proved that apatite mineral has the highest affinity for Pb and removed more than 94% from initial Pb concentration; the rest of contaminants followed the descending order of: Zn > Mn >Cu > Co > Ni. The sorption of Pb, Zn and Mn onto apatite mineral was well characterized by the Langmuir model. Ternary-metal addition induced competitive sorption among the three metals, with the interfering effect of Pb > Zn > Mn.

Pb, Zn and Mn desorption depended on the pH of the extracting solutions. The percentage of Zn^{+2} and Mn^{+2} desorption decreased with pH increased reached to up to 30% and 50% of total adsorbed, respectively. However, the behavior of Pb^{+2} desorption was different from Zn and Mn from two sides. First, much less Pb^{+2} were desorbed, less than 14% in the pH range of (3-9). Second, the Pb^{+2} desorption increased from 9.77% to 15.49% as pH increased from (3) to (5). Decreasing Pb desorption in pH (3) may referred to that in high acidity is likely to induce dissolution of both weakly-bound Pb^{+2} and apatite mineral, facilitating formation of hydroxypyromorphite and leading to reduction of Pb^{+2} desorption.

Obtained results suggested that there are two general mechanisms for the ability of apatite mineral to take up Pb^{2+}, Zn^{+2} and Mn^{+2}. The first is (ion – ion exchange mechanism) concerned with adsorption of ions on the solid surface followed by their diffusion into apatite mineral and the release of cations originally contained within apatite, the second is (dissolution – precipitation mechanism) concerned to the dissolution of apatite in the aqueous solution containing Pb^{2+}, Zn^{+2} and Mn^{+2} followed by the precipitation or coprecipitation. Pb^{+2} desorption responding to solution pH may indicate that not all the Pb^{+2} was chemisorbed by precipitating as hydroxypyromorphite and fraction of Pb^{+2} was weakly adsorbed or complexed on the surface of apatite mineral.

ACKNOELEDGEMENTS

This research was supported via program to support research and researchers at King Khalid university , Saudi Arabia, under number (kku_s014_33)

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