

## **TOWARDS A SAFETY ENVIROMENT: HOW APATITE MINERALS REMEDIATE Pb, Zn and Mn FROM WASTE WATER?**

**Abdallah, S. M.**

**Department of Soils, Faculty of Agriculture, Ain Shams University**

### **ABSTRACT**

To evaluate the effectiveness of apatite minerals 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 adsorption. The greatest increase of calcium and the largest phosphate reduction were found with Pb<sup>2+</sup>sorption. This is suggested that Pb<sup>2+</sup>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 two general mechanisms for the ability of apatite mineral to take up Pb<sup>2+</sup>, Zn<sup>2+</sup>and Mn<sup>2+</sup>. 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<sup>2+</sup>, Zn<sup>2+</sup>and Mn<sup>2+</sup>followed by the precipitation or coprecipitation. Pb<sup>2+</sup>desorption responding to solution pH may indicate that not all the Pb<sup>2+</sup> was chemisorbed and fraction of Pb<sup>2+</sup> 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'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.. 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.

Increaseing use of metals and chemicals in process of industries has resulted in generation of large quantities of effluents 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 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 metal contaminants from low quality water in the industrial city of abha, Asir region, southwestern of Saudi Arabia.
- 2- Answer the question of how apatite mineral remediates  $Pb^{2+}$ ,  $Zn^{2+}$  and  $Mn^{2+}$  from waste water?

## **MATERIALS AND METHODS**

### **Materials**

#### **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:

<b>Sample location</b>	<b>Latitude</b>	<b>Longitude</b>
Aswan(rock phosphate) (P1)	25° 15' 22" N	32° 38' 8" E
Aswan ( rock phosphate) (P2)	25° 14' 45" N	32° 38' 46" E

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

#### **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.

### **Methods**

#### **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 to 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 retained by apatite minerals was taken as the difference between the initial concentration in wastewater and that remaining in solution after the equilibration.

#### **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:

#### **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 minerals were examined as follows:

##### **Mono metal 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 metal 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 supernatants were 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 for the 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.

**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.

**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 reacted 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  $Mn^{2+}$ .

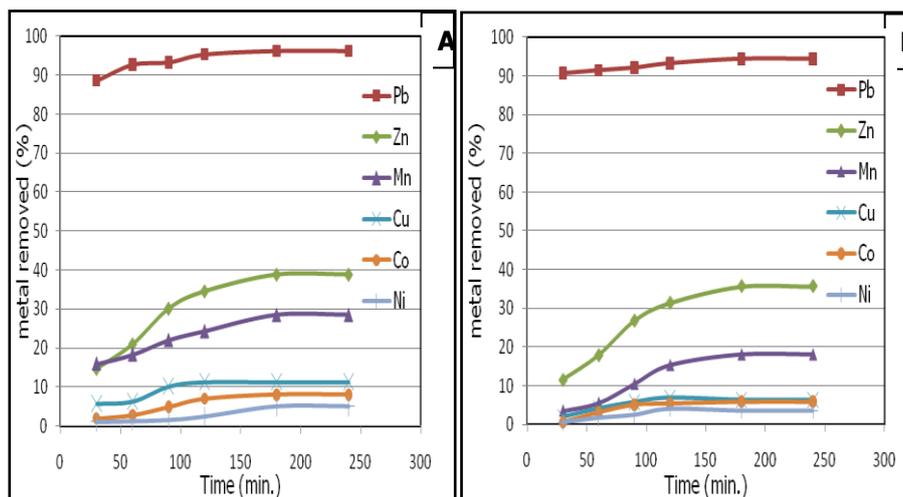
## **RESULTS AND DISCUSSION**

**In situ remediation experiment:**

Data of Table 1 show that the industrial wastewater used in this study contains several heavy metal contaminants i.e. Pb , Zn , Mn , Cu , Co , and Ni (Pescod, 1992).

Both apatite minerals are 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 show 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.



**Figure 1: Percentage of ions removed from wastewater by apatite mineral (A) (P1) and (B) (P2)**

The previous discussion proved that apatite mineral was effective to remediate heavy metals as contaminant ions from wastewater, this is achieve the first aim of the current study. Regarding the 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 <sub>4</sub>	32	Cr	0.4
Na	79	PO <sub>4</sub>	17	Hg	0.1
K	16	NO <sub>3</sub>	32	V	0.02
Fe	176	NO <sub>2</sub>	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

**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).

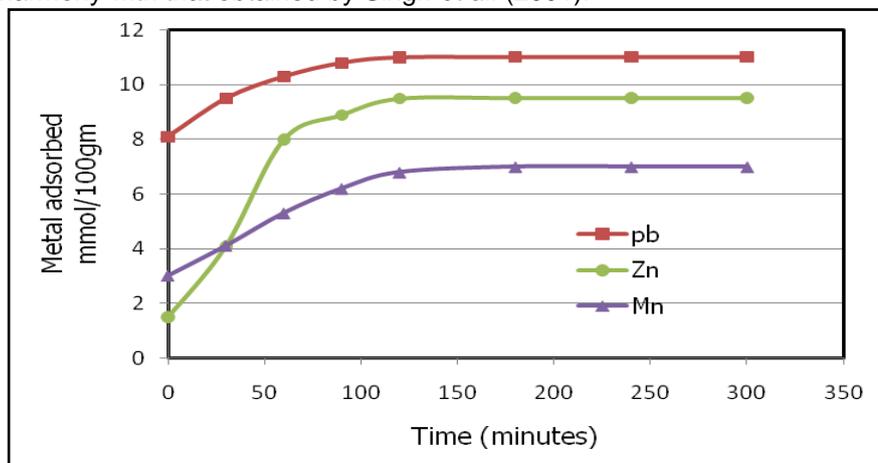


Figure 2: Adsorbed amount of studied heavy metals as a function of time

**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) are 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 (Mavrouboulos *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.

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 the constant related to 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 ( $Q_m$ ) 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 ( $Q_m$ ) 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 as compared to mono – metal system, the competition leads to reduce the maximum adsorbed amount of Pb 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 ( $1.2\text{\AA}$ ) with the  $Ca^{+2}$  ion ( $0.99\text{\AA}$ ).  $Zn^{2+}$  with ionic radius  $0.74\text{\AA}$  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  $0.46\text{\AA}$  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 exanimate 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 5A. During metal retention by apatite mineral solution  $Ca^{2+}$  increased with increasing metal disappearance. The greatest increase was found with the Pb sorption.

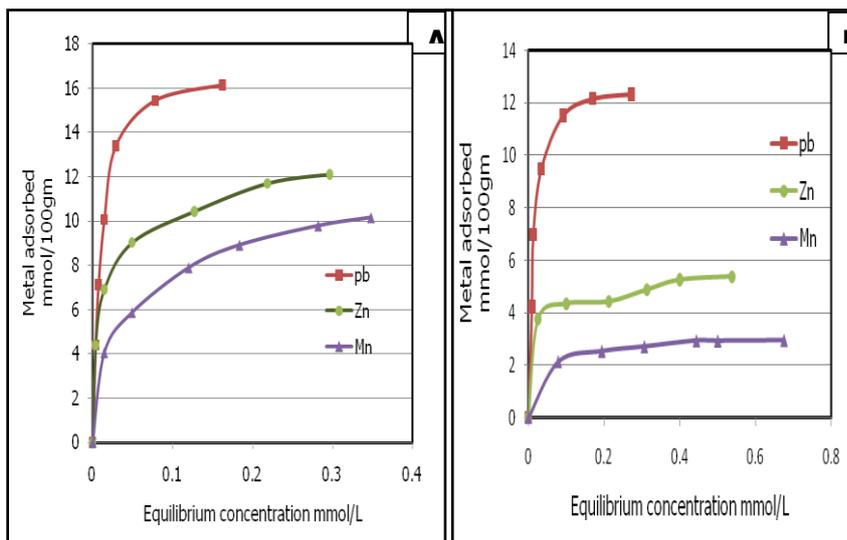


Figure 3: Adsorption isotherms of (A) mono-metal and (B) ternary-metal on apatite mineral at pH (6)

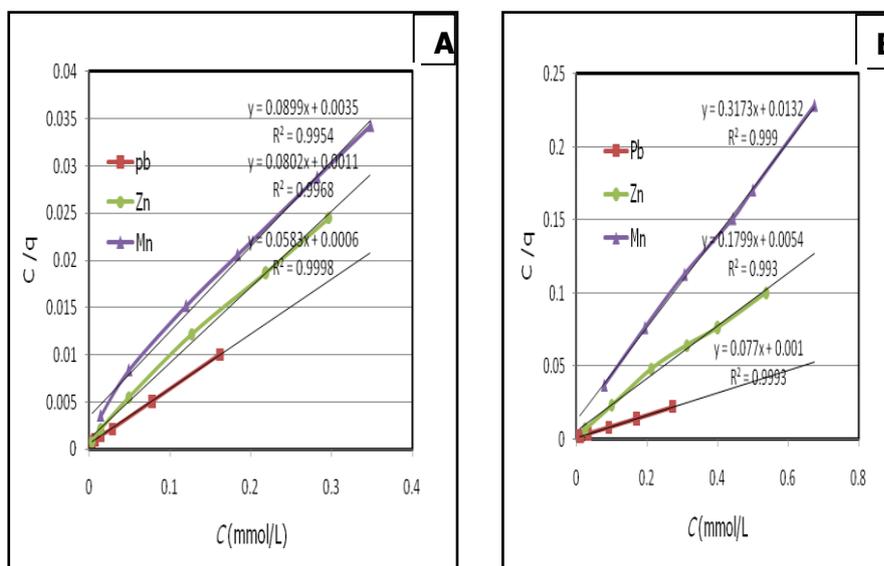


Figure 4: Langmuir adsorption isotherm of  $Pb^{2+}$ ,  $Zn^{2+}$  and  $Mn^{2+}$  on apatite mineral (A) mono-metal and (B) ternary-metal

The largest P (phosphate) reduction was also found with  $Pb^{2+}$  sorption Figure 5B. 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.

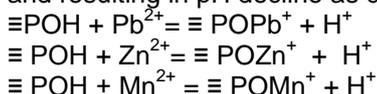
In addition, Ca levels increased and P levels decreased upon reaction of  $Zn^{2+}$  and  $Mn^{2+}$  with apatite mineral but to a lesser extent. So, it cannot exclude the possibility of Zn and Mn phosphate precipitation or coprecipitation of  $Zn^{2+}$  and  $Mn^{2+}$  with apatite mineral. In this 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 fluoro and hydroxyl pyromorphite, respectively, Chen *et al.*(1997).

#### **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) represent the obtained data for mono-metal and 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 retention caused a significant decrease of solution pH 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), Mavropoulos *et al.*, (2002) and Wei Zheng *et al.* (2007). 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:



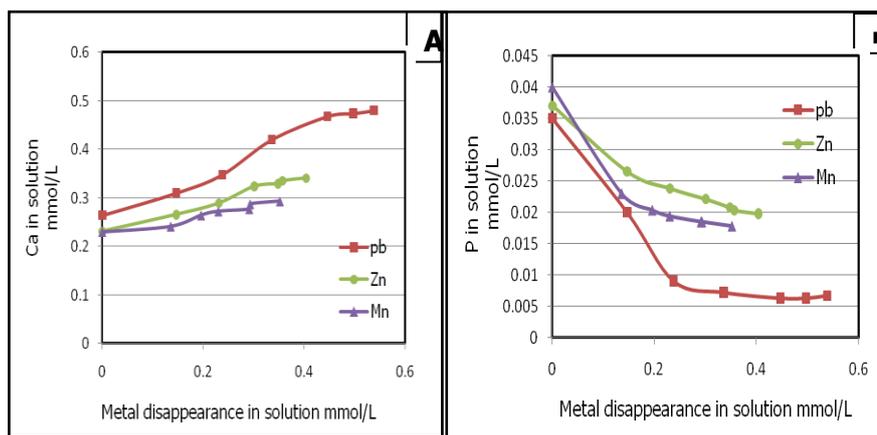
**Desorption of ternary metal solution experiments:**

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 30% and 50% of total adsorbed amount, respectively. However, the behavior of  $Pb^{+2}$  desorption was different than  $Zn^{+2}$  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) then  $Pb^{2+}$  desorption decreased as pH increased from (5) to (9) similar to  $Zn^{2+}$  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).

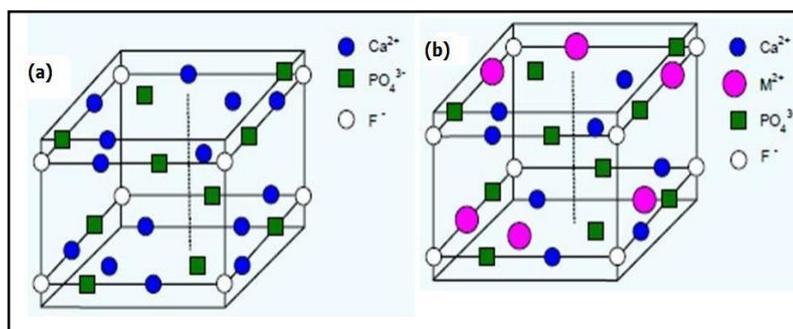
$Zn^{2+}$  and  $Mn^{2+}$  was weakly bound by complexation with apatite mineral, (again it is may be another reason of why no solid phase formed between Zn and Mn with apatite minerals), thus pH reduction induced greater  $Zn^{2+}$  and  $Mn^{2+}$  solubility. In consistent  $Pb^{2+}$  desorption responding 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  $^{2+}$  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  $Mn^{2+}$ .



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

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.



**Figure 6: Unit cell of apatite mineral (a) before and (b) after interaction with heavy metal ions ( $M^{2+}$ ) (after Sona Saxena and Disouza, 2006)**

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´io,*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.

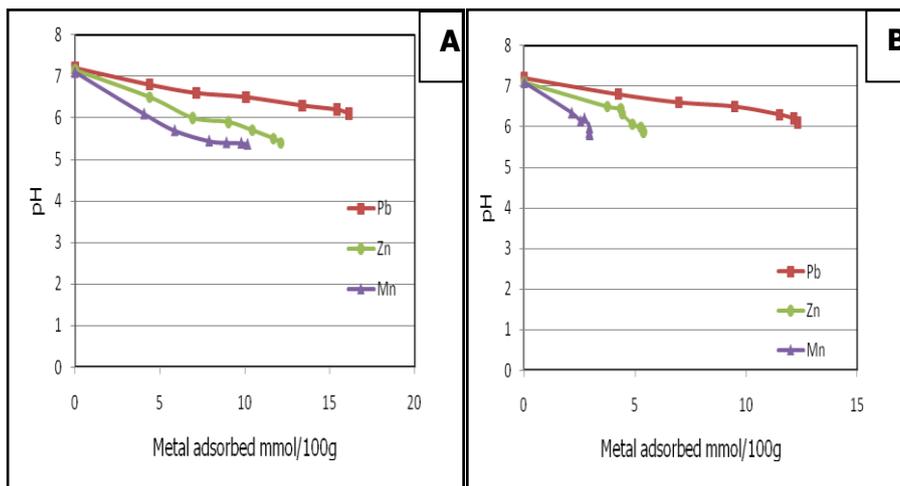


Figure 7: Final pH as a function of metal adsorbed mmol/100g free control system (A) mono-metal (B) ternary -metal

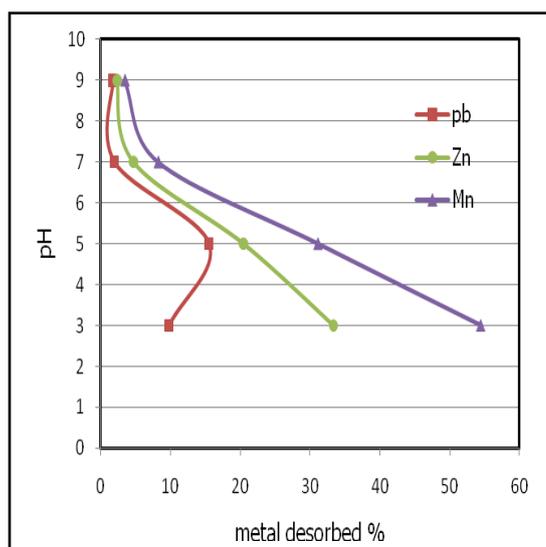


Figure 8: Percentage of metal desorption as a function of pH

Apatite minerals were 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 single 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<sup>2+</sup> and Mn<sup>2+</sup> desorption decreased with pH increased reached to up to 30% and 50% of total adsorbed amount, respectively. However, the behavior of Pb<sup>2+</sup> desorption was different than Zn and Mn from two sides. First, much less Pb<sup>2+</sup> were desorbed, less than 14% in the pH range of (3-9). Second, the Pb<sup>2+</sup> 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<sup>2+</sup> and apatite mineral, facilitating formation of hydroxypyromorphite and leading to reduction of Pb<sup>2+</sup> desorption.

Obtained results suggested that there are two general mechanisms for the ability of apatite mineral to retained Pb<sup>2+</sup>, Zn<sup>2+</sup> and Mn<sup>2+</sup>. 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 initially contained within apatite, the second is (dissolution – precipitation mechanism) concerned to the dissolution of apatite in the aqueous solution containing Pb<sup>2+</sup>, Zn<sup>2+</sup> and Mn<sup>2+</sup> followed by the precipitation or coprecipitation. Pb<sup>2+</sup> desorption responding to solution pH may indicate that not all the Pb<sup>2+</sup> was chemisorbed by precipitating as hydroxypyromorphite and may be fraction of Pb<sup>2+</sup> was weakly adsorbed or complexed on the surface of apatite mineral.

## REFERENCES

- Abdallah, S.M. (2004). Towards a more safe environment: (3) phosphatic clays as solution for removing Pb<sup>2+</sup> from wastewater. *Egyptian Journal of Soil Science.*, 44: 585-599.
- Abdallah, S.M. (2006) Towards a more safe environment (1) A new modified clay for removing heavy metals from low quality water. *Journal of Applied Science Research*, 2: 391-396.
- Abdallah, S.M., El-hussaini, O.M., and Mahdy, R.M. (2005) Towards a more safe environment: (4) Sorpability of vanadium by some clay sediments in Egypt. *Journal of Applied Science Research*, 1: 168-175.
- Abdallah, S.M., El-Hussaini, O.M. and Mahdy, R.M. (2007) Towards a more safe environment (2) Characterization of some clay sediments in Egypt for safe environmental applications. *Australian Journal of Basic and Applied Sciences*, 1: 813-823.

- Akliil, A., Mouflih, M. and Sebti, S. (2004). Removal of heavy metal ions from water by using calcined phosphate as a new adsorbent; *J. Hazard. Mater.*, 112: 183–190.
- Basta, N.T., Gradwohl, R., Snethen, K.L. and Schroder, J.L., (2001). Chemical immobilization of lead, zinc, and cadmium in smelter contaminated soils using biosolids and rock phosphate. *J. Environ. Qual.*, 30: 1222-1230.
- Buerge-Weirich, D., Hari, R., Xue, H., Behra, P. and Sigg, L. (2002). Adsorption of Cu, Cd and Ni on goethite in the presence of natural groundwater ligands. *Environ. Sci. Technol.*, 36: 328–336.
- 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.
- Dong, D.M., Hua X.Y., Zhang, J., Li, Y. and Yan D. (2003). Chemical processes at the Water-manganite ( $\gamma$ -MnOOH) interface. *Environ. Sci. Technol.*, 37: 4106–4112.
- Echeverria, J.C., Morera, M.T., Mazkarian, C. and Garrido, J.J. (1998). Competitive sorption of heavy metal by soils. Isotherms and fractional factorial experiments. *Environ. Pollut.*, 101:275-284.
- Elouear, Z., Bouzid, J., Boujelben, N., Feki, M., Jamoussi, F. and Montiel, A. (2008). Heavy metal removal from aqueous solutions by activated phosphate rock. *Journal of Hazardous Materials*, 156:412–420
- Fred Jr. D.T., Shannon, L.B.H., Vinka, A.S., James A.S. and George, R.A. (2005). Relative metal ion sorption on natural and engineered sorbents: batch and column studies. *Environ. Eng. Sci.*, 22: 400–409.
- Gómez del Río, J.A., Morando, P.J. and Cicerone, D.S. (2004). Natural materials for treatment of industrial effluents: comparative study of the retention of Cd, Zn and Co by calcite and hydroxyapatite. Part I: batch experiments. *J. Environ. Manag.*, 71:169–177.
- 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
- LeGeroes, R.Z. and LeGeroes, J.P., (1984). Phosphate minerals in human tissues. In: Nariagu, J.O. (Ed.), *Phosphate Minerals*. Springer- Verlag, Berlin, 351-385.
- Ma, Q.Y., Traina, S.J., Logan, T.J. and Ryan, J.A., (1994). Effects of aqueous Al, Cd, Cu, Fe(II), Ni, and Zn on Pb immobilization by hydroxyapatite. *Environ. Sci. Technol.*, 28: 1219-1228.
- Manning, B.A., Fendorf, S.E., Bostick, B. and Suarez, D.L. (2002). Arsenic (III) oxidation and arsenic (V) adsorption reactions on synthetic birnessite. *Environ. Sci. Technol.* 36 976–981.
- 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.

- Mouflih, M., Aklil, A., Jahroud, N., Gourai, M. and Sebti, S. (2006). Removal of lead from aqueous solutions by natural phosphate, Hydrometallurgy, 81:219–225.
- Pescod, M.B. (1992). Wastewater treatment and use in agriculture. Food and Agriculture organization of the United Nations Rome, 1992 FAO irrigation and drainage paper 47
- 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.
- Sona Saxena, and D'Souza S.F. (2006). Heavy metal pollution abatement using rock phosphate mineral. Environment International 32:199 – 202
- Trivedi, P. and Axe, L. (2000). Modeling Cd and Zn sorption to hydrous metal oxides; Environ. Sci. Technol., 34 :2215–2223.
- Wei Zheng, Xiao-ming Li, Qi Yang, Guang-ming Zeng, Xiang-xin Shen, Ying Zhang and Jing-jin Liu (2007). Adsorption of Cd(II) and Cu(II) from aqueous solution by carbonate hydroxylapatite derived from eggshell waste. Journal of Hazardous Materials, 147: 534–539
- Xinde cao, X., Ma, L. Q., Rhue, D.R. and Appel, C.S. (2004). Mechanism of lead, copper and zinc retention by phosphate rock. Environ. Poll., 131:435-444.
- Xu, Y., Schwartz, F.W. and Traina, S.J. (1994). Sorption of  $Zn^{2+}$  and  $Cd^{2+}$  on hydroxyapatite surfaces. Environ. Sci. Technol., 28:1472-1480.

### نحو بيئة أكثر أماناً:

### كيف تزيل معادن الأباتيت كل من الرصاص والزنك والمنجنيز من مياه الصرف؟

سامي محمد عبد الله

قسم الأراضي – كلية الزراعة – جامعة عين شمس

لتقييم مدى كفاءة معادن الأباتيت في إزالة الملوثات المختلفة من المياه المنخفضة الجودة تم إختيار نوعين من صخر الفوسفات التي يسود بها معدن الأباتيت وتجربته علي معالجة مياه الصرف من المنطقة الصناعية في مدينة أ بها – منطقة عسير - جنوب غرب المملكة العربية السعودية.

أكدت نتائج إزالة العناصر الثقيلة من المياه المنخفضة الجودة *in situ remediation* علي وجود علاقة ارتباط قوية بين عنصر الرصاص ومعدن الأباتيت حيث أزال حوالي 94% من الرصاص الموجود في مياه الصرف أما باقي العناصر فكانت تتبع الترتيب التالي: الزنك < المنجنيز < النحاس < الكوبلت < النيكل.

لوضع ميكانيكة لمعرفة كيف تزيل معادن الأباتيت كل من الرصاص والزنك والمنجنيز تم إجراء بعض التجارب (إدمصاص لكل عنصر بمفرده *mono-metal* – إدمصاص لمخلوط من الثلاث عناصر معا *ternary – metal mixture* - مع التحكم في ال pH – تجربة لإدمصاص العناصر بدون التحكم في ال pH – إنطلاق للعناصر المدمصة من علي الأباتيت). وأثناء حدوث ارتباط للعناصر الثقيلة مع الأباتيت تم تقدير كلا من الكالسيوم والفوسفات في محلول الإتران وأظهرت النتائج زيادة نسبة الكالسيوم وإنخفاض نسبة الفوسفات مع زيادة إحتفاء العناصر الثقيلة من المحلول. كما أكدت النتائج أن أعلى تركيز للكالسيوم وأقل تركيز للفوسفات يحدث مع إدمصاص الرصاص. وإقتترحت الدراسة أن ارتباط الرصاص بالأباتيت يكون عن طريق حدوث تحلل للأباتيت

وهو ما يعني زيادة تركيز الكالسيوم والفوسفات في المحلول ثم تكوين معدن البيرومورفيت (فوسفات الرصاص) وهو ما يعني إستهلاك الفوسفات ونقصه من محلول الإتزان.

وأظهرت نتائج إنطلاق العناصر من معدن الأباتيت بواسطة محاليل الإستخلاص المختلفة ال pH أن نسبة الزنك والمنجنيز المنطلقة تقل مع زيادة ال pH لمحلول الإستخلاص ووصلت أعلي نسبة إنطلاق إلي 30% و 50% علي التوالي. أما نتائج إنطلاق الرصاص فقد أظهرت سلوك مختلف يؤكد ما تم التوصل إليه من ميانيكية الإزالة للعناصر الثقيلة من مياه الصرف. فلقد اختلف سلوك الرصاص من ناحيتين:

الأولي: نسبة منخفضة جدا من الرصاص هي التي تم إنطلاقها حيث كانت أقل من 16% في مدي ال pH من (3-9).

الثانية: نسبة الرصاص المنطلقة زادت من 9.77% إلي 15% عند زيادة ال pH من 3 إلي 5 ثم إنخفضت بعد ذلك مع زيادة ال pH مثل باقي العناصر. تم تفسير ذلك علي حدوث إنحلال للرصاص ومعدن الأباتيت في ال pH المنخفض فزادت نسبة الرصاص المنطلق ثم تم تكوين هيدروكسي بيرومورفيت والذي أدي بدوره إلي نقص عنصر الرصاص بعد ذلك.

إقترحت نتائج الدراسة أن هناك ميكانيكيتين مختلفتين لإرتباط أيونات الرصاص والزنك والمنجنيز بمعدن الأباتيت. الميكانيكية الأولى حدوث ion – ion exchange mechanism وهي حدوث تبادل أيوني للأيونات علي سطح المعدن الصلب. الميانيكية الثانية: dissolution – precipitation mechanism عن طريق حدوث إنحلال لمعدن الأباتيت في المحلول المحتوي علي العناصر الثقيلة ثم يحدث ترسيب مع الأيونات الموجودة بالمحلول وقد يتكون طور صلب جديد أو لا يتكون.

قام بتحكيم البحث

أ.د / خالد حسن الحامدي

أ.د / عيد مرسى خالد

كلية الزراعة – جامعة المنصورة

كلية الزراعة – جامعة عين شمس

