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PREPARATION AND CHARACTERIZATIONS OF BARIUM HYDROXYAPATITE AS ION EXCHANGER

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ABSTRACT

The aim of this study was preparation and characterization of barium hydroxyapatite, $Ba_{10}(PO_4)_6(OH)_2$, BHP, to be used as ion exchanger for removal of some toxic cations from their aqueous solutions. The starting materials were barium hydroxide and phosphoric acid. The effects of the ratio between phosphoric acid and barium hydroxide on the produced hydroxyapatite were studied. X-ray diffraction, IR spectra, Transition electron microscope, and surface area were used for characterization of the produced barium hydroxyapatite. The x-ray patterns indicated the formation of the crystalline barium hydroxyapatite by using 0.02M H_3PO_4, while the other normality gives more than one phase. The IR spectrum exhibits specific absorption peaks at 558.2, 693.28, 1008.11, 1428.99, 1751.53, 1941.97, 3440.87, which characterizes the barium hydroxyapatite. It is observed that the intensity of the specific peaks on the x-ray charts increases with increasing of the acid normality, this indicate that the crystallinity improves by the increase of the acid normality. The TEM showed that: (1) the particle size of the barium hydroxyapatite lies in the scale of nanoparticles (40- 180 nm). (2) the size of the barium hydroxyapatite increases with increasing the ratio of phosphoric acid. (3) the particles have irregular shape and not depend on the ratio of phosphoric acid. (4) The sample produced by using phosphoric acid = 0 .04 M showed a bone structure. The measurements of the surface area indicated that it depends on the morphology of the produced samples which by turn depends on the normality of phosphoric acid. The more suitable sample was used to remove Cu, Cd, Ni, and Zn from their aqueous solutions.

Keywords: Barium hydroxyapatite, preparation, charsacterization, removal, metals.

INTRODUCTION

The objective of this work was preparation and characterization of barium hydroxyapatite, $Ba_{10}(PO_4)_6(OH)_2(BHAP)_2$, to be used as ion exchanger to remove some heavy metals from their aqueous solutions. The more conventional technologies for heavy metal ions removal are chemical precipitation, ion exchange, reverse osmoses, electrochemical treatment, sorption, solvent extraction and filtration. Among these methods, sorption and ion exchange technologies are the most promising methods due to their high efficiency, easy handling, availability of different materials and cost effectiveness. Phosphate minerals have been shown to possess the potential to remove heavy metal ions from aqueous solutions (Monteil – Rivera and Fedoroff, 2002). Of all the inorganic phosphate sources, apatite is most readily available. Different origins of apatite (mineral or synthetic) have been used to remove heavy metal cations (Elouear *et al*., 2008). Peld *et al.* (2004) studied the effects of different factors on removing Cd^{+2}, Zn^{+2}, by some synthetic types of hydroxyapatite. Removal of single, binary and tertiary divalent cations, i.e Pb^{+2}, Cu^{+2}, Cd^{+2} respectively, from their chloride or nitrate aqueous solutions were carried out by using hydroxylapatite. The results indicated that Pb^{+2} were adsorbed on the apatite structure very fast than the other cations **(**Takeuchi and Arai, 1990**)**. Bailliez *et al.* (2004) studied the mechanism of the removal of Pb^{+2}on the structure of hydroxyapatite, and used the chemical analysis and the x-ray techniques for the solution and the solid respectively. They found that the slightly dissolution of HAP is followed by formation of hydroxy pyromorphite, a solid solution of $Pb_{10-x}Ca_x(PO_4)_6(OH)_2$ formula, with Pb ions mostly occupying Ca(II) sites, and that the Ca/P molar ratio of this solid solution decreases continuously. Sugiyanaa *et al.* (2000) identified the formation of lead hydroxyapatite in the solid state after exchange with Pb^{+2}, while no copper analogue of HAP was found. Also, they found that the addition of HCl enhance the exchangeability. It is noteworthy that most of the work was focused on Ca - hydroxyapatite due to its natural occurrence in the rock, bones and teeth, beside the ability of Ca^{+2} in CaHAP to substituted by various other cations. A few works was devoted to the other hydroxyapatite such as SrHAP, BaHAP to study the effect of the atomic radius on the exchangeability (Sugiyanaa *et al*., 2000**;** Sgiyama, 1998). For this reason our work was aimed to prepare barium hydroxyl apatite by simple method and using as ion exchanger agent for removing the more toxics metals such as Cd^{+2}, Zn^{+2}, Cu^{+2} and Ni^{+2} where these cations interaction with the biological apatite

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of bones, leading to a disease producing effects similar to osteoporosis (Miyahara, 1980; Christoffersen, 1988). BaHAP have been synthesized by many researchers using solid state reactions (Fowler, 1974, 1974), wet process and sol- gel route (Bigi *et al*., 1984)˙ BaHAP, $Ba_{10}(PO_4)_6(OH)_2$ possesses unique properties as catalysts and immobilization reagents. For example, catalysts activities on BaHAP into metal conversion (Sgiyama and Moffat, 2002) and oxidative dehydration of alkanes (Sgiyama *et al*., 1999, 2001) were reported together with the removal properties of BaHAP with aqueous heavy metals (Bailliez *et al*., 2004).

MATERIALS AND METHODS

Pure grade chemicals were used without further purification. Barium hydroxyapatite, BaHAP, was prepared from $Ba(OH)_2.8H_2O$ and H_3PO_4(85%) according to the procedure reported by (Yasukawa *et al* 1999). 0.2 M of $Ba(OH)_2.8H_2O$ and different molarities of H_3PO_4(0.02, 0.04, 0.06, 0.08, and 0.1 M) were prepared as stock materials. H_3PO_4 solution was added to the barium hydroxide with continuous stirring at 100°C under nitrogen atmosphere. Phosphoric acid was added with low rate (4cm^3/min) to avoid the local depression in the pH of the solution. The resultant white suspensions were aged at 100°C for 16hr. and the formed precipitates were filtered off. The precipitates were washed with di-ionized water and methanol and dried at the room temperature for 16hr. The produced samples were calcinated at 500°C for 4 hr. to study the effect of the calcinations on the structure of the samples (Matsumoto *et al*., 2001). The obtained particles were characterized by various techniques. Infrared absorption spectra (IR) were performed by the KBR disc technique using a Fourier transformer infrared spectrometer (Nexus 670 FTIR, USA) in the range between 400 to 4000 cm-1.X-ray diffraction (XRD) was carried out by using Brukur D8 advance diffractometer (Germany) using CuKα radiation. The surface area of the prepared samples was performed by using Quantachrome Inst., Quantachrome Nova Automated gas sorption system version 1.12.

The dried BHA was used as ion exchanger to remove some divalent cations, Cu, Ni, Cd, and Zn from their aqueous solutions, In this work, 0.4gm of the BaHAP powder were dispersed in 100 cm^3 aqueous solutions containing concentrations of the divalent cations nitrates. The pH value of the solutions were adjusted between 5 to 7 by adding 1 N HNO_3 solution at 30°C. The solutions were left for 60 min to attain the equilibrium state. After this period the solid part were separated by filtration, dried at 70°C. The filtrate was analyzed by using atomic absorption route to determine the remainder amounts of Cu, Ni, Cd, and Zn. The effects of the concentration of the divalent cations between 10^{-4} to 10^{-2} M and the time of immersion between 10 to 75 min were investigated. The efficiency of removing was calculated by using the following formula $f\ \% = (C_o - C) / C_o$ where C_o and C are the initial and the concentration of the divalent cations in the solution after removing respectively.

RESULTS AND DISCUSSION

Figure 1, represents the IR spectra of the five prepared samples (a, b, c, d and e). At all samples, a broad band at ~3425.3 - 3440 cm^{-1} was appeared, this band attributed to the vibration of the OH^- in the lattice as proposed by (Yasukaua *et al*., 1999). The intensity of this band decrease with increasing the concentration of H_3PO_4 and becomes very weak at sample (e), this may due to the presence of some difference in the orientation of OH^- groups through the structure of the lattice (Reisner and Klee, 1982). Also, curve (a) shows a strong band at 1000-1100cm^{-1} beside a week one at ~ 930cm^{-1} due to the stretching vibrations of PO_4^{-3}. Two other sharp bands at ~580 and 558 were specified due to the deformation vibrations of the phosphate ions $(PO_4)^{-3}$ (Baddiel and Berry, 1966). In addition, a sharp band was appeared at ~1420 corresponding to CO_3^{-2} ions incorporated with OH^- sites on the surface hydroxyl apatite. (Cheng *et al*., 1998) suggested that the presence of the CO_3^- group in the lattice of the hydroxyl apatite may due to the atmospheric carbon dioxide. For the other samples (b,c,d, and f), the IR spectrum shows the same character as that proceeded for sample (a) with some shifts which may due to the orientation in the lattice. In general the IR spectrum indicate that the BaHAP is formed in agreement with the previous work (1,2,3). In previous study, the authors found that the CaHAP powder is converted from amorphous state to crystalline phase by increasing the calcinations temperature (El-sayed and Mousa, 2006). According to these results, a sample from the prepared BaHAP was exposed to calcinations at 500°C for 4hr. The results of the X-ray diffraction were presented in fig 2, for the prepared samples by using 0.02, 0.04, 0.06, 0.08, and 0.1 M H_3PO_4. The X-ray patterns of the produced powder showed that only sample (a) which prepared by using 0.02 M of phosphoric acid gives BaHAP (JCPDS 36-0272). For the other four samples (b-e) which prepared by using (0.04-0.1M) of phosphoric acid. The produced phases are BaHAP with traces of $Ba_3(PO_4)_2$, $Ba_3(PO_4)_2$, and a mixture of $Ba_3(PO_4)_2$ and $Ba_2(P_2O_7)$ and $Ba_2(P_2O_7)$, respectively at high molarities of H_3PO_4 due to the formation of pyrophosphate. According to the results of the X-ray diffraction, sample (a) is the preferable one to be used as ion exchanger. The results indicate that the formed BaHAP have a nanoparticle size in the range between 40 and 180 nm. Also it is observed that the particle size of BaHAP increased by increasing the molarities of H_3PO_4, this may due to the crystal growth.

Figure 3, displays TEM images of the prepared samples by using different molarities of H_3PO_4. The average

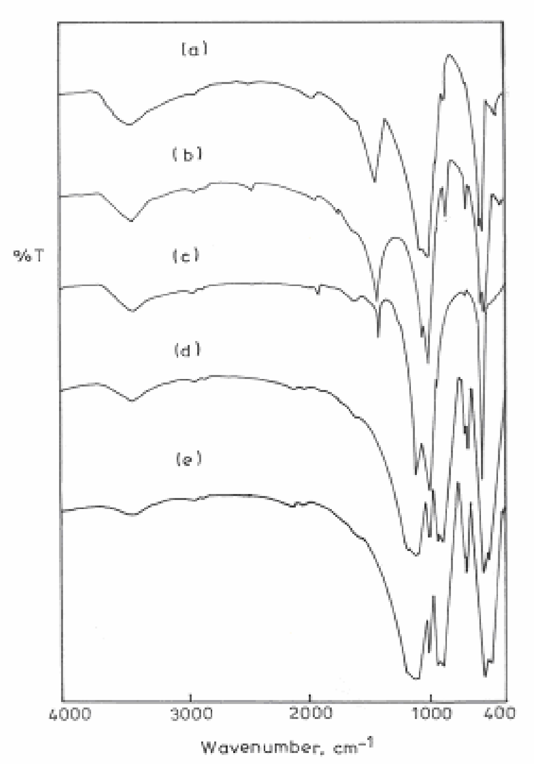


Fig. 1. IR spectrum of prepared samples
a= sample with 0.02 M H_3PO_4
b= sample with 0.04 M H_3PO_4
c= sample with 0.06 M H_3PO_4
d=sample with 0.08 M H_3PO_4
e= sample with 0.1 M H_3PO_4

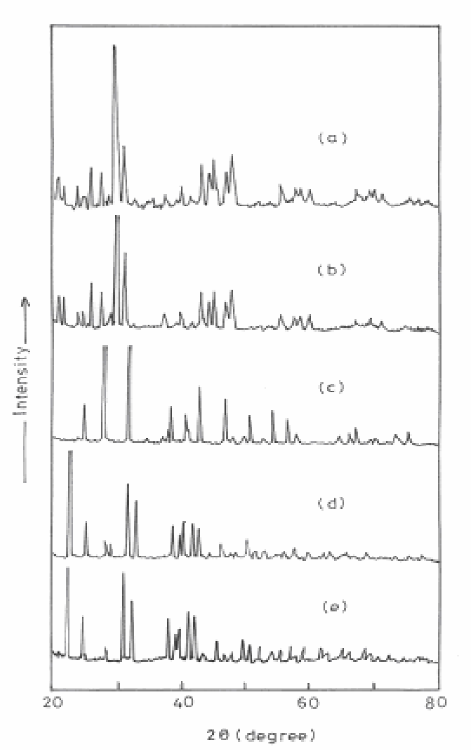


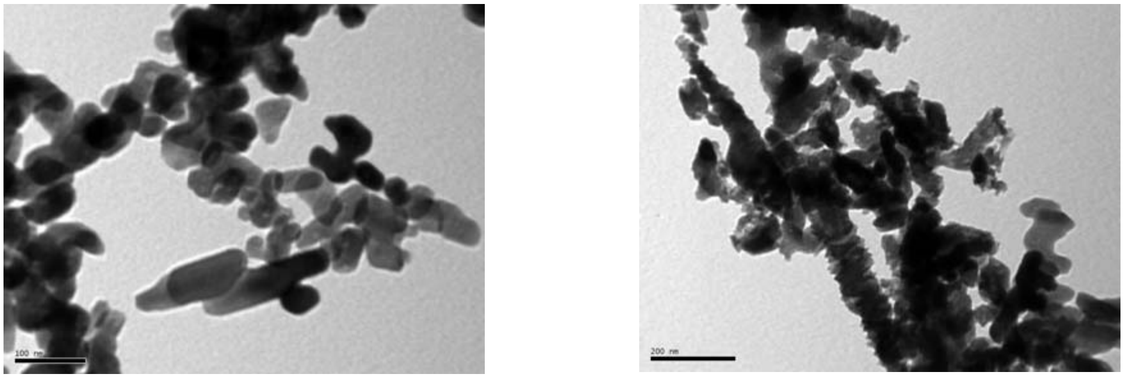
Fig. 2. X-ray diffraction of prepared samples.
a= sample with 0.02 M H_3PO_4
b= sample with 0.04 M H_3PO_4
c= sample with 0.06 M H_3PO_4
d=sample with 0.08 M H_3PO_4
e= sample with 0.1 M H_3PO_4

particle size estimated from the TEM image are increase from 40 to 180nm as the molarities of the used phosphoric acid increases from 0.02 to 0.1. On other hand, it is observed that the short rod particles elongated as the molarities of H_3PO_4 increases. The formed BaHAP are arranged in irregular shape and this increased by increasing the molarities of H_3PO_4 forming a structure lake bone at the high molarities of H_3PO_4 samples (d,f). The results of the measured surface area indicate that the surface area of the produced BaHAP decrease as increasing in the molarities of H_3PO_4 (Table 1). This finding is in agreement with the results of X-ray diffraction, where the crystallinity of the BaHAP increased with the molarities of the acid which leads to decrease in the surface area.

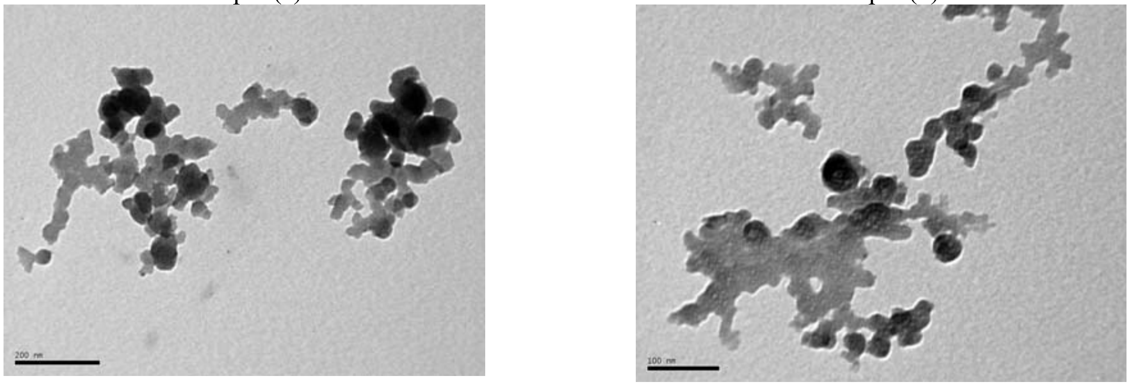
To study the effects of the surface area of BaHAP on the efficiency of removing copper cations with concentration = $5x10^{-4}$ M, was used as example of the divalent cations. The results indicate that the sample with high surface area exhibiting high efficiency to removal the copper from its aqueous solution (Table 2). These results are in agreement with the fundamental bases and the obtained results.

The prepared sample of Barium hdroxyapatite calcinated at 500°C for 4hr with 0.02 M H_3PO_4 was used as ion exchanger to remove some heavy metals M^{+2}(M^{+2} =Zn, Cu, Cd, and Ni). In this study, the batch process was performed, where a certain weight of BaHAP was immersed in nitrate solutions of the divalent cations with continuous stirring to attain the equilibrium. The effect of the pH values at pH = 5,5.5,6 and 7 on the efficiency of the up taking the cations was studied. At the pH values > 7, some problems were observed in performing the experiments such as complex formation or dissolution of the precipitated salts. Also, the effect of the initial concentration C(C =10^{-4}, $5x10^{-3}$, 10^{-3}, $5x10^{-2}$, 10^{-2}) and the time of removing (t), (t=10, 20, 30, 45, 60min) on the efficiency of removing was investigated.

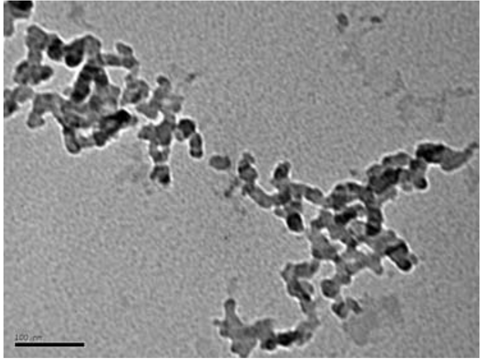
Figure 4, represents the variation of the efficiency to removing the metal cations with the pH values by using sample (a) [prepared from 0.02M H_3PO_4 and having the higher surface area]. For the four cation under investigation, it was observed that the efficiency of removing decreases with increased in the pH values. At low pH value ranges, the decrease in the efficiency is



Sample (a) Sample (b)



Sample (c) Sample (d)



Sample (e)

Fig. 3. TEM of prepared samples.
a= sample with 0.02 M H_3PO_4 b= sample with 0.04 M H_3PO_4
c= sample with 0.06 M H_3PO_4 d=sample with 0.08 M H_3PO_4
e= sample with 0.1 M H_3PO_4

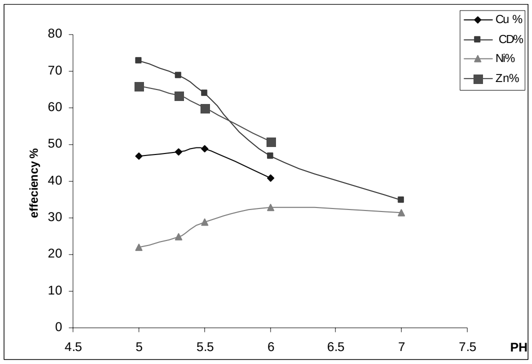


Fig. 4. Effects of pH on adsorption process.

more remarkable than that at high pH value. This behavior is in agreement with the results obtained by (Sgiyama *et al*., 2000), where they observed that the addition of HCl to the medium of solution enhances the up taking of the divalent cations. On other hand, (Suzuki *et al*., 1981) reported that hydroxylapatites are quite suitable as an a desorbent in the acidic medium of the aqueous solution

In general figure 4, shows that the removing of the four cations take place the same trends by the variation of the pH values and following the sequence Cu > Zn > Cd > Ni. This arrangement may depend on the nature of cations such as their electronegativity, ionic radius atc. Literatures indicated that there are two mechanisms for the ability of the hydroxyapatites to take up the cations from their solutions (Lower *et al*., 1998).

1) ion–ion exchange mechanism, where the cations were adsorbed on the solid surface, followed by diffusion into the HAP and release of cations, whatever they are Ca^{+2},Ba^{+2},Sr^{+2} .

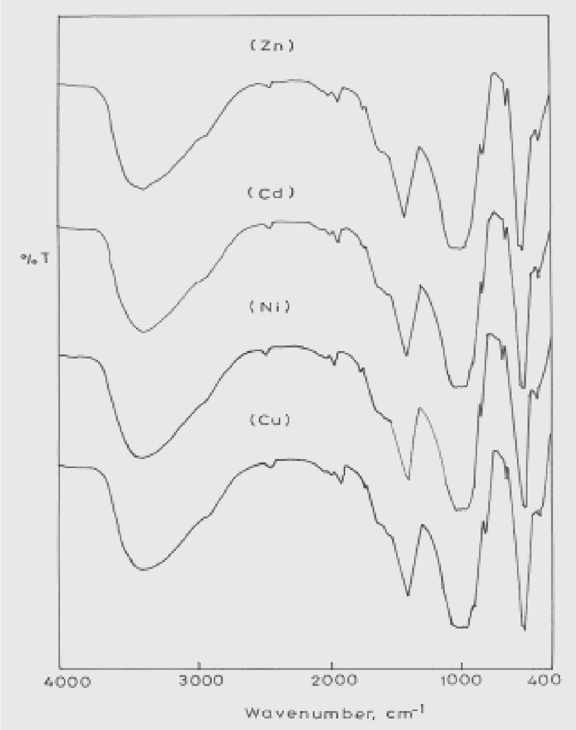


Fig. 5. IR spectrum of produced BaHAP samples after adsorption process.

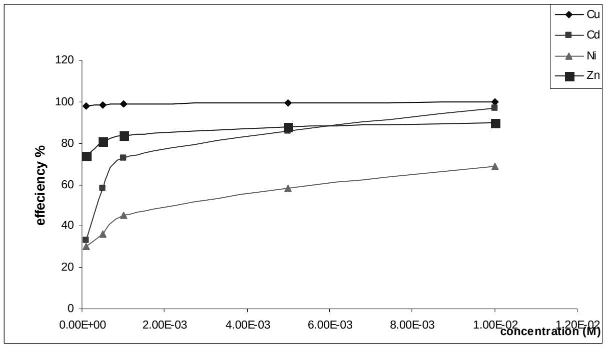


Fig. 6. Effects of the initial concentrations on adsorption process.

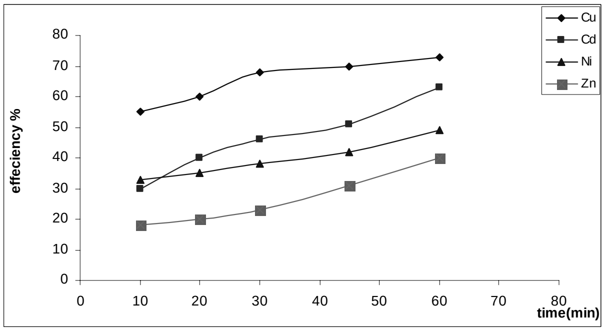


Fig. 7. Effects of the time on adsorption process.

2) Dissolution – precipitation mechanism, where a few amounts of HAP was dissolved in the aqueous solution containing the divalent cations followed by precipitation or coprecipitation.

The mechanism of the removal of divalent cations by hydroxyapatites depends on the nature of these cations such as their ionic radius and the electromotivities as well as the type of the hydroxyapatites whatever it is strontium, calcium, barium. On other hand, the morphology and the structure of the hydroxyapatites affected greatly on the efficiency of the removing for the cations. Because no detection on the formation of the substituted hydroxyapatites on the IR spectrum for the BaHAP after removing, fig. 5, the most acceptable mechanism is the solubility of some barium hydroxyapatites particles from the surface (the coprecipitation mechanism).

The effect of the initial concentration of the divalent cations on the efficiency of up taking was illustrated in fig. 6, In all adsorption cases, the efficiency of absorption increases with the increase the initial concentration of cations, but this increase is more remarkable at the low concentration than that at high concentration. This may due to the low solubility of barium hydroxyapatite and their interaction with the divalent cations. This results are in agreement with the obtained results by (Fedoroff *et al.*, 1999**)**, where they observed that no significant difference are noted between experiments performed with initial concentration of $3.96x10^{-3}$ and $3.96x10^{-4}$ mol.l^{-1} of cadmium cation and using CaHAP.

Figure 7, represents the dependence of the efficiency of removing on the time of immersion. In general it is observed that the efficiency increases rapidly at the first stages (>30 min) of removing, and increases slightly with time of immersion between 30-60min. This results support the mechanism of removing which depend on the dissolution and precipitation on the surface of the barium hydroxyl apatite.

CONCLUSION

The preparation of barium hydroxyapatite depends on the normality of H_3PO_4 as well the conditions of preparation and the calcination temperatures. The prepared BaHAP from 0.02M H_3PO_4 and barium hydroxide shows a single phase with higher surface area than the other samples. The up taking of the heavy metals from their aqueous solutions was depended on the initial concentration, time of contact and the pH values.

Table 1. Surface area measurements of BaHAP samples.

Samples	Surface area
a(0.02M) H_3PO_4	89.7 m^2/g
B(0.04M) H_3PO_4	37.9 m^2/g
c(0.06M) H_3PO_4	30.8 m^2/g
d(0.08M) H_3PO_4	33 m^2/g
e(0.1M) H_3PO_4	29 m^2/g

Table 2. the efficiency of removal of Cu metal by BaHAP with different molarities.

Samples of Cu solutions	Samples of BaHAP	Efficiency %
a	a(0.02M) H_3PO_4	35.9
b	b(0.04M) H_3PO_4	28.6
c	c(0.06M) H_3PO_4	5.58
d	d(0.08M) H_3PO_4	4.88
e	e(0.1M) H_3PO_4	3.59

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