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Metal Ion Binding on Hydroxyapatite (Hap) and Study of the Velocity of Sedimentation

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Abstract

The objective of this study is to develop by chemical synthesis of hydroxyapatite, an adsorbent powder to be used for the decontamination of waters by metal ions. Moreover, the effectiveness of chitosan produced from shrimp waste to flocculate turbid suspensions produced from the previous treatment is evaluated. The study of adsorption of Cu and Zn on hydroxyapatite showed a removal efficacy of 88-95% with relatively fast kinetics. Between the two metals, copper presents the higher adsorbing tendency. However, the use of hydroxyapatite, as an adsorbent, generates turbid suspensions which are hardly settleable. For this reason we evaluated the effectiveness of chitosane to flocculate the hydroxyapatite turbid suspensions. The outcome of this study is the great efficacy exhibited by the chitosan to remove the turbidity of various samples of hydroxyapatite of different fractions. The elimination rate after 30 minutes of settling in all cases exceeds 98%.
The effect of the dose of chitosane and the effect of pH on the coagulation-flocculation process were studied and the respective results show that the optimal doses range from 0.2 to 2 mg of chitosane/ L corresponding at optimal pH between 6 and 7.

Keywords: ion binding, hydroxyapatite; Chitosane; settling velocity; nano-particles

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1. Introduction

Pollution from heavy metals is becoming an increasing concern, since pollution can affect different environmental compartments namely, soil, air and water. Especially, the increased production and utilization of these metals in various industries results to a larger quantity of wastes, mostly liquids, emitting into the environment. Moreover, a vast amount of heavy metal ions is discharged annually by many human activities. Heavy metals are toxic for the environment and belong to the most important group of water pollutants. Cadmium and lead are frequently used in industrial processes such as metallurgy, mining, painting, smelting, batteries, and alloys industries [1, 2]. The high toxicity of these metals results to serious ecological damages. Water contamination by heavy metals may also be the result of natural processes that involve essentially the leaching of the rock metal content to surface water or groundwater.

Thus, there is an increased necessity to develop processes to eliminate heavy metals, or at least to minimize their concentration in wastewaters prior to their release into the environment. The World Health Organization (WHO)[03], recommends maximum allowable concentrations, which in the case of cadmium and lead are 0.005 mg/L and 0.05 mg/L, respectively.

The methods used to remove heavy metal ions are chemical precipitation, adsorption, cations-exchange, reverse osmosis, electrodialysis, electrochemical reduction, etc. Adsorption process is the most frequently applied method in industries with many studies having been carried out in this field [4-6]. The use of activated carbon as an adsorbent is less effective for the removal of some metals (Cu, Zn, Cd,) being also an expensive adsorbent especially for the developing countries. Hence the idea to investigate the applicability of other adsorbent becomes more than a necessity.

The hydroxyapatites are known for their natural ability to retain various metals and metalloids, due to their surface characteristics; these are calcium phosphates that exist in some phosphate rocks, but especially in teeth and bone tissue of animals.

2. Materials & Methods

2.1. Obtaining hydroxyapatite (HA$_0$ sample)

The sample of hydroxyapatite was prepared according to the conventional wet way published by Hayek & Newesely [5], or alternatively with the replacement of $Ca(NO_3)_2$ into $CaCO_3$ (available at minimal cost) which has the advantage of not transforming into nitrogen oxides during the calcination, which in turn are harmful for the environment.

Two solutions are prepared and subsequently mixed: the first consisting of 20.3167 g of calcium carbonate suspended in 50 ml of distilled water, the second consisting of 13.8954 g of diammonium phosphate dissolved in the same volume of distilled water. The resulting mixture is stirred vigorously for 72 h at room temperature. The resulting product is then filtered and washed with distilled water. The solid (filtrate) collected was dried in an oven at 60 ° C thereby obtaining a white powder which is subjected to calcination at 900 °C.

In fact, the calcination can convert unreacted $CaCO_3$ into CaO (calcium oxide), with the latter one being removed from the powder by washing it, until reaching a stable pH [7].

The hydroxyapatite powder obtained by this method contains a large proportion of grains of large size (hundreds of microns). In this case a screening is conducted for all particles that are smaller than 63 microns and the collected powder is named fraction or sample HA$_0$.

2.2. Obtaining samples of different sizes (HA$_A$, HA$_B$, HA$_C$, HA$_D$, HA$_E$)

The fraction retained by the previous sieving, is designated by HA$_A$. The different size fractions HA$_B$, HA$_C$, HA$_D$ and HA$_E$ are all obtained from the same initial sample, HA$_0$, by successive operations of suspension-settling. The principle of division is as follows:

An amount of 10 g of HA is placed into suspension in 1 L of distilled water and stirred for 5 minutes. Once the shaking stops, the suspension is left to settle down for 1 hour. After this, the supernatant is aspirated and then dried in open air. The resulting powder consists normally of particle sizes smaller than those of HA_0 (fraction HA_B). The production of HA_C is made in the same manner: decanting the supernatant of the suspension of HA_B, once dried and receiving fraction HA-C. For the two remaining fractions, HA_D and -HA_E, a similar procedure is followed.

2.3. Adsorption procedure

The batch experiments were carried out using a digital heating controlled magnetic stirrer (Stuart®). Batch mode adsorption studies were carried out to determine the metal sorption. A known volume (100 ml) of metal solutions of varying initial concentrations (100–1000 ppm), taken in 100 ml stoppered glass conical, was shaken with a fixed dose of adsorbent (0.25 g) for a specified period of contact time in a digital heating controlled magnetic stirrer (agitation speed 250 rpm). The residual metal was analyzed by means of a selective ion electrode (Denver Instrument, USA). All the experiments were carried out in duplicate and mean values are presented. The metal ion measurements were repeated three times to obtain an accurate cadmium concentration. The percentage error in the measurement of metal ion concentration is ± 0.1. The average values were obtained and used for calculating the percentage ions removal by the adsorbent according to the following Eq. (1):

$$\% R= ((C_o-C)/C_o)* 100 \tag{1}$$

Where R is the ions removal, C_o is the initial concentration of the metal ions in the solution, and C is the final metal ion concentration in the aqueous solution after phase separation.

In order to elucidate the uptake capacity of the metal ion, the up take amounts per gram of HAP was evaluated from the change in solution concentration using Eq. (2)

$$Q (mg/g) =V (C_o-C)/M \tag{2}$$

Where

Q is the uptake capacity (mg/g),
V is the volume of the solution (ml) and
M is the mass of the solid material (g).

Kinetic studies of adsorption were also carried out at different concentrations of adsorbent (1–5 g) where the extent of adsorption was investigated as a function of time.

After a contact time sufficient to reach equilibrium, the final pH of the suspension is optionally measured and it is subsequently filtered using a paper disk of 0.45 microns. The metal solution collected is then assayed by atomic absorption spectroscopy (AAS) to determine the metal ion residual concentration.

2.4. Coagulation-flocculation experiments (Jar Test)

The simulation of coagulation-flocculation process was carried out through a conventional Jar Test (Janke and Hunkeler®) having 5 agitators with variable speed and five trains each one equipped with a 1 liter beaker.

As soon as chitosan solution was added to the suspension, the mixture was strongly stirred at 200 rpm for 3 minutes. This step was followed by a slow mixing (40 rpm) for 20 minutes. Thereafter, the solution was allowed to settle for 10, 15, 30, 60 and 120 minutes. To analytically assess the coagulation-flocculation effectiveness, the supernatant was removed from the top of the solution by siphoning through measurement of the turbidity using a turbimeter (HANNA INSTRUMENTS®: LP2000). This setup was developed to comply with the International Standard ISO 7027. The turbidity is expressed in nephelometric turbidity units. The pH of the solution was adjusted by the addition of 0.1N HCl solution.

3. Results and Discussion

3.1.Optimization of the adsorption of Cu, Zn on hydroxyapatite

3.1.1. Study of adsorption kinetics

From Figure (1) it can concluded that the adsorption of Cu and Zn on the hydroxyapatite is very quick for both metals. Within a short period of 20 minutes of contact, over 90% of the copper ions are removed from the solution. In this case the adsorption capacity is 30.6 mg / g, while the adsorption of Zn^{2+} on the same material is a bit slower: the removal of 85% of the initial ionic charge occurs only after 50 minutes of contact corresponding to an adsorption capacity of 31 mg/g.
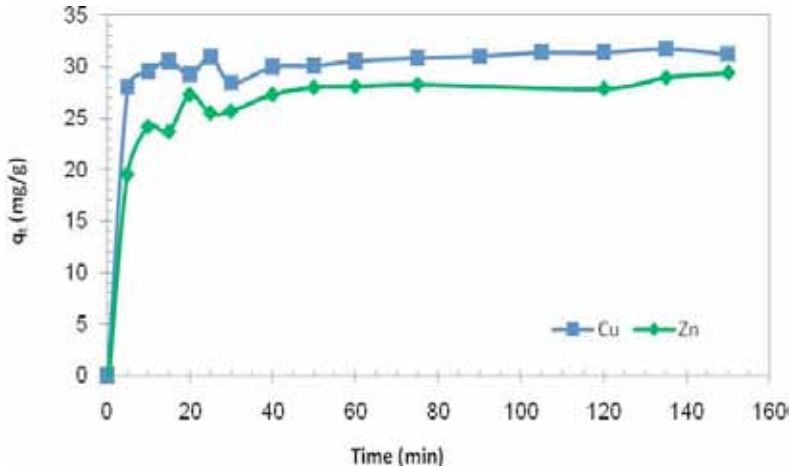

Fig. 1. Evolution of the adsorption capacity of Cu and Zn on hydroxyapatite as function of time.

The time of the rapid adsorption is followed by a relatively long time during which the adsorption process continues until it reaches an equilibrium (setting stage). In the equilibrium phase the adsorption capacities for both metal ions are slightly increased as shown in Table 1. For all remaining experiments, a contact time of 2 hours was chosen to ensure that the equilibrium is reached for all tested metals.

Table 1. Experimental values of adsorption capacities and removal rates

metal	Adsorption capacity at equilibrium *(mg/g)*	Removal rate at the balance *(%)*	Equilibration time *(min)*
Cu^{2+}	31,4	94,21	105
Zn^{2+}	28,9	87,9	120

3.1.2. Effect of solution pH on the adsorption

The hydrolysis and precipitation of metals begin at a pH ranging from 5.2 for Cu, and 6.2 for zinc. At alkaline pH all metals form insoluble precipitates (CuO, ZnO). That is why we limited the study with pH values ranging from 3 to 8. The adsorption of the two metal ions on hydroxyapatite at various pH is shown in Figure 2.We note that the adsorption capacity of the material increases as the pH increases. This behavior is similar for the two metals. Thus, at acidic pH 3, the adsorption capacity is almost zero for both metals, progressively reaching values of about 31 mg/g at pH 5-6 and maintained at pH 7 and 8.

At alkaline pH, Fig 2 clearly shows the further removal of metal cations, which reaches 100%. This is due to the increased precipitation of ions as hydroxides or metal oxides that occurs especially at alkaline pH. However, for slightly acid to neutral pH (5-7), elimination is largely due to the adsorption proper ion exchange that occurs between cationic species and Ca^{2+} of the hydroxyapatite. These results lead to the conclusion that the optimum pH for the adsorption is judged between 5 to 6. Such a pH value will result to both a good adsorption of all cations and an unwinding of the process under mild conditions, avoiding by this way the generation of sludge and the corrosion of materials.
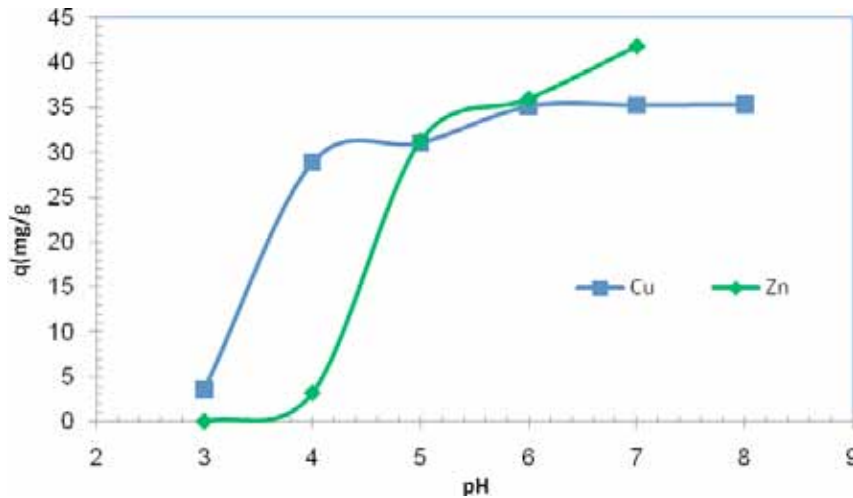

Fig.2. Effect of initial pH of the solution on adsorption of Cu and Zn on Apatite. Operating conditions: t=120 min, C_A= 3g/L, C_0= 100mg/l

3.1.3. Effect of Hydroxyapatite (HAP) concentration

To determine an optimum concentration of adsorbent which takes account of both the adsorption capacity and the rate of removal of heavy metals, we presented the responses in terms of adsorption capacity (q mg/g) and in terms of elimination rate (E%). The results are shown in Figures 3.a and 3.b, respectively.
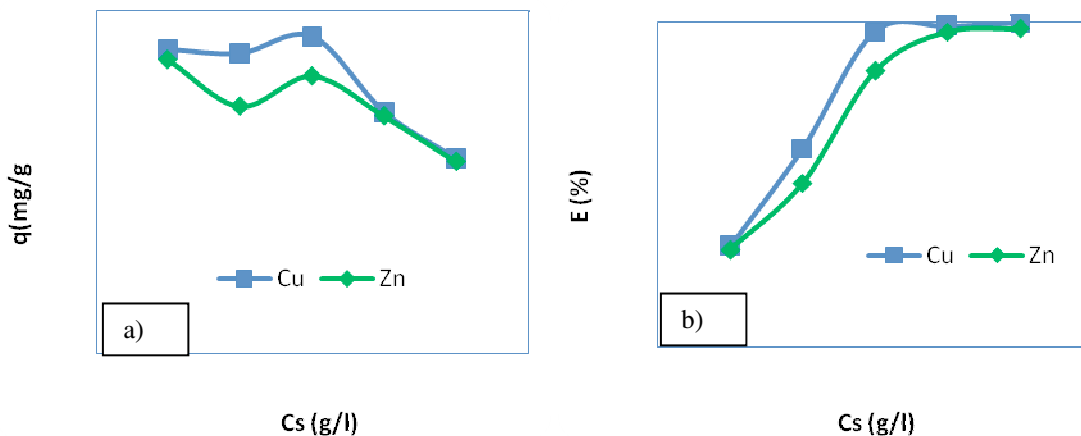

Fig.3. Effect of initial concentration of PAHs on the adsorption of Cu and Zn on hydroxyapatite. Operating conditions: t=120 min, pH 5, C_0= 100mg/l

From Figure 3 it can be observed that, the removal of metals by hydroxyapatite increases with the amount of adsorbent in the solution. Indeed, the more hydroxyapatite the higher the number of retention sites on the surface of the adsorbent. This behavior is consistent with the results of Karapinar et al [8] who used bentonite as an adsorbent.

3.2. Flocculation of turbid suspensions of hydroxyapatite

3.2.1. Monitoring the natural settling samples hydroxyapatites

Figure 4 shows the reduction of the turbidity as function of time. For all samples studied, much of the particulate matter settles rapidly during the first 5minutes. The removal rate within the first 5 minutes is 46% for the ADT and 65 to 75% for all other samples. As time goes by the turbidity of all samples continues to decline until the water becomes clear. Thus, after 6 hours of decanting, the abatements of 90% and 98% are established for the ADT and the remaining samples, respectively.
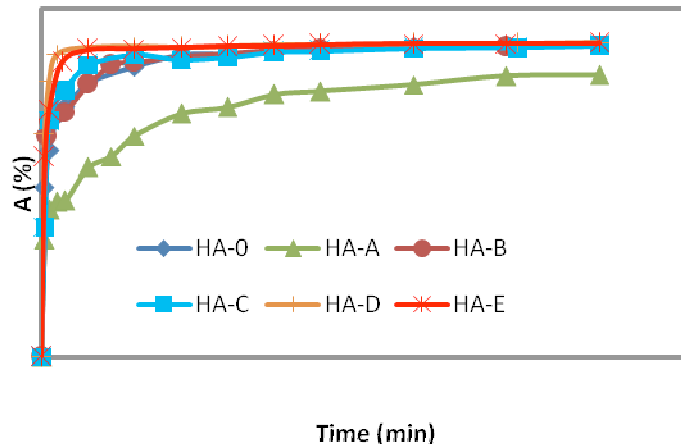

Fig.4. The natural settling of turbid suspensions based on hydroxyapatite HA_0, HA_A, HA_B, HA_C, HA_D and HA_E; C_A=3 g/l

3.2.2. Dose effect of chitosan

By analyzing the evolution curves of the turbidity of chitosane with amounts ranging from 0.02 to 2.5 mg (Fig. 5), we derive the following remarks: The removal of turbidity resulting from any type of suspension is feasible with chitosane as a coagulant; the resulting turbidity after 2 hours of settling varies between 11.4 and 60 NTU (reduction of 99.5 % and 97.2 %) depending on the dose and the sample. For all samples, a sharp drop in turbidity is observed during the first 10 minutes, so the reduction is about 57 % for the HA_A and 99.16 for HA_0. Very good removal of turbidity was observed with doses of chitosane ranging between 0.05 and 0.5 mg. We deduce that the optimal doses of chitosane samples for HA_0 and HA_A are 0.05 mg, for HA_B is 0.2 mg, and for the samples HA_C, HA_D and HA_E the optimal dose is 0.5mg. These doses have been adopted in the subsequent study of the effect of pH on the coagulation-flocculation process.

3.2.3. Effect of pH of turbid suspensions

The results of the experimental work performed for various pH values of different hydroxyapatite solutions are shown in Figure 6. It is remarkable that at acidic pH (pH 4 and 5) and at slightly alkaline (pH 8) suspensions a slight decrease in the effectiveness of chitosan is observed for all samples. The optimum pH is 6 for HA_0, 8 for HA_D and 7 for the remaining samples. However, to facilitate coupling between the two processes, adsorption, flocculation and coagulation, it would be convenient to choose a single pH for both stages of treatment. In this case pH 6 was adopted, since the rate of reduction caused by the pH 6 is no far from the one generated by the pH 7 and 8.
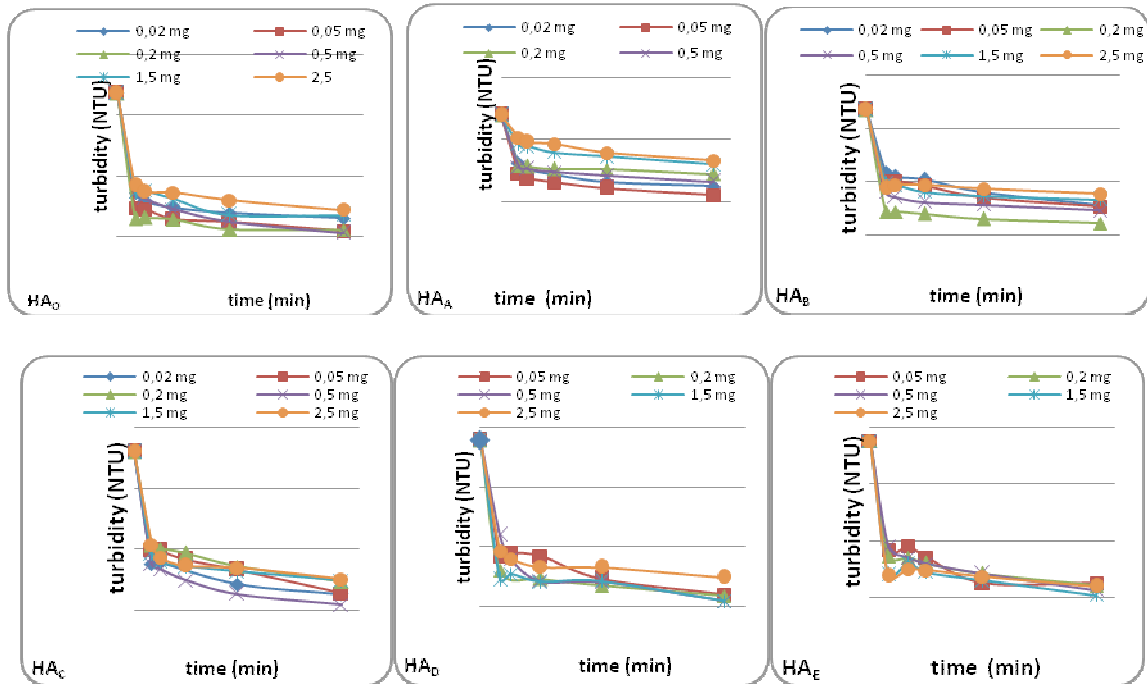
Fig.5. Kinetics of sedimentation of different suspensions of hydroxyapatite after coagulation-flocculation with different doses of chitosan. Operating conditions: pH 7, v_1 (200rpm/3min), v_2 (45rpm/20min), V=250 ml.
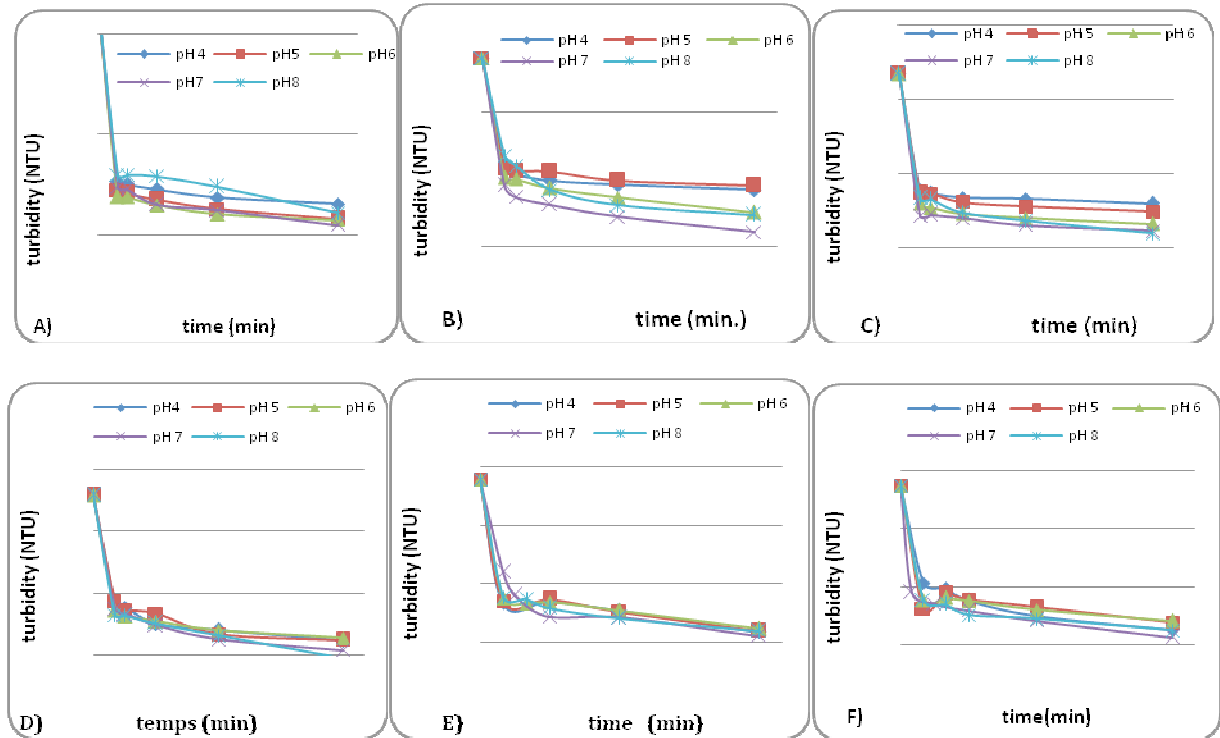

Fig.6. Kinetics of sedimentation of different suspensions of hydroxyapatite after coagulation flocculation at different pH. Operating conditions: v_1 (200rpm/3min), v_2 (45rpm/20min), V=250 ml.) HA_0 (0,05 mg of chitosan) B) HA_A (0,05 mg of chitosan) C) HA_B (0,2 mg of chitosan) D) HA_C (0,5 mg of chitosan) E) HA_D (0,5 mg of chitosan) F) HA_E (0,5 mg of chitosan)

4. Conclusion

The objective of the present study was the treatment of synthetic water containing heavy metals, such as copper and zinc, through adsorption on a mineral carrier, hydroxyapatite, originated from a slaughterhouse waste bone. The study of adsorption of both metals on hydroxyapatite showed the effectiveness of the process. More specifically, the following aspects have been observed:

- Hydroxyapatite presents an adsorption capacity of around 30 mg/g, with removal rates that range between 88 and 96%.

-The mechanism for adsorption to hydroxyapatite is based on an ion exchange transport with exchangeable cations, such as Ca^{2+} and H^+, coming from the apatite structure.

- An optimal pH of the suspension is found to be 5 to 6 while the best adsorbent's concentration is 3 g/l for both adsorbents tested (hydroxyapatite, chitosan).

- Monitoring the natural sedimentation showed that the process is slow, because a reduction in turbidity of 98% is only reached after 6 hours of decanting.

- A very good efficiency is shown by chitosan to remove the turbidity of various samples of hydroxyapatite of different fractions. The elimination rate after 30 minutes of settling in all cases exceeds 98%.

- The study of the effect of the dose of chitosan and the effect of pH on the coagulation-flocculation showed optimal doses ranging from 0.2 to 2 mg of chitosan / l at an optimum pH between 6 and 7.

- The coupling between adsorption and coagulation-flocculation has also proven the effectiveness of the latter, even in the presence of metal cations, with the residual turbidity ranging from 10 to 40 NTU (more than 99% abatement). In conclusion, the results of the present study are regarded as very important, encouraging, and original, placing a particular emphasis on the benefits of nanotechnology for environmental preservation.

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