REMOVAL OF HEAVY METAL FROM INDUSTRIAL WASTEWATER BY APATITE MINERAL

THĂM DÒ KHẢ NĂNG XỬ LÝ KIM LOẠI NẶNG TRONG NƯỚC THẢI CÔNG NGHIỆP BẰNG KHOÁNG APATIT CỦA VIỆT NAM

Dao Thi Thu Hang, Dang Kim Chi

Hanoi University of Technology

ABSTRACT

The study on removal of heavy metal ions from aqueous solution was studied in batch experiments using Apatite-a natural and abundant mineral in Vietnam. The effects of some factors on adsorption were investigated: initial pH, the contact time, the amount of absorbent and the initial concentrations. The sorption process fitted to Langmuir adsorption equation model. The adsorption capacity was found to follow the order: $Pb^{2+}>Cd^{2+}>Cu^{2+}>Zn^{2+}$ with values of 43.48; 18.3; 7.36; 5.49 mg/g respectively. The research demonstrated that natural Apatite mineral in Vietnam can effectively remove heavy metal ions from solution and it can be effectively applied in industrial wastewater treatment.

TÓM TẮT

Nghiên cứu thăm dò khả năng xử lý kim loại nặng trong nước thải công nghiệp bằng khoáng Apatit của Việt Nam được thực hiện bằng phương pháp hấp phụ theo mẻ. Một số yếu tố ảnh hưởng tới quá trình hấp phụ được nghiên cứu như: pH ban đầu, thời gian tiếp xúc, lượng vật liệu sử dụng và nồng độ kim loại ban đầu. Quá trình hấp phụ các kim loại nặng bởi Apatit phù hợp với mô hình đẳng nhiệt hấp phụ Langmuir. Dung lượng hấp phụ tối đa của các kim loại được xác định giảm theo thứ tự $Pb^{2+}>Cd^{2+}>Cu^{2+}>Zn^{2+}$ với các giá trị lần lượt là 43.48; 18.3; 7.36; 5.49 mg/g. Kết quả nghiên cứu bước đầu cho thấy, Apatit của Việt Nam có khả năng xử lý tốt một số kim loại nặng trong môi trường nước. Từ kết quả này có thể áp dụng hiệu quả vào thực tế xử lý kim loại nặng trong nước thải công nghiệp.

I. INTRODUCTION

The removal of heavy metal ions in aqueous solution has been performed by chemical precipitation, ion exchange, coagulation, membrane filtration and adsorption. Recently, the adsorption method has gained more attention thanks to its high efficiency, easy handling and cost effectiveness. The studies are now focusing on new natural adsorbents with low-cost as well as the local availability [1]. In this study, the removal of four heavy metal ions (Pb^{2+}, Cd^{2+}, Cu^{2+}, Zn^{2+}) was investigated by using Apatite mineral-an available natural mineral in Vietnam as well as a new adsorbent for heavy metal treatment.

II. MATERIALS AND METHODS

2.1 Materials

The Apatite mineral used in this study was from Laocai Province in Vietnam. It was preliminary treated by flotation process and the size range of 160-212 μm was used. The mineralogical composition of sample was analyzed by X-ray diffractometer. Fluoroapatite-$Ca_{10}(PO_4)_6F_2$ was identified as a major component of this mineral. The result is given in Table 1.

Table 1. Composition of Apatite mineral in Vietnam

Constituents	Weight percent
Fluoroapatite	51-53
Chlorite	5-7
Quartz	13-15
Mica	13-15
Amphibole	3-5
Goethite	4-6

2.2 Bath experiments

Stock solutions (1000mg/l) of different metal ions (Pb^{2+}, Cd^{2+}, Cu^{2+}, Zn^{2+}) were prepared from nitrate solution and diluted to various initial concentration. The mineral Apatite sample was equilibrates with 100ml of heavy metal ions solution. The solution pH was adjusted with different concentration of HNO_3 and NaOH. The suspensions were shaken on orbital shaker at 25^oC, 150 rpm with different initial pH, contact time, amount of adsorbent and initial concentration. Suspensions were then filtered through 0.45 μm filter. The metal concentrations of the filtrates were analyzed by Atomic Absorption Spectrophotometer (AAS).

III. RESULTS AND DISCUSSION

3.1.Effect of initial pH

An initial heavy metal solution concentration of 10mg/l was used in conjunction with the Apatite sample of 8g/l. The mixture was shaken at speed of 150rpm and temperature of 25^oC in 120min. The pH values were adjusted to 2, 3, 4, 5, 6 and 7 to avoid metal precipitation as hydroxides at higher pH values. The results are shown in Fig. 1.

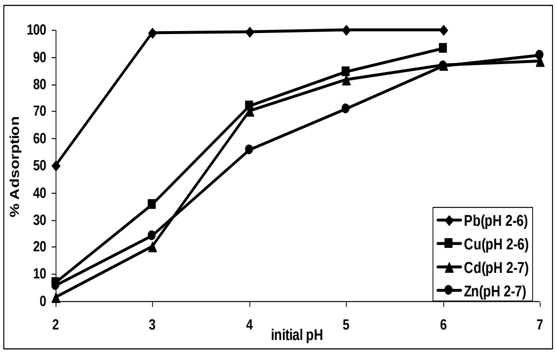

Fig.1 Effect of initial pH on heavy metal adsorption on Apatite

As the result, the pH values strongly affect the efficiency of heavy metal adsorption. It is observed from the Fig. 1 that the removal of heavy metal ions increases with the increase of initial pH value. With the same initial pH values, the percent removal of lead ion is highest. This can be attributed by the largest diameter of lead ion compared to other ions [2]. For Pb^{2+}, the maximum of adsorption capacity was reached at pH=3 to pH=6. With other metal ions, the maximum adsorption capacity was reached at the highest value of pH surveyed range of each metal; Cu^{2+} at pH=6 and Zn^{2+}, Cd^{2+} at pH=7

3.2 Effect of contact time

The effect of contact time was studied from 5 to180 min with initial heavy metal concentration is 10mg/l and in the optimized pH condition for each metal ion. The results are given in Fig. 2.

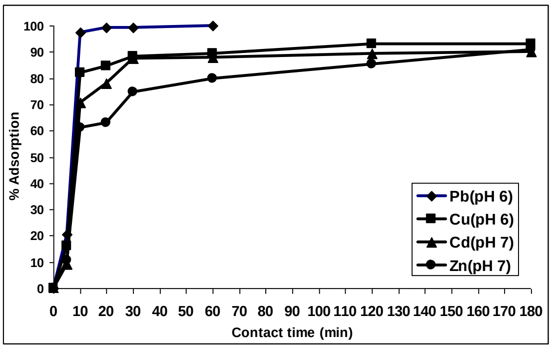

Fig.2 Effect of contact time on heavy metal adsorption on Apatite.

It is observed from Fig. 2 that the percentage of heavy metal ions removed increases with the increase of time contact. The adsorption rate of Pb^{2+} is very fast as the equilibrium was reached after 30 min; it is noticeable that the time equilibrium of lead is shorter than other heavy metals. For Cd^{2+}, Cu^{2+}, Zn^{2+}, the equilibrium was reached after 120 min.

3.3. Effect of adsorbent amount

To study the effect of adsorbent amount on percent adsorption of heavy metal, 0.25-12 g/l Apatite mineral was equilibrium with 10 mg/l of each heavy metal ions solution. The results are shown in Fig. 3.

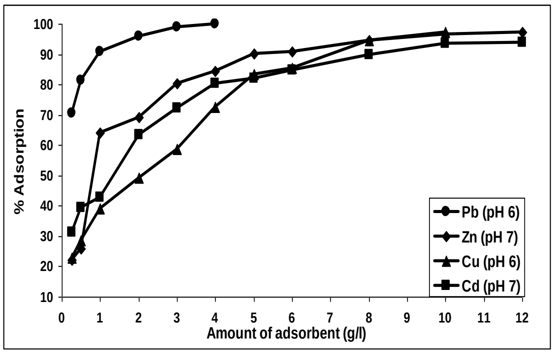

Fig.3 Effect of time on heavy metal adsorption on Apatite

It is observed that, with the increase in the amount of Apatite mineral, the percent adsorption of metal ions also increases. However, it is noticeable again that with the same amount of adsorbent the percentage removal of lead is highest. For the subsequent experiments 4g/l was used for adsorption of Pb^{2+} and 8g/l for Cd^{2+}, $Cu^{2+}$and Zn^{2+}

3.4 Effect of initial metal ions concentration

The experiments were conducted with initial concentration of metal ions ranging from 5-100mg/l at the optimum condition in terms of pH, amount of adsorbent and contact time.

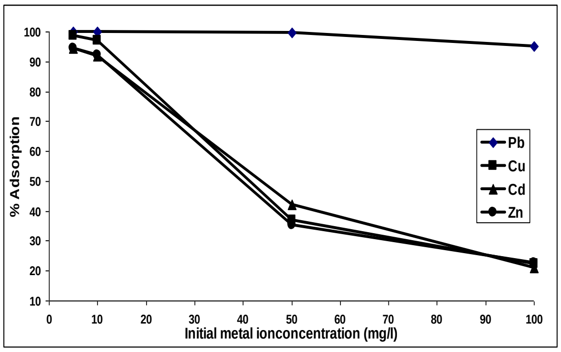

Fig.4 Effect of initial metal concentration on heavy metal adsorption on Apatite

As shown in Fig. 4 that, the heavy metal ions removed decrease with the increase in initial concentration of metal solution. This is can be explained that due to the lack of biding sites on adsorbent surface at higher concentration of metal ions. Similar observation was also reported by Sona Saxena, 2006 [3]

3.5 Adsorption isotherms

Both Langmuir and Freundlich isotherm models were used to interpret and evaluate the experimental results.

The Langmuir equilibrium equation is represented as: $q_e = q_m K C_e/(1+KC_e)$

Where C_e is the equilibrium liquid-phase concentration (mg/l), q_e is the equilibrium amount adsorbed (mg/g), q_m is the maximum amount of adsorbate adsorbed per unit sorbent, K is the Langmuir constant.

The Freundlich isotherm is expressed by the following equation: $q_e = K_f.C_e^{1/n}$

The equation is convenient used in the linear form by taking the logarithm of both side as:

$\ln q_e = \ln K + (1/n).\ln C_e$ where K_f and n are Freundlich constants. The results and examination data are shown on Table 2 and Table 3.

Table 2. Langmuir adsorption isotherm constants for lead, copper, zinc and cadmium.

Metal Ions	Equation	q_m (mg/g)	K_L (l/g)	R^2
Pb^{2+}	y=0.073x+0.0231	43.48	0.32	0.9866
Cd^{2+}	y=0.9141x+0.0542	18.40	0.06	0.9661
Cu^{2+}	y=0.7247x+0.1358	7.36	0.19	0.9404
Zn^{2+}	y=0.2972x+0.1821	5.49	0.62	0.9733

Table 3. Freundlich adsorption isotherm constants for lead, copper, zinc and cadmium

Metal Ions	Equation	K_f	1/n	R^2
Pb^{2+}	$q = 10,8.C^{0,6416}$	10.80	0.6416	0.9203
Cd^{2+}	$q = 0,89.C^{1,1324}$	0.89	1.1324	0.9329
Cu^{2+}	$q = 1,17.C^{0,7248}$	1.17	0.7248	0.9506
Zn^{2+}	$q = 1,87.C^{0,615}$	1.87	0.615	0.9570

The examination of data show that both of the Langmuir and Freundlich isotherm are good description of the data for all the metal ions over the concentration of range studied. However, the values of the correlation coefficients indicate that the results obtained with Langmuir isotherm are better than those obtained with the Freundlich isotherms. From this results, it can be concluded that the mechanism of heavy metal ions mentioned adsorption on Apatite based on the monolayer sorption onto surface of Apatite.

3.6 Mechanism of removal of metal ions by Apatite mineral

For Pb^{2+}: the XRD patterns of the solid isolated after reaction between Apatite and Pb at pH 2-3 and pH 6 are presented in Fig. 5. At pH 2-3 the presence of Cl- ion in solution probably caused the formation of Pyromorphite-$Pb_{10}(PO_4)_6Cl_2$ which is more thermodynamically stable than Fluoroapatite $Ca_{10}(PO_4)_6F_2$ [4]. It is suggested that at pH=2-3 the dissolution of Fluoroapatite and precipitation of Pyromorphite is primary mechanism for Pb removal by Apatite. This can be expressed by equation (1), (2)

$$\underset{\textit{Floapatite}}{Ca_{10}(PO_4)_6F_2} + 6H^+ \xrightarrow{\textit{dissolution}} 10Ca^{2+} + 6HPO_4^{2-} + 2F^- \qquad (1)$$

$$10Pb^{2+} + 6HPO_4^{2-} + 2Cl^- \xrightarrow{\textit{precipitation}} \underset{\textit{Pyromorphite}}{Pb_{10}(PO_4)_6Cl_2} + 6H^+ \qquad (2)$$

The similarity result was also obtained in the study of M. Mouflih [5].

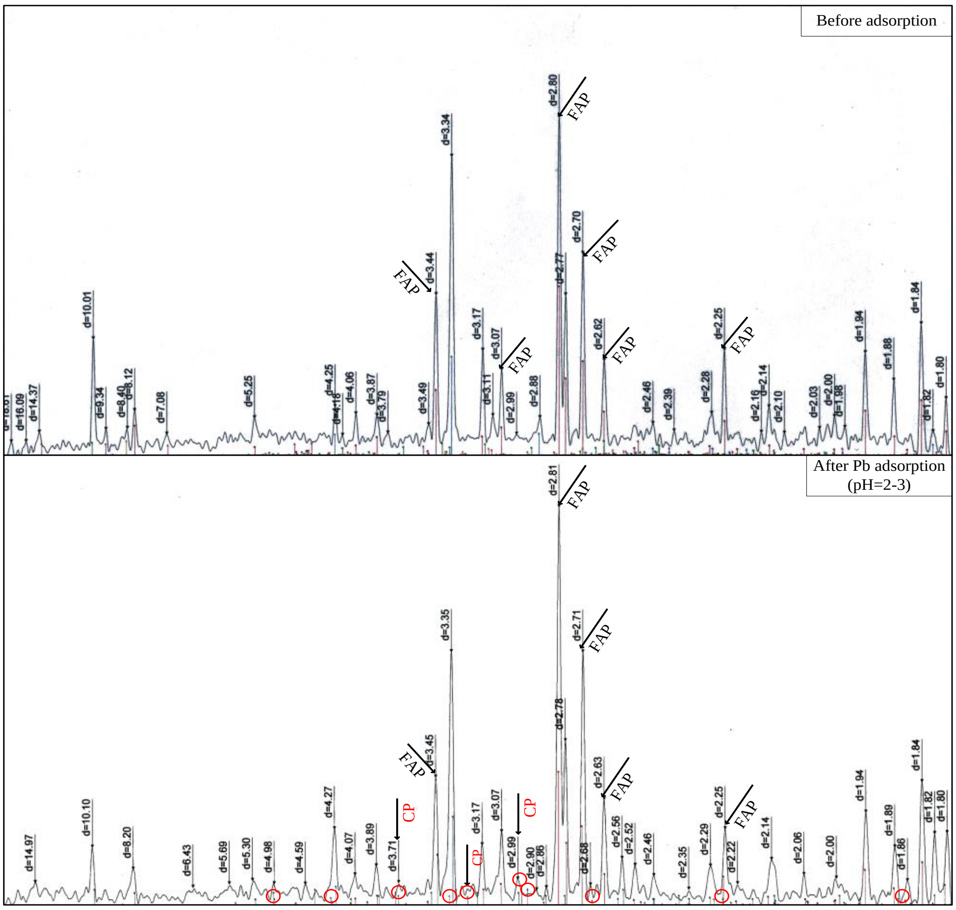

Fig.5 XRD patterns of the solid after reaction between Apatite and Pb^{2+}. (FAP: Floapatite, CP: Pyromorphite)

At pH=4-6, the Apatite surface is thought to consist of distinct surface groups included $\equiv$Ca-OH, $\equiv$P-OH and $\equiv$P-O^- [6], at pH<3 the surface is fully protonated. Therefore it can be suggested that at pH=4-6, the mechanism of Pb adsorption is responsible by the functional groups on the surface through forming surface complexation. The process can be described:

$$\equiv Ca\text{-}OH + Pb^{2+} \rightarrow \equiv Ca\text{-}OPb^{+} + H^{+} \quad (3)$$

$$\equiv P\text{-}O^{-} + Pb^{2+} \rightarrow \equiv P\text{-}OPb^{+} \quad (4)$$

$$\equiv P\text{-}OH + Pb^{2+} \rightarrow \equiv P\text{-}OPb^{+} + H^{+} \quad (5)$$

For Cd^{2+}, Cu^{2+}, Zn^{2+}: Similar to the mechanism of Pb adsorption at pH=4-7 the common processed can be descried (Me^{2+}: Cd^{2+}, Cu^{2+}, Zn^{2+})

$$\equiv Ca\text{-}OH + Me^{2+} \rightarrow \equiv Ca\text{-}OMe^{+} + H^{+} \quad (6)$$

$$\equiv P\text{-}O^{-} + Me^{2+} \rightarrow \equiv P\text{-}OMe^{+} \quad (7)$$

$$\equiv P\text{-}OH + Me^{2+} \rightarrow \equiv P\text{-}OMe^{+} + H^{+} \quad (8)$$

IV. CONCLUSIONS

The objective of this study was to evaluate the adsorption ability of natural Apatite mineral in Vietnam for removal of heavy metal ions. The conclusions obtained are:

- Apatite mineral in Vietnam can be used as a sorbent for removal of heavy metal in wastewater with high efficiency
- The Langmuir isotherm is suitable for fitting experimental data. The adsorption capacity of each metal ion were in the descending order: Pb^{2+}>Cd^{2+}>Cu^{2+}>Zn^{2+} with the values of 43.48; 18.3; 7.36; 5.49 mg/g.

From the results obtained, it can be concluded that the natural Apatite mineral in Vietnam is efficient for removal of heavy metal ions in wastewater, especially for the high concentration of Pb (II) in industrial wastewater.

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Contact: Dao Thi Thu Hang, Dang Kim Chi - Tel: (+844)3868.1686 – Fax: (+844)3869.3551
Email: hangbelq@gmail.com
Institute for Environmental Science & Technology, Hanoi University of Technology
No.1, Dai Co Viet Road, Hai Ba Trung, Hanoi.