

Adsorption of cobalt(II) from aqueous solution onto hydroxyapatite/zeolite composite

Neha Gupta, Atul K. Kushwaha and M.C. Chattopadhyaya*

*Environmental Chemistry Research Laboratory, Department of Chemistry
University of Allahabad, Allahabad, 211002, India*

*Corresponding author. Tel/Fax: (+91) 532 2462393; E-mail: mcc46@rediffmail.com

Received: 25 Dec 2010, Revised: 06 March 2011 and Accepted: 02 July 2011

ABSTRACT

The Hydroxyapatite/Zeolite (HApZ) composite were synthesized by precipitation method and used as an adsorbent for the removal of cobalt ions from the aqueous solution. The materials were characterized by scanning electron microscope (SEM) and Fourier transform infrared (FTIR) spectroscopy. It has been observed that there was slight enhancement in the % removal of cobalt ions from aqueous solution by HApZ (63%) than HAp (58%) and zeolite (47%). Batch experiments were performed to observe the effect of pH, adsorbent dose, contact time and initial cobalt (II) concentration. Kinetic study shows that the adsorption process follow pseudo-second order kinetic model. Equilibrium data were well fitted to Langmuir and Freundlich isotherm model. Copyright © 2011 VBRI press.

Keywords: Adsorption; hydroxyapatite/zeolite composite; cobalt; isotherm; kinetics.



Neha Gupta has obtained her B.Sc. and M.Sc. (Environmental Science) from University of Allahabad, India and joined as D. Phil. scholar under the supervision of Prof. M.C. Chattopadhyaya in 2009 in Department of chemistry, University of Allahabad. She is working in the field environmental chemistry. She has presented several papers in national and International conferences. She received two young scientist awards in International conferences on "Recent

Research trends in Chemical Sciences" VIT University, Vellore and International Conference on "Recent Advances in Chemical Sciences, Pt. Ravishankar Shukla University, Raipur. She has published four research papers.



Atul K. Kushwaha is working as Junior Research Fellow (CSIR) in University of Allahabad (U.P.) India. He has done his B.Sc. and M.Sc. (Chemistry) from University of Allahabad and M. Tech. (Pharmaceutical Chemistry) from VIT University, Vellore (T.N.) India. He joined as D. Phil. scholar under the supervision of Prof. M.C. Chattopadhyaya in 2009 in Department of chemistry, University of Allahabad. He received young scientist award in International Conference on "Recent

Advances in Chemical Sciences, Pt. Ravishankar Shukla University, Raipur. He has published ten research papers in different national and international journals. His main research interests are Pharmaceutical chemistry, organic synthesis and Environmental Chemistry.



M.C. Chattopadhyaya is Professor in Department of Chemistry, University of Allahabad, Allahabad (U.P.) India. He did his Post Graduation in Chemistry from Gorakhpur University with specialization in Inorganic Chemistry in 1967. He was selected for P.G. course in Radiological Physics by Bhabha Atomic Research Centre. After completion of the course he joined IIT Bombay for Ph.D. He did a short course of American Chemical Society on "Interpretation of Infra-red Spectra". He was elected as Fellow of

Cambridge Philosophical Society, Fellow of Chemical Society, London, Indian Chemical Society, Institution of Chemists, India. Presently he is President of Indian Chemical Society. He has published ninety research papers in different national and international journals. Twenty four research scholars have been awarded doctoral degree under his supervision. Currently he is working on solid oxide fuel cells, synthesis of inorganic materials and development of sensors for estimation of surfactants.

Introduction

Cobalt containing compounds are widely used in many industries such as mining, metallurgical, paints, pigments and electronics [1]. However, higher concentration of cobalt may cause paralysis, diarrhoea, low blood pressure, lung irritation and bone defects. The tolerance limit of cobalt in potable water has been fixed as 0.05mg/L [2]. Different organic and inorganic sorbents have been considered for heavy metal ions adsorption: hydroxyapatite [3, 4], resin [5], zeolite [6], chitosan [7], agro-based waste materials [8] and algae [9].

Hydroxyapatite [$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$] (HAp) is a main mineral constituent of teeth and bones. It can accept a series of anionic and cationic substitution in its structure due to which it was proposed for removal of heavy metals from contaminated soil and water. Zeolites are naturally occurring hydrated aluminosilicate minerals. The structures of zeolite with high cation exchange and molecular adsorption capacity is also a candidate for the adsorption of heavy metals and radioactive elements from the soil and water.

The aim of present work is to synthesize HApZ composite by precipitation method and use as an adsorbent material for removal of Co (II) from aqueous solution.

Experimental

Synthesis of adsorbent

The zeolite was purchased from Sigma Aldrich and the n-HAp was synthesized by the mixing of the solution of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Merck) and $(\text{NH}_4)_2\text{HPO}_4$ (Merck) with stoichiometric ratio of Ca/P (1.67) and pH (10-11) was maintained by adding ammonia solution. The precipitate formed was rinsed with double distilled water to bring the pH level to 7 and was dried at 80°C for 24 h.

The HApZ composite was also prepared by precipitation method. The suspension of 5 wt% of zeolite was added to solution of calcium nitrate with stirring. The aqueous solution of $(\text{NH}_4)_2\text{HPO}_4$ was added to above mixture at a slow rate and stirred for 24 h. The precipitate formed was rinsed with double distilled water and dried at 80°C .

Adsorption experiments

The stock solution of Co^{2+} was prepared from $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Merck) and double distilled water. The solution of desired concentration was obtained by successive dilution of stock solution. In each experiment, 50 mL of aqueous metal ion solution of desired concentration was taken in 100 mL of conical flask and a

fix amount of adsorbent was added into that, the resulting mixture was agitated on a stirrer for given length of time. The adsorption was monitored by determining the concentration of Co (II) in solution by atomic absorption spectrophotometer (ECIL). The quantity of Co (II) adsorbed on adsorbent at the time of equilibrium (q_e) was calculated by following expression:

$$q_e = (C_o - C_e) V/m \text{ ----- (1)}$$

where C_o and C_e is the initial and equilibrium concentration (mg/L) of Co (II) ion in solution. V is volume (L) of solution and m is weight of adsorbent (g) taken for experiment.

Results and discussion

Characterization of adsorbent

The morphology of the prepared adsorbents were recorded using scanning electron microscope (SEM) (FEI Quanta 200) operated at 20KV accelerating voltage. As shown in **Fig. 1**, it has been observed that there is no significance change in morphology and granular size/shape of HAp (**Fig. 1b**) and HApZ (**Fig. 1a**) composite with introduction of zeolite (5 wt%). Fourier transform infra-red (FTIR) studies were carried out on FTLA 2000 spectrophotometer and spectrum of the adsorbent materials (**Fig. 2**) shows formation of HApZ composite. The band of Si-O-Si and PO_4^{3-} groups overlapped around 1100 cm^{-1} and this band was due to asymmetric stretching vibration. The band at 1035 cm^{-1} was due to asymmetric stretching vibration of Si-Al-O group. The band around 715 and 672 cm^{-1} was due to symmetric stretching vibration of Si-Al-O and PO_4^{3-} group respectively. The broad peak around 3200 cm^{-1} to 3500 cm^{-1} corresponds to the adsorbed water. The peak at 1632 cm^{-1} was due to bending mode of water (O-H).

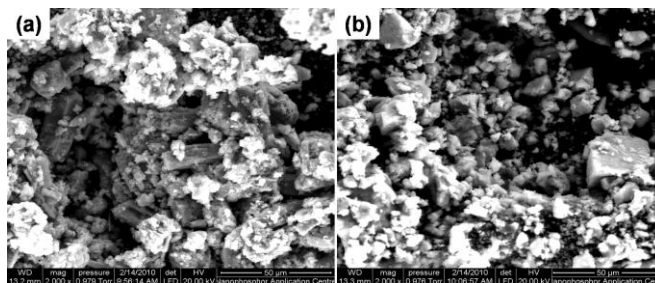


Fig. 1. SEM micrograph of HApZ composite and HAp.

Effect of pH

The % removal increases as the pH increases. Maximum removal occurs around pH 6. Heavy metal ions tend to form a precipitate at pH higher than 6 and therefore

adsorption is difficult to quantify at the higher pH value of 6. Thus, pH 6 was used for further experiments.

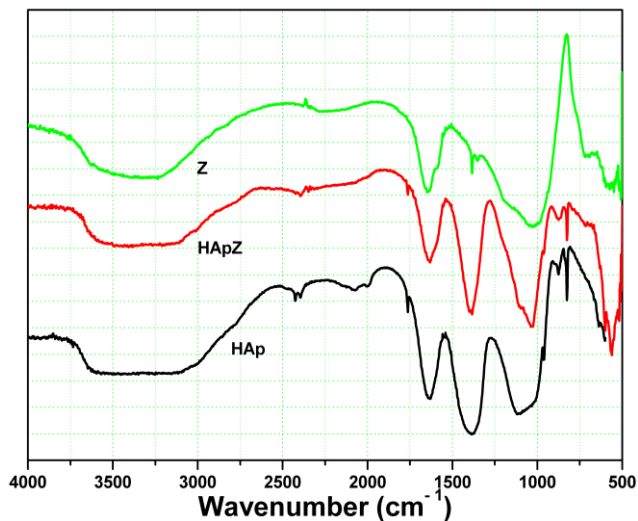


Fig. 2. FTIR spectra of adsorbent materials.

Effect of adsorbent dose

Initially, the rate of adsorption was very rapid up to 2 g/L. This is because at higher dose of the adsorbent, more adsorption sites are available causing higher removal of Co (II). Above 2g/L removal of metal ions becomes very slow, as the surface Co (II) concentration and the solution Co (II) concentration come to equilibrium with each other. Therefore adsorbent dose of 2 g/L was used for all further experiments.

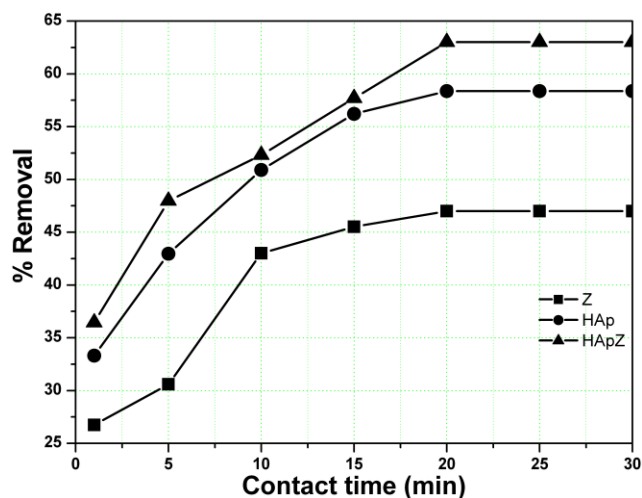


Fig. 3. Effect of contact time on adsorption capacity of the adsorbents (pH: 6; Adsorbent dose: 2g/L; initial Co²⁺ concentration: 5 mg/L).

Effect of contact time and initial metal ions concentration

Fig. 3 indicates that maximum removal occurs within 20 minutes and thereafter the system has reached equilibrium point. The slight enhancement in % removal of cobalt ions from aqueous solution was observed by HApZ (63%) than

HAp (58%) and zeolite (47%). The percentage removal of Co (II) decreased with increase in initial Co (II) concentration due to lesser availability of binding sites.

Kinetics of adsorption

In the order to investigate the mechanism of adsorption kinetics of Co (II) onto HApZ composite, the kinetics models: Lagergren's pseudo-first order and McKay and Ho's pseudo-second order models were applied to the experimental data. The linearised form of the pseudo-first order can be expressed as follows:

$$\log (q_e - q_t) = \log q_e - (k_1/2.303)t \quad \text{----- (2)}$$

where q_t and q_e are the amount adsorbed at time t (mg/g) and at equilibrium (mg/g) respectively, k_1 is the rate constant (min^{-1}) of the pseudo-first order adsorption process. The values of k_1 and $q_{e,cal}$ were calculated from slope and intercept of the plot of $\log (q_e - q_t)$ vs. t respectively.

The pseudo-second order kinetic model can be written as follows:

$$t/q_t = 1/k_2q_e^2 + t/q_e \quad \text{----- (3)}$$

where k_2 is the pseudo-second order rate constant (g/mg min). A linear plot of t/q_t vs. t verifies the pseudo-second order kinetics with the slope and intercept yielding the values of $q_{e,cal}$ and rate constant k_2 respectively.

Table 1. Pseudo-first and Pseudo-second order kinetic parameters for adsorption of Co (II) onto HApZ.

Initial Co (II) concentration	$q_{e,exp}$	Pseudo-first-order			Pseudo-second-order		
		$q_{e,cal}$	k_1	R^2	$q_{e,cal}$	k_2	R^2
5 mg/L	1.611	0.719	0.109	0.990	1.577	0.385	0.994
10 mg/L	2.90	1.345	0.102	0.989	3.035	0.179	0.992
15 mg/L	4.125	1.683	0.132	0.978	4.295	0.176	0.997
20 mg/L	5.10	2.378	0.128	0.959	5.333	0.120	0.994

Table 1 shows that the pseudo-second order model with high R^2 value was better fitted than pseudo-first order and the calculated q_e values are very close to that of experimentally obtained q_e for pseudo-second order model. By comparing the constants of the two kinetic models, the pseudo-second order kinetic model seems to be best fitted for the experiment.

Adsorption isotherms

The Langmuir and Freundlich equations are commonly used for describing adsorption equilibrium of adsorbate onto the adsorbent. The Langmuir isotherm is applicable to monolayer chemisorptions while Freundlich isotherm is used to describe adsorption on surface having heterogenous energy distribution:

$$\text{Langmuir isotherm: } C_e / q_e = (1/bq_{\max}) + (1/q_{\max})C_e \quad \text{----- (4)}$$

$$\text{Freundlich isotherm: } \ln Q_e = \ln K_F + (1/n) \ln C_e \quad \text{----- (5)}$$

where C_e is concentration of dye solution at equilibrium (mg/L), q_e is the amount of dye at equilibrium in unit mass of adsorbent (mg/g), q_{\max} and b are the Langmuir coefficient related to adsorption capacity (mg/g) and adsorption energy (L/mg) respectively, K_F and n are the Freundlich coefficient related to adsorption capacity [$\text{mg g}^{-1} (\text{mg L}^{-1})^{-1/n}$] and adsorption intensity of adsorbent respectively.

Table 2. Langmuir and Freundlich adsorption isotherm constants for the adsorption of Co (II) on HApZ composite.

Langmuir constant			Freundlich constant		
q_{\max}	b	R^2	K_F	n	R^2
10.892	0.089	0.996	1.027	1.401	0.998

Values of constants of both the isotherms are presented in **Table 2**. The good correlation coefficients show that adsorption of Co (II) on HApZ follows both, Langmuir and Freundlich isotherm models.

Conclusion

HApZ composite is better adsorbent than HAp. The small amount of adsorbent (2mg/L) is able to adsorbed 65% of Co (II) within 20 min at pH 6 and 30 °C of temperature. The rate of adsorption decreases with increases initial metal ions concentration. The kinetics of adsorption of Co (II) onto HApZ composite was well represented by the pseudo-second order kinetic model. The sorption of Co (II) onto the HApZ composite follows both, Langmuir and Freundlich isotherm models.

Acknowledgement

Authors are thankful to Prof. Avinash C. Pandey and Mr. Prashant K. Sharma of Nanotechnology Application Centre, University of Allahabad, Allahabad for extending their kind help during the characterization of the samples.

Reference

1. H. Ghassabzadeh, M.T. Mostaedi, A. Mohaddespour, M.G. Maragheh, S.J. Ahmadi, P. Zaheri, Desalination, 261 (2010) 73.
2. D.M. Manohar, B.F. Noeline, T.S. Anirudhan, Applied Clay Sci. 31 (2006) 194.
3. G. Lusvardi, G. Malavasi, L. Menabue, M. Saladini, Waste Manage. 22 (2002) 853.
4. Smiciklas, S. Dimovic, I. Plecas, M. Mitric, Water Res. 40 (2006) 2267.
5. S.H. Lin, S.L. Lai, H.G. Leu, J. Hazard Mater. 76 (2000) 139.
6. E. Erdem, N. Karapinar, R. Donat, J. Colloid Interf. Sci. 280 (2004) 309.
7. Gamage, F. Shahidi, Food Chemistry, 104 (2007) 989.
8. Demirbas, J. Hazard Mater. 157 (2008) 220.
9. O.M.M. Freitas, R.J.E. Martins, C.M. Delerue-Matos, R.A.R. Boaventura, J. Hazard Mater. 153 (2008) 493.

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