Asian Journal of Chemistry Vol. 21, No. 8 (2009), 6005-6014

Sorption of Lead(II) in Aqueous Solution on Chitin

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The present research was aimed at the development of chitin as an adsorbent that it can be used in the removal of lead(II) ions to obtain equilibrium, kinetics and thermodynamic parameters. The experimental results show that the optimal pH for the sorption of lead(II) ions was 6.72 in the CH_3COOH-CH_3COONa system and the maximum adsorption capacity was estimated to 44.0 mg g^{-1} chitin by saturated capacity method. The apparent sorption rate constant was $k_{298K} = 2.70 \times 10^{-5}$ s^{-1}. Experimental results were found to fit to Freundlich isotherm model over the entire studied concentration range. Effect of temperature on the equilibrium distribution values has been studied to evaluate the changes. The thermodynamic parameters, ΔG_{298K} was calculated to be -16.1 kJ mol^{-1}, ΔH and ΔS were found to be 13.1 kJ mol^{-1} and 97.8J mol^{-1} K^{-1} and the results show that the adsorption was feasible, spontaneous and endothermic under examined conditions. Adsorption mechanism was also proposed for the adsorption of lead(II) ions onto chitin using infrared spectroscopy technique.

Key Words: Chitin, Sorption, Lead(II), Kinetics, Thermodynamic.

INTRODUCTION

As we know, environmental conservation is of increasing social and economic importance. A particularly intractable pollution problem is that of the contamination of waters by heavy metals. Most of them are well-known toxic and carcinogenic agents and represent a serious threat to human populations as well as the fauna and flora of receiving water bodies as discharged in wastewater[1]. Lead(II) is one of the heavy metals considered toxic to humans and aquatic life. In recent years, there has been a sharp rise in the global use of lead(II) for batteries and other applications, such as pigments, polyvinyl chloride stabilizers and plating[2]. The lead(II) ions concentrations were approximately the range of 200-500 mg dm^{-3} in industrial wastewaters. According to water quality standards, this value is very high and must be reduced to a value of 0.10-0.05 mg dm^{-3} before discharge to water ways or sewage systems[3].

Conventional methods for removing metals from industrial waste solutions (which include chemical precipitation, chemical oxidation or reduction, filtration, ion exchange, electrochemical treatment, application of membrane technology and evaporation recovery) may be ineffective or extremely expensive, especially when the metals are dissolved in large volumes of solution, at relatively low concentrations

(around 1-100 ppm)[4]. This situation has in recent years led to a growing interest in the application of biomaterials technology for the removal of trace amounts of toxic metals from dilute aqueous wastes. Biomaterials including algae, bacteria, fungi, higher plants and products derived from these organisms, have been demonstrated to remove certain chemicals species[5]. *Cephalosporium aphidicola*[6], *Sargassum natans*[7], *Neurospora crassa*[8], *Aspergillus niger*[9] and *Bacillus* sp[10] have been used to remove lead(II) ions from aqueous solutions by adsorption. As environmental friendly materials, natural polymers are biodegradable and biocompatible, therefore, they can be expected to be a potential suitable materials and have attracted much attention.

Chitin, a polymer composed of N-acetyl-d-glucosamine residues[11], is considered the second most plentiful organic resource on the earth; occurring in plants, marine invertebrate, insects, cell walls of some fungi and microorganisms. It exhibits numerous interesting physico-chemical, biological and mechanical properties with great potential applications. It carries one -NHCO- group per glucose ring, thus allowing excellent complexation capacity with metal ions, particularly transition and post-transition metals. The formation of a coordination complex between the metal and the chitin nitrogen or oxygen has been reported[12-14]. Consequently, chitin may be used in water treatment for the removal of cations such as lead(II) ions.

The present work is undertaken in order to determine the optimum conditions on the biosorption of lead(II) by chitin in static conditions. Both equilibrium and kinetic characterization of the biosorbent material are crucial for quantitative assessment of its performance. In the other words, they are an important tool to understand the adsorption mechanism for the theoretical evaluation[15].

EXPERIMENTAL

The lead(II) was determined with Shimadzu UV-2550 UV-Vis spectrophotometer. Chitin dosage was measured by electronic balance of METTLER TOLEDO AL204. Mettler toledo delta 320 pH meter was used for measuring pH. The sample was shaken in the DSHZ-300A temperature constant shaking machine. The water used in the present work was purified using Molresearch analysis-type ultra-pure water machine.

Chitin from crushed crab shells (purchased from Zhejiang University) in the form of 0.2-6.3 mm particle size flakes, was used throughout this work with proper treatment.

Its structures are illustrated in Fig. 1. Standard solutions of 1 mg mL^{-1} metal ions were prepared by dissolving appropriate amounts of analytical grade $Pb(NO_3)_2$ in purified water and further diluted prior to use. CH_3COOH-CH_3COONa with pH 3.40-6.99 and $C_6H_{12}N_4$-HNO_3 with pH 5.40 buffer solutions were prepared from the 0.4 mol L^{-1} CH_3COOH, 0.4 mol L^{-1} CH_3COONa and 0.08 g L^{-1} $C_6H_{12}N_4$ solutions. The colour reagent of 0.05 % xylenol orange solution was obtained by dissolving 0.05 g xylenol orange into 100 mL purified water. All other chemicals were of analytical grade and purified water was used throughout.

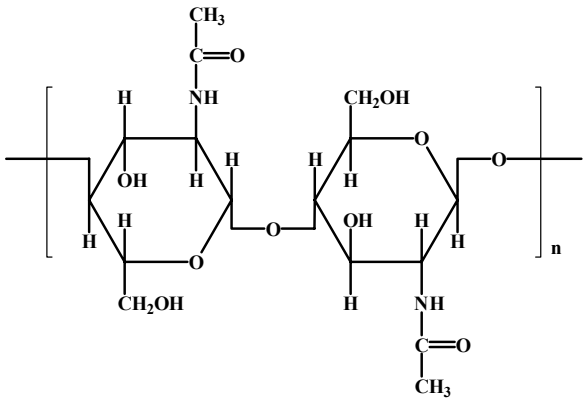

Fig. 1. Structure of chitin

Adsorption experiments: The amount of absorbed metal (Q) and distribution coefficient (D) were determined as a difference of metal ions concentration before and after adsorption based on the equation:

$$Q = (C_o\text{-}C_e)V/W,\ D = Q/C_e$$

where C_o = initial concentration of Pb^{2+} in solution (mg mL^{-1}), C_e = equilibrium concentration of Pb^{2+} in solution (mg mL^{-1}), V = total volume of solution (mL), W = chitin weight (g).

All batch experiments were carried out at certain temperature in a 100 mL iodine flask and equilibrated to elucidate the optimum conditions. However, the effect of the contact time, initial pH of the solution and temperature were investigated to determine the optimum conditions for Pb^{2+} adsorption.

An analysis of the relationship between adsorption capacity of chitin and metal ion concentration was performed using the Langmuir adsorption equations and the Freundlich adsorption equations.

For kinetic studies, 40.0 mg of chitin was contacted with 55 mL of metal solutions in a 100 mL iodine flask stirred vigorously in a shaker of 100 rpm, maintained at a constant temperature. At appropriate time intervals, stirring was briefly interrupted while 0.1 mL volumes of supernatant solutions were pipetted from the reactor and were analyzed to determine the residual metal concentration in the aqueous solution.

Further characterization was performed by infrared spectroscopy. IR spectra is generally recorded in the range of 4000-500 cm^{-1}. The sample was prepared as a thin disc-formed samples made from a mixture of KBr and chitin as solid forms.

Measurement of heavy metal ions: The concentration of unadsorbed Pb^{2+} ions in the sorption medium was determined spectrophotometrically. A solution containing lower than 75 µg of Pb^{2+} was accurately added into a 25 mL colorimetric tube and then 1 mL colour reagent of 0.05 % xylenol orange solution and 5 mL pH 5.40 $C_6H_{12}N_4$-HNO_3 buffer solutions were added. After the addition of purified water to the mark of colorimetric tube, the absorbency was determined in a 1 cm colorimetric vessel at wavelength of 570 nm and compared with the blank test.

RESULTS AND DISCUSSION

Effect of pH and the treatment to chitin on the sorption of Pb^{2+} onto chitin: We make a comparison through experiments on the efficiency between the three different methods of treatment methods of chitin. The first one is directly mashing the chitin and drying. The second method employs only one step for drying the chitin without mashing. The last one is immersing the mashing chitin in HCl solution and then drying for use after washing to neutral with purified water. The results are presented in the Fig. 2. Compared with batch method, the first method was the best. So we chose the first method to handle the chitin.

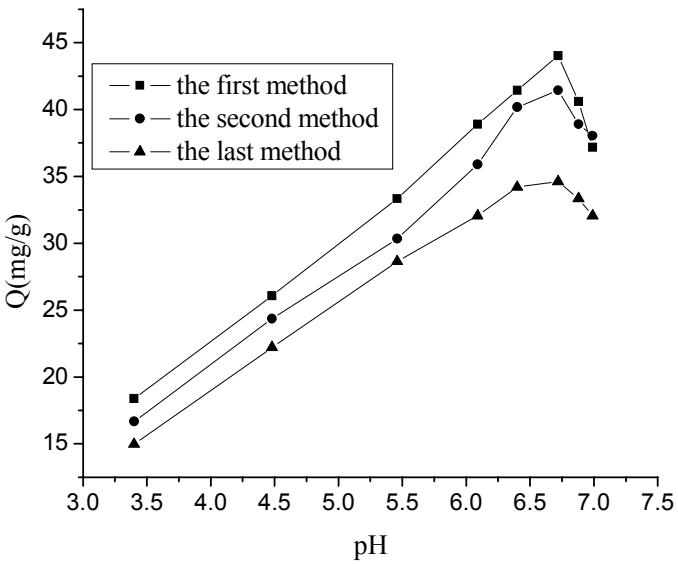

Fig. 2. Influence of pH on adsorption capacity

On the other hand, the initial pH of sorption medium is one of the most significant parameters affecting the sorption process[16]. It is well known that pH could affect the protonation of the functional groups on the chitin as well as the metal chemistry. The effects of pH on lead(II) adsorption capacity of chitin have been studied.

The results demonstrated that the sorption percentage was highest at pH 6.72 and decreased either raising or lowing. At low pH, chitin's ligands are protonated to a higher extent and restrict the approach of metal cations as a result of the repulsive force. As pH increases, interactions between H^+ and chitin are destabilized, leading to an improvement of the adsorption of Pb^{2+} onto chitin because more ligands groups would be exposed and the biosorption of the metal ions with positive charge (Pb^{2+}) process was reached maximum. However, above the threshold pH, decrease in biosorption is due to the precipitation of some Pb^{2+} ions. The same trend was observed by several authors that investigated the effect of pH on biosorption of heavy metal by using different biomaterials[17].

Hence, the following experiments were performed in the solution pH of 6.72. As can be observed in Fig. 2, it can be noted that the maximum sorption capacity of Pb^{2+} is 44.0 mg g^{-1} chitin. This is an important parameter because it determines how much sorbent is required quantitatively to adsorb the metal from a solution.

Effect of container walls adsorbing: Review the veracity of sorption capability, the effect result of container walls adsorbing were also discussed. For this experiment, ions solution and butter solution were directly added to without chitin. We detected absorbance of Pb^{2+} and calculated the content of Pb^{2+} in different time. The results were shown in Table-1. From the results, there is not influence to absorbance. On the other hand, the experiment result proves the method we used is veracity.

TABLE-1
EFFECT OF CONTAINER WALLS ADSORBING

t (h)	0	0.25	0.5	1.0	1.5	2.5	3.5	5.5	7.5
A (absorbance)	0	0.220	0.219	0.219	0.217	0.219	0.217	0.218	0.218

Equilibrium isotherms: Sorption isotherms describe how adsorbates interact with adsorbents. In order to successfully represent the equilibrium adsorptive behaviour, it is important to have a satisfactory description of the equation state between the two phases composing the adsorption system. Two kinds of several isotherms equations were tested[18]:

Langmuir equation: $C_e/Q = C_e/Q^0 + 1/(Q^0 b)$

Freundlich equation: $\lg Q = 1/n(\lg C_e) + \lg K$

where Q is the amount adsorbed at equilibrium (mg g^{-1}) and C_e is the equilibrium concentration of metal ions in solution (mg mL^{-1}). The other parameters are different isotherm constants, which can be determined by regression of the experimental data. In the Langmuir equation, Q^0 is satured sorbing capacity and b is a constant related to the energy of adsorption (mL mg^{-1}). The Q^0 of chitin was found to be 45.1 mg g^{-1} for Pb^{2+} at 298 K. Moreover, the b value was found as 222 mL mg^{-1} for Pb^{2+}. Freundlich treatment gives the parameters, n, indicative of bond energies between metal ion and the adsorbent and K, related to bond strength.

The values of R^2 are regarded as a measure of the goodness-of-fit of experimental data on the isotherm's models (Table-2). The data indicated that Freundlich and Langmuir isotherms offer very good fits for all metal ions studied with R^2 values above 0.9. The intensity parameter, 1/n indicates the deviation of the adsorption isotherm from linearity. n = 1 indicates the adsorption is linear with homogeneous adsorption sites and there is no interaction between the adsorbed metals. $1/n < 1$ shows that the adsorption is favourable, new adsorption sites are available and the adsorption capacity increases. $1/n > 1$ indicates that the adsorption bonds are weak, adsorption capacities decrease and unfavourable[19]. Results in Table-2 indicate that adsorptions are favourable for Pb^{2+} with $1/n < 1$. The Freundlich isotherm model best fitted the equilibrium data since it presents higher R^2 values. This may be that besides the formation of a coordination complex between the metal and the chitin

nitrogen or oxygen, Sorption of Pb^{2+} occur by precipitation onto chitin with the formation of nodules of metal, a mechanism referred to the Eiden-Jewell effect[20]. This possible mechanism implies a multilayer sorption or heterogenous sorption induced by variation in sorption energies on various sites or by several different sorbed species.

TABLE-2
LANGMUIR AND FREUNDLICH ISOTHERM EQUATION
AT DIFFERENT TEMPERATURES

T (K)	Langmuir isotherm equation	R^2	Q^0 (mg g^{-1})	b (J mg^{-1})
288	$C_e/Q = 0.0251\ C_e + 0.0003$	0.9833	43.1	77.3
298	$C_e/Q = 0.0222\ C_e + 0.0001$	0.9778	45.1	222.0
308	$C_e/Q = 0.0193\ C_e + 0.0002$	0.9786	51.8	96.5
318	$C_e/Q = 0.0183\ C_e + 0.0001$	0.9642	54.6	183.0
	Freundlich isotherm equation	R^2	n	
288	$\lg Q = 0.4898 \lg C_e + 2.1258$	0.9918	2.04	–
298	$\lg Q = 0.4734 \lg C_e + 2.1906$	0.9974	2.11	–
308	$\lg Q = 0.4341 \lg C_e + 2.1883$	0.9756	2.30	–
318	$\lg Q = 0.4194 \lg C_e + 2.2259$	0.9670	2.38	–

Kinetics of sorption of metal ions: The time-dependent behaviour of lead(II) adsorption was studied by varying the contact time between the chitin and lead(II). It is observed a quick adsorption for lead(II) occurred in first 2 h. After this period, the adsorption became slow and the equilibrium was reached. In present investigations, the Brykina method was used to test adsorption kinetics data to investigate the mechanism of biosorption.

The sorption rate curves (Fig. 3) of the chitin towards lead(II) was obtained by plotting the sorption capacity against the sorption time allowed. The sorption rate constants (k) were calculated using the following equation of Brykina method[21]:

$$-\ln(1-F) = kt, \text{ where } F = Q_t/Q$$

where Q_t is the sorption capacity at sorption time t and Q is the sorption capacity at equilibrium. Therefore, the sorption rate constant can be found from the slope of the straight line. The calculated sorption rate constants (k) are $k_{288K} = 2.00 \times 10^{-5}\ s^{-1}$, $k_{298K} = 2.70 \times 10^{-5}\ s^{-1}$, $k_{308K} = 3.10 \times 10^{-5}\ s^{-1}$ and $k_{318K} = 4.40 \times 10^{-5}\ s^{-1}$, respectively.

Rather high correlation coefficient ($R^2_{288K} = 0.9949$, $R^2_{298K} = 0.9949$, $R^2_{308K} = 0.9956$, $R^2_{318K} = 0.9935$) were obtained *via* linear fitting. According to Boyd *et al.*[22], if the beeline accord with the linear relationship of -ln(1-F)~t, it can be deduced that the liquid film spreading is the predominating step of the sorption process.

According to the formula of Arrhenius $\log k = -E_a/RT + \text{Constant}$, the slope of straight line, which is made by plotting -log k *versus* 1/T can be obtained (Fig. 4). The equation was y = -2.2885x-0.5723 ($R^2 = 0.973$). The apparent activation energy of $E_a = 8.314 \times 2.2885 = 19.0$ kJ mol^{-1}. It can be seen from the rate constant that the sorption speed accelerated when the temperature raised within the scope of experimental temperature.

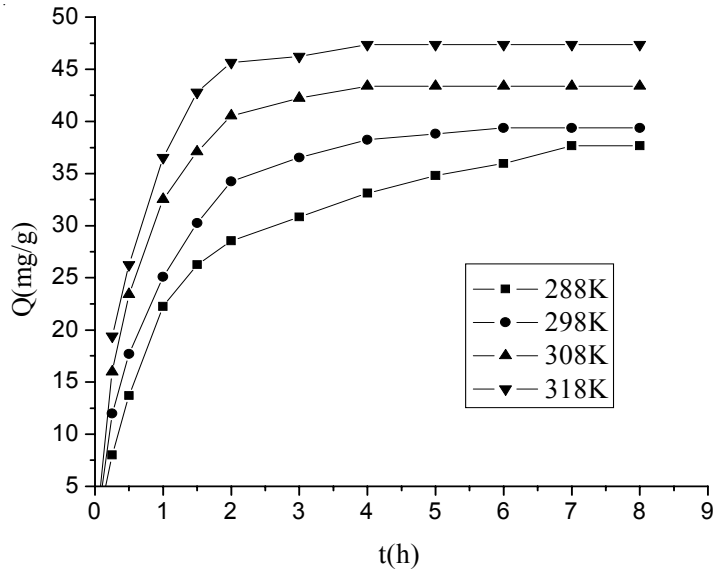

Fig. 3. Adsorption curves

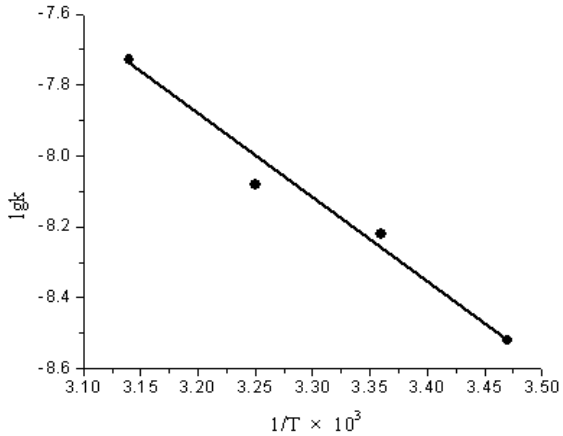

Fig. 4. Determination of E_a

Effect of temperature: The temperature of the adsorption medium could be important for energy dependent mechanisms in metal adsorption by chitin. For an increase in temperature from 288 to 318 K, an increase in the adsorption of lead(II) was observed (34.8 mg/g at 288 K to 49.1 mg/g at 318 K at experimental conditions). The results indicated that an increase of the temperature deals induce an increase in the capacity of sorption. Meena *et al.*[23], reported that the increase in sorption with temperature may be attributed to either increase in the number of active surface sites available for sorption on the adsorbent or due to the decrease in the boundary layer thickness surroundings the sorbent, so that the mass transfer resistance of absorbate in the boundary layer decreased.

The free energy change ΔG^o, enthalpy change ΔH^o and entropy change ΔS^o for adsorption process were calculated using following equations:

$$\lg D = -\Delta H^o/(2.303\ RT) + \Delta S^o/2.303R$$

$$\Delta G^o = \Delta H^o - T\Delta S^o$$

The equation was $y = -0.6823x + 5.1094$ ($R^2 = 0.9833$) and the slope of straight line is:

$$K_{slope} = -0.6823.$$

According to

$$\lg D = -\Delta H^o/(2.303RT) + \Delta S^o/2.303R$$

where

$$\Delta H^o = -K_{slope} \times 2.303R$$
$$= -0.6823 \times 2.303 \times 8.314$$
$$= 13.1\ (\text{kJ mo1}^{-1}).$$
$$\Delta S^o = 2.303 \times 8.314 \times 5.1094$$
$$= 97.8\ (\text{J K}^{-1}\ \text{mol}^{-1})$$
$$\Delta G^o_{298K} = \Delta H^o - T\Delta S^o$$
$$= -16.1\ \text{kJ mol}^{-1}$$

The Gibbs free energy change, ΔG^o, is the fundamental criterion of spontaneity, reaction occurring spontaneously at a given temperature if it is a negative value. ΔG^o_{298K} values were negative indicating that the sorption process led to a decrease in Gibbs free energy and confirm the feasibility of the process and spontaneous nature of the sorption under the experimental condition[24]. Positive values of ΔS^o refer to an increase in entropy. If sorption decreases with increasing temperature, it may be indicative of physical sorption and the reverse is generally true for chemical sorption. However, there are a number of contradictory cases in the literature[25]. The positive values of ΔH^o indicate that the sorption process is an endothermic process. So the sorption reaction is a chemical sorption.

IR analyses: The IR spectra of the chitin and metal-loaded chitin are shown in Fig. 5. The IR spectrum of α-chitin exhibited major peaks at 3443 cm^{-1} for -OH stretching vibration. In addition, for α-chitin, the amide I band splitted at 1661 and 1626 cm^{-1}, the amide II band is unique at 1555 cm^{-1}. The absorption peaks at 1373 and 1312 cm^{-1} were the $\delta(CH_3)$ and ν(C-N) of the acetylamino. A comparison of the spectra for free chitin with that of Pb-loaded chitin reveals characteristic changes of acety1 groups, $\delta(CH_3)$ and ν(C-N), which shift from 3443, 1661, 1555, 1373 and 1312 cm^{-1} before Pb^{2+} adsorption to 3438, 1646, 1561, 1377 and 1316 cm^{-1} after Pb^{2+} adsorption. At the same time, the infrared absorption band of 1626 cm^{-1} disappeared. The spectral analysis indicated that the complex reactions took place between the the acetylamino (-CONH-), the hydroxyl group (-OH) and Pb^{2+}.

Conclusion

In this study, the sorption of lead(II) on chitin has been studied. The effected results such as solution pH, temperature, sorption rate constant, container walls adsorbing have been evaluated. It was concluded that the chitin can be used for removal of lead(II) very effectively. It was observed that lead(II) sorption is highly

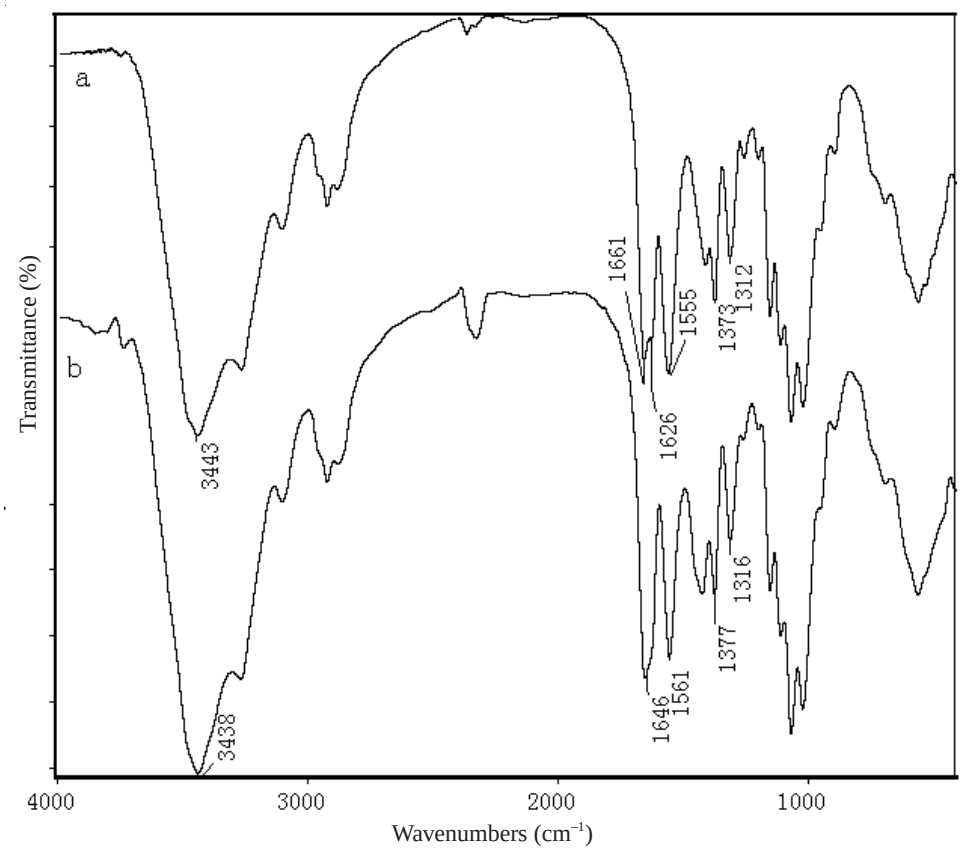

Fig. 5. IR analyse (a) chitin before sorption; (b) chitin after sorption

dependent on pH. In addition, chitin dosage and initial lead(II) concentration are effective on lead(II) sorption. The sorption behaviour could be modeled using the Langmuir isotherm and Frendlich isotherm, but the Freundlich isotherm model gives better fitting than Langmuir. Batch studies clearly suggest that the high adsorption capacity (44.0 mg g^{-1}) of chitin for the lead(II) ions was obtained at pH 6.72. The apparent sorption rate constant is $k_{298K} = 2.70 \times 10^{-5}$ s^{-1} and the liquid film spreading is the predominating step of the sorption process. The sorption parameters of thermodynamic obtained from experiments indicated a chemical, feasible, spontaneous endothermic adsorption.

In summary, chitin has many advantages to remove lead(II) in the solution. It can be used in wastewater including lead(II) disposal and purification.

ACKNOWLEDGEMENTS

Project supported by the Natural Science Foundation of Zhejiang Province (No. Y404279) and the Analysis Project (No. 2008F70059) under Zhejiang Provincial Scientific and Technological Research Planning.

REFERENCES

1. D. Zhou, L.N. Zhang, J.P. Zhou and S.L. Guo, *Water Res.*, **38**, 2643 (2004).
2. E. Pehlivan, B.H. Yanik, G. Ahmetli and M. Pehlivan, *Biores. Technol.*, **99**, 3520 (2008).
3. H. Ucun, Y.K. Bayhan, Y. Kaya, A. Cakici and O.F. Algur, *Desalination*, **154**, 233 (2003).
4. B. Benguella and H. Benaissa, *Colloids and Surfaces A: Physicochem. Eng. Aspects*, **201**, 143 (2002).
5. B. Benguella and H. Benaissa, *Water Res.*, **36**, 2463 (2002).
6. S. Tunali, T. Akar, A.S. Özcan, I. Kiran and A. Özcan, *Sep. Purif. Technol.*, **47**, 105 (2006).
7. Z.R. Holan and B. Volesky, *Biotechnol. Bioeng.*, **43**, 1001 (1994).
8. I. Kiran, T. Akar and S. Tunali, *Process Biochem.*, **40**, 3550 (2005).
9. J.L. Wang, X.M. Zhan, D.C. Ding and D.J. Zhou, *Biotechnol.*, **87**, 273 (2001).
10. S. Tunali, A. Çabuk and T. Akar, *Chem. Eng. J.*, **115**, 203 (2006).
11. N.Q. Hien, D.V. Phu, N.N. Duy and T.H. Huy, *Nucl. Instrum. Methods Phys. Res.*, **236**, 606 (2005).
12. A.Y. Dursun and C. Seda Kalayci, *J. Hazard. Mater.*, **B123**, 151 (2005).
13. K.M. Peiselt da Silva and M.I. Pais da silva, *Colloids and Surfaces A: Physicochem. Eng. Aspects*, **237**, 15 (2004).
14. W. Kaminski and Z. Modrzejewska, *Sep. Sci. Technol.*, **32**, 2659 (1997).
15. M. S.ölener, S. Tunali, A. Safa Özcan, A. Özcan and T. Gedikbey, *Desalination*, **223**, 308 (2008).
16. P.K. Roy, A.S. Rawat and P.K. Rai, *Talanta*, **59**, 239 (2003).
17. B.Y.M. Bueno, M.L. Torem, F. Molina and L.M.S. de Mesquita, *Miner. Eng.*, **21**, 65 (2008).
18. C.H. Xiong, C.P. Yao and X.M. Wu, *Hydrometallurgy*, **90**, 221 (2008).
19. H.A. Aziz, M.N. Adlan and K.S. Ariffin, *Biores. Technol.*, **99**, 1578 (2008).
20. Y. Sag and Y. Aktay, *Process Biochem.*, **36**, 1187 (2001).
21. G.D. Brykina, T.V. Marchak and L.S. Krysina, *Zh. Anal. Khim.*, **35**, 2294 (1980).
22. G.E. Boyd, A.W. Adamson and L.S. Myers, *J. Am. Chem. Soc.*, **69**, 2836 (1947).
23. A.K. Meena, G.K. Mishra, P.K. Rai, C. Rajgopal and P.N. Nagar, *J. Hazard. Mater.*, **B113**, 119 (2005).
24. T.S. Singh and K.K. Pant, *Sep. Pur. Technol.*, **36**, 139 (2004).
25. M. Kara, H. Yuzer, H. Sabah and M.S. Celik, *Water Res.*, **37**, 224 (2003).

(*Received*: 10 November 2008; *Accepted*: 22 May 2009) AJC-7574