Bull. Chem. Soc. Ethiop. **2008**, 22(3), 349-360.	ISSN 1011-3924
Printed in Ethiopia

# REMOVAL OF LEAD(II) IONS FROM AQUEOUS SOLUTIONS USING ACTIVATED CARBON FROM *MILITIA FERRUGINEA* PLANT LEAVES

Alemayehu Abebaw Mengistie[1*], T. Siva Rao[1], A.V. Prasada Rao[1] and Malairajan Singanan[2]

[1]Department of Inorganic and Analytical Chemistry, School of Chemistry, Andhra University, Vishakhapatnam, Andhra Pradesh, India
[2]Department of Applied Chemistry, Ambo College–Jimma University, P. O. Box 19, Ambo Town, Western Shoa, Ethiopia

(Received October 4, 2007; revised July 22, 2008)

**ABSTRACT.** The adsorption of lead(II) on to activated carbon developed from an indigenous Ethiopian medicinal plant leaves namely Birbira (*Militia ferruginea*) was investigated to assess the possible use of this adsorbent. The influences of contact time, adsorbent dose, Pb(II) concentration, pH and temperature on adsorption were investigated. The maximum adsorption took place at 3 h. at a dose of 4.0 g of adsorbent, and 97.3 % of $Pb^{2+}$ adsorption at pH of 4.0. The amount of lead ion adsorbed per gram of the adsorbent increased with decreasing concentration of $Pb^{2+}$. The percentage of adsorption had increased with the increasing temperature. The positive value of $\Delta H$ indicated that the adsorption of lead ions on the adsorbent was an endothermic process. The values of free energy ($\Delta G$) were negative as expected for a spontaneous process. The decrease in $\Delta G$ value with increasing temperature revealed that adsorption of the ion on the adsorbent became favorable at a higher temperature. The calculated value of $\Delta H$ was 25.05 kJ $mol^{-1}$, $\Delta S$ was 135.48 $JK^{-1}$ $mol^{-1}$ and $\Delta G$ was also calculated for each temperature. The two theoretical adsorption isotherms, namely, Langmuir and Freundlich were used to describe the experimental results. The Freundlich adsorption isotherm best fits and adsorption capacity was calculated to be 3.3 mg of Pb(II) per g of adsorbent. The adsorption followed the first order kinetics and was found to be pH dependent being maximum at pH 4.0. The pH effect and desorption studies showed that ion exchange mechanism might be involved in the adsorption process. Reuse of the desorbed bio-adsorbent is possible. The effect of foreign ions on the removal of Pb(II) has been investigated. The removal of Pb(II) from industrial wastewater sample was also tested and showed that more than 97 % removal was possible. The results showed that activated carbon prepared from Birbira (*Militia ferruginea*) leaves could be used for the removal of Pb(II) from wastewater.

**KEY WORDS:** Industrial wastewater, Lead removal, Adsorbent, *Militia ferruginea*

## INTRODUCTION

Heavy metals are toxic pollutants released into the surface and ground water as a result of different activities such as industries, mining and agriculture [1]. The rapid pace of industrialization has led to severe problem of water pollution. Awareness encouragement of pollutant toxicity has forced industries and municipal authorities to treat wastewater before discharging to the natural water bodies [2].

Lead is one of the industrial pollutants; possibly enter to the ecosystem through soil, air and water. Inorganic lead causes disturbance in the central nervous system by changing the characteristics of the early organism [3, 4]. According to WHO, the maximum permissible limit (MPL) of lead in drinking water is 0.1 mg/L [5]. Hence, the appropriate treatment of industrial wastewater which releases lead into the aquatic and terrestrial systems is very important.

At present, a number of technologies can be used to remove heavy metals from the contaminated wastewater such as filtration, adsorption, chemical precipitation, ion exchange, membrane separation methods and electro-remediation methods [6-12]. However, most of these methods might not efficient in removing heavy metal at very low concentrations, and could be relatively expensive. These methods are also not effective due to their secondary effluent impact on the recipient environment. Hence, the simple, effective, low cost and eco-friendly techniques

---

*Corresponding author. E-mail: alemayehuabebaw@yahoo.com

are required for the fine tuning of effluent wastewater treatment. The search for low cost, and easily available adsorbents has led to the investigation of materials of agricultural and biological origin, alongside those of industrial by-products as adsorbents for removal of heavy metals [13-17]. Examples of such low cost adsorbents are clay [18], cotton [19], wool fiber [20], tea leaves [21] and other materials [22-25].

A search for newer eco-friendly adsorbents is still under investigation. The aim of this study is to propose new biomaterial involving application of an Ethiopian indigenous medicinal plant leaves (*Militia ferruginea*) also known in the vernacular as Birbira, in the removal of heavy metals from synthetic wastewater (spiked with lead) and subsequently its application to industrial wastewater. In our earlier studies, we had used *Tridax procumbers* (Asteraceae), for removal of color, lead and cadmium ions from wastewater [26-28]. In our earlier study the removal of lead ion from wastewater has its maximum capacity at high concentrations. The application of indigenous abundantly available biomaterials for low concentration heavy metal removal is of high importance for the country. It will be also a valuable contribution and novel development to adsorption research, since conventional methods for the removal of heavy metals from wastewater is with inadequate efficiencies at law metal concentrations particularly in the range of 1-100 mg/L. For environmental degradation, industries are not the only contributors but deforestation of indigenous trees for agriculture does also contribute. It is therefore, of great value to solve these problems simultaneously. The search for indigenous biomaterials especially, those with high social value and economically important trees for tackling both deforestation and environmental pollution are sounding. In the present work we have used the leaves of *Militia ferruginea* an Ethiopian indigenous for the removal of lead ions from synthetic wastewater and its application to real wastewater. Selection of these indigenous trees for this application will increase the farmer’s attention towards planting the trees since the value of these trees will increase in terms of economy.

## EXPERIMENTAL

### *Preparation of activated carbon of the bio-adsorbent*

The leaves of Birbira (*Militia ferruginea*) were collected from the nearby forest around Ambo town, Ethiopia. It was dried in open air and thereafter powdered using electrical grinding equipment. The resultant homogenous powder was then used for experimental purpose during these studies. Activated carbon of the biomaterial was later prepared by treating with concentrated sulfuric acid (Sp. Gr 1.84) in a weight ratio of 2:1 (biomaterial:acid). The generated black product was kept in air-free oven monitored at 195 $^{o}$C ± 5 $^{o}$C for three hours, followed by washing with distilled water several times until the complete removal of excess acid, and dried at 105 ± 5 $^{o}$C. The activated carbon obtained from the biomaterial was grounded and the portion retained between 90 and a 125 μm sieve was used for the metal adsorption experiments [29].

### *Preparation of synthetic wastewater*

Synthetic wastewater samples were prepared by using analytical grade lead nitrate (99 % Labosi, India) by using double distilled water. The stock solution was prepared by dissolving the salt in double distilled water, which contains 1000 mg/L. Working solutions of 5, 10, 20, 50, 60 and 100 mg/L were prepared by dilution.

### *Batch adsorption experiments*

The batch experiments were performed by adding the desired amount of the stock solution in 250 mL of volumetric flask at the designated adsorbent dose, pH, and temperature. The solution was shaken using a mechanical Gemmy orbit shaker (model: VRN-480, USA) at 250 rpm for a definite period. Adsorbent dose, contact time, temperature and pH were optimized by continuous variation method (studying one, keeping the other parameters constant). After equilibrating, the system was allowed to settle for 20-30 min, filtered and analyzed for lead. The pH of the original solution and the filtrate solution was determined using HANNA instruments pH meter (pH 209 model, Portugal).

The difference in the lead content before and after adsorption experiments represents the amount of lead adsorbed by the bio-adsorbent. All experiments were performed at room temperature (23 ± 2 $^{o}$C) except for the samples used to study temperature effect. The free ion concentrations of $Pb^{2+}$ in the test solution were measured by flame atomic absorption spectrometer model AA-6200, Shimadzu Japan. The concentration was measured at wavelength of 283.3 nm with slit width (nm) 0.7 by using Photron hollow cathode lamp system in AAS. Experiments were carried out in triplicate and mean values were taken for calculation. All the results are statistically significant at $p < 0.05$.

The percent removal of metal ions can be calculated by using the formula.

$$Percent\ \ removal = \frac{C_i - C_f}{C_i} X\,100 \tag{1}$$

where, $C_i$ = initial concentration of the metal ion, $C_f$ = final concentration of the metal ion in the solution.

### *Temperature study*

The effect of temperature was studied using 50 mL of 10, 20, 40 and 60 mg/L of $Pb^{2+}$ solutions for 3 h at adsorbent dose of 4.0 g. The temperatures were varied from room temperature (23 $^{o}$C) to 30, 35, 40, 45, 50 and 60 $^{o}$C, respectively.

### *Desorption studies*

The adsorbent of known quantity (50 mg) that was used for the adsorption of 5, 10, 20, 40, 50 and 80 mg/L of $Pb^{2+}$ solution was separated from the solution by filtration using Whatman filter paper No. 41 and washed gently with distilled water three times for 15 min to remove the unadsorbed $Pb^{2+}$. The water was immediately removed. Then the adsorbent was mixed with 50 mL of distilled water, adjusted to a pH value in the range of 2.0–10.0 using dilute HCl/NaOH and agitated at time interval longer than the equilibrium time (4 h). The desorbed lead was estimated as before. The adsorbent after desorption of the ion was checked for further adsorption capacity.

## RESULTS AND DISCUSSION

### *Effect of contact time on adsorption*

It is evident from Figure 1 that the removal of metal ion increases at the contact time increases. Initially, the rate of uptake is fast. However, equilibrium was attained in 3 h. Further increase in contact time to 24 h, the percentage adsorption decreases very slowly. Therefore, the contact time can be optimized to 3 h.

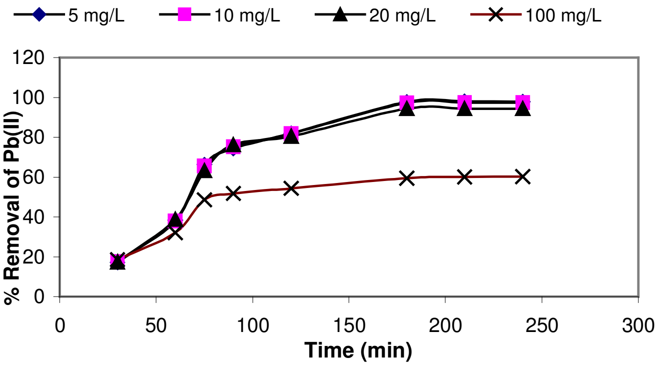

Figure 1. Effect of contact time (pH = 4, adsorbent dose = 4 g).

*Effect of quantity on adsorbent*

The adsorption of lead ions is observed to increase linearly as the amount of adsorbent is increased gradually from 0.25 g to 4.0 g (Figure 2). The maximum adsorption is obtained at the adsorbent dose of 4.0 g where a further increase thereafter, in the quantity of the adsorbent up to 5 g has no more effect to the adsorption rate. Therefore, the study indicated that 4.0 g of the adsorbent is sufficient to adsorb the maximum ions. The study further alluded that the removal efficiency is associated with the adsorbent dose increases which is due to the availability of more adsorbing sites at higher doses.

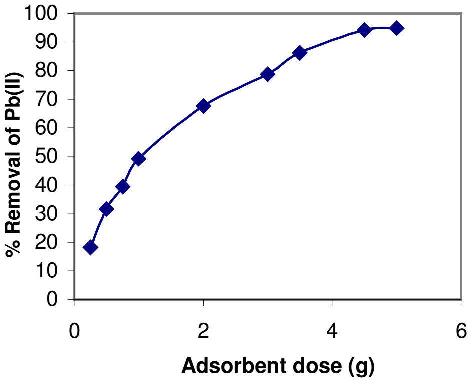

Figure 2. Effect of adsorbent dose (pH = 4, initial concentration = 20 mg/L, time = 3 h).

*Effect of initial concentration of lead ions*

Removal of Pb(II) from aqueous solution was studied for concentrations ranging from 5 to 100 mg/L. The percentage adsorption of Pb(II) at different concentrations at 23 ± 2 $^{o}$C from 50 mL solution of different initial concentration (equilibrated with 4.0 g of adsorbent) is shown in Figure 3. As observed from the figure the removal of metal ion is found to increase with decrease in initial concentration. At the experimental condition of 4.0 g dose of adsorbent and adjusting the pH at 4, maximum adsorption is obtained for the concentrations of 5 and 10 mg/L.

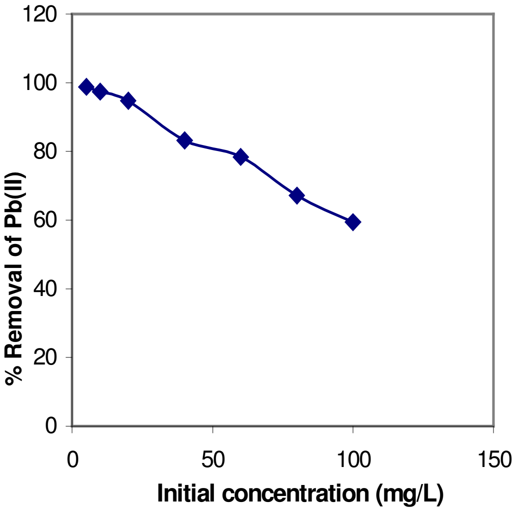

Figure 3. Effect of initial concentration (pH = 4, adsorbent dose = 4 g, time = 3 h).

### *Effect of pH*

The pH value of the solution is an important controlling parameter in the adsorption process, and the initial pH value of the solution has more influence than the final pH, which influences both the adsorbent surface metal binding sites and the metal chemistry in water [30]. The pH of feed solution was examined from solution a different pH levels, covering a range of 1.0-7.0. In the case of Pb(II) the maximum adsorption was obtained at pH 4.0 for both 10 and 50 mg/L. Removal of $Pb^{2+}$ onto the activated carbon is pH dependent as shown in Figure 4. At pH < 2.5, $H^+$ ions compete with Pb(II) ions for the surface of the adsorbent which would hinder Pb(II) ions from reaching the binding sites of the sorbet caused by the repulsive forces. At pH > 6.0, the Pb(II) gets precipitated due to hydroxide anions forming a lead hydroxide precipitate. For this reason the maximum pH value was selected to be 4.0. The highest efficiency was observed when 97.3 % level at pH of 4.0 for 10 mg/L and 80.3 % for 50 mg/L was attained. Change in pH of the solution after adsorption was observed in this study for example, the pH value changes from 5.6 (solution pH of 5 mg/L initial concentration) to 3.7 for adsorbent dose of 1.5 g, to pH value of 3.1 for adsorbent dose of 2.5 g and to pH values of 2.82 for adsorbent dose of 4.0 g. In all cases, pH of the solution decrease after equilibrium was achieved. Therefore the study indicated that a change in pH value is dependent on the amount of adsorbent dose. Thus higher the adsorbent dose the larger the change in pH until the equilibrium is attained. The study further alluded that adsorption of the metal ions on the surface could result in the release of more $H^+$ ions from the surface, indicating ion exchange mechanism as shown from the decrease of the pH from the initial pH value.

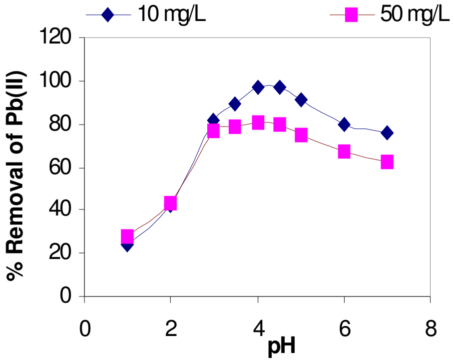

Figure 4. Effect of pH (adsorbent dose = 4 g, time = 3 h).

*Effect of temperature*

The extent of lead ion adsorption on the activated carbon at various temperatures is shown in Figure 5. As observed from the figure temperature rise therein resulted to an increase in the removal of the metal as expressed as a percentage. The enhancement of the adsorption capacity when temperature is increased could be due to increased mobility and diffusion of ionic species. Since diffusion is an endothermic process, it would be expected that an increased solution temperature would result in the enlargement of pore size due to 'activated diffusion' causing the micro-pores to widen and deepen and create more surface for adsorption.

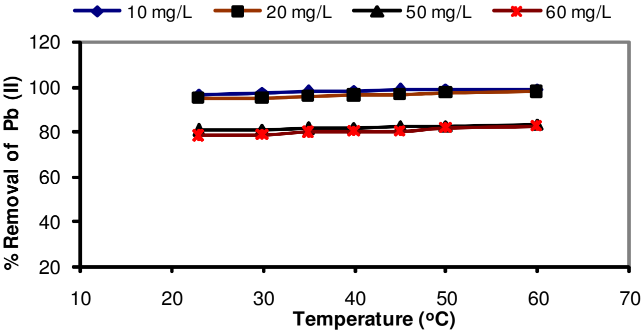

Figure 5. Effect of temperature (pH = 4, adsorbent dose = 4 g, time = 3 h).

*Calculation of thermodynamic parameters*

The value ΔH and ΔS were calculated from the slope and intercept of the linear Van't Hoff plot, respectively, using the relation:

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (2)$$

where $\Delta S$ = entropy change for the process, $\Delta H$= enthalpy change for the process, R = gas constant, T = absolute temperature

The distribution coefficient ($K_d$) on activated charcoal surface were calculated using the equation

$$K_d = \frac{C_i - C_e}{C_e} x \frac{V}{m} \left( mLg^{-1} \right) \tag{3}$$

The changes in free energy ($\Delta G$) for the specific adsorption have also been calculated using the equation

$$\Delta G = - RT \ln K_d \tag{4}$$

where, the symbols have their usual significance.

The thermodynamic quantities $\Delta H$, $\Delta S$, $\Delta G$ of Pb(II) adsorption on activated carbon were calculated from the $K_d$ values using equations (3) and (4). Values of $\Delta H$ and $\Delta S$ were computed from the slope and intercept of linear variation of ln $K_d$ with the reciprocal of temperature (Figure 6.) and was found to be 25.05 kJ mol$^{-1}$ and 135.48 JK$^{-1}$mol$^{-1}$, respectively (Table 1).

Table 1. Adsorption studies of $Pb^{2+}$ ions on activated carbon as a function of temperature.

| T (K) | 1/T (K$^{-1}$ x 10$^{-3}$) | $K_d$ (mLg$^{-1}$) | ln $K_d$ | $\Delta H$ (kJmol$^{-1}$) | $\Delta S$ (JK$^{-1}$mol) | $\Delta G$ (kJmol$^{-1}$) |
|---|---|---|---|---|---|---|
| 296 | 3.38 | 446.2 | 6.10 | | | -15.01 |
| 303 | 3.30 | 558.0 | 6.32 | | | -15.92 |
| 308 | 3.25 | 677.8 | 6.52 | | | -16.69 |
| 313 | 3.19 | 816.7 | 6.70 | 25.05 | 135.48 | -17.43 |
| 318 | 3.14 | 963.7 | 6.87 | | | -18.16 |
| 323 | 3.09 | 1094.4 | 6.99 | | | -18.78 |
| 333 | 3.00 | 1372.2 | 7.22 | | | -19.98 |

The values of free energy of specific adsorption, $\Delta G$ at various temperatures were calculated by using equation (4) and were listed in Table 1. The positive value of $\Delta H$ shows that the adsorption of lead ions on the adsorbent is an endothermic process. The values of free energy ($\Delta G$) are negative as expected for a spontaneous process. The decrease in $\Delta G$ value with increasing temperature reveals that adsorption of the ion on the adsorbent becomes favorable at higher temperature. The positive value of $\Delta S$ reveals the increase in randomness at solid solution interface during the fixation of lead ions on the active site of the adsorbent.

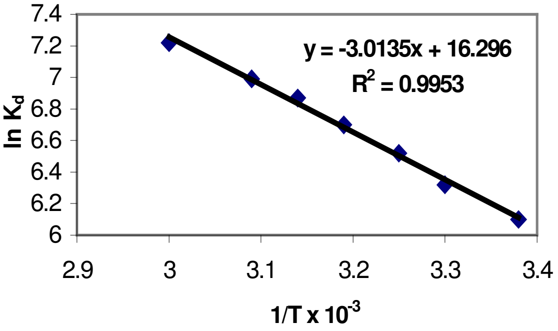

Figure 6. Plot of ln $K_d$ vs 1/T (pH = 4, initial concentration = 10 mg/L).

*Effects of anion and cations*

The effects of anions such as $F^-$, $Cl^-$, $NO_3^-$, $SO_4^{2-}$ and $PO_4^{3-}$ as well as the effect of cations such as $Fe^{2+}$, $Ca^{2+}$, $Na^+$ and $K^+$ on the adsorption efficiency of $Pb^{2+}$ with the bio-adsorbent were studied. There was no significant reduction in the adsorption of $Pb^{2+}$ when the concentration of the above ions increased up to 100 mg/L in the synthetic water. It is evident that with the proper treatment of the wastewater, it is possible to adsorb $Pb^{2+}$ ions on the surface of the adsorbent up to 97 % in the presence of the above mentioned anions and cations up to 100 mg/L.

*Adsorption isotherm*

Equilibrium batch adsorption experiments resulted in points of the adsorption isotherm, which was approximated by the *Langmuir* model.

$$q = \frac{q_{\max} b C_{\max}}{1 + b C_{eq}} \tag{5}$$

where $q_{\max}$ is maximum adsorbate uptake and b is the *Langmuir* constant related to energy of adsorption, which quantitatively reflects the affinity between the adsorbent and the adsorbate. The evaluation of the specific uptake q was performed according to

$$q = \frac{V\left(C_i - C_{eq}\right)}{m} \tag{6}$$

where V is the volume, $C_i$ and $C_{eq}$ is the initial and the unadsorbed concentration of the metal ion at equilibrium and m is mass of the biomaterial.

The Langmuir parameters were obtained by fitting the experimental data to linearized equation derived from equation (7)

$$1/q = \frac{1}{q_{\max}} + \frac{1}{\left(C_{eq} q_{\max} b\right)} \tag{7}$$

The Freundlich isotherm can be derived from the Langmuir isotherm by assuming that there exists a distribution of sites on the adsorbent that have different affinities for different adsorbates with each site behaving according to the Langmuir isotherm. According to Freundlich adsorption from solution can be expressed by the equation

$$q = KC^{1/n} \tag{8}$$

where K is the measure of the capacity of the adsorbent (mass of adsorbate/mass of adsorbent) and n is a measure of how affinity for the adsorbate changes with changes in adsorption density. Where $n > 1$ indicates the affinities decrease with increasing adsorption density. Evaluation of the coefficient of K and n can be accomplished using the linearized form of equation (8).

$$\log q = \log K + \frac{1}{n} \log C \tag{9}$$

From the values obtained for these parameters the theoretical Freundlich curves were calculated and plotted in Figure 7. The Freundlich parameters as well as the correlation coefficient are also indicated in the Figure.

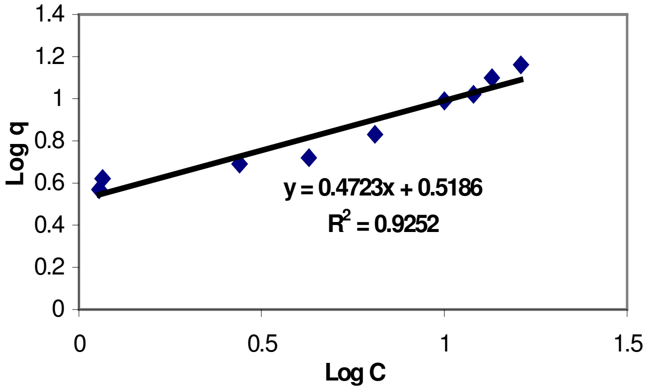

Figure 7. Freundlich adsorption isotherm.

It can be observed that experimental data fit the isotherm adequately. The applicability of the Freundlich model to the experimental data indicates monolayer coverage on heterogeneous adsorbent surface by each of Pb(II) ions. For comparison the Langmuir adsorption isotherm is also given in Figure 8.

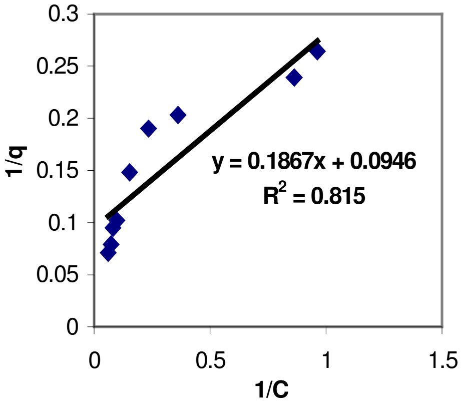

Figure 8. Langmuir adsorption isotherm.

*Order of reaction of Pb(II) adsorption*

The rate constant (K) of the Pb(II) adsorption at the adsorbent surface was calculated at 25 °C keeping the equilibration time (t) 180 min using the following equation [31].

$$K = \frac{1}{t}\ \ln\left(C_o / C_e\right) \tag{10}$$

Here $C_o$ and $C_e$ are the initial and equilibrium concentrations of lead ions, respectively. The values of $C_e$ and rate constant for the adsorption process at different initial concentrations of lead ions ($C_o$) are calculated. The plot of rate constant (K) versus ln ($C_o/C_e$) is observed to be a straight line as shown in Figure 9. The results indicate that, the adsorption process of Pb(II) at the surface of the adsorbent followed the first order of reaction kinetics.

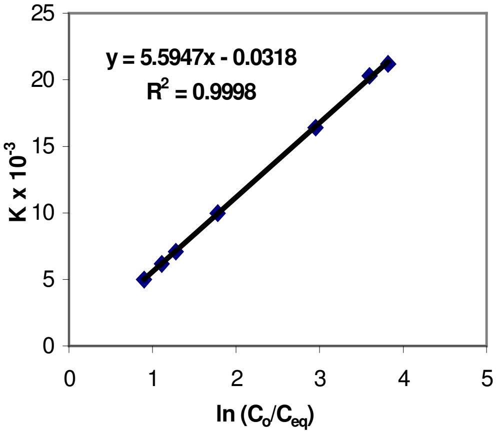

Figure 9. Adsorption kinetics.

*Treatment of industrial wastewater*

The suitability of the bio-adsorbent materials for the removal of Pb(II) was tested with the electroplating industrial effluent. The wastewater sample pH was maintained between 4.0-4.5. The effect of contact time with the adsorbent dose of 4.0 g of 50 mL of 20 mg/L Pb(II) is shown in Figure 10 and the determined composition of electroplating industrial effluent is tabulated in Table 2.

Table 2. Experimentally determined composition of electroplating industrial effluent.

| Parameter | Results |
|---|---:|
| pH | 3.5 |
| Electrical conductivity (µmhos/cm) | 4367.75 |
| Total dissolved solids (mg/L) | 6846.21 |
| Turbidity (NTU) | 1.25 |
| COD (mg/L) | 33.44 |
| Chloride (mg/L) | 468.36 |
| Sulfate (mg/L) | 1228.52 |
| Iron (mg/L) | 38.10 |
| Cadmium (mg/L) | 964.13 |
| Lead (mg/L) | 116.42 |
| Calcium (mg/L) | 86.68 |
| Sodium (mg/L) | 177.55 |
| Potassium | 32.14 |
| Zinc | 16.11 |

It has been found that the treatment of Pb(II) in industrial wastewater is significantly good ($p < 0.05$). Almost 97 % removal from wastewater was possible with 4.0 g of the selected bio-adsorbent. Thus, the results are in good agreement with what is obtained from batch experiments conducted for Pb(II) removal in synthetic wastewater samples. Preliminary treatment of the industrial wastewater is essential before application of activated carbon of the bio-adsorbent.

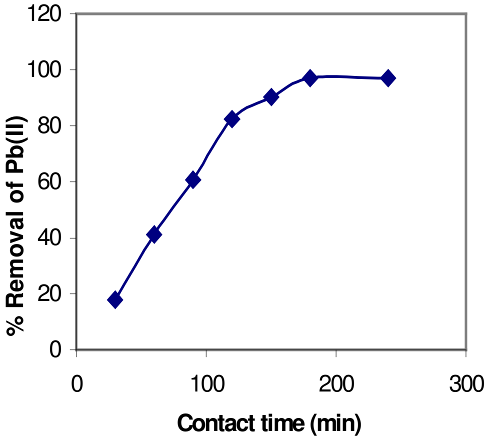

Figure 10. Treatment of wastewater (pH = 4.0, Adsorbent dose = 4.5 g).

*Desorption studies*

Disposal of the exhausted adsorbent loaded with heavy metal ions creates another environmental problem, as it is hazardous material, which pollutes environment. Regeneration of the adsorbent material is of crucial importance in economic development. Regeneration must produce small volume of metal concentrates suitable for metal recovery process without damaging of the capacity of the adsorbent. In this experiment 99.2 % of the adsorbed metal ion was removed at pH value of 8.0 and complete removal at pH value of 9.0. The reuse of regenerated activated carbon was found to be efficient.

## CONCLUSIONS

The removal of Pb(II) in synthetic water by using bioremediation technology was studied in the batch experimental systems. Based on the results, the following conclusions can be drawn. The prepared activated carbon is an efficient biomaterial for removal of lead ion from industrial wastewater. Equilibrium metal adsorption decreased with the increase in the initial concentration of Pb(II) ions suggesting the applicability of the biomaterial at lower concentrations. The adsorption of Pb(II) is a monolayer according to Freundlich adsorption isotherm. The percent removal of Pb(II) by adsorption under the conditions employed in this study is 97.3 % with an effective dose of 4.0 g of bio-adsorbent. Adsorption equilibrium for the metal was reached in about 3 h and was endothermic in nature based on the calculated value of $\Delta H$ and $\Delta G$ as well as its dependence on temperature. Adsorption efficiency increased with increasing pH showing a maximum at pH 4.0 and then decreases, at high pH value, greater than pH 8 desorption was complete in the desorption procedure. The study further demonstrated that the adsorption process was on first order in kinetics. This methodology can be applied to the removal of toxic metals from wastewater efficiently. Moreover efficient reuse of the regenerated bio-adsorbent was found to be possible. The method was simple, cost effective and environmental friendly.

## REFERENCES

1. Bounheng, S.; Kazunori, N.; Munehiro, N.; Nobou, C.; Osamu, N. *Water Res.* **2006**, 40, 2295.
2. Auradha, B.; *Proceedings of the International Conference on Water and* Environment (WE-2003), Bhopal, India, **2003**; pp 299-309.
3. Paulino, A.T.; Tessari, J.A.; Nogami, E.M.; Lenzi, E.; Nozaki, J. *Environ. Contam. Toxicol.* **2005**, 75, 42.
4. Johnson, F.M. *Mutat. Res*. **1998**, 410, 123.
5. WHO *Guideline Values for Drinking Water Quality*, Vol. 1, Recommendations, World Health Organization: Geneva; **1984**; p. 81.
6. Horsfall, J.M.; Abia, A.A. *Water. Res*. **2003**, 37, 4913.
7. Amritphale, S.S.; Prased, M.; Sexena, S.; Chandra, N. *Main Group Met. Chem.* **1999**, 22, 557.
8. Abou-El-Sherbini, K.S.; Kenaway, I.M.M.; Hamed, M.A.; Issa, R.M.; Elmorsi, R. *Talanta* **2002**, 58, 578.
9. Akhatar, S.; Qadeer, R. *Adsorp. Sci. Technol.* **1997**, 15, 815.
10. Ho, Y.S.; McKay, G. *Water Res*. **1999**, 33, 578.
11. Mier, M.V.; Challejas, R.R.; Gehr, R.; Cisneros, B.E.J.; Alvarez, P.J.J. *Water Res*. **2001**, 35, 373.
12. Reddad, Z.; Gerente, C.; Andeers, Y.; Pierrele, C. *Environ. Sci. Technol*. **2002**, 36, 2067.
13. Paulino, A.T.; Simonato, J.I.; Garcia, J.C.; Nozaki, J. *Carbohydr. Polym*. **2006**, 64, 98
14. Murphy, B.; Hathaway, B. *Coord. Chem. Rev*. **2003**, 243, 237.
15. Gupta, V.K.; Mittal, A.; Gajbe, V. *J. Colloid Interface Sci*. **2005**, 284, 89.
16. Kumar, K.V.; Ramamurthi, V.; Sivanesan, S. *J. Colloid Interface Sci*. **2005**, 284, 14.
17. Tahir, S.S.; Rauf, N. *J. Chem. Thermodynamics* **2003**, 35, 2003.
18. Farrah, H.; Pickering, W.F. *Aus. J. Chem.* **1977**, 30, 1417.
19. Robert, E.J.; Rowland, S.P. *Environ. Sci. Technol*. **1973**, 7, 552.
20. Balkose, D.; Balatacioglu, H. *J. Chem. Technol. Biotechnol*. **1992**, 54, 393.
21. Tee, T.W.; Khan, R.M. *Environ. Technol. Lett.* **1988**, 9, 1223.
22. Prasad, M.N.V.; Freitas, H. *Environ. Pollut*. **2000**, 110, 277.
23. Babel, S.; Kurniawan, T.A. *J. Hazard. Mater*. **2003**, B97, 219.
24. Drake, L.R.; Rayson, G.D. *Anal. Chem*. **1996**, 68, 22A.
25. Sheng, P.X.; Ting, Y.P.; Chen, J.P.; Hong, L. *J. Colloid Interface Sci*. **2004**, 275, 131.
26. Singanan, M. *Proceedings of the International Conference on Water and Environment (WE-2003)*, Bhopal, India, **2003**; pp 45-49.
27. Malarajan, S.; Alemayehu, A.; Singanan, V. *Bull. Chem. Soc. Ethiop.* **2005**, 19, 289.
28. Malarajan, S.; Singanan, V; Alemayehu, A. *Ethiopian J. Health Sci.* **2006**, 16, 59.
29. Stephen, I.B.; Sulochana, N. *Proceeding of the International Conference on Water and Environment (WE- 2003)*, Bhopal, India, **2003**; pp 22-28.
30. Waranusantigul, P.; Pokethityook, P.; Kruatrachue, M.; Upatham, E.S. *Environ. Pollut.* **2003**, 1, 385.
31. Raj, G. *Chemical Kinetics in Advanced Physical Chemistry*, 4th ed., Geol Publishing House: Meerut, India; **2001**; pp. 669-676 and 149-150.