Asian Journal of Chemistry Vol. 21, No. 9 (2009), 7149-7154

Evaluation of Lead(II) Adsorption on A Column Packed With Phosphorylated Tamarind Nut Carbon

N. SUGANTHI† and K. SRINIVASAN*
Department of Chemistry, College of Engineering, Salem-636 011, India
Tel: (91)(427)2346157; E-mail: srini_vasank@hotmail.com

The continuous adsorption of lead ions from aqueous solutions on phosphorylated tamarindnut carbon and commercial activated carbon was studied. The aim of carrying the continuous flow studies is to assess the effect of pH, flow rate and bed height on the adsorption of lead ion. This has helped in ascertaining the practical applicability of the adsorbent in large scale. The effect of common anions and cations on adsorption of lead ions was examined. The regeneration capacity of carbons was analyzed by repeated adsorption and desorption processes. Breakthrough capacities were found out using wastewater containing lead ions and phosphorylated tamarindnut carbon was found to be superior to commercial activated carbon in the removal of lead ions.

Key Words: Lead(II) removal, Phosphorylated tamarind nut carbon, Adsorption.

INTRODUCTION

The presence of heavy metal pollution in water and waste water has been of great concern to environmentalists, due to their toxicity and impact on human health and environment. Unlike organic pollutants, heavy metals are non-degradable and can accumulate in living tissues. Lead is an important environmental pollutant that acts as a cumulative poison. Lead has been introduced into natural water from a variety of sources such as storage batteries, lead smelting, tetraethyl lead manufacturing, mining, plating, ammunition, the ceramic and glass industries[1].

Limit values of lead in drinking water and surface water intended for drinking as set by EU, USEPA and WHO are 10, 50 and 10 µg/L, respectively[2]. However, more recently an EPA document prescribes a zero lead value in national primary drinking water standard[3]. In India limit value of lead in drinking water is 0.01 mg/L[4].

The presence of excess lead in drinking water causes diseases such as anemia, encephalopathy and hepatitis[5]. Lead poisoning in human causes severe damage to the kidney, nervous system, reproductive system, liver and brain[6]. The removal of

†Department of Chemistry, S.S.M. College of Engineering, Komarapalayam-638 183, India; E-mail: suganthi_saravanan@yahoo.co.in

lead from wastewaters by conventional methods includes its precipitation with lime or alkali hydroxide, coagulation, electrolytic deposition, reverse osmosis and ion exchange. These conventional methods are expensive and have significant disadvantages such as generation of metal bearing sludge or wastes, incomplete metal removal and disposal of secondary waste.

Activated carbon is one of the most popular adsorbents for the removal of metal ions from aqueous solutions[5,7]. The high cost of commercially available activated carbon limits its use as an adsorbent in developing countries. Hence there is growing need to prepare activated carbon from cheaper and readily available waste materials. While several researchers adopted various low cost adsorbents, there is still a need to develop activated carbon from cheaper and readily available material, which can be effective and economical for the removal of lead from aqueous solution.

The aim of this study is to investigate the application of activated carbon prepared from tamarind nuts (seeds) for the removal of lead by continuous adsorption method. This paper describes the investigation carried out with respect to the removal of lead ions from aqueous by phosphorylated tamarind nut carbon (PTNC) by column studies.

EXPERIMENTAL

Preparation of carbon: Tamarind nuts (seeds) procured from the market was washed with distilled water, dried and pulverized to 300 to 800 µm particle size. It was treated with phosphoric acid under a weight ratio of 1:1 and heated in the hot air oven at a temperature of 160 ± 5 °C for 24 h. The carbonized material was washed with distilled water to remove the excess acid and dried at 100 ± 5 °C. The carbon was soaked in 1 % sodium carbonate solution for 24 h to remove any free acid. It was washed with distilled water to remove excess sodium carbonate, dried at 100 ± 5 °C and again sieved to 300 to 800 µm particle size. Preliminary studies were carried out with raw tamarind nut, phosphorylated tamarind nut carbon and phosphorylated tamarind nut carbon (PTNC) soaked in 1 % sodium carbonate for Pb(II) removal. Based on their efficiency, PTNC was chosen for further studies. The commercial activated carbon (CAC) was procured from SD fine chemicals, was sieved to 300 to 800 µm particle size and subsequent experiments were carried out with PTNC and CAC. The characteristics of PTNC and CAC are summarized in Table-1.

All the chemicals used for this study were of analytical reagent grade obtained from E. Merck, Ranbaxy, SD Fine and BDH.

Preparation of solutions: A stock solution of Pb(II) ions 1000 mg/L was prepared by dissolving $Pb(NO_3)_2$ in distilled water and acidified with 2 mL concentrated HNO_3 to prevent hydrolysis. The stock solution was diluted with distilled water to obtain working solutions of desired concentration. The pH of the solutions was adjusted to the required value by using 0.1 M NaOH or 0.1 M HNO_3 solutions.

TABLE-1
CARBON CHARACTERISTICS

Parameter	PTNC	CAC
Bulk density (g/mL)	0.619	0.668
Moisture (%)	5.736	15.84
Ash (%)	4.400	0.900
Solubility in water (%)	1.761	0.594
Solubility in acid (%)	6.365	6.725
pH	6.98	9.40
Decolourizing power (%)	1.8	1.05
Phenol number	20	40
Ion exchange capacity (meq/g)	0.4172	Nil
Surface area (m^2/g)	316.21	214
Iron (%)	0.18	0.44

Column studies: The stock solution was diluted to obtain 200 mg/L of Pb(II) and used for column studies. Cylindrical glass column of 2.5 cm diameter and 30 cm height with a Teflon stopper valve to control the flow of solution was used for this study. Optimum weights of carbon under proper flow rate and bed height conditions were used for column studies. For PTNC, Pb(II) of concentration 200 mg/L at an optimum flow rate of 15 mL/min with optimum bed height of 11.6 cm was employed to assess the potential. For CAC, 200 mg/L of Pb(II) at an optimum flow rate of 3 mL/min and bed height of 7.4 cm was maintained. Percolation of Pb(II) solution was stopped as soon as Pb(II) concentration in the effluent exceeded the permissible limit[8] at 0.5 mg/100 mL, which is the break point. Lot volumes of 100 mL were collected and analyzed for Pb(II). An atomic absorption spectrometer model Elico SL 163 was used to determine Pb(II) concentration in the aliquots.

Regeneration and recycling of PTNC was done by treating with dilute solution of 0.3 N hydrochloric acid (optimum concentration) followed by soaking in 1 % sodium carbonate. Commercial activated carbon was also regenerated with 0.35 N HCl, thoroughly washed and reloaded in the column under wet conditions.

Breakthrough capacities pertaining to Pb(II) adsorption in the presence of common impurities such as chloride, calcium and magnesium were done under optimum bed height and flow rate conditions for both the carbons.

The application of PTNC and CAC for removal of Pb(II) from synthetic waste-water related to lead battery industry has been evaluated.

RESULTS AND DISCUSSION

Examination of carbon characteristics shows that PTNC has higher surface area and ion exchange capacity than CAC. The high surface area shows the availability of more sites for adsorption of Pb(II). The moisture content of PTNC suggests that the acid treatment has made the carbon more porous. Phosphorylated tamarind nut carbon has high ion exchange capacity and was the main mechanism for the adsorption of the heavy metal.

Effect of pH: pH is one of the most important parameters affecting adsorption yield. The pH of the solution affects the degree of ionization and speciation of the surface functional groups[9]. Fig. 1 shows the effects of pH on the adsorption yield of Pb(II) ions by PTNC and CAC. As can be seen, metal removal increased with increasing solution pH and a maximum value was reached over a pH range 6.0-7.0 for PTNC and sharply at 6.0 for CAC (optimum pH). Similar results were reported for adsor-ption of lead on agricultural wastes such as maize bran[10], sulphuric acid treated wheat bran[11] and activated carbon prepared from coconut shell[12].

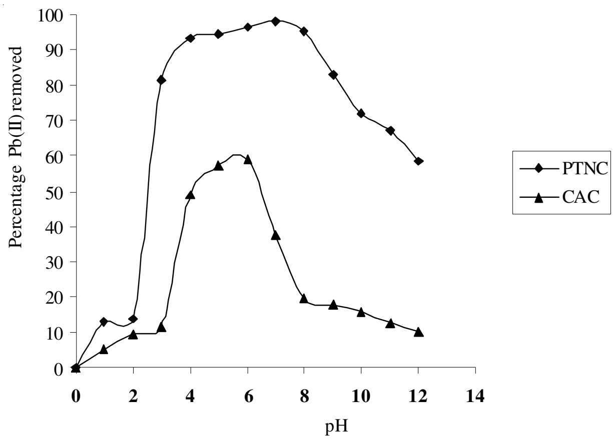

Fig. 1. Effect of pH on the adsorption of Pb(II) of concentration 10 mg/L on PTNC of dose 100 mg/100 mL, agitation time 4 h and on CAC of dose 100 mg/100 mL, agitation time 4 h

The adsorption of Pb(II) ions was very low at acidic pH values. This can be explained by the fact that at low pH values, electrostatic repulsion forces act between H_3O^+ and Pb^{2+} ions. As pH increases adsorption of Pb(II) ions takes place on the surface of the adsorbent replacing H_3O^+. Above optimum pH, Pb(II) starts precipi-tating as $Pb(OH)_2$ and hence causing a decrease in the adsorption yield.

In the case of PTNC, the following mechanism is suggested. Based on the work of Frumkin[13], the surface oxide groups available on the surface of a carbon can undergo hydrolytic reaction resulting in the formation of proton exchangeable sites such as $C_xOH_2^{2+}$, C_xOH^+. Since PTNC was prepared on treatment with phos-phoric acid followed by sodium carbonate soaking, groups such as C_xONa^+, C_xONa^{2+}, C_xPO_3H and C_xPO_3Na may be present. Hence it is expected that Na^+ in the group get exchanged with Pb(II).

$$2C_xOH^+ + Pb^{2+} \rightleftharpoons (C_xO)_2Pb^{2+} + 2H^+$$

$$C_xOH_2^{2+} + Pb^{2+} \rightleftharpoons C_xOPb^{2+} + 2H^+$$

$$2C_xONa^+ + Pb^{2+} \rightleftharpoons C_xOPb^{2+} + 2Na^+$$

$$C_xONa_2^{2+} + Pb^{2+} \rightleftharpoons C_xOPb^{2+} + 2Na^+$$

$$2C_xPO_3H + Pb^{2+} \rightleftharpoons (C_xPO_3)_2Pb + 2H^+$$
$$2C_xPO_3Na + Pb^{2+} \rightleftharpoons (C_xPO_3)_2Pb + 2Na^+$$

In order to find out optimum flow rate and optimum bed height conditions for the removal of Pb(II) by PTNC and CAC, experiments were carried out with 200 mg/L Pb(II) solutions at pH of 4.5, since precipitation of Pb(II) occurred at pH more than 4.5.

Table-2 indicates the breakthrough capacities of carbon under optimum flow rate and bed height conditions of PTNC and CAC from which it can be concluded that PTNC showed a higher removal capacity when compared to CAC.

TABLE-2
BREAKTHROUGH CAPACITIES OF CARBONS
Optimum flow rate (PTNC) = 15 mL/min; Optimum flow rate (CAC) = 3 mL/min; Optimum weight of carbon (PTNC) = 20 g (11.6 cm); Optimum weight of carbon (CAC) = 20 g (7.2 cm)

Condition	Breakthrough capacity (mg)	
	PTNC	CAC
Room temperature	859.08	119.93

Table-3 indicates the effect of common anions and cations available in water on the removal of Pb(II) by PTNC and CAC. Decrease in capacities was noted for both PTNC and CAC. The decrease in the removal of Pb(II) may be due to the competence of calcium, magnesium and chloride ions for the ion exchange sites during the adsorption process.

TABLE-3
EFFECT OF COMMON ANIONS AND CATIONS ON THE REMOVAL OF Pb(II) UNDER OPTIMUM FLOW RATE AND BED HEIGHT CONDITIONS

Carbon	None	Cl^- (1000 mg/L)	Ca^{2+} (1000 mg/L)	Mg^{2+} (1000 mg/L)
PTNC	859.08	579.46	0	0
CAC	119.93	39.73	0	0

Phosphorylated tamarind nut carbon showed constant breakthrough capacity values in distilled water under different regeneration cycles indicating that carbon is effective in the removal of Pb(II) over the number of cycles and it was not undergoing any significant degradation in particle size because of its hardness. However in CAC, the capacity was much affected by the different cycles and also showed nil adsorption during the second cycle of regeneration as shown in Table-4.

TABLE-4
REGENERATION CYCLES

Cycle	PTNC	CAC
I	879.44	120.00
II	900.00	19.55
III	880.00	–
IV	859.60	–
V	860.00	–

The experiments with synthetic wastewater and its characteristics similar to that of lead battery manufacturing industry are shown in Table-5. It could be seen that PTNC showed the adsorption capacity to an extent of 203.06 mg/ 20 g whereas CAC showed nil adsorption capacity after 10 times dilution of wastewater.

TABLE-5
Pb(II) WASTEWATER CHARACTERISTICS

Parameter	Amount (mg/L)
Lead	1015.3
Chlorides	182.7
Calcium	204.8
Sulphur	Nil

Conclusion

Tamarind nut was generated as a waste biomaterial in the agricultural sector and could be used effectively in treating water and wastewaters. From the foregoing experiments it could be concluded that the activated carbon prepared from tamarind nut is an efficient adsorbent for the removal of Pb(II) from aqueous solution. Characterization of the carbon showed the presence of large surface area and higher ion exchange capacity, which favours the adsorption process. From column studies applied to wastewater containing Pb(II) ions, PTNC is found to have much higher adsorption capacity compared to commercial activated carbon. Hence it may be concluded that PTNC could be effectively employed for the removal of Pb(II). However the economic factors will be considered before utilizing the same.

REFERENCES

1. S. Manahan, Environmental Chemistry Books, Colei, CA (1984).
2. Lead, Pollution Prevention and Abatement Handbook, World Bank Group, Effective July (1998), http://wbln0018.worldbank.org/essd.nsf/Global View/PPAH/ $File/37 lead. PDF.
3. Current Drinking Water Standards, EPA. Office of water, http://www.epa.gov/safewater/mcl.html (2002).
4. Indian Standard, Drinking Water Specification, (First Revision) (Amendment 1) Reaffirmed 1993. IS:10500 (1991).
5. M. Sekar, V. Sakthi and S. Rengaraj, *J. Colloid. Interface Sci.*, **279**, 307 (2004).
6. J. Goel, K. Kadirvelu, C. Rajagopal and V.K. Garg, *J. Hazard. Mater.*, **B125**, 211 (2005).
7. Y. Kikuchi, Q. Qian, M. Machida and H. Tatsumoto, *Carbon*, **44**, 195 (2006).
8. N. Manivasakam, Industrial Effluents: Origin, Characteristics, Effects, Analysis and Treatment, First Reprint, Sakthi Publications, Coimbatore, India pp. 498 (1997).
9. Z. Reddad, C. Gerente, Y. Andres and P.L. Cloirec, *Environ. Sci. Tech.*, **36**, 2067 (2002).
10. K.K. Singh, M. Talat and S.H. Hasan, *Bioresour. Tech.*, **97**, 2124 (2006).
11. A. Ozer, *J. Hazard. Mater.*, **141**, 753 (2007).
12. M. Sekar, V. Sakthi and S. Rengaraj, *J. Colloid Interface Sci.*, **279**, 307 (2004).
13. A. Frumkin, *Kolloidz*, **51**, 123 (1981).

(*Received*: 8 January 2009; *Accepted*: 17 August 2009) AJC-7744