

Pb (II) Removal from Aqueous Solution by Chemically Activated Carbon Composite using fixed bed Column

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Abstract— Lead (II) adsorption over chemically activated carbon composite coconut shell and cashew nut husk (CSCNHCAC) of 20-50 mesh ASTM size packed in a fixed column has been reported for aqueous solutions. The results were also compared with commercial activated carbon (CAC). The effects of operational parameters like pH, adsorbent dose and contact time by batch studies were already established along with isotherm, kinetics and morphological studies. Column experiments were performed using the prepared adsorbent CSCNHCAC to find out optimum flow rate, bed height. The results showed that an optimum flow rate of 15mL /min and bed height of 6 cm. The breakthrough capacity for CSCNHCAC was found to be 133.33 mg/g which is superior to CAC. The adsorbed Pb(II) could be quantitatively recovered by 1M HCl which could be put into reuse. The effect of common anions was also studied. The capacity of CSCNHCAC remained unaffected even after 5 cycles of operation and the treated water was found to be free from Pb(II) ion. The application of surfactants was also investigated. From the results obtained, the prepared low cost adsorbent CSCNHCAC can be considered as an alternative and an effective one in the removal of heavy metal ions.

Keywords— Lead (II), Column study, Carbon composite, Breakthrough capacity, Coconut shell, Cashew nut husk

I. INTRODUCTION

Contamination of various natural resources including water by heavy metals is a worldwide concern nowadays. The purity of water plays an important role to determine the health of the people. Large volumes of waste water generated by rapid industrialization are one of the main causes for the contamination of water source and other environmental resources with heavy metal ions [1]. At present, various ill effects of health are caused by the use of polluted water on the horizons of developing countries [2]. The demand for water now a days has forced man to assess water reuse technology. Proper treatment of wastewater from industries represents another source of reusable water mass prevents health problems and also recovery of the heavy metal ions which can be reused [3]. Heavy metal ions are not bio-degradable and they tend to be accumulated in organisms and cause numerous diseases and disorders [4].

Lead contamination is known as one of the most pervasive and elusive environmental health threats as considered by the fact that exposure of lead (II) ions has been associated with death and disease in humans, birds and animals. The majority of lead pollution has been through automobiles, battery manufactures, cable coverings, radioactivity shields, plumbing fixtures, painting pigments, solder, textile industry, printed circuit boards, electroplating and petroleum industries. [5,6].The lead (II) ion concentrations were approximately in the range of 200-500 mg dm⁻³ in industrial wastewaters and according to water quality standards, this value is very high and must be reduced to a value of 0.10 - 0.05 mgdm⁻³ [7].

Traditional treatment methods such as chemical precipitation and filtration, chemical oxidation and reduction, electrochemical treatment, reverse osmosis, solvent extraction, ion-exchange and evaporation were employed for the removal of heavy metal ions namely, lead (II) ions from aqueous solutions. These methods have some disadvantages such as high cost, incomplete metal removal, low selectivity, high energy requirements and the generation of toxic slurries [8,9].

Adsorption is one of the most respective methods applied for lead (II) ion removal from toxic wastes due to its low maintenance cost, high efficiency, ease of operation [10]. Activated carbon adsorbents are used widely in the removal of organic contaminants as well as heavy metal ions. In spite of this prolific use, commercial activated carbon remains an expensive material and higher the quality of activated carbon, the higher it's cost [11]. Hence low cost adsorbents were prepared from a variety of agricultural wastes like coconut shell [12], tamarind nut [13], pongamia leaf powder [14], dates nut [15] walnut [16] *Delonix regia* [17] *Cocos nucifera* [18] sugarcane bagasse [19] date tree leaves [20] etc., have been used for the removal of toxic inorganics from wastewater. Cashewnut husk is also a potential agricultural waste. Since the carbon derived from different source differs in nature, studies were carried out using chemically activated carbon composite prepared from coconut shell and cashew nut husk. The carbon composite and a commercial activated carbon of same particle size were used for the removal of Pb(II) from wastewater.

II. COLUMN STUDIES

A. *Materials and Methods*

Adsorption Studies were carried out systematically by batch and column experiments as the adsorbents are economical, ecofriendly and effective [21]. The influence of parameter such as effect of pH, carbon dose and equilibration time were determined by batch studies. The optimum values of pH, carbon dose and equilibration time are shown in the table 1 for the carbon composite and CAC.

TABLE I
BATCH STUDIES

Carbon	Optimum pH	Optimum carbon dose (g/L)	Optimum equilibration time (hrs)
CSCNHCAC	3.0	0.08	2
CAC	5.0	0.2	4

Adsorption of the carbon conforms to Langmuir isotherm and reversible second order kinetics. Column studies were performed with 12g each of CSCNHCAC and 14.5 g of CAC packed in a glass column of 2.5 cm diameter to evaluate the flow rate and bed height. The carbon under study was made into slurry with distilled water and it was slowly transferred to the glass column packed at the bottom with glass wool. After completing the transfer of the carbon the bed was washed several times with water.

Pb(II) solution was stored in polythene bottles of 5L capacity. Polythene tubes were connected to the bottles with a tap at the bottom. The other end of the tubing was connected to a glass socket containing a flow regulating valve. The outlet of the valve was fixed to the top of the glass column which was kept at a lower level. The column is provided with pinch cocks at the bottom to control the flow rates. A pressure head of 10-15 cm (4"-6") was maintained over the carbon beds for all the column experiments. The inflow and outflow rates were maintained constant [22].

Solutions containing 200mg/L of Pb(II) maintained at pH 3.0 for CSCNHCAC and 5.0 for CAC were used as the influent solutions. Each of lot of 200 mL fraction of the effluent was separately collected and it is analysed for metal ion content. Percolation of metal ion solutions was stopped as soon as the Pb (II) content in the effluent lot exceed 0.05 mg/L.

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III. RESULTS AND DISCUSSION

A. Influence of flow rate

In order to find out the optimum flow rate for the maximum uptake of the metal ion, the influent solutions were allowed to flow through the column of constant bed height of 6cm at separate flow rates from 10,13,15,18 and 20 mL/min. The effluent was analysed until break through point of 0.05 mg/L occurred for each lot and the capacity of Pb (II) in each instant was established. The results indicate that for both the carbons the rate of flow has considerable influence on the removal Pb (II) was maximum when the flow rate was maintained at 15 mL/min with the maximum removal of Pb (II) were 1599.98 mg and 1159.98 mg were achieved in the case of CSCNHCAC and CAC. Hence, in all the subsequent experiments, it was decided to maintain a flow rate of 15 mL/min for both the carbons. The influence of flow rate with respect to the removal capacity of the metal ion is shown in figure 1.

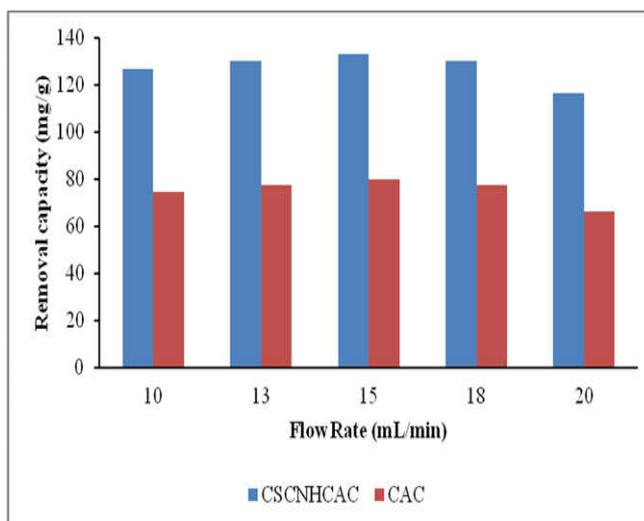


Fig. 1 Influence of flow rate

It reveals that the removal capacity is maximum at a flow rate of 15 mL/min and minimum at 20 mL/min for both the carbons.

B. Influence of bed height

The experiments were conducted using different weights of carbon ranging from 8.00 to 29.00 g in order to find out the influence of optimum bed height or maximum removal of Pb (II) at a constant flow rate of 15 mL/min with various bed heights of 4,6,8,10 and 12cm respectively. Percolation of Pb (II) solution was done through the carbon bed under study. Each lot of 200mL fractions were collected and analysed for Pb (II) content and the percolation of Pb (II) solution was stopped as soon as the Pb (II) in the efficient lot collected exceeded 0.05 mg/L. The capacity of the carbon for Pb (II) was calculated and it was found that the amount of Pb (II) removal is affected to a significant extent by bed height. A minimum bed height of 6cm provided by 12g of CSCNHCAC and 14.5g of CAC is capable of removing 1599.98 mg and 1159.98 mg of Pb (II). This corresponds to the removal of 133.33 mg/g and 80mg/g per g of CSCNHCAC and CAC respectively. Figure 2 represents the removal capacity in terms of bed height. It is evident that a bed height of 6 cm is needed for the removal of Pb (II) ions.

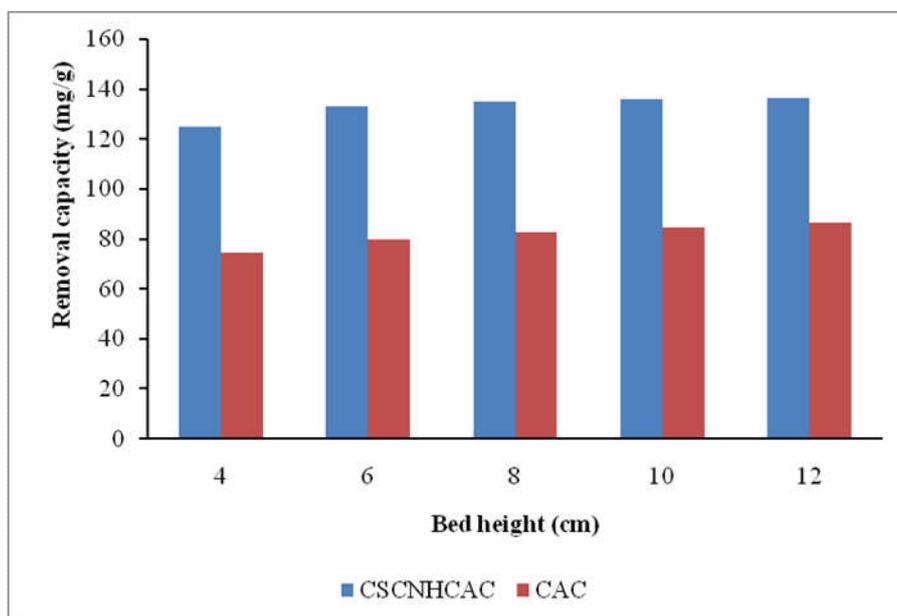


Fig. 2 Influence of bed height

C. Regeneration of carbon

Having optimised the conditions for the quantitative adsorption of Pb (II) on CSCNHCAC and CAC, attempts were made to desorb the metal ions from the carbon surface bed. As batch studies have shown that HCl was effective for the quantitative removal of Pb (II), the use of this reagent was therefore examined for the regeneration of column.

Experiments were done with 12g of carbon for CSCNHCAC and 14.5g of CAC packed in 2.5 cm diameter glass column. The solution containing 200 mg/L of Pb(II) adjusted to pH 3.0 for CSCNHCAC and 5.0 for CAC were passed through the carbon columns at a flow rate of 15 mL/min. Percolation of the solution was stopped as soon as the concentration of Pb(II) in the effluent lot collected exceeded 0.05 mg/L. After washing the column thoroughly with water attempts were made to desorb the metal ion using HCl of varying concentration from 0.5 to 1 M. It is evident that a maximum of 99.09% and 99.39% and 99.39% can be removed as Pb (II) from the column by CSCNHCAC for 0.5, 1.0 and 2.0M HCl and 98.05%, 99.15% and 99.67% can be removed by CAC respectively.

D. Recycling of carbon bed

The regenerated carbons were put to repeated use after washing the column with 1M HCl followed by distilled water to remove the bicarbonate till the pH of the wash water was 7.0. The removal percentage is around 99.5 % for CSCNHCAC and 97.15 for CAC which is shown in figure 3. There is no change in the capacity even after 5 cycles of operation.

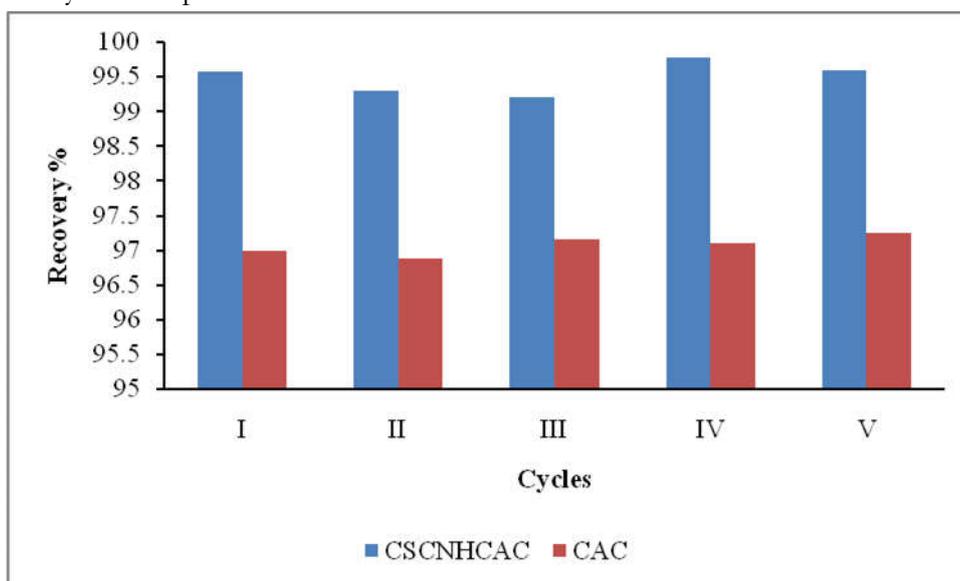


Fig. 3 recycling of carbon bed

The summary of the results obtained in the column studies of Pb (II) are tabulated in Table 2.

TABLE III

REMOVAL AND RECOVERY OF Pb (II) BY COLUMN STUDIES

Sl. No	Description	CSCNHCAC	CAC
1	Pb (II) removal, mg	1599.98	1159.98
2	Pb (II) recoverd, mg	1590.30	1126.90
3	Pb (II) recovery, %	99.39	97.15

E. Effects of Co-existing anions

The effect of co-existing anions like Cl^- and SO_4^{2-} on Pb (II) removal efficiency of both the carbons was also studied using column experiments.

The ions in the concentration range 200mg/L of Pb (II) solution adjusted to pH 3.0 and pH5.0 for CSCNHCAC and CAC and the influence of each were evaluated. Here 12g of CSCNHCAC and 14.5g of CAC were used for charging the 2.5 cm diameter glass columns. The solutions were passed through the beds at a flow rate of 15mL/min for both the carbons. When the Pb(II) content in 200ml effluent lot collected exceeded 0.05 mg/L, the percolation of the solutions was stopped and the capacity of the materials was established in each instance. It is evident that the presence of Cl^- to the extent of 10,000mg/L does not affect the capacity of both the carbons as the capacity is found to be 133.33 mg/g for CSCNHCAC and 80mg/g for CAC. The effect of SO_4^{2-} on the capacity of CSCNHCAC and CAC for Pb (II) is also not affected by the presence of sulphate upto 300mg/L and possessing similar capacity as that of Cl^- ions.

F. Application of CSCNHCAC and CAC on surfactants

Surfactants are usually present in plating wastewaters and their influence on their presence on the uptake of Pb (II) was investigated. Lead (II) solution of 200 mg/L containing 0.01% of the surfactant under study was prepared. After adjusting the pH 3.0 and pH 5.0 in the case of Pb (II) using CSCNHCAC and in the case of CAC, the Pb (II) solution is allowed to flow through the 2.5 cm diameter column containing 12g of CSCNHCAC and 14g of CAC under study at a flow rate of 15mL/min. Each lot of 200mL fractions of the effluent were separately collected and analysed for metal ion content. As soon as the concentration of Pb (II) in the effluent exceeded 0.05 mg/L, percolation of the solution is stopped and the removal capacity is calculated. The removal capacity is found to be 133.35 mg/g and 79.5 mg/g for CSCNHCAC and CAC. From the result, it is evident that the presence of surfactants had no effect on Pb (II) for both the carbons.

IV. CONCLUSIONS

This study clearly revealed that coconut shell and cashew nut husk chemically activated carbon composite (CSCNHCAC) is highly superior to CAC for the removal of Pb (II) from aqueous solution. From the column study results, it is clear that the breakthrough capacity of CSCNHCAC is 133mg/g which is 1.67 times higher than CAC. The presence of Pb (II) was recovered to the extent of 99.5 % for CSCNHCAC and 97.15 % for CAC using 1M HCl. The carbon can be regenerated and the capacity remains the same even after five cycles of operation. The capacity of the carbon remained unaffected which reveals that the carbon materials developed can be used for the removal of Pb (II). The presence of surfactants had no effects on Pb(II) for both the carbons. The preparation of CSCNHCAC is inexpensive and it was highly abundant in tropical countries. From the experimental results it has been successfully proved that the carbon (CSCNHCAC) can be potentially used for Pb (II) removal from aqueous solution to save the living community from health hazards.

CONFLICT OF INTEREST

On behalf of all authors, the corresponding author states that there is no conflict of interest.

REFERENCES

- [1] Abdel-Raouf MS and Abdul-Rabeim ARM (2017) Removal of Heavy Metals from Industrial Waste Water by Biomass-Based Materials: A Review, *Journal of Pollution Effects & Control* 5: 1-13. Doi: 10.4172/2375-4397.1000180
- [2] Ake CL, Mayura K, Huebner H, Bratton GR and Phillips TD (2001) Development of porous clay-based composites for the sorption of lead from water, *J.Toxicol Environ. Health Part A* 63(6): 459 – 475. <https://doi.org/10.1080/152873901300343489>
- [3] Angelina Thanga Ajisha M and Rajagopal K (2014) Characterization and Adsorption Study using *Cocos nucifera* midribs for Fluoride Removal, *Journal of the Institution of Engineers (India) Series A* 94:209-217. <https://doi.org/10.1007/s40030-014-0060-4>
- [4] Angelina Thanga Ajisha M and Rajagopal K (2015) Fluoride removal study using pyrolyzed *Delonix regia* pod, an unconventional adsorbent, *International Journal of Environmental Science and Technology* 12:223-236. <http://dx.doi.org/10.1007/s13762-013-0485-8>
- [5] Boudrahem F, Aissani-Benissad F, and Soualab A (2011) Adsorption of Lead(II) from Aqueous Solution by Using Leaves of Date Trees As an Adsorbent, *Journal of Chemical Engineering Data* 56 (5):1804–1812 Doi: 10.1021/je100770j
- [6] Chuah TG, Jumasiab A, Azni I, Katayon S and Choong SYT (2005) Rice husk as a potentially low-cost biosorbent for heavy metal and dye – removal: an overview. *Desalination* 175: 305- 316. <https://doi.org/10.1016/j.desal.2004.10.014>
- [7] Cun HU, Bayhan YK, Kaya Y, Cakici A and Algur OF (2003) Biosorption of lead (II) from aqueous solution by cone biomass of *pinus sylvestris*, *Desalination* 154 (3): 233-238. [https://doi.org/10.1016/S0011-9164\(03\)80038-3](https://doi.org/10.1016/S0011-9164(03)80038-3)
- [8] David William O. Connell, Colin Birkinshaw and Thomas Francis O. Dnyer (2008) Heavy metal adsorbents prepared from the modification of cellulose: A review, *Bio resource Technology* 99: 6709-6724. <https://doi.org/10.1016/j.biortech.2008.01.036>
- [9] Dubey SS and Gupta RK (2005) Removal behaviour of Babool bark (*Acacia nilotica*) for submicro concentrations of Hg²⁺ from aqueous solutions: a radiotracer study, *Sep. Purif. Technol.* 41(1): 21-28. <https://doi.org/10.1016/j.seppur.2004.03.012>
- [10] Kannan K and Balamurugan J (2005) Removal of lead ions by adsorption onto coconut shell and dates nut carbons-A comparative study, *Indian J. Env. Prot.*, 25(9): 816 - 823.
- [11] Muthukumaran K and Sophie Beulah S (2010) SEM and FT-IR studies on nature of adsorption of Mercury (II) and Chromium (VI) from wastewater using chemically activated *Syzygium jambolanum* nut carbon. *Asian Journal of Chemistry* 22(10): 7857 – 7864.
- [12] Muthukumaran K, Balasubramanian N and Ramakrishna TV (1995) Removal of lead and cadmium from plating wastes, *J. Indian Assoc. Env. Manage.* 22: 136-141.
- [13] Ozer A and Pirincci HB (2006) The adsorption of Cd(II) ions on sulphuric acid – treated wheat bran. *Journal of Hazardous Materials* 137 (2): 849 – 855. <https://doi.org/10.1016/j.jhazmat.2006.03.009>
- [14] Pehlivan, Erol and Turkan Altun (2008) Biosorption of chromium (VI) ion from aqueous solutions using walnut, hazelnut and almond shell, *J. Hazard. Mater.*, 155 (1-2): 378-384. <https://doi.org/10.1016/j.jhazmat.2007.11.071>
- [15] Salih IU, Kutty SRM and Isa MH (2017) Adsorption of Lead ions onto Activated Carbon derived from Sugarcane bagasse, *Materials Science and Engineering* 201 doi:10.1088/1757-899X/201/1/012034
- [16] Sivamani S and Prince Immanuel V (2008) Batch adsorption studies for Chromium removal, *J. Env. Sci. Eng* 50(1):11-16. PMID:19192921
- [17] Sivasankari C and Arulanantham A (2014) Evaluation of Polymer- Agglomerated Granular tricalcium phosphate for fluoride removal from drinking water, *Indian Journal of Chemical Technology* 21:70-77. Doi: <http://hdl.handle.net/123456789/26253>.
- [18] Sophie Beulah S and Muthukumaran K (2010) Chromium (VI) sorption and recovery by chemically activated high temperature *Syzygium jambolanum* Nut carbon by column studies. *IJEP* 30 (1): 62-66. DOI: 10.1016/j.proenv.2011.03.032

- [19] Suganthi N and Srinivasan K(2011) Adsorptive removal of nickel and lead ions from aqueous solutions using phosphorylated tamarind nut carbon, *J Environ Sci Eng*, 53(2):163-174 PMID:23033699
- [20] Tunalı S, Akar T, Özcan AS, Kiran I and Özcan A (2006) Equilibrium and kinetics of biosorption of lead (II) from aqueous solutions by *Cephalosporium aphidicola*, *Sep. Purif. Technol.* 47 (3): 105-112. <https://doi.org/10.1016/j.seppur.2005.06.009>
- [21] Volesky B (2001) Detoxification of metal bearing effluents: biosorption for the next century, *Hydrometallurgy* 59 (2-3): 203-216. [https://doi.org/10.1016/S0304-386X\(00\)00160-2](https://doi.org/10.1016/S0304-386X(00)00160-2)
- [22] Volesky B (1990) Removal and recovery of heavy metals by biosorption', in B.Volesky (Ed.), *Biosorption of Heavy Metals*, CRC Press, Boca Raton, FL, 1990, 7-43.