

**Article Info**

Received: 18 Jan 2019 | Revised Submission: 30 Jan 2019 | Accepted: 05 Feb 2019 | Available Online: 25 Mar 2019

**Study of Adsorption of Lead Ions from Wastewater by Polyaniline Coated bel Leaf Powder in a Packed Bed**

*Achla Kaushal\* and SK Singh\*\**

**ABSTRACT**

Bio sorbents are commonly used in removing toxic heavy metal ions from wastewater. Bel leaves are used in temples and immersed in water after offering prayers since ancient times. In the present study, a packed bed continuous column was used to remove lead ions from contaminated water with modified bel leaf powder. The bel leaf powder was polymerised during in-situ polymerisation of aniline in the presence of strong oxidant at low temperature. This modified polyaniline coated bel leaf powder had more capacity to adsorb lead ions. It adsorbed 97.6% lead ion as compared to 90% adsorbed by raw bel leaf powder. Packed column dynamics were also studied for different flow rates (5-25 mL/min) of the adsorbate at different depths along the column. Clogging of the pores and channelization was observed along the column with passage of time, which led to change in lead ion concentration, % removal, adsorption capacity and time of exhaustion along the length of the column. Maximum lead ion removal obtained was 19.1mg, 18.7 mg, 18.36 mg and 18.05 mg at the ends of sections S1, S2, S3 and S4. The exhaustion time was 46 mins, 51 mins, 61 mins and 70 mins respectively for sections S1, S2, S3 and S4. Desorption study showed 96.3% desorption of lead with 0.1 M HCl as eluent.

**Keywords:** Adsorption; desorption; lead ions; packed bed; polyaniline coated bel leaf powder.

**1.0 Introduction**

Lead is a heavy metal which is toxic, non-biodegradable and non-essential for growth of body. It enters the body through food chain, bio-accumulates and absorbed by the body tissues. Its presence in human body is very harmful. It affects the metabolism, liver, pancreas, kidneys and other vital organs. Its presence in body results in retardation of growth, both physical and mental, in children. It has been classified as a 2B carcinogen by IARC (Kaushal and Singh, 2017). Agriculture waste is a well-known bio sorbent used to remove toxic heavy metal ions from wastewater samples. Researchers have prepared adsorbents from (i) agricultural waste such as fruit and vegetable peels, pulps, skin, seeds etc. (ii) horticulture waste such as leaves, barks, stems and roots of trees such as mango, bel, Ashoka, peepal, neem etc. (c) agriculture waste based adsorbents modified by physical or chemical treatment and (d) activated carbon prepared from hard shells and stones etc. to study the removal of heavy metal ions from

contaminated water solutions (Kaushal and Singh, 2016). They have exhibited good results in removing the heavy metal ions under optimum conditions of pH, temperature and optimum quantities of adsorbent dose and initial metal ion concentration. Increase in adsorption capacity and removal efficiency was observed in modified adsorbents due to change in surface morphology.

Polyaniline (PA), PA-composites and nanocomposites and PA-coated materials have shown good results in removing cationic-dyes and heavy metal ions from waste water (Ghorbani et al., 2010; Zang et al., 2010; Ansari and Mosayebzadeh, 2011; Kanwal et al., 2011; Mansour et al., 2011; Ghorbani et al., 2012; Kolaei et al., 2012; Fang et al. 2013; Rathinum & Sankaran, 2014; Rafiqi and Majid 2015). PA (emeraldine base) prepared by oxidative polymerisation of aniline is used for waste water treatment. In-situ polymerisation of agriculture based adsorbent during the synthesis of dil. PA resulted in changes in physical and structural properties of the adsorbents. The resultant modified adsorbent was more stable and had more active sites for adsorption.

\*Corresponding Author: Department of Environmental Technology, Delhi Technological University, Delhi, India  
(E-mail: achla001@hotmail.com)

\*\*Department of Environmental Technology, Delhi Technological University, Delhi, India  
(E-mail: sksinghdce@gmail.com)

Spent adsorbents were desorbed or ignited to recover the adsorbed heavy metal ions before disposing them on land or in water (Cheung et al., 1997; Stockton & Rubner, 1997; Kumar et. al., 2008).

## 2.0 Materials and Method

### 2.1 Preparation of adsorbents

Bel tree were collected from the local area, Rohini, Delhi, India. They were washed thoroughly to remove dirt and other impurities, dried in hot air oven for 48 hours and pulverized to 200 mesh size. The crushed bel leaf powder (BLP) was again washed repeatedly till clear solution was obtained. The BLP was finally dried for 60 hours at 50°C in a hot air oven and stored in air tight container.

### 2.2 Modification of adsorbents

The BLP were modified by in-situ polymerization of aniline in the presence of ammonium persulfate, a strong oxidant, in 1M HCl.

### 2.3 Polyaniline-coated bel leaf powder (PA-BLP)

Dry BLP was added during in-situ oxidative polymerization of aniline resulting in synthesis of PA-BLP. 10 ml purified aniline was dissolved in 100 ml of 1M HCl solution. 5g of BLP was added to this solution and kept at 0°C temperature for an hour. 1.25 g ammonium persulfate [(NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] was dissolved in 100 ml of 1M HCl solution.

This oxidant solution was added dropwise to the aniline solution at ice-cold temperature for 1 hour, stirring continuously to restrict the secondary reactions.

PA-BLP precipitates, a highly stable polymeric compound at room temperature were formed by the exothermic reaction. PA-BLP precipitates were filtered, washed first with 0.1 M HCl and then with distilled water before drying at 50°C for 24 hours. Small quantity of oxidant [(NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] was used for fast oxidation reaction, to prevent the newly formed polymer from degrading. Higher conductivity and yield was obtained for [(NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] : aniline molar ratio < 1 (Syed and Dinesan, 1991).

### 2.4 Dynamic study of lab-scale packed adsorption column

A lab-scale 230 mm L \* 44 mm ID fibre glass column was used to study the adsorption of lead ions on PA-BLP. A sprinkler at the top of the column ensured uniform distribution of the adsorbate throughout the packed column. The adsorbate flowed down the column by gravity. The study was performed for the known flow rates of 5 ml/ min, 10 ml/ min, 15 ml/ min, 20 ml/ min and 25 ml/ min. The extent of adsorption was calculated at regular intervals from sections S1, S2, S3 and S4 of the column spaced at a gap of 50 mm each. The outlet solutions from these sections were analysed for lead ion concentration with respect to time and distance. The concentration of lead ions (m<sub>f</sub>) at the end of each section found to be directly proportional to the time taken to reach the exhaustion stage and the flow rate of the adsorbate through the column. Final concentration of lead ions, adsorption capacity and % removal efficiency was calculated using equations 1, 2 and 3.

$$m_f = F \cdot m_i \cdot t \quad \dots (1)$$

$$Q = (m_i - m_f)/m_a \quad \dots (2)$$

$$\eta (\%) = [(m_i - m_f)/m_i] * 100 \quad \dots (3)$$

m<sub>i</sub> and m<sub>f</sub> denotes the initial and final concentration of lead ions in the solution. It was directly proportional to the flow rate and the time taken to reach the exhaustion limit.

Q represents the adsorption capacity of the adsorbent. It was calculated as the mg of metal ions adsorbed/mass of the adsorbent.

$$m_a = \text{mass of the adsorbent(g)}$$

The amount of lead ions adsorbed was computed from the difference of the initial and the final lead ion concentration in the solution.

η = Metal removal efficiency of the adsorbent (%) is calculated as the amount of metal ions adsorbed/initial lead ion concentration in solution.

## 3.0 Results and Discussion

Adsorption of lead ions on PA-BLP in a packed column was studied for known flow rates; 5

mL/min, 10 mL/min, 15 mL/min, 20 mL/min and 25 mL/min.

At the ends of all the four sections (S1, S2, S3 and S4), the outlet concentration of lead ions was measured. It was observed that time taken to reach the exhaustion state was high at low flow rates. Along the length of the column, the void space in the adsorbent was reduced as the voids were clogged by the lead ions. This resulted in decrease in flow rate along the column, and hence the exhaustion state was obtained after a longer time.

Therefore, the outlet concentration of lead ions in lower sections of the column was higher as compared to that in the upper section due to less adsorption. On increasing the flow rate of the contaminated solution, the time taken for the exhaustion state was reduced. At high flow rates i.e. 20 mL/min and 25 mL/min, the contact time for adsorption was very less. Channelling prevented wetting of the adsorbent in the column resulting in very less contact and hence partial adsorption of the adsorbate with adsorbent.

Therefore, the solution came out of the column with high concentration of the lead ions (Treybal, 1980; Coulson and Richardson, 1998; McCabe et al., 1993).

The concentration of lead ions at the end of sections S1 and S2 was quite high. The performance of packed column was better in the lower sections as

the flow rate were reduced due to better contact between the adsorbate and the adsorbent. Optimum flow rate for adsorption of was found to be 15 mL/min.

At this flow rate, 18.072 mg of lead ions were removed in section S1. 18.7 mg, 18.36 mg and 18.05 mg were removed in the sections S2, S3 and S4 respectively, which was the highest amount removed for all the flow rates.

For the optimum flow rate of 15 mL/min, time taken by the adsorbents in each section to reach the state of exhaustion. The time obtained was 46 mins, 51 mins, 61 mins and 70 mins respectively for sections S1, S2, S3 and S4 respectively. This was due to the fact that in the section S1, the flow rate was high and the adsorbent was fresh, with open pores to take the lead ions.

As per equation 1, the amount of lead ions adsorbed was directly proportional to the flow rate and time taken to exhaust the adsorbents. Hence in section S1, the removal was higher and the adsorbent exhausted very fast i.e. in 46 mins.

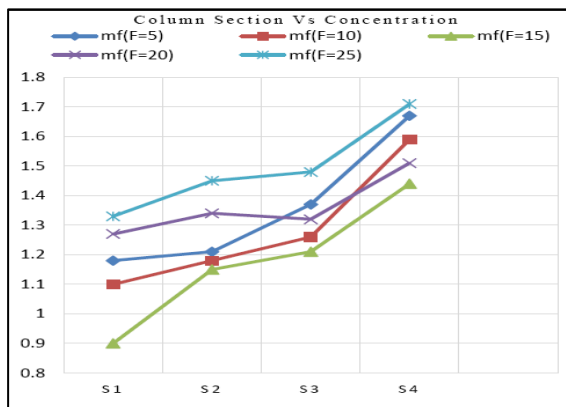
In lower sections, the flow rate was reduced from S2 to S4 due to clogged pores and hence the adsorption of lead ions was less. Hence the adsorbent exhausted slowly.

For the optimum flow rate of 15 mL/min, the 97.6% lead ion removal and maximum adsorption capacity of 0.925 was obtained.

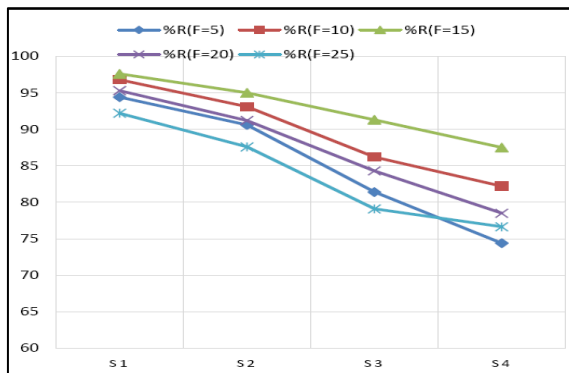
**Table 1: Process characteristics of the packed column for adsorption of lead ions**

Column sections	Outlet concentration of the adsorbate, mg					% Removal					Adsorption capacity				
	5	10	15	20	25	5	10	15	20	25	5	10	15	20	25
1	1.18	1.1	0.9	1.27	1.33	94.4	96.8	97.6	95.3	92.2	.856	.901	.925	.88	.823
2	1.21	1.18	1.15	.34	1.45	90.6	93.1	95.0	91.2	87.6	.79	.831	.893	.81	.77
3	1.37	1.26	1.21	.32	1.48	81.4	86.2	91.3	84.3	79.1	.76	.815	.880	.801	.732
4	1.71	1.59	.44	.59	1.71	75.4	82.2	87.5	72.1	65.0	.698	.788	.868	.75	.65

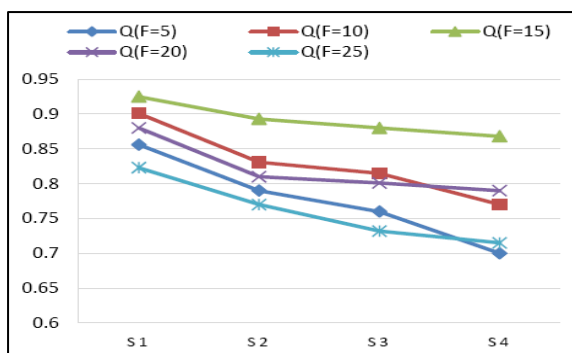
**Fig 1: Concentration of Lead Ions by PA-BLP at Sections S1, S2, S3 and S4**



**Fig 2: % Removal of Lead Ions by PA-BLP at Sections S1, S2, S3 and S4**



**Fig 3: Adsorption Capacity of PA-BLP for Lead Ions at Sections S1, S2, S3 and S4**



#### 4.0 Conclusions

In the present study, a packed bed continuous column was used to remove lead ions from contaminated water with modified bel leaf powder. Clogging of the pores and channelization was observed along the column with passage of time, which led to change in lead ion concentration, % removal, adsorption capacity and time of exhaustion along the length of the column. Maximum lead ion removal obtained was 19.1mg, 18.7 mg, 18.36 mg and 18.05 mg at the ends of sections S1, S2, S3 and S4. The exhaustion time was 46 mins, 51 mins, 61 mins and 70 mins respectively for sections S1, S2, S3 and S4. Desorption study showed 96.3% desorption of lead with 0.1 M HCl as eluent.

#### References

- [1]. JH Cheung, WB Stockton, MF Rubner. Molecular-level processing of conjugated polymers. 3. Layer-by-layer manipulation of polyaniline via electrostatic interactions, *Macromolecules*. doi: 10.1021/ma970047d, 1997.
- [2]. M Ghorbani. Application of polyaniline and polypyrrole composites for paper mill wastewater treatment, *Desalination*. doi: 10.1016/j.desal.2010.06.072, 2010.
- [3]. M Ghorbani, H Eisazadeh, AA Ghoreyshi. Removal of zinc ions from aqueous solution using polyaniline nanoco - 8.pdf, *Iranica Journal of Energy and Environment*. doi: 10.5829/idosi.ijee.2012.03.01.3343, 2012.
- [4]. F Kanwal. Adsorption studies of cadmium (II) using novel composites of polyaniline with rice husk and saw dust of *Eucalyptus camaldulensis*, *Electronic Journal of Environmental, Agricultural and Food*

- Chemistry, 2011.
- [5]. R Karthik, S Meenakshi. Adsorption study on removal of Cr(VI) ions by polyaniline composite, *Desalination and Water Treatment*. doi: 10.1080/19443994.2014.909330, 2015.
- [6]. A Kaushal, SK Singh. Critical analysis of adsorption data statistically', *Applied Water Science*, 7(6), 2017, 3191–3196. doi: 10.1007/s13201-016-0466-4.
- [7]. PA Kumar, S Chakraborty, M Ray. Removal and recovery of chromium from wastewater using short chain polyaniline synthesized on jute fiber, *Chemical Engineering Journal*. doi: 10.1016/j.cej.2007.11.004, 2008.
- [8]. MS Mansour, ME Ossman, HA Farag. Removal of Cd (II) ion from waste water by adsorption onto polyaniline coated on sawdust', *Desalination*. doi: 10.1016/j.desal.2011.01.037, 2011.
- [9]. WB Stockton, MF Rubner. Molecular-level processing of conjugated polymers. 4. Layer-by-layer manipulation of polyaniline via hydrogen-bonding interactions, *Macromolecules*. doi: 10.1021/ma9700486, 1997.
- [10]. AA Syed, MK Dinesan. Review: Polyaniline-A novel polymeric material, *Talanta*. doi: 10.1016/0039-9140(91)80261-W, 1991.
- [11]. R Zhang, H Ma, B Wang. Removal of chromium(VI) from aqueous solutions using polyaniline doped with sulfuric acid', *Industrial and Engineering Chemistry Research*. doi: 10.1021/ie1008794, 2010.