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# Chemical carbonization of papaya seed originated charcoals for sorption of Pb(II) from aqueous solution

Sunil Kumar Yadav [a], Dhruv Kumar Singh [a,*], Shishir Sinha [b]

[a] Analytical Research Laboratory, Department of Chemistry, Harcourt Butler Technological Institute, Kanpur 208002, U.P., India
[b] Department of Chemical Engineering, Indian Institute of Technology, Roorkee 247667, U.K., India

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ABSTRACT

The potential of chemically carbonized papaya seed charcoals (PSCs) for the effective removal of Pb(II) ions from aqueous solution has been investigated in batch experiments. Lead adsorption significantly depends on the initial concentration of Pb(II), contact time, pH, adsorbent dosage and particle size. The adsorption behavior of Pb(II) was best described by the pseudo-second order model and it can be seen that the calculated $q_e$ (cal) values agree with the experimental values. Langmuir, Freundlich, Temkin and Dubinin–Radushkevich (D–R) adsorption isotherm models were applied to represent adsorption data. The equilibrium data were well fitted by the Langmuir isotherm model by revealing the maximum sorption capacity values 188.6 and 238.09 mg/g of $PSC_1$ and $PSC_2$, respectively. Thermodynamic parameters showed that the process is spontaneous, feasible and endothermic. The mechanism of adsorption was also studied using Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy (SEM) analysis before and after the adsorption of lead(II) ions. $PSC_2$ was regenerated using HCl (0.2 M) as eluent and reused for four adsorption–desorption cycles.



## Introduction

There is a growing interest to the health risks on human and animal due to water pollution by heavy metals. Some of these heavy metal ions in traces play a significant role in human metabolic system; their higher concentrations are toxic which can cause severe physiological or neurological damage. Lead is regarded as one of "the big three" of the heavy metals (others are Cd and Hg) due its severe toxicity and great potential hazard to the environment and organisms [1]. They have the ability to bioaccumulation in biological species even at very low concentration [2]. Lead, is one of the typical heavy metals even at very low concentration, may bring substantial threat to human health through the food chains [3]. Increasing concentration of heavy metals in the water constitutes is a severe health hazard, for their toxicity, persistent in nature particularly when it exceeds the permissible limits. In industrial wastewater, Pb(II) concentrations range was 200–500 mg/L [4]. The permissible level of Pb(II) in wastewater, given by the Environmental Protection Agency (EPA) is 0.05 mg/L and that of the Bureau of Indian Standards (BIS) is 0.1 mg/L [5]. World Health Organization (WHO) have recommended 0.01 mg/L, for safe drinking water containing Pb(II) ions [6]. These metal ions exist in wastewater from many industries such as lead acid storage battery [7], solders [8], painting [9], pigments [10], pesticides [11], smelting, metal plating, mining, galvanizing and agricultural activities [12,13]. Lead can cause severe damage to the nervous system, kidney, brain [14] and reproductive system even at mg/L levels [15,16]. Therefore, the removal of Pb(II) in wastewater has received much attention in recent years. Consequently, the development of reliable methods for the removal of lead in environmental samples is particularly significant from aquatic environment.

Among the several methods to treat metal polluted effluents are chemical precipitation [17], reverse osmosis [18], ion exchange [19], solvent extraction, flocculation, membrane separation, electrolysis [20,21], photochemical reactions [22], activated sludge [23], magnetic separation [24], and adsorption [25–29]. In ion exchange, an ion sorbs to the surface by removing another ion of the same valence or multiple ions of lower valence. Ion exchange never changes surface charge. Specific sorption describes the inner sphere complexing of an ion to the surface without the need of other ions to be removed. Specific sorption is able to alter the surface charge. Adsorbents combine chemical and physical processes to remove metal ions, organic contaminants and the compounds that impart color, taste and odor to water.

Among various water purification and recycling technologies, adsorption is a fast, less expensive and universal method. The industrial application of the conventional methods is frequently restricted by their high cost and disadvantages like slow process,

* Corresponding author. Tel.: +91 9450333734; fax: +91 512 2533812.
*E-mail addresses:* dhruvks123@rediffmail.com, hbti_sky@rediff.com (D.K. Singh).

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incomplete removal low selectivity, high-energy consumption, and generation of toxic sludge, which is difficult to be eliminated. The spent adsorbent goes to hazardous waste landfill and is a long terms liability for the society. The development of low-cost adsorbents has led to the rapid growth of research interests in this field. The present protocol describes salient features of adsorption and detailed experimental methodologies for the development and characterization of low-cost adsorbents, water treatment and recycling using adsorption technology including batch operations. Although continuous sorption process is preferred in large scale water treatment applications with the some advantages such as simple operation, high yield, easily scaled up from a laboratory scaled procedure and easy regeneration of packed bed. In batch experiments metal ion sorption by adsorbent is fast, the residence time of the metal solution in the packed column may not be sufficient to reach sorption equilibrium. In the continuous sorption process, the sorption break through is strongly dependent on the liquid flow rate and height of the bed.

Removal of Pb(II) from aqueous solution by adsorption using activated tea waste has been reported [30]. Mango peel waste was evaluated for the removal of Cd(II) and Pb(II) from aqueous solution. The maximum sorption capacity for Cd(II) and Pb(II) was found to be 68.92 and 99.05 mg/g, respectively [31]. Removal of Pb(II) from aqueous solution by adsorption on chemically modified musk melon peel has been reported [32]. Alkaline treated waste cashew nut shell has been studied for the removal of Pb(II), Cd(II) and Zn(II) from aqueous solution [33]. Its adsorption capacity was found 8.82 mg/g for Pb(II). Leaves of date trees [34], coffee residue treated with phosphoric acid and zinc chloride [35], dried cactus cladodes [36], functionalized coconut active charcoal [37], formaldehyde treated onion skin [38], chemically treated rubber leaf powder [39] and xanthated date palm trunk [25] have been studied to remove and recover toxic contaminants from industrial effluents and wastewater.

Papaya seed is widely available as waste material, is mechanically stable and most importantly is environmentally appealing. The purpose of this work is to exploit and utilize PSC as a new modified agricultural waste for enhanced treatment of wastewater containing lead(II). It was also important that by the elaborated chemical procedure one could design the number of surface functional groups to obtain a charcoal having optimal lead(II) adsorption capacity. Another goal was the comparative study of the adsorption properties of the produced activated charcoals and the suggestion of a binding mechanism. The lactone groups and the carboxylic groups formed coordinative bond with the Pb(II) ions, as it could be concluded from the FTIR spectra of Pb(II) loaded $PSC_1$ and $PSC_2$. $PSC_2$ has a greater tendency to form stable complexes with lead(II) ions and leads to the elimination of Pb(II) from aqueous solutions.

## Materials and methods

### Materials

$Pb(NO_3)_2$ (A. R. grade) was purchased from Merck, India. A stock solution of lead(II) (1000 mg/L) was prepared by dissolving 1.61 g of $Pb(NO_3)_2$ in deionized water (DIW) and acidified with concentrate $HNO_3$ (5 ml).

### Preparation of papaya seed charcoals

#### Charcoal labeled $PSC_1$

The crushed papaya seed (10 g) was mixed with concentrated sulfuric acid (11 mL, 98% m/m) in for carbonization and activation. The black slurry was heated in a hot air oven (Shivam Instruments 181/4, Delhi, India) at 150 ± 2 °C for 24 h. The carbonized material was stirred with DIW and centrifuged. The process was repeated until the washing did not show a change in color with methyl orange, indicating that the sorbent was acid free. The washed carbon was dried in a hot air oven at 110 ± 2 °C, ground, sieved (177–149, 149–125 and 125–105 μm) and labeled as $PSC_1$.

#### Charcoal labeled $PSC_2$

In preparation of $PSC_2$ (10 g) the papaya seed powder was mixed in concentrated sulfuric (11 mL, 98% m/m). After 10 min reaction time, concentrated nitric acid (6.6 mL, 65% m/m) was added. The mixture was heated in a hot air oven at 150 ± 2 °C for 24 h and the rest procedure continued same way as given in preparation of $PSC_1$.

### Adsorption experiment

Batch adsorption experiments were carried out in Erlenmyer flasks (100 mL) containing 50 mL of Pb(II) solution with concentration between 25 and 200 mg/L. pH (1–6) was adjusted using NaOH or $HNO_3$ before the adsorbent was added and measured with pH meter (EI Digital pH meter 111, Chandigarh, India). Then, the adsorbent ($PSC_1$ and $PSC_2$; 0.05 g each; particle size 125–105 μm) was added and flasks were shaken in a rotator shaking machine (160 rpm) at room temperature (30 °C) until the equilibrium was reached (120 min). After equilibrium, the adsorbent was separated from the solution by filtration using Whatman No. 4 filter paper and the remaining concentration of Pb(II) ions in the filtrate was analyzed by spectrophotometric method using 1,5-diphenyl thiocarbazone in aqueous miceller solutions [40]. Systronic double beam spectrophotometer 2203, Ahmedabad (India) was used for absorbance measurements. All experiments were performed in triplicate, and mean values were considered in data analysis. The percentage of Pb(II) removal '*R*' and $q_e$ (mg/g) amount of Pb(II) adsorbed per unit mass of the adsorbent were determined using Eqs. (1) and (2), respectively.

$$\%R = \left(\frac{C_i - C_e}{C_i}\right) \times 100 \quad (1)$$

$$q_e\,(\mathrm{mg/g}) = \left(\frac{C_i - C_e}{M}\right) V \quad (2)$$

where $C_i$ and $C_e$ (mg/L) are the initial and equilibrium Pb(II) concentrations, respectively, $V$ is the solution volume (L) and $M$ is the weight of the adsorbent (g).

### Elemental analysis

Elemental analyses of PS, $PSC_1$ and $PSC_2$ samples were performed using Perkin-Elmer 2400 Series CHNS Analyser, Chennai (India). This analysis allows the determination of the percentage of C, H, N, and the O content was calculated by difference to 100%.

### FTIR spectroscopy

In order to determine the functional groups involved in the Pb(II) adsorption process, the unloaded and Pb(II) loaded $PSC_1$ and $PSC_2$ were analyzed by using FTIR spectra (Bruker FTIR Vertex 70, Germany).

### Desorption studies

$PSC_2$ (0.1 g) was saturated with 50 mL of Pb(II) solution (100 mg/L) in Erlenmeyer flask (100 mL) for 120 min, at room temperature at optimum pH (5.0). In order to elute Pb(II) ions adsorbed, the adsorbent was washed with DIW for several times, further it was treated with the HCl (0.2 M, 50 mL) and shaken for 120 min at room temperature. Supernatant was collected and analyzed for Pb(II) ion.