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Research Paper

REMOVAL OF CERIUM (IV) ION FROM AQUEOUS SOLUTIONS USING SAWDUST AS A VERY LOW COST BIOADSORBENT

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Abstract: In this paper adsorption of Ce (IV) ion from aqueous solution using wood sawdust obtained from a local carpentry (termed as SD) as a very cheap and efficient adsorbent has been investigated. Radioisotopes of cerium are a common constituent of liquid radioactive wastes arising from nuclear facilities. So, the removal of cerium ions from the wastewater of nuclear plants is in great importance. Adsorption experiments were carried out using both batch and column systems. The influence of some important experimental conditions such as dosage of adsorbent, initial concentration, contact time has been investigated. In order to have a better comparison, the sorption capacity of sawdust was compared with a commercial grade of activated carbon. It was found that sawdust is a very efficient adsorbent for uptake of cerium ion from aqueous solutions such as nuclear power plants wastewaters.

Keywords: Removal, Ce (IV) ion, sawdust, activated carbon

INTRODUCTION

Cerium with electron configuration of $[Xe]6S^24f^15d^1$ is a lanthanide series rare earth element, and is the most abundant of these rare earths, and forms about 0.0046% the earth's crust [1]. Cerium can exist in either the free metal or oxide form, and can cycle between the cerous, cerium (III), and ceric, cerium (IV), oxidation states [1]. Radioisotopes of cerium are marked products of nuclear fission and hence, they are a common constituent of liquid radioactive wastes arising from nuclear power operations. Many methods have been used to remove the heavy metals from effluents namely oxidation, membrane filtration, coagulation, adsorption, ion exchange, and precipitation, but few of them were accepted due to cost, low efficiency, inapplicability to a wide

variety of pollutants. Unfortunately there is a very limited report for removal of cerium ions from aqueous solutions [2,3]. Heavy metals, for example, can be precipitated as insoluble hydroxide at high pH or sometimes as sulfides. A major problem with this type of treatment is the disposal of the precipitated waste. Another weak point is that in most time the precipitation itself cannot reduce the contaminant far enough to meet current water-quality standards. Adsorption and ion exchange treatment is the most widely used methods for heavy metal ions removal [4-12]. These methods do not present a sludge disposal problem and has the advantage of reclamation of metals. Adsorption can reduce the metal ion concentration to a very low from a cost stand point. Adsorption with activated carbon can also be highly efficient for the removal of numerous trace elements from water, but the high cost of activated carbon inhibits its large-scale use as adsorbent [13-15]. Then, the need for effective and economical removal of unwanted materials resulted in a research for unconventional methods and materials that might be useful in this field. Scientists have, therefore, centered their interest on low cost adsorbents research in recent years. Raw agricultural solid wastes and waste materials from forest industries such as sawdust has been used as adsorbent. It is available in large quantities and may have potential as sorbents due to its physico-chemical characteristics and low cost. Sawdust is an abundant by-product of the wood industry that is either used as cooking fuel or as packing material. Sawdust is easily available in the countryside at zero or negligible price. It contains various organic compounds (lignin, cellulose and hemicellulose) with polyphenolic groups that might be useful for binding pollutants such as heavy metal ions, dyes, etc. from aqueous solutions [16-21].

The objective of the current research is to investigated the possibility of removal of Ce(IV) ion as heavy or superheavy metal ion from aqueous solution using sawdust as a very available biomaterial waste byproduct. A commercial grade of activated carbon as a commonly used and popular adsorbent was used at the same time for comparison.

MATERIALS AND METHODS

All chemicals used were analytical reagents grade and prepared in distilled water. The starting materials (purity 99.99%) were $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$. Sawdust sample was prepared from balsam fir tree and collected from a local carpentry workshop. It was washed with distilled water and sieved before use. Activated carbons were purchased from Merck Company and used without any pretreatment.

Adsorption experiments

For investigation of the effect of adsorbent dosage on removal percentage of Ce (IV) ion, different weights (10 -125 mg) of the selected adsorbents (SD and GAC), were treated for 40 min with 50 mL of of 100 mg/L cerium (IV) ion solution. For investigation of the effect of in initial concentration on removal percentage of Ce (IV) ion, 25 mg of each adsorbent of GAC and SD were treated with 50 mL of Ce (IV) ion solutions containing different initial concentration (10-100 mg L⁻¹). The exposure/shaking time was selected 40 min. For investigation of the effect of contact time on removal percentage of Ce (IV) ion, 50 mg of different selected adsorbents were treated with constant volume of cerium ion solution (50 mL) with the initial concentration of 50 mg L⁻¹ accompanied by mild stirring using a mechanical shaker. Due to strong tendency of Ce (IV) ions in aqueous media, in order to prevent of hydrolysis of Ce (IV) ions all adsorption experiments were carried out in H_2SO_4 0.10M (pH~ 0.6).

For preparing breakthrough curves, a glass column with 1.0 cm diameter and 15 cm height was employed. 1.0 g of the each selected adsorbent were packed into the column separately.

Ce (IV) solution with initial concentration of 10 mg L⁻¹ was passed through the column at a flow rate of 2 mL min⁻¹ at room temperature. The outlet solution was analyzed for residual or unadsorbed cerium ion. All adsorption experiments (both batch and column studies) were carried out in acidic conditions (H₂SO₄ 0.10 M) due to the high tendency of Ce (IV) ions to hydrolysis and room temperature.

Analysis of Ce(IV) ion

Ce(IV) ion was measured using electrochemical method (redox titration) [22]. A standard solution of Fe²⁺ prepared from Fe (NH₄)₂ (SO₄)₂ .6H₂O salt was used as titrant. The end point was detected employing biamperometric technique using double Pt microelectrodes (polarizable) as indicator electrodes with applying a small potential (0.20V). The endpoint is marked by a sudden increase in the current from zero. The percentage adsorption was calculated using the following equations (eq. 1 and eq.2):

$$\% \text{Adsorption} = \frac{(C_i - C_f)}{C_i} \times 100 \quad (1)$$

$$\frac{x}{m} = \frac{(C_i - C_f) V}{m} \quad (2)$$

Where, C_i and C_f are the initial and equilibrium or unadsorbed concentrations of Ce (IV) ion solution, x/m (mg g⁻¹) is the amount of sorption per unit mass of sorbent, V is the volume of adsorbate (L) and m is the amount of adsorbent (g). Each data reported is the average of at least three measurements with maximum uncertainty (RSD) of 2%.

RESULTS AND DISCUSSION

Effect of adsorbent dosage

The results obtained from this investigation are shown in Figure 1. As our data show, increasing sorbent dosage led to a considerable increase in removal of Ce(IV) ions. 0.10 g of SD can clean 100 mL Ce(IV) polluted solution with concentration of 100 mg L⁻¹. Therefore, SD seems to be a very efficient adsorbent for removal of Ce (IV) ions from industrial wastewaters polluted with this ion such as nuclear power plants.

Its sorption capacity is interestingly comparable to a commercial grade activated carbon (GAC, Merck) which was used in this study. AC is a common and well established adsorbent for heavy and super heavy metal ions from aqueous solutions. However, due to the high cost of GAC, its use has been limited. Sorption of Ce(IV) ions by SD can be mainly due to chelating reactions between cerium ions with the different functional groups present in the cellulosic and noncellulosic constituents in sawdust which helps to binding the heavy metal ions. Removal of Ce(IV) ions by sawdust, can also be due to the redox reaction between Ce (IV) ion (E⁰= 1.44 V) and the reducible functional groups present in sawdust constituents such as lignin (e.g. phenolic, carbonylic and hydroxyl) and the subsequent complex formation of the Ce (III) ion (the reduced product of Ce⁴⁺)

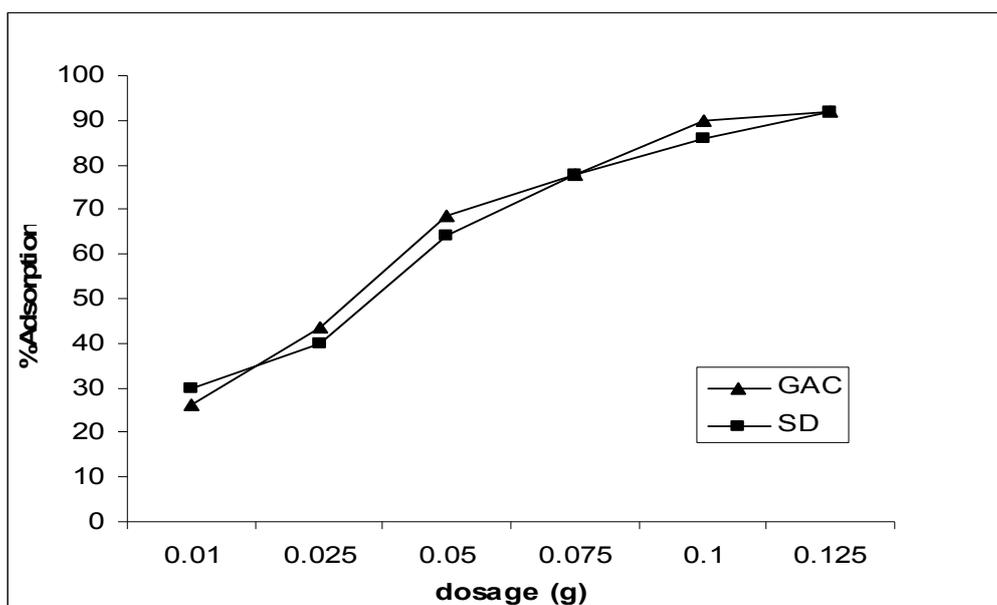


Fig. 1: Effect of GAC and SD dosage on the adsorption of Ce (IV) ion (pH=0.6).

Using powdered form of activated carbon (PAC), it was found that it was more efficient than GAC because of its higher surface area. For instance it was observed that using only 0.05 g of PAC, it is possible to remove 98% of Ce(IV) ions under the experimental conditions as described in Fig. 1. Since PAC can not be used in column system because of pressure drop of liquid and very low flow rate, so our study was mainly focused on GAC instead of PAC. Sorption of Ce (IV) ions by activated carbon can be mainly due to its porous structure and partly due to its surface chemistry (presence of functional groups) which helps to uptake the heavy metal cations.

Effect of initial concentration

For this investigation, 0.025 g of SD or GAC were selected to be treated with 100 mL of Ce(IV) ion solution with different initial concentrations. The results obtained in this investigation are summarized in Table 1. According to the data obtained in this study, SD was found to be more efficient adsorbent for removal of Ce (IV) ions for each initial concentration. It is very interesting to note that each 25 mg of sawdust can remove about 97% of Ce (IV) ions from 100 mL polluted solution of this ion with concentration of 25 mg L⁻¹.

Table 1: Effect of initial concentration on removal percentage (%R) of Ce (IV) ion

Adsorbent	C _i (mg L ⁻¹)				
	10	25	50	75	100
% R (SD)	98	97	66	52	40
X/m (mg g ⁻¹) (SD)	19.6	48.4	66.0	78.0	80.0
%R (GAC)	84	54	50	46	44
X/m (mg g ⁻¹) (GAC)	16.8	26.8	50.0	69.2	87.2

The data also shows that with increasing the initial Ce (IV) concentration, the amount of sorbed Ce(IV) ions per unit mass of adsorbent is increased too. The increase in X/m was also higher for SD compared to GAC from 10 to 75 ppm of Ce(IV) ion initial concentration.

Effect of contact time

For investigation of the effect of contact time, 0.05 g of adsorbents (SD and GAC) were treated with 50 mL of Ce(IV) solutions with constant initial concentration of 50 mg L⁻¹ at pH about 0.6 accompanied by mild shaking at room temperature for various time intervals. The filtrates were then analyzed for unadsorbed Ce(IV) ions. The results obtained are shown in Figure 2.

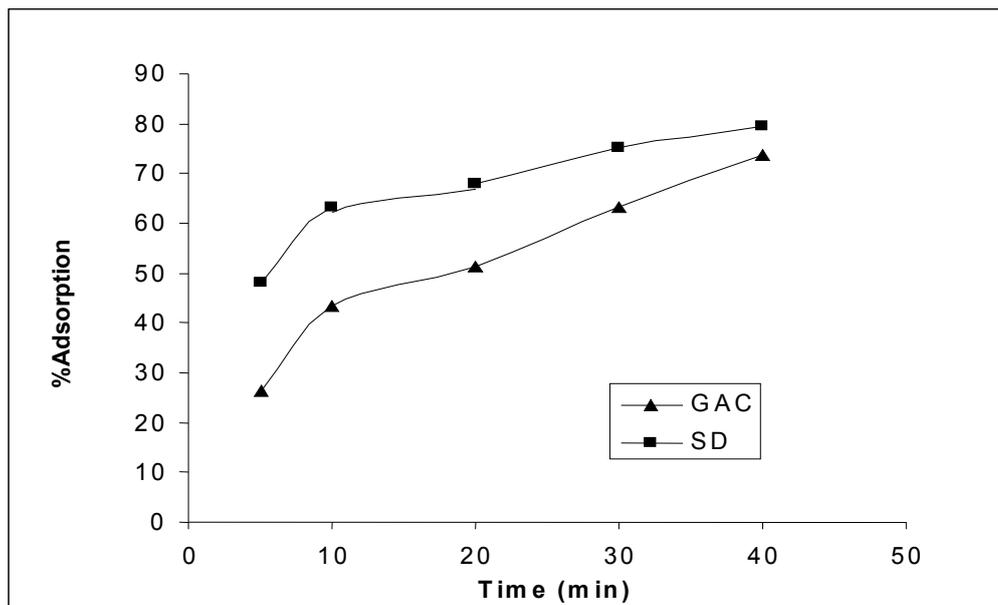


Fig. 2: Effect of contact time on adsorption of cerium ion by GAC and SD.

As our data show, with increasing exposure time, a gradual increase in removal percentage is observed. About 80% of the Ce(IV) was removed within 40 minutes of exposure. This implies the high kinetics as well as higher sorption capacity of SD compared to GAC which is quite consistent with our previous findings in this research.

Treatment of data using adsorption isotherms

In order to model the sorption behavior, adsorption isotherms were studied at room temperature. Both Langmuir and Freundlich equations were employed to plot the isotherms [23-25]. Langmuir and Freundlich equations can be shown as the following (eq. 3-eq.6):

$$\text{Langmuir, non-linear form} : X = \frac{X_m b C_f}{1 + b C_f} \quad (3)$$

$$\text{Langmuir, linear form} : \frac{1}{X} = \frac{1}{X_m} + \frac{1}{b C_f} \quad (4)$$

$$\text{Freundlich, non-linear form} : X/m = K C_f^{\frac{1}{n}} \quad (5)$$

$$\text{Freundlich, linear form} : \log X/m = \log K + \frac{1}{n} \log C_f \quad (6)$$

Where C_f is the equilibrium concentration of Cerium(IV) solution (mg L⁻¹), X is the amount sorbed by adsorbent (mg g⁻¹), X_m is the maximum amount sorbed (mg g⁻¹), b a Langmuir's constant

signifying energy of sorption ($L \text{ mg}^{-1}$), K ($L \text{ g}^{-1}$) and n are Freundlich's constants indicating sorption capacity and intensity, respectively.

The isotherm obtained (both Freundlich and Langmuir) indicate that adsorption of Ce (IV) ion by GAC and SD can be modeled by both Freundlich and Langmuir isotherm equations (Figures 3 and 4). The high correlation coefficient obtained for SD ($R^2 = 0.9917$) using Langmuir model indicates high affinity between adsorbent surface and Ce (IV) ions which plays the major role in the adsorption mechanism and also imply a better fit to the adsorption system of Ce (IV) ions by SD to Langmuir model and also confirms a monolayer sorption process(Figure 3).

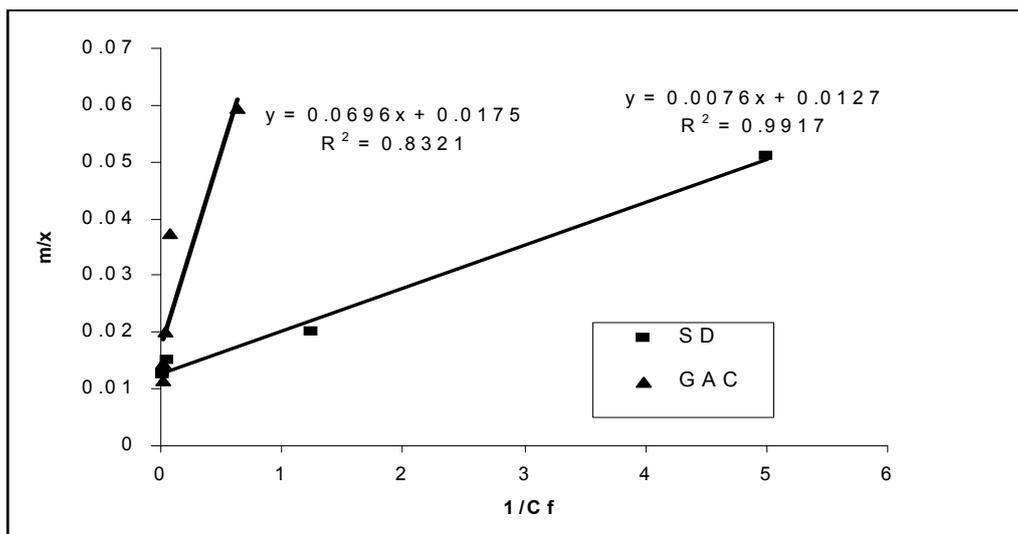


Fig. 3: Langmuir adsorption isotherm for the sorption of Ce (IV) ion: SD ■, GAC ▲

From the higher correlation coefficient obtained for GAC ($R^2 = 0.9246$) using Freundlich model it could be concluded that the adsorption isotherm of Ce (IV) ions using GAC in contrast to SD, give a better fit to the Freundlich model (Figure 4).

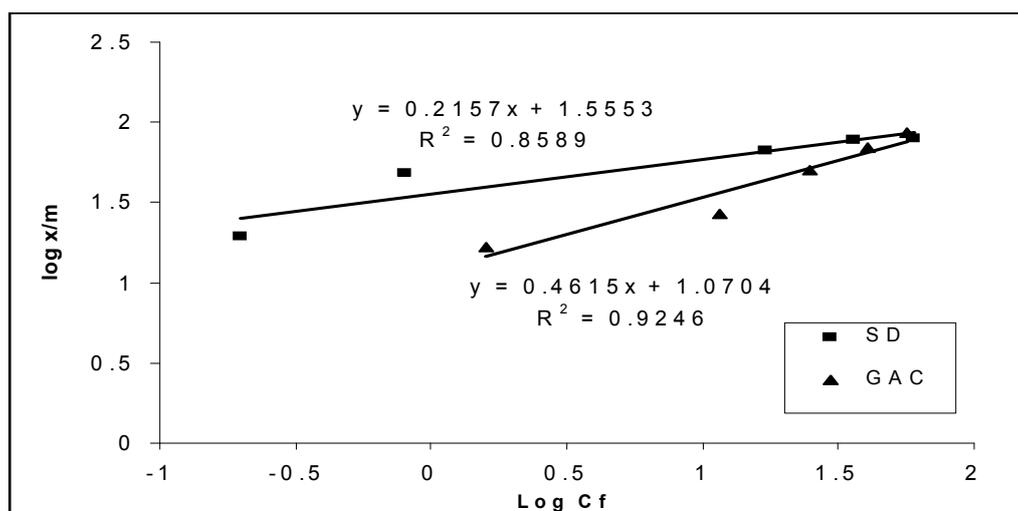


Fig. 4: Freundlich isotherm for the sorption of Ce (IV) ion: SD ■, GAC ▲

On the basis of slopes and intercepts of the straight lines Langmuir and Freundlich constants derived from these straight lines are presented in Table 2.

Table 2: Freundlich and Langmuir constant values obtained for adsorbents

Adsorbent	n	k	b	$X_m(\text{mg g}^{-1})$
GAC	2.2	12	0.25	57.0
SD	4.6	36	1.7	79

The values of n obtained for SD and GAC indicates that both adsorbents are suitable for uptake of Ce(IV) ions from aqueous solutions. For a suitable sorbent/adsorbate system, the value of n is normally between one and ten [26]. More over, SD has a higher value for n than GAC indicating its more heterogeneous surface than GAC which is due to its various chemical functional groups. The higher adsorption capacity (X_m), b and K values obtained for SD also confirms a higher sorption capacity and superior performance of SD adsorbent for Ce (IV) ions adsorption from aqueous solution compared to GAC (Table 2).

Breakthrough curves (column system).

Sorption isotherms which are obtained from batch study do not give accurate scale-up data for industrial systems since sorption in a column is not normally in a state of equilibrium. Besides this, the problem of regeneration can not meaningfully study in a batch experiment. Consequently, there is a need to perform flow test using column prior to scale-up. When working adsorption experiments with columns, the breakthrough curves (a plot of effluent solute concentration vs. time) are very useful. The point where the effluent solute concentration reaches 95% of its influent value is usually called the point of column exhaustion [20].

For this investigation, 1.0 g of each adsorbent (SD and GAC) was packed into a glass column (fixed bed depth of 5 cm). After conditioning the column with distilled water, Ce (IV) solution with initial concentration of 10 mg L^{-1} was passed through the column (flow rate = 2 mL min^{-1}). The outlet solutions were analysed for unadsorbed Ce (IV) ion. The breakthrough curves obtained are shown in Figure 5.

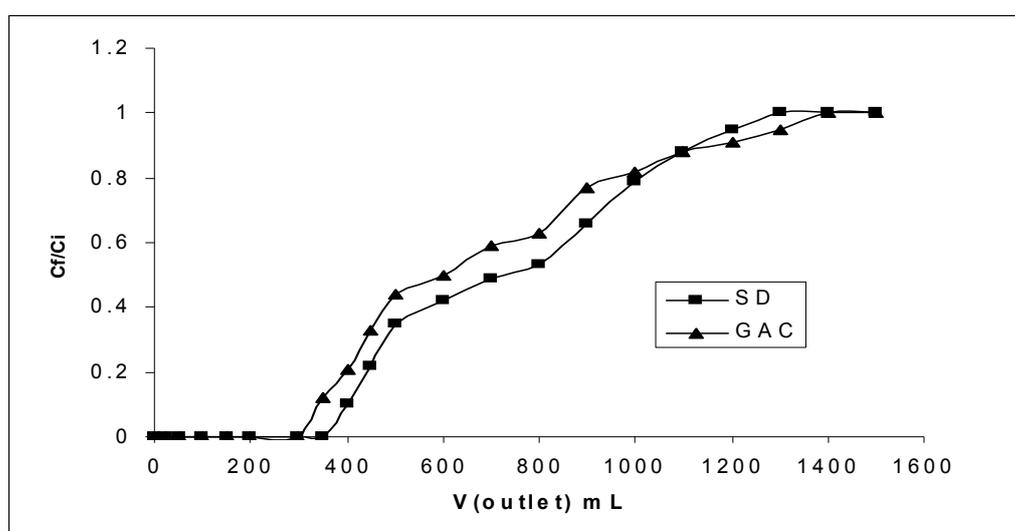


Fig. 5: Breakthrough curve obtained for removal of Ce (IV) ion using GAC and SD adsorbents.

As our breakthrough curve analysis is interestingly show (Figure 5), SD is more efficient adsorbent for Ce (IV) ions even in flow or non-equilibrium system, compared to GAC as well. In consistent with our other investigation in this paper, higher removal efficiency of Ce (IV) ions was observed when SD compared to GAC in our fixed bed column or flow system.

CONCLUSIONS

Sawdust obtained from balsam fir tree has proven to be a promising material for the removal of Ce (IV) ions from wastewaters. The sorption capacity and removal efficiency toward Ce (IV) ions of SD was found to be comparable or even higher than GAC in both batch and column adsorption systems. SD is also a very abundant, low cost and environmentally friendly adsorbent, so its use is very economic and favorable for uptake of Ce (IV) ions from the wastewaters polluted with this ion such as nuclear activities plants wastewaters.

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