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# Removal of Toxic Cadmium from Aqueous Solution using Natural Adsorbents: An Eco-friendly Method 

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#### Abstract

The industrialization has led to the environmental pollution and pollutant removal from waste water is intensively studied. The wastes that are produced in large quantities in the form of solid or liquid wastes are disposed directly to the environment. These wastes from some industries like tannery may contain heavy metals that are toxic to plants, animals and to the environment. When they are present in quantities more than permisible limits they result in heavy metal pollution. Adsorbents for removal of pollutants from waste water is an efficient technique to remove them from aqueous solutions. Wood materials like bark from trees can be used to remove heavy metals from solution. The present study was an attempt to remove the toxic cadmium from the aqueous solution using Pongamia glabra, Tamarindus indicus, Tesphesia populnea and Mangifera indica bark materials in different concentrations. The bark materials were found to be effective in removing cadmium from the solution.


Key words: Tree bark, adsorbents, aqueous solution, heavy metal, cadmium

## INTRODUCTION

Cadmium is used for production of dye, pigment, batteries, ceramics, wooden and plastic products. The metal is also used in electroplating, semiconductors, rectifiers and solder for aluminum. Smelters produce one million kilogram of Cd which is released in to the atmosphere every year. Cadmium factories account for $45 \%$ of the total cadmium pollution. From the incineration of cadmium bearing products such as automobile tyres, motor oils, fungicides, plastics and coals, $52 \%$ of the cadmium pollutes the atmosphere. Its volatility is the reason for its quick distribution in to the atmosphere. Cadmium discharge in to the natural water is from electroplating and $\mathrm{Ni}-\mathrm{Cd}$ batteries industries (Dara, 2001).

Adsorption is an effective purification and separation technique used in industry for water and waste water treatment to remove toxic materials from aqueous and non aqueous solutions. The heavy metals result from different industries like electroplating, cadmium-nickel batteries and alloy industries. Heavy metals need to be treated and avoid direct discharge to the environment due to its harmful effects. Cadmium is respiratory irritant and its continuous exposure causes anosmia and alloy stains on the necks of the teeth and copper may cause keratinisation of the hands and soles of the feet (Sitting, 1981). The concentration of these metals should be reduced to the lower levels, set by the environmental agencies. Adsorption process is advantageous over other regular methods
as it is selective, effective and removes very low levels from the solutions (Patterson and Minear, 1975). Biological materials are found to be extensively applied for the adsorption process as it is effective in its sorption cap acity (Singh et al., 1993).

Bark are obtained in large quantities from saw mills that can be used as adsorbents for heavy metals. They primarily contain lignin and cellulose. The modified or carbonated wood materials may be efficient for removing metals from solutions and effective and economical alternative to expensive treatments (Gaballah and Kilbertus, 1998). Therefore in the present investigation it was proposed to make use of the readily available low-cost plant barks such as Pongamia glabra, Tamarindus indicus, Tesphesia populnea and Mangifera indica as adsorbents to remove the heavy metal ion Cd (II) in synthetic solutions.

Such a study may pave the way to make use the barks for the removal of Cd (II) from the tannery effluent. In a similar manner the study may certainly of immense use for the removal of excess metal ions which let out polluting the water bodies, land and air from the industries where Pb (II), Cd (II) and Hg (II) are liberally made use of.

## METHODOLOGY

Batch studies were conducted at $31^{\circ} \mathrm{C}$ with constant amount of bark adsorbents ( $1-3 \mathrm{~g} \mathrm{~L}^{-1}$ ) at the constant pH 2 and 4.5 to evaluate the bark materials for the removal of cadmium ions. Prior to the introduction of the metal ions, the flasks were vigorously stirred for 90 min to hydrate the material. Stock solution of cadmium was prepared by dissolving 0.203 g of cadmium chloride in 1000 mL of double distilled de-ionised water to give 1000 ppm . Using suitable volumes of this solution 2.038, 6.091 and $10.130 \mathrm{mg} \mathrm{L}^{-1}$ solutions were prepared in Erlenmeyer flasks. In the first batch of the experiment 0.1 g of bark was added and in the second batch 0.3 g of bark was added to 95 mL of aqueous solutions. The pH of these solutions was adjusted to 4.5 using $\mathrm{HNO}_{3}$ and the flasks were agitated for 1 h . After the experiment the samples were filtered through a $0.45 \mu \mathrm{~m}$ membrane filter. In the similar experiments with all these concentrations of the solutions and barks, the flasks were agitated 2 h and the filtration was done similarly. All the clear filtrates were analyzed for Cd (II) using atomic absorption spectrophotometer at 228.8 nm .

## RESULTS AND DISCUSSION

Effect of initial metal concentrations on the removal of Cadmium (II) using PGBM, TIBM, TPBM and MIBM: For PGBM, as initial concentration of Cd (II) is varied from 2.038-10.130 $\mathrm{mg} \mathrm{L}^{-1}$ for 1 h contact time and for $1 \mathrm{~g} \mathrm{~L}^{-1}$ bark concentration percentage removal of Cd (II) decreased from 49-37.7 (Fig. 1, Table 1) At similar conditions when the bark dose is increased to $3 \mathrm{~g} \mathrm{~L}^{-1}$, the increase of initial concentration of Cd (II) has resulted in the decrease of percentage of removal from 70-58.3 (Fig. 1, Table 1). Variation of initial concentrations, keeping the contact time 2 h and the bark concentration $1 \mathrm{~g} \mathrm{~L}^{-1}$, percentage of removal of Cd (II) decreased from 56.3-40.7 (Fig. 2). At the same contact time and at the bark dose of $3 \mathrm{~g} \mathrm{~L}^{-1}$ also a decrease of percentage of removal of Cd (II) is found from 85.2-61.3 when the initial concentration of Cd (II) increased (Fig. 2). When the experiment is conducted with TIBM, TPBM and MIBM the results obtained are similar to that of PGBM.

The results obtained in the present investigation are similar to that of obtained by the use of tea waste (Oboh and Aluyou, 2008) and Nile Rose Plant (Abdel-Ghani and Elchaghaby, 2007) as an adsorbent for Cd (II) as reported in the literature.

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Fig. 1: Effect of initial metal concentration on the removal of Cd (II) using PGBM, TIBM, TPBM and MIBM at contact time 1 h

Table 1: Percentage removal of Cd (II) by four plant barks at different parameters ( $\mathrm{pH}: 4.5$ Temperature: $31^{\circ} \mathrm{C}$ )

| Initial concentration of Cd (II) ( $\mathrm{mg} \mathrm{L}^{-1}$ ) | 1 h contact time |  | 2 h contact time |  |
| :---: | :---: | :---: | :---: | :---: |
|  | --------- | ------------ | - | ---- |
|  | $1 \mathrm{~g} \mathrm{~L}^{-1}$ bark | $3 \mathrm{~g} \mathrm{~L}{ }^{-1}$ bark | $1 \mathrm{~g} \mathrm{~L}^{-1}$ bark | $3 \mathrm{~g} \mathrm{~L}{ }^{-1}$ bark |
| PGBM |  |  |  |  |
| 2.038 | 49.0 | 70.0 | 56.3 | 85.2 |
| 6.091 | 45.4 | 67.4 | 50.5 | 73.5 |
| 10.130 | 37.7 | 58.3 | 40.7 | 61.3 |
| TIBM |  |  |  |  |
| 2.038 | 42.7 | 64.5 | 52.2 | 79.8 |
| 6.091 | 38.2 | 56.9 | 47.2 | 69.7 |
| 10.130 | 34.8 | 53.1 | 45.6 | 58.4 |
| MIBM |  |  |  |  |
| 2.038 | 40.6 | 55.6 | 50.8 | 73.4 |
| 6.091 | 35.8 | 47.7 | 45.5 | 64.8 |
| 10.130 | 33.8 | 44.6 | 39.6 | 60.3 |
| TPBM |  |  |  |  |
| 2.038 | 38.1 | 52.4 | 46.9 | 69.8 |
| 6.091 | 34.6 | 45.6 | 44.0 | 63.7 |
| 10.130 | 32.7 | 43.6 | 39.6 | 58.8 |

Effect of contact time on the removal of Cadmium (II) using PGBM, TIBM, TPBM and MIBM: For the plant material TIBM, keeping the initial concentration of Cd (II) as $2.038 \mathrm{mg} \mathrm{L}^{-1}$ and the bark dose as $1 \mathrm{~g} \mathrm{~L}^{-1}$, contact time is varied from 1-2 h . Percentage of Cd (II) removal is found to increase from 42.7-52.2 (Fig. 3a, Table 1). For the same experiment for a bark dose concentration of $3 \mathrm{~g} \mathrm{~L}^{-1}$ for the increase of contact time from 1 to 2 h percentage of removal is also found to increase from 64.5-79.8(Fig. 3b). When the initial concentration of Cd (II) is kept as $6.120 \mathrm{mg} \mathrm{L}^{-1}$ and the bark as $1 \mathrm{~g} \mathrm{~L}^{-1}$ increase of contact time from $1-2 \mathrm{~h}$ has increased the percentage removal of Cd (II) from 38.2-47.2 (Fig. 3b). When the same experiment is conducted with $3 \mathrm{~g} \mathrm{~L}^{-1}$ of bark dose percentage removal of Cd (II) increased from 56.9-69.7\% as the contact time increased from 1-2 h (Fig. 3b).

At the initial concentration of $10.130 \mathrm{mg} \mathrm{L}^{-1}$ of Cd (II) at a bark dose of $1 \mathrm{~g} \mathrm{~L}^{-1}$ percentage of removal is increased from 34.8-45.6 (Fig. 3c). Under similar circumstances at $3 \mathrm{~g} \mathrm{~L}^{-1}$ bark dose percentage removal of Cd (II) is found to increase from 53.1-58.4\% for an increase of contact time from 1-2 h (Fig. 3c). When this experiment is carried out with plants PGBM, TPBM and MIBM increase of contact time is found to increase the percentage removal (Table 1).


Fig. 2: Effect of initial metal concentration on the removal of Cd (II) using PGBM, TIBM, TPBM and MIBM at contact time 2 h


Fig. 3(a-c): Effect of contact time on the removal of Cd (II) using PGBM, TIBM, TPBM and MIBM with initial concentration (a) $2.038 \mathrm{mg} \mathrm{L}^{-1}$, (b) $6.091 \mathrm{mg} \mathrm{L}^{-1}$ and (c) $10.130 \mathrm{mg} \mathrm{L}^{-1}$

It has been already reported that increase of contact time has increased the amount of removal of Cd (II) from polluted water when leaves (Sayrafi et al., 1996) of reed, oak, pine, cypress saw dust, rice husk and chemically activated saw dust (Saravanane et al., 2002) have been made use of.

Abdel-Ghani and Elchaghaby (2007) have also reported such an observation by conducting the experiment with Nile Rose Plant as adsorbent for Cd (II).

Effect of bark dose on the removal of Cadmium (II) using PGBM, TIBM, TPBM and MIBM: Keeping the Cd (II) initial concentration as $2.038 \mathrm{mg} \mathrm{L}^{-1}$ and contact time as 1 h and the bark dose of TPBM is varied from $1-3 \mathrm{~g} \mathrm{~L}^{-1}$ (Fig. 4a, Table 1). The percentage removal of Cd (II) is found to increase from 40.6-55.6. For the same concentration of Cd (II), for the contact time 2 h and increase of bark dose from $1-3 \mathrm{~g} \mathrm{~L}^{-1}$ there is an increase of percentage removal from $50.8-73.4 \%$ (Fig. 4b). When the experiment is conducted with the initial concentration of Cd


Fig. 4(a-b): Effect of bark dose on the removal of Cd (II) using PGBM, TIBM, TPBM and MIBM at contact time (a) 1 h and (b) 2 h
(II) as $6.091 \mathrm{mg} \mathrm{L}^{-1}$ and contact time 1 h increase of bark dose from $1-3 \mathrm{~g} \mathrm{~L}^{-1}$ has increased, the percentage removal from 35.8-47.7\% (Fig. 4a) for 2 h contact time variation of bark of dose from $1-3 \mathrm{~g} \mathrm{~L}^{-1}$ resulted in the increase of percentage of Cd (II) removal from 45.5-64.8\% (Fig. 4b). When the initial concentration of Cd (II) is kept constant as $10.130 \mathrm{mg} \mathrm{L}^{-1}$ and the contact time as 1 h an increase of percentage removal of Cd (II) from 33.8-44.6 is found when the bark dose is increased from $1-3 \mathrm{~g} \mathrm{~L}{ }^{-1}$ (Fig. 4a); for 2 h contact time increase of percentage removal of Cd (II) is found to be $39.6-60.2 \%$ for the increase of $1-3 \mathrm{~g} \mathrm{~L}^{-1}$ (Fig. 4b). When this experiment is conducted under the same conditions with the plants PGBM, TIBM and MIBM increase of bark dose is found to increase the percentage of Cd (II) removal as noticed in TPBM.

The results are in agreement with tea wastes (Mahvi et al., 2005) and Nile Rose Plant (Panikar et al., 2003) used for Cd (II) adsorption.

Efficacy of the PGBM, TIBM, TPBM and MIBM plant barks for the removal of Cd (II): For an initial concentration of Cd (II) 10.130 ppm , for 1 h contact time at $1 \mathrm{~g} \mathrm{~L}^{-1}$ bark dose, percentage of Cd (II) removal by PGBM, TIBM, TPBM and MIBM are compared (Fig. 5a). It is found that PGBM shows maximum removal as $37.7 \%$, for $3 \mathrm{~g} \mathrm{~L}^{-1}$ concentration, the value of maximum $58.3 \%$ for PGBM compared to other four plant materials (Fig. 5a). For the same concentration of $10.130 \mathrm{mg} \mathrm{L}^{-1}$ for 2 h contact time at $3 \mathrm{~g} \mathrm{~L}^{-1}$ of bark concentration the value obtained is $61.3 \%$ which is high when compared to other plants (Fig. 5a). Keeping the initial concentration of Cd (II) as $6.091 \mathrm{mg} \mathrm{L}^{-1}$ contact times as 1 h with bark doses of the plants as 1 and $3 \mathrm{~g} \mathrm{~L}^{-1}$ of all the plants employed only PGBM adsorbs maximum amount of Cd (II) as shown in the Fig. 5b. In this experiment when contact time is changed to 2 h and the experiment is conducted with two different bark doses viz., 1 and $3 \mathrm{~g} \mathrm{~L}^{-1}$, similar results are obtained (Fig. 5b).


Fig. 5(a-c): Efficacy of the PGBM, TIBM, TPBM and MIBM plant barks on the removal of Cd (II) at initial matal concentration (a) $10.130 \mathrm{mg} \mathrm{L}^{-1}$, (b) $6.091 \mathrm{mg} \mathrm{L}^{-1}$ and (c) $2.038 \mathrm{mg} \mathrm{L}^{-1}$

When the same experiment is repeated with all the condition described above with all the four plant barks only PGBM is found to take up maximum amount of Cd (II) (Fig. 5c). It is said that during the adsorption of cadmium by the plant $S$. cervisiae, it is found to be drawn inside the vacuoles of the plant as reported by Voleskey (1993).

Earlier studies have reported that the adsorption by carbon aerogel depends on the concentration, pH , contact time, adsorbent dose and temperature dependent. Calotropis procera roots were found efficient in removing the cadmium ion. The adsorption was dependent on the initial metal ion concentration, adsorbant dosage, contact time and agitation speed and the adsorption efficiency were appreciable (Ramalingam et al., 2013). Argun et al. (2007) have also reported that bark is an efficient adsorbent and rapid uptake of heavy metals makes it as an effective alternate for sorption of heavy metals. The Gmelina arborea bark was found to be an effective adsorbent by Jover and Salvacon (2012). The pine bark was found as an environment friendly adsorbent by Nehreinheim et al. (2011). These materials could be effectively used for treatment of industrial effluents.

## CONCLUSION

Plant barks are mainly composed of macromolecules or natural polymers, decomposition of which has no adverse impact on the environment and are considered to be economic, flexible, eco friendly and able to eliminate metal ions from contaminated wastes. The use of this material for metals remediation requires knowledge of the reactivity and the exact content of chelating surface sites to determine the main properties. In the present study, four different plant bark materials (PGBM, TIBM, TPBM and MIBM) have been harnessed for heavy metals removal. The sorption of heavy metal Cd as a function of pH and metal concentration has been performed in single solution. These studies show that adsorbent prepared from all the plant bark materials are efficient sorbent for cadmium removal from aqueous solutions, owing to its very low cost and its relatively interesting sorption capacity which could be related to the abundance of cellulose, lignin and fatty acid moieties.

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