Adsorption of cadmium from water using activated carbon derived from *Ipomoea Carnea* using chemical impregnation

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Abstract. *Ipomoea Carnea* is a wild shrub, and because of its abundance, it was chosen as precursor for making activated carbon. Adsorbent preparation method involved the impregnation of dried precursor with zinc chloride followed by activation at 500°C. Surface morphology of prepared adsorbent was compared with the raw *Ipomoea Carnea* by Scanning Electron Microscope analysis. Batch adsorption studies were carried out to understand the effect of parameters like, metal initial concentration, contact time, adsorbent dose and pH on percent removal of cadmium. More than 96% removal of Cd(II) was obtained at the adsorbent dose of 0.3 g/L in 20 minutes at pH 6. Experimental data were fitted to isotherm and kinetic models to understand the mechanism of adsorption. Adsorption of Cd(II) onto raw *Ipomoea Carnea* followed the Langmuir isotherm, whereas adsorption onto activated *Ipomoea Carnea* followed the Freundlich isotherm. Kinetic study reveal that the experimental data of adsorption of Cd(II) onto activated *Ipomoea Carnea* followed the second order kinetic.

Keywords: Water Treatment, *Ipomoea Carnea*, Adsorption, Cadmium.

1. Introduction

Application of cadmium is very common in industries like electroplating, alkaline batteries, smelting, pigments, mining and metallurgical processes. It is BI carcinogen according to United States Environmental Protection Agency which upon accumulation in the human bodies causes the diseases such as neuralgia, nephritis, hypertension and anemia [1]. According to Minimal National Standard (MINAS), Ministry of Environment and Forest, Government of India, the safe discharge limit for cadmium in effluent is 0.2 mg/L [2]. Techniques such as electrochemical treatment, ion-exchange, filtration, membrane separation, precipitation and adsorption are used to treat wastewater. These methods have the drawbacks like large sludge production, large capital cost and high operational and maintenance cost [3]. The adsorption onto activated carbon (AC) has emerged as a promising method for wastewater treatment, but AC is not economical due to its high manufacturing cost. Many researchers have focused on reducing the cost of manufacturing of AC by using wastes like crab shell, peanut hull pellets, corn starch, soybean hull, rice husk, de-oiled soya, turmeric waste, pomegranate peel as the precursor to make activated carbon [4-10].

*Ipomoea Carnea* plant is an abundantly available shrub and the extract of different parts of this plant has the medicinal values such as anti-bacterial, anti-fungal, anti-oxidant, and tranquilizing properties.
Due to its abundant availability and adsorption property, Ipomoea Carnea has been used for adsorptive removal of the pollutant from wastewater. Ipomoea Carnea was activated with ZnCl₂ to adsorb copper from water [11]. Krishnaveni and Thirumurugan, studied the removal of Chromium using Ipomea Carnea and observed 74% removal efficiency within 60 min of operation for an adsorbent dose of 2g/L from the solution containing 20 PPM of chromium initially [12]. Pandian et al. prepared the adsorbent from Ipomoea Carnea leaves by acid treatment for nickel adsorption [13].

In the present work, AC was derived from the stems of Ipomoea Carnea plant using ZnCl₂ as an activating agent and the efficiency of prepared adsorbent in Cd(II) removal from water was tested. Surface morphology of the raw Ipomoea Carnea and prepared activated carbon were compared to understand the effect of activation on surface. To gain insight of adsorption phenomena, different isotherms and the kinetic models were fitted to the experimental data.

2. Materials and method

2.1. Adsorbate and adsorbent
Ipomoea Carnea stems (figure 1) were collected from Guru Ghasidas Vishwavidyalaya, Bilaspur, India. Synthetic aqueous solution of cadmium was prepared by cadmium nitrate. Standard HCl/NaOH solution was used to maintain the pH of the solution.

2.2. Adsorbent preparation method
The stems were first washed thoroughly with deionized water to remove adhered impurities; dried at room temperature for one week; ground to obtain particles of size 1-2 mm which is termed as RIC (Raw Ipomoea Carnea). RIC were added to solution of zinc chloride (10% w/v) at the ratio of 1:1 in the stem to ZnCl₂. The solution was kept at the temperature of 85 °C and stirred for 14 h. The paste was then carbonized at the temperature of 500 °C under closed conditions for 3 h. Excess reagent from the sample after carbonization was removed by washing with distilled water. After washing the material was dried in hot air oven at 110 °C until a constant weight was obtained. This prepared adsorbent was termed as AIC (Activated Ipomoea Carnea) and stored in sealed container for further use.

2.3. Batch adsorption study
A batch study was done to investigate the effect of solution pH, contact time, adsorbent dose, and initial Cd(II) concentration in solution. For the batch study, a known amount of adsorbent was added in aqueous solution (100 mL) in a 250 mL Erlenmeyer flask; shaken in orbital shaker for a predefined time at a constant speed of 100 rpm. The Cd(II) concentration in the solution was determined through UV-visual spectrophotometer at 200 nm wavelength. The removal of Cd(II) and the uptake capacity (qe) were determined by equation (1) and (2), respectively.

\[ % \, Cd(II) \, removal = \frac{c_0 - c_e}{c_0} \times 100 \]  

\[ q_e = \frac{c_0 - c_e}{m}V \]
Where, \( C_0 \) and \( C_e \) are the initial and equilibrium concentrations, respectively. \( V \), volume of aqueous solution and \( m \), adsorbent mass.

3. Results and Discussions

3.1. SEM analysis
Surface micrograph of the prepared adsorbents were obtained by SEM analysis using JOE-JSM-840 field emission SEM. Surface morphology of the prepared adsorbent AIC was compared with the RIC (figure 2). The adsorbent's SEM images showed that the prepared adsorbent had more porous structure compared to raw material, suggesting that the activation process was successful. It can be observed from Fig 2 (a) that RIC has irregular surface with little or no pores. The porous structure of the AIC might have resulted due to degradation of cellulosic compound and aromatization of the carbon after impregnation with ZnCl\(_2\) [14].

![SEM images](image_url)

**Figure 2.** SEM images (a) raw Ipomoea Carnea (b) prepared activated carbon.

3.2. Effect of initial concentration
Figure 3 shows the effect of adsorption parameters on the percent Cd(II) removal and \( q_e \). To examine the effect on adsorption, initial concentration was varied from 5 to 40 mg/L, while other parameters were fixed as adsorbent dose 0.5 g/100mL, initial pH 6 and time 60 min. It can be observed from Figure 3a that both percent removal of Cd(II) and uptake capacity increased with the increase in initial concentration of cadmium in the solution as with increased difference in concentration between adsorbent and solution, the driving force would be high and more Cd(II) ions would have adsorbed on the surface of the adsorbents [15].
3.3. Effect of AIC Dose
As shown in figure 3(b), the adsorbent dose was varied from 0.1 g to 0.7 g per 100 ml of solution. The percent removal of Cd(II) ions increased with increase in adsorbent dose upto 0.3 g/100 mL and after that change was not much significant. With increased dose, the adsorption sites also increased leading to more adsorption of Cd(II)\[16\]. Only slight increase in percent removal after 0.3 g of dose might be due to the non-availability of free ions to be absorbed by the adsorbent for a fixed initial concentration of 20 mg/L. The uptake capacity decreased with increase in adsorbent dose suggesting insufficient use of adsorbent by the Cd(II) ions and the extra mass of adsorbent resulted in lower uptake capacity.

3.4. Effect of Time
Figure 3c shows the change in percent removal of Cd(II) and uptake capacity for variation in contact time from 5 - 90 minutes. The pH, adsorbent dose, and initial concentration were fixed at 6.0, 0.5 g/100 mL and 20 mg/L, respectively. Figure 3(c) shows that adsorption was rapid during the initial 30 min and then it became slow. This can be attributed to large driving force and the more available adsorption sites at initial period of adsorption, later it became slower due to competition of cadmium and hydrogen ions for the available active sites to reach the equilibrium [17].
3.5. Effect of initial pH
The effect of initial pH of solution on Cd(II) adsorption and uptake capacity is presented in figure 3(d).

Initial pH was maintained at 1 to 9 and the other parameters used were time 60 min, dose 0.5 g/100 mL and initial concentration 20 mg/L. It can be noted that both percent removal of Cd(II) and uptake capacity increased with increase in pH up to pH 6, which might have due to lower competition between protons and metal cations at higher pH [18]. Beyond pH 6.0 the Cd(II) ions precipitate in the form of hydroxides, hence decrease in adsorption of Cd(II) at these conditions [19].

3.6. Comparison of AIC and RIC
Figure 4 shows the comparison of RIC and AIC for the percent removal of Cd(II) at different initial metal concentration. It indicates that for the initial concentration up to 0.8 mg/L Cd(II), the performance of AIC was much better than RIC. It advocates that the activation process increases the surface area and porosity of adsorbent. It is evident from the figure that the percent removal by AIC was 95% compared to 89% for RIC after 60 minutes. Goswami and coworkers have also reported a similar higher removal efficiency, such as more than 94% cadmium removal using non-activated Biochar and above 98% removal by KOH activated Biochar obtained from Ipomea Carnea [20].

![Figure 4. Comparison of RIC and AIC for percent removal of Cd(II). (pH-6.0, time-60 min, dose-0.5 g/100 mL).](image)

3.7. Isotherm study
Data obtained from batch adsorption study were fitted to Langmuir and Freundlich isotherms models to understand the mechanism. Langmuir model assumes that the adsorption surface has uniform energy of adsorption and the adsorbed sorbate does not transmigrate in the plane of the surface [21]. The Freundlich isotherm assumes that the surface has the exponential distribution of energies and adsorption sites [3]. Linear equations of the two models are given by equation (3) and (4).

\[
\frac{C_e}{q_e} = \frac{1}{K_L Q_o} + \frac{C_e}{Q_o}
\]  

(3)

\[
\log q_e = \log K_f + \frac{1}{n} \log C_e
\]  

(4)

where, \(Q_o\) (mg/g) is maximum adsorption capacity, \(K_L\) (L/mg) is Langmuir constant related to adsorption energy. \(K_f\) is Freundlich constant related to adsorption capacity and \(n\) is adsorption intensity.

Linear plot of the two models are shown in figure 5 and figure 6 and the parameters are presented in table 1. It was found that data for AIC were best fitted with Freundlich isotherm model with \(R^20.984\)
and the Langmuir model were best fitted to data for RIC with $R^2$ 0.997. This might have due to the effect of modification of Ipomoea carnea.

| Adsorbent | Langmuir | Freundlich |
|-----------|----------|------------|
|           | $Q_0$, mg/g | $K_L$, L/mg | $R^2$ | $N$ | $K_F$ | $R^2$ |
| AIC       | 5.2952    | 2.3387     | 0.9042 | 0.4153 | 33.7119 | 0.9847 |
| RIC       | 1.5447    | 62.6073    | 0.9974 | 1.4622 | 7.6701 | 0.9763 |

**Figure 5.** Langmuir isotherm plot (a) AIC and (b) RIC.

![Langmuir isotherm for AIC and RIC](image)

**Figure 6.** Freundlich isotherm for (a) AIC and (b) RIC

| Adsorbent | Log $q_e$ vs Log $C_e$ |
|-----------|------------------------|
|           | Intercept | Slope | R-Square |
| AIC       | 3.51785    | 2.40755 | 0.98466 |
| RIC       | 2.03733    | 0.68391 | 0.9763 |

**Table 1.** Isotherm parameter obtained from the linear plot of Langmuir and Freundlich isotherm models.

3.8. **Kinetic Study**

Adsorption kinetic studies were carried out by fitting the experimental data of Cd(II) adsorption using AIC by pseudo-first-order (PFO) and pseudo-second order (PSO) kinetic models. Linear form of these two models is given by equation (5) and (6), where $q_e$ is the metal uptake at equilibrium and $q_t$ is the metal adsorbed at time ($t$). $K_F$ and $K_s$ is the rate constant for PFO and PSO kinetic model, respectively. PFO model is based on the assumption that the adsorption rate is proportional to the number of vacant sites of the adsorbate [22]. PSO model is based on the consideration of chemical adsorption as
controlling mechanism for adsorption and related to the concentration of the active sites of the adsorbent surface [23].

\[
\log(q_e - q_t) = \log q_e - \frac{K_F}{2.303} t \\
\frac{t}{q_t} = \frac{1}{K_s q_e^*} + \frac{1}{q_e}
\]

Linear plot of PFO and PSO kinetic models is shown in figure 7 and the table 2 presents the parameters of the kinetic models. Based on the correlation coefficient, the kinetic data was fitted more closely with PSO kinetic model as compared to PFO kinetic model with correlation coefficient of 0.999. Equilibrium capacity of the second order kinetic was close to the Langmuir monolayer adsorbent capacity as compared to the pseudo first order kinetic model, which suggests that process of adsorption started with physisorption and after initial rapid period adsorption process was dominated by chemisorption [24].

| Table 2. Kinetic model parameters for the linear models for the adsorbent AIC. |
|---|---|---|
| **Pseudo-first order model** | **Pseudo-second order model** |
| K_F, h⁻¹ | q_e, mg/g | R² | K_s, g/mg/h | q_e, mg/g | R² |
| 0.0071 | 0.801291883 | 0.897 | 0.164 | 3.78 | 0.999 |

**Figure 7.** Linear plot of (a) PFO and (b) PSO kinetic models.

4. Conclusion

In this study, activated carbon was prepared from the Ipomoea Carnea stem using chemical impregnation with zinc chloride and carbonization. Porous structure of AIC was found to be increased as compared to RIC by surface morphology. Batch adsorption factors pH, time, dose and initial concentration was investigated for the effect on percent removal of Cd(II) and adsorbent capacity of AIC. Adsorbent capacity and percent removal of Cd(II) were increased with increase in adsorption time and initial concentration. Percent removal of Cd(II) was increased and uptake capacity was decreased with increase in adsorbent dose. For both percent removal and capacity, optimum pH was found 6 after that adsorption was decreased. The Langmuir isotherm and Freundlich isotherm provided a best fit description for Cd(II) sorption onto AIC and RIC. Cd(II) adsorption data onto RIC was best fitted to Langmuir isotherm model indicating the physisorption. Cd(II) adsorption onto AIC was best described by combination of physisorption and chemisorption. Kinetic study suggests that the adsorption of Cd(II) ions onto AIC
involves the ion interaction between the cadmium and the surface functional group of the adsorbent. By virtue of the conducted experimental study, it can be concluded that the heavy metal like Cd (II) can efficiently be adsorbed using AIC.

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