

Adsorption of Cd (II) ions from Waste Water using Calotropis Procera as an Adsorbent (PVAC-CP)

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ABSTRACT

The mobilization of heavy metals in the environment due to industrial activities is of serious concern due to the toxicity of these metals in humans and other forms of life¹. The Contamination of water by toxic heavy metals is a world-wide environmental problem. Discharges containing Cadmium, in particular, are strictly controlled due to the highly toxic nature of this element and its tendency to accumulate in the tissues of living organisms². Cadmium is a highly toxic metal that is rather ubiquitous in its distribution in the ecosystem⁵. The major objective of this paper was to investigate the removal of Cadmium (II) from synthetic wastewater using poly vinyl alcohol coated activated carbon prepared from leaves of Calotropis Procera (PVAC-CP) an unconventional adsorbent. The dried leaves of calotropis procera plant were used at different adsorbent/metal ion ratios. The influence of pH, contact time, metal concentration, and adsorbent loading weight on the removal process was investigated. Batch adsorption studies were carried out at room temperature. The results showed removal of 88.1% of Cadmium in the 60 ppm Cadmium solutions, the adsorbent required at saturation was 15g/L. Kinetic experiments revealed that the dilute Cadmium solutions reached equilibrium within 120 min. The adsorptive capacity of the Calotropis Procera was dependent on the pH of the cadmium solution, with pH 6 being optimal. Removal efficiency increased with an increase in contact time before equilibrium is reached. The adsorption data fit well with the Langmuir and Freundlich isotherm models. This research focuses on understanding adsorption process and developing a cost effective technology for treatment of heavy metals-contaminated industrial wastewater. Comprehensive characterization of parameters indicates Calotropis Procera to be a good material for adsorption of Cd (II) to treat wastewaters containing low concentration of the metal.

Keywords: *Water Pollution, Wastewaters, Heavy metals, Calotropis Procera, Adsorption isotherms*

1. INTRODUCTION

The mobilization of heavy metals in the environment due to industrial activities is of serious concern due to the toxicity of these metals in humans and other forms of life¹ Removal of toxic heavy metals from industrial waste waters is essential from the stand point of environmental

pollution control. Industrial wastewater particularly in electroplating metal finishing industry, chemical manufacturing and battery manufacturing industries is an important pathway for entry of heavy metals in the environment¹⁷. Heavy metals are common pollutant found in various industrial effluents. The stricter environment regulation on the discharge of heavy metals make it necessary to develop various technologies for the removal⁷. Heavy metals cannot being metabolized and bio-accumulate in organism body. Discharge and treatment of industrial wastewater containing heavy metals and precise identification of the actual sources of heavy metal contamination of water resources is urgent, due to the acute, severe, and persistent impacts of these pollutants on human health and on the sustainability of ecosystems are important issues in environmental protection.¹⁶ Heavy metal toxicity can result in damage or reduced mental and central nervous function, lower energy levels and damage to blood composition, lungs, kidneys, liver and other vital organs. Presence of heavy metals in water streams and marine water causes a significant health treat to the aquatic community – most common being the damage of the gill of the fish. Many toxic heavy metals have been discharged into the environment as industrial wastes, causing serious soil and water pollution¹¹. Pb+2, Cu+2, Fe+3, and Cr+3 are especially common metals that tend to accumulate in organisms, causing numerous diseases and disorders¹². Cadmium (Cd), which is widely used and extremely toxic in relatively low dosages, is one of the principle heavy metals responsible for causing kidney damage, renal disorder, high blood pressure, bone fraction and destruction of red blood cells. The permissible limit for Cd(II) as described by WHO is 0.01 mg/dm³. Numerous processes exist for removing dissolved heavy metals, including ion exchange, precipitation, phytoextraction, ultrafiltration, reverse osmosis, and electro dialysis¹³⁻¹⁴. Adsorption of heavy metal ions onto activated carbon has been applied widely as a unit operation in the treatment of industrial wastewater. In recent years considerable attention has been devoted to develop surface modified carbons from locally available materials for the treatment of heavy metal-bearing wastes⁶. The removal of heavy metal ions from industrial wastewaters using different adsorbents is currently of great interest.

Preparation of Poly Vinyl Activated Charcoal from Calotropis Procera (PVAC-CP): The naturally dried leaves of the plant Caltropis procera obtained locally. It cut into small pieces. The leaves treated with concentrated sulphuric acid (five times its volume) and kept in oven at 150°C for 24 hours. It filtered and washed with distilled water repeatedly to remove sulphuric acid (washings tested with two drops of barium chloride solution) and finally dried. The adsorbent sieved to 40-60-mesh size and heated at 150 °C for 2 hours. 1 gm of PVA dissolved in 10ml hot water (10% solutions) as a result gel formation occurs. Now 2.5gm of furnace black added in it to form a thick paste. This paste mixed with activated carbon obtained from the leaves of the plant Caltropis procera. Now the thick paste obtained, and then dried to form lumps. The lumps further

ground into fine powder. This powder used as an adsorbing material. When 2.5gm furnace black used the results were better

Preparation of Cd (II) solution: A stock solution of cadmium (2mg/ml) was prepared by dissolving Cd (NO₃)₂·4H₂O in 0.1M HNO₃. The solution was standardized complex metrically with EDTA (disodium salt) using Xylenol orange indicator.

Adsorption isotherms -Two important physiochemical aspects for the evaluation of the adsorption process as a unit operation are the equilibria of the adsorption and the kinetics. Equilibrium studies give the capacity of the adsorbent¹⁸. The equilibrium relationships between adsorbent and adsorbate are described by adsorption isotherms, usually the ratio between the quantity adsorbed and that remaining in solution at a fixed temperature at equilibrium. There are two types of adsorption isotherms : Langmuir adsorption isotherms and Freundlich adsorption isotherms. Each adsorption studies were carried out to study the effect of pH (3,4,5,6,7and 8), contact time (15-150 min), adsorbent dose (3-18 g/l) and initial metal ion concentration (50-150mg/l) at room temperature using stopper bottles. The initial pH of solution was adjusted by using 0.05 N HCl or 0.1N NaOH without changing the volume of the sample. After agitating the sample for the required contact time, the contents were centrifuged and filtered through whatman No.41 filter paper and unreacted chromium and cadmium (work was done separately for both ions) in the filtrate was analyzed spectrophotometrically. The removal efficiency (E) of adsorbent was defined as:

$$E (\%) = [(C_o - C_e) / C_o] \times 100$$

Where C_o and C_e are the initial and equilibrium concentration of metal ion solution (mg/l), respectively.

Langmuir isotherm:- The Langmuir equation was chosen for the estimation of maximum adsorption capacity corresponding to complete monolayer coverage on the adsorbent surface (Langmuir, 1918). This model is based on following assumptions:-

- 1)Metal are chemically adsorbed at a fixed number of well define sites;
- 2)Each site can hold only one ion;
- 3)All sites are energetically equivalent & there is no interaction between the ions

The saturation of monolayer can then be represented by the expression:

$$C_e/q_e = 1/Q_{mb} + C_e/Q_m$$

Where, C_e is equilibrium concentration (mg/l), q_e is the amount at equilibrium time per unit adsorbent (mg/g) .

Q_m and b is Langmuir constants related to adsorption capacity (maximum specific uptake corresponding to the site saturation) and energy or intensity of adsorption respectively. They can be evaluated from the slope and intercept of linear equation. The plot of C_e/q_e Vs C_e gives a straight line relationship indicating the applicability of Langmuir Isotherm. The essential characteristics of the Langmuir Isotherm can be expressed in terms of a dimensionless constant, Separation factor or equilibrium parameter R_L that defined as $R_L = 1/(1+b C_0)$

This parameter indicates the shape of the isotherm as follows:

If R_L value Type of isotherm

$R_L > 1$ Unfavorable

$R_L = 1$ Linear

$R_L < 1$ Favorable

$R_L = 0$ Irreversible

Values of dimensionless equilibrium parameter R_L show the adsorption to be favorable ($0 < R_L < 1$). The Langmuir and Freundlich constants increase with the rise in temperature.

Freundlich adsorption isotherm:-The Freundlich isotherm is the earliest known relationship describing the heterogeneous adsorption equilibria and the adsorption equation is expressed as: (X/m) or $q_e = K_f C_e^{1/n}$

This equation is conventionally used in the linear form by taking the logarithmic of both sides as: $\log q_e = \log K_f + 1/n \log C_e$

Where: q_e = the amount of the adsorbate adsorbed per unit mass of adsorbent (mg adsorbate/g adsorbent); X = the amount of the adsorbate; m = mass of adsorbent used (g); K_f = adsorption capacity. (higher the K_f value becomes the greater the adsorption intensity); n = adsorption intensity are (the empirical constants) dependent on several environmental factors. The values of $1/n$, less than unity is an indication that significant adsorption takes place at low concentration but the increase in the amount adsorbed with concentration becomes less significant at higher concentrations and vice versa. The values of n between 1 to 10 represent beneficial adsorption. The equilibrium concentration was calculated using following formula: $C_e = C_0 - (\% \text{ adsorption} \times C_0 / 100)$

C_0 = initial concentration of adsorbate (mg/l) C_e = equilibrium concentration of adsorbate (mg/l).

2. RESULTS AND DISCUSSION

Effect of contact time: In adsorption system, the contact time play a vital role irrespective of the other experimental parameters, affecting the adsorption kinetics. Figure-1 depicts that there was an

appreciable increase in percent removal of of cadmium 120 thereafter further increase in contact time the increase in removal was very small. Thus the effective contact time (equilibrium time) is taken as 120 min.for Cd (II) and it is independent of initial concentration.

Effect of pH: The influence pH of solution on the extent of adsorption of adsorbent material used is shown in figure-2 .The removal of metal ions from solution by adsorption is highly dependent on the pH of the solution. It was found that 85.2 % removal of Cd (II) achieved at pH 6 and there after the percent removal decreases with increases in pH as 7and 8. Thus the optimum adsorption pH for Cd (II) removal was found to be 6

Effect of adsorbent dose: The effect of adsorbent dose on percent removal of cadmium is shown in figure-3 Adsorbent dose was varied (3,6,9,12,15,18 g/L) and performing the adsorption studies at pH 6 The present study indicated that the amount of Cd(II) adsorbed on (PVAC-CP) increase with increase in the dose upto 15g/l and thereafter further increase in dose the increase in removal was very small. Thus the effective dose is taken as 15 g/L

Effect of Adsorption Capacity: Adsorption capacity increased with the initial concentration of asorbate studied as shown in figure- 4 To obtain the maximum adsorption capacity of (PVAC-CP) for metal ions of interest, we increased the initial concentration of metal ions up to 150ppm. The maximum adsorption capacities found were as follow: 3.432 mg Cd (II)/g (PVAC-CP).

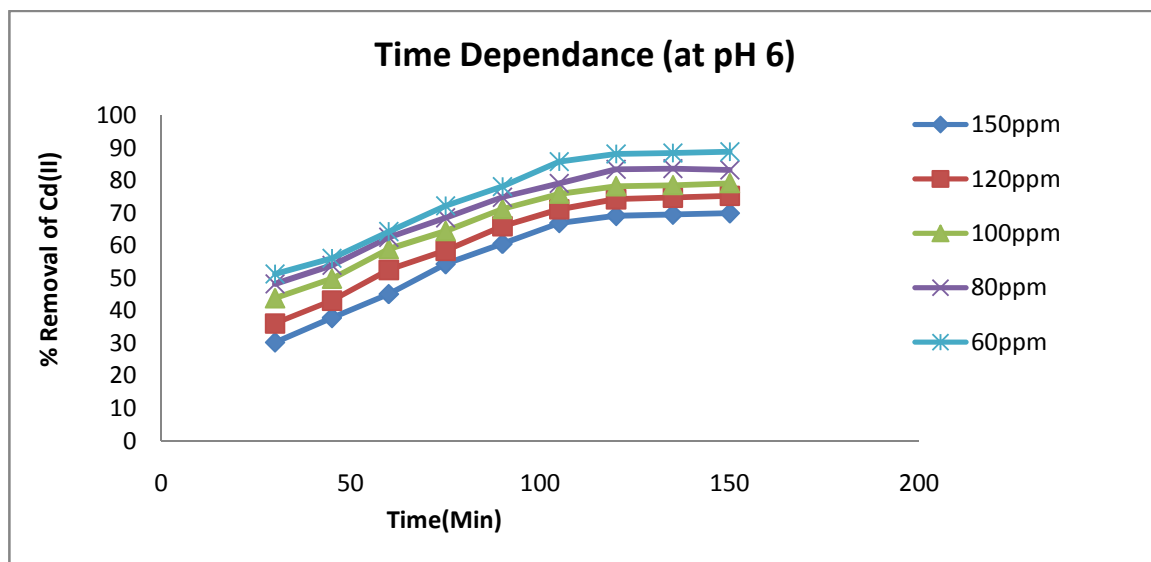


Figure1: Effect of contact time on removal of Cd (II) at different concentration by PVAC-CP at pH 6.

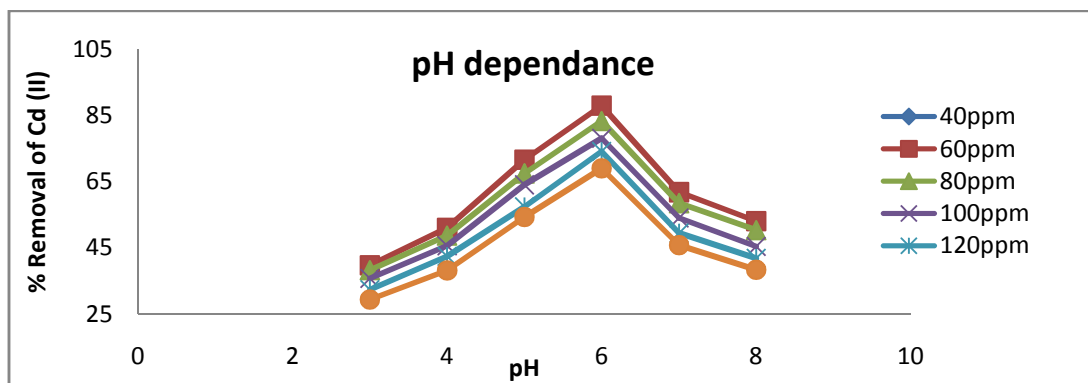


Figure 2: Effect of pH on removal of Cd (II) at different concentrations by 15 g/L of PVAC-CP at constant contact time 120 min.

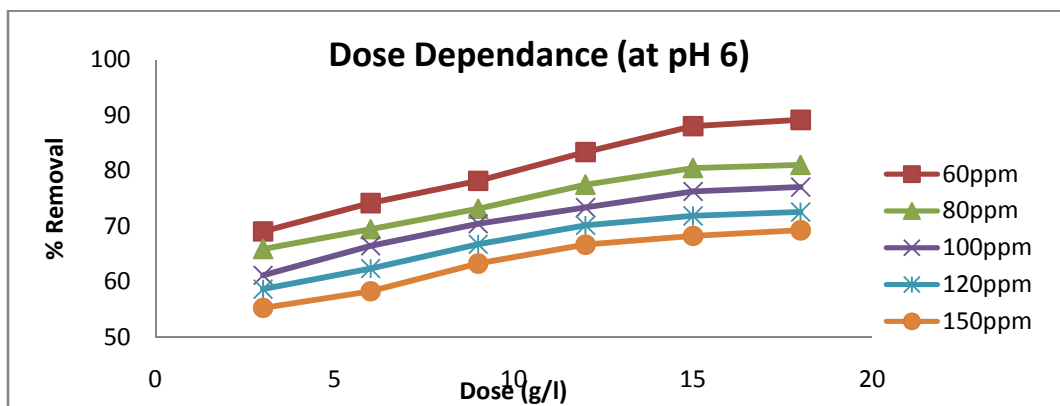


Figure 3 : Effect PVAC-CP dose on percent removal of Cd(II) at equilibrium contact time 120min. and effective at pH 6.

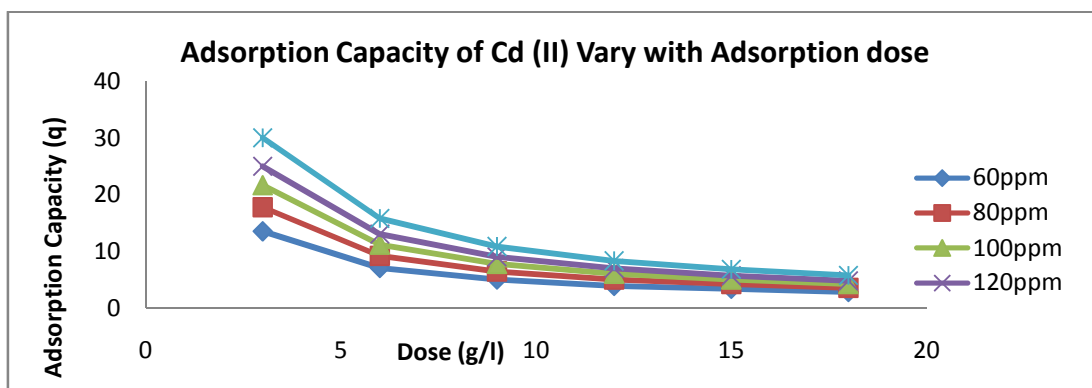


Figure 4 :Effect of initial concentration of Cd (II) on adsorption capacity at equilibrium contact time 120 and at effective pH 6

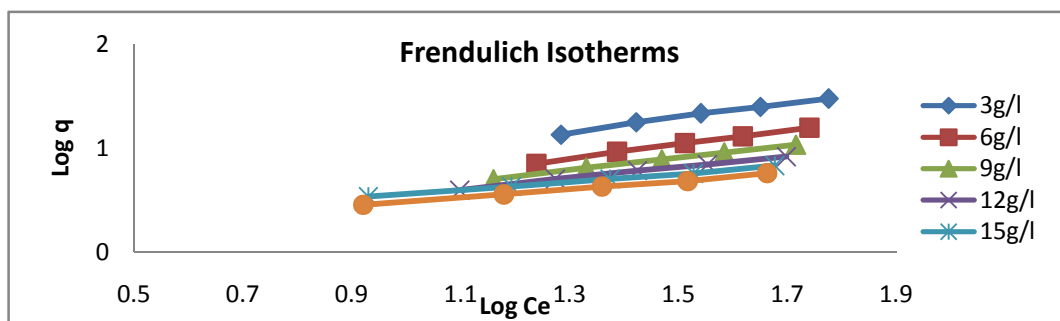


Figure 5 : Freundlich Isotherm plot for Cd(II) adsorption by PVAC-CP at optimum conditions.

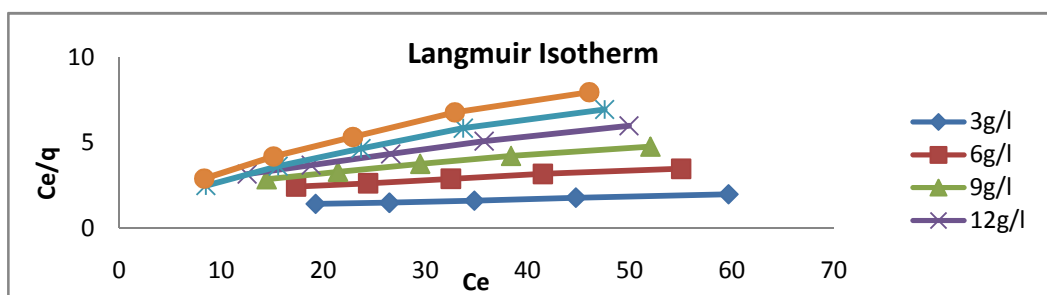


Figure 6 : Langmuir Isotherm plot for Cd(II) adsorption by PVAC-CP at optimum conditions.

Table -1

Langmuir and Freundlich constants for adsorption of Cd(II)

Dose (gm/l)	Freundlich isotherm (linear equation)	Langmuir isotherm (linear equation)	R ² Freundlich	R ² Langmuir
15	Y=0.3948X+0.1645	Y= 0.1142X+1.7712	0.9973	0.9822

Dose (gm/l)	Freundlich constants			Langmuir constants		
	Kf	n	c	Qm (mg/g)	b(l/ mg)	R _L
15	1.46049	2.532928	0.1645	8.756567	0.064476	0.99614

3. CONCLUSION

This study indicates that PVAC-CP has rapid adsorption rate and good adsorption capacity for Cd. The Cd⁺² adsorption was found to be dependent on initial Cd concentration, contact time, pH, temperature and amount of adsorbent.

The adsorption of Cadmium follows Freundlich and Langmuir isotherm models. Maximum adsorption 88.1 % of Cd occurred at pH 6 and the effective dose is taken as 15 g/L and The maximum adsorption capacities found were as follow: 3.432 mg Cd (II)/g (PVAC-CP). Since Calotropis Procera plant are highly abundant and can be easily synthesized at relatively low cost, the adsorbent could be applied for the removal of Cadmium from wastewaters.

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