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Removal of Pb (II) and Cd (II) ions from Industrial waste water using *Calotropis Procera* roots

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ABSTRACT: *The adsorption of Pb (II) and Cd (II) on calotropis procera has been studied using UV* ***spectrometer to estimate metal*** *analysis. Parameter like Heavy metal concentration, adsorbent dose, contact time and agitation speed were studied. Langmuir and Freundlich isotherm were employed to describe adsorption equilibrium. The* ***significant study*** *of this paper is the utilization of low cost adsorbent available in abundance for the removal of heavy metal ion from dilute aqueous solution.*

Keywords: *Adsorption, Freundlich isotherm, Heavy metal, Langmuir isotherm.*

I. INTRODUCTION

Rapid industrialization is the major cause of inclusion of heavy metals into the environment particularly in the water bodies all over the world. Heavy metal ion contamination of aqueous stream is becoming a serious threat to aquatic system, because of their high toxicity even at very low concentration. Heavy metals ions released by number of industrial processes are the major pollutants in marine, ground, industrial and **even in treated waste** waters. However they can be extremely toxic because they damage nerves, liver, kidney, bone and also block functional groups of vital enzyme.

A conventional method used for removing metals from industrial effluent includes chemical precipitation, coagulation, solvent extraction, electrolysis, membrane separation, ion exchange and adsorption [1] but due to high cost of the materials these methods are not generally used. Therefore, recently very innovative and cost effective methods are used for the removal of toxic substances from waste water. Biosorption **is an effective** and versatile method and can be easily adopted to remove heavy metals **from the** large amount of industrial waste water [2]. Recent studies shows that heavy **metals can be removed** using plant materials such as palm pressed fiber and coconut husk [3] lignocellulosic substrate extracted from wheat bran [4], cork and yohimbe bark waste [5] and leaves of indigenous biomaterials tridax procumbens [6].

Apart from that plant based material chemical modification of various adsorbents, phenol formaldehyde cationic matrices [7], polyethylonamid modified wood [8], and sulphur containing silica gels [6], and commercial activated charcoal are utilized [9].

The toxic heavy metals Cu (II) and Zn (II) were successfully removed using *calotropis procera* by Hifsa Mubeen et al. [10] and Vaishnav Vinod et al [11] respectively. The aim of present work is to study the removal of Lead (Pb) and Cadmium (Cd) ions by modified shrub *calotropis procera* roots materials from synthetic solution, and the maximum adsorption capacity of adsorbent, adsorption intensity of the adsorbate on adsorbent surface and adsorption potentials of adsorbent were estimated by Langmuir and Freundlich isotherms [12-14], respectively. The change in metal ion concentration due to adsorption was carried out using UV-Vis-NIR spectrophotometer PerkinElmer (Lampda 35).

II. MATERIAL AND METHODS

2.1. Preparation of Biomass:

The biomass was collected from the local shrub roots in Thirubuvanam village, Papanasam (T.k), Thanjavur (Dt). The bio mass was extensively washed with running tap water for 30 to 40 minutes to remove dirt and particulate matter followed by washing in double distilled water. The outer part of the root was removed and cut into the small pieces. The pieced bio mass was then immersed in 1:1 HCl solution for 10 minutes and then washed with double deionized water and was finally put in an electric oven at 60°C for two hours.

Afterward the biomass kept at a temp of 45 °C for overnight. The dried biomass was ground in a lab blends and sorted using standard test sieves.

The following operating condition such as pH, adsorbent amount, contact time, and metal ion concentration were investigated.

2.2 Chemical and Reagent

The stock solution containing the 1000 mgL^{-1} concentration of Lead and cadmium were prepared by dissolving Lead nitrate, and Cadmium chloride in milli Q water. The salts of these chemicals were of analytical grade, procured from s.d.fine.chem limited, Mumbai.

2.3 Metal analysis

The change in Pb(II) ion concentration due to adsorption was determined by UV-vis spectrometer. A brick red color soluble complex was developed by diphenylthiocarbazone in the presence of ammonia in alkaline condition. Absorbance was measured at wavelength 530 nm.

The percentage of Pb ion removal due to bioadsorption was calaculated as % Pb as removal =$[C_o$-$C_i/C_o]$ x 100 %, where C_i and C_o are the initial and final concentration of Pb (II) solution (mg/L) respectively.

2.3.2 Cd (II) ion determination

The change in Cd ion concentration due to adsorption was determined by UV-VIS spectrometer. A violet colour was developed by diphenyl carbazide in acidic condition. Absorbance was measured at wavelength 540 nm. The percentage of Cd ion removed due to bioadsorption was calculated as % Cd as removal =$[C_o$-$C_i/C_o]$ x 100 %, where C_i and C_o are the initial and final concentration of Cd (II) solution(mg/L) respectively.

2.4 Study of process parameter

The effect of four parameters, Heavy metal concentration, adsorbent dose, contact time, and agitation speed were studied. To study the effect of certain parameter, that parameter has been changed progressively keeping the other three constant .After adsorption content of the flasks were filtered and filtrate were subjected to add suitable reagent for absorption of UV-vis- Spectrometer.

2.5 Study of adsorption Isotherm

Varying metal ion solution with concentration 30, 50, 60 and 90 gmL^{-1} were made by proper dilution of stock solution of Lead and Cadmium. p^H was adjusted to 4-8. 1.5 g of biosorbent was added to 50 mL of each metal solution and was agitated for half an hour. At the end it is filtered and the filtrate with added suitable reagent was analyzed for metal ion by UV-visible spectrophotometer.

2.6 Assessment of sorption performance

Langmuir (eq(1)) ,Freundlich (eq-2) isotherm were plotted by using standard straight line equation and corresponding two parameters for lead (II) and Cadmium (II) ion were calculated from their respective graphs.

$$\frac{1}{qe} = \frac{1}{q\max} + \left(\frac{1}{q\max.b}\right)\left(\frac{1}{Ce}\right) \qquad \text{….. (1)}$$

$$\ln qe = \ln kf + \left(\frac{1}{n}\right)\ln Ce \qquad \text{…. (2)}$$

qe (mg g^{-1}) is the amount of metal adsorbed and Ce (lg mL^{-1}) is concentration at equilibrium. qm (mg g^{-1}) and b (L g^{-1}) are Langmuir isotherm parameter. 'KF' and 'n' are Freundlich isotherm parameters.

III. RESULTS AND DISCUSSIONS

3.1 Effect of Initial ion concentration

Effect of Pb (II) and Cd (II) ion concentration was studied by varying the metal ion concentration from 1 to 10 mg/L with 0.5 g of adsorbent, at contact time of 30mins. There is an increase in the adsorption and then it was stable (Fig. 1). The decrease in percentage biosorption may be **caused** by the lack of sufficient surface area to accommodate more Lead and Cadmium ions available in the solution.

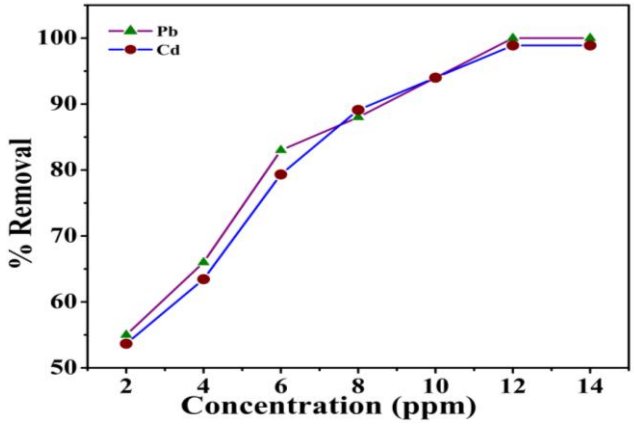


Fig.1 Effect of concentration on the adsorption of Pb and Cd by *calotropis procera*

3.2 Effect of adsorbent dosage

Effect of adsorbent dosage on adsorption of Lead and Cadmium is studied by changes the biosorbent dosage from 0.5 to 5g and there is no change in other parameter like initial concentration .The contact time was 30mins for Pb and Cd as stated earlier. **The graph has shown** an increase in the biosorption percentage as dosage of biosorbent **increases to certain level and then decreases** (Fig. 2). This is because of the availability of more binding sites in the surface of the biosobent for complexation of Lead and Cadmium ions.

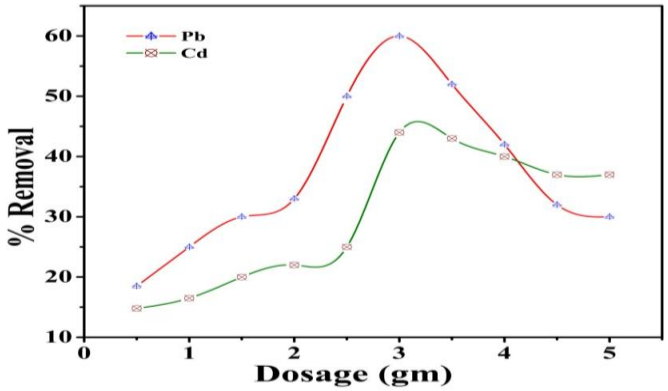


Fig. 2 Effect of dosage on the adsorption Pb and Cd by calotropis procera

3.3 Effect of Contact Time

Contact time profile for the biosorption of Lead for a solution of 90 mg/L and 80 mg/L is shown in the data obtained from the biosorption of Lead and Cadmium ions on the calotropis procera showed that a contact time 90 mins is needed to achieve equilibrium and the biosorption **decreased** significantly with further increase in contact time **(Fig. 3).**

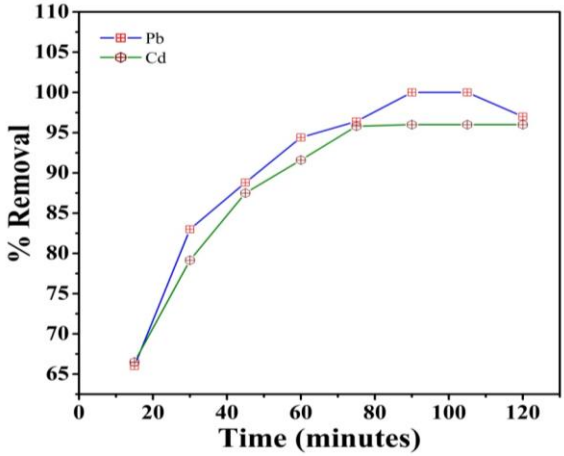


Fig. 3 Effect of time on the adsorption Pb and Cd by *calotropis procera*

3.4 Effect of Agitation speed

The agitated speed varied from 100 to 400 rpm is carried out with a magnetic shaker. As agitation rate on adsorption increased from 100 to 400 rpm, adsorption capacity of *calotropis procera* **increased** and then **decreased** (Fig. 4). The effect of increasing the agitation rate was to decrease the filter resistance to mass transfer surrounding the adsorbent particle.

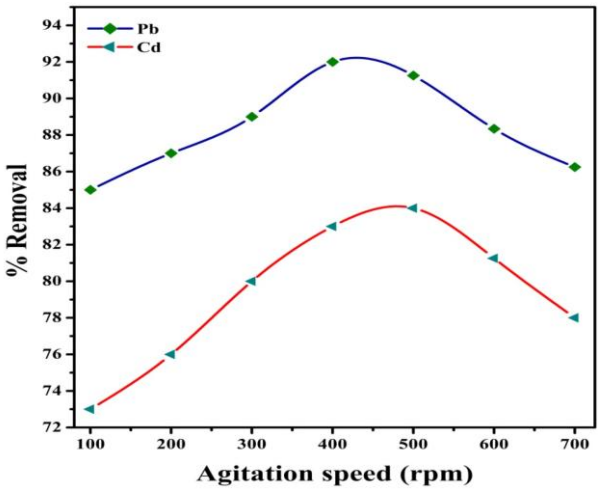


Fig. 4 Effect of agitation speed on the adsorption Pb and Cd by *calotropis procera*

3.5 Adsorption Isotherm

The equilibrium data of adsorption are in good agreement with Langmuir and Freundlich adsorption isotherm. Value of equilibrium parameter RL from a(lg mL^{-1}) is concentration at equilibrium, qm (mgg^{-1}) and b (Lg^{-1}) one Langumuir Isotherm parameters 'KF' and 'n' are Frendlich isotherm parameters. The values of Langmuir and Freundlich parameters for the removal of both Pb (II) and Cd (II) metal ions are shown in the figure 5 and 6. The correlation coefficient R^2 for the biosorption Pb (II) and Cd (II) are 0.9734 and 0.96131 respectively. The linearity of the two plots Fig-5 (a) and (b) indicate application of the Langmuir equations, supporting monolayer formation of the surface of the biosorption.

The Freundlich expression is an empirical equation based on heterogeneous surface. The variable qe and Ce are the amount of metal ion adsorbed and the equilibrium metal ion concentration in solution. The Freundlich biosorption models are shown in Fig. 6. The correlation coefficient R^2 for the biosorption Pb (II) and Cd (II) are 0.99961 and 0.97887 respectively. It is also observed that the Freundlich isotherm modelfig- 6(a) and (b) were well fitted for two metal ions.

Fig. 5 (a) Langmuir isotherm Pb by calotropis procera

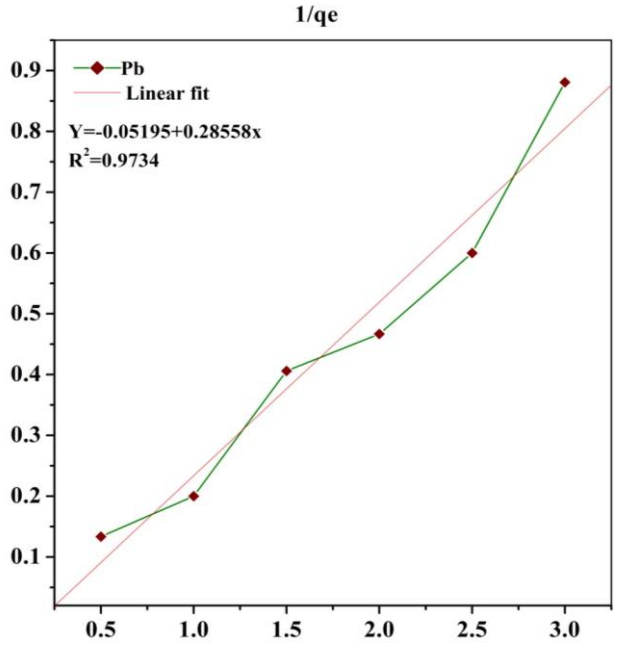


Fig. 5 (b) Langmuir isotherm Cd by *calotropis procera*

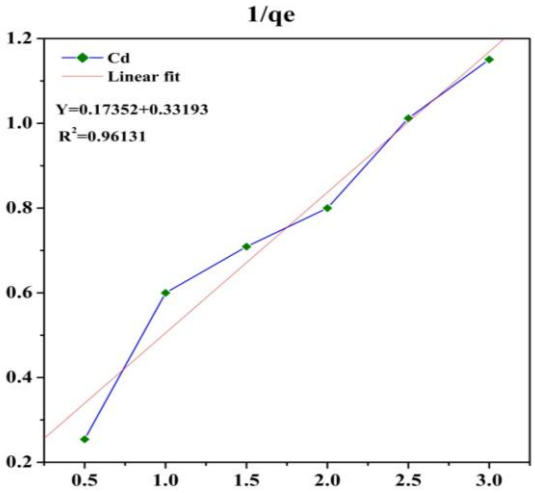


Fig. 6 (a) Freundlich isotherm Pb by *calotropis procera*

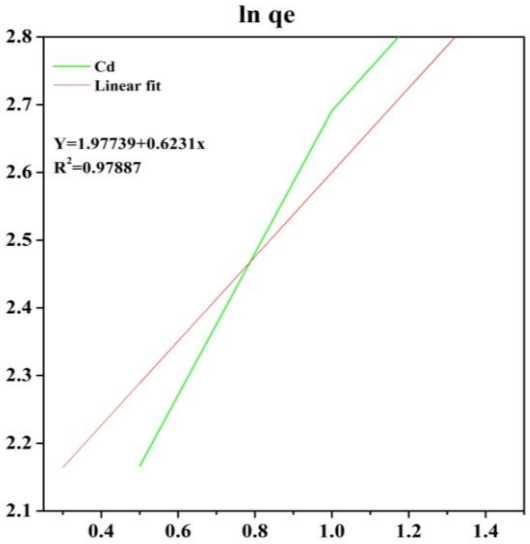
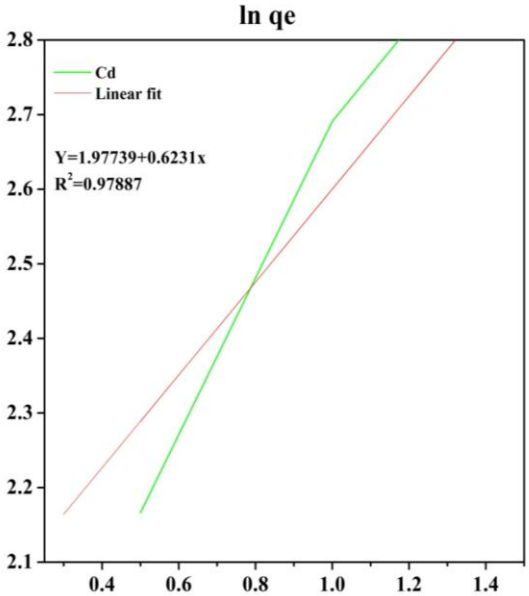


Fig. 6 (b) Freundlich isotherm Cd by *calotropis procera*



IV. CONCLUSION

In this study the adsorption behavior of Pb (II) and Cd (II) onto *Calotropis Procera* roots were **investigated** in the batch experiment. The adsoption was found to be drastically **depending** on initial metal ion concentration, adsorption dosage, contact time and agitation speed. Further more the equilibrium data of adsorption are in good agreement with the models of Freundlich and Langumir. This **adsorption can be a good** choice for adsorption of not only Pb (II) and Cd (II) ions but also other heavy metal ion in waste water stream.

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