

An Experimental Investigation on Biosorption of Cadmium by *Erythrina Variegata Orientalis* as an Adsorbent

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Abstract— An unauthorized activity of releasing harmful contaminants arising from domestic, municipal and industrial establishments into the environment is continuing unabated due to expensive treatment process and ineffective implementation of environmental legislation. In developing countries with the result there is a study increase in concentrations of pollutants sometimes reaching alarming levels and causing serious human health hazards of the life, sustaining water resource due to release of industrial effluents is one of the serious environmental problems encounter today. In the present work an attempt is made to study to effect of parameters like p^H , temperature, time of contact, biosorbent dosage, size of biosorbent etc. on removal of Cadmium and determination of equilibrium, kinetics and thermodynamic parameters in a batch biosorption of cadmium by the leaf powder of *Erythrina Variegata Orientalis* as biosorbent.

IndexTerms—Biosorption,pollutants,cadmium, environmental issues.

I. INTRODUCTION

Water is the most essential requirement in daily life that has been contaminated by the disposal of domestic, municipal and industrial wastes. Anything, which is not needed, finds its way to the nearest watercourse or land, which further pollutes the ground water. Though 80% of the earth's surface is covered by water, but only small part is available for drinking, agriculture, domestic and industrial purposes. So, there is a need to utilize the available resources effectively without polluting the water. The discharge of non-biodegradable heavy metals into water is a major concern because they tend to accumulate in living organisms, causing various diseases and disorders thereby interfering with the designated best use of water. It is well perceived that there is permissible limit of each metal, above which they are generally toxic and some forms are even fatal to human and animal beings. Keeping in view of these problems, strict environmental regulations on the discharge of heavy metals have been laid by Pollution Control Board. These laws make it necessary to develop efficient technologies for removal of heavy metals. The harmful effects of these pollutants have been identified since long, but only recently, the public concern has led to the enforcement of strict legislative laws governing the discharge of toxic pollutants. This act has provisions for controlling pollution caused by

industries or communities so as to meet even the minimum standards for any function and purpose. The trace metals are divided as heavy metals and light metals on the basis of their densities. The metals having density above 5gm/cc are called heavy metals. Trace metals are of environmental interest both as limiting nutrients and as toxins.

Toxic heavy metals include cadmium, mercury, silver, lead, tin and chromium, although several nutrient metals, notably zinc, copper and nickel, are toxic at elevated concentrations. The industrial and domestic wastewater, if not properly managed, is responsible for severe damage to the environment and adversely affecting the health of the people. The major resources of consumption of cadmium are: Ni-Cd batteries (79%), cadmium pigments (11%), cadmium stabilizers (2%), cadmium coatings (7%) and cadmium alloys and others (1%). Prolonged exposure to bivalent cadmium plating baths causes serious toxicity problems. The presence of cadmium in the body causes hypertension, emphysema, renal cancer, prostate cancer, kidney disease, bones problem and human carcinogen. The allowable cadmium concentrations specified for different purposes are: <2 mg/L for inland surface water and < 0.01 mg/L for drinking water. It is Herculean task to purify the effluent before discharging it into the environment. Several methods such as precipitation, filtration through lime stone beds, ion exchange, reverse osmosis, evaporation, electro-dialysis and chelating polymer are available for the removal of cadmium from industrial effluents. The capital and operating costs for the removal of metals using these methods is very high. Adsorption also plays an important role in the removal of metals from the effluents. Present work is extension study of the different parameters with different values [5].

II. MATERIALS AND METHODS

Preparation of adsorbent

Mature *Erythrina variegata orientalis* leaves collected from nearby places and are washed with water to remove dust and used for the experimental study for measuring the parameters like pH, adsorbent dosage, adsorbent concentration and kinetic, temperature effects.

Preparation of Cadmium stock solution

2.135 gm of 99% $3CdSO_4 \cdot 8H_2O$ is dissolved in 1L of distilled water to prepare 1000 mg/l of cadmium stock solution. 80ml of 1000mg/l cadmium stock solution is taken in a 1000 ml volumetric flask and made up to the mark with distilled water to obtain 81 mg/l of cadmium concentration. Similarly cadmium solutions with other metal concentrations such as 23mg/l, 44mg/l, 65mg/l, 117mg/l, 144mg/l and 188mg/l are prepared. The pH of the aqueous solution is varied by adding required amounts of 1N H_2SO_4 and 1N NaOH.

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Studies on Equilibrium, Kinetics and Thermodynamics of Adsorption

The initial concentration of cadmium in the aqueous solution is analyzed in an Atomic Absorption Spectroscopy (AAS) and found to be 81 mg/l. The procedure adopted for the removal of cadmium is as follows. 50 ml of aqueous solution is taken in a 250 ml conical flask and 0.5 gm of 53µm size biomass is added. This sample is shaken on an orbital shaker at 160 rpm at room temperature (303 K) for 1 min. Similarly 15 more samples are prepared in conical flasks adding 0.5gm of 53µm size adsorbent and exposed to varying agitation times (2, 3, 4, 5, 10, 20, 30, 40, 50, 60, 120, 180, 240, 300 and 360 min).

These samples are filtered separately with 40 no. Whatman filter papers and the filtrates are analyzed in AAS to obtain final concentrations of cadmium. The same experimental procedure is repeated with other adsorbent sizes (106 and 212 µm) for various agitation times and for other dosages (1.0, 1.5, 2.0 and 2.5 gm). The percentage removal of cadmium is calculated as $(C_0 - C_t) \times 100 / C_0$. From these data, the optimum agitation time, particle size and dosage are identified. The experiments are repeated at these optimum values by varying the initial concentrations of cadmium in the aqueous solution, volume of the aqueous solution, pH of the aqueous solution and temperature of the adsorption.

III. RESULTS AND DISCUSSION

Effect of Agitation Time

The optimum agitation time is determined by plotting the % removal of cadmium against agitation time in fig.1 for different dosages. The % removal is found to increase up to 50 min and thereafter, negligible increase in % biosorption is noticed with agitation time. Duration of adsorption equilibrium is defined, as the time required for heavy metal concentration to reach a constant value during adsorption. The rate of biosorption is fast in the initial stages up to 20 minutes because adequate surface area of the adsorbent is available for the biosorption of cadmium. As time increases beyond 20 minutes, more amount of cadmium is adsorbed onto the surface of the adsorbent and surface area available decreases. The adsorbate, normally, forms a thin one molecule thick layer over the surface. When this monomolecular layer covers the surface, the capacity of the adsorbent is exhausted. So, the % removal of cadmium has become constant after 50 min. Different equilibrium agitation times were reported in literature. Agarwal et al (1) obtained equilibrium agitation time at 30min with manganese nodule residue as an adsorbent for the removal of cadmium. Bayat (2 & 3) obtained 2 hours as

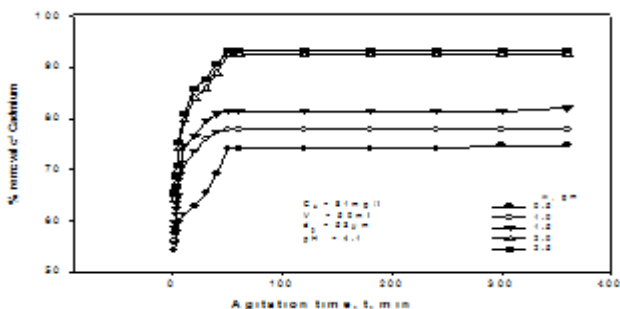


Fig.1 Effect of agitation time on % removal of Cadmium

equilibrium agitation time with the adsorbent Turkish fly ash

for the removal of cadmium and cadmium - zinc mixture from aqueous solutions. 4 hours equilibrium agitation time was reported by Veeraraghavan and Mathalagan [14] with the adsorbent vermiculate.

Effect of Adsorbent Size

The variations in % removal of cadmium with particle sizes (53µm, 106µm and 212µm) are obtained at different biomass dosages of 1.5, 2 and 2.5 gm at the optimum agitation time. The results are drawn in fig.2 with % removal of cadmium as a function of adsorbent size. The percentage removal of cadmium is increased from 87.03% to 92.59 % as the particle size decreases from 212 to 53 µm. This phenomenon is expected, as the size of the particle decreases, surface area of the adsorbent increases, thereby the number of active sites on the biomass are better exposed to the adsorbate. For manganese nodule residue adsorbent Agarwal and Sahu [1] results obtained percentage removal of Cadmium is increased from 85.23% to 98.1% as the particle size 0.053 to 0.152 mm.

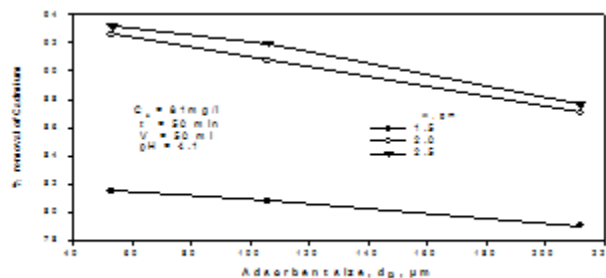


Fig.2 Variation of % removal of Cadmium with adsorbent size

Effect of Adsorbent Dosage

The percentage removal of cadmium is drawn against adsorbent dosage for different adsorbent sizes in fig.3. It is evident from the plots that the percentage removal of metal from the aqueous phase increases with increase in the adsorbent dosage. The % removal of cadmium increases from 74.1 % to 93.2 %, for the adsorbent size 53 µm, as dosage is increased from 0.5 to 2.5 gm. Such behaviour is obvious because the number of active sites available for metal removal would be more as the amount of the adsorbent increases. The change in % removal of cadmium is marginal when 'w' is increased from 2 gm to 2.5 gm. Similar to the present work, was reported for the adsorbent activated carbon Madava rao et al (4) % removal of cadmium is increased with increasing the adsorbent dosage from 0.5 gm to 10 gm.

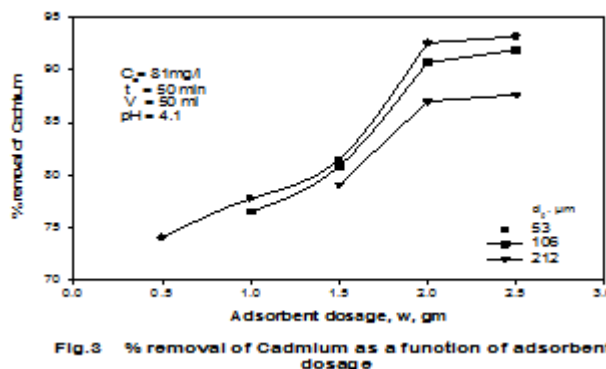


Fig.3 % removal of Cadmium as a function of adsorbent dosage

Effect of Initial Concentration of Cadmium in the Aqueous Solution

The effect of initial concentration of cadmium on the

percentage removal of cadmium is shown in fig.4 for different temperatures. The percentage removal of cadmium is decreased from 98.7 % at 333 K to 86.2 % at 283 K by increasing the initial concentration of cadmium from 23 mg/l to 188 mg/l. Such behaviour can be attributed to the increase in the amount of adsorbate to the unchanging number of available active sites on the adsorbent, since the amount of adsorbent is kept constant. From the reference of Agarwal and sahu [1] manganese nodule residue as adsorbent results are obtained % removal of Cadmium is decreased from 99.75% to 85% by increasing the concentration of cadmium from 100 to 500 mg/l. Similarly % removal of Cadmium is decreased from 95% to 82% by increasing the concentration of cadmium from 10 to 400 mg/l by a Heechancho et al [7] using adsorbent is fly ash.

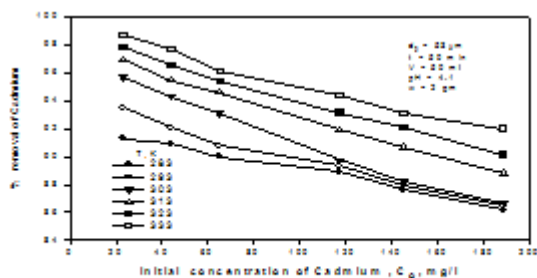


Fig. 4 Variation of % removal of Cd with initial concentration of cadmium

Effect of Volume of the aqueous solution

Change in percentage removal of cadmium with variation in volume of the aqueous solution from 10 to 150 ml is shown in fig.5 for a dosage of 2 gm of 53 μm size adsorbent for an optimum agitation time of 50 min for various temperatures. It is clear that % removal of cadmium is gradually decreased with an increase in the volume of the aqueous solution. The % removal is decreased from 98.75 % at 333 K to 85.8 % at 283 K. As the volume of the aqueous solution increases, the amount of cadmium present in the solution also increases. This implies that % metal removal by unaltered surface area of the adsorbent decreases as the amount of cadmium in the solution is increased.

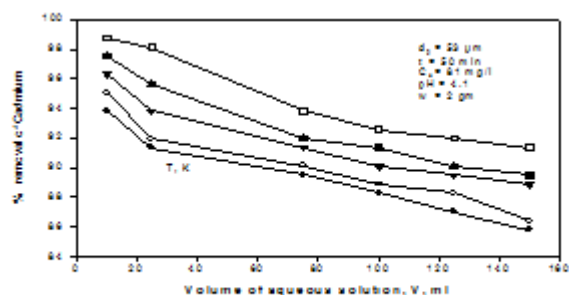


Fig.5 Variation of % removal of Cd with volume of aqueous solution

Effect of pH of the Aqueous Solution

pH is an important factor controlling the process of adsorption as it influences the surface charge of the adsorbent, the degree of ionization and the species of adsorbate. In the present investigation, adsorption data are obtained in the pH range of 1 to 14 for $C_0 = 81 \text{ mg/l}$ and 2 gm of 53 μm size adsorbent. The effect of pH of aqueous solution on % removal of cadmium is drawn in fig.6. The % removal of metal is increased from 69.1% to 95.1% as pH is increased from 1 to 7. The graph reveals that % removal of

cadmium from the aqueous solution is increased significantly with an increase in pH value from 1 to 4 (69.4% to 92.7 %). Increase in percentage adsorption is marginal for pH values from 4 to 7 (92.8 % to 95.5%)

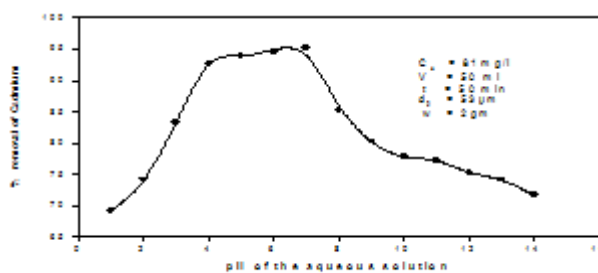


Fig.6 Effect of pH of aqueous solution on % removal of Cadmium

Freundlich Isotherm for Adsorption of Cadmium

The adsorption isotherm is an equilibrium relationship between the concentration of the metal in the fluid phase and its concentration in the adsorbent at a given temperature. Freundlich [12] relationship is an empirical equation. It does not indicate a finite uptake capacity of the adsorbent and can thus only be applied in case of low and intermediate concentration ranges. However, it is easier to handle mathematically in more complex calculations. Freundlich isotherm is given by $q_e = K_f C_e^n$. Freundlich isotherms are drawn between $\log C_e$ and $\log q_e$ in fig.7. The resulting lines have the correlation coefficient of 0.99. The following equations are obtained from the plots drawn in fig.7 for various initial concentrations of cadmium in aqueous solution

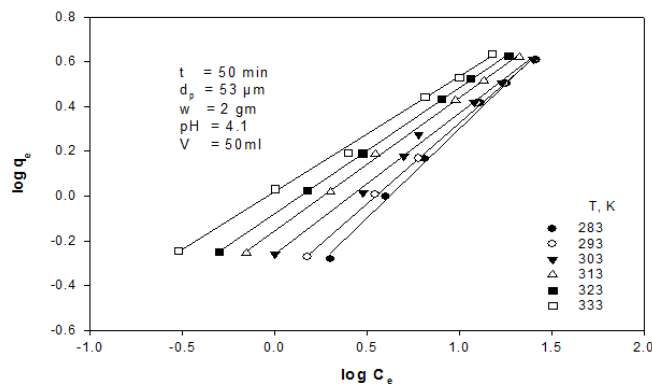


Fig.7 Freundlich isotherm for removal of Cadmium w.r.t. initial concentration of Cadmium

Langmuir Isotherm for Adsorption of Cadmium

Since the chemical forces fall off very rapidly with distance, it is probable that chemisorption does not extend beyond a single layer of adsorbate on the surface of the solid. It can be anticipated as first pointed out by Langmuir [13] that chemisorbed adsorbate layers may be only one molecule thick. The Langmuir isotherm is the most widely used two-parameter equation. The relationship is of a hyperbolic type form: $q_e/q_m = bC_e / (1 + bC_e)$ and this can be rearranged as $(C_e/q_e) = 1/bq_m + C_e/q_m$. From the plots between (C_e/q_e) and C_e , we can calculate the slope $(1/q_m)$ and the intercept $(1/b)$. Further analysis of the Langmuir equation is made on the basis of separation factor (RL) and $0 < RL < 1$ indicates favourable adsorption. Langmuir isotherms for the present data, drawn in fig.8, have good linearity (correlation coefficient, $R \sim$

0.99).

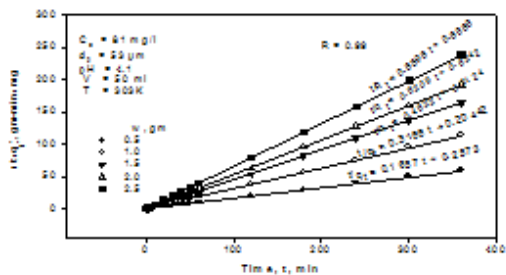


Fig.8 Langmuir isotherm for removal of Cadmium with initial concentration of Cadmium

Kinetics of Adsorption

In the case of adsorption preceded by diffusion through a boundary, the kinetics in most cases follows the pseudo first order rate of equation of Lagergren: $(dq_t/dt) = K_{ad} (q_e - q_t)$. This can be written as $\log (q_e - q_t) = \log q_e - (K_{ad}/2.303) t$. For the present study, Lagergren plot of $\log (q_e - q_t)$ versus agitation time (t) gives a straight line for first order kinetics, which allows computation of the adsorption rate constant. K_{ad} attained in the value for the current work is 1.74 and r^2 is 0.90. On the other hand, several authors have shown that pseudo second order kinetics, given by $(dq_t/dt) = K (q_e - q_t)^2$, can describe these interactions very well in certain specific cases. This equation can be written as $(t/q_t) = (1/K q_e^2) + (1/q_e) t$. If the pseudo second order kinetics, which considers the rate limiting step as the formation of chemisorption bond involving sharing or exchange of electrons between the adsorbate and adsorbent, is applicable, the plot of (t/q_t) vs t gives a linear relationship that allows computation of q_e and K. The pseudo second order model, are therefore applied to find the suitability for the present data. The plots (t/q_t) versus t for the present data are studied. The linearity of the plots ($r^2=0.99$) in fig.9 confirms the suitability of pseudo second order rate equation and the average rate constant (K) is found to be 0.4684 L/mol.min. The following second order rate equations are obtained from the graph for $w = 0.5, 1.0, 1.5, 2.0$ and 2.5 gm of $d_p = 53\mu m$

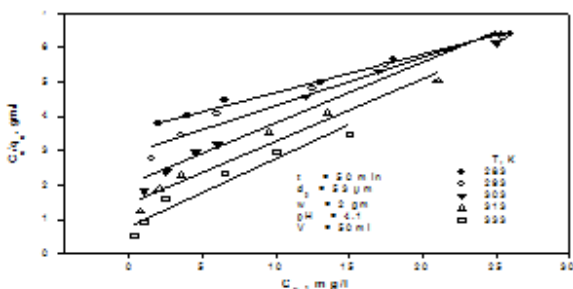


Fig.9. Second order kinetics for adsorption of Cadmium

Thermodynamics of Cadmium Adsorption

The changes occurring during adsorption process can be explained by the three main important thermodynamic parameters enthalpy of adsorption (ΔH), entropy of adsorption (ΔS) and Gibbs free energy (ΔG) due to transfer of unit mole of solute from solution to the solid - liquid interface. The Vanthoff's equation is $\log(q_e/C_e) = -\Delta H/(2.303RT) + \Delta S/(2.303R)$ ΔH and ΔS values are calculated from the plots between $\log(q_e/C_e)$ and $(1/T)$. From the plot

Slope = $\Delta H/2.303R$ and Intercept = $\Delta S/2.303R$ Gibbs free energy (ΔG) is related to enthalpy (ΔH) and entropy (ΔS) of adsorption as $\Delta G = \Delta H - T (\Delta S)$ the adsorption data are obtained for $w = 2$ gm, $d_p = 53\mu m$ at different temperatures and initial concentrations of the cadmium and shown in fig.10. The positive value of enthalpy indicates that the adsorption process is endothermic in nature. The value of entropy above zero confirms the irreversibility of the adsorption process. The negative value of Gibbs free energy shows the reaction as spontaneous

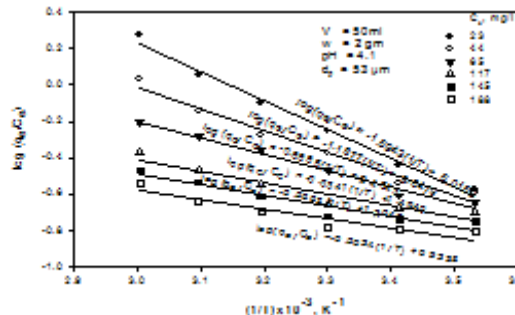


Fig.10 Effect of temperature on adsorption of Cadmium (Van't Hoff plot)

IV. CONCLUSION

The *Erythrina variegata orientalis* leaf powder can be used as an effective adsorbent for the removal of cadmium from its aqueous solutions. The equilibrium agitation time for the cadmium biosorption onto *Erythrina variegata orientalis* leaf powder is 50 min. The percentage removal increases with a decrease in the size of the adsorbent from 212 to 53 μm . The percentage removal is increased with an increase in the adsorbent dosage from 10 to 50 g/L. Percentage removal is increased significantly with increase in pH from 2 to 4. The percentage removal decreases as pH is increased beyond 7. The data are well represented by Freundlich and Langmuir isotherms indicating favourable biosorption. The percentage removal increases with an increase in temperature indicating biosorption as endothermic. Also, the biosorption is endothermic as ΔH is positive. The biosorption follows pseudo-second order kinetics with a rate constant of 0.25 g/(mg-min) for a dosage of 40 g/L. The biosorption is irreversible as ΔS is varied from 17.69 to 96.86 J/(mol-K).

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