

# KINETIC STUDIES ON ADSORPTIVE REMOVAL OF Cd (II) FROM AQUOUS SOLUTION USING MICROALGAL RESINS

# **R. RAM SENTHIL and R. M. MEYYAPPAN**<sup>\*</sup>

Department of Technology, Annamalai University, ANNAMALAI NAGAR - 608 002 (T.N.) INDIA

## ABSTRACT

The removal of Cd from aqueous solution using micro algal resin has been studied. The percentage removal of Ni was carried out by varying experimental conditions viz. initial metal ion concentration, contact time, and pH. It was found that more than 70% removal was achieved within 120 minutes. This process followed first order Lagergren kinetic model. First order rate constant  $K_{ad}$  was calculated. Both; Langmuir and Freundlich isotherms was found to fit and the experimental uptake, the adsorption capacity and adsorption intensity were calculated. The studies showed micro algal resin that can be used as an efficient removal of Cd(II) from waste water.

Key words: Micro algal resin, Removal of Cd (II), Ion exchange, Lagergren kinetic model, Langmuir and Freundlich isotherms.

# **INTRODUCTION**

Electrochemical industries like metal finishing, electroplating and battery industries, metal fabrication paint and pigment industries contribute considerably to pollution load. Cadmium is used in a wide variety of industrial processes such as alloy preparation, metal plating and electronics.

Chemical precipitation and filtration, chemical oxidation or reduction, electrochemical treatment, evaporation, ion exchange and reverse osmosis are some of the most commonly used procedures for removing metal ions from aqueous streams<sup>1</sup>. Wastewaters from these industries have permanent toxic effects to human and the environment. Cd (II) is the common pollutant introduced into natural waters from a variety of industrial wastewaters. Cadmium is used in dipped coatings on metals bearing and low-melting alloys, fire protection systems and batteries. Cadmium is highly toxic elements and considered to be

<sup>\*</sup>Author for correspondence; E-mail: rmmeyyappan@yahoo.co.in

carcinogenic. Cadmium in humans can cause serious damage to kidney and bones. Typical discharge requirements in secondary effluents for cadmium is  $1-2 \text{ g/L}^2$ .

Biosorption of heavy metals from aqueous solutions is a relatively new technology for the treatment of some industrial wastewaters. It is defined as the accumulation and concentration of pollutants from aqueous solutions onto biological materials; thus, allowing the recovery and/or environmentally acceptable disposal of pollutants<sup>3</sup>. The major advantages of the biosorption technology are its effectiveness in quickly reducing the concentration of heavy metals ions to very low levels with high efficiency with the use of inexpensive biosorbent materials<sup>4</sup>. These characteristics make biosorption an ideal alternative for treating high volumes of low concentration complex wastewaters<sup>5</sup>.

A review on the various technologies available for recovery of Ni, Cu, Cr and Zn from plating solution was made by Olthof<sup>6</sup>. Removal of nickel, lead and iron by electrochemical method has been described elsewhere<sup>7</sup>. Pretreatment of tannery wastewater by ion exchange process for the removal of Cr (III) was studied by Tiravanti et al.<sup>8</sup> Rengaraj et al.<sup>9</sup> studied the removal of chromium from water and wastewater by ion exchange resins.

In the present study, micro algal resin was used for the removal of Cd (II) from aqueous solution. The objective of this work was to investigate equilibrium and kinetic parameters of the ion exchange resin for the removal of Cd (II) from aqueous solution. The parameters, which influence adsorption such as initial metal concentration, contact time and pH, were investigated.

#### EXPERIMENTAL

#### Methods

The removal of Cd from aqueous solution by micro algal resin has been studied using cadmium sulphate solution. A stock solution of 1000 mg/L of cadmium was prepared. This solution was diluted as required to obtain initial concentration 100, 150 and 200 mg/L of cadmium. Different pH were adjusted using dilute acid or dilute sodium hydroxide. Known amounts of resin were added to each bottle and the pH was adjusted. The solutions were agitated for a predetermined period in a shaking incubator and for each time, the samples were taken out and filtered. The solution was analyzed by AAS. All experiments were conducted at room temperature i.e  $30^{\circ}$ C, Adsorption isotherm and kinetic studies were carried out with different initial concentrations of cadmium viz. 100, 150 and 200 mg/L and different pH viz. 2, 4, 6 and 8.

#### **RESULTS AND DISCUSSION**

#### Effect of initial concentration

Fig. 1 shows the effect of reaction time on the removal of Cd (II). Cd (II) removal increased with time for all the initial metal ion concentrations. The metal removal versus time curves were smooth and continuous indicating monolayer adsorption of metals on the surfaces of the resin.



Fig. 1: Effects of reaction type and initial concentration of Cd (II)

#### Effect of pH

In order to investigate the effect of pH, the batch experiments were conducted in the pH range 2-7 and the results are shown in Fig. 2.



Fig. 2: Effect of pH on the removal of Cd (II)

As the pH was increased, the removal of metal ion increases. The maximum capacity of Cd adsorption was found out in the pH range 4- 5.

#### Adsorption kinetics

The pseudo-second order kinetics is given by this equation:

$$\frac{\mathrm{d}qt}{\mathrm{d}t} = \mathrm{K}_2 \left(\mathrm{q}_2 - \mathrm{q}_t\right)^2 \qquad \dots (1)$$

q<sub>2</sub>: Maximum uptake for the pseudo-second order kinetics (mmol/g of biomass).

k<sub>2</sub>: Rate constant of the pseudo-second order sorption (g/mmol.min).

Assuming that the metal uptake is proportional to the number of biomass binding sites with sorbed metal and integrating at the limit conditions from t = 0 to t and from  $q_t = 0$  to q, the pseudo-second order model can be expressed as:

$$t/q_t = 1/k_2 q_2^2 + t/q_2 \qquad \dots (2)$$

The values of  $q_2$  and  $k_2$  can be deduced from the linear plot of  $t/q_t$  vs. t.

Metal uptake q (mg of metal / g of resin) was calculated as follows -

$$q = V (C_{initial} - C_{final})/1000 m \qquad \dots (3)$$

were V - Volume of metal solution (mL),  $C_{initial}$  - Initial concentration of metal ion solution (mg/L),  $C_{final}$  - Final concentration of metal ion in the solution (mg/L) and m - Mass of the resin (g).

Fig. 3 is a the linear plot of  $t/q_t$  vs. t, which showed that the removal of Cd (II) by this cation resin follow second order expression. The kinetics of Cd (II) adsorption on micro algal resin followed second order expression given by Lagergren.  $k_2$  values were calculated from the slopes of the linear plots and are presented in Table 1.

Table 1: Adsorption rate constants of Lagergren plots for Cd (II) on micro algal resin

Initial concentration of Cd(II) (mg/L)	<b>k</b> <sub>2</sub>
200	0.0525
150	0.0516
100	0.0410



Fig. 3: Lagergren plot for the adsorption of Cd (II) on micro algal resin

#### **Adsorption isotherm**

The experimental results were fit into Freundlich adsorption isotherm.

 $x/m = kc_e^{1/n}$ 

The logarithmic form of the equation becomes -

 $\log (x/m) = \log k + 1/n \log c_e$ 

x/m = The amount of metal adsorbed per unit mass of the resin

c<sub>e</sub> – Concentration of the metal in solution at equilibrium

The experimental results obtained for the adsorption of cadmium on microalgal resin was found to obey Freundlich adsorption isotherm. Fig. 4 shows the plot of log (x/m) versus log  $c_e$  for various initial concentrations, which was found to be linear indicating the adsorption capacity (k) and adsorption intensity (n). The adsorption capacity (k) and adsorption intensity (n) were calculated from Fig. 4 and the values are 4.3957, and 1.557, respectively.

Value of n shows a favorable adsorption of metal on micro algal resin

### CONCLUSION

The present study showed that micro algal resin could be used as an adsorbent for the effective removal of cadmium from aqueous solution. The removal efficiency increases with increase in contact time, decrease in initial metal ion concentration, and increase in pH. Langmuir isotherm was found to fit the experimental metal uptake rates. Application of this micro algal resin to waste water treatment is economical and efficient.



Fig. 4: Freundlich adsorption isotherm for Cd (II) on micro algal resin

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