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Kinetic and Adsorption Isotherm studies for the removal of Heavy Metals by *Rhizoclonium* Species.

Kirti Srivastava^{1*}, Ashima Srivastava¹, and Pratibha Singh².

¹Department of Chemistry, JSS Academy of Technical Education, Sector 62, Noida, India.

²Enviro Infra Solutions Pvt. Ltd., Sector 9, Vasundhara, Ghaziabad 201012, India.

ABSTRACT

The intrinsic characteristic of algae for the uptake (adsorption) and accumulation of heavy metals is the one of the best eco-friendly techniques used for the removal of toxic pollutants from wastewater. In the present work, removal efficiency of microalgae *Rhizoclonium species* was determined for Cd(II) and Cu(II) removal at different initial concentration of metal ions, pH and contact time. With increase in concentration of metal ions, removal efficiency was diminished. With respect to the contact time, it was found that maximum removal of Cd(II) by *Rhizoclonim* sp. was 75.48% at 30 minutes and 79.21% for Cu(II) at same contact time. Maximum removal of metal ions occurred at optimum pH range of 6-8. The isotherm study was carried out for each metal by applying the experimental results onto the Langmuir and Freundlich models. The results suggested that *Rhizoclonim* sp. followed Freundlich adsorption model for Cu uptake whereas for Cd uptake, Langmuir model gave better correlation values ($R^2 > 0.9$). The experimental data of adsorption was also applied to different kinetic models and it could be established that adsorption kinetics followed the pseudo-second-order kinetics.

Keywords: Rhizoclonim, Heavy metals, Adsorption, Chemical kinetics, Isotherm

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**Corresponding author*

INTRODUCTION

Industrial activity frequently produces wastewater containing heavy metals which flows into natural waters and poses a potential damaging effect to plants, animals and human beings (Volesky and Holan, 1995). Heavy metals in soil and water are persistent in nature and are carcinogenic too. Conventional methods applied to remove excessive heavy metals from aqueous solutions include chemical precipitation, ion exchange, evaporation, electroplating and membrane processes. These methods are either inefficient or expensive in operation especially when heavy metals exist in low concentrations (Pan et al., 2009). Globally, use of biomass for the biosorption of organic and inorganic pollutants especially heavy metals has been widely investigated (Sreelakshmi, 2008; Ramola and Rajput, 2017).

As per Kord et al. (2010) recent advances in environmental research have uncovered the fact that many living organisms can accumulate high concentrations of toxins in their bodies. Living and algae biomass has been used for bioremediation processes of heavy metal contaminated wastewaters (Sahan et al., 2010, et al, Tuzen and Sari, 2010, Priyadarshani, 2011, Amin Keyvan Zeraatkar, Hossein Ahmadzadeh, Ahmad Farhad Talebi, Navid R. Moheimani, Mark P. McHenry, Potential use of algae for heavy metal bioremediation, a Cuitical review, Journal of Environmental Management, Volume 181, 2016, Pages 817-831). They can aggregate various lethal contaminants in significant level into their biomass by two unique biochemical pathways: Biosorption (*adsorption* of metal ions onto the cell surface) and Bioaccumulation (*absorption* of metal into the cell) (Rangsayatorn et al., 2002). The probable binding sites present for the heavy metals present in the cell wall of algae are polysaccharides, proteins, glycoproteins, lipids, acids, etc. (Ozer et al., 1999).

In the search suitable cost-effective technique for the bioremediation of heavy metals, filamentous green algae *Rhizoclonium sp* is selected in current investigation. *Rhizoclonium* is a genus of green algae in the family Cladophoraceae. It grows in fresh, brackish as well as marine waters. It consists of unbranched filaments, occasionally short, unicellular, or few-celled rhizoidal branches arise at right angles to axis. Cells are usually more than twice as long as broad, sometimes with walls thick and lamellate, each with a parietal, reticulate chloroplast and several pyrenoids and nuclei. In the present study, removal efficacy of *Rhizoclonium sp* is studied for Chromium (Cu) and Cadmium (Cd) from their aqueous solutions at different parameters such as initial metal ion concentration, pH and contact time.

MATERIALS AND METHODS

Preparation of the Algae (Biosorbent)

Fresh algal biomass of *Rhizoclonium sp* was collected from the stagnant pond of the Garhi Mandu Forest, New Delhi. Prior to utilize, it was washed with tap water and then with distilled water for eliminating dirt. For optimum growth, biomass was kept in the nutrient medium consisting of sodium nitrate and sodium hydrogen phosphate. After considerable growth, it was sun-dried for 4 days and further dried in oven at 378K for 24 h. Later it was grounded in a Basalt stone mortar and pestle. For final use, it was sieved through a 150 and 250 μm mesh.

Metal Solutions

Stocks of 1000 mg L⁻¹ metal ion solutions were prepared using CdCl₂ and CuSO₄ in distilled water. The solutions were then diluted to the desired concentrations and analyzed. All the chemicals used were of Analytical Grade supplied by Sigma-Aldrich.

Batch experiments for single metal-ion solution

Effect of contact time

The pH of the test solution was adjusted to 5 ± 0.2 , with a constant metal concentration of 100 mg L⁻¹ and a biomass dose of 1.0 g L⁻¹ in 50 mL of solution. Samples were taken out after regular intervals at 5, 10, 15, 20, 30, 40, 50, and 60 min.

Effect of pH

The experiment was conducted for biosorption at a concentration of 100 mg L⁻¹ of Cd(II), Cu(II) ions and 1.0 g L⁻¹ of bio-adsorbent dose in a 50 mL metal ion solution for 60 min with varying pH from 3 to 7. Solution pH value was adjusted using 1 M HCl or 1 M NaOH.

Effect of initial metal ions concentration

Effects of initial metal ion concentration on the biosorption of Cd(II) and Cu(II) from 50 to 300 mg L⁻¹ were studied.

Analysis of experimental data

Kinetic Model

To determine the effect of contact time on Cd and Cu uptake by *Rhizoclonium* sp. two kinetic models were applied: pseudo first order and pseudo second order kinetic models.

Pseudo-first order: The pseudo-first order kinetic equation considers that the rate of adsorption sites to get filled is proportional to the number of unoccupied sites on algae. The linear equation is as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (1)$$

Here, q_e is the amount of Cd and Cu adsorbed by algae at equilibrium (mg/g), q_t is amount adsorbed at time t (mg/g), k_1 is rate constant of first order adsorption (min⁻¹). Straight line plots of $\log(q_e - q_t)$ against time (Ozer and Ozer, 2003) were used to determine q_e , k_1 and R^2 .

Pseudo-second order: In the pseudo-second-order model, the rate of adsorption sites to get filled is proportional to the square of the number of unoccupied sites and the number of occupied sites is proportional to the fraction of the metal ions, the pseudo-second order chemisorption kinetic rate equation is given by equation 2:

$$\frac{t}{q_t} = \left(\frac{1}{k_2 q_e^2} \right) + \frac{t}{q_e} \quad (2)$$

Here k_2 is the rate constant of pseudo second order kinetics (mg/g/min), q_e , k_2 and R^2 values were determined from the slope and intercept of the plots of t/q against time (Ho and McKay, 2000).

Analysis of Cd(II) and Cu(II)

Amounts of Cd(II) and Cu(II) adsorbed by the biomass were calculated using the following equation:

$$q = (C_o - C_e) V/W \quad (3)$$

$$\% \text{ Removal} = (C_o - C_e) \times 100 / C_o \quad (4)$$

where q is the amount of Cd(II) or Cu(II) adsorbed by biomass (mg/g), C_o is the initial concentration of Cd(II) or Cu(II) ions (mg/L), C_e is the concentration of Cd(II) or Cu(II) at equilibrium (mg/L), V is the volume of the metal solution (L), and W is the mass of adsorbent (g). All experiments were conducted at room temperature.

Biosorption isotherm

Adsorption data for a wide range of adsorbate concentrations are best conveniently described by various adsorption isotherms, such as the Langmuir and Freundlich isotherms.

The Langmuir adsorption isotherm assumes that monolayer adsorption exists at all surface sites that is homogeneity, with the ability of no interaction of adsorbed molecules with the neighbouring adsorption sites.

The linear Langmuir equation is represented as:

$$C_e/q_e = 1/Q_{max}b + 1/C_e(Q_{max}) \tag{5}$$

where q_e is the amount of metal ions adsorbed (mg/g) and C_e is the equilibrium concentration (mg/L). Q_{max} represents maximum adsorption and b is the affinity between bio-adsorbent and bio-adsorbate.

The Freundlich isotherm is given as:

$$q_e = K_F C_e^{1/n} \tag{6}$$

The logarithmic form of the equation is given as:

$$\log q_e = \log K_F + 1/n \log C_e$$

K_F and $1/n$ are isotherm constants, respectively.

RESULTS AND DISCUSSION

Effect of contact time

Ideal bio-adsorption materials are able to rapidly adsorb high concentrations of heavy metals from waste emissions and use chemical agents to desorb heavy metals from biosorption material (Singh et al., 2007). For these reasons, the results of *Rhizoclonium sp.* adsorption on Cd(II) and Cu(II) used the relationship between heavy metal adsorption and contact time as a function, as shown in Fig.1.

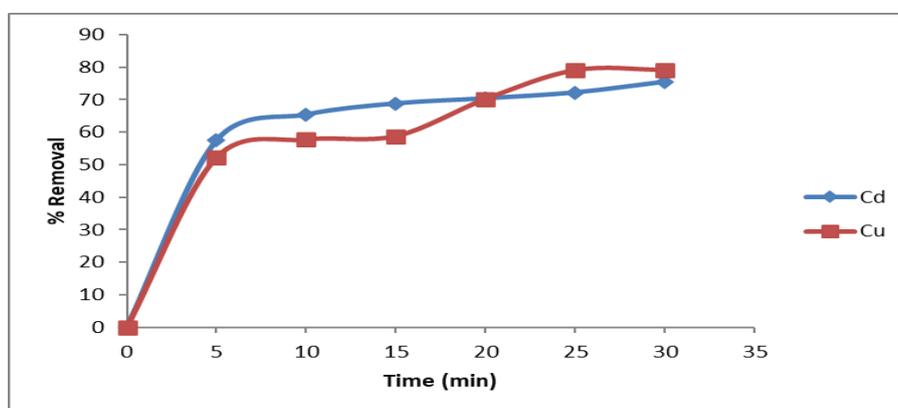


Figure 1: Effect of contact time on % Removal of Heavy metal ions

During the first 10 minutes, adsorption rate of both metals was extremely high, comprising approximately 87% of the total adsorption. This may be due to the availability of large surface area of the adsorbent in the beginning (physical adsorption). Then, the rate began to drop toward a steady state as the surface pores of the adsorbent became agglomerated with heavy metal ions which leads to binding site saturation. This study observed three phases of *Rhizoclonium sp.* in the contact time adsorption curve: the initial phase, with rapid adsorption of heavy metal ions; the second phase, with gradual slowing of the adsorption rate; and the equilibrium phase, with no significant increase in the removal rate.

Effect of pH

Numerous studies show that pH is an important factor affecting adsorption of heavy metals by biosorbents (Fourest and Roux, 1992). During this process, the functional groups, surface charges, degree of ionization and solubility of the adsorbent are frequently responsible for the binding of metal ions onto the adsorbent. In Fig. 2, the optimum pH values ranged from 6 to 8 for the Cd (II) and Cu (II). It was observed that further increase in pH above their optimum caused the formation of precipitates. At lower pH, the adsorbent is protonated and the protons compete with the metal ions, resulting in less adsorption ((Gupta and Rastogi, 2008). In case of Cd(II) the capacity to adsorb decreases when pH exceeded 6 whereas in case of Cu(II), it diminished when the pH went beyond 8. This may have been due to the precipitation of hydroxides of cadmium and copper.

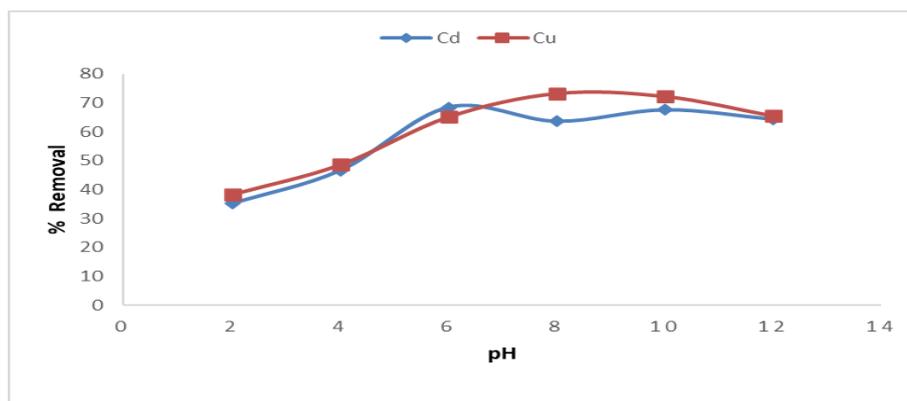


Figure 2: Effect of pH on % Removal of Heavy metal ions

Effect of initial concentration

The effect of the initial concentration of the metal ions (10–30 mg/L) on their adsorption on the biosorbent is shown in Fig 3. The results show that as the initial concentration of heavy metal ion was increased, at constant temperature, pH and biosorbent mass for the respective optimum times, the % removal of the metal ions decreased. This behaviour is attributed to binding site saturation. At lower concentrations, the ratios of available binding sites to the initial metal ion concentrations were larger, while at higher concentrations, the saturation of the adsorption sites occurred.

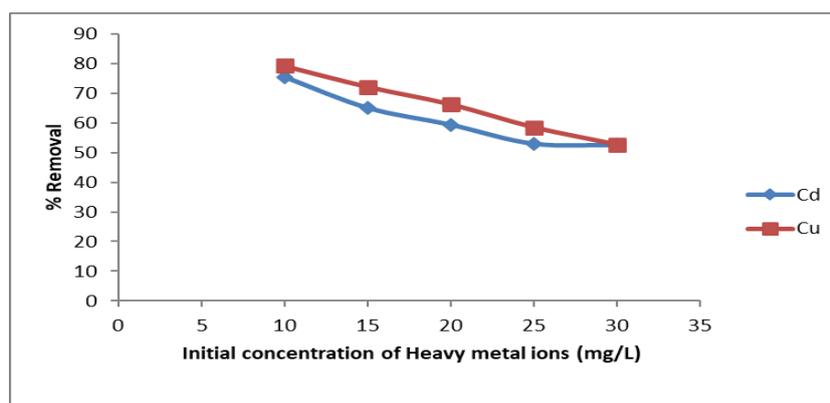


Figure 3: Effect of initial metal ion concentration on % Removal

Kinetic Model Analysis

Kinetic Model provides information on the reaction pathways and the mechanisms of the adsorption of sorbate by the *Rhizoclonium sp.* Table 1 describes the kinetics of the adsorptions of studied metal ions on algae using pseudo-first and pseudo-second-order models. For the pseudo-first-order model, the low k_1 suggests that a slow adsorption process takes place, while for the pseudo-second

order model, k_2 values were high indicating an increase in adsorption rates. The R^2 values for the adsorption kinetics of the metal ions were higher for the pseudo-second-order model compared to those of the pseudo-first-order model (Fig 4,5). Thus, it appears that pseudo-second-order model is a better model fitting the kinetics of the adsorption of the metal ions employed in this study.

Table 1: Kinetics Parameters of pseudo-first and pseudo-second-order adsorption model

Kinetic Model	Constants	Metal ions	
		Cd	Cu
Pseudo-first order	k_1	0.1834	0.1239
	R^2	0.7153	0.5715
Pseudo-second order	k_2	0.7592	0.6491
	R^2	0.9950	0.9870

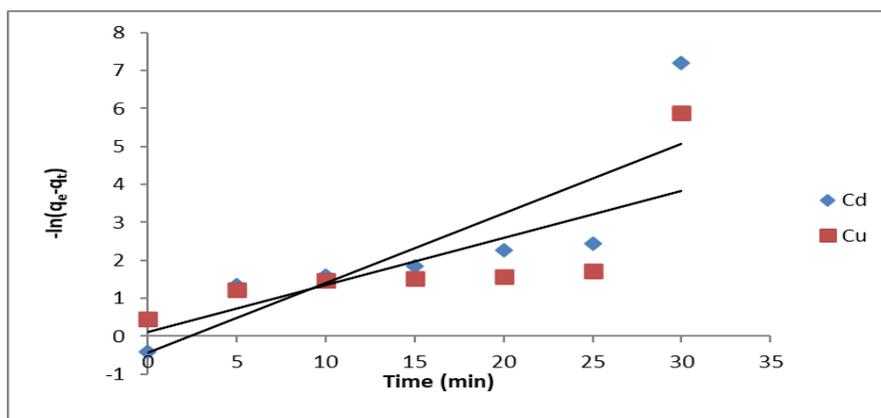


Figure 4: Pseudo- first order plot for Heavy metal ion removal at different time intervals

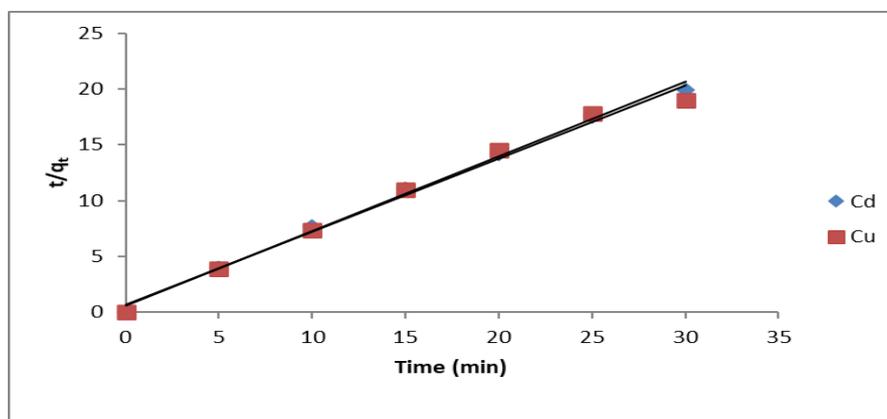


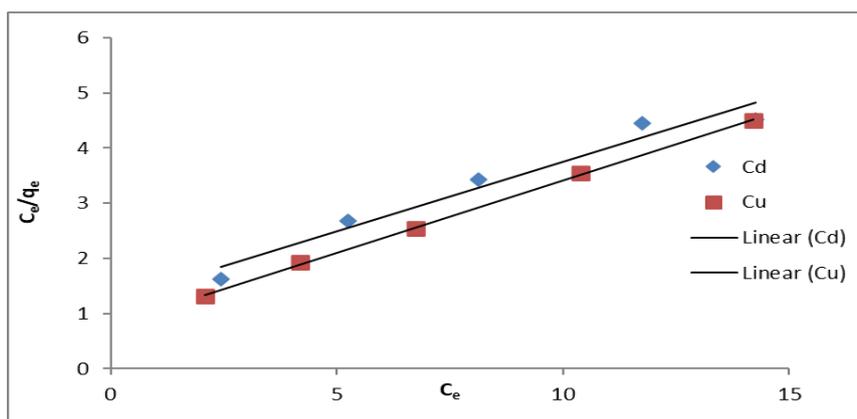
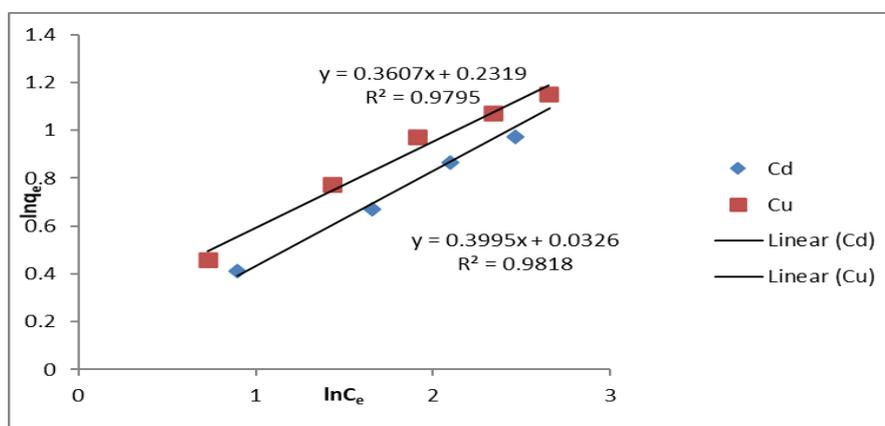
Figure 5: Pseudo- second order plot for Heavy metal ion removal at different time intervals

Adsorption Isotherm Model Analysis

The graph for the Langmuir adsorption isotherm (Fig 6) was plotted between of C_e (x-axis) and C_e/q_e (y-axis) and Langmuir parameters were computed from the same. The graph for the Freundlich adsorption isotherm (Fig 7) was plotted between of $\ln C_e$ (x-axis) and $\ln q_e$ (y-axis) and Freundlich parameters were computed from the same. The Langmuir and Freundlich parameters are given in Table 2.

Table 2: Parameters of Langmuir and Freundlich adsorption isotherm models

Adsorption Isotherm Model	Constants	Metal ions	
		Cd	Cu
Langmuir	Q_{max}	3.8168	3.9840
	b	0.3287	0.2034
	R^2	0.999	0.960
Freundlich	K_F	1.03	1.2599
	n	2.5062	2.7778
	R^2	0.981	0.979


Figure 6: Langmuir Isotherm for Heavy metal ion removal at various concentrations

Figure 6: Freundlich Isotherm for Heavy metal ion removal at various concentrations

From the Table 2, it can be observed that the value of correlation coefficients for Cu(II) strongly support Freundlich adsorption isotherm in comparison to Langmuir isotherm equation. It suggests that multilayer adsorption with non-uniform distribution of adsorption heat and affinities over the heterogenous surface for Cu(II). However, for Cd (II) Langmuir isotherm showed better fit to the experimental data. The maximum adsorption capacities of the algae were found to be 3.8168 (Cd) mg/g and 3.9840 (Cu) mg/g.

CONCLUSIONS

From the above investigation and results it can be well established that *Rhizoclonium sp.* serves as natural, promising, economic and environmentally friendly adsorbent for waste water remediation. Its easy availability, low-cost operation and maintenance makes it as an ideal choice of biosorbent for the removal of selected heavy metals from their aqueous solutions. The batch adsorption method for the

uptake of Cd(II) and Cu(II) by algae is dependent on the contact time, solution pH and initial metal ion concentrations. The experimental data in the adsorption process of Cd(II) indicated good correlations with the pseudo-second-order kinetic model and Langmuir isotherm whereas Cu (II) adsorption process exhibited good correlations with the pseudo-second-order kinetic model and Freundlich isotherm.

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