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Bio-adsorption of copper (II) from synthetic wastewater using *vaucheria* sp. Dead biomass

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Abstract

The ability of the yellow-green alga *Vaucheria* sp. to remove Copper (II) from synthetic wastewater through the adsorption process was investigated in this communication. The pH of the solution, the adsorbent dose, the initial concentration of Cu (II) ions, the contact period, and the temperature are all factors that influenced Cu (II) sorption. The adsorption capacity at 5 pH, 80 minutes of contact time, 318 K, and 250 mg/L initial copper metal ion concentration was calculated using the Langmuir adsorption model as 46.29 mg/g. By comparing the coefficient correlation (R^2) values, both the Langmuir and Freundlich equations were found to fit the equilibrium data. The parameters (ΔG^o, ΔH^o, and ΔS^o) were examined during thermodynamic tests at three distinct temperatures: 298, 308, and 318 K, suggesting that the process was sustained, spontaneous, and endothermic. Pseudo-second-order kinetic models accurately described adsorption kinetics when compared to pseudo-first-order kinetic models. Finally, the current research revealed that the bio-adsorption technique utilizing *Vaucheria* sp. alga could be an inexpensive and effective way to adsorb and remove Cu (II) metal ions from synthetic wastewaters.

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1. Introduction

Water is the most important component of the earth's ecosystem and a necessary commodity for the survival of all living things, including humans. Because of the exponential growth of the world population, industrialization, and civilization, the quality of our water resources is fast degrading. Water contains over one thousand pollutants, including organic, inorganic, and biological contaminants. Heavy metals are non-biodegradable inorganic contaminants that are very hazardous and carcinogenic [1]. Furthermore, some metal ions form complexes with specific enzymes, proteins, and other molecules, altering their physiological functions. Copper (II) is one of the hazardous heavy metals found in wastewater effluents that needs to be extracted [2]. Chemical precipitation, membrane separation, evaporation, electrowinning, and resin ionic exchange are examples of traditional metal removal techniques that can be costly and ineffective [3-5]. These techniques are applied by many researchers earlier. Moreover, adsorbent techniques, mainly utilizing biological matter either living or non-living bacteria, yeast, algae, and plants to reduce hazardous metals, are both cost-effective and environmentally beneficial methods [6-10]. Therefore, in need of acceptable, natural, readily available, renewable, and low-cost sorbents, algae are examined for their ability to remove toxic heavy metal ions by scientists [11-15].

Algal biomass is commonly used as an adsorbent material because it is plentiful, easy to prepare, and has a high adsorption capacity. In the current study, *Vaucheria* sp., a yellow-green alga from the Xathophyceae family, is used to adsorb and extract Cu (II) from synthetic wastewater. A network of mats is generated by apical filament growths, in almost every wetland habitat (ponds. riverside, etc.). This biomaterial was chosen for investigation because it has significant adsorption capabilities for methyl orange and methylene blue dyes, as indicated in our previous publications [16-17], and there are few studies on its applicability for heavy metal ion sequestration [18]. Thus, the key aim of the present study is to determine the influence of key variables affecting the sorption phenomenon, followed by estimation of adsorption isotherms, kinetic models, and thermodynamic studies. The physical and chemical characterization of the algal biomass was performed and the adsorption capacity of the test alga for copper (II) metal was compared with the earlier reported alga.

2. Material and Methods

2.1. Preparation and characterization of Bio-adsorbent (*Vaucheria* sp.)

This study used pond-collected *Vaucheria* sp. algae as an adsorbent. The biomaterial was washed with tap water and distilled water to remove extraneous materials. After two days in the Sun, it's baked at 343 K for a day. The dried biomass is pulverized and sieved to collect 50-100 µm mesh particles. Prepared algal biomass was stored in a vacuum desiccator. The surface area of the adsorbent was calculated using the BET method [19], and the elemental analyzer Vario MICRO CHNS V3.1.1 (GmbH, Germany) was used to estimate Carbon, Nitrogen, and Sulphur percentages. The primary chemical functional groups on the adsorbent's surface were determined using KBr pellets and a Thermo-Nicolet FTIR (Germany) in the 4000-400 cm^{-1} region.

2.2. Synthetic wastewater preparation

Synthetic wastewater is artificially produced and contains Cu (II) as adsorbate. Anhydrous $CuSO_4$. $5H_2O$ was dissolved in double-distilled water to make a 1000 mg/L Cu (II) stock solution, which was then diluted for experiments. All chemicals and reagents used in this study were analytical grades from Merck, Germany, or S.D Fine Chem. Ltd., India. A digital pH meter (PERFIT, India) was used to measure solution pH and an atomic absorption spectrophotometer was used to record the sample absorbance.

2.3. Procedural design

Each flask with the optimal adsorbent dose was filled with 250 mg/L Cu (II) solution and swirled at 150 rpm until equilibrium was reached. Adding 0.1 M HCl kept the pH at 5. A 0.45 µm membrane filter separated the biomass and the filtrate was diluted before analysis. The filtrate's Cu (II) content was measured with a Hitachi (Japan) atomic absorption spectrophotometer at 324.8 nm. Mass balance equation was used to calculate *Vaucheria* sp. adsorption capacity in each flask

$$q_e = (C_o - C_e)V / M \qquad (1)$$

Where qe is algal adsorption capacity (mg/g), C_o and C_e are initial and equilibrium Cu (II) metal ion concentrations (mg/L), V is reaction mixture volume (L), and M is adsorbent mass (g). Each case presented the average result and the standard deviations were roughly ±1.5%.

2.4. Operational parameters impact

The operational parameters assessed for the maximal adsorption uptake by alga for Cu(II) were contact time (1-140 minutes), and solution pH (3-7) adsorbent dosage (0.1-1 g/L), and temperature (298, 308, and 318 K).

2.5. Adsorption isotherms and kinetic modeling

The Langmuir and Freundlich isotherms [20-21] were used to calculate the maximal adsorption capacity, q_e (mg/g). The Langmuir adsorption isotherm assumes monolayer coverage on the sorbent surface and is expressed as;

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{bQ_0C_e} \qquad (2)$$

Where q_e and Q_0 are equilibrium and maximum adsorption capacity (in mg/g) respectively. C_e represents the equilibrium concentration of adsorbate (mg/L) and b refers to the Langmuir constant. The Freundlich isotherm is valid for multilayer sorption onto a heterogeneous surface, represented by the equation;

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \qquad (3)$$

Where, K_F (mg g^{-1}) represents the Freundlich constant and n, the intensity of adsorption.

Two kinetic models that were applied and that allow the understanding of the mechanism of Cu (II) adsorption onto the algal surface are pseudo-first-order and pseudo-second-order models [22, 23]. The linearized forms of these models are given as:

Pseudo-first-order model- $\log(q_e - q_t) =$

$$\log q_e - \frac{k_{1,\,ads}}{2.303} t \qquad (4)$$

Pseudo-second-order model -

$$\frac{t}{q}=\frac{1}{k_{2,ads}q_e^2}+\frac{1}{q_e}t \qquad (5)$$

Where q_t (mg/g) refers to the amount of Cu (II) adsorbed at time t and q_e (mg/g) is equilibrium sorption uptake. Further, $k_{1,ads}$ (min^{-1}) and $k_{2,ads}$ (g mg^{-1} min^{-1}) are the pseudo-first-order and pseudo-second-order rate constant respectively.

2.6. Thermodynamic Studies

The thermodynamic parameters (Gibbs free energy change (ΔG^o), enthalpy change (ΔH^o), and entropy change (ΔS^o)) were analyzed to understand the system's overall performance, using the standard general equations presented as;

$$\Delta G^0 = -RT\ln(b) \qquad (6)$$

$$\ln\left(\frac{b_2}{b_1}\right) = -\frac{\Delta H_o}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right) \qquad (7)$$

$$\Delta G^o = \Delta H^o - T\Delta S^o \qquad (8)$$

3. Results and Discussion

3.1. Adsorbent Characterization

The Quantasorb surface area analyzer measured the test alga's surface area to be 3.248 m^2/g. The element composition as determined by element analyzer is found to be Carbon, Hydrogen, Nitrogen, and Sulphur (%) as 35.92, 4.59, 4.28, and 0.744% respectively.

The functional groups and the surface properties of the dried *Vaucheria* sp. algal biomass were examined using the FT-IR technique, before and after Cu (II) adsorption. The interpretation of the spectra revealed the possible presence of several functional groups including carboxylic, hydroxyl, amino, and carbonyl groups. When fresh-dried and metal-loaded biomass spectra were compared, it was discovered that there were slight changes in the wavenumber of dominant peaks associated with the loaded metal, implying that the metal-binding process has taken place on the alga's surface [24].

Table 01: FTIR absorption bands of Vaucheria sp. alga before and after Copper (II) adsorption.

Algae before Cu (II) adsorption (wavenumber in cm^{-1})	Algae after Cu (II) adsorption (wavenumber in cm^{-1})	Bonds associated with Functional groupings
3423	3417	Carboxylic/OH stretch and N-H stretch
2925	2920	Phenolic/ carboxylic
1644	1649	C=O chelate stretching, Amide I band
1535	1541	Amide II band, OH Bonds
1432	1427	Symmetric bending of CH_3 of the acetyl moiety
1068	1074	–C–N stretching

3.2. Impact of Key variables

Among the main variables optimized were pH, algal dosage, alga-Cu (II) contact time, and temperature on Cu (II) uptake by the test alga *Vaucheria* sp.

3.2.1. Impact of pH on Cu (II) uptake

The residual Cu (II) metal ion uptake following batch equilibration with algae was determined at pH values ranging from 2 to 7. As shown in figure 1, adsorption reaches a maximum at pH 5 and then begins to decline. This is most likely due to the intense competition for sorption sites between metal ions and protons at low pH. As pH increases, the concentration of hydrogen ions decreases, resulting in increased heavy metal adsorption. Further pH changes beyond pH 6.0 result in precipitation and the formation of soluble hydroxylated metal ion complexes that begin to compete with the active sites, making it impossible to ascertain the precise adsorption capacities. According to previous research, the maximum adsorption capacity of Cu (II) metal ion onto biomass was observed at pH 5 [24].

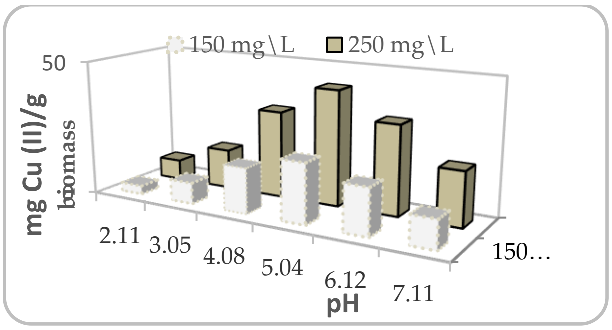

Figure 1. Influence of pH on Copper (II) adsorption onto *Vaucheria sp*. biomass.

3.2.2. Impact of algal dosage on Cu (II) uptake

To test the impact of the adsorbent dose, 0.1–1.0 g/L of *Vaucheria* sp. was suspended in 50 ml Cu (II) solution at optimal pH and contact time. Figures 2a and 2b show the effect of adsorbent dosage on Cu (II) adsorption on algal metal adsorption in mg/g and adsorption extent (%) respectively. Metal ion adsorption increased with adsorbent dosage, becoming almost constant at 0.8 g/L. This pattern could be explained by biomass agglomeration at higher concentrations, reducing adsorption's effective surface area. For the rest of the studies, the effective algal dosage was set to 0.8g/L, where adsorption is about 82%. Similar results were found with other adsorbent systems [10].

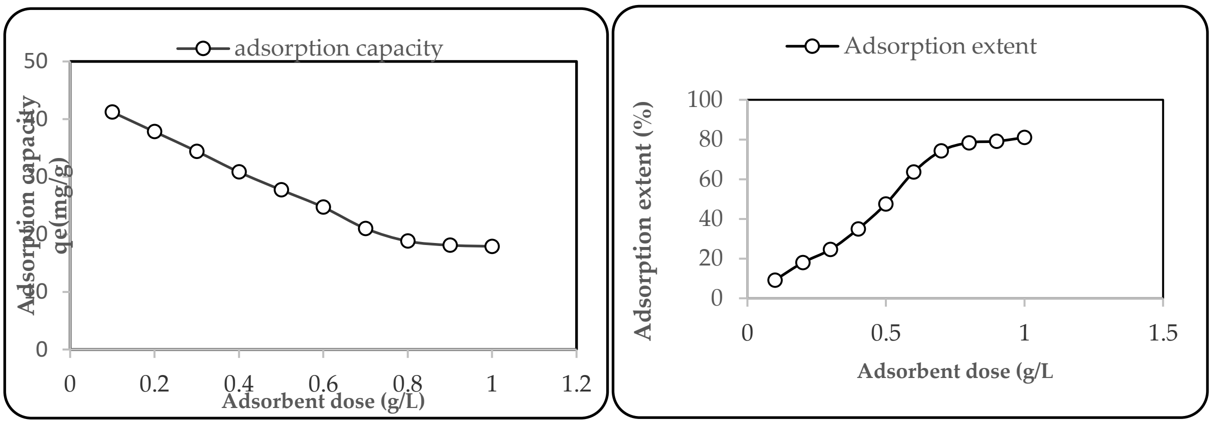

Figure 02. Effect of Adsorbent dosage on copper (II) adsorption in terms of (a) Adsorption capacity (qe) (b) Adsorption extent (%), onto *Vaucheria* sp. algal biomass.

3.2.3. Impact of Temperature on Cu (II) uptake

The temperature of adsorption media may be crucial for energy-dependent microbial metal sorption mechanisms. Figure 3 shows the effect of temperature on the adsorption of Copper (II) ions onto *Vaucheria* sp (298, 308, and 318 K). Figure 3 shows that adsorption capacity (q_e) rose from 298 K to 318 K, indicating that sorption is endothermic. Similar results have been seen with other adsorbents [24]. For additional adsorption studies, the optimal solution temperature was determined to be 318 K.

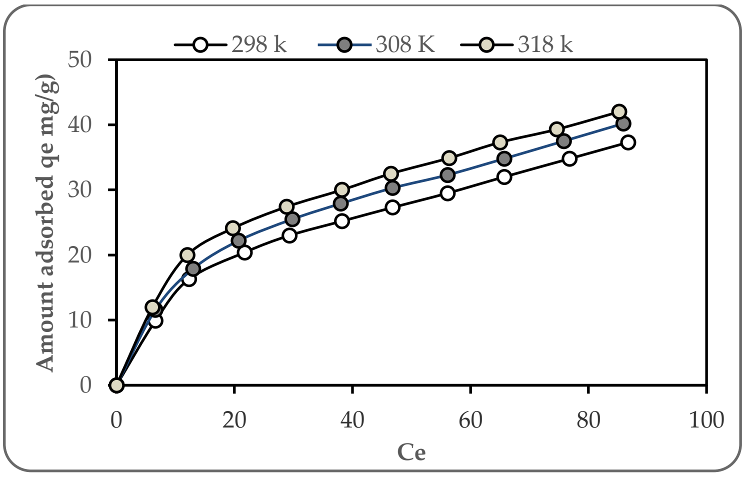

Figure 03. Effect of Temperature on copper (ii) adsorption onto *Vaucheria sp*. algal biomass.

3.2.4. Impact of contact time on Cu (II) uptake

This experiment timed the absorption of metal ions from a solution. Figure 4 shows the effect of contact time (measured in the range of 1-140 minutes) between Cu(II) and algal biomass using 0.8g algal dose, 50 ml of 150 and 250 ppm Cu(II) solution at pH 5.0, and temperature 318 K. Due to enough heavy metal ion adsorption surfaces and non-saturated active sites, adsorption started quickly. After 80 minutes, saturation occurs. Phase one involves physical adsorption, while phase two involves complexation, micro-precipitation, or binding site saturation. All adsorption studies were therefore performed at an 80-minute contact period.

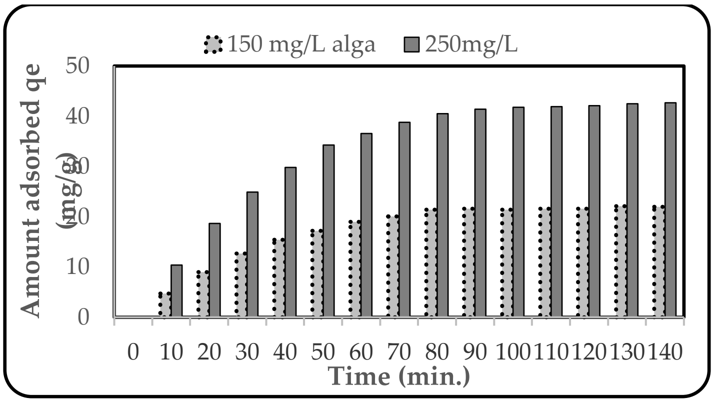

Figure 04. Effect of contact time on the uptake of copper (II) onto *Vaucheria sp.* algal biomass at two concentrations (150 mg/L and 250 mg/L).

3.3. Adsorption Isotherms

Adsorption data must be analyzed in order to develop an equation that accurately describes the results and can be used in the design. Langmuir and Freundlich isotherms (linearized equations 2 and 3) were used to match the experimental results, and the values of adsorption constants and correlation coefficients were calculated using the plots (Figures 5a and 5b) and listed in Table 2. The Langmuir isotherm assumes a homogeneous binding site distribution on a monolayer surface.

The Freundlich isotherm is an empirical equation based on the distribution of sorption sites and energy on an exponential scale. The fact that the values of parameter n in Table 2 are greater than one indicates that Cu (II) metal ions adsorb favorably and heterogeneously onto algal biomass. On comparing correlation coefficient values (R^2) for both the isotherms, it was observed that the experimental data fit well with both Langmuir (R^2 =0.99) and the Freundlich adsorption isotherm (R^2=0.99) indicating both monolayer and heterogeneous surface conditions. Using the Langmuir model, the value of q_e responsible for demonstrating adsorption capacity for the test alga, was determined to be 46.29 mg/g at 318 K with high R^2 values. When compared with several other algal systems, the present yellow-green alga, *Vaucheria* sp., was found to show comparable or higher adsorption capacity values for Cu (II). Green algae like *Gelidium* sp., *Oscillatoria limnetica*, *Anabaena Spiroides*, *Eudorina elegans*, and *Chlorella vulgaris* have been reported to show maximum Cu (II) uptake of 33.0, 23.96, 0.24, 1.08 and 9.47 mg/g respectively [10, 25-26].

Table 02: Langmuir and Freundlich isotherms constants for the bio-adsorption of Cu (II) onto *Vaucheria* sp. at different temperatures and pH 5.0.

Biomass	***Temp* (K)**	***Langmuir Constant***				***Freundlich Constant***		
		b **(L mg^{-1})**	**B (Lm mol^{-1})**	***Q_0*** **(mg g^{-1})**	**R^2**	***n***	***K_F*** **(mg g^{-1})**	**R^2**
***Vaucheria* sp.**	298	0.048	3.060	41.32	0.989	2.109	4.493	0.992
	308	0.054	3.444	43.48	0.992	2.1925	5.277	0.989
	318	0.058	3.678	46.29	0.992	2.290	6.123	0.976

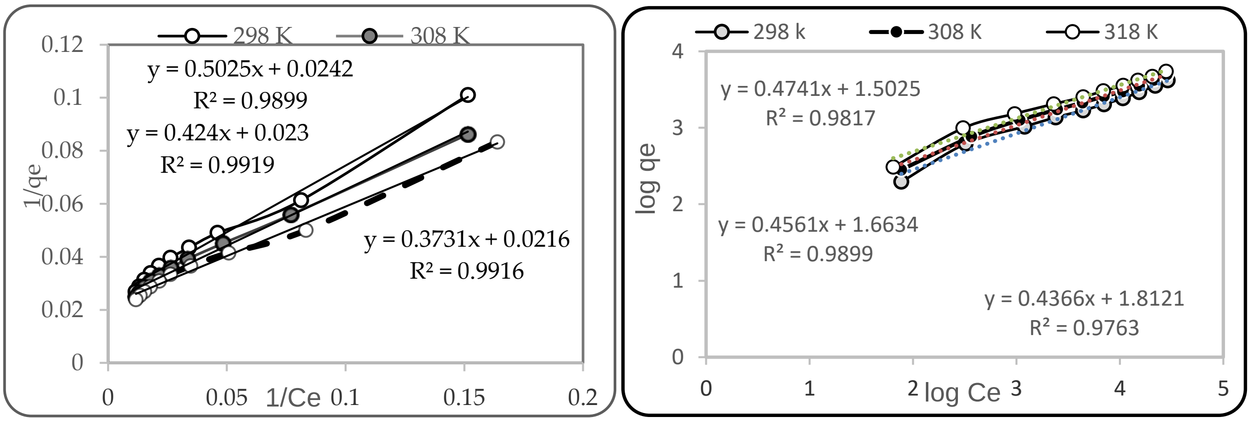

Figure 05. Adsorption isotherms of Copper (II) onto *Vaucheria sp.* algal biomass (a) Langmuir model (b) Freundlich model

3.4. Thermodynamic studies

The values of different thermodynamic parameters deduced using eq. 6,7 and 8, are summarized in table 3. The ΔG^o value is negative, indicating spontaneous adsorption of Cu (II) by *Vaucheria* sp. This value increased with increasing temperature implying more favorable adsorption at higher temperatures. The positive value of ΔH^o indicates the endothermic nature of Cu (II) adsorption by test alga, which is already evidenced by the increase in adsorption capacity with temperature. The positive value of ΔS^o reflects the increased disorderliness at the solid-solution interface. These results are quantitatively similar to those obtained by other researchers for the removal of Cu (II) by algal biomass [11].

Table 03: Thermodynamic Parameters for the bio-adsorption of Cu (II) onto *Vaucheria* sp. at different temperatures.

Biomass	**Temp (K)**	**$\Delta G°$ (kjmol^{-1})**	**$\Delta S°$ (kj mol^{-1} K^{-1})**	**$\Delta H°$* (kjmol^{-1})**
***Vaucheria* sp.**	298	-19.885	0.0910	7.249
	308	-20.855	0.0912	
	318	-21.706	0.0910	

*measured between 298 K to 318 K

3.5. Kinetic Models

The findings of the adsorption kinetics of copper (II) onto the adsorbent surface are shown in Table 4. The slope of the linear plot of ln (q_e-q_t) *vs.* time (Figures 6a) and t/q_t *vs.* t (Figure 6b) was used to compute the adsorption rate constants k_1 for pseudo-first-order and k_2 for pseudo-second-order, as given in Table 4. Despite the fact that both kinetic models have good correlation coefficients (better than 0.98), table 4 data show that q_e, cal. values for the pseudo-second-order are substantially closer to q_e, exp. values than pseudo-first-order values. As a result, it appears that Cu (II) sorption onto the adsorbent is more pseudo-second-order. Other researchers came up with similar conclusions [27].

Figure 06. (a) Pseudo-first order (b) Pseudo second-order kinetic modeling of copper (II) adsorption onto *Vaucheria* sp.

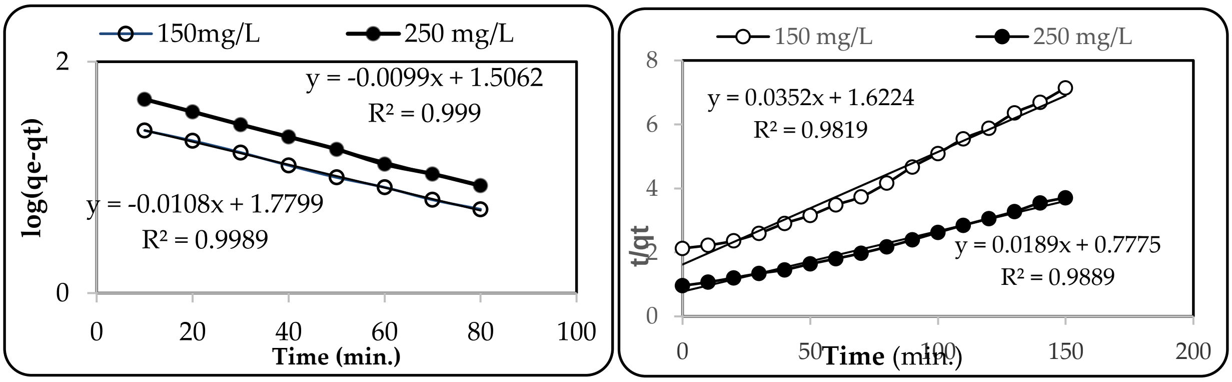

Table 04: Comparison between adsorption rate constants, q_e estimated and coefficient of correlation associated to the Lagergren pseudo-first and second-order adsorption for the *Vaucheria* sp. (pH 5.0).

Bio-mass	**Initial Cu (II) conc. (mg/L)**	**q_e, (exp.) (mg g^{-1})**	**Pseudo-First-order model**			**Pseudo-Second-order model**		
			k_1x10^{-3} (min^{-1})	**q_e cal. (mg g^{-1})**	**R^2**	**k_2 x 10^{-3} (g mg^{-1} min^{-1})**	**q_e, cal. (mg g^{-1})**	**R^2**
***Vauche-ria* sp.**	150	21.4	22.79	32.07	0.999	0.763	28.41	0.982
	250	40.5	24.87	60.24	0.998	0.459	52.91	0.989

4. Conclusion

In this study, the effect of adsorbent dose, pH, temperature, and contact time on Cu (II) adsorption onto *Vaucheria* sp. biomass was observed. At 5 pH, 318 K, 80 minutes contact time, and 0.8 g algal dose, the adsorption capacity was 46.29 mg/g. The Freundlich and Langmuir adsorption isotherms, both adequately describe equilibrium sorption. Cu (II) adsorption onto biomass was found to be feasible, spontaneous, and endothermic based on its thermodynamic characteristics. Compared to the pseudo-first-order model, the pseudo-second-order model better reflects adsorption kinetics. It has been discovered that functional groups (–COOH, –OH, and –NH_2) on algal surfaces are involved in the adsorption of Cu (II). As demonstrated in this study, *Vaucheria* sp. algal biomass could serve as an effective and cost-effective adsorbent material for the removal of Copper (II) from synthetic wastewater.

5. Acknowledgement

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6. Conflict of Interest

The author declares that there is no conflict of interest.

7. Funding

No Funding

8. References

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