PREPARATION, CHARACTERIZATION, AND ADSORPTIVE REMOVAL STUDIES OF HEAVY METAL COPPER FROM AQUEOUS SOLUTION USING CHITOSAN OLIGOSACCHARIDE-BASED SCHIFF BASE

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Abstract

Low molecular weight chitosan, known as chitosan oligosaccharide (COS), is derived from prawns, crab shells, and other microorganisms. Since COS dissolves in water, it cannot be directly applied to water treatment applications. However, because of their better qualities, COS derivatives and blends indicate that there is still room for improvement in the manufacture of derivatives that may be tailored for a range of uses. Heavy metals are thought to be extremely hazardous to health. Heavy metal-contaminated water needs to be treated before being used for washing or irrigation. Adsorption is a significant and inexpensive technique used to extract metals from water. To remove Cu(II) ions from the aqueous solution, a novel hybrid material called COS-SB-MBA (chitosan oligosaccharide Schiff base with 4-methoxy benzaldehyde) was utilised as the adsorbent in the batch adsorption procedure in the present work. The prepared Schiff base was characterised using different analytical techniques such as FTIR, XRD, DSC, and SEM studies which proved the effective formation of the Schiff base. Studies on the adsorption isotherm and the kinetics of the adsorption process were carried out. The results demonstrated how COS-SB-MBA removed copper from aqueous solutions. The process exhibits pseudo-second-order kinetics and a Freundlich adsorption isotherm, demonstrating that the adsorption is multilayer in nature.

Key Words: Chitosan Oligosaccharide Schiff base, 4-Methoxy benzaldehyde, adsorption, Copper

1. Introduction

Heavy metals' toxicity, non-degradability, biomagnification, and ability to accumulate via a food chain make water pollution by these metals a serious worldwide problem (Sun et al., 2014). Water bodies are known to be contaminated by heavy metals. Copper, zinc, lead, nickel, cadmium, mercury, chromium, and so on are examples of heavy metals (Lakatos et al., 2002). Additionally, inorganic contaminants known as heavy metals can be detected in industrial, ground, marine, and even treated effluent (Mahvi, 2008). Even while certain heavy metals, including copper, selenium, zinc, and others, are necessary for human existence and health, excessive use of these metals can be harmful to other living things (Nuhoglu et al., 2002). A variety of techniques, including filtration, electrodialysis, ion exchange adsorption, and precipitation, have been developed to separate and remove metal ions from aquatic environments (Zhou et al., 2014). Adsorption using inexpensive non-traditional adsorbents has been utilised recently to remove contaminants from contaminated water.

Biopolymers—such as the amino polysaccharide chitosan—have drawn interest as effective, affordable adsorbents. Chitosan Oligosaccharide (COS), a low-molecular-weight derivative of chitosan, has the same function but is soluble in water. Therefore, to increase its mechanical strength and functionality and make it insoluble in water COS is altered both chemically and, more appropriately, physically. Because COS contains free amino groups, aldehydes can react with ease to generate Schiff bases by a straightforward condensation process. Therefore, 4-methoxy benzaldehyde was used to condense COS in the current study (MBA). The resulting COS-MBA Schiff base was utilised for the adsorption of copper and heavy metals from an aqueous solution after its synthesis was confirmed through characterization.

2. Materials and Methods

The India Seafood Company, with its headquarters located in Cochin, Kerala, India, provided chitosan oligosaccharide. Copper (Cu (II)) solutions with a concentration of 1000 mg/L were prepared. Ultrapure copper sulfate was used to prepare the copper solutions. During the preparation procedure, potassium dichromate can be utilized as a stabilizer or oxidizing agent. Working solutions were prepared by diluting the Cu (II) stock solutions. Presumably, standard solutions of different concentrations were produced by further diluting the working solutions.

2.1. Synthesis of chitosan oligosaccharide-4-methoxy benzaldehyde Schiff Base (COS-MBA-SB)

Approximately 1 g of chitosan oligosaccharide was dissolved in 100 ml of deionized water and the mixture was rapidly stirred for 30 min using a magnetic stirrer to ensure complete dissolution. The prepared chitosan oligosaccharide solution was then supplemented with approximately 1 ml of 4-methoxy benzaldehyde. Subsequently, the resultant mixture was continuously stirred on a magnetic stirrer for 12 h at 60 °C until it became an evenly distributed solution. The crude product was filtered, cooled, rinsed with ethyl alcohol, and vacuum dried at 60°C.

2.2. Characterization

The reactive groups in the sample were identified using a SHIMADZU FTIR Spectrometer making it pellets with potassium bromide at ambient temperature. The FTIR spectrum was recorded within wavenumbers 400–4000 cm^{-1}. To confirm the crystalline and amorphous nature of the adsorbing material, powder XRD analysis was performed using a SHIMADZU XD–D1 X-ray diffractometer, which uses Ni-filtered Cu Kα as the X-ray energy source. The diffractometer was operated at 40 kV voltage and 30 mA, with λ=0.154 nm in the 2θ range of 5° to 80°.

2.3. Batch Adsorption studies

The biosorption of copper was assessed by batch adsorption experiments using a chitosan-oligosaccharide-based Schiff base sample. 100 mg/L standard mixture containing $CuSO_4$ was first prepared by dissolving 0.1809 g of $CuSO_4$ in 1000 mL of deionized H_2O. One hundred milliliters of standard $CuSO_4$ solution were taken separately and placed in two conical flasks. Approximately 1 g of the prepared chitosan-oligosaccharide-based Schiff base was added to each solution. The mixture was then vigorously agitated for 60 min. After agitation, the solution was allowed to acclimatize before being removed from the shaker. Once the resultant mixture was filtered, the metal content in the filtrate was estimated using AAS assays. Adsorption has been studied in batch mode. Optimal conditions were obtained by varying the working adsorption factors, such as pH, time of contact, adsorbent dosage, and initial metal ion concentration while maintaining the other parameters constant. The percentage removal of the test metal ions was calculated using the following equation:

$$\% \, Adsorption = \frac{C_i - C_e}{C_e} \, x \, 100$$

Where Ce is the metal ion equilibrium concentration and Ci is the initial metal ion concentration.

3. Results and discussion

3.1. Fourier Transform Infrared Spectroscopy (FTIR)

The functional groups in the prepared COS-SA-SB and their interactions with each other were determined using FT-IR spectroscopy. The FTIR spectra of the prepared chitosan oligosaccharide – MBA Schiff base Schiff base before and after Cu(II) adsorption are presented in **Figures 1 and 2.**

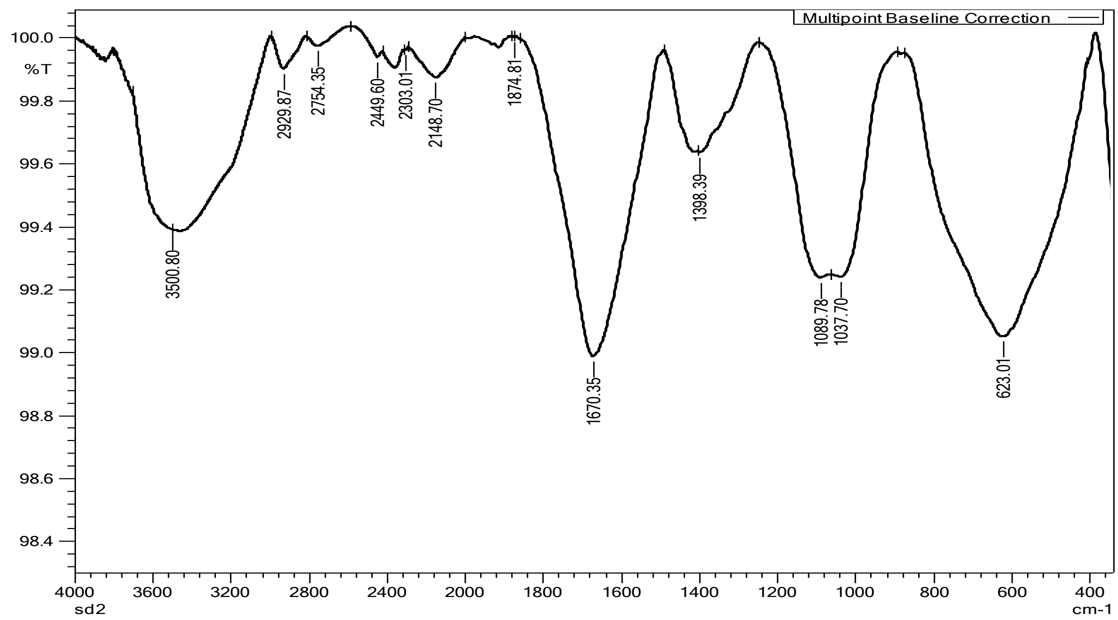

Figure 1: FTIR spectrum of the COS-MBA Schiff base

Figure 1 shows the FTIR spectrum of the synthesized COS-MBA Schiff base. The occurrence of the hydroxyl –OH group was indicated by a broad and visible band at 3500.80 cm^{-1} spectral area, which is related to the stretching vibrations of the OH, -NH2 groups and intermolecular H-bonding. Intermolecular hydrogen bonding, OH bond stretching, and NH2 group stretching vibrations were initiated by the broad spectrum at 3423.65 cm^{-1} as mentioned by Sharef et al., (2022). A notable band in the spectrum for the -carbon-nitrogen double bond was observed at 1670.35 cm^{-1}, which represents the imine C = N vibration that most often formed between the C=O group of aldehydes and the NH_2 group of chitosan oligosaccharide (Vadivel et al., 2019). The saccharide group structure (chitosan oligosaccharide) exhibited distinct peaks at 1089.78 cm^{-1}, 1037.70 cm^{-1}. These peaks demonstrate the existence of C-O-C linking, C-O stretching, and C-C extension. The unique absorption at the 623.01 cm^{-1} wavelength range reveals metal-oxygen binding fingerprint areas (Antony et al., 2019)

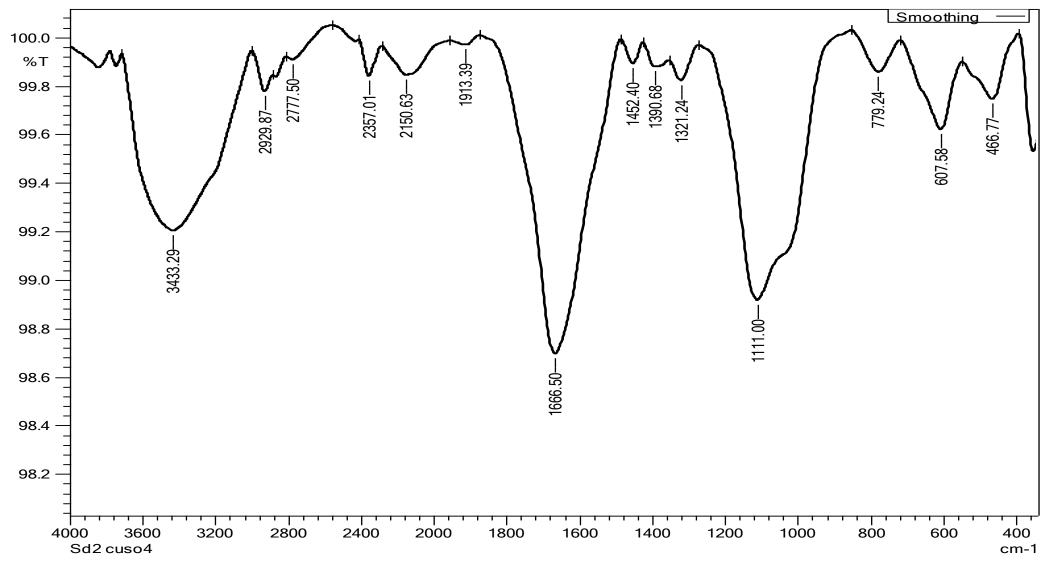

Figure 2: FTIR spectrum of the COS-MBA Schiff base after Copper adsorption

Figure 2 shows a shift to the lower wavelength of the peak at 3433.29 cm^{-1} showing the interaction of the metal copper with the lone pair of electrons on the -O-H and -NH_2 groups. Similarly, the peak representing the imine group – C=N is shifted to a lower wavelength of 1666.50cm^{-1}proving the copper adsorption on the functional groups of the Schiff base. The -C-O-C- linkage band also is shifted. The new bands are observed at 779.24cm^{-1} and 466.77cm^{-1} showing the adsorption of heavy metal copper on the COS-MBA Schiff base. These changes indicate the interaction between the metal ions and the adsorbent surface. Overall, some of the adsorption peaks shifted or disappeared and new peaks were formed which was due to the adsorption of copper onto the adsorbent surface (Rao, 2021)

3.2. XRD Analysis

X-ray diffraction patterns of the COS-MBA Schiff base are represented in **Figure 3.** The normal peaks that are observed in COS at around 10^0 and 20^0 are changed and merged as a single peak at 25^0 in the case of the COS-MBA Schiff base.

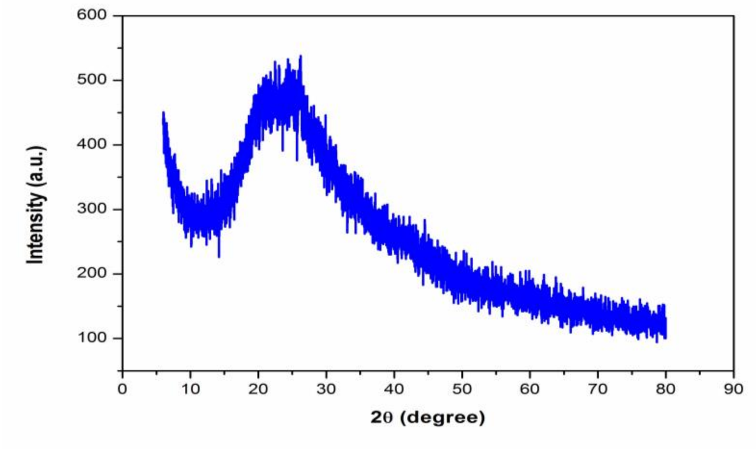

Figure 3: X-Ray diffractogram of COS-MBA Schiff base

The peak has become very broad and the amorphous area under the peak also has been reduced indicating the conversion of crystalline to amorphous nature of the Schiff base. During reactions of functional groups, such as the covalent and noncovalent interactions between the COS and MBA, the NH_2 of oligosaccharide polymers, and the aldehyde of MBA form new imine bonds which may induce disturbance in the fundamental structure. The amorphous nature of the produced material means, that it is expected to serve as an effective adsorbent for the adsorption of metal ions into and out of the Schiff base surface and lead to effective binding (adsorption) (Balaji et al., 2021).

3.3. Scanning Electron Microscopic Studies

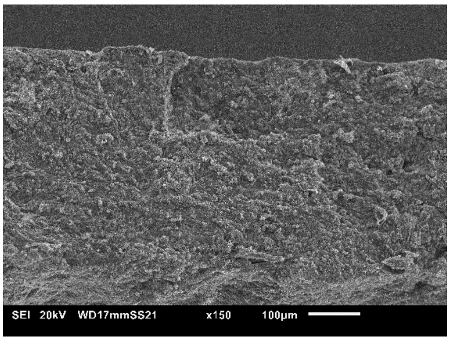

Figure 4: SEM Cross-sectional image of COS-MBA Schiff base

Figure 4 represents the cross-sectional SEM image of COS-MBA Schiff base. There is a complete preservation of the porous network structure of the material (Zhang et al., 2020). The rough texture even in the cross section confirms the availability of many pores with available functionalities throughout the material which facilitates efficient adsorption of metal copper onto the Schiff base material.

3.4. Studies on batch adsorption

Removal of heavy metal copper had been performed in a discontinuous mode ie. Batch mode under different operational conditions. By varying the pH, contact time, adsorbent dose, and initial concentration of the metal solutions, the chitosan-oligosaccharide-based Schiff base efficiency to remove copper (II) metal ions was examined using a batch adsorption technique.

3.4.1. Effect of pH

The efficiency of sorption processes during wastewater treatment depends significantly on the pH of the solution. Furthermore, changing the pH of a metal ion-containing solution can significantly affect the rate at which the ions are absorbed into the biosorbent. This is because the surface charge of the metal ions and absorbent material are both affected by the pH (Beni, and Esmaeili, 2020). The pH can affect the adsorption properties of a Schiff base towards metal ions. To study the effect of pH on the chitosan oligosaccharide-based Schiff base as an adsorbent, the adsorption process was carried out at various pH values (2.0 to 9.0) at room temperature.

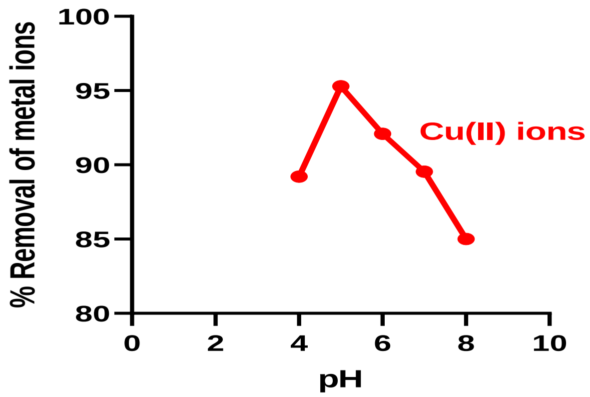

Figure 5: Effect of pH on Cu (II) adsorption by COS-MBA Schiff base

The degree of functional group protonation on the Schiff base surface based on chitosan oligosaccharide varied at different pH values, as shown in **Figure 5.** The attraction or repulsion of electrostatic forces between the adsorbent material and metal ions may be affected by a shift in the surface charge. Changes in pH can have a significant impact on the reactive groups present on ionized adsorbent surface materials (Yu et al., 2016). The graphical data demonstrate that increasing the pH value for Cu (II) ions from 3 to 5 enhances the efficiency of metal ion removal from the adsorbent. At pH 5, the copper (II) ion removal efficiency was optimized, yielding a 95.3% removal percentage. Furthermore, a notable reduction in the percentage of Cu (II) ions removed from the adsorbent was noted at pH values higher than 6 (Ramteke and Gogate, 2016).

Because harmful metal ions aggregate as OH- at higher pH levels, the rate of adsorption slows down, which reduces the ability to eliminate heavy metals.

3.4.2. Effect of dosage of adsorbent

The objective of this study was to determine whether the addition of the COS-MBA-SB adsorbent dosage influences Cu(II) sorption from the solution under specific circumstances. In a series of batch adsorption studies, different sorbent weights of an aqueous solution containing Cu(II) metal ions were used, ranging from 1 g to 5 g. Other variables were maintained constant, such as pH, the volume of the Cu (II) metal solution (100 mL), the initial concentration at 200 ppm, the duration of contact (60 min), and the effect of Cu(II) sorption on the COS-MBA-SB adsorbent dose were assessed.

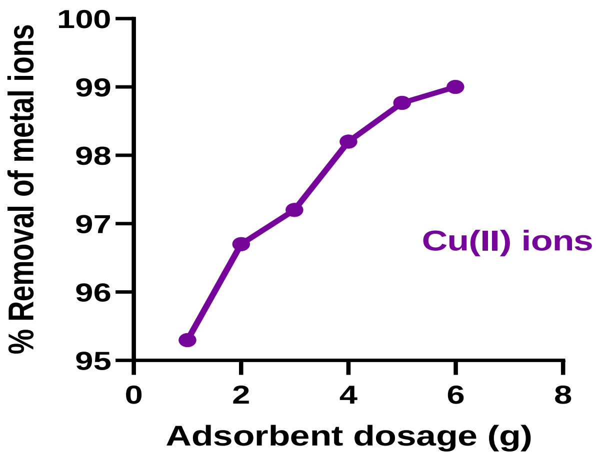

Figure 6: Effect of dosage of adsorbent on Cu (II) removal by COS-MBA Schiff base

In a batch experiment, as represented by **Figure 6** demonstrates how the dosage of the adsorbent, the COS-MBA Schiff base interacts to effectively adsorb toxic heavy-metal copper ions. The adsorption of Cu (II) ions using various adsorbent doses is depicted graphically in **Figure 6**. According to the given data, it was confirmed that using more adsorbent than the recommended dosage of 5 g had no discernible impact on the adsorption process for Cu (II) metal ions. Hence, it was found that the ideal dosage for copper and chromium ions was 5 g of the adsorbent. By increasing the sorbent weight from 1 g to 5 g, there are several ways in which this alteration can affect the removal efficiency of metal ions from a solution. One significant effect is the increase in the number of active sites free of interactions with the target metal ions. The functional groups on the sorbent surface and metal ions in the solution interact to form association bonds. The formation of coordination bonds is facilitated by the release of more active sites as the sorbent weight increases (Normi et al., 2023).

3.4.3. Effect of time in contact

Cu(II) adsorption on COS-MBA-SB was studied in the time interval of 1–8 h. **Figure 7** illustrates the impact of the duration of contact on the efficacy of Cu (II) adsorption while maintaining the adsorbent dose (1 g/100 mL), constant temperature (25 °C), pH 5, initial copper concentration (200 mg/L), and agitation rate (200 rpm). Under particular operating conditions, usually at equilibrium, the optimum adsorbent ability, which adsorbs the maximum amount of metal ions onto the adsorbent, is measured (Ojedokun, and Bello, 2016). This made it feasible to calculate the ideal amount of time required for the adsorption process.

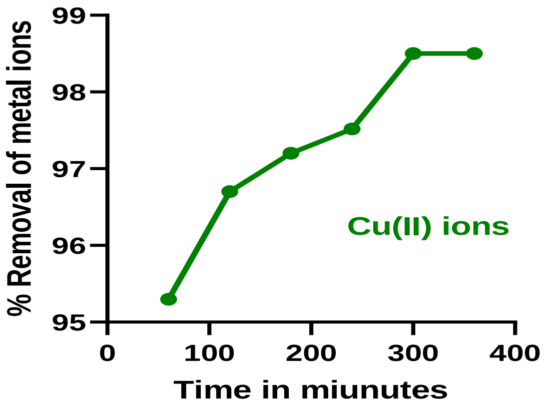

Figure 7: Effect of time of contact on the adsorption of Cu (II) by COS-MBA Schiff base

The graphical illustration in **Figure 7** shows that the duration of the interaction between the heavy metal ions and the COS-SA-SB adsorbent increased the availability of copper (II) ions on the surface of the adsorbent. The rate of adsorption of Cu(II) metal ions was greater up to 180 min and later decreased considerably between 180 and 300 min. Finally, after 300 minutes, it subsequently exhibited a lack of development. Consequently, the capacity of the adsorbent to eliminate Cu (II) ions from the solution is aided by its greater availability (Elhag et al., 2020). The ideal contact duration for the adsorption of Cu (II) metal ions was determined to be 300 min based on the results of studies performed at different time intervals. This finding suggests that the adsorption process decreased after 300 min because the number of binding sites became less accessible with time.

3.4.4. Effect of initial concentration of metal ion

The chitosan oligosaccharide-based Schiff base adsorption capacity may be influenced by the concentration of Cu (II) metal ions in the batch adsorption system. To determine the initial metal ion concentration for the removal of Cu (II), 1 g of the COS-MBA-SB adsorbent was used during a 1-hour contact period at an ambient temperature. To remove Cu(II) metal ions, the metal ion concentration was initially adjusted to 1000, 500, 200, 100, and 50 mg/L at pH 6. **Figure 8** shows the results.

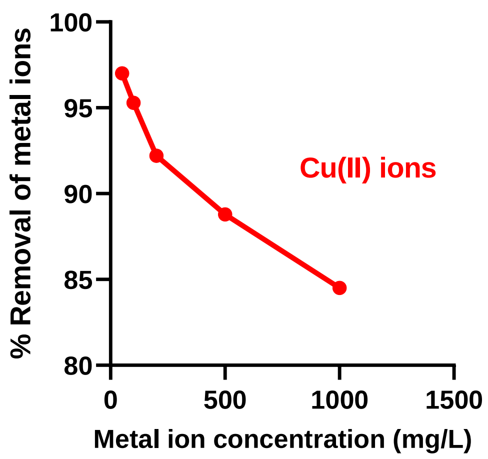

Figure 8: Effect of Initial Concentration of Metal Ion on adsorption of Cu(II) by COS-MBA Schiff base

Based on the observed results, it was determined that the Schiff base based on chitosan oligosaccharide adequately reduced Cu (II) ions from metal solutions at lower concentrations than other metal ion concentrations. This also implies that the reactive molecules of the Schiff base have a greater affinity for Cu (II) ions, facilitating effective removal, even at lower concentrations. Compared to the amount of metal ions in the solution, there are comparatively more accessible surface-active sites on the adsorbent when the metal concentrations are low. This suggests that a greater percentage of metal ions can bind to readily available locations on the adsorbent efficiently, increasing the removal percentage (Wu et al., 2022). In conclusion, the large ratio of metal ions to accessible surface-active sites enables efficient removal even at low metal concentrations. The elimination percentage decreased as the concentration increased because the available areas quickly became saturated.

3.5. Adsorption Isotherms

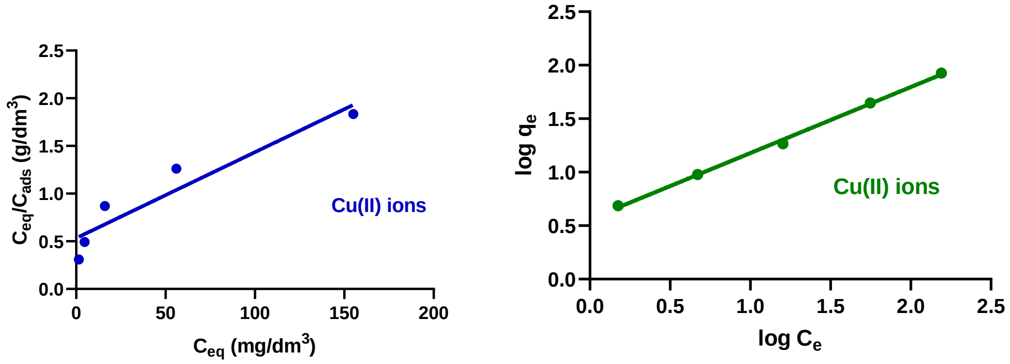

Figure 9a) Plot of Langmuir adsorption Isotherm b) Plot of Freundlich adsorption Isotherm

Table 1: Adsorption Isotherm constants of Copper adsorption on COS-MBA Schiff base

Adsorbent	Langmuir constants				Freundlich constants		
	K_L (dm^3/g)	b	C_{max}	R^2	K_F	n	R^2
COS – MBA - SB	1.87546	0.0169	110.963	0.8942	1.1378	1.62074	0.9979

Table 1 and Figures 9a and b represent the Isotherm parameters of the adsorption process of copper metal on the prepared COS-MBA-Schiff base. The calculated value indicates that the adsorption follows more of Freundlich isotherm when compared to Langmuir isotherm indicating more of physical interactions than chemical interactions. The functions groups such as -OH, -NH2, -C=N and so on makes copper to interact with the Schiff base with dative bonds, Vander Waals forces and little number of electrostatic interactions. Similar results were obtained by Mittal et al., (2023) proving physisorption and multilayer adsorption.

3.6. Adsorption kinetics

Adsorption kinetics studies are vital before employing any adsorbent in an operational setup. Adsorption kinetics refers to the rate of adsorption, including the degree to which adsorbate molecules attach to the surface of the sorbent material. Several models, including pseudo-first-order(PFO) and pseudo-second-order (PSO) equations, describe the kinetics of adsorption reactions. This study used the chitosan oligosaccharide-based Schiff base adsorbent to remove Cu(II) heavy metal ions. They are commonly used in adsorption methods due to their affordability and high capacity.

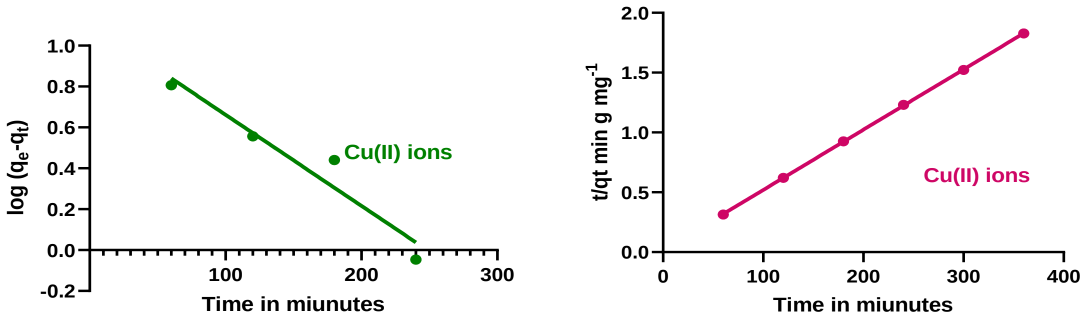

Figure 10: a) Plot of PFO kinetics of Cu adsorption b) Plot of PSO kinetics of Cu adsorption

Table 2: Kinetic parameters of Copper adsorption on COS-MBA Schiff base

Sample	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
	q_e (mg/g)	k_1 (min^{-1})	R^2	q_e (mg/g)	k_2 (g mg^{-1} min^{-1})	R^2
COS-MBA SB	90.74	0.00199	0.9301	198.72	0.005167	0.9995

On analysing **Figures 10a and b and Table 2**, it was confirmed that the adsorption of metal copper on the COS-MBA adsorbent followed pseudo Second Order. Similar results were obtained in the investigation by Rekha et al., (2023)

4. Conclusion

Thus, Chitosan oligosaccharide and 4-Methoxy benzaldehyde were condensed to form a COS-MBA Schiff base and characterized for its formation, crystallinity, and morphology to confirm its suitability for the adsorption process. Copper a toxic heavy metal in larger doses was adsorbed onto the prepared Schiff base by changing the operational parameters such as pH, contact time, dosage of the material, and initial metal concentration. The obtained values helped in the calculation of the adsorption isotherm parameters which confirmed multilayer physisorption following Freundlich isotherm. The kinetics study also confirmed second-order kinetics proving the complete involvement of the sorbate and sorbent in the adsorption process. Overall, the material prepared proved to be an efficient one for the removal of heavy metals.

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