



Sorption studies on the removal of copper onto biopolymer derivative: chitosan-g-maleic anhydride-g-ethylene dimethacrylate

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The current work suggests employing an unique Chitosan-g-Maleic anhydride-g-ethylene dimethacrylate copolymer to remove the harmful heavy element copper. By adjusting variables like the concentration of the monomer, the concentration of the initiator, and the temperature during the chain polymerization reaction, the graft copolymer was developed. The copolymer obtained at the optimum condition was picked out to study its adsorption property towards Cu²⁺ ions. The adsorption factors, such as the amount of adsorbent, contact time, pH, and initial concentration of the metal solution, which affect the adsorption process, were looked at using the batch adsorption mode. Freundlich and Langmuir isotherm models were applied to analyse the equilibrium adsorption.

[**Keywords:** Grafting, Chitosan-g-MA, adsorption]

Introduction

Due to the rapid and unregulated industrialization that is occurring to satisfy the tremendous demand for heavy metals from the expanding population, heavy metals are being released into the ecosystem. Because some heavy metals are extremely hazardous even at small levels, aquatic habitats are seriously threatened by pollution from these metals. Furthermore, because they are difficult to biodegrade and have a propensity to accumulate in living things, heavy metals could have a major detrimental effect on both human and animal health¹.

Toxic metals, noble metals, and radionuclides are the three categories of heavy metals that are deemed dangerous². Lead, chromium, zinc, arsenic, cadmium, nickel, and copper are toxic heavy metals³. Chemical precipitation, coagulation, reverse osmosis and ion exchange are the conventional methods typically used for effluent treatment⁴.

The primary drawback of using conventional procedures is that they are expensive and unsustainable. Other downsides include insufficient metal removal, high energy needs, and the requirement for careful waste disposal of toxic sludge⁵. Wastewater treatment is of vital importance because it has become

obligatory to analyse all effluents and need strict integrated pollution documentation before their ultimate release due to the health concerns posed by heavy metals. The utilisation of industrial waste products or readily accessible natural materials as adsorbents is also possible^{6,7}.

Chitosan is a semicrystalline polymer when it is solid⁹. Chitosan has been shown to be physiologically effective, non-toxic, non-antigenic, biocompatible, and biodegradable¹⁰. Two key goals of chemically altering chitosan are to change its solubility in water or acidic medium and to enhance its metal adsorption capabilities. This encompasses chain elongation processes including cross-linking, graft copolymerization and enzymatic depolymerization¹¹.

The comparatively large number of nitrogen sites can be used to explain the strong attraction of metal ions in these sorbents. Chitosan's ability to bind to metals depends on its crystallinity, water affinity, deacetylation level (DD), and amino group concentration¹². These variables may have an impact on its biological, physicochemical, and conformation in solution¹³. The percentage of free NH₂ groups that will be available for interactions with metal ions depends on the quantity of deacetylation. The two

most used techniques for determining the degree of deacetylation are FTIR and NMR analysis¹⁴.

According to kinetic studies, the raw material, preparation technique, chemical modification, and particle shape all determine how fast metallic ions bind to chitosan. Numerous investigations have shown that chitosan has a strong ability for solubilizing metals and favourable kinetics for the majority of metals¹⁶. Guibal¹² and Gerente¹⁵ have provided reviews.

The major goal of this work was to determine whether a brand-new hybrid material called CS-g-MAH-g-EDMA could effectively remove Cu(II) ions. To assess the metal adsorption capability of the CS-g-MAH-g-EDMA copolymer, batch adsorption tests were carried out.

Materials and Methods

Chitosan was purchased from India Sea Foods in Cochin, India. Both the chemical ethylene dimethacrylate and the analytical-grade monomer maleic anhydride were purchased from Merck. All of the analytical-grade compounds required for the other substances were obtained.

Preparation of Chitosan-g-Maleic anhydride

100 ml of acetic acid were combined with 2 g of chitosan, 5 g of maleic anhydride, and 0.5 g of ceric ammonium nitrate in 10 ml of nitric acid. The mixture was then agitated for three hours at 70 °C. The end product was precipitated by adding the resulting solution to 10 % NaOH after it had cooled to room temperature. The finished product underwent many filters and washes in diethyl ether before being dried under vacuum at 40 °C. N-maleilated chitosan was obtained as a greyish white powder.

Preparation of Chitosan-g-Maleic anhydride-g-Ethylene Dimethacrylate

The co-polymer was consistently created in aqueous solution using ceric ammonium nitrate as the initiator. 2 g of ethylene dimethacrylate dissolved in ethanol was added after 0.5 g of maleilated chitosan had been dissolved in 150 mL of formic acid. At 70 °C, the reaction went on for 30 minutes. To precipitate the graft co-polymer, the flask's contents were cooled to room temperature and then kept in a 10 percent NaOH solution. Aspects like the yield and efficiency of the grafting process, the monomer concentration, the reaction temperature, and the initiator and monomer concentrations were all researched.

Characterization of CS-g-MA-g-EDMA

The Perkin Elmer Spectrum FTIR spectrometer was used to record the FTIR spectra of the samples, with range of 400 to 4000 cm^{-1} . The X-ray diffractometer (D8 Advance Bruker, Germany) and SEM (Hitachi - S3400N), was used to study the crystalline nature and surface morphology of the copolymer CS-g-MA-g-EDMA.

Preparation of stock solution

The stock solutions were made by combining 1 liter of double-distilled water with 0.786 mg of CuSO_4 . The mass-based concentration of the metal ion solution was determined using the mg L^{-1} unit of measurement. The required lower concentrations were made by dilutions from stock solution over time.

Batch adsorption studies

Stoppered bottles were filled with a synthetic Cu(II) ion solution, and the bottles were shaken in an orbit shaker with composite films at a preset speed of 160 rpm. Through independent adjustments to the adsorption dose, contact time of shaking, and solution pH, the extent of heavy metal removal was assessed. After reaching equilibrium, the adsorbent was separated using filter paper, and the quantity of metal in the aqueous phase was calculated using an AAS.

Results and Discussions

Preparation and characterization of CS-g-MAH-g-EDMA

The investigation of the FTIR spectra of the CS-g-MAH and CS-g-MAH-g-EDMA copolymer is shown in Figure 1(a & b). The massive bands in the FTIR spectrum of the copolymer CS-g-MAH copolymer were designated as follows: 3451 cm^{-1} for the stretching vibrations of the OH and NH, 2897 and 2832 cm^{-1} for the stretching vibration of the CH in CH and CH_2 , 1769 cm^{-1} for the stretching vibration of the C=O, 1643 cm^{-1} for the stretching vibration of the C=C of grafted maleic anhydride, 1558 cm^{-1} for the NH deformation.

The FTIR spectrum of the synthetic CS-g-MAH-g-EDMA copolymer (Fig. 1b) reveals a shift in the bands for the OH and NH stretching vibrations from 3451 to 3361 cm^{-1} and the C=O stretching from 1769 to 1719 cm^{-1} . The second grafting of CS-g-MA utilising EDMA monomer is what caused the alterations in band locations that were noticed. The number of carbonyl groups (C=O), ester groups, and C=C groups increased when EDMA formed the graft copolymer, which is anticipated to lead to greater metal-ligand interaction during the metal ion removal

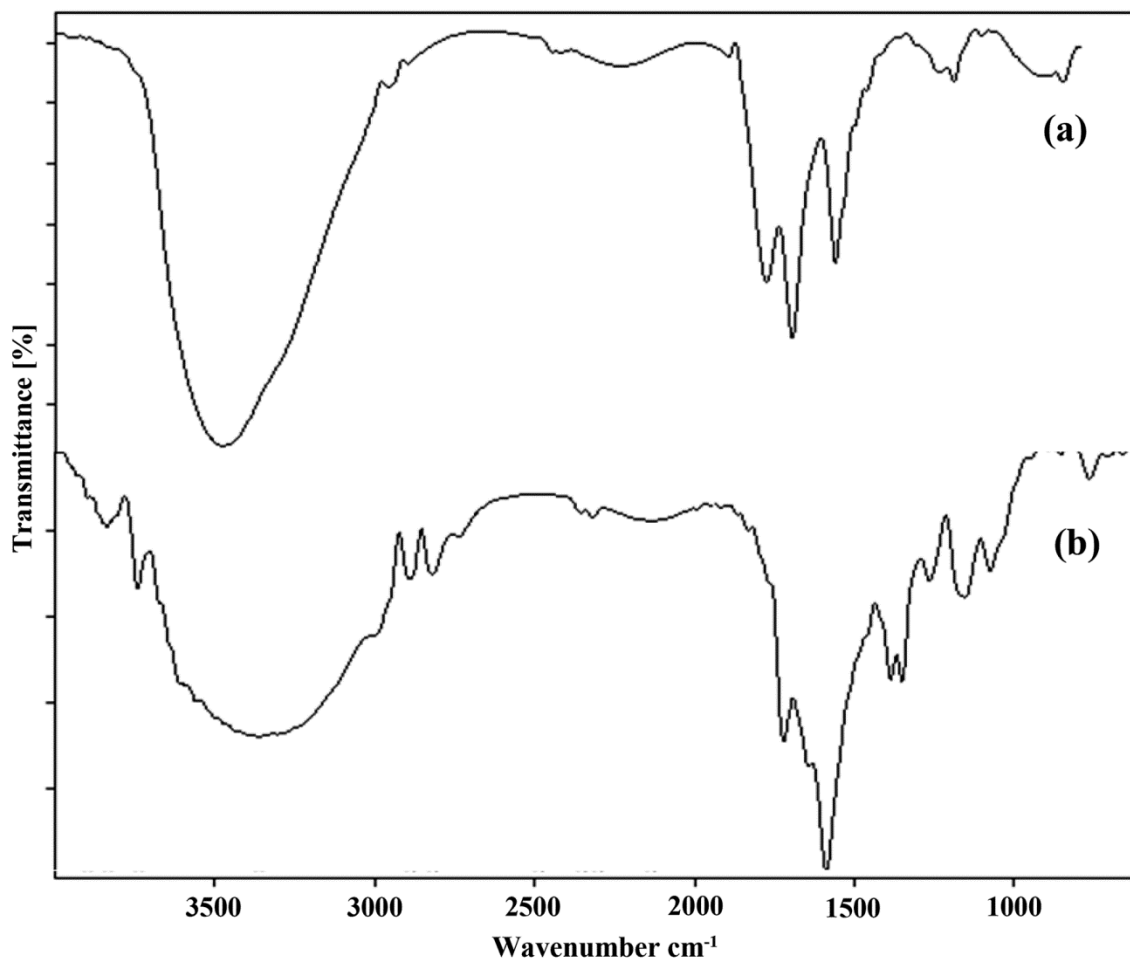


Fig. 1 — a) FTIR spectrum of Chitosan-g-Maleic anhydride; and b) FTIR spectrum of Chitosan-g-Maleic anhydride-g-Ethylene dimethacrylate copolymer

process. The molecular miscibility during double grafting may be the cause of the change^{17,18}.

Additionally, the intensity of the C-H and C=C groups bands increased when comparing the FTIR spectra of single graft and double grafted copolymers, demonstrating the effectiveness of double grafting utilising EDMA¹⁹. When copper ions were adsorbed onto the double-grated CS-g-MAH-g-EDMA copolymer, a similar observation was anticipated. Based on this, Figure 2 provides the adsorption mechanism.

Additionally, the amorphous character of the prepared double grafted copolymer, a crucial quality for adsorption was supported by the XRD and SEM analyses. Peaks at $2\theta = 44^\circ$ and $2\theta = 45^\circ$ were visible in the XRD patterns of CS-g-MAH and CS-g-MAH-g-EDMA copolymers, respectively, in Figure 3(a & b) and was shown to have less crystallinity when compared to the other grafted

copolymers. Due to the addition of additional molecules onto a single grafted copolymer, the polymeric chains have become less regular, which may be the cause of the lack of crystalline²⁰. Therefore, it is anticipated that metal ions will penetrate the copolymer's surface. This resulted from the CS-g-MAH and EDMA copolymer's strong contact when they mixed well at the molecular level.

Figure 4(a & b) show SEM images of prepared composites. The amorphous nature of the material is evidenced by the rough surface morphology visible in the SEM pictures. The surface of the CS-g-MAH-g-EDMA copolymer was very rough and had a greater number of pores when compared to the CS-g-MAH copolymer, which is evident in Figure 3(b). This demonstrated that the prepared copolymer would be an effective adsorbent for the removal of metal ions.

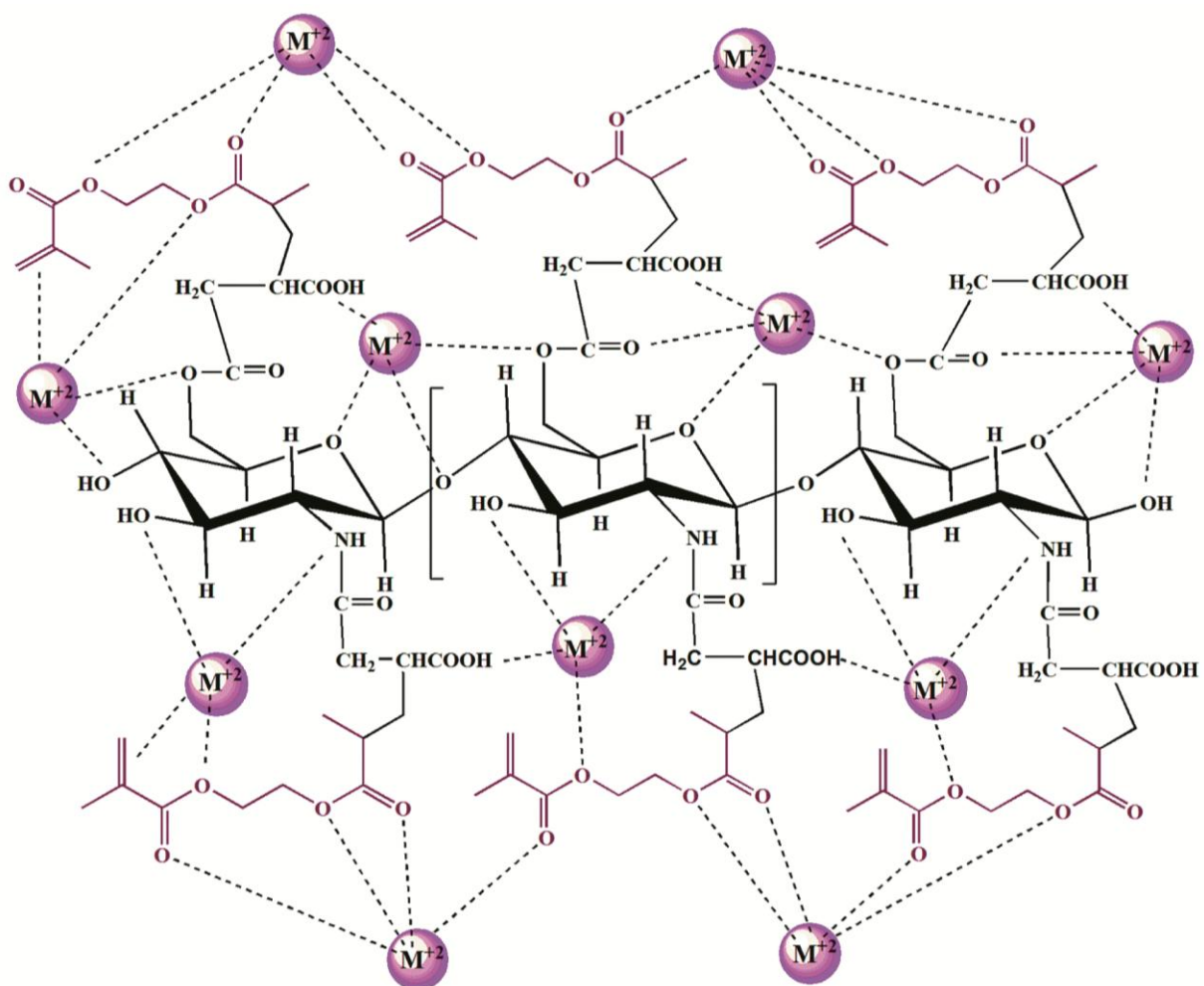


Fig. 2 — Proposed mechanism for the adsorption of copper on to double grafted Chitosan-g-Maleic anhydride-g-Ethylene dimethacrylate copolymer

Factors influencing the adsorption of Cu (II) ions

Influence of dosage

The experiment's other parameters remained constant while the adsorbent concentrations, which ranged from 1 to 6 g, were changed. It was found that when the dosage of adsorbent increases, the percentage of Cu^{2+} ions removed steadily rises (Fig. 5). This increase resulted from more surface area becoming available when the adsorbent dose increased during the adsorption process²¹. At a dosage of 6 g, the percentage of Cu(II) that could be removed most effectively was about 90.1 %. The minimal surface area is accessible for additional metal ion adsorption after a specific dose of adsorbent because maximal adsorption has already taken place²². As a result, even when the adsorbent dose is increased, the quantity of free ions in the solution and the ratio of ions bound to the adsorbent both stay unchanged.

Effect of contact time

The effect of contact time was studied by varying the contact time from 60 to 360 min and the results were given in Figure 6. The effective adsorption occurred because there was initially a larger surface area accessible for the adsorption of Cu^{2+} ions²³. However, as contact duration increases, the absorption of metal ions decreases, which may be because there are fewer active sites for adsorption until equilibrium is reached²⁴. The results demonstrate that after 360 min of increasing contact time, the rate of metal ion removal remained constant (91.7 %). As an outcome, the ideal contact time for the highest removal was 360 min²⁵, proving that this is one of the key elements for a sustainable wastewater treatment.

Effect of pH

Through protonation and deprotonation, a little pH change affects the sorbent surface as well as the

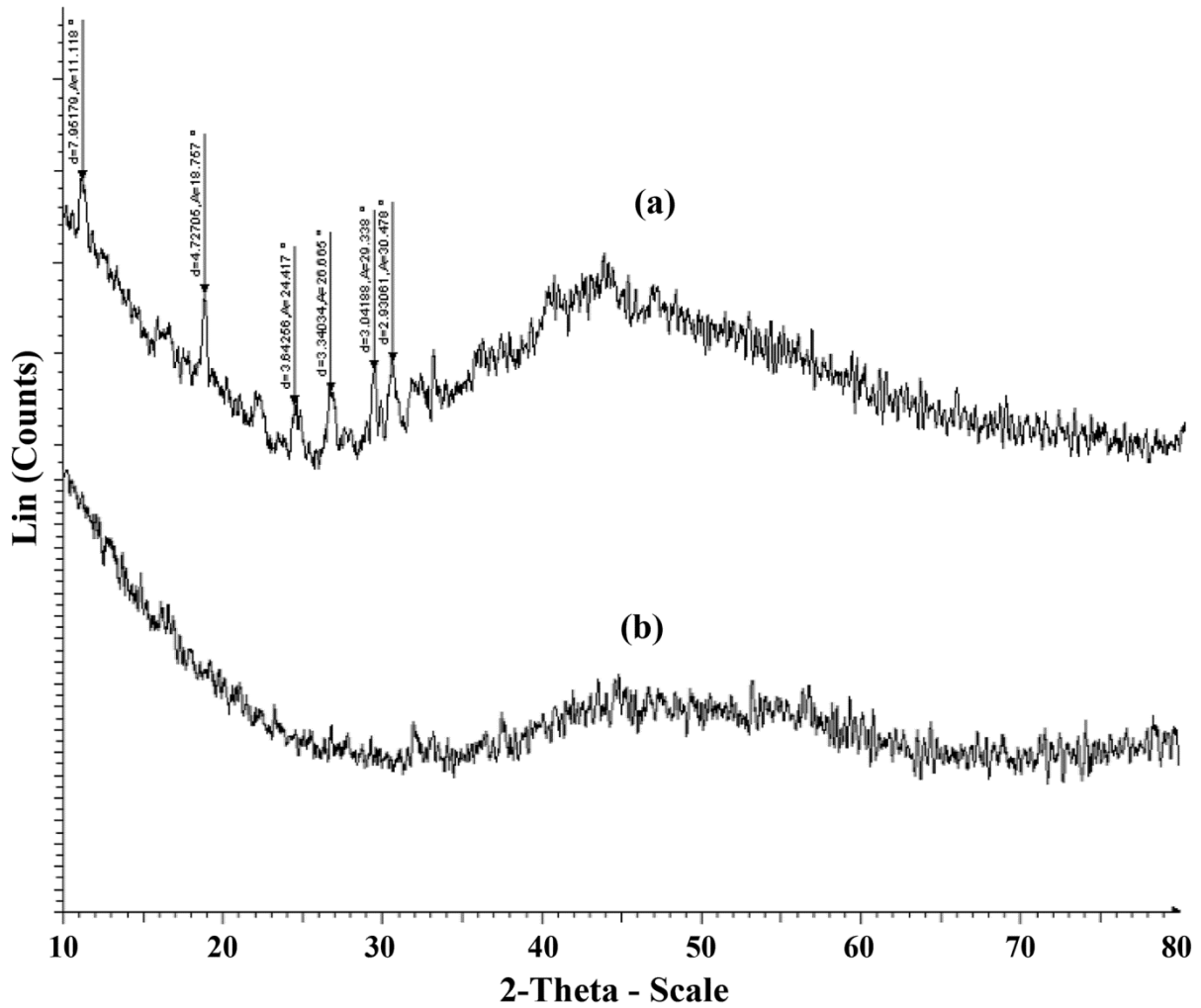


Fig. 3 — a) XRD pattern of Chitosan-g-Maleic anhydride; and b) XRD pattern of Chitosan-g-Maleic anhydride-g-Ethylene dimethacrylate copolymer

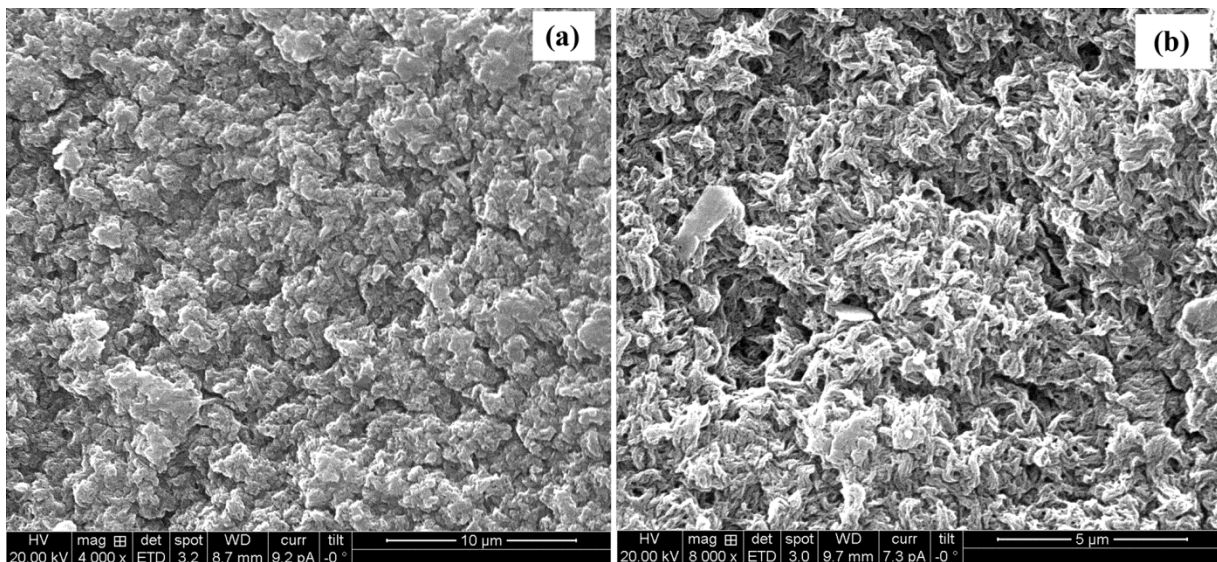


Fig. 4 — a) SEM image of Chitosan-g-Maleic anhydride; and b) SEM image of Chitosan-g-Maleic anhydride-g-Ethylene dimethacrylate copolymer

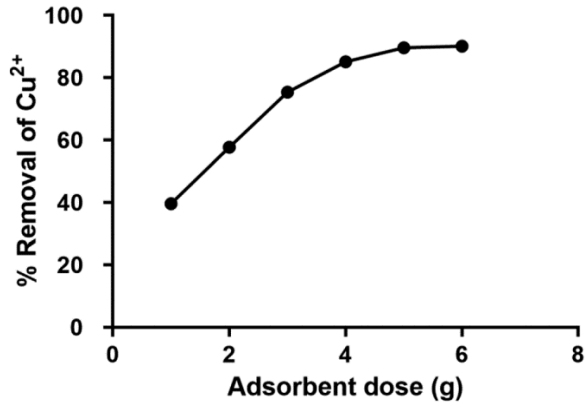
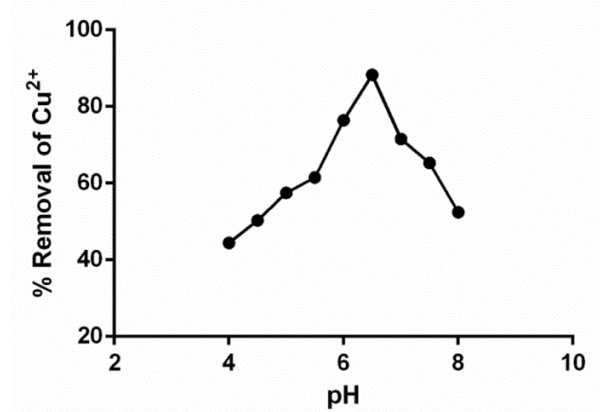
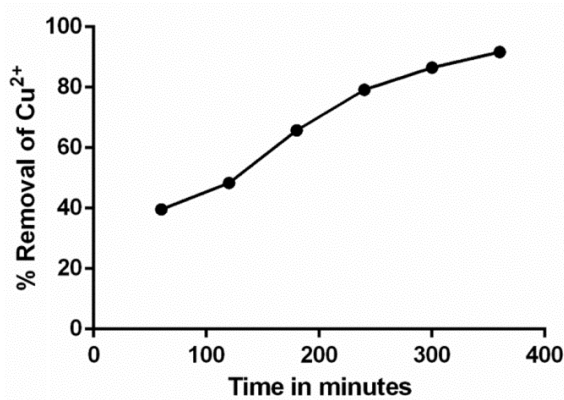
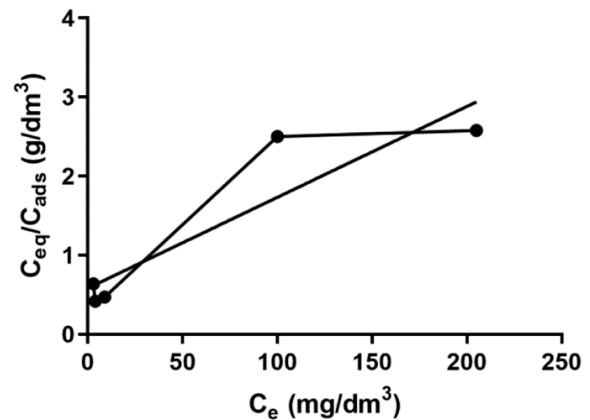
Fig. 5 — Effect of adsorbent dose on the removal of Cu²⁺ ionsFig. 7 — Effect of pH on the removal of Cu²⁺ ionsFig. 6 — Effect of contact time on the removal of Cu²⁺ ions

Fig. 8 — Langmuir isotherm for the removal of Copper (II) ions

ionic species of metal ions in water^{26,27}. Figure 7 shows that as the pH of the metal ion solution increases, the adsorption gradually increases and then gradually declines. The highest rate of Cu(II) removal was around 88.3 % at pH 6.5. 6.5 was shown to be the optimal pH for the adsorption process²⁸. The electrostatic repulsion between surface and metal ions was reduced at this pH due to a decrease in the rivalry between proton and metal ion attraction²⁹ to the same functional groups as well as a drop in the positive surface charge on the adsorbent³⁰.

Adsorption isotherms

Langmuir sorption isotherm

The monolayer adsorption on an energetically homogeneous surface with no intermolecular interactions is explained by the Langmuir model³¹⁻³³. Once the monolayer formation is fully saturated, equilibrium is reached³⁴. Every sorption site was thought to be similar, and whether or not sorbate could bind there regardless of whether or not nearby sites were occupied³⁵. The Langmuir model written as:

Table 1 — Langmuir isotherm constant, C_{max} and correlation coefficient

Metal ion	Langmuir constants			
	K _L (dm ³ .mg ⁻¹)	b (dm ³ .mg ⁻¹)	C _{max} (mg.g ⁻¹)	R ²
Cu ²⁺	1.7155	0.01973	86.95	0.8370

$$C_{eq}/C_{ads} = bC_{eq}/K_L + 1/K_L$$

Where, C_{ads} = amount of metal ions adsorbed (mg g/1); C_{eq} = equilibrium concentration of metal ion in solution (mg dm/3); K_L = Langmuir constant (dm³.g/1); b = Langmuir constant (dm³.g/1)³⁶.

The Langmuir equation's constants 'b' and 'K_L' are its two distinguishing features, and the linearized version of the equation allows for their determination³⁷.

Figure 8 and Table 1 for every gram of copolymer, the C_{max} value is 86.95 mg of copper. R² value indicates a linear or correlative relationship. R_L factor determines whether an adsorption system is favour or unfavour, can be utilised to define the key characteristics of a Langmuir isotherm³⁸.

Metal ion	Initial concentration C_o (mg.dm ⁻³)	Final concentration C_f (mg.dm ⁻³)	R_L values
Cu ²⁺	1000	795	0.0599
	500	393	0.1142
	200	191	0.2097
	100	96	0.3455
	50	47	0.5189

Metal ion	K_f	n	R^2
Cu ²⁺	0.5883	1.7879	0.9230

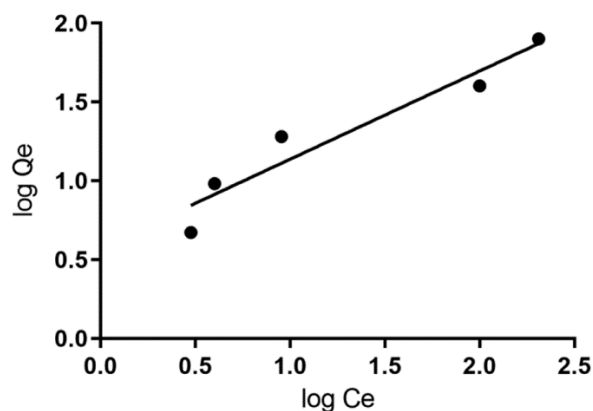


Fig. 9 — Freundlich isotherm for the removal of Copper (II) ions

Since the values for the adsorption of Cu(II) onto composite are in the range of $0 < R_L < 1$ (Table 2), the graft copolymer is a successful adsorbent³⁹.

Freundlich isotherm

To describe multilayer adsorption, including particles of different sizes that have been adsorbed⁴⁰. The adsorbate concentration in the solution is expected to rise, according to the model. The model is applicable to reversible and uniformly distributed energy adsorption onto heterogeneous surfaces equation follows:

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

Where, C_e = Equilibrium concentration of adsorbate in solution after adsorption (mg dm³); K_f = Empirical Freundlich constant or capacity factor (mg g/1); $1/n$ = Freundlich exponent or Freundlich intensity factor⁴¹.

The Freundlich isotherm of copper (II) ion is shown in Figure 9. Mathematical modeling revealed that the values of n , which reflect favourable sorption, range between 1 and 10^(ref. 42).

K_f and n , the Freundlich constants, are equal to 0.5883 and 1.7879 (Table 3). The Freundlich equation can be used for surfaces other than homogeneous surfaces⁴³. The creation of multilayer adsorption is

demonstrated by a heterogeneous surface⁴⁴ and an adsorption isotherm. Since $1/n$ is less than unity, it can be concluded that there is significant adsorption even at low concentrations.

Conclusion

FTIR spectroscopy verified with the prepared composites. In order to determine the most effective way of removing metal ions, the effects of adsorbent dosage, contact time, and medium pH were examined. The Freundlich adsorption isotherm and Langmuir were better matched in terms of the regression coefficient. As a result, the CS-g-MAH-g-EDMA performs well as an adsorbent.

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Conflict of Interest

The authors declare that there is no conflict of interest.

Ethical Statement

This work was not published in any mean and no endangered species are being used in this study.

Author Contributions

MRGR: Experimental data analysis and manuscript writing; TG: Manuscript formatting and result interpretation; SP: Plagiarism and reference formatting; JAKF: Data interpretation; RS: Data analysis; and PNS: Conceptualization and editing the manuscript.

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