Synthesis, Characterization, Kinetics, and Thermodynamics of EDTA-Modified Chitosan-Carboxymethyl Cellulose as Cu(II) Ion Adsorbent

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ABSTRACT: A new adsorbent derived from the naturally occurring biopolymers, chitosan (CS) and carboxymethyl cellulose (CMC) was prepared by cross-linking them using EDTA. EDTA having high affinity for metal ions can be used to enhance the chelation properties of the adsorbent enormously. The product obtained (chitosan-EDTA-CMC, CSEC) was characterized by different techniques: FTIR, XRD, SEM/EDAX, TGA, and XPS. The parameters for evaluation of the adsorption properties for removal of Cu(II) ions from the aqueous solution were determined using the batch adsorption method by studying the effect of pH, contact time, initial ion concentration, and temperature on adsorption. Pseudo-first-order, pseudo-second-order, and intra-particle diffusion kinetic models were applied to study the kinetics of the adsorption process, whereas Langmuir, Freundlich, Temkin, and D-R models were applied to evaluate the thermodynamics of the adsorption process. The kinetic adsorption parameters were in best agreement with the pseudo-second-order model, while thermodynamic parameters best fitted to the Langmuir isotherm at different temperatures for adsorption of Cu(II) ions from aqueous solution with a maximum adsorption capacity of 142.95 mg/g at pH 5.5. CSEC showed excellent regeneration capability and recovery of the Cu(II) ion up to five cycles without the loss of the adsorption efficiency, which is the best characteristic to select the appropriate choice of the adsorbent. The adsorbent was also employed in batch experiments to evaluate the adsorption of hardness, producing common metal ions in single and real wastewater solutions.

1. INTRODUCTION

Increasing industrialization has led to serious ecosystem concerns due to intake of excessive toxic pollutants into either underground or exposed water bodies. Toxic pollutants in large quantities such as heavy metal ions (copper, cadmium, lead, arsenic, and mercury), dyes, etc., are discharged into the water bodies on a daily basis, all of which are highly toxic to all forms of living systems at higher concentration above the permissible limits proposed by the WHO. The permissible limits of Cu(II) from industrial effluents is 0.25 mg/L, whereas the permissible limit in the drinking water is 1.3 mg/L. Cu(II), being the low-cost metal ion and with its extensive application in various industries, is the most discharged heavy metal pollutant from industries. Hence, degradation or removal of these toxic heavy metal ions from wastewater is essential to save the biological life on Earth.1−3 Copper in bonded form, however, is essential as a cofactor for many enzymes in low concentrations including cytochromes and in ceruloplasmin (the major copper-carrying protein in blood), which reduces oxidative stress, but it is toxic in its unbounded form. When its concentration increases slightly, it results in impairment of zinc homeostasis, which further causes disruption of antioxidant enzyme function and finally increases oxidative stress.4 Deposition of copper in hepatic parenchyma cells, brain, periphery of the iris, and kidneys excessively causes serious disorders, such as Wilson’s disease.5,6 Several methodologies have been implemented for copper removal such as professionally installed reverse osmosis,9 backwashing media filtration systems or an ion exchange system,10−12 precipitated materials,13 carbon nanotubes,14 and biopolymeric membranes.15,16 Moreover, the electrochemical precipitation17 and adsorption are the most significant methods.20−25 Adsorption is one of the most cost-effective and environmentally sustainable approach for decontamination of wastewater at a low concentration.26−28 Numerous materials ranging from inorganic composites to nature-derived activated charcoal from various biomass have been evaluated for removal of toxic pollutants dyes, heavy metal ions, organic pollutants, etc. Although these materials have comparable removal efficiencies, however, there are more disadvantages such as the source from which adsorbents are derived, environmental sustainability, cost efficiency, regeneration ability, and source renewability, which force the researchers for further investigation and development of new adsorbent systems. Biopolymers from natural resources, which are nontoxic, environment-friendly, and renewable, provide an extensive ability to undergo chemical transformation through simple cross-linking and condensation reactions due to the presence of a large number of functional groups.29,30

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All the techniques cited above compel toward the engineering of polymeric systems that are contacted with water for everyday functions for the handling of wastewater for a variety of pollutants as researchers are striving to improve the favorable surface interaction of polymers with water bodies. Biopolymers provide an alternative by which surface hydrophilicity and biodegradability can be introduced for acquiring the environmental sustainability.

Among biopolymers, chitosan and carboxymethyl cellulose have heteroatoms such as nitrogen and oxygen in their backbones, which are exercised for surface modification to increase the adsorption efficiency. In the present work, chitosan-carboxymethyl cellulose-based adsorbent is synthesized through single-pot synthesis in the presence of EDTA to modify the surface of the biopolymers, which simultaneously increases the adsorption efficiency and mechanical properties while decreasing their swelling on contact with wastewater. Besides adsorption of Cu(II) ions, CSECM, furthermore, effectively decreases the hardness of water by chelating the calcium and magnesium ions. To fulfill the gap of knowledge, different studies were carried out: (i) effect of pH, contact time, initial ion concentration, and temperature; (ii) thermodynamics and kinetics, which were carried out by using different models; (iii) applicability of data fit on the basis of error analysis; and (iv) regeneration of CSECM and recovery of the Cu(II), which are important characteristics to justify the selection of the material; biodegradability test was also further investigated by burying the worn-out samples into the soil.

2. EXPERIMENTAL SECTION

2.1. Materials and Methods. Carboxymethyl cellulose (low viscosity) was purchased from Sigma Lifescience, chitosan (degree of deacetylation, ≥75%) was provided by HiMedia India, and p-toluene sulfonyl chloride (TsCl) was purchased from SDH Fine Chemicals (India). Copper nitrate was obtained from Fisher Scientific India. EDTA (dipotassium salt), sodium hydroxide, glacial acetic acid (99–100%), and phenolphthalein were purchased from Merck India. Throughout the experiment, doubly distilled water was used.

2.2. Preparation of Chitosan-EDTA-CMC (CSECM). An effective protocol for waste-minimized, environmentally benign thermal condensation of carboxylic acids with amines has been identified. One gram of chitosan (2 × 10⁻³ mol) was dissolved in 0.01 M acetic acid solution until a clear solution was obtained; the solution was centrifuged several times to remove the impurities. Similarly, solutions of CMC (0.524 g, 2 × 10⁻³ mol) and EDTA (1.168 g, 4 × 10⁻³ mol) were prepared in doubly distilled water. Initially, the EDTA solution was mixed with TsCl in the molar ratio of 1:2 to obtain the tosylated form of EDTA in a three-necked round-bottom (RB) flask. The solutions of CS and CMC were added simultaneously to the RB flask containing the tosylated EDTA solution, at one drop per 30 s. The contents of the RB flask were kept on continuous stirring for 72 h at 80 °C until the reaction was complete as slightly higher temperatures are required for challenging the starting materials. The product was precipitated out as such in the reaction vessel due to intense intramolecular hydrogen bonding, washed several times with distilled water, and dried in oven at 50 °C. The
approach leads to the corresponding esters in good yields (Scheme 1).

### 2.3. Characterization of Materials

#### 2.3.1. Degree of Epoxy Content

The number of epoxy groups formed in the product was determined by the titration method using acetone/hydrochloride (1:1) solution. HCl reacts with the adsorbent and causes the protonation of the epoxy groups. The remaining H⁺ concentration is determined by titration of the solution with NaOH using phenolphthalein as an indicator. The number of equivalents of H⁺ reacted is equal to the number of epoxy groups in the adsorbent.

\[
E_{\text{pr}} = \frac{V_0 - V_f}{W_g} \times C_{\text{NaOH}}
\]  

where \(V_0\) (mL) and \(V_f\) (mL) is the volume of NaOH consumed by acetone/HCl solution before and after reaction with the adsorbent, respectively, \(C_{\text{NaOH}}\) (M) is the concentration of NaOH used in the titration, and \(W_g\) is the weight of the adsorbent in grams.

#### 2.3.2. Characterization of CSECM Product

FTIR was carried out by using a Bruker Tensor 37 spectrophotometer by scanning the product in the wavelength range from 4000 to 650 cm⁻¹. SEM micrographs were obtained by using an FEI Quanta 200 FESEM (50–500 X). XRD analyses were carried out with a D8 Advance diffractometer (Bruker) with Cu target \(\lambda = 0.154\) nm at 40 kV, and 2θ was 10°–80°.

The crystallinity index was calculated using the equation

\[
\text{CrI} = \frac{I_{200} - I_m}{I_{200}}
\]  

where \(I_{200}\) is the intensity at 2θ ≈ 20.72°, and \(I_m\) is the intensity of baseline at 2θ ≈ 70.5°.

### 3. RESULTS AND DISCUSSIONS

Adsorption parameters such as the effect of pH, initial ion concentration, contact time, temperature, and rate of adsorption were evaluated through the batch adsorption method. To maintain the criterion of optimality, an entire set of the experimental parameter(s) were varied individually one by one, keeping the remaining ones as fixed. A series of solutions with concentrations varying from 100 to 200 ppm, an adsorbent dose of 100 mg, temperature ranging from 303 to 323 K, contact time of 10 to 80 min, and pH from 3 to 8 were prepared; 10 mL of each solution was used for the adsorption study, and thus, effective optimization of each parameter is achieved for the best results.

Both naturally occurring and synthetic compounds widely consist of the amide bond linkages. There is considerable interest in the development of new approaches to direct amidation. In the presented work, there is a focus on the development of novel, atom-economic, environmentally benign methods for this process in engineering newer combinations of biopolymers for designing the technologies for wastewater treatment. An important consideration here is the direct thermal amide formation from the naturally occurring amines present in chitosan and carboxylic acid in CMC (Scheme 1). Importantly, a solid-phase purification procedure is reported that enables the product to be obtained without aqueous workup or chromatography, henceforth, the simplicity in separating the reagents from the resulting products.

The presence of amine and hydroxyl groups both in chitosan and CMC is responsible for the adsorption feature in the polymer backbone. EDTA had been reported to have strong chelation with the metal ions as a hexadentate ligand and generally employed in the determination of hardness of water by complexometric titrations among the crude experiments. Thus, as a result of chelation of heavy metal ions, the CSECM can effectively remove the hardness of water via coordination with calcium and magnesium ions from their salts responsible for hardness. CSECM hypothetically must show strong affinity for positively charged heavy metal ions. This procedure is more convenient for general use and could be potentially used in establishing its employment in removing not only copper but the other common ions from the wastewater discharges.

### 3.1. Structure Characterization

#### 3.1.1. Quantitative Estimation of Epoxy Content

The titration used for determination of epoxy groups using HCl/acetone solution was carried out three times simultaneously under similar laboratory conditions. Calculations using eq 1 revealed that the epoxy groups in the product were ~0.15 mmol g⁻¹.

#### 3.1.2. FTIR Characterization

FTIR spectra of chitosan, CMC, CSECM, and metal-loaded adsorbent are shown in Figure 1. The major differences in the FTIR spectra of CS, CMC, and CSECM among the appearance of the bands are at 1705 cm⁻¹, 1686 cm⁻¹, 1157 cm⁻¹, 897 cm⁻¹, and other bands in the fingerprint region. The peak at 1705 cm⁻¹ can be
assigned to C=O due to stretching vibration of the ester group formed by reaction of the carboxyl group of EDTA and the hydroxyl group of CMC, while the bands appearing at 1399, 1580, and 1650 cm$^{-1}$ appear due to C-N stretching, N-H bending, and C-O stretching of amide vibrations, respectively.49 Absorption bands appearing at 1624 and 1481 cm$^{-1}$ are likely due to asymmetrical stretching of C=O of the carboxylate group.50,51

Furthermore, the bands appearing in the fingerprint region, particularly at 1152 and 899 cm$^{-1}$, are attributed to the glycosidic bridge. The bands appearing at 1036, 1020, 1052, and 1036 cm$^{-1}$ are the characteristic C-O-C stretching vibrations of the glucopyranose ring. Besides, the bands at 3400, 3200, 3000, and 2850 cm$^{-1}$ are the characteristic peaks of $\equiv$NH$_2$, $\equiv$OH, C-H, and $\equiv$C-H (next to carbonyl group of ester) stretching vibrations appearing in all the FTIR spectra, respectively. However, a slight shift toward lower frequency in the bands of the metal-adsorbed adsorbent can be assigned to the adsorption of metal ion, leading to slight reduction in frequency.35,52–54

3.1.3. SEM and EDAX Characterization. The surface morphologies of all the reactants and products are reported in Figure 2a. As observed from the figure above, both CMC and chitosan have smooth and nonporous surfaces; however, the surface of the adsorbent appears to be porous and granular with increased surface area, which certainly enhances the adsorption.

The elements present in the adsorbent CSECM were detected by EDAX, as shown in Figure 2b. The peak heights resemble the relative concentrations of metals. The EDAX spectrum confirms the presence of copper ions on the surface of the adsorbent besides C, N, and O, which are the main constituents of the adsorbent.

3.1.4. XRD Characterization. The XRD patterns of chitosan, CMC, and CSECM are given in Figure 3. In chitosan, the diffraction maximum at $2\theta = 20.25$ is characteristic of the crystalline form of chitosan with a crystallinity index of $\sim 76.57\%$, while that of CMC at $20.45$ is $81.36\%$ due to the lesser crystalline nature of CMC. However, in CSECM, the diffraction maximum at $2\theta = 21.05$ has a crystallinity index of $94.89\%$, which indicates the higher crystallinity of CSECM.

Figure 1. FTIR spectrum of (a) CS, (b) CMC, (c) CSECM, and (d) metal-loaded CSECM.

Figure 2. (a) SEM micrographs of (i) CMC, (ii) CS, (iii) CS-ES-CMC, and (iv) CSECM-Cu(II) (2000× magnification) and (b) EDX micrographs of (i) CSECM and (ii) CSECM-Cu(II).
The higher crystallinity index indicates the ordered structure of the CSEM probably due to cross-linking.

3.1.5. Thermal Stability of CS, CMC, and CSEM. Figure 4 shows the thermogram of the cross-linked adsorbent (CSECM) and the biopolymers CS and CMC from which it was synthesized; as evident from the figure, the adsorbent CSECM is thermally more stable than the corresponding biopolymers from which it was synthesized. The degradation of chitosan begins at 10 °C with 30% loss, whereas that of CMC starts at 250 °C with 60% degradation. In comparison, the degradation of CSECM starts at 170 °C with just 10% loss, making it thermally more stable than the native material from which it is synthesized.55,56

3.1.6. XPS Analysis. XPS analysis was carried out on the adsorbent before and after adsorption to account for the adsorbent surface, as shown in Figure 5. The high-resolution full survey spectrum of the adsorbent shows the peaks at 40.5, 289.9, 399.6, and 534.17 eV, which correspond to O2s, C1s, N1s, and O2s, respectively; however, the spectrum of the adsorbent after copper adsorption shows an extra peak at 932.5 eV, which corresponds to Cu2p.57 The peaks of Cu(II) in the XPS spectrum confirm its surface deposition on the adsorbent. The binding energy peaks of O1s at 531.60 and 534.09 eV in the high-resolution XPS spectrum correspond to C=O and C−O of the carbonyl and hydroxyl moieties in CSECM, respectively. Furthermore, a slight shift in these peaks can be observed clearly in the XPS spectrum after Cu(II) adsorption, which suggests the involvement of these functional groups in the Cu(II) adsorption.58,59

3.1.7. Surface Charge Analysis by Zero Point Charge. Zero point charge (ZPC) is the pH at which the net charge on the surface of the adsorbent is zero. Below the pHZPC, the surface of the adsorbent becomes positively charged, whereas above pHZPC, the adsorbent surface is negatively charged. The mechanism of adsorption however does not depend only on pHZPC, but there are other factors that affect the adsorption of species onto the adsorbent. To determine the pHZPC of CSECM, salt addition method60 was used in which a series of 10 mL flasks containing 0.5 mg of CSECM were filled with 50 mL of 0.1 M KNO3 and the initial pH was adjusted from 1 to 12 using 0.1 M HCl and 0.1 M NaOH. The flasks were kept on a constant-temperature water bath and left for 24 h. The supernatant solution was filtered, and final pH was determined using a pH meter. The pH of the solutions affects the ionization of the different pollutants as well as the surface of

Figure 3. X-ray diffractograms of (a) CS, (b) CMC, and (c) CSECM.

Figure 4. TGA thermogram of (a) CS, (b) CMC, and (c) CSECM.

Figure 5. High-resolution XPS spectrum of (a) CSECM and (b) CSECM-Cu and the corresponding spectra of relevant bands.
the adsorbent. The pHZPC was obtained to be 5.4 from the plot of ΔpH versus initial pH (Figure 6).61

3.2. pH Effect on Adsorption of Cu(II) Ions. The pH of a solution is the main factor that affects all other parameters of adsorption behavior by influencing the surface properties of the adsorbent as well as association/dissociation of the adsorbate molecules.62 The variation of adsorption of Cu(II) ions on CSECM with pH is shown in Figure 7a. As clearly shown from the plot, initially, when pH is increased from 3 to 5.5, the H₃O⁺ ion concentration decreases in the solution, rendering the surface of the adsorbent more negative as depicted by zero point charge, thereby increasing the vacant adsorption sites, which results in increased adsorption of Cu(II) ions onto the adsorption sites, attaining maximum adsorption at pH 5.5. However, increasing the pH beyond 5.5 does not yield an increase in adsorption of metal ions probably due to equilibrium as well as competition between metal ions and H₃O⁺. Increasing pH above 7.0 leads to formation of metal hydroxides, which are highly stable and preferentially formed, resulting in decreased adsorption.63

3.3. Contact Time Effect on Adsorption of Cu(II) Ions. The variation of adsorption with contact time is shown in Figure 7b. Contact time is the major parameter used for the evaluation of the kinetics of the adsorption process.64 Initially, all the sites on the adsorbent are vacant, and hence, with increasing contact time between the adsorbent and the adsorbate, the interactions result in an increase in the uptake of Cu(II) ions until the adsorption equilibrium is reached at 40 min. After 40 min, there is no net increase in adsorption as the amount of Cu(II) ions adsorbed equals the amount of Cu(II) ions desorbed.65

3.4. Initial Concentration Dependence of Adsorption. Initial concentration of adsorbate plays an important role in studying the kinetics of adsorption. For studying the effect of initial concentration of the adsorbate, different concentrations of Cu(II) ion, 50, 100, 150, and 200 ppm, were taken at different temperatures: 303, 313, and 323 K. It was observed that, with higher initial concentration, the higher quantity of Cu(II) ion was adsorbed by the adsorbent at equilibrium (Figure 7c). This can be attributed to the fact that, with higher initial ion concentration, the probability of the adsorbent–adsorbate interaction increases exponentially, thereby resulting in increased adsorption.66
3.5. Kinetic Study. For understanding the kinetic behavior of the adsorption of Cu(II) ion onto CSECM, different models were used to correlate the adsorption process. Generally, linear forms of the models are used for obtaining the plots of pseudo-first-order, pseudo-second-order, and intraparticle diffusion models (eqs 3–5; Figure 8) from which the maximum adsorption capacities and other parameters are calculated. The model that explains the adsorption in the best way is obtained by comparing the correlation coefficients ($R^2$), as shown in Table 2.

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$$\ln(q_e - q_t) = \ln q_e - k_1t$$

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

$$q_t = K_{id}^{1/2} + C$$

where $q_e$ and $q_t$ (mg g$^{-1}$) are the adsorption capacities at equilibrium and at time $t$, respectively, $k_1$ and $k_2$ (g mg$^{-1}$ min$^{-1}$) are the first- and second-order rate constants, and $K_{ad}$ (mg g$^{-1}$ min$^{-1/2}$) and $C$ are the intraparticle diffusion rate constants. The results of the plots are summarized in Table 2.

On comparing $R^2$ values, the adsorption of Cu(II) ions onto CSECM is best explained by the pseudo-second-order model ($R^2 = 0.993, 0.999, and 1.000$ at temperatures of 303, 313, and 323 K, respectively) than the other two models, suggesting that the adsorption of Cu(II) ions follows the second-order kinetics.

For obtaining the initial rate $h_0$, the following equation is used

$$h_0 = k_2 q_e^2$$

where $k_2$ and $q_e$ are the second-order rate constant and equilibrium adsorption capacity, respectively.

3.6. Adsorption Isotherms. For establishing the relation between the amounts of adsorbate molecules adsorbed at constant temperature, different models are used. In the present study, four models, Langmuir model, Freundlich model, Temkin model, and D-R model, were applied to interpret the adsorption data.

Table 2. Kinetic Parameters for Adsorption of Cu(II) Ions on CSECM

| metal ions | $k_1$ (min$^{-1}$) | $q_{e,cal}$ (mg g$^{-1}$) | $R^2$ | $k_2$ (min$^{-1}$) | $q_{e,cal}$ (mg g$^{-1}$) | $h_0$ (mg g$^{-1}$ min$^{-1}$) | $R^2$ | initial conc. (mg/L) | $K_{ad}$ (mg/g min$^{-1/2}$) | C (mg/g) | $R^2$
|------------|-------------------|--------------------------|-------|-------------------|--------------------------|-----------------------------|-------|----------------------|-----------------------------|--------|-------
|            |                   |                          |       |                   |                          |                             |       |                      |                             |        |       
| 303 K      | $6.14 \times 10^{-05}$ | 144.57                   | 0.969 | 0.009              | 136.60                   | 17.42                       | 0.999 | 50                   | 0.180                       | 140.431 | 0.794 |
| 313 K      | $6.10 \times 10^{-05}$ | 145.41                   | 0.967 | 0.010              | 141.84                   | 19.39                       | 0.999 | 100                  | 0.287                       | 139.616 | 0.773 |
| 323 K      | $6.10 \times 10^{-05}$ | 145.56                   | 0.977 | 0.010              | 146.62                   | 21.99                       | 0.989 | 150                  | 0.302                       | 139.368 | 0.773 |
|            |                   |                          |       |                   |                          |                             |       | 200                 | 0.378                       | 138.920 | 0.994 |

Figure 8. Kinetic plots of (a) pseudo-first-order, (b) pseudo-second-order, and (c) intraparticle diffusion models for adsorption of Cu(II) ion onto CSECM at various initial concentrations.
the results for the adsorption of Cu(II) ions onto CSECM in the best possible way (Table 3).

The Langmuir model is given as eq 7 (Figure 9a) and assumes that one molecule is adsorbed per site of the adsorbent and the energy of adsorption is constant.

$$\frac{1}{q_e} = \left( \frac{1}{K_L q_m} \right) \frac{1}{C_e} + \frac{1}{q_m}$$

where $q_e$ (mg g$^{-1}$) and $q_m$ (mg g$^{-1}$) are the adsorption capacity at equilibrium and maximum adsorption capacity, respectively, while $C_e$ (mg L$^{-1}$) is the Langmuir constant determined from the slope of the plot between $\frac{1}{q_e}$ and $\frac{1}{C_e}$, also known as the binding energy of adsorption.

Freundlich adsorption is based on the concept of nonuniform distribution of heat of adsorption over a heterogeneous surface and multilayer adsorption. The linear form of the Freundlich model (Figure 9b) is given as $^{71}$

$$\ln q_e = \frac{1}{n} \ln C_e + \ln K_F$$

where $q_e$ and $C_e$ have the usual meaning as noted earlier, and $b_T$ (J mol$^{-1}$) and $A_T$ (L mg$^{-1}$) are the Temkin constants for binding energy and heat of adsorption, respectively.

The Temkin isotherm (Figure 9c) also describes the adsorption behavior of the heterogeneous systems and is given as

$$q_e = \frac{RT}{b_T} \ln A_T + \frac{RT}{b_T} \ln C_e$$

where $C_e$ (mg L$^{-1}$) and $q_e$ (mg g$^{-1}$) are the concentration and adsorption capacity at equilibrium, respectively. The constants $K_F$ and $n$ represent the adsorption capacity and adsorption intensity, respectively.

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$$q_e = \frac{RT}{b_T} \ln A_T + \frac{RT}{b_T} \ln C_e$$

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Relation between the porous structure and adsorption by the adsorbent is explained by the Radushkevich and Dubinin model (Figure 9d) given in linear form\[75,74\] as

\[
\ln q_e = -\beta \left( RT \ln \left| 1 + \frac{1}{C_e} \right| \right) + \ln q_m
\]  

where \(q_m\) and \(C_e\) have the usual meaning as noted earlier, and \(\beta\) (mol\(^2\) kJ\(^{-2}\)) is the constant related to the mean free energy of adsorption \(E\) (kJ mol\(^{-1}\)) as

\[
E = \frac{1}{\sqrt{2\beta}}
\]

The constants \(\beta\) and \(q_m\) were determined from the slope and intercept, respectively. The values of \(E\) between 8 and 16 kJ mol\(^{-1}\) suggest the occurrence of physisorption, while the values higher than 16 kJ mol\(^{-1}\) correspond to chemical adsorption. In the current study for adsorption of Cu(II) on the CSECM adsorbent, the values of \(E\) are calculated as 1.207, 1.303, and 0.950 at temperatures 303, 313, and 323 K, respectively. The best fit model cannot only be decided from the linearization of the plots, but various error analysis parameters (Table 4) are also used for choosing the best fit model. In this study, the Langmuir model best fits the adsorption of Cu(II) on the CSECM adsorbent with \(R^2\) equal to 0.991 and the lowest values for statistical error analyses. Furthermore, the experimental values calculated for \(q_m\) have the highest value for the Langmuir isotherm, as shown in Figure 9b.

### 3.7. Adsorption Thermodynamics

The feasibility and the physiochemical characteristics were determined by evaluation of thermodynamic parameters. The change in free energy, enthalpy, and entropy on the adsorption of Cu(II) onto the adsorbent was evaluated by using the van’t Hoff equation\[75\]

\[
\Delta G^o = -RT \ln K_C
\]

\[
\ln K_C = -\frac{\Delta H^o}{R} \left( \frac{1}{T} \right) + \frac{\Delta S^o}{R}
\]

\[
K_C = \frac{q_m}{C_e}
\]

where \(\Delta G^o\), \(\Delta H^o\), and \(\Delta S^o\) are the standard free energy, enthalpy, and entropy of adsorption respectively, \(R\) is the gas constant (\(\sim 8.314\) J K\(^{-1}\) mol\(^{-1}\)), \(T\) is the temperature, and \(K_C\) is the equilibrium constant, while \(q_m\) and \(C_e\) are the adsorption capacity at equilibrium and equilibrium concentration, respectively.

The values of \(\Delta H^o\) and \(\Delta S^o\) were determined from the slope and intercept of the van’t Hoff plot of \(\ln K_C\) versus \(\frac{1}{T}\) (Figure 10 and Table 5). The increasing negative values of Gibbs free energies obtained at different temperatures correspond to the spontaneous nature of the adsorption process, whereas the increasing negative \(\Delta G^o\) values with increasing temperature suggest that adsorption of Cu(II) ions increased with temperature. As reported in the literature, the \(\Delta G^o\) values up to \(-20\) kJ mol\(^{-1}\) for the adsorption process are usually assigned to the physisorption process that usually occurs due to electrostatic interaction between the groups on the adsorbent and the adsorbate molecules/ions.\[68,76\] In the current study, the values of \(\Delta G^o\) are \(-12.33, -12.82,\) and \(-13.32\) kJ mol\(^{-1}\) at temperatures 303, 313, and 323 K, respectively, suggesting the physisorption of Cu(II) ions onto the adsorbent. The positive value of \(\Delta H^o\) (2.732 kJ mol\(^{-1}\)) corresponds to the endothermic nature of the adsorption process, which is further supported by the increase in negative \(\Delta G^o\) values with temperature. The positive value of \(\Delta S^o\) (49.718 J mol\(^{-1}\) K\(^{-1}\)) indicates the interaction of adsorbate molecule/ions at the interface of solid–liquid junction.

### 3.8. Mechanism of Cu(II) Ion Adsorption

The adsorption of metal ions onto the adsorbent can occur through a number of possible interactions at the interface of the adsorbent, which include coordination of metal ion by the functional groups (–OH, –NH\(_2\), –SH, and COO\(^-\)), electrostatic interactions, or ion exchange. Biopolymers contain high density of functional groups such as –OH, –NH\(_2\), and COO\(^-\), which can be further increased by cross-linking two different biopolymers using an appropriate cross-linker. In the current work, the adsorption of Cu(II) ion onto CSECM can be explained properly by FTIR (Figure 1) and XPS (Figure 4).
analysis. From the FTIR spectrum of the CSECM before and after adsorption in Figure 1, it is clearly evident that there is only a slight change in the stretching vibrations of $-\text{NH}_2$ and $-\text{OH}$ bands, which indicates that there are no coordination linkages between $-\text{NH}_2/-\text{OH}$ and $\text{Cu}(\text{II})$ ion, negating the removal of $\text{Cu}(\text{II})$ ions through complexation. Furthermore, slight changes in the stretching frequencies of $-\text{NH}_2/-\text{OH}$ indicate the strong electrostatic interaction of these groups with the $\text{Cu}(\text{II})$ ions. These results were further supported by the data of XPS analysis. The increase in the binding energy of $-\text{NH}_2$ before and after the adsorption of $\text{Cu}(\text{II})$ ion by CSECM shows the strong interaction between $-\text{NH}_2$ and $\text{Cu}(\text{II})$ due to the fact that the electron density on the N atom decreases on interaction with $\text{Cu}(\text{II})$ ion. Similar changes in binding energies can be noticed in the XPS spectra of C–C, C–O, and C=O.

3.9. Desorption Studies. The adsorption–desorption behavior is an important factor to evaluate the efficiency, regeneration capacity, recovery, reusability, and the economic benefits of the synthesized adsorbent. To evaluate the reusability, 0.01 M EDTA solution was used for desorption characteristics of CSECM. The adsorbent with maximum $\text{Cu}(\text{II})$ ions adsorbed on it was treated several times with 0.01 M EDTA solution, and complete desorption of $\text{Cu}(\text{II})$ ions was obtained in just five adsorption–desorption cycles shown in Figure 11. The results were verified in three concurrent measurements, and it was found that the adsorbent was regenerated completely.

3.10. Soil Biodegradability Test. For testing the soil degradability of the synthesized adsorbent, it was buried under the soil for 50 days, and the samples were characterized by SEM analysis, as shown in Figure 12a, b. It was observed that the synthesized adsorbent began to decompose within 20 days from burial under the soil. The weight of the sample was taken every second day, and the graph (Figure 12c) plotted shows the degradation behavior.

4. CONCLUSIONS

In the present study, a biodegradable-cum-compostable EDTA-modified CS-CMC biopolymer-based adsorbent has been prepared. The exquisiteness of the designed polymer as an adsorbent for copper(II) removal is a one-pot approach in synthesizing it. Further, the distinctive addition is the lessening of the hardness of the water under assessment. CSECM is prepared from natural biopolymers chitosan and CMC by cross-linking them with EDTA and characterized by FTIR, XRD, and SEM/EDX. The adsorption parameters were evaluated by using the batch adsorption method, and adsorption equilibrium was obtained in 40 min at pH 5.5 with a removal efficiency of 142.95 mg/g. The kinetics of the experimental values were fitted with the pseudo-second-order model and Langmuir model for understanding the thermodynamics of the adsorption process with a higher adsorption of 142.86 mg/g for $\text{Cu}(\text{II})$ than the other adsorbents. Adsorption–desorption studies showed that CSECM was completely regenerated up to five cycles using 0.01 M EDTA with the loss of adsorption efficiency to a larger extent. Keeping in view the economic perspective as well as the environmental sustainability, CSECM can be efficiently used for removal of $\text{Cu}(\text{II})$ ions from wastewater. This material extracts the copper out of wastewater, thereby helping the environment sustainability toward generating reusable water and producing fertilizers, increasing the soil fertility post-use dump. It is assumed that the material, by treating the copper containing hard water, will help in protecting the water resources, spurring toward the appropriate, cost-effective, and easily available solutions.

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