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Adsorption of Copper from an Aqueous Solution by Chemically Modified Cassava Starch

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Abstract

The present research work demonstrated removal of Copper (II) ions from an aqueous solution by grafting cassava starch with 5-chloromethyl-8-hydroxyquinoline (CMQ). A copolymer was prepared by grafting CMQ on cassava starch and was characterized by Scanning Electron Microscopy (SEM), Energy Dispersive X-Ray (EDX) and Fourier Transform Infrared (FTIR). The study was performed under different experimental conditions of initial metal ion concentrations, adsorbent dose, time and pH. The maximum adsorption was found to occur at pH value of 6.0 and within 90 min of contact time. The adsorption has been explained in the terms of Langmuir and Freundlich isotherm. The experimental data was found to obey with the Langmuir adsorption isotherm. Although the R^2 value for both the isotherms were close to unity the low chi square value for Langmuir isotherm indicate the applicability of this Cassava Starch CMQ copolymer (CSCMQ) for Cu removal in monolayer with several possible functional groups responsible for sorption of the metal ions. This work suggests that the present CMQ starch copolymer can be more useful for the removal of copper from effluents discharged by industries.

Keywords: Adsorption, Copper metal ions, Cassava starch, Langmuir, Freundlich, adsorption isotherm, kinetics.

Introduction

Rapid industrialization has led to increased disposal of wastewater into the environment. This often exceeds the admissible sanitary standards and results in the adverse impact on aquatic environment and consequently on human health. Wastewater treatment has received greater attention over the years due to the global awareness of the environmental deterioration. A large volume of effluent with hazardous species, namely heavy metals and semimetals, is being discharged every day from industries into aquatic systems [1]. Migration of Heavy metals into non contaminated areas as dust or leachates through the soil and spreading of heavy metals containing sewage sludge are a few examples of events contributing towards contamination of the ecosystems [2].

Most of heavy metals above trace quantities are harmful to humans, animals and plants. Federal and local agencies have therefore stipulated discharge limits on the levels of these heavy metals into the environment. In the course of tissue mineral research, copper toxicity is a common finding. By correlation thousands of tests with symptoms and diagnosis, a picture has emerged of the detrimental effects of copper toxicity on human health as well as on aquatic environment. Copper toxicity is much overlooked because of many important health conditions like fatigue, premenstrual syndrome, anorexia, depression anxiety, migraine headache, and allergies (food and environmental allergies) [3]. In mammals due to copper toxicity wide range of effects such as liver cirrhosis, necrosis in kidneys and the brain, gastrointestinal distress, lesions, low blood pressure, and fetal mortality are found [4–6]. Too much copper in water may damage marine and freshwater organisms such as fish and molluscs [7]. The chronic effect of sublethal concentrations of copper on fish and other creatures is damage to gills, liver, kidneys and the nervous system. It also interferes with the sense of smell in fish, thus preventing them from choosing good mates or finding their way to mating areas [8].

A variety of conventional methods can be used for the removal of copper from an effluent which includes membrane filtration [9], chemical precipitation [10], electro coagulation [11], reverse osmosis [12], solvent extraction [13], biological degradation [14], ion exchange [15] and adsorption [16]. Most of these methods suffer from some drawback, such as the high capital or high operational cost or the disposal of the resulting sludge [17]. Among these techniques, adsorption is generally preferred due to its high efficiency, easy handling, and availability of different adsorbents. So the search for cost-effective adsorbents has become the focus of attention for many studies [18].

Recently, with respect to the ability to remove heavy metal ions from aqueous solutions, modified cellulose, chitin and its derivative and modified starch have been studied. Starch is one of important agricultural biopolymers used in the industry due to its low cost, renewability and biodegradability. There are many starches available like potato starch, maize starch, sago starch, cassava starch, etc. but cassava starch [19] (Manihot esculenta, also known as manioc or yucca) was chosen for the study as it has many remarkable characteristics, including high paste viscosity, high paste clarity, and high freeze – thaw stability, which are advantageous [20–22]. The present study focused upon adsorption of copper metal from its aqueous solution by substitution of starch with 5-choloromethyl-8-hydroxyquinoline (CMQ), which forms chelates with various heavy metal ions in aqueous medium. The chloromethylation of CMQ is a simple process and cassava starch is relatively cheap, the derivative can be produced at an economical level.

2. Material and Methods

2.1 Reagents

All chemicals used in this study were of analytical grade and were used without further purification. Cassava starch was purchased from Sigma Aldrich, India and all other chemicals used were of analytical reagent grade and were obtained from ACS Chemicals Pvt. Ltd. (Ahmadabad). The stock solution of copper metal ion (1,000 mg/L) was prepared in double distilled water and working solutions were obtained by appropriate dilution.

2.2 Biosorbent preparation

Dried Cassava starch (10 g) was mixed with an appropriate amount of Triethyl amine and Tetra hydro Furan and was allowed to stir for 30 minutes and then 5-chloromethyl-8-hydroxyquinoline (CMQ), which was synthesized, purified and characterized by previously reported routes [23], was added to that mixture with constant stirring and was allowed to heat for 6 hours at 60 ^{0}C. The synthesized product was dried and further used for the adsorption of copper metal ion from an aqueous solution.

2.3 Contrivance used

FT-IR, Nicolet IR-200, USA, potassium bromide was used to identify the functional groups present on the adsorbent. Scanning electron micrographs and EDX spectra were obtained by using SEM–EDX (SNE-15 00M, Korea and CarlZeiss, EVO MA 15, England). Atomic absorption spectrophotometer (Model novAA$^®$ 400 P, Analytic Jena, Germany) was used for the determination of metal ion concentrations before and after biosorption.

2.4 Batch Sorption Experiment

The studies of the kinetics of adsorption were carried out at room temperature. 100 ml of the solution containing the desired quantity of the copper metal ion was treated with 0.1 g of starch-CMQ copolymer in stoppered conical flasks for the different time period.

The solution–starch-CMQ copolymer mixtures were stirred at 100 rpm and at the end of predetermined time interval the reaction mixtures were filtered out and analyzed for its metal ion concentrations using Atomic Absorption Spectrometer, AAS (Model novAA$^®$ 400 P, Analytic Jena, Germany). The batch equilibrium studies for the determination of the effect of optimum metal ion concentration were conducted for the equilibrium time mixing at a constant speed of 200 rpm to obtain value of maximum adsorption. The effect of pH of the initial solution on the equilibrium uptake of Cu(II) ion was analyzed over a pH ranges from 2 to 7. The effect of pH of the solution was adjusted by either 0.1 M NaOH or 0.1 M HCI solutions. The adsorption studies were also conducted in batch experiments as function of adsorbent dosage (10 mg to100 mg), contact time (15, 30, 45, 60, 75, 90, 105 and 120, min) and metal ions concentration (10, 20, 30, 40 and 50 mg/L) for maximum adsorption. The percentage of metal adsorption by the adsorbent was computed using the equation:

$$R\ \% = \frac{(C_i - C_e)}{C_i} \times 100\ \% \tag{1}$$

$$q_e = \frac{(C_i - C_e)\ V}{W} \tag{2}$$

Where q_e is the adsorption capacity (mg/g), C_i is the initial concentration of Copper in the solution (mg/L), C_e is the equilibrium concentration of Copper (mg/L), V is the volume of metal ion solution (mL) and W is the weight of the adsorbent (mg).

3. Results and discussion

3.1. FT-IR

The grafted copolymer, non grafted starch and CMQ were characterized by IR spectrophotometer. The IR spectrum of cassava starch in Figure.1a (Starch**)** gave adsorption band –OH broad at 3400 cm^{-1}and single intermolecular polymeric band the C-H stretching at 2930 cm^{-1} and 1078 cm$^{-1,}$ characteristic of amylase containing in starch. The peak of starch at 1640-1650 is controversial as has been reported in many articles. The bending mode of water is shown at 1800-1600 cm^{-1}, while the δ (OH) bend of absorption of water was assigned at the wave number at 1640 cm^{-1}and at 1650 cm^{-1}. The wave number at 1658 cm^{-1}was assigned as a peak of the first overtone of OH bending. On the other hand, 1650 cm^{-1} was assigned as -C=C- alkene stretching.

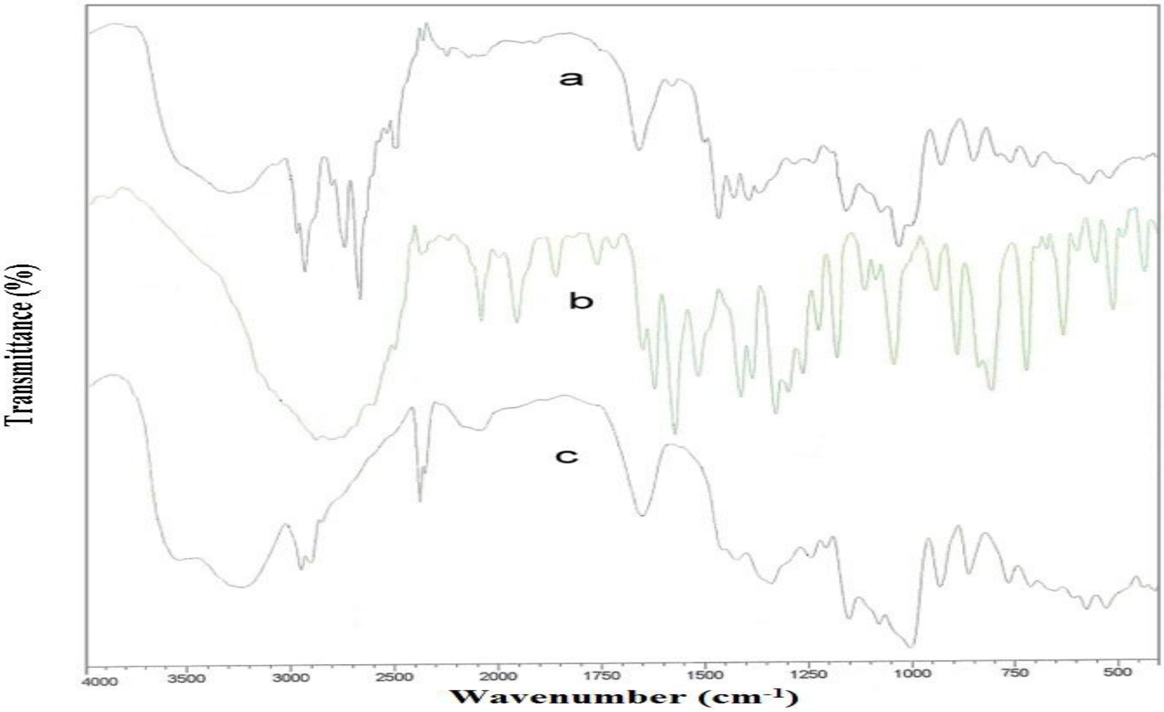

Figure 1: FT-IR Spectra of Starch (**a**); CMQ (**b**); Copolymer CSCMQ (**c**)

In Figure.1b (CMQ) a sharp peak is seen at 1491cm^{-1} which confirms C=N aromatic nitro compound in CMQ. The broad band at 3283 cm^{-1} observed in the case of ligand was shifted at 3343 cm^{-1}, which was attributed to (O–H) of coordinated water molecule. In the investigated metal complexes, the bands observed in the regions of 1267–1284cm^{-1} and 865–875 cm^{-1} are attributed to –OH stretching, bending, rocking and wagging vibrations respectively, due to the presence of water molecules.

The spectra of grafted copolymer showed the existence of sharp peak at 785 cm^{-1}as observed in Figure 1c. CSCMQ copolymer which arises from the stretching vibration mode of C-Cl bond and a small peak is observed at 1500 cm^{-1}which confirms the presence C=N aromatic nitro compound and a weak symmetrical stretching band 1431-1396 cm^{-1}, characteristics of C=O group indicated the occurrence of grafting it is evidence of grafting. Most other peaks are related to polymer backbone (starch).

3.2. SEM

The SEM images at different magnifications reveal the nature of the surface of copolymer CSCMQ as shown in Figure 2. It can be seen in Figure 2a that the surface morphology of copolymer is quite rough and porous, which will be favorable for metal ions to diffuse and penetrate into the interior part of each adsorbent and be trapped on the copolymer. During the adsorption process, it is also observed that the surface of copolymer will become smooth as shown in Figure 2b, while the filtered liquid is still clear, meaning that thus modified copolymer has the acceptable resistance to the possible solubility in the aqueous solution.

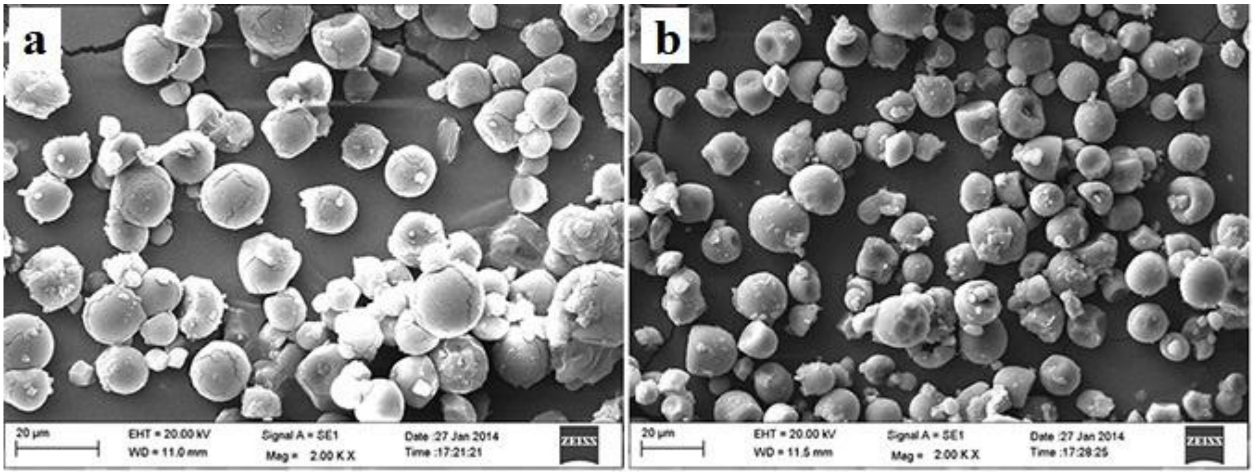

Figure 2: SEM images of Copolymer CSCMQ Before (a) and After (b) Copper adsorption

3.3. Effect of pH

The pH of solution has been identified as the most important variable governing metal adsorption on adsorbent. This is partly because hydrogen ions themselves are strongly competing with adsorbates. Figure 3 indicates the effect of pH on the removal of copper (II) by CSCMQ grafted cassava starch from an aqueous solution. It can be seen from figure that adsorption capacity are low at strong acidic medium. After pH 3, uptake increase sharply up to pH 6 since more metal binding sites could be exposed and carried negative charges, with subsequent attraction of metal ions with positive charge and adsorption onto the adsorbent surface. A decrease in adsorption of copper (II) was noticed above pH 6. Experiments were carried out with the pH values of up to 6 due to the fact that metal precipitation appeared at higher pH values and interfered with the accumulation or adsorbent deterioration.

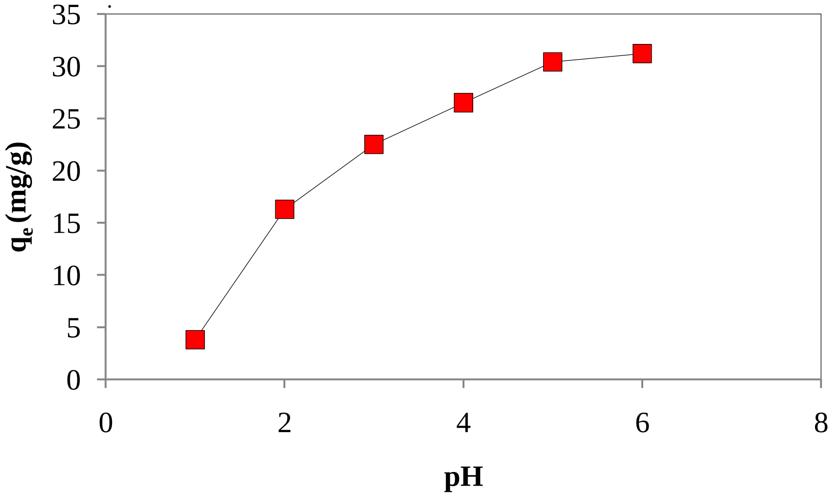

Figure 3: Effects of pH on the adsorption capacity of Cu(II) onto CSCMQ Copolymer [C_0= 50 mg/L; contact time = 90 min; dosage of adsorbent = 100 mg/100 mL; agitation speed = 200 rpm].

3.4. Effect of initial concentration and contact time:

The effect of time and amount of Cu (II) adsorbed (in mg/g) is presented in Figure. 4. The adsorption of Cu(II) has been shown to increase with time and attains a maximum value at 90 min and then remains almost constant. When initial Cu (II) concentration is increased from 20 to 50 mg/L, the amount adsorbed increases from 13.9 to 30.4mg/L, showing that adsorption of Cu (II) depends upon the initial concentration because amount of Cu (II) adsorbed increases by increasing the initial concentration. The rate of percent metal removal is higher in the beginning due to a larger surface area of the adsorbent being available for the adsorption of the metals.

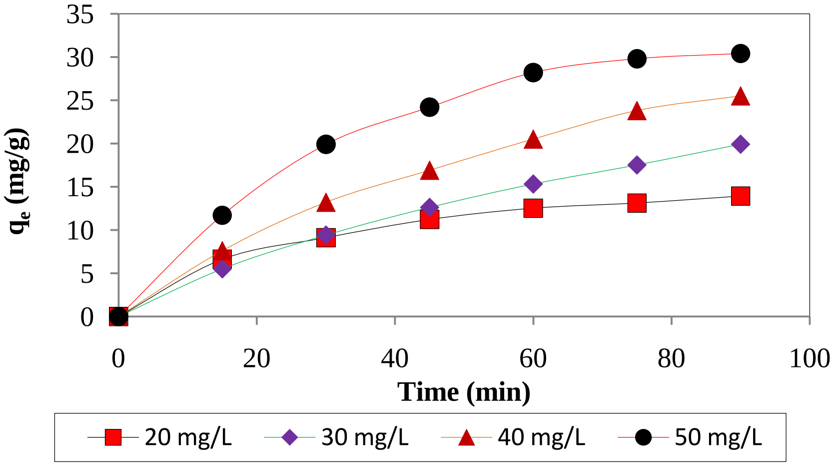

Figure 4: Effects of initial metal ion concentrations and contact time on the adsorption of Cu (II) by CSCMQ Copolymer
[pH = 6.0; dosage of adsorbent = 100 mg/100 mL; agitation speed = 200 rpm].

3.5. Effect of dosage of adsorbent:

The dependence of adsorption of copper on the dosage of CMQ grafted cassava starch copolymer is shown in Figure 5. The amount of copper adsorbed (mg/g) was found to decrease from 117 to 45.4 mg/g with increasing adsorbent dosage from 10 mg to 100 mg. But further increase in adsorbent dosage from 100 to 120 mg showed minor depreciation in adsorption capacity. Normally it has been seen that the decrease in adsorption capacity (mg/g) with increase in adsorbent dosage is due to the high number of unsaturated adsorption sites. However, the percent copper removal increased from 23.4 to 90.8% for adsorbent dosage of 10 to 100 mg, respectively. This is due to the availability of more binding sites as the dosage of adsorbent increased.

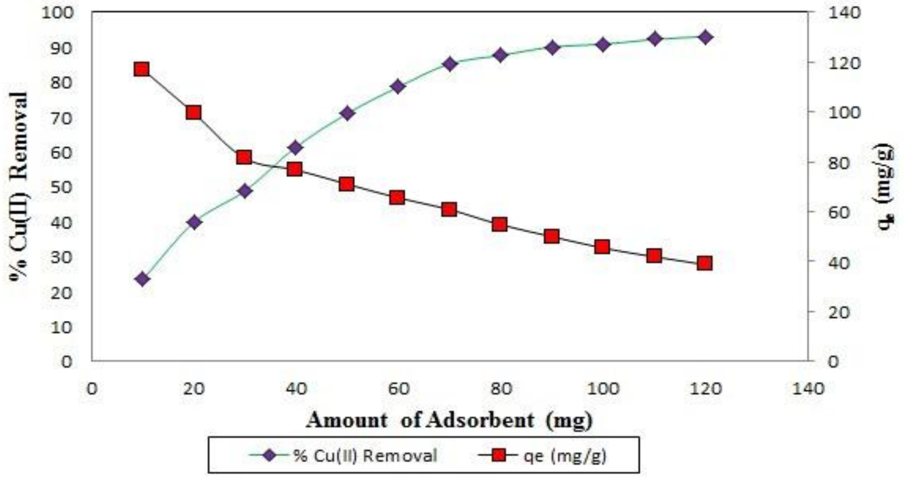

Figure 5: Effects of amount of adsorbents on the adsorption of Cu(II) by CSCMQ Copolymer
[C_0= 105 mg/L; pH = 6.0; contact time = 90 min; agitation speed = 200 rpm].

3.6. Isotherm studies

Adsorption Isotherms:

The adsorption isotherm data were analyzed with Langmuir and Freundlich isotherms. The most widely used isotherm models for solid–liquid adsorption are the Langmuir and Freundlich.

3.6.1. Langmuir model:

This model assumes that the adsorptions occur at specific homogeneous sites on the adsorbent and is used successfully in many monolayer adsorption processes:

The Langmuir model assumes that the each adsorbate molecule is located at specific homogenous sites within the adsorbent. Thus, it predicts the formation of a monolayer of the adsorbate on the homogenous adsorbent surface and does not consider surface heterogeneity of the adsorbent. The linear form of the Langmuir adsorption isotherm is represented as [24]:

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L}.C_e \quad (3)$$

Where, C_e (in milligrams per liter) is the equilibrium concentration of the Cu(II) in the solution. q_e (in milligrams per gram) is the equilibrium adsorption capacity per gram dry weight of the adsorbent corresponding to complete coverage of the adsorptive sites. a_L (in liter per milligram) and K_L (in liter per gram) are the Langmuir isotherm constants. The values of a_L and K_L are calculated from the slope $(\frac{a_L}{K_L})$ and intercept $(\frac{1}{K_L})$ of the plot of $\frac{C_e}{q_e} \rightarrow C_e$. Ratio of $\frac{K_L}{a_L}$ gives the value of monolayer sorption capacity of the adsorbent, q_m (in milligrams per gram). Table 1 indicates that the maximum adsorption capacity of CSCMQ copolymer was 28.75 mg/g which is equivalently high and can be compared with previously reported adsorbents (Table 2)

The essential characteristic feature of Langmuir isotherm can be expressed in terms of "R_L", a dimensionless constant referred to as "separation factor" or "equilibrium parameter". The value of R_L is calculated using the following equation:

$$R_L = \frac{1}{(1+a_L .C_0)} \quad (4)$$

The value of R_L lies between 0 and 1 for favorable adsorption, while $R_L > 1$ represents unfavorable adsorption, and $R_L = 1$ represents linear adsorption while the adsorption process is irreversible if $R_L=0$ [25]. R_L values of CSCMQ copolymer (0.008665) for the initial Cu(II) concentration of 50 mg/L indicate favorable adsorption of Cu(II) onto CSCMQ copolymer.

3.6.2. Freundlich model:

Freundlich adsorption isotherm defines the adsorption onto the adsorbent with heterogeneous surface. The linear form of Freundlich isotherm model is as follows [26]:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (5)$$

Where, K_F (in liter per gram) is the Freundlich adsorption isotherm constant, relating to the extent of adsorption. n (in grams per liter) is the Freundlich exponent. The values of K_F and $\frac{1}{n}$ are calculated from the slope and intercept of the plot of $\log q_e \rightarrow \log C_e$ and are listed in Table 1.

Table 1: Constants for equilibrium isotherm models with error analysis values for CSCMQ Copolymer

Langmuir Isotherm					
Adsorbents	**K_L (L/g)**	**q_m (mg / g)**	**R_L^***	**R^2**	**χ^2**
CSCMQ copolymer	65.79	28.75	0.009	0.999	0.003
Freundlich Isotherm					
Adsorbents	**K_F (L/g)**	**1/n**	**n**	**R^2**	**χ^2**
CSCMQ copolymer	3.48	0.74	1.35	0.996	40.32

* C_0 = 50 mg/L

The equilibrium adsorption of Cu (II) using CSCMQ copolymer (q_e Vs. C_e) is shown in Figure 6 and the isotherms are plotted together with the experimental data points. For the adsorbent Langmuir isotherm model show good fit with the experimental data.

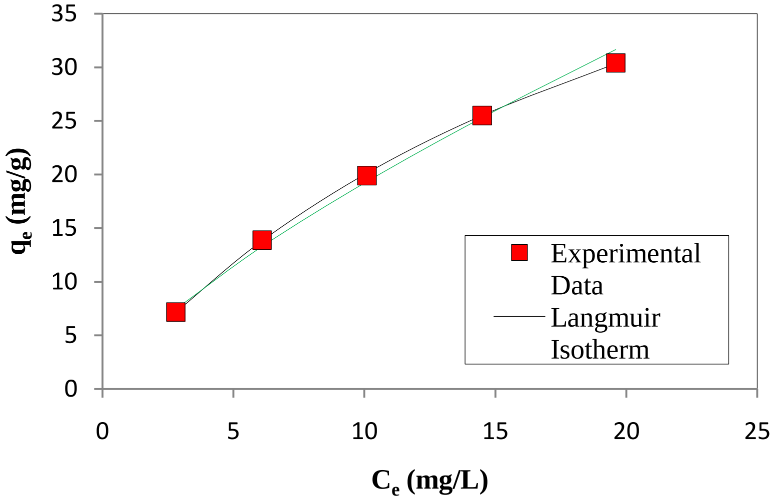

Figure 6: Plot of q_e Vs. C_e for the adsorption of Cu(II) onto CSCMQ Copolymer
[pH = 6.0; contact time = 90 min; dosage of adsorbent = 100mg/100 mL; agitation speed = 200 rpm]

Table 2: Adsorption capacity of copper by different adsorbents reported in other studies.

Sr. No.	Adsorbent	qm (mg/g)	Reference
1	Starch-g-acrylic acid copolymer	5.08	[27]
2	2,Amino4,6Dihydroxylpyrimidine modified corn Starches:	7.71	[28]
	a)DASAP 1		
	b) DASAP 2	8.12	
3	Activated nylon-based membrane	10.8	[29]
4	Cellulose-g-acrylic acid copolymer	18.17	[30]
5	Starch graft copolymer with aminoethyl group	21.05	[31]
6	Clinoptilolite	25.4	[32]
7	CSCMQ	28.75	Present study

3.7. Error analysis

In the single component isotherm studies, the optimization procedure requires an error function to be defined in order to be able to evaluate the fit of the isotherm equation to the experimental equilibrium data. In this study, linear coefficient of determination (R^2) and a non-linear Chi-square test (χ^2) were performed for both the isotherms.

The Chi-square test statistics is basically the sum of the squares of the differences between the experimental data and the data obtained by calculating from models, with each squared difference divided by the corresponding data obtained by calculating from models. The mathematical equation can be represented as:

$$\chi^2 = \sum \frac{\left(q_{e(\exp)} - q_{e(cal)}\right)^2}{q_{e(cal)}} \qquad (6)$$

Where, $q_{e(exp)}$(in milligrams per gram) is the experimental data of the equilibrium capacity; $q_{e(cal)}$ (in milligrams per gram) is the equilibrium capacity obtained by calculating from the model. If data from the model are similar to the experimental data, χ^2 will be a smaller number, and if they differ, χ^2 will be a bigger number. Therefore it is necessary to analyze the data using the non-linear Chi-square test to confirm the best fit isotherm for this adsorption system [33, 34].

3.8. Kinetic studies

The rate constants were calculated by using pseudo-first-order and pseudo-second-order kinetic equations. Pseudo-first-order expression is given by equation [35]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}\, t \qquad (7)$$

where q_e is the amount adsorbed at equilibrium, q_t the amount adsorbed at time t and k_1 (per minute)is the adsorption rate constant. The linear plot of log $(q_e - q_t)$ versus t is observed in (Figure. 4).

The linear pseudo-second-order kinetic equation is given as [36]:

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{t}{q_e} \qquad (8)$$

Where, k_2 (in grams per milligram per minute) is the pseudo-second-order rate constant. The values of k_2 and q_e for pseudo-second-order rate model calculated from intercept and slope of the $\frac{t}{q_t}$Vs. t plots and given in Table 3. The plots of pseudo-first order and second-order were shown in Figure. 7 and 8.

Table 3: Kinetic parameters for the adsorption of Cu(II) onto CSCMQ copolymer.

Adsorbent			**CSCMQ copolymer**		
Pseudo-first-order Constants	**C_0 (mg/L)**	**$q_{e(exp)}$ (mg/g)**	**$q_{e(cal)}$ (mg/g)**	**k_1 (min^{-1})**	**R^2**
	20	13.9	13.89	0.038	0.995
	30	19.9	24.64	0.029	0.978
	40	25.5	37.33	0.037	0.934
	50	30.4	55.08	0.056	0.961
Pseudo-second-order Constants	**C_0 (mg/L)**	**$q_{e(exp)}$ (mg/g)**	**$q_{e(cal)}$ (mg/g)**	**k_2 (g/mg/min)**	**R^2**
	20	13.9	17.83	0.0021	0.997
	30	19.9	39.06	0.00028	0.997
	40	25.5	49.75	0.00024	0.991
	50	30.4	48.54	0.00046	0.993

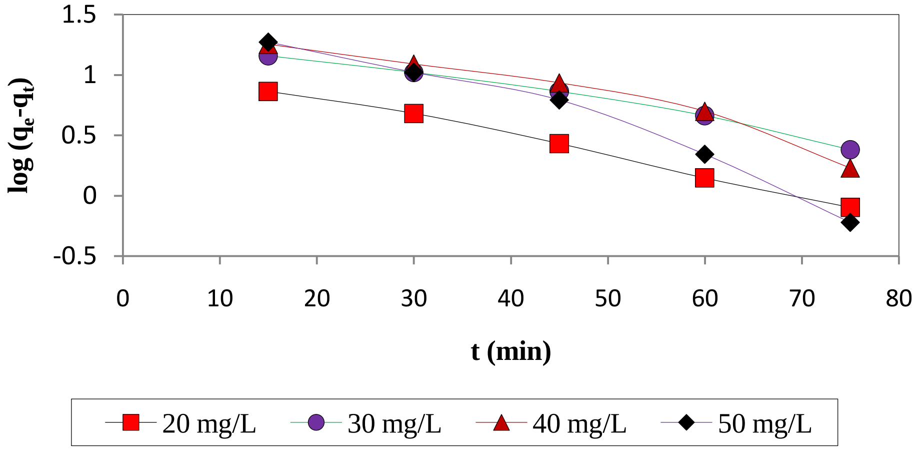

Figure 7: Pseudo-first-order rate model for the adsorption of Cu(II) onto CSCMQ Copolymer [pH = 6.0; dosage of adsorbent = 100mg/100 mL; agitation speed = 200 rpm]

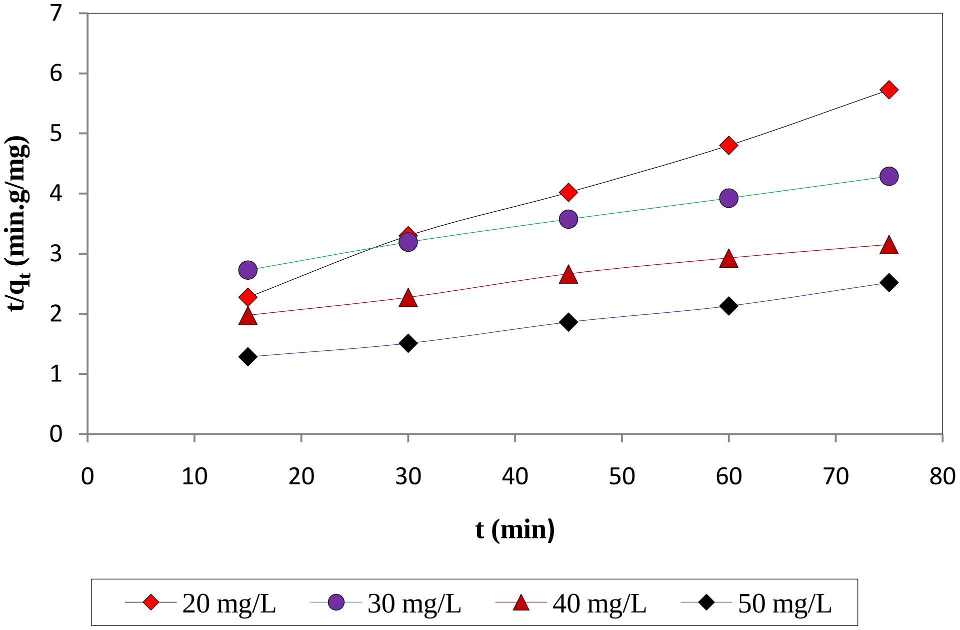

Figure 8: Pseudo-second-order rate model for the adsorption of Cu(II) onto CSCMQ Copolymer [pH = 6.0; dosage of adsorbent = 100mg/100 mL; agitation speed = 200 rpm]

It is observed that the values of the correlation coefficient for both the pseudo-first-order and pseudo-second-order rate models were closer to unity. However, the pseudo-second-order model described very well the adsorption of Cu(II) onto CSCMQ copolymer because the experimental q_e values were very close to the calculated q_e values for pseudo-second-order rate model. As shown in table the values of the rate constant k_2 decreases with increasing initial Cu(II) metal ion concentration because higher metal ion concentration corresponds to higher surface loading which decreases the diffusion efficiency.

Conclusions

This study demonstrated that CSCMQ copolymer can be effectively used as adsorbent for the removal of copper metal from aqueous solutions. The adsorbent was characterized by SEM and FT-IR. The SEM image of CMQ starch copolymer showed that the porous structure of the sorbent surface could improve the adsorption capacity. Several parameters were studied and maximum adsorption was found to occur at pH value of 6.0 and within 90 min of contact time. The Langmuir isotherm was the best fit adsorption isotherm model for the experimental data obtained from the non-linear chi-square statistic test. The maximum adsorption capacity was 28.75 mg/g for CSCMQ copolymer. Further, the pseudo-first-order and second-order kinetic models were used to describe the kinetic data and rate constants were evaluated. The dynamical data fits well with the second-order kinetic model. This work suggests that the present CMQ starch copolymer can be more useful for the removal of copper from effluents discharged by industries.

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