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Synergistic removal of Cu(II) and nitrazine yellow dye using an eco-friendly chitosan-montmorillonite hydrogel: Optimization by response surface methodology

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ABSTRACT: A comprehensive feasibility study on adsorption of Cu(II) and a water-soluble nitrazine yellow (NY) dye by chitosan-montmorillonite (CS-MMT) hydrogel as the biosorbent was investigated as a function of biosorbent dosage, initial concentration, pH, temperature, and the presence of salts. Box–Behnken methodology was applied to optimize the adsorption experiments. Maximum adsorption values were determined as 132.74 mg/g and 144.41 mg/g at pH = 5.0, for Cu(II) and NY dye, respectively. Equilibrium isotherms of Langmuir and Freundlich were analyzed by the non-linear regression model. The equilibrium data were well described by Freundlich model and the adsorption process well fitted pseudo-second order kinetics. The enthalpy change of adsorption ($\Delta H°$) were calculated as −3.78 kJ/mol and −5.75 kJ/mol for Cu(II) and NY dye, respectively, indicating that the adsorption processes were exothermic. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43664.

KEYWORDS: adsorption; hydrogels; modelling; response surface methodology; swelling

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INTRODUCTION

The efficient removal of toxic heavy metal ions and dyes from water is an important and widely studied research area because, the existence of these pollutants results in ecological problems.[1,2] Although it is difficult to remove heavy metal ions and dyes from water due to their complex structure and binding affinity,[3–5] a number of technologies have been developed over the years. A widely used technique in removing dyes and heavy metal ions from wastewaters is adsorption by hydrogels, which are crosslinked hydrophilic three-dimensional network polymers with enormous capacity for water and are insoluble due to the presence of chemical or physical crosslinks.[4,6,7]

As of recent years, several studies have been focused on the development of cheap, effective, and eco-friendly new biosorbents including chitosan (CS) which has exceptional characteristics such as hydrophilicity, biocompatibility, biodegradability, non-toxicity, and high adsorption capacity due to the presence of amino and hydroxyl groups.[8–10]

Montmorillonite (MMT) is a natural occurring phyllosilicate clay which exhibits good adsorption abilities. The clay is composed of a layered structure consisting of alumina (Al_2O_3) octahedral sheet situated between two silica (SiO_4) tetrahedral sheets. Substitution of Al^{3+} for Si^{4+} in the tetrahedral layer alongside Mg^{2+} or Fe^{2+} for Al^{3+} in the octahedral layer generates a net negative charge on the surface layers. Therefore, MMT exhibits good adsorption for dyes and heavy metal ions in aqueous solutions by exchangeable cations.[11,12]

Copper is a widely used heavy metal based on its excellent physical and mechanical properties, such as electrical and thermal conductivity, better corrosion resistance etc. The most water soluble form of copper is Cu(II) and minimum amount of Cu(II) is important for human body, animals, and microorganisms but consumed in excess may cause toxic and harmful effects. Thus, it is of prior interest to remove excess Cu(II) from wastewater because of their high toxicity.[13–15]

Nitrazine Yellow (NY) is a pH sensitive dye and widely used in cell biology, hematological, and histological stains. NY is also harmful and can cause life-threatening diseases and skin irritation.

Adsorption is one of the most suitable treatment techniques used in removing heavy metal ions and dyes from water. Notwithstanding other known techniques such as biological processes, combined chemical and biochemical degradation, chemical oxidation, coagulation, and membrane treatments have been used but are time consuming, expensive and do have some drawbacks.[4,16,17]

Notwithstanding, CS can adsorbs both cationic and anionic species from aqueous solution but demonstrate some limitations such as low mechanical property and low specific gravity which causes CS to swell and float when immersed in water.[11] Thus for enhancement of this limitations, CS is encapsulated with negatively charge MMT surface to form CS-MMT hydrogel with improved swelling and stability which increases metal and dye adsorption. Therefore, in the present study, chemically crosslinked Schiff based chitosan-montmorillonite (CS-MMT) hydrogels were prepared using glutaraldehyde as a crosslinker. To the best of our knowledge, this is the first report on chemically crosslinked Schiff based CS-MMT hydrogels, which was simultaneously applied for removal of Cu(II) and NY dye from water. The main objectives of this study were: (1) to synthesize chemically crosslinked stable CS-MMT hydrogels; (2) to understand the removal performance of the different contaminant species by CS-MMT hydrogel during water treatment; and (3) to optimize the treatment process by using an integrated approach of isothermic modelling and response surface methodology (RSM, by Box–Behnken model) at dynamic parametric conditions.

EXPERIMENTAL

Materials

All reagents were of analytical grade. Medium molecular weight chitosan (85% deacetylation), commercial grade K10 montmorillonite (K10-MMT) with a CEC of 26 meq/100 g and glutaraldehyde (25%) were all supplied by Sigma Aldrich and used without further purification. Sodium tripolyphosphate (Na-TPP), NaOH, HCl (37%), copper nitrate trihydrate, and nitrazine yellow dye (Figure 1) (dye content: 85%, molecular formula: $C_{16}H_8N_4Na_2O_{11}S_2$, M_w: 542.36 g mol^{-1}, and λ_{max}: 586 nm) were also used without further purification. Distilled water was used for preparation of all experimental solutions.

Preparation of Chitosan-Montmorillonite (CS-MMT) Solution

Chitosan solution was prepared by dissolving 2% (w/w) chitosan flakes in 1% (v/v) acetic acid on a stirrer at 350 rpm for 6 h. Then, 10% (w/v) montmorillonite (MMT) was dispersed in distilled water for 30 min and added into the already prepared chitosan solution. The mixture was continuously stirred for 3 h at 70 °C to obtain a homogenous solution. Into the stirring mixture of CS-MMT, 4 mL of 0.1 M HCl was added for acid activation of montmorillonite to reduce the number of cation exchange sides and increase the dissolution rate thereby improving the exfoliation of the silicate sheets at higher pH values.[18,19]

Synthesis of CS-MMT Hydrogel

Step 1: Crosslinked hydrogel beads were synthesized using sodium tripolyphosphate (Na-TPP) solution (2% w/w; V = 100 mL) as coagulant for ionic crosslinking. CS-MMT solution was added dropwise into Na-TPP solution at constant time interval using a 0.6 mm diameter needle syringe. The obtained hydrogel beads were then allowed to stir for 12 h.[9,20,21] Step 2: The hydrogel beads were then transferred into a beaker containing 2% (v/v) glutaraldehyde solution placed in an ice bath and the mixture was continuously stirred for 2 h to obtain chemically crosslinked hydrogel beads. The obtained chemically crosslinked hydrogel beads were washed severally with deionized water to remove unreacted monomers and used for further investigations.[14,22,23]

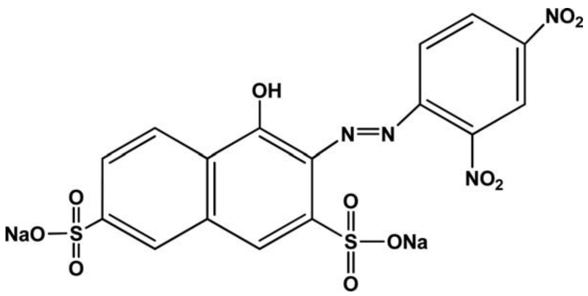


Figure 1. Chemical structure of Nitrazine Yellow dye.

Characterization Techniques

Fourier Transform Infrared (FTIR) spectral analysis was performed using FTIR spectrophotometer (Bruker, Tensor 27 IR) in the range of 4000–400 cm^{-1} to determine the functional groups of CS-MMT hydrogel. The concentrations of Cu(II) and NY dye solutions were qualitatively determined via atomic absorption spectrophotometer (Perkin-Elmer, Analyst 800) at 324 nm and UV/vis Spectrophotometer (Agilent, Cary 60) at 586 nm, respectively. Triplicate readings were collected for each sample and the average value determined.

Swelling Investigation of CS-MMT Hydrogel

Wet hydrogel samples (0.06 g) were immersed in 50 mL deionized water solutions, at varying pH (1–9) and temperatures (293 K, 303 K, and 313 K) for 2 h to evaluate the swelling properties of CS-MMT. The weight of the swollen samples were then measured in replicates after excess surface water was removed by gently blotting the surface with dry filter paper. The swelling ratio for each hydrogel sample was calculated using the formulation below.

$$\text{Swelling ratio} = \frac{M_s - M_w}{M_w} \quad (1)$$

where M_s and M_w represent the weight of the swollen and wet state samples, respectively. The water content (WC) was calculated from following equation:

$$\text{Water content }\% = \frac{M_w - M_d}{M_w} \times 100 \quad (2)$$

where M_d represents the weight of dry hydrogel sample.

pH Point Zero Charge (pH_{pzc}) Determination

The pH point zero charge (pH_{pzc}) of CS-MMT hydrogel was investigated via pH drift method. A solution of 0.01 *M* NaCl was initially prepared and pH of solution adjusted to values between 1 to 9 by addition of small amounts of either 1 *M* HCl or 1 *M* NaOH solution. Weighed amounts of 0.05 g CS-MMT hydrogels were added into 50 mL of the pH adjusted solutions in capped vials and equilibrated for 24 h. The final pH then measured in duplicates and the average value plotted against the initial pH. The pH at which the curves crossed was determined as the pH_{pzc}.

Batch Adsorption Investigations

Batch adsorption experiments were conducted in 100 mL conical flasks at different conditions, in the presence of different sodium salts (PO_4^{3-}, SO_4^{2-}, NO_3^-, and Cl^-), biosorbent dosage (60–100 mg), initial concentration (40–100 ppm), pH (2–6), and temperature (293–313 K). Standard stock solutions of

Cu(II) and NY dye were prepared by dissolving known amounts of copper nitrate trihydrate and NY dye in 250 mL flasks to obtain 500 ppm and 200 ppm of Cu(II) and NY dye stock solutions, respectively. The equilibrium uptake capacity (q_e) and percentage removal (%R) of the hydrogel were calculated using the following equations:

$$q_e = (C_o - C_e)\frac{V}{M} \tag{3}$$

$$\%R = \frac{C_o - C_e}{C_o} \times 100 \tag{4}$$

where C_o represents initial concentration (ppm) of the metal ion and dye, C_e is the equilibrium concentration (ppm), M is the mass of biosorbent (g), V is the volume of metal ion and dye (L), q_e is the equilibrium amount of metal ion and dye adsorbed (mg/g), and $\%R$ is the percentage removal.[24–26]

Design and Optimization of Parameters

For batch adsorption system, optimization was performed by means of response surface methodology (RSM) to improve efficiency and simplicity of the adsorption process. RSM was used to optimize and determine the optimum operating conditions for the uptake efficiency of Cu(II) and NY dye onto CS-MMT hydrogel by Box–Behnken design model. In this model, numeric factors of biosorbent dosage (g), initial concentration (ppm), pH, and temperature (K) were investigated.[27]

RESULTS AND DISCUSSION

FTIR Analysis

Figure 2 shows the spectral analysis for CS-MMT hydrogel, CS-MMT Cu(II), and NY dye. It is observed that the broad band between 3550 cm^{-1} to 3200 cm^{-1} for CS-MMT indicates N–H and O–H stretching overlaps of chitosan. The observed enhanced and broadened bands for CS-MMT/Cu(II) and CS-MMT/NY were attributed to the binding of Cu(II) and NY dye to amide and hydroxyl groups of CS-MMT hydrogel.[28] Peaks at 2918 cm^{-1} and 2871 cm^{-1} are attributed to C–H stretching on methyl and methylene of the hydrogels, respectively. The peaks at 2360 cm^{-1} and 2341 cm^{-1} represent alkyl C–H stretching vibration of chitosan and glutaraldehyde. The peak at 1637 cm^{-1} indicates the stretching bands of C = N (Schiff base or imine bond), formed by the reaction of chitosan amine groups and the aldehyde groups of glutaraldehyde. The peak at 1535 cm^{-1} represents N–H group stretching vibration of acetyl glucosamine in chitosan. The bands between 1375 cm^{-1} and 1313 cm^{-1} indicates deformation vibration of protonated amine group (NH_3^+) and this band is observed to be more intense for hydrogel containing Cu(II) and NY dye, demonstrating the binding capacity and affinity of Cu(II) and NY dye onto CS-MMT hydrogel. Spectral peaks at 1026 cm^{-1} are related to stretching vibrations of etheric C–O groups.

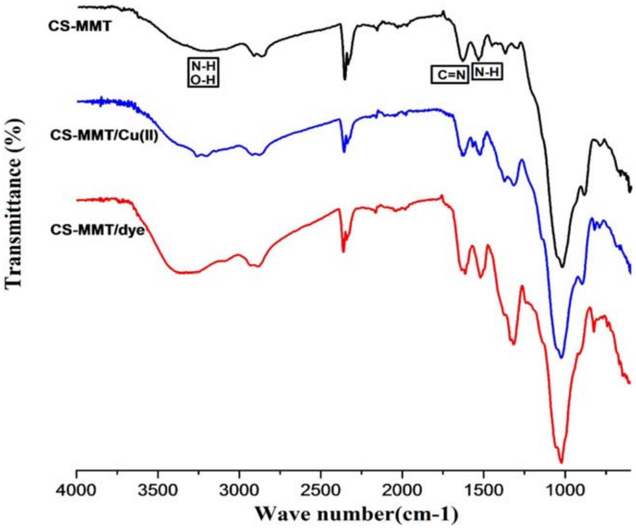


Figure 2. FTIR spectra of CS-MMT hydrogel. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

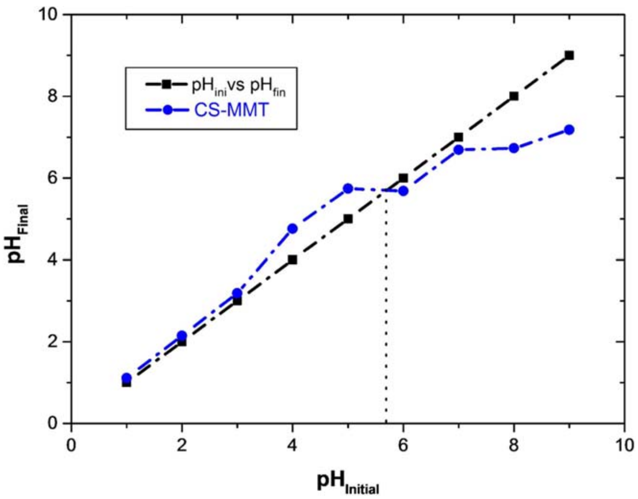


Figure 3. pH_{pzc} of CS-MMT hydrogel by pH drift method. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

pH_{pzc} Analysis

The pH_{pzc} of CS-MMT hydrogel was determined for better understanding of adsorption mechanism. A plot of the initial pH versus final pH determined the pH_{pzc} of CS-MMT hydrogel to be 5.6 as represented in Figure 3. Therefore, for adsorption solutions of $pH < 5.6$, CS-MMT hydrogel surface becomes positively charged thereby enhancing electrostatic interaction with negatively charged species. However, solutions of $pH > 5.6$ enabled CS-MMT hydrogel surface to be negatively charged which increases electrostatic interaction with positively charged species.

Swelling Analysis

The swelling properties of polymeric hydrogels in solvents can be measured by their sorption ability. This process involves the diffusion of solutes into the hydrogel bulk induced by mobility of polymeric chains and free-volume among chains.[29] Figure 4(A) shows the water swelling ability of CS-MMT hydrogel in different pH solutions. The obtained results demonstrated the swelling properties of the hydrogel network varied with change in pH of swelling solution. Water uptake significantly decreased with increasing pH and then increased for investigated pH range. This is because at low pH, protonation of the amino groups of CS-MMT occurs leading to repulsion in the polymer chains and dissociation of secondary interactions via

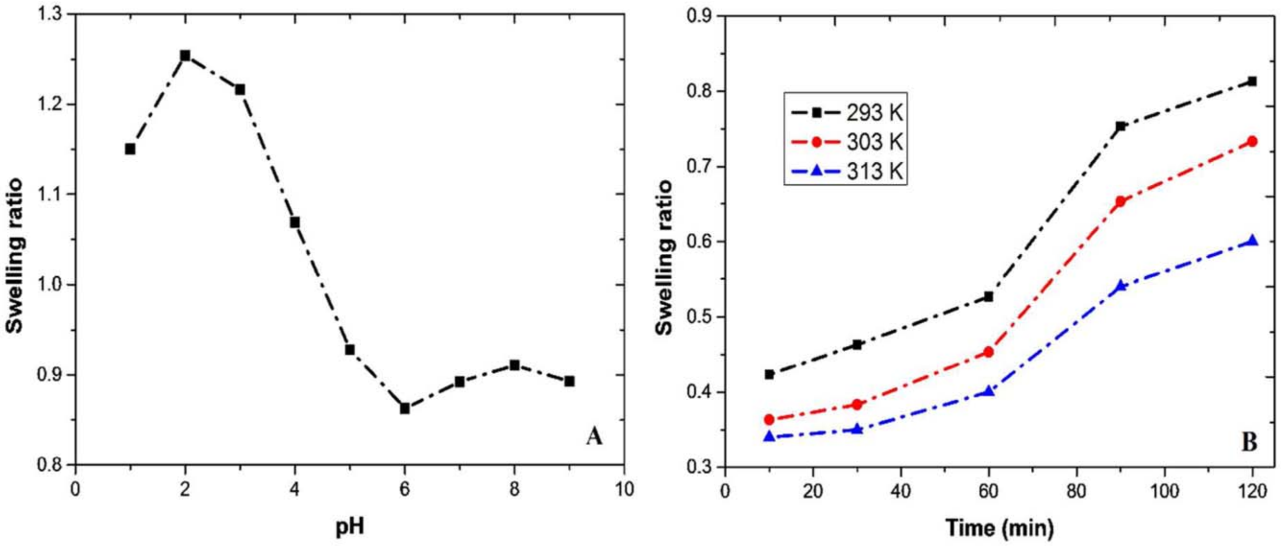


Figure 4. Swelling investigation of CS-MMT hydrogel in aqueous solution with (A) pH and (B) temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

intramolecular hydrogen bonds, which allowed diffusion of more water into the hydrogel network. As the pH increased, the ionized NH_3^+ groups are transformed to hydrophobic NH_2 thus repulsion in the polymer chains recedes allowing shrinking.[30] The maximum swelling value for the investigated parameter was obtained as 1.25 g/g at pH solution 2. The temperature dependent equilibrium swelling response of the hydrogels in water (pH 6) at temperature range from 293 to 313 K in the time interval of 0 to 2 h is shown in Figure 4(B). As the time of the hydrogels in solution increased, the swelling ratio of the hydrogel samples increased. CS-MMT hydrogel exhibited a temperature responsive swelling behavior with highest swelling values of 0.84 g/g at 293 K. The decrease in swelling with increasing temperature was attributed to low dissociation of hydrogen bonding of amine groups in CS-MMT at higher temperature, which decreased the relaxation of the polymer chains in the hydrogel thereby limiting penetration of water molecules into the hydrogel network.[12,31] In addition, CS-MMT hydrogel water content was determined as 84% indicating swelling was favorable due to ease in hydration of the hydrophilic groups of CS-MMT hydrogel.

Adsorption Mechanism

Several studies have been reported[13,14,26,32] on chitosan for adsorption of metal ions or dyes to determine the optimum pH for maximum adsorptions. In the present study CS-MMT hydrogel was used to remove Cu(II) and NY dye. It is expected that the adsorption sites for Cu(II) and NY dye are at the nitrogen atoms of –NH_2 groups and the oxygen atoms of –OH groups in chitosan. Due to the stronger attraction for lone pair of electrons to the nucleus in an oxygen atom to nitrogen atom, there is a greater tendency for nitrogen atoms to share lone pair of electrons with Cu(II) and NY dye to form complexes as shown in Scheme 1. On this note, the following chemical reactions may be expressed to account for the adsorption of Cu(II) and NY dye onto CS-MMT hydrogel.

$$R{-}NH_2 + H^+ \longleftrightarrow R{-}NH_3^+ \qquad \text{Protonation}$$

$$R{-}NH_3^+ + Dye{-}SO_3^- \longrightarrow R{-}NH_3^+\ {}^-O_3S{-}Dye \qquad pH<5.6$$

$$R{-}NH_3^+ + OH^- \longrightarrow R{-}NH_2 + H_2O \qquad \text{Deprotonation}$$

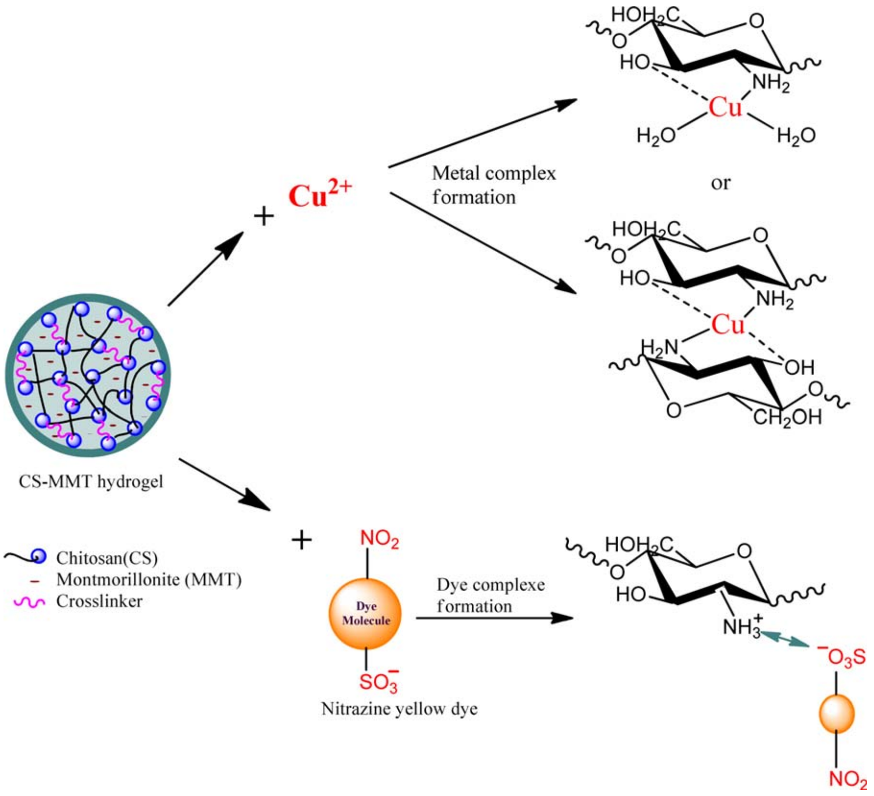
$$R{-}NH_2 + Cu^{2+} \longrightarrow R{-}NH_2Cu^{2+} \qquad pH>5.6$$

The reactions above demonstrate the behavior and interaction of the functional groups on the surface CS-MMT hydrogel. At $pH < 5.6$, free NH_2 groups on the hydrogel surface are protonated to form NH_3^+ charge species, which enhances the binding capacity of NY dye molecules. On the other, solutions of $pH > 5.6$ enhance the binding of Cu(II) via formation of coordinate bonds with the nitrogen atoms in the amine groups.

Batch Analysis

Biosorbent Dosage Effect. This parameter determines the uptake capacity of a biosorbent for a given initial concentration of the adsorbate. The CS-MMT dosage (60, 80, and 100 mg) on adsorption of Cu(II) and NY dye were monitored at constant initial concentration (80 ppm) and time 2 h at 293 K. Figure 5 shows that as dosage increases, the uptake capacity for Cu(II) and NY dye decreased. Increasing biosorbent dosage increases surface area and the availability of more adsorption sites. However, the adsorption capacity decreased with increasing dosage. The adsorption capacity of CS-MMT hydrogel decreased from 156.33 to 115.10 mg/g and 167.61 to 126.25 mg/g with increasing biosorbent dose from 60 to 100 mg/100 mL for Cu(II) and NY dye, respectively. The decrease can be attributed to remained unsaturation of the adsorption sites during the process whereas the number of sites available increases by increasing the CS-MMT dose.[33,34]

Effect of Initial Concentration. The adsorption of Cu(II) and NY dye was investigated at varying initial concentrations (60, 70, 80, 90, and 100 ppm) at constant CS-MMT dosage (80 mg), temperature (293 K), and time 2 h. As can be seen in Figure 6, adsorption capacity of CS-MMT increases from 106.41 to 154.66 mg/g



Scheme 1. Adsorption process of Cu(II) and NY dye by CS-MMT hydrogel. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and 109.60 to 171.53 mg/g with increasing initial concentrations from 40–100 ppm for Cu(II) and NY dye, respectively. This reveals that initial concentrations plays important roles in the adsorption process by providing driving forces to overcome the mass transfer resistance between the solution and solid phases.[14,35]

pH Effect. Several experiments were performed at different pHs (2–8) to investigate the effect of pH. The amount of biosorbent dosage (80 mg), initial concentration (60 ppm), temperature (293 K), and time 2 h were kept constant for adsorption of Cu(II) and NY dye by CS-MMT hydrogel. Figure 7 shows the adsorption of Cu(II) and NY dye with change in pH of solution from 2 to 8. As observed, Cu(II) adsorption increased and then decreased with increasing pH while NY dye adsorption decreased significantly for the entire studied pH range. The increase in Cu(II) adsorption from pH 2 to 6 was due to increasing number of coordinate bonds between Cu(II) and nitrogen atoms of amine groups on CS-MMT hydrogel. The decrease in adsorption from pH 6 to 8 was attributed to the gradual precipitation of Cu(II) ions to form $Cu(OH)_2$. NY dye adsorption decreased with increasing pH which was due to the

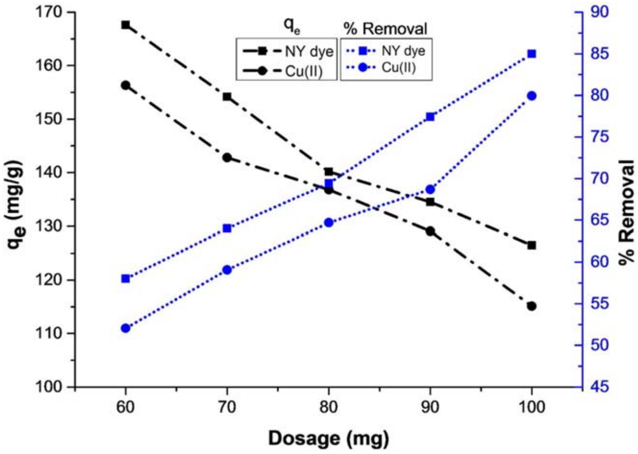


Figure 5. Effect of dose on Cu(II) and NY dye adsorption at initial concentration 80 ppm and 293 K. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

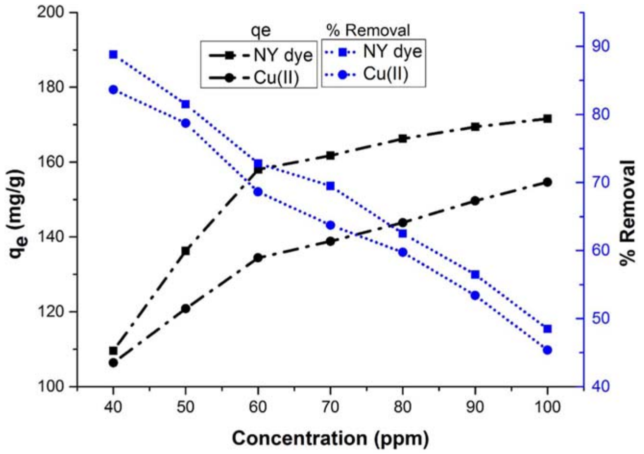


Figure 6. Effect of Initial concentration on Cu(II) and NY dye at constant dosage (80 mg) and 293 K. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

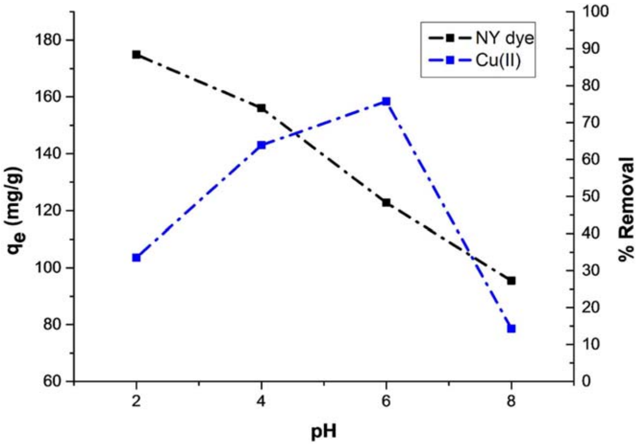


Figure 7. pH effect on Cu(II) and NY dye removal at constant dosage (80 mg), initial concentration (80 ppm) and 293 K. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

gradual deprotonation of NH_3^+ on CS-MMT hydrogel to hydrophobic NH_2 thereby increasing electrostatic repulsion between the hydrogel and NY dye molecules.[24,36] Maximum adsorption capacities of CS-MMT hydrogel were obtained as 158 mg/g and 174 mg/g for Cu(II) at pH 6 and NY dye at pH 2, respectively.

Effect of Ionic Strength. Wastewater from textile and dying industries do not only contain heavy metal ions and dyes but also several sodium salts such as phosphates, sulfates, nitrates, and chlorides thereby affecting adsorption efficiency of the system.[25,37] For this purpose, several experiments were carried out to see the effect of sodium salts (PO_4^{3-}, SO_4^{2-}, NO_3^-, and Cl^-) on the adsorption of CS-MMT hydrogel for Cu(II) and NY dye. The presence of salts affects the adsorption process via columbic potential and preferential adsorption on the active sites of the CS-MMT hydrogel.[34] In this study, 0.01 *M* corresponding sodium salts of PO_4^{3-}, SO_4^{2-}, NO_3^-, and Cl^- were used to investigate the salts effect on adsorption of Cu(II) and NY dye at constant CS-MMT dosage (80 mg) initial concentration (80 ppm) and temperature (293 K). From Figure 8, the presence of the salts significantly decreased the adsorption capacity of Cu(II) and NY dye with increasing salt ionic strength. This was due to the increase competition of the salt ions with the investigated adsorbate species for CS-MMT adsorption active sites. The effect of the investigated sodium salts on the adsorption of Cu(II) and NY dye was in the magnitude of $Cl^- < NO_3^- < SO_4^{2-} < PO_4^{3-}$. The maximum adsorption capacities were determined as 142.3 mg/g and 157.6 mg/g for Cu(II) and NY dye, respectively.

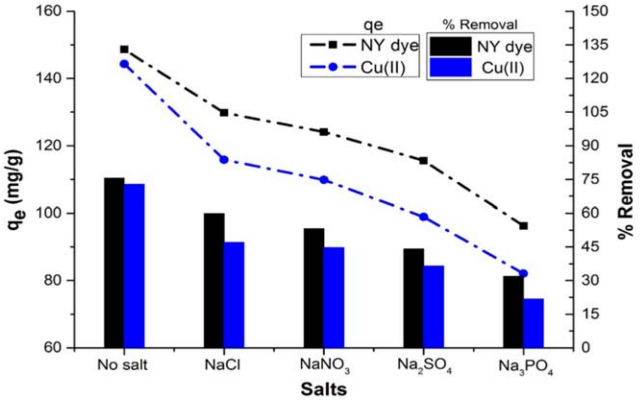


Figure 8. Effect of salts on the adsorption of Cu(II) and NY dye at constant CS-MMT dosage (80 mg), initial concentration (80 ppm), temperature (293 K) and pH 6. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

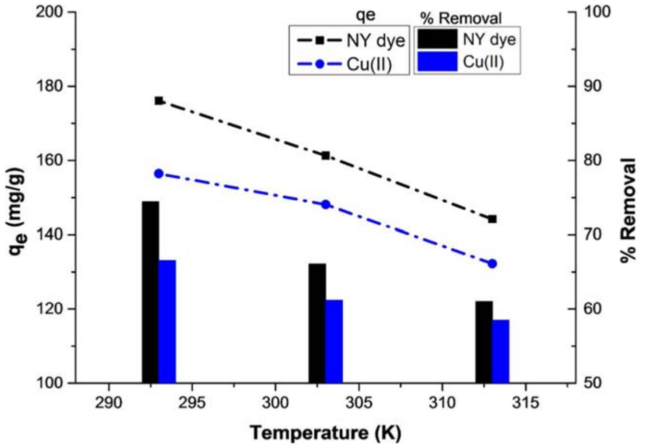


Figure 9. Temperature effect on adsorption of Cu(II) and NY dye onto CS-MMT hydrogel at constant CS-MMT dosage (80 mg), initial concentration (80 ppm) and pH 6. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Effect of Temperature. A study on the effect of temperature was performed for adsorption of Cu(II) and NY dye at constant CS-MMT dosage (80 mg), initial concentration (80 ppm), pH 6, and time 2 h. As shown in Figure 9, Cu(II) and NY dye adsorptions decreased with increasing temperature from 293 K to 313 K. This was mainly due to the decreased adsorbent-adsorbate attractive interaction ascertaining the adsorption process was exothermic. In addition, this decrease in uptake capacity with increasing temperature was associated to the decrease in swelling of the hydrogel as temperature increase cause shrinkage at higher temperature and thereby limiting the accessibility of CS-MMT active sites by adsorbate species.[38] The maximum adsorption capacities were obtained as 156 mg/g and 176 mg/g for Cu(II) and NY dye onto CS-MMT hydrogel, respectively at 293 K.

Isotherm Models

A comprehensive investigation is necessary to understand the nature of interaction between adsorbates and biosorbent for the most effective use. In this study, the experimental data of equilibrium adsorption by CS-MMT hydrogel were evaluated using Langmuir and Freundlich isotherm models. Langmuir model describes the thickness of the adsorbed layer as monolayer in nature. The equation is depicted below:

$$q_e = \frac{Q_o K_L C_e}{1 + K_L C_e} \tag{5}$$

where C_e and q_e are the equilibrium concentrations (ppm) and adsorbed capacity (mg/g), respectively. By plotting q_e versus C_e (Figure 10), Q_o (mg/g), and K_L (L/mg) which

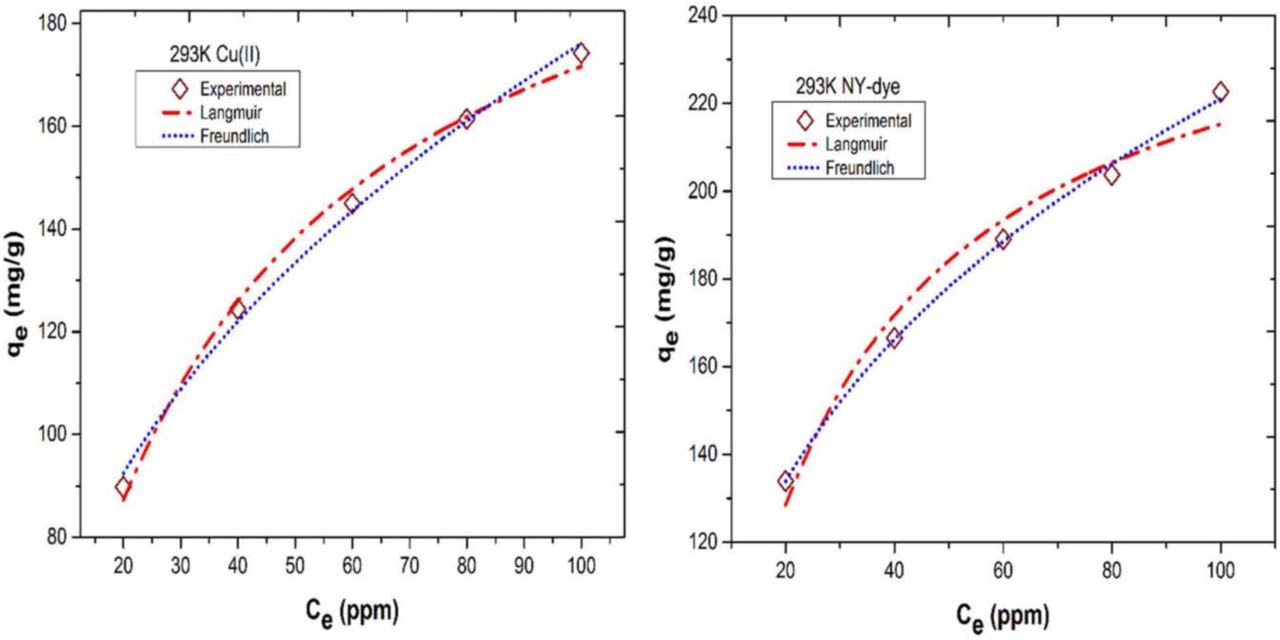


Figure 10. Langmuir and Freundlich isotherms for Cu(II) and NY dye at 293 K. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

represent the maximum adsorption capacity and Langmuir constant, respectively, were determined. The dimensionless constant, R_L, was also determined as shown by the equation below:

$$R_L = \frac{1}{1+K_L C_o} \tag{6}$$

R_L demonstrates the type of adsorption either favorable ($0 < R_L < 1$), unfavorable ($R_L > 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$).

Freundlich isotherm explains the adsorption on a heterogeneous (multilayer) surface with uniform energy distribution. The Freundlich equation is:

$$q_e = K_F C_e^{1/n} \tag{7}$$

where n indicates the intensity level of the adsorption and K_F is the Freundlich constant. A plot of q_e versus C_e (Figure 10) is used to determine the values of n and K_F.

The adsorption constants were determined from Langmuir and Freundlich isotherms for varying temperatures (293 K, 303 K, and 313 K) and summarized in Table I. Higher correlation coefficients (R^2) indicate that Freundlich isotherm best describes the adsorption process and the adsorption on CS-MMT surface was heterogeneous. However, the highest adsorption capacities were observed as 240.68 mg/g and 259.00 mg/g for Cu(II) and NY dye, respectively, at 293 K. As can be seen in Figure 10, the experimental data of present study best correlated with the isotherm plots at low temperature.

Thermodynamic Investigations

Thermodynamic parameters including entropy change ($\Delta S°$), enthalpy ($\Delta H°$), and Gibb's free energy ($\Delta G°$) are useful for the better understanding of the effect of temperature on the

Table I. Isotherm Adsorption Values of Cu(II) and NY Dye for CS-MMT Hydrogel

	Temperature (K)					
	Cu(II)			Nitrazine yellow		
Isotherm model	293 K	303 K	313 K	293 K	303 K	313 K
Langmuir						
Q_o (mg/g)	240.68	228.15	226.47	259.00	246.95	238.19
K_L (L/mg)	0.031	0.030	0.028	0.057	0.054	0.049
R^2	0.994	0.993	0.987	0.971	0.941	0.935
R_L	0.254	0.239	0.223	0.382	0.379	0.363
Freundlich						
K_F ($mg^{1-1/n}L^{1/n}/g$)	34.14	31.03	27.86	74.35	66.37	52.69
N	2.66	2.61	2.49	3.21	2.82	2.98
R^2	0.996	0.995	0.993	0.998	0.984	0.983

Table II. Thermodynamic Parametric Values of the Adsorption Process

Thermodynamics parameters	Temperature (K)					
	Cu(II)			Nitrazine yellow		
	293 K	303 K	313 K	293 K	303 K	313 K
ΔG° (kJ/mol)	−15.93	−16.35	−16.76	−18.45	−18.89	−19.32
ΔH° (kJ/mol)		−3.78			−5.75	
ΔS° (J/mol K)		−41.47			−43.36	

removal of Cu(II) and NY dye by CS-MMT hydrogel. Using the eqs. (8)–(10), ΔG°, ΔH°, and ΔS° were calculated:

$$\Delta G^\circ = -RT\ln K_L \tag{8}$$

$$\ln K_L = -\frac{\Delta G^\circ}{RT} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{9}$$

$$\Delta G^\circ = \Delta H - T\Delta S \tag{10}$$

where R (J/mol K) is the gas constant, T (K) temperature, and K_L (L/mol) is Langmuir constant. ΔH° and ΔS° values were obtained by plotting a graph of ln K_L versus $1/T$ and tabulated in Table II. ΔG° is used to describe the spontaneity of the adsorption system. The more negative the value, the more energetic and favorable the adsorption process. The ΔG° values suggest that Cu(II) and NY dye adsorption by CS-MMT was spontaneous and favorable at low temperatures. The obtained ΔG° values were between −20 kJ/mol to 0 kJ/mol indicating the adsorption process was dominated by physical adsorption. ΔH° and ΔS° values for studied temperatures on the adsorption of Cu(II) and NY dye were negative. The negative ΔH° values confirm the adsorption process was exothermic in nature. The negative values of ΔS° suggested decrease randomness at the solid–solution interface during Cu(II) and NY dye adsorption. This was due to the low displacement of the adsorbate molecules leading to the generation of less translational entropy by the adsorbate ions, thus preventing the prevalence of randomness in the system.

Kinetics Modeling

Different adsorption kinetic models have been employed to evaluate the interactions between adsorbates and biosorbents. In the present study, the pseudo-first order, pseudo-second order, and intraparticle diffusion model were applied to evaluate the adsorption kinetics using eqs. (11)–(13). The calculated results are shown in Table III.

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \tag{11}$$

$$\frac{t}{q_t} = \frac{1}{K_2 \, q_e^2} + \frac{t}{q_e} \tag{12}$$

$$q_t = K_i t^{1/2} + C_i \tag{13}$$

where q_e and q_t (mg/g) represent the adsorbed capacities at equilibrium and time, t (min), respectively, K_1 (min^{-1}) is the pseudo-first order adsorption rate constant, K_2 (g/mg min) is the rate constant of second-order of adsorption process, K_i (mg/g min$^{1/2}$) is the rate parameter for intraparticle diffusion model,

Table III. Kinetic Data for Adsorption of Cu(II) and NY for CS-MMT Hydrogel

	Cu(II)			Nitrazine yellow		
CS-MMT	293 K	303 K	313 K	293 K	303 K	313 K
Pseudo-first order model						
K_1 (min^{-1}) × 10^{-4}	4.90	4.55	4.53	13.2	11.4	14.1
$q_{e,cal}$ (mg/g)	130.26	124.55	133.93	149.49	154.06	142.53
$q_{e,exp}$ (mg/g)	166.41	163.08	161.25	173.08	169.25	161.17
R^2	0.974	0.999	0.991	0.987	0.983	0.980
Pseudo-second order model						
K_2 (g/mg min) × 10^{-4}	32.32	32.29	32.28	5.73	7.78	4.28
$q_{e,cal}$ (mg/g)	168.63	167.69	164.78	185.69	176.36	173.67
$q_{e,exp}$ (mg/g)	166.41	163.08	161.25	173.08	169.25	161.17
R^2	0.999	0.999	0.999	0.991	0.993	0.988
Intraparticle diffusion model						
k_i (mg/g min$^{1/2}$)	2.08	1.75	2.87	7.21	5.59	8.81
C_i	105.35	103.47	101.49	144.70	149.72	131.30
R^2	0.909	0.995	0.949	0.991	0.988	0.977
Activation energy						
Ea (kJ/mol)		4.5			6.74	
$A \times 10^{-6}$ (s^{-1})		31.73			8.08	

Table IV. Model Factors for High and Low Level Experimental Coding

Factor	Name	Low level	Medium level	High level	Coding
X_1	Dosage	60	80	100	Actual
X_2	Concentration	60	80	100	Actual
X_3	pH	2	6	8	Actual
X_4	Temperature	293	303	313	Actual

and C_i is the boundary layer effect which contributes to the surface adsorption at the rate-controlling step and in addition which describes the thickness of the adsorbed layer. Using pseudo-first order equation, a plot of $\log(q_e - q_t)$ versus t was deduced. The values of K_1 and $\log q_e$ were obtained from the slope and intercept, respectively. A graph of t/q_t versus t was also plotted to calculate K_2 and $1/K_2q_e^2$ from the slope and intercept, respectively, for pseudo-second order. As for intraparticle diffusion, a plot of q_t versus $t^{1/2}$ was deduced to determine K_i and C_i. Calculation of the activation energy was performed following the equation below:

$$\ln K_2 = \ln A - \frac{Ea}{RT} \tag{14}$$

where K_2 (g/mg min) is the pseudo-second order rate constant, Ea (kJ/mol) is the Arrhenius activation energy of CS-MMT adsorption, A is the Arrhenius factor, and R (8.314 J/mol K) is the gas constant. $\ln K_2$ was plotted against $1/T$ to determine Ea from slope ($-Ea/R$) and A as intercept. Ea values, which fall between the range of 5 kJ/mol to 40 kJ/mol, confirmed that the adsorption of Cu(II) and NY dye by CS-MMT was dominated by physical adsorption.[39]

Evaluations based on the obtained R^2 values (Table III) and close agreement between $q_{e,cal}$ and $q_{e,exp}$ values confirmed the adsorption of Cu(II) and NY dye onto CS-MMT best fitted the pseudo-second order kinetic model. However, the boundary layer thickness (C_i) for the intraparticle diffusion model decreased with increasing temperature as can be seen in Table III. This indicates that the adsorption of Cu(II) and NY dye was highly favorable at low temperature as earlier discussed.

Design and Optimization of Adsorption Process

The adsorption process was optimized by simultaneously studying the adsorption parameters of dosage, concentration, pH, and temperature using the Box–Behnken model via Design-Expert 9.0 for the different independent parameters.[40,41] Box–Behnken model helped to reduce the number of experimental replicates, thereby allowing the linear, quadratic effects, and first order interactions to be well estimated.[27] The Box–Behnken design of quadratic model comprised of 29 experimental runs for Cu(II) and NY dye. The number of experiments needed for Box–Behnken design can be determined with the equation below:

$$N = K^2 + K + C_p \tag{15}$$

where N is the number of experiments, K is the factor number, and C_p is the replicate number of the central points. For the good accuracy, the second order model is used. The equation is given below:

$$Y = b_o + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_4 + b_{12}X_1X_2 + b_{13}X_1X_3 + \;\ldots\ldots \tag{16}$$

where Y is the response, b is the coefficient associated with factor n, and X_1, X_2, X_3, and X_4 stands for the variables in the model.[37,42]

The polynomial equation for predicting the optimal adsorption point was obtained using the Box–Behnken experimental design model with the experimental parameters of low and high levels as shown in Table IV. The relationship between the response Y and the critical variables X_1, X_2, X_3, and X_4 in the coded forms were expressed by:

$$\begin{aligned}\text{Cu(II) (mg/g)} = {} & 128.52 + 5.40\ X_1 - 20.87\ X_2 + 175.97\ X_3 - 7.25 \\ & X_4 - 0.01\ X_1\ X_2 + 0.40\ X_1\ X_3 - 0.03\ X_1\ X_4 - 0.09 \\ & X_2\ X_3 + 0.09 X_2\ X_4 - 0.50\ X_3\ X_4 + 0.01 \\ & X_1^2 - 0.03\ X_2^2 - 5.69\ X_3^2 + 0.01\ X_4^2\end{aligned} \tag{17}$$

$$\begin{aligned}\text{NY dye (mg/g)} = {} & 148.71 - 9.94\ X_1 + 9.41\ X_2 - 24.27\ X_3 \\ & -36.60\ X_4 + 5.54\ X_1\ X_2 - 0.28\ X_1\ X_3 + 2.06\ X_1\ X_4 \\ & -9.91\ X_2\ X_3 - 12.34\ X_2\ X_4 + 19.21\ X_3\ X_4 - 8.15\ X_1^2 \\ & +5.86\ X_2^2 + 9.41 X_3^2 - 2.38\ X_4^2\end{aligned} \tag{18}$$

The Analysis of Variance (ANOVA) results of the response surface quadratic model analysis are summarized in Table V below. With good R^2 values of 0.913 and 0.989 for Cu(II) and NY dye responses, respectively, demonstrate that this model is sufficient to predict the adsorption process. F-values of 10.49 and 8.59 for Cu(II) and NY dye, respectively, indicate that this model is significant. "Prob > F" less than 0.0500 indicates that the model terms are significant.

Table V. ANOVA Statistical Analysis for the Adsorption of Cu(II) and NY Dye

Source	Sum of squares Cu(II)	Sum of squares NY-dye	Degree of freedom	*P*-value prob > F Cu(II)	*P*-value prob > F NY-dye
Model	43413.11	26982.19	14	<0.0001	0.0001
Residual	4137.06	3141.85	14		
Lack of fit	3949.93	2926.43	10	0.0272	0.0586
Pure error	7.13	5.42	4		
Adjusted R^2	0.913	0.986			
Predicted R^2	0.886	0.897			

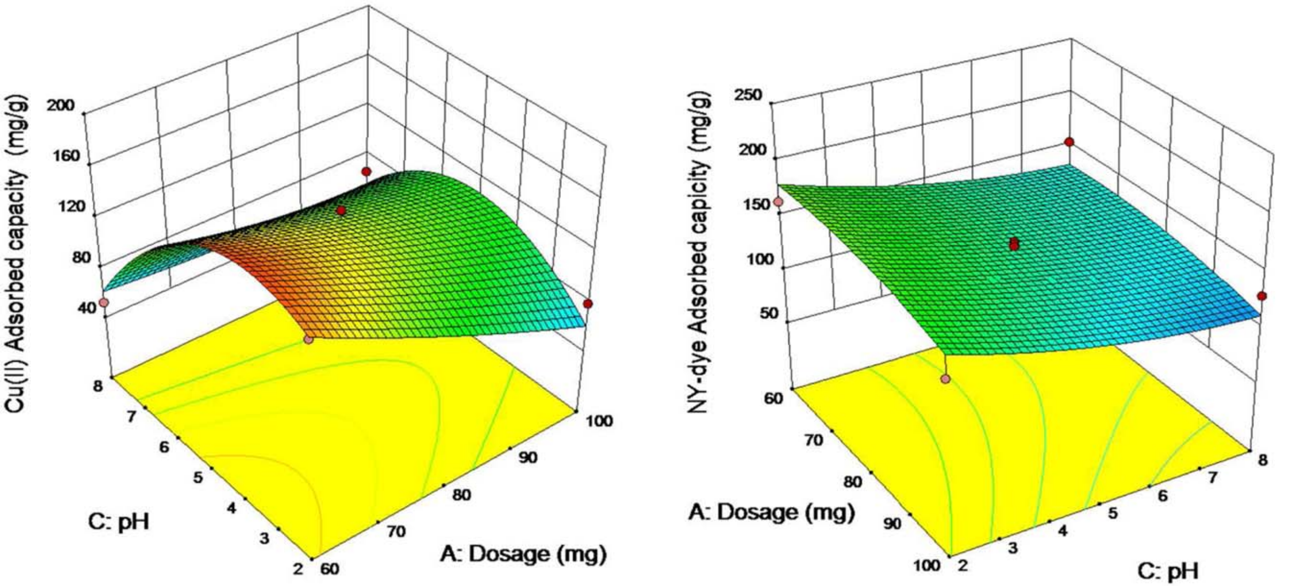


Figure 11. 3D response surface plots. Effects of pH and dosage on the adsorption capacity of Cu(II) and NY dye at constant initial concentration (80 ppm) and temperature (303 K). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Interactive Effect of Two Variables

An experimental design RSM model was applied with four process variables to evaluate their effect on Cu(II) and NY dye uptake process, as discussed above. Three-dimensional plots were created to evaluate the interactive effect on adsorption capacity of CS-MMT hydrogel. The obtained inferences are discussed below.

Effect of Initial pH and CS-MMT Dosage on Cu(II) and NY Dye Uptake. Figure 11 represents the 3D interactive plots of CS-MMT dosage and pH on Cu(II) and NY dye uptake. The uptake capacities increased with increasing dosage and maximum removal was attained when 80 mg adsorbent was consumed. Then, the sorption capacities decreased with increasing dosage. This can be attributed to saturated sorption sites and possible competition between adsorbed adsorbates and adsorbates in solution.[43] High adsorption values for Cu(II) and NY dye at low pH was due to the increase in available binding sites caused by increased swelling of hydrogel at low pH, thus enhancing the diffusability and adsorption of the adsorbates onto CS-MMT hydrogel. The maximum adsorption capacities of CS-MMT hydrogel were obtained as 127 mg/g and 143 mg/g at optimum dosage (80 mg) and pH 5 for Cu(II) and NY dye, respectively.

Effect of pH and Initial Concentration on Cu(II) and NY Dye Uptake. Figure 12 depicts the 3D plots of the combined effect of pH and initial concentration on the uptake of Cu(II) and NY dye onto CS-MMT hydrogel. Uptake of Cu(II) increased with increasing initial concentration, while a constant uptake was observed for NY dye as initial concentration increased. This

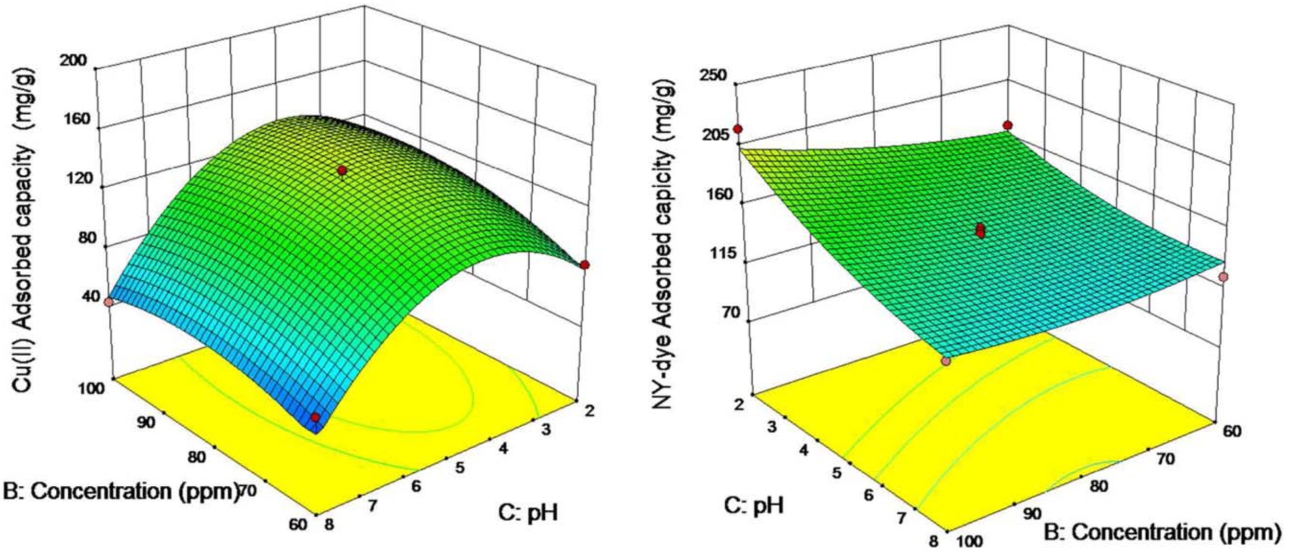


Figure 12. 3D response surface plots on the effect of pH and initial concentration on the adsorption of Cu(II) and NY dye. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

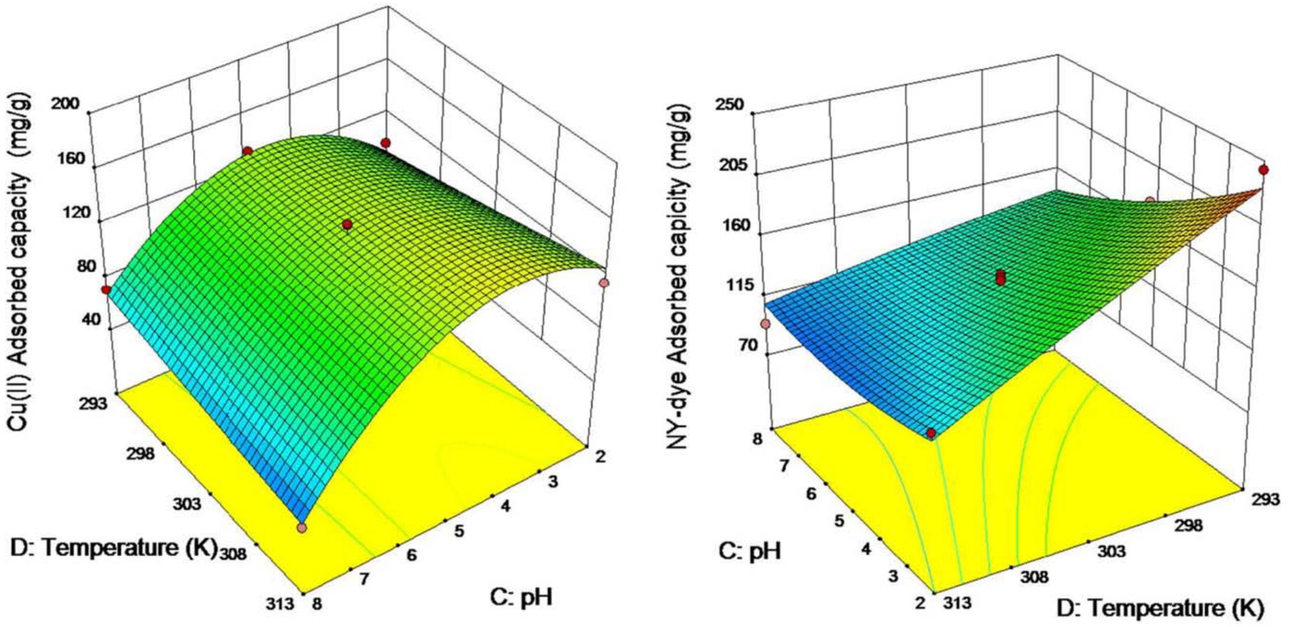


Figure 13. 3D response surface plots. Effects of temperature and pH on the adsorption of Cu(II) and NY dye at constant initial concentration (80 ppm) and dosage (80 mg). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

increasing uptake in Cu(II) was as a result increased driving force of the concentration gradient rather than an increase in the initial concentration of Cu(II).[32,43] The Cu(II) uptake increased until pH 5, after which a decreasing trend was observed. This was due to increase coordinate bond formation between Cu(II) and nitrogen atom of NH_2 on CS-MMT hydrogel followed by gradual precipitation of Cu(II) ions to form $Cu(OH)_2$. The decrease in NY dye adsorption with increasing pH which was due to the gradual deprotonation of ammonium ion on CS-MMT hydrogel to hydrophobic amine which enhanced electrostatic repulsion in adsorption solution. The maximum adsorption capacities of Cu(II) and NY dye were determined as 134 mg/g and 146 mg/g, respectively, for optimum initial concentration (80 ppm) and pH 5.

Effect of Temperature and pH on Cu(II) and NY Dye Uptake. Based on literature,[44,45] pH and temperature variables are very significant and considered the most influencing variables in the adsorption process. Figure 13 shows 3D plots on the adsorption of Cu(II) and NY dye which decrease with increasing the temperature. This behavior demonstrated that the adsorption of Cu(II) and

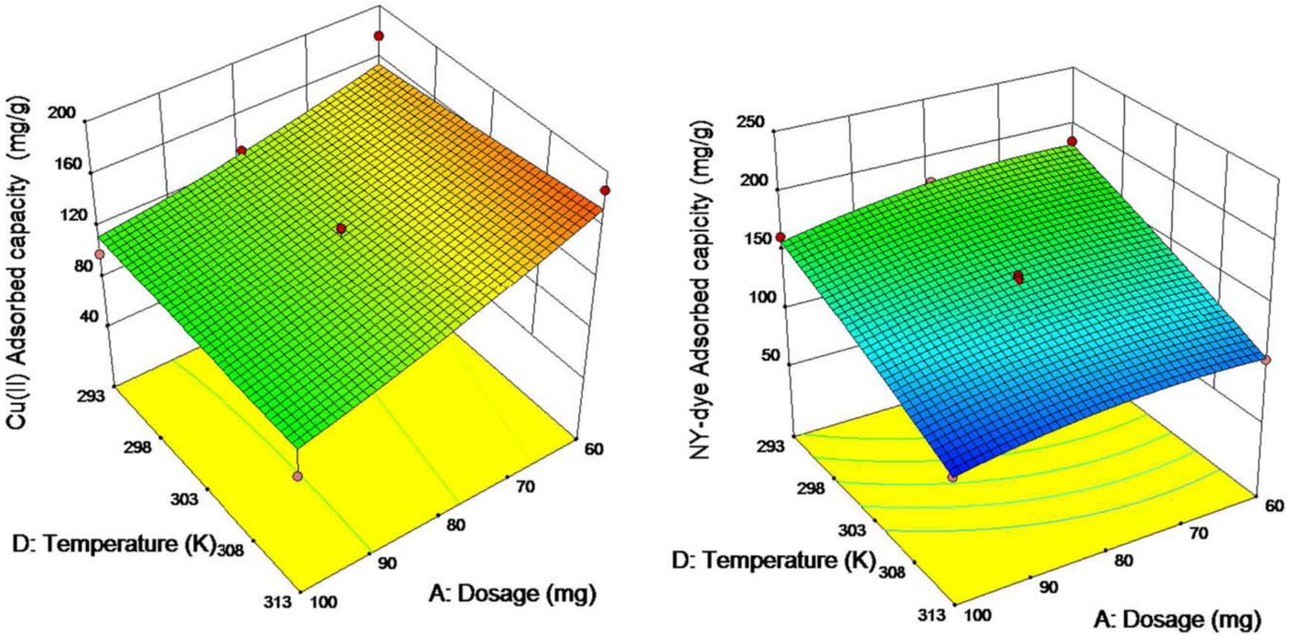


Figure 14. 3D response surface plots. Effects of temperature and dosage on the adsorption of Cu(II) and NY dye at constant initial concentration of 80 ppm and pH 5. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

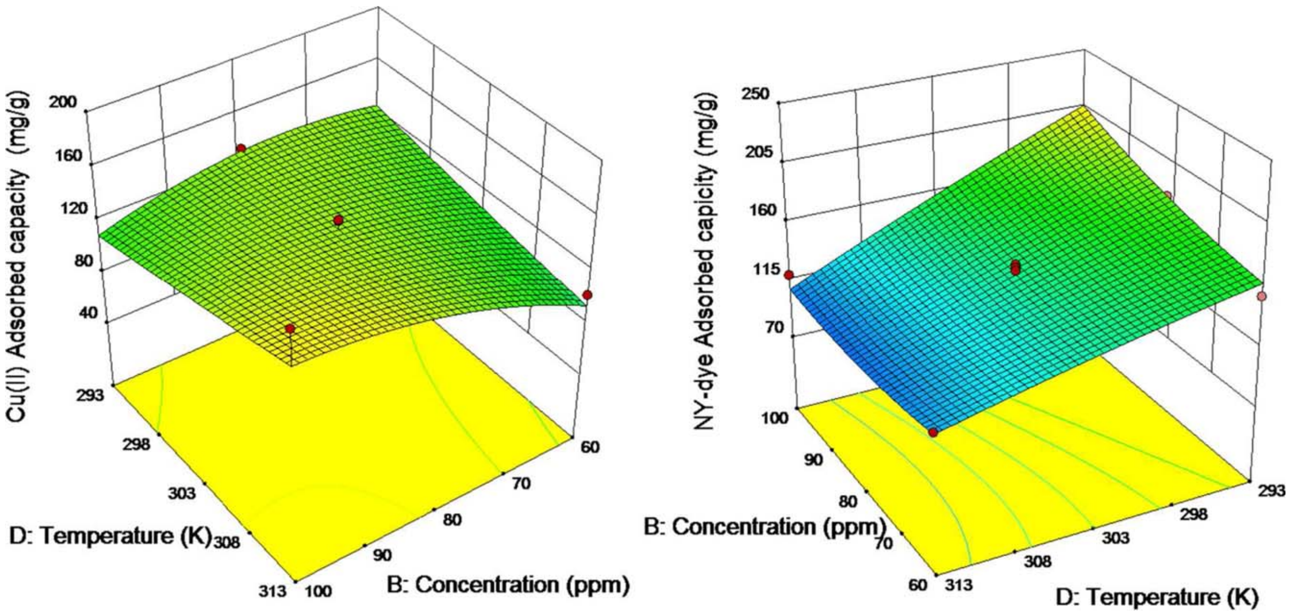


Figure 15. 3D response surface plots. Effects of temperature and initial concentration on the adsorption of Cu(II) and NY dye at constant CS-MMT dosage (80 mg) and pH 5. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

NY dye onto the CS-MMT surface was more favorable at low temperatures and thus exothermic. Cu(II) uptake increased from pH 2–6 then decreased at pH > 6, due to the precipitation of Cu(II) ions to form $Cu(OH)_2$. NY dye uptake decreased with increased pH attributed to decrease in available NH_3^+ ions on CS-MMT hydrogel surface at high pH. Maximum adsorptions were obtained as 133 mg/g and 144 mg/g for Cu(II) and NY dye, respectively, at optimum temperature of 303 K and pH 5.

Effect of CS-MMT Dosage and Temperature on Cu(II) and NY Dye Uptake. The interactive effect of temperature and CS-MMT dosage on Cu(II) and NY dye adsorption is represented in Figure 14. The adsorption capacity of CS-MMT decreased with increased CS-MMT dose. This decrease can be attributed to the decreasing in the number of adsorbate molecules in the solution. Maximum adsorptions were obtained as 133 mg/g and 147 mg/g for Cu(II) and NY dye, respectively, at constant pH 5 and initial concentration (80 ppm).

Effect of Temperature and Initial Concentration on Cu(II) and NY Dye Uptake. The combined effect of temperature and initial concentration for the adsorption of Cu(II) and NY dye by CS-MMT hydrogel is represented in Figure 15. The adsorption rate decreased with increasing temperature as expected. The decreased in adsorption rate was attributed to the decreased in force of attraction between CS-MMT and adsorbate

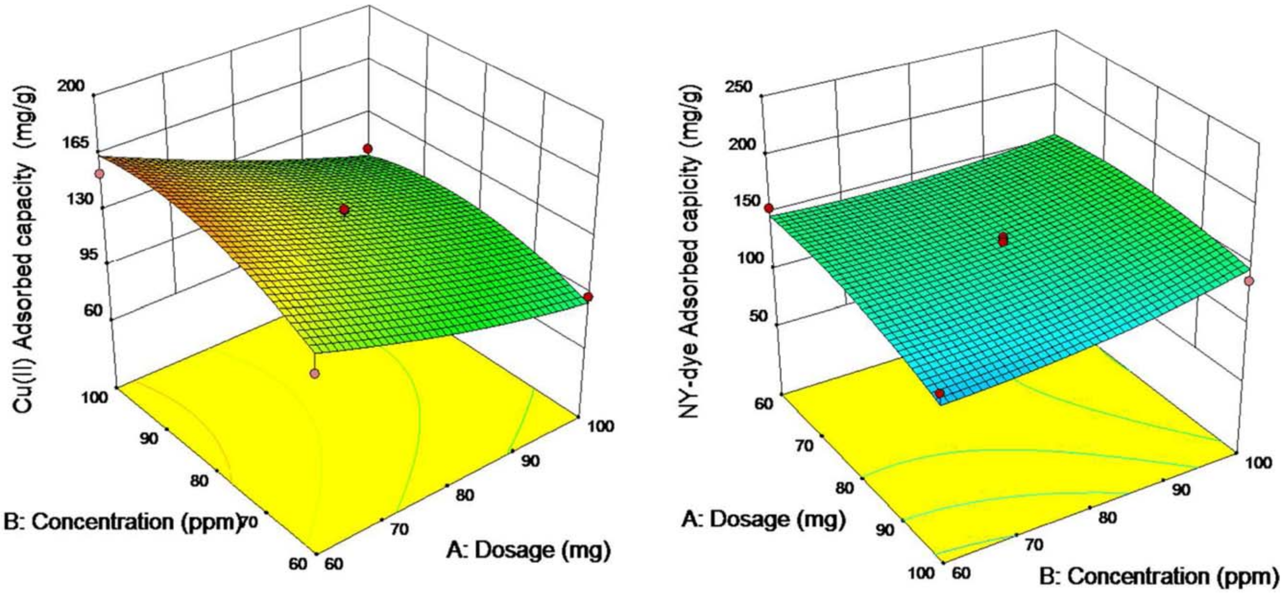


Figure 16. 3D response surface plots. Effects of dosage and initial concentration on the adsorption of Cu(II) and NY dye at constant temperature (303 K) and pH 5. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Table VI. Predictive Response Data for Cu(II) and NY Dye Adsorption

Response	Predicted	Std. Dev.	SE Mean	95% CI low	95% CI high
Cu(II) (mg/g)	132.74	17.19	7.53	116.58	148.91
NY dye (mg/g)	144.41	14.98	6.57	130.32	158.50

species at the solid–solution interface for higher temperature induced by decrease in swelling of hydrogel with increasing temperature.[46,47] The phenomenon of increasing adsorption rate with decreasing temperature depicts that the adsorption of Cu(II) and NY dye onto CS-MMT is exothermic. However, increasing adsorbates concentration increased uptake capacity on adsorption sites of CS-MMT. Maximum adsorptions were obtained as 131 mg/g and 146 mg/g for Cu(II) and NY dye, respectively, at optimum temperature (303 K) and pH 5.

Effect of CS-MMT Dosage and Initial Concentration on Cu(II) and NY Dye Uptake. Figure 16 represents the effect of adsorbent dosage and initial concentration uptake Cu(II) and NY dye under predefined conditions. The uptake capacity of Cu(II) and NY dye decreased with increased CS-MMT dosage and increased with increasing initial concentration of Cu(II) and NY dye which is in agreement with previous studies.[48,49] The increase in uptake capacity with increasing initial concentration was due to a high driving force for mass transfer.[43] The maximum adsorptions were obtained as 133 mg/g and 142 mg/g for Cu(II) and NY dye, respectively, at optimum CS-MMT dosage (80 mg) and initial concentration (80 ppm).

Process Optimization. The goal and objective of the present study was to reach the most effective values of process variables to optimize Cu(II) and NY dye removal by CS-MMT hydrogel from aqueous medium. This aim was reached via quadratic model within the investigated experimental range of the dynamic parameters. The optimization model determined the optimum variable values as temperature 303 K, CS-MMT dosage 80 mg, initial adsorbate concentration 80 ppm, and pH 5, yielding the maximum adsorption capacities as 132.74 mg/g and 144.41 mg/g for Cu(II) and NY dye, respectively, as given in Table VI. Comparatively, the experimental adsorption capacities were determined as 168.63 mg/g and 185.69 mg/g for Cu(II) and NY dye under the same optimal conditions.

The maximum adsorption capacities of CS-MMT hydrogel for the removal of Cu(II) and NY dye were compared to crosslinked chitosan hydrogel adsorption results at same optimum conditions and other similar adsorbents of previous research studies as seen in Table VII. From Table VII, we can definitely conclude that CS-MMT hydrogel is a good biosorbent for Cu(II) and NY dye, in addition can serve as a good alternative biosorbent for adsorption of other heavy metal ions and dyes.

CONCLUSIONS

An eco-friendly and chemically crosslinked chitosan montmorillonite (CS-MMT) hydrogel was synthesized, characterized, and the adsorption capacities for Cu(II) and NY dye in aqueous solutions were investigated. Different isotherms and response surface methodology (RSM) model were applied to the present adsorption study to evaluate the adsorption kinetics and equilibrium uptake at varying adsorption parameters. The obtained results indicate that the pseudo-second order model fits the experimental data preferably and Freundlich model better fitted the experimental data. The results reveal that the removal of Cu(II) and NY dye decreased with increasing CS-MMT dosage, temperature, and ionic strength but increased with increasing initial concentration and pH. Finally, we can conclude that CS-MMT hydrogel is an effective, eco-friendly, low cost material, and suitable biosorbent for Cu(II) and NY dye and can serve as a good alternative for adsorption of other heavy metal ions and dyes.

NOMENCLATURE

C_i	Intraparticle diffusion model constant
K_1	Pseudo-first order kinetic rate constant (min^{-1})
K_2	Pseudo-second order kinetic rate constant (g/mg min)
K_L	Langmuir adsorption constant (L/g)
K_F	Freundlich adsorption constant (L/g)
K_i	Intraparticle rate constant (mg/g min)
M	Mass of adsorbent (g)
n	Freundlich constant
V	Volume of adsorbate (mL)
C_o	Initial concentration of adsorbate (ppm)

Table VII. Comparison of Various Biosorbents

Biosorbent	Adsorbate	Parameter condition	Max. adsorption (mg/g)	Reference
Crosslinked chitosan	Cu(II)	pH = 6	130.72	13
Chitosan-cellulose	Cu(II)	pH = 7	53.2	14
Alumina-chitosan	Cu(II)	pH = 6	315.46	36
Chitosan-coated sand	Cu(II)	pH = 6	8.18	32
Crosslinked chitosan	Cu(II)	pH = 5	47.51	Present study
Crosslinked chitosan	NY dye	pH = 5	89.74	Present study
Chitosan-MMT	Cu(II)	pH = 5	132.74	Present study
Chitosan-MMT	NY dye	pH = 5	144.41	Present study

C_e	Concentration of adsorbate at equilibrium (ppm)
q_e	Amount adsorbed onto CS-MMT at equilibrium (mg/g)
$q_{e,exp}$	Experimental amount adsorbed at equilibrium (mg/g)
Q_o	Maximum adsorption capacity for CS-MMT (mg/g)
R	Ideal gas constant (8.314 J/mol K)
R^2	Correlation coefficient
T	Absolute temperature (K)
t	Time (min)
ΔG°	Free energy change (kJ/mol)
ΔH°	Enthalpy change (kJ/mol)
ΔS°	Entropy change (J/mol K)
Std.	Dev. Standard deviation
SE	Sum of error
CI	Confidence interval

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