Sulphate-Crosslinked Chitosan as an Adsorbent for the Removal of Congo Red Dye From Aqueous Solution

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ABSTRACT: Dyes are a major cause of concern nowadays as large quantities are being released into water bodies causing pollution. In this article, modified chitosan (sulphate crosslinked) has been studied for the removal of Congo red (a benzidine-based anionic diazo dye) which is a toxic dye introduced into water bodies from textile industries. Sulphate-crosslinked chitosan (SCC) was prepared in the laboratory and the characterization of SCC was done by Fourier-transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDX). Various parameters such as pH, contact time, adsorbent dosage, and concentration of adsorbent were optimized. The adsorption capacity was determined at pH 3.0, at which the percentage recovery was about 90% and followed Freundlich adsorption isotherm with an adsorption capacity of 91.8 mg/g. The adsorption followed pseudo-second-order kinetics. Various thermodynamic parameters were also determined for the change in adsorption with temperature. The SCC was regenerated with NaOH and showed good recycling capacity. The modified chitosan was applied for the removal of Congo red from industrial wastewater samples (spiked).

KEYWORDS: Biodegradable polymers, chitosan, Congo red, spectrophotometer, sulphate crosslinking

Introduction

Dyes are a major constituent of industries like paper, textile, and plastics and their presence in wastewater is a matter of serious concern to environmentalists.[1] A number of these dyes are stable to light and oxidation and also resistant to aerobic digestion.[2] Congo red (CR; 1-naphthelene sulphonic acid, 3,3′-(4,4′-biphenylene bis (azo)) bis (4-amino) disodium salt) is a benzidine-based anionic diazo dye which enters water bodies due to their use in textile and paper industries.[3] They are carcinogenic in nature. Removal of these dyes from water has been a major challenge and a large number of methods have been adopted for the same like photocatalysis for degradation,[4–7] nanocomposites, and carbon nanotubes.[8–12] Various processes have been used for the removal of CR specifically like coagulation, ion exchange, membrane filtration, irradiation, and ozonation, but these methods are very expensive and cannot be used at a large scale.[13–19]

Adsorption has been found to be a highly useful method as it is cost effective and also can be used in large scale. Materials like ricehusk,[20] activated carbon from waste rubber,[21] ash,[22] graphene oxide,[23] and other bioadsorbents[24] have been reported for the removal of different dyes. Natural adsorbents like biowaste material,[25] activated carbon from coir pith,[26] radish peel,[27] sawdust,[28] papaya seeds,[29] pine cone,[30] and eucalyptus wood[31] have been studied for the removal of CR.

Chitosan is obtained by deacetylation of chitin which is a component of crustacean shells (shrimp and crab) as well as fungal biomass. It has a wide range of applications in fields like food, cosmetics, medical, and pharmaceutical. It shows properties like biocompatibility and is biodegradable. The degradation products are nontoxic.[32] Due to its chemical stability, high reactivity, good chelation property, and so on, it can be used for the removal of dyes.[33] Chitosan is obtained from chitin in the form of flakes or powder and has limited use for adsorption, but the main advantage is that it is insoluble in sulphuric acid. The free amino groups react with the acid to form salt. Since sulphate is divalent, on treatment with sulphuric acid the cross links are formed. The crosslinking with hydrochloric acid has been used in medicinal applications.[34]

Kahu et al[35] have reported the use of sulphate-crosslinked chitosan (SCC) for the removal of Cr(VI), but the applicability in the removal of dyes has not yet been explored. In this article, the removal of CR dye from wastewater has been reported using batch adsorption method. The kinetic and isotherm studies have also been studied.

Experimental

Materials

Chitosan was obtained from Uniloid Bio-Chemicals India Limited, Hyderabad (India). This chitosan had 85% degree of acetylation. CR dye, sulphuric acid, and sodium hydroxide were purchased from Merck, India, and used without further purification. All the solutions were prepared in double distilled water.

Preparation of SCC

The SCC was prepared as per the method reported by Kahu et al.[35] Approximately 5 g of chitosan powder was taken in round-bottom flask and 4% v/v sulphuric acid solution was added to it and stirred with a magnetic stirrer for about an hour. The stirring was done at room temperature (298 K). The

mixture was then filtered and the residue was washed with distilled water. The complete removal of sulphate ions was tested and a final solid residue of SCC was obtained. The residue was dried at 60°C for 1 hour in a hot air oven.

Characterization

The Fourier-transform infrared spectroscopy (FT-IR) spectrum and X-ray diffraction (XRD) measurements along with scanning electron microscopy (SEM) gave the same results as reported by Kahu et al.[35]

Batch adsorption experiments

Fifty millilitres of CR solution with concentration of 5 mg/L at pH 3.0 was taken in a flask and 0.1 g of SCC was added to it. The flask was stirred in a mechanical shaker for 30 minutes at room temperature. The amount of CR adsorbed at equilibrium was calculated as follows:

$$q_e = \left(C_o - C_e / W\right) \times V$$

where C_o and C_e are the initial and equilibrium liquid phase concentrations (mg/L) of CR, respectively; V is the volume of the solution taken; and W is the weight of SCC added for the study. All the experiments were performed a minimum of 3 times to get reliable results.

Analysis

The concentration of CR was determined using UV-Visible spectrophotometer (Shimadzu UV-1800) at 498 nm. The pH measurements were done using pH meter (Systronics-335) and it was adjusted using NaOH and HNO₃ solutions. The absorbance for each solution was recorded before and after adsorption and the quantitation was done accordingly.

Regeneration of SCC

Reusability of the adsorbent is important from an environmental point of view. Reagents like sodium hydroxide, ammonium hydroxide, hydrochloric acid, and sodium chloride were considered for desorption studies. One gram of the SCC with the adsorbed CR was placed in a round-bottom flask and 100 mL of the regeneration solution (5%) was added to it. The solution was stirred for about 1 hour and then cooled, filtered, and washed with distilled water. The chitosan obtained was crosslinked as shown previously and reused.

Zero point charge

The zero point charge is the pH value at which the net charge on the surface of the adsorbent is zero. The pH of zero point charge (pH_{zpc}) plays an important role in the adsorption process. For this purpose, 50 mL of a 0.01M sodium chloride (NaCl) solution was placed in a 100-mL Erlenmeyer flask. The
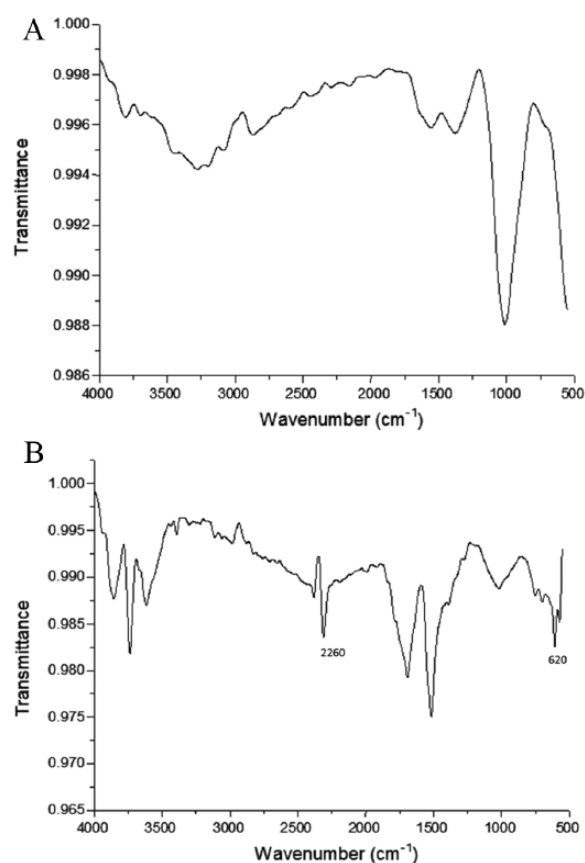

Figure 1. FT-IR spectra of (A) chitosan and (B) SCC.

pH was then adjusted to successive initial values between 1 and 10, using either sodium hydroxide or hydrogen chloride (0.1N), and 0.1 g of modified chitosan was added to the solution. After a contact time of 24 hours, the final pH was measured and plotted against the initial pH. The pH at which the curve crosses the line, pH (final) = pH (initial) is taken as the pH_{zpc}. In this case, zero point charge was observed at pH 4.6.

Results and Discussion

Characterization of SCC

FT-IR spectral characterization. The FT-IR analysis showed broad peaks in the region of 3350 cm⁻¹ and 3550 cm⁻¹ which corresponds to O-H and N-H stretching vibration as well as at 1588 cm⁻¹ for N-H bending vibration, 1375 cm⁻¹ for C-N bending vibration, and C-O and C-H stretching peaks at 2880 cm⁻¹ and 1070 cm⁻¹. The sulphate peaks were observed at 620 and 1110 cm⁻¹ which match with reported values[34] (Figure 1).

XRD studies. The diffraction pattern for chitosan and SCC is shown in Figure 2. Sulphate-crosslinked chitosan showed a peak at 2θ = 10.428° and 19.69°. On cross linking with sulphuric acid, new peaks were observed at 2θ = 11.55° and 18.26° which confirm the formation of SCC.

SEM and EDX spectral studies. The SEM micrographs showed that only chitosan showed irregularly shaped particles while that of SCC showed a regular arrangement (Figure 3). It clearly
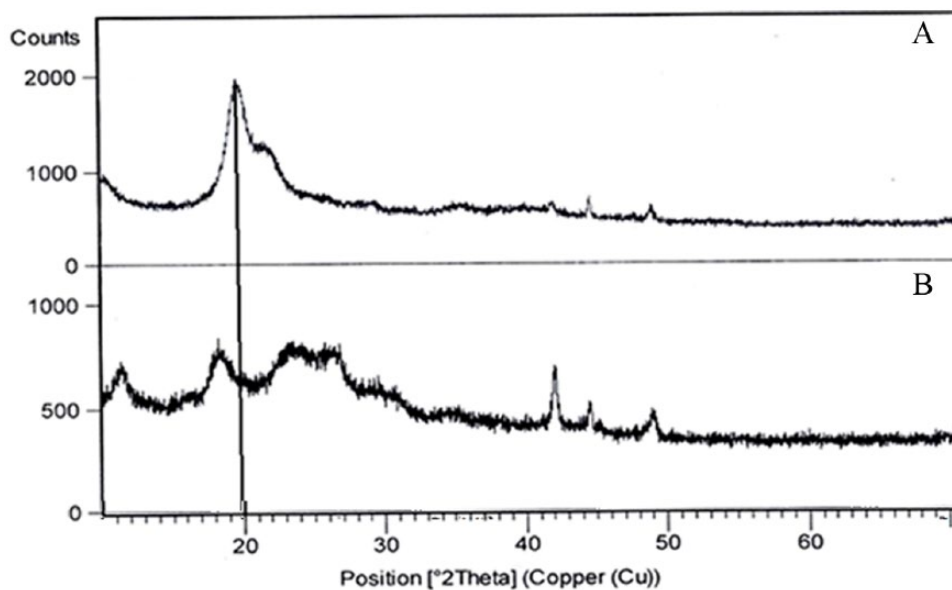
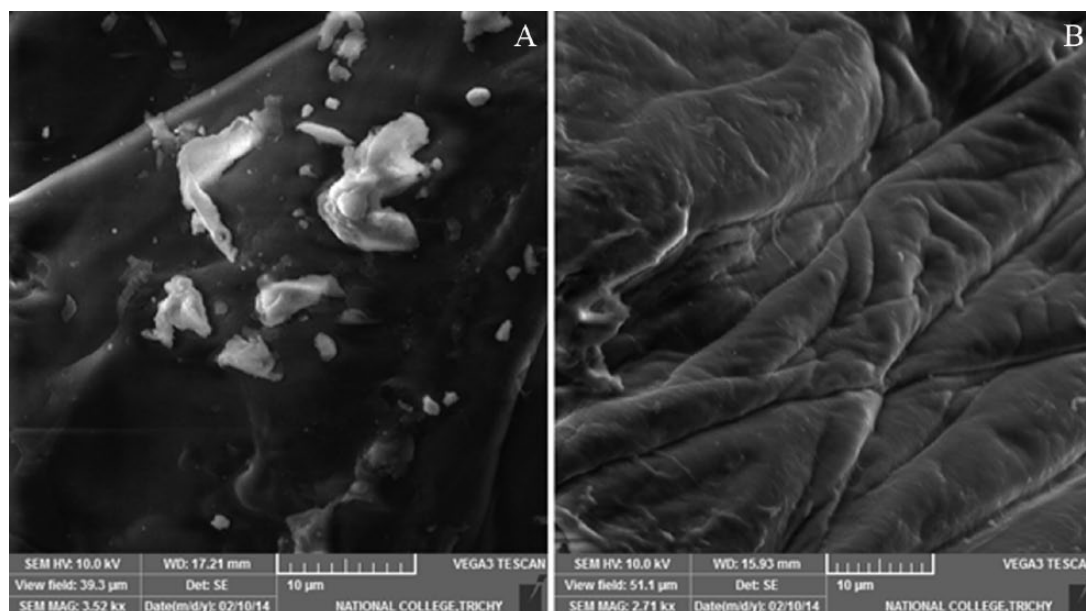**Figure 2.** XRD pattern of (A) chitosan and (B) SCC.

Figure 3. SEM micrographs of (a) chitosan and (b) SCC.

shows that the crosslinking leads to stable and ordered morphology of the material. The peaks of C, H, and N were observed in the energy-dispersive X-ray spectroscopy (EDX) spectrum and after treatment with sulphuric acid the peak for S is also clearly observed. This indicates that sulphate crosslinking has taken place and the material has been clearly modified (Figure 4).

Effect of contact time

The contact time was varied from 15 to 180 minutes. It was observed that the extent of adsorption initially increased with increase in contact time after which it became constant. The equilibrium was attained at about 90 minutes. This may be due to the lack of availability of adsorption sites after a certain period of time. Thus, 90 minutes was optimized as optimum for further studies (Figure 5A).

Effect of adsorbent dosage

The effect of adsorbent dosage was varied by adding 0.02 to 0.2 g of the crosslinked chitosan at room temperature with fixed initial concentration, pH, and contact time. There was an increase in the percentage removal of CR with increase in concentration indicating the increase in the number of adsorption sites (Figure 5B).

Effect of concentration of adsorbate

The adsorption studies were performed by increasing the concentration of CR from 0.5 to 5 mg/L. The percentage removal was found to be nearly steady and then decreases. This can be explained as, even though there is an increase in concentration of adsorbate, the available sites for adsorption become a limiting factor (Figure 5C).

Effect of pH

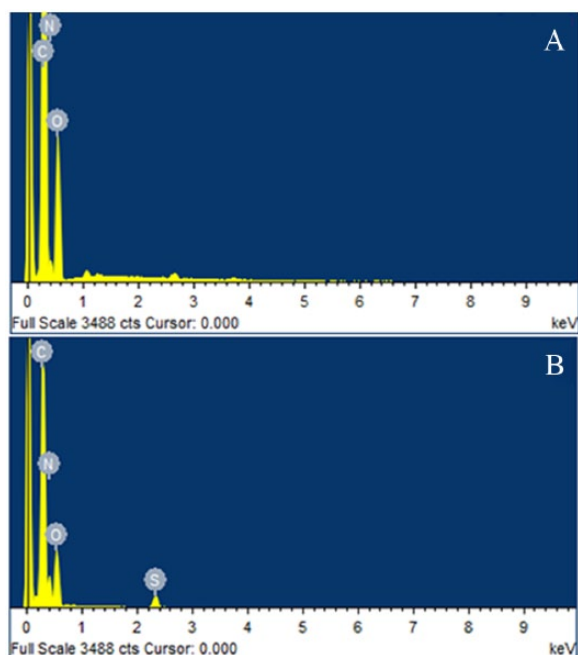The pH of the solution was varied from 1.0 to 10.0 at constant initial concentration, contact time, and temperature to determine the pH at which the percentage removal of CR was maximum. It was observed that at pH 3.0 the percentage removal was the highest. The colour of CR dye is red around pH 7.0, dark blue in acidic pH, and red at alkaline pH. (This red is slightly different from the original red at neutral pH.) It exists in its anionic form in basic pH (sulphonate group) and cationic form in acidic pH. Adsorption of cation is favoured at $pH > pH_{zpc}$ and anion at $pH < pH_{zpc}$.[36,37] In alkaline pH, there is an excess of negative ions as well as the SCC has negatively charged groups, so the anionic form of CR does not get adsorbed easily. But in acidic pH, the adsorption of CR is higher and thus pH 3.0 was optimized for further studies (Figure 5D).

Kinetics of adsorption

The percentage recovery of the dye depends on the contact time and thus the study of kinetics is essential. The experimental data were correlated using pseudo-first-order and pseudo-second-order kinetic models. The study was done using 50 mL of 5 mg/L CR solution at pH 3.0 along with the addition of 0.1 g of SCC at 298 K at increasing time intervals.

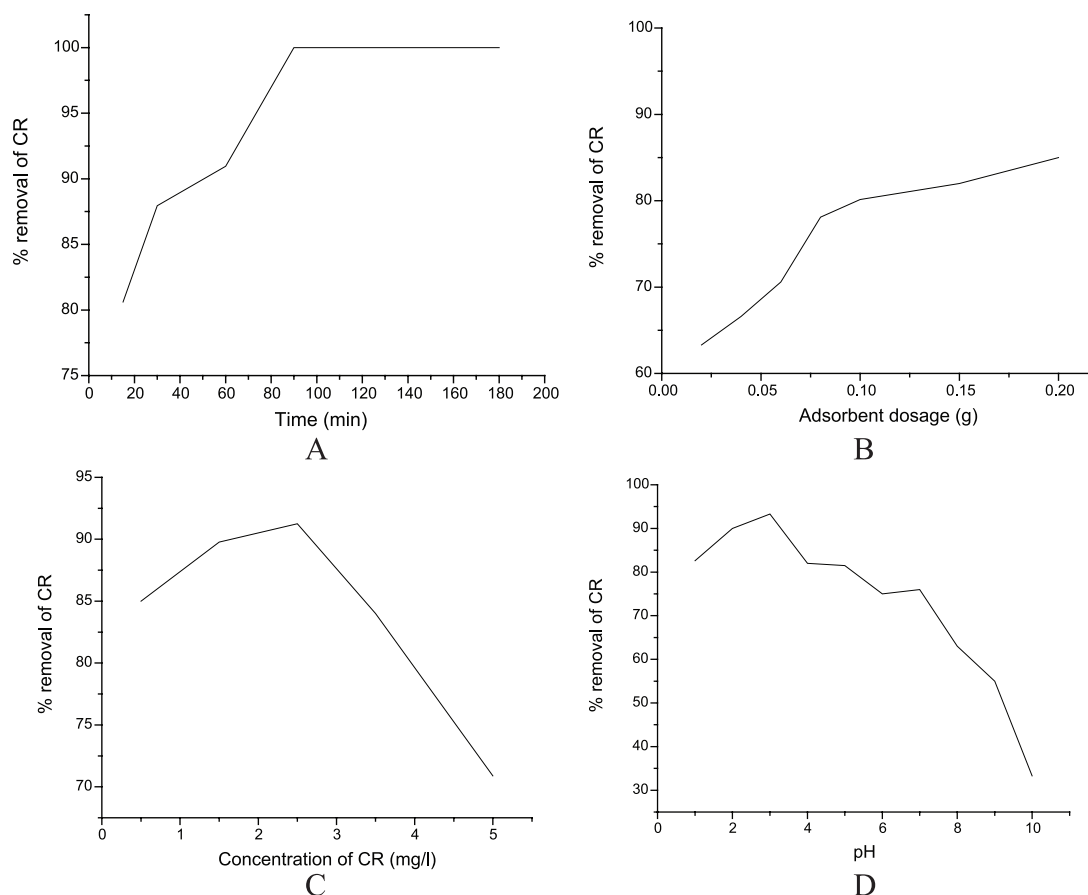*Pseudo-first-order kinetics.* The pseudo-first-order kinetics is given by the following equation[38]:

Figure 4. EDX spectra of (a) chitosan and (b) SCC.

Figure 5. Effect of (A) contact time, (B) adsorbent dosage, (C) concentration of Congo red, and (D) pH.
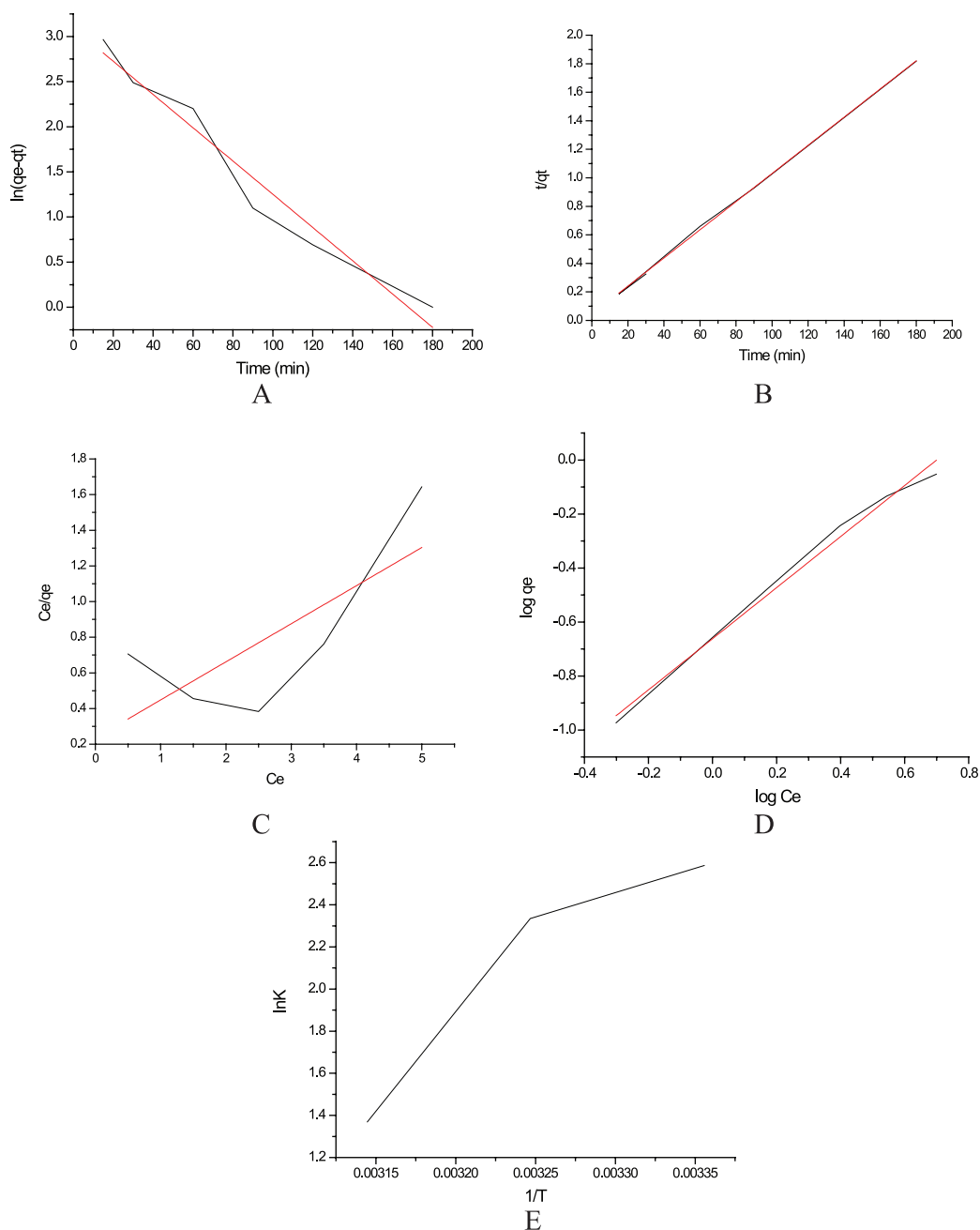
Figure 6. (A) Pseudo-first-order kinetics, (B) pseudo-second-order kinetics, (C) Langmuir adsorption isotherm, (D) Freundlich adsorption isotherm, and (E) van't Hoff plot.

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

where q_e and q_t refer to the amount of CR adsorbed at equilibrium and time, t respectively with first-order rate constant k_1. The plot of $\log(q_e - q_t)$ against t gave the regression coefficient as 0.935 (Figure 6A).

Pseudo-second-order kinetics. The pseudo-second-order equation is given as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

where k_2 is the pseudo-second-order rate constant in g/(mg min).[39] The plot of $\log t/q_t$ against t gave a regression coefficient of 0.999. The high value of regression coefficient shows that pseudo-second-order kinetic model is followed (Figure 6B).

Adsorption isotherms

Adsorption isotherms are an important tool to explain the partition of the dye between the adsorbent and liquid phases. The studies were performed using 50 mL of CR solution with varying concentrations (0.5-5 mg/L) with the addition of 0.1 g of SCC at 298 K for 30 minutes.

Langmuir isotherm. The Langmuir adsorption isotherm is the most commonly used monolayer adsorption model which correlates the maximum adsorption capacity and adsorption energy.[40] The adsorption capacity and Langmuir constant can be calculated by the following equation:

$$\left(C_e / q_e\right) = \left(1 / q_0 b\right) + \left(C_e / q_0\right)$$

The plot between C_e / q_e and C_e gave a correlation coefficient of 0.556 (Figure 6C). A dimensionless parameter R_L can be calculated by the following equation:

$$R_L = 1 / \left(1 + b C_0\right)$$

If the value of R_L lies between 0 and 1, it indicates efficient adsorption. The value of R_L for CR is found to be 0.18, which shows that there is an electrostatic interaction between the modified chitosan and CR under optimized conditions.

Freundlich isotherm. The linearized form of Freundlich[41] isotherm for studying adsorption from aqueous solution is given as follows:

$$\text{Log } q_e = \log kf + \left(1/n\right) \log C_e$$

where kf and n are Freundlich constants that indicate adsorption capacity and adsorption intensity, respectively. Value of n between 1 and 10 indicates favourable adsorption. The plot of log q_e by log C_e shows a straight line with r value of 0.989. The value of n is found to be 1.06 (Figure 6D).

The value of r clearly shows that Freundlich isotherm model is followed indicating multilayered adsorption over a heterogeneous surface.

Thermodynamics of adsorption

The effect of temperature on the adsorption of CR was studied to obtain the thermodynamic parameters (Figure 6E). The free energy change is calculated as follows:

$$\Delta G = -RT \ln K$$

The entropy and enthalpy changes were determined by van't Hoff equation[42]:

$$\ln K = \left(\Delta S / R\right) - \left(\Delta H / RT\right)$$

where R is the gas constant (8.314 J/mol/K) and T is the absolute temperature (K). The equilibrium constant K was calculated as the ratio of concentration of CR on SCC to that in the solution phase. The value of ΔH and ΔS from the slope and intercept of the graph between ln K and $1/T$ was found to be –47.62 and –0.137 kJ/mol, respectively. The
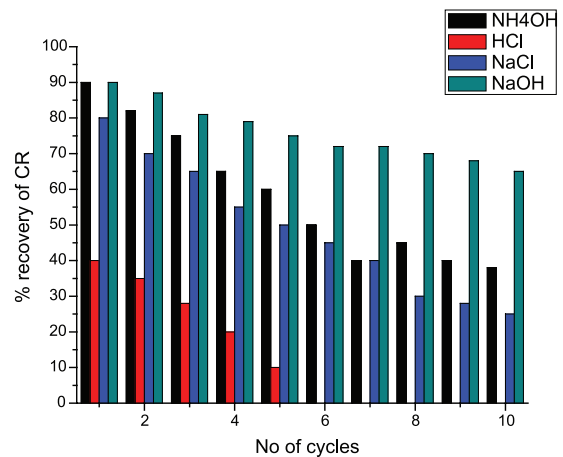

Figure 7. Graphical representation of reusability studies.

Table 1. Comparison of adsorption capacity of various reported materials.

S. NO.	ADSORBENT	ADSORPTION CAPACITY (MG/G)	REFERENCES
1	Chitosan bead	93	Chatterjee et al[43]
2	Chitosan bead modified with CTAB	94.39	Rouf et al[44]
3	*N,O*-carboxymethyl chitosan	81.23	Wang and Wang[45]
4	*N,O*-carboxymethyl chitosan/ montmorillonite nanocomposite	74.24	Wang and Wang[46]
5	Sulphate-crosslinked chitosan	91.8	This study

Abbreviations: CTAB: Cetyl tribormide ammonium bromide.

van't Hoff plot is shown in Figure 6E. The negative free energy change indicates the spontaneous nature of adsorption process. Negative enthalpy change shows that the process is exothermic and negative entropy indicates the decrease in randomness as it goes from solution to adsorbed state.

Reusability of SCC

Various reagents were analysed for desorption studies like 5% solutions of NH4OH, HCl, NaCl, and NaOH for 10 cycles. The regeneration of SCC in 5% NaOH solution was found to be maximum (Figure 7). The regenerated SCC was found to be as effective as the original SCC.

Comparison with other adsorbents

Adsorption capacity is an important parameter for an adsorbent. A comparison with other similar adsorbents shows that

SCC shows a better adsorption capacity for CR dye as compared to some of the previously reported ones (Table 1). Thus, this method is a novel, efficient, and simple method for the removal of CR dye from aqueous solutions.

Conclusions

The effectiveness of using a modified biopolymer (sulphur crosslinked) for the removal of CR dye has been shown in this study. The various parameters studied gave optimum values at pH 3.0, contact time of 90 minutes, and concentration of SCC as 0.1 g. The system was observed to follow pseudo-second-order kinetics and the type of adsorption was shown by the high r value using Freundlich isotherm. The thermodynamic parameters showed that the process is spontaneous and exothermic. A comparison with other modified chitosan samples previously reported showed that SCC has a good adsorption capacity and can be reused with nearly 100% efficiency. The method gave good results with spiked wastewater samples also.

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Author Contributions

Conceived and designed the experiments: CJ. Analyzed the data:NC. Wrote the first draft of the manuscript: NC. Contributed to the writing of the manuscript: RJ. Agreed with manuscript results and conclusions: NC,RJ. Jointly developed the structure and arguments for the paper: CJ, RJ. Made critical revisions and approved the final version: CJ. All the authors reviewed and approved the final manuscript.

REFERENCES

1. Ho YS, Chiang CC. Sorption studies of acid dye by mixed sorbents. *Adsorption*. 2001;7:139–147.
2. Chen H, Zhao J. Adsorption study for removal of congo red anionic dye using organ-attapulgite. *Adsorption*. 2009;15:381–389.
3. Mall ID, Srivastava VC, Agarwal NK, Mishra IM. Removal of congo red from aqueous solution by bagasse fly ash and activated carbon – kinetic study and equilibrium isotherm analysis. *Chemosphere*. 2005;61:492–501.
4. Gupta VK, Jain R, Nayak A, Agarwal S, Shrivastava M. Removal of hazardous dye–Tartrazine by photodegradation on titanium dioxide surface. *Mater Sci Eng C*. 2011;31:1062–1067.
5. Saleh TA, Gupta VK. Photo-catalyzed degradation of hazardous dye methyl orange by use of a composite catalyst consisting of multi-walled carbon nanotubes and titanium dioxide. *J Colloid Sci Inter Sci*. 2012;371:101–106.
6. Saravanan R, Karthikeyan S, Gupta VK, Sekaran G, Narayanan V, Stephen A. Enhanced photocatalytic activity of Zno/Cuo nanocomposite for the degradation of textile dye on visible light illumination. *Mater Sci Eng*. 2013;33:91–98.
7. Saravanan R, Mansoob Khan M, Gupta VK, et al. ZnO/Ag/CdO nanocomposite for visible light-induced photocatalytic degradation of industrial textile effluents. *J Colloid Inter Sci*. 2015;452:126–133.
8. Gupta VK, Kumar R, Nayak A, Saleh TA, Barakat MA. Adsorptive removal of dyes from aqueous solution onto carbon nanotubes: a review. *Adv Colloid Interface Sci*. 2013;193-194:24–34.
9. Mohammadi N, Khani H, Gupta VK, Amereh E, Agarwal S. Adsorption process of methyl orange dye onto mesoporous carbon material – kinetic and thermodynamic studies. *J Colloid Inter Sci*. 2011;362:457–462.
10. Saravanan R, Karthikeyan N, Gupta VK, et al. ZnO/Ag nanocomposite: an efficient catalyst for degradation studies of textile effluents under visible light. *Mater Sci Eng*. 2013;33:2235–2244.
11. Ghaedi M, Hajjati S, Mahmudi Z, et al. Modeling of competitive ultrasonic assisted removal of the dyes – methylene blue and Safranin-O using Fe_3O_4 nanoparticles. *Chemical Eng*. 2015;268:28–37.
12. Asfaram A, Ghaedi M, Agarwal S, Tyagi I, Gupta VK. Removal of basic dye Auramine-O by ZnS:Cu nanoparticles loaded on activated carbon: optimization of parameters using response surface methodology with central composite design. *RCS Adv*. 2015;5:18438–18450.
13. Liu HL, Chiou YR. Optimal decolorization efficiency of reactive red 239 by UV/ZnO photocatalytic process. *J Chinese Inst Chem Eng*. 2006;37:289–298.
14. Kapdan IK, Kargi F. Simultaneous biodegradation and adsorption of textile dyestuff in an activated sludge unit. *Process Biochem*. 2002;37:973–981.
15. Pala A, Tokat E. Color removal from cotton textile industry wastewater in an activated sludge system with various additives. *Water Res*. 2002;36:2920–2925.
16. Clark T, Bruce M, Anderson S. Decolorisation of extraction stage bleach plant effluent by combined hypochlorite oxidation and anaerobic treatment. *Water Sci Technol*. 1994;29:421–432.
17. Solozhenko EG, Soboleva NM, Goncharuk VV. Decolourization of azodye solutions by Fenton's oxidation. *Water Res*. 1995;29:2206–2210.
18. Treffry GK, Buckley CA, Groves GR. Reverse osmosis treatment and reuse of textile dyehouse effluents. *Desalination*. 1983;47:313–320.
19. Gupta VK, Srivastava SK, Mohan D. Equilibrium uptake, sorption dynamics, process optimization and column operations for the removal and recovery of Malachite green from wastewater using activated carbon and activated slag. *Ind Eng Chem Res*. 1997;36:2207–2218.
20. Ahmaruzzaman M, Gupta VK. Rice husk and its ash as low-cost adsorbents in water and wastewater treatment. *Ind Eng Chem Res*. 2011;50:13589–13613.
21. Gupta VK, Nayak K, Agarwal S, Tyagi I. Potential of activated carbon from waste rubber tire for the adsorption of phenolics: effect of pre-treatment conditions. *J Colloid Surface Sci*. 2014;417:420–430.
22. Mittal A, Mittal J, Malviya A, Gupta VK. Removal and recovery of Chrysoidine Y from aqueous solutions by waste materials. *J Colloid Inter Sci*. 2010;344:497–507.
23. Robati D, Mirza B, Rajabi M, et al. Removal of hazardous dyes-BR 12 and methyl orange using graphene oxide as an adsorbent from aqueous phase. *Chem Eng J*. 2016;284:687–697.
24. Gupta VK, Nayak A, Agarwal S. Bioadsorbents for remediation of heavy metals: current status and their future prospects. *Environ Eng Res*. 2015;20:1–18.
25. Kaur S, Rani S, Mahajan RK. Adsorption kinetics for the removal of hazardous dye congo red by biowaste materials as adsorbents. *J Chem*. 2013;2013:628582.
26. Namasivayam C, Kavitha D. Removal of congo red from water by adsorption onto activated carbon prepared from coir pith, an agricultural solid waste. *Dyes Pigments*. 2002;54:47–58.
27. Abbas A, Murtaza S, Munir M, Zahid T, Abbas N, Mushtaq A. Removal of congo red from aqueous solutions with *Raphanus sativus* peels and activated carbon: a comparative study. *Am Eur J Agricult Environ Sci*. 2011;10:802–809.
28. Nimkar DA, Chavan SK. Removal of congo red dye from aqueous solution by using saw dust as an adsorbent. *J Eng Res Applicat*. 2014;4:47–51.
29. Patel H, Vashi RT. Removal of congo red dye from its aqueous solution using natural coagulants. *J Saudi Chem Soc*. 2012;16:131–136.
30. Dawood S, Sen TK. Removal of anionic dye Congo red from aqueous solution by raw pine and acid-treated pine cone powder as adsorbent: equilibrium, thermodynamic, kinetics, mechanism and process design. *Water Res*. 2012;46:1933–1946.
31. Mane VS, Vijay Babu PS. Kinetic and equilibrium studies on the removal of congo red from aqueous solution using eucalyptus wood (*Eucalyptus globulus*) saw dust. *J Taiwan Inst Chem Eng*. 2013;44:81–88.
32. Rinaudo M. Chitin and chitosan: properties and applications. *Prog Polymer Sci*. 2006;31:603–632.
33. Vakili M, Rafatullaha M, Salamatinia B, et al. Application of chitosan and its derivatives as adsorbents for dye removal from water and wastewater: a review. *Carbohydr Polym*. 2014;113:115–130.
34. Mayyas MA. Properties of chitosan nanoparticles formed using sulphate anions as cross linking bridges. *Am J Appl Sci*. 2012;9:1091–1100.
35. Kahu S, Saravanan D, Jugade R. Effective detoxification of hexavalent chromium using sulfate-crosslinked chitosan. *Water Sci Tech*. 2014;70:2047–2055.
36. Mondal MK. Removal of Pb(II) ions from aqueous solution using activated tea waste: adsorption on a fixed-bed column. *J Environ Manage*. 2009;90:3266–3271.
37. Roy TK, Mondal NK. Biosorption of congo red from aqueous solution onto burned root of *Eichhornia crassipes* biomass. *Appl Water Sci*. 2017;7:1841–1854.
38. Lagergren S. Zur theorie der sogennanten adsorption geloster stoffe. *Sven Vetenkapsakad Handl*. 1989;24:1–39.
39. Ho YS, Mckay GA. A multi-stage batch sorption design with experimental data. *Adsorp Sci Technol*. 1999;17:233–243.

40. Langmuir I. The adsorption process of gases on planes surfaces of glass, mica and platinum. *J Am Chem Soc*. 1918;40:1361–1403.
41. Freundlich HMF. Over the adsorption in solution. *Z Phys Chem*. 1906;57:385–470.
42. Donia AM, Atia AA, El-Boraey HA, Mabrouk D. Uptake studies of copper(II) on glycidyl methacrylate chelating resin containing Fe_2O_3 particles. *Separat Purificat Technol*. 2006;49:64–70.
43. Chatterjee S, Chatterjee S, Chatterjee BP, Guha AK. Adsorptive removal of congo red, a carcinogenic textile dye by chitosan hydrobeads: binding mechanism, equilibrium and kinetics. *Colloid Surfaces A*. 2007;299:146–152.
44. Rouf S, Nagapadma M, Ramakoteswara Rao R. Removal of harmful textile dye congo red from aqueous solution using chitosan and chitosan beads modified with CTAB. *Int J Eng Res Applicat*. 2015;5:75–82.
45. Wang L, Wang A. Adsorption properties of congo red from aqueous solution onto N,O-carboxymethyl-chitosan. *Biores Technol*. 2008;99:1403–1408. doi:0.1016/j.biortech.2007.01.063.
46. Wang L, Wang A. Adsorption behaviors of congo red on the N,O-carboxy-methyl-chitosan/montmorillonite nanocomposite. *Chem Eng J*. 2008;143:43–50. doi:10.1016/j.cej.2007.12.007.