
Synthesis and characterization of eco-friendly polymer for removal of dye from wastewater

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Abstract

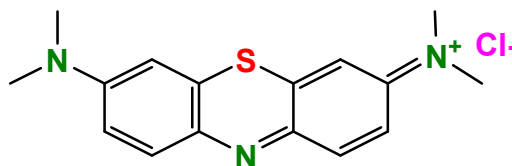
Using eco-friendly chitosan based hydrogel adsorption system was studied to remove Methylene Blue from aqueous medium. Fourier transform infrared spectroscopy and desorption studies ensure the involvement of amino and hydroxyl groups in dye adsorption. X-ray diffraction of the composite pointed out the reflections of both chitosan and NIPAM ($2\theta = 16.18^\circ$ and 30.98°). The maximum percentage removal was found to be 94.36 % for this anionic dye. The kinetics follows pseudo second order kinetics and Langmuir isotherm.

KEYWORDS: Chitosan, hydrogel, dye, composite.

INTRODUCTION

Colour is the chief attraction of every fabric and textile industry. Since 3500 BC imparting colour to fabric art is prevalent to mankind. Owing to wide range of bright colour, the use of synthetic dyes for fabric dyeing has therefore, becomes the centre of attraction at present days. But use of the synthetic dyes has the adverse impact on human being, aquatic lives, and microorganisms as these organic materials are often carcinogenic or mutagenic and therefore pose to hazard to health of them [1]. They also decline soil fertility and productivity by clogging the pores of the soil and reduce the quality of water through water pollution. So it is very much essential to develop new technologies for the waste water treatment and recycling of dye contaminated water before their final disposal because water plays a vital role for preserving ecological balance and sustainable life on earth. One of the notorious hazardous dyes is methylene blue (MB) which creates severe toxicity central nervous system, skin and eye infection and allergic reaction [2]. Due to low biodegradation of dyes, the conventional treatments such as chemical precipitation, membrane separation, coagulation/flocculation etc. are not very effective in treating dyed aquatic wastewater [3]. Adsorption is one of the most effective methods for removing dyes from effluents to solid phase [4]. Several workers studied the adsorption of different materials by chitosan complex [5]. But there is no works about NIPAM/chitosan based hydrogel for the removal of anionic dyes. Hence a cross-linked interpenetrating network polymer (IPN), namely chitosan based hydrogel, a low-cost,

simple and environmentally supported biopolymer composite adsorbent has been designed for adsorptive removal of MB dye.



Structure of Methylene Blue

EXPERIMENTAL SECTION

A. Adsorbate materials

Methylene blue ($C_{16}H_{18}N_3S^+Cl^-$) was purchased and Chitosan was procured from Sigma-Aldrich. All of the other materials were used as received, and the solutions were prepared in double distilled water.

B. Preparation biopolymer supported adsorbent

Biopolymers are most convenient for their pore size and surface morphology. Chitosan is regarded as appropriate functional resources according to its biodegradability, biocompatibility, adsorption properties and non-toxicity [6]. The free-radical polymerization mainly involves the dissolution of a functional monomer and template ion in a definite quantity in the solvent during co-polymerization, followed by the addition of a definite amount of cross-linking agent and initiator. This polymerization is an environmentally benign synthesis, as surfactants or stabilizers are not required during the imprinting process; the spherical particles are obtained as products; particles having uniform range is formed; usually compounds with desired size and shape are obtained; and rapidly produce polymer microspheres in an approximately quantitative yield [7]. A conventional dye, Methylene Blue (MB) adsorption from water was explained by Xu et al. [8] using Chitin/clay microspheres (CCM2) nanocomposite adsorbents. Hydrogels are cross-linked, covalently bonded three-dimensional (3D) networks. Without affecting the three dimensional structure, hydrogels can absorb and preserve large amounts of water prepared hydrogels with high capacity of dye adsorption with chitosan and

cellulose [9]. Herein, the preparation and the dye adsorbing capacities of the some of the chitosan hydrogels and their derivatives are comprehensively scrutinized. Hydrogel has been synthesized via solution copolymerization of monomers in presence of natural polymers, using a crosslinker and a redox pair of initiators (Fig. 1). Selected materials for synthesis of hydrogel are Chitosan (CS), N-isopropyl acrylamide (NIPAM), Sodium acrylate (SA) and Methylene-bis-acrylamide (MBA). CS is natural fibrous polymer which is constituent of exoskeleton of crustaceans (such as crabs and shrimp) and NIPAM, being a synthetic monomer shows thermosensitivity. SA also acts as monomer showing pH sensitivity. MBA a crosslinker helps to form network structure. Potassium peroxydisulfate (PPS) and sodium metabisphite (SBS), redox pair of initiators, are used for free radical formation.

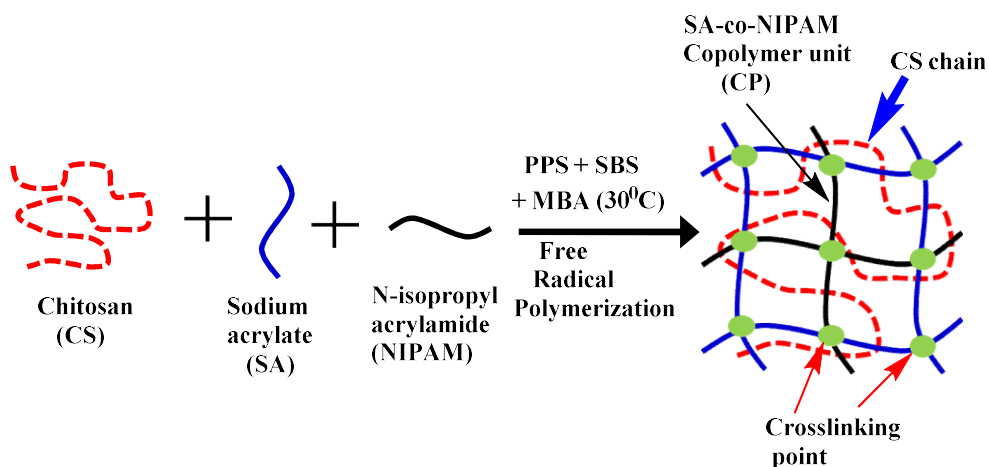


Fig.1: Probable structure of hydrogel

The prepared material was analyzed using FTIR, XRD and UV-spectrophotometer. The parameters influencing in adsorption of dye adsorbates including initial dyes concentration, pH range of solution, temperature and adsorbent polymer dosage were studied.

C. Characterization of Chitosan composite

FTIR spectra were measured on a Perkin Elmer (model no. LS55) (USA) fluorescence FTIR spectrophotometer with the attenuated total reflectance (ATR) technique. A LiTiO₃ detector was used to record this spectrum. The process involved obtaining samples on a diamond plate, adjusting the pressure, and conducting measurements within the wavelength range of 500 to 4000 cm⁻¹. The X-ray diffraction (XRD) pattern was taken on a D/MAX/2500PC X-Ray diffractometer (Rigaku, Japan). Ultraviolet-visible (UV-Vis) absorption was performed on a Cary 5000 UV-Visible spectrophotometer (Agilent, USA).

RESULTS AND DISCUSSION

A. FTIR study

From FTIR spectra (Fig. 2) it is found that the monomer characteristic vinyl absorption at 1680 cm^{-1} is not observed in the CP and CSCP, confirming its polymerization. The basic characteristic absorption peaks of O–H, N–H and C=O are observed in these spectra. This absorption data reveals that —NH_2 , —NHCO and —OH of CS took part in the polymerization reaction with CP. As CS is incorporated in the CP gel network, the characteristic absorption bands are also observed with shifting or disappearance of some of the peaks of CP or CS in CSCP hydrogel. Similar trend was reported by [10].

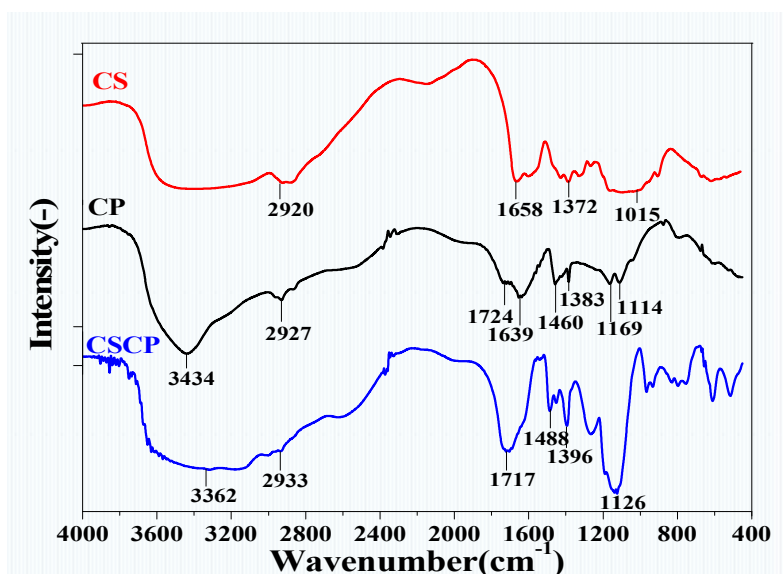


Fig. 2: Variation of intensity against wavenumber

B. XRD study

The nature of the polymers in terms of order/ disorder arrangement has been confirmed via XRD analysis. From Fig. 3 CS shows two strong crystal diffraction peaks at $2\theta = 10.6^\circ$ and $2\theta = 20.1^\circ$ and the crystallinity of CS arises from the intermolecular and intra-molecular hydrogen bonding. CP shows broad peaks at $2\theta = 22.62^\circ$ and very weak peak at $2\theta = 36.18^\circ$ due to formation of H-bonding between carboxylic and amide groups of SA and NIPAM unit respectively. In CSCP, 10.6° peak is disappeared and 20.1° is shifted to 16.4° . This result indicates that CS takes part in

the copolymerization reaction of CP and thus its crystallinity changes due to disordered structure. This type of observation is similar as found by Can et al [11].

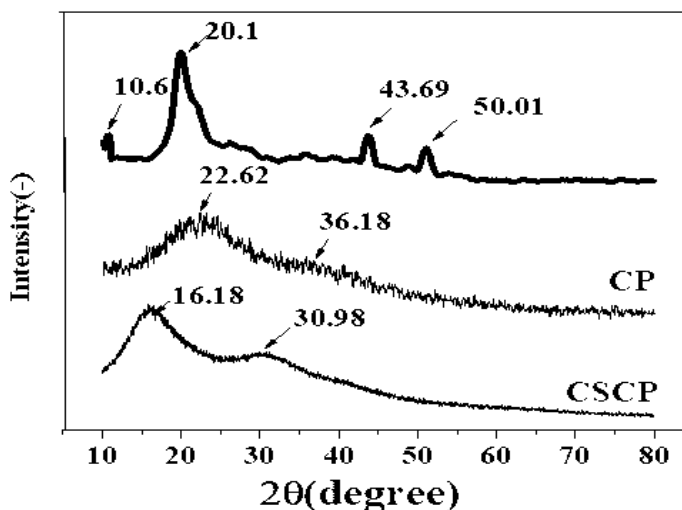


Fig.3: Variation of intensity against angle of incident rays

C. Adsorption studies

The concentrations of dye solutions before and after addition of hydrogel were determined by spectrophotometric measurement from a pre-calibrated curve of absorbance versus concentrations using UV-visible Spectrophotometer. The concentration ranges of MB were 2.5–40 mg/L and approximately, 0.025 g of hydrogel was taken for performing absorption study. The equilibrium adsorption or adsorption capacity (q_e) and dye removal % (R) was obtained by the following equations

$$q_e = \frac{(C_i - C_e) \times V}{m}$$

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

D. Effect of pH

Several observations were made for the significant role of pH. Low pH solution results in a decrease in the percentage of MB dye removal because of the electrostatic repulsion between cationic dye and the positive surface charge of the adsorbent. At higher solution pH, electrostatic attraction is found between the negatively charged surface and positively charged dye molecules increases the

adsorption capacity and percentage removal of cationic dyes. In the Fig. 4 the CP/CSCP hydrogels show q_e of 17.65/17.76 mg/g and R% of 88.26/88.81 for MB dye at optimum solution pH of 9 and concentration of 10 ppm.

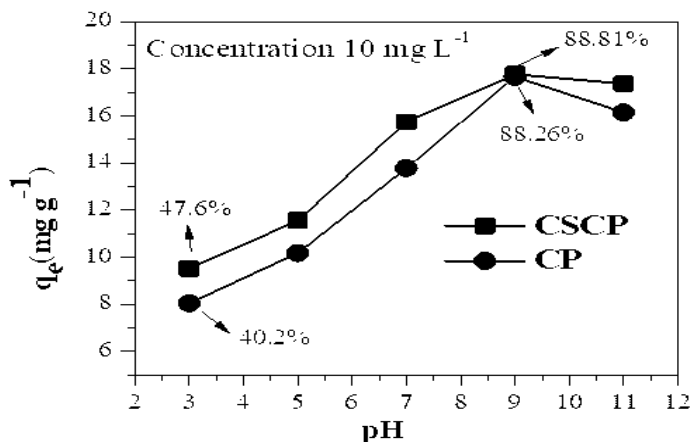


Fig. 4: Adsorption capacity vs $[H^+]$ of dye solution

E. Effect of contact time

Adsorption of dye increases at a very fast rate at the initial stage of the experiments, and finally, it reaches a dynamic equilibrium within 4 h. Fig. 5 shows that at higher contact time, the rate of adsorption decreases, gradually leading to equilibrium due to decrease in total adsorbent surface area and less available binding sites. Adsorption kinetic experiment was performed at λ_{max} of 644.11 nm in UV-Vis spectrophotometer.

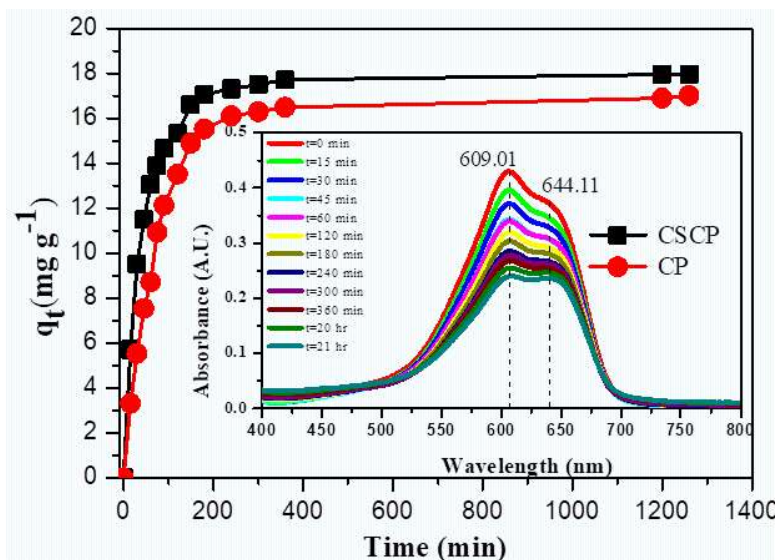


Fig. 5: Effect of contact time of dye on chitosan composite

F. Kinetics and isotherm

The mechanism of dye adsorption was evaluated in terms of adsorption kinetics by measuring adsorption (q_t) at various time intervals (Fig.6) . The dye adsorption data were verified by fitting in Langmuir isotherm. The experimental values give better fittings for 2nd order kinetics, indicating that the rate-determining step of the present adsorption process is governed by chemical sorption. Similarly, the experimental values give better fittings for Langmuir isotherm, indicating that adsorption occurs at homogeneous sites of the hydrogels.

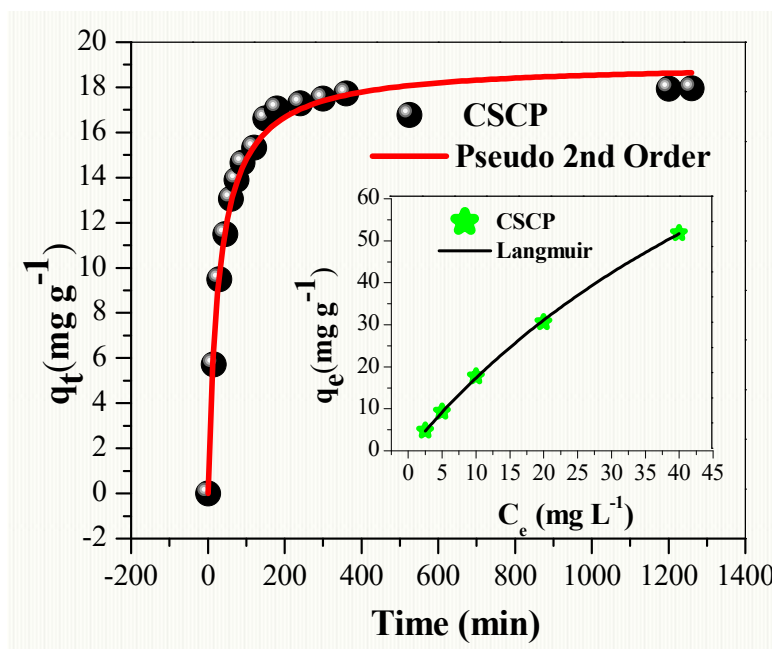


Fig. 6: Adsorption profile at different times

CONCLUSION

In this work, several IPN type hydrogels were synthesized by free radical solution polymerization. The synthesized hydrogels were optimized in terms of ESR and the optimized hydrogels were further characterized by FTIR and XRD analyses. The optimized hydrogels then used for adsorptive removal of toxic cationic MB dye from water. It is one of the most promising materials that can be used as an effective material for the adsorption of organic dyes [12]. Here adsorption is most encouraging techniques. Based on this consideration, the adsorption appears to be simple to design, available, easy to operate, does not produce toxic materials and does not require high cost. The adsorption data were verified by fitting in pseudo

nd
 2nd order kinetics and Langmuir isotherm. The optimized CP/CSCP shows maximum adsorption capacity (q_{\max}) 51.8/50.6 (mg/g) and removal % (R) of 96.72/94.36 for MB, respectively. The composite has well flocculation ability in aqueous solution, and shows excellent adsorption capacity. Altogether, we can conclude that synthesized hydrogel shows excellent adsorption capacity. So, it can be used for removal of other cationic dyes and/or metal ions from wastewater.

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