A CHITOSAN-TiO₂ IMPRINTED POLYMER FOR THE QUANTITATIVE REMOVAL OF CONGO RED DYE FROM TEXTILE WASTEWATERS

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Received April 25, 2018

Removal of Congo red (CR) dye from textile waste effluents is a challenging task. Therefore, a new molecularly imprinted polymer (MIP) based on Chitosan-TiO₂ nanocomposite (CTNC) was synthesized for the quantitative and selective removal of CR as a brand anionic dye from textile wastewaters. The physicochemical features and efficiency of the prepared MIP-nanoparticles were investigated using various spectral techniques including FTIR, XRD, SEM, and N₂-adsorption-desorption isotherm. The mechanism and kinetics of CR removal were systematically investigated. The data fitted well into the Langmuir and the pseudo-second order models, revealing monolayer dye molecules formation. The prepared CTNC-MIPs was successfully applied to the elimination of CR, as a brand anionic dye, from highly polluted textile wastewaters. Moreover, the exceptionally high adsorption capacity, stability, and recyclability of the prepared CTNC-MIPs make it an excellent competitive to previously reported adsorbents.

INTRODUCTION

The fabric dye process is a key step in clothes and footwear production but unfortunately, it is also one of the extremely polluting stages of the textile industry, which annually utilizes 6-9x10⁹ cubic meter of water.¹ Treating these massive effluents contaminated with dyes resulting from textile, biocides, dyes, detergents, paints, and inks industries have become a challenging problem that faces many countries.² Anionic azodyes, including Congo red (CR, CI 22120) are used in the textile, printing, dyeing, paper, rubber, plastic industries, and diagnostic purposes.^{1,2} However, CR dye was banned in some advanced countries because of its toxicity and carcinogenic effects to living

organisms and mammals but it is still in use in many developing countries.^{1,2}

Some nano-adsorbents have been used to remove CR from effluents, before its discharge to the environment, e.g., activated carbon,³⁻⁷ metal oxides,⁸⁻¹³ shells,^{14,15} clays,¹⁶⁻¹⁸ chitosan,¹⁹⁻²² algae,²³ fungi,^{24,25} and plant materials.²⁶⁻³⁴ Recently, molecular imprinted polymers (MIPs) have been applied to treat wastes and reduce pollutants, as a cheap, safe, and highly effective technique compared to other classical removal methods.³⁵ The MIPs had first appeared in 1930 and its structure was explained by Polyakov in 1931.³⁶ This new class of polymers is prepared by copolymerization of a functional monomer, a cross-linker, a proper initiator and a propogenic

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solvent along with the template. After polymerization, the imprinted template is extracted to leave complementary cavities that are almost specific to the template molecules, and thus explaining the extraordinary selectivity of MIPs.³⁷ Therefore, MIPs have been applied to numerous fields, *e.g.*, sensors, chemical separations, catalysis, and solid phase extraction. Recently, different supporting materials have been used during MIPs preparations; *e.g.*, silica, magnetic nanoparticles, steel fiber and TiO₂ that is adopted in the current work due to its thermal stability, low toxicity, and wide industrial applications.³⁷

Chitosan is a low-cost, safe, water-soluble polysaccharide and powerful adsorbent that can be prepared by treating the chitin shells of shrimp or other crustaceans with alkalis. Chitosan was reported to remove some dyes, metal ions and other hazardous pollutants from wastewaters.^{37,38}

Herein, we report for the first time the preparation of Chitosan-TiO₂-Congo red nanocomposite based molecularly imprinted polymer (CTNC-MIPs) for removing Congo Red (CR) dye from wastewaters. The prepared nanocomposite particles were characterized by FTIR, XRD, SEM, and N₂ adsorption-desorption isotherms. Further, the efficacy of our prepared MIPs for the quantitative removal of CR, as a typical anionic dye, from wastewaters was monitored by UV-Visible spectrophotometry at 498 nm. Various parameters including the effects of MIP dose, dye concentration, temperature, contact time and pH on CR uptake were carefully examined and optimized. Four mechanistic models; Langmuir, Freundlich, Dubinin–Radushkevich and Temkin³⁹ have been used to examine the sorption process of CR dye on CTNC-MIPs. In addition, the kinetics of CR adsorption on CTNC-MIPs was explored using the pseudo-first-order, the pseudo-second-order, Elovich, and weber-Morris models.³⁹ Further, the prepared CTNC-MIPs was successfully utilized in the removal of CR along with other dye wastes, from highly polluted textile wastewaters.

MATERIALS AND METHODS

Materials

Chitosan (Practical grade 190000–375000 Da, from shrimp, %de-acetylation $\geq 75\%$; viscosity ≥ 200 cP), titanium isopropoxide, epichlorohydrin, and ammonium persulfate were obtained from

Sigma (St. Louis, MO, USA). Congo red, Isopropanol and glacial acetic acid were purchased from Merck (Merck, Darmstadt, Germany). Bidistilled water was used throughout.

Instruments

Absorption spectra were made on a Shimadzu-1601 UV-Visible spectrophotometer (Kyoto, Japan), that is controlled by UV-probe 2.5 software, in 10 mm cells. The pH measurements were performed using a calibrated Adwa pH/mV pH meter model 1000 (Szeged, Hungary). Temperature was controlled using a thermostating bath SCI LOGEX Ms 7-H550-pro (Rocky Hill, USA). Centrifugation was performed using an NF815 centrifuge (Ankara, Turkey). Fourier-transform (FT-IR) spectra were recorded on ATT Genesis II Mattson series FTIR spectrometer using the KBr disk technique. The nanostructure of the synthesized CTNC-MIPs was explored by scanning electron microscopy (JEOL, JEM-1200X II). The X-ray diffractions of the prepared CTNC-MIPs were obtained using XRD-6100 X-ray diffractometer in the 2θ range of 10–90° using continuous scanning mode. The N₂ adsorption/desorption isotherms were recorded using a typical volumetric apparatus with a vacuum system and prior outgassing to 10⁻⁵ Torr residual pressure.

Preparation of chitosan-TiO₂ imprinted and non-imprinted polymer

A 10⁻³ mol.L⁻¹ CR dye stock solution was prepared by dissolving the desired dye amount in water. Working CR solutions were prepared daily by suitable dilution of the parent stock. A 0.1 mol.L⁻¹ sodium hydroxide or acetic acid solutions were used to adjusted pH. A 1% chitosan solution was prepared in a 100 mL of 5% acetic acid. The chitosan solution was added to a 10 mL titanium isopropoxide that is dissolved in 50 mL isopropanol with stirring for 1h. A 25 mL of 5 $\times$ 10⁻⁵ mol.L⁻¹ aqueous CR dye template was added drop-wise with stirring. Then, 5 mL Epichlorohydrin cross-linker was added drop-wise and the pH of the reacting mixture was adjusted to 5.0 $\pm$ 1.0 where a white coloration of Ti(OH)₄ was detected. After that, a 0.30 g of initiator (ammonium persulfate) was added and the reacting mixture was stirred at 60°C for 3h. Then, the mixture was set aside overnight for complete polymerization, at room temperature. The obtained MIP was filtered using a Whatman no 1 filter paper, air dried for 24h and then dried in an

oven for another 24 hours at 50 °C. Thereafter, it was characterized by FTIR, SEM, XRD, and N₂ adsorption/desorption techniques. Then, the MIP was washed with 50% ethanol and distilled water in a Soxhlet extractor to remove the CR template from the MIP to give the leached molecularly imprinted polymer (LMIP). The non-imprinted polymer (NIP) was similarly prepared but without CR template. The schematic representation of the synthesis is shown in Scheme 1.

Adsorption experiments

Batch adsorption experiments were performed by adding fixed doses of CTNC-LMIP to a series of 250 mL beakers, containing 1-10×10⁻⁵ mol·L⁻¹ CR dye solutions. The homogeneous mixtures were stirred at 700 rpm at ambient temperature (30°C) for 1 h to achieve equilibrium. Every 5 minutes, aliquot samples were withdrawn from the stirred solution, centrifuged and the absorbance values were recorded spectrophotometrically, Figure 1.

The amount adsorbed of CR dye onto CTNC-LMIP nanoparticles cavities was calculated using equation (1):

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where q_e is the adsorption capacity of CR per unit mass of CTNC-LMIP adsorbent (mg·g⁻¹), V is the volume of CR solution (L), C_0 and C_e are initial and equilibrium concentrations of CR (mg·L⁻¹), and m is the adsorbent mass in (g).

RESULTS AND DISCUSSION

FT-IR spectra

FTIR analysis was conducted to explore the structure of the synthesized MIPs and to estimate the possible interactions between MIPs and the CR template dye. Figure 2 shows the FTIR spectra of Chitosan, CR dye, TiO₂, MIP, LMIP and NIP.

Scheme 1 – Molecular imprinted polymer preparations.

Fig. 1 – Absorption spectra of Congo red solutions after adsorption on CTNC-LMIP nanoparticles at different contact times.

Fig. 2 – FT-IR of (a) Chitosan, (b) TiO_2 , (c) Congo red, (d) Non imprinted polymer, (e) Molecularly imprinted polymer and (f) Leached molecularly imprinted polymer.

Fig. 3 – SEM of CTNC-MIP (a), CTNC-LMIP (b).

The spectra of the prepared MIPs exhibited interesting bands characteristic of both TiO_2 and Chitosan. Absorption bands at 1630 and 3400 cm^{-1} were attributed to $-\text{NH}_2$ and $-\text{OH}$ groups stretching vibrations for primary amine and hydroxyl groups of Chitosan, Figure 2e. Bands at 1420, 1530, and 3400 cm^{-1} were attributed to bending deformations of hydroxyl groups. However, the bands at 1261, 1383, and 1635 cm^{-1} were attributed to the amine/amide functional groups. The fingerprint broad band at 1250–

850 cm^{-1} was assigned to C-O stretching vibrations overlapped with C-N stretching. The characteristic band at 612 cm^{-1} proves the existence of TiO_2 backbone. The presence of the characteristic bands of amine, amide, and hydroxyl functional groups together with TiO_2 metal oxide verify the formation of a Chitosan- TiO_2 nanocomposite (CTNC) particles. Examination of FTIR spectra of the MIP containing the CR template and the bare CR dye, clearly reflect the strong interactions between the polymer functional groups and CR

template dye in the prepared MIPs. Some of the characteristic peaks were slightly shifted or completely disappeared, while some new peaks were also identified in CTNC-MIP after interaction with CR template dye.

Scanning electron microscopy (SEM)

The SEM-micrograph of the prepared CTNC-MIPs-CR shown in Figure 3a represent a closely packed non-porous structure revealing the clear interactions between CR template molecules and the CTNC polymeric matrix that resulted in the formation of Large sized agglomerated MIP-CTNC particles with large inter-agglomerate voids. However, leaching of the bound template CR molecules led to disintegration of the aggregated nanocomposite particles with pronounced shrinkage of LMIP-CTNC particle size along with a decreased voids' size, Figure 3b.

X-ray diffraction (XRD) analysis

The XRD patterns of Chitosan, MIP and LMIP are shown in Figure 4. Chitosan exhibited characteristic peaks at $2\theta = 9.45$ and 20.4° , while TiO₂ exhibited five primary peaks at $2\theta = 25.23^\circ$, 37.83° , 48.12° , 54.93° , 62.64° attributable to anatase TiO₂. Patterns 1 and 2 of LMIP and MIP exhibited peaks at $2\theta = 9.45$, 25.26° , 37.73° , 47.66° , 54.4° and 62.8° characteristic of chitosan

and titania anatase and thus proving the existence of CTNC-MIP nanocomposite. The very small shift from bare TiO₂ peaks upon imprinting indicates that the creation of CTNC-MIP did not destroy the structural properties of TiO₂.

Textural analysis

The experimental N₂-adsorption/desorption isotherm of the prepared CTNC-LMIP nanoparticles, given in Figure 5a, was classed as type (IV) with H1-hysteresis loop that is characteristic for mesoporous spherical particles that are ordered in a uniform manner with cylindrical pore arrangement and indicating a pretty high pore size uniformity and facile pore connectivity. The specific surface area (A_{BET}) was $184.96 \text{ m}^2 \cdot \text{g}^{-1}$ and was estimated by the BET equation and adopting a $16.2 \text{ \AA}$ as the N₂ cross-sectional area. However, the total pore volume (V_p) measured at saturation pressure and expressed as liquid volume was $0.257 \text{ cc} \cdot \text{g}^{-1}$ and the average pore radius was $27.8 \text{ \AA}$ revealing the mesoporosity of the prepared CTNC-MIP, Figure 5a. The pore size dissemination was created according to BJH analysis as illustrated in Figure 5b, and exhibited a main narrow peak positioned at $27.8 \text{ \AA}$ in addition to a smaller shoulder peak centered at $32 \text{ \AA}$, confirming the mesoporous nature of CTNC-LMIP and revealing the existence of two groups of relatively wide mesopores.

Fig. 4 – XRD of CTNC LMIP (a), CTNC MIP (b), TiO₂ (c), and Chitosan (d).

Fig. 5 – N_2 adsorption/desorption isotherm of CTNC-MIP (a), The Pore size dissemination according to BJH analysis (b).

Fig. 6 – a) Effect of contact time on CR adsorption by CTNC, b) Effect of concentration on CR adsorption by CTNC-LMIP, c) Influence of pH on the adsorption capacity of CR on CTNC LMIP, d) The adsorption heat capacity of CR on CTNC LMIP. ($C_0=50 \text{ mL}$ ($5 \times 10^{-5} \text{ mol.L}^{-1}$), stirring rate 700 rpm and $m=0.03 \text{ g}$ the contact time was 60 min. The pH was 5.0).

Dye Adsorption Analysis

CR dye was selected as a typical anionic dye pollutant to explore the removal efficiency of CTNC-LMIP nanoparticles.

Effect of Contact Time on CR adsorption

A 0.03 g LMIP was added to 50 mL of 5×10^{-5} mol·L⁻¹ CR in a 100 mL beaker and the reacting mixture was stirred for 1 h at 700 rpm. At 5 min intervals, solution aliquots were withdrawn, centrifuged and monitored spectrophotometrically. The results indicated that about 85% of CR dye was adsorbed within 20 min as shown in Figure 6a. The amount of CR dye adsorbed (Q_t) decreased from 74.88 to 40.19 mg·g⁻¹ with increasing the CTNC-LMIP dose from 0.02–0.04 g. This is due to decrease in the number of available adsorption sites as a result of aggregation of adsorbent molecules at higher CTNC-LMIP doses. The amount of CR adsorbed per unit mass of LMIP and the %uptake were calculated from equations (2) and (3):

$$Q_t = \frac{(C_o - C_t)V}{m} \quad (2)$$

$$\% \text{ uptake of CR} = \frac{(C_o - C_t)}{C_o} \times 100 \quad (3)$$

where C_o (mg·L⁻¹) represents the initial concentration of CR, and C_t (mg·L⁻¹) is the concentration of CR at different contact times. V is the volume in liters of CR solution and m is the CTNC-LMIP adsorbent mass in grams.

Effect of CR Concentration on adsorption

The initial CR dye concentration plays a crucial role as a fixed mass of the CTNC-LMIP adsorbent solid can adsorb a fixed amount of the dye. Experiments were performed as described above, to explore the influence of varying initial CR concentration ($5\text{--}10 \times 10^{-5}$ mol·L⁻¹) on adsorption. Results showed that the adsorption capacity increased from 54.61 to 102.33 mg·g⁻¹ upon increasing the CR dye concentration from 5×10^{-5} to 1×10^{-4} mol·L⁻¹ as shown in Figure 6b.

The effect of pH on CR adsorption

The medium pH is a key factor influencing the CR dye uptake by LMIPs nanoparticles, Figure 6c. The maximum adsorption ($q_{\max} = 57.85$ mg·g⁻¹) was

observed at pH=5.0. At pH values < 4.0, the CR dye is involved in protolytic equilibria and its color changed from red to blue. However, at pH > 6.8, no adsorptions occurred, probably due to the formation of a less reactive CR species.

Effect of temperature on Adsorption

The adsorption capacity of CR on CTNC-LMIP was investigated in the temperature range of 20 to 40 °C at initial dye concentration 5×10^{-5} and pH 5 and was found to increase with raising the temperature in the studied range, indicating that high temperature favored the CR adsorption onto CTNC-LMIP, Figure 6d.

Generally, raising the temperature would decrease the solution viscosity and thus increase the rate of diffusion of CR adsorbed molecules into the internal pores of the adsorbent CTNC-LMIP particles. Therefore, varying temperature will change the adsorption capacity of the CR dye. The Gibbs free energy change (ΔG°), the enthalpy change (ΔH°) and entropy change (ΔS°) were calculated from equations (4-6):

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (4)$$

$$\Delta G^\circ = -RT \ln K_c \quad (5)$$

$$\text{where: } K_c = \frac{q_e}{C_e}$$

$$\log(K_c) = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (6)$$

where T is temperature (K), R is gas constant (kJ·mol⁻¹·K⁻¹), K_c is the standard thermodynamic equilibrium constant, q_e is the amount of adsorbed CR dye per unit mass of CTNC-MIP at equilibrium (mg·g⁻¹) and C_e is the aqueous concentration of CR dye at equilibrium. The calculated ΔG° , ΔH° and ΔS° of CR adsorption on CTNC-LMIP were given in Table 1, as derived from the slope and the intercept of van't hoff plot Figure 6d. The negative values of the free energy (ΔG°) indicated that the process is spontaneous and the positive value of ΔH° indicated that the reaction was endothermic.

Adsorption Kinetics

The kinetics of adsorption was systematically investigated and the resulting data were shown in Figure 7. Addition of CTNC-LMIP showed good performance in the first 30 min, after that there is no marked change from 30 to 60 minutes. Various models have been applied to investigate the adsorption kinetics. These are the pseudo-first-

order model Figure 7a, the pseudo-second-order model Figure 7b, the Elovich model and the Weber-Morris model; Table 2. The calculated equilibrium adsorption capacities for pseudo-first-order and pseudo-second-order models were $Q_{e, cal}$ 44.305 and 88.496 mg.g^{-1} with correlation coefficients of =0.939 and =0.998, respectively; where, the calculated pseudo-second-order Q_e was very close to the experimental maximum adsorption capacity (Q_{eq} =81.368 mg.g^{-1}). Therefore, the adsorption of CR dye on CTNC-LMIP was believed to fit well with pseudo-second-order model. The used kinetics equations are shown below:

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \quad (7)$$

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{t}{Q_e} \quad (8)$$

$$q_t = \frac{1}{\beta} \ln \alpha \beta + \frac{1}{\beta} \ln t \quad (9)$$

$$q_t = K_{id} t^{1/2} \quad (10)$$

where Q_e and Q_t refer to the amounts of CR (mg.g^{-1}) at equilibrium and at any time (min), respectively. K_1 is the equilibrium rate constant of pseudo-first-order sorption (min^{-1}); and K_2 is the rate constant of pseudo-second-order adsorption derived from the t/Q_t vs t plot as shown in Table 2. The initial adsorption rate (α , $\text{mg.g}^{-1}.\text{min}^{-1}$) and the desorption constant (β , g.mg^{-1}) were calculated from the intercept and slope of the q_t - $\ln t$ plot. Moreover, q_t is the amount of CR dye adsorbed per unit mass of adsorbent (mg.g^{-1}) at time t and K_{id} is the intra-particle diffusion rate constant ($\text{mg/g.min}^{-1/2}$).

From Weber and Morris model, it was noticed that the intra-particle diffusion of CR dye presumably proceeded in two stages (k_{1d} , k_{2d}) as given in Table 2. In the first stage, CR molecules are adsorbed onto the available empty sites of the external surface of the CTNC-LMIP. However, in the second stage, the CR molecules penetrated into

the porous structure of the CTNC-LMIP and finally are adsorbed on the active internal surfaces of CTNC-LMIP cavities.

Adsorption isotherm models

In these experiments, 0.03 g of CTNC-LMIP was added to 50 mL of different initial dye concentration solutions. Results revealed that the CR dye uptake depended largely on the initial CR concentration. The equilibrium adsorption capacity increased with the initial CR dye concentration and reached a plateau that was considered as the maximum adsorption capacity (q_{max}). The equilibrium data for CR dye were analyzed by fitting into the Langmuir Figure 8a, Freundlich Figure 8b, Temkin Figure 8c, and Dubinin Figure 8d, models to find out the most suitable model for describing the adsorption mechanism. The obtained Data showed that the adsorption of CR dye fitted well into the Langmuir isotherm model ($R^2 = 0.9623$) compared to Freundlich isotherm model ($R^2 = 0.9439$). The Langmuir isotherm gave an exceptional dye uptake of Q_m =138.89 mg.g^{-1} , where the CR dye uptake took place on specific homogenous sites by monolayer adsorption without any lateral interaction between CR dye molecules and solid surface. The expression of Langmuir equation is:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{K_L Q_m} \quad (11)$$

where Q_m (mg.g^{-1}) is the maximum CR adsorption capacity corresponding to a complete monolayer coverage. The K_L is the Langmuir constant (L.mg^{-1}). However, the energy of adsorption derived from Temkin plot was 32 J.mol^{-1} indicating that the physisorption process was endothermic with a strong interaction between CTNC-LMIP and CR. The value of free energy obtained from The Dubinin–Radushkevich isotherm model was (1.118 kJ.mol^{-1}) showing a strong physisorption interaction between CR dye and CTNC-LMIP.

Table 1

Thermodynamic parameters of CR adsorption onto CTNC MIP

Temp (°C)	ΔG (kJ.mol^{-1})	ΔH^0 (kJ.mol^{-1})	ΔS^0 ($\text{J.mol}^{-1}.\text{K}^{-1}$)	R^2
20	-3.179	67.79	242.23	0.9513
25	-4.738			
30	-4.932			
35	-7.077			
40	-8.079			

Table 2

Kinetic parameters of pseudo-first-order, pseudo-second-order, Elovich and Weber-Morris models for CR adsorption on CTNC MIP

kinetic models		First-order-kinetic model			second-order-kinetic model			Elovich model			Weber-Morris model			
Wt. of														
MIP	q _e , exp	q _e , cal	K ₁		q _e , cal	K ₂		α (mg.(g.min ⁻¹))	β		K ₁ d		K ₂ d	
(g)	(mg.g ⁻¹)		(min ⁻¹)	R ²	(mg.g ⁻¹)	(g.mg ⁻¹ .min ⁻¹)	R ²		(g.mg ⁻¹)	R ²	(mg.g ⁻¹ .min ^{-1/2})	R ²	(mg.g ⁻¹ .min ^{-1/2})	R ²
0.02	81.368	44.305	0.0526	0.939	88.496	0.00179	0.998	45.3758	0.0666	0.968	11.042	0.978	2.7534	0.979
0.03	54.612	24.117	0.0995	0.993	56.818	0.00786	0.999	37.0539	0.0336	0.923	4.6803	0.9118	0.5117	0.912
0.04	41.783	10.643	0.0784	0.915	42.735	0.01525	0.998	31.9867	0.0354	0.855	2.2778	0.729	0.6713	0.811

Fig. 7 – a) The pseudo-First-order model, b) The pseudo-second-order model.
(The initial CR concentrations were 5×10^{-5} mol.L⁻¹; pH = 5.0; at 30 °C).

Fig. 8 – The Langmuir isotherm model (a), Freundlich isotherm model (b), Temkin isotherm model, and The Dubinin–Radushkevich isotherm model (d), ($C_0=50$ mL (5×10^{-5} mol.L⁻¹), stirring rate 700 rpm and $m=0.03$ g the contact time was 60 min. The pH was 5.0).

Fig. 9 – a) The adsorption of CR dye on CTNC-LMIP and Chitosan ($C_0=50$ mL (5×10^{-5} mol.L⁻¹), stirring rate 700 rpm and $W=0.03$ g the contact time was 60 min. The pH was 5.0; b) The regeneration cycles of CTNC LMIP; c) Application for CTNC LMIP to the removal of CR, AR and MB mixture from highly polluted textile wastewater ($W = 0.05$ g).

Comparison between the efficiency of CTNC-LMIP and pure Chitosan for removing CR dye from aqueous solutions

Figure 9a showed that the CTNC-LMIP had considerable potential for removing CR, as a typical anionic dye. The % uptake of CR on pure chitosan was 38 and 49 after 10 and 30 min, respectively. However, our prepared CTNC-LMIP exhibited a marginally improved %uptake of 80 and 93% after 10 and 30 min respectively, revealing the high efficiency of our prepared CTNC-LMIP in CR dye removal.

CTNC-LMIP regeneration

The regeneration of the LMIP nanoparticles is one of the essential parameter that increases its economic usage from industrial point of view. The

used LMIP nanoparticles is washed with 50% ethanol solution, then, the adsorption–desorption processes was repeated. The %uptake of dye was 95%, 80% and 60% after the 2nd, 3rd and 4th cycles, respectively; showing the high possibility of adsorption Capacity and reuse, as represented in **Figure 9b**.

Application for real sample analysis

The prepared CTNC-LMIP was applied to highly polluted textile wastewaters. Samples containing CR as a sole dye exhibited excellent dye removal of 99% within 30 min of contact with 0.05 g CTNC-LMIP. However, other aliquot samples that have been spiked with 50 mg L⁻¹ Alizarine (AR), or Methylene blue (MB) exhibited excellent dye removal of $\geq 95\%$ within 50 and 90 min of contact, respectively. On the other hand, an

aliquot of the waste sample containing CR when spiked with 50 mg L⁻¹ of each of AR and MB exhibited quantitative dye removal of > 97% after a contact time of 120 min, as shown in Figure 9c, showing the excellent CR dye removal even in the presence of other dyes in the waste effluent. This selectivity arises from the fact that Congo red molecules penetrated selectively into the specifically tailored template cavities of the CTNC-LMIP; while the AR and MB dye molecules can be adsorbed only onto the external surfaces of the CTNC nanoparticles as their molecular sizes do not allow its fitting into the specifically tailored template cavities of the CTNC-LMIP. The delay time required for the complete removal of CR along with other dyes of the mixture may be ascribed to the competition of various molecules towards the adsorbent active surface sites and the complex interaction between oppositely charged dyes' molecules found in the complex waste matrix. It is worthy to emphasize

the advantage of the current method as not requiring any photo-degradation to quantitatively remove other interfering dyes from the very complex dye matrix.⁴⁰

Comparison with other studies

The maximum CR adsorption capacity ($q_{\max}$) of our CTNC-LMIP NP's as determined from the Langmuir isotherm along with literature values of $q_{\max}$ (expressed as mg CR/g dry weight adsorbent) of various adsorbents for CR removal are listed in Table 3. All of the listed adsorbents previously used for CR adsorption have considerably lower $q_{\max}$ values compared to the CTNC-LMIP NP's adopted in this work. Moreover, the current method does not require any photo-assisted treatment of waste effluent to quantitatively remove CR along with the associated dyes encountered in complex textile wastes.⁴⁰

Table 3

Some recently reported adsorbent systems for CR removal

Adsorbents	Adsorption (mg.g ⁻¹)	capacity	Reference
Bagasses fly ash	11.89		3
AgNPs-coated AC	64.8		4
AuNPs-coated AC	71.05		4
Magnetic (Fe ₃ O ₄) cellulose activated carbon	66.09		5
Activated carbon from coir pith	6.72		6
activated carbon Activated carbons from date pit	105		7
MnFe ₂ O ₄	92.4		8
Nanospheres Fe ₃ O ₄	68.5		8
NiFe ₂ O ₃	97.1		8
Fe _{2.95} La _{0.05} O ₄	107.64		9
Hollow Zn-Fe ₂ O ₄ nanospheres	16.1		10
Co _{0.3} Ni _{0.7} Fe ₂ O ₄	131.75		11
Ni(OH) ₂ nanosheets Hierarchical	82.9		12
ZrO ₂ hollow spheres	59.5		13
ZrO ₂ reagent	4.8		13
ZrO ₂ solid spheres	21.4		13
Eggshells	69.45		14
Cashew nut shell	5.184		15
Vaterite calcium carbonate	32.6		16
Kaolin (Clay materials)	5.44		17
NaBentonite (Clay materials)	35.84		17
Zeolite (Clay materials)	3.77		17
Ca-bentonite	107.41		18
chitosan coated magnetic iron oxide in batch mode	42.62		19
Chitosan/montmorillonite nanocomposite	54.52		20
N,O-CMC-MMT, Chitosan	74.24		21
Chitosan hydrobeads	93.71		22

Table 3 (continued)

Marine alga	71.46	23
Aspergillus niger	14.72	24
Fungal biomass	51.81	25
Jujuba seed	55.56	26
Hydrogen peroxide treated tendu waste	134.4	27
Rice bran	14.63	28
Wheat bran	22.73	28
Palm kernel seed coat	66.23	29
Pine cone Activated	40.19	30
Sugarcane bagasse	38.2	31
Neem leaf powder	72.4	32
Banana peel	18.2	33
Orange peel	14	33
Modified wheat straw	71.2	34
CTNC-MIP	138	This work

CONCLUSION

Novel CTNC-LMIP nanoparticles were synthesized, characterized and conveniently applied to the quantitative and selective removal of CR, as a brand anionic dye, from highly polluted textile wastewaters. The adsorption models of Freundlich, Langmuir, Dubinin-Radushkevich and Temkin were applied to explore the nature and mechanism of CR dye adsorption. The pseudo-first order, the pseudo second order, and the Elovich, and Weber-Morris models were used to investigate the kinetics of the CR dye uptake. Experimental data fitted well into the Langmuir and pseudo-second order models. The Gibbs free energy was negative reflecting the spontaneous nature of the uptake process.

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