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Recyclable Crosslinked O-Carboxymethyl Chitosan for Removal of Cationic Dye from Aqueous Solutions

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Abstract

Carboxymethyl chitosan have been investigated for many biomedical applications as well as for the removal of metal ion and cationic dye from aqueous solution. But, carboxymethyl chitosan is soluble in water and therefore, it is difficult to reuse. The aim of the work was to prepare cross-linked O-carboxymethyl chitosan (OCMCTS) with different degree of substitution for the removal of Crystal Violet (CV) cationic dye from aqueous solution. The influence of the parameters such as initial pH of the dye solution, initial dye concentration, adsorption temperature, degree of substitution of OCMCTS and adsorption time on the adsorption capacity was studied using batch method. The results showed that the adsorption capacity of modified CTS increased from 28.49 mg/g to 239.54 mg/g. The kinetic study of OCMCTS showed that it follows the pseudo-second-order kinetic rather than pseudo-first-order kinetic. The adsorption equilibrium showed that the experimental data could be best fitted to the Langmuir equation. The desorbed OCMCTS can be reused to absorb the cationic dyes. Therefore, cross-linked OCMCTS may be favorable adsorbent and could be employed as low-cost alternatives for the removal of cationic dyes in wastewater treatment.

Keywords: O-Carboxymethyl chitosan; Cross-linked; Crystal violet; Isotherms; Desorption

Introduction

Water is a basic necessity for the entire living organism in this world. When, water gets contaminated due to presence of various pollutants in it, it becomes dangerous for the living beings and causes several diseases and harmful effects by consumption in different ways. Therefore, availability of pure water for drinking is fast becoming a scarce resource due to wide spread pollution. Among the different pollutants of aquatic ecosystems, dyes are the largest and most important industrial chemicals for which world production in 1978 was estimated at 640,000 tons [1]. Substantial volume of water is consumed daily by many industries such as textile, rubber, cosmetics, paper, plastics as well as dyestuffs and they also use chemicals during manufacturing and dyes to color their products. As a result, they generate a considerable amount of polluted wastewater [2-5]. Due to their possible toxicity, carcinogenicity and resistant to environmental conditions like light, effects of pH and microbial attack [6], it is desirable to remove coloring material from wastewater. Colored dyes can be removed from wastewater by several methods including coagulation and flocculation [7], membrane separation [8], oxidation [9], electro-coagulation [10], and adsorption on activated carbon and clays [11]. Adsorption process is the most widely used technique for decontamination of dye-containing effluents. Currently, activated carbon is the most widely used commercial adsorbent due to its excellent adsorption capacity [12]. But, high cost and regeneration are the main drawbacks for the use of activated carbon as adsorbent [13]. To overcome this problem, most researchers have focused on the development of low cost and effective new adsorbents [14]. In recent years, many works on low-cost adsorbents have been studied for dye removal such as cotton, fly ash, guava leaf powder, sugarcane bagasse pith, rice husk, coconut coir and chitosan [15-21].

Recently, most researchers have concentrated towards natural polymeric materials, because they are renewable, biodegradable, non-toxic and an environment friendly material [22]. Among the natural polymeric materials, chitosan is the most attractive polymer due to its low cost and ready availability. Chitosan (CTS) is a linear copolymer composed of (1–4)-linked D-glucosamine and N-acetyl-D-glucosamine and it is obtained by alkaline hydrolysis of chitin (second abundant polymer in nature after cellulose) [23]. Chitin is obtained from crustaceans (crab, krill, crayfish) primarily because a large amount of the crustacean's exoskeleton is available as a by-product of food processing. CTS is widely used for the removal of heavy, transition metals and dyes as a well-known sorbent [24-26]. Because of its cationic nature, CTS adsorbs the anionic dyes and in very small amount of the cationic dyes. Recently, researchers showed interest in chemical modification of CTS to enhance their properties and consequently their potential applications [27,28]. Carboxymethylation of chitosan is very attractive method among the various chemical modifications, because it introduces active carboxyl (–COOH) groups into the molecule. This leads to an increase in the adsorption capacity of chitosan for heavy, transition metals and dyes [29,30]. But, carboxymethyl chitosan cannot regenerate after adsorption because it is soluble in water, which is the main drawback of carboxymethyl chitosan to use an effective adsorbent for dye waste water treatment. To overcome this problem of carboxymethyl chitosan, here we prepared cross-linked O-carboxymethyl chitosan for cationic dye, crystal violet (CV) as a model cationic dye separation from aqueous solution. No one reported the cationic dye adsorption by cross-linked O-carboxymethyl chitosan (OCMCTS) till date. Therefore, the aim of this study was to investigate the adsorption of CV onto cross-linked OCMCTS in detail. The effects of initial pH of the dye solution, dye concentration, adsorption temperature and degree of substitution of OCMCTS were investigated. The adsorption kinetics and isotherms for CV dye onto OCMCTS and the desorption study were also carried out.

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Experimental

Materials

Chitosan was obtained from Acros Organics (USA). The degree of deacetylation and weight average molecular weight (determined by Gel Permeation Chromatography, Waters, USA) are 86% and 222 kDa, respectively. Monochloroacetic acid was purchased from Loba Chemie (India) and glutaraldehyde (GA) was obtained from Merck, India. Other reagents used were all analytical grade and used without further purification.

Crystal violet stock solution

Crystal violet, also known as hexamethyl pararosaniline chloride, λ_{max} = 590 nm is a basic dye and it was purchased from RFCL Limited, India. The molecular formula and molecular mass of CV are $C_{25}H_{30}ClN_3$ and 407.98, respectively. The chemical structure of CV is shown in Figure 1. Crystal violet stock solution of 2000 mg/L was prepared by dissolving 2 g of the dye into 1000 ml double distilled water. The pH of the dye solution was adjusted by dilute HCl or NaOH. The stock solution was used throughout the whole experiment by fresh dilution.

Preparation of crosslinked O-Carboxymethyl chitosan

O-carboxymethyl chitosan was prepared according to the previous report [31] with slight modification. Briefly, 2 g of CTS was swelled in 40 ml isopropanol and water mixture (8:2 v/v ratio) containing 6 g sodium hydroxide at a temperature of 50°C for 1 hr. Then, different amounts of monochloroacetic acid dissolved in isopropanol was added drop wise into the reaction mixture over the period of 30 min to prepare carboxymethyl chitosan with different degree of substitution (DS). The reaction was continued with constant stirring for another 4 hr at the same temperature. Finally, the reaction was stopped by adding 70% ethyl alcohol. Then, the product was filtered and washed with 80% ethyl alcohol to remove salt and water. The OCMCTS was dried under vacuum overnight.

To prepare cross-linked OCMCTS, carboxymethyl chitosan was dissolved in distilled water and then, the OCMCTS solution was added drop wise into 1% (v/v) glutaraldehyde solution with constant stirring at high speed. The mixture was kept at 50°C for 30 min for complete cross-linking. The cross-linked OCMCTS was collected by centrifugation at 5000 rpm. and washed with water for few times to remove unreacted glutaraldehyde. Finally, the product was vacuum dried for 24 hr at 50°C.

Determination of degree of substitution

The degree of substitution (DS) of OCMCTS was determined by potentiometric titration [32]. 0.2 g OCMCTS was dissolved in 40 mL distilled water and the pH of the solution was adjusted to pH<2 by adding hydrochloric acid. Then, the OCMCTS solution was titrated with 0.1 M aqueous NaOH and the corresponding pH values of the solution was simultaneously recorded by a laboratory pH meter (Make-CD, Model: APX175 E/C, India). The volume of aqueous NaOH was determined by the second order differential method. The degree of substitution (DS) can be calculated as follows:

$$DS = \frac{161 \times A}{m_{CMCTS} - 58 \times A}$$

$$A = V_{NaOH} \times C_{NaOH}$$

Where, V_{NaOH} and C_{NaOH} are the volume and concentration of aqueous NaOH, respectively, m_{CMCTS} is the mass of OCMCTS (g), 161 and 58 are the respective molecular weights of glucosamine (repeating unit of chitosan) and carboxymethyl group.

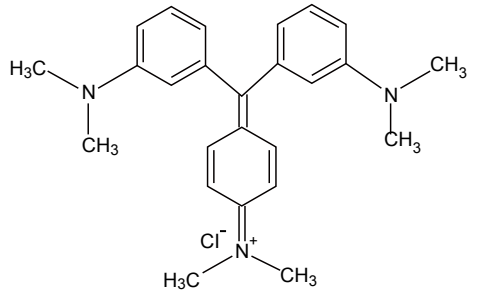

Figure 1: Chemical structure of crystal violet.

Characterization of OCMCTS

OCMCTS was characterized by infrared (FT-IR) spectrophotometer. The infrared spectra were recorded at the frequency range of 4000-500 cm^{-1} with 42 consecutive scans at a 4 cm^{-1} resolution on a Bruker Alpha ATR FT-IR spectrometer.

X-ray diffraction spectrometry of chitosan, OCMCTS and cross-linked OCMCTS in the powder form were performed by a wide angle X-ray scattering diffractometer (Panalytical X-Ray Diffractometer, model- X'pert Pro) with Cu K_α radiation (λ=1.5444) in the range 5–35° (2θ) at 40 kV and 30 mA.

Adsorption Studies of CV by Batch Technique

Adsorption kinetics and isotherms were carried out by batch technique. All the batch experiments were carried out on a water bath and stirring with a magnetic stirrer at a speed of 120 rpm. In each experiment, a fixed mass of OCMCTS (50 mg) was added into 25 ml of an aqueous solution of CV at a known concentration in a 250 ml conical flask. The influence of pH on CV removal was studied by adjusting CV solutions (800 mg/L) to different pH values (2.0, 4.0, 6.0, 8.0 and 10.0) using pH meter at 30 °C for 4 hr. The effects of initial dye concentrations on the adsorption were carried out at 30 °C (pH 8.0) for 4 hr. The effect of temperature on dye adsorption was carried out at different temperatures (30 °C, 40 °C, 50 °C and 60 °C) in 25 mL of dye solution (800 mg/L, pH 8.0) with 0.05 g of OCMCTS for 4 hr. For kinetic study, 800 mg/L dye solutions (25 mL, pH 8.0) were agitated with 50 mg of adsorbent at 30 °C for 4 hr. Batch equilibrium adsorption experiments were carried out by agitating 25 mL of various dye concentrations of CV solution at pH 8.0 with 50 mg of adsorbent at 30 oC until equilibrium was established.

For kinetic study, the samples were withdrawn from the flask at predetermined time intervals. The absorbencies of the samples were measured using a UV-vis spectrophotometer (LAMBDA 25, PerkinElmer) at 590 nm corresponding to a maximum absorbency of CV. The amount of adsorption, q (mg/g) was calculated by the following equation

$$q = \frac{(C_0 - C_t)V}{W}$$

where C_0 and C_t (mg/L) are the concentrations of dye at initial and at time *t*, respectively. *V* is the volume of solution (L) and W is the mass of dry adsorbent used (g).

Desorption study

For the desorption studies, 50 mg of OCMCTS was loaded with CV using 25 mL of 800 mg/L CV solution at pH 8.0. Agitation period was 180 min and agitation rate was fixed at 200 rpm. CV loaded OCMCTS was collected by centrifugation and gently washed with distilled water to remove any unadsorbed CV. The amount of CV adsorbed per gram of OCMCTS was determined by using the supernatant of CV solution. The loaded OCMCTS was agitated with 25 mL 0.2M HCl solution (pH 2.0) at 30 °C for 2 hr and the sample was collected at different time intervals for determination of the eluted dye concentration to calculate the percentage of desorption.

Results and Discussion

FT- IR Spectra of OCMCTS

The synthetic route of OCMCTS and cross-linked OCMCTS is shown in Figure 2. The FT-IR spectrums of chitosan and OCMCTS are shown in Figure 3. Figure 3a shows the basic characteristic peaks of CTS at: 3427.73 cm^{-1} (O-H stretch and N-H stretch, overlap), 2922.49 and 2859.82 cm^{-1} (C-H stretch), 1652.90 cm^{-1} (NH-CO (I) stretch), 1597.66 cm^{-1} (N-H bend), 1154.09 cm^{-1} (bridge-O- stretch) and 1092.74 cm^{-1} (C-O stretch) [33]. The H form of OCMCTS shows the strong peaks at 1711.57 cm^{-1} (-COOH), 1604.96 and 1543.66 cm^{-1} (-NH_3^+), which are the characteristic peaks of O-carboxymethyl chitosan (Figure 3b) [34]. Figure 3c shows the IR spectrum of Na salt of OCMCTS. The characteristic peak at 1601.15 cm^{-1} is due to the asymmetric stretching vibrations of $-COO^-$ Carboxylate ions and N-H bending vibrations and the symmetric stretching vibration of $-COO^-$ with GA, a superimposed band for asymmetric stretching vibration of carboxylate ion and $C=N$ bond is appeared at 1643.81 cm^{-1} and the peak intensity for $-CH_2$ at 2928.64 cm^{-1} increases due to the introduction of GA (Figure 3d) [35]. The FTIR result confirms the cross-linking of OCMCTS by GA.

The X-ray diffraction of chitosan, OCMCTS and cross-linked OCMCTS is shown in Figure 4. Chitosan shows two different peaks at 2θ= 10° and 2θ= 20°. The peak at 10° was assigned to crystal form I and the strong peak at 20° was assigned to form II (Figure 4a). But, for both OCMCTS (Figure 4b) and cross-linked OCMCTS (Figure 4c), the peaks at 10° was disappeared and the reflection at 20° also significantly decreased. The reason may be attributed to the destruction of the intermolecular hydrogen bonds between the amine groups and hydroxyl groups of chitosan due to the graft copolymerization. These results indicate that the graft copolymerization caused destruction of the ordered crystal structure of the chitosan.

Effect of pH on Adsorption

During dye adsorption from aqueous solution, the pH of the aqueous solution is an important factor for dye separation, as it affects the surface charge of the adsorbent material as well as the degree of ionization of the dye molecule [36]. Therefore, the adsorption experiments are carried out at different pH values between 2 and 10 to evaluate the effect of the pH of the dye solution on the adsorption capacity of cross-linked OCMCTS. Figure 5 shows the effect of pH variations on the CV adsorption from the aqueous solutions, for initial CV concentration of 800 mg/L and 50 mg of dry OCMCTS at 30°C for 4 h. From Figure 5, the adsorption capacity of OCMCTS increases

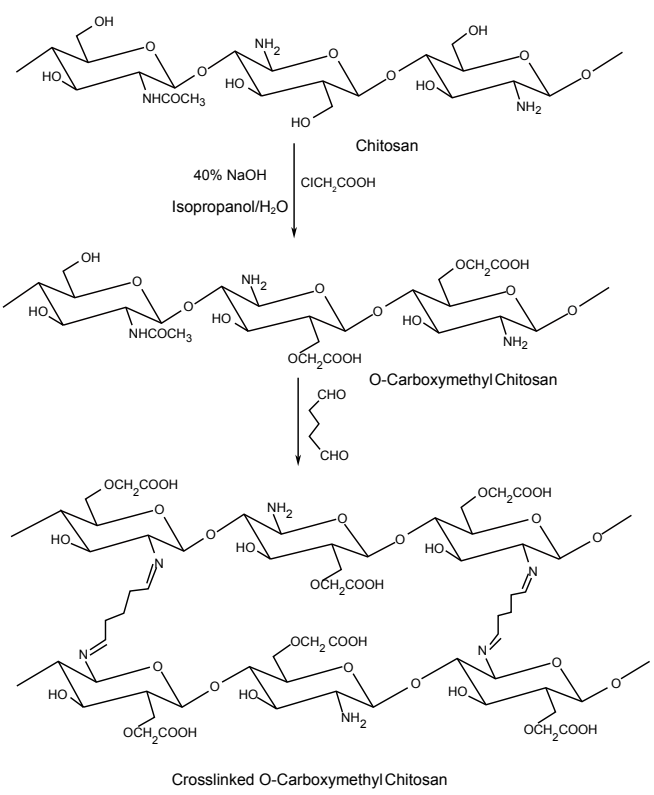

Figure 2: Synthetic route for synthesis of cross-linked o-carboxymethyl chitosan.

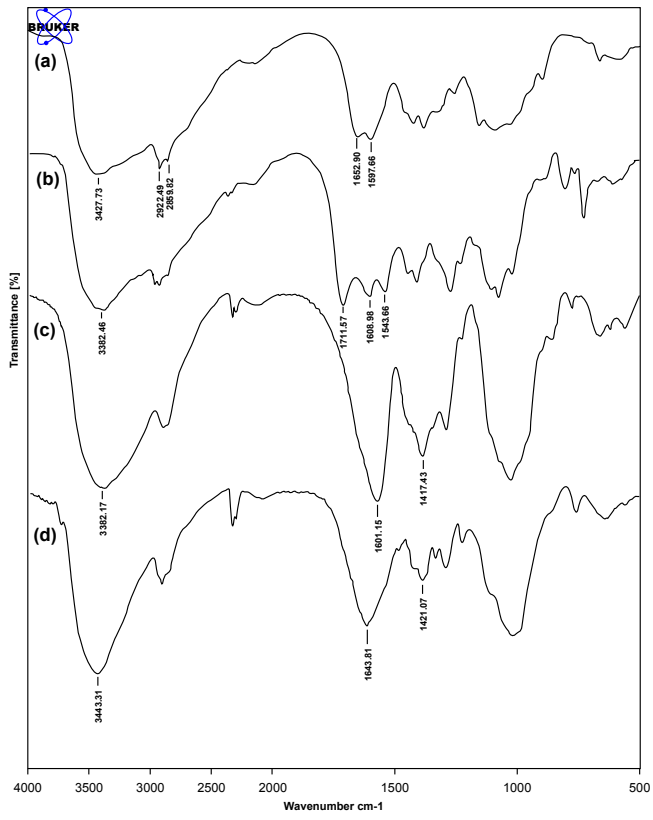

Figure 3: FT-IR spectrum of CTS (a), H form of OCMCTS (b), Na salt of OCMCTS (c) and cross-linked OCMCTS (d).

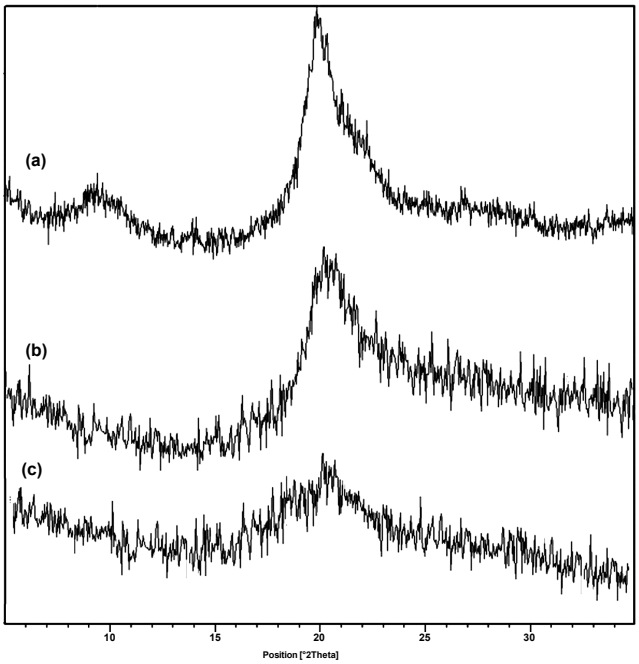

Figure 4: XRD of CTS (a), OCMCTS (b) and cross-linked OCMCTS (c).

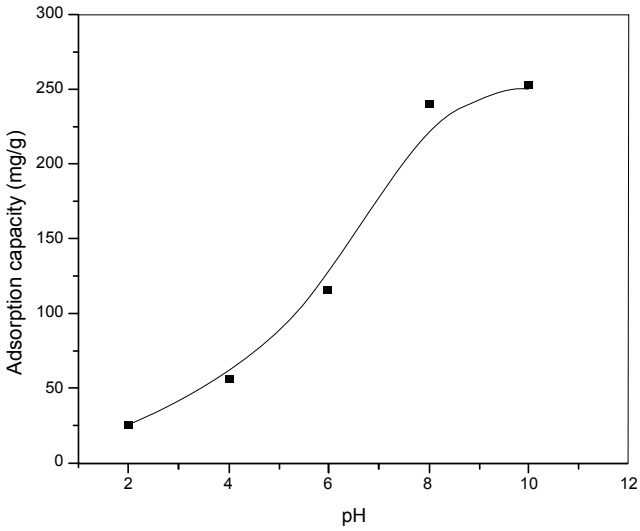

Figure 5: Effect of pH of the dye solution on adsorption capacity of OCMCTS for CV.

smoothly from 25.23 mg/g to 115.62 mg/g, when the value of pH is increased from 2 to 4. In the pH range from 6 to 8, a sharp increase in the adsorption capacity (from 115.62 mg/g to 239.54 mg/g) of OCMCTS is observed. A further increase in dye adsorption between pH 8.0 and 10 is insignificant. Since, the optimum pH for dye adsorption by OCMCTS is found to be 8.0 because; the isoelectric point of OCMCTS with different DS was around 7.3 to 7.9, determined by potentiometric titration (data not shown). This pH was used for further studies. As the pH increases, the charge density of the dye solution decreases, leading to the lowering of the electronic repulsion between the positively charged dye molecule and the surface of the adsorbent [37]. This results in an increase in the sorption of the dye. A little adsorption of the dye onto OCMCTS is observed at lower pH due to chemical interaction between CV dye and OCMCTS.

Effect of temperature on adsorption

The effect of temperature on adsorption capacity of cross-linked OCMCTS is investigated at different temperatures such as, 30, 40, 50 and 60°C at pH 8.0. From Figure 6, it is found that the adsorption capacity of CV on OCMCTS increased from 239.54 mg/g to 467.21 mg/g with an increase of temperature from 30°C to 50°C. This result suggests that the adsorption of CV on OCMCTS is endothermic in nature. The increase in adsorption capacity is due to the swelling of OCMCTS with increasing temperature, facilitating the penetration of dye molecules into the internal structure of OCMCTS [38]. This phenomenon also leads to an increment in the availability of active surface sites, increased porosity and in the total pore volume of the adsorbent. But, the adsorption capacity slightly decreased from 467.21 mg/g to 445.26 mg/g with increasing the temperature from 50°C to 60°C. This may be attributed by the fact that the mobility of the dye molecule increases with increasing the temperature, which may responsible for the decrease of adsorption capacity of cross-linked OCMCTS. The similar result was also obtained in our previous study [39].

Effect of initial dye concentration on CV sorption

The adsorption capacity of cross-linked OCMCTS for CV as a function of initial dye concentration is shown in Figure 7. Initial concentration of dye has an important role on the adsorption capacity. The initial concentrations of dye solution were varied within the range of 50-1000 mg/L. It is observed that the adsorption capacity of OCMCTS sharply increased with an increase in the initial concentration of the dye solution and then reaches a plateau, indicating the saturation of the active sites of the adsorbents i.e. maximum adsorption of the adsorbents. As shown in Figure 5, the adsorption capacity of OCMCTS sharply increased from 10 mg/g to 230 mg/g with increasing dye concentration from 50 mg/L to 600 mg/L and remained almost constant with further increase in the dye concentration. The adsorption capacity of OCMCTS is observed to be much higher than

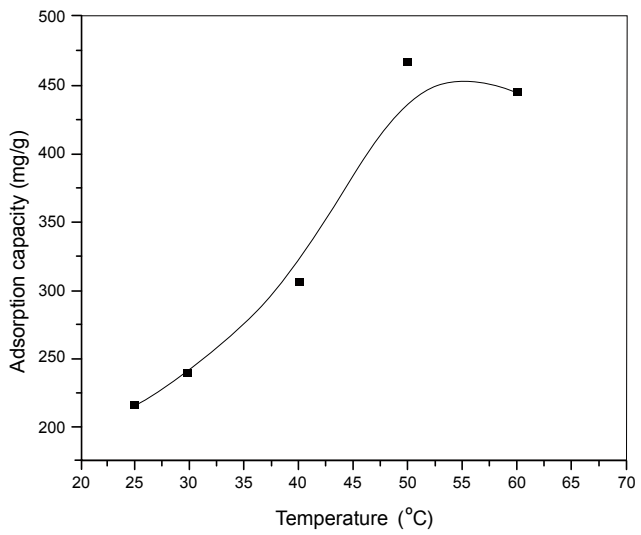

Figure 6: Effect of reaction temperature on adsorption capacity of OCMCTS for CV.

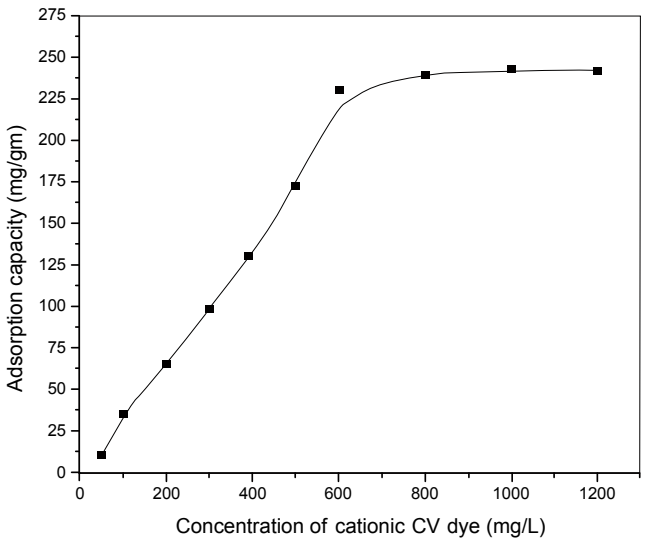

Figure 7: Effect of initial dye concentration on crystal violet adsorption by OCMCTS.

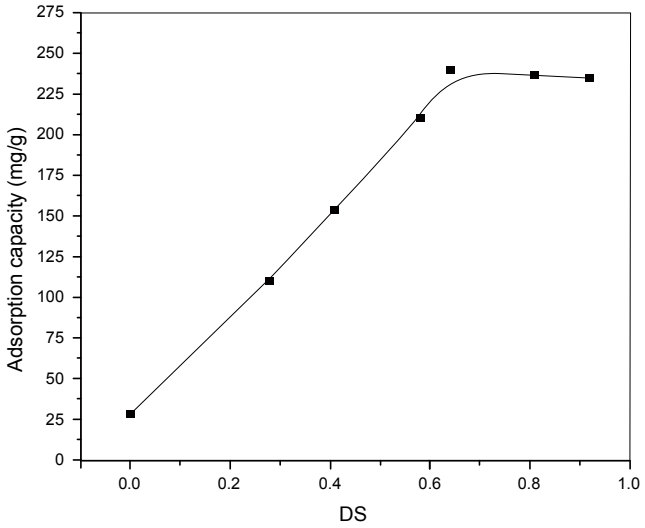

Figure 8: Effect of degree of substitution of OCMCTS on CV adsorption.

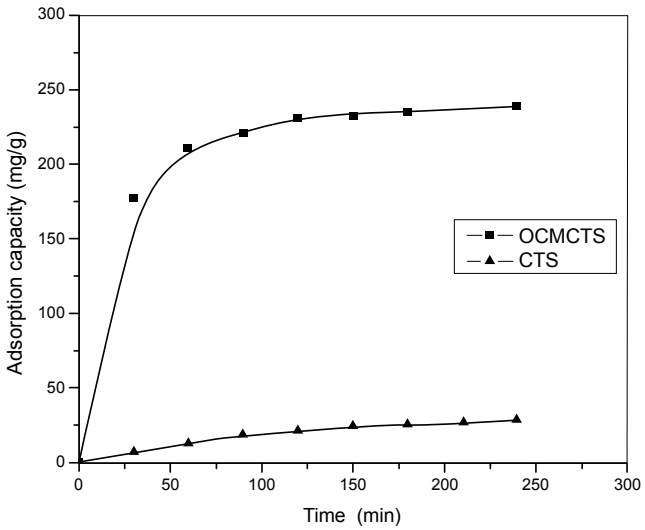

Figure 9: Adsorption of crystal violet by OCMCTS and CTS as a function of time.

that for other materials previously reported as adsorbents for the removal of CV basic dye such as 65 mg/g by activated carbon obtained from rice husk [40] and 60 mg/g by activated carbon from male flowers of coconut tree [41].

Effect of DS On CV adsorption

The adsorption of CV dye onto cross-linked O-carboxymethyl chitosan with different degree of substitution is shown in Figure 8. It is found that the adsorption capacity of OCMCTS sharply increased with increasing the DS of OCMCTS from 0.28 to 0.64 and then it slightly decreased with further increasing the DS from 0.64 to 0.92. This result may be explained by the fact that the number of anionic carboxyl group (-COO-) increased with increasing the degree of substitution of OCMCTS. As a result, the electrostatic interaction between the positively charged dye molecule and the negatively charged OCMCTS molecule also increased which results the enhancement of adsorption capacity of OCMCTS. On the other hand, the number of hydroxyl groups (-OH) in repeating units of chitosan decreases with increasing the DS of OCMCTS, which may be resulted the slight decrease of adsorption capacity of OCMCTS.

Adsorption kinetics

Figure 9 shows the adsorption of CV onto cross-linked OCMCTS as a function of contact time. As observed in Figure 9, the adsorption of CV on OCMCTS occurs in two phases, firstly a rapid phase followed by a slow phase. The first phase involves a rapid adsorption of dye during the first 30 min followed by a slow phase of dye removal spread over a significantly longer period of time (>120 min) until the equilibrium is reached. According to the previous study [42], the rapid phase may last for several minutes to a few hours, while the slow stage continues for several hours to a day. The rapid phase probably occurs due to the availability of more active sites on the adsorbent. The active sites are gradually decreased by the occupancy of adsorbate and results in the slower phase.

To examine the kinetic mechanism of the adsorption process of CV on the cross-linked OCMCTS, the pseudo-first-order and the pseudo-second-order kinetics models are used to test the experimental data.

The pseudo-first-order rate equation of Lagergren model [43] is as follows:

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

The pseudo-second-order rate equation is given as below [44]:

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

where q_e and q_t are the adsorption capacity (mg/g) at equilibrium and at time t (min), respectively. k_1 (min^{-1}) and k_2 (g mg^{-1} min^{-1}) are the adsorption rate constants of pseudo-first-order and pseudo-second-order adsorption rates, respectively. The linear plot of $\log(q_e - q_t)$ versus t for pseudo-first-order model (Figure 10) and that of (t/qt) versus t for pseudo-second-order model (Figure 11) are drawn. The values of q_e and the rate constants k_1 and k_2 can be obtained from the plot of experimental data.

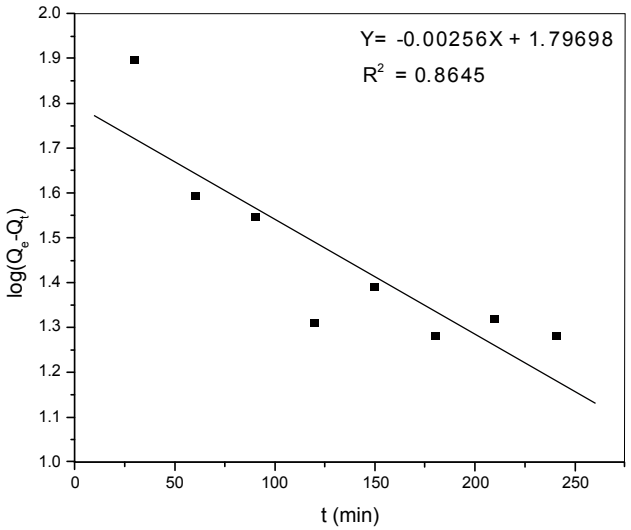

Figure 10: Linearized pseudo-first-order plot for the adsorption of crystal violet by OCMCTS.

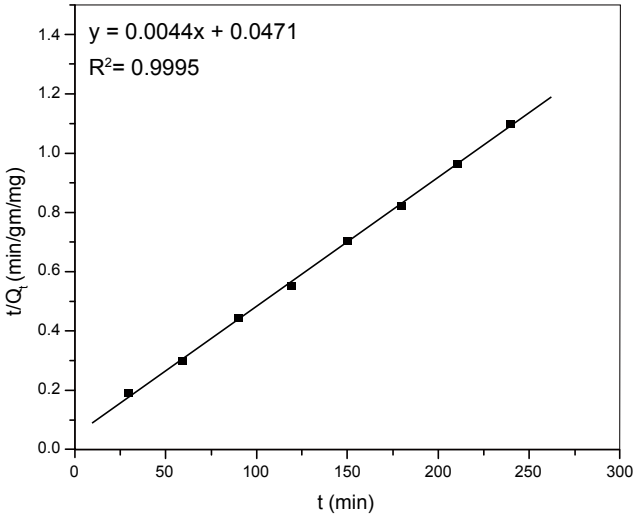

Figure 11: Linearized pseudo-second-order plot for the adsorption of crystal violet by OCMCTS.

The calculated q_e, the rate constants and the correlation coefficients for two kinetic models of OCMCTS are shown in Table 1. The values of correlation coefficient (R^2) of pseudo-first-order and pseudo-second-order models are 0.8644 and 0.9996, respectively. The calculated q_e value of the pseudo-second-order model is 244.5 mg/g, which is close to the experimental data (239.54 mg/g). The higher value of correlation coefficient (0.9996) and the close calculated q_e value indicate that these data are well fit for pseudo-second order model. On the other hand, the theoretical q_e value (62.65 mg/g) obtained from the pseudo-first-order model is significantly different from the experimental data and the correlation coefficient was also found to be lower than that of pseudo-second-order model. These results indicate that the adsorption of CV on cross-linked OCMCTS is not following the pseudo-first-order kinetic. Thus, it is suggested that the adsorption of CV obeys the pseudo-second-order kinetics.

Experimental q (mg g^{-1})	Pseudo-first-order constants			Pseudo-second-order constants		
	qe (mg g^{-1})	k_1 (x10^{-5} min^{-1})	R^2	qe (mg g^{-1})	k_2 (x10^{-4}g mg^{-1} min^{-1})	R^2
239.54	62.65	5.89	0.8645	244.5	5.51	0.9996

Table 1: Theoretically determined constants of the pseudo-first and the pseudo-second-order reaction kinetics based on the sorption of crystal violet from 25 mgL^{-1} solutions. pH 8.0, by 0.05g cross-linked OCMCTS during shake flask sorbent–sorbate contact at 30°C for 240 min.

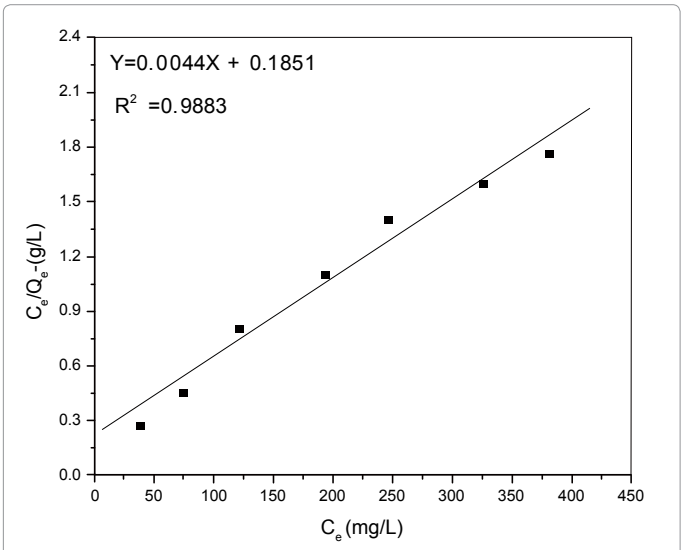

Figure 12: The linearized Langmuir adsorption isotherms for the adsorption of crystal violet by OCMCTS.

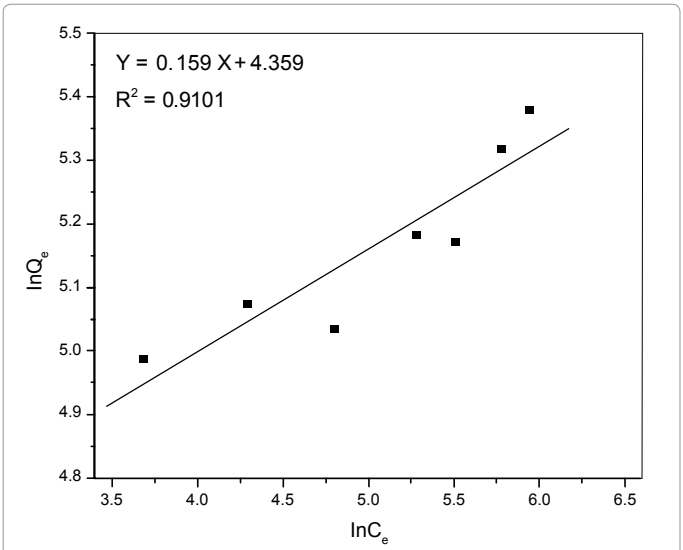

Figure 13: The linearized Freundlich adsorption isotherms for the adsorption of crystal violet by OCMCTS.

Adsorption isotherms modeling

Adsorption isotherms are important for the description of how molecules of adsorbate interact with adsorbent surface. Hence, the correlation of equilibrium data using either a theoretical or empirical equation is essential for the adsorption interpretation and prediction of the extent of adsorption. The obtained adsorption data are interpreted by the two well known isotherm equations namely, the Langmuir and the Freundlich isotherm equations [45].

The Langmuir isotherm equation can be represented as:

$$\frac{C_e}{q_e} = \frac{1}{q_{max} b} + \frac{C_e}{q_{max}}$$

where, b is constant of the adsorption equilibrium (L/mg) and q_{max} is the maximum dye adsorption capacity (mg/g). The values of q_{max} and b can be obtained from linear plot of Ce/qe versus Ce.

The Freundlich isotherm equation based on adsorption on a heterogeneous surface is given as follows:

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

This equation can be rewritten as below for its linearized form:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$$

Where, K_F and n are the Freundlich constants, which represent adsorption capacity and adsorption intensity, respectively. K_F and n can be obtained from intercept and slope of a linear plot of $\ln q_e$ against $\ln C_e$.

A linear plot of C_e/q_e versus C_e for the Langmuir model of adsorption of CV on cross-linked OCMCTS is shown in Figure 12. Figure 13 shows the linear plot of Freundlich isotherm model for the adsorption of CV on cross-linked OCMCTS. The calculated values of various parameters of Langmuir and Freundlich equation are reported in Table 2. The comparison of correlation coefficients (R^2) of the linearized form of both the Langmuir and Freundlich adsorption equations indicates that the Langmuir model yields a better fit for the experimental equilibrium adsorption data than the Freundlich model. This result suggests the monolayer coverage of the dye on the surface of the OCMCTS. Similar results are also observed in previous studies like, the adsorption of methylene blue onto quaternary ammonium compounds modified monmorillonite [46], clay [47] and chitosan-g-poly (acrylic acid)/montmorillonite [48]. The maximum adsorption of CV on cross-linked OCMCTS is found to be 230.41 mg/g (from the plot), which is close to the experimental data 227.27 mg/g (Table 2). This adsorption capacity of cross-linked OCMCTS for CV is found to be quite higher than previous reported adsorbents, such as 85.47 mg/g by skin almond waste [49], 64.87 mg/g by activated rice husk [38] and 113 mg/g by activated sludge [50].

The affinity between the adsorbate and adsorbent can be obtained from the Langmuir parameter with the help of the dimensionless separation factor (R_L), which can be presented as below [51]:

$$R_L = \frac{1}{1 + bC_i}$$

In accordance with criteria of R_L (Table 3), R_L can be used to predict whether an adsorption system is "favorable" or "unfavorable". The R_L value for this adsorption system is 0.18 (Table 2), which is lower than 1 and higher than zero. This suggests that the adsorption of CV onto OCMCTS is "favorable".

Proposed adsorption mechanism

Figure 14 represents the FT-IR spectra of cross-linked OCMCTS before and after adsorption of CV dye. Figure 14b shows that there was no significant change in the absorption intensity at wave numbers 3443.31 cm^{-1} (-OH stretching vibration) and 1643.81 cm^{-1} (superimposed of asymmetric vibration of carboxylate ion and C=N bond). Two new absorption peaks appeared at 1574.52 cm^{-1} and at 1355.15 cm^{-1} after adsorption due to adsorption of CV dye molecule onto cross-linked OCMCTS. This implies that the adsorption processes are physical adsorption and may not involve a chemical interaction. The proposed mechanism of CV adsorption on OCMCTS is shown in Figure 15.

Experimental q (mg g^{-1})	Langmuir				Freundlich		
	qmax (mg g^{-1})	b (L mg^{-1})	R_L	R^2	KF [(mg g^{-1}/ (mg $L^{-1})^{1/n}$]	1/n	R^2
239.54	227.27	0.023	0.18	0.9883	78.16	0.159	0.9101

Table 2: The Langmuir and Freundlich isothermsmodel constants, and their respective correlation coefficients R^2 for the sorption of crystal violet from aqueous solution by OCMCTS.

Separation factor (R_L)	Types of isotherms
R_L>1	Unfavorable
R_L=1	Linear
0>R_L<1	Favorable
R_L=0	Irreversible

Table 3: Characteristics of the Langmuir adsorption isotherms.

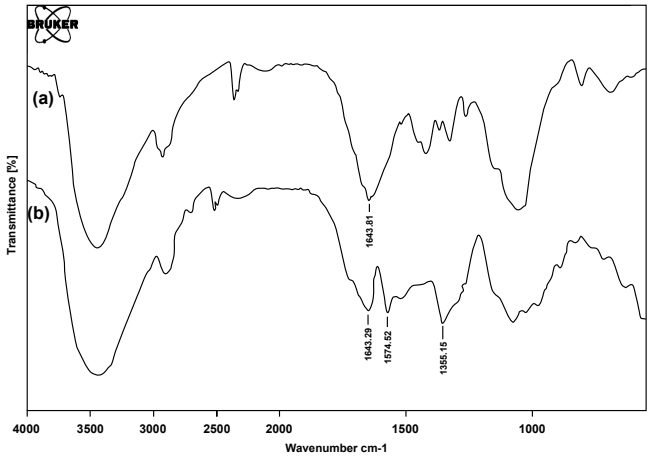

Figure 14: FT-IR spectrum of OCMCTS: before adsorption (a) and after adsorption (b).

Desorption

For economic viability of adsorbent for water purification, it is necessary to re-generate the spent adsorbent. Figure 16 illustrates the desorption of CV from cross-linked OCMCTS at different time intervals. For desorption, the reaction responsible may be as follows:

$$R - COO^- CV - NMe_2^+ + HCl \rightarrow R - COOH + CV - NMe_2Cl$$

In order to study the regeneration of the cross-linked OCMCTS, three cycles of adsorption/desorption were carried out. Percentage of desorption of CV from cross-linked OCMCTS are shown in Figure 16. It is found from Figure 16 that desorption process was reasonably fast and the equilibrium was almost reached within 60 minutes. It may be observed that the percentage of desorption was quite high and the desorption percent slightly decreased with increasing the cycle number. This result is in accordance with the previous report [52].

Conclusion

The FT-IR and XRD characterization show that O-carboxymethyl chitosan and cross-linked OCMCTS are successfully synthesized. From this study, it is observed that the adsorption capacity of cross-linked OCMCTS increases largely that of CTS. The results also show that the adsorption process of CV on cross-linked OCMCTS is depended on pH, temperature, initial dye concentration, degree of substitution of

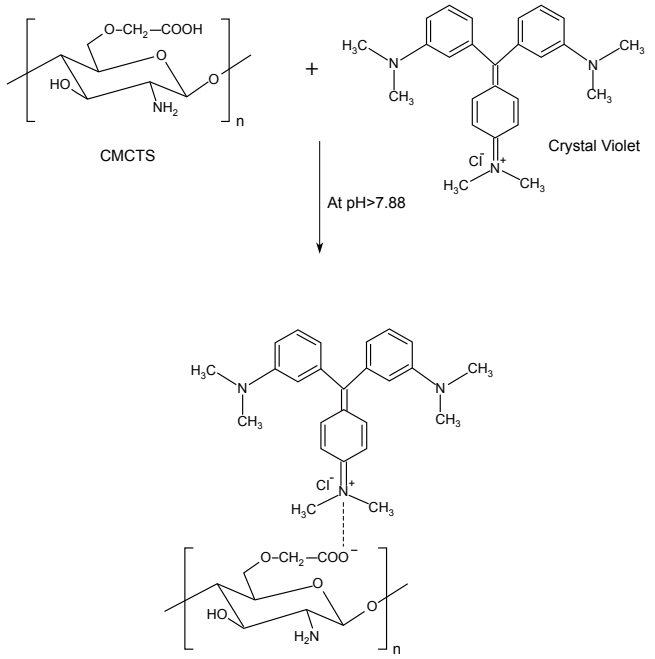

Figure 15: The proposed mechanism of CV adsorption onto OCMCTS.

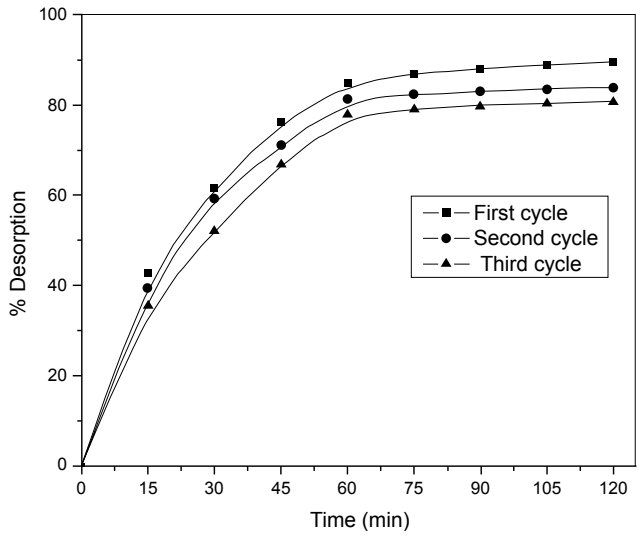

Figure 16: Desorption study of adsorbed cross-linked OCMCTS in 0.2 M HCl solution at different time interval.

OCMCTS and contact time. The adsorption process follows a second-order-kinetic model, rather than the first-order-kinetic model. At optimized conditions, the experimental equilibrium adsorption data obtained from batch studies fits well to the Langmuir adsorption isotherm equation, rather than the Freundlich equation, indicating the formation of monolayer of CV on OCMCTS during adsorption. The dimensionless parameter R_L is calculated from the Langmuir constant b and the value of R_L is found to be between 0 and 1, which again suggest favorable adsorption of CV on OCMCTS. The FT-IR analysis also indicates that the adsorption of CV onto cross-linked OCMCTS is physical interaction rather than chemical interaction. From desorption study, it is found that cross-linked OCMCTS can be re-used repeatedly with slight loss of the adsorption capacity of OCMCTS. Therefore, it may be concluded that cross-linked recyclable OCMCTS can find an application as a low-cost effective adsorbent and it can be an alternative to high-cost commercial activated carbon for the removal of basic dyes from water and wastewater.

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