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Functionalization of Microcrystalline Cellulose with *N,N*-dimethyldodecylamine for the Removal of Congo Red Dye from an Aqueous Solution

Dongying Hu, Peng Wang, Jian Li, and Lijuan Wang*

Microcrystalline cellulose (MCC) was functionalized with quaternary amine groups for use as an adsorbent to remove Congo Red dye (CR) from aqueous solution. The ultrasonic pretreatment of MCC was investigated during its functionalization. Characterization was conducted using infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and scanning electron microscopy (SEM). The batch adsorption of the functionalized MCC was studied to evaluate the effects of dye concentration, pH of solution, temperature, and NaCl concentration on the adsorption CR. The adsorbent (FM-1) obtained using ultrasonic pretreatment of MCC under 10.8 kJ•g^{-1} exhibited an adsorption capacity of 304 mg•g^{-1} at initial pH under a dose of 0.1 g•L^{-1} and initial concentration of 80 mg•L^{-1}. After functionalization, the FT-IR and XPS results indicated that the quaternary amine group was successfully grafted onto the cellulose, the surface was transformed to be coarse and porous, and the crystalline structure of the original cellulose was disrupted. FM-1 has been shown to be a promising and efficient adsorbent for the removal of CR from an aqueous solution.

*Contact information: Key Laboratory of Bio-based Material Science and Technology of Ministry of Education, Northeast Forestry University, 26 Hexing Road, Harbin 150040, P. R. China; * Corresponding author: donglinwlj@163.com*

INTRODUCTION

The development of industry in recent years has resulted in many potential dangers to the environment. The discharge of colored wastewater has caused a great impact on industry as well as causing harm to the environment, especially, the textile, leather, paper, and plastic industries (Ravikumar *et al.* 2005). There are over an estimated 100,000 kinds of commercially available dyes with an output of $> 7 \times 10^5$ tons per year. However, around 10 to 20% of dyes used in textile dyeing processes have been estimated to have been lost into dye wastewater because of the low fixation between dyes and fibers, and the washing operations needed (Lee *et al.* 2006; Noroozi and Sorial 2013). Organic dyes are synthetic, aromatic compounds that possess intense color and high toxicity. Due to their complex chemical structures, most of them are stable to light and oxidizing agents. Some dyes have been reported to cause allergic dermatitis or skin irritation, and they may be potentially carcinogenic and mutagenic in humans (Sun and Yang 2003; Bhatnagar and Jain 2005; Silva *et al.* 2013). Congo Red dye (CR) has a molecular weight of 696.68 g•mol^{-1} and has a benzidine-based structure. CR causes allergic reactions and is a known human carcinogen (Mall *et al.* 2005). It is a popular anionic diazo dye used in

many industries (Purkait *et al.* 2007). It is highly water soluble and has been applied in the textile, printing, dyeing, paper, rubber, and plastics industries (Chiou *et al.* 2004). In addition, CR possesses a very stable chemical structure, which makes it difficult to remove from wastewater (Wang and Wang 2007). Therefore, there is a constant need to develop an effective process that can efficiently remove CR from wastewater.

Although the effectiveness of a removal method is important for treating dye wastewater, methods such as coagulation, chemical oxidation, membrane separation processes, electrochemical, and aerobic and anaerobic microbial degradation, all suffer from one or more limitations (Sulak *et al.* 2007). In comparison with these methods, adsorption is a low cost and highly efficient method that can be used to remove colored matter from dye wastewater, and as such it has attracted increasing attention for improving the purity of water resources (Leitão and Serrão 2005; Qadeer 2007). Adsorption using activated carbon as adsorbent is an important method to purify colored wastewater because of its excellent physical properties (Yin *et al.* 2008). However, it is still considered a relatively expensive material and is difficult to recycle (Gouamid *et al.* 2013). Therefore, it is necessary to develop new promising alternatives for wastewater purification.

Cellulose and its derivatives are low-cost, widely resourced, non-toxic, biodegradable, and renewable raw materials (Carlmark *et al.* 2012). In addition, they can effectively remove metal ions and some organic compounds from wastewater (Cai *et al.* 2013). Cellulose has been used in the removal of colored matter from dye wastewater (Hwang and Chen 1993). In addition, some adsorption materials obtained from cellulose-based waste products have also been used for the adsorption of dyes, including sawdust (Ofomaja 2008), rice husk (Zou *et al.* 2011), wheat shell (Vieira *et al.* 2009), and banana and orange peel (Annadurai *et al.* 2002). However, most of them reported have a low adsorption capacity, and the characteristic that limits the development of the class of renewable adsorbents. Cellulose is a linear 1,4-β-glucan polymer, which possesses a macromolecular structure containing many free hydroxy groups that are prone to undergo intra-molecular or intermolecular reactions with organic compounds. Chemical modification of biomass materials for dye adsorption has also been investigated (Zhang *et al.* 2012). Therefore, in order to improve the maximum adsorption capacity of the material, chemical modification of cellulose is an important method to improve the adsorption performance of cellulose in dye wastewater.

In the adsorption process, anionic and cationic surfactants can adsorb basic dyes and anionic dyes, respectively (Janos and Smidova 2005; Zhu and Ma 2008). Amine functional groups in adsorbents play an important role in the effectiveness, capacity, and selectivity for the adsorption of water pollutants (Lin *et al.* 2011). The properties resulting from the cationization of microcrystalline cellulose using 3-chloro-2-hydroxypropyltriethylammonium chloride have been reported (El-Shishtawy and Hashem 2001). Quaternization of cellulose is advantageous for the adsorption of anionic dyes and greatly improves the adsorption capacity in dye wastewater.

To the best of our knowledge, there have been no previous reports on the removal of dye using cationized microcrystalline cellulose (MCC) using *N,N*-dimethyldodecylamine. We now study the synthesis of adsorbents from MCC modified with *N,N*-dimethyldodecylamine. Ultrasonic pretreatment technology was used to increase the accessibility and chemical reactivity of MCC to obtain the cationic cellulose with ideal adsorption ability for removing anionic dyes. The influence of ultrasonic pretreatment on the cationic treatment of cellulose was analyzed. The properties of the

adsorbents (FM) were characterized using infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and scanning electron microscopy (SEM). The dye adsorption capacity was analyzed to determine the optimal conditions for the ultrasonic pretreatment used in the MCC modification process. The influences of dye concentration, pH of solution, and NaCl concentration were considered.

EXPERIMENTAL

Materials and Reagents

Microcrystalline cellulose (MCC) was purchased from HengXin Chemical Reagent Co. Ltd (Shanghai, China). N,N-dimethyldodecylamine ($C_{14}H_{31}N$; 98% pure; M.W: 213.4) was obtained from Heowns Business License (Tianjin, China). Epichlorohydrin was purchased from Kemiou Chemical Reagent Co. Ltd. (Tianjin, China). Congo Red dye (CR; $C_{32}H_{22}N_6Na_2O_6S_2$; M.W: 696.68) was purchased from BoDi Chemical Reagent Co. Ltd (Tianjin, China). All other chemicals and reagents used in this work were of analytical grade. All the solutions used in this work were prepared using distilled water.

Preparation of the Adsorbents

MCC (10 g) was suspended in a 20 wt% NaOH solution (250 mL). Ultrasonic pretreatment of the suspension was carried out at 20 °C at a power of 10.8 kJ•g^{-1}, 16.2 kJ•g^{-1}, and 21.6 kJ•g^{-1}, respectively. The mixture was stirred at room temperature for 2 h and the liquid removed using filtration. A 10 wt% NaOH solution (250 mL) and epichlorohydrin (240 mL) were added to the residue in a 500 mL three-necked flask and the resulting mixture heated at 65 °C for 6 h. The liquid was removed using filtration, and 40 v/v% of N,N-dimethyldodecylamine in isopropanol (100 mL) was added to the residue and the resulting mixture heated at 80 °C for 3 h. The product was filtered, and washed with ethanol (1000 mL), 0.1 mol•L^{-1} NaOH solution (1000 mL), 0.1 mol•L^{-1} HCl (1000 mL) and distilled water (2000 mL). The product was dried in vacuum at 60 °C for 10 h. The products were termed FM-0, FM-1, FM-2, and FM-3, according to the power of the ultrasonic pretreatment used. The possible reactions are shown in Fig.1.

Characterization

The chemical structure of all the samples was characterized by Fourier transform infrared spectroscopy (FT-IR) using a Nicolet 6700 instrument (Thermo Fisher Scientific Co., Ltd., USA) with the ATR technique, 32 scans were recorded for each spectrum with a resolution of 4 cm^{-1}. The nitrogen content (N%) of all samples was determined using a K-Alpha XPS Analyzer (ThermoFisher Scientific Company). The results of XPS analysis can be used to evaluate the substitution of the hydroxyl groups in the modified cellulose (Alila *et al*. 2009). The surface morphological analysis was carried out using a Quanta Zoo device, Philips-FEI Co., Netherlands. Absorption spectra were recorded directly on a UV-visible spectrophotometer (TU-1900) from the dye solution after adsorption. The wavelength of maximum adsorption (λ_{max}) for the CR dye is 494 nm. The crystalline structures of MCC and FM were characterized by X-ray diffraction (XRD) using a Rigaku D/max-2200 diffractometer with a Cu K$_\alpha$ target, operated at 1200 W (40 kV, 30 mA). The point of zero charge (pH$_{pzc}$) of the adsorbents tested was determined using a

literature method (Vieira *et al.* 2009). A NaCl solution (0.01 mol•L^{-1}, 20 mL) was added to a series of 100 mL conical flasks, the initial pH (pH$_i$) values of the solutions were adjusted in the range of pH 2 to 11, FM-1 (100 mg) was added to every flask and the resulting suspensions were shaken in an acclimatized shaker at 298 K for 10 h. After this time, the final pH (pH$_f$) was determined, and the difference between the initial and final pH values was calculated according to ΔpH= pH$_i$ - pH$_f$, a plot of ΔpH as a function of pH$_i$ was subsequently constructed. The ΔpH value where the pH$_i$ is 0 is called the point of zero charge (pH$_{pzc}$) of FM-1.
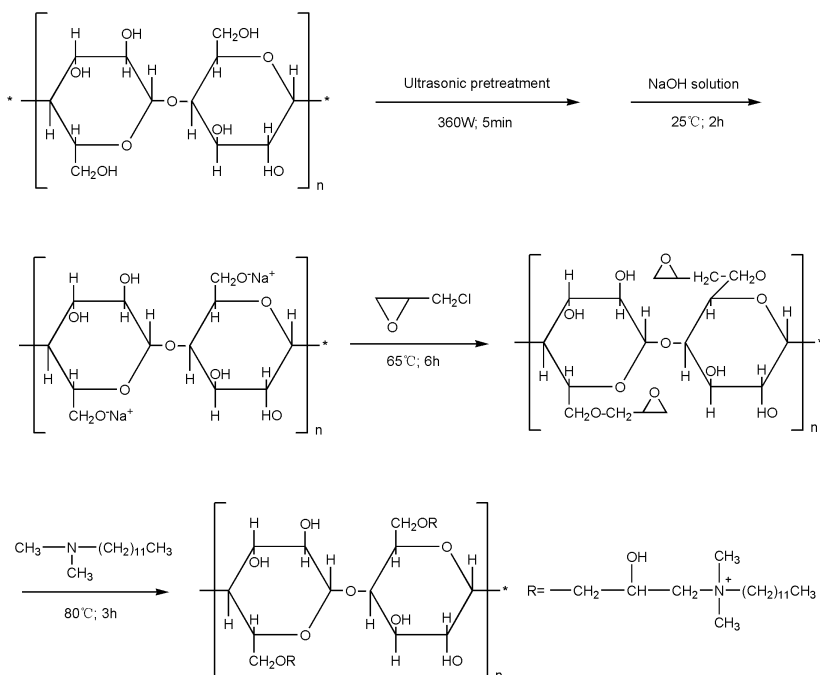

Fig. 1. Synthetic reactions for the FM

Dye Adsorption Experiments

The influence of various parameters on the adsorption capacities was investigated and included the adsorbent dosage, contact time, initial dye concentration, temperature, pH, and NaCl concentration. In order to study the influence of initial pH on the adsorption capacity, the scope of pH studied ranged from 5 to 11. The initial pH was adjusted using a solution of 10 mol•L^{-1} NaOH or 5 mol•L^{-1} HCl. The adsorption experiments for CR were carried out in a water bath oscillator at 120 rpm. A quantity of the adsorbent and 100 mL of dye solution were placed into a 250 mL beaker. After adsorption, the mixture was subjected to centrifugation at 4000 rpm for 10 min to remove the adsorbent. The concentration of the residual dye in the remaining solution was determined using UV spectrophotometry.

The amount of dye adsorbed by the FM and the dye removal efficiency (R) was calculated using the following equations, where the amount of dye adsorbed q_t (mg•g^{-1}) and the amount of dye adsorbed at equilibrium q_e (mg•g^{-1}) at a time t are,

$$R = \frac{C_0 - C_t}{C_0} \times 100\% \tag{1}$$

$$q_e = \frac{(C_0 - C_e) \times V}{M} \tag{2}$$

$$q_t = \frac{(C_0 - C_t) \times V}{M} \tag{3}$$

where C_o (mg•L^{-1}) is the initial dye concentration in the solution before adsorption, C_e (mg•L^{-1}) is the dye concentration of the residual solution at equilibrium, C_t (mg•L^{-1}) is the dye concentration at a time t in the solution, V (mL) is the volume of the solution, and M (mg) is the mass of the adsorbent on a dry basis.

RESULTS AND DISCUSSION

Characterization of the Adsorbents

Effect of ultrasonic pretreatment

The effects of ultrasonic pretreatment on the adsorption of FMs are shown in Fig. 2(a). The adsorption capacities of FM-0, FM-1, FM-2, and FM-3 were 23.38 mg•g^{-1}, 158.03 mg•g^{-1}, 131.57 mg•g^{-1}, and 117.95 mg•g^{-1}, respectively. The results indicate that the ultrasonic pretreatment improved the adsorption capacity of the FM. The mechanical effect of acoustic cavitation is advantageous for improving the accessibility of the reactants (Rattaz *et al*. 2011). However, the use of an excessively high power ultrasonic pretreatment decreased the adsorption properties. This was attributed to the cellulose molecules interacting with each other intensely and gathering together in the cavitation area at higher ultrasonic power levels, which decreases the accessibility of the reactive sites in the FM (Dong *et al*. 1998). Therefore, an appropriate power level of pretreatment using ultrasonic radiation favors the functionalization of cellulose.
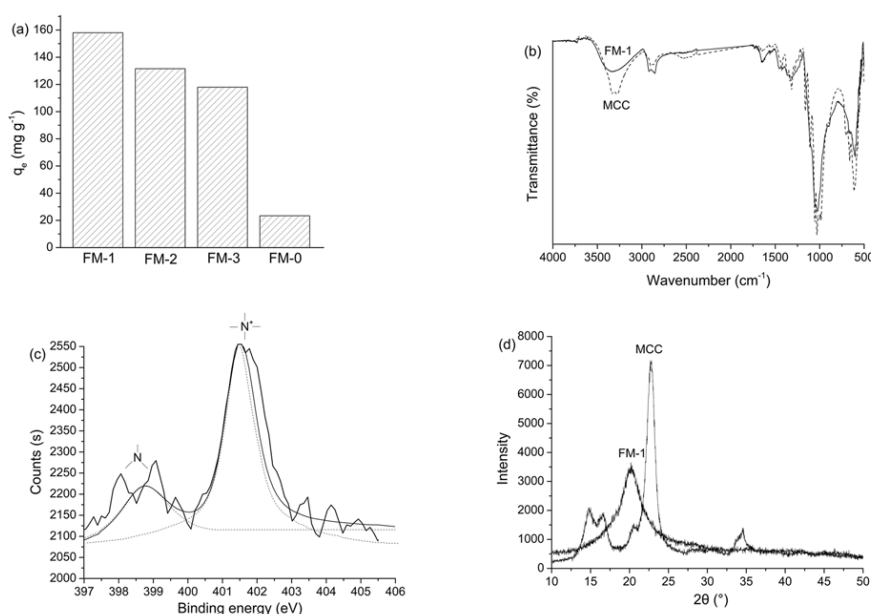

Fig. 2. (a) The effects of ultrasonic pretreatment on adsorption capacity for CR (dosage 20mg, T=303K, t=10h, C=80mg•L-1, V=50mL), (b) FT-IR spectra of MCC, FM-0 and FM-1, (c) N 1s spectrum of FM-1, (d) XRD patterns of MCC and FM-1

FT-IR and XPS analysis

The FT-IR spectra of MCC and FM-1 are shown in Fig. 2(b). For MCC, the band at 3343 cm^{-1} was attributed to the O-H stretching vibration of the hydroxy groups in cellulose. The band at 2874 cm^{-1} corresponds to C-H stretching vibration of the –CH$_2$– groups. The band at 1644 cm^{-1} was assigned as the carbonyl group in the aldehyde on the terminal anhydroglucose unit. The band at 1315 cm^{-1} was assigned as the C-O stretching vibration of the CH$_2$-OH groups. A series of bands at 1028 cm^{-1}, 1053 cm^{-1}, 1107 cm^{-1} and 1162 cm^{-1} correspond to the -C-O-C- bonds in the anhydroglucose unit of the cellulose molecule (Wang and Li 2013). In the spectrum of FM-1, the peak at 3330 cm^{-1} became weaker and shifted to 3353 cm^{-1}. The band at 2874 cm^{-1} became stronger and was observed as a broad shoulder peak, which indicates that new –CH$_2$– groups were introduced in the chemical structure of FM-1. Moreover, there was a new adsorption peak associated with the stretching vibration of a C-N bond at 1457 cm^{-1} (Anirudhan *et al*. 2006). This indicates that the quaternary amine groups were successfully grafted onto the cellulose skeleton. In addition, the band at 1640 cm^{-1} was significantly strengthened, which further demonstrates that more terminal anhydroglucose units were produced. In addition, these results show that treatment with NaOH in the initial stage of the chemical modification of MCC makes the cellulose swell and gives rise to chain breaks in cellulose.

In order to confirm that FM-1 contains nitrogen in the quaternary state, XPS analysis was carried out. As shown in Fig. 2(c), the nitrogen content (N%) of FM-1 reached 2.1%. The peaks at 398.68 and 401.48 eV in the XPS spectrum represent the two different valence forms of nitrogen in tertiary amine and quaternary amine groups, respectively (Tastet *et al*. 2011). The average DS value of the quaternary amine groups was 0.26.

XRD analysis

The XRD patterns of MCC and FM-1 are presented in Fig. 2(d). The XRD pattern of MCC shows a typical cellulose I structure, with a sharp peak at 22.74°, a wide peak between 14.26° and 17.16°, and a typical peak at 34.56° (Hao *et al*. 2009). However, these characteristic peaks either disappeared or were weakened in the XRD pattern of FM-1.

For example, a weaker peak at 20.24° was observed, in which the diffraction intensity decreased significantly upon ultrasonic pretreatment in an alkaline solution. Therefore, crystalline structure of cellulose was damaged, and cellulose I was converted to cellulose II. This indicates that the intermolecular and intra-molecular hydrogen bonds of the original MCC were broken in the modification process (Raymond *et al*. 1995).

Surface morphology properties

The SEM photographs of MCC and FM-1 at 10,000 × magnification are shown in Fig. 3. Figure 3(a) clearly shows that the surface of MCC had a smooth and compact structure.

By contrast, Fig. 3(b) shows that the surface structure visibly changed after the modification process. The surface of FM-1 becomes coarse and porous. These changes in the surface morphology are important for dye adsorption.
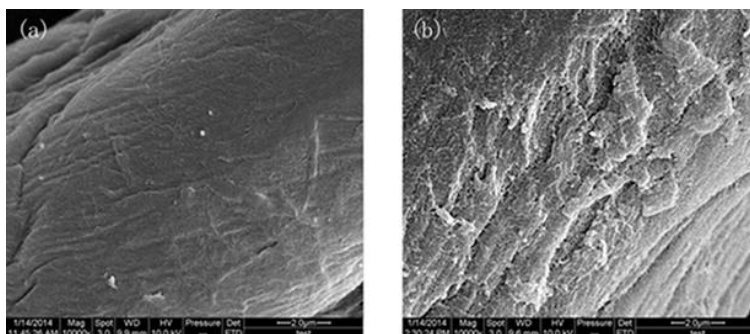
Fig. 3. SEM photographs of MCC (a) and FM-1 (b)

Adsorption Behavior for CR Dye

Effect of initial dye concentration

In order to study the influence of the dye concentration on the adsorption capacity, studies were carried out at different temperatures (303 K, 308 K, and 313 K). As shown in Fig. 4(a), the adsorption amount of FM-1 for CR increased with increasing dye concentration ranging from 70 to 120 mg•L^{-1} when using 40 mg of FM-1 in a 100 mL solution. The amount adsorbed increased owing to an increase in the driving force resulting from the increase in dye concentration (Chiou and Li 2002). In particular, the adsorption increased significantly from 192.13 mg•g^{-1} to 212.31 mg•g^{-1} at different dye concentrations at 313 K. However, the results show that the adsorption capacity increased less from 144.25 mg•g^{-1} to 153.85 mg•g^{-1} at different dye concentrations at 303 K. These results illustrate that an increase in temperature was advantageous for the adsorption of CR on FM-1. However, the growth trend of adsorption capacity indicates that FM-1 did not reach its maximum absorption capacity, and the absorbent had not reached saturation under the dye concentrations tested (Safa and Bhatti 2011).

Effect of pH

The initial pH of the dye solution had an important effect on the adsorption process. Fig. 4(b) shows the graph of potential of zero charge (pH$_{pzc}$), which shows the charge behavior of the surface of FM-1. The surface of the adsorbent retains few protons within the scope of the low pH values, and this retention gradually diminishes with an increase in pH. Thereafter, the positive and negative charges are equivalent at a pH of 7.68; this equivalence point is called the point of zero charge (pH$_{pzc}$). After this point, the FM-1 begins to release protons at higher pH values, which makes the surface of the adsorbent anionic. Overall, it is advantageous for an adsorbent for anionic dye adsorption that the pH of the solution is < pH$_{pzc}$. Conversely, it is conducive for an adsorbent for cationic dye adsorption that the pH of the solution is > pH$_{pzc}$ (Calvete *et al*. 2010).

After the pH$_{pzc}$ studies, the effects of initial pH on the adsorption of CR onto the surface of the FM-1 were investigated within a pH range of 5 to 10. The results in Fig. 4(c) show that the adsorption capacity decreased from 191.71 mg•g^{-1} to 160.1 mg•g^{-1} with an increase in pH from 5 to 7.68. The adsorption capacity increased at higher pH values. At a lower pH, the –NH$_2$ groups in the dye molecule are protonated (–NH$_3^+$ groups). The dye molecules are adsorbed onto the adsorbent via ion exchange between the quaternary amino groups in the FM and the –SO$_3^-$ groups of the CR. Subsequently, the adsorbed dye molecules can absorb free dye molecules *via* electrostatic bonding interactions. Upon increasing the pH, the amount of –NH$_3^+$ group's present decreases;

therefore, the adsorption capacity decreases. Under alkaline conditions, there is competition occurring between the excess OH⁻ ions and the CR anions to interact with the quaternary amino groups in the FM-1, so one would expect the adsorption capacity to decrease. However, the adsorption capacity did not follow this prediction and can be explained by hydrogen bonding between the –OH groups on the glucoside and the –NH$_2$ groups in the CR.
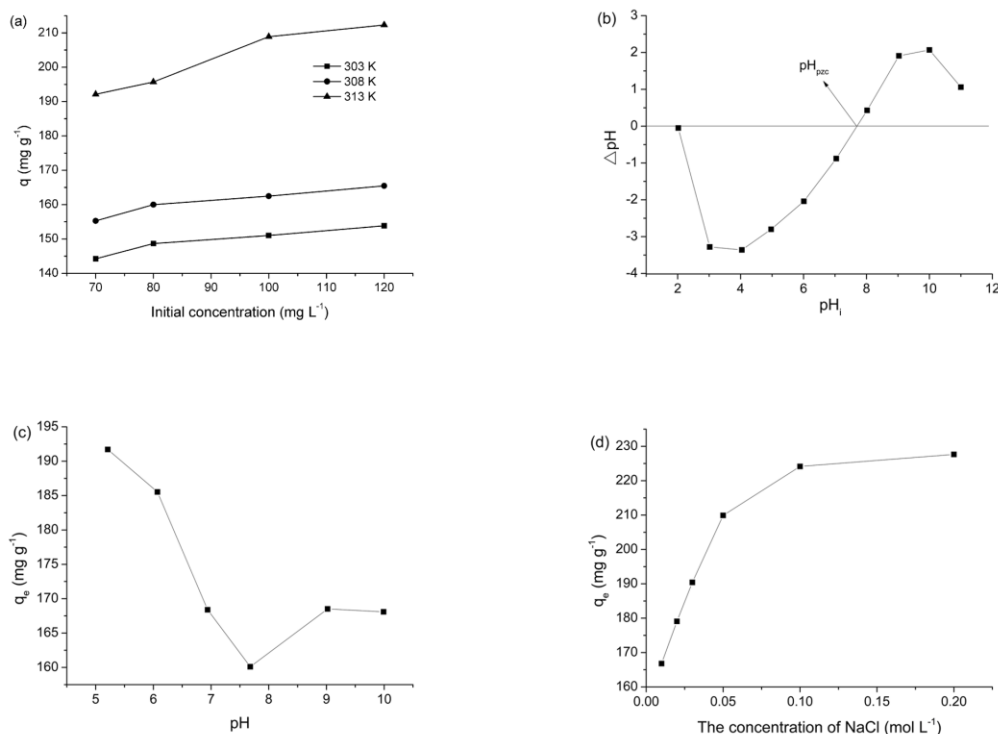

Fig. 4. (a) Effect of initial dye concentration for the adsorption of CR on FM-1 (initial pH, dosage 35 mg, T=303 K, t=10 h, C=80 mg•L^{-1}, V=100 mL), (b) point of zero charge of FM-1, (c) effect of pH on the uptake of CR on FM-1 (dosage 35 mg, T=303 K, t=10 h, C=80 mg•L^{-1}, V=100 mL), and (d) effect of ionic strength on the uptake of CR on FM-1 (initial pH, dosage 35 mg, T=303 K, t=10 h, C=80 mg•L^{-1}, V=100 mL)

Effect of ionic strength

Ionic strength may have an impact on adsorption of a dye from a solution. As a common substance, NaCl was used to investigate the effect of ionic strength in this study. The influence of ionic strength on the adsorption of CR is shown in Fig. 4(d). Adsorption capacity increased from 166.80 to 227.65 mg•g^{-1} with an increase in the NaCl concentration from 0.01 mol•L^{-1} to 0.2 mol•L^{-1}. Generally, an increase in ionic strength will decrease the adsorption capacity due to the existence of electrostatic screening. However, the experimental data from this study did not follow this trend, which was attributed to NaCl ions inducing the aggregation of the CR molecules, enhancing the extent of adsorption on adsorbent (Alberghina *et al*. 2000). Therefore, higher ionic strength was favorable for the adsorption of CR on FM-1.

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CONCLUSIONS

1. A new and eco-friendly adsorption material was successfully prepared by modification of MCC using *N,N*-dimethyldodecylamine, which has a specific structure and selective adsorption performance for CR.

2. The method of ultrasonic pretreatment was used to improve the treatment of MCC with *N,N*-dimethyldodecylamine in this process. The most appropriate power level of ultrasonic radiation was 10.8 kJ•g^{-1}.

3. After functionalization, the FT-IR and XPS results indicated that the quaternary amine group was successfully incorporated onto the cellulose.

4. The adsorption of CR is dependent on its dye concentration, pH of solution, NaCl concentration, and temperature. The maximum adsorption capacity of adsorbent for CR dye reached 304.34 mg•g^{-1} (with a dye concentration of 80 mg•L^{-1}, a volume of 100 mL, a temperature of 40 °C and an adsorbent dosage of 10 mg).

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