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Application of cross-linked porous chitosan films for Congo red adsorption from aqueous solution

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ABSTRACT

The preparation, characterization, and environmental application of cross-linked porous chitosan (CPCS) films for Congo red adsorption have been investigated. The adsorbent was characterized by Fourier transform infrared spectrophotometer and scanning electron microscope. The adsorption experiments were carried out in a batch system to optimize operation variables: contact time, Congo red concentration, temperature, and pH. The results indicated that CPCS films could successfully remove 96% of Congo red. The adsorption kinetics and equilibrium isotherms showed that the sorption processes were better fitted by pseudo-second-order equation and Langmuir equation, respectively. Adsorption thermodynamics indicates the spontaneous nature and endothermic of the adsorption process.

Keywords: Chitosan; Adsorption; Congo red; Film

1. Introduction

As a result of the rapid development of the textile industries, synthetic dyes have become one of the main sources of severe water pollution. These substances can bring on environmental problems as most of these compounds were recognized as toxic carcinogens [1]. Congo red is a benzidine-based dye. That is expected to metabolize to benzidine, which is a known human carcinogen [2]. Adsorption is considered an effective and economical method for removal of pollutants from wastewater. This technique is quite popular due to its simplicity as well as the availability of a wide range of adsorbents, and it proved to be an effective and attractive process for the removal of non-biodegradable pollutants (including dyes) from wastewater [3]. In order to decrease the cost of treatment, some attempts have been made to find low-cost adsorbents.

Chitosan, a naturally occurring linear polymer of glucosamine, has exhibited excellent adsorption capacity for anionic dyes because chitosan molecules contain a large number of active amine (–NH_2) groups. Cross-linking of chitosan film with formaldehyde [4], epichlorohydrin (ECH) [5], or polyethylene glycol (PEG) [6] has been proposed to improve pore

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size distribution, mechanical resistance, chemical stability, and adsorption properties. However, these chemicals can attack the amino groups, which play an important role in adsorption. In this study, formaldehyde was used as a pre-crosslinking agent to protect amino group. Chitosan can easily reaction with aromatic aldehyde (or ketone), aliphatic aldehydes to form Schiff's bases in the neutral medium. This reaction can use to protect amino group and react with hydroxyl radical thereafter. Besides, the protecting group can easily take off after the reaction, which made it useful in chitosan application.

The aim of this study was to prepare a novel type of cross-linked porous chitosan (CPCS) film by incorporating formaldehyde, ECH, and PEG, and evaluated its potential in terms of the adsorption of Congo red.

2. Materials and methods

2.1. Materials

Chitosan with a weight-average molecular weight of 230 kDa and the degree of deacetylation of 90.8% was obtained from Yuhuan Biochemical Co. (Zhejiang, China). All other chemicals and reagents used were of analytical grade.

2.2. Adsorbent preparation

In a 2% (v/v) aqueous acetic acid solution, 3 g chitosan was dissolved to prepare a 3% (w/v) solution. Then, 0.1 mL formaldehyde was added to pre-crosslinking for 3 h. After that 0.75 g PEG was added. The resulting solution was stirred, filtered, and degassed; and then was spread over a glass plate. The films obtained were washed intensively and bathed in distilled water at 80℃ for 2 h to remove PEG and form porous. To cross-link with ECH, the wet films obtained were immersed in a certain amount of 0.1% (v/v) ECH solution at 50℃ for 3 h. Afterwards, the films were rinsed with distilled water to remove unreacted ECH. The cross-linked films were kept in 0.5 mol/L HCl solution for 3 h and latter placed in 2% NaOH solution overnight. Finally, the obtained CPCS films were washed thoroughly with distilled water and then dried in air.

2.3. Characterization of CPCS film

The samples were grounded into powder for the preparation of KBr pellets. IR spectra of the powdered samples were recorded on Nicolet-360 Fourier transform infrared (FTIR) spectrometer with KBr pellet. The spectrum was corrected for the background noise. Micrographs of these samples were taken by Nova 400 Nano SEM. Before observation of SEM, all samples were fixed on aluminum stubs and coated with gold.

2.4. Batch adsorption studies

In general, adsorption experiments were conducted by adding 0.1 g of CPCS films (unless otherwise stated) into 50 mL CR solutions in 250 mL glass vials. The batch adsorption was carried out on a shaker at 120 rpm under room temperature (25℃). After adsorption, the solutions were filtered and analyzed at a wavelength of 498 nm using UV–visible spectrophotometer. According to the decreasing of CR concentration in the adsorption, absorbance, and adsorption percent were calculated.

3. Results and discussion

3.1. FTIR spectra of CPCS film

FTIR spectroscopy has been shown to be a powerful tool for the study of the physicochemical properties of polysaccharides. Curves *a*, *b*, *c*, *d*, *e*, and *f* in Fig. 1 show the IR spectra of chitosan, pre-crosslinked film, pre-crosslinked porous film (unwashed), pre-crosslinked porous film (washed), ECH cross-linked film, and CPCS film. The adsorption bands at 3,442, 1,602, 1,259, 1,646, 1,389, and 1091 cm^{-1} in chitosan are attributed to –NH$_2$ and –OH stretching, –NH$_2$ deformation, –OH deformation, C=O stretching, C–H deformation, and C–O stretching, respectively.

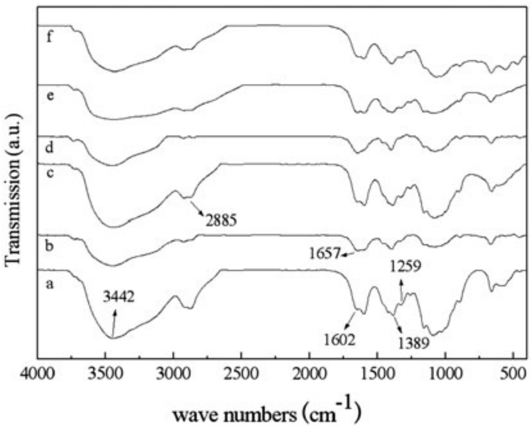

Fig. 1. FTIR spectra of chitosan (a), pre-crosslinked film (b), pre-crosslinked porous film (unwashed) (c), pre-crosslinked porous film (washed) (d), ECH corss-linked film (e), and CPCS film (f).

Compared with the chitosan to the chitosan films treated with formaldehyde (Curve *b*), the amount of $-NH_2$ group on the films decrease and the peak intensity increases at 1,645 cm^{-1} which results from the reaction between formaldehyde and $-NH_2$ group, and the –N–C bond changed into –N=C bond to form Schiff base and protect amino group. When the pre-crosslinked films treated with PEG (Curve *c*), the peak at 2,885 cm^{-1} is attributed to the character peak of PEG, overlapping with the absorption peak of chitosan. After muggy treatment (Curve *d*), the character absorption band of PEG and amino weakened obviously. It is indicted that PEG was separated in muggy treatment which depressed amino content of the film.

As film cross-linked with ECH (Curve *e*), the peak intensity decrease at 1,100 cm^{-1} attributes to C–O bond. It is obviously that the carbon atom of the hydroxyl groups of chitosan has participated in cross-linking reaction. After the film washed with hydrochloric acid solution finally (Curve *f*), absorption of amino band significantly increased, moving to the higher wave number, and the peak at 1,657 cm^{-1} of Schiff base decreased, indicating that hydrochloric acid treatment can neutralize Schiff base efficiently.

3.2. Morphology of CPCS film

SEM micrographs of pure chitosan film (a), CPCS film (b), and cross-section of CPCS film (c) are shown in Fig. 2, the morphologies of both films are different. The surfaces of pure chitosan films were relatively flat, homogeneous, and smooth. However, the surface of CPCS films were roughness and the cross-section showed lamellar and porous microstructure. This is attributed to the formation of 3D macroporous layered structure. The adsorption capacity for aromatics substances depends mainly on the available immobilized groups, the presence of amorphous domains in the membrane structure, and the surface area of the adsorbent [7]. The presence of porous surface structure provides suitable sites for Congo red adsorption leading a higher degree of adsorption of the films.

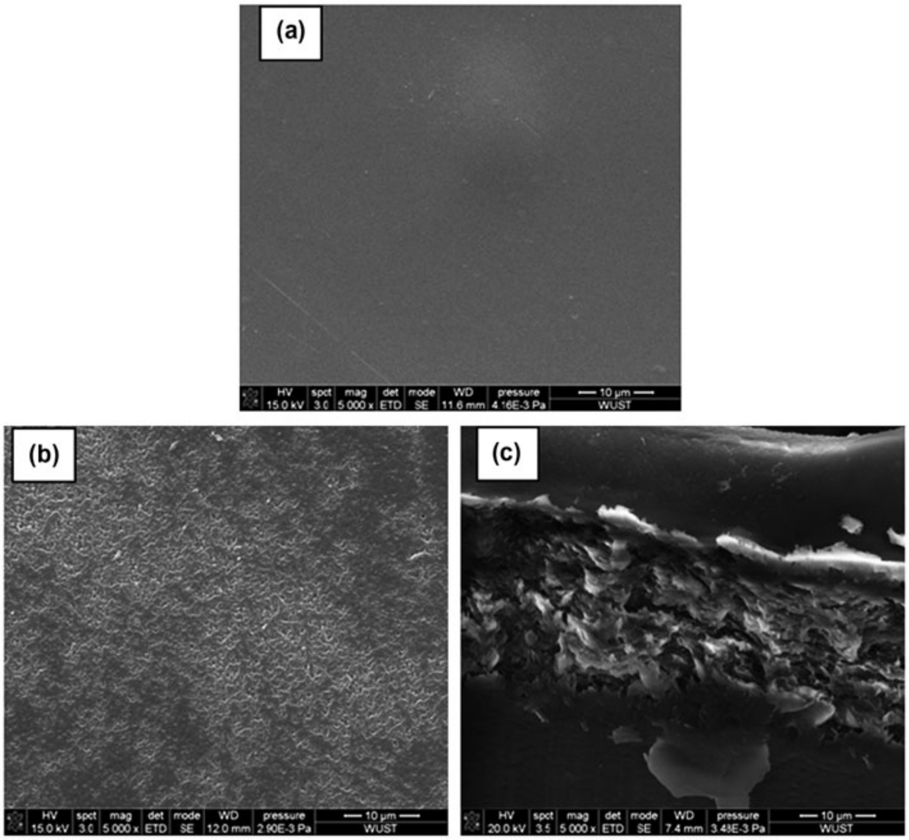

Fig. 2. SEM micrographs of chitosan film (a), CPCS film (b), and the cross-section of CPCS film (c).

3.3. Effect of contact time on adsorption percent

In the test for investigation of the effect of contact time on adsorption capacities of CR experiments, 0.1 g adsorbent and 50 mL CR solution (initial concentration 50 mg/L) were used. It is observed from Fig. 3 that the adsorption of CR is rapid from the beginning of the experiment and thereafter it proceeds at a slower rate and finally reaches to equilibrium. As illustrated in Fig. 3, the adsorption efficiency of CR onto CPCS films by adsorption for 1 h can reach up to 69.8%. The adsorption increases to 88.9% in the condition of double time. According to resent paper, there are four common steps involved in an adsorption process [8]. The first step is bulk diffusion process in which adsorbates migrate from bulk solution onto the surface of the adsorbent. Secondly, is the film diffusion where the adsorbates diffused through boundary layer to the adsorbent surface. Pore diffusion or intraparticle diffusion then takes place which allows adsorbates to diffuse from the surface to the inner part of the adsorbent particles and finally adsorbed on the active sites. That is why the adsorption becomes slower near the equilibrium. Fig. 3 also shows that the adsorption rate of CR can reach to 94.4% after adsorption for 4 h. Based on the above results, 4 h was fixed as equilibrium time throughout this study.

3.4. Effect of initial CR concentration on adsorption percent

The effect of the initial CR concentration on dye removal was carried out by vibrating 50 mL various dye concentrations of CR solution and adding 0.1 g adsorbent at room temperature for 4 h. The test show that the amount of CR molecule adsorbed onto CPCS film increased from 9.64 to 37.5 mg/g with an increase of the initial CR concentration from 20 to 200 mg/L in the initial concentration of dye solution, while adsorption percent decreased from 96.4 to 37.5% (Fig. 4). The adsorbing capability increasing with the initial CR concentration is due to the increase in the driving force of the concentration gradient with the higher initial dye concentration [9]. The adsorption of dyes by CPCS film is very intense and reaches equilibrium very quickly at low initial concentration. This is because, in the case of lower concentrations, the ratio of initial number of dye molecules to the available adsorption sites is low and subsequently the molecules form itself into monolayer coverage at the outer interface of the adsorbent. In the case of higher concentrations, the removal of dyes depends on the concentration gradient and the diffusion of exchanging molecules within CPCS film, because of the number of available adsorption sites is a constant [10]. So, the amounts of unadsorbed molecules increase with the initial dye concentration, leading to the decrease of adsorption.

3.5. Effect of pH on adsorption percent

Fig. 5 shows the adsorption percent of CR at different pH of initial CR solution. It can be observed that the adsorption efficiency of the adsorbents increases with an increase in pH of the initial solution from 3 to 5, and decrease thereafter. In acidic medium, the free amino groups of chitosan are protonated and this facilitates electrostatic interaction between the adsorbent and the anionic (R–SO_3^-) group in the CR molecule [11]. Consequently, high adsorption capacity of CR on adsorbent occurs when pH is around 4~6. Below this range, a large excess of competitor anions limits adsorption efficiency [12]. Hence adsorption percent decreases from 94.9 to 54.5% with pH decrease from 4 to 3. On account of successive deprotonation of positive charged groups on the adsorbent and electro-

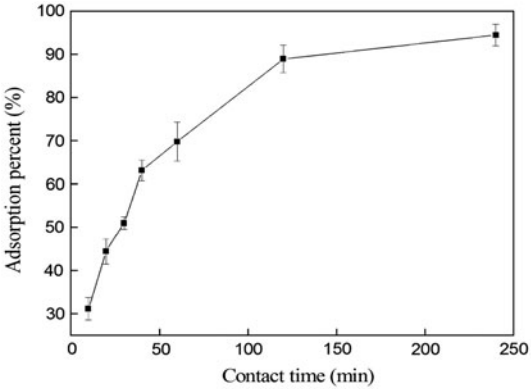

Fig. 3. Influence of contact time on adsorption percent.

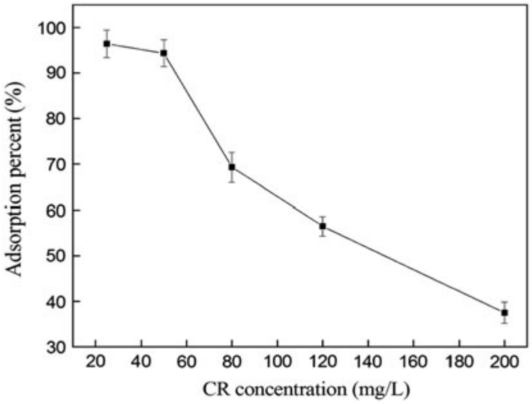

Fig. 4. Influence of CR concentration on adsorption percent.

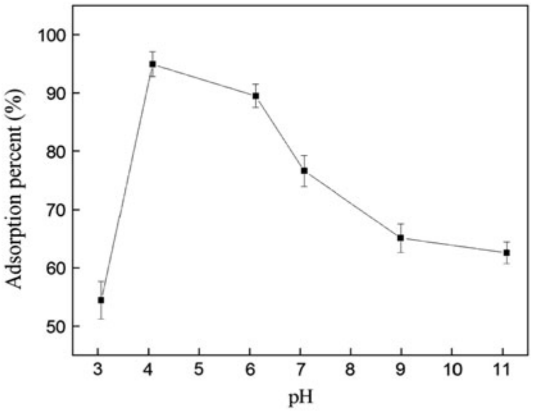

Fig. 5. Influence of pH on adsorption percent.

static repulsion between negatively charged sites on the adsorbent and CR molecules, the adsorption percent of CPCS film decreases from 90.5 to 62.6% with the initial pH of CR solution increases from 6 to 11. Moreover, the decrease in adsorption percent could also be interpreted by enhanced formation of OH^- ions that compete with the dye anionic species for the adsorption sites.

3.6. *Effect of temperature on adsorption percent and adsorption thermodynamics*

The effect of temperature on dye removal was carried out in the 50 mL dye solution (50 mg/L,) by adding 0.1 g adsorbent under vary temperature for 4 h. Table 1 shows that uptake of Congo red by CPCS films appear to increase (25–45℃) firstly and then keep balance (45–65℃) with an increase in temperature. An increase in temperature is followed by an increase in the diffusivity of the dye molecule, moreover, the dimensions of the chitosan pores increased with temperature, which reduce the contribution of intraparticle diffusion resistance [13]. So, the increase with the temperature seems to decrease the impact of the boundary-layer effect. Thus, the adsorption percent increases as the temperature increases from 25 to 45℃. However, with the increase of temperature, the solubility of the dye also increase, the interaction forces between the solute and the solvent become stronger than those between solute and adsorbent, consequently the solute is more difficult to adsorb with further increasing temperature [14]. Consequently, the dyes are more difficult to further adsorb, and the adsorption percent keep still while the temperature increases from 45 to 65℃.

To better understand the effect of temperature on the adsorption, it is important to study the thermodynamic parameters such as standard Gibbs free energy change ΔG^0, standard enthalpy ΔH^0, and standard entropy ΔS^0. The Gibbs free energy of adsorption by using equilibrium constant (K_c) is calculated from the following equation:

$$\Delta G^0 = -RT \ln K_c \tag{1}$$

Standard enthalpy, ΔH^0, and standard entropy, ΔS^0, of adsorption can be estimated from van't Hoff equation given in:

$$\ln K_c = \frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \tag{2}$$

where R is the gas constant, K_c is adsorption equilibrium constant. The K_c value is calculated from the equation [6].

$$K_c = \frac{C_{\mathrm{Ae}}}{C_{\mathrm{Se}}} \tag{3}$$

where C_{Ae} is the equilibrium concentration of the dye ions on adsorbent (mg L^{-1}) and C_{Se} is the equilibrium concentration of the dye ions in the solution (mg L^{-1}).

Thermodynamic parameters obtained are given in Table 1. As shown in the table, the negative values of ΔG^0 at different temperatures indicate the spontaneous nature of the adsorption process. Positive ΔH^0 reveals endothermic adsorption. The positive value of ΔS^0

Table 1
Effect of temperature on adsorption percent and thermodynamic parameters for the adsorption of Congo red onto CPCS film

Temperature (℃)	Adsorption (%)	K_c	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (kJ/mol K)
25	68.6	2.19	−1.940	3.881	0.124
35	78.6	3.68	−3.336	–	–
45	91.9	11.45	−6.450	–	–
55	95.5	21.13	−8.324	–	–
65	96.5	28.29	−9.399	–	–

suggests the increased randomness at the solid/solution interface during the adsorption of the dye onto CPCS film. A similar trend has been reported for the adsorption of Congo red onto fly ash [15].

3.7. Adsorption isotherm

Adsorption isotherms are important for the description of how molecules of adsorbate interact with adsorbent surface. The Langmuir isotherm model assumes monolayer coverage of adsorbate on a homogeneous adsorbent surface. This model does not consider surface heterogeneity of the sorbent. It assumes adsorption will take place only at special site on the adsorbent. The Freundlich isotherm model is an empirical equation that describes the surface heterogeneity of the sorbent. It considers multilayer adsorption with a heterogeneous energetic distribution of active sites, accompanied by interactions between adsorbed molecules.

The Langmuir isotherm is expressed:

$$\frac{1}{q_e} = \frac{1}{q_{\max}} + \frac{1}{bq_{max}C_{\mathrm{e}}} \tag{4}$$

where C_{e} is the equilibrium concentration of the adsorbate (mg L^{-1}), $q_{\max}$ (mg g^{-1}) and b (L mg^{-1}) are the Langmuir constants related to the maximum adsorption capacity and the energy of adsorption, respectively. $q_{\max}$ and b are calculated from the slopes and intercepts of the straight lines of plot of $1/q_{\mathrm{e}}$ vs. $1/C_{\mathrm{e}}$.

The Freundlich adsorption isotherm can be expressed as:

$$\ln q_{\mathrm{e}} = \ln k_{\mathrm{f}} + \frac{1}{n}\ln C_{\mathrm{e}} \tag{5}$$

where k_{f} and n are Freundlich adsorption isotherm constants, being indicative of the extent of the adsorption and the degree of nonlinearity between solution concentration and adsorption, respectively. k_{f} and $(1/n)$ can be determined from the linear plot of ln q_{e} vs. ln Ce.

Table 2 shows the calculated values of Freundlich and Langmuir model's parameters. The values of R^2 of Langmuir and Freundlich models are 0.9955 and 0.8979, respectively. It can be concluded that the Langmuir isotherm best represents the equilibrium adsorption of CR on CPCS film, which suggests the monolayer coverage of the dye on the surface of the adsorbent. And the maximum sorption capacity ($q_{\max}$) calculated from Langmuir isotherm was 40.65 mg g^{-1}

Table 2
Adsorption isotherm constants for adsorption of Congo red on CPCS films at 25°C

Freundlich adsorption model			Langmuir adsorption model		
n	k_{f}	R^2	$q_{\max}$ (mg g^{-1})	b (L mg^{-1})	R^2
4.75	15.14	0.8979	40.65	0.21	0.9955

3.8. Kinetics of adsorption

To investigate the adsorption kinetics of CR onto CPCS film, pseudo-first-order, pseudo-second-order rate models, and intraparticle diffusion models were used in this study.

The pseudo-first-order rate equation is expressed:

$$\log(q_{\mathrm{e}} - q_{\mathrm{t}}) = \log q_{\mathrm{e}} - \frac{k}{2.303} \times t \tag{6}$$

In the above equation, q_{e} and q_{t} denote the amount adsorbed at equilibrium and at any time t, respectively, and k_1 is the first-order rate constant.

The pseudo-second-order rate equation is represented as:

$$\frac{t}{q_{\mathrm{t}}} = \frac{1}{k_2 q_{\mathrm{e}}^2} + \frac{t}{q_{\mathrm{e}}} \tag{7}$$

In the above equation, q_{e} and q_{t} denote the amounts adsorbed at equilibrium and at any time t, respectively, and k_2 is the second-order rate constant.

The intraparticle diffusion equation is given by:

$$q_{\mathrm{t}} = k_p t^{0.5} + C \tag{8}$$

where C is the intercept and k_{p} is the intraparticle diffusion rate constant (mg g^{-1} $min^{-0.5}$) which are determined from the linear plot of q_{t} vs. $t^{0.5}$.

The calculated parameters are given in Table 3. On comparing the R^2 values obtained for first-order and second-order kinetics, it can be easily concluded that the ongoing reaction proceeds via a pseudo-second-order mechanism rather than a pseudo-first-order mechanism. It indicates that chemisorptions might be the rate-limiting step that controls these adsorption processes [16]. The high R^2 value for the intraparticle diffusion model indicates that intraparticle diffusion might play a significant role in the adsorption. The adsorption of CR probably takes place via surface exchange reactions in the initial

Table 3
Adsorption parameters of kinetic for the adsorption of 50 mg/L Congo red on CPCS films

Pseudo-first-order kinetic models			Pseudo-second-order kinetic models			Intraparticle diffusion models		
k_1 (min^{-1})	q_{e1} (mg/g)	R^2	k_2 (g mg^{-1} min^{-1})	q_{e2} (mg/g)	R^2	k_p (g mg^{-1} min$^{-0.5}$)	C	R^2
7.3926×10^{-3}	7.87	0.8118	0.1395×10^{-2}	25.91	0.9982	1.29	5.95	0.9472

stage of the adsorption, thereafter dye molecules diffuse into the polymer network for further interactions and/or reactions.

4. Conclusion

This study demonstrates that CPCS film is a promising adsorbent for the removal of CR from aqueous solution. The results demonstrated that the adsorption process is dependent on contact time, initial CR concentration, adsorbent dosage, solution pH, and temperature. When 0.1 g adsorbent were used to deal with 50 mL CR solution (initial concentration 50 mg/L), with the solution pH of 4–6, adsorption for 4 h under 25℃, the adsorption percent could reach up to 96%. The maximum sorption capacity ($q_{\max}$) of CPCS film at 25℃ calculated from Langmuir isotherm was 40.65 mg g^{-1}. Several studies have been investigated on removal of CR in aqueous solution using different adsorbents, such as waste orange peel [17], bagasse fly ash [2], activated red mud [18], and kaolin [19]. The $q_{\max}$ of these adsorbents was 22.44, 11.88, 7.08, and 5.44 mg g^{-1}, respectively. CPCS film exhibits higher adsorption capacity in CR adsorption. However, the high cost may be the limitation in use of CPCS film.

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