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Adsorption properties of nano-cellulose hybrid containing polyhedral oligomeric silsesquioxane and removal of reactive dyes from aqueous solution

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ABSTRACT

Dyeing wastewater is an important class of pollutants, which can be identified by human's eye. The release of some dyes in water streams has serious environmental impacts. Nano-cellulose hybrids containing polyhedral oligomeric silsesquioxane with multi-*N*-methylol (R-POSS) could be used as novel biosorbents for dyes. Adsorption properties of nano-cellulose hybrid for reactive dyes from aqueous solution were investigated. Reactive dyes, Yellow B-4RFN, and Blue B-RN, were used. The surface chemical ingredient of the hybrid was analyzed by X-ray photoelectron spectroscopy (XPS). The removal capacities of nano-cellulose hybrid materials for reactive dyes from aqueous solution were significantly higher than that of control cellulose. The adsorption kinetics of two reactive dyes, Reactive Yellow B-4RFN and Reactive Blue B-RN, were good fit with the second-order models. Nano-cellulose hybrids have potential application as biosorbents in the low concentration dyeing wastewater.

1. Introduction

Dyeing and finishing of textile fabrics are generally performed in water based media. This process has environmental problems including water pollution due to discharge of various chemical additives (Donia, Atia, Al-Amrani, & Ei-Nahas, 2009; Hou, Chen, Dai, & Zhang, 2010). Reactive dyes are mainly dyes for cellulose fabrics. However, the fixation of the reactive dyes on cellulose fabrics is lower and a lot of unfixed dyes may be lost to the effluent during dyeing processes. Removing pollutant from wastewater has grown with rapid industrialization (Hou, Wang, & Yu, 2009; Sang & Hudson, 2004; Wang & Lewis, 2002). Recently, many new treating wastewater methods have been developed for decontaminating purposes, including electrochemical process, biological technique, chemical oxidation, membrane separation, and adsorption (Donia et al., 2009; Husain, 2006; Qada, Allen, & Walker, 2008). Adsorption is one of the important methods for removing dyes. However, some adsorption materials used are either ineffective or expensive; especially dyes in wastewater are present at low concentration (Gupta and Suhas, 2009; Xue, Hou, & Zhu, 2009). The development of low-cost or new effective composition for adsorption attracts a large number of researchers. New biomasses and their composites from natural polymers should be developed because of their nature and reproduce (Hasan, Ahmad, & Hameed, 2008; Tastan, Ertugrul, & Donmez, 2010; Vimonses, Lei, Jin, Chow, & Saint, 2009).

Cellulose fiber is one of the excellent natural biomaterials and easy to be reused. Cellulose has been explored as a substrate for composite materials because of the presence of functional groups that may be employed in various activation processes (Hou & Sun, 2009). The polyhedral oligomeric silsesquioxane (POSS) derivatives as functional and reactive reagents play an important role in preparation of hybrid materials (Liu, Kondo, Tanaka, Oku, & Unno, 2008). Reactive polyhedral oligomeric silsesquioxane containing multi-*N*-methylol (R-POSS) is a functional and attractive staring monomer for new reinforcement materials. In our previous work, high-reactive polyhedral oligomeric silsesquioxane containing multi-*N*-methylol groups was synthesized and utilized for preparing nano-cellulose hybrids. Nano-structure of R-POSS was observed by field emission scanning electro microscope (FSEM) and AFM. (Xie, Gao, & Zhao, 2010) R-POSS monomer imparted a nano-sized inorganic core and organic corner with multi-*N*-methylol groups. R-POSS could readily crosslink to cellulose polymer and improve elastic recovery of hybrids. Thermal degradation properties of the nano-cellulose hybrids were reported (Xie, Zhang, & Chen, 2010). The incorporation of R-POSS in the cellulose slightly decreased the thermal degradation temperature. Nano-cellulose hybrids has a nanometer-sized cubic core and numerous organic functional groups (–C–N–), which impart significant adsorption for reactive dyes. Isotherm adsorption mathematical model on the nano-cellulose for reactive dyes were also analyzed (Xie, Gao, &

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Gao, 2010). The adsorptions of dyes on the hybrids were good fit with Langmuir isotherm equation.

In this paper, adsorption properties of nano-cellulose hybrid for Reactive Yellow B-4RFN and Reactive Blue B-RN aqueous solutions were further investigated. Adsorption kinetics of nano-cellulose hybrid for Reactive Yellow B-4RFN and Reactive Blue B-RN were investigated, respectively. The effects of temperature and time on the adsorption properties of nano-cellulose hybrid were discussed.

2. Experimental

2.1. Materials

Reactive dyes, Yellow B-4RFN and Blue B-RN, were obtained from Shanghai Matex Chemical Company, Shanghai, China. Scoured and bleached cellulose fabric (cotton fiber, control sample) was obtained from Jinqiu Textile Company, Shaoxing, China. R-POSS was obtained from National Engineering Research Center of Dyeing and Finishing of Textiles, Shanghai, China. Dimethyloldihydroxyethylene urea (DMDHEU) was obtained from Handa Chemical Company, Shanghai, China. Other chemicals were obtained from Shanghai Chemical Reagent Plant, Shanghai, China.

2.2. Preparation of nano-cellulose hybrid containing R-POSS

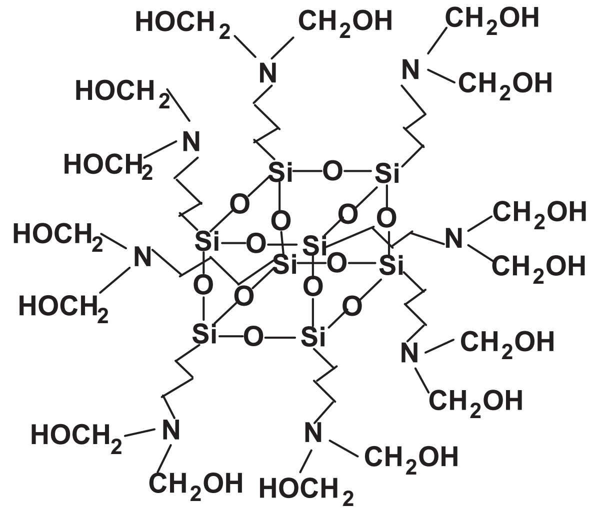
Nano-cellulose hybrid containing R-POSS was prepared according to the reference method (Xie, Zhang, et al., 2010). However, there is some difference in ingredient. The ingredient of mixture used: R-POSS 2.4% (w/w), DMDHEU 5% (w/w), citric acid 1% (w/w) and $MgCl_2{\cdot}6H_2O$ 1.5% (w/w). After crosslinking finish, the sample was rinsed in hot water at 65 °C for 15 min at liquor ratio 1:15. Then, the sample was removed and air-dried.

2.3. Surface chemical component analysis and FT-IR spectra

X-ray photoelectron spectroscopy (XPS) was carried out with a Thermo ESCALAB 250 (USA), using Al Kα excitation radiation ($h\nu$ = 1486.6 eV). FT-IR spectra of the samples were measured by a OMNI Sampler of the Nexus-670 FT-IR-Raman spectrometer (Nicolet Analytical Instruments, Madison, WI) using a single ART reflecting method.

2.4. The adsorption removal ratio of dyes on the hybrid

Batch adsorption investigations were performed in 100 ml solution of initial dye concentrations 40 mg/l. The samples (nano-cellulose hybrid and control sample) were cut into a piece of square sample (0.2 g), respectively. The experiments were carried out at 303 K. The concentrations of dyes were measured by a 723 UV-Vis spectrophotometer (Shanghai Analysis Co., China). The adsorption removal ratio (E, %) was calculated by Eq. (1).



Scheme 1. Chemical structure of reactive polyhedral oligomeric silsesquioxane containing multi-*N*-methylol groups.

$$E(\%) = \left(\frac{C_0 - C_1}{C_0}\right) \times 100\% \tag{1}$$

where C_0 is the initial concentration of reactive dyes, C_1 is the final concentration of reactive dyes. Each experiment was repeated three times independently and the means were taken.

2.5. Effect of temperature and time on adsorption properties of dyes on the hybrid and its kinetics

Adsorption investigations were performed in the solution (100 ml) of the initial dye concentration, 40 mg/l. The nano-cellulose hybrids were cut into pieces of square sample (0.2 g). The experiments on the effect of time were carried out at 303 K. The samples were taken at interval time, and the concentrations of dyes were measured by a 723 UV-Vis spectrophotometer. The experiments on the effect of temperature were carried out for 5 h at desired temperatures, 303 K, 313 K, 323 K and 333 K, respectively.

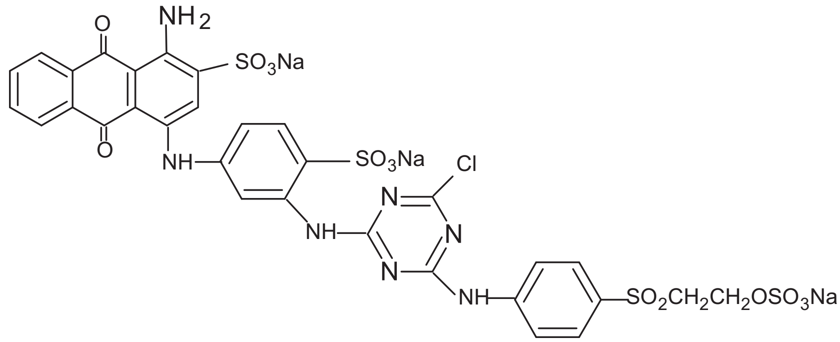
The q_t (mg/g) is the amount of adsorption at time t, and is calculated with Eq. (2).

$$q_t = \frac{(C_0 - C_t) \times v}{m} \tag{2}$$

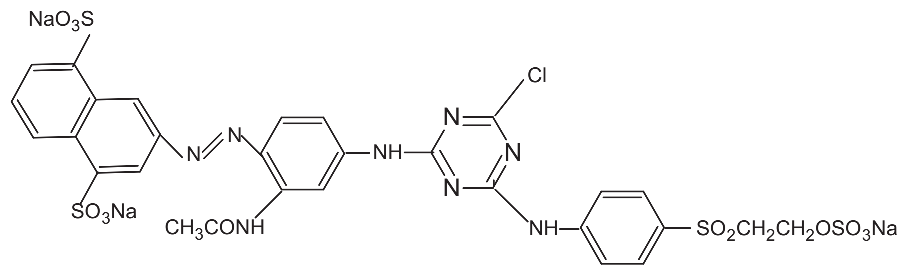
where q_t was the adsorbed amount per unit mass of adsorbent at time t. C_0 was the initial concentration of dyes. C_t was the dye solution concentration at time t; m was the mass of adsorbent (g) and v was volume of solutions (l).

Table 1
XPS data of samples.

	Name	Peak BE	FWHM (eV)	Area (P) CPS (eV)	At. (%)
Control sample	C1s (C–C, C–H)	284.80	1.59	10301.63	16.03
	C1s (C–O)	286.56	1.59	22627.09	35.23
	C1s (C=O)	288.16	1.59	4410.30	6.87
	O1s (–O–)	533.00	1.91	62179.08	41.40
	Si2p	101.51	0.23	358.51	0.48
Hybrid	C1s (C–C, C–Si)	284.79	1.38	19847.20	30.78
	C1s (C–O)	286.48	1.30	17318.08	26.87
	C1s (C=O)	287.97	1.30	3880.18	6.59
	O1s (–C–O–)	532.83	1.59	45492.92	30.19
	O1s (Si–O–)	531.46	1.59	6562.72	4.35
	Si2p	102.21	1.69	912.74	1.22



Reactive Blue B-RN



Reactive Yellow B-4RFN

Scheme 2. Chemical structures of two reactive dyes.

3. Results and discussion

3.1. Surface component analysis of nano-cellulose hybrids with R-POSS

Reactive polyhedral oligomeric silsesquioxane bearing multi-*N*-methylol groups (R-POSS) is high reactive POSS monomer. The structure of R-POSS is shown in Scheme 1.

The high-reactive multi-*N*-methylol of R-POSS can be used to crosslink cellulose and forms network structure containing nano-sized inorganic particles. The FT-IR spectrum of crosslinked cellulose showed the typical absorption bands for Si–O– were located at 1650 and 810 cm^{-1}. Meantime, the characteristic absorption band of the –OH near 3470 cm^{-1} became weaker. It can be seen that R-POSS had been grafted to cellulose macromolecule. In order to further investigate the surface ingredient, X-ray photoelectron spectroscopy (XPS) was applied for this study. The C1s, O1s and Si2p spectrum data of samples are summarized in Table 1. The peak area of C1s for the hybrid at 284.80 noticeably increased. The peak area of C1s for the hybrid at 284.80 was attributed to C1s (C–C, C–Si). The peak area of Si2p for the hybrid at 102.21 also significantly increased. It indicates that C–C and C–Si bonds in the nano-cellulose surface significantly increased. The atom percent of silicone in the hybrid was higher than that of control sample.

3.2. Adsorption properties of nano-cellulose for reactive dyes from aqueous solution

It is well known that the adsorption by activated carbon is an effectively and commercially applicable method for removing color and other pollutants from dyeing wastewater. However, activated carbon is expensive, with high regeneration cost and 10–15% loss in the adsorption procedure (Kobya, Demirbas, Senturk, & Ince, 2005). Nano-cellulose macromolecules have numerous aminos, which impart positive charge on cellulose. They could form numerous new adsorptive positions for reactive dyes. The reactive dyes, Yellow B-4RFN and Blue B-RN, were used. Chemical structures of them are shown in Scheme 2. The chemical structures of the reactive dyes are simple and have high water-solubility in the aqueous solution.

The adsorption ratios of nano-cellulose for Reactive Yellow B-4RFN and Reactive Blue B-RN aqueous solutions were measured (shown in Fig. 1). The adsorption ratios of control sample for Reactive Yellow B-4RFN and Reactive Blue B-RN were small, and did not access 10%. Comparing with control sample, the adsorption capacity of nano-cellulose hybrid for Reactive Yellow B-4RFN and Reactive Blue B-RN significantly increased. It can be attributed to the organic functional groups (–C–N–) and numerous nanometer-sized cubic cores in nano-cellulose hybrids. The organic functional groups (–C–N–) impart cationic properties on the hybrid cellulose surface. It could improve surface adsorption capability of the hybrids for reactive dyes. The adsorption ratios of two dyes on hybrid increased with the adsorption time.

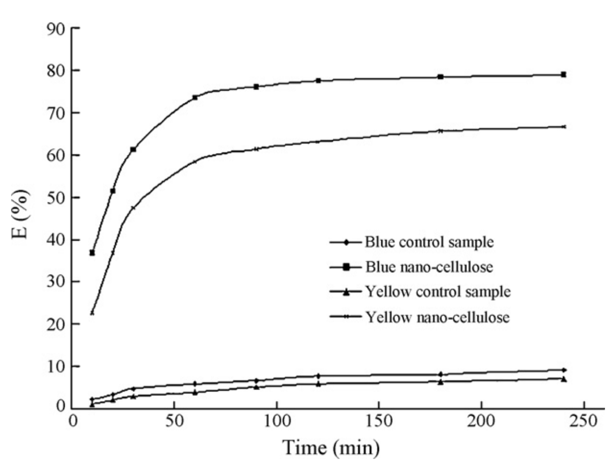


Fig. 1. Adsorption ratio of reactive dyes from aqueous solution.

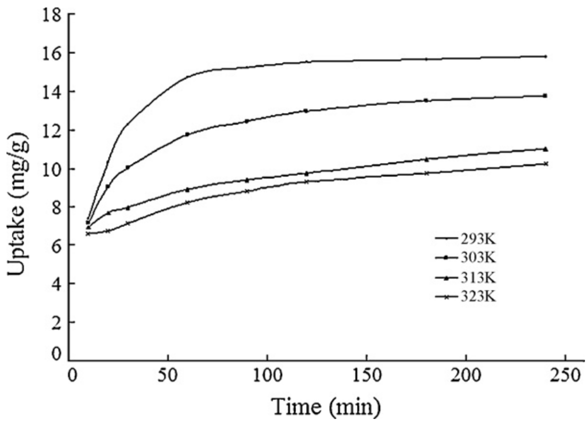


Fig. 2. Effects of adsorbing time and temperature on Reactive Blue B-RN.

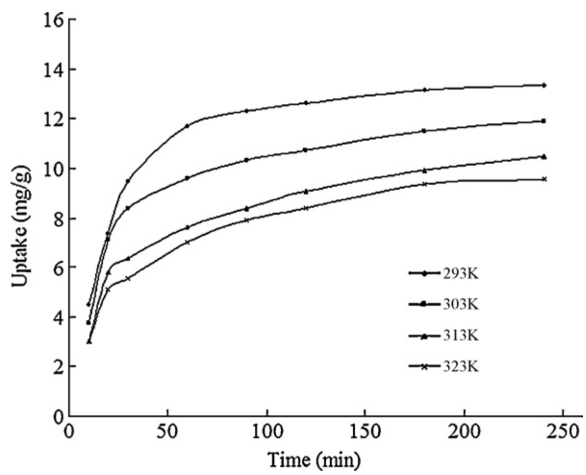


Fig. 3. Effects of adsorbing time and temperature on Reactive Yellow B-4RFN.

3.3. Effect of temperature and time on the adsorption properties of nano-cellulose hybrid

The effects of temperature and time on the adsorption of reactive dyes on control sample and the hybrid were investigated at pH 7. The results are shown in Figs. 2 and 3. The uptakes of two dyes, Reactive Yellow B-4RFN and Reactive Blue B-RN, increased initially with the adsorption time, and then slowed down after 100 min, and reached equilibrium at 240 min. The temperature had significant influences on the uptakes of Reactive Yellow B-4RFN and Reactive Blue B-RN. The adsorption curves of Reactive Yellow B-4RFN were similar with that of Reactive Blue B-RN. The higher the temperatures were, the lower the amounts of adsorbed dyes by the hybrid were. It could be explained that desorption rate increased in adsorption–desorption balance at higher temperature.

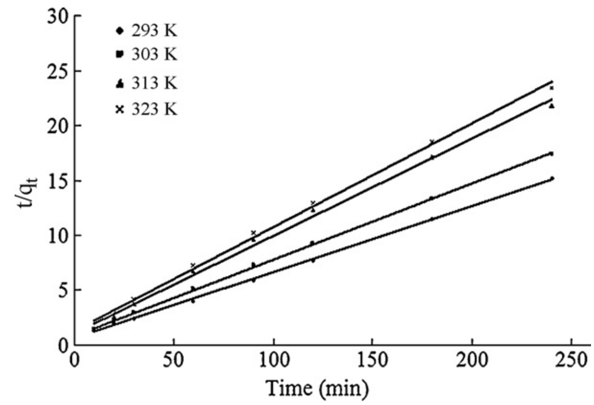


Fig. 4. Adsorption curves of Reactive Blue B-RN on the nano-cellulose hybrid.

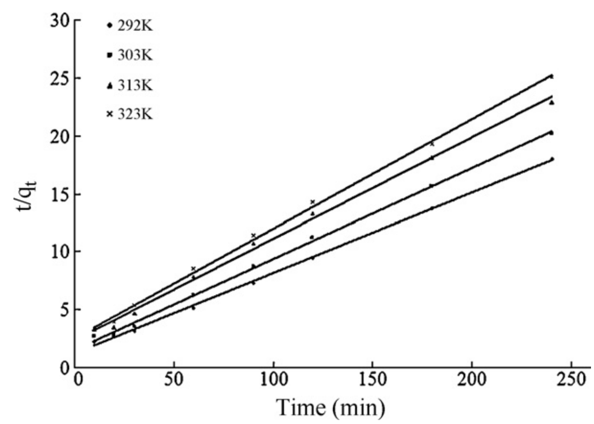


Fig. 5. Adsorption curves of Reactive Yellow B-4RFN on the nano-cellulose hybrid.

3.4. Adsorption kinetics of dye on the nano-cellulose hybrids

The adsorption kinetics of Reactive Yellow B-4RFN and Reactive Blue B-RN were studied at different temperatures, respectively. The dynamic experimental data were treated according to the second-order equation model (Eq. (3)).

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{3}$$

where q_e and q_t refer to the amount of dye (mg/g) at equilibrium and at t time (min), k_2 is the overall rate constant of the pseudo-second order of adsorption (g mg^{-1} min^{-1}). The kinetic parameters were obtained from the straight-line plots between t/q_t vs. t.

The straight-line plots of t/q_t vs. t of Reactive Yellow B-4RFN and Reactive Blue B-RN on the nano-cellulose hybrids are shown in Figs. 4 and 5, respectively.

Adsorption curves of Reactive Blue B-RN and Reactive Yellow B-4RFN on the nano-cellulose hybrid at different temperatures showed good line relationship. The kinetic equations and kinetic

Table 2
Kinetic parameters at different temperatures.

Dyes	Temperature (K)	k_2 (10^{-2}) [g (mg min)$^{-1}$]	q_e (mg/g)	R^2
Reactive Blue B-RN	293	0.42	14.40	0.9957
	303	0.40	12.76	0.9945
	313	0.398	11.16	0.9986
	323	0.39	10.35	0.9990
Reactive Yellow B-4RFN	293	0.71	16.61	0.9970
	303	0.69	14.43	0.9963
	313	0.55	11.28	0.9997
	323	0.55	10.56	0.9994

parameters of the dyes are shown in Table 2. It can be seen that the adsorptions of Reactive Yellow B-4RFN and Reactive Blue B-RN on hybrid at certain temperatures were good fit with the second-order model. Equilibrium adsorption uptakes of two dyes on the hybrid decreased with increasing temperature.

4. Conclusion

Nano-cellulose hybrids could form new adsorptive position for reactive dyes. The adsorption capacities of the hybrid materials were obviously higher than that of control cellulose. The higher the temperature, the lower the amount of the adsorbed dyes by the hybrids was. The adsorptions of two reactive dyes, Reactive Yellow B-4RFN and Reactive Blue B-RN, on nano-cellulose hybrid at certain temperatures were good fit with the second-order models.

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