Chemosphere 141 (2015) 297–303

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Effective removal of cationic dyes using carboxylate-functionalized cellulose nanocrystals

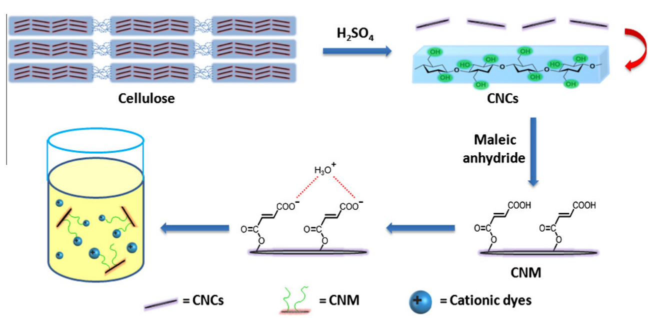
Han Qiao, Yanmei Zhou *, Fang Yu, Enze Wang, Yinghao Min, Qi Huang, Lanfang Pang, Tongsen Ma

Institute of Environmental and Analytical Sciences, College of Chemistry and Chemical Engineering, Henan University, Kaifeng, Henan 475004, PR China

HIGHLIGHTS

- The graft rate of maleic anhydride on cellulose nanocrystals can reach a high value of 88.8%.
- CNM exhibited wide adsorption capacities to cationic dyes.
- CNM displayed a rapid adsorption rate and an efficient adsorption capacity to crystal violet.
- CNM could be regenerated and reused for adsorption of crystal violet at least four times.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 8 May 2015
Received in revised form 27 July 2015
Accepted 29 July 2015

Keywords:
Cellulose nanocrystals
Maleic anhydride
Adsorption
Cationic dyes
Crystal violet

ABSTRACT

A novel carboxylate-functionalized adsorbent (CNM) based on cellulose nanocrystals (CNCs) was prepared and adsorptive removal of multiple cationic dyes (crystal violet, methylene blue, malachite green and basic fuchsin) were investigated. The maximum cationic dyes uptakes ranged from 30.0 to 348.9 mg g^{-1} following the order of: CNM > CNCs > raw cellulose. Furthermore, the removal of crystal violet by CNM was investigated representatively where kinetics, thermodynamics and isotherm analysis were employed to explain in-depth information associated with the adsorption process. The adsorption kinetics fitted well to the pseudo-second-order model and thermodynamic analysis revealed that the adsorption process was spontaneous and exothermic. Meanwhile, isothermal study demonstrated a monolayer adsorption behavior following the Langmuir model with a calculated maximum absorption capacity of 243.9 mg g^{-1}, which is higher than those of many other reported adsorbents. These findings prefigure the promising potentials of CNM as a versatile adsorbent for the efficient removal of cationic dyes from wastewater.

1. Introduction

Nowadays, dyes and pigments are widely consumed in the leather, textile dyeing, pharmaceutical, and cosmetic industries. Release of the dye contaminants to the environment have aroused worldwide concerns due to their toxic effects, such as teratogenetic, mutagenic and carcinogenic action to aquatic biota and humans. Hence, removing the dyes from wastewater to an acceptable level before discharging into the natural environment is a challenge for industries (El-Sayed, 2011). To date, various physicochemical and biological strategies, including catalytic degradation (Wang et al., 2015), photocatalysis (Dong et al., 2010), chemical precipitation (Yuan et al., 2014), membrane filtration (Staicu et al., 2015) and adsorption (Wu et al., 2014) have been developed to lessen dyes' pollution and hazards. Among these

* Corresponding author.
E-mail address: zhouyanmei@henu.edu.cn (Y. Zhou).

http://dx.doi.org/10.1016/j.chemosphere.2015.07.078
0045-6535/

techniques, adsorption is considered as one of the competitive methods because of its low costs, simple operation and high efficiency. Thus, developing new adsorbents with high adsorption capacities is of great significance and challenge for persistent dyes pollution in the environment.

Over the past years, cellulose and its modified forms have been developed as a new class of versatile adsorbents for various pollutants removal from aqueous solutions (Liu et al., 2011; Li et al., 2014; Qiu et al., 2014). As a long-chain polysaccharide, cellulosic fiber is made up of repeating β-D-glucopyranose units and consists of three hydroxyl groups per an hydroglucose unit, which provide numerous active adsorption sites and give the cellulose molecule a high degree of functionality to improve its removal capacity. Native cellulose consists of amorphous and crystalline regions through hydrogen bonds and van der Waals forces, and the amorphous regions have lower density compared to the crystalline regions (Domingues et al., 2014). When subjected to the proper combination of mechanical, chemical and/or enzymatic treatments, individualized nanofibers can be released by breaking down the amorphous regions, resulting in so-called cellulose nanocrystals (CNCs) (Abdul Khalil et al., 2014). In contrast to cellulose fibres, CNCs possess high aspect ratio, large specific surface area, high specific strength and large number of reactive surface groups and are well suited for the scaffolds fabrication of functional adsorbents (Lin et al., 2012; Habibi et al., 2010). Particularly, the low ecotoxicological risk, excellent biodegradability and high relatively reactive surface of CNCs cannot only match the desirable eco-friendly sustainability but also introduce intriguing application prospects. Moreover, when cellulose reacts with sulfuric acid, the charged surface sulfate esters can promote dispersion of the CNCs in water and provide high adsorption capacity to remove positively charged species (Moon et al., 2011; Batmaz et al., 2014; Mu and Gray, 2014; Araki et al., 1998). These special characters of CNCs expanded their potential applications as functional adsorbents for water purification and pollutants removal. On the basis of the predominant advantages, several adsorbent materials based on CNCs have already been proposed for the efficient adsorption of toxic pollutions (Zhou et al., 2013a, 2014a; He et al., 2014; Wang et al., 2014b).

The aim of this work is to ascertain the potentials of carboxylate-functionalized adsorbent based on cellulose nanocrystals as a versatile adsorbent in the removal of multiple cationic dyes. Maleic anhydride was utilized for introducing carboxylic groups onto CNCs via ring-opening esterification reaction. Adsorption capacities for cationic dyes including crystal violet (CV), methylene blue (MB), malachite green (MG) and basic fuchsin (BF) by CNM, CNCs and raw cellulose were compared. Furthermore, the adsorption behavior of CV onto CNM and CNCs, including the factors potentially affecting the adsorption and the adsorption kinetics, thermodynamics, isotherms were investigated representatively. Finally, the recyclability of CNM for the CV adsorption was also examined.

2. Experimental

2.1. Materials

All solvents used in this study were of analytical grade, and the chemicals used for synthesizing were of reagent grade and commercially available. Cellulose (99.5%) was purchased from Henan Xiren Cellulose Co., Ltd. and used as received. Maleic anhydride (99.5%) was purchased from the Tianjin No. 1 chemical reagent factory. Deionized water was used throughout the experiments.

2.2. Preparation of CNM

Acid hydrolysis was utilized in the preparation of cellulose nanocrystals referring previously described in the literatures (Rosa et al., 2010; Kos et al., 2014; Wang et al., 2014a). A total of 10 g cellulose was mixed with 85 mL of 64 wt% sulfuric acid at 45 °C for 30 min under vigorous mechanical stirring. After that, the resulting suspension was diluted with three times amount of water to stop the reaction, and then washed with deionized water by repetitive centrifugations (3000 rpm, 20 min per cycle) until the pH remained constant. Then the CNCs were obtained after repeated dialysis and freeze-dried process for further usage.

CNM was synthesized by grafting maleic anhydride on the hydroxyl groups of CNCs. Dried CNCs were dispersed in pyridine with constant magnetic stirring. Excess maleic anhydride was added then refluxed 24 h at 120 °C in an oil bath. The result mixture was filtered and washed with ethanol, distilled water and acetone in turns. Finally, CNM was obtained by drying process. The detailed information of characterization methods (SEM, AFM, FT-IR, XRD and TGA) are presented in supporting information.

2.3. Adsorption measurement

2.3.1. Adsorption of cationic dyes and comparison

The extensive sorption behaviors of CNM for cationic dyes, such as CV, MB, MG and BF were investigated and the results were compared with those of cellulose and CNCs. 25 mg of adsorbent was accurately weighed in a conical flask, and 25 mL of cationic dyes aqueous solutions (400 mg L^{-1}) was added. The conical flask was subjected to a table concentrator for 240 min at 30 °C. The precipitate was separated and the residual concentration of supernatant solution was determined by UV–Vis spectrophotometer (TU-1900, Beijing Purkinje General Instrument. Co., Ltd. Beijing, China). The detection wavelength of CV, MB, MG, BF were record at 588, 664, 617 and 542 nm, respectively.

2.3.2. Adsorption experiments of CV

The adsorption behaviors of CNCs and CNM for CV were systematically investigated by changing the factors of adsorption time, solution pH, initial concentration and adsorption temperature. Adsorption kinetic studies were conducted with an initial CV concentration of 400 mg L^{-1} at 30 °C and the independent samples were measured at time intervals ranging from 25 to 250 min. Thermodynamic parameters were evaluated by conducting the experiments at different temperature of 10–50 °C. The adsorption isotherms experiments were performed with various initial CV concentrations (C_0 = 50–600 mg L^{-1}) for 240 min. The effect of pH on adsorption was examined by changing the initial pH value from 3.0 to 9.0 (0.1 mol L^{-1} NaOH and/or HCl solution was used to adjust the pH value). All experiments were performed in duplicate and the average values are reported. Additional analyses were conducted whenever two measurements showed a difference of larger than 5%. The removal efficiency (E, %) and the equilibrium adsorption capacity (q_e, mg g^{-1}) of dyes were calculated according to the equation evaluated of Eqs. (S1) and (S2), respectively.

2.3.3. Desorption and reusability behaviors of the adsorbents

After the sorption experiments, the spent CNM was separated by centrifugation, and dried. Then, 25 mL of 50% ethanol solution (pH 3.0) was added and the mixture was shook at 30 °C for 240 min. After that, solid–liquid separation was conducted by centrifugation. Desorption ratio was calculated by Eq. (S3).