



# Adsorptive removal of anionic dyes from aqueous solutions using microgel based on nanocellulose and polyvinylamine



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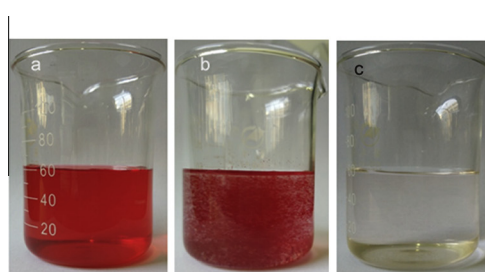
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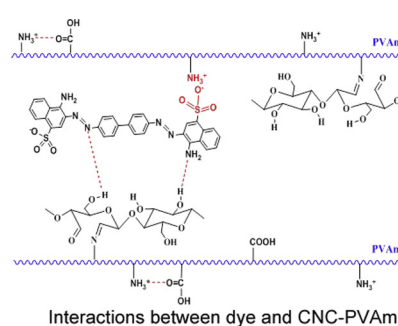
## HIGHLIGHTS

- A novel microgel was fabricated via nanocellulose and amphoteric polyvinylamine.
- It demonstrated highest dye removal efficiency at acidic pH.
- The sorption kinetic follows pseudo-second-order model.
- The experimental data fit well with Sips isotherm.
- The microgel was an excellent adsorbent for the removal of anionic dyes.

## GRAPHICAL ABSTRACT



a, before adsorption; b, dye adsorption after 120min; c, after dye removal



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## ABSTRACT

A novel nanocomposite microgel based on nanocellulose and amphoteric polyvinylamine (PVAm) was fabricated via a two-step method. Firstly, cellulose nanocrystal was oxidized by sodium periodate to yield dialdehyde nanocellulose (DANC). DANC was then used as a crosslinker to react with PVAm to obtain a pH responsive microgel with high density of free amine groups. The microgel was characterized using FTIR, XRD, AFM and elemental analysis. AFM images revealed that the nanocomposite was microspherical particles with a diameter ranging from 200 to 300 nm. The microgel was found to be effective in anionic dye removal at acidic conditions. The adsorption isotherms for congo red 4BS, acid red GR and reactive light yellow K-4G fit well with the Sips model, and the maximum adsorption capacities were 869.1 mg g<sup>-1</sup>, 1469.7 mg g<sup>-1</sup> and 1250.9 mg g<sup>-1</sup>, respectively. The adsorption for these three anionic dyes all followed pseudo second order kinetics, indicating a chemisorption nature.

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## 1. Introduction

Dyes are widely used in industries such as textiles, leather, paper, printing, plastics, food, cosmetic, etc. Approximately 15% of the dyes remain as industrial waste and are discharged into water bodies (Kayranli, 2011). Their discharges into hydrosphere have posed serious environmental problems due to their recalcitrant

nature. Dyes are usually non-biodegradable and stable to light, heat and oxidizing agents (Wang et al., 2006), hence, physical methods, especially sorption of synthetic dyes on inexpensive and efficient solid supports have been considered a simple and economical process for the removal of dyes from wastewater (Bonetto et al., 2015).

The adsorbents used in water treatment include activated carbons, agricultural solid wastes, industrial by-products, clay minerals, biomass and polymeric resins, etc. (Unuabonah and Taubert, 2014; Yagub et al., 2014). However, conventional adsorbents are

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usually limited by the lack of selectivity and lower adsorption kinetics due to the limited surface area or active sites (Qu et al., 2013). A large surface area and the abundance of adsorption sites are essential for adsorption and removal of contaminants from wastewater (Liu et al., 2014). Nanomaterials, due to their higher surface area and greater number of active sites for interaction with pollutants, are increasingly used in dye removal (Savage and Diallo, 2005). Nanocellulose, extracted from lignocellulosic materials, has attracted increasing attention from many diverse areas due to its unique properties such as high aspect ratio, large specific surface area, good biocompatibility and chemical accessibility. Its high surface area can provide many more active sites on the surface, resulting in high adsorption capability. Zhou et al. (2014) reported a series of partially hydrolyzed polyacrylamide/cellulose nanocrystal (HPAM/CNC) nanocomposite hydrogels with various amounts of CNCs, which were used to remove methylene blue (MB) dye from an aqueous solution. The maximum dye adsorption capacity of HPAM/CNC nanocomposite hydrogels can be improved by the incorporation of CNCs. Maatar et al. (2013) prepared a highly porous organogel from cellulose nanofibrils hydrogel and investigated its adsorption properties towards a wide range of organic solutes. It was shown that by functionalizing the native cellulose nanofibrils of the organogel with hydrophobic hydrocarbon chains, the adsorption capacity of the material is meaningfully boosted.

The adsorbability of biosorbents can be further increased by appropriate functionalization (Ong et al., 2007). Recently, amino-functionalized nanocellulose showed an outstanding adsorption capability for heavy metal ions and anionic dyes, since amino groups are easily protonated under acidic conditions. Jebali et al. (2015) evaluated the adsorption of humic acid by nanocellulose modified with N-(2-aminoethyl)-3-aminopropylmethyldimethoxy silane. It was found that amine-modified nanocellulose could be used for removal of humic acid from wastewater. Hokkanen et al. (2014a) investigated the adsorption properties of aminopropyltriethoxysilane (APS) modified microfibrillated cellulose (MFC) in aqueous solutions containing Ni(II), Cu(II) and Cd(II) ions. The results showed that the modified MFC was very effective for Ni (II), Cu(II) and Cd(II) removal from contaminated water. In our previous work (Jin et al., 2015), cellulose nanocrystal was oxidized by sodium periodate and then grafted with ethylenediamine to obtain amino-functionalized nanocellulose with free primary amino groups. The modified nanocellulose was effective in removal for anionic dyes. Nevertheless, most of the researches are dealing with nanocellulose modified using low molecular weight amines. To our knowledge, nanocellulose modified with polyamine, which was applied in contaminant removal, are not reported.

Polyvinylamine is a potent tool for the modification of macroscopic and nanoparticle surfaces due to its high primary amine groups content (Pelton, 2014). It adsorbs spontaneously and irreversibly on most surfaces in water, generating cationic interfaces. Polyvinylamine could be applied in separation membranes, flocculation, chromatography stationary phases, encapsulation, oil recovery and gene delivery. It is expected that the adsorbability of nanocellulose modified with polyvinylamine would be boosted due to its high content of amine groups.

In this work, a pH responsive nanocomposite microgel based on cellulose nanocrystal and amphoteric PVAm was prepared and applied in dye removal. Firstly, cellulose nanocrystals (CNCs), extracted from bleached kraft pulp, were oxidized by sodium periodate to yield dialdehyde nanocellulose (DANC). DANC was then used as a crosslinker to react with PVAm through a Schiff-base reaction to obtain the nanocomposite microgel (CNC–PVAm). Properties of the microgel were characterized by FTIR, XRD, AFM and elemental analysis. Furthermore, its adsorption capacity for anionic dyes was evaluated.

## 2. Methods

### 2.1. Materials

Fully bleached aspen kraft pulp, as an original material used for preparation of the nanocrystalline cellulose, was provided by the Silver Star Paper Co., Ltd, Jinan, China. Amphoteric polyvinylamine with carboxyl as the anionic groups and a molecular weight of 150 kDa was provided by BASF (China) Co. Ltd. Sodium periodate was purchased from Sigma–Aldrich Co. Ltd. The commercial anionic dyes, acid red GR (acid dye), congo red 4BS (direct dye), and reactive light yellow K-4G (reactive dye) were supplied by Tianjin Ruiji Chemical Co. Ltd. Their chemical structure and characteristics are shown in Table 1.

### 2.2. Preparation of CNC and DANC

CNC was prepared by sulfuric acid hydrolysis of fully bleached kraft pulp and then periodate oxidized to obtain DANC according to the method by Jin et al. (2015). 9 mmol sodium periodate per gram of cellulose nanocrystal was used. The aldehyde group content was determined by the Schiff base reaction between aldehyde groups and hydroxylamine hydrochloride. It was calculated through Eq. (1),

$$\text{CHO (mmol/g)} = C(V_2 - V_1)/m \quad (1)$$

where,  $V_1$  is the amount of sodium hydroxide for DANC titration, mL;  $V_2$  is the amount of hydrochloric acid for control titration in mL;  $C$  is the concentration of sodium hydroxide, mol L<sup>-1</sup> and  $m$  is the weight of each sample, g.

### 2.3. Nanocomposite microgel preparation of DANC and PVAm

The dialdehyde cellulose nanocrystals were mixed with PVAm at the mass ratio of 1:1 for reaction of 24 h. Unreacted PVAm and DANC were removed with deionized water by centrifugation. The obtained nanocomposite microgel, namely CNC–PVAm, was stored at a temperature of 5 °C as its original wet state.

### 2.4. Characterization

#### 2.4.1. Elemental analysis

The percentage of carbon, hydrogen, nitrogen and sulfur of nanocellulose, PVAm and the microgel were determined with a Vario EL III Elemental Analyzer (Elementar, Germany). The quantity of each element is expressed in a percentage of dry mass.

#### 2.4.2. FT-IR

FT-IR spectra of cellulose nanocrystals and CNC–PVAm were conducted on an IRPrestige-21 Fourier Transform Infrared Spectrometer (Shimadzu Company, Japan). The samples were freeze-dried before preparing the KBr tablets. The spectra were recorded with width ranging from 400 to 4000 cm<sup>-1</sup>, and resolution of 2 cm<sup>-1</sup>.

#### 2.4.3. X-ray diffraction analysis

X-ray diffraction analyses were performed with a D8 Powder X-ray Diffractometer (Bruker AXS, Germany), which was equipped with a CuXa X-ray tube. The crystallinity index (Crl) was calculated based on the Eq. (2) below (Segal et al., 1959),

$$\text{Crl} = (I_{002} - I_{\text{am}})/I_{002} \quad (2)$$

where, Crl is the crystallinity index;  $I_{002}$  is the intensity of the crystalline peak at the maximum at  $2\theta$  between 22° and 23° for cellulose I, and  $I_{\text{am}}$  is the intensity at minimum at  $2\theta$  between 18° and 19° for cellulose I.

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