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Development of self-assembled nanocrystalline cellulose as a promising practical adsorbent for methylene blue removal

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ABSTRACT

This study is focused on nanocrystalline cellulose (NCC) flakes for methylene blue (MB) removal via adsorption. NCC flakes exhibit a high adsorption capacity (188.7 mg/g fixed at 0.7 g/L adsorbent dosage, 25 °C and pH 6) compared to other nanomaterials, such as carbon nanotube and other cellulosic materials, such as coffee husks. Unlike NCC powder, it was observed that NCC flakes can be easily separated from wastewater containing MB. Further adsorption studies were conducted on NCC flakes, and it was found that 0.7 g/L was the optimum adsorbent dosage, which fitted well with the Langmuir Isotherm. The mean free energy value from Dubinin-Radushkevich isotherm was less than 8 kJ/mol. ΔG_o values at different temperatures were within the -20 kJ/mol to 0 kJ/mol range. In conclusion, NCC flakes is a promising and practical 'green' nanomaterial that can be further developed for industrial applications.

1. Introduction

The textile industry has been a major contributor to the world economy. However, pollution level from dyes is rising and sustainability concerns are being addressed at each point of the supply chain. Most dyeing factories have a high polluting footprint, and it is estimated that up to 200,000 tons of dyes escape in effluents that are released into water bodies due to inefficient wastewater treatment process (Chequer et al., 2013). Methylene blue (MB) is a common cationic dye that is widely used to dye textiles, such as cotton, cellulose, wood, and silk (Rafatullah, Sulaiman, Hashim, & Ahmad, 2010). Most dyes in the industry are potentially injurious to human health and MB was reported to cause chronic toxicity (Gillman, 2006), particularly to central nervous system (Vutskits et al., 2008). Hence, there is an urgent need to remove these pollutants for a healthier environment (Alswat, Ahmad, & Saleh, 2016). Adsorption is reported to be the process of choice for dye treatment as it is inexpensive, simple, and easy to be operated (Saleh, Sarı, & Tuzen, 2017; Sani et al., 2017; Vakili et al., 2017).

Industrial processes commonly use activated carbon as an adsorbent due to its high porosity and surface area (Matsis & Grigoropoulou, 2008). Commercial activated carbon is relatively expensive due to its high production cost as regeneration requires high pressure steam (Aksu, Açıkel, Kabasakal, & Tezer, 2002). Recently, interest in the application of nanomaterials as adsorbents is growing (Alansi, Alkayali, Al-qunaibit, Qahtan, & Saleh, 2015). The future development and commercialization of nanomaterial-based adsorbents for dye removal are wrought with challenges, particularly on environmental concern as nanomaterials, such as carbon nanotube, titania nanotube, and nano zerovalent iron are toxic (Tan et al., 2015).

Cellulose is the most abundant polysaccharide in the world, which has been proven to be non-toxic, low cost, sustainable, and renewable (Ali, Rachman, & Saleh, 2017). By exposing cellulose to acid, particularly sulfuric acid, its amorphous region would be selectively degraded, leaving the rod-shape crystalline region of the nano-size cellulose intact (Zhou & Wu, 2012). The nanocrystalline cellulose (NCC) is an anionic nano-size cellulose that is unlike regular cellulose. It is reported to be tougher than steel (Mitchell, 2004), and more effective towards removal of cationic dyes, such as MB dye. As an adsorbent, NCC is relatively cheaper compared to other nanomaterials, such as carbon nanotube (Huang & Rodrigue, 2015), and more environmentally friendly (Peng, Dhar, Liu, & Tam, 2011). Hence, environmentally friendly, and

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effective NCC-based adsorbents for dye removal could be developed as an alternative to activated carbon.

Even with this advantage, all nanomaterials share a similar drawback. Nanomaterials will form either stable suspension or dispersion in treated wastewater, making separation a major challenge. NCC adsorbent could not be separated from treated water, despite being exposed to vigorous centrifugation. The use of calcium chloride ($CaCl_2$) is reported in the separation of NCC adsorbent from MB water, which will cause aqua-toxicity in excessive amount (Mallick, Mohapatra, & Sarangi, 2014). This drawback proves the necessity of developing an alternative approach. Thermal treatment as a self-assembly method for NCC could overcome the separation problem by taking advantage of its anisotropic property (Peng et al., 2011).

While self-assembly of NCC is widely used in optical application and protein immobilization (Peng et al., 2011), to the authors' knowledge, there are no reported studies on thermal treated NCC for adsorption application. In addition, the effect of heat on self-assemble curing of NCC on dye uptake has not been reported. Efficient production of self-assembled NCC film can be potentially increase by reducing the curing time. There is a knowledge gap on the changes that occur under thermal conditions for intensified self-assembled NCC flakes. The properties of the flake could affect the performance of the material, in particular for water treatment applications. This highlights the necessity of characterizing the NCC films to assume unchanged properties.

Therefore, in this work, NCC powder had self-assembled into NCC flakes via the evaporation method, whereby curing conditions, namely, curing temperature and curing time during the self-assembly process, were varied to study their effects on MB uptake. The NCC flakes were characterized using several techniques. These include Fourier Emission Scanning Electron Microscope (FE-SEM) for surface morphology, Fourier Transform Infrared Spectroscopy (FTIR) for chemical functional group, mercury porosimeter for surface area, and zeta potential for surface charge at different pHs. In addition, the adsorption isotherm and thermodynamics of the removal of MB could provide insights on the adsorption mechanism of the self-assembled NCC adsorbent. A performance comparison with other adsorbents was also conducted to determine any changes to the adsorption mechanism by the self-assembled NCC.

2. Materials and methods

2.1. Materials

NCC powder (sulfur content 0.89 wt%) was supplied by University of Maine, USA. MB powder (98% purity) was supplied by Sigma-Aldrich, while nitric acid and sodium hydroxide were supplied by Merck, Germany. Calcium chloride ($CaCl_2$) was supplied by R&M Chemicals, Malaysia. All chemicals were of analytical grade.

2.2. Preparation of adsorbent

Initially, 4.8 g of pure NCC powder was added into 40 mL of deionized water. The NCC mixture was sonicated using a sonicator (Qsonica, USA) for 5 min, with 3 s of pulse-on, and 1 s of pulse-off at 60% amplitude in an ice bath to avoid any rise of temperature by means of ultrasonic. The NCC dispersion was poured into 50 mL centrifuge tubes and was centrifuged at 6000 rpm (revolution per minute) using a centrifuge (Thermofisher Heraeus Multifuge X3R, USA) until all bubbles were removed. Then, 40 mL of NCC dispersion was poured into standard size glass petri dishes (9.5 cm in diameter, 3.8 cm in height). The samples were then cured at varying ranges of temperature (50–90 °C) and time (5–25 h). The resulting NCC films were pealed from the petri dishes and grounded using a blender (Panasonic MX GM-1011, Japan) for 10 min to form NCC flakes. The NCC flakes were stored in an incubator prior to adsorption studies.

2.3. Dye uptake experiment

For the adsorption studies, 0.035 g of NCC flakes was added into 50 mL of 100 ppm (parts per million) MB solution. The MB solution was shaken using an orbital shaker at 300 rpm and 1 mL samples were drawn at 0.5 min intervals until no changes were observed in the removal percentage. The treated dye solution was then centrifuged at 6000 rpm using a micro-centrifuge (Vitaris ScansSeed Mini Personal Micro-centrifuge, Switzerland) for 1 min to separate the NCC flakes from the dye wastewater. The final absorbance number was measured at 663 nm using a UV–vis spectrophotometer (Thermo Genesys 10UV, USA), followed by obtaining the final dye concentration via a calibration curve prepared beforehand. Dye uptake was then calculated using the following equation:

$$\mathbf{Q_e} = [(\mathbf{C_o} - \mathbf{C_f})\mathbf{V}]/\mathbf{m} \quad (1)$$

where, C_o represents the initial dye concentration, C_f represents the final dye concentration, Q_e represents dye uptake in mg/g, V represents the volume of the dye solution, and m represents the mass of NCC flakes. All data points were repeated 3 times to obtain average values. Similar procedure and protocol for measurements of dye concentration have also been reported by Dil et al. (2017). To compare the behavior of NCC powder in MB wastewater with the self-assembled NCC flakes, adsorption experiment was also conducted. However, instead of curing, 0.292 mL of the NCC dispersion was directly added into 50 mL of 100 ppm MB solution, as proposed by Batmaz et al. (2014) and was shaken at 300 rpm using an orbital shaker. Upon equilibrium, the solution was added into a centrifuge tube and 0.44 mL of CaCl2 (0.09 M) solution was added to separate NCC from the dye. The mixture was centrifuged using the Thermo-fisher Heraeus Multifuge X3R (USA) machine for 2 min at 6000 rpm.

2.3.1. Isotherm studies and thermodynamics

Analysis of adsorption isotherm data for different materials is essential to predict the adsorption mechanism. To describe the adsorption isotherm, four widely used models were applied, namely, the linear forms of the Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich (Chang, Lai, & Lee, 2016). Thermodynamics studies are essential to study the spontaneity of the process with temperature, by taking into consideration both energy and entropy. This can be performed using the Van Hoff's equation (Tan, Abdullah, Horri, & Salamatinia, 2016).

2.3.2. Effects of adsorbent dosage, initial dye concentration, and dye pH

The adsorbent dosage was varied between 0.1 and 1.3 g/L, while the initial dye concentration was varied from 10 to 1000 ppm. The pH of the dye was adjusted using 0.01 M of nitric acid and sodium hydroxide, in the range of pH 2 to pH 10. Similar procedure and protocol were also reported by Asfaram et al. (2016).

2.4. Characterization

The morphology of the NCC flakes was observed using FE-SEM (Hitachi SU8000, Japan) at an accelerating voltage of 2–5.7 kV. The samples were coated with platinum using a coater (Quarum Q150R S) prior to conducting the analysis. Energy-dispersive X-ray (EDX) spectroscopy was also conducted for the elemental analysis of the NCC flakes. The sample was scanned for 3 times at the respective location, and the best results have been chosen for the discussion.

The chemical functional groups of the samples were analyzed using an FTIR Spectroscope (Thermo Scientific Nicolet IS10, USA), at the range of 4000 cm^{-1} to 800 cm^{-1}. (Recoreded at 0.4 cm^{-1} resolution and averaged by 64 scans) under transmittance mode using ATR technique.

X-ray diffraction (XRD) analysis was done using XRD diffractometer (D8 Discover from Bruker, Germany) to understand the crystallinity NCC flakes. The analysis was run at 40 kV and 4 mA with a copper tube as the radiation source (λ = 1.54060 Å). Scan range of 5–50 with a step