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Nanocellulose based biosorbents for wastewater treatment: Study of isotherm, kinetic, thermodynamic and reusability

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ABSTRACT

The advance technology in 21st century has given human ease of life and huge problem in environmental sector. Recently, the improvement on nanomaterial has attracted researchers in the preparation of nanocellulose adsorbents. The stability of nanocellulose as adsorbent also shows good prospects in upgrading scale as regenerative aspects indicates good performance after several adsorption-desorption cycle. This review paper provides a comprehensive review on the use of nanocellulose and its modified forms for the wastewater treatment. Various aspects on the validity of adsorption isotherms and kinetic models as well as theoretical aspects of the thermodynamic of adsorption are also given in this paper. Future perspective on the use of NCC and its modified forms for industrial application is also discussed.

1. Introduction

Water as source of life, is essential to every aspect in human's life. However, at present our world faces water scarcity due to rapid growth of population, development of industry, climate change, mismanagement of water use, etc. Currently, around 700 million peoples suffer from water scarcity in 43 countries and more than two million children under the age of five died every year by water-related disease (UN-Water, 2007, 2014). The contamination of water and water pollution are big problems for more than 60% of the world human population. Industrial and urban activities are likely to give major contribution to water pollution. Since water scarcity and water pollution are major global problems, therefore, a strict water usage policy and water management is urgently required.

Hazardous contaminants enter water mostly through the direct discharge of industrial effluents and urban activities. The presence of hazardous contaminants in water environment creates severe problems for human and water ecosystem. Currently, a number of technologies are available for the removal of hazardous substances from industrial effluents such as biological treatments using aerobic and anaerobic microorganisms, advanced chemical oxidation, membrane separation, photo catalysis oxidation and adsorption. Among all available methods for the treatment of industrial effluents, adsorption is still the most widely used method in wastewater treatment due to low capital cost, can remove most of all kinds of pollutants, and easy regeneration (Crini, 2005). Several types of adsorbents have been used for the removal of various kinds of pollutants such as are activated carbon, montmorillonite, zeolites, kaolin, microorganism, and agricultural wastes (Veglio and Beolchini, 1997; Yin et al., 2007; Demirbas, 2008; Bhattacharyya and Gupta, 2008; Malamis and Katsou, 2013). Due to its abundant availability and broad range of applicability, lignocellulosic materials have attracted the attention of various researchers to utilize it for environmental application. One of the promising applications of lignocellulosic material is as the adsorbent for water purification or wastewater treatment. Cellulose is one of the major components in lignocellulosic material. This natural polymer has been investigated as bio-sorbent in its natural or chemically modified form. In natural form, it exists in agricultural wastes such as banana peel, saw dust, corncob, and bagasse (Annadurai et al., 2002; Ngah and Hanafiah, 2008). Modified cellulose can be divided into two groups, which are direct modification and monomer grafting. The main routes of direct cellulose modification in the preparation of adsorbent materials are esterification, etherification, halogenation, oxidation, alkaline treatment, and silynation (O'Connell et al., 2008; Hokkanen et al., 2016a, 2016b). Monomer grafting or graft copolymerization is a process where side chain grafts are covalently attached to the main chain of a polymer backbone to form a branched copolymer. Well known techniques that commonly used in graft copolymerization are photografting, high energy radiation grafting, and chemical initiation grafting (O'Connell et al., 2008; Hokkanen et al., 2016a, 2016b).

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Nomenclature

TC	Tetracycline hydrochloride
JG	Janus green
MB	Methylene blue
CV	Crystal violet
AR	Acid red GR
CR	Congo red 4BS
RY	Reactive light yellow K-4G
RB	Reactive blue 21
NC	New coccine
U	Ultrasonication

Superscripted letters

a	Consisted of carboxylated NCF, amine functionalized magnetite nanoparticles and poly(vinyl alcohol) (PVA) blended chitosan
b	T = 55 °C
c	T = 65 °C
d	T = 75 °C
e	T = 75 °C + LiCl
f	Stirred for 2 days
g	Stirred for 13 days
h	P = %Polyacrylamide, C = %NCC, number = pH (example: p30C20-6.5 means that the material consisted of 30% polyacrylamide, 20% NCC, pH 6.5)
i	Second region
j	Third region
k	After 2 cycles, 15 s of ultrasonication was done

Currently, isolation of cellulose in the form of nanocrystal and nanofibers has been extensively studied due to its wide application in industry such as enzyme immobilization, adsorption, catalysis, drug delivery, biosensors and bio-imaging (Lam et al., 2012). The separation of nanocrystalline cellulose (NCC) can be conducted by acid hydrolysis, esterification, oxidation, silylation, cationization, acetylation, and polymer grafting (Peng et al., 2011). Whilst the extraction of nanofibrils cellulose (NFC) must be carried out by mechanical treatment such as homogenization, cryo-crushing, microfluidization, grinding and sonication (Zhao et al., 2007; Siro and Plackett, 2010; Spence et al., 2011) or via fermentation by bacteria (Klemm et al., 2009). Both NCC and NFC have nanometer scale in diameter, but the length of NFC is in micrometer while NCC has nanometer length (Brinchi et al., 2013). This nanomaterial has already been studied as adsorbent for removal of various kinds of hazardous pollutants, and the results of the studies indicate that these materials possess high adsorption capacity, are environmental friendly and low cost adsorbent (Lam et al., 2012). Despite that many review articles have been published dealing with the use of lignocellulosic materials as the adsorbent in water and wastewater treatment (most of them mention in specific type of adsorbate such as heavy metals and organic compounds), however, there is no review discuss about the use of nanocellulose for environment remediation especially as adsorbent. In this review, we discuss recent studies on the use of nanocellulose adsorbents for adsorption of heavy metals, dyes, and organic compounds. The emphasis of this review paper is to provide a comprehensive discussion on the adsorption mechanisms of hazardous pollutants onto nanocellulose and its modified forms through equilibrium and kinetic studies. Future perspective on the use of nanocellulose adsorbents for water remediation is also given in this review.

2. Preparation of various nanocellulose adsorbents

Cellulose is a linear polysaccharides consisted of two anhydroglucose rings linked by β-1,4 glycoside bonds in a repeated manner (Eichhorn et al., 2010). It can be found within the fiber walls of plants, the lateral size of cellulose chains is around 0.3 nm (Ioelovich, 2008). Cellulose fibrils are arranged in crystalline and amorphous region, where the length of crystalline is 50–150 nm and the amorphous length is 25–50 nm (Fig. 1) (Ioelovich, 2008; Moon et al., 2011). To produce NCC, the removal of amorphous region is needed. The most common procedure to eliminate this amorphous part is through acid hydrolysis using sulfuric acid; this method is first published by Ranby and Ribi (1950). Apart from acid hydrolysis, there are other procedures like oxidation, enzymatic hydrolysis, ionic liquid (IL), carbamation, amidation, esterification, silylation, and cationization. For oxidation, there are two well-known commonly used chemicals: 2,2,6,6-tetramethylpiperidinyl-1-oxyradical (TEMPO) and ammonium persulfate (APS). TEMPO oxidation is always combined with NaBr and NaOCl as the co-oxidizing agent (Montanari et al., 2005; Saito et al., 2007; Lin et al., 2012). Unlike TEMPO, APS does not require any chemical addition (Zhang et al., 2016a, 2016b). This oxidation is exceptionally different from any other procedures that transform the hydroxyl groups in cellulose fiber; it converts the hydroxymethyl groups of cellulose fibers (Habibi et al., 2010). The oxidated NCC by TEMPO can be further modified by amidation by using carbodiimides derivatives as the amidation agent, and N-Hydroxysuccinimide (NHS) is added as the amine source to allow the migration O → N of *O*-acylisourea (Bulpitt and Aeslichmann, 1999; Habibi, 2014). Another method called carbamation can also be used to modify hydroxyl groups of NCC by reacting it with an isocyanate (Eyley and Thielemans, 2014).

For the IL pretreatment, it is definitely affected by the anion side than cation. The reaction occurred in the NCC preparation is also completely depends on the anion type in the IL. Han reported the use of $[BMIM]^+[Cl]^-$ to produce NCC, the free $[Cl]^-$ associates with the hydroxyl group of cellulose, while $[BMIM]^+$ attacks the oxygen atom in the hydroxyl group (Han et al., 2013). On the other hand, Man used $[BMIM]^+[HSO_4]^-$ which resulted in sulfate-NCC (Man et al., 2011). From the works of Han (2013) and Man et al. (2011), it can be concluded that anion completely control the formation of NCC.

Esterification is the reaction that usually occurs when acid is used as the reactant to produce NCC. The most common reactant used is sulfuric acid, which results in NCC–OSO_3H due to the grafting of anionic sulfate ester groups (Dufresne, 2013). Other reactants that have been investigated to produce NCC by Fischer esterification is the combination of HCl and organic acid like acetic, citric, malonic, and malic acid (Braun and Dorgan, 2009; Spinella et al., 2016). Using phosphoric acid also can form NCC with better thermal stability than sulfonated NCC; Espinosa et al. (2013) assumed the formation of NCC by one ester bond. Kokol et al. (2015) reported that there is tautomeric equilibrium occurred in the process, where two possible products can be formed: a) P-NCC that behaves as monobasic acid and b) P-NCC that exhibits two acid groups.

Enzymatic hydrolysis has been favorably considered to produce NCC because it does not use harsh chemicals, has lower energy

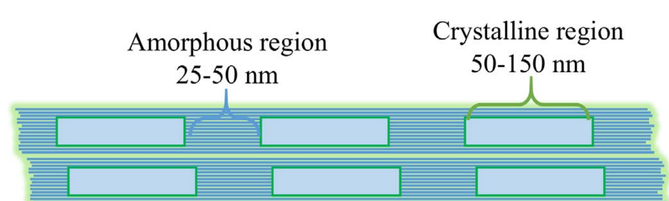

Fig. 1. Cellulose fiber.