Chemical Engineering Journal 331 (2018) 587–596

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

# New spherical nanocellulose and thiol-based adsorbent for rapid and selective removal of mercuric ions

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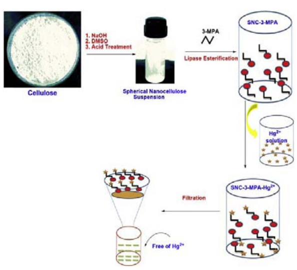
## GRAPHICAL ABSTRACT




## ARTICLE INFO

*Keywords:*
Spherical nanocellulose
3-Mercaptopropionic acid
$Hg^{2+}$ ions uptake
Adsorption kinetics
Adsorption isotherm

## ABSTRACT

In the present study, we report synthesis of new cellulose-based functional adsorbent for the adsorption of $Hg^{2+}$ ions from their aqueous solutions. The nanocellulose spheres or the spherical nanocellulose (SNC) was synthesized via acid hydrolysis which was followed with lipase catalyzed esterification using 3-mercaptopropionic acid. The thiolated-SNC was well characterized and it was found to be rapid, efficient and selective absorbent for $Hg^{2+}$ ions with ~98.6% removal within 20 min from a 100 ppm solution. Contrary to this, the SNCs does not show adsorption under these conditions. The adsorbent can be regenerated and its reusability was studied up to nine cycles with cumulative adsorption capacity of 404.95 mg/g. The maximum %removal achieved was 88% from tap water and 78% in the presence of some common competing ions, thus exhibiting the specificity of the adsorbent for $Hg^{2+}$ ions. Regeneration studies were carried out by using 0.1*N* HCl, $HNO_3$, NaCl, $NaNO_3$ and $CH_3COONa$ and among these 0.1*N* HCl returned the best results. This study thus embodies multiple aspects of environmental sustainability right from the utilization of the most abundant biopolymer to develop a smart material for use to correct the environmental imbalances.

## 1. Introduction

It is now increasingly becoming imperative that cost-effective and the environmentally-friendly materials can be derived from the biomass [1–3]. Cellulose, being the major component of the biomass, is highly suitable to synthesize materials for various applications [4–6]. Its nanoform, nanocellulose, is a highly useful material and its relevance in different fields is increasing due to its high aspect ratio, strength and light weight [7]. From the perspective of sustainable chemistry nanocellulose is a promising material in different area of nanotechnology [8–12]. Apart from the structural properties, nanocellulose offers the ease of functionalization to different derivatives with high accessibility of reagents to its rich pool of hydroxyl (–OH) groups [13]. One of the most attractive transformations of cellulose is to develop its spherical nanocellulose (SNC) by various modes [14–16]. Acid hydrolysis is the common route to prepare SNC [17–19]. However, the sulfuric acid hydrolysis generates sulfonate groups on the SNC particles, and have low thermal stability. Hence, desulfonation of SNC has to be

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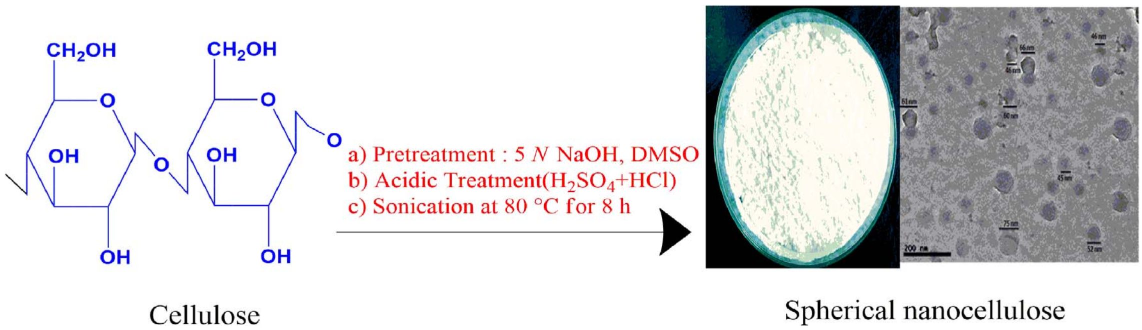
http://dx.doi.org/10.1016/j.cej.2017.08.128
Received 12 July 2017; Received in revised form 28 August 2017; Accepted 30 August 2017
Available online 21 September 2017
1385-8947/ 




**Scheme 1.** Synthetic route for spherical nanocellulose via acid hydrolysis.

adjusted [20]. The SNC generated from the HCl hydrolysis and subsequently treated with $H_2SO_4$ has the same particle size as those directly obtained from the hydrolysis using the latter alone, and the combination of both the acids generate SNC that has better thermal stability mainly because their surface has lesser number of the sulfate groups those are solely generated from sulfuric acid hydrolysis [21]. Also, the acid combination results in SNC particles of uniform morphology with narrow size distribution [22–23]. SNC has been evaluated in various applications such as synthesis of adsorbents for metal ions from the wastewater [24–26], supercapacitors [27], supports for the drug loading [28], theranostics [29] and cellular uptake [30]. However, there is scanty information on its applications in environmental technologies especially with respect to the removal of $Hg^{2+}$ ions from wastewater, which is the theme of the present work. Removal of $Hg^{2+}$ ions is a major concern given their toxicity, volatility, abnormal functions of vital organs like brain, kidney and lungs, and their bioaccumulation is a major health threat. Maximum contaminant level of mercury is 0.002 mg/L set by Environmental Protection Agency (EPA) [31] and World Health Organization (WHO) has also set a very low permissible limit [32]. Various techniques for sensing and adsorption of $Hg^{2+}$ ions have been reported in literature [33–37]. Thiol groups have been reported to be highly selective adsorption sites for these ions from wastewater [38–40]. In our earlier study we functionalized cellulose to synthesize a sensor-cum-adsorbent for $Hg^{2+}$ ions with high adsorption efficiency and recyclability [37].

So, in view of the preceding discussion, in the present work, cellulose was converted to SNC via acid hydrolysis using both HCl and $H_2SO_4$. SNC was functionalized with 3-mercptopropionic acid (3-MPA) to incorporate thiol groups on SNC to generate a thiol-based new adsorbent (SNC-3-MPA). Because of their serious toxic effects to human health and lack of bio-remedial mechanisms, and extremely low permissible levels, there is a strong urgency to develop a bio-friendly, highly efficient, selective and rapid absorbent for their removal from the contaminated water. The $Hg^{2+}$ ions adsorption mechanism on SNC-3-MPA can be elucidated with the help of HSAB concept where hard and soft acids prefer to react with hard bases and soft bases, respectively. As $Hg^{2+}$ ions are soft acids and the synthesized SNC-3-MPA adsorbent having thiol (R-SH) active side groups act as soft base and provide better interactions with soft acid $Hg^{2+}$ ions which enhance its selective nature even when competitive ions are present. Also, high $Hg^{2+}$ ions adsorption was anticipated mainly due to two factors – the large surface area of the SNC than cellulose and presence of thiol groups those have high affinity for these ions. Effect of different parameters affecting adsorption behaviour of the adsorbents was studied to determine optimum conditions for the maximum $Hg^{2+}$ ions and adsorption isotherms were used to understand the mechanism of the adsorption process. Also, adsorption is a reversible phenomenon so attention was paid to recycling of the used adsorbent and recovery of $Hg^{2+}$ ions by desorption process.

## 2. Experimental

### 2.1. Chemicals

Cellulose from cotton linters (Hi-media, India), sodium hydroxide, iso-propanol (SD Fine Chemicals, Ltd., India), mercuric acetate, sodium acetate, (Sigma- Aldrich, Germany), isopropyl alcohol, 100% (glacial) acetic acid, Michler's thioketone [4,4′-bis(dimethylamino) thiobenzophenone (TMK)], and 1-propanol (Merck, Germany), were of reagent grade and used as received. The concentration of $Hg^{2+}$ ions was determined with a Photolab 6600 ultraviolet–visible (UV − Vis) programmable spectrophotometer, and pH values were measured with a pH meter (Eutech 20).

### 2.2. Synthesis of spherical nanocellulose (SNC)

Synthesis of spherical nanocellulose (SNC) was carried out by a previously reported method after some modifications [14]. Briefly, cellulose powder (30 g) was transferred into 5*N* NaOH solution (250.0 mL). Heating the resultant suspension at 80 °C for 4 h resulted in slurry formation which was filtered and repeatedly washed with distilled water until it was ensured that the pH of the washings was 7.0. The resulting cellulose powder was air-dried for 24 h and then added to dimethyl sulfoxide (250.0 mL) at 80 °C in a water bath and kept undisturbed for 4 h. Finally, the treated cellulose was filtered. It was washed with the distilled water and treated with a solution consisting 300.0 mL distilled water, 50.0 mL of 12.1*N* HCl and 150.0 mL of 36*N* $H_2SO_4$ (in a 1:3 ratio of HCl and $H_2SO_4$) and the resulting suspension was sonicated, under vigorous stirring, in Cole-Parmer 8890 ultrasonicator with an internal heating at 70 °C for 8 h (Scheme 1). The hydrolysed cellulose slurry turned into milky suspension which was centrifuged. The SNC obtained after centrifugation was washed with the distilled water 5 times and neutralized with 2*N* NaOH to attain washings with the neutral pH. The purified product was further washed with the distilled water. The purified SNC was freeze dried and stored at 5 °C.

### 2.3. Functionalization of spherical nanocellulose-3-mercaptopropionic acid (SNC-3-MPA)

SNC was enzymatically esterified with 3-mercaptopropionic acid to obtain its ester derivative as SNC (1.218 g) and 3-mercaptopropionic acid (3-MPA) (1.0 mL) were suspended in hexane (20.0 mL) and a specific amount of lipase was added [41]. The mixture thus obtained was stirred in chemical reactor at 45 °C for 8 h. The product obtained was washed thoroughly with methanol and water. The material obtained was named as SNC-3-MPA, Scheme 2.

### 2.4. Characterization of SNC and SNC-3-MPA

The synthesized SNC was characterized by using Fourier transform