International Journal of Biological Macromolecules 76 (2015) 109–118

Contents lists available at ScienceDirect

International Journal of Biological Macromolecules

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

# Distinctive green recovery of silver species from modified cellulose: Mechanism and spectroscopic studies

Amarendra Dhar Dwivedi[a,*], Shashi Prabha Dubey[a,b], Mika Sillanpää[a], Henrikki Liimatainen[c], Terhi Suopajärvi[c], Jouko Niinimäki[c], Young-Nam Kwon[b], Changha Lee[b]

[a] Lappeenranta University of Technology, LUT Green Tech, Laboratory of Green Chemistry, Sammonkatu 12, 50130 Mikkeli, Finland
[b] School of Urban and Environmental Engineering, Ulsan National Institute of Science and Technology (UNIST), 100 Banyeon-ri, Eonyang-eup, Ulju-gun, Ulsan 698-805, Republic of Korea
[c] Fibre and Particle Engineering Laboratory, University of Oulu, P.O. Box 4300, FI-90014, Finland

ARTICLE INFO

*Article history:*
Received 2 December 2014
Received in revised form 17 February 2015
Accepted 23 February 2015
Available online 27 February 2015

*Keywords:*
Desorption
Nanocrystallization
Taurine-cellulose

ABSTRACT

The present study aimed to recover precious silver in order to identify the adsorption coupled reduction pathways that determine this process. A combination technique of adsorption and nanocrystallization was used to investigate the recovery of silver species from taurine-cellulose (T-DAC) samples. The non-synthetic route of nanocrystallization yielded spherical zero-valent silver sized ~18 nm. Rate-controlling steps were modeled by adsorption parameters by the best fit of Langmuir capacity (55 mg/g), pseudo-second order curves, and exothermic chemical reactions. The T-DAC was an excellent sorbing phase for the treatment of silver-polluted waters over a broad range of pH (2.1–10.1) and varying ionic strengths (8.5–850 mM, as NaCl), which are the conditions often encountered in industrial and mining effluents. A good recovery of silver (40–65%) was also obtained in the presence of Cd(II), Co(II), Cr(VI), Ni(II), and As(V) at lower or equivalent concentrations with Ag(I), either from individually added metals or from all metal ions mixed together. Desorption was compared with a series of five eluents including complexing agents. In these experiments acidified thiourea yielded 86% desorption of Ag(I). Aqueous silver reduced to metallic silver on the surface of the T-DAC samples, which was confirmed by X-ray photo electron spectroscopy.



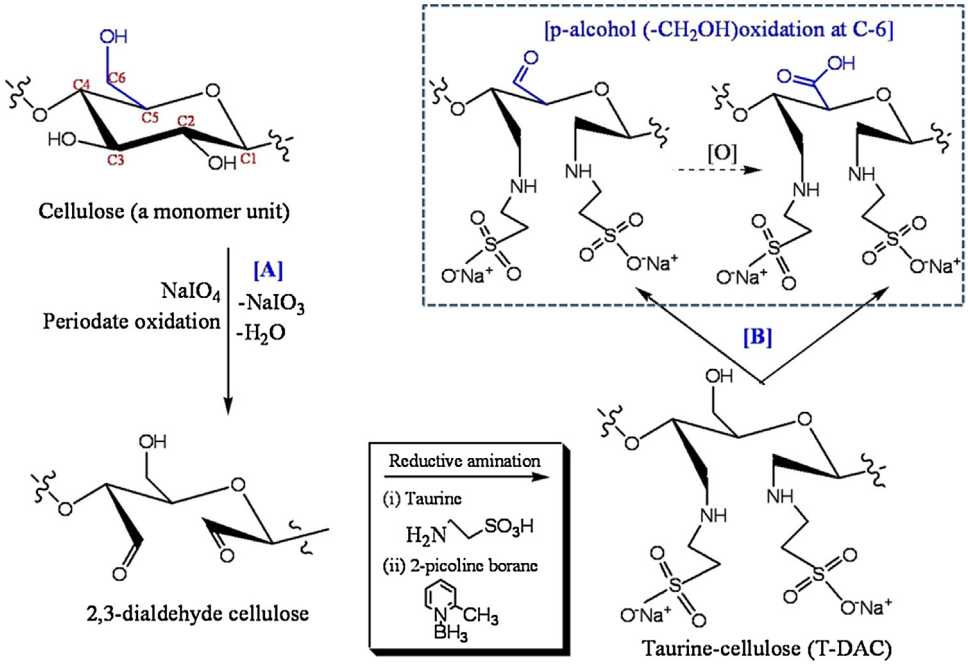
## 1. Introduction

There is increasing interest in using silver for a variety of new applications due to its excellent malleability, ductility, electro-thermal conductivity, and photosensitivity. The World Silver Survey (2013) by Thomson Reuters for the Silver Institute showed that the overall supply of silver increased by 0.9% to 32,604 tons in 2012 alone [1]. Demand for silver is continually growing due to its commercial success in a wide range of market sectors such as textiles, electronics, materials, and medical instruments. Significant silver volumes are lost in the effluents discharged from such industries. Another key source of silver waste is mine sites, where silver species may be released directly into the environment. Silver has also been employed as a popular antimicrobial in various types of filters in the water purification units of hospital, community and domestic drinking water distribution systems [2]. Silver levels may sometimes be elevated in tap water during the disinfection of water supplies. Thus, the impact of aqueous silver species possesses a general appeal in terms of their human, ecological and environmental influences; however, their toxicity potential varies significantly depending on dissolved complex and free (hydrated) cationic forms [3].

The predominant ligand species of Ag depend on its redox state and abundance in both natural water and aerobic–anaerobic soils. Metallic Ag forms silver oxide with $O_2$ which in water dissociates to Ag(I). Therefore, the catalytic action of Ag with oxygen provides a powerful sanitizer [4]. Silver is reactive toward commonly occurring ligands in water and sediment materials which are easily adsorbed by clay and organic matter. These ligands may be in the form of simple organic or inorganic compounds, or they may be the functional groups on complex organic molecules. Chloride ($Cl^-$) and sulfide ($S^{2-}$) ions are often present in natural water and have a strong affinity to the oxidized silver metal. Their chemical speciation is dominated by inorganic chloride complexes in aerobic water systems [5]. In contrast, the sulfidation of silver species

* Corresponding author. Tel.: +358 505639740.
*E-mail addresses:* amarendradhar@gmail.com, amarendra.dhar.dwivedi@lut.fi (A.D. Dwivedi).

http://dx.doi.org/10.1016/j.ijbiomac.2015.02.032
0141-8130/




**Scheme 1.** (a) Taurine-cellulose (T-DAC) synthesis pathway from the cellulose; (b) oxidation products (C-6 aldehydic and carboxylic derivative) from the primary alcoholic group of T-DAC.

can be observed in anaerobic environments [6]. Moreover, silver species such as AgCl, $Ag_2SO_4$ and $Ag_2CO_3$ are commonly insoluble in environmental matrices [7].

The recovery of precious metals from mine and industrial waters is always of great interest because they are often present in these waters in considerable amounts. The available technologies include precipitation, electrolysis, solvent extraction, ion-exchange resins, and chelating agents. Most of these processes can be used profitably on a large scale when the metal concentrations in the effluents are sufficiently high (>100 mg/L) [8,9]. Studies have also been conducted on the adsorption of Ag(I) on (un)modified natural materials, which strengthen the adsorption behavior of precious metals [10,11].

As abundant and renewable material, cellulose is a potential bioresource for the recovery of soft metals due to its strong electrostatic and chemical interactions, selectivity, stability in acid–base changes, non-corrosiveness and low environmental impact. In our previous work we used modified cellulose based on oxidative treatment as an excellent green material for the recovery of gold species [12,13]. The oxidative product of cellulose, 2,3-dialdehyde cellulose (DAC) obtained from periodate oxidation, can undergo selective modifications to produce carboxylic, sulfonate, and imine derivatives [14–16]. These modifications increase the feasibility of cellulose for various high-end applications [17]. As an example, cellulose modifications have recently been transformed into environmentally friendly film materials for packaging applications [18]. Similarly, cationic and anionic celluloses were investigated for water treatment as nano-sorbents [19] and in coagulation–flocculation [20].

The green recovery of precious metal by adsorptive-reduction pathways has received limited attention so far, few studies being concerned with gold [12,13]. In the present work, we investigated the unique capability of taurine-cellulose (T-DAC) obtained from regioselective oxidation route for the recovery of silver species through a combination technique of adsorption and nanocrystallization. Silver nanoparticles (Ag NPs) containing biodegradable material are in high demand for smart composites in material, biochemical, and medical research. Here nanoparticulate Ag was obtained from silver-polluted waters, and adsorption capacity, selectivity, desorbability and stability of taurine modified cellulose were explored. The mechanistic evidences of nanocrystallization were supported by comprehensive characterization methods.

## 2. Materials and methods

### 2.1. Materials

A 1000 mg/L stock solution of Ag(I) was prepared using silver nitrate ($AgNO_3$). All working solutions were prepared from the stock at the required concentrations. Millipore Milli-Q water was used in all experiments. All reagents, unless otherwise specified, were analytical grade, obtained from the Sigma-Aldrich Co. The pH was adjusted by the addition of either 0.1 M HCl or 0.1 M NaOH solution under agitation. After filtering with a 0.45 μm acetate filter and diluting with 2% $HNO_3$, metal concentrations in the solution were analyzed by inductively coupled plasma optical atomic emission spectrometer (ICP-OES), model iCAP 6000 series (Thermo Electron Corporation, USA). The test sample measurements were performed in triplicate. All the experiments were carried out at least twice and sample-free controls were performed concurrently. Preparation of taurine-modified cellulose is provided in supplementary information (SI Section A) and also presented in Scheme 1a.

### 2.2. Adsorption and desorption experiments

The adsorption of Ag(I) onto T-DAC in an aqueous solution was investigated through batch experiments with different process variables. The Ag(I) solution concentration (range 1–300 mg/L) was incubated with different T-DAC dosages (0.1–1.5 g/L) for a given range of temperature (300–338 K) and contact time (5–1440 min).