A Comparative Study on the Rare Earth Elements Recovery of Cross-linked Cellulose Adsorbents and Capacitive Deionization with Cellulose Derived Carbon as Electrode Materials

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Abstract The increasing demand for Rare Earth Elementals (REEs) due to their exponential use in various applications has stimulated research on the development of an efficient technology for the separation and recovery of REEs. Adsorption is one of the best and most typical methods, while capacitive deionization (CDI) is increasingly being considered as a promising solution for desalination and ions recovery.

Cellulose, the most abundant and low-cost polysaccharides in the nature, has attracted great attention for its potential applications in adsorbent and energy storage fields, due to its excellent mechanical, abundant –OH functional groups, as well as the outstanding electronic and thermal properties after carbonization. With an objective to develop a cost-efficient and exceptional CDI electrode material with high specific surface area, low electrical resistance and durability, in this work, we developed a novel cellulose derived carbon electrode, and it was further applied for REEs recovery. The material exhibits the above-mentioned characteristics along with superior adsorption capability. As a comparison, a cellulose adsorbent was synthesized by crosslinking cellulose nanocrystal (CNC) with polyethylenimine (PEI). The adsorbent and electrode materials were characterized by Fourier Transform Infrared (FT-IR) spectroscopy, elemental analysis, Brunauer–Emmett–Teller (BET) analysis, Scanning Electron Microscope (SEM), Transmission Electron Microscopy (TEM). The electrochemical capacitive behavior of the electrode material was determined by cyclic voltammetry (CV). Their adsorption behaviors of the cellulose adsorbent for the removal of REEs by varying experimental conditions were investigated in bath. The CDI recovery performance was also studied using a laboratory CDI module, under varying voltage and REE concentrations. The REEs uptake ability, and the kinetics and isotherms of the both methods for REEs uptake were further compared. The REEs uptake mechanisms of the both methods were studied via FTIR and XPS as well.

Such a comparison is not only useful for further understanding the fundamental of the traditional adsorption and electrosorption, but also for promoting the CDI application in water treatment.

Introduction

Rare Earth Elementals (REEs) have been applied in various advanced applications, including lasers, optics, super-magnets, catalysts, and batteries [1-3]. However, as the name suggests, the mining storage of REE is very limited and dispersed. The exponential use of REEs has skyrocketed the prices in the past decades due to the limited supply for “geopolitical” reasons. Therefore, the separation and recovery of REEs from residues and wastes would be crucial for both economical and sustainable reasons [4, 5]. In particular, the reproduction of REEs from diluted aqueous streams such as secondary resources and industrial wastewater has attracted great interest.

A number of methods have been employed for the recovery of REEs from aqueous solution, such as precipitation[6], solvent extraction [2], and ion-exchange [7]. However, most of these methods might bring some defects such as high energy consumption and secondary pollution [2, 8]. Adsorption is currently one of the best main methods used to recover REEs from water solutions, due to its low cost, efficiency, and sustainability [9]. In our previous works, a β-cyclodextrin-based material (EDTA-β-CD) has been prepared by using EDTA as cross-linker [10], and the obtained product was further applied as an advanced adsorbent to separate REEs from seawater [3]. Recently, capacitive deionization (CDI) is increasingly being considered as a promising solution for ions recovery [11]. The CDI technology is defined as an electric potential-driven adsorption of ions onto charged porous electrode surfaces [12]. By applying low voltages to a CDI cell, the charged ions are attracted to the electrodes and are kept in the electric double layer (EDL); when the voltages are removed, the attracted ions can be released into the solution again, reaching the purpose of enrichment of the targeted ions [13]. CDI technology has been widely applied in desalination [14], and occasionally applied in the removal of heavy metals [15, 16] and fluorine [17], but it has never been applied in REE recovery.

Cellulose, the most abundant and low-cost polysaccharides in the nature, has attracted great attention for its potential applications in adsorbent and energy storage fields, due to its excellent mechanical, abundant –OH functional groups, as well as the outstanding electronic and thermal properties after carbonization [18]. However, cellulose has rarely been applied in REE adsorption due to the lack of enough functional groups for REE complex. In this work, a cellulose adsorbent was synthesized by crosslinking cellulose nanocrystal (CNC) with polyethylenimine (PEI), which contains abundant of amino groups [19]. In this set, PEI acts not only cross-linker but also as functional groups for REEs. The PEI-cross-linked CNC was characterized and its REE uptake properties were investigated in bath experiments. Moreover, we fabricated a porous carbon electrode derived from cellulose in this study. The physical and electrochemical properties of the obtained carbon electrode were analyzed by cyclic voltammetry (CV); then the electrode was applied to build CDI cells. The CDI recovery performance was also studied under varying voltage and REE concentrations.

Materials and methods

Materials.

CNCs were supplied by CelluForce, Inc. (Canada). All other reagents were purchased from Sigma-Aldrich and were used without further purification. The branched PEI had an average molecular weight of 75 000 Da (50 wt. % in H_2O). Stock solution of 1000 mg/L Ce(III) was prepared via dissolving appropriate amounts of 99.99% trace metals basis $Ce(NO_3)_3{\cdot}6H_2O$ in deionized water.

Preparation of PEI-modified cellulose.

The PEI-modified cellulose (PEI-CNC) was prepared via two steps: firstly, the pristine CNCs were oxidized according to previous reported method, obtaining TEMPO-oxidized CNCs (TEMPO-CNC) with carboxylic groups [20]; secondly, the 0.25 g of as-prepared TEMPO-CNC was further reacted with 0.50 g of PEI in the presence of 250 mg of N-(3-(dimethylamino)propyl)-N’-ethylcarbodiimide hydrochloride (EDC) and 250 mg of N-hydroxysuccinimide (NHS) via a carbodiimide-mediated amidation reaction [20, 21] for 24 h. The prepared cellulose adsorbent was rinsed and freeze-dried at – 42 °C for 48 h.

Preparation of carbon electrodes.

A porous carbon electrode was fabricated using carbon powder derived from cellulose according to a previously reported method [12]. Briefly, 5.0 g of carbon powder and 0.6 g of Poly(vinylidene fluoride) (PVDF) were suspended in 10 ml of di-methylacetamide, and then the mixture was stirred for 1 h to get well-dispersion. After that the mixture was casted onto a graphite sheet (VWR, Finland) with a thickness of 500 µm. Then the graphite sheet was dried at room temperature in a fuming hood for 20 h and then in an oven at 60 °C for 2 h to remove the residual organic solvent in the pores of the carbon electrode.

Characterization

Fourier transform infrared (FTIR) spectroscopy of the type Nicolet Nexus 8700 (U.S.A.) was used to identify the surface groups. The morphology of the sample was investigated using a Jeol JSM-5800 scanning electron microscope (SEM) and a Philip CM 10 transmission electron microscope (TEM). The surface and pore properties of the electrodes were measured using a NOVA4000 analyzer based on the Brunauer–Emmett–Teller (BET) method. The cyclic voltammetry (CV) was conducted by a potentiostat (AUTOLAB).

Adsorption tests using PEI-CNC adsorbent

The batch experiments of Ce(III) sorption onto PEI-CNC adsorbent were carried out by mixing 10 mg of adsorbent with 10 mL of REE solutions (dose: 2 g/L) at designated concentrations ranging from 5 to 300 mg/L. After adsorption, the adsorbent was separation from the solution by using 0.45 µm polypropylene syringe filter, and the residual Ce(III) concentration was analyzed at a wavelength of 333.75 nm by an inductively coupled plasma optical atomic emission spectrometer (ICP-OES) Model Icap 6300 (Thermo Electron Corporation). The REE uptake capacity (mg/g) was calculated as [22, 23]:

$$q = \frac{(C_0 - C_e)}{M} V \qquad (1)$$

where C_o and C_e are the initial and equilibrium Ce(III) concentrations (mg/L), respectively, while M and V represent the adsorbent weight and solution volume, respectively.

Electrosorption tests using the capacitive deionization cell

The electrosorption performance of the carbon electrodes was investigated in bath as well. The CDI cell was laboratory made. Briefly, a pair of electrodes was kept parallel and separated by a non-electrically conductive spacer (glass filter, 250 µm thickness). The size of the electrode was 6×6 cm, and each electrode was 2 g. The feed solution (200 mL) was continuously pumped into the CDI cell by a peristaltic pump at a flow rate of 48 mL/min under a potential of 10 V and the effluent returned to the feed solution for next run. The electrosorption was repeated for 16 times. The Ce(III) concentrations before and after electrosorption using CDI were also analyzed by ICP-OES and conductivity meter (EC-500, SUNTEX).

Results and discussion

Characterization

The presence of additional functional groups on the surface of the cross-linked cellulose was studied by FT-IR. As shown in Figure 1a, the characteristic vibration peaks of the amino and amide groups were observed at 1642, 1561 and 1452 cm^{-1}. The SEM image (Figure 1b) shows the pore structure and the pore wall could be assign to the cross-linked cellulose. The optical image in Figure 1c (Figure 1c) suggests the light weight of the material. In the TEM image (Figure 1d), it is easy to find the aggregation of the cellulose nanocrystals after cross-linking with PEI. This is beneficial for the practical application in water treatment.T

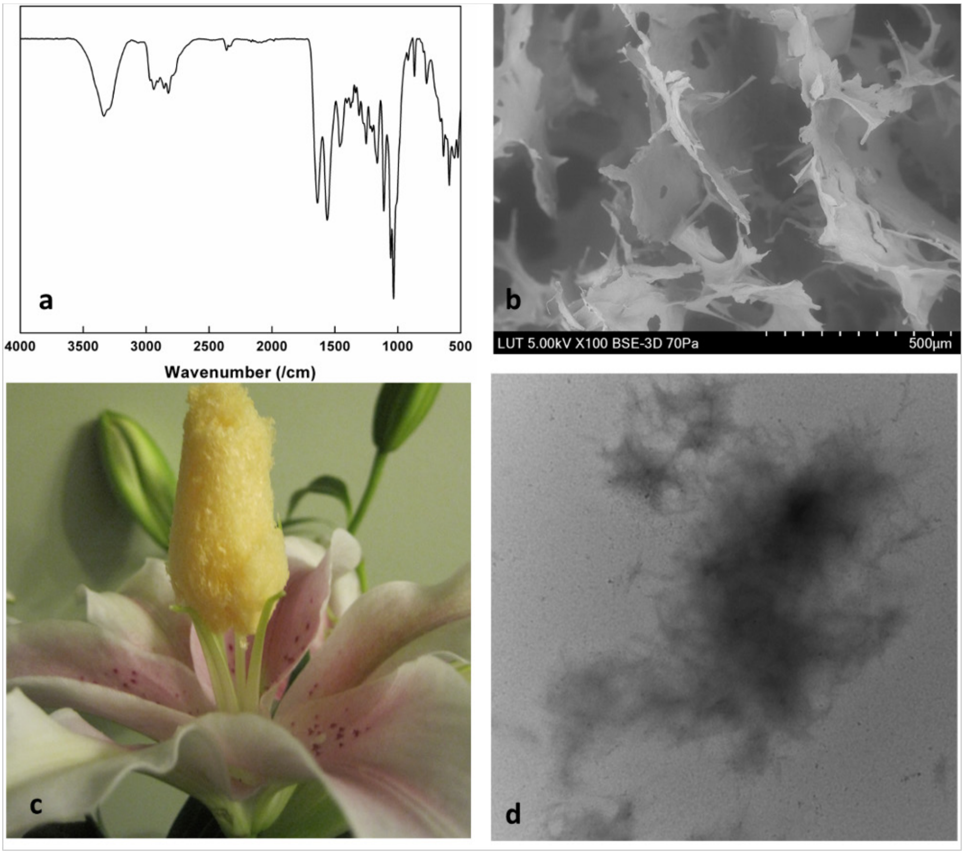

Figure 1. *(a) FT-IR spectrum, (b) SEM, (c) optical image, and (d) TEM of the obtained cross-linked cellulose.*

As shown in Figure 2a, the prepared carbon electrodes have a smooth surface and the carbon were well-spread on the surface. Importantly, the carbon powders were binded firmly and no fracture was observed. Figure 2b shows the practical CDI cell and its inner structure was illustrated in Figure 2d. The parallel electrodes were separated by a 250 μm thickness of spacer and graphite sheets act as the current collector. Whole the CDI system was sealed in a Teflon house (10×10 cm). Figure 2c shows the CV curves of carbon electrode after three scans and the specific capacity was 86 F/g. All the CV curves were asymmetric, with two small peaks at 5.5 and 8.0 V. The specific surface area and the total pore volume of the obtained carbon electrodes were 39.48 m^2/g and 0.117 cm^3/g, respectively (Table 1). The good surface and pore properties resulted in the high specific capacity.

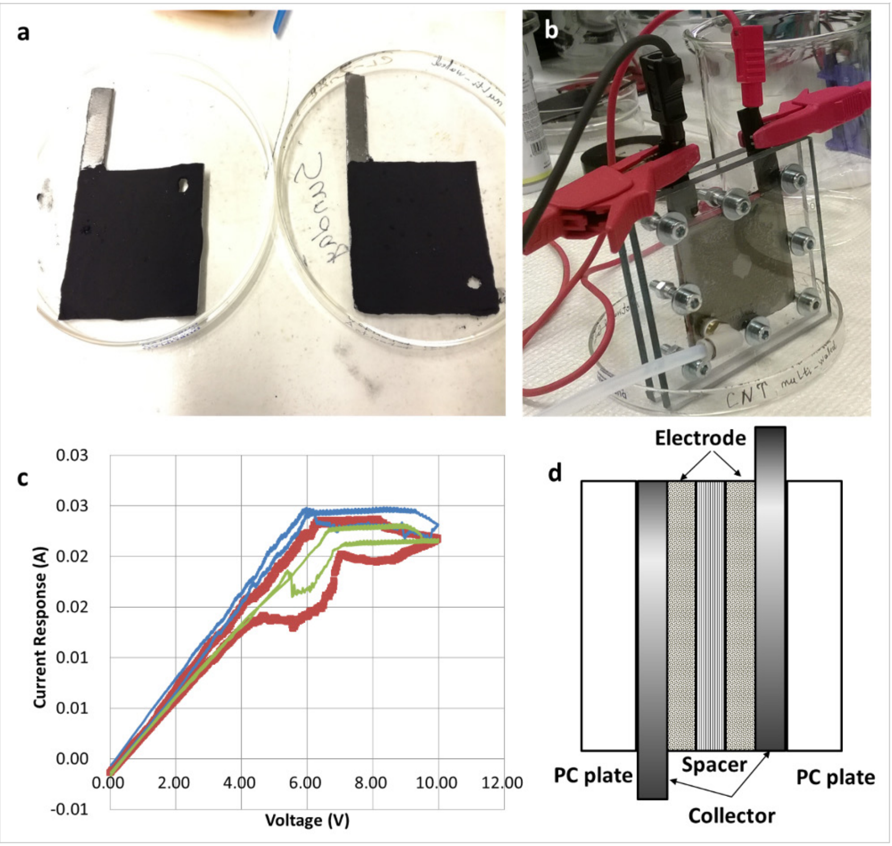

Figure 2. *(a) the as-prepared carbon electrodes; (b) CDI cell; (c) Cyclic voltammograms of carbon electrode (blue, first scan; red, second scan; green, third scan); (d) schematic diagram of CDI cell.*

Table 1. *Surface and pore parameters of cellulose-derived carbon electrodes from nitrogen isotherms at -196 °C.*

Parameter	Value
S_{BET} (m^2/g)	39.48
V_{total} (cm^3/g)	0.117
$D_{pore\ size}$ (nm)	16.386

Adsorption tests using PEI-CNC adsorbent

To investigate the adsorption performance of the as-prepared cellulose adsorbent, the batch sorption experiments were carried out at varying initial concentrations, involving 50, 100, 200, and 315 mg/L with adsorbent dosage of 1 g/L for 16 h. The linearized Langmuir model (Eq. 2) was employed to simulate the experimental data as below:

$$1/Q = 1/(Q_m KC) + 1/Q_m \qquad (2)$$

where C is the equilibrium concentration (mg/L), Q is the amount of adsorbed Ce(IIl) (mg/g), Qm is the maximum adsorption capacity and K_L is Langmuir constant related to binding energy (L/mg). The fitting results were shown in Figure 3 and the fitting parameters were presented in Table 2. It is clearly found from Figure 3 that the Langmuir model correlated with the experimental data well, in the basis of the high correlation coefficient. This indicated that monolayer adsorption might be the primary mechanism in the adsorption process. Moreover, the high maximum adsorption capacity of 82.645 mg/g could be attributed to the fact that the cross-linking introduced abundant of amino groups. PEI plays roles not only as cross-linker but also as functional groups.

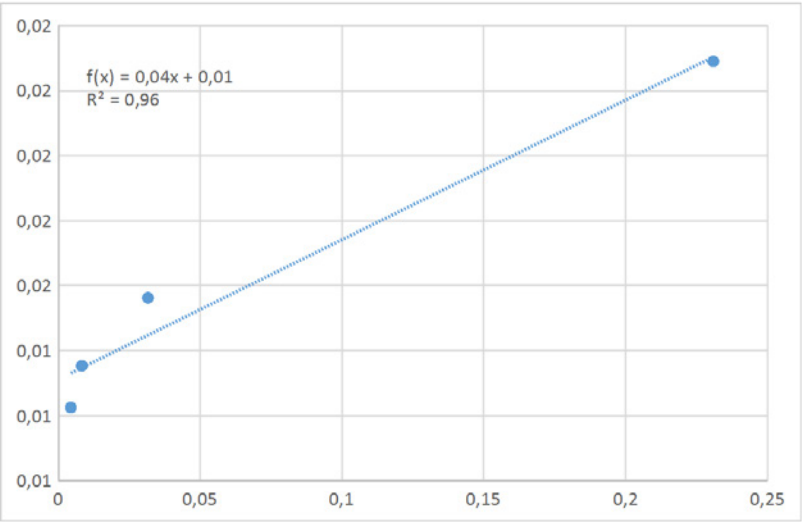

***Figure 3**. Linearized Langmuir isotherm of Ce(III) onto cross-linked CNC.*

***Table 2**. Determined parameters of Langmuir isotherm of Ce(III) onto cross-linked CNC.*

Parameter	Value
Q_m (mg/g)	82.645
K_L (L/mg)	0.282
R^2	0.964

Electrosorption tests using the capacitive deionization cell

Ce(III) ions were separated from the solution with the initial concentration of 27.18 ppm by passing through the CDI cell while the electric potential (10.0 V) was applied to the porous carbon electrodes. The total treatment time was 66 min for 16 runs. Figure 4 shows the electrosorption performance. The separation efficiency was slow at the first 5 cycles but it soared after the sixth cycle. The final recovery efficiency of Ce(III) by the CDI system was found to be 76.39% after 16 cycles. The high efficiency could be attributed to the high specific surface area and high specific capacity.

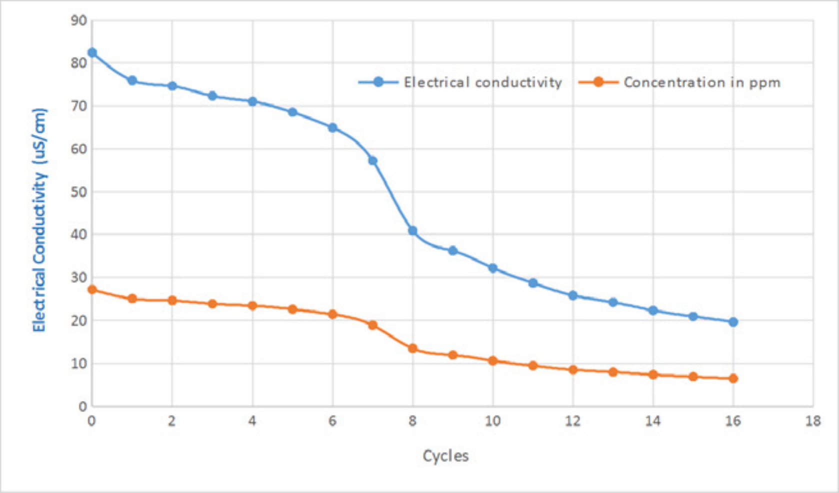

Figure 4. *Electrosorption of Ce(III) onto cellulose-derived carbon electrode at voltage of 10.0 V and flow rate of 48 mL/min.*

Conclusion

In this study, a cellulose-based adsorbent was synthesized by crosslinking cellulose nanocrystal (CNC) with polyethylenimine (PEI) for REE recovery. As a comparison, a cellulose derived carbon electrode was developed and further applied for REEs recovery via CDI system. The cellulose adsorbent showed high maximum adsorption capacity of 82.645 mg/g toward Ce(III) after 16 h. The recovery of CDI was very fast that the recovery efficiency reached 76.39% after 66 min. Such a comparison is not only useful for further understanding the fundamental of the traditional adsorption and electrosorption, but also for promoting the CDI application in water treatment.

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