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# In situ preparation of "Cr-keeper" nanoparticles – Separation of trace vanadium (V) from chromium (VI) in aqueous solution



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#### ABSTRACT

"Cr-keeper" nanoparticles (CKN) are in-situ synthesized based on the challenge of separation trace vanadium (V) from chromium (VI) in aqueous solution. Kelp is used as the bio-template and it can react with chromium (VI). Transmission electron microscopy (TEM) results reveal that CKN can copy the cell structure from kelp and the specific surface area of CKN is 343.20 m<sup>2</sup>/g. Fourier transform infrared (FT-IR) and X-ray photoelectron spectroscopy (XPS) analysis confirm the formation of hydroxyl and Cr (III) species in CKN. The adsorption capacity of V (V) onto CKN is 51.20 mg/g and the maximum separation coefficient ( $\beta_{V/Cr}$  = 3900) is achieved at pH 3.00. The adsorption kinetics follow pseudo-first-order model and Weber-Morris intra particle diffusion model. The adsorption isotherms follow the Sips model. The regeneration and reusability of CKN are discussed. All the results suggest that the utilization of biomass's cell structure as the template for the fabrication of adsorbent with "Cr-keeper" function is excellent, which will bring new directions for Cr (VI) system purification.

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#### 1. Introduction

Chromium is an important strategic element widely used in steel manufacturing, mining, electroplating and leather tannery, etc. [1–3]. Vanadium and chromium are normally coexist in the ore due to their similar chemical characteristics [4]. The mineral mining and the utilities of chromium will produce industrial effluents, which contain trace vanadium and large amount of chromium. It is not an easy task for the separation of trace vanadium from chromium. The partition of V (V) from Cr (VI) has drawn considerable attention in recent years [5–8]. Several technologies can be used to separate V (V) from Cr (VI), including solvent extraction [4], ion exchange [6], electro-oxidation [7] and adsorption [9]. Adsorption technology has been widely employed for the separation of metal ions due to its easy operation and low cost [10–14]. Bio-adsorbents have attracted much attention for the adsorption of metal ions from aqueous, such as cellulosic biomass [15], sugarcane bagasse [16] and Phanerochaete chrysosporium [17]. However, the utilization of the biomass's fine cell structure to in situ synthesize cell-templated adsorbent has seldom been reported to

\* Corresponding author. E-mail address: chmawv@yahoo.com (W. Ma). the best of the authors' knowledge. In addition, literature has been rarely discussed about the selective separation of trace V (V) from Cr (VI), because the organic groups in bio-adsorbent can simultaneous remove V (V) and Cr (VI) from the solution.

Therefore, in this work, "Cr-keeper" nanoparticles (CKN) are in situ synthesized based on the cell structure from kelp. The presence of Cr element in the bio-adsorbent will prevent Cr (VI) adsorption from V (V) and Cr (VI) mixture solution, which means "Cr-keeper" function. The structure of CKN was characterized by transmission electron microscopy (TEM) and nitrogen adsorption analyses. The constituent of CKN was confirmed by Fourier transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS). The separation capacity for trace V (V) from Cr (VI) solution was evaluated through batch adsorption experiments.

#### 2. Materials and methods

#### 2.1. Chemicals

Sodium chromate (Na<sub>2</sub>CrO<sub>4</sub>), sodium metavanadate (NaVO<sub>3</sub>), NaOH and HCl were purchased from Sinopharm Chemical Reagent Co., Ltd., China. All the above reagents are of analytical grade and used as received without any further purification.

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#### 2.2. In situ preparation of CKN

The fresh kelp was pre-treatment with deionized water and then cut into the fixed size (2 cm  $\times$  2 cm). Then the kelp samples were dipped in 5% HCl solution for 4 h and then washed with deionized water for further use. The kelp was placed in a 0.5 M Na<sub>2</sub>CrO<sub>4</sub> solution at 60 °C for 10 h, then the kelp impregnation with Na<sub>2</sub>CrO<sub>4</sub> was heated at 150 °C for 6 h. After the sample cooling down to room temperature, the product was washed several times with 0.05% HCl and deionized water until the concentration of Cr (VI) in the liquid supernatant was below 0.5 mg/L. Then the final "Cr-keeper" nanoparticles (CKN) were dried at 80 °C for 12 h and grinded to powder for subsequent use.

#### 2.3. Characterization

Fourier transform infrared spectroscopy (FT-IR) spectra was obtained using Bruker TENSOR 27 FTIR and the spectra was recorded in 400–4000 cm<sup>-1</sup> range. Transmission electron microscopy (TEM) analysis was conducted with JEM-2100F field emission electron microscopy. The surface area of CKN was measured by N<sub>2</sub> adsorption-desorption technique (JW-BK122W). The surface electronic states were analyzed by X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi). The content of Cr in CKN was analyzed by Inductive Coupled Plasma Emission Spectrometer (ICP, Optima 2000DV, USA).

#### 2.4. Batch adsorption experiments

The adsorption of V (V) and Cr (VI) on CKN was studied by batch experiments in an isothermal shaker (150 r/min). Unless otherwise stated the parameters were: temperature 293.15 K, solution volume 50 mL, sorbent dose 0.01 g, contact time 12 h, Cr (VI) concentration 200 mg/L, V (V) concentration 10 mg/L. The effect of initial pH was from 1.0 to 7.0 adjusted by HCl and NaOH solution. Then the supernatant was centrifuged at 4000 rpm for subsequent centration analysis.

The adsorption capacity (q, mg/g), distribution ratio (D, L/g) and separation coefficient ( $\beta_{V/Cr}$ ) between V (V) and Cr (VI) were calculated according to the follow equations:

$$q = \frac{(C_i - C_e)V}{m} \tag{1}$$

$$D = \frac{(C_i - C_e)V}{C_e \times m} = \frac{q}{C_e}$$
(2)

$$\beta_{\rm V/Cr} = \frac{D_{\rm V}}{D_{\rm Cr}} \tag{3}$$

where  $C_i$  (mg/L) and  $C_e$  (mg/L) are the initial and final metal ions concentration, respectively. *V* (L) is the volume of the solution, and *m* is the weight of the adsorbent.

D (L/g) is the distribution ratio.  $D_v$  and  $D_{Cr}$  are the distribution ratio of V (V) and Cr (VI), respectively.

The amount of V (V) ions desorbed from V (V) loaded CKN was determined by the remaining concentrations of V (V) ion solution after desorption and the desorption rate was calculated from the equation as below:

$$w = \frac{q_d}{q_a} \times 100\% \tag{4}$$

where *w* is the desorption rate (%),  $q_d$  and  $q_a$  are the amount of V (V) desorbed from V (V) loaded CKN and the amount of V (V) adsorbed on CKN, respectively.

#### 2.5. Analytical methods

The concentrations of V (V) and Cr (VI) were determined by Inductive Coupled Plasma Emission Spectrometer (ICP, Optima 2000DV, USA). The pH of the solution was measured by an acidimeter (PHS-2 Model, China). Three replicates were measured on each sample.

#### 3. Results and discussion

#### 3.1. In situ synthesis of CKN and characteristics

The natural kelp contain a mass of crude fiber, protein and alginic acid [18]. The above constituents could provide large organic reducing substances and Cr (VI) is strong oxidability [19], which could react with the reductive groups present in kelp. In addition, the natural kelp contains epidermis, exodermis, endoderm and pith [20], which endowing the kelp with elaborate cell organization and the resulting CKN samples could copy the special structure from kelp cell. For kelp, the dipping process of Cr (VI) ensured the full occupation of active sites by Cr (VI). Hence, kelp was selected as the bio-template for the in situ fabrication of "Cr-keeper" absorbent.

The digital microscope image of nature kelp was showed in Fig. S1, and we can see clearly the cells in kelp were wellaligned. The microstructural properties of CKN were investigated by TEM. As shown in Fig. 1(A), CKN copied the cell structure from the nature kelp and the results confirmed the effect of the cell template. In the detail observation (Fig. 1(B)), we can see clearly that a mass of nanowires with a length of 10-20 nm are dispersed onto the surface of the samples, seemingly like caterpillars. The N<sub>2</sub> adsorption-desorption isotherm and corresponding pore size distribution curves of CKN were displayed in Fig. 2. To determine the surface area and pore size of CKN, BET and Barrett Jouner Halenda (BJH) analysis were performed, respectively. The specific surface area of CKN was 343.20 m<sup>2</sup>/g and the pore volume was 0.679 cm<sup>3</sup>/g. A narrow pore size distribution of CKN samples with the average pore diameter of 0.67 nm is observed, which suggests that CKN would possess a good adsorption capacity for V (V) since CKN have abundant intra channels and the pores are nano-sized.

To determine the functional groups of CKN, FT-IR analysis was performed. As shown in Fig. S2, CKN displayed the vibrations at  $3412 \text{ cm}^{-1}$  (O—H and N—H stretch),  $1629 \text{ cm}^{-1}$  (C—O asymmetric vibration from —COO<sup>-</sup>),  $1430 \text{ cm}^{-1}$  (C—O symmetric vibration from —COO<sup>-</sup>) and  $1056 \text{ cm}^{-1}$  (C—C vibration) [21]. The peak at  $532 \text{ cm}^{-1}$  was due to the vibration of Cr—O [22]. Meanwhile the peaks observed at 3412, 1629,  $1430 \text{ cm}^{-1}$  for CKN shifted respectively to 3415, 1621 and  $1423 \text{ cm}^{-1}$  after V (V) was loaded onto CKN (CKN-V), indicating that hydroxyl groups in CKN participated in the adsorption of V (V). It is likely attributed to the coordination with the oxygen-containing group vanadate. Besides, a new peak appeared at around 609 was attributed to the symmetric vibration of V-O-V after vanadate loaded onto CKN [23].

The content of Cr in CKN was 25.65% according to the ICP results. The chemical constituents and the surface electronic states of CKN were further confirmed by XPS analysis. As shown in Fig. S3, the XPS signals originating from Cr 2p (575.48 eV), O 1s (529.86 eV), N 1s (398.54 eV) and C 1s (284.21 eV) can be identified. By contrast, the peak of V 2p (515.6) can be found in the amplified region from 508 to 526 eV for vanadate loaded on CKN (CKN-V), suggesting that vanadate had been involved into CKN. The Gaussian-resolved result for V 2p spectrum displayed the peak at around 515.6 eV, which could be attributed to V (V), a high oxi-

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