



# Cerium oxide cadmium oxide nanomaterial as efficient extractant for yttrium ions

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## ABSTRACT

The present study describes a developed methodology for selective extraction of yttrium ions based on cerium oxide cadmium oxide (CeO<sub>2</sub> CdO) nanomaterials. The elaborated characterization of CeO<sub>2</sub> CdO nanomaterial was provided by SEM, EDS, XRD, XPS and FTIR techniques. CeO<sub>2</sub> CdO nanomaterial was employed as solid-phase extractant for heavy metal ions from aqueous media. Based on the results, CeO<sub>2</sub> CdO nanomaterial exhibited high selectivity for Y(III) with a maximum uptake capacity of 84.67 mg g<sup>-1</sup> at pH 6.0. Adsorption isotherm data were well-correlated with Langmuir isotherm and pseudo-second order models. Yttrium ions were easily recovered from CeO<sub>2</sub> CdO nanomaterial using 0.3 M HCl solution, and the adsorbent showed high stability for reusing several times. Ultimately, the developed methodology was successfully applied for real water specimens.

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## 1. Introduction

Rare earth elements (REEs) considered as surface active elements, which play a significant role in metallurgy, such as refinement of microstructure materials, alloying and purification of materials as well as production of super-conductors, super-magnets, storage, conservation and transport of energy. They possess unique physicochemical characteristics that lead them indispensable for a growing number of delicate technologies. This group of elements is fall into two categories, the light rare earth elements including cerium, lanthanum, neodymium, praseodymium, promethium and samarium, and the heavy rare earth elements which are more valuable involving dysprosium, gadolinium, erbium, europium, holmium, lutetium, scandium, terbium, thulium, ytterbium and yttrium. Yttrium is one of the most REEs that industrially used in large quantity due to its importance in manufacturing devices of visual displays [1–3]. Yttrium-90 isotope is also employed in therapy as a replacement for radioactive elements. However, yttrium considered harmful to human health and may cause several diseases. As a result of industrial and medical wastes, yttrium could be released to environmental waters leading to health concern for human and other organisms. Therefore, it is of importance to find effective methods that selectively separate yttrium from aqueous media [3,4].

Several techniques have been utilized for the selective extraction or preconcentration of REEs that involves coprecipitation, ion-exchange, liquid–liquid and solid-phase extractions. Liquid–liquid extraction considered as ineffectual method because it requires large volume of toxic solvents, which cause health problems. Other conventional techniques are usually time-consuming, high operational cost, low selectivity and may create the generation of secondary pollutants [5–7]. Solid-phase extraction is the more preferable separation technique for wide range of analytes owing to its versatility, simplicity and availability of various adsorbents. Traditional adsorbents, such as activated carbon, alumina, silica and polymeric resins are efficient for removing many kinds of analytes but mostly suffer from selectivity that restricts their practical use [8–10]. Therefore, development of new advanced materials as adsorbents is of great interest nowadays in order to achieve high selectivity toward target analyte besides high uptake capacity.

Recently, nanostructured materials as promising adsorbents have been extensively employed for wide range of target pollutants; owing to their unique physicochemical characteristics and distinct performance as solid-phase extractants [11–16]. Semiconductor nanostructured materials, especially mixed transition metal oxides, have received plentiful attention by researchers since it offered stable morphologies composed of number of irregular phases that lead them suitable for versatile applications, such as adsorption, sensing and catalysis [17,18]. Specifically, ZnO and CdO are well known n-type semiconductors with band gaps of 3.3 eV and 2.2 eV, respectively, that provide enhanced characteristics [19]. Extensive efforts have been made for improving ZnO nanostructured semiconductors by transition metal

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oxides in order to use in sophisticated technologies. For example, CdO ZnO nanocomposites have been synthesized by sol-gel route as a sensor for CO gas [20]. An ammonia vapor sensor was developed using vanadium doped ZnO synthesized by coprecipitation route [21]. Photocatalytic degradation of methylene blue dye has been reported by using ZnO/CeO<sub>2</sub> nanorods developed by thermal decomposition method [22]. Our group reported the fabrication of CuO ZnO nanosheets and nanofibers by wet-chemical method for selective extraction of lead ions and photocatalytic degradation of Remazol brilliant orange 3R, respectively [23,24]. ZnO CdO nanoblocks were also reported as effective solid-phase extractant and photocatalyst for pollutants removal [25]. Up to our knowledge, few studies were reported on transition metal oxide CdO nanostructures for environmental applications, and most of them have been used CdO with ZnO as nanocomposites. Accordingly, we report a facile synthesis and structure elucidation for cerium oxide cadmium oxide nanomaterials (CeO<sub>2</sub> CdO). The synthesized CeO<sub>2</sub> CdO nanomaterial was employed as solid-phase extractant for metal ions from aqueous media. Several parameters were investigated for yttrium ions adsorption onto CeO<sub>2</sub> CdO nanomaterial. The developed methodology was then applied onto extraction of Y(III) from real water samples.

## 2. Experimental

### 2.1. Chemicals and reagents

Stock standard solutions of Cr(III) and Cr(VI) as well as sodium hydroxide (NaOH) were purchased from Sigma-Aldrich. Metal ion salts of CeCl<sub>2</sub>, CdCl<sub>2</sub>, Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, CuCl<sub>2</sub>, Na<sub>2</sub>WO<sub>3</sub>·2H<sub>2</sub>O, Pb(NO<sub>3</sub>)<sub>2</sub>, Y(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and ZnCl<sub>2</sub> were purchased from BDH. Ethanol was also obtained from BDH. All employed reagents were of analytical and spectral purity grade, and 18.2 MΩ cm distilled deionized water was utilized throughout experiments.

### 2.2. Synthesis of CeO<sub>2</sub> CdO nanomaterial

CeO<sub>2</sub> CdO nanomaterial was prepared by mixing 0.1 M of CeCl<sub>2</sub> solution and 0.1 M of CdCl<sub>2</sub> solution in a ratio of 2:1. The mixed solution was first kept on stirring for 30 min at room temperature. Then, the pH was adjusted to around 10 by drop wise addition of NaOH solution. The resultant solution was further stirred at 60 °C for 10 h. A white precipitate was obtained after terminating the reaction, which was washed with water and ethanol several times, dried and calcined at 400 °C for 5 h.

### 2.3. Apparatus

A field emission-scanning electron microscope (FESEM), JEOL (JSM-7600F, Japan) was utilized to investigate the morphologies of CeO<sub>2</sub> CdO nanomaterial. The elemental analysis of CeO<sub>2</sub> CdO nanomaterial was performed by employing the Energy dispersive X-rays spectrometry (EDS), oxford-EDS system. The crystal structures of CeO<sub>2</sub> CdO were analyzed using X-ray diffraction (XRD), Thermo scientific diffractometer with a Cu Kα radiations (λ = 0.154 nm) source. Thermo scientific FTIR spectrometer was also used in characterization order to analyze common functional groups in CeO<sub>2</sub> CdO nanomaterial. The surface chemical composition of CeO<sub>2</sub> CdO nanomaterial was studied using X-ray photoelectron spectroscopy (XPS). A Perkin Elmer ICP-OES model Optima 4100 DV, USA was employed for ICP-OES measurements using the parameters reported in our previous study [26]. Selected metal ions concentrations were detected at wavelengths of 238.892 nm for Co(II), 327.393 nm for Cu(II), 267.716 nm for Cr(III) and Cr(VI), 220.353 nm for Pb(II), 324.227 nm for Y(III), 207.912 nm for W(VI) and 213.857 nm for Zn(II).

### 2.4. Batch adsorption procedure

In this investigation, static adsorption method was carried out in order to evaluate the selectivity and extraction efficiency of selected metal ions by CeO<sub>2</sub> CdO nanomaterial. An amount of 10.0 mg CeO<sub>2</sub> CdO was added to 25 mL of 5 mg L<sup>-1</sup> sample solution of Co(II), Cu(II), Cr(III), Cr(VI), Pb(II), W(VI), Y(III) and Zn(II), and vigorously shaken for 60 min at room temperature. Then, the effect of other empirical parameters influenced the adsorption performance of Y(III) was inspected including adsorbent dose (10–25 mg), pH of the solution (1.0–8.0), initial Y(III) concentration (0–200 mg L<sup>-1</sup>), contact time (2–120 min) and temperature (298–338 K). The isolation of CeO<sub>2</sub> CdO adsorbent from the solutions was achieved by filtration, and the concentration of each metal ion was determined by employing inductively coupled plasma–optical emission spectroscopy (ICP-OES). The desorption of Y(III) was studied by transferring 15 mg CeO<sub>2</sub> CdO nanomaterial saturated with Y(III) after performing adsorption experiments to 25 mL of HCl solution (0.1–0.5 M).

## 3. Results and discussion

### 3.1. Characterization of CeO<sub>2</sub> CdO nanomaterial

#### 3.1.1. Field emission scanning electron microscopy (FESEM)

Morphologies of CeO<sub>2</sub> CdO were investigated using FESEM, as displayed in Fig. 1. We can clearly observe small dots of less than 100 nm proliferated on fibers like elongated structures, which suggest the formation of mixed metal oxides (CeO<sub>2</sub> CdO nanomaterial). According to the low and high magnification of FESEM images, the prepared CeO<sub>2</sub> CdO nanomaterial is possessing unsmooth surface. The average diameter of the fiber like structures is below 100 nm are covered with small particles having average diameter less than 100 nm while in some part the particles exist in aggregated form. These two types of morphology suggest the growth of CeO<sub>2</sub> CdO mixed metal oxides nanomaterial.

#### 3.1.2. Energy-dispersive X-ray spectroscopy (EDS)

EDS analysis was conducted in order to confirm the presence of CeO<sub>2</sub> CdO in the synthesized mixed oxide nanomaterial. Results reveal a successful preparation of CeO<sub>2</sub> CdO mixed oxide nanomaterial, in which Ce, Cd and O elements can be clearly observed in the composition of CeO<sub>2</sub> CdO (Fig. 2).

#### 3.1.3. X-ray diffraction (XRD)

Crystal structure and crystallinity of the CeO<sub>2</sub> CdO nanomaterial were analyzed by XRD which is represented in Fig. 3(a). The strong diffraction peaks of CeO<sub>2</sub> and CdO were noticed in the as-grown CeO<sub>2</sub> CdO nanomaterial. The peaks which are marked with “\*” could be indexed to (111), (200), (220), (311), (222), (400), (331) and (420) phases, which illustrate that the synthesized nanomaterial have well-crystalline distinct fluorite-type structure of CeO<sub>2</sub> [27]. Besides the CeO<sub>2</sub> peaks, the peaks marked with “φ” are referred to CdO [28,29]. All featured peaks in XRD pattern are well compatible with that of CeO<sub>2</sub> and CdO, which suggest that as-grown nanomaterial is CeO<sub>2</sub> CdO mixed oxides.

#### 3.1.4. Fourier transforms infrared spectroscopy (FTIR)

Fig. 3(b) illustrates the typical FTIR spectrum of CeO<sub>2</sub> CdO nanomaterial recorded in the range of 400–4000 cm<sup>-1</sup>. The band centered at 3424 and 1634 cm<sup>-1</sup> was assigned to bending and stretching vibrations of O—H bond owing to the presence of water absorbed from the environment [30]. The high intense band at 1385 cm<sup>-1</sup> is attributed to CO<sub>2</sub> or CO<sub>3</sub> bonds, which comes from the environment or precursor. The broad band located at 560 cm<sup>-1</sup> is responsible for M—O (M = Ce and Cd) bonds.

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