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Samaria-doped ceria nanopowders for heavy metal removal from aqueous solution

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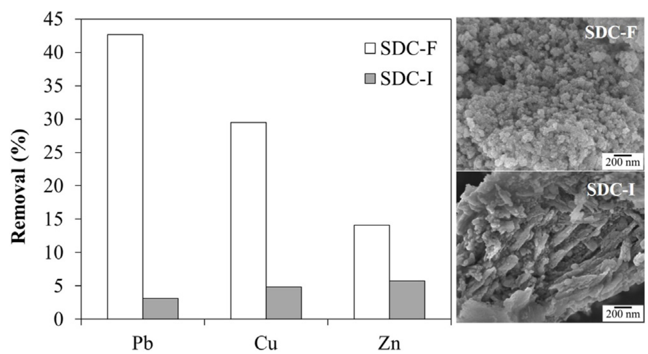
HIGHLIGHTS

- SDC nanoparticles can efficiently remove Pb(II) and Cu(II) from water by adsorption process.
- Spherical SDC nanoparticles show higher performance than plate-like SDC nanoparticles.
- Pb(II) sorption on SDC is represented by the pseudo-second order and Langmuir isotherm model.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, the feasibility and performance of samaria-doped ceria nanopowder (SDC) as an absorbent for Pb(II), Cu(II) and Zn(II) removal from synthetic wastewater is investigated in batch studies. Two commercial SDC nanopowders; SDC-I and SDC-F, are comparatively studied their morphology, crystal structure, specific surface area and pore volume in order to distinguish the effect of above features on the adsorption capability for metal-ion removal. The spherical SDC-F nanopowder is more effective for removal those three metals than SDC-I nanopowders having a cluster plate-like structure. Among those three metal ions, Pb(II) shows the highest sorption amount on the SDC-F surface. The adsorption parameters for Pb(II) on SDC-F are optimized via variable pH values, metal-ion concentrations, adsorbent dosages, temperatures and contact times. Adsorption capacity of Pb(II) on SDC-F nanopowder is maximum at pH = 5.6. Higher removal ability is found at lower metal-ion concentration but higher adsorbent dosage, temperature and contact time. Kinetic studies reveal that the adsorption of Pb(II) on SDC-F nanopowder follows the pseudo-second-order model. The maximum adsorption capacity of SDC-F for Pb(II) ions calculated by Langmuir isotherm is 23 mg g^{-1}. Adsorption of Pb(II) on SDC-F is confined by the agglomeration of spherical nanoparticles. The outcome of this study shows that the SDC-F nanoparticles is possible candidate for removal of Pb(II) ions from wastewater.

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1. Introduction

Heavy metal ions, such as Cr(VI), Cd(II), Co(II), Ni(II) and Pb(II), are frequently found in wastewater coming from metal plating, textile dyeing and battery industries [1]. Among these toxic ions, Lead ion or Pb(II) shows an extreme toxicity and high-level contamination in aquatic environments. This results in serious damage of, kidney, liver, nervous and brain system to all livings [2]. Pb and its compounds are found in a wide variety of products including pipes and plumbing materials, batteries, gasoline, solders, paints, ceramics cosmetics, and ammunition [3]. Pb-compound are stable substances and cannot be naturally decomposed from environmental system. The treatment of Pb-contaminated wastewater is therefore a serious issue for our aquatic environments.

In contaminated water, Pb(II) ions can be eliminated by several techniques such as precipitation into a metal-hydroxide form, ion-exchange, chemical extraction and adsorption process. The elimination of metal ions in water via an adsorption is a mass transfer process by which a heavy metal ion (absorbate) is transferred from the liquid phase to the surface of a solid (adsorbent), and becomes bound by physical and/or chemical interactions. The adsorption mechanism, therefore, takes place at the whole surface of the adsorbent where the absorbate molecules can move to. Recently, various metal-oxide nanopowders such as Fe_2O_3, MnO_2, Al_2O_3, TiO_2, MgO and CeO_2 have been used as the absorbent for toxic-metal ion removal from polluted water [4]. High surface area of metal-oxide nano-sized particles provides the large adsorbed area for metal ions leading to a high effectiveness for cleaning up contaminated water.

In addition to the high surface area of the adsorbent, other criterias for selecting absorbent metal-oxide powder are sensitivity in low concentration of metal-ion contamination, nontoxicity and reusable [5]. Cerium oxide (CeO_2) is a non-harmful rare-earth oxide, which is used in several applications including an absorbent in wastewater treatment [6–10]. CeO_2 incorporated with other metal oxides such as Gd_2O_3, Sm_2O_3, and La_2O_3 are also reported their effectiveness in solid oxide fuel cell (SOFC) [11–13] and photocatalytic heavy-metal removal applications [14,15]. However, none of the study is revealed the feasibility and performance of doped-CeO_2 materials instead of solely CeO_2 [6,16] on the elimination of heavy metal in wastewater via adsorption process.

In this work, Sm_2O_3-doped CeO_2 or SDC nanopowder, which is previously used in our studies on SOFC application, has been investigated for metal-ion removal from contaminated water in order to reveal another usefulness of nano-sized SDC powder. The SDC nanoparticles from two different commercial sources are employed for comparative study in their metal-ion adsorption capabilities. The SDC nano-sized powder has never been fully investigated so far on eliminating toxic metal ions, particularly Pb(II) from contaminated water via adsorption process. However, there are some reports on enhancing metal catalyst adsorption of CeO_2 powder by increasing oxygen vacancies and providing more structural defects and surface active sites for the adsorption via the Sm_2O_3 doping into CeO_2 structure [17].

To the best of our knowledge, the present study is the first report on the feasibility of the SDC nano-sized powders and their utilities in the removal of metal ions from synthetic wastewater. The two commercial SDC nanopowders are comparatively characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM) and BET surface area analyzing techniques. The efficiency of the SDC nanoparticles related to their morphology and surface properties for effective removal of Pb(II) ions from aqueous solution is explored. The optimal parameters contributed to the adsorption capability of the SDC nanoparticles are investigated and compared. The experimental data are fitted with various kinetic and isotherm models in order to understand the adsorption kinetics of metal-ion adsorption on the surface of SDC nano-sized powders.

2. Materials and methods

2.1. Characterization of SDC nanopowders

Commercial samaria-doped ceria nanopowders ($Sm_{0.2}Ce_{0.8}O_{2\text{-}x}$ or SDC) having different physical features are used in this study. They are obtained from two suppliers that are coded as SDC-F and SDC-I. Morphology of SDC nanoparticles is examined by a field emission-scanning electron microscope (FE–SEM, JEOL JSM-7610F). TEM images of the SDC nano-sized powders are collected on a high-resolution transmission electron microscope (HRTEM, JEOL JEM 2010 USA). Specific surface area and pore volume of the SDC nanopowders are obtained by surface analyzer (Quantachrome, Autosorb-1). Crystal structure of the SDC nanopowders is analyzed by an X–ray diffractometer (Bruker AXS-D8 Discover). The 2θ scan is in a range between 20° and 80° with a step size of 0.2 s.

2.2. Ion adsorption test

100 mg L^{-1} of each $Pb(NO_3)_2$ (Loba Chemie), $CuSO_4{\cdot}5H_2O$ (Fisher Scientific), and $ZnSO_4{\cdot}7H_2O$ (J.T. Baker) aqueous solutions is prepared for adsorption experiments. A 100 mg SDC-F and SDC-I nanopowders is individually added into a 50 mL of each aqueous solution in a glass beaker to obtain suspension samples for adsorption activity test. Each suspension is individually agitated at a speed level 6 for 60 min by a magnetic stirrer (VELP-AM4). After test, All the suspensions are centrifuged at a speed of 5000 rpm min^{-1} for 20 min in order to separate the absorbent nanoparticle from the metal ion solution. The residual concentration of metal ions in the aqueous solutions is measured by atomic adsorption spectrophotometer (AAS, Varian-AA280FS). An ion removal percentage is calculated from an initial metal-ion concentration (C_i) and a residual concentration after test (C_f) in a certain time using Eq. (1). Any SDC sample showing the highest capability is further selected to study optimal adsorption parameters for metal-ion removal via the adsorption process.

$$\%Removal = \frac{C_i - C_f}{C_i} \times 100 \tag{1}$$

2.3. Optimized parameters for Pb(II) adsorption

Adsorption experiments are conducted to study the effect of various parameters i.e. pH, metal-ion concentration, adsorbent dosage, contact time and temperature. Effect of pH on metal-ion adsorption is investigated by changing the pH of Pb(II) solution from 5.6 to 5, 4, and 3 by using 0.1 mol L^{-1} hydrochrolic acid solution (HCl). A 150 mg SDC nanopowder is added into a 50 mL pH-adjusted solutions and agitated at a speed level 6 for 60 min by a magnetic stirrer (VELP-AM4) before solid-liquid separation using centrifuge method.

In order to study the effect of adsorbent dosage, the amount of SDC nanopowder from 0.5 to 5 g L^{-1} is used in the experiments. The effect of metal-ion concentration is studied by changing the respective metal concentration from 25 to 100 mg L^{-1}. The SDC nanopowder is added into Pb (II) solution and agitated with the same speed and time as mentioned above prior to centrifuge and determine the maximum adsorption capacity of SDC nanopowder.