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Evaluation of cerium doped tin oxide nanoparticles as a sensitive sensor for selective detection and extraction of cobalt



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ABSTRACT

Chemo-sensor technology demands to design a single, preconcentrator based sensing system having higher sensitivity, sufficient selectivity and efficient removal of metal ions with simple operating and recognition methodology. Here we effectively deliberated Ce doped SnO₂ nanoparticles based sensing system which can be exploited for the recognition and extraction of Co(II) ions in a single step by strong interaction between Ce doped SnO₂ nanoparticles and Co(II). The sensing ability of Ce doped SnO₂ nanoparticles were deliberated for a selective removal of cobalt using inductively coupled plasma-optical emission spectrometry. The sensing ability of Ce doped SnO₂ is studied for various metal ions, such as Cd (II), Co(II), Cr(III), Cu(II), Fe(III), Ni(II) and Zn(II) but the designed sensor was most selective toward Co(II) which was 5000 time more sensitive to Co(II) rather than different interfering metal ions. In addition, the desorption study for regeneration of Ce doped SnO₂ nanoparticles was carried out. This novel approach provides a new route for simultaneous detection and removal of Co(II) in a single step and can be a time and cost alternative tool for environmental safety.

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1. Introduction

Many industries such as nuclear power plant and tanneries acts as rich source of heavy metal contamination present in waste streams [1–3]. These heavy metals existence contribute chiefly in ground and surface water contamination. Metals like cadmium, chromium, cobalt, lead and mercury play key role in initiating various diseases and disorders as these metals are not biodegradable [1]. Only trace amount of these metals is vital to life as it occurs in ores of the Earth's crust in the form of several salts. Pure cobalt has the physical properties such as odorless metal, steely-grayish in color, shiny in appearance and hard metal. Humans are

open to a little quantity of cobalt in food and environment. Cobalt ions have useful as well as hurtful effects on human health. Sea water and soil are the vital resources of cobalt in the natural atmosphere. Cobalt and its precursors have been utilized for different purposes by pharmaceutical and painting industries [1]. The main use of cobalt and its precursors have been found in medicine, painting on glass and porcelain, lacquers, varnishes and paints. The allowable confines of cobalt in water using both for irrigation purposes and livestock are 0.0005 and 0.0010 g/L, respectively (Environmental Bureau of Investigation, Canadian Water Quality Guidelines). Cobalt has severe poisoning and adverse effect on humans. It generally causes asthma like allergy and heart failure. It is also harmful to heart, thyroid and liver. Cobalt also causes cancer by exposing to ionizing radiation. With a healthier wakefulness of the harms related with cobalt, exploration associated to the techniques of extracting cobalt from wastewater has gained great attention [1–5].

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Various skills and analytical tools have been established for analyzing and extraction of toxic cobalt from wastewater such as chemical precipitation, electroflotation, coprecipitation, ion exchange, cloud point extraction, reverse osmosis and liquid–liquid extraction (atomic absorption spectrometry, anodic stripping voltammetry and ion chromatography) [6–16]. However, these methods cannot quantify the toxic cobalt at ultra-trace level due to their less sensitivity and selectivity [17]. The second reason is their high cost which restricts their importance. However, simple, cost effective and efficient alternative methods for management of metal polluted waste water and monitoring of cobalt in the environment are required [18–20].

Solid phase extraction is deliberated to be one of the cost effective and potent techniques because it is simple, quick, and competent [21]. Solid phase extraction requires least amount of solvent usage and removal time. Several adsorbents have been utilized for the selective extraction of metal ions [22–29] but lower sorption capacity and less selectivity makes their limitation as super adsorbents for waste water treatment. Recently hard work has been carried out to improve the heavy metal binding aptitudes and also their selectivity towards metals using nanomaterials [30].

Nanomaterials have idiosyncratic and copious applications concerning human health as it bestow substantially to medicine and environment [31,32]. Nanomaterials exhibit a unique competence to adsorb metal ion which is rarely possible regarding conservative systems [33]. Nanomaterials possess particular shape, trivial size, great active surface to volume ratio, and extraordinary surface activity. Tin oxide is multipurpose nanomaterial relating to its applications but it still requires reformation in order to enhance its properties [34]. Among different techniques, one is doping of nanomaterials known to reveal outstanding properties in numerous areas. Dopants increase the surface area, reduce the mass and alter the morphologies of the nanomaterials resulting in much improved properties of nanomaterials [35].

In the current investigation, Ce doped SnO₂ nanoparticles were prepared and characterized by XRD, FESEM, FTIR, and XPS. Ce doped SnO₂ nanoparticles were applied as adsorbent for the selective extraction of Co(II). The selectivity of Ce doped SnO₂ nanoparticles toward diverse metal ions, such as Cd(II), Co(II), Cr(III), Cu(II), Fe(III), Ni(II) and Zn(II), was explored in order to examine the efficacy of Ce doped SnO₂ nanoparticles on the extraction of nominated metal ions. Based on the selectivity study, the Ce doped SnO₂ nanoparticles accomplished the utmost selectivity toward Co(II). Ce doped SnO₂ nanoparticles displayed 77.85 mg g⁻¹ of static uptake capacity for Co(II). Adsorption isotherm data of Co(II) with Ce doped SnO₂ nanoparticles were well fit with the Langmuir adsorption isotherm, strongly confirming that the adsorption process was mainly monolayer on homogeneous adsorbent surfaces.

2. Experimental

2.1. Chemicals and reagents

Tin chloride and cerium nitrate and stock standard solutions of 1000 mg L⁻¹ Cd(II), Co(II), Cr(III), Cu(II), Fe(III), Ni(II), and Zn(II) were purchased from Sigma-Aldrich (Milwaukee, WI, USA). All reagents used were of high purity and of spectral purity grade, and doubly distilled deionized water was used throughout.

2.2. Synthesis of Ce doped SnO₂ nanoparticles

Tin chloride and cerium nitrate were collectively added to distilled water and prepared 0.1 M aqueous solution according to

each metal salt. The aqueous solution was titrated till pH 10.0 by using 0.5 M NaOH solution. This subsequent basic solution was kept for stirring at 60.0 °C for overnight. The solution was filtered and the solid product was washed thoroughly, dried and calcined at 400.0 °C for 5 h.

2.3. Samples preparation and procedure

For the detection and selectivity study of the designed sensor toward metal ions, standard solutions of 5 mg L⁻¹ of each metal ion were prepared and adjusted to pH value of 5.0 with acetate buffer. Each standard solution was individually mixed with 25 mg of the Ce doped SnO₂ nanoparticles. A fixed pH value of 5.0 was chosen in this study for all metal ions in order to avoid any precipitation of other species, in particular for Fe(III). Fe(III) is usually forms a precipitation of Fe(OH)₃ with buffer solutions above pH value of 5.0. For investigation of the Co(II) adsorption capacity, standard solutions of 0, 5, 10, 15, 20, 25, 30, 50, 75, 125 and 150 mg L⁻¹ were prepared as above, adjusted to the optimum pH value of 5.0 and individually mixed with 25 mg of Ce doped SnO₂ nanoparticles. All mixtures were mechanically shaken for 1 h using a mechanical shaker at 150 rpm and room temperature. The recovery time was fixed for 1 h because minimum to no change was observed in the uptake capacity of Ce doped SnO₂ nanoparticles for Co(II) under batch conditions. The reversibility of adsorption of 25 mg Ce doped SnO₂ nanoparticles for Co(II) was investigated by desorption study at different concentrations (2 and 6 mg L⁻¹) of Co(II). The saturated Ce doped SnO₂ nanoparticles with Co(II) was removed from solution and transferred to 25 mL of (0.1–0.3 mol L⁻¹) HNO₃ solution once equilibrium was reached. The mixture was mechanically shaken for 1 h at 150 rpm and room temperature using a mechanical shaker. The Ce doped SnO₂ nanoparticles was then removed by centrifugation, and the concentration of Co(II) in the aqueous solution was determined by inductively coupled plasma-optical emission spectrometer (ICP-OES).

2.4. Apparatus

The morphology of the synthesized product was studied at 15 kV using a JEOL company Field Emission Scanning Electron Microscope (JSM-7600F, Japan). Energy dispersive spectroscopy was used for the composition of nanomaterials. X-ray diffraction patterns (XRD) were taken with a computer controlled RINT 2000, Rigaku diffractometer using the Ni-filtered Cu-K_α radiation ($\lambda = 0.15405$ nm). FT-IR spectrum was recorded in the range of 400–4000 cm⁻¹ on PerkinElmer (spectrum 100) FT-IR spectrometer. ICP-OES measurements were acquired by use of a Perkin Elmer ICP-OES model Optima 4100 DV, USA. The ICP-OES instrument was optimized daily before measurement and operated as recommended by the manufacturers. The ICP-OES spectrometer was used with following parameters: FR power, 1300 kW; frequency, 27.12 MHz; demountable quartz torch, Ar/Ar/Ar; plasma gas (Ar) flow, 15.0 L min⁻¹; auxiliary gas (Ar) flow, 0.2 L min⁻¹; nebulizer gas (Ar) flow, 0.8 L min⁻¹; nebulizer pressure, 2.4 bar; glass spray chamber according to Scott (Ryton), sample pump flow rate, 1.5 mL min⁻¹; integration time, 3 s; replicates, 3; wavelength range of monochromator 165–460 nm. Selected metal ions were measured at wavelengths of 228.80 nm for Cd(II), 238.90 nm for Co(II), 267.72 nm for Cr(III), 327.39 nm for Cu(II), 259.94 nm for Fe(III), 221.65 nm for Ni(II), and 206.20 nm for Zn(II).

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