

Exploration of silver oxide nanoparticles as a pointer of lanthanum for environmental applications



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ABSTRACT

Solid phase extraction technique is a promising advancement in the fundamental science and has vital role in the environmental and health monitoring. A huge number of solid phase materials have been studied but the prospective for industrial development as an environmental supplement is still limited. Therefore, silver oxide (Ag_2O) nanoparticles have been prepared and applied as a selective adsorbent for the adsorption and determination of lanthanum ion using simple eco-friendly solid phase adsorption method. Pure Ag_2O nanoparticles powders were illustrated by field emission scanning electron microscopy (FEEM), X-ray diffraction, X-ray photoelectron spectroscopy (XPS), and Fourier transform infrared spectroscopy (FTIR). The analytical potential of Ag_2O nanoparticles was studied for a selective extraction of nickel prior to its determination by inductively coupled plasma-optical emission spectrometry. The selectivity of Ag_2O nanoparticles was investigated toward different metal ions, including Cd(II), Cu(II), Hg(II), La(III), Mn(II), Pb(II), Pd(II) and Y(III). Data obtained from the selectivity study showed that the selectivity of Ag_2O nanoparticles was the most toward La(III). The uptake capacity for La(III) was experimentally calculated to be 94.30 mg/g. Moreover, adsorption isotherm data of La(III) on Ag_2O nanoparticles, were well fit with the Langmuir adsorption isotherm, strongly supporting that the adsorption process was mainly monolayer on homogeneous adsorbent surfaces. Kinetic study revealed that the adsorption of La(III) on Ag_2O nanoparticles followed the pseudo-second-order kinetic model.

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1. Introduction

Rare earth elements (REEs) have continued to be one of interest due to their unique properties, such as, the production of superconductors, super-magnets and geochemical natures. REEs are important elements not only in industrial applications but also in energy and environmental applications [1]. For example, lanthanum is one of lanthanide elements found in rare earth minerals such as cerite, monazite, allanite and bastnasite. It has unique physical and chemical characteristics attracted great attention because of increasing demands for advanced new materials [2,3]. Monazite and bastnasite minerals are principal ores that contain up to 25% and 38% Lanthanum, respectively.

Mischmetals are used in making lighter flints, in which lanthanum occurs in percentages about 25%. Lanthanum is also used for the manufacture of specialized lenses because of special optical qualities in glass attained by lanthanum compounds. For the motion picture industry, lanthanum compounds containing fluorine or oxygen are used in making carbon arc lamps [4].

However, there are several contaminants, such as, contamination with heavy metals, radionuclides and lanthanides, usually caused by human activities and natural resources [5]. The environmental pollution has been taken under consideration due to the population density and growth of technology. Concern over this problem has led to the development of sensitive and efficient methods for monitoring metal ions in the environment. Different analytical methods have been implemented to estimate the concentration level of metal ions in aqueous media, such as atomic absorption spectrometry [6], inductively coupled plasma-optical emission spectrometry (ICP-OES) [1], anodic stripping voltammetry [7], and ion chromatography [8]. However, metal ions, in particular at ultra-trace concentration, cannot be directly

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measured in aqueous systems by analytical techniques due to the lack of sensitivity and selectivity of these methods. Therefore, an efficient separation step is often required prior to the determination of metal ions for sensitive, accurate and interference-free determination of metal ions [9].

There are different analytical methods for extraction of analyte of interest prior to its determination by an appropriate analytical method, involving liquid–liquid extraction [10], ion exchange [11], coprecipitation [12], cloud point extraction [13] and solid phase extraction (SPE) [14,15]. SPE is considered to be one of the most popular techniques because it reduces solvent usage and exposure, disposal costs, and extraction time for sample preparation. Because of the popularity of SPE for selective extraction of analytes, several adsorbents have appeared, such as alumina, C18, molecular imprinted polymers, cellulose, silica gel, activated carbon and carbon nanotubes [16–19].

Nanoscience and technology have attracted significant attention due to its potential application in various fields and especially in metal ion adsorption [17,18]. Silver oxide nanomaterials have potential applications in many fields such as electronics, optical devices, biological devices, in the treatment skin, antimicrobial, sensors, etc. [20,21]. In this investigation, we prepared Ag₂O nanoparticles by simply hydrothermal method and characterized by XRD, FESEM, FTIR, XPS and UV. Ag₂O nanoparticles were applied to investigate their utility and the analytical efficiency as adsorbent for La(III). The selectivity of Ag₂O nanoparticles toward eight metal ions, including Cd(II), Cu(II), Hg(II), La(III), Mn(II), Pb(II), Pd(II) and Y(III), was studied in order to investigate the effectiveness of Ag₂O nanoparticles on the extraction of selected metal ions. Data obtained from the selectivity study, displayed that the Ag₂O nanoparticles was most selective toward La(III) in comparison to other metal ions. The adsorption capacity for La(III) was experimentally found to be 94.30 mg/g. Results of adsorption isotherm also confirmed that the adsorption process was mainly monolayer adsorption onto a completely homogeneous surface with a finite number of identical sites.

2. Experimental

2.1. Chemicals and reagents

Silver nitrate (AgNO₃), sodium hydroxide (NaOH), mercuric nitrate [Hg(NO₃)₂], lanthanum nitrate [La(NO₃)₃], palladium nitrate [Pd(NO₃)₂] and yttrium nitrate [Y(NO₃)₃] were purchased from Sigma–Aldrich (Milwaukee, WI, USA). Stock standard solutions of 1000 mg/L Cd(II), Cu(II), Mn(II) and Pb(II) were also obtained from Sigma–Aldrich. All reagents used were of high purity and of spectral purity grade, and doubly distilled deionized water was used throughout.

2.2. Preparation of Ag₂O nanoparticles

Ag₂O nanoparticles were prepared by thermal stirring method in which 0.1 M of silver nitrate aqueous solution was titrated with 0.1 M solution of NaOH till pH reached above 10. The resulting

basic solution was stirred at 70 °C for overnight and the resulting product was washed and dried. The dried product was calcined at 450 °C for 4 h.

2.3. Possible growth mechanism of Ag₂O nanoparticles

The formations of Ag₂O might be takes place by following probable chemical reactions:



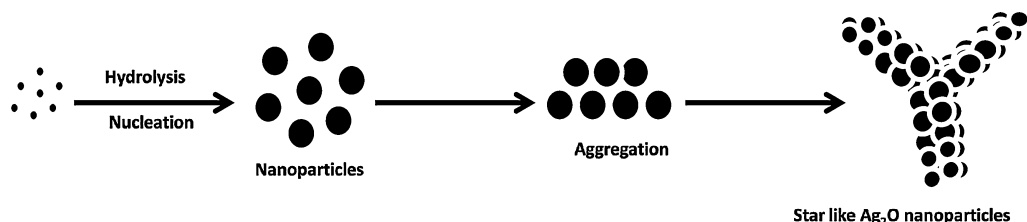
Initially AgNO₃ and NaOH undergo hydrolysis in water and produces Ag⁺ and OH[−] which later produces AgOH. The AgOH produces Ag₂O by thermal dehydration. During growth process (Scheme 1), first Ag₂O nucleus growth takes place which then aggregate and produce Ag₂O nanoparticles by Ostwald ripening. Nanoparticles crystallize and aggregate with each other through Van der Waals forces and hydrogen bonding and give aggregation of ZnO nanoparticles.

2.4. Characterization

The morphology of the synthesized product was studied at 15 kV using a JEOL Scanning Electron Microscope (JSM-7600F, Japan). X-ray diffraction patterns (XRD) were taken with a computer controlled RINT 2000, Rigaku diffractometer using the Ni-filtered Cu K_α radiation (λ = 0.15405 nm). FT-IR spectrum was recorded in the range of 400–4000 cm^{−1} on PerkinElmer (spectrum 100) FT-IR spectrometer. XPS spectrum was recorded in the range of 0–1350 eV by using Thermo Scientific K-Alpha KA1066 spectrometer (Germany). ICP-OES measurements were acquired by use of a Perkin Elmer ICP-OES model Optima 4100 DV, USA.

2.5. Samples preparation and procedure for metal uptake study

Stock solutions of Cd(II), Cu(II), Hg(II), La(III), Mn(II), Pb(II), Pd(II) and Y(III) were prepared in 18.2 MΩ cm distilled deionized water and stored in the dark at 4 °C. For studying the selectivity of Ag₂O nanoparticles toward metal ions, standard solutions of 2 mg/L of each metal ion were prepared and adjusted to pH value of 5.0 with a buffered aqueous solution (0.1 mol/L CH₃COOH/CH₃COONa). Standard solutions were adjusted at pH value of 5.0 in order to avoid the formation of suspended gelatinous lanthanides hydroxides with buffer solutions at pH values beyond 5.0. Each standard solution was individually mixed with 25 mg of the Ag₂O nanoparticles. For investigation of the La(III) adsorption capacity, standard solutions of 0, 5, 10, 15, 20, 25, 30, 50, 75, 125 and 150 mg/L were prepared as above, adjusted to pH value of 5.0 and individually mixed with 25 mg Ag₂O nanoparticles. All mixtures were mechanically shaken for 1 h at room temperature.



Scheme 1. Schematic representation of Ag₂O nanoparticles growth mechanism.

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