



Magnetic iron–cobalt/silica nanocomposite as adsorbent in micro solid-phase extraction for preconcentration of arsenic in environmental samples



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ABSTRACT

A new method for separation/preconcentration of trace As in environmental samples by micro solid-phase extraction (μ -SPE) using $\text{CoFe}_2\text{O}_4/\text{SiO}_2$ magnetic nanoparticles (MNPs) prior to ICP-OES determination, has been developed. The morphological characteristic of the magnetic nanomaterial was characterized by scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM-EDS), and X-ray diffractometer (XRD). Optimal experimental conditions including pH, adsorbent mass, and eluent acid concentration were found to be 3, 100 mg and 5 mol L^{-1} HCl, respectively. The adsorption capacity of the MNPs of As was found to be 8.5 mg g^{-1} . Under optimum conditions, the analytical limits of detection (LOD) and limits of quantification (LOQ) were found to be 2.8 and 9.2 $\mu\text{g L}^{-1}$, respectively. The accuracy of the method was tested by analyzing certified wastewater (CWW-TM-D) and the recoveries were found to be greater than 90%. The method was successfully applied to the determination of trace amounts of As in river and tap water samples.

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1. Introduction

Arsenic is a naturally occurring element that is widely distributed in the environment as a number of complex minerals mainly arsenides of copper, nickel and iron. Since arsenic is the 20th most abundant element in the earth's crust, it has served in many uses such as herbicides, fertilizers, wood preservatives, animal feed additives, paint pigments, and metal alloys, among others [1]. However, arsenic is very toxic at sufficiently high levels. In South Africa arsenic-based compounds have been used to treat East Coast Fever in cattle for about half a century [2]. Long-term exposure to arsenic may lead to arsenicosis, a chronic illness that produces skin disorders, gangrene, and cancer of the kidneys and bladder while exposure to high levels of arsenic is lethal [2]. The importance of human health and the impact of arsenic in the environment explain the increasing interest for the behavior and removal processes of arsenic. Because of the health threat imposed by arsenic, the World Health Organization (WHO) changed the acceptable content of arsenic in drinking water from 50 to 10 $\mu\text{g L}^{-1}$ [3]. Arsenic is introduced into the water and groundwater systems through a number of natural processes such as weathering reactions, dissolution of minerals and biological activity as well as through man-made activities such as mining, agriculture, and manufacturing. Mine dumps are heavily polluted with arsenic, levels are in the range of 0.9–62 g kg^{-1} thus they act as the

main sources of arsenic in ground/surface water [3,4]. In the surface water, arsenic is mostly present in two forms: arsenate (As(V)) and arsenite (As(III)). The stable form which dominates in surface water is arsenate while arsenite exists in anaerobic underground water [5]. The toxicity of arsenic depends on its oxidation and its various forms, that is, As(III) is more toxic than As(V) , and the organic arsenic is less toxic than inorganic forms [6].

To overcome arsenic toxicity which has become a major concern worldwide, it is necessary to develop methodologies for removal with improved extraction materials which have high efficiency. A number of different techniques can be used for removal of arsenic in drinking water. The most commonly used methods for removing arsenic from aqueous solution are ion exchange resin, adsorption, co-precipitation, reverse osmosis, membrane filtration, modified coagulation or filtration. The adsorption method offers a number of advantages as compared to other methods, these include simple and stable operation, easy handling of waste and generally lower operation cost [6]. A wide variety of adsorbents has been used for water purification such as biological materials, mineral oxides, activated carbons and polymer resins [7]. Numerous studies are still being conducted to develop cheaper effective adsorbents because the current water and wastewater treatment technologies are reaching their limit for providing suitable water quality to meet human and environmental needs. Adsorption based on microextraction techniques such as micro-solid phase extraction (μ -SPE) shows a remarkable improvement of the traditional solid phase extraction method since nanotechnology plays an important role in providing clean and affordable water to meet human requirements. The

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advantages of μ -SPE include reduced solvent consumption, sorbents usage and sample handling [7]. Nano-adsorbents offer significant improvement with their extremely high specific surface area and associated sorption sites, short intraparticle diffusion distance, and tunable pore size and surface chemistry. Usually, adsorption of arsenic on nano-adsorbents occurs by transporting the adsorbate molecule to the adsorbent surface by diffusion through the boundary phase. The adsorbate then diffuses from the external surface into the pores of the adsorbent and the adsorbate binds on the active sites of the internal pores [8]. Magnetic nanoparticles have shown great potential as adsorbents for removal of arsenic due to their strong adsorption activity and ease of separation on the application of an external magnetic field. Iron oxide-based materials have been widely studied as the arsenic adsorbents because of their low costs, high stability, environmental friendliness, and a strong affinity for arsenic species [9]. Mesoporous silica is known to be one of the most ideal coating layers for magnetite nanoparticles due to its reliable chemical stability, high surface area, and facile surface modification. Different applications of mesoporous silica core-shell nanoparticles containing magnetite nanocrystals ($\text{Fe}_3\text{O}_4@ \text{SiO}_2$) for the removal of pollutants from water have been reported elsewhere [5].

The objective of this study was to prepare and to characterize magnetic cobalt-ferrite/silica nanoparticles. The prepared magnetic nanoparticles were applied for the adsorptive preconcentration of As in tap and river water samples collected around Doornfontein area. The factors affecting the preconcentration of As were optimized. The variables under investigation include pH, the mass of adsorbent and eluent type and concentration. Contact time, sample volume and eluent volume were kept constant. It should be noted that univariate strategy was used for optimization of experimental parameters.

2. Experimental

2.1. Materials and reagents

All the chemicals used were of analytical grade unless otherwise stated and ultra-pure water was used for the preparation of all solutions. The adsorbent precursors: iron (III) nitrate, cobalt (II) nitrate, tetraethoxysilane (TEOS), traceSELECT nitric acid (70%), traceSELECT hydrochloric acid (37%), and ammonia solution (25%) were purchased from Sigma-Aldrich (St. Louis, MO, USA), and solid NaOH pellets were purchased from Merck (Germany, GmbH). As standards and model solutions were prepared by appropriate dilution of single element stock solution (1000 mg L^{-1} , Sigma-Aldrich) using ultra-pure water. Certified wastewater was purchased from High-Purity Standards (CWW-TM-D, Charleston, USA). The pH of the model solutions and samples was adjusted to desired values with diluted ammonia solution (0.1 mol L^{-1}) and glacial acetic acid. Before every use the lab glassware and plastic containers were soaked in 5% nitric acid overnight, rinsed thoroughly with deionized water and dried in an oven.

2.2. Instrumentation

The quantification of As was performed using an ICP-OES (iCAP 6500 Duo, Thermo Scientific, UK) equipped with a charge injection device (CID) detector. The samples were introduced with a concentric nebulizer and a cyclonic spray chamber. The instrumental operating

parameters are given in Table 1. Arsenic was detected at a wavelength of 189.0 nm. All pH measurements were made with an OHAUS STARTER 2100 pH meter. Eppendorf Centrifuge 5702, ultrasonic bath (Branson Electronic 5800) was used for adsorption experiments. The particles were calcined on a tubular electric furnace. For characterization, the X-ray diffractometer, Panalytical X'Pert X-ray Diffractometer, and Cu K α radiation spectrometer were used and the scanning area covered the range $2\theta = 4.00\text{--}80.00$ and a step time of 196.9 s. The surface morphology of the material was examined using SEM (TECAN VEGA 3 XMU) coupled with EDS (TECAN VEGA 3 XMU) technique at an accelerating voltage of 30 kV.

2.3. Synthesis of magnetic cobalt-ferrite/silica

The CoFe_2O_4 nanoparticles were prepared by co-precipitation method reported by Murat et al. [10]. Briefly, a portion 8.08 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was mixed with 2.91 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 100 mL deionized water at room temperature. An aliquot of 3.0 mol L^{-1} NaOH (25 mL) was added slowly while constantly stirring. A volume of 1.0 mL TEOS and 0.5 mL of NH_4OH were added to the reaction mixture and stirred for 12 h at room temperature. The particles were washed with ethanol, filtered and dried in an oven at 100°C . The particles were then heated in a furnace at 600°C for 3 h.

2.4. General procedure

The preconcentration procedure was carried out by adding an appropriate (10–100 mg) of $\text{CoFe}_2\text{O}_4@ \text{SiO}_2$ to 20 mL of $100 \mu\text{g L}^{-1}$ As solution in a 50 mL propylene sample bottles and immersed in an ultrasonic bath for 15 min. It should be noted that for optimization of pH, 50 mg was used. The adsorbent and supernatant were separated by centrifugation at 7830 rpm for 10 min. An aliquot of 10 mL of either HCl or HNO_3 (1.0–5.0 M) was used to elute adsorbed arsenic from the magnetic nanoparticles. The eluent and adsorbent mixture was sonicated for 10 min and separated by centrifugation at 7830 rpm for 10 min. The supernatant was filtered through a $0.2 \mu\text{m}$ syringe filter and the arsenic concentration in the eluent solution was determined by ICP-OES technique. It is important to note that for the optimization of pH and amount of sorbent, 3.0 mol L^{-1} nitric was selected as an eluent solution. For validation of the developed method certified wastewater (CWW-TM-D) containing 250 mg L^{-1} of As was diluted with ultra-pure water to a final concentration of $25 \mu\text{g L}^{-1}$ and the general preconcentration procedure was applied.

2.5. Adsorption studies

The determination of adsorption capacity of the $\text{CoFe}_2\text{O}_4@ \text{SiO}_2$ nanocomposite was performed on a batch scale using the ultrasound assisted system. Equilibrium adsorption experiments were carried out with initial concentrations of arsenic ranging from 10 to 300 mg L^{-1} while maintaining other parameters at optimum conditions. After reaching equilibrium, solutions were filtered and analyzed using ICP-OES. The adsorption capacity of the nanocomposite at different concentrations was estimated using Eq. (1).

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where q_e (mg g^{-1}) is the equilibrium adsorption capacity, C_0 and C_e (mg L^{-1}) are the initial and equilibrium concentrations of the analyte in solution, V (L) is the volume, and m (g) is the amount of the nanocomposite.

Table 1
Instrumental analytical conditions.

Instrument	Condition
RF power	1150 W
Auxiliary argon gas flow rate	0.5 L/min
Nebulizer flow rate	0.7 L/min
Sample pump rate	50 rpm
Sample flush time	30 s
Flush pump rate	100 rpm

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