

Synthesis, characterization and performance of polyurethane foam nanocomposite for arsenic removal from drinking water



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ABSTRACT

A new nanocomposite material is developed for arsenic removal from drinking water, in ppb concentrations, by incorporating 15–20 nm iron oxide nanoparticles (IONPs) inside a porous polyurethane foam (PU) with an open cell structure. To obtain the best removal capacity of arsenic species, the composition ratio of Polypropylene glycol (PPG) and Toluene di-isocyanate (TDI) in the PU foam, as well as, the percentage loading weight and size of the IONPs, were investigated. Scanning Electron Microscope and Energy Dispersive X-ray analysis (SEM/EDX) were used to examine the microstructure and distribution of IONPs inside the foam matrix. Atomic absorption spectrometer (AAS) analysis was conducted to measure the removal capacity of the nanocomposite foams. Sorption isotherms models were applied to determine the adsorption mechanisms and modeling parameters. It was found that the composition ratio of PPG:TDI (1:2) with 12% IONPs (15–20 nm) yields the highest affinity towards arsenic species, compared to other possible combinations, with a removal capacity of 40% using single stage batch analysis. Multi-stage setup and applications can increase the removal capacity significantly. Polyurethane nanocomposite adsorbents provide low-cost solutions to water filtration applications with high versatility and potentials.

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1. Introduction

Water contamination by various heavy metal pollutants; such as, Lead, Arsenic, Cadmium and Mercury, have serious toxic effects on living organisms and humans. Considerable research work, aimed at finding and developing various separation and treatment techniques, has been conducted over the past few decades. Arsenic contamination of ground water poses a serious concern in many countries throughout the world, including the United States. High concentrations of arsenic in drinking water cause serious damage to the central and peripheral nervous systems, as well as the dermal, cardiovascular, gastrointestinal, and respiratory systems [1,2].

The removal of dissolved arsenic, essentially, involves a selective separation of As(V) and As(III) oxyanions or oxyacid. The conventional treatment methods of arsenic involve a coagulation with ferric chloride or aluminum sulfate coagulants, followed by the separation of the produced insoluble by settling, or by direct filtration through sand beds. Other treatment techniques for arsenic removal are: reverse osmosis, ion exchange, lime softening, flotation and adsorption on hydrated iron oxide, zero valent iron, or activated

carbon [3–11]. These methods have been reported to be effective, mainly, for the removal of pentavalent arsenic As(V). Therefore; a pre-oxidation step is usually required in order to achieve efficient removal of trivalent arsenic As(III). Solid phase nano adsorbents are becoming the core of most recent works in removing heavy metals due to their high capacity and affinity to heavy metal ions. Nano adsorbents; such as, HFO [12] and MgO [13], have been deposited on the surface of porous materials like: polymeric anion exchanger D-201 [12] and polyurethane foam [13], while others were incorporated inside electrospun polymers [14–16]. However, the preparation of these adsorbents often involves complex and costly methods.

In this research work, a new bulk modified nanocomposite material (adsorbent) is developed using iron oxide nanoparticles (IONPs) impregnated in open cell polyurethane (PU) foams in order to exploit the inherent advantages of porous PU foam structures and flexibility. In addition, the incorporation of the adsorbent particles in a foam media allows for easier post treatment cleaning of the filtration system. The ability of iron compounds to react with arsenic species by adsorption and ion exchange mechanism offers higher removal capacities. The proposed system of the nanocomposite foam offers a potential for the removal of arsenic with high capacity at lower costs than conventional arsenic removal systems.

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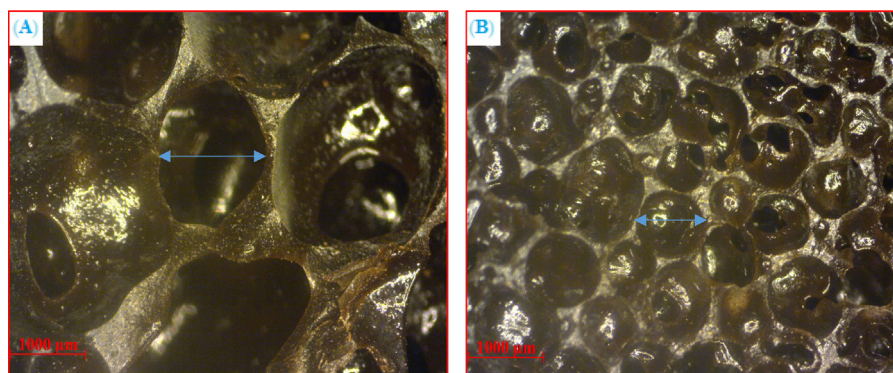


Fig. 1. Optical micrographs of PU-IONPs foams, (A): PPG:TDI ratio 1:2, (B): PPG:TDI ratio 1:1.75.

2. Materials and methods

2.1. Materials

The following is a list of raw materials which were used in the synthesis of PU foam nanocomposite: polypropylene glycol 1200 (PPG; Sigma Aldrich Co. LLC) dehumidified in a vacuum oven at 70 °C, toluene di-isocyanate (TDI; 2,4–80%, 2,6–20%, Alfa Aesar), polysiloxane surfactant (Sigma Aldrich), nitrogen gas (Air-gas, O₂ free UHP), iron oxide nanoparticles (IONPs; Fe₃O₄, high purity 99.5%, US Research Nanomaterials Inc.) with two size ranges: 50–100 nm and 15–20 nm, and 18.2 MOhm-cm deionized water. For the batch sorption experiments, 1 ppm standard arsenic solution, from Inorganic Ventures Co., was diluted to 100 ppb. The solution contained both As(III) & As(V). The solution was equilibrated with atmospheric CO₂, no acid or base addition.

2.2. Preparation and characterization of PU nanocomposite

The experimental set up used in this study is described in a previous publication of similar work for the removal of lead ions from drinking water using polyurethane foam functionalized with sulfonic groups in BES chain extenders [17]. A 3-neck round bottom reaction flask was placed in an oil bath and fitted with a mechanical stirrer and a condenser at the center neck. A nitrogen gas inlet was fitted at the right neck and a drop funnel was fitted at the left neck. The reaction between PPG and TDI was conducted at 75 °C in an inert atmosphere.

Initially, the 3-neck flask was charged with TDI and allowed to stabilize at 75 °C in a saturated nitrogen atmosphere. A drop funnel was filled with a pre-weighted amount of PPG which was added drop wise and allowed to react with TDI for 4–5 h until an initial isocyanate content of 11–12% is reached, according to ASTM D5155. IONPs was manually added to the mixture in different weight percentages (4%, 8%, 12%, and 16%). Based on the amount of PPG used, a pre-weighted amount of deionized water was added as a blowing agent along with the polysiloxane surfactant. The compound was mixed using a mechanical stirrer at 2500–3000 rpm for 10–15 s. The reaction of water with the remaining isocyanate groups released CO₂ gas to form the final foam structure [18].

A total of eight samples were prepared using two PPG:TDI ratios; 1:1.75 and 1:2, and four concentrations of 15–20 nm IONPs (4%–16%). Table 1 lists the composition of the various PU foam samples prepared for this study. Two additional foam samples were prepared using different range of nanoparticle sizes; 50–100 nm, at 12% loading amount for (1:1.75) and (1:2) PPG:TDI compositions.

The cellular structure of PU-IONPs adsorbents was investigated for (1:1.75) and (1:2) PPG:TDI compositions by ZEISS Stereo Microscope Stemi 2000-C. The elemental analysis and distribution of

Table 1

Compositions of PU-IONPs Samples for Batch Sorption Analysis.

Group	Sample ID	Molar Ratio of (PPG:TDI)	Loaded IONPs (%)
I	I-1	01:02	4
	I-2		8
	I-3		12
	I-4		16
II	II-1	01:01.8	4
	II-2		8
	II-3		12
	II-4		16

IONPs in the foam matrix were characterized using JEOL JSM-6460 LV Scanning Electron Microscope with Energy Dispersive X-ray Microscope (SEM/EDX). The adsorption capacity of the foam was measured with a Thermo Electron Corporation S4 Atomic Absorption Spectrometer (AAS). The detection limit, for the vapor technique used in AAS, was 0.2 ppb.

2.3. Batch sorption experiments

Batch sorption experiments were conducted in two stages. In the first stage, 1 g cubic samples were prepared from Group I and Group II compositions, and were soaked in 50 ml of 100 ppb arsenic solutions for 24 h. The cubes were shaken in normal solutions (pH = 6.5) at 200 rpm and at room temperature (22 °C). The aim of the first stage is to investigate the effect of the foam composition; i.e., PPG:TDI ratio and %IONPs, on the removal capacity of arsenic. In the second stage, foam samples with different IONPs sizes; i.e., 15–20 nm and 50–100 nm, were used under similar conditions of the first batch sorption experiments for 6 and 24 h to study the effect of the nanoparticles size and contact time on the adsorption capacity. After each batch test, 25 ml of each treated solution was filtered and preserved with 2% HNO₃ for AAS analysis.

3. Results and discussion

3.1. Structure analysis and characterization

3.1.1. Optical microscope

The optical micrographs obtained for PU-IONPs foam samples at 1X, reveal a distinct difference in the cellular structure between the two compositions. Fig. 1 shows the microstructure of (1:1.75) and (1:2) PPG:TDI compositions. It can be noticed that the 1:2 PPG:TDI composition exhibits larger cell size than the 1:1.75 PPG:TDI composition. However, a disordered distribution of the cells can be observed for both compositions. The polyurethane chemistry (i.e., foam composition) and the foaming reaction are substantial fac-

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