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γ-Al_2O_3-based nanocomposite adsorbents for arsenic(V) removal: Assessing performance, toxicity and particle leakage

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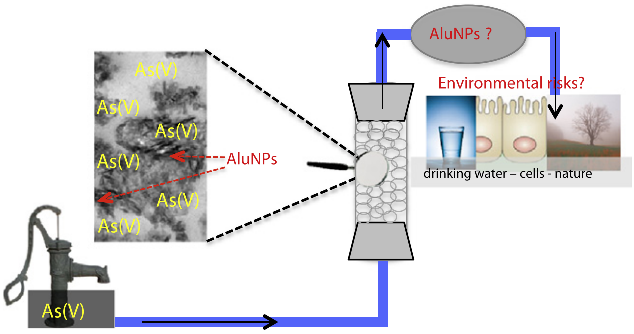
HIGHLIGHTS

- Adsorption performance and environmental risks with nanomaterial were investigated.
- Nanocomposites embedded with γ-Al_2O_3 nanoparticles show no particle leakage.
- High stability in flow-through experiments was confirmed from examined materials.
- Monomer leakage was linked to reduction in viability on epithelial cells.

GRAPHICAL ABSTRACT



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ABSTRACT

The generation and development of effective adsorption materials for arsenic removal are urgently needed due to acute arsenic contamination of water sources in many regions around the world. In the search for these new adsorbents, the application of nanomaterials or nanocomposites, and especially the use of nanoparticles (NPs), has proven increasingly attractive. While the adsorptive performance of a range of nanocomposite and nanomaterial-based systems has been extensively reviewed in previously-published literature, the stability of these systems in terms of NP release, i.e. the ability of the nanomaterial or nanocomposite to retain incorporated NPs, is less well understood. Here we examine the performance of nanocomposites comprised of aluminium oxide nanoparticles (AluNPs) incorporated in macroporous polyacrylamide-based cryogels (*n*-Alu-cryo, where n indicates the percentage of AluNPs in the polymer material ($n = 0$–6%, w/v)) for As(V) adsorption, and evaluate AluNP leakage before and after the use of these materials. A range of techniques is utilised and assessed (SEM, TEM, mass weight change, PIXE and in vitro toxicity studies). The 4-Alu-cryo nanocomposite was shown to be optimal for minimising AluNP losses while maximising As(V) removal. From the same nanocomposite we were further able to show that NP losses were not detectable at the AluNP concentrations used in the study. Toxicity tests revealed that no cytotoxic effects could be observed. The cryogel-AluNPs composites were not only effective in As(V) removal but also in immobilising the AluNPs. More challenging flow-through conditions for the evaluation of NP leakage could be included as a next step in a continued study assessing particle loss and subsequent toxicity.

1. Introduction

Contamination of water sources by arsenic is a global environmental problem. While particularly severe in Bangladesh, arsenic contamination is also a major issue in many other regions: e.g. South Asia, southern

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parts of Europe, the USA, South America and China (Chowdhury et al., 2000; Nickson et al., 1998; Nordstrom, 2002; Winkel et al., 2008). Due to different groundwater conditions (Hug et al., 2008), and indeed varying levels of economic development and water pre-treatment, there are currently no universal treatment solutions for As-contaminated water. In order to provide regional and local solutions, a range of technologies have to be developed and implemented. Arsenic remediation is challenging; arsenic can for instance be present in different oxidation states, show high temporal and spatial variability in concentration, and co-exist with other (competing) ions depending on the pollution source as well as the sedimentary and geochemical characteristics of the groundwater source area (Chowdhury et al., 2000; Hug et al., 2008; Nickson et al., 1998; Smith et al., 2000). While dissolved concentrations of arsenic can vary significantly, the guide line value concentration for arsenic in drinking water is set to 10 μg/l (WHO, 2001). From a treatment point of view, considering the environmentally relevant concentrations for arsenic in groundwater, arsenic is most optimally removed using adsorption processes (Mohan and Pittman, 2007; Nordstrom, 2002). A wide range of adsorbent-based solutions for As removal have been proposed (see review in Mohan and Pittman, 2007), including recently a range of nanomaterial-based sorbents (Ali, 2012; Khin et al., 2012). These nanomaterials, incorporating different metal nanoparticles (NPs, e.g. Al, Fe, Mn, Zr, and Ti oxides and oxyhydroxides) are interesting since they offer a much greater surface area per unit volume in comparison to the corresponding micro-sized metal (and consequently may show enhanced reactivity and adsorption capacity), and the adsorption kinetics are often improved for particles of smaller size (Khin et al., 2012). There remain, however, a number of concerns over the toxicity of metal (and other) NPs, particularly in a “free” or mobile form in solution and/or suspension.

Evidently, NPs of different elements (or compounds of one or more elements) may give different toxicity responses. In addition, the direct toxicity from the NP itself must be distinguished from any toxic soluble contaminant derived from the NP, such as ions or surfactants (Ali, 2012; Klaine et al., 2008). There have been a number of discussions regarding solubility aspects of NP materials involved in toxicity studies, especially for aluminium ions (Al^{3+}), which show phytotoxicity and are released and dissolved at higher pH-values (Murashov, 2006; Yang and Watts, 2005). Comparing toxicity for different bulk concentrations of NPs can however be difficult. Using concentration as a metric is not straightforward as surface area, particle charge, size and coating are also important parameters (Arvidsson et al., 2011; Klaine et al., 2008; Teeguarden et al., 2007). As an example, the available surface area of NPs is related to the surrounding conditions, such as pH and ionic strength. More generally, both the environmental toxicity and fate of NPs remain poorly constrained, even for more toxic (and more intensely studied) NP types such as AgNPs. Recent observations indicate that AgNPs show little discharge into surface waters as a result of the urban waste water cycle (Kaegi et al., 2013). In contrast, in other studies synthetic nanoparticles have been observed to readily distribute through environmental systems, e.g. after an exposure period of 12 days in an aquatic mesocosm, gold nano-rods could be found in biofilm, the water column, clams and other biota (Ferry et al., 2009).

Polymers and other materials can be used as a support for adsorbent particles or NPs, i.e. forming nanocomposites (Gupta et al., 2012; Onnby et al., 2012; Sankar et al., 2013; Savina et al., 2011; Zhu et al., 2012) which have been proposed as water clean-up devices. These can harness the high reactivity of NPs while preventing their environmental release, and also allow application of these adsorbent devices in a variety of end-use configurations (e.g. as beads, column filters, and surface coatings). Besides applying nanocomposites for adsorption of toxic ions, nanocomposites have also been studied for disinfection purposes or used as membranes in water treatment. In the case of the latter, NPs have been shown to result in less bio-fouling and improved permeate quality (Kim and Van der Bruggen, 2010; Loo et al., 2013). For most research dedicated to nanocomposites, however, little attention is paid to possible environmental consequences arising from their application, e.g. if NPs are lost to, or dissolved in, the treated water. Despite the prototype status of many nanocomposite devices, such environmental risk assessments are a key to characterize any potential risk from the devices prior to up-scaling and practical application. Here we examine adsorbent nanocomposite materials based on highly porous polymers. These polymers, so-called cryogels, are produced at temperatures below the freezing point of water allowing them to possess a beneficial three-dimensional interconnected continuous pore system of micrometre size (Lozinsky, 2002). Ideally, the use of nanocomposite materials should reduce the release and potential toxic effects of NPs while the adsorption of the target contaminant(s) by the nanocomposite should be comparable (or higher) than that obtained from the free NPs. Herein, we test the As(V) removal performance of a nanocomposite of AluNPs incorporated in a polyacrylamide (pAAm) cryogel matrix, referred to subsequently as Alu-cryo. In addition, we investigate the possible loss of incorporated NPs from the Alu-cryo with respect to robustness of the material following application as a water filter, and examine the release of AluNPs to filtered water by means of particle induced X-ray emission (PIXE) mass analysis. The potential toxicity of the filtrate using human epithelial cells in cell culture is also evaluated.

2. Material and methods

2.1. Chemicals

Acrylamide (AAm, >99%), D_3-acrylamide (98%), N′,N′,-methylene-bisacrylamide (MBAAm), *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TEMED), ammonium persulphate (APS) and aluminium oxide nanoparticles (AluNPs, nanopowder, γ-Al_2O_3, <50 nm, >40 m^2/g, 4 g/cm^3) were purchased from Sigma Aldrich. Arsenic standard stock solution, As(V), and palladium nitrate were from analytical standards (Germany). Ultrapure water (18.2 MΩ cm at 25 °C) was used throughout the study (Millipore system, France) except for the cytotoxicity studies where water from an ELGA Purelab flex purification system (Veolia, UK) was used. The ultrapure water is referred to subsequently as Milli-Q water.

The cell media used in the cytotoxicity studies, was a DMEM/Ham's F12 medium supplemented with 10% foetal bovine serum, 2.5 mM L-glutamine, and 100 IU/ml penicillin–streptomycin; (PAA, UK).

2.2. Preparation of Alu-cryo nanocomposite

Nanocomposites were prepared following (Onnby et al., 2012) but with slight modifications, hence we prepared a pAAm cryogel without addition of allylamine, as the stability was improved with the pAAm cryogel (Onnby et al., 2012). In detail, different amounts of AluNPs were added to a 6% monomer solution with 1:7 molar ratio of MBAAm:AAm, resulting in a nanocomposite with 1–6% (w/v) particle loading. The monomer and NP suspension were activated with TEMED and further initiated with APS, both added as 1 wt.% of the total monomer concentration respectively. Prior to the initiation of the reaction, the monomer solution was degassed with nitrogen while cooling on ice. Aliquots of monomer-nanoparticle suspension (0.5 ml) were thereafter added to glass tubes (inner diameter = 10 mm, length 30 mm) and allowed to freeze in an ethanol bath for 1 h at −12 °C. Samples were thereafter kept overnight in a dry freezer (−12 °C). We hereby obtained 0.5 ml monoliths, which we have chosen to denote 1-, 2-, 3-, 4-, 5- and 6-Alu-cryo respectively (depending on the corresponding percentage of NP loading). The small size of the monoliths was chosen to facilitate laboratory handling and minimise volumes of As-spiked water used in the subsequent tests. The most optimally loaded adsorbent was thereafter screened for potential leakage of NPs as well as toxicity. Before any samples were applied for adsorption studies, all composites were thoroughly washed with 20 ml Milli-Q water (40 bed volumes) in order to