

Towards developing a low-cost gravity-driven arsenic filtration system using iron oxide nanoparticle-loaded PU foam

Arundhati Pillai, M. Amin F. Zarandi, Faten B. Hussein, Krishna M. Pillai and Nidal H. Abu-Zahra

ABSTRACT

Arsenic contamination of water sources is a global problem, affecting numerous (especially developing) countries across the world. Exposure to exorbitantly high concentrations reaching 400 parts per billion of arsenic in water sources lead to numerous health complications, including the development of respiratory, neurological, and cancerous diseases. This study focused on developing an innovative, low-cost, and gravity-driven filtration system using a novel iron oxide nanoparticle-loaded polyurethane (PU) foam by which people in developing countries may have easy access to an effective, affordable, and easily fabricated filtration system. After successfully synthesizing the new iron oxide nanoparticle-loaded PU foam, effectiveness of the foam was tested by developing a filtration system consisting of vertical polyvinyl-chloride tubing inserted with 10 and 20 cm of PU foams. Samples of arsenic-contaminated water with known concentrations of 100 and 200 ppb were run through each of the systems numerous times for one and five run cases. The system with 20 cm of PU foam and five runs successfully filtered out around 50–70% of the arsenic from the 100 and 200 ppm samples. The filtration process was quite fast (and hence practical) with each run completing in 5–10 minutes' time. Future research is expected to improve this promising start.

Key words | arsenic, clean water, filtration, foams, polyurethane, PU foam

Arundhati Pillai

Department of Biochemistry and Molecular Biophysics,
University of Chicago,
924 E. 57th Street BSLC, Suite 104, Chicago, IL 60637,
USA

M. Amin F. Zarandi

Krishna M. Pillai (corresponding author)
Mechanical Engineering Department,
University of Wisconsin-Milwaukee,
3200 N Cramer St., EMS Building, Laboratory for Flow & Transport Studies in Porous Media,
Milwaukee, WI 53211,
USA
E-mail: krishna@uwm.edu

Faten B. Hussein

Civil and Environmental Engineering Department,
Marquette University,
1637 W Wisconsin Ave., Milwaukee, WI 53233,
USA

Nidal H. Abu-Zahra

Material Science Department,
University of Wisconsin-Milwaukee,
3200 N Cramer St., EMS Building, Room 351,
Milwaukee, Wisconsin, 53211,
USA

INTRODUCTION

Arsenic contamination of water is a widespread problem that affects many different parts of the world. Natural weathering and anthropogenic sources, such as mining and use of coal-fired power plants, leads to the exacerbation of this issue. Ranging from the developed nations, including the United States and Canada, to developing countries such as Bangladesh, India, and China, arsenic contamination has affected numerous different populations across the world and proven to be extremely injurious to human health. Arsenic exposure has many dermal, gastrointestinal (Yang *et al.* 2011; Alava *et al.* 2015; Calatayud & Laparra Llopis

2015; Chávez-Capilla *et al.* 2016), neurological (Halatek *et al.* 2009; Yorifuji *et al.* 2016), and cardiovascular effects (Mehta *et al.* 2015; Phung *et al.* 2017), some of which include hemorrhagic gastroenteritis, skin, lung, and bladder cancer (Lesueur *et al.* 2012; Melak *et al.* 2014; Yeh *et al.* 2015; Lynch *et al.* 2017), and peripheral neuropathy (Brocato & Costa 2015; Duan *et al.* 2015; Ameer *et al.* 2017). The International Agency for Research on Cancer (IARC) and U.S. Environmental Protection Agency (EPA) have both classified and established inorganic arsenic as a known human carcinogen (Gehle 2009). This carcinogenic inorganic

arsenic compound is what is contaminating water sources across the world, as compared to the less harmful organic arsenic compounds that are commonly found in seafood (World Health Organization 2018).

The bodies of water that are most affected by arsenic contamination are groundwater sources. The arsenic primarily present within said sources are oxy anions with two different oxidation states: arsenite (As(III)) and arsenate (As(V)) (Ferguson & Gavis 1972; Cullen & Reimer 1989). Although the introduction of arsenic into these sources of water can occur naturally due to its presence in surrounding bedrock, especially in areas of West Bengal and China, this arsenic contamination can be exacerbated through numerous human activities. These include industrial activities of mining, smelting, coal-fired power plants, and the environmental effects of various agricultural pesticides used for wood preservation (Garelick *et al.* 2009).

Although many countries are affected by arsenic water contamination, including Argentina, China, Chile, Mexico, India, and USA, Bangladesh is an important example of a country affected by severe arsenic exposure. Since the early 2000s, around 35–77 million of its people have been exposed to dangerously high levels of arsenic in water sources (Anthamatten & Hazen 2012). This is due to the fact that an extremely high percentage of Bangladesh's population depends on tube wells to access groundwater sources since they avoid taking water from the pathogen-contaminated surface-water sources such as lakes and ponds. In rural areas, over 97% of the rural population depends on such groundwater sources, which has resulted in a large-scale exposure to high arsenic levels due to the lack of access to clean water. Thus, in 2009, 65 million people were surveyed for national quality of water and were found to be exposed to concentrations above the national standard of 50 parts per billion (ppb) and the World Health Organization's international standard of 10 ppb (Flanagan *et al.* 2012). These concentrations were found to reach extremely high and dangerous concentrations of arsenic, in some areas reaching as high as 400 ppb (Figure 1, (Wilson 2009)).

The removal of arsenic, essentially, involves a selective separation of As(V) and As(III). 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 (Wickramasinghe *et al.* 2004; Terracciano *et al.* 2015; Mahdavi *et al.* 2017). Other treatment techniques for arsenic removal are: reverse osmosis (McNeill & Edwards 1997; Ning 2002; Teychene *et al.* 2013; Abejón *et al.* 2015; Schmidt *et al.* 2016); flotation and adsorption on hydrated iron oxide or activated carbon (DeMarco *et al.* 2003; Gu *et al.* 2005; Gupta *et al.* 2005; Wu *et al.* 2008; Di Natale *et al.* 2013; Asadullah *et al.* 2014; Siddiqui & Chaudhry 2017; Xiong *et al.* 2017; Xu *et al.* 2017); and absorptive media (Adsorptive arsenic removal media modelled 2007; Baig *et al.* 2013; Chen *et al.* 2015; Yazdani *et al.* 2016; Chatterjee & De 2017). 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).

As mentioned above, there are numerous available options for arsenic filtration, including reverse osmosis and anionic exchange systems (Oregon Health Authority), but there is a newer type of filtration material that is showing potential to be used in filtration systems: polyurethane (PU) foam. There has been some research into the synthesis and characterization of this synthetic foam, especially for its porous-medium properties of permeability and porosity that mark its potential as a filter (Cao *et al.* 2005). Properties such as low costs, recyclability, and easy room-temperature fabrication has made this material very attractive as a filter. Progressively, these PU foams have been modified to incorporate various compounds for specific water-filtration applications, such as the silver nanoparticle-coated PU foams developed as an antibacterial water filter (Jain & Pra-deep 2005). However, to date, limited research has been conducted for the specific application of arsenic removal using this novel synthetic foam.

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, hydrous ferric oxide (HFO) (Zhang *et al.* 2008) and magnesium oxide (MgO) (Choi *et al.* 2014), have been deposited on the surface of porous materials. However, the preparation of these adsorbents often involves complex and costly methods. Iron oxide has proven to be a popular compound used for arsenic filtration that is even

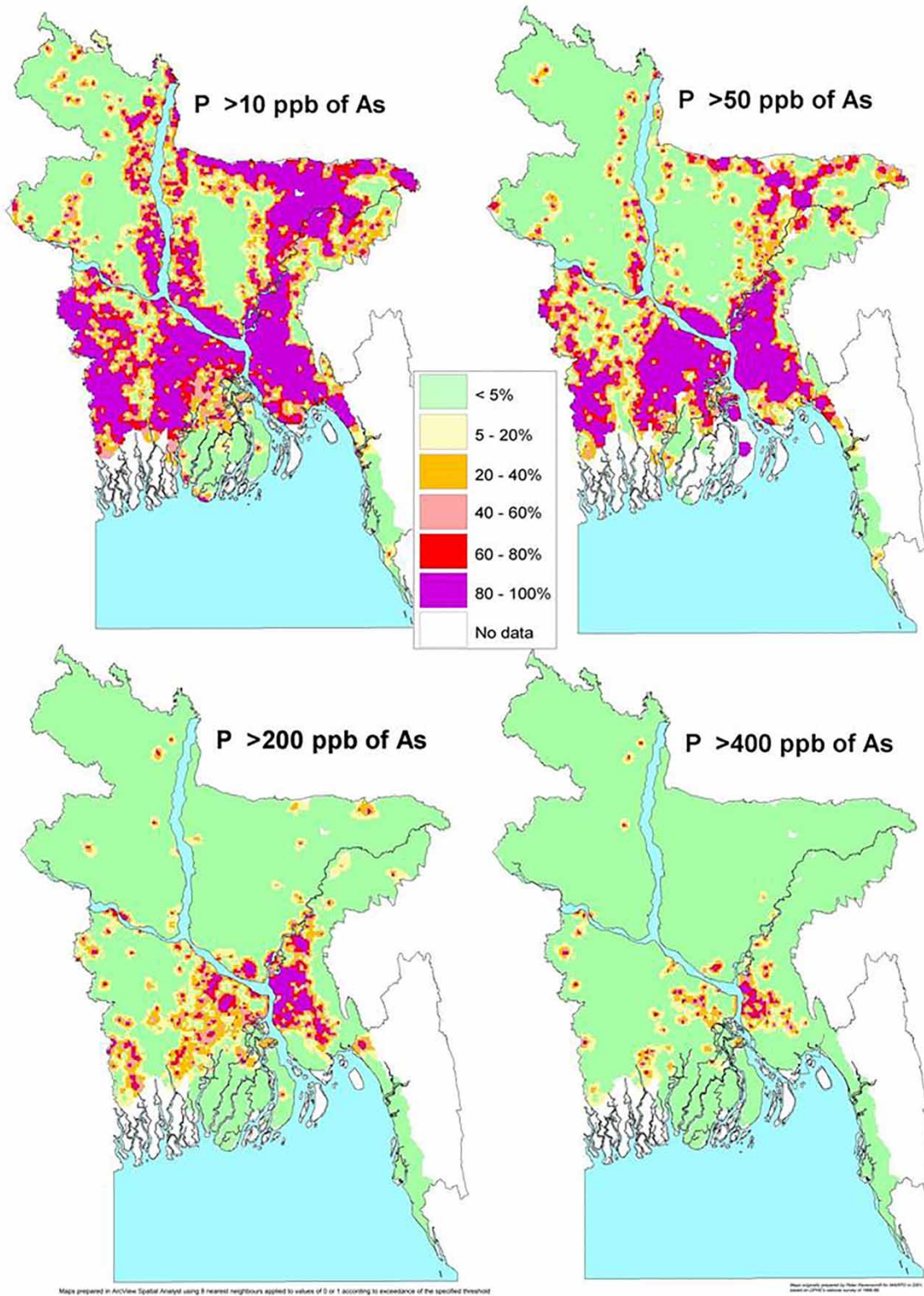


Figure 1 | These are four maps of Bangladesh that show four worsening levels of arsenic contamination in various areas. As presented through the map, there are alarming concentrations that surpass the World Health Organization's international standard of 10 ppb of arsenic in water sources, with concentrations beyond 400 ppb in certain areas. (Adapted from (Wilson 2009), reprinted with permission from Dr. Richard Wilson).

incorporated into many commercial arsenic-filtration products. The high affinity that this compound has for arsenic contaminants allows iron oxide to play an important role in arsenic filtration research (Katsoyiannis & Zouboulis 2002). Iron oxide-coated polymers and various other synthetic materials have been researched to understand their filtration capabilities, and the incorporation of iron oxide into PU foam has also been investigated (Hussein & Abu-Zahra 2017b).

Prior research has been successful in synthesizing an open-cell PU foam with iron oxide nanoparticles (IONPs) embedded within it. Through a single column study, all arsenic species within the arsenic samples of 60 ppb were removed after 22 cycles (approximately 9 days) of the operating period (Hussein 2016). In addition, modified versions of the PU foam were tested through batch and column studies and showed 87–88% lead removal efficiency (Gunashekar 2015). Therefore, the potential for these specialized PU foams to have a significant impact in the future of water filtration is evident.

RESEARCH AIM

The purpose of this study is to synthesize a nanocomposite PU foam embedded with iron oxide nanoparticles by incorporating these adsorbent particles within the foam media. After creating such a composite, the second part of the overall purpose is developing a low-cost and gravity-driven filtration system with iron oxide nanoparticle-infused PU foam to not only test the effectiveness of the foam in filtering out arsenic present in contaminated water, but also develop an alternative option for filtration that is less expensive, more sustainable, and usable in the third-world rural areas marked with low-supply/absence of electricity. By developing such a prototype device, this study hopes to present another option of an adsorptive filtration system that can successfully extract the harmful arsenic from water.

The novelty in this work lies in developing a new gravity-driven low-cost filtration system capable of utilizing the previously synthesized PU foam nanocomposites to remove arsenic from water with comparable removal

efficiency at a fraction of the time, compared to what has been reported in previous works.

METHODOLOGY

Synthesis of polyurethane foam with iron oxide

To synthesize the nanocomposite polyurethane foam, modifications need to be made to the current PU foam synthesis processes in order to incorporate the iron oxide nanoparticles. In the standard process, the two main components that create the PU foam are 2,4-toluene diisocyanate (TDI) and polypropylene glycol (PPG). TDI is an important aromatic isocyanate that is used within the polyurethane industry. It acts as the unique and basic monomer that PU foams are comprised. The PPG is a polyol that determines the final properties of the PU foam. It is a polymer of propylene glycol and is chemically a polyether. The presence of the hydroxyl groups within this compound makes PPG the optimum raw material used in polyurethanes as the hydroxyl groups react with the TDI monomers to produce the polyurethane monomer.

Therefore, within this study, PPG was used as the only polyol to react with the TDI to control the pre-polymer chemistry and allow for the iron oxide nanoparticles to be incorporated into the PU foam synthesis process and, ultimately, functionalize the final PU foam product. The molar ratio of TDI to PPG used in this synthesis process was 2:1 (Hussein 2016), thus requiring 18.4 g of TDI to 50 g of PPG, based on molar mass values. Before the start of the synthesis and mixing process of the chemical compounds of the PU foam, the PPG was heated and sealed in a vacuum furnace at around 70 °C for 24 hours in order for the PPG to be effectively expressed.

An experimental setup was established using a three-necked round-bottom reaction flask to correctly mix and allow for the PPG and TDI chemical molecules to thoroughly react with one another (Figure 2). The round-bottom flask was submerged halfway in a mineral oil bath in order to provide uniform heating for the reaction between the chemical constituents of TDI and PPG. This entire system was placed on a hotplate stirrer, and a

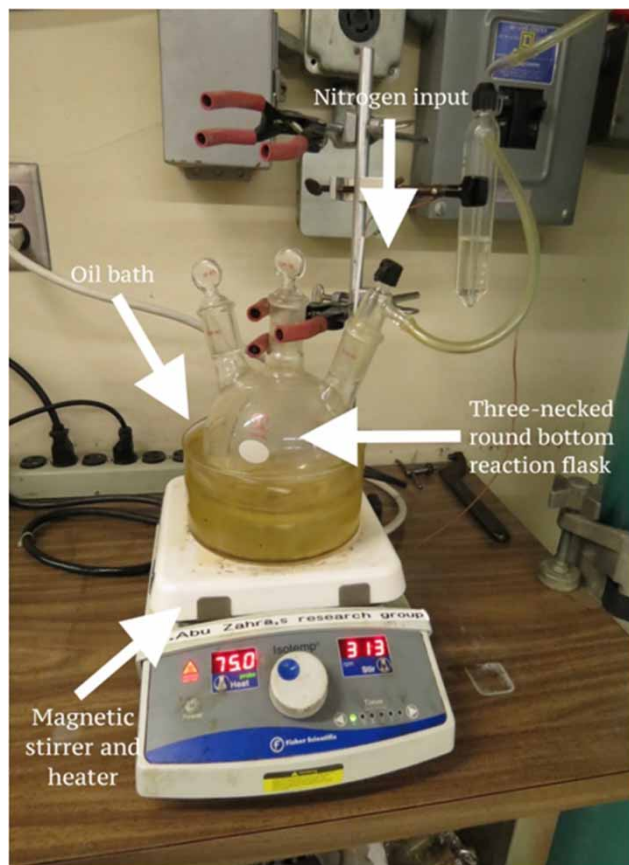


Figure 2 | The setup for making PU foam – mixing PPG and TDI under inert (nitrogen-filled) conditions at 75 °C temperature.

magnetic stir bar was placed inside the round-bottom flask in order to mix the components during the reaction process. As shown in Figure 2, as the round-bottom flask was clamped to a stand, the middle neck was plugged in order to maintain a sealed environment during the synthesis. After the measured 18.4 g of TDI was added to the flask, the leftmost neck of the reaction flask was plugged shut with a separating funnel, which was also used to drip the 50 g of vacuum-treated and heated PPG into the reaction flask. In the rightmost neck of the reaction flask, an inlet of nitrogen gas was plugged into the opening and the closed environment was supplied with nitrogen gas from a low-flowing source in order to maintain an inert atmosphere. Thus, the reaction was allowed to go to completion in 4–5 hours with the magnetic-bar rotation rate of approximately 200–300 rpm and a hot-plate temperature of 75 °C (Figure 2).

After the reaction had been sustained for 4–5 hours, the round-bottom flask was disconnected from the system, and its contents were emptied into a glass container greased with silicone spray lubricant. Then the iron oxide nanoparticles (of size 15–20 nm and forming 10% of mass) in powder form and a few drops of polysiloxane surfactant were added to the PPG-TDI mixture. The polysiloxane surfactant was used within the synthesis of the polyurethane foam because it helps to lower surface tension, promote the nucleation of bubbles during mixing, and stabilize the rising foam by reducing stress concentrations in thinning cell-walls (The Dow Chemical Company). Approximately 6.5–7 mL of deionized water was then added to the entire mixture before all of the components of this novel PU foam were mixed thoroughly for 15 seconds with the use of a mechanical mixer. A homogeneous distribution and dispersion of the nanoparticles was sought by high shear mixing with the polymer mixture before foaming. The distribution of the iron oxide nanoparticles in the foam is likely to have an amplified effect at the local pore levels with more homogeneous distribution likely to enhance the arsenic removal.

After the mixing process, the glass containing the now well-incorporated components is set aside in an environment with minimal movement to allow for the natural rising and development of the foam for 24 hours as the water reacts with the remaining isocyanate groups to release CO₂, thus forming the final structure of iron oxide nanoparticle-loaded polyurethane (IONP-PU) foam.

Based on the porosity analysis, the cell size distribution is bimodal or falls into two pore sizes: (0.001–0.1) μm and (0.1–10) μm, and the open/closed cell ratio is 2:1 (66% open cell and 33% closed cell). The molar ratio of TDI: PPG (2:1) provides flexible structure of PU foam which, in turn, facilitates the water flow during filtration (high content of opened cells). In a preliminary test, the pure PU foam did not show a removal capacity toward arsenic.

Now we add some more nuts-and-bolt details on the materials used in our foam preparation. The following is a list of raw materials which were used in the synthesis of PU foam nanocomposite: polypropylene glycol1200 (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, O₂free UHP), iron oxide nanoparticles (IONPs; Fe₃O₄, high purity 99.5%, US Research Nanomaterials Inc.) in the size range 15–20 nm, and 18.2 M Ohm-cm deionized water.

Creating the gravity-driven low-cost filtration system

For the development of such a water-filtration system, the two key goals focused on in this specific model were the low overall cost of production and the user-friendly nature of the product. The majority of the Bangladeshi population that suffers from chronic arsenic exposure primarily lives in rural areas and has little education or understanding about the severity of the problem (Human Rights Watch 2016). Therefore, our system was devised and developed to be not only low cost and simple, but also gravity-driven, which would eliminate the need for electricity to power any components of the filtration system.

For the development of this product, 0.95 m wide polyvinyl chloride (PVC) tubing was purchased for only \$10.42. From Darcy's law used for predicting flow inside a porous medium where flow rate is proportional to applied pressure gradient (Bear 1972), one can see that the greater the pressure build-up above the foam, the greater the flow rate through the filtration medium, if all other variables remain constant. Therefore, the synthesized IONP-PU foam was compressed into the lower end of the tubing, in order to allow for the greatest build-up pressure on the other side into which the water was envisioned to be

poured. For the first initial model, a block of 10 cm length of the synthesized IONP-PU foam was lodged in the PVC tubing, and for the second, 20 cm of synthesized IONP-PU foam was placed in the PVC tubing as presented in Figure 3. In order to avoid lateral flow through the filtration system, a non-toxic polyurethane-based adhesive was used to seal the circumference of the IONP-PU foam pieces inserted into the PVC tubing for each of the two models (Figure 3(b)). In addition, to allow for the greatest gravitational force to act upon the system, the flexible PVC tubing was zip-tied to a vertical metal ruler (Figure 4) in order to increase the overall straightness and verticalness of the system.

A certain volume of arsenic polluted water, when poured into the top of the vertical tube, created a water column that used the hydrostatic pressure at its bottom to push water through the pores of IONP-PU foam. The liquid laden with arsenic comes in contact with iron oxide nanoparticles embedded on the walls of the porous medium and thus get adsorbed, filtering the polluted water. The foam, as a porous medium, is preferred for this process as the circuitous flow path of water particles through the interconnected pores forces repeated contact of arsenic-laden water with the iron oxide nanoparticles of the pore walls, thus improving the chances of arsenic removal. The high specific area (i.e., total pore-wall area divided by the outer volume of the foam) of the foam makes this forced contact (and hence filtration) quite thorough and efficient.

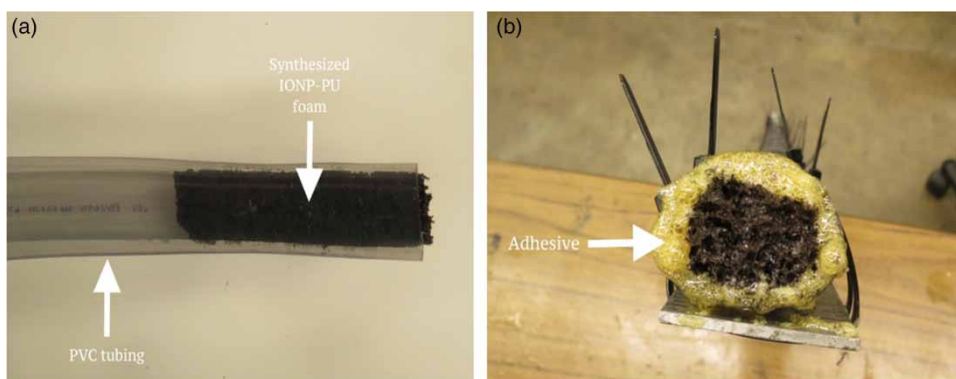


Figure 3 | (a) After cutting the synthesized IONP-PU foam down to the circumference of the PVC tubing, 20 cm of the foam was inserted into the tubing, as seen in this image. (b) To avoid lateral flow, a non-toxic polyurethane-based adhesive was used to seal the circumference of the specific end of the PVC tubing with the synthesized IONP-PU foam inserted into it. This decrease in the side flow due to leakage allows for more thorough arsenic removal from water as water particles spend more time within the porous filtration system.



Figure 4 | The final layout of the proposed gravity-based low-cost arsenic filtration system attached to a vertical metal ruler to allow for maximum gravitational force to act upon the passing liquid. The water, poured at the top for creating a certain column above the sponge, was collected at the bottom after its seepage.

Testing the filtration of arsenic-laden water by the proposed system

In order to test the effectiveness of the synthesized ION-PU foam and the developed filtration system, water samples containing arsenic in varying concentrations were created and then run through the system. For the batch sorption

experiments, 1,000 ppm standard arsenic solution, from Inorganic Ventures Co., was diluted to the concentrations required. The solution contained both As(III) and As(V). The solution was equilibrated with atmospheric CO₂, no acid or base addition.

To create the samples, 1,000 ppm arsenic stock solution was diluted down to a new stock solution of only 1 ppm of arsenic, using deionized water. With this lower concentration, there was increased flexibility to create realistic dilutions of arsenic within water with concentrations that correlate well with concentrations of arsenic that are typically present within groundwater sources.

For the case of Bangladesh, especially in rural locations, concentrations often exceed 100 ppb and can be as high as 400 ppb, i.e., over 10–40 times the maximum concentration that the World Health Organization (WHO) recommends for coming into contact with or for ingesting. Therefore, for this study, the concentrations of 100 and 200 ppb of arsenic in water samples were tested through the filtration system, in order to analyze the effectiveness of the synthesized ION-PU foam and the gravity-driven low-cost system's ability to filter out higher and increasingly dangerous concentrations of arsenic present in many rural Bangladeshi groundwater sources.

The aforementioned created stock solution of 1 ppm of arsenic water samples was diluted down to sample volumes corresponding to 100 and 200 ppb that could be run through the designed filtration system. These samples of 100 and 200 ppb of arsenic water were poured into the filtration system, but approximately 50 mL of the arsenic water samples before filtration were separated from the testing samples in order to act as the control, or point of comparison. A specific variable that was tested for was the number of runs that would allow for the optimal amount of arsenic removal. Therefore, for both the 10 and 20 cm systems (corresponding to the lengths of the synthesized ION-PU foam plugs lodged in the tube), three separate trials of the samples were run through the system for the following two cases: (a) one batch of the three-sample filtering through the system *only once*, and (b) the other batch of the three-sample filtering through the system *five times*. If there is any exponential decrease in the residual arsenic concentration over the course of five runs vis-à-vis the single run, the hypothesis is that such a decrease should be able to

capture the broad trends in the graph. Note that every time, after running contaminated water through the foam, it retains a little of that water. Hence, in order to minimize the effect of the retained contaminated water, we washed the filter by running clean distilled water for each of the three separate trials.

The collected filtered samples, along with the aforementioned controls, were all preserved with 2% nitric acid (HNO_3) in a ratio of sample to acid being 50:1 mL, and then they were all tested for the percentage change in arsenic concentrations using atomic absorption spectroscopy (AAS).

RESULTS AND DISCUSSION

Trials with shorter (10 cm) PU plugs

For the 10 cm model of the filtration system, three trials were conducted to analyze the effect of one run on the overall concentration of arsenic in the water samples. In the first trial, there was only around an 8–11% decrease in the overall arsenic concentrations. (Note that in 8–11%, the first value of 8% stands for arsenic concentration reduction achieved for the 100 ppb solution while the second value of 11% stands for arsenic concentration reduction achieved for the 200 ppb solution.) In the second trial, a better 18–24% decrease was observed in the overall arsenic concentrations. Finally, in the third trial, an 11–21% decrease was observed for the overall arsenic concentrations. Ultimately, across the three trials conducted, there was an average of a 13–20% decrease in arsenic concentration when running the samples of 100 and 200 ppb arsenic just once through the filtration model containing 10 cm of the IONP-PU foam (Figure 5(a)–5(c)).

Now, for the second batch of three trials of arsenic water samples run through the 10 cm filtration system, the five runs, repeated one after another, of filtration achieved very similar percentages of arsenic removal as was achieved with just one run. For the first trial, 8–38% removal was achieved; in the second trial, 15–10% removal was achieved; finally, in the third and last trial, 18–8% removal of arsenic was achieved (Figure 6). With the filtration system containing only 10 cm of the synthesized IONP-PU foam, there were no drastic improvements in the filtering capabilities

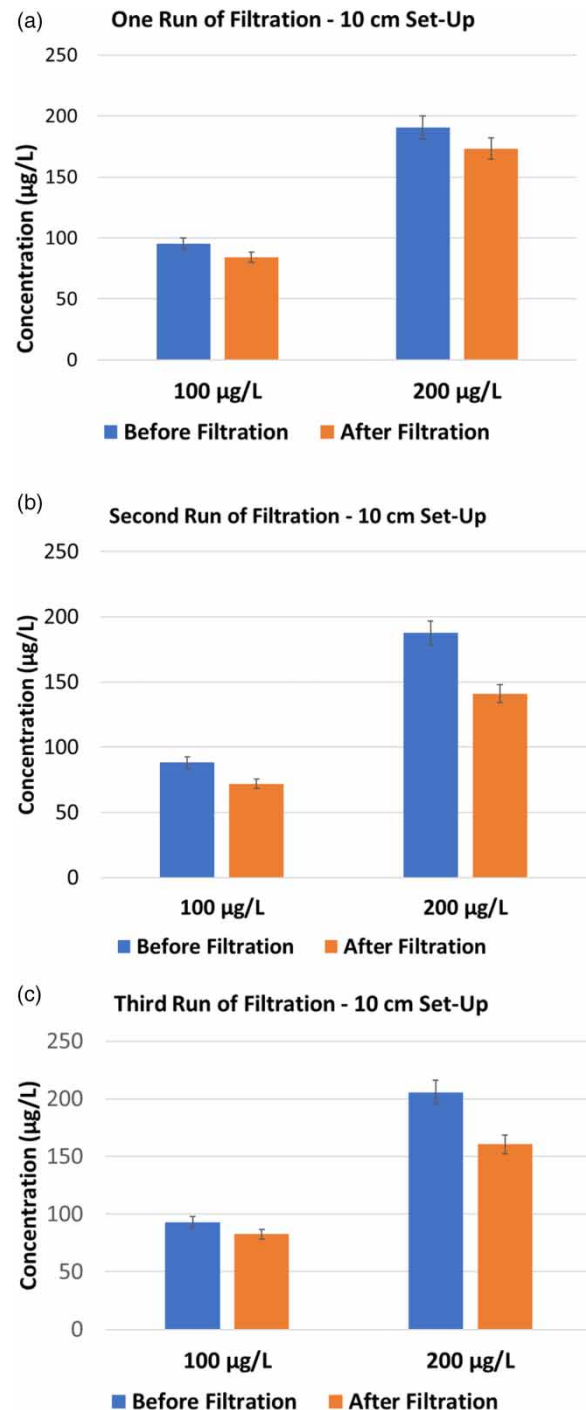


Figure 5 | First, second, and third round of the trials for running the 100 and 200 ppb arsenic water samples through the 10 cm filtration system once. Note that 1 $\mu\text{g/L}$ = 1 ppb.

due to five repetitions. Therefore, a filtration system with 20 cm of the synthesized IONP-PU foam, instead of the hitherto 10 cm, was tested with the arsenic water samples

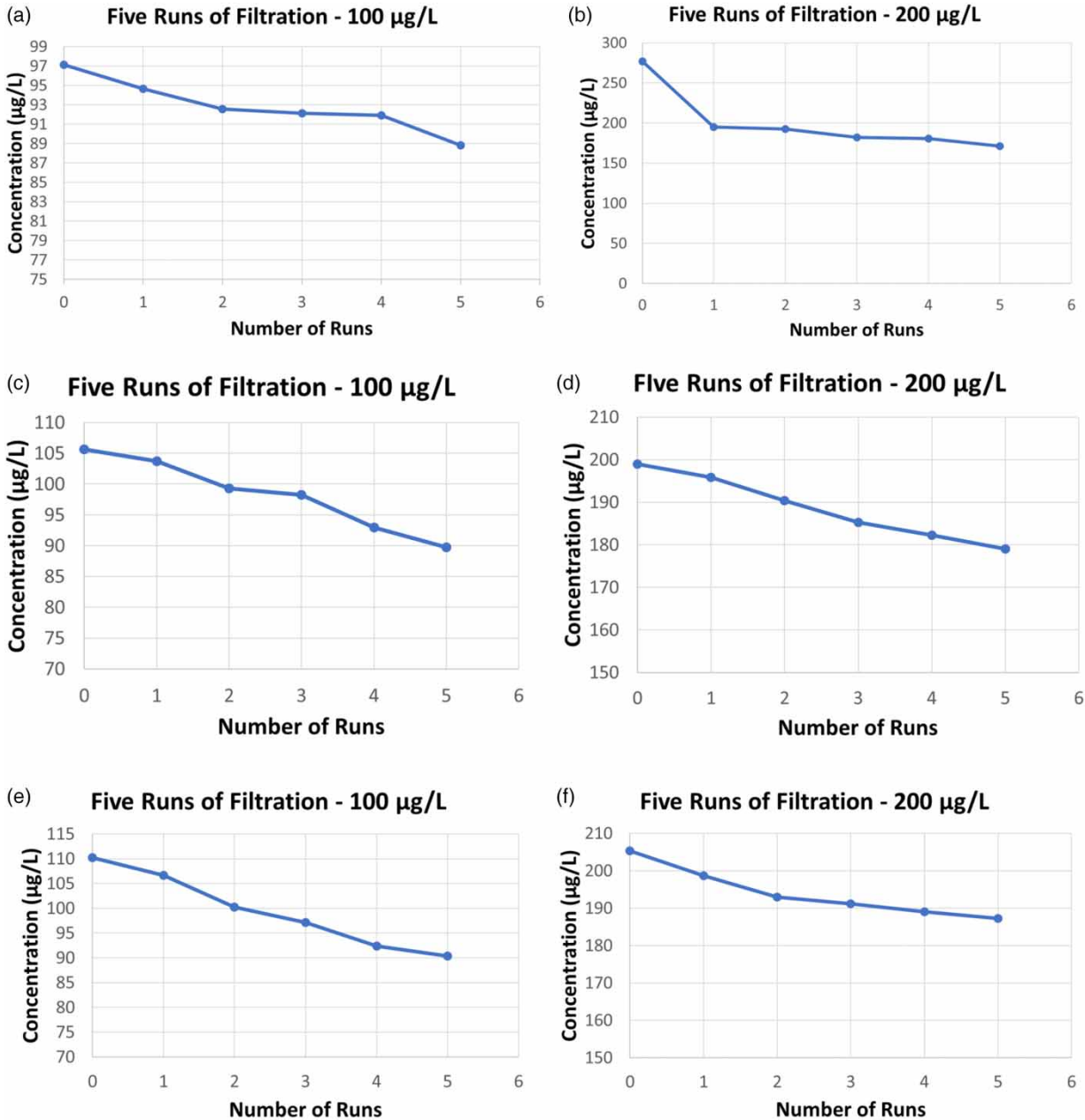


Figure 6 | Results of running the 100 and 200 ppb arsenic water samples through the 10 cm filtration system five times: (a) and (b) first trial, (c) and (d) second trial, (e) and (f) third trial.

to see whether an increased length of the foam plug increases filtration capabilities.

Trials with longer (20 cm) PU plugs

For the first three trials conducted using the 20 cm filtration system for just one filtration run, an average of

48–50% of arsenic was being filtered from the water samples. In the first trial, 47–51% of arsenic was filtered; in the second, 49–50% of the arsenic was filtered; in the final third trial, 50–51% of arsenic was filtered from the samples (Figure 7). We note, with pleasant surprise, that merely by doubling the length of the synthesized ION-PU foam plug, the arsenic removal capabilities for just

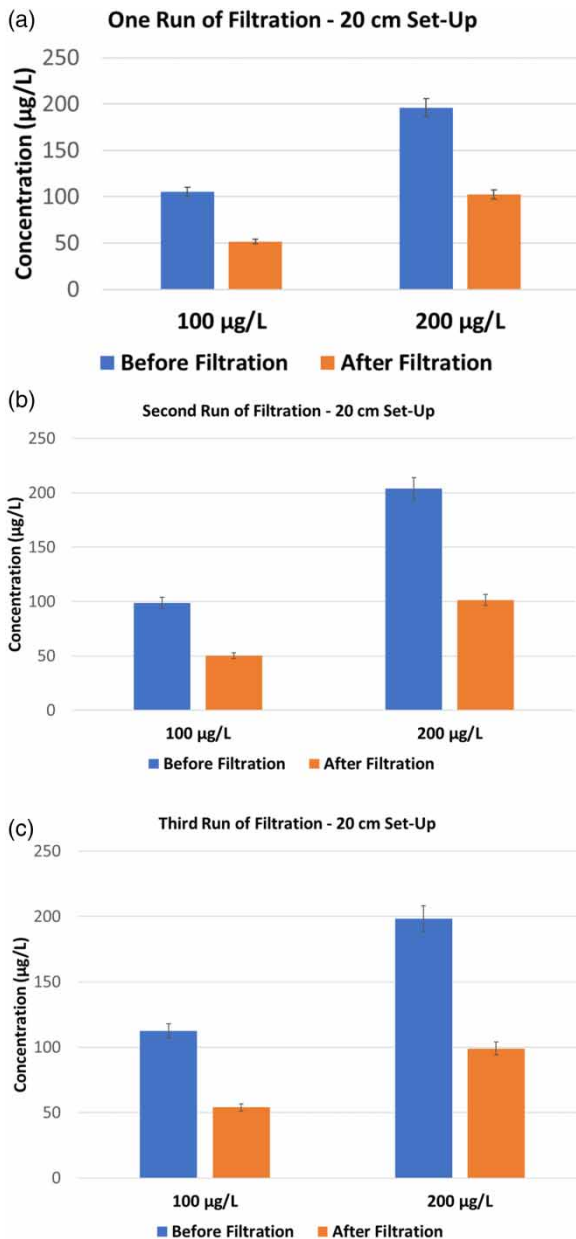


Figure 7 | The first, second, and third trials for running the 100 and 200 ppb arsenic water samples through the 20 cm filtration system once.

one round of filtration have increased by *three- to four-fold* compared to the 10 cm case.

Finally, for the second three trials conducted on the 20 cm filtration system for five runs or cycles of filtration, the highest percentage of arsenic removal within this study was recorded. In the first trial, 59–64% of the arsenic was filtered from the 100 ppb and 200 ppb samples of arsenic-tainted water that were run through the system. In the

second trial, 64–69% of the arsenic was removed from the water samples. Finally in the third trial, 61–73% of the arsenic was filtered from the water samples (Figure 8).

Comparison of filtration performance

On comparing the 20 cm and 10 cm systems under five runs, we see once again a significant improvement in performance. For the 100 ppb samples, the gains in the arsenic removal percentages are around a staggering *seven-, six-, and seven-fold*, while for the 200 ppb samples, the gains are less modest, around *one-and-half-, five-, and four-fold*. Out of the two primary filtration systems created (i.e., 10 cm and 20 cm), the trials conducted with the 20 cm system were most successful.

Some explanation for this amazing effect of increasing the filter length on the extent of arsenic removal is in order. The presence of IONPs on the pore walls of PU foam is the dominant cause of removal of arsenic by adsorption. Note that increasing the filter length provided higher removal efficiency as the tortuous path of water traveling through the porous foam lengthened and, consequently, the number of the IONPs coming in contact with contaminated water increased significantly.

We should comment on the time required to conduct one trial as that is relevant to the usefulness of the proposed low-cost, gravity-driven arsenic filtration device. Note that the time required for one sample to be completely filtered (Table 1) was found to be much lower than the prior filtration study that required approximately 9 days for the arsenic to be completely removed from a vertical column (Hussein 2016). After 20 runs, the filtration time did double, possibly due to swelling or saturation of the foam, but it still amounted to less than 10 minutes. Hence, this indicates the practical utility of the proposed system.

Regarding the removal efficiency in an earlier study of our research group (Hussein 2016), a column test was conducted to measure the removal efficiency of the PU/IONP foam composite. Complete 100% arsenic removal was attained with 22 cycles of the water flow through the foam at a slow flow-rate of 1.5 mL/min. The flow rate was slow due to high foam density. Optimizing the foam morphology can improve flow rate and the exposure of the IONPs to the contaminated water. With regards to the capacity of the filtration system, we refer the reader to our previous study

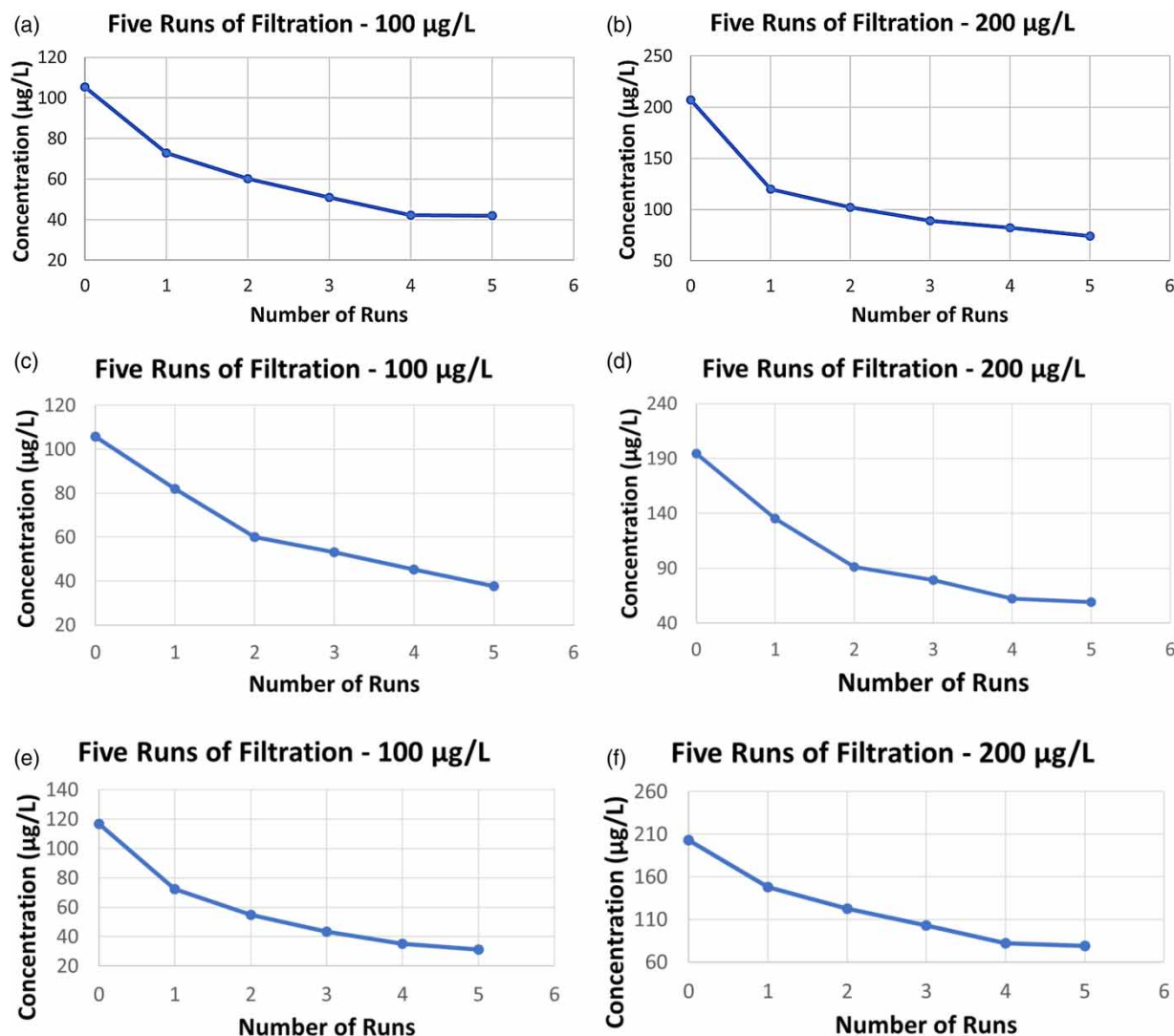


Figure 8 | Results of running the 100 and 200 ppb arsenic water samples through the 20 cm filtration system five times: (a) and (b) first trial, (c) and (d) second trial, (e) and (f) third trial.

Table 1 | Total filtration time for one run of the 20 cm system

	At start	After 20 runs
Time (min)	4.74	8.23

where we investigated this issue thoroughly (Hussein & Abu-Zahra 2017a).

Error estimation

A brief comment on the estimation of errors in the present study is now presented. The error bars displayed in the bar

graphs were calculated using the Excel software, which calculated the standard error of mean of the input values and, accordingly, used those calculations to place the error bars. Statistical analysis was done to confirm that the difference in the arsenic concentrations before and after filtration is statistically significant. A paired two-sample t-test (Excel) was conducted and a significance level (α) of 0.05 was used to compare the P values calculated (Table 2). All of the differences that resulted in each trial of using the filtration system were deemed as statistically significant, with the only exception being the trials conducted with arsenic samples containing 200 ppb run five times through

Table 2 | Paired two-sample T-test statistical analysis of efficacy of 10 and 20 cm PU foam models

	Model with 10 cm of PU foam		Model with 20 cm of PU foam	
	1 run	5 runs	1 run	5 runs
100 ppb	0.031	0.031	0.003	5.97×10^{-5}
200 ppb	0.023	0.1	1.95×10^{-5}	0.0002

the filtration model with 10 cm of PU foam. This was due to an outlier in the data, and it further confirmed the less significant outcome that resulted from using the PU foam model with only 10 cm of PU foam. The filtration model containing 20 cm of PU foam, on the other hand, performed more effectively and produced P values that suggest more significant statistical differences in the arsenic concentration of the samples before and after filtration. Note: The $P(T < =t)$ one-tail results were calculated using the Excel algorithm for the PU foam model containing 10 and 20 cm of the PU foam ($\alpha = 0.05$).

A discussion on system cost

We present here some facts that indicate that the proposed system has the potential to develop into a low-cost water filtration system. Since the gravity-driven systems are rather rare in the commercial market and our system is in the preliminary research stage, no commercial system has been compared with the proposed system in terms of costs in this paper. The fabrication costs of our system are expected to be low since, as mentioned earlier, the cost of the PVC tube used to house the PU-IONP slug was merely \$10.42 in the US – in developing countries with an abundant supply of low-cost plastics, this will be much lower. (In the case where PVC is not available, any other similar material of low cost can be used.) In the absence of the use of electric components such as a pump in the design, the device cost will remain substantially low. Let us now compare the costs of filter ‘cartridge’. One pound of PU-IONPs typically costs \$182 which is lower compared to other similar materials. For example, the average cost of activated alumina, hydrated iron oxide, and nanoscale zero valent iron, are \$225/lb, \$586/lb, and \$4,850/lb, respectively. All these points indicate that the final cost of such a gravity-

based system is expected to be quite low and hence suitable for developing countries.

SUMMARY AND CONCLUSIONS

Many countries suffer from the problem of arsenic in groundwater, which can lead to severe health issues if the polluted water is used without filtration. Here, we demonstrate that the nanocomposite polyurethane foam, with embedded iron oxide nanoparticles, could be used to develop a simple, low-cost, gravity-driven filtration device that has shown the promise of effectively removing (or at least reducing significantly) arsenic from polluted water. Through the testing of water samples with 100 and 200 ppb arsenic, it was shown that the 20 cm PU foam plug, compared to the 10 cm plug, was more effective at removing arsenic from the water samples. With only one run, it was able to effectively remove close to half of arsenic present within the water sample, and with just five runs in only 28 minutes, up to 70% of the arsenic was filtered. In addition, the models created performed better for higher (200 ppb) concentrations of arsenic, thus providing a viable filtration mechanism for nations affected by higher arsenic concentrations. The time taken for one run increased from around 4.7 minutes to around 8.2 minutes at the end of 20 runs. This performance was much better than reported in a previous published study where it took several days to purify similarly polluted water.

FUTURE INVESTIGATIONS

Future work will look into optimizing and studying further the overall filtering capability of the proposed simple, inexpensive, gravity-driven filtration system. The reusability and regeneration capabilities will also be studied for the proposed designed system.

Already, if close to 70% of arsenic within water can be filtered from water with just 20 cm of iron oxide nanoparticle-loaded PU foam plug, an increased length of foam plug could potentially lead to even 100% filtration of contaminated water samples. This will be studied in the near future. We will also look into correlating the time needed for one

trial with the permeability of the porous plug as well as with the effectiveness in arsenic removal. By the falling head permeability test, the permeability, a property of porous foam which determines how fast water will flow through the foam (Bear 1972), will be determined. In fact, such a determination can easily be made using the data recorded for the change in water level with time in the proposed setup. We also plan to propose a detailed mathematical model for predicting spatial changes in arsenic concentration within the PU foam plug. Using the volume averaging method, often employed for upscaling transport phenomena in porous media, we will aim to couple the adsorption of arsenic ion on pore walls with the macroscopic flow of water and transport of arsenic ions through the porous plug.

Usage of this device (or its suitable derivative) within the rural areas of developing countries will be planned to confirm the effectiveness and reliability of this filtration system in realistic operating situations. Given the fact that this model was simply a prototype, more research can be attempted into making the system easier to synthesize and fabricate for starting the regular production of this model. For example, more work can be done to make the overall insertion and removal of foam within the plastic tube easier. Research will also be done for recharging of the PU foam filter by removing the arsenic adsorbed on pore walls through some chemical treatment as well as safe disposal of adsorbed arsenic obtained from this process.

In addition, the efficiency of the device will be evaluated in the presence of other heavy metal contaminants, such as lead and mercury, and at different water pH levels. The multiple functionalization of the foam surface may be used to target various contaminants simultaneously.

If successful, this innovative low-cost technology has the potential to have a tremendously significant impact on the well-being of numerous communities in developing countries across the globe and ultimately help those people live healthier and longer lives.

ACKNOWLEDGEMENTS

We would like to acknowledge the help of Dr. Steve Hardcastle in the use of the AAS system.

REFERENCES

- Abejón, A., Garea, A. & Irabien, A. 2015 Arsenic removal from drinking water by reverse osmosis: minimization of costs and energy consumption. *Separation and Purification Technology* **144**, 46–53.
- Adsorptive arsenic removal media modelled 2007 *Membrane Technology*, **6**.
- Alava, P., Du Laing, G., Tack, F., De Ryck, T. & Van De Wiele, T. 2015 Westernized diets lower arsenic gastrointestinal bioaccessibility but increase microbial arsenic speciation changes in the colon. *Chemosphere* **119**, 757–762.
- Ameer, S. S., Engström, K., Bakhtiar Hossain, M., Concha, G., Vahter, M. & Broberg, K. 2017 Arsenic exposure from drinking water is associated with decreased gene expression and increased DNA methylation in peripheral blood. *Toxicology and Applied Pharmacology* **321**, 57–66.
- Anthamatten, P. & Hazen, H. 2012 *An Introduction to the Geography of Health*. Routledge, Abingdon, UK.
- Asadullah, M., Jahan, I., Boshir Ahmed, M., Adawiyah, P., Malek, N. H. & Sahedur Rahman, M. 2014 Preparation of microporous activated carbon and its modification for arsenic removal from water. *Journal of Industrial and Engineering Chemistry* **20**, 887–896.
- Baig, S. A., Sheng, T., Hu, Y., Lv, X. & Xu, X. 2013 Adsorptive removal of arsenic in saturated sand filter containing amended adsorbents. *Ecological Engineering* **60**, 345–353.
- Bear, J. 1972 *Dynamics of Fluids in Porous Media*. American Elsevier Publishing Company, New York, USA, p. 764.
- Brocato, J. & Costa, M. 2015 10th NTES conference: nickel and arsenic compounds alter the epigenome of peripheral blood mononuclear cells. *Journal of Trace Elements in Medicine and Biology* **31**, 209–213.
- Calatayud, M. & Laparra Llopis, J. M. 2015 Arsenic through the gastrointestinal tract. In: *Handbook of Arsenic Toxicology* (S. J. S. Flora, ed.). Academic Press, Oxford, UK.
- Cao, X., Lee, L. J., Widya, T. & Macosko, C. 2005 Polyurethane/clay nanocomposites foams: processing, structure and properties. *Polymer* **46**, 775–785.
- Chatterjee, S. & De, S. 2017 Adsorptive removal of arsenic from groundwater using chemically treated iron ore slime incorporated mixed matrix hollow fiber membrane. *Separation and Purification Technology* **179**, 357–368.
- Chávez-Capilla, T., Beshai, M., Maher, W., Kelly, T. & Foster, S. 2016 Bioaccessibility and degradation of naturally occurring arsenic species from food in the human gastrointestinal tract. *Food Chemistry* **212**, 189–197.
- Chen, A. S. C., Sorg, T. J. & Wang, L. 2015 Regeneration of iron-based adsorptive media used for removing arsenic from groundwater. *Water Research* **77**, 85–97.
- Choi, H., Woo, N. C., Jang, M., Cannon, F. S. & Snyder, S. A. 2014 Magnesium oxide impregnated polyurethane to remove high levels of manganese cations from water. *Separation and Purification Technology* **136**, 184–189.

- Cullen, W. R. & Reimer, K. J. 1989 Arsenic speciation in the environment. *Chemical Reviews* **89**, 713–764.
- DeMarco, M. J., SenGupta, A. K. & Greenleaf, J. E. 2005 Arsenic removal using a polymeric/inorganic hybrid sorbent. *Water Research* **37**, 164–176.
- Di Natale, F., Erto, A. & Lancia, A. 2013 Desorption of arsenic from exhaust activated carbons used for water purification. *Journal of Hazardous Materials* **260**, 451–458.
- Duan, X., Li, J., Zhang, Y., Li, W., Zhao, L., Nie, H., Sun, G. & Li, B. 2015 Activation of NRF2 pathway in spleen, thymus as well as peripheral blood mononuclear cells by acute arsenic exposure in mice. *International Immunopharmacology* **28**, 1059–1067.
- Ferguson, J. F. & Gavis, J. 1972 A review of the arsenic cycle in natural waters. *Water Research* **6**, 1259–1274.
- Flanagan, S. V., Johnston, R. B. & Zheng, Y. 2012 Arsenic in tube well water in Bangladesh: health and economic impacts and implications for arsenic mitigation. *Bulletin of the World Health Organization* **90**, 839–846.
- Garelick, H., Jones, H., Dybowska, A. & Valsami-Jones, E. 2009 Arsenic pollution sources. In: *Reviews of Environmental Contamination Volume 197* (H. Garelick & H. Jones, eds). Springer, New York, USA, pp. 17–60.
- Gehle, K. 2009 *Arsenic Toxicity, Agency for Toxic Substances and Disease Registry*. Agency for Toxic Substances and Disease Registry. Available from: www.atsdr.cdc.gov/csem/csem.asp?csem=1&po=0.
- Gu, Z., Fang, J. & Deng, B. 2005 Preparation and evaluation of GAC-based iron-containing adsorbents for arsenic removal. *Environmental Science & Technology* **39**, 3833–3843.
- Gunashakar, S. 2015 *A Study on the Synthesis-Structure-Property-Performance Relationship of Bulk Functionalized Polyurethane Foams for Water Filtration Applications*. PhD dissertation, University of Wisconsin-Milwaukee.
- Gupta, V. K., Saini, V. K. & Jain, N. 2005 Adsorption of As (III) from aqueous solutions by iron oxide-coated sand. *Journal of Colloid and Interface Science* **288**, 55–60.
- Halatek, T., Sinczuk-Walczak, H., Rabieh, S. & Wasowicz, W. 2009 Association between occupational exposure to arsenic and neurological, respiratory and renal effects. *Toxicology and Applied Pharmacology* **239**, 193–199.
- Human Rights Watch 2016 *Bangladesh: 20 Million Drink Arsenic-Laced Water*. Human Rights Watch, New York, USA.
- Hussein, F. B. 2016 *Synthesis and Performance Analysis of Polyurethane Foam Nanocomposite for Arsenic Removal From Drinking Water*. Thesis, The University of Wisconsin-Milwaukee.
- Hussein, F. B. & Abu-Zahra, N. H. 2017a Adsorption kinetics and evaluation study of iron oxide nanoparticles impregnated in polyurethane matrix for water filtration application. *Journal of Minerals and Materials Characterization and Engineering* **5**, 298.
- Hussein, F. B. & Abu-Zahra, N. H. 2017b Extended performance analysis of polyurethane-iron oxide nanocomposite for efficient removal of arsenic species from water. *Water Science and Technology: Water Supply* **17**, 889–896.
- Jain, P. & Pradeep, T. 2005 Potential of silver nanoparticle-coated polyurethane foam as an antibacterial water filter. *Biotechnology and Bioengineering* **90**, 59–63.
- Katsoyiannis, I. A. & Zouboulis, A. I. 2002 Removal of arsenic from contaminated water sources by sorption onto iron-oxide-coated polymeric materials. *Water Research* **36**, 5141–5155.
- Lesueur, C., Gilbert-Diamond, D., Andrew, A. S., Ekstrom, R. M., Li, Z., Kelsey, K. T., Marsit, C. J. & Karagas, M. R. 2012 A case-control study of polymorphisms in xenobiotic and arsenic metabolism genes and arsenic-related bladder cancer in New Hampshire. *Toxicology Letters* **210**, 100–106.
- Lynch, H. N., Zu, K., Kennedy, E. M., Lam, T., Liu, X., Pizzurro, D. M., Loftus, C. T. & Rhomberg, L. R. 2017 Quantitative assessment of lung and bladder cancer risk and oral exposure to inorganic arsenic: meta-regression analyses of epidemiological data. *Environment International* **106**, 178–206.
- Mahdavi, M., Ebrahimi, A., Azarpira, H., Tashauoei, H. R. & Mahvi, A. H. 2017 Dataset on the spent filter backwash water treatment by sedimentation, coagulation and ultra filtration. *Data in Brief* **15**, 916–921.
- McNeill, L. S. & Edwards, M. 1997 Arsenic removal during precipitative softening. *Journal of Environmental Engineering* **123**, 453–460.
- Mehta, A., Ramachandra, C. J. A. & Shim, W. 2015 Arsenic and the cardiovascular system. In: *Handbook of Arsenic Toxicology* (S. J. S. Flora, ed.). Academic Press, Oxford, UK, pp. 459–492.
- Melak, D., Ferreccio, C., Kalman, D., Parra, R., Acevedo, J., Pérez, L., Cortés, S., Smith, A. H., Yuan, Y., Liaw, J. & Steinmaus, C. 2014 Arsenic methylation and lung and bladder cancer in a case-control study in northern Chile. *Toxicology and Applied Pharmacology* **274**, 225–231.
- Ning, R. Y. 2002 Arsenic removal by reverse osmosis. *Desalination* **143**, 237–241.
- Oregon Health Authority. *Drinking Water Program Fact Sheet: Recommendations for Arsenic Removal From Private Drinking Water Wells in Oregon*. Available from: <http://www.oregon.gov/oha/PH/HealthyEnvironments/DrinkingWater/SourceWater/Documents/gw/arsenicremoval.pdf>.
- Phung, D., Connell, D., Rutherford, S. & Chu, C. 2017 Cardiovascular risk from water arsenic exposure in Vietnam: application of systematic review and meta-regression analysis in chemical health risk assessment. *Chemosphere* **177**, 167–175.
- Schmidt, S.-A., Gukelberger, E., Hermann, M., Fiedler, F., Großmann, B., Hoinkis, J., Ghosh, A., Chatterjee, D. & Bundschuh, J. 2016 Pilot study on arsenic removal from groundwater using a small-scale reverse osmosis system – towards sustainable drinking water production. *Journal of Hazardous Materials* **318**, 671–678.

- Siddiqui, S. I. & Chaudhry, S. A. 2017 Iron oxide and its modified forms as an adsorbent for arsenic removal: a comprehensive recent advancement. *Process Safety and Environmental Protection* **111**, 592–626.
- Terracciano, A., Ge, J. & Meng, X. 2015 A comprehensive study of treatment of arsenic in water combining oxidation, coagulation, and filtration. *Journal of Environmental Sciences* **36**, 178–180.
- Teychene, B., Collet, G., Gallard, H. & Croue, J.-P. 2013 A comparative study of boron and arsenic (III) rejection from brackish water by reverse osmosis membranes. *Desalination* **310**, 109–114.
- The Dow Chemical Company. *Dow Polyurethanes – Surfactants Role in Foam Formulations*. Available from: <https://www.dow.com/en-us/product-technology/pt-polyurethanes/pg-polyurethanes-additives-surfactants.html>.
- Wickramasinghe, S. R., Han, B., Zimbron, J., Shen, Z. & Karim, M. N. 2004 Arsenic removal by coagulation and filtration: comparison of groundwaters from the United States and Bangladesh. *Desalination* **169**, 231–244.
- Wilson, R. 2009 *Chronic Arsenic Poisoning: History, Study and Remediation*. Available from: <http://users.physics.harvard.edu/~wilson/>.
- World Health Organization 2018 Arsenic. Available from: www.who.int/mediacentre/factsheets/fs372/en/.
- Wu, Y., Ma, X., Feng, M. & Liu, M. 2008 Behavior of chromium and arsenic on activated carbon. *Journal of Hazardous Materials* **159**, 380–384.
- Xiong, Y., Tong, Q., Shan, W., Xing, Z., Wang, Y., Wen, S. & Lou, Z. 2017 Arsenic transformation and adsorption by iron hydroxide/manganese dioxide doped straw activated carbon. *Applied Surface Science* **416**, 618–627.
- Xu, X., Chen, C., Wang, P., Kretzschmar, R. & Zhao, F.-J. 2017 Control of arsenic mobilization in paddy soils by manganese and iron oxides. *Environmental Pollution* **231**, 37–47.
- Yang, Z., Wu, X., Li, T., Li, M., Zhong, Y., Liu, Y., Deng, Z., Di, B., Huang, C., Liang, H. & Wang, M. 2011 Epidemiological survey and analysis on an outbreak of gastroenteritis due to water contamination. *Biomedical and Environmental Sciences* **24**, 275–283.
- Yazdani, M., Tuutijärvi, T., Bhatnagar, A. & Vahala, R. 2016 Adsorptive removal of arsenic(V) from aqueous phase by feldspars: kinetics, mechanism, and thermodynamic aspects of adsorption. *Journal of Molecular Liquids* **214**, 149–156.
- Yeh, T.-C., Tai, Y.-S., Pu, Y.-S. & Chen, C.-H. 2015 Characteristics of arsenic-related bladder cancer: a study from Nationwide Cancer Registry Database in Taiwan. *Urological Science* **26**, 103–108.
- Yorifuji, T., Kato, T., Ohta, H., Bellinger, D. C., Matsuoka, K. & Grandjean, P. 2016 Neurological and neuropsychological functions in adults with a history of developmental arsenic poisoning from contaminated milk powder. *Neurotoxicology and Teratology* **53**, 75–80.
- Zhang, Q., Pan, B., Zhang, W., Pan, B., Zhang, Q. & Ren, H. 2008 Arsenate removal from aqueous media by nanosized hydrated ferric oxide (HFO)-loaded polymeric sorbents: effect of HFO loadings. *Industrial & Engineering Chemistry Research* **47**, 3957–3962.

First received 7 June 2018; accepted in revised form 22 January 2020. Available online 6 April 2020