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**Removal of arsenate and ammonia from water by molecularly
imprinted polymers**

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ABSTRACT

Arsenic and ammonia in ground and surface waters pose significant health risks globally, especially for remote areas where access to safe drinking water is a concern for U.S. military personnel. Current removal materials and methods lack contaminant specificity. This study developed adsorptive resins and membranes specifically targeting arsenate and ammonia removal using molecularly imprinted acrylate polymers supported on graphitic carbon nitride. These materials showed comparable arsenate removal capacity to commercial resins. Higher ammonia removal capacity but lower selectivity was demonstrated by these materials in comparison to commercial resins. This research aims to enhance water treatment materials for ensuring clean drinking water access in remote military locations.

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1. INTRODUCTION

Arsenic contamination in groundwater poses a significant threat to drinking water supplies worldwide. The presence of arsenic ions, arsenate (As(V)) being the most

common, in ground and surface waters is a pressing health concern for U.S. military operations around the world. These toxic ions can infiltrate water sources through various pathways such as air, soil, and industrial runoff, leading to severe adverse effects on human health. Other than naturally occurring

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arsenic species, anthropogenic sources – such as insecticides, herbicides, food additives and medicinal preparations - also contribute to groundwater contamination. High arsenic concentrations have been reported in Taiwan, Mexico, Japan, Poland, and China, among others [1], emphasizing the necessity for mobile water treatment availability in remote locations to effectively address such contamination risks.

Ammonia likewise poses a threat to clean drinking water. It enters the environment through nitrogen fixation, animal waste deposition, agricultural runoff, and municipal discharge [2]. Elevated levels of ammonia in drinking water can lead to severe health complications, including organ damage, skin burns, or death [3]. Given the potential for ammonia contamination in remote locations where access to clean drinking water may be limited, the need is imminent for effective mobile water treatment to safeguard the health of military personnel deployed in such areas.

The removal of As(V) and ammonia from water is traditionally achieved through filtration, adsorption, ion exchange, and membrane processes [4,5]. Recent advancements have introduced novel materials and methods for more efficient removal. Among these methods, adsorption and membrane processes offer distinct advantages. Membrane processes have shown over 95% pollutant rejection under optimal conditions, though pollutant rejection rates are influenced by factors that typically lack controllability, such as membrane pore size and selectivity [6,7,8]. Adsorptive membranes, however, offer rapid removal of contaminants and low energy consumption compared to conventional membranes [9]. On the other hand, adsorption processes are simpler than traditional filtration methods, environmentally benign, and cost-effective.

However, commonly used adsorbents like activated carbon may lack selectivity.

To resolve the lack of selectivity presented by commonly used polymers, molecularly imprinted polymers (MIPs) are currently being used specifically for their selectivity, as well as for their relatively high tolerance to different temperatures and pH [10].

In this study, molecular imprinting polymerization benefits from the addition of graphitic carbon nitride (g-C₃N₄), which acts as both a cross-linker and initiator during polymerization due to its unique properties such as high porosity, chemical versatility, strong mechanical stability, and large surface area [11]. This composite nature enhances the strength and adsorptive properties of the resulting material. Nanostructured g-C₃N₄ decorated with acrylate MIPs templated for arsenate or ammonia was used to create adsorbents and adsorptive membranes to remove arsenate and ammonia from water. This study aims to evaluate the polymer's performance in removing these contaminants and assess its overall performance.

2. MATERIALS AND METHODS

Methacrylic acid (99%), methacrylamide (98%), acetonitrile, urea, sodium arsenate (98%), ethylene glycol dimethacrylate (EDMA, 98%), ammonium chloride (*NH₄Cl*) were obtained from Sigma Aldrich, USA. Concentrated HCl (12 M) was obtained from Fisher Scientific, USA. Deionized ultra-filtered (DIUF) water was obtained from an E-Pure water purification system (Barnstead E-Pure D4641) and collected at 18 M Ohm. The DIUF water was used to synthesize the chemical solutions, non-imprinted (NIP) and imprinted polymers (MIP).

2.1. Preparation of NIP and MIP Resins for Arsenate and Ammonia Removal

For non-imprinted resins, g-C₃N₄ was prepared by heating 20 g of urea in a muffle furnace at 550 °C (heating rate of 2.5 °C/min) for 4 h. The NIP was prepared by adding 0.9 g g-C₃N₄ to a 500 mL flat-bottomed reaction vessel. It was dissolved in 75 mL of DIUF water and 75 mL of acetonitrile. Methacrylamide (9.01 g, 0.106 mol, 0.7 eq for arsenate, or 3.061 g, 0.3 eq for ammonia) and methacrylic acid (4.00 mL, 0.047 mol, 0.3 eq for arsenate or 7.046 mL, 0.7 eq for ammonia) were added to the mixture and homogenized with a mechanical stirrer. For the ammonia NIP, 13.6 μL of EDMA (0.0005 eq) was also added to the mixture prior to polymerization. For both arsenate and ammonia NIP resins, the mixture was polymerized under two blue lights (GloGlow E27 18 W LED 460 nm) spaced at 12 inches for 48 h. Nitrogen was bubbled into the solution throughout the polymerization. The NIP was filtered using a Buchner funnel and lyophilized to remove water from the product. The MIP was synthesized using the same process as the NIP with Na₂HAsO₄ (0.05 g, 0.0002 mol, 0.001 eq) added as the template for arsenate removal or 1.5 g NH₄Cl added as the template for ammonia removal. The template was removed from the MIP by dialysis with DIUF water. The polymer was lyophilized to remove water.

2.2. Fabrication of Membranes for Arsenate and Ammonia Removal

Membranes for removal were fabricated by filtration for arsenate, and phase inversion for ammonia. These processes are similar with the exception that, for filtration, polymerization is done in two steps; while phase inversion includes adding 8 mL hexane prior to bubbling nitrogen into the mixture.

For both arsenate and ammonia, NIP membranes were synthesized by mixing 0.9 g of g-C₃N₄ with 22.5 mL DIUF water and 22.5 mL acetonitrile. This mixture was then stirred at 200 rpm. While stirring the mixture, 5.4096 g of methacrylamide (5.4096 for arsenate or 1.836 g for ammonia) and methacrylic acid (2.4 mL for arsenate or 4.114 mL for ammonia) were added. For the arsenate NIP, 0.1 M HCl was added for protonation. For the ammonia NIP, 3.46 μL of EDMA was added for additional cross-linking. The mixture was then stirred in a sonicator for 30 minutes. After sonicating, the mixture was stirred under blue light for 2 hours, then dried under the blue light by pouring the mixture over a glass filter paper using a Buchner funnel. For the imprinted membrane, 0.03 g sodium arsenate (Na₂HAsO₄) for the arsenate resin or 0.3786 g ammonia chloride (NH₄Cl) for the ammonia resin was added as the template molecule prior to sonicating, and the membrane was dialyzed to remove the contaminant template.

2.3. Arsenate and Ammonia Adsorption Resin Performance Evaluation

Column tests for arsenate and ammonia adsorption capacity were performed by swelling 0.2 g of the polymer with ≤ 250 μm particle size in 20 mL DIUF water for 24 h. 20 mL of solution with different concentrations (5, 10 and 20 mg/L for arsenate and 2, 4 and 8 mg/L for ammonia) were poured into the columns packed with the MIP or NIP. The eluent was collected into vials for concentration measurements. Competition column experiments for arsenate were conducted by pouring a 20 mg/L arsenate solution (50%:50% sodium arsenate, 20 mg/L: sodium chloride solution, 20.0 mL) into the column containing the MIP resin. The eluent was collected and analyzed.

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Arsenate concentrations were measured using Inductively Coupled Plasma-Optical Emission Spectroscopy (Agilent 5800 series ICP-OES, model G8020-90002) after digesting samples with 2% HNO₃ (60 µL). Arsenic concentrations were determined at wavelengths 188.980 nm and 193.696 nm.

Ammonia concentrations were measured using an ammonia electrode (Thermo Scientific Orion Star A214 Benchtop pH/ISE Meter, USA).

2.4. Arsenate and Ammonia Adsorptive Membrane Performance Evaluation

Membrane capacity was determined for arsenate and ammonia by passing a known concentration of arsenate or ammonia solution through the respective NIP or MIP membrane. Competition experiments in MIP membranes used a 50%:50% sodium arsenate: sodium chloride solution (20 ppm, 20 mL) for sodium arsenate. A 50%:50% ammonia: calcium ion (Ca²⁺) solution (8 mg/L, 20 mL) was used for ammonia. The filtered eluent of each experiment was collected for analysis, using the same arsenate and ammonia analytical methods noted in the previous section.

3. Results

Column experiments demonstrated that the MIP removed more contaminant compared to the NIP for both arsenate and ammonia (Figures 1 and 2). This demonstrates the higher capacity and binding strength of the MIP compared to the NIP in both contaminants. The competition experiments for arsenate and ammonia showed some removal, although lower compared to the MIP. Despite the competing ion binding more strongly to the ionic sites in the resin, arsenate and ammonia were still removed

from water. However, the binding strength towards the contaminants has to be improved.

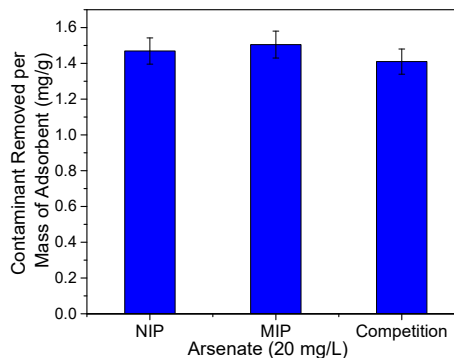


Figure 1: Mass of arsenic removed per mass of adsorbent by columns.

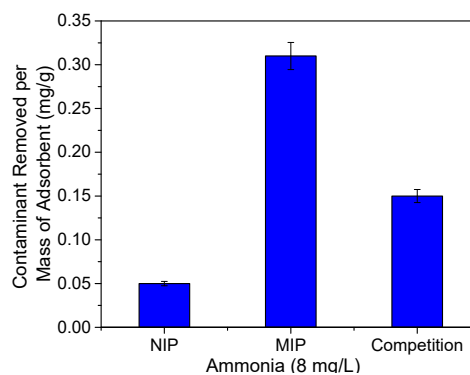


Figure 2: Mass of ammonia removed per mass of adsorbent by columns.

Membrane experiments showed higher removal in the MIP membrane compared to the NIP membrane for both arsenate and ammonia (Figures 3 and 4). This means that the higher binding strength of the imprinted binding sites allows for increased specificity of the MIP membranes. In the competition experiment for arsenate, the MIP membrane shows the highest removal, suggesting that the binding of arsenate happens faster than the competing ion, and proving the increased selectivity of the membrane.

The experiment for ammonia demonstrated lower removal for the MIP membrane in the competition experiment, suggesting that the speed of binding needs improvement (Figure 4).

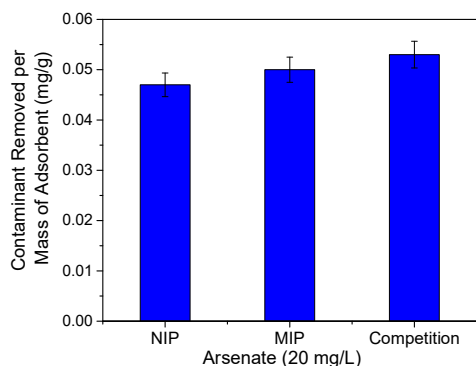


Figure 3: Mass of arsenate removed per mass of adsorbent by membranes.

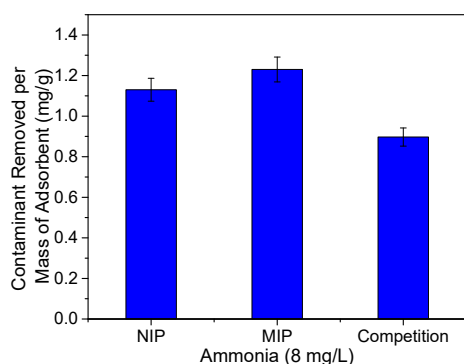


Figure 4: Mass of ammonia removed per mass of adsorbent by membranes.

Overall, the MIP resins for arsenate and ammonia demonstrated higher selectivity, and greater adsorption capacity. The membrane adsorption experiments indicate a need to continue optimizing binding strength and adsorption kinetics. Further work must also be done to improve the preparation and the mechanical stability of the membranes.

4. REFERENCES

(Note: Use IEEE style)

[1] C. Jain, and I. Ali, "Arsenic: occurrence, toxicity and speciation techniques," *Water Res.*, vol. 34, pp. 4304–4312, 2000.

[2] S. Khuntia, S. K. Majumder, and P. Ghosh, "Microbubble-aided water and wastewater purification: a review," *Reviews in Chemical Engineering*, vol. 28, no. 4–6, Jan. 2012, doi: 10.1515/revce-2012-0007.

[3] P. Jiri, and K. Kamil, "Irritant compounds: respiratory irritant gases". *Milit Med Sci Lett*. Vol. 83, no. 2, pp. 73-82, 2014.

[4] T. C. Alex, Er, E. Gullede, and F. X. Han, "Arsenic Occurrence, Ecotoxicity and its Potential Remediation," *Journal of Bioremediation and Biodegradation*, vol. 7, no. 4, Jan. 2016, doi: 10.4172/2155-6199.1000e174.

[5] S. Alka, S. Shahir, N. Ibrahim, M. J. Ndejiko, D. N. Vo, and F. A. Manan, "Arsenic removal technologies and future trends: A mini review," *Journal of Cleaner Production*, vol. 278, p. 123805, Jan. 2021, doi: 10.1016/j.jclepro.2020.123805.

[6] N. Tanne, R. Xu, M. Zhou, P. Zhang, X. Wang, and X. Wen, "Influence of pore size and membrane surface properties on arsenic removal by nanofiltration membranes," *Frontiers of Environmental Science & Engineering*, vol. 13, no. 2, Feb. 2019, doi: 10.1007/s11783-019-1105-8.

[7] M. C. Shih, "An overview of arsenic removal by pressure-driven membrane processes," *Desalination*, vol. 172, pp. 85–97, 2005.

[8] M. R. Adam *et al.*, "Current trends and future prospects of ammonia removal in wastewater: A comprehensive review on adsorptive membrane development," *Separation and Purification Technology*, vol. 213, pp. 114–132, Apr. 2019, doi: 10.1016/j.seppur.2018.12.030.

[9] D. Roper and E. N. Lightfoot, "Separation of biomolecules using adsorptive membranes," *J. Chromatogr. A*, vol. 702, pp. 3–26, 1995.

[10] B. Murat, and G. Olgun, "RAFT mediated grafting of poly (acrylic acid) (PAA) from polyethylene/polypropylene (PE/PP) nonwoven fabric via pre-irradiation," *Polymer*, vol. 54, no. 18, pp. 4838-4848, 2013.

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[11] W. Aiyu, W. Chundong, F. Li, W. Winnie and L. Yucheng, "Recent advances of graphitic carbon nitride-based structures and applications in catalyst, sensing, imaging, and LEDs", *Nano-micro letters*, vol. 9, pp. 1-21, 2017.