

Removal of Arsenic (III) from Groundwater by Adsorption onto Duckweed (*Lemna minor*)

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Authors' contributions

This work was carried out in collaboration between all authors. Author MNA designed the study. Authors MNA, AIM and SBQ supervised the present study. Authors TRC and TA carried out the experimental works according to the plan. Author TRC prepared the manuscript. Author MNA wrote the final draft of the manuscript. All authors read and approved the final manuscript.

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ABSTRACT

Duckweed used as adsorbent material for arsenic (III) removal from groundwater. The results of this study showed that adsorption of arsenic (III) by duckweed without any pretreatment. Various parameters are investigated that affect arsenic adsorption/desorption. Maximum arsenic (III) removal was obtained under the following conditions: initial As (III) concentration, 100 µg/L; Duck weed amount, 3 g; average particle size, 0.595 mm; treatment flow rate, 1.67 mL/min; and pH, 5.5, respectively. The desorption efficiencies with 1M H₂SO₄ was observed 97.67%. The present work meets the arsenic concentration required for drinking water recommended by Bangladesh and the World Health Organization (WHO) water quality criteria for drinking water.

Keywords: Arsenic; adsorption; duckweed; aqueous solution; groundwater; desorption.

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1. INTRODUCTION

Arsenic (As) is a naturally occurring element, due to the presence of arsenical minerals, (e.g., arsenolite, arsenopyrite, enargite, tennantite etc.), volcanic emissions and inputs from geothermal sources, as well as a consequence of anthropogenic activities, such as mining activities, combustion of fossil fuels and the use of arsenical pesticides [1]. A large number of sites worldwide have been contaminated by arsenic from natural and anthropogenic sources [2]. Global concern as a pollutant of drinking water and groundwater, which has been reported in Bangladesh, India, Taiwan, Argentina, Mexico, Hungary, and Chile [3,4]. Increased usage of groundwater for drinking has caused serious health problems [5], because arsenic is known to be highly detrimental to human beings and animals. They include several neurological [6], dermatological [7], gastrointestinal [8] and cardiorenal diseases [9]; arsenic also is a suspected carcinogen [10]. Furthermore, recent research has suggested that As is toxic to living organisms at high concentration, and inorganic arsenicals are proven carcinogens to human [11]. Recently, because of its high nuisance value, various regulatory agencies have revised the maximum contaminant arsenic level 50 to 10 µg/L in drinking water [12,13]. This situation will require the development of simple and low-cost methods for the removal of As from groundwater for drinking water.

Arsenic toxicity depends on its speciation, and generally inorganic arsenic species are more toxic than organic species [11,14]. As(III) is more toxic than As(V), and dimethylarsinic acid (DMAA) and monomethylarsonic acid (MMAA) are more toxic than their parent compounds [15]. In general, in anaerobic groundwaters, arsenite [As (III)] predominates, whereas arsenate [As (V)] is more prevalent in surface waters. The As(V) species exists as oxyanions (H_2AsO_4^- and HAsO_4^{2-}) at neutral pH, whereas the predominant As(III) species is neutral H_3AsO_3 [16]. As(III) is more toxic and more difficult to remove with the conventionally applied physicochemical treatment methods than As(V). Coprecipitation with iron or alum, ion-exchange resin, adsorption onto coagulated floc, reverse osmosis and membrane techniques are widely used to remove As from aqueous solution [17–20].

Among these methods, the adsorption techniques are simple and convenient. This method also have the potential for regeneration

and sludge-free operation. Metal-loaded coral limestone, activated carbon, activated alumina, reverse osmosis and hydrous zirconium oxide, etc. adsorbents are used for arsenic removal [20–25]. But most of these adsorbents are expensive and several problems in terms of efficiency. The purpose of this study was to evaluate the feasibility of using of duckweed without any pretreatment as an alternate adsorbent for removing arsenite from Bangladeshi As-contaminated drinking water samples in a single-step column operation.

2. MATERIALS AND METHODS

2.1 Reagent

All reagents are analytical grade (Merck, Germany) were used in this study. Standard As (III) solution was supplied by Varian Inc, USA with highest purity level (99.98%). Stock solutions (1000 mg/L) of As(III) was prepared by dissolving appropriate weighted quantity of solid KAsO_2 in distilled water. Standard dilute solutions were prepared daily before use. Water was purified with an ultrapure water making system (Advantec MFS, Inc., Tokyo, Japan) with a resistivity of $>18 \text{ M}\Omega \text{ cm}$.

2.2 Preparation of Adsorbent

The dhoicha, duckweed, water hyacinth and wheat husk were collected from local area of Bangladesh. The proximate analysis of dry duckweed is as follows (wt.%): moisture – 3.7; total volatiles (120–950°C) – 78.0 (including volatiles evolved at 120–650°C – 67); fixed carbon – 8.8; ash – 9.5. The ultimate analysis of a dry duckweed is as the following (%): C – 39.11; H – 6.13; O – 37.74; N – 5.52; S – 0.67; balance – mineral matter [26].

The Duckweeds were washed with pure water several times to remove dust and fines until the color of the wash water was transparent. The washed materials were then dried in an oven at 60°C for 24 h. The dried material was sieved into particle size of 0.105–2.3 mm. The materials were used for the removal of arsenic without further treatment.

2.3 Adsorption and Analytical Procedures

The Duckweeds were washed with pure water several times to remove dust and fines until the color of the wash water was transparent. The washed materials were then dried in an oven at

60°C for 24 h. The dried material was sieved into particle size of 0.105–2.3 mm. Duckweed kept to the treatment glass columns (2 x 30 cm). The arsenic adsorption were carried out in columns with a stopper for controlling the column eluate flow rate. The adsorption factors including duckweed amount, particle size, pH, initial sample concentration, and treatment flow rate were evaluated. The sample solution was passed through the adsorption column, after the pH had been fixed with HCL and NaOH, at a given flow rate. The flow rates of 0.41, 0.55, 0.83, 1.67 and 3.3 mL/min correspond to 3 g of adsorbent. During the treatment, a small piece of tissue paper was inserted in the bottom of the column to prevent loss of adsorbent and kept constant the flow rate with the controlling of the stopper valve. The treatment was performed at ambient temperature. Five experiments for the removal of As. Analyses were performed using Varian Atomic Absorption Spectrometer (Model Spectr AA 240) with a Hydride generation system and controlled with software Version 5.01. During the analysis time, acid container contains 5M HCl and reductant container contain 0.6% sodium borohydride in 0.5% (w/v) sodium hydroxide.

The adsorption efficiency was calculated as the following equation,

$$\text{Removal (adsorption) efficiency} = \frac{C_o - C_t}{C_o} \times 100$$

Where C_o and C_t are the As (III) concentration before and after treatment, respectively.

2.4 Regeneration of Adsorbent

Recovery of the adsorbed material and regeneration of As (III) is also an important aspect of wastewater treatment. Attempt was made to desorb of As (III) from duck weed surface with acid solutions of sulfuric, nitric acid, and hydrochloric and base solutions of sodium hydroxide and potassium hydroxide. This desorption process was performed by the column method. 100 mL of desorption solution was added to the column and was kept for a fixed period of time for each experiment. The solution was passed through the column after the fix time.

3. RESULTS AND DISCUSSION

First, the performances of four adsorbents (Dhoincha, duckweed, water hyacinth and wheat husk) were evaluated for the removal of As (III) from aqueous solutions. The removal efficiencies with dhoincha, duckweed, water hyacinth and

wheat husk were 3.31%, 22.72%, 7.03% and 3.74%, respectively. The adsorbents dhoincha, water hyacinth and wheat husk had lower removal efficiencies than duckweed. Therefore, they were not considered for further investigations. The duckweed used was an available material in the local pond. Because the main component of duckweed is carbon, duckweed has the potential to be used. Duckweed was chosen as an adsorbent material because of its absorption ability of metals.

3.1 Effect of Adsorbent Amount

The effect of the amount of duckweed on the removal of As (III) was investigated. The results are presented in Fig. 1. The removal efficiencies of As (III) increased gradually with increasing amount of Duckweed. It is readily understood that the adsorption capacity of Duck weed depends on the surface activity, that is, the specific surface area available for As-surface interactions that is accessible to the As. Hence, increasing the amount of Duckweed will increase removal capacity of As. Until now, various kinds of adsorbents have been studied for the removal of arsenic. The maximum As (III) removal efficiency achieved was 99% for iron oxide-coated sand at an adsorbent dose of 20 g/L with an initial As concentration 100 µg/L in batch studies [27]. The removal efficiencies for As (III) from an aqueous solution (100 µg/L, 100 mL) by 0.1 g of modified fungal biomass were 75%, respectively, after a 12-h batch treatment [28]. When an aqueous As (III) solution of 10 mg/L concentration was stirred in the presence of both 1.0 g/L TiO_2 and 1.0 g/L activated alumina under sunlight irradiation, the arsenic removal increased with time and reached 89% after 24 h [29]. Although the removal efficiencies in the proposed system were similar to those obtained with the other adsorbents, the treatment time was very short because of the flow method (column system).

3.2 Effect of Flow Rate

The treatment flow rate is one of the most effective factor in column adsorption process. The effect of the flow rate on the removal of As (III) is presented in Fig. 2. The removal efficiency of As (III) increased gradually with decreasing flow rate. Since the flow rate was slow, As (III) in the sample solution got more contact time with the active surface of the adsorbents.

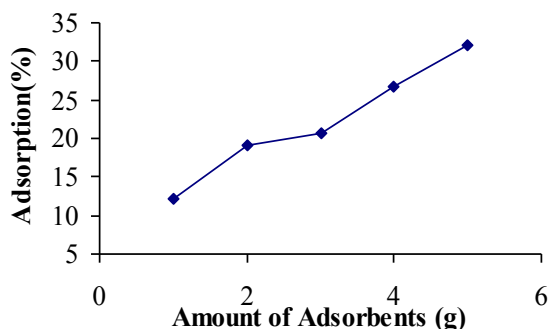


Fig. 1. Effect of adsorbent amount on the removal of As (III) by adsorption onto duckweed (initial As concentration, 100 µg/L; pH, 5.5; treatment flow rate, 1.67 mL/min)

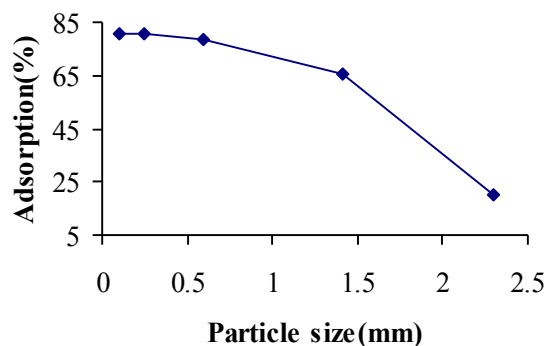


Fig. 3. Effect of particle size on the removal of As (III) by adsorption onto duckweed (initial As concentration, 100 µg/L; pH, 5.5; amount of adsorbent, 3 g; treatment flow rate, 1.67 mL/min)

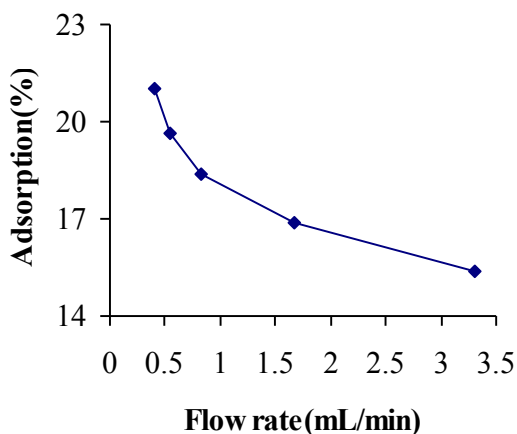


Fig. 2. Effect of treatment flow rate on the removal of As (III) by adsorption onto duckweed (initial As concentration, 100 µg/L; pH, 5.5; amount of adsorbent, 3g)

3.3 Effect of Particle Size

Column adsorption experiments were carried out for the removal of arsenic from aqueous solution using five different particle sizes (0.105 mm, 0.25 mm, 0.595 mm, 1.41 mm and 2.3 mm). The results are shown in Fig. 3. The removal efficiency for As (III) decreased gradually with decreasing particle size. It is reported that, when particles size of adsorbent increased, the adsorption of metal ions decreased [30]. Similar results have been reported by Wong et al. [31]. These phenomena may be due to the fact that the smaller particles offer comparatively larger surface areas and greater numbers of adsorption sites.

3.4 Effect of Initial Concentration

The removal efficiency depends on the initial concentrations of As (III) in the sample solution. The initial concentration was investigated in the range of 50-500 µg/L, and the results are illustrated in Fig. 4. The removal efficiency decreased with increasing adsorbate concentration of the solutions. These phenomena may be at low concentration most of As (III) in the sample solution get contact with active sites. With increasing arsenic concentration in solution, active sites on the adsorbents were not increased. Therefore arsenic removal efficiencies were decreased.

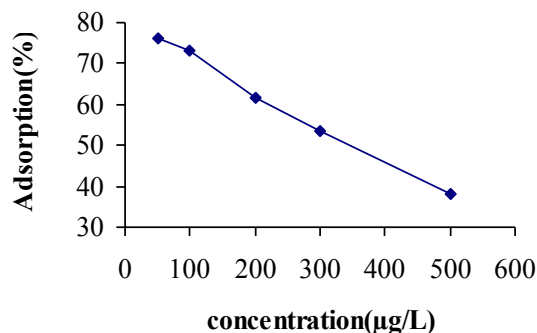


Fig. 4. Effect of initial adsorbate concentration on the removal of As (III) by adsorption onto duck weed (Particle size, 0.595 mm; pH, 5.5; amount of adsorbent, 3 g; treatment flow rate, 1.67 mL/min)

3.5 Effect of pH

pH is one of the most important parameters controlling the metal ion sorption process [30,31]. Fig. 5 depicts the effect of pH on As(III) removal with duckweed. The removal efficiency of As (III) tended to decrease with increasing pH and then decreased markedly at pH 12. At low pH values, i.e., higher hydrogen ion concentration, internal pore of surface were neutralized by the negative charge and developed some more new adsorption sites which provided a positive charge for anionic As(III) complex to get adsorbed on the surface. Again it is observed that the final pH of the solution was always greater than the initial pH of the solution, which confirmed the neutralization of H⁺ ions with the negative charge at the surface and envelopment of more H⁺ ions in formation of positively charged surface. As a result, the concentration of H⁺ ions decreased in the solution and hence the pH of the solution increased. Many authors also reported similar results [32]. The removal efficiency for As (III) observed 76% was in comparatively neutral regions. These results should be of great advantage for arsenic removal from groundwater.

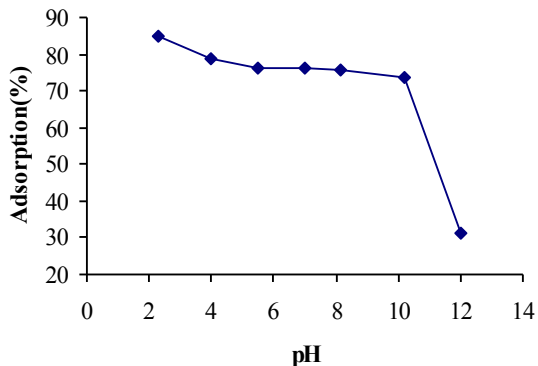


Fig. 5. Effect of pH on the removal of As (III) by adsorption onto duckweed (initial As (III) concentration, 100 µg/L; particle size, 0.595 mm; amount of adsorbent, 3g; treatment flow rate, 1.67 mL/min)

3.6 Adsorption Mechanism

Arsenic adsorption can be occurred mainly through two routes: (i) Affinity adsorption and (ii) Anion exchange between the arsenic in the water and the carbon surface of the duckweed. Affinity adsorption is related to the behavior of duckweed surface, while anion exchange relates to the arsenic species of the existing forms. During the

activation process, the OH groups are created on the carbon surface [33,34]. The adsorption mechanism of metal anions onto activated carbon is well explained by the electrochemical theory, carbon in contact with water reduces oxygen to a hydroxyl group [35].



And thus, the carbon become positively charged with losing electrons. Electrical neutrality is maintained with hydroxyl ions, resulting in their adsorption. Although the duckweed used was not subjected to any activation treatment, a large number of OH groups will remain on the surface of the duckweed after the drying process. The physical adsorption and interaction between the duckweed surface and the H₃AsO₃ species might be partly responsible for the removal of As(III).

3.7 Desorption

The results are illustrated in Table 1. It has been reported that although arsenic elution obtained using strong acidic or alkaline solutions [36], the present work showed that effective desorption was achieved with acidic solutions. These phenomena are consistent with the results observed due to the effect of pH. Consequently, sulfuric acid solution was useful for the desorption of arsenic from the surface of duckweed in the present study.

Table 1. Influence of eluents on the desorption of As (III)

Desorption agent	Desorption (%)
NaOH (1M)	72.0
KOH (1M)	57.42
HCl (1M)	84.84
H ₂ SO ₄ (1M)	97.67
HNO ₃ (1M)	58.13

Adsorption process: duckweed, 3g; initial As(III) concentration, 100 µg/L; treatment flow rate, 1.67mL/min; average particle size, 0.595 mm; volume of desorption agent, 100 mL.

3.8 Application of the Developed Treatment System

The utility of the duckweed was evaluated for the removal of as contaminated Bangladeshi groundwater samples. The total arsenic concentration in the samples was 233.03 µg/L. It has been reported that the content of total arsenic in the tubewell water is in the range 0.25-

1.0 mg/L, with 60-90% of the arsenic present as As (III) species [37]. Because the pH of these groundwater samples was around 7.0, the arsenic species might be H_3AsO_3 for As (III) [16,38]. The results are presented in Table 2. Although 3 g of adsorbent was applied in the treatment, the concentration of arsenic in the treated sample water could be lowered to 50 $\mu\text{g/L}$. The desorption efficiencies was 96.53% with 100 mL of 1M H_2SO_4 . From the present study, the arsenic was successfully removed from real As-contaminated groundwater, and As could be recovered from the surface of duckweed.

Table 2. Removal and desorption of as from the contaminated groundwater of Bangladesh

	Sample
pH	7.50
initial As conc. ($\mu\text{g/L}$)	233.03
final As conc. ($\mu\text{g/L}$)	50.71
removal ^a (%)	86.51
desorption ^b (%)	96.53

^aRemoval: Duckweed; 3 g; treatment flow rate, 1.67 mL/min; average particle size, 0.595 mm. ^bDesorption: 1M H_2SO_4 , 100 mL, flow rate 1.67 mL/min.

4. CONCLUSION

The proposed treatment column systems are suitable and appropriate for homemade approaches to arsenic removal in rural and local areas, because of their easy operation, simplicity and handling. The present method is effective for a wide range of concentrations (i.e., 50-500 $\mu\text{g/L}$), which were quite similar to real contaminated Bangladeshi groundwater. There is no secondary-pollution problem will occur, because desorption of the arsenic is possible. Direct removal of arsenic (III) can be achieved without first oxidizing, whereas the traditional methods require the oxidation process. Based on the results of this research, duckweed can be considered as low cost, effective, available and natural adsorbent for removing arsenic and other heavy metals like Hg, Pb, Cr etc. from ground water and aqueous medium.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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