Biosorption of arsenic from contaminated water by anaerobic biomass

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ABSTRACT

The potential of an anaerobic sludge from an anaerobic wastewater treatment plant to remediate (inorganic) arsenic contaminated water was evaluated. The granular biomass was chemically modified as PO_4-biomass and Cl-biomass. The biomass was then investigated in equilibrium batch experiments and continuous flow fixed-bed column operation. Initial arsenic concentration, contact time and solution pH affected the biosorption capacity. Arsenate exhibited greater removal rates than arsenite. Adsorption data fitted better with the Langmuir than the Freundlich isotherm model. Kinetic data followed a pseudo-second-order model. In column operation, at pH 5, 90 and 220 bed volumes of water with the respective arsenate concentrations of 500 and 200 µg/L were treated. Desorption of almost 40% arsenate was achieved by using 0.5 M NaCl solution. Protein/amino acid–arsenic interaction was proposed as the dominant mechanism in the biosorption process. The arsenic–laden biomass satisfied USEPA's Toxicity Characteristic Leaching Procedure (TCLP) test and can be safely disposed of as non-hazardous waste.

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1. Introduction

Arsenic is known around the globe in recent history due to the consequence of mass poisoning through the exposure of drinking water. Due to its carcinogenic and many other adverse health effects, the regulatory authorities like the World Health Organization (WHO) and United States Environmental Protection Agency (USEPA) have reduced the maximum contamination level (MCL) of total arsenic in drinking water from 50 to 10 µg/L. However, much higher concentrations of arsenic than the permissible limit still exist in many parts of the world such as Argentina, Bangladesh, India, Pakistan, Mexico, Mongolia, Germany, Thailand, China, Chile, USA, Canada, Hungary, Romania, Vietnam, Nepal, Myanmar, and Cambodia [1,2]. The worldwide awareness of the arsenic crisis has motivated researchers to develop emerging technologies or the modification of the conventional ones which would be technologically sound and efficient as well as cost effective.

Arsenic, a metalloid, possesses both metallic and non-metallic properties, is ubiquitously present in air, soil, natural water, mineral deposits and rocks and biota [3,4] in varying concentrations. It can be released into the environment by both natural and anthropogenic processes. Natural processes are volcanic emissions, biological activities, burning of fossil fuels and weathering of arsenic bearing rocks and minerals such as realgar (AsS), orpiment (As_2S_3), arsenopyrite (FeAsS), and lollingite (FeAs_2) [5].

Anthropogenic sources include applications of arsenical pesticides, insecticides [6,7], wood preservatives, paints, drugs, dyes, semiconductors, incineration of arsenic containing substances, industrial wastewater discharge, mine tailing/landfill leaching, and manufacturing of arsenic compounds [8,9]. Arsenic can be present both in inorganic and organic forms depending on the ambient environment (i.e. pH, Eh) and microbial activity [10]. Naturally occurring inorganic arsenic is stable in oxidation state of −3 as in arsine gas (AsH_3), 0 as in crystalline/elemental arsenic, +3 as in arsenite, and +5 as in arsenate. The elemental state is extremely rare whereas −3 oxidation state is found only in extremely reducing conditions. Arsenate species are stable in oxygenated waters. Under mildly reducing conditions, arsenite predominates [11].

Arsenite is generally more difficult to remove than arsenate by conventional treatment methods [12]. Hence, most methods require an oxidation step as pre-treatment that converts arsenite to arsenate for effective arsenic removal. If oxidation is considered as a separate subject, all of the arsenic removal technologies can be put in two categories, membrane separations and adsorbents. Membrane separations include reverse osmosis, nanofiltration and electrodialysis [13]. Adsorbents include fixed bed adsorbent media, metal hydroxides precipitated from solution and ion exchange resins. Fixed bed adsorbent media can be both engineered and biological materials. Biological materials have merits over synthetic/engineered materials regarding cost, energy requirements, and disposal.

The biosorption technology, a process of passive sequestration of contaminant materials by some dead and inactive biomass [14], specially industrial by-product or wastes from food, pharmaceutical or waste water treatment [15] could be an alternative to remove

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Table 1
Physicochemical properties of the anaerobic biomass.

Parameters	Value
COD (mg O_2/L)	66,700
Total solids, TS (mg/L)	39,700
Total volatile solids, TVS (mg/L)	27,800
Total fixed solids, TFS (mg/L)	11,900
Total suspended solids, TSS (mg/L)	1,240
Total volatile suspended solids, TVSS (mg/L)	1,140
Specific surface area (m^2/g)	3.5
Specific gravity (SG)	0.78
Wet bulk density (g/mL)	0.46

metals from aqueous solution due to its low cost and eco-friendly nature. A number of investigations have been reported for removal of arsenic from water using biological materials. Some of them are: fungal biomass [16,17], coconut coir pith [18], sea nodule, *Lessonia nigrescens* [19], orange waste [20,21], chitosan [22,23], coconut husk carbon (CHC) [24], bone char [25], crab shell [26], powder egg shell [27], activated carbon (AC) produced from oat hulls [28], lignite, peat chars [29,30], water hyacinth [31]. However, there is a continuous search for better and easily available biological materials with high sorption capacity, low cost and well-explained sorption mechanism.

The objective of this study is to investigate the potential of non-viable anaerobic biomass granules to remove inorganic arsenic from an aqueous solution through a biosorption phenomenon. It is a material that is already in granular form and is highly available due to the number of anaerobic reactors worldwide. In this study, the kinetics of sorption, Langmuir and Freundlich isotherms as well as the influence of pH, initial arsenic concentration, and contact time on the sorption of arsenic on anaerobic granules were studied.

2. Materials and methods

2.1. Biomass preparation

Anaerobic sludge was collected from an anaerobic wastewater treatment plant treating effluents from the cheese production located at Agropur, Notre Dame de Bon Conseil, Quebec, Canada. The sludge was first centrifuged for 20 min at 3000 rpm. The pellets that were left by centrifugation at the bottom of the centrifuging tubes were dried in an oven at 50 °C for 6 days. Thereafter, the dried biomass was ground and sieved into mesh sizes 16 and 20, corresponding to a particle size ranging from 0.84 mm to 1.18 mm, and was termed as 'untreated biomass'. The biomass was then impregnated with PO_4 and Cl separately. The PO_4-impregnation was done by mixing the untreated biomass with 0.01 M and 0.02 M KH_2PO_4 separately in a 2 L beaker for 3 h at a biomass concentration of 20 g/L and pH values of 7 and 12, adjusted by 0.1 M NaOH. The Cl-impregnation was prepared by the same method as PO_4-biomass except for mixing the untreated biomass with 0.02 M KCl at pH values of 4 and 7. Subsequently the KH_2PO_4 and KCl solutions were drained and the biomass was washed with distilled water 4 or 5 times. Finally, the wet biomass loaded with PO_4 and Cl were dried in the oven at 50 °C for 48 h.

2.2. Biomass characterization

Several parameters were determined to characterize the biomass. According to American Public Health Association [32], chemical oxygen demand (COD), sludge solid parameters, and specific gravity were determined. The specific surface area of the samples was determined by using the Micromeritics ASAP 2000 BET surface area analyzer. The measured parameters are given in Table 1.

2.3. Chemical reagents

Stock solutions of arsenate and arsenite were prepared in distilled water using dibasic sodium arsenate ($Na_2HAsO_4·7H_2O$) and arsenic trioxide (As_2O_3) respectively. The concentrations of both stock solutions were made to 1000 ppm (mg/L) and stored in high density polyethylene (HDPE) bottles at room temperature. The stock solutions were subsequently diluted to different concentrations according to the requirements of the experiment.

2.4. Batch experiments

A biomass dose of 500 mg was suspended in 50 mL of arsenic solution in centrifuge tubes. The tubes were placed on a shaker at 100 rpm and left to equilibrate for 24 h. The supernatant solution was then filtered with the Whatman No. 42 (0.45 μm pore size) filter paper. The concentration of arsenic in the filtrate was initially scrutinized by the Hach colorimetric method (Hach, CO, USA; range: 0–500 μg/L, detection limit of 10 μg/L). Some representative samples were analyzed by a certified laboratory, Exova (Pointe Claire, Quebec, Canada) using ICP-MS to cross check the results. Arsenic sorption capacity of the biomass was calculated from the difference between the initial and the final supernatant concentrations. Since there was potential for arsenic adsorption onto the surface of the glassware or plastic ware, biomass-free known concentration of arsenic considered as blanks were used as controls with every set of experiments. All experiments were carried out at room temperature (22 ± 2 °C). Three forms of dried granular biomass were used for batch experiments; (i) untreated biomass; (ii) PO_4-biomass and (iii) Cl-biomass. To study the sorption behavior of treated and untreated biomass, 4 g/L of both types of biomass were suspended in arsenate and arsenite solution separately. To analyze the influence of pH different pH values from 3 to 10 in a single interval were used for both sets of experiments. The pH of the solutions was also monitored after the sorption experiment. Different initial arsenic concentrations were used to evaluate its effects on the sorption capacity of biomass. To find out the effect of contact time on sorption capacity a biomass dose of 4 g/L was kept in contact with 500 μg/L arsenate solution over different time periods (10–120 min) at a pH value of 5. Each set of experiments was performed in duplicate within the error limit ±5% and the average of these results is presented.

2.5. Fixed bed column experiments

Column experiments were carried out to investigate the arsenate sorption capacity of untreated biomass in the column system. Plastic columns with 70 mm height and 15 mm inner diameter were loaded with 4.6 g dried untreated biomass. For homogeneous distribution of the influent at the inlet of the column a bed of glass spheres was placed at the bottom of the column before placing the biomass. The arsenate bearing solution was stored in a 2 L Erlenmeyer flask and the pH value of 5 was adjusted using HCl and NaOH solution. A peristaltic pump connected to a flow meter was used to feed this solution into the column from the bottom at a flow rate of 1.5 BV/h (bed volume, BV = dry weight of biomass used in the column/wet bulk density of the biomass = 10 mL) allowing an approximate retention time of 40 min in the column. The effluent samples were collected from the top using a fraction collector at preset time intervals for subsequent analysis. The column operation was terminated after the effluent concentration had reached its breakthrough point of 10 μg/L. The effluent pH was measured to ensure whether any change occurred after column operation. Finally to check the reusability of the biomass, desorption was done by feeding a 0.5 M NaCl solution from the bottom of the column (ini-
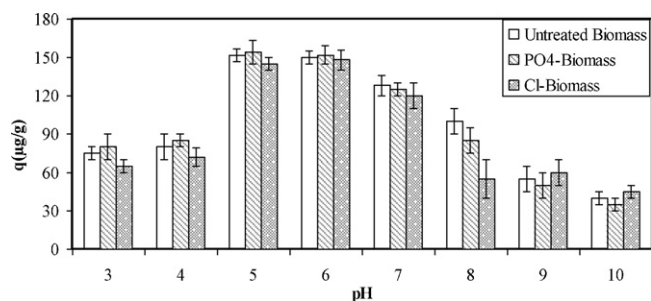
Fig. 1. Effect of pH on arsenate sorption capacity of three forms of biomass.

Fig. 3. Effect of initial concentration on arsenate sorption.

tial concentration 500 μg/L) with an upward flow rate of 1.5 BV/h allowing a residence time of 40 min.

2.6. TCLP procedure

In the TCLP (Toxicity Characteristic Leaching Procedure), the solid waste was mixed with an acidic extraction liquid (dilute acetic acid) that is to simulate the acid fluid at the bottom of a landfill. The solid sample weighed 100 g and the extraction liquid was equal to 20 times the weight of the solid sample. This sample and the extraction fluid was then placed into a tumbler and mixed for 18 h. This tumbling simulated the leaching action of water seeping through waste in a landfill. After tumbling, the mixture was filtered and the filtrate/extract was analyzed. If it contains arsenic at or greater than 5 mg/L, the waste is considered hazardous [33].

3. Results and discussion

3.1. Batch experiments

3.1.1. Effect of pH

The pH of the solution is one of the most important controlling factors that affect the biosorption process [34]. Bio-materials can act as a synthetic mixed resin having the properties of both anionic and cationic exchange capacity. It was anticipated that the Cl-loaded biomass would act like a Cl-form synthetic anion exchange resin. The PO4-loaded biomass was prepared because of the competing behavior of phosphate with arsenate. In the solution of KH_2PO_4 K^+ and $H_2PO_4^-$ ions are liberated. The anion $H_2PO_4^-$ then dissociates further into HPO_4^{2-} and PO_4^{3-} at pH 7.20 and 12.38 respectively, corresponding to their pKa values. At pH values of 4 and 7, KCl produces Cl^- ions. It was presumed that the anionic species would be attracted by the cationic sites of the biomass. A wide range of pH values from 4 to 12 for the treatment of the biomass keeping in mind this concept.

The effect of pH on the untreated and treated biomass was examined at pH 3–10 for both arsenate and arsenite solutions and the results are shown in Figs. 1 and 2. It can be seen from these figures that the adsorption of arsenate was maximum at a pH range of 5–6
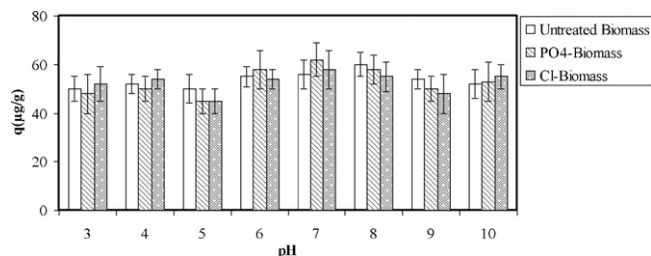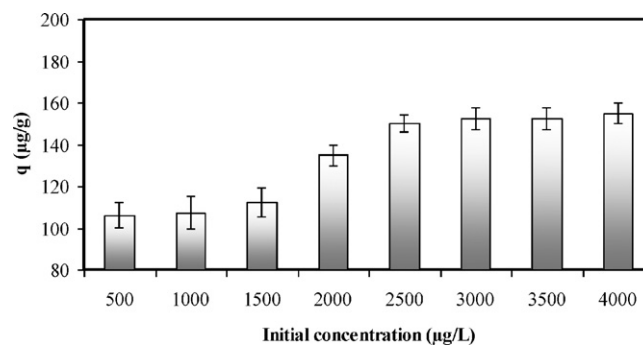
whereas the adsorption of arsenite did not vary significantly over a pH range of 3–10. It was observed that the chemical treatment had an insignificant effect on the sorption capacity of the biomass. The sorption capacity of arsenate was found higher than that of arsenite. Arsenate exists mostly as the monovalent ($H_2AsO_4^-$) anion in between pH 2.2 and 6.97 (pKa1 = 2.2, pKa2 = 6.97) [35]. The sorption of arsenate at pH 5 could be favorable due to the interaction between protein/amino acid in the biomass surface and the charged arsenate species. Arsenite (H_3AsO_3) exists as neutral below the pH of its first pKa value of 9.22. The reason behind poor adsorption of arsenite is the lack of interaction of the protein/amino acid with the arsenite due to its neutrality.

3.1.2. Effect of initial concentration

Different initial arsenate concentrations (500–4000 μg/L) with a biomass dose of 4 g/L were used at a pH value of 5. Fig. 3 represents the sorption capacity per unit dry mass of the biomass and Fig. 4 shows the percentage removal efficiency. It was found that the amount adsorbed increased from 106 to 155 μg/g with the increase of initial concentration from 500 to 4000 μg/L but the removal efficiency decreased from 85 to 16%. In the case of low initial concentration, a relatively slow transport due to decreased diffusion coefficient and decreased mass transfer coefficient was observed [36]. It was noticed that biosorption of arsenate with *L. nigrescens* increased with an increase in initial concentration [19]. The removal efficiency depends on the number of active sites present on the biomass surface. At higher initial concentration the interaction of arsenic species with the available sites on the biomass surface could be higher due to increased diffusion and mass transfer; this may contribute to more sorption at higher initial concentration. On the other hand, for a fixed dose of biomass, the number of active sites is limited. When the initial concentrations are increased with the same biomass dose, the active sites become fewer for adsorption thereby decreasing the removal efficiency.
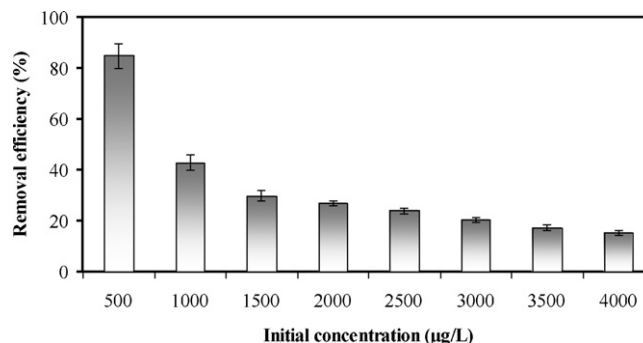

Fig. 2. Effect of pH on arsenite sorption capacity of three forms of biomass.

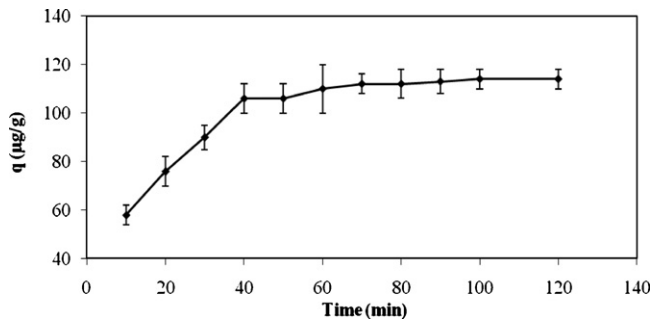**Fig. 4.** Effect of initial concentration on arsenate removal efficiency.

Fig. 5. Effect of contact time on arsenate sorption by untreated biomass.

Table 2
Langmuir and Freundlich isotherm coefficients for untreated biomass.

Langmuir model		Freundlich model	
q_{max} (µg/g)	164	K_F (L/µg)	59.27
b (L/µg)	0.00397	n	8.771
R^2	0.9873	R^2	0.7059

3.1.3. Effect of contact time

An untreated biomass dose of 4 g/L was maintained in contact with 500 µg/L arsenate solution over different time periods (10–120 min) at a pH value of 5 and the results are shown in Fig. 5. It was found that the rate of sorption increased rapidly up to 40 min and slowly reached saturation at about 90 min. The adsorption of arsenate remained almost constant after 90 min implying that equilibrium had been reached.

Again different initial arsenate concentrations with an untreated biomass dose of 4 g/L were used at a pH value of 5 (Fig. 6). The plots also show that the time of equilibrium as well as time required to achieve a definite fraction of equilibrium adsorption for all the concentrations is independent of initial concentration.

3.1.4. Bioadsorption isotherm

An adsorption isotherm describes the interaction between the adsorbate and the adsorbent. Langmuir and Freundlich adsorption isotherm models were used to describe the sorption behavior of arsenate on anaerobic granular biomass. The details of the isotherms can be found elsewhere [37–39]. The linearized models of Langmuir and Freundlich isotherm are fitted with the experimental data in Figs. 7 and 8 and the estimated parameters are given in Table 2. It is observed from the correlation coefficient that the data fits better to the Langmuir isotherm model than the Freundlich isotherm model. The significance of following the Langmuir isotherm model of the experimental data is that the adsorption
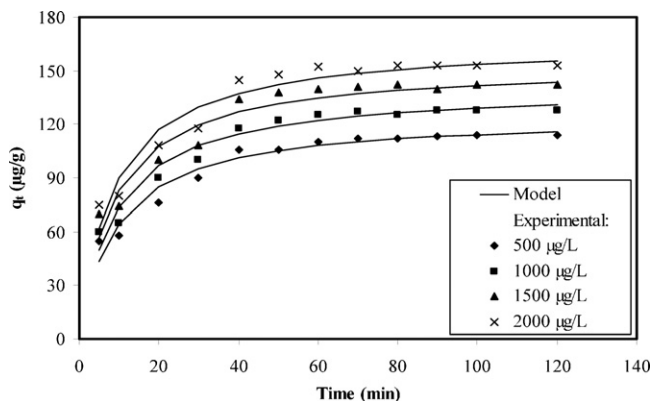

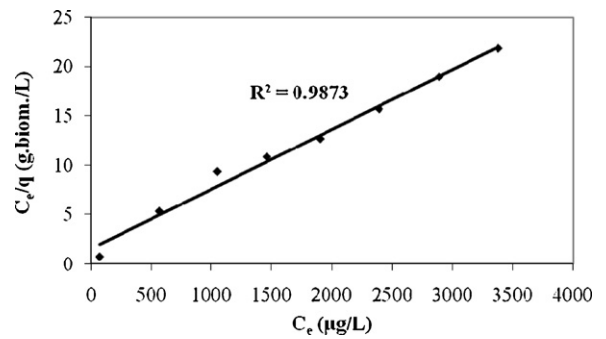**Fig. 6.** Time profile of arsenate sorption of untreated biomass at different initial concentrations.

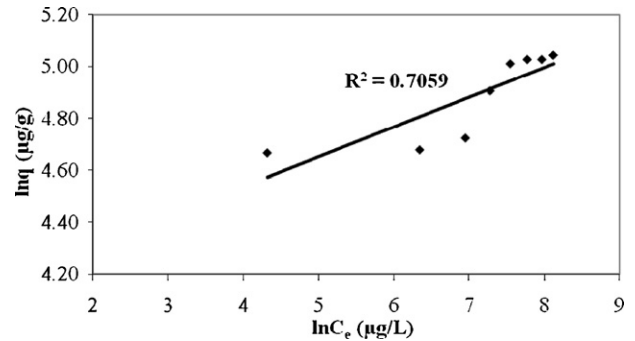**Fig. 7.** Langmuir (linearized) isotherm model for untreated biomass.

Fig. 8. Freundlich (linearized) isotherm model for untreated biomass.

holds the monolayer pattern which is eventually limited by the number of participating sites on the biomass surface.

From Fig. 9, it can be seen that at an initial stage the sorption capacity increases almost in a linear way with rising equilibrium concentration and finally reaches its saturation limit where a plateau can be observed. This is due to the fixed number of active sites on the biomass which take part in the sorption yielding a maximum sorption capacity. The experimental sorption capacity (q) for arsenate was 155 µg/g compared to 164 µg/g found from the Langmuir isotherm model. This also validates that the Langmuir model suitably describes the experimental data.

Hall et al. [40] showed that the Langmuir constant, b can be expressed in terms of an equilibrium parameter known as a separation factor, R based on which adsorption can be described as unfavorable ($R > 1$), linear ($R = 1$), favorable ($0 < R < 1$), and irreversible ($R = 0$).

The values of the Hall dimensionless separation factor R were found between 0.059 and 0.33, which indicate the favorable adsorption of arsenate on anaerobic biomass. Moreover, the considerably lower cost of the anaerobic biomass and its physical characteristics make it an attractive biosorbent.
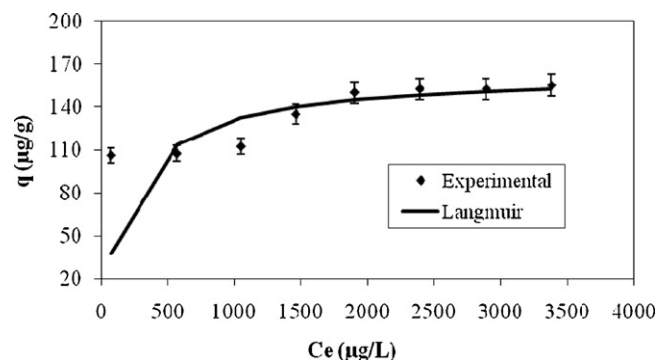

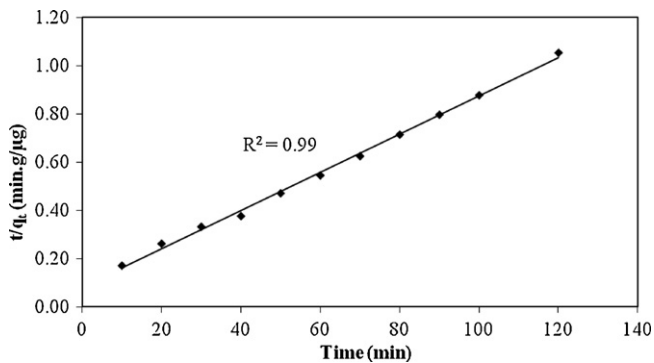**Fig. 9.** Bioadsorption isotherm for untreated biomass.

Fig. 10. Pseudo-second-order reaction kinetic model of untreated biomass.

Fig. 11. Desorption of arsenate from the exhausted biomass.

3.1.5. Adsorption kinetics modeling

Adsorption kinetics were used to explain the adsorption mechanism and adsorption characteristics of the untreated biomass. The rates of reaction of the biomass were determined by equilibrium batch tests. The biomass with a concentration of 4 g/L was suspended in an arsenate solution of 500 μg/L for varying time periods. The experimental data were analyzed by four reaction kinetic models: first order, pseudo-first order, second order and pseudo-second order described elsewhere [41–43]. Fig. 10 represents the pseudo-second order reaction kinetic model (others are not shown for brevity). It was found from the correlation coefficients that all forms of biomass including untreated followed a pseudo-second-order reaction kinetic model. Based on the initial sorption rate (kq_e^2) the untreated biomass was found to be better than the other two biomasses as its value (11.806 μg/g min) for the untreated biomass was higher than those for PO_4-biomass (8.319 μg/g min) and Cl-biomass (9.380 μg/g min). The significance of following the pseudo-second-order reaction kinetics of an adsorption process is that the mechanism of removal is mainly through chemical bonding or chemisorption [44].

3.2. Fixed bed column experiments

Column experiments were performed to produce the breakthrough curves with two different influent concentrations of arsenate such as 500 and 200 μg/L at the same pH value of 5. The upward flow rate was 1.5 BV/h with an approximate empty bed contact time (EBCT) of 40 min based on batch experiment. At up to 90 BV, the effluent concentration remained below 10 μg/L and after that it gradually increased. This happened due to the formation of a mass transfer zone in the column [45]. When the arsenate bearing solution comes in contact with a layer of fresh biomass in the column, arsenate is adsorbed onto the biomass until it reaches equilibrium with the influent concentration. At this point, the portion of the biomass reaches its capacity and becomes exhausted. As the mass transfer zone moves upward towards the direction of flow sorption continues to next layer of fresh biomass making it again exhausted. This way the mass transfer zone moves up through the column until it reaches at the outlet. In the column system, arsenate bearing solution percolates through the active bed of biomass which acts like a series of batch reactors.

It was observed that the breakthrough occurred after 90 bed volumes when the effluent concentration reached 10 μg/L which is the maximum allowable concentration according to most regulatory authorities like the WHO and the USEPA. The average arsenate sorption capacity of the anaerobic granules found was 96 μg/g. This sorption capacity is considered as the operating capacity of the biomass in the column system. This capacity is 16% less than the equilibrium sorption capacity found in the experimental batch test. One of the reasons behind this 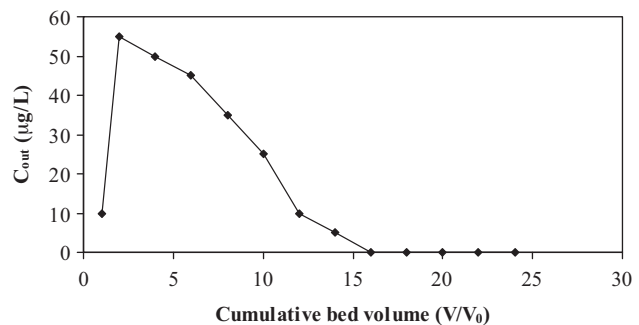could be the formation of channels that lead to development of zones of unexposed biomass in the column. Another reason is that there was still some unsaturated portion of the biomass at the exiting end of the column after the breakthrough occurred. This occurred as the column was not run until the full saturation of biomass, at which the sorption should have reached its maximum level.

It was found that the breakthrough occurred at the bed volume of 220 when the influent arsenate concentration was 200 μg/L. For lower initial concentrations, less arsenate is available to be adsorbed compared to the same amount of water with higher initial concentration. As a result, the number of treated bed volumes increased from 90 to 220 when the influent arsenate concentration decreased from 500 to 200 μg/L.

3.2.1. pH in the column bed

One of the challenges in column operation is to maintain the pH in the column. As it is difficult to control the pH inside the column, adsorbents with minimum influence on pH change with good buffering capacity during column operation are preferable. The change of pH after column operation was measured along with the effluent concentration analysis. The pH of the feed solution was 5 and it was observed that the pH change in the column was insignificant (±0.5 pH units). This once again justifies the anaerobic biomass as a potential candidate for biosorption.

3.2.2. Desorption

Fig. 11 shows the concentration profile of arsenate during desorption in the column. It is observed from Fig. 11 that up to 15 bed volumes, an average elution of arsenate reached a concentration of 1.56 mg/L. The mechanism of arsenate desorption could be due to the exchange of arsenate ion with the chloride ion. The comparison between the amount of arsenate retained by the biomass and that of the amount eluted by NaCl shows that only 40% was recovered. On the basis of this result it is recommended that the spent biomass should be disposed of without regeneration.

3.3. Disposal of spent biomass

It is equally important, like arsenic removal, to handle the arsenic–laden wastes with due care as improper disposal can be a boomerang posing the same threat to the environment. For sanitary landfill disposal, the solid waste/sludge requires to meet specific criteria that determine its hazard. In the case of arsenic containing residuals, toxicity is the primary characteristic of concern. The EPA [33] has established an analytical method (method 1311), the Toxicity Characteristic Leaching Procedure (TCLP), to measure the toxicity of a waste. The current TCLP limit for arsenic is 5 mg/L.

As per the conditions of TCLP, if we mix 100 g of spent sludge from the first column (containing 96 μg/g of arsenate) with 2 L of extraction liquid, then in that case even if all arsenate leached out

of the sludge, the concentration of arsenate in the extraction fluid would be 4.8 mg/L which is still less than the TCLP limit of 5 mg/L. This fact indicates that the sludge can be disposed of in the sanitary landfill as a non-hazardous material.

3.4. Arsenic sorption mechanism

Heavy metal removal by sludge is a consequence of the interaction between metals in the aqueous phase and the microorganism cell surface [46]. The cell wall consists of covalently linked polysaccharide and polypeptide chains, which form a bag-like structure that completely encases the cell [47]. The amine groups in amino acids may be ionized in solution and may contribute to the metal binding capacity [48].

Many functional groups such as hydroxyl, carboxyl, sulfhydryl, sulfonate and phosphonate are neutral when protonated and negatively charged when deprotonated. When the pH of the solution exceeds their pKa, these groups become mostly available for the attraction of cations. Amine, imine, amide and imidozole groups on the other hand, are neutral when deprotonated and positively charged when protonated. Therefore, they attract anions if the pH is lowered such that the groups are protonated [45].

The solid matter present in the anaerobic sludge is mostly organic in nature and protein constitutes the major part of the solid matter. It was found that the major part of the amino acids present in the biomass has isoelectric points in the pH range of 4.0–8.0 [49,50]. In this pH range the majority of the amino acid molecules contain cationic sites. If pH is increased, the carboxylic group of the amino acid would progressively be deprotonated as the carboxylate ligands, simultaneously protonating the amino groups. These positively charged NH_3^+ ions could facilitate the biomass–arsenic binding. Protein/amino acid–arsenic interaction was also supported by arsenic induced loss in protein content in several plant biomasses [51]. Such arsenic induced decrease in protein content might be due to an increase in the breakdown of amino acid [52] at higher arsenic concentrations.

The arsenate ion occurs mainly in the monovalent form of $H_2AsO_4^-$ in the pH range between 2.2 and 6.9 while a divalent anion $HAsO_4^{2-}$ dominates at a higher pH range between 6.9 and 11.5. So, it can be said that the negatively-charged species will interact with the positively charged amino acids. A decrease in the pH below 5 shows a decrease in the adsorption even though the adsorption surface is positively charged and the sorbate species are negatively charged. In this case, more protonated arsenate species are less adsorbable than the less protonated one. This could be attributed to a lack of electrostatic attraction between the surface and the protonated arsenate species. The decrease in the adsorption at a pH above 8 may be attributed to the increasing electrostatic repulsion between the negative surface sites and the negative arsenic species.

In the case of arsenite the nonionic form H_3AsO_3 exists at a pH below its first pKa value of 9.22. Monovalent arsenite, $H_2AsO_3^-$ and divalent arsenite, $HAsO_3^{2-}$ exist above the pHs of their pKa values of 9.22 and 12.13 respectively. But at these high pHs the amino acid molecules present in the biomass surface do not provide any cationic sites to interact with the anionic arsenic species. The arsenite remains undissociated below pH 9.22 on the other hand, amino acid molecules remain dissociated between pH 4 and 8, when the cationic sites may be available. The dissociation of arsenite and amino acid molecules at different pH values contributes to the least or no interaction between them resulting in lower arsenic removal efficiency. The adsorption of arsenite does not vary significantly over the pH range of 3–10. The poor removal of arsenite could be due to the non-specific adsorption on the biomass surface.

Table 3
Arsenic removal efficiency of different media [53].

Adsorbents	Biosorbent dose (g/L)	Adsorption capacity (µg/g)	
		As(III)	As(V)
Kimberlite tailing	10	25	40
Water hyacinth	10	45	70
Wood charcoal	10	19	37
Banana pith	10	12	18
Coal fly ash	10	20	28
Spent tea leaf	10	25	42
Mushroom	10	22	35
Saw dust	10	28	36
Rice husk ash	10	5	12
Sand	10	15	22
Activated carbon	10	50	65
Bauxite	10	58	80
Hematite	10	40	60
Laterite	10	45	70
Iron-oxide coated sand	10	72	90
Activated alumina	10	90	96
CalSiCo	5	180	196
Hydrous granular ferric oxide	2	460	495

3.5. Comparison of arsenic sorption capacity

The sorption capacity of the anaerobic biomass determined in this work was 152 µg/g at pH 5 with an initial arsenate concentration of 2000 µg/L. The results of our experiments are compared with those found in the literature. It is crucial to compare different test results as varying experimental conditions are employed in different studies; high removal/technical efficiency alone can misinterpret the viability of particular technology if it does not meet the economical feasibility. Saha et al. [53] conducted batch adsorption studies on different materials with an arsenic concentration of 1 mg/L for a 6 h contact time as shown in Table 3. It is seen from Table 3 that the anaerobic biomass was superior to all but two of the sorbents. The biomass is available as a by-product of the commonly used anaerobic wastewater treatment plants. The USEPA [54] estimates that the publicly owned wastewater treatment works (POTWs) generate over 8 million tons (dry weight) of anaerobic sludge annually. This huge amount of sludge can easily be recycled to treat arsenic-rich water. The novelty of the anaerobic biomass, due to its simple preparation without any chemical modification, huge availability, low cost, good physical characteristics, easy disposability and biodegradability, makes it a favorable sorbent material.

4. Conclusions

Anaerobic granular biomass was investigated in batch and column experiments to remove inorganic arsenic from contaminated water. pH, initial concentration, and contact time affected the removal efficiency. Maximum removal occurred for arsenate at a pH range of 5–6. Adsorption of arsenite was insensitive in the pH range of 3–10. An additional oxidation step is required, prior to biosorption, if arsenite is dominant in the influent. Higher initial concentrations decreased the removal efficiency without affecting the equilibrium time. In 40 min, 95% of the adsorption took place and the equilibrium was reached in 90 min. This result shows that the sorption of arsenic by anaerobic biomass is a fast phenomenon; the implication is that the materials would be suitable for a continuous flow system. The Langmuir isotherm best described the equilibrium data. The rate of adsorption of untreated biomass followed a pseudo-second-order kinetic model. This implies that the mechanism of removal is mainly by chemical bonding or chemisorption. A possible binding mechanism was proposed as protein/amino acid–arsenic interaction. Direct disposal of the spent

biomass in the landfill as a non-hazardous material is possible. Finally, it could be concluded that the anaerobic biomass is a cost-effective and eco-friendly biosorbent due to its availability, particulate shape, sufficient mechanical strength, fast sorption rate, and ease of disposal.

Arsenic speciation needs to be studied as the natural water generally contains both arsenate and arsenite in different proportions. An additional oxidation step is to be considered if arsenite is present. Natural water contains many impurities; the effect of these impurities on arsenic removal efficiency needs to be examined. Biosorption of arsenic by viable biomass should be considered for comparative studies. Pilot scale investigation with naturally contaminated water is recommended to determine scale-up parameters.

Acknowledgments

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