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Adsorption of arsenate on untreated dolomite powder

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Abstract

Raw dolomite powder was evaluated for its efficiency in adsorbing As(V) from water. An experimental setup comprised of a fluidized dolomite powder bed was used to assess the impact of various test variables on the efficiency of removal of As(V). Test influents including distilled water (DW), synthetic groundwater (SGW) and filtered sewage effluent (FSE) were employed to assess the effect of influent parameters on the adsorption process and the quality of the effluent generated. Dolomite exhibited good As(V) removal levels for distilled water (>92%) and synthetic ground water (>84%) influents at all initial As(V) concentrations tested (0.055–0.600 ppm). Breakthrough of dolomite bed occurred after 45 bed volumes for DW and 20 bed volumes for SGW influents with complete breakthrough taking place at more than 300 bed volumes. As(V) removal from FSE influents was relatively unsuccessful as compared to the DW and SGW influents. Partial removal in the order of 32% from filtered sewage effluent at initial concentration of 0.6 mg/L started at 75 bed volumes and gradually stopped at 165 bed volumes. Varying degrees of As(V) adsorption capacities were observed by the different test influents employed, which indicate that the adsorption of As(V) is adversely affected by competing species, mainly sulfates and phosphates present in the influent. The adsorptive behavior of dolomite was described by fitting data generated from the study into the Langmuir and Freundlich isotherm models. Both models described well the adsorption of dolomite. The average isotherm adsorptive capacity was determined at $5.02 \mu g/g$. Regeneration of the dolomite bed can be achieved with the use of caustic soda solution at a pH of 10.5. © 2007 Elsevier B.V. All rights reserved.

Keywords: Water; Wastewater; Arsenate; Adsorption; Dolomite; Fluidized bed

1. Introduction

Arsenic is found widely in surface and groundwaters in many parts of the world. Its occurrence in the environment is primarily from natural sources and therefore may form a significant constituent even in areas where industrial or other anthropogenic sources are limited. Arsenic has long been recognized to be a toxic element that negatively impacts health when ingested, inhaled or skin absorbed [1]. Its consequences range from acute lethality to chronic effects, such as cancer and diseases of the vascular system. Laboratory studies on animals have demonstrated that the toxicity of arsenic is dependent on its form and its oxidation state. It is generally established that the soluble inorganic arsenicals are more toxic than the organic ones, and the trivalent forms are more toxic than the pentavalent ones [2].

Conventional treatment processes to remove arsenic from drinking water, domestic and industrial wastewater have

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employed physical, chemical, and biological processes. Treatment processes for arsenic removal such as coagulation/precipitation/filtration, adsorption by hydrous ferric oxides, activated alumina, iron oxide-coated sand, iron filings, manganese green sand filtration, neutralized red mud (Bauxsol), ion exchange resins in Fe³⁺ form, mine tailing wastes, and polymeric/inorganic hybrid sorbents have been reported [3–25]. Evaluation studies of various treatment methods used in arsenic removal were reported by Murcott [26] and more recently by Pokhrel et al. [27].

Chemical treatment processes (coagulation/precipitation) entail excessive chemical use and hence excessive production of sludge. Biological treatment technologies are reported to be cheap and produce minimal sludge but could be only applied to treat wastewater. On the other hand, physico-chemical treatment technologies are known for their well-defined performance and high removal efficiency, whereby arsenic removal is attained through sorption/membrane techniques without excessive chemical use and the absence of sludge generation [28,29].

In the context of the search for new methods that may be efficiently used in the removal of chemical pollutants, a study

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conducted by Ayoub and Kalinian [29] has shown that phosphate could be successfully removed from water using dolomite as an adsorbent. The fact that phosphate has a chemistry that is very similar to that of arsenate (e.g. their pK_a values, surface complexation reactions) [21,22], it was hypothesized that dolomite could also be successfully used in the removal of arsenate. The reported study aimed at assessing the efficiency of raw dolomite [CaMg(CO₃)₂], a material that is available very cheaply and in abundance around the world, in removing arsenic in the form of As(V) from water and wastewater matrices. The process employs fixation of As(V) during the passage of As(V) laden influent through a fluidized bed of raw untreated dolomite powder.

2. Materials and methods

2.1. Dolomite powder

Dolomitic rock was obtained from a quarry that was identified by Hadda [30] to have dolomitic formations in the Sibline area, South of Beirut. As a naturally occurring mineral deposit, specimens of the rock showed a variety of both physical and chemical properties. The specific suitability of the collected dolomite rocks for this study was principally based on the magnesium and calcium oxides content of the different samples. Table 1 summarizes the chemical properties of the dolomite utilized in this study as determined by X-ray diffraction.

The rocks identified to be suitable for this study were crushed and the powder generated was further sieved to various size ranges, using a variety of standard mesh sieves (sieve numbers 80-200), i.e. 0.177-0.075 mm. The dolomite powder passing through the standard sieve number 200 (<0.075 mm) was selected as the optimum dolomite size for the study based on a series of tests conducted earlier [31]. The powder was further analyzed by ion chromatography for specific constituents including chlorides, sulfates and nitrates in which the values were found to be 121, 268, and 48 mg/kg, respectively. The physical properties of the powder were determined and reported by Kalinian [31]. The particle size distribution of the sieved powder was determined by the Hydrometer method described in the "American Society for Testing and Materials" [32]. Fig. 1 shows the percent size distribution of sieved dolomite particle sizes <0.075 mm (200 sieve size).

 Table 1

 Chemical composition of the dolomite rocks collected from Sibline

Compound	Percent composition (%)		
SiO ₂	0.77		
Al ₂ O ₃	0.14		
Fe ₂ O ₃	0.19		
CaO	30.85		
MgO	21.55		
K ₂ O	0		
TiO ₂	0.09		
P ₂ O ₅	0		
Loss on ignition	46.26		



Fig. 1. Percent size distribution of sieved dolomite particle sizes <0.075 mm.

2.2. Experimental setup

To arrive at the most practical and feasible experimental setup, different experimental approaches were assessed utilizing a variety of configurations including: (1) mixing the adsorbent using jar test apparatus; (2) a fixed dolomite bed down-flow column setup; (3) a mixed dolomite/sand bed downflow column setup; and (4) a fuidized dolomite bed up-flow column setup. The fluidized bed setup was deemed to be the most practicable system because of the following reasons: (1) it has shown to be easier to control and operate; (2) permeability problems encountered in the fixed bed setup were overcome by the fluidization of the bed; (3) contact between the influent and the dolomite powder particles were enhanced due to the mixing attained during fluidization; and (4) better removal values were recorded.

The experimental fluidized bed setup consisted of an unpacked dolomite bed placed in a vertical glass column of 1.5 cm internal diameter and a height of 120 cm. The length of the column was selected in order to control bed expansion at moderate flow velocities while preventing loss of medium. The test water was introduced through the bottom by means of an external flow-adjustable peristaltic pump (Masterflex, Cole Parmer) so as to fluidize the powder at a velocity that was maintained below the terminal velocity of the dolomite particles. In each experiment, 15 g of unpacked powder dolomite with a depth of about 10 cm were utilized. This provided a bed volume of 11 mL with a 7 mL pore volume.

2.3. Experimental test influents

In order to assess the effect of solvent characteristics on the arsenic adsorption process, various types of water were used as feed influent, namely: distilled water (DW), synthetic ground water (SGW) and filtered sewage effluent (FSE). Synthetic ground water influents were prepared by dissolving MgSO₄·7H₂O (35 mg), CaSO₄·2H₂O (12 mg), NaHCO₃ (12 mg), NaCl (6 mg) and KNO₃ (6 mg) in 1 L of distilled water [33]. The filtered wastewater was originally collected as raw sewage from an open sewer outfall located at Ras-Beirut in the vicinity of the American University of Beirut (AUB). After allowing for a settling period of 2 h, the clarified supernatant was filtered using 90 mm diameter plain Whatman No.1 filters (particle retention >11 µm). A specific amount of arsenate

 Table 2

 Average physico-chemical composition of the test influents

Parameter	Influent type			
	DW	SGW	FSE	
PH	6.9	7.1	7.0	
TDS, ppm	340	391	2090	
Conductivity, µS	680	785	4150	
SO_4^{2-} , ppm	20	44	670	
Cl ⁻ , ppm	30	40	42000	
Ca hardness, ppm as CaCO ₃	20	45	800	
Mg hardness, ppm as CaCO ₃	70	80	1200	

 $Na_2HAsO_4 \cdot 7H_2O$ was added to each of the test influents. Table 2 displays the average physico-chemical composition of the test influents used.

2.4. Experimental procedures

Preliminary experiments were conducted to evaluate the impact of using dolomite as an adsorbent for arsenic removal. Both arsenite [As(III)] and arsenate [As(V)] were tested for posssible removal. The results indicated very low removals (<10%) for As(III) with high removals (>90%) for As(V). Accordingly it was decided to conduct the study using As(V) as the target parameter. In the context of removal of arsenite using dolomite, pretreatment of the arsenite by oxidation to arsenate using ozone would be a possible solution, which at the same time would provide the necessary disinfection requirements [27].

Five sets (I–V) of experiments were thus conducted to evaluate As(V) adsorption efficiencies under varying experimental conditions. Each set consisted of at least two experiments to confirm reproducibility of results. All experiments were conducted at room temperature (22 ± 1 °C).

The first set consisted of trial experiments using DW that aimed at determining optimum operating flow rates denoted by fluidization of dolomite particles without causing overflow of the dolomite from the upper end of the column. Flow rates of 5.5 mL/min and 10 mL/min were investigated. Using an influent concentration of 0.20 mg/L As(V), the experiments simultaneously assessed the dynamic effect of the different flow rates on the removal efficiency.

Set II experiments were conducted in an attempt to evaluate removal with respect to varying pH (7.08 and 5.31) while maintaining constant dolomite particle size (<0.075 mm) and flow rate (5.5 mL/min). The feed influents (DW and SGW) were spiked with different arsenate doses to yield a final concentrations of 0.3 mg As(V)/L.

Set III experiments were conducted in an attempt to evaluate removal with varying initial arsenate concentrations. Concentrations of 0.055, 0.19, 1.08 mg/L at a pH of 5.8 and a concentration of 0.055 at pH 6.88 were tested for DW and concentrations of 0.1, 0.3, and 0.59 mg/L at pH 6.9 were tested for SGW. In all the tests the dolomite particle size (<0.075 mm) and flow rate (5.5 mL/min) were maintained constant.

Experiments in set IV were directed at testing the various influent types (DW, SGW and FSE) under similar operational conditions (about pH 7.0, flow 5.5 mL/min, and dolomite powder with size <0.075 mm) in order to assess influent characteristics on the effectiveness of the adsorption process. Variations in the physical and chemical characteristics of the feed solutions were assessed by measuring effluent pH, conductivity, total dissolved solids, arsenate, calcium and total hardness.

Finally, set V involved two trial experiments where regeneration of the spent dolomite material was investigated. A dilute basic solution, characterized by its relatively high pH of 10.5, was employed as a potential regenerant to release the fixed arsenate.

Table 3 summarizes the experiments conducted in the course of the study to evaluate dolomite as a potential arsenate adsorbent.

2.5. Analytical procedures

Analysis of the effluent resulting from the columns was performed directly without further processing because of the clear effluent samples produced. However, wastewater effluents needed to be digested because of their greenish turbid color. Physico-chemical characterization of the effluent samples collected throughout the experimental runs as well as the digestion procedure were performed in accordance to the "Standard Methods for the Examination of water and wastewater" [34]. Arsenic, phosphate, sulfate, nitrate and nitrite measurements were performed as per the instructions listed in the Hach Company manual. Parameters under assay, methods of analysis and instrumentation employed are presented in Table 4.

Borosilicate glassware were used and carefully kept in dilute acidic solution and rinsed with distilled water prior to use in order to remove all arsenic residues from previous usage. Moreover, this glassware was reserved specifically for arsenic determination during the entire experimental period.

Table 3

Summary of experiments conducted in the course of the study to evaluate dolomite as a potential arsenate adsorbent

Experimental set	Technique of arsenic measurement adopted	Objective
I	SDDC	Determination of optimal experimental flow rate under steady pH and arsenic initial concentration
II	SDDC	Evaluation of process efficiency with respect to varying pH under steady flow rate
III	SDDC	Evaluation of process efficiency with respect to varying initial concentration under steady pH using DW and SGW
IV	ICP-MS	Assessment of influent (DW, SGW, FSE) characteristics on the efficacy of arsenate adsorption under optimal operational conditions
V	ICP-MS	Regeneration of exhausted dolomite using alkaline solution of 10.5 pH

Table 4
List of parameters under assay, methods of analysis and instrumentation

Parameter	Type of analysis	Reference	Method number	Instrument
pН			4500-H ⁺ B	Orion Research, Model 811
TDS, EC	Potentiometric		2510 B	Cole Parmer
Chlorides	Argentometric titration	St. Meth.	4500-Cl ⁻ B	
Calcium	EDTA titration	APHA 1999	3500-Ca D	Not applicable
Magnesium	EDTA titration		3500-Mg E	
Sulfates			8051	
Arsenic			3500	HACH DR/2010 spectrophotometer
Phosphates	Colorimetric	HACH	8048	
Nitrates			8039	
Nitrites			8153	
K ⁺	Flame emission	St. Meth.	3500-K D	Flame photometer
Na ⁺	Photometry	APHA 1999	3500-Na D	-

2.6. Isothermal analysis

Batch sorption experiments were carried out to determine the sorptive capacity of raw dolomite powder for arsenate using multi-point isothermal analysis. The adsorptive capacity of raw dolomite powder was determined by incorporating the data obtained from the multi-point isothermal analysis into two most widely used models: the Freundlich isotherm model and the Langmuir isotherm model. The parameters K and 1/n for the Freundlich isotherm and a and b for the Langmuir isotherm were evaluated from the amounts of As(V) adsorbed.

The isothermal test was conducted by applying arsenic solution of known concentration (0.62 mg As/L) to a series of five Erlenmeyer flasks containing dolomite doses (2.5-20 g) carefully weighed using a sensitive Mettler digital balance, Model AE100. The selection of a concentration of 6.2 mg/L was based on the fact that a higher concentration relative to the adsorbent dozes was needed compared to those adopted in the testing in order to maintain a residual at the end of the equilibrium phase. Dolomite samples used in the isothermal analysis were dried at 105 °C in a Fisher Scientific isotemp oven, Model 655G, to free pores from moisture or vapor. The flasks were then shaken at 150 rpm on an orbit shaker for 4 h at room temperature. Subsequently, the mixtures were centrifuged using a Fischer Scientific Centrific, model 228.

Following the sorption experiment, the samples were centrifuged and the residual arsenate concentration of each of the sample effluents was determined. The removal of arsenate accomplished by the different doses of dolomite was calculated by subtracting the residual concentration from the initial arsenate concentration. The Langmuir and Freundlich adsorption capacity of each dose of dolomite was calculated using the respective equations [29].

3. Results and discussion

3.1. Effect of hydraulic flow rates

The results of the first series of experiments have shown the optimum operating flow rate to be $5.5 \text{ mL/min} (1.9 \text{ m}^3/\text{m}^2/\text{h})$.

Operating at a flow rate of $10 \text{ mL/min} (3.4 \text{ m}^3/\text{m}^2/\text{h})$ resulted in the dolomite overflowing from the column.

The effect of flow rate on the efficiency of arsenate sorption on a fixed amount of dolomite was found to be more pronounced as the adsorption sites became scarcer. As depicted from Fig. 2, average arsenate removal efficiencies varied between 97.4 and 95.2% at the start of the experimental run and declined to 59.7 and 47.1 percent at the end of the experimental run (105 bed volumes) for the flow rates of 5.5 and 10 mL/min, respectively. A difference in removal efficiency of 2.2% at the start of the run to 12.6% at the end of run. Higher removal efficiencies attained with lower influent flow rates is attributed to the longer contact time between the adsorbent (dolomite) and the adsorbate (arsenate).

3.2. Effect of pH on removal efficiency

In representing the removal efficiencies versus the flow treated, the commonly used expression of "bed volumes" is adopted to express the quantity of water treated in terms of a number of medium bed volumes. Fig. 3 illustrates the effect of varying pH on the adsorption process. At 25 bed volumes, removal efficiency was almost the same (86%) under both acidic



Fig. 2. Arsenate removal percentages as a function of flow rate.



Fig. 3. Effect of pH on arsenate removal (SGW).

and neutral conditions. At 45 bed volumes, dolomite accomplished higher removal (56%) at pH 5.31 than it did under neutral conditions (45%) at pH 7.08 showing an 11% difference. However, this difference was reduced to less than 7% at 75 and 105 bed volumes. This behaviour is expected as it is established that adsorbents operate more efficiently under acidic conditions [35]. In this context, the solution pH relative to the point of zero charge, pH (ZPC) for the Dolomite, needs to be regarded. Pokrovsky et al. [36] reported the pH (ZPC) of Dolomite to be about 8. As the tests were conducted at pH values less than the ZPC, the anionic adsorption capacities of the adsorbent are expected to increase at lower pH values [21,37]. Genç-Fuhrman et al. [22] reported a value of 4.5 as the optimal pH for arsenate adsorption using Bauxsol as adsorbent.

3.3. Effect of initial arsenic concentration

Fig. 4 shows the effect of varying initial arsenic concentrations on the removal of arsenate using DW and SGW, respectively. Arsenate adsorption followed the general pattern of decreasing percent sorption with major increase in concentration. Such a pattern was mostly evident with DW where an increase in initial arsenate concentration from 0.055 to

120 100 Arsenate removal (%) 80 60 40 20 0 0.6 mg/L 0.055mg/L 0.192mg/L 1.00 mg/L 0.1 mg/L 0.3 mg/L DW SGW DW - Flow = 5.5 ml /min - pH = 5.8☑ 22.5 bed volumes 45 bed volumes

Fig. 4. Effect of initial arsenate concentration on removal over 45 bed volumes.

1.000 mg/L (about 18 fold) led to reductions in removal efficiencies of 11% and 16% at 22.5 and 45 bed volumes, respectively. Minor reductions were noted when the initial concentration was increased by about four fold (0.055 to 0.193 mg/L). This was in contrast to the relatively insignificant effect attained when using SGW, where a maximum increase in concentration by six fold (0.1 to 0.6 mg/L) was investigated. However, the rate of reduction in removal efficiencies with increased bed volumes from 22.5 to 45 was noted to be more pronounced for SGW than for DW for all the tested concentrations.

3.4. Efficiency of system in arsenate removal

The arsenate removal patterns by dolomite from the different types of test influents were assessed using optimal experimental conditions established throughout the course of the study. Key process variables including flow rate and pH set at 5.5 mL/min and about 7.0, respectively, were held constant during the assessment of influent characteristics on the efficiency of arsenate adsorption. Varying degrees of arsenate adsorption capacities were observed by the different test influents employed.

3.4.1. DW

Dolomite exhibited high arsenate removal levels for influents prepared with distilled water. Complete (100%) removal of low arsenate concentrations (0.055 ppm) was achieved for the first 45 bed volumes and about 96% removal for the following 75 bed volumes, after which breakthrough was realized as depicted from Fig. 5, which represents the average of two experiments.

At higher concentrations (Ci = 0.58 mg/L), complete removal was not observed, however, a 93% removal was attained for the first 22.5 bed volumes. Breakthrough occurred between 22.5 and 45 bed volumes where the removal was reduced to 75%.

3.4.2. SGW

Dolomite showed good removals from synthetic groundwater. Fig. 6 depicts the breakthrough curves for three different initial arsenate concentrations of 0.1, 0.3 and 0.6 mg/L, where



Fig. 5. Arsenate breakthrough curves for DW.



Fig. 6. Arsenate breakthrough curve for SGW.

high removals of 85, 86 and 81% were respectively attained at the 22.5 bed volumes. At 45 bed volumes, the removals drop respectively to 65, 57 and 62%. However, breakthrough occurred at an earlier stage (about 22.5 bed volumes) compared to DW.

3.4.3. FSE

Experiments with FSE were performed to determine the arsenate removal efficiency and to investigate the effect of interfering compounds present in the filtered wastewater on the adsorption of arsenate by dolomite powder.

Arsenate removal from FSE influents was relatively unsuccessful as compared to the distilled water and groundwater influents. No removal of arsenate from FSE at initial arsenate concentration of 0.6 ppm was achieved over the first 45 bed volumes. Partial removal in the order of 32% started at 75 bed volumes. Total exhaustion of the dolomite bed was attained at 165 bed volumes as depicted from Fig. 7. This behaviour may be explained by the presence of high concentrations of competing anionic solutes.

3.5. Competing effects of solutes

Defining the anion competition during arsenate adsorption is an important factor in designing effective arsenate removal



Fig. 7. Arsenate breakthrough curve for FSE.



Fig. 8. Selectivity sequence of dolomite for anions present in FSE influent.

systems. Fig. 8 depicts graphically the selectivity sequence of dolomite powder under room temperature and neutral pH. Phosphates, present at an initial concentration of 33 mg/L, were the first anions to be removed by dolomite at a rate of 22%. At 45 bed volumes, sulfate removal occurred at a rate of 28% (Ci = 670 mg SO₄^{2–}/L). At 45 bed volumes, nitrates were adsorbed by dolomite as well, however, unlike sulphate, nitrate removal dropped to 5% (Ci = 109 mg NO₃⁻/L) at the next sampling point (75 bed volumes). Arsenate removal started at the 75th bed volume (Ci = 0.60 mg HAsO₄^{2–}/L) with a removal efficiency of 31% and dropped by 3%, 30 bed volumes later. After 90 bed volumes, arsenate removal efficiency dropped to zero (exhaustion of the dolomite bed). Consistent decrease in the competing anions concentration of the test influent suggested fixation of those anions by dolomite.

Chlorides, however, showed no significant removal during the whole run: the removal started at 75 bed volumes $(Ci = 10200 \text{ mg Cl}^{-}/L)$ at a rate less than 5% and dropped to zero at the very next sampling point (30 bed volumes later), the fact that led to rank chlorides, as a non-competing element to arsenate, at the end of the selectivity sequence of dolomite powder as presented in the following order: PO_4^{3-} > $SO_4^{2-} > NO_3^- > HAsO_4^{2-} > Cl^-$. These results are in conformity with studies reported by Genç et al. [18,21,22]. In one study [18] it was concluded that the order of suppression on arsenic removal on a molar basis was in the following order: phosphate > silicate > sulphate > bicarbonate. Another study [21] conducted on the effect of ions present in tap water (e.g. Ca^{2+} , Cl^{-} , and HCO_{3}^{-}) on the uptake by Bauxsol concluded that the presence of HCO₃⁻ ions decreases the arsenate removal efficiency as these ions compete with H₂AsO₄⁻ ions for positively charged adsorption sites. Furthermore, the presence of Ca²⁺ ions diminishes the negative charges, and NaCl has a minimal effect on arsenate adsorption, probably because Cl⁻ does not compete with H₂AsO₄⁻. The positive effect of Ca²⁺ on arsenate removal was found to be in agreement with findings of Wilkie and Hering [37] and Smith et al [38]. A third study [22] reported the selectivity sequence to be in the following order: phosphate \gg sulphate > bicarbonate, and concluded that the initial arsenate and competing anion concentrations are a function of the magnitude of the suppression. The extent of the competition between arsenate and the other anions will not only depend on the affinity of each anion to the surface, but also on their concentrations relative to each other [39].

3.6. Regeneration of dolomite

Regeneration of the saturated dolomite bed was attempted using 0.01N HCL solution of pH 2.0 and caustic soda solution of pH 10.5. Arsenate desorption experiments were conducted at the end of column loading experiments, after complete exhaustion of the dolomite bed was attained through the passage of 285 bed volumes of synthetic groundwater influent (Ci = 0.10 mg As(V)/L). Regeneration with the acidic solution of pH 2.0 was discontinued due to the dissolution of the dolomite. Regeneration with an alkaline solution involved feeding about 120 bed volumes of distilled water with pH raised to 10.5 using NaOH into the column at a flow rate of 5.5 mL/min. Re-feeding of arsenate jacked groundwater influent into the column led to better removal of arsenate during the first 22.5 bed volumes where removal increased by 2%.

This improvement in removal efficiency of the regenerated dolomite bed by the alkaline solution may be attributed to desorption of other chemicals or impurities that could have been present on the original raw dolomite particles, which could have interfered with the adsorption of arsenate.

Fig. 9 shows the effluent arsenate concentration profile of the regeneration run using an alkaline solution as regenerant (pH 10.5) and synthetic groundwater jacked with 0.1 mg As(V)/L as feed influent (pH 6.90). The whole run was performed under room temperature ($23 \,^{\circ}$ C).



Fig. 9. Effluent arsenate concentration profile at regeneration.



Fig. 10. Langmuir/Freundlich isotherm equilibrium curves.

Table 5	5
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Arsenate adsorption data at equilibrium employing various dolomite doses

Dolomite dose (g)	HAsO4 ²⁻ at equilibrium (mg/L)	HAsO ₄ ^{2–} removed (mg/L)	Percent HAsO4 ²⁻ removed (%)	Adsorptive capacity (mg/g)
2.5	0.484	0.136	21.94	0.00544
5	0.38	0.24	38.71	0.0048
10	0.2	0.42	67.74	0.0042
15	0.151	0.469	75.65	0.003127
20	0.116	0.504	81.29	0.00252

3.7. Adsorption isotherms

The results from the sorption study (Table 5) were fitted in the Langmuir and Freundlich models. The differences between the Langmuir and the Freundlich adsorption isotherms were determined to be insignificant. In both cases the data attained fitted well with correlation coefficients of 0.98 and 0.96, respectively. The model coefficients for the Langmuir model, *a* and *b* were computed based on the regression analysis of the data plotted, to yield 0.0088 mg/g and 3.607 L/mg, respectively. While the model coefficients for the Freundlich model, *K* and 1/*n* yielded values of 0.008 mg/g and 0.5, respectively. The equilibrium curves for the Langmuir and Freundlich isotherms attained at 23 °C by dolomite powder are depicted in Fig. 10.

4. Conclusions

Results of the present study on the efficacy of untreated dolomite powder in the adsorption of arsenate from various water matrices revealed the following:

- Raw dolomite powder was found to be a good adsorbent capable of removing residual arsenate concentrations from distilled and groundwater effluents. Early breakthrough (relative to the number of bed volumes treated) is attributed to the relatively high arsenate concentrations adopted in the experiments. Had the concentrations been in the µg/L range then the number of bed volumes treated would have increased appreciably.
- Effective operation of the fluidized dolomite-bed system was attained at a flow rate of 5.5 mL/min, which sustained expansion of the dolomite bed without overflow.
- The arsenate fixation efficiency on dolomite is affected by the hydraulic flow conditions, dolomite particle size, large variations in initial arsenate concentrations, pH and the presence and concentration of competing anionic solutes.
- Assessment of the competing effects of phosphate, sulfate, and nitrate ions with targeted arsenate ions for sorption sites demonstrated an inverse relation between initial influent anions concentration and efficiency of arsenate removal.
- Regeneration of arsenate-saturated dolomite with caustic soda solution at a pH of 10.5 showed complete regeneration of the exhausted dolomite particles.
- Adsorption isotherm of arsenate on dolomite is well described by both the Langmuir and Freundlich isotherms.

References

- R. Zaldivar, Arsenic contamination of drinking water and foodstuffs causing endemic chronic poisoning, Beitr. Path. Bd. 151 (1974) 384–400.
- [2] I.P.C.S. (International Program on Chemical Safety), Environmental Health Criteria no. 224: Arsenic and Arsenic Compounds, World Health Organization, Geneva, 2001.
- [3] A. Joshi, M. Chaudhuri, Removal of arsenic from groundwater by iron oxide-coated sand, J. Environ. Eng. 122 (8) (1996) 769–771.
- [4] K.S. Subramanian, T. Viraraghavan, S. Tanjore, T. Phommavong, Removal of arsenic (III): role of manganese greensand, in: Proc., 1995 Water Quality Technology Conference, November 12–16, 1995, New Orleans, LA, American Water Works Association, Denver, Colo., 1996, pp. 1063–1089.
- [5] D.A. Clifford, A.G. Ghurye, A.R. Tripp, Development of a novel anion exchange process for arsenic removal from water, in: Proceedings of the 3rd International Conference on Arsenic Exposure and Health Effects. Society of Environmental Geochemistry and Health/EPA/ERPI, San Diego, CA, July 12–15, 1998.
- [6] T. Viraraghavan, K.S. Subramanian, J.A. Aruldoss, Arsenic in drinking water—problems and solutions, Water Sci. Technol. 40 (2) (1999) 69–77.
- [7] K. Karschunke, V.L. Cacers, M. Jekel, Arsenic removal by corrosion induced adsorption. Water sanitation and hygiene: challenges of the millennium, in: Proceedings of the 26th WEDC Conference Dhaka, Bangladesh, Water and Waste Engineering for Developing Countries (WEDC), Loughborough University of Technology, Leicestershire, England, 2000, pp. 221–223.
- [8] A.H. Khan, S.B. Rasul, A.K.M. Munir, M. Habibuddowla, M. Alauddin, S.S. Newaz, A. Husaam, Appraisal of a simple arsenic removal method for ground water of Bangladesh, J. Environ. Sci. Health Part A Tox. Hazard. Subst. Environ. Eng. 35 (7) (2000) 1021–1041.
- [9] A. Ramaswami, S. Tawachsupa, M. Isleyen, Batch-mixed iron treatment of high arsenic waters, Water Res. 35 (18) (2001) 4474–4479.
- [10] B. Petrusevski, S.K. Sharma, F. Kruis, P. Omeruglu, J.C. Schippers, Family filter with iron-coated sand: solution for arsenic removal in rural areas, Water Sci. Technol.: Water Supply 2 (5–6) (2002) 127–133.
- [11] O.S. Thirunavukkarasu, T. Viraraghavan, K.S. Subramanian, Removal of arsenic in drinking water by iron oxide-coated sand and ferrihydrite-batch studies, Water Qual. Res. J. Canada 36 (1) (2001) 55–70.
- [12] O.S. Thirunavukkarasu, T. Viraraghavan, K.S. Subramanian, S. Tanjore, Organic arsenic removal from drinking water, Urban Water 4 (2002) 415–421.
- [13] O.S. Thirunavukkarasu, T. Viraraghavan, K.S. Subramanian, Arsenic removal from drinking water using iron oxide-coated sand., Water, Air, Soil Pollut. 142 (2003) 95–111.
- [14] N. Selvin, J. Upton, J. Simms, J. Barnes, Arsenic treatment technology for groundwaters, Water Sci. Technol. 2 (1) (2002) 11–16.
- [15] S.A. Mokashi, K.M. Paknikar, Arsenic (III) oxidizing *Microbacterium lacticum* and its use in the treatment of arsenic contaminated groundwater, Lett. Appl. Microbiol. 34 (2002) 258–262.
- [16] N.P. Nokolaidis, G.M. Dobbs, J.A. Lackovic, Arsenic removal by zerovalent iron: field, laboratory and modeling studies, Water Res. 37 (2003) 1417–1425.
- [17] R.C. Vaishya, S.K. Gupta, Coated sand filtration: an emerging technology for water treatment, J. Water Supply: Res. Technol.–AQUA 52 (4) (2003) 299–306.
- [18] H. Genç, J.C. Tjell, Effects of phosphate, silicate, sulphate, and bicarbonate on arsenate removal using activated seawater neutralise red mud (bauxsol), J. phys. IV France 107 (2003) 537–540.

- [19] M.J. DeMarco, A.K. SenGupta, J.E. Greenleaf, Arsenic removal using polymeric/inorganic hybrid sorbent, Water Res. 37 (2003) 164–176.
- [20] J.S. Ahn, C.-M. Chon, H.-S. Moon, K.-W. Kim, Arsenic removal using steel manufacturing by products as permeable reactive materials in mine tailing containment systems, Water Res. 37 (2003) 2478–2488.
- [21] H. Genç, J.C. Tjell, D. McConchie, O. Schuiling, Adsorption of arsenate from water using neutralized red mud, J. Colloid Interface Sci. 264 (2003) 327–334.
- [22] H. Genç-Fuhrman, J.C. Tjell, D. McConchie, Increasing the arsenate adsorption capacity of neutralized red mud (Bauxsol), J. Colloid Interface Sci. 271 (2004) 313–320.
- [23] H. Genç-Fuhrman, J.C. Tjell, D. McConchie, Adsorption of arsenic from water using activated neutralized red mud, Environ. Sci. Technol. 38 (8) (2004) 2428–2434.
- [24] I.A. Katsoyiannis, A.I. Zouboulis, Application of biological processes for the removal of arsenic from groundwaters, Water Res. 38 (2004) 17–26.
- [25] P. Lakshmipathiraj, B.R.V. Narasimhan, S. Prabhakar, G.B. Raju, Adsorption of arsenate on synthetic goethite from maqueous solutions, J. Hazard. Mater. 136 (2) (2006) 281–287.
- [26] S. Murcott, Appropriate remediation technologies for arseniccontaminated wells in Bangladesh, in: Presented at Arsenic in Bangladesh Ground Water, Wagner College, Staten Island, New York, February 27–28, 1999.
- [27] D. Pokhrel, T. Viraraghavan, L. Braul, Evaluation of treatment systems for the removal of arsenic from ground water, Pract. Periodical Hazard., Toxic, Radioactive Waste Manage. 9 (3) (2005) 152–157.
- [28] G.M. Ayoub, B. Koopman, N. Pandya, Iron and aluminum hydroxy (oxide) coated filter media for low-concentration phosphorus removal, Water Environ. Res. 73 (4) (2001) 478–485.
- [29] G.M. Ayoub, H. Kalinian, Removal of low concentration phosphorus using a fluidized raw dolomite bed, Water Environ. Res. 78 (4) (2006) 353–361.
- [30] F. Haddad, Evaluation of raw materials for the magnesia industry: selected dolomites from southern Lebanon and Qartaba. M.S. Thesis, American University of Beirut, Lebanon (1990).
- [31] H. Kalinian, Low concentration phosphorous removal using raw dolomite powder, M.S. Thesis, American University of Beirut, Lebanon (1991).
- [32] ASTM (American Society for Testing and Materials), Standard Test Methods for Particle-Size Analysis of Soils. vol. 04.08, Method D422-63, Easton. (2000a).
- [33] D.R. McCaulou, R.C. Bales, J.F. McCarthy, Use of short-pulse experiments to study bacteria transport through porous media, J. Contam. Hydrol. 15 (1) (1994).
- [34] American Public Health Association (APHA)/American Water Works Association (AWWA)/Water Environment Federation (WEF), Standard Methods for the Examination of Water and Wastewater, twentieth ed., Washington, D.C. (1999).
- [35] T.J. McGhee, Water Supply and Sewerage, McGraw-Hill Inc., New York, NY, 1991.
- [36] O.S. Pokrovsky, J. Schott, F. Thomas, Dolomite surface speciation and reactivity in aquatic systems, Geochim. Cosmochim. Acta 63 (19/20) (1999) 3133–3143.
- [37] J.A. Wilkie, J.G. Hering, Adsorption of arsenic on to hydrous ferric oxide: effects of adsorbate/adsorbent ratios and co-occuring solutes, Colloids Surf., A 107 (1996) 97–110.
- [38] E. Smith, R. Naidu, A.M. Alston, Chemistry of inorganic arsenic in soils: II. Effect of P, Na, Ca, J. Environ. Qual. 31 (2002) 557–563.
- [39] J.G. Hering, P.E. Kneebone, in: W.T. Frankenberger Jr. (Ed.), Environmental Chemistry of Arsenic, Dekker, New York, 2002, p. 167.