

Bayoxide: An effective adsorbent for making arsenic free drinking water

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ABSTRACT

Batch sorption experiments were carried out to remove As(III) from aqueous solution by using iron based commercial adsorbent Bayoxide. The effects of various experimental parameters, such as initial concentration, contact time and solution pH on the adsorption of As(III) on adsorbent was investigated. The adsorption density increased with increased initial arsenic concentration and contact time. The suitability of Langmuir and Freundlich adsorption models to the equilibrium data was investigated for As(III)-adsorbent system. The results showed that equilibrium data fitted Langmuir model best. The monolayer sorption capacity was 7.88 mg/g. Adsorption data were modeled using the pseudo-first-order and pseudo-second-order kinetic equation. It was shown that the second-order kinetic equation could best describe the sorption kinetics.

Key words: Bayoxide, adsorption, isotherm, kinetics, pH.

INTRODUCTION

Arsenic is a naturally occurring toxic element, and is also introduced into environments through a number of industrial processes and agricultural practices, including mining, poultry farming and the production and use of arsenical pesticides. A decision by the US Environmental Protection Agency in 1999 to reduce the maximum contamination level (MCL) for As in drinking water from 50 µg/L to 10 µg/L reflects a re-evaluation of health risks associated with ingestion of this metalloid. In Bangladesh, the MCL of arsenic in drinking water is 50 µg/L. A higher than acceptable level of arsenic in surface and ground water has caused serious health problem in many countries, including Argentina, Chile, Taiwan and United States¹. Particularly high arsenic levels have been reported in Bangladesh and in West Bengal, an Indian province bordering Bangladesh²⁻⁴.

Arsenic occurs in -3, 0, +3 and +5 oxidation states in aquatic systems. The elemental state is extremely rare where as -3 oxidation state is found only at extremely reducing conditions. Arsenate species (pentavalent state) are stable in oxygenated waters. Under mildly reducing conditions, arsenites (trivalent state) predominate. Arsenic combines strongly with carbon in arsenical organic compounds, which are used as pesticides, chemotherapeutic agents and chemical warfare agents.

The presence of arsenic in water causes toxic and carcinogenic effects on human beings. It has been reported that long-term uptake of arsenic contaminated drinking water has produced gastrointestinal, skin, liver and nerve tissue injuries. The toxicity of arsenic firmly depends on its oxidation state and trivalent arsenic has been reported to be more toxic than pentavalent and organic arsenicals⁵.

Various treatment methods such as ion exchange, adsorption, ultrafiltration, reverse osmosis, and adsorption-co-precipitation by metals (predominately ferric chloride) followed by coagulation have been so far proposed and adopted for the removal of arsenic from aqueous media. In general, the removal of arsenic by precipitation is most effective for small quantities of highly concentrated arsenic waste liquid. The most common arsenic removal method is precipitation-coagulation with lime and iron (III) salts followed by adsorption onto the resulting iron (III) hydroxide flocs. However, a problem with this technique is the safe separation, filtration, and the handling of the contaminated coagulant sludge. The cost effectiveness of precipitation is diminished when disposing of large quantities of low concentration arsenic wastes. As it is easy to remove the adsorbent from aqueous media after treatment, adsorption technique is generally considered to be a promising method and has been studied for arsenic removal as well. Adsorption is a mass transfer process where a substance is transferred from the liquid phase to the surface of a solid and becomes bound by chemical or physical forces. A number of papers have focused on the strong adsorption affinity of As on iron based adsorbents⁶⁻¹³.

Iron oxides, oxyhydroxides and hydroxides, including amorphous hydrous ferric oxide (FeO-OH), goethite (α -FeO-OH) and hematite (α -Fe₂O₃), are promising adsorbents for removing both As(III) and As(V) from water¹⁴⁻¹⁸. Amorphous Fe(O)OH has the highest adsorption capability since it has the highest surface area. Surface area is not the only criterion for high removal capacities of metal ions and other mechanisms (ion exchange, precipitation) play an important role. Most iron oxides are fine powders that are difficult to separate from solution. In the present study, suitability of a commercial iron based adsorbent Bayoxide (Bayer Chemicals, Germany) is explored for the removal of As (III) from aqueous solution. Compared to iron oxide, it is harder and can be separated from aqueous medium easily. This adsorbent may be highly suitable for column adsorption for both ground and wastewater. Both equilibrium and kinetic study over a wide range of operating conditions are undertaken to evaluate the effectiveness of Bayoxide to remove As (III) from water. The effects of pH, contact time

and concentrations on the adsorption of As (III) are also studied.

MATERIAL AND METHODS

Materials

An iron based adsorbent; Bayoxide (Bayer Chemical, Germany) has been used as an adsorbent. It has a very high surface area and high adsorption capacity. At the same time, the granules are stable to the stream of water. The specification of the adsorbent is given in Table 1. The inorganic form of arsenic, As(III) in single component aqueous solutions was used to assess experimental behaviour during the equilibrium adsorption studies. As(III) stock solution (1000 mg/L) was prepared by dissolving 1.32 g As₂O₃ (Merck, Germany) in double distilled water. Experimental solutions of the desired concentration were obtained by successive dilutions with double distilled water.

Table 1: Specification of Bayoxide

Parameter	Value
Chemical designation	Synthetic iron oxide
Fe ₂ O ₃ content	> 70 %
Specific surface area	120 – 200 m ² /g
Particle size	0.5-2 mm
Bulk density	0.4-0.6 g/cm ³

Analysis

Concentrations of arsenic were determined by finding out the absorbance at the characteristic wavelength (535 nm) using a UV/vis spectrophotometer (Shimadzu Model UV-1601), by the silver dithiodiethylcarbamate method (minimum detectable quantity: 1 µg As), commonly known as the SDDC method¹⁹.

Adsorption experiments

To study the effect of important parameters like pH, initial concentrations and contact time on the adsorptive removal of As(III), batch experiments were conducted at 25±2 °C. For each experimental run, 260 ml of As(III) solution of known concentration, amount of the adsorbent and pH was taken in a 300 mL stopper plastic conical flask and was agitated using a flash shaker (Stuart Scientific Co. Ltd. Model SF1, U.K.) at constant oscillation of

500 osc/min. Samples were withdrawn at appropriate time intervals and were centrifuged and the left out concentration in the supernatant solution were analyzed.

The effect of pH on the removal of As(III) was studied over a pH range of 3–12 with a solution of 1 mg/L at an adsorbent dose of 0.1 g /260 ml and a contact time of 6 h. The kinetics of adsorption was determined by analyzing adsorptive uptake of As(III) from the aqueous solution at different time intervals. The adsorption density defined as the amount of As (III) adsorbed per unit weight of adsorbent at time t , q_t (mg As (III)/g adsorbent), was calculated by:

$$q_t = \frac{(C_0 - C_t)V}{M} \quad \dots(1)$$

where C_0 and C_t (mg/L) are the liquid-phase concentrations of As(III) at initial and any time t , respectively. v is the volume of the solution (L), and M is the mass of dry adsorbent used (g).

For adsorption isotherms, 260 ml As (III) solutions of different initial concentrations (0.8–1.4 mg/L) were agitated with 0.1 g adsorbent till the equilibrium was attained. The adsorption density at equilibrium, q_e (mg/g), was calculated by:

$$q_e = \frac{(C_0 - C_e)V}{M} \quad \dots(2)$$

where C_e (mg/L) is the liquid-phase concentrations of As(III) at equilibrium.

Equilibrium time for the isotherm studies was kept as 6 h. Experiments for the batch tests were duplicated to check the reproducibility and the results are given as the average of the duplicates \pm (maximum value-minimum value)/2. The blank experiments showed no detectable As (III) adsorbed on the walls of the flask.

RESULTS AND DISCUSSION

Effect of pH

The effect on the uptake of As(III) at

various initial pH levels (3.–12) for arsenic concentrations of 1 mg/L was studied to determine the optimum pH and is shown in Fig. 1 As is evident from Fig. 1, the adsorption of As (III) over the pH range studied is not strongly dependent on pH, which is highly advantageous for practical operation. This may be due to specific chemical interaction between the adsorbate and the alkaline adsorbent surface. In the acidic pH range, when the non-ionic As (III) species comes in contact with the adsorbent,

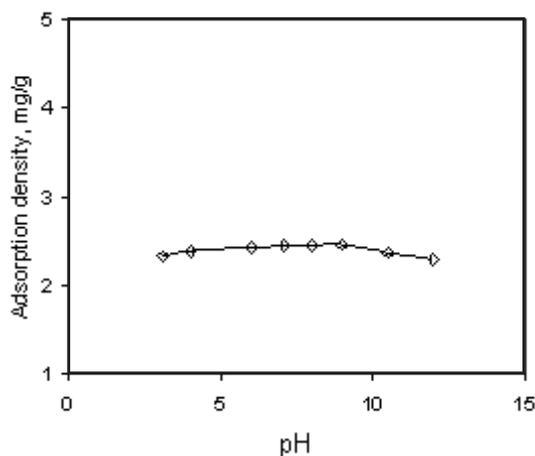


Fig. 1: Effect of pH on the adsorption of As(III) onto Bayoxide

the alkaline adsorbent surface possibly helps in the conversion of non-ionic arsenic to its anionic form in the acidic pH range, which in turn assists in the adsorption process. As very little effect on As (III) uptake was observed with varying pH, all further experiments were carried out at pH ~7.

Effect of contact time and concentration

Arsenic solutions of 260 ml at different concentration of 0.6 mg/L, 0.8 mg/L, 1.2 mg/L, and 1.5 mg/L were treated with 0.1g of adsorbent. Fig. 2 shows the effect of concentration on the adsorption density of As (III) onto Bayoxide. The adsorption density increased with increasing concentration of arsenic and finally reached a saturation point. This is due to the fact that by increasing the concentration of As (III) in solution, the availability of arsenic at the interface also increased, thus enhancing the amount of adsorption. When the surface active sites were covered fully, the extent

of adsorption reached a limit resulting in saturated adsorption.

Fig. 2 also demonstrates the effect of contact time on the adsorption of As (III). It is clear from Fig. 1 that the adsorption efficiency increases rapidly with an increase in contact time; and a maximum adsorption (more than 90%) was

achieved and remained fairly constant up to the end of the experiment (360 min). The results also show that most of the adsorption (80%) occurs in a contact time of 120 min.

Adsorption isotherm

To examine the relationship between adsorption density, q_e and aqueous concentration,

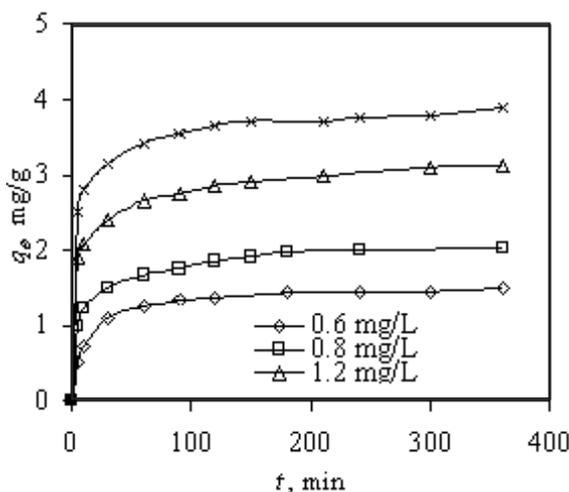


Fig. 2: Effect of concentration and contact time on the adsorption of As(III) onto Bayoxide

Table 2: Equilibrium constants for As(III) adsorption onto Bayoxide

Freundlich isotherm parameters			Langmuir isotherm parameters		
K_f	n	r^2	q_0 (mg/g)	K_L	r^2
1.467	9.23	0.9948	7.88	2.44	0.9988

C_e at equilibrium, sorption isotherm models are widely employed for fitting the data, of which the Langmuir and Freundlich equations are most widely used. The Langmuir model assumes that the uptake of ions occurs on a homogenous surface by monolayer adsorption without any interaction between adsorbed ions. To get the equilibrium data, initial As(III) concentrations were varied while the adsorbent mass in each sample was kept constant. 6 hrs of equilibrium periods for sorption experiments were used to ensure equilibrium conditions. The Langmuir model takes the form:

$$q_e = \frac{q_0 K_L C_e}{1 + K_L C_e} \quad \dots(3)$$

Where q_0 and K_L are Langmuir parameters related to maximum adsorption capacity and free energy of adsorption, respectively. The linearized form of Langmuir equation can be written as

$$\frac{1}{q_e} = \frac{1}{q_0} + \frac{1}{q_0 K_L} \cdot \frac{1}{C_e} \quad \dots(4)$$

The Langmuir constant q_0 and K_L can be calculated by plotting $1/q_e$ versus $1/C_e$. On the other hand, the Freundlich equation is an empirical equation based on adsorption on a heterogeneous surface. The equation is commonly represented by:

$$q_e = K_F C_e^{1/n} \quad \dots(5)$$

Where K_F and n are the Freundlich constants that indicate adsorption capacity and adsorption intensity, respectively.

The linearized form of Freundlich isotherm can be written as.

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad \dots(6)$$

The value of K_F and n can be calculated by plotting $\ln q_e$ versus $\ln C_e$.

The Langmuir and Freundlich equations were used to describe the data derived from the adsorption of As(III) by Bayoxide over the entire concentration range studied. Fig. 3 and Fig. 4 show the Freundlich and Langmuir curves for As(III) adsorption onto Bayoxide, respectively. The isotherm constants and correlation coefficients are shown in Table 2. From Table 2 it is obvious that, Langmuir isotherm has a better fitting model than

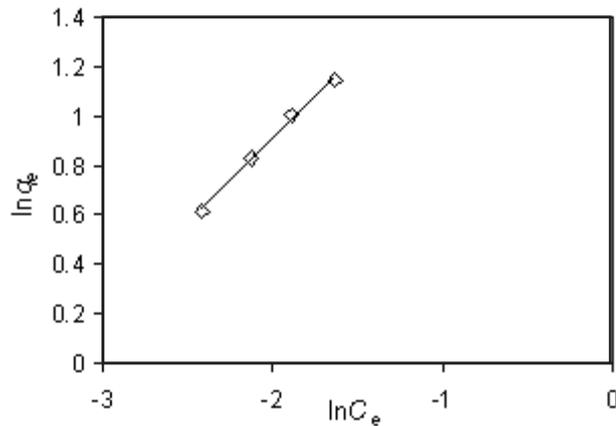


Fig. 3: Freundlich isotherm for As(III) adsorption onto Bayoxide

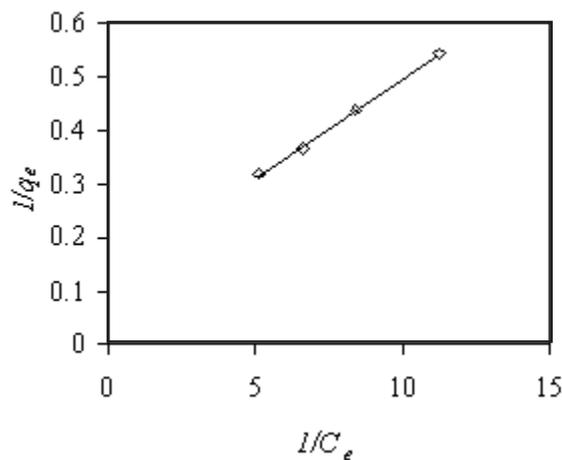


Fig. 4: Langmuir isotherm for As (III) adsorption onto Bayoxide

Freundlich as the former have higher correlation regression coefficient than the latter thus, indicating to the applicability of a monolayer coverage of the As(III) on the surface of adsorbent. From table 2, it was also observed that the maximum sorption capacity of Bayoxide for As(III) was found to be 7.88 mg/g.

Adsorption Kinetics

In order to determine the sorption kinetics of As(III), the first-order and second-order kinetics models were examined. The first-order rate expression of Lagergren²⁰ based on solid capacity is expressed as follows:

$$\frac{dq}{dt} = k_1(q_e - q_t) \quad \dots(7)$$

where k_1 is the rate constant of the first order (min^{-1}). Integrating Eq. (6) for the initial and end conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q$, and

after some rearrangement, a linear plot is obtained:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad \dots(8)$$

The rate constant for the first-order equation was determined from the slope of the plot

$\ln(q_e - q_t)$ vs. t . If first-order kinetics is applicable to the system under study, the plot of $\ln(q_e - q_t)$ vs. t of Eq. (7) should give a linear relationship. Further, the k_1 obtained from the plot should also be close to the k_1 obtained from experiment.

The experimental data were also analysed using the pseudo-second-order model²¹.

$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \quad \dots(9)$$

Table 3: Kinetic parameters for As(III) adsorption onto Bayoxide

C_0 (mg/L)	$q_{e,exp}$ (mg/g)	First-order kinetic model			Second-order kinetic model		
		$q_{e,cal}$ (mg/g)	k_1 (min^{-1})	r_1^2	$q_{e,cal}$ (mg/g)	k_2 ($\text{g mg}^{-1}\text{min}^{-1}$)	r_2^2
0.6	1.48	0.72	0.0121	0.895	1.52	0.055	0.9998
0.8	2.03	1.73	0.0164	0.965	2.07	0.043	0.9989
1.2	3.12	1.43	0.0133	0.935	3.17	0.033	0.999

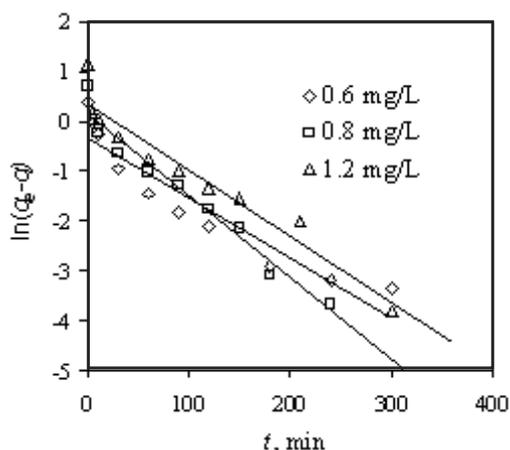


Fig. 5: Pseudo-first-order kinetics for the adsorption of arsenic (III) onto Bayoxide

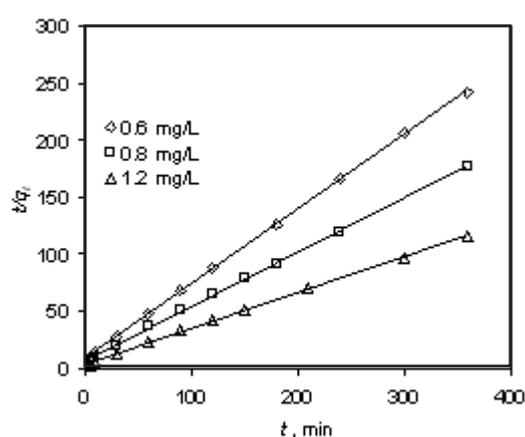


Fig. 6: Pseudo-second-order kinetics for the adsorption of arsenic (III) onto Bayoxide

Where k_2 is the rate constant of pseudo-second-order sorption ($\text{g mg}^{-1}\text{min}^{-1}$). Integrating Eq. (8) for the initial and end conditions $t = 0$ to $t = t$ and $q_t = 0$ to $2qt$, and after some rearrangement, a linear plot is obtained:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad \dots(10)$$

If the second order kinetic equation is applicable, the plot of t/q against t of Eq. (9) should give a linear relationship. The q_e and k_2 can be determined from the slope and intercept of the plot. Figs. 5 and 6 show the pseudo-first-order and pseudo-second-order curves for the adsorption of As(III) onto Bayoxide. Table 3 lists the results of the rate constant studies for different initial As(III) concentrations by the pseudo-first-order and second-order models. The correlation coefficient, r^2 for the pseudo-second-order adsorption model has high value (>99%), and its calculated equilibrium adsorption capacity, is consistent with

experimental data. These facts suggest that the pseudo-second-order adsorption mechanism is predominant.

CONCLUSION

Bayoxide is found to be a suitable adsorbent for the removal of As(III) from drinking water. The adsorption was found to be independent on pH. The kinetics of adsorption could be described by pseudo-second order kinetic model. The equilibrium of adsorption is best described by Langmuir isotherm rendering an adsorption capacity of 7.88 mg/g.

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$q_{e,cal}$

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