

REMOVAL OF ARSENIC FROM AQUEOUS SOLUTION BY SYNTHETIC HEMATITE

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Accepted:07/06/11

Abstract

An hematite was synthesized and subjected to batch equilibration of arsenic and its desorption processes that control the mobility, toxicity and availability of arsenic in the water environment. The pH_{pzc} of the synthesized hematite as determined by mass and potentiometric titration techniques are 9.18 and 9.20 respectively. The effect of background electrolyte concentration affected the pH_{pzc} values obtained from Potentiometric titration method. Adsorption of As(III) was influenced by ionic strength and pH of the adsorbate medium. Maximum adsorption was obtained at pH 7.8. The adsorption data fit fairly well into Langmuir, Freundlich and Temkin isotherms with correlation coefficient, r^2 values of 0.96, 0.94, and 0.92 respectively. The $n < 1$ value obtained from Freundlich plot was an indication of favourable adsorption of As(III), over the entire range of concentrations studied. From the kinetic studies, a significant amount of As(III) was sorbed within 240 min. About 53% and 81% of the amount at 100% coverage were sorbed at 120 and 240 min respectively. Desorption of As(III) is pH dependent with 86% maximum desorption at pH 1 and 7% at pH 6.

Key words: Hematite, Arsenic, Adsorption kinetics, desorption, Temkin isotherm, Lagergren plot

Introduction

Scientific and technological development of the world has brought about tremendous development in industrial and agricultural processes as well as health and social systems. One of the negative consequences of this development is in the accumulation of toxic metals in our environment. The buildup of heavy metals in the ecosystem is a global source of concern because of its persistence in the environment and known health implications [1-4]. Arsenic is one of the most toxic metals of concern [4] in the environment. It contaminates both surface and subsurface water through natural and anthropogenic sources. Contamination of aquifer and wells are largely due to geological processes and partly due to particulate emission or liquid effluent discharges into water cycles [5-7].

Arsenic has been reported to be toxic and carcinogenic metalloid. The degree of toxicity is reflected in the low guide-line limit ($10\mu\text{g/l}$) set by international regulatory bodies [8, 9]. Arsenic is predominantly found as arsenite [As (III)] or arsenate [As (IV)]. Arsenate is present as negatively charged ion at typical drinking water pH (pH 6.5-8.5), whereas, arsenite is neutral in the same pH range. Elevated concentrations ($>50\mu\text{g/l}$) in drinking water have been reported with attendant endemic poisoning of man in different parts of the world such as in Bangladesh [10-14]. The potential toxicity and

bioavailability of arsenic species is a product of several factors which include redox potential, pH, presence and type of surface, microbial population which can reduce inorganic arsenic to methylated arsenic species, presence and concentration of competing ions [15, 16]. Many reports of As (IV) sorption on variable mineral oxides (Al, Mn and Fe oxides) agreed to the formation of inner sphere complexes [17, 18]. An earlier study showed that As formed three different complexes with goethite [19]. These are monodentate, bidentate mononuclear and bidentate binuclear complexes.

Iron oxides are abundant in the natural soil and natural remediation of toxic metals is essentially due to oxides of Al, Mn and Fe. Goethite and hematite are the most abundant forms of iron oxides. Due to the positive surface characteristic of hematite and goethite couple with their high surface area, synthetic hematite and goethite have been subjected to sorption of heavy metals and anions such as SO_4^{2-} and HPO_4^{2-} from aqueous solution to mimic natural soil environment [20-23]. The potential toxicity and mobility of arsenic is controlled by sorption onto metal oxide surface. In this study we synthesized hematite and evaluated its sorption capacity and behaviour in the removal of arsenic from aqueous solution.

Material and Methods

Synthesis: Hematite was synthesized by dissolution of 40g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (97% purity) in 500 mL

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distilled water preheated to 90°C followed by careful addition of 1 M KOH solution previously equilibrated at 90°C until precipitate is formed. 50mL of 1M NaHCO₃ also maintained at 90°C was added to quantitatively precipitate hematite. The resulting suspension was aged in a thermostatic oven set at 90°C [24]. As (III) stock solution was prepared by dissolving 1.32g As₂O₃ in 200gdm⁻³ KOH solution and neutralized by 1% (v/v) H₂SO₄ in a 1L standard flask. The solution was made up the mark with de-ionised water. The working standard solutions (40-120mg/l) were prepared from these by appropriate dilutions.

Characterisation: Elemental analysis of the synthesised hematite was determined by atomic absorption spectrometer (AAS). The surface charge characteristic was determined using potentiometric and mass titration methods [25, 26]. The mass titration method involves two steps: the mass concentration sufficient to obtain a limiting pH is first determined. The amount of solid phase is then used for the second acid-base titration [27].

Sorption Studies: Batch equilibration of 20mL of As (III) of initial concentration range between 40-120mg/l was separately contacted with 0.2g of hematite. Blank solutions containing no hematite were also included. Batch adsorption experiments were carried out in a series of Erlenmeyer flasks of 100mL (or 250mL) capacity. All samples were agitated on a motorised orbital shaker, Mk V shaker, type Lh Fermentation for 24hr. After equilibration, the mixtures were filtered and filtrate were analysed for un-adsorbed As(III) using Apel PD - 303 UV - visible spectrophotometer at 340nm. The quantity sorbed was calculated from the equation [2]:

$$q_e = \frac{C_i - C_f}{M} \times V \quad (1)$$

Where q_e is the quantity of metal sorbed (mg/g); C_i and C_f are the initial and final concentrations of As(III) (mg/l) respectively; V is the volume of As(III) solution (l); and M is the mass of hematite used (g).

The sorption isotherm of As was tested against three commonly employed isotherm theories in their linearised forms. These are: Langmuir, Freundlich and Termkin isotherms. Sorption data were subjected to the three forms of Langmuir equations:

$$\text{Langmuir: } \frac{C_e}{Q_e} = \frac{1}{bQ_m} + \frac{C_e}{Q_m} \quad (2)$$

$$\text{Freundlich: } Q_e = K_f C_e^{\frac{1}{n}} \quad (3)$$

$$\text{Termkin: } Q_e = B \ln A + B \ln C_e \quad (4)$$

The linearised forms of Freundlich and Termkin equations used are:

$$\text{Freundlich: } \log Q_e = \log K_f + \frac{1}{n} \log C_e \quad (5)$$

$$\text{Termkin: } Q_e = B \ln A + B \ln C_e \quad (6)$$

Where Q_e is the quantity sorbed at equilibrium (mg/g); A is a constant related to the energy of adsorption (l/mg); Q_m is the mass of adsorbed solute required to completely saturate a unit mass of adsorbent (mg/g); C_e is the equilibrium concentration of the remaining metal in the liquid phase (mg/l); K_f is the sorption capacity when metal equilibrium concentration is 1 (mg^{1/n} g⁻¹ Lⁿ) and B is the degree of dependence of sorption with equilibrium concentration.

Sorption kinetics: A pre-determined concentration (100mg/l in 0.1M KNO₃ solution) of As (III) was contacted with 0.2g of hematite in a 50mL Erlenmeyer flask. The ratio of As (III) concentration to hematite used corresponds to the optimum sorption capacity obtained from the sorption capacity experiment. The mixture was agitated on an orbital shaker for varying contact time ranging from 30 to 420 min. The mixtures were filtered and filtrates were analysed for residual As using Apel PD - 303 UV - visible spectrophotometer at 340nm. The quantity adsorbed was calculated using equation 1.

Effect of ionic strength: Hematite (0.2g) was variously suspended in different concentrations of KNO₃ (0.001-0.2M) solution in 100mL flask. 20mL of 100mg/l As(III) solution was added to each and equilibrated for 320 min. The mixtures were then filtered and the filtrates analysed for residual As (III) using Apel PD - 303 UV - visible spectrophotometer at 340nm. The quantity adsorbed was calculated using equation 1.

Influence of pH: The pH of five different solutions of 20mL of 100mg/l As (III) was adjusted between pH 2 and 10 by gradual addition of 0.1M HNO₃ or 0.1M KOH solution. The pH was taken as initial pH. 0.2g of hematite was added to the solution and equilibrated on an orbital shaker for 320 min. After equilibration, the mixtures were filtered and the content of each flask was analysed for un-adsorbed As using Apel PD - 303 UV - visible spectrophotometer at 340nm. The quantity adsorbed was calculated from equation 1.

Desorption experiment: 20cm³ of 100mg/l As(III) solution was pipette into 6 different 100ml capacity Erlenmeyer conical flasks containing 0.2g of hematite and the pH in each flask was adjusted to 7.5 by addition of HNO₃ or KOH of known concentration. The mixture was agitated for 320 min at room temperature and then filtered. The residue from each flask was then transferred into new set of conical flasks and 20cm³ of HNO₃ of concentration between 10⁻¹ to 10⁻⁶ was added and the pH taken. The mixture was agitated for 320 min after which it was filtered and the filtrate was analyzed using Apel PD -

303 UV - visible spectrophotometer at 340nm to determine the quantity of arsenic desorbed.

Results and Discussion

A reddish brown, fine textured hematite was synthesized. The elemental analysis of the hematite by AAS revealed the presence of some minor elements which constitute impurity (Table 1). The presence of other metals are attributed to the purity level of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ used which was 97%.

Table 1: Adsorbent Characterization

PROPERTIES	SAMPLE
Colour	Reddish brown
Texture	Fine
Density (g/cm^3)	4.0
% by weight of Fe	63.7%
% by weight of Mn	2.02%
% by weight of Cu	1.53%
% by weight of Zn	1.22%
% by weight of Mg	0.32%
PZC	9.2
pH	6.3

The pH_{pzc} is the pH of the surface carrying a net zero charge and is a measure of the propensity of the oxides surface to become either positively or negatively charged as a function of pH. The point of zero charge of hematite determined using mass titration method was found to be 9.18 as illustrated in Fig. 1, while 9.20 was obtained in potentiometric titration method using 0.1M KNO_3 as background electrolyte (Fig. 2). The result of point of zero charge as determined by mass titration in acidic medium agrees more with literature value of pH_{pzc} of hematite on the extreme end [26]. The high pH_{pzc} is an indication of impurity in the synthesized hematite [26] as revealed by elemental analysis.

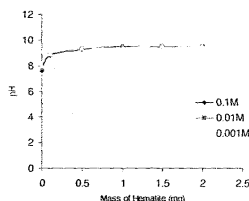


Fig 1: Mass Titration of Hematite

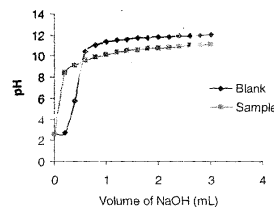


Fig 2: Potentiometric Titration of Hematite in 0.1M KNO_3

Batch adsorption: The sorption data of hematite for As (III) are as shown in Fig 3. The amount of hematite used for all samples was constant (0.20g). The initial concentrations of As (III) were varied and volume kept constant. It could be observed from Fig 3, that the sorption of As (III) on hematite increased steadily up to a maximum of 4.1mgAs/g hematite at equilibrium concentration of 100mg/L. According to Giles's classification of adsorption isotherms, Fig. 3 conforms with L2- type isotherm which is an indication of a medium affinity of hematite for As(III) at low surface coverage coupled with a decreasing amount of adsorbing surface remaining as the surface coverage increases [28]. The adsorption reached a maximum with the presence of a plateau.

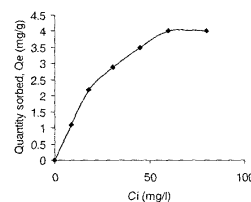


Fig 3: Sorption Capacity

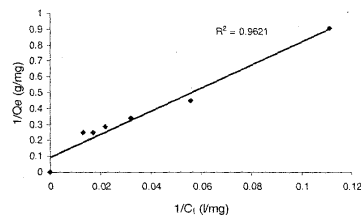


Fig 4a: Linearised Langmuir isotherm curve

The adsorption data were fitted into the three adsorption equations (eqs. 2, 5 and 6). Figs. 4a-c indicate that Langmuir, Freundlich and Temkin isotherms with correlation coefficient, $r^2 = 0.96, 0.94$ and 0.92 respectively fit fairly well to the experimental data, with Langmuir isotherm found to yield the best fits to the experimental data. The results therefore showed that As (III) sorption can also be modeled by Freundlich and Temkin isotherms. The fitness of data indicates that the coverage of the adsorption sites was in the form of monolayer coverage and all surface sites have almost the same adsorption energies [2].

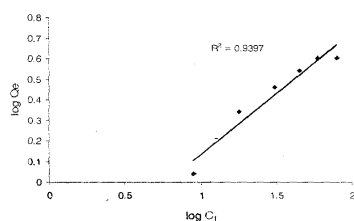


Fig.4b: Linearised Freundlich isotherm curve

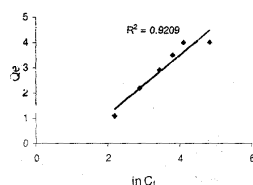


Fig. 4c: Linearised Temkin isotherm curve

The isotherms parameters as obtained from figs. 4a-c are reported in Table 2. The k_f and n parameters estimated from the Freundlich isotherm are useful information that determines how favourable the sorption of As (III) on hematite is. A high value of k_f suggests that adsorption capacity of the adsorbent is high; n indicates whether the nature of sorption is favourable or unfavourable. A steep slope n that is far less than 1 indicates that sorption intensity is good (or favourable) over the entire range of concentrations studied, while a steep slope $n > 1$ means that sorption intensity is good (or favourable) only at high concentrations, but much less at lower concentrations. Low $1/n$ values (<1) suggested that any large change in the equilibrium concentration of arsenic would not result in a marked change in the amount of arsenic adsorbed [6, 29]. From Table 2 the n value is less than one, which indicates that sorption intensity is good (or favourable) over the entire range of concentrations studied and the $1/n$ value is high indicating that change in equilibrium concentration of As(III) will have effect on amount adsorbed on hematite. These results were consistent with previously published data, where adsorption of As(III) on different substrates (e.g. activated carbon, gibbsite, goethite and Fe-oxide coated sand) also followed Langmuir isotherms [30].

Adsorption kinetics

The data obtained for the effect of time on sorption of As(III) on hematite at an initial As(III) concentration of 100mg/L are illustrated in Fig 5. The amount of As(III) adsorbed on hematite increased with an increase in contact time and the curve began to flatten at 320 min contact time which indicate that the equilibrium was reached. The experimental data were analyzed according to the Lagergren rate equation [31]:

Table 2: Linearized Langmuir, Temkin and Freundlich Model Parameters

Parameters	$b(\text{L/mg})$	$Q_{\text{max}}(\text{mg/g})$	n	$1/n$	r^2	k_f
Langmuir Isotherm	0.60	4.81	—	—	0.91	—
Langmuir Isotherm	0.014	10.73	—	—	0.96	—
Langmuir Isotherm	0.005	13.0	—	—	0.03	—
Temkin Isotherm	0.67	—	0.98	—	0.94	—
Freundlich Isotherm	—	—	0.59	1.69	0.94	0.347

Note: Unit of k_f is $\text{mg}^{-1/n} \text{g}^{1/n} \text{L}^n$ [Chen et al (1999)]

$$\log(q_e - q_t) = \log q_e - \frac{k}{2.303} t \quad (7)$$

Where q_e and q_t are the quantities of As (III) adsorbed at pseudo-equilibrium condition and at time t respectively; k is the adsorption rate constant. Experimental data were fitted

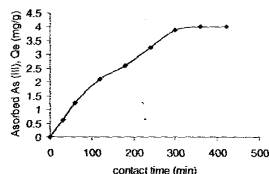


Fig. 5: Effect of contact time on As (III) adsorption

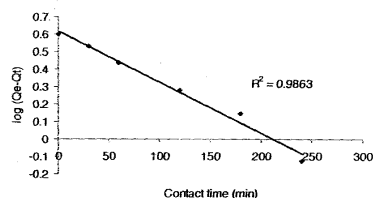


Fig. 6: Lagergren plot

into equation 7 and plotted as illustrated in Fig 6 and it gave a linear relationship with correlation coefficient of 0.99. The rate constant k and quantity adsorbed at equilibrium Q_e , calculated from the slope and intercept were $0.0067 \text{ mgg}^{-1}\text{s}^{-1}$ and 4.15 mgg^{-1} respectively. The linearity of the relationship indicates the first order nature of sorption of arsenic, as reported in the previously published literature [6]. The calculated Q_e (4.15 mg/g) from Lagergren plot agreed well with the value obtained in the sorption experiment as illustrated in Fig 3.

Influence of Ionic Strength on Sorption of As(III) on Hematite

Sorption of As (III) on hematite was investigated at different concentrations of background electrolyte and As (III) initial concentration of 100 mg/L . The data obtained are as shown in Fig 7. It could be observed that As (III) sorption on hematite is dependent on ionic strength of the background electrolyte. The sorption capacity increased linearly up to the optimum at 0.05 M KNO_3 , after which there

was no appreciable change with increase in the ionic strength.

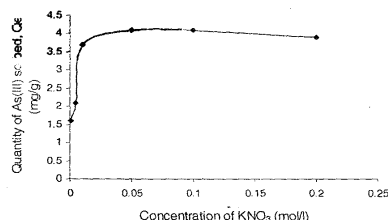


Fig. 7: Effect of ionic strength on As (III) adsorption

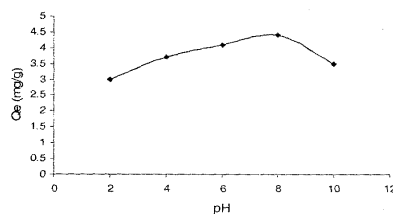


Fig. 8: Effect of pH on adsorption of As(III)

Influence of pH on Sorption of As(III) on Hematite

The effect of pH on As(III) sorption on hematite was studied at an initial pH between 2 and 10 for 320 min contact time and As(III) initial concentration of 100 mg/L . The data obtained are as illustrated in Fig 8. Sorption increased with pH up to a maximum of 4.4 mg/g which correspond to pH_{pzc} of 7.8, after which sorption decreased with pH. The result showed that pH had significant effect on sorption of As(III) on synthetic hematite. The pH effect on As(III) sorption is generally related to the point of zero charge (pzc) of hematite. At $\text{pH} > \text{pHpzc}$, hematite surface acquires a net negative charge and at $\text{pH} < \text{pHpzc}$ a net positive charge [25]. Arsenic (III) exist as H_3AsO_3 at $\text{pH} < 2$, H_2AsO_3^- within the pH range of 3-6, HASO_3^{2-} at pH 8-12 and AsO_3^{3-} at $\text{pH} > 12$. The predominant As-oxyanion involved in the adsorption below pH 7.8 is HASO_3^{2-} [32]. Above the pH_{pzc}, hematite exists as monomeric anionic form which account for the insensitivity of the surface to adsorption of As (III). This result is in variance with an earlier published article [6], where it was observed

that pH has no effect on As(III) sorption on natural hematite

Desorption experiment

Desorption of As(III) from the surface of hematite was investigated and the data obtained are illustrated in Fig 9. It can be observed that 86% desorption was achieved at pH of 1, and that desorption decreases with increase pH of equilibrium solution. Desorption experiment was carried out in 10^{-6} – 10^{-1} mol/dm² HNO₃, and above the concentration of 10^{-1} mol/dm², the synthetic hematite dissolved in the acid. Conclusion 1.

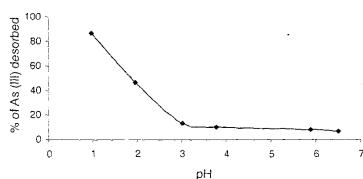


Fig. 9: Desorption of As (III) from used hematite

Conclusion

Studies of factors influencing sorption and desorption of As(III) onto and from synthetic hematite is important in understanding the behaviour of As(III) with hematite. It will also help to predict the efficiency of hematite in removing As(III) from contaminated water. pH is an essential factor that influence the amount of As(III) adsorbed onto and desorbed from the hematite surface. An optimum adsorption was achieved at pH 7.8 while greater percentage (86%) was desorbed at pH 1. Adsorption of As(III) onto hematite could be modeled by Langmuir, Freundlich and Temkin adsorption isotherms. This suggests that adsorption sites have almost the same adsorption energies which gave a monolayer type of coverage. The sorption of As (III) on hematite is dependent on ionic strength of the background electrolyte. There was an initial increase in As(III) sorption with pH up to a maximum of 4.4mg/g which correspond to pH_{pzc} of 7.8, after which sorption decreased with pH. Therefore, pH had significant effect on sorption of As(III) on synthetic hematite. The kinetics of adsorption followed a pseudo-first kinetics with rate constant k and Q_e obtained as 0.0067 mgg⁻¹s⁻¹ and 4.15mgg⁻¹ respectively

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