# Adsorption of arsenate on synthetic goethite from aqueous solutions

P. Lakshmipathiraj, B.R.V. Narasimhan*, S. Prabhakar, G. Bhaskar Raju

*National Metallurgical Laboratory (Madras Centre), CSIR Madras Complex, Taramani, Chennai 600113, India[1]*

## Abstract

Goethite was synthesized from the oxidation of ferrous carbonate precipitated from the double decomposition of ferrous sulfate doped with sodium lauryl sulfate (an anionic surfactant) and sodium carbonate in aqueous medium. The specific surface area and pore volume of goethite were $103 \, m^2 \, g^{-1}$ and $0.50 \, cm^3 \, g^{-1}$. Batch experiments were conducted to study the efficacy of removal of arsenic(V) using this goethite as adsorbent for solutions with $5–25 \, mg \, l^{-1}$ of arsenic(V). The nature of adsorption was studied by zeta-potential measurements. The adsorption process followed by Langmuir isotherm and diffusion coefficient of arsenate was determined to be $3.84 \times 10^{11} \, cm^2 \, s^{-1}$. The optimum pH of adsorption was found to be 5.0. The kinetics of adsorption was evaluated with $10 \, mg \, l^{-1}$ and $20 \, mg \, l^{-1}$ of As(V) solutions and activation energy of adsorption, as calculated from isoconversional method was in the range of $20 \, kJ \, mol^{-1}$ to $43 \, kJ \, mol^{-1}$. This suggests that the adsorption process is by diffusion at the initial phase and later through chemical control. FT-IR characterization of arsenic treated goethite indicated the presence of both As—O—Fe and As—O groups and supported the concept of surface complex formation.
© 2005 Elsevier B.V. All rights reserved.

*Keywords:* Goethite; Arsenate; Kinetics; Isoconversional method; Langmuir isotherm

## 1. Introduction

Arsenic is known to cause various ailments to humans ranging from skin rashes to carcinoma and its presence in exceedingly higher concentrations in drinking water poses threat to millions of people in West Bengal of India and Bangladesh [1]. United States Environmental Protection Agency (USPEA) has revised the maximum contaminant level for arsenic in drinking water from $50 \, \mu g \, l^{-1}$ to $10 \, \mu g \, l^{-1}$ because of its proven toxic effects on human health. Under reducing conditions, arsenic occurs in trivalent form (arsenious acid species) whereas the pentavalent state (arsenic acid species) is common in oxidizing conditions in aqueous systems [2]. In order to combat the problem of arsenic contamination, various treatment methods are proposed. The most common methods include the application of aluminum and iron salts that are used in water purification [3]. The removal of arsenic is accomplished by adsorption techniques wherein adsorbents such as amorphous ferric hydroxide [4], ferrihydrite [5], natural iron ores [6], ferruginous manganese ores [7], iron oxide coated polymers [8], lanthanum compounds [9], zero valent iron [10], silica containing iron oxide [11], activated carbon [12], have been recommended. In another study, it has been demonstrated that arsenic in the form of arsenate could be removed up to 95% by adsorption on to hardened paste of Portland cement [13]. Iron filings (40 mesh) immersed in water was used to remove arsenic in batch type adsorption and a removal efficiency of 90% was reported [14]. The arsenic uptake from aqueous solutions by iron bearing minerals such as goethite, lipidocrocite, mackinawite and pyrite was studied and found to be better [15]. In a comparative study [16], that evaluated the arsenic removal from water using a variety of adsorbents, viz., zirconia-impregnated activated carbon, AM3 (a commercial adsorbent comprising calcite, fluorite and iron oxide) and granules iron hydroxide (GIH), the sorption capacity was found to be 2.8 mg, 2.0 mg and 2.3 mg of arsenic per gram of adsorbent. It is observed that in most of these cases, the adsorption efficiency is dependent on the surface properties of the adsorbent such as specific surface area, surface charge, pore volume and pore sizes.

Among the various adsorbents, iron bearing minerals especially goethite was observed to be more effective and economically viable. Various synthesis methods of goethite [17] were reviewed and found that the particle size, shape and

**Nomenclature**

| | |
|---|---|
| $a$ | amount adsorbed (mg g$^{-1}$) |
| $a_s$ | amount of adsorbed at equilibrium (mg g$^{-1}$) |
| $A$ | pre-exponential factor |
| $C_e$ | equilibrium concentration of adsorbate |
| $C_o$ | initial concentration of adsorbate |
| $C_\infty$ | concentration of adsorbate at infinite time |
| $D$ | diffusion coefficient (cm$^2$ s$^{-1}$) |
| $E_a$ | activation energy (kJ mol$^{-1}$) |
| $k$ | rate constant |
| $K$ | adsorption coefficient |
| $R$ | universal gas constant |
| $x/m$ | adsorbate: adsorbent ratio (mg g$^{-1}$) |
| $\alpha$ | degree of adsorption or conversion fraction |

surface area of goethite depend on the Fe(III):OH ratio, the rate of base titration of iron salt, temperature of neutralization and time of crystallization. Most of the synthesis methods were based on neutralization of ferric nitrate with an alkali and subsequent aging spanning from 20 h to 336 h. The specific surface area of goethite specimens obtained by the above method ranges from 11 m$^2$ g$^{-1}$ to 150 m$^2$ g$^{-1}$. In another method, goethite nano crystals with mean size ranging from 1 nm to 10 nm and specific surface area around 300 m$^2$ g$^{-1}$ by hydrolysis of aqueous solutions of ferric salts followed by membrane purification and freeze drying was reported [18].

In the present investigation, the synthesis of goethite was carried out by oxidation of ferrous carbonate precipitated from ferrous sulfate solution doped with sodium lauryl sulfate and sodium carbonate solution, wherein $CO_3^{2-}/Fe^{2+}$ molar ratio of the resultant solution was maintained at 1.0. The interaction of arsenate with goethite surface, the kinetics of adsorption process and the activation energy of adsorption by isoconversional method were also studied. An attempt was made to elucidate the mechanism of arsenic(V) adsorption on goethite synthesized from the oxidation of ferrous carbonate.
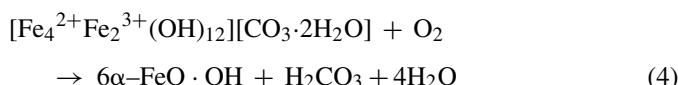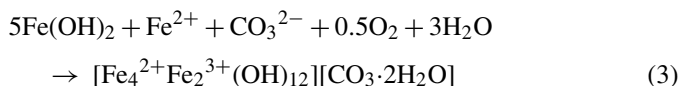
## 2. Experimental

### 2.1. Reagents

Electrolytic grade (99.9% purity) iron powder was treated with sulphuric acid to prepare 0.5 M ferrous sulfate solution. 2.0 M stock solutions of sodium carbonate and sodium hydroxide were prepared by using analar grade chemicals obtained from E. Merck sodium lauryl sulfate obtained from British Drug House (BDH) was used to prepare 1% (w/v) solutions. Arsenic(V) test solutions were prepared from $H_3AsO_4$ (E. Merck-NIST Certified: 1000 ppm As) standard reference solution. The test solutions were freshly prepared from the stock solution using double distilled water.

### 2.2. Preparation of goethite and its characterization

One hundred milliliters of sodium lauryl sulfate solution was added to 0.5 M ferrous sulfate under continuous stirring. Sodium carbonate (2.0 M) was added to ferrous sulfate solution through a burette under stirring conditions, till the slurry pH of 10.0 was obtained. At this juncture, ferrous ions were precipitated as ferrous carbonate in the form of a pale green precipitate. An aliquot portion of sodium hydroxide (2.0 M) was further added to the slurry to raise the pH to 12.0. Oxygen was passed through the solution using a perforated glass impinger and the rate of scrubbing was maintained at 2.0 l min$^{-1}$. The ferrous carbonate precipitated, dissolves partially to produce ferrous hydroxide and the oxidation triggers the formation of another compound known as Green Rust Carbonate (GRC1). With the onset of further oxidation, GRC1 was oxidized to iron oxy hydroxide (α-FeO·OH). The scrubbing time of oxygen was maintained for a period of 12 h. The precipitate was filtered and washed with copious amounts of double distilled water to get rid of excess alkali. The wet cake was dried at 90 °C for 6 h and a fine iron oxy hydroxide powder was obtained and preserved for adsorption studies. The sequence of reactions underlying the synthesis method can be written as follows:

$$FeCO_3 + OH^- \rightarrow FeOH^+ + CO_3^{2-} \tag{1}$$

$$FeOH^+ + OH^- \rightarrow Fe(OH)_2 \tag{2}$$

Green Rust Carbonate 1:

$$5Fe(OH)_2 + Fe^{2+} + CO_3^{2-} + 0.5O_2 + 3H_2O$$
$$\rightarrow [Fe_4^{2+}Fe_2^{3+}(OH)_{12}][CO_3 \cdot 2H_2O] \tag{3}$$

$$[Fe_4^{2+}Fe_2^{3+}(OH)_{12}][CO_3 \cdot 2H_2O] + O_2$$
$$\rightarrow 6\alpha-FeO \cdot OH + H_2CO_3 + 4H_2O \tag{4}$$

The Green Rust Carbonates are widely studied because of their occurrence in nature in hydromorphic soils and corrosion products of iron in carbonate/bicarbonate media. The specific surface area and pore volume of goethite were estimated by using ASAP-2020 Micromeritics BET Surface Analyzer and the same were found to be 103 m$^2$ g$^{-1}$ and 0.50 cm$^3$ g$^{-1}$, respectively. The particle size of goethite was measured using CILAS-1180 particle size analyzer. The mean size of goethite particles was found to be 8.77 μm. The iron oxide prepared was subjected to X-ray diffraction and the d values obtained were found to match with that of goethite.

### 2.3. Adsorption experiments

Known quantity of arsenic test solution was taken in 250 ml conical flask and its pH was adjusted to the desired value by using dilute NaOH/HCl. Known weight of goethite was added to the test solution and equilibrated for 1 h with the help of laboratory shaker at constant temperature. After the equilibration time of 1 h, the solutions were filtered through 0.2 μm membrane filter and filtrates were analyzed for arsenic.

Arsenic in the filtrates was analyzed by a hydride generator (HG-2000) coupled with an atomic absorption spectrophotometer (GBC-Avanta). The samples were stored in polyethylene containers and the analysis was performed the same day after conducting the adsorption experiments. The detection limit of arsenic was estimated to be $2 \, \mu g \, l^{-1}$.

The adsorption kinetics was studied by choosing arsenic solutions of $10 \, mg \, l^{-1}$ and $20 \, mg \, l^{-1}$. These values were chosen keeping in the view of the industrial effluents. One hundred milliliters of test solution and an adsorbent dose of 100 mg were taken in 250 ml flasks. The pH of the slurry was maintained constantly at 5.0. Batch adsorption experiments were conducted at $30 \,^\circ C$, $40 \,^\circ C$ and $60 \,^\circ C$, using the constant-temperature water bath fitted with a temperature indicator having a resolution of $\pm 1 \,^\circ C$. After an adsorption time of 15 min, 30 min, 60 min, 90 min, 120 min and 150 min, aliquot portions were taken out, filtered and analyzed for arsenic. The residual concentration at infinite time was determined after elapsing 24 h.

## 2.4. FT-IR characterization studies

The FT-IR spectra of pure goethite and arsenic adsorbed goethite were recorded in KBr media using a Perkin-Elmer spectrophotometer. Ten milligrams of the dried samples was dispersed in 200 mg of spectroscopic grade KBr to record the spectra. Forty scans were collected on each sample at a resolution of $4 \, cm^{-1}$.

## 2.5. Zeta-potential measurements

Zeta-potential measurements were conducted using zeta-meter (zeta-meter Inc., USA). Goethite sample was suspended in 0.1 N KCl solution (electrolyte) and the aqueous suspension was equilibrated at different pH values for 30 min. The equilibrated slurry was injected in to the micro-electrophoresis cell using disposable syringes. The experiments were also conducted in the presence of arsenate. Minimum of ten readings were taken and the mean value was reported. Prior to each measurement, the electrophoresis cell was thoroughly washed and rinsed with deionized water followed by rinsing with the sample solution to be measured.

## 3. Results and discussion

### 3.1. Effect of pH on arsenic adsorption

The effect of pH on the adsorption of arsenic at goethite surface was studied with an initial concentration of $10 \, mg \, l^{-1}$ of arsenic solution. One hundred milligrams of goethite was added to each of the test solution and equilibrated for 1 h. After equilibration, unadsorbed arsenic and the final pH of the solution were measured and the results are shown in Table 1.

From the results, it is apparent that maximum adsorption of arsenic on goethite was observed around pH 5.0. In general, arsenate removal was slightly better in acidic region compared to basic conditions. It was also observed that pH of the slurry was shifted slightly towards higher pH, i.e., towards basic. This

Table 1
Effect of pH on the adsorption of arsenate on goethite

| Initial pH | pH after equilibrium | $x/m$ (mg g$^{-1}$) |
| --- | --- | --- |
| 4 | 4.52 | 4.125 |
| 5 | 6.04 | 4.7 |
| 6 | 6.75 | 3.623 |
| 7 | 7.25 | 2.0 |
| 8 | 8.05 | 1.1 |

Initial concentration of arsenate: $10 \, mg \, l^{-1}$.

slight shift in pH may be attributed to the sorptions reactions of As(V) which releases OH groups from sorbent, as a result of ligand exchange [19]. For better understanding, zeta-potential measurements were also conducted and the results of the same are presented in Fig. 1. The isoelectric point (iep) of goethite was observed at pH 6.7 that is consistent with the value reported in the literature [20]. Below this pH, the goethite particles are predominantly charged positive and above this they are negatively charged. The surface reactions can be represented as [21].

$$=FeOH + H^+ \rightarrow \; =FeOH_2^+ \qquad (5)$$

$$=FeOH \rightarrow \; FeO^- + H^+ \qquad (6)$$

Arsenic acid ($H_3AsO_4$) with $pk$ values of 3.6, 7.3 and 12.5 [22] predominantly exists as $H_2AsO_4^-$ and $HAsO_4^{2-}$ anions in the pH range studied. The maximum adsorption of arsenate on goethite was observed around 6.0 that is close to the iep value. In other words, better adsorption of arsenate is taking place on FeOH sites. The shift in pH indicates that the adsorption of arsenate is taking place by ion exchange mechanism where OH$^-$ ions are replaced with arsenate anions. Further, the shift in iep clearly indicates specific adsorption of arsenate on goethite rather than by purely electrostatic interaction. This type of electro kinetic behavior is generally interpreted due to chemisorption [23].

$$=FeOH + H_2AsO_4^- \rightarrow \; =FeH_2AsO_4 + OH^- \qquad (7)$$
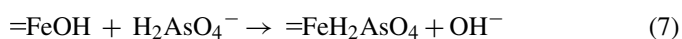
Researchers have shown that arsenate is specifically adsorbed on to iron oxides such as goethite through an inner-sphere complex
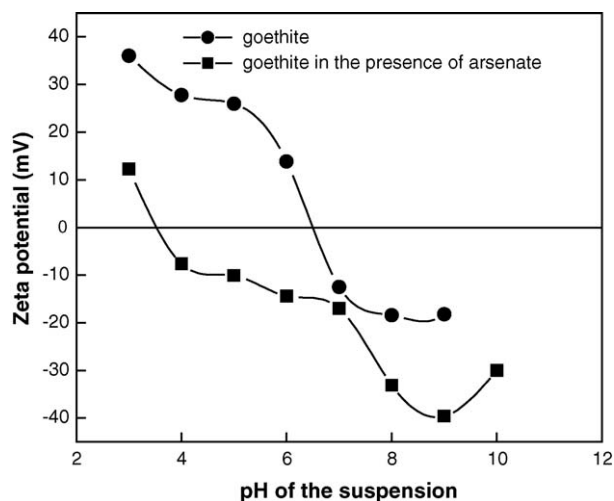


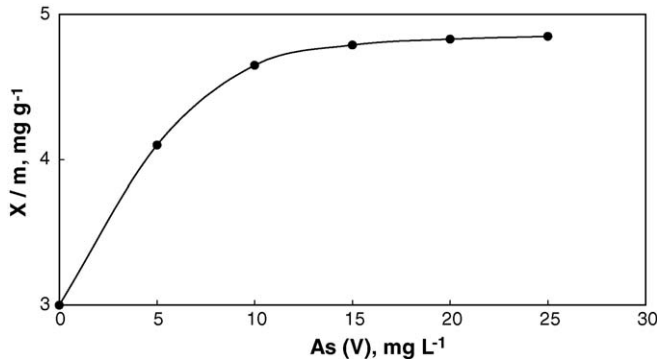Fig. 1. Zeta-potential of goethite in the presence and absence of arsenate.

Fig. 2. Effect of varying concentration of As(V) on adsorption of goethite at pH: 5.0 °C and 29 °C.

via ligand exchange mechanism [24,25]. It was proposed that, at extremely low surface coverage, a ligand exchange reaction of $H_2AsO_4^-$ with surface OH groups formed the monodentate complex. At high surface loadings, the sorption of arsenate was dominated by the formation of bidentate surface complexes after the second ligand exchange reaction.

### 3.2. Effect of initial arsenate concentration

Arsenic solutions at different concentration of $5 \, mg \, l^{-1}$, $10 \, mg \, l^{-1}$, $15 \, mg \, l^{-1}$, $20 \, mg \, l^{-1}$ and $25 \, mg \, l^{-1}$ were treated with 100 mg of goethite at pH 5.0. Fig. 2 shows the effect of varying arsenate concentration against the amount of arsenic adsorbed. The amount of adsorption increases with increasing concentration of arsenic and finally reaches a saturation point. This is due to the fact that by increasing the concentration of arsenate ions in solution, the availability of arsenate ions at the interface also increases, thus enhancing the amount of adsorption. When the surface active sites are covered fully, the extent of adsorption reaches a limit resulting in saturated adsorption.

The adsorption data was analyzed in terms of Langmuir model Fig. 3 and found to obey the same with a correlation coefficient of 0.989. The sorption isotherms of As(V) ions on to akaganeite (β-FeOOH) were determined by Deliyanni et al. [26] and found to fit in to typical Langmuir equation. Adsorption coefficient ($K$) was calculated according to the well-known Langmuir's equation

$$\frac{C_e}{a} = \frac{1}{a_s K} + \frac{C_e}{a_s} \tag{8}$$

where $C_e$ is the equilibrium concentration of adsorbate, $K$ the adsorption coefficient, $a$ and $a_s$ the amount of adsorbate (mg gm$^{-1}$) at equilibrium and saturation, respectively. From the Langmuir adsorption isotherm (Fig. 3), using the ratio of slope to intercept of the linear plot, the value of adsorption coefficient was calculated as $194 \, l \, mol^{-1}$. The diffusion coefficient ($D$) can also be calculated, assuming a Fickian diffusion model. As per this model, the adsorbed mass at any given time $q(t)$ is derived as
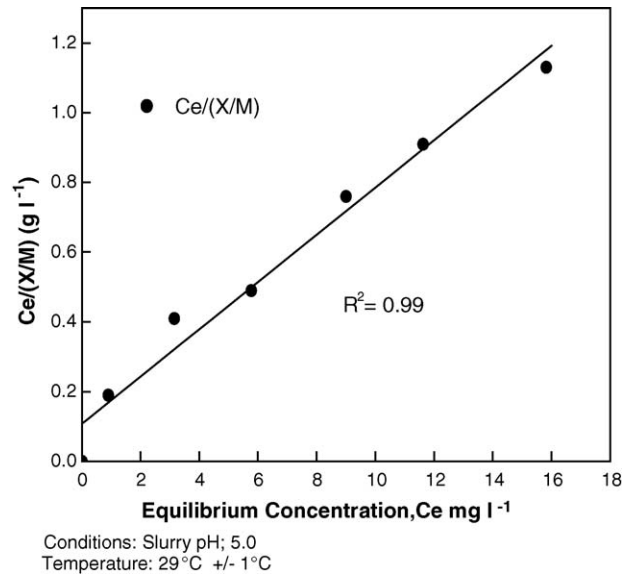
$$q(t) = \frac{2C_0\sqrt{Dt}}{\sqrt{\pi}} \tag{9}$$



Fig. 3. Langmuir adsorption isotherm plot. Conditions: slurry pH: 5.0; temperature: 29 °C ± 1 °C

where $C_0$ is the initial concentration. The diffusion coefficient $D$ for $10 \, mg \, l^{-1}$ arsenic was calculated as $3.84 \times 10^{11} \, cm^2 \, s^{-1}$.

### 3.3. Kinetics of adsorption

The rate of the adsorption can be described as the amount of adsorbate that is adsorbed in unit time and can be written as

$$R_{ad} = \frac{d\alpha}{dt} \tag{10}$$

where $\alpha$ denotes the fraction of adsorbate that has adsorbed (conversion factor) and a dimensionless number. It can also be stated that $\alpha$ denoted the degree of adsorption and can be written as

$$\alpha = \frac{C_0 - C_i}{C_0 - C_\infty} \tag{11}$$

where $C_0$ is the initial concentration of As, $C_i$ the concentration of As in the aqueous phase at time $t$ and $C_\infty$ the concentration of As in the aqueous phase at infinite time.

For a particular isothermal process, the rate of chemical reaction is given by the general formula

$$\frac{d\alpha}{dt} = kf(\alpha) \tag{12}$$

where $k$ is the reaction constant and $f(\alpha)$ the reaction model. On integrating this equation, we get the integral rate law:

$$g(\alpha) = kt \tag{13}$$

where $g(\alpha)$ is the integral form of reaction model.

The temperature dependence of the rate is given by Arrhenius equation
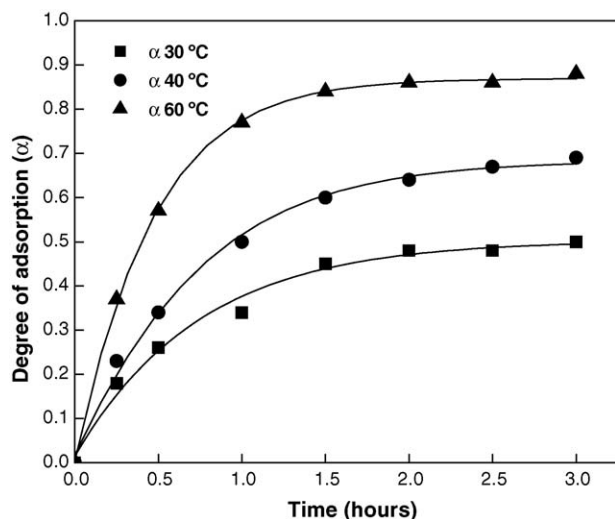
$$k = A \exp{-\frac{E_a}{RT}} \tag{14}$$

Fig. 4. Degree of adsorption ($\alpha$) vs. time. Adsorption conditions: $10\,mg\,l^{-1}$ of arsenic(V), pH: 5.0 mg and 100 mg of goethite.



Fig. 5. Degree of adsorption ($\alpha$) vs. time. Adsorption conditions: $20\,mg\,l^{-1}$ of arsenic(V), pH: 5.0 mg and 100 mg of goethite.

where $A$ is the frequency factor, $E_a$ the activation energy, $R$ the universal constant and $T$ the absolute temperature. Substituting Eq. (13) in the rate Eq. (11), we have

$$\frac{d\alpha}{dt} = A \, \exp -\frac{E_a}{RTf(\alpha)} \qquad (15)$$

and hence

$$g(\alpha) = A \, \exp -\frac{E_a}{RTt} \qquad (16)$$

Kinetic analysis of isothermal data can be conveniently done by either using conventional model-fitting methods or model free isoconversional methods. In the first option, it is possible to calculate activation energy ($E_a$) and frequency factor ($A$) while in the second, activation energy ($E_a$) can only be calculated.

The standard isoconversional method [27] is based on taking natural logarithm of Eq. (16) and can be written as

$$-\ln\, t = \ln \left[ \frac{A}{g(\alpha)} \right] - \frac{E_a}{RT} \qquad (17)$$

A plot of $-\ln t$ against $1/T$ at each $\alpha$ yields $E_a$ from the slope for that $\alpha$ regardless of the model.

The reason for choosing the 'model free' method of kinetic analysis is based on the fact that any misidentification of the kinetic model has got a profound effect on the values obtained for the Arrhenius parameters. Sewry and Brown [28] and Galwey [29] have critically reviewed the usage of various kinetic models and asserted that caution has to be exercised in choosing the right kinetic model.

The alpha versus time plots (Figs. 4 and 5) of $10\,mg\,l^{-1}$ and $20\,mg\,l^{-1}$ arsenic show that adsorption of arsenic progressively increased with time and attained almost saturation after 1–2 h. Also, it is seen that with increase in temperature, the extent of adsorption also increased. Using these conversion-time plots, for various quantities of fixed alpha, the conversion time were known and subsequently, $-\ln t$ versus $1/T$ were plotted. From the slope, activation energy ($E_a$) was calculated. Fig. 6 shows the
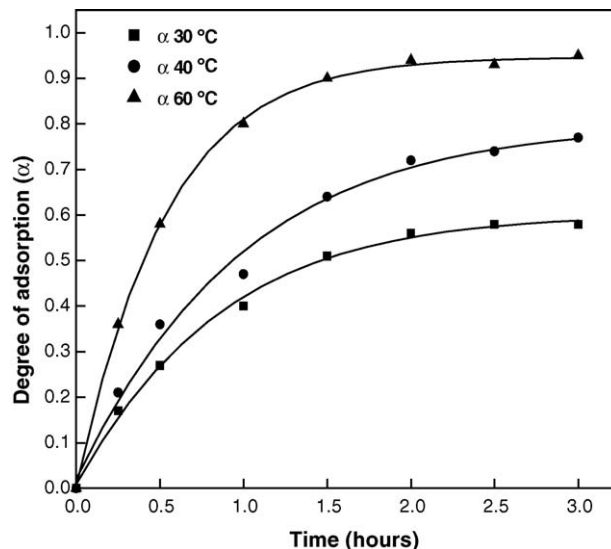
graph drawn for $\alpha$ versus $E_a$ for $10\,mg\,l^{-1}$ and $20\,mg\,l^{-1}$ arsenic and it is seen that $E_a$ varies from $20\,kJ\,mol^{-1}$ to $40\,kJ\,mol^{-1}$ and $22\,kJ\,mol^{-1}$ to $43\,kJ\,mol^{-1}$, respectively. The $E_a$ values indicate that the low values of adsorption ($<25\,kJ\,mol^{-1}$) suggest that the initial phase adsorption is diffusion controlled whereas the latter part ($>25\,kJ\,mol^{-1}$) by chemically controlled processes. Though the concept of variation of $E_a$ is not accepted theoretically, in reality there is no conflict because the condition of simple homogeneous system is seldom encountered in practice. An elementary reaction could also show variation in activation energy during its progress because of heterogeneous nature of solids. The change in kinetics is attributed to product formation and other factors like crystal defects, steric hindrances or electrostatic repulsion of adsorbed molecules to the forthcoming adsorbate species. Liu and Huang [30], in their study of adsorption of lead on iron oxides found that increasing temperatures promoted the adsorption and reported $E_a$ values ranging
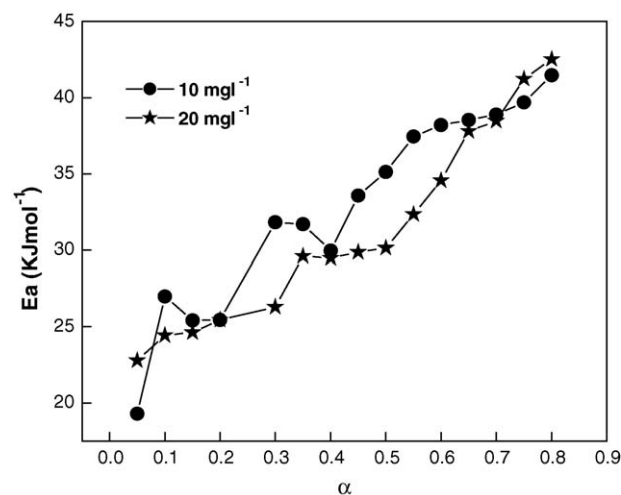


Fig. 6. Degree of adsorption ($\alpha$) vs. activation energy ($E_a$) for $10\,mg\,l^{-1}$ and $20\,mg\,l^{-1}$ arsenic(V), pH: 5.0 mg and 100 mg of goethite.
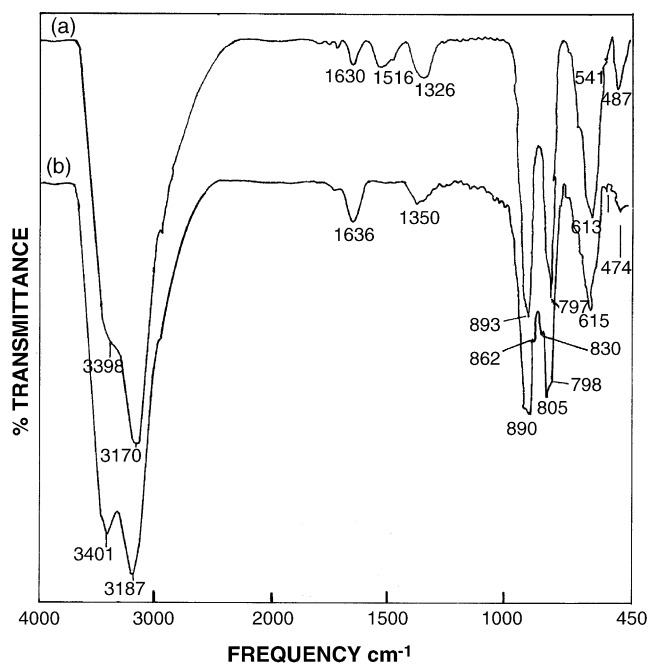
Fig. 7. FT-IR spectra: (a) pure goethite; (b) As adsorbed goethite (100 mg of goethite treated with 15 mg l$^{-1}$ arsenic(V) at pH: 5.0 °C and 30 °C).

from 21 kJ mol$^{-1}$ to 53 kJ mol$^{-1}$ and they concluded that the first phase was by diffusion but changed to chemical later.

## 4. FT-IR studies

Fig. 7 shows FT-IR spectra in which spectrum (a) is for pure goethite and spectrum (b) is for goethite treated with 15 mg l$^{-1}$ arsenic at pH 5.0 at 30 °C. The bands at 797 cm$^{-1}$ and 893 cm$^{-1}$ in spectrum (a) are characteristic of goethite and arise due to $\gamma$ and $\delta$ −OH bending modes of out and in plane modes. The intense band at 3170 cm$^{-1}$ is due to the bulk −OH stretching. The symmetric stretching of Fe−O is indicated by a band at 613 cm$^{-1}$ [31]. In spectrum (b), bands at 862 cm$^{-1}$ and 830 cm$^{-1}$ could be assigned to HAsO$_4^-$ ion and As−O−Fe groups. This clearly indicates that arsenate is not only bound through Fe−O bonding but also by non-surface complexed As−O bonds of adsorbed arsenate species. The bands at 805 cm$^{-1}$ and 890 cm$^{-1}$ matches well with the stretching frequencies of As−O bonds in AsO$_4^{3-}$ and H$_2$AsO$_4^-$ groups. The spectral data is in good agreement with the results of FT-IR characterization of arsenic adsorbed on ferric oxide reported by Goldberg and Johnston [32] and supports the concept of surface complex formation. Arienzo et al. [19] studied the adsorption of arsenic and found that the electrochemically generated hydrous ferric oxide removed both arsenite and arsenate from aqueous phase. But they confirmed that there was no formation of ferric arsenate phase such as scorodite. The EXFAS studies of O' Reilly et al. [33] indicated that arsenate predominantly sorbed on goethite as a bidenate binuclear complex and interestingly this bond was quite stable for months.

The surface area analysis indicated that specific surface area of goethite after adsorption (50 mg l$^{-1}$ arsenate at pH 5) increased from 103 m$^2$ g$^{-1}$ to 120 m$^2$ g$^{-1}$. But there was a decrease in specific pore volume from 0.50 cm$^3$ g$^{-1}$ to 0.36 cm$^3$ g$^{-1}$. The enhanced area with simultaneous decrease in volume could be interpreted due to surface complexation that could create "microcontours". According to literature, pore volume and size are considered to be more important factor rather than surface area [34] for effective adsorption processes.

## 5. Conclusion

Goethite with high surface area was synthesized from ferrous sulfate treated with sodium lauryl sulfate and sodium carbonate. Batch experiments of adsorption were conducted to study the efficacy of removal of arsenic(V) from aqueous solutions. The optimum pH of adsorption was determined to be 5.0. The zeta-potential measurements have indicated that the arsenate is adsorbed on goethite by chemisorption. The adsorption data showed that Langmuir isotherm was the best fit and using the plot, the diffusion and adsorption coefficients of arsenate ion were calculated to be $3.84 \times 10^{11}$ cm$^2$ s$^{-1}$ and 194 l mol$^{-1}$. Isoconversional methods were employed to study the kinetics of adsorption process. The activation energy of adsorption reaction was of the order of 20 kJ mol$^{-1}$ to 43 kJ mol$^{-1}$, indicating that the initial phase of arsenic adsorption is through diffusion control, later switching over to chemical mode. FT-IR characterization of arsenic adsorbed goethite conclusively proved the formation of As−O−Fe bonds and also the presence of As−O bonds due to adsorbed arsenate species and these results eventually support the theory of surface complex formation.

## References

[1] D. Das, A. Chatterjee, B.K. Mondal, G. Samanta, B. Chanda, D. Chakraborti, Arsenic in ground water in six districts of West Bengal, India: the biggest calamity in the world. Part 2. Arsenic concentration in drinking water, hair, nail, urine, skin scale and liver tissues (biopsy) of the affected people, Analyst 120 (1995) 217–224.
[2] J.F. Ferguson, J. Gavis, Review of the arsenic cycle in natural waters, Water Res. 6 (1972) 1259–1274.
[3] J.G. Hering, P.Y. Chen, J.A. Wilkie, M. Elimelech, Arsenic removal by ferric chloride, J. Am. Water Works Assoc. 88 (1996) 155–167.
[4] M.L. Pierce, C.B. Moore, Adsorption of arsenite and arsenate on amorphous iron hydroxide, Water Res. 16 (1982) 1247–1253.
[5] A. Jain, K.D. Ravene, R.H. Loeppert, Arsenite and arsenate adsorption on ferrihydrite: surface charge reduction and net OH$^-$ release stoichiometry, Environ. Sci. Technol. 33 (1999) 1179–1184.
[6] W. Zhang, P. Singh, W. Paling, S. Delides, Arsenic removal from contaminated water by natural iron ores, Miner. Eng. 17 (2004) 517–524.
[7] S. Chakravarty, V. Durej, G. Bhattacharyya, S. Maity, S. Bhattacharjee, Removal of arsenic from ground water using low cost ferruginous manganese ores, Water Res. 36 (2002) 625–632.

[8] I.A. Katsoyiannis, A.I. Zouboulis, Removal of arsenic from contaminated water sources by sorption onto iron-oxide-coated polymeric materials, Water Res. 36 (2002) 5141–5155.

[9] S. Tokunaga, S.A. Wasay, S.W. Park, Removal of arsenic(V) ion from aqueous solution by lanthanum compounds, Water Sci. Technol. 35 (1997) 71–78.

[10] B. Sunbaek, K.P. George, M. Xiaoguang, Removal of arsenic from water by zero-valent iron, J. Hazard. Mater. 121 (2005) 61–67.

[11] L. Zeng, A method for preparing silica-containing iron(III) oxide adsorbents for arsenic removal, Water Res. 37 (2003) 4351–4358.

[12] L. Lorenzen, J.S.J. Van Deventer, W.M. Landi, Factors affecting the mechanism of the adsorption of arsenic species on activated carbon, Miner. Eng. 8 (1995) 557–569.

[13] S. Kundu, S.S. Kavalakatt, A. Pal, S.K. Ghosh, M. Mandal, T. Pal, Removal of arsenic using hardened paste of portland cement: batch adsorption and column study, Water Res. 38 (2004) 3780–3790.

[14] R. Anuradha, S. Tawachsupa, M. Isleyen, Batch-mixed iron treatment of high arsenic waters, Water Res. 35 (2001) 4474–4479.

[15] M.L. Farquhar, J.M. Charnock, F.R. Livens, D.J. Vaughan, Mechanisms of arsenic uptake from aqueous solution by interaction with goethite, lepidocrocite, mackinawite and pyrite: an X-ray absorption spectroscopy study, Environ. Sci. Technol. 36 (2002) 1757–1762.

[16] B. Daus, R. Wennrich, H. Weiss, Sorption materials for arsenic removal from water; a comparative study, Water Res. 38 (2004) 2948–2954.

[17] M. Kosmulski, S. DurandVidal, E. Maczka, J.B. Rosenholm, Morphology of synthetic goethite particles, J. Colloid Interface Sci. 271 (2004) 261–269.

[18] D.N. Bakayannakis, E.A. Deliyanni, A.I. Zouboulis, K.A. Matis, L. Nalbandian, Th. Kehagias, Akaganeite and goethite-type nanocrystals: synthesis and characterization, Microporous Mesoporous Mater. 59 (2003) 35–42.

[19] M. Arienzo, P. Adamo, J. Chiarenzelli, M.R. Bianco, A.D. Martino, Rentiontion of arsenic on hydrous ferric oxides generated by electrochemical peroxidation, Chemosphere 48 (2002) 1009–1018.

[20] I. Iwasaki, S.R.B. Cooke, A.F. Colombo, U.S. Bureau of Mines, RI 5593, 1960.

[21] D. Suvasis, G.H. Janet, Comparison of arsenic(V) and arsenic(III) sorption onto iron oxide minerals: implications for arsenic mobility, Environ. Sci. Technol. 37 (2003) 4182–4189.

[22] K.W. Whitten, K.D. Gailey, R.E. Davis, General Chemistry with Quantitative Analysis, fourth ed., Saunders College Publishers, Orlando, 1999.

[23] Pradip, On the interpretation of electro kinetic behaviour of chemisorbing surfactant system, Trans. Indian Inst. Met. 41 (1988) 15–25.

[24] T. Hiemstra, W.H. Van Riemsdijk, Surface structural ion adsorption modeling of competitive binding of oxyanions by metal (hydr)oxides, J. Colloid Interface Sci. 210 (1999) 182–193.

[25] D.M. Sherman, S.R. Randall, Surface complexation of arsenic(V) to iron(III) (hydr)oxides: structural mechanism from ab initio molecular geometries and EXAFS spectroscopy, Geochim. Cosmochim. Acta 67 (2003) 4223–4230.

[26] E.A. Deliyanni, D.N. Bakoyannakis, A.I. Zouboulis, K.A. Matis, Sorption of As(V) ions by akaganeite-type nanocrystals, Chemosphere 50 (2003) 155–163.

[27] S. Vyazovkin, Computational aspects of kinetic analysis. Part C. ICTAC kinetics project—the light at the end of the tunnel, Thermochim. Acta 355 (2000) 155–163.

[28] J.D. Sewry, M.E. Brown, Model-free kinetic analysis, Thermochim. Acta 390 (2002) 217–225.

[29] A.K. Galwey, Eradicating erroneous Arrhenius arithmetic, Thermochim. Acta 399 (2003) 1–29.

[30] C. Liu, P.M. Huang, Kinetics of lead adsorption by iron oxides formed under the influence of citrate, Geochim. Cosmochim. Acta 67 (2003) 1045–1054.

[31] R.M. Cornell, U. Schwertmann, The Iron Oxides Structure, Properties, Reaction Occurrences and Uses, VCH Publishers, New York, 1996.

[32] S. Goldberg, C.T. Johnston, Mechanisms of arsenic adsorption on amorphous oxides evaluated using macroscopic measurements vibrational spectroscopy and surface complex modeling, J. Colloid Interface Sci. 234 (2001) 204–216.

[33] S.E. O' Reilly, D.G. Strawn, D.L. Sparks, Residence time effect on arsenate adsorption/desorption mechanism on goethite, Soil Sci. Soc. Am. J. 65 (2001) 67–77.

[34] E. Diamadopoulos, P. Samaras, G.P. Sakellaropoulos, The effect of activated carbon properties on the adsorption of toxic substances, Water Sci. Technol. 25 (1995) 153–160.