

A Comparative Study of Sorption Of As (V) Ions On Nanoparticle Hematite, Goethite and Magnetite

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Abstract

Hematite (α -Fe₂O₃), magnetite (Fe₃O₄) and goethite (α -FeOOH) nanoparticles were synthesized by transformation of ferrihydrite and precipitation methods, these materials were used for the removal of arsenic (V) ions from aqueous solution. The synthesized nanoparticles were characterized by some physico chemical and spectroscopic methods such as bulk density, point of zero charge (pzc), micropore volume, surface area, x-ray diffraction, x-ray fluorescence, fourier transform infra-red, Scanning and Transformation electron microscopy. The characteristic properties of the iron oxides show that the samples were nanoparticle in size with surface area in the range 45.3 to 56.1m²/g. The x-ray diffraction showed the sample had crystal structures of hematite, goethite and magnetite of 84.3% - 95% respectively.

The adsorption experiment results revealed that equilibrium was reached within 120 minutes of the adsorption process and it was pH dependent where optimum pH was at 3 – 4. Furthermore, batch adsorption isotherm studies were performed to determine the adsorption capacity of As (V) on the nanoparticles. The adsorption data was found to fit the Langmuir, Freundlich, Temkin and Dubinin Radushkevich isotherm. The overall results of this study showed that the synthesized nanostructured hematite, goethite and magnetite are very effective for the removal of As (V) from aqueous solution. These materials offer great potential for environmental technological applications in industries and it is recommended for the decontamination of real industrial effluent.

Keywords: Sorption, Arsenate, Nanoparticles, Hematite, Goethite, and Magnetite.

1.0 Introduction

Arsenic, a toxic and possible carcinogenic element [1] is occurring in many natural waters, as well as in various industrial wastes, solid or liquid. It is one of the most toxic of contaminants found in the environment. It enters the environment from anthropogenic sources such as petroleum refineries, fossil fuel power plants, non ferrous smelting activities and from ceramics, semi conductors, pesticides and fertilizer production [2-4]. The discharge of arsenic waste into waterways, even at low concentration may adversely affect human health as well as that of flora and fauna. Exposure to elevated arsenic levels has been attributed to adverse health related issues such as changes in skin pigmentation, diabetes, lung ailments and cancers of the kidney and bladder [5]. According to World Health Organization (WHO), the maximum allowed concentration of arsenic in drinking water is 10.0µg/L [WHO].

Arsenic can be found in two different oxidation states, As (V) which dominates under oxidizing conditions and As (III) which is the predominant species in reducing environments. Bangladesh and the West Bengal in India are the two areas in the world that shows the most severe arsenic ground water contamination [6]. Several technologies including membrane filtration, coagulation and phytoremediation have been developed for arsenic removal from aqueous solutions, and adsorption is

considered as an effective technology. Adsorption offers many advantages including simple and stable operation, easy handling of waste, absence of added reagents, compact facilities and generally lower operation cost.

Iron oxides have been proven to be excellent adsorbent with high affinity towards inorganic arsenic species and selectivity in the adsorption process [2, 3, 7]. Mamindy-Pajany et al carried out sorption studies of arsenic onto commercial hematite and goethite at different pH and ionic strength. They observed more than 80% arsenic removal at pH values corresponding to natural water for both hematite and goethite. The result of the sorption experiments showed that there was no effect of ionic strength on arsenate adsorption suggesting the formation of inner sphere surface complex.

In order to obtain useful information on the adsorption characteristics of nanostructured iron oxides and compare their adsorption characteristics we reported simple synthetic approach to produce hematite (α -Fe₂O₃), magnetite (Fe₃O₄) and goethite (α -FeOOH). The produced iron oxides were characterized by FTIR, transmission electron microscopy (TEM), scanning electron microscopy (SEM), x-ray diffraction (XRD) and x-ray fluorescence (XRF), the adsorption capacity of As (V) on the iron oxides types was investigated in order to compare their adsorption effectiveness.

2.0 Experimental

2.1 Preparation of Nanoparticle Iron Oxides

Three different types of iron oxides (hematite, goethite and magnetite) were prepared in this study. All chemicals used in the preparation were of reagent grade obtained from Sigma Aldrich and Merck.

Nanoparticle hematite was prepared by preheating 40g of $\text{Fe}(\text{NO}_3)_3$ (Sigma Aldrich 99.9% purity) dissolved in 500ml of deionized water at 90°C . Three hundred milliliters (300ml) of the preheated 1M potassium hydroxide was added to the solution to precipitate ferrihydrite, 50ml of preheated 1M NaHCO_3 was then added to the brown voluminous precipitate. The suspension at pH 8 - 9 in a close polyethylene flask was held at 90°C for 48 hours. The brownish-red voluminous precipitate was washed by dialysis and filtered by millipore glass membrane vacuum filtration system and dried at 40°C [8].

Nanoparticle goethite was prepared by the method proposed by Schwertmann and Cornell [8]. The preparation was carried out under nitrogen atmosphere. 100ml of freshly prepared 1M $\text{Fe}(\text{NO}_3)_3$ solution by dissolving ferric nitrate hepta hydrate salt in milliQ water of $18.2\text{M}\Omega$ resistivity was poured out into a 2L flask and 180ml of 5M KOH added with stirring. The suspension was diluted with milliQ water to 2L capacity and held in closed polyethylene flask at 70°C for 60 hours. The precipitate was washed by dialysis, filtered by millipore glass membrane vacuum filtration system and dried at 60°C . Nanoparticle magnetite was prepared by dissolving 9.05g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in 500ml deionized water of $18.2\text{M}\Omega$ resistivity. The pH of solution which was initially 3.82 was adjusted to pH 11 by slowly adding 35ml of 2 M NaOH. The mixture was homogenized by stirring at 1800rpm in order to obtain the precipitate of magnetite. The precipitate was aged at room temperature for 24 hours, washed several times by dialysis and filtered using a $0.45\mu\text{m}$ millipore filter paper in a vacuum filtration system. The precipitate was dried at room temperature.

2.2 Nanoparticle Characterization

The particles were characterized using infrared spectroscopy (Perkin Elmer FT-IR Spectrometer 1000) The morphology of the particles were determined using scanning electron microscopy (SEM) (Leo 1430VP and FEI Nova NanoSEM) 230 scanning electron Microscope). The particle size of

Results and Discussion

3.1 Surface and physico-chemical properties of $\alpha\text{-Fe}_2\text{O}_3$, Fe_3O_4 and FeOOH nanoparticles

the Nanoparticle iron oxides were determined by transmission electron microscopy (TEM). The TEM images were taken with a Technai G²20 high resolution transmission electron microscope fitted with a Lanthanum hexaboride (LaB_6) filament and operated at 200kv.

The surface area, micropore volume and micropore area of the nanoparticles were measured according to Brunauer- Emmett-Teller (BET) Micrometrics TRISTAR 3000 through Nitrogen adsorption at -196°C .

The crystal structure of $\alpha\text{-Fe}_2\text{O}_3$, $\alpha\text{-FeOOH}$ and Fe_3O_4 were analyzed by x-ray diffraction (XRD) on a PW 3050/60 Goniometer x-ray power diffractometer using $\text{CuK}\alpha$, with scanning speed of 2°min^{-1} . X-ray fluorescence was used for the elemental composition of the synthesized iron oxides. The measurement was carried out using a PAnalytical Xpert Pro MPD x-ray fluorescence.

2.3 Batch Arsenic (VI) Adsorption Experiments

2.3.1 Adsorption capacity

Adsorption experiments were carried out at room temperature and pH 7 in 50ml polyethylene tubes. A constant mass of adsorbent (20mg) was put in contact with 20cm^3 of arsenate solution of concentrations 1, 2, 4, 5, 10 and 20 mg/L. The arsenate As (V) stock solution was prepared by dissolving 4.164g $\text{NaHASO}_4 \cdot 7\text{H}_2\text{O}$ (Sigma-Aldrich, $\geq 98.0\%$) in a standard flask using boiled milliQ water of $18.2\text{M}\Omega$ resistivity. The suspension were shaken on an orbital shaker (GEFRAN 600 model) for 240 minutes until equilibrium was attained or reached. All samples were tested in duplicate for statistical purposes. The suspensions were filtered and analyzed after equilibration using spectro-inductively coupled plasma (ICP) for total arsenate. The amount of As (V) adsorbed was calculated by subtracting final concentration in aqueous solution from the initial arsenic concentration. The amount adsorbed (q) was calculated as follows:

$$\text{Amount adsorbed (q)} = \frac{(C_i - C_f)V}{W}$$

Where C_i and C_f (mg/L) are the initial and final concentration of As (V) at time t in the solutions respectively, W the amount of the adsorbent used in grams and V is the volume of As (V) solution in litres.

The analysis was performed using calibration curves with correlation coefficient (R^2) of 0.99 or better.

The surface and physicochemical properties of the synthesized iron oxides nanoparticles are shown in Table 1.

Table 1: The physico-chemical properties of synthesized iron oxide nanoparticles

Iron oxides	Colour	pH	Bulk density (g/cm ³)	Pzc	Texture	% yield
Hematite	Reddish brown	9.06	1.417	9.35	Fine	81.3
Goethite	Yellowish brown	9.48	1.648	9.10	Fine	93.4
Magnetite	Black	7.1	1.354	7.56	Fine	92.9

As shown in Table 1, the colour of hematite, goethite and magnetite are reddish brown, yellowish brown and black respectively. These are in line with the colour for different iron oxides reported by different authors Schwertmann [8], Duhan and Devi [9] and Mohapatra et al (2010). The BET surface area of the iron oxides nanoparticles were 45.3m²/g, 56.1m²/g and 52.48 m²/g for hematite, goethite and magnetite respectively. The micropore volume for the nanoparticles were in the range 0.0004 -0.0142 cm³/g. These nanoparticles have relatively large

surface areas and pore volumes which are desirable qualities for good adsorption capacity.

3.3 Morphology and crystal structure of iron oxide nanoparticles

Scanning Electron Microscopy (SEM) images show that the iron oxides have different sizes and shapes. The figures show agglomeration of particles that are plate-like in shape, goethite nanoparticles were needle-like in shape while that of magnetite revealed agglomerates of different spherical

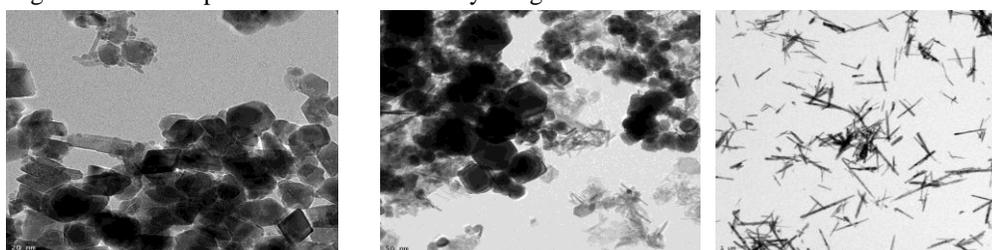


Fig. 1a,b,c: TEM micrograph of hematite, magnetite and goethite

The diffraction pattern confirmed the peaks at 2θ for crystalline hematite, goethite and magnetite nanoparticles. No diffraction line corresponding to other phases were observed indicating high purity of samples. Therefore, it can be confirmed that iron

oxides synthesized were in the form of α- Fe₂O₃, Fe₃O₄ and α- FeOOH. The results of X-ray diffraction was also supported by the X-ray Fluorescence (XRF) and Energy dispersive X-ray (EDX) analysis.

Table 2: Kinetics Parameters For As (V) Adsorption on Iron Oxide Nanoparticles

Kinetic Models	Hematite	Goethite	Magnetite
Pseudo- First order			
q _e	1.21	1.38	2.10
K ₁ (min ⁻¹)	4.61x10 ⁻³	9.21x10 ⁻³	4.6x10 ⁻³
R ²	0.818	0.767	0.924
Pseudo-Second order			
q _e	2.67	2.99	4.29
K ₂	3.77x10 ⁻²	2.01x10 ⁻²	2.62x10 ⁻²
R ₂	0.991	0.992	0.983

Due to the good agreement between the kinetic model fit and experimentally observed equilibrium

adsorption capacity in addition to the high correlation coefficients, this suggests that arsenate adsorption

followed pseudo second-order kinetics and As (V) ions were adsorbed onto iron oxide surfaces via a chemical interaction.

The Langmuir adsorption isotherm fitted the experimental data for all samples: hematite, magnetite and goethite with q_m values ranging from 0.299 to 1.47 mg/g and correlation coefficients (R^2) of 0.937 to 0.971 respectively. The Freundlich constants K_f which is related to the adsorption capacity and n related to adsorption intensity were determined from the slope and intercept of the plot of $\log q_e$ versus C_e . In this study n value was greater than unity indicating chemisorptions for goethite sample with a correlation coefficient of 0.895. The experimental data does not fit the Freundlich isotherm model for hematite and magnetite with a correlation coefficient of 0.403 and 0.460 respectively. The linear plots of Temkin adsorption isotherm which consider chemisorption of an adsorbate onto adsorbent also describe the isotherm data fairly with correlation coefficients in the range ($0.633 < R^2 < 0.979$) for As (V) adsorption. Hematite and goethite fitted Temkin isotherm best. The

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Temkin isotherm constants and the constant related to heat of sorption are in the range of 0.989 to 112.2L/mg and 2.33 to 4.44kJ/mol for the different iron oxides respectively. This further supports the findings that the adsorption of arsenate onto iron oxides particles is a chemisorption process.

Conclusion

Nanoparticles hematite, goethite and magnetite were prepared using different methods and their performance for As (V) removal from aqueous solution were investigated by batch adsorption experiments. As (V) maximum adsorption capacities were in the range 0.266-1.47mgg⁻¹ for the iron oxide types. Adsorption experiments were performed under different physico-chemical conditions (pH, initial arsenic concentration, time) on three synthetic adsorbents: hematite, goethite and magnetite nanoparticles. Results showed that arsenate adsorption rate is dependent on pH, initial concentration and the time. Hematite, magnetite and goethite showed good adsorption characteristics.

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