



Sorption of Arsenic (III) by Oxides of Coated Sand

Dharmendra^{1,*}, R.C.Vaishya², S.C. Prasad²

¹Department of civil engineering, NIT, Hamirpur (H.P) – 177005 (India)

²Department of Civil engineering, Motilal Nehru National Institute of Technology, Allahabad, India

*E-mail: djha24@yahoo.com

Abstract

A granular media known as Iron Oxide-Coated Sand (IOCS) developed in the laboratory by coating ferric nitrate on quartz sand surface by a simple and easy process has proved more effective than plain sand. Isothermal studies showed that the uptake potential of IOCS media dependent on pH, sorbate concentrations, ionic strength of sorbate. Uptake capacity of IOCS studies based on Langmuir and Freundlich model. The main aim of these studies was to develop economic and efficient IOCS for removal of As in which less skill required. In the present studies, Fe oxide coating and uptake capacity of As (III) were achieved 5.08 mg Fe/g and 0.230 mg/g respectively. The result of column studies indicated that it has the desired characteristics for successful continuous flow mode operations. The IOCS proved to be viable and cost effective alternative as a filter medium for arsenic removal from contaminated groundwater of developing countries.

Key words: adsorption, Iron oxide-coated sand, sorption, oxides

Introduction

Arsenic is omnipresent in the environment and is a toxic element for the general population, which is mainly exposed to arsenic via drinking water and marine food. While organic arsenic species like dimethylarsinic acid (DMA), for example, with a median lethal doses in animals LD^{50} (DMA) = 1200 mg/kg, are found as non-toxic compounds, the inorganic arsenite with LD^{50} (As^{3+}) = 4.5 mg/kg and arsenate LD^{50} (As^{5+}) = 14 mg/kg which makes no great difference, should be considered to be rather toxic. Most of the international drinking water standards are in the range of 0.04–0.05 mg/L. In India, per BIS 10500 (1991), a maximum arsenic level of 50 μ g/L has been permitted in groundwater supplies for drinking purposes. Based on human health data, an As concentration of 10 μ g/L has been recommended by WHO as a guideline value for drinking water (WHO, 1993) Consequently, there is growing interest in using low-cost materials to remove arsenic from water. One promising method appears to be adsorption from solution. In the study stage this removal technique is carried out in batch experiments, columns or fixed bed reactors, and

offers remarkable advantages. Trivalent and pentavalent arsenic species in aqueous solutions were adsorbed onto activated carbon impregnated with silver and copper (Rajaković, 1992). The adsorption of arsenic, both as As (III) and as total arsenic, has also been studied using a variety of natural materials including sand, clay, kaolinite, bentonite, montmorillonite, goethite (Pokonova, 1998), spodic, (Lindberg *et al.*, 1997) and aquifer material from mining areas, (Carrillo *et al.*, 1998). The removal of As (III) and As (V) has been studied in detail using antimony pentoxide and manganese dioxide (Galer *et al.*, 1997) as well as anthranol compounds (Tokunaga *et al.*, 1997), iron hydroxides (Driehaus *et al.* 1998; Raven *et al.*, 1998) and iron-coated catalyst (Huang *et al.*, 1997). However, comparatively few published papers deal with ion exchange for arsenic elimination (Vagliasindi *et al.*, 1998).

Recently, several researchers have developed techniques for coating iron oxide onto the surface of sand to overcome the problem of using iron oxide powders in water treatment. Iron-coated sand has been tested for removal of cationic as well as anionic metals from synthetic and real wastes (Edwards *et al.*, 1989; Stahl *et al.*, 1991; Bailey *et al.*, 1992; Lai *et al.*, 1994; Lo *et al.*, 1994). The results from these studies confirm that the utilization of iron-coated sand for trace element removal from water is worth developing. The applications of iron-coated sand are influenced by the coating techniques. Iron oxide formed from $\text{Fe}(\text{NO}_3)_3$ is composed of mainly amorphous iron oxides and a small amount of crystalline iron oxides (Lo *et al.*, 1994; Baltpurvins *et al.*, 1996). But the type of iron oxide coating produced depends on the physical and chemical environments at which iron oxide was prepared and coated.

Materials and Methods

Reagents and stock solution

All the chemicals used in the study were of analytical grade and used without further purification. Distilled water was used in preparation of all the solutions. For all the batch adsorption experiments, stock solutions containing 100 mg/L of As(III) were prepared by dissolving 0.1734 g of Sodium arsenite (Na AsO_2) (LOBA Chemie) in 1000 ml distilled water. Working solutions, as per the experimental requirements, were freshly prepared from the stock solution for each experimental run. Ferric nitrate $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Merck) was used for the coating process. 0.1N HCl (Merck) and 0.1N NaOH (Merck) solutions were used for pH adjustment.

All glassware (Borosil make) used was made of borosilicate glass. All glassware was chromic acid washed and rinsed with DI water. All the chemicals were of AR grade and used without further purification. A stock solution of As (III) was made using distilled water.

Equipment

pH measurements were made on a pH meter, Model Thermo Orion 420A+. Arsenic determination was carried out with Genesys-20 by Thermo spectronic.

Synthesis and characterization of the adsorbent

In this study sand was used as base of adsorbent materials and Ferric nitrate ($\text{Fe}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$) salts used as coating material for arsenic removal. The sand was procured from the bank of river Yamuna. Sand washed by tap water until completely clean, and dried under the sunlight. The sand dried in the oven overnight at temperature 105°C . Oven dry sand sieved and size of sand selected on geometric mean size $[(d_1d_2)^{0.5}]$, where d_1 and d_2 are the sieve openings for particles retained and particle passed respectively].

Coating method: IOCS-I

Above mentioned cleaned and sieved size sand (geometric size of 0.547 mm) taken by weight and 10% of sand, ferric nitrate homogeneously dry mixed. Mixed sand poured with water at the rate of 30% by weight of sand, and then after heated over gas stove into the iron frying pan, and continuously stirred by iron spoon. After reaching to the boiling point, lowering to gas flame and continuously stirred until completely dried and within 60 minute (approx) coated over the sand. Coated sand cooled at room temperature. The coated sand washed with tap water until washing were clear, also washed with distilled water. The washed coated sand is dried in oven at 105°C until dry. The coated sand cooled and stored in plastic jar for further use.

Coating method: IOCS-I-A (without water)

Above mentioned cleaned and sieved size sand taken by weight and 10% of sand, ferric nitrate homogeneously dry mixed, then after heated over gas stove in iron frying pan and continuously stirred by iron spoon. Within 10 minute ferric nitrate completely dried and coated over the sand. Coated sand cooled at room temperature. The coated sand washed with tap water till washing were clear, also washed with distilled water. The washed coated sand is dried in oven at 105°C till dry. The coated sand cooled and stored in plastic jar for further use.

Coating method: IOCS-II (dry under sunlight)

Above mentioned cleaned and sieved size sand taken by weight and 10% of sand, ferric nitrate homogeneously dry mixed, then after heated over gas stove in iron frying pan and continuously stirred by iron spoon. Within 10 minute ferric nitrate completely dried and coated over the sand. Coated sand cooled under sunlight at ambient temperature. Again it dried because sand become sticky and the coated sand washed with tap water till washing were clear, also washed with distilled water. The washed coated sand is dried in oven at 105°C till dry. The coated sand cooled and stored in plastic jar for further use.

Coating method: IOCS-III (pressure cooker)

Above mentioned cleaned and sieved size sand taken by weight and 10% of sand, ferric nitrate homogeneously dry mixed, then after heated over gas stove in pressure cooker with water and continuously heated till water vapor end. Within 30 minute ferric nitrate completely dried and coated over the sand. Coated sand cooled under room temperature. The coated sand washed with tap water till washing were

clear, also washed with distilled water. The washed coated sand is dried in oven at 105 °C till dry. The coated sand cooled and stored in plastic jar for further use.

To measure the total iron on the surface of the coated sand, 1g of IOCS was poured in 30ml of (1:1 HNO₃) and heat gently on a hot plate until volume-reduced approx 5 ml. It was cooled at room temperature and again boiled with 10ml of (1:1 HNO₃) until volume-reduced approx 5 ml. After digestion, the solution was filtered through whatman filter paper. The sand was rinsed with distilled water during filtration to remove the remaining iron. The quantity of Fe in the filtrate was determined by atomic absorption spectrophotometer (perkin-Elmer).

Experimental methods

Batch studies

To evaluate the feasibility of arsenic removal by different IOCS were used as adsorbents with a dose of 20 g/L and solution pH was 7 ± 0.1. The parameters of reaction at room temperature (31 °C) and revolution per minute of shaker were controlled 38 rpm. The adsorption time was set at 8 h for all adsorption isotherm experiments. All the above criteria were fixed based on earlier studies observations (Vaishya & Gupta 2003; 2004). Isotherm studies were conducted with varying initial As (III) concentration (1mg/L to 8mg/L). Batch sorption experiments were conducted to obtain sorption capacity of IOCS, using 300 ml BOD bottle kept at room temperature; an end-to-end shaker was used to agitate the solution. The reaction mixture consisted of 100 ml As (III) solution of known concentration and the adsorbent, which was weighed and added to the solution. Each bottle was removed after the required reaction time and the solution was filtered through whatman No.40 filter paper. The measured arsenic data were statistically analyzed for the fitting of isotherm models of both the Langmuir and Freundlich.

Fixed bed adsorption studies

Column experiments were performed on a laboratory scale to study the effect of different IOCS for the reduction of As (III) concentration in aqueous solutions. The column used was prepared using glass tubes of length 100cm and internal diameter 22 mm. The column was filled with glass wool at the bottom, up to a height of 60 cm IOCS with a geometric size of 0.547 mm was filled in.

To study As (III) uptake of different IOCS were performed at constant filtration rate and depth, an As solution of 1mg/L was pumped through the column at the required filtration rate, and samples were collected at 1hour interval and after six hour column run samples were collected at 2 hours intervals. The samples were analyzed for residual arsenic concentration.

Results and Discussion

Adsorption isotherms

In general, adsorption isotherm is used to describe the equilibrium state of adsorbate, adsorbent and solute at a given temperature. Arsenic adsorption isotherm

experiments were carried out to compare their adsorption capacities under various conditions. Two adsorption models were proposed, including Langmuir (Eq.-1) and Freundlich (Eq.-2) models, the equation of which are expressed below, respectively (J. Wiley & sons)

$$q_e = \frac{Q^0 bc}{(1 + bc)} \quad (\text{Langmuir equation}) \quad (1)$$

$$\text{And } q_e = K_F C^{1/n} \quad (\text{Freundlich equation}) \quad (2)$$

Where Q^0 and q_e represent saturated adsorption capacity at equilibrium concentration of adsorbate (C), respectively; b, K_F , and n stand for empirical constants.

The linearized form of Langmuir (Eq.-3) and Freundlich (Eq.-4) which are expressed below, respectively were used for obtained the respective empirical constants.

$$\frac{1}{q_e} = \left(\frac{1}{bQ^0} \right) \left(\frac{1}{C} \right) + \frac{1}{Q^0} \quad (3)$$

$$\log q_e = \log K_F + \frac{1}{n} \log C \quad (4)$$

Where

K_F = Sorption capacity. Unit will be $\text{mg}^{n-1/n} \text{g}^{-1} \text{L}^{1/n}$
 $1/n$ = Adsorption intensity.

Table 1 Fitting of As (III) adsorption isotherm

Methods	Langmuir model			Freundlich model		
	Q^0 (mg/g)	b(L/g)	R^2	$K_F (\text{mg}^{n-1/n} \text{g}^{-1} \text{L}^{1/n})$	1/n	R^2
IOCS-I	0.20	2.44	0.96	1.06	0.059	0.93
IOCS-I-A	0.11	0.43	0.96	1.02	0.014	0.93
IOCS-II	0.23	0.12	0.99	1.02	0.014	0.95
IOCS-III	0.13	0.80	0.92	1.02	0.018	0.74

Based on the above two equations, the profile of As (III) adsorption isotherm were transformed into the linearized form, as illustrated in figure (1-8) given below. In addition, the respective empirical constants (b, K_F , and n) of these two models are presented in Table 1. Note that the linearized form of Langmuir and Freundlich equations is expressed in terms of $1/q_e$ vs. C and $\log q_e$ vs $\log C$, respectively. As (III) depicted in Table 1, the As (III) adsorption isotherm fits the Langmuir model ($R^2 = 0.96, 0.96, 0.99, 0.92$) with better degree than the Freundlich model ($R^2 = 0.93, 0.93, 0.95, 0.74$) for the four different IOCS. The most useful aspect of this Langmuir

model is for obtaining the saturated adsorption capacity (SAC), while magnitude of the “b” is probably devoid of any physical-chemical meaning with respect to the forces involved in the sorption process. Quantitatively speaking, the SAC’s of As (III) adsorbed onto IOCS-I, IOCS-I-A, IOCS-II, and IOCS-III were statistically calculated to be 0.20, 0.11, 0.23, and 0.13 mg g⁻¹ respectively. The result are shown in table 1, according to Freundlich isotherm model, the trends in sorption capacity are largely captured in the parameter KF, while n reflects the steepness of the curve where plotted on arithmetic or logarithmic scale. Treybal (1968) reported that the value of N > 1, represent favorable sorption condition.

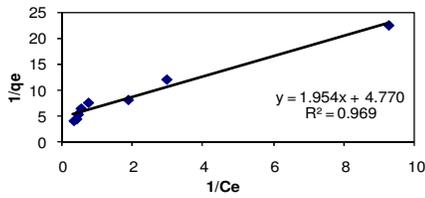


Fig.1 Langmuir adsorption isotherm for As (III) on IOCS-I, sorbent dose 20g/L

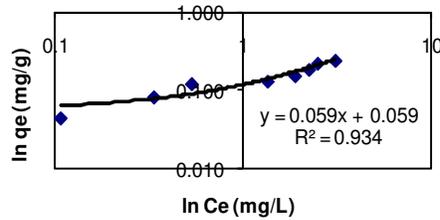


Fig.2 Freundlich adsorption isotherm for As (III) on IOCS-I, sorbent dose 20g/L

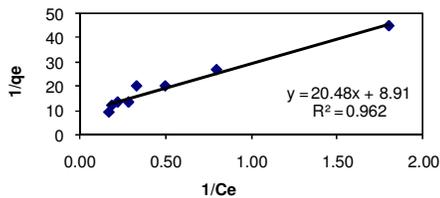


Fig.3 Langmuir adsorption isotherm for As (III) on IOCS-IA, sorbent dose 20g/L

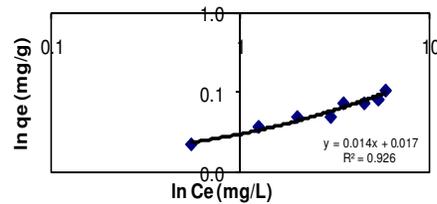


Fig.4 Freundlich adsorption isotherm for As (III) on IOCS-IA, sorbent dose 20g/L

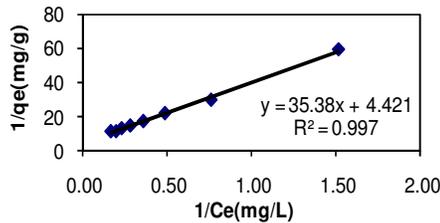


Fig.5 Langmuir adsorption isotherm for As (III) on IOCS-II, sorbent dose 20g/L.

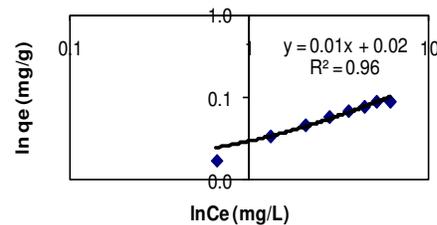


Fig.6 Freundlich adsorption isotherm for As (III) on IOCS-II, sorbent dose 20g/L

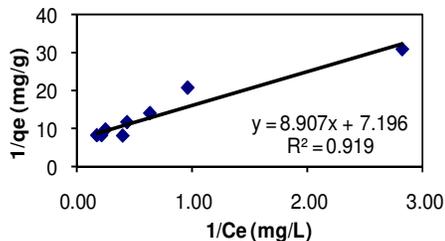


Fig.7 Langmuir adsorption isotherm for As (III) on IOCS-III, sorbent dose 20g/L.

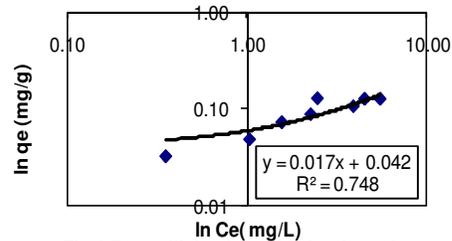


Fig.8 Freundlich adsorption isotherm for As (III) on IOCS-III, sorption dose 20mg/L

Column studies

Comparative sorption by different IOCS

The initial As (III) concentration was kept at 1mg/L for all the adsorbents used in the column studies. Fixed bed adsorption column operated in the down flow mode may perform two functions, namely adsorption and filtration. Breakthrough or exhaustion curves were developed from the column data by plotting the ratio of C_e/C_0 with the time of water processed. Where, C_e is the effluent adsorbate concentration (mg/L); C_0 , the influent adsorbate concentration (mg/L).

As shown in above figure-9 the breakthrough curve among all the adsorbents As (III) removal with the IOCS-I, 28 hours achieved < 0.05 mg/L residual As (III), and overall removal capacity was highest among all other media used. Based on the present column studies; the performance of IOCS-I was better than that of other IOCS because in the preparation of IOCS-I, an effective coating of iron oxide was achieved on sand. Poor performance was observed with IOCS-I-A and IOCS-III. It means, pressure doesn't effective in coating process and water play an important role in dissolve Ferric nitrate salts as well as attachments over sand surface.

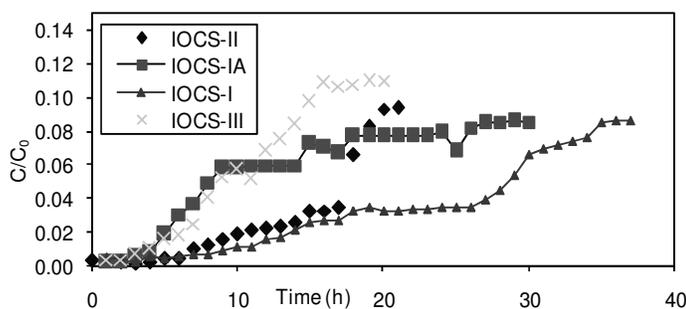


Fig.9 Breakthrough curves for As-III adsorption by different IOCS

Effect of bed depth

The initial As (III) concentration was kept at 1mg/L and discharge 1.58 m³/m²/h. for all the adsorbents used in the column studies. Fixed bed adsorption column operated in the down flow mode may perform two functions, namely adsorption and filtration. Breakthrough or exhaustion curves were developed from the column data by plotting the ratio of C_e/C_0 with the time of water processed. Where, C_e is the effluent adsorbate concentration (mg/L); C_0 , the influent adsorbate concentration (mg/L).

Sorbent bed height strongly affects the volume of solution treated. Effect of bed height on adsorption of As (III) by IOCS-I is as shown in fig.10. As it is evident from the figure, as increase in column depth increased the treated volume due to high contact time. The curve followed characteristics S-shape profile, which is associated with the adsorbate of smaller molecular diameter and more simple structure. The increase in the metal uptake capacity with the increase of bed height in the column is probably due to improvement in surface properties of the adsorbent, which provide more binding sites for the adsorption. The breakthrough time also increased with increase in bed height. For As (III) removal by IOCS-I the breakthrough time increase from 8 to 32 hours as the bed, height was increased from 20 to 60 cm when the exit As (III) concentration was below the permissible limit 0.05 mg/L.

Fig.10 depicts the breakthrough time achieved at different bed depths on coated sand.

Conclusions

IOCS filtration, an emerging technology may be suitable for small water facilities, especially in developing countries such as Bangladesh, Chile, India and Mexico because of its simplicity, and easy of operation. Present studies clearly showed that quick developed IOCS are capable of removing arsenic from groundwater as well as easy in develop iron oxide.

The arsenic removal capacities of the media used in column studies decreased in the following order: IOCS-I > IOCS-II > IOCS-I-A > IOCS-III. The breakthrough time also increased with increase in bed height. For As (III) removal by IOCS-I the breakthrough time increase from 8 to 32 hours as the bed, height was increased from 20 to 60 cm when the exit As (III) concentration was below the permissible limit 0.05 mg/L.

Authors' contribution: Dr. Dharmendra (Assistant professor), Research scholar, contributed in experiment design and final editing of the manuscript; Dr. R.C.Vaishya, (Professor), Supervisor, contributed in experiment design; S.C. Prasad(Professor), co-supervisor, contributed in experiment design.

REFERENCE

- Bailey. R. P., Bennett T., Benjamin M. M., 1992. Sorption onto and recovery of Cr(VI) using iron-oxidecoated sand, *Water Science & Technoogy*. 26, 1239-1244.
- Baltpurvins K. A., Bums R. C., Lawrance G. A., Stuart A. D., 1996. Effect of pH and anion type on the aging of freshly precipitated iron (B1) hydroxide sludges, *Environment Science & Technology* 30(3), 939-944.
- Carrillo A., Drever J.I., 1998. Adsorption of arsenic by natural aquifer material in the San Antonio-El Triunfo mining area, Baja California, Mexico, *Environment Geology*. 35, 251-257.
- Driehaus W., Jekel M., Hildebrandt U., 1998. Granular ferric hydroxide a new adsorbent for the removal of arsenic from natural water, *Journal of water supply: Research & Technology-AQUA*. 47(1), 30-35.
- Edwards M., Benjamin M. M., 1989. Adsorption filtration using coated sand: a new approach for treatment of metal-bearing wastes, *Journal of the Water Pollution Control Federation* 61, 1523-1533.
- Galer J.M., Delmas R., Loos-Neskovic C., 1997. Decontamination of arsenic-containing aqueous solutions using inorganic sorbents. Investigation of the arsenic species in solution by means of capillary electrophoresis, in: A. Dyer, M.J. Hudson, P.A. Williams (Eds.), *Progress in Ion Exchange: Advances and Applications, The Royal Society of Chemistry*, 187 pp.
- Huang J.G., Liu J.C., 1997. Enhanced removal of As(V) from water with iron-coated spent catalyst, *Separation science & Technology*. 32, 1557-1569
- Lai C. H., Lo S. L., Lin C. F., 1994. Evaluating an iron-coated sand for removing copper from water, *Water Science & Technoogy*. 30(9), 175-182.
- Lindberg J. Sterneland J., Johansson P.O., Gustafsson J.P, 1997. Spodic material for in situ treatment of arsenic in ground water, *Ground Water Monitoring Remediation* 17, 125-130
- Lo S. L., Jeng H. T., Lin C. F., Lee D. Y., 1994. Adsorption of heavy metals by the iron-coated filter medium, *Journal of the Chinese Institute of Civil & Hydraulic Engineering*. 6(1), 101-110.
- Lo S. L., Shiu S. H., Lin C. F., Lee D. Y., 1994. Adsorption of Metals on oxides formed from Fe (NO₃)₃, FeCl₃ and Fe (ClO₄)₃ solutions, *Environmental Geochemistry and Health*, 16, 89-99.
- Pokonova Yu.V. 1998. Carbon adsorbents for the sorption of arsenic, *Carbon* 36, (4) 457-459.
- Rajakovi'c L.V. 1992. The sorption of arsenic onto activated carbon impregnated with metallic silver and copper, *Separation Science & Technology* 27, 1423.
- Raven K.P., Jain A., Loeppert R.H., 1998. Arsenite and arsenate adsorption on ferrihydrite: kinetics, equilibrium, and adsorption envelopes, *Environment Science & Technology* 32, (3) 344-349.

- S. Tokunaga S.A., Wasay S., Park W., 1997. Removal of arsenic (V) ion from aqueous solutions by lanthanum compounds, *Water Science and Technoogy* 35, 71-78.
- Stahl R. S., James B. R., 1991. Zinc sorption by iron-oxide-coated sand as a function of pH, *Soil Science Society of americ Journal*. 55, 1287-1290.
- Treybal, R.E., 1968. Mass-Transfer operations, *Mc Graw Hill*, Koga Kusha Co., Tokyo, Japan.pp29-31
- Vagliasindi F.G.A., Benjamin M.M., 1998. Arsenic removal in fresh and non-preloaded ion exchange packed bed adsorption reactors, *Water Science & Technoogy*. 38, 337-343.
- Vaishya R.C., Gupta S.K., 2003.Coating sand filtration: an emerging technology for water treatment. *Journal of water supply: Research & Technology-AQUA*, 52.4, 299-306.
- Vaishya, R.C., Gupta, S.K., 2004. Modeling arsenic (V) removal from water by sulfate modified iron-oxide coated sand (SMIOCS), *Separation Science Technology*. 39 (3), 645-666.
- WHO, 1993. Guidelines for drinking water quality: 1. Recommendations, World Health Organization, Geneve, Volume 1: 3rd edition pp 188