Optimisation of 3D-Organized Mesoporous Silica Containing Iron and Aluminium Oxides for the Removal of Arsenic from Groundwater

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The development of mesoporous adsorbents coated with iron and aluminium oxides has been optimised for the removal of arsenic. 3D-organised mesoporous silica KIT-6 was used as a host for iron and aluminium oxides loading in single or mixed conditions. Material properties were characterized using BET and TEM analysis. The high surface area and porosity of the sorbents and their 3D organization has been ascertained. Materials produced were used in adsorption studies for removing both As(III) and As(V). KIT-6 coated with 8 % iron oxides showed an As(III) and As(V) removal capacity of 10.47 and 6.26 mg.g^{-1} while the same silica matrix coated with 8 % aluminium oxides displayed an As(III) and As(V) removal capacity of 7.73 and 38.78 mg.g^{-1} respectively. The use of mixed Fe-Al oxides coated sorbents showed the possibility to tailor the adsorption towards one of the two arsenic species. These materials are expected to be superior adsorbents when used in column systems as they will be saturated simultaneously with both As(III) and As(V) thus avoiding the use of an oxidation step.

1. Introduction

Arsenic groundwater contamination is a severe environmental concern and public health issue affecting millions of people. As arsenic accumulates in human body, people exposed to arsenic contaminated water develop different kind of cancers affecting the skin and internal organs (Kemper and Minnatullah, 2005). This worldwide contamination is affecting many countries and especially Bangladesh where aquifer contamination has been reported to be extensive (Kinniburgh and Smedley, 2001).

Different techniques have been developed to remove arsenic from groundwater; among them adsorption is probably the most widely applied technology (Walker and Weatherley, 2001). The main advantages of adsorption technologies are low running costs, low maintenance needs, low electrical demand and low chemical addition needs (Walker and Weatherley, 1997). Many materials have been tested to remove arsenic; and the review by Mohan and Pittman presents a good overview of the work that has been carried out (Mohan and Pittman, 2007). Adsorption processes are very dependent on the surface area of the materials as well as their surface chemical properties. Iron and aluminium oxides and hydroxides have been shown to be very efficient in removing As(III) and As(V). In some studies it was demonstrated a better removal capacity of iron oxides at removing As(III) and of aluminium oxides at removing As(V) (Mohan and Pittman, 2007).

This study aims at developing an efficient arsenic adsorbent using the superior surface area and porosity of organised mesoporous silica. Two organised mesoporous silica; SBA-15 and KIT-6; were investigated as host for iron and aluminium coating. These two materials have been used for support on a wide range
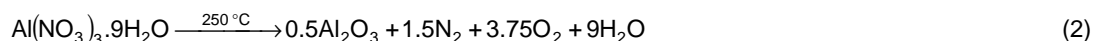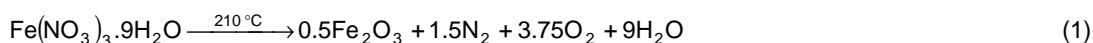
of application (Davis, 2002). Previous studies shown that iron coated activated carbon or mesoporous have good removal capacity for arsenic removal (Gu et al., 2005). In the present study the effect of mixed aluminium and iron coating has been investigated as a way to control the relative removal of As(III) and As(V). By doing so it may be possible to produce an adsorbent with removal capacity tailored for each specific component. An adsorption unit using such a material would be saturated simultaneously with both arsenic species without the requirement of an oxidation stage.

2. Materials and methods

2.1 Adsorbents synthesis

KIT-6 and SBA-15 were produced using the method presented by Anja Rumplecker (Rumplecker 2007). For the production of SBA-15, a solution of 252 g of deionised water and 7.7 g of HCl at 37% was used to dissolve 13.9 g of Pluronic P123. After dissolution of the surfactant, 25.0 g of TEOS was added. The solution was stirred in a Duclan glass bottle for 24 h at 35 °C using a silicon oil bath. The bottle was then placed in an autoclave to undergo a hydrothermal treatment (at 40 °C, 60 °C, 80 °C or 100 °C) for 24 h under static conditions. The solid product was then filtered without washing and dried for 48 h at 95 °C in an oven. The surfactant was removed by calcination in flow of air at 550 °C for 6 h with a temperature ramp of 1 °C.min^{-1} and a flow of air set at 100 mL.min^{-1}. Differences between KIT-6 and SBA-15 are in the chemicals used during the synthesis and the time used for drying. For KIT-6 synthesis, 9 g of P123 was dissolved in 325 g of deionised water and 17.4 g HCl (37 %) under vigorous stirring. After complete dissolution of the surfactant, 9 g of butanol was added. Further steps were the same as SBA-15 synthesis except the drying time which was reduced to 24 h. Mesoporous silica were named KIT-XX °C and SBA-XX °C where XX is the hydrothermal temperature used in the synthesis.

The 3D-organised mesoporous silica KIT-100 °C was selected for aluminium and iron doping because of its higher mesoporosity. This process was carried out using a solvent evaporation method. 0.8 M aluminium and iron nitrate in absolute ethanol solutions were used to coat the mesoporous silica. Different loading percentage were studied; 1 % to 8 % in one impregnation step and 15 % to 30 % in three impregnation steps. The percentage loading is based on the internal pores filling by Al_2O_3 and Fe_2O_3. The selected amount of iron or aluminium solution was added at once onto the mesoporous silica and was left under stirring for 1 h. After homogeneous dispersion of the solution; the HDPE bottles were placed in an oven at 60 °C to undergo solvent evaporation. The resulting powder was then calcined at 210 °C or 250 °C into a chamber furnace to eliminate the nitrate salts following the reactions presented in equation (1) and (2). Coated mesoporous silica were named KIT-YY % ZZ where YY is the percentage of coating and ZZ the metal salt corresponding (Al or Fe).

$$Fe(NO_3)_3.9H_2O \xrightarrow{\;210\,°C\;} 0.5Fe_2O_3 + 1.5N_2 + 3.75O_2 + 9H_2O \tag{1}$$

$$Al(NO_3)_3.9H_2O \xrightarrow{\;250\,°C\;} 0.5Al_2O_3 + 1.5N_2 + 3.75O_2 + 9H_2O \tag{2}$$

A set of mixed iron and aluminium coated mesoporous KIT-100 °C was produced by varying the relative percentage of iron and aluminium while keeping constant the total metal loading percentage at 8 %. Same coating procedure as single metal oxide coating was followed. Mixed metal coated mesoporous silicas were named KIT-8%-Fe/Al-AA/BB where AA and BB are the iron and aluminium relative content.

2.2 Adsorbent characterization

Adsorbents surface characteristics were studied using a BET surface analyser and a TEM. The BET analyser was a Nova 4200e Surface area and pore size analyser form Quantachrome Instruments run with nitrogen. Samples were degassed overnight at 60 °C under vacuum and analysed at 77 K with 45 adsorption points and 30 desorption points. The TEM equipment was a FEI Tecnai F20 field emission high-resolution transmission electron microscope having a 200kV accelerating voltage.

2.3 Arsenic removal using adsorbents

Adsorbents produced were tested in removing arsenic using synthetic water solutions. Sodium arsenate dibasic heptahydrate and sodium (meta)arsenite were dissolved in deionised water to produced corresponding stock solutions. Sodium hydrogencarbonate provided ionic strength and pH buffering capacity to solutions.

Arsenic removal studies were carried out in batch mode using 50 mL solution and 1 g.L^{-1} adsorbent dosage in 60 mL glass flasks. Solutions were let to reach pseudo-equilibrium onto a horizontal shaker set at 100 rpm for 48 h. pH was controlled using 1 M HCl or 1 M NaOH solutions and equilibrium pH was

recorded by the mean of a Thermo Scientific Orion 3 Star pH meter equipped with a Camlab pH probe calibrated with 3 standard solutions. Starting concentration of 50 ppm was selected for the single arsenic specie removal study. In experiments studying the simultaneous removal of As(III) and As(V) starting solution having 50 ppm As(III) and 50 ppm As(V) were used.

All samples taken were filtered using 13 µm cut off filter papers, 2 % acidified with HNO_3 and analysed using an ICP-AES HR duo IRIS Intrepid model from Thermo Elemental. In order to differentiate As(III) and As(V) some anionic exchange cartridges Waters Sep-Pak® were used to remove As(V) prior to ICP analysis while a second sample was analysed for total arsenic.

3. Results and discussion

3.1 TEM analysis

Figure 1 presents the TEM images of some of the mesoporous silicas synthesized. It can be noticed the 3D organisation of the KIT-6 materials, Figure 1 (a) and (b), varies compared with the 2D organised SBA-15 silica, Figure 1 (c) and (d). Coating SBA-15 internal walls with iron oxide appears to lead to iron oxide particles growth in-homogeneously distributed into the pores (e) and (f).
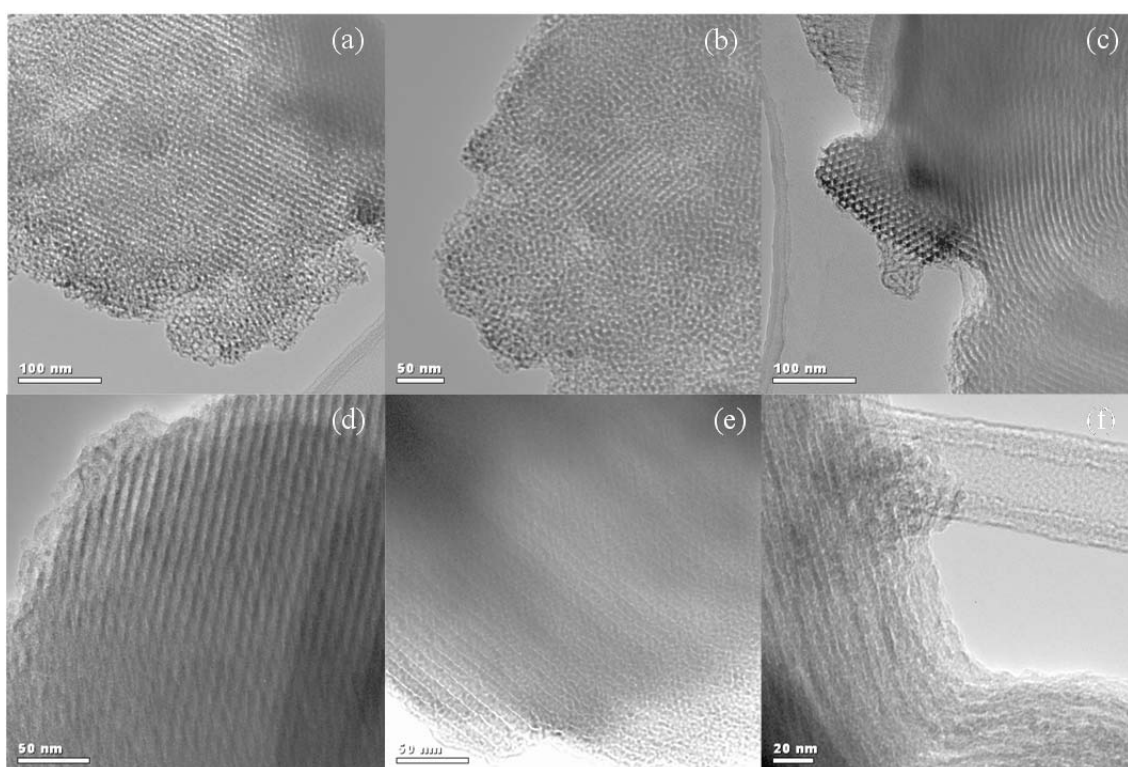

Figure 1: TEM images of KIT-6 (a), (b); SBA-15 (c), (d) and SBA-8 % Fe (e), (f)

3.2 BET

Physical surface area analyses of the adsorbents produced are showed in Figure 2. Figure 2 (a) illustrates the evolution of the mean pore diameter for silica KIT-6 produced at different temperatures. As the hydrothermal temperature increases the average pore size diameter increases which is due to the thermal sensitivity of the polymer P123 used in the synthesis (Galarneau et al., 2001). Figure 2 (b) compares the N_2 adsorption isotherms for KIT-100 °C and SBA-100 °C. It can be noticed that both materials possess approximately the same micropore volume while KIT-100 °C possess a higher mesoporous volume. Both isotherms follow the type IV isotherm with a sharp increase and rather wide hysteresis loop type H1 as defined by IUPAC (Sing et al., 1985). These features are characteristic of organized mesoporous materials with a narrow pore size distribution. The high surface area of materials produced can be compared to commercial unorganised silica gel with surface area around 500 $m^2.g^{-1}$, average pore diameter of 6 nm and porosity of 0.84 $cm^3.g^{-1}$ (Seo et al., 2009). The KIT-100 °C mesoporous silica was then selected for iron and aluminium oxides coating.

The BET analysis summary presented in Table 1 shows that the wall coating process by iron and aluminium oxides decreases the surface area and fills the pores of the materials produced.
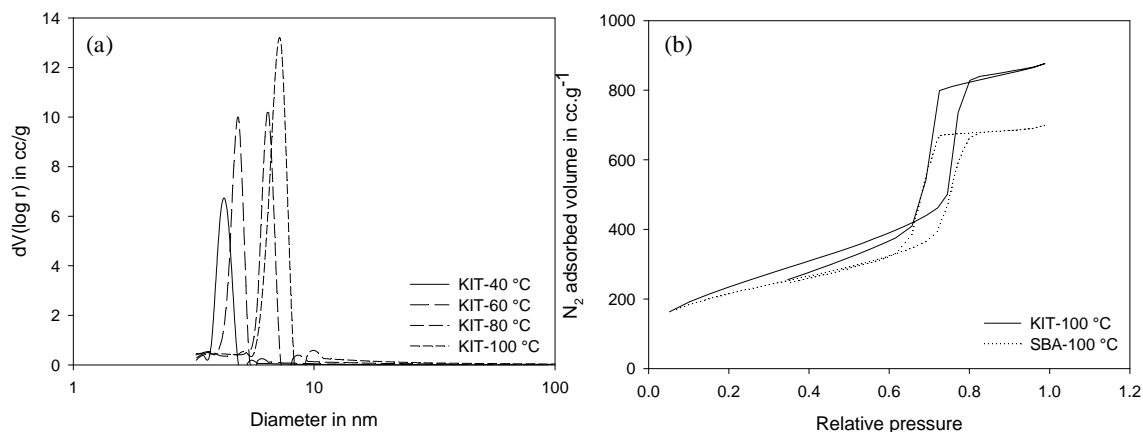
Figure 2: Pore size distribution in KIT materials produced at different hydrothermal temperatures (a) and BET isotherms of KIT-100 °C and SBA-100 °C (b)

As the metal loading percentage increases the surface area decreases for both Fe and Al coating. Nevertheless the aluminium oxides coating fill the pores at lower metal loading percentage and pores are nearly filled at 30 % Al loading. This difference may be due to incomplete nitrate removal during the oxidation step in the chamber furnace at 250 °C. External metal oxides growth may also interfere in the BET analysis even if no evidence was noted during TEM examination.

Table 1: BET analysis of mesoporous silica KIT-6 coated with increasing iron oxides content

Silica	Fe loading %	Surface area $m^2.g^{-1}$	Porosity $cc.g^{-1}$	Average pore size nm	Silica	Al loading %	Surface area $m^2.g^{-1}$	Porosity $cc.g^{-1}$	Average pore size nm
KIT	0	853.2	1.356	6.36	KIT	0	853.2	1.356	6.36
KIT	1	607.2	0.866	5.70	KIT	1	591.3	1.034	7.00
KIT	3	530.0	0.671	5.06	KIT	3	442.2	0.770	6.97
KIT	8	520.9	0.575	4.42	KIT	8	207.8	0.434	8.36
KIT	15	267.2	0.311	4.65	KIT	15	252.4	0.359	5.69
KIT	20	271.9	0.315	4.64	KIT	20	294.1	0.387	5.26
KIT	30	222.0	0.241	4.33	KIT	30	83.2	0.118	5.68

3.3 Metal loading effect onto As adsorption
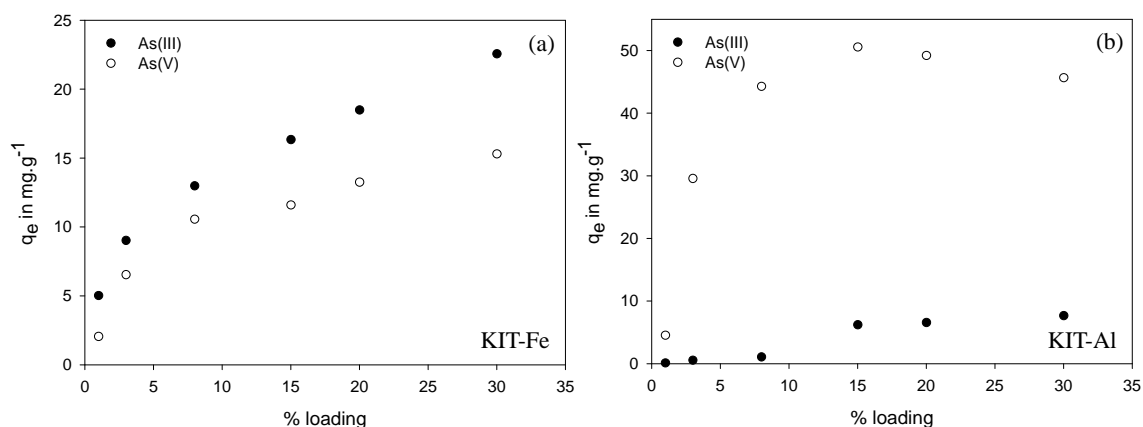

Figure 3: Arsenic adsorption onto KIT-Fe (a) and KIT-Al (b) adsorbents loaded with increasing metal content (adsorbent concentration is 1 $g.L^{-1}$; initial corresponding arsenic concentration is approx. 50 ppm and equilibrium pH is 7)

Figure 3 presents the efficiency of the materials produced in removing As(III) and As(V) as single components. The KIT-Fe materials series removes As(III) more efficiently than As(V) for any iron coating percentage tested. As the iron percentage loading increases the arsenic adsorption capacity of the materials increases. This is especially noticeable at low loading percentage. For Fe loading higher than 15 % the increase in arsenic removal capacity is less visible.

On the contrary KIT-Al adsorbents reach a very high As(V) removal capacity, while As(III) removal efficiency remains low. The effect of increasing Al coating percentage onto the arsenic adsorption capacity is even more pronounced than in the case of Fe coating. At 15 % Al loading no more improvement of As(V) removal capacity is evident This effect can be related to the decrease in the surface area of the materials when corresponding metal oxides were coated (Table 1).

For further experiments 8 % metal oxides coating was selected as the optimum balance between surface area and porosity availability and arsenic removal efficiency.

3.4 Iron and aluminium relative loading effects onto As(III) and As(V) removal in single and simultaneous configuration

Figure 4 presents the removal of As(III) and As(V) in single or mixed conditions by the materials produced using different iron to aluminium oxides ratio during the coating process. In Figure 4 (a) it can be noticed that the As(V) removal capacity of the material decreases when the iron coating percentage increases. This is due to the relative decrease of aluminium oxides into the material which possesses a higher removal capacity for As(V) than the iron oxides as previously shown (Figure 3). The points 0 % and 100 % correspond to the material KIT-8 % Al and KIT-8 % Fe respectively. The figure reveals the better As(III) removal efficiency of the material with at least 75 % iron oxides coated.

Figure 4 (b) shows the simultaneous removal of As(III) and As(V) with the same materials. The total arsenic removal of the materials is very close to the As(V) removal capacity of the materials when removing As(V) only. Materials produced with Fe percentage ranging from 25 to 75 show a total arsenic 15 % higher than the single As(V) capacity of the material. When iron loading ratio increases over 75 % As(III) removal is favoured over As(V) removal. Finally it should be noted that the low increase of As(III) removal capacity occurs when iron loading percentage is increased. This can be explained by the low KIT-8 % Fe As(III) and As(V) adsorption capacity difference (around 13 mg As(III).g^{-1} and 10 mg As(V).g^{-1} in the experiments conditions; see Figure 3). Moreover it must be pointed out that a higher As(III) removal capacity of the KIT-8 % Al materials was found in this experiment.
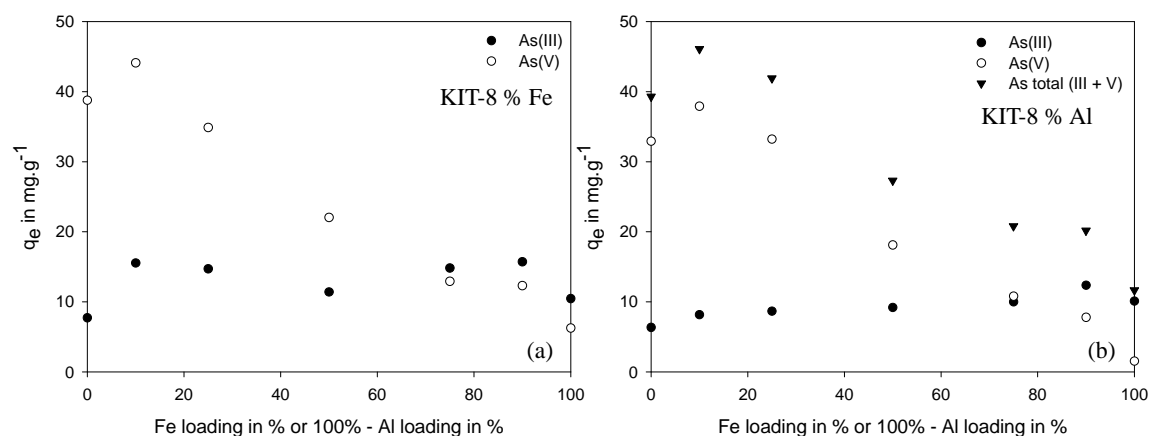

Figure 4: As(III) and As(V) single compound removal study (a) and simultaneous As(III) and As(V) removal study (b) using KIT coated with mixed Al and Fe oxides (adsorbent concentration is 1 g.L^{-1}; initial corresponding arsenic concentration is approx. 50 ppm and equilibrium pH is 7)

The arsenic adsorption capacities obtained in this study are compared to results from the literature in Table 2. Granular Activated Carbon or Ordered Mesoporous Carbon coated with iron present similar arsenic adsorption capacity than the mesoporous silica coated with iron from this study. The materials produced with aluminium oxides displayed a As(V) adsorption capacity of an order of magnitude higher than the one produced with iron oxides coating. It must be noticed that the concentration range used in this study is higher than that used in the Gu *et al.* studies.

Table 2: Comparison of arsenic adsorption capacity of materials produced with other porous adsorbents

Material	Surface area	Adsorption capacity		Reference
	$m^2.g^{-1}$	mg As(III).g^{-1}	mg As(V).g^{-1}	
GAC - 8 % Fe	380	-	6.57	(Gu et al., 2005)
OMC - 4 % Fe	466	8.156	6.465	(Gu et al., 2007)
KIT-8 % Fe	521	10.47	6.26	This study
KIT-8 % Al	208	7.73	38.78	This study
KIT-8 % Fe/Al-10/90	348	8.17	37.92	This study
KIT-8 % Fe/Al-90/10	510	12.37	7.8	This study

Figure 4 and Table 2 show that it is possible to tailor the selectivity of materials towards either of the arsenic species.

4. Conclusion

A range of 3D-organized mesoporous silica was produced and successfully coated with iron, aluminium and mixed Fe-Al oxides. The optimal iron and aluminium oxides loading was evaluated at 8 % of the total pore volume in terms of available surface area and arsenic adsorption capacity. Mesoporous silica coated with iron removed As(III) more efficiently than As(V) while mesoporous silica coated with aluminium oxides presented a very high As(V) removal capacity and a very low As(III) removal capacity. The materials produced in this study possess higher As removal capacity of equivalent materials present in the literature. Using the difference of As adsorption capacity of both metal oxides offers the possibility to tailor the removal selectivity of the adsorbents toward one or other As species. The degree of control does not allow a perfect tailoring of the sorbent to match every water quality. Nevertheless it is thought that the idea presented in this paper can be extended to other metal oxides and hydroxides. Materials having the proper characteristics to be exhausted simultaneously for different pollutants, which match specific water characteristics would extend the lifetime of the adsorption units.

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