

Optimization of oxide coating process on quartz sand for arsenic (III) removal from groundwater

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ABSTRACT

This paper presents optimization of various oxide coating processes on quartz sand surface. The chemical characteristics of quartz sand collected from the Yamuna river, Allahabad, India, shows 82.022% SiO₂ besides other oxides. The optimal coating temperature was 60°C; optimal pH_{coating} ≈ 0.5; optimal heating time was 60 hours and percentage iron salt [Fe(NO₃)₃·9H₂O] was 8–10% w/w for iron oxide coated sand (IOCS) with maximum As(III) removal efficiency. The 60 h heating time in iron oxide coating process yields maximum Fe (mg/g) on the sand surface. The pH_{coating} has shown considerable effect on arsenic removal efficiency during optimization of sulfate modified iron oxide coated sand (SMIOCS) media. The SMIOCS prepared at pH_{coating} < 1.0 was quite efficient compared to media prepared at pH_{coating} ≈ neutral and pH_{coating} ≈ 12.05. The mixed oxide coated sand (MOCS) prepared at pH_{coating} < 1.0 has shown better arsenic removal efficiency in comparison to other mixed oxide coated sand media. The BET surface area varied between 2.55 and 7.895 m²/g for particle size ranging from 0.324 mm to 0.716 mm for different coated sand media. The pH_{zpc} values indicate that the IOCS and SMIOCS media are positively charged at neutral pH, whereas uncoated sand is negatively charged. Equilibrium and column studies results show that IIS and MIOCS media have better As(III) removal potential compared with other media.

Key words | column studies, iron oxide coated sand (IOCS), mixed oxide coated sand (MOCS), optimization, pH_{zpc}, sulfate modified iron oxide coated sand (SMIOCS)

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INTRODUCTION

The occurrence of arsenic in groundwaters in different parts of the world has attracted worldwide attention due to the severity of the adverse impact on human health (Karim 2000). The recent epidemiological evidence on arsenic carcinogenicity suggests that the standard of 50 µg/L may not be sufficient to reduce the risk of cancer (Smith *et al.* 1992). Studies in Taiwan have shown that long-term human exposure to arsenic can cause cancers of the skin, liver, lung, kidney and bladder. The actual toxicity of arsenic to the human body varies depending on several factors such as general health and diet (Smith *et al.* 1998). The weathering process

contributes a significant flux of arsenic in groundwater and surface water. Arsenic trioxide is only slightly soluble in water, forming arsenious acid (H₃AsO₃), but arsenic pentoxide (As₂O₅), formed by oxidation of As₂O₃, is readily soluble in water, forming arsenic acid (H₃AsO₄). In groundwaters generally As(III) is the dominant species of arsenic and toxicity of As(III) is nearly 60 times that of As(V). These two inorganic arsenicals are more acutely toxic than most organic forms. There are suggestions that the chronic toxicity of many organic forms of arsenic, especially those found in fish and shellfish, is also less than that of inorganic arsenic.

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The World Health Organization (WHO) has recommended a provisional guideline value of 0.01 mg/L for arsenic in drinking water (WHO 1993).

Treatment methods for removal of arsenic from water include adsorption-co-precipitation with hydrolysing metals, such as aluminium or iron. Ion exchange can also be used but the high cost of resins and regeneration is likely to make it a less appropriate technology. Low-cost adsorbents have shown great promise in achieving a low level of 'Arsenic' in drinking waters. The adsorption process also offers more reliable and more efficient removal of complex inorganic and organic metals that would not have been removed by conventional treatment methods. As(V) is removed more effectively than As(III) due to its neutral status at normal pH of water. Arsenite also exhibits a strong affinity for sulfur due to potential formation of insoluble arsenic sulfide minerals in the reduced environment (Hounslow 1980). The iron oxide coating on the sand surface has been modified using both Ba and S, to evaluate the feasibility of sulfate modified iron oxide coated sand (SMIOCS) media for arsenic (III) removal from water. Merkle *et al.* (1997) developed many methods for manganese oxide coating on the sand surface. Bajpai & Chaudhuri (1999) prepared manganese dioxide coated sand (MDCS) by using MnCl_2 , KMnO_4 and NaOH and heating at 105°C for 48 hrs for arsenic removal from groundwater. Knocke *et al.* (1991) successfully used $\text{MnO}_{x(s)}$ -coated filter media to obtain significant removal of soluble Mn.

Coated sand filtration is one of the emerging technologies for arsenic and other heavy metals removal from groundwaters (Vaishya & Gupta 2003). The coating of Fe oxides onto the surface of sand to effectively remove/recover trace heavy metals has been used by many researchers (Edwards & Benjamin 1989; Bailey *et al.* 1992; Vaishya & Gupta 2002). However, very limited research papers are available on the optimization of the iron oxide coating on quartz sand. In the majority of the papers, coated sand developed by a single method has been used as an adsorbent. The various techniques of oxide coating on quartz sand surface has been tried in the laboratory using new approaches, because iron is the best metallic material for environmental remediation due to its strong character as a reducer, as well as being non-toxic and inexpensive. Apart from iron, manganese and sulfur were also used for development of IOCS, SMIOCS and MOCS media. The MOCS was also optimized for achieving maximum

arsenic removal efficiency by varying the dose of chemicals etc. The optimized media were used as adsorbents for testing arsenic (III) removal efficiency from aqueous groundwater.

The research work described here aims to achieve maximum removal of As(III) by oxide coated sand media prepared by varying the temperature of the coating, dose of chemical, heating time and $\text{pH}_{\text{coating}}$ etc. The study also includes determination of BET surface area, determination of pH_{zpc} , isothermal studies and column studies on selected media.

MATERIALS AND METHODS

Materials

Chemicals and glassware

All chemicals used were of analytical reagent grade. Stock As(III) solution of 1000 mg/L was prepared using arsenic trioxide (As_2O_3), [M/s Loba Chem. (India)]. Preservation of As(III) solution was done using 1000 mg/L ascorbic acid solution (Eaton 1996). The ionic strength of the synthetic water system was maintained using sodium nitrate (NaNO_3). All glassware used was made by M/s Borosil Glass Works Limited, Mumbai, India, after following appropriate cleaning procedures.

Sand

Quartz sand was procured from the banks of the Yamuna river at Allahabad (India). The sand used in this process was soaked in an acid solution (1.0 M HCl) for 24 h, rinsed with distilled water and dried at 105°C . The geometric mean (GM) sizes of 324 μm , 498 μm and 716 μm by British Standard Sieves were used in the present study. Dried sand was kept in PVC cans for further experiments.

Coated sand

Coated sand was prepared by using different salts of Fe, Mn, Ba, oxidant (KMnO_4) and alkali like NaOH in certain proportions. The detailed coating procedures for different types of coated sand are given below along with their abbreviations.

Methods of coating for different media

Iron oxide coated sand (IOCS)

Coating was applied as per Edwards & Benjamin (1989) by evaporating a ferric nitrate solution in the presence of sand. In this process, 200 g acid-soaked dried sand, 20 g $\text{Fe}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$ and about 60 mL water to cover the sand were placed in a 1.0 L glass flask. The total mixture was agitated by a glass rod for about 10 minutes. The uncovered flask was placed in an oven at $110 \pm 1^\circ\text{C}$ for 20 h to drive off all visible water. The coated media was washed with distilled water until the washings were clear. After washing it was dried again in an oven at $100 \pm 1^\circ\text{C}$.

Modified iron oxide coated sand (MIOCS)

The iron oxide was coated on sand by using a modified coating procedure. 200 g acid-soaked dried sand, 20 g $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 50 mL distilled water (DW) were placed in a 1.0 L glass flask. The flask was agitated gently to dissolve the $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ before placing it in an oven at 60°C for 60 h (optimized temperature and time) to remove all visible water. The coated media was washed gently with distilled water until the washings were clear. The sand was re-heated at 60°C for another 16 h to ensure all grains were dry. When MIOCS was cooled, the coating became quite moist i.e. it was hygroscopic. To remove moisture, the sand was subjected to three more drying cycles, each consisting of 3 h at 100°C with cooling to room temperature in between. The coating became less hygroscopic after these cycles. This procedure yielded distinctly red-coloured sand.

Iron-impregnated sand (IIS)

This media was prepared by taking 25 g $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 150 mL water in a 500 mL porcelain bowl and the mixture was stirred for about 10 minutes with a glass rod until all ferric nitrate was dissolved. Then 250 g acid-soaked sand (size = $498 \mu\text{m}$) was poured into this solution and the total mixture was again mixed for about 20 minutes with the glass rod. The bowl was heated on an electric heater at 100°C until dry. After cooling to room temperature, the impregnated sand was washed with tap water until the washings were clear.

The washed impregnated sand was dried in sunlight. This procedure yielded distinct red-coloured sand.

Sulfate modified iron oxide coated sand (SMIOCS)

This coating was applied by taking 100 mL of 0.5 M BaCl_2 solution in a 1.0 L glass beaker. In this solution 12 mL of 5 N H_2SO_4 was added drop by drop with simultaneous shaking of the beaker until a dense white floc of BaSO_4 formed in the beaker. In this solution 100 mL 0.5 M ferric nitrate [$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$] salt was added and mixed in a horizontal shaker at 30 strokes/minute for 10 minutes. After 10 minutes 500 g quartz sand was added to the mixture and again the beaker was shaken for an additional 30 minutes to ensure proper mixing of sand and solution. Thereafter, the beaker was kept in an oven at 105°C for 24 h. The coated sand was washed by distilled water until the washings were clear. The washed sand was again kept in an oven for drying. The coated sand was kept in a capped bottle for further analysis. This procedure yielded slightly red-coloured sand.

Mixed oxide coated sand - pre modified (MOCS-PM)

The mixed oxide (Fe + Mn) coated sand (MOCS) was prepared by oxidation of manganous iron by permanganate in the presence of ferric nitrate and sand. In 100 mL of 0.2 M KMnO_4 solution, 10 mL of 0.4 M NaOH was added to neutralize the acid produced and to keep the pH of the mixture basic throughout the preparation. Thereafter, 50 mL of 0.3 M MnCl_2 solution was added drop wise, while the mixture was kept well mixed with a shaker or by glass rod. After 30 min of mixing, 10 g of ferric nitrate [$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$] salt was added to this solution and the mixture was mixed for another 30 minutes. A 250 g sample of washed and acid-soaked river sand (GM size = 0.498 mm) was added to this mixture and was mixed by glass rod for another 10 minutes. Thereafter, the total mixture was kept in an oven for 20 h at 100°C . The coated sand was washed with distilled water until the washings were clear.

Mixed oxide coated sand (MOCS)

Mixed oxide coated sand (MOCS) was prepared by taking 40 mL 0.2 M KMnO_4 and 40 mL 0.2 M MnCl_2 solution and

properly mixing it in a 500 mL glass beaker. An 8.0 g sample of ferric nitrate $[\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}]$ was added to this beaker and the total mixture was again mixed by glass rod until all ferric nitrates were dissolved. A 200 g sample of acid-soaked sand was poured into the beaker and mixed by a glass rod for another 15 minutes. The uncovered beaker was placed in an oven at 60°C for 60 h. After this heating cycle, the oven temperature was raised to 102°C for an additional 12 h. The coated sand was washed by distilled water until the washings were clear and again it was dried at 102°C for 24 h. Cooled, coated sand was stored in PVC bottles for further studies. The colour of the coated sand was blackish and slightly reddish.

Mixed oxide coated sand - I (MOCS-I)

The coated sand was prepared by taking 2.24 g $\text{MnSO}_4 \cdot 7\text{H}_2\text{O}$ salt, 7.22 g ferric nitrate $[\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}]$ and 100 mL distilled water in a 500 mL glass beaker. A 200 g sample of acid-soaked quartz sand was mixed into this solution and the total mixture was manually mixed using a glass rod for 20 minutes. The beaker was kept in an oven at 105°C for heating. During the heating process the colour of the sand turned black. The coated sand was washed with distilled water until the washings were clear. The washed sand was again heated in an oven at 105°C until dry. The dried sand was kept in PVC bottles for further use.

Chemical properties of media

Total metal and acid/alkali resistance measurement

The total coated metals on the sand surface were determined by dissolving 5 g of coated sand into 50 mL of 6.0 M HCl for 24 h (Kuan *et al.* 1998). The total coated barium and sulfur were determined by dissolving 5.0 g SMIOCS in 50 mL concentrated HNO_3 for 24 h. Measurement of alkali resistance was performed in the laboratory by soaking 5.0 g of coated sand into NaOH ($\text{pH} = 12.67$, 50 mL) for 24 h. Measurement of acid resistance was conducted in the laboratory by soaking 5.0 g coated sand into HCl ($\text{pH} < 1.0$, 50 mL) for 24 h (Kuan *et al.* 1998). The suspensions from these experiments were filtered by 'Whatman-42' (ashless) filter paper and the contents were determined by ICP-AES (model -8440 Plasmalab, GBC, Australia).

The percentage alkali or acid resistance was measured using the following equation:

$$\% \text{ Alkali/acid resistance} = \frac{\text{Dissolved metal}}{\text{Total metal}} \times 100 \quad (1)$$

The lower percentage values of alkali/acid show that those media are more resistant to alkali or acid. Similarly, higher percentage values of alkali/acid show lower resistance to alkali or acid.

Chemical properties of quartz sand

The quartz sand procured from the banks of the Yamuna river, Allahabad, India, was cleaned and all foreign matters were removed, then it was soaked in acid (0.1 M HCl) for 24 hours. The sand was then washed and dried in an oven at 100°C . The dried sand was used for its chemical property determination as per the method described by Shapiro & Brannock (1956).

pH of quartz sand

The quartz sand pH was determined by taking 1 : 2 sand : water suspensions in a glass beaker. The suspensions were mixed intermittently for 30 minutes before pH measurement (Jackson 1967).

Measurement of arsenic concentration

The analysis of As(III) was carried out as per Johnson & Pilson's (1972) method. The absorbance was measured at 865 nm using a spectrophotometer (Spectronic 20 Genesys, USA). The minimum detection limit is $4 \mu\text{g As}$. All samples were measured in duplicate.

BET surface area and pH_{zpc} of coated sand determination

The surface area of quartz and coated sand was measured by BET method using ASAP- 2000 model (Micromeritics Corp., USA). The pH_{zpc} of the medium was determined by the potentiometric titration method as described by Smith (1998).

Column studies

The column experiments were conducted in a fixed-bed reactor (glass column) in down-flow mode employing distilled water spiked with 0.01 M NaNO₃ ionic strength using arsenic (III) as adsorbate. Glass columns of 15 mm internal diameter with media depths of 200 mm were used to generate data for this study. The influent concentration was maintained constant at 1.0 mg/L. The influent flow rate was maintained at 1.56 m³/m²/h in all studies using a peristaltic pump (Watson Marlow, model 502 S, USA). The average diameter of adsorbent particles (d) was 0.498 mm and bulk densities (ρ) were ~1.48 g/cm³. The samples were collected at different time intervals and were analysed for arsenic concentrations. The column was run until the effluent concentration reached near 95% of influent concentration.

Screening of coated sand

Six different coated sand media were screened for their arsenic uptake potentials. These experiments were conducted using the protocol of isotherm experiments. Accordingly, 20 g/L of sorbent dosage of different media (geometric mean size, 0.498 mm) were added to different glass-stopper bottles containing 100 mL of As(III) using different concentrations of As(III) from 0.5 to 3.5 mg/L, and pHs were maintained by using 0.1 M NaOH and 0.1 N HCl. The bottles were rotated on an end-to-end rotary shaker at 44 rpm. Several duplicate samples were included to determine time required to reach equilibrium. The allowed equilibrium was 8 h and the solution was filtered using 'Whatman 42' (ash-less) filter paper. The filter paper used was pre-saturated with corresponding solutes to avoid errors due to possible adsorption of arsenic by the filter paper.

RESULTS AND DISCUSSION

The aim of the present research work was development of suitable cost-effective oxide coated sand media using innovative methods and optimization of the coating process for efficient removal of arsenic from water. Determination of quartz and coated sand properties was also a main objective

of the study. Accordingly, the results obtained have been discussed under the appropriate headings.

Optimization, properties and screening of media

In the present study, six new media have been developed using iron and other metal oxides, either by changing the process of coating or by optimizing oxide-coating processes on sand by changing the number of parameter variables. The selection of medium was dependent especially on its arsenic uptake potential and other properties like BET surface area, pH_{ZPC}, alkali and acid resistance. The following subsections deal with properties of quartz and coated sand along with optimization procedures.

Table 1 presents the chemical composition of quartz sand. It is evident that the major composition of quartz sand is SiO₂. Aluminium oxide (Al₂O₃) is the second largest oxide. Total iron in the form of oxides is 2.74% (W/W).

The optimization of different oxide coated media was carried out as per the following procedures.

Optimization of oxide coated sand media

Optimization of IOCS media

Several researchers (Edwards & Benjamin 1989; Benjamin *et al.* 1996; Joshi & Chaudhuri 1996) have used iron oxide

Table 1 | Chemical characteristics of quartz sand

No.	Contents	% Composition
1.	SiO ₂	82.022
2.	Al ₂ O ₃	9.447
3.	P ₂ O ₅	0.375
4.	TiO ₂	0.383
5.	Total Fe (Fe ₂ O ₃ + FeO)	2.741
6.	Na ₂ O	1.078
7.	K ₂ O	2.040
8.	CaO	ND
9.	MgO	0.600
10.	SO ₄ ²⁻	0.11
11.	Cl ⁻	0.023

Note: ND represents not detected

coated sand for the removal of heavy metals including arsenic. In this study the iron oxide coating on sand surface was optimized using the following parameter variations.

- Temperature of coating
- pH of coating ($\text{pH}_{\text{coating}}$)
- Heating time of coating
- Dose of iron oxide salt

The results of As(III) removal on these optimized media are presented in Tables 2–7. Only Fe and Mn were considered as main oxides for coating on sand surface because aluminium oxide (Al_2O_3) has shown poorer arsenic removal capacity compared with Fe_2O_3 (Jeong *et al.* 2007).

Table 2 shows that *iron oxide coated sand* (IOCS) coated at a lower temperature (60°C) has shown better removal efficiency (97%) of As(III) compared with higher temperatures (100°C upwards) of coating under similar experimental conditions. Also Fe on the surface of media coated at 60°C was highest compared with other media coated at higher temperatures. Therefore, 60°C was chosen as the optimum temperature of coating. Similar to the present finding Xu & Axe (2005) have also obtained maximum Fe_{conc} (mg Fe/g) at 60°C on silica. The quartz sand used in this study for oxide coating contains nearly 82% SiO_2 (Table 1). Thus the observed result is similar to the findings of previous researchers. The oxide coating decreased at a higher temperature (100°C), which is similar to observations by Stahl & James (1991), where the iron oxide coating decreased as the temperature increased from 105 to 500°C . Sorensen *et al.* (2000) also supported these findings and reported that at higher temperature amorphous iron oxides transform to crystalline structures and the availability of the oxalate extractable iron fraction was quite low compared to that at 50°C . For the

removal of copper and lead from water, Lai *et al.* (2000a) have also prepared iron coated sand at $50 \pm 1^\circ\text{C}$ by heating in an oven for 96 h.

Table 3 shows the effect of heating time on coating. The results show that 60 h heating time in iron oxide coating process yields maximum As(III) removal. The media prepared at this heating time has the highest Fe (mg/g) on the sand surface. Previous literature (Thirunavukkarasu *et al.* 2002; Gupta *et al.* 2005) suggests that iron plays a major role in the removal of As(III) and organic arsenic from water. Therefore, all further optimization studies for coating were conducted at 60°C for 60 h. Table 3 also shows that Fe_{conc} (mg Fe/g-sand) ranges from 4.78 to 11.59 (mg Fe/g-sand) for 24 to 76 h heating time. Lai *et al.* (2000b) have also reported that the amount of iron on the sand surface was 5.7 ± 0.3 (mg Fe/g-sand).

In the literature, a number of researchers have used different $\text{pH}_{\text{coating}}$ for the removal of cations and anions (Kuan *et al.* 1998; Lai *et al.* 2000a); therefore, it was imperative to see the effect of pH on coating for its arsenic removal potential. The effect of pH on coating was studied at pH values ranging from 0.5 to 12.0. The results are given in Table 4. The results show that better As(III) removal efficiency was obtained when iron coating at the sand surface was conducted at lower pH. During coating of quartz sand at low pH regime, more iron may have been associated on the quartz sand surface. This statement is also supported by results shown in Table 4, which shows higher Fe concentration on the sand surface (12.51 mg/g) at low $\text{pH}_{\text{coating}}$ (≈ 0.5).

The effect of iron salt dose on coating was also studied to optimize the dosage of salt necessary for maximum removal of arsenic (Table 5). The iron salt [$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$]

Table 2 | Effect of temperature on coating for 60 h heating time

No.	Coating temp. ($^\circ\text{C}$)	Fe conc. (mg/g)	Mn conc. (mg/g)	As(III) removal (%)
1.	60	12.61	0.12	97
2.	100	7.65	0.14	92
3.	150	4.76	0.11	80
4.	250	5.4	0.16	80
5.	350	6.75	0.18	85
6.	450	7.54	0.15	93

Table 3 | Effect of heating time on coating at 60°C heating temperature

No.	$\text{pH}_{\text{coating}}$ (<)	Heating time (h)	Fe conc. (mg/g)	As(III) removal (%)
1.	0.5	24	4.78	83
2.	0.5	30	5.12	87
3.	0.5	36	6.02	89
4.	0.5	48	8.56	94
5.	0.5	60	12.6	97
6.	0.5	72	12.45	97
7.	0.5	76	11.59	97

Table 4 | Effect of pH_{coating} at 60°C heating temperature and 60 h heating time

No.	pH _{coating}	Fe conc. (mg/g)	As(III) removal (%)
1.	0.5	12.51	97
2.	1.65	6.2	84
3.	3.0	4.36	66
4.	4.65	6.8	93
5.	8.10	6.2	73
6.	10.19	4.85	62
7.	13.00	7.25	84

percentage was varied from 4 to 14 and the mixture was kept in an oven at 60°C for 60 h at pH_{coating} = 0.5. The evaluation of media on the basis of As(III) removal capacity shows that a ferric nitrate dose of 8–10% (weight of salt/eight of sand) may be the optimum dose of iron coating on the sand surface. The medium developed at optimized temperature, time and pH_{coating} (60°C, 60 h and <1.0) was denoted as *modified iron oxide coated sand* (MIOCS).

Optimization of SMIOCS media

The optimization of SMIOCS media was carried out with pH_{coating} variation and change in dose of iron before coating. The pH_{coating} has shown a considerable effect on arsenic removal efficiency. The SMIOCS prepared at pH_{coating} < 1.0 was quite efficient compared to media prepared at pH_{coating} ≅ neutral and pH_{coating} ≅ 12.05. When the iron concentration in the mixture was increased from 0.5 M ferric nitrate to 1.0 M ferric nitrate, keeping all other conditions similar in solution before coating, the coated media prepared using

Table 5 | Effect of iron salt dose on coating at 60°C heating temperature

No.	pH _{coating}	Salt (%)	Fe conc. (mg/g)	% Fe ₂ O ₃	As(III) removal (%)
1.	0.5	4	5.58	7.98	95.3
2.	0.5	6	6.03	8.62	95.3
3.	0.5	8	6.36	9.09	96
4.	0.5	10	7.09	10.14	97.5
5.	0.5	12	7.66	10.95	97.5
6.	0.5	14	6.16	8.81	95.3

1.0 M ferric nitrate has shown slightly higher arsenic removal efficiency.

Optimization of MOCS-PM media

Mixed oxide coated sand (MOCS-PM) medium was also optimized using the following parameter variations:

- Chemical requirement
- Temperature
- pH of coating
- Fe/Mn ratio

From Table 6, it can be seen that MOCS-PM is quite effective for As(III) removal if coated at a lower temperature (100°C). The drawback of this method of coating was that it requires more chemicals (i.e. KMnO₄ and MnCl₂) for media preparation compared to MOCS [MOCS and MOCS-I]. The high development cost of this medium could not justify this method of coating. Therefore, further studies were conducted using mixed oxide coated sand (MOCS).

The effect of pH_{coating} was also measured using MOCS. This effect is shown in Table 7. Table 7 shows that MOCS prepared under acidic medium is more effective for arsenic removal than basic medium. Also, the chemical dose requirement is less than in MOCS-PM media. Initial low-temperature heating in an oven may have enhanced the surface area of the media and, thus, increased arsenic sorption capacity. Table 7 also presents MOCS-I media, which were prepared using a different set of chemicals for the evaluation of arsenic removal potential. The efficiency of this medium was also comparable with MOCS developed under acidic medium.

Physical and chemical characteristics of media

The physical and chemical characteristics of plain quartz sand, IOCS, MIOCS, SMIOCS, MOCS, MOCS-I and iron

Table 6 | Effect of heating temperature (MOCS-PM)

No.	Coating temp. (°C)	Heating time (h)	Fe conc. (mg/g)	Mn conc. (mg/g)	As(III) removal (%)
1.	100	12	6.61	3.72	100
2.	200	12	4.07	1.3	76
3.	400	12	5.44	2.6	64

Table 7 | Effect of pH_{coating} and dosage of chemicals

Media	Coating temp. (°C)	Heating time (hr)	pH _{coating}	Fe conc. (mg/g)	Mn conc. (mg/g)	As(III) removal (%)
MOCS	60 + 102	60 + 12	<1.0	7.29	1.48	89
MOCS	60 + 102	60 + 12	≅ 10.0	2.15	0.53	48
MOCS-I	105	24	<1.0	7.22	1.97	85

impregnated sand (IIS) are shown in Table 8. Acid and alkali resistance shows that the amount of Fe or Mn gets dissolved in an acidic or alkaline medium. The MOCS media has better acid resistance than IOCS and SMIOCS media whereas alkali resistance for all the media is less than 1%. Thus, oxide coated sand media prepared at low pH have less capability for acid resistance but very high capability for alkali resistance. Therefore, regeneration may be limited with alkaline regenerating solution. The total iron content was higher on MOCS compared with IOCS and SMIOCS, but lower than MIOCS and IIS. This may be the reason that MOCS has shown high arsenic (III) removal efficiency with respect to IOCS and SMIOCS. Barium and sulfur presence on the SMIOCS media is also shown in Table 8.

BET surface area

The surface area of an adsorbent is an important property. It has been used for the calculation of mass transfer coefficients from the sorption kinetic data by many researchers (Matthews & Weber 1977; Allen *et al.* 1992). It was necessary to measure the surface area of coated sand to find out the

relation between surface area and adsorption potential of the medium. The high adsorption potential is widely attributed to high specific surface area of the medium. Table 9 shows BET surface areas of coated sands.

The measured BET surface areas of these media range from 1.795 to 4.268 m²/g for 0.498 mm size particles. This is not uncommon as the BET method always under-estimates the surface area of particles (Smith 1998). The obtained result of this study is close to the reported BET surface area of IOCS (5.0 m²/g) in the literature (Stenkamp & Benjamin 1994). Benjamin *et al.* (1996) have also reported the BET surface area of IOCS as 5.8 m²/g. Lai *et al.* (2000b) have reported the BET surface area as 2.76 m²/g for un-adsorbed IOCS during adsorption of copper ions.

Table 9 shows that the BET surface area of SMIOCS increases from 2.95 to 7.895 m²/g when the size of quartz sand particles reduces from 0.716 mm to 0.324 mm. The BET surface areas of MIOCS, SMIOCS and IIS media were higher compared with other media for 0.498 mm size particles. The media having higher BET surface areas have shown better removal efficiency compared with media having poor BET surface areas (Figure 1).

Table 8 | Physical and chemical properties of different media used for experimental study

No.	Characteristics	Quartz sand	IOCS	MIOCS	IIS	SMIOCS	MOCS	MOCS-I
1.	Geometric mean size (μm)	498	≅ 498	≅ 498	≅ 498	≅ 498	≅ 498	≅ 498
2.	Diameter of particle (mm)	≅ 0.5	≅ 0.5	≅ 0.5	≅ 0.5	≅ 0.5	≅ 0.5	≅ 0.5
4.	Fe salt used for coating: (Fe salt/sand) w/w × 100	–	10	10	10	4	4	≅ 4
5.	Total iron on coated sand: mg Fe/g sand	–	4.61	12.61	15.2	5.31	7.28	7.22
6.	Acid-resistance at pH ≅ 1.0 (%)	0.02	40.3	47.4	40.1	45.67	33.8	32.67
7.	Alkali-resistance at pH ≅ 12.67 (%)	0	0.25	0.05	0.015	0.94	0.07	0.03
8.	Total manganese on coated sand: mg Mn/g sand	–	–	0.12	–	–	1.48	1.97
9.	Acid-resistance at pH ≅ 1.0 (%)	–	–	41.54	–	–	10.74	20.2
10.	Alkali-resistance at pH ≅ 12.67 (%)	–	–	0.14	–	–	0.02	0.014

Table 9 | BET surface area of coated sands

Size	0.324 mm (m ² /g)	0.498 mm (m ² /g)	0.716 mm (m ² /g)
Media			
Quartz sand	–	1.795	–
IOCS	2.4875	3.21	2.168
SMIOCS	7.895	3.75	2.95
MOCS	2.89	2.70	2.55
MOCS-I	–	2.90	–
MIOCS	–	3.44	–
IIS	–	4.268	–

pH zero point charge (pH_{zpc})

The surface of the sorbent can be characterized by zero point charge (zpc), which is defined as the pH value at which the total charge on the sorbent, arising from all the sources, is zero and is indicated as pH_{zpc}. The surface will be positive for pH < pH_{zpc} and negative for pH > pH_{zpc}. The results of pH_{zpc} are presented in Table 10.

The pH_{zpc} values indicate that the IOCS and SMIOCS media are positively charged at neutral pH, whereas uncoated sand is negatively charged. Stumm & Morgan (1981) reported that the pure iron oxides typically have zero point charges (ZPCs) in the pH range of 7–9. The measured pH_{zpc} of IOCS and SMIOCS in the present study actually fall in this pH range. Though the value pH_{zpc} of IOCS is on the higher side, it may be that incorporation of some cations into Fe oxides

Table 10 | pH_{zpc} of media

Media	pH _{zpc}
Plain quartz sand	2.3
IOCS	8.9
SMIOCS	8.2
MOCS	6.2

can increase the pH_{zpc} of the media. But there was no evidence of any such cation incorporations in the coating. This result also suggests that the iron oxide may dominate at least in the acid–base interactions between surface and solution.

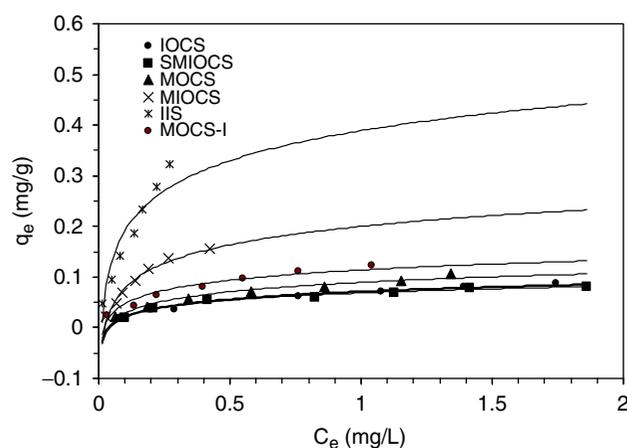
MOCS showed a pH_{zpc} value (6.2) below neutral pH. The reported values of pH_{zpc} of Mn oxides are in the pH range of 2–3.5, but Healy *et al.* (1966) have reported the value of pH_{zpc} = 5.5 ± 0.2 for γ-MnO₂. There is evidence that incorporation of cations increases the pH_{zpc} of media (Benjamin *et al.* 1996). The measured pH_{zpc} of MOCS was towards the higher side (6.2). This may be due to the presence of Fe on the sand surface.

Isothermal studies

Isothermal studies were conducted to determine sorption capacities of coated sand media. The isotherm data were fitted to both Langmuir and Freundlich isotherms. Linearized forms of Langmuir and Freundlich isotherms are shown below:

$$\frac{C_e}{q_e} = \frac{C_e}{Q_0} + \frac{1}{bQ_0} \quad (2)$$

$$\ln(q_e) = \ln K_F + 1/n \ln(C_e) \quad (3)$$

**Figure 1** | Equilibrium curves for the uptake of As(III) by different media.

The saturation capacity, Q_0 (mg/g) in the Langmuir isotherm is equal to the solid phase arsenic concentration, at liquid-phase equilibrium arsenic concentration, C_e (mg/L). Here Q_0 represents the maximum quantity of the sorbate which a sorbent can sorb, at a given initial concentration range. The value Q_0 represents the sorption capacity of the medium. In Equation (3), if $C_e = 1.0$ mg/L then the value of

K_F may be taken as the sorption capacity of a medium for a given range of concentrations.

The sorption equilibria experiments were conducted for the sorption of arsenic (III) onto six different coated sand media developed in the laboratory. Figure 1 presents the sorption isotherm of these six selected media. Qualitatively, all the isotherms have similar shape and in all cases the Freundlich isotherm provides a good fit ($C_c > 0.90$). Isotherm parameters are presented in Table 11. From the table it can be seen that the sorption capacity coefficient K_F and the saturation capacity Q_0 for IOCS and SMIOCS media are almost equal (difference $< 15\%$). It can also be concluded from the table that MOCS media have higher sorption capacities compared to IOCS and SMIOCS. The IIS and MIOCS media have shown little higher sorption capacity compared with other media. The MOCS media have higher sorption capacities compared to IOCS and SMIOCS media. The uptake capacities of other media were almost uniform with slight variations. Figure 1 also shows that the media which have shown higher Fe_{conc} (mg Fe/g-sand) in Table 8 have shown higher adsorption potentials for As(III).

Column studies

Figure 2 shows breakthrough curves for As(III) removal from simulated groundwater by different media during column studies. The operating conditions were similar for all these media. It can be seen from the figure that IIS and MIOCS media are able to treat As(III)-containing simulated water, considerably higher number of bed volumes till breakthrough. It may be due to higher Fe concentration and higher BET

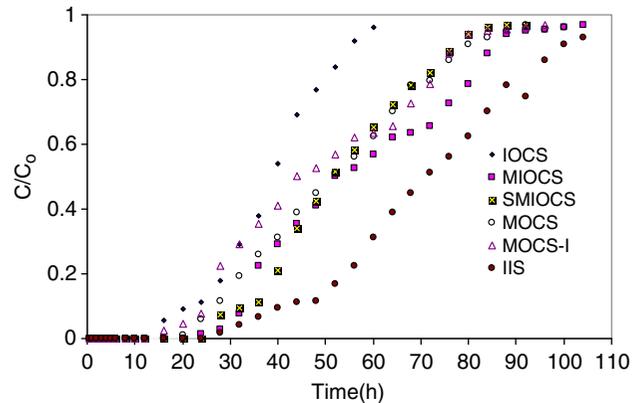
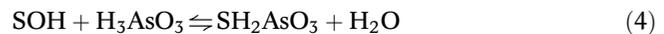


Figure 2 | Breakthrough curves for As(III) removal from simulated groundwater by different media.

surface area of IIS and MIOCS media (Table 8). The possible removal mechanism may be explained using surface complexation theory. As per this theory, the media are assumed to have oxide on the hydroxylated surface sites in the solution such as $>SOH_2^+$ and $>SOH$ representing positive and neutral charged sites. Since Fe is present on the coated sand surface, these surface sites may be $>FeOH_2^+$ and $FeOH^{+2}$. An example of surface complexation of arsenite (H_3AsO_3) is as follows:



Here, SOH is a hydroxide surface site. Equation (4) represents un-indentate surface complexation in the near-surface plane and incorporates the impact of pH on adsorption equilibria (Smith 1996). Another possibility is the formation of arsenic polymers at the surface of the medium analogous to polyphosphate, allowing single arsenic (III) species on the chain to sorb onto the coated sand surface while removing several arsenic atoms. Based on this concept, the surface of the media may develop a high adsorption density for As(III). Jain *et al.* (1999) also reported that As(III) forms bidentate complexes with ferrihydrite.

CONCLUSIONS

The results of optimization of iron oxide coated sand (IOCS) show that better arsenic removal efficiency can be achieved in comparison with traditional coating process. The MIOCS

Table 11 | Langmuir and Freundlich isotherm parameters for As(III) removal by various coated sand media

No.	Media	Langmuir parameters		Freundlich parameters	
		Q_0 (mg/g)	b (L/g)	K_F ($mg^{n-1}/n \cdot g^{-1} L^{1/n}$)	$1/n$
1.	IOCS	0.083	3.54	0.070	0.472
2.	SMIOCS	0.096	3.06	0.067	0.442
3.	MOCS	0.129	2.46	0.091	0.5
4.	MIOCS	0.269	3.57	0.351	0.729
5.	IIS	0.491	5.76	0.677	0.612
6.	MOCS-I	0.151	3.55	0.125	0.483

media developed at an optimal coating temperature of 60°C optimal $\text{pH}_{\text{coating}} \approx 0.5$, optimal heating time 60 hours and 10% w/w percentage iron salt $[\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}]$ have shown better As(III) removal efficiency compared with media developed at different process parameter variables. The 60 h heating time in the iron oxide coating process yields maximum Fe (mg/g) on the sand surface. The $\text{pH}_{\text{coating}}$ has shown a considerable effect on arsenic removal efficiency during optimization of sulfate modified iron oxide coated sand (SMIOCS) media. The SMIOCS prepared at $\text{pH}_{\text{coating}} < 1.0$ was quite efficient compared to media prepared at $\text{pH}_{\text{coating}} \cong \text{neutral}$ and $\text{pH}_{\text{coating}} \cong 12.05$. The mixed oxide coated sand (MOCS) prepared at $\text{pH}_{\text{coating}} < 1.0$ has shown better arsenic removal efficiency in comparison to other mixed oxide coated sand (MOCS) media developed. The BET surface area varied from 2.55 to 7.895 m^2/g for particle sizes ranging from 0.716 mm to 0.324 mm for different coated sand media. The IOCS and SMIOCS media were found to be positively charged at neutral pH, whereas uncoated sand was negatively charged on the basis of measured pH_{zpc} values. Thus optimized media developed after optimization of the oxide coating process on quartz sand result in relatively higher As(III) removal efficiency during column studies as compared with coated sand media prepared using simple traditional processes available in the literature.

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