

Iron and manganese amended activated alumina – a medium for adsorption/oxidation of arsenic from water

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ABSTRACT

In a laboratory study, iron and manganese amended activated alumina (IMAA) showed promise as an effective medium for removing arsenic [As(III) and As(V)] from groundwater. Batch adsorption/oxidation kinetic test indicated that the effectiveness of the IMAA medium was due to *in situ* oxidation of As(III) to As(V) and higher adsorption of As(V) by the medium. A home arsenic removal unit, containing 4 L of IMAA or AA and operated at 6 L/h, produced 2400 L and 2340 L or 1392 L and 1320 L of water in two cycles of runs when the influent arsenic concentration was 1.0 mg/L [0.6 mg/L of As(III) and 0.4 mg/L of As(V)]. The IMAA medium should be subjected to field trials to assess the long-term effects on performance, such as loss of medium capacity, attrition of the iron and manganese coating, fouling by organics, and pH and competing ion effects.

Key words | activated alumina, adsorption/oxidation, arsenic removal, iron, manganese

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INTRODUCTION

The presence of arsenic in drinking water even at low concentrations poses a threat to human health, as arsenic is a well-known toxic element and a documented human carcinogen. Arsenic occurs in groundwater in two valence states, as trivalent arsenite [As(III)] and as pentavalent arsenate [As(V)]. Adsorption by activated alumina, with oxidative pretreatment using chlorine or potassium permanganate is most commonly used for small municipal drinking water systems and point-of-use treatment.

Based on the evidence of oxidation of As(III) to As(V) by iron and manganese oxides (Oscarson *et al.* 1981, 1983; Moore *et al.* 1990; Driehaus *et al.* 1995; Scott & Morgan 1995), adsorption of As(III) and As(V) by iron hydroxide (Pierce & Moore 1980, 1982) and adsorption of As(V) by hydrous manganese oxide (Takamatsu *et al.* 1985), it appeared that iron or manganese oxide, or a porous support medium coated (impregnated) with iron/manganese oxide, would serve as an effective medium for removing arsenic from water. Granular ferric hydroxide (Driehaus *et al.* 1998) and granulated Fe–Si binary oxide (Zeng 2003), iron oxide-coated sand (Joshi & Chaudhuri 1996), iron oxide-impregnated activated carbon

(Reed *et al.* 2000), iron-coated sand and iron-impregnated activated carbon (Petrusevski *et al.* 2002), iron oxide-coated polystyrene and polyHIPE (Katsoyiannis & Zouboulis 2002), iron-impregnated sand (Vaishya & Gupta 2003), manganese dioxide-coated sand (Bajpai & Chaudhuri 1999) and manganese dioxide-loaded polystyrene (Lenoble *et al.* 2004) media were developed and found to be effective in removing arsenic from groundwater.

In examining the adsorption/oxidation of arsenic by manganese dioxide-coated sand, Verma (2000) reported that the sand matrix under the coating also played a role in the adsorption of As(III) and As(V), suggesting that iron oxide/manganese dioxide-coated (impregnated) on a support medium with high As(V) adsorption capacity, such as activated alumina, would be a more effective medium for adsorption/oxidation removal of arsenic [As(III) and As(V)] from water. Subsequently, a manganese amended activated alumina (manganese dioxide-impregnated activated alumina) medium was developed (Kunzru & Chaudhuri 2005).

An electron microprobe study has shown that microscopic accumulation of manganese in soil is always accompanied by

relatively high concentration of iron (McKenzie 1975), suggesting that iron oxide may promote accumulation of manganese oxide and successive coatings of iron oxide and manganese dioxide is possible. This paper describes a method for the preparation of an iron and manganese amended activated alumina (iron oxide and manganese dioxide-impregnated activated alumina) medium and examines adsorption/oxidation of arsenic and its removal from groundwater by the medium *vis-à-vis* activated alumina. Suitability of the medium *vis-à-vis* activated alumina for use in home arsenic removal units is also assessed.

METHODS

Activated alumina used in the study was commercially available (Grade AS-37, Oxide India Ltd., Durgapur, India). The characteristics of the activated alumina were: particle size 0.3–0.6 mm, bulk density 960 kg/m³, surface area (BET) 275 m²/g, pore volume 0.46 cm³/g, loss on attrition 0.10% and loss on ignition at 1000°C 5.60%, and Al₂O₃ 93.60%, Fe₂O₃ 0.05%, SiO₂ 0.18% and Na₂O 0.27%. Before use, the activated alumina was subjected to alkali–acid treatment: treatment with a 4% sodium hydroxide solution, followed by rinsing with distilled water and treatment with a 0.05 N hydrochloric acid solution, followed by rinsing with distilled water until the pH of the rinse water was in the range 7.5–8.0.

Iron and manganese amended activated alumina was prepared by impregnating activated alumina with iron oxide and manganese dioxide, using a procedure similar to that of Kapteijn *et al.* (1994) for preparation of the alumina-supported manganese oxide catalyst. In the first phase of impregnation, 7.0 mL of a 2 M ferric nitrate [Fe(NO₃)₃·9H₂O] solution were slowly added to 10.0 g of activated alumina by mixing. The mixture was then dried at 150°C for 3 h and calcined in dry air at 550°C for 3 h, giving an iron oxide-impregnated activated alumina. In the second phase of impregnation, 3.0 g of manganese acetate [(CH₃COOH)₂Mn·4H₂O] were dissolved in 6.5 mL of distilled water and the solution was slowly added to 9.0 g of iron oxide-impregnated activated alumina by mixing. The mixture was then dried at 150°C for 3 h and calcined in dry air at 400°C for 3 h, giving an iron and manganese amended activated alumina (IMAA) medium. The IMAA was washed with distilled water until the runoff was

clear, dried overnight at 105°C for 3 h, and stored in capped bottles. X-ray diffraction analysis confirmed the impregnation to be of iron oxide (α -FeO(OH), goethite) and manganese dioxides (δ -MnO₂, birnessite, and α -MnO₂, cryptomelane). The amount of iron and manganese impregnation, estimated by nitric acid digestion, was found to be 52 mg Fe/g and 61 mg Mn/g of activated alumina. The surface area (BET) of the IMAA was 256 m²/g.

The arsenic-bearing water was a groundwater (pH 7.5–8.0, alkalinity 240–250 mg CaCO₃/L, hardness 145–195 mg CaCO₃/L, phosphate 0.02–0.07 mg P/L and conductivity 450–550 $\mu\Omega^{-1}$ /cm) spiked with 1.0 mg/L of As(V), using sodium arsenate (Na₂HAsO₄), or 1.0 mg/L of As(III), using sodium arsenite (NaAsO₂), or 0.6 mg/L of As(III) and 0.4 mg/L of As(V).

The molybdenum blue spectrophotometric method (Johnson & Pilson 1972) was used for the determination of As(V). By the use of an oxidising agent (potassium iodate), As(III) was oxidised to As(V) and determined along with As(V) as total arsenic. As(III) was given by the difference between total arsenic and As(V). In a recovery experiment [adding a known quantity of As(III) or As(V) to the water and measuring the concentration], up to 0.005 mg/L of As(V) or As(III) was detected with good precision.

Batch kinetic tests, using the arsenic-bearing water and the activated alumina (AA) (10 g/L) or IMAA (10 g/L) in 250 mL glass bottles, were conducted to examine adsorption/oxidation of As(V), As(III), and As(III) and As(V) (present together) in groundwater by the IMAA and AA. The bottles were placed in an end-over-end shaker at 30 rpm, and at predetermined time intervals bottles were withdrawn, the supernatant was filtered through a 0.45 μm membrane filter and the filtrate was analysed for residual arsenic.

Downflow column tests, using 63 mL (52 g) of AA or 63 mL (66 g) of IMAA medium in a 20 mm ID glass column (bed depth 200 mm) and a flow rate of 3.14 mL/min (bed flowthrough time of 20 min), were conducted with the arsenic-bearing [1.0 mg/L of arsenic – 0.6 mg/L As(III) and 0.4 mg/L As(V)] water, to compare the performance of the two media and to assess durability of the IMAA medium. The columns were run until the effluent arsenic exceeded the World Health Organization (WHO) guideline value of 0.01 mg/L for arsenic in drinking water (WHO 2004). Following termination of a run, the AA medium was

regenerated *in situ* by backwashing at 2 mL/cm²·min with 1 L of a 4% sodium hydroxide solution followed by a rinse with 1 L of a 0.5 N hydrochloric acid solution, whereas the IMAA medium was regenerated *in situ* by backwashing with 2 L of a 1% sodium hydroxide solution. The columns were then equilibrated by passing distilled water until the influent and effluent pH were comparable. This constituted one cycle of the column test. The spent regenerant and the backwash water were analysed for the recovered arsenic.

RESULTS AND DISCUSSION

Adsorption/oxidation of As(V), As(III), and As(III) and As(V) (present together) by IMAA and AA are shown in Figure 1. Adsorption of As(V) by both IMAA and AA was rapid – 88.5 and 76% removal in 5 min, and 100 and 99.5% removal in 30 and 120 min, respectively (Figure 1(a, b)). Initial rapid adsorption of As(III) by AA was significantly lower than that of As(V) – 38% removal in 5 min (Figure 1(d, b)). This was presumably due to the fact that As(III) was present as a neutral species (H₃AsO₃), and hence was not strongly adsorbed to the positively charged AA surface as was the As(V) species (H₂AsO₄⁻ and HAsO₄²⁻). For IMAA, both As(III) and As(V) were present in the water up to 30 min (Figure 1(c)) – As(V) resulted from As(III) oxidation by iron oxide and manganese dioxide, and the As(V) produced was adsorbed onto IMAA. Due to oxidation of As(III) to As(V) and subsequent adsorption of As(V) by IMAA, removal of As(III) by IMAA was much higher than that by AA – 82% in 5 min, compared to 38% by AA (Figure 1(c, d)). However, for IMAA, As(V) concentration in water showed a maxima at 5 min, due probably to simultaneous formation of As(V) from As(III) oxidation and adsorption of As(V) by IMAA. Initially when the concentration of As(III) was high, oxidation of As(III) to As(V) was rapid and the rate of adsorption of As(V) was lower than the rate of formation, causing a build-up of As(V). As time progressed, all As(V) adsorbed onto IMAA and removal by IMAA became higher (100% in 100 min) than that by AA (83% in 120 min) (Figure 1(c, d)). When both As(III) and As(V) were present together [0.6 mg/L As(III) and 0.4 mg/L As(V)], for AA, initial (5 min) removal of total arsenic was intermediate between that of As(III) and As(V) when

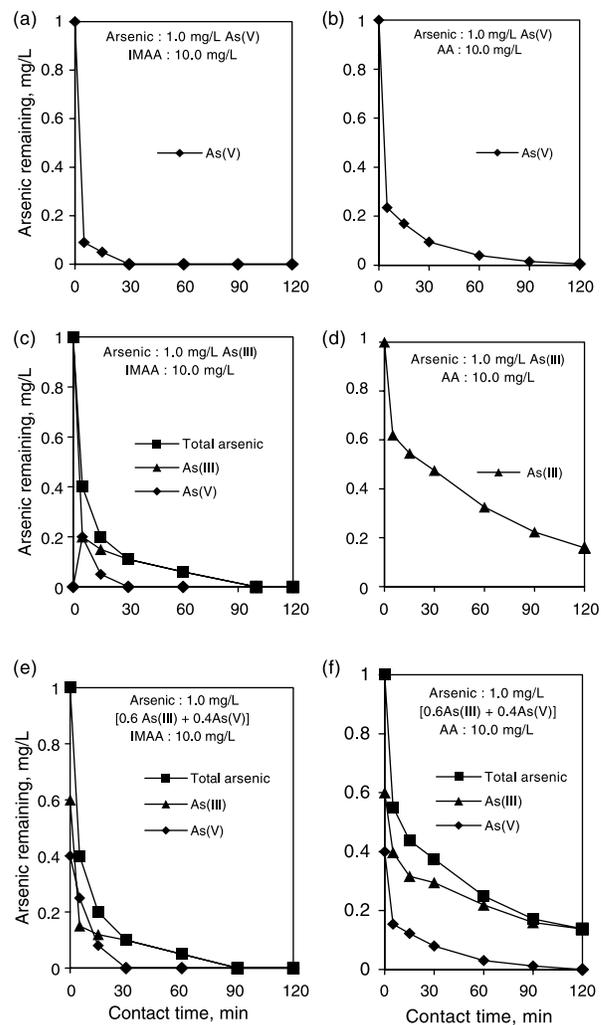


Figure 1 | Kinetics of adsorption/oxidation of arsenic from groundwater by iron and manganese amended activated alumina (IMAA) and activated alumina (AA).

present alone, and the initial rate of adsorption of both As(III) and As(V) was lower than the rates when they were present alone (Figure 1(b, d, f)). For IMAA, when both As(III) and As(V) were present together, removal of total arsenic was similar to that of As(III) when present alone (Figure 1(e, c)), and no maxima in As(V) concentration was observed at any time.

The performance of IMAA and AA in arsenic removal in three cycles of column test are shown in Figure 2. The top three panels show As(III) and As(V) in the effluent at breakthrough in the first, second and third cycles, whereas the bottom panel shows total arsenic in effluent in three cycles. Total arsenic content and the ratio of As(III) to

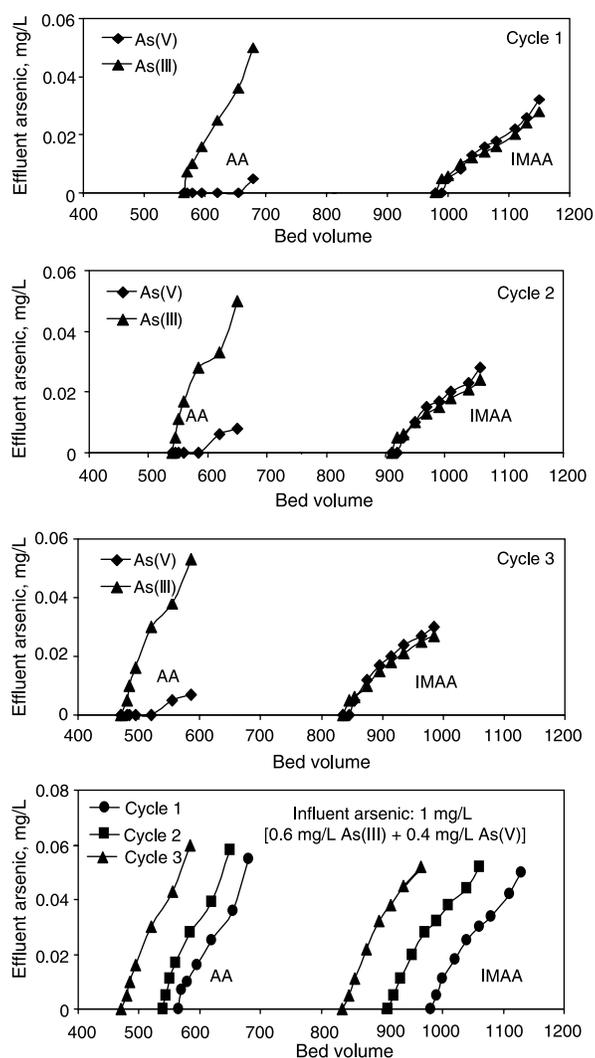


Figure 2 | Performance of iron and manganese amended activated alumina (IMAA) and activated alumina (AA) in arsenic removal in column test.

As(V) in the influent remained unchanged during the three cycles. At the WHO guideline value of 0.01 mg/L for arsenic in drinking water, AA treated 580, 550 and 485 bed volumes in the first, second and third cycles, respectively. The corresponding values for IMAA were 1000, 930 and 855 bed volumes, respectively. In a similar test, manganese amended activated alumina (MAA) treated 825, 770 and 695 bed volumes, respectively (Kunzru & Chaudhuri 2005). At breakthrough, the IMAA column effluent contained both As(III) and As(V), whereas the AA column effluent contained As(III) only. By comparison, the ratio of As(V) to As(III) in the IMAA column effluent at breakthrough was

higher than that in the MAA column effluent (Kunzru & Chaudhuri 2005). During regeneration of AA, 88, 85 and 84% of the removed arsenic was recovered after the three cycles, whereas for IMAA, 87, 86 and 85% of the removed arsenic was recovered. Aluminium concentration in the AA column effluent was 0.15–0.16 mg/L and that in the IMAA column effluent was 0.06–0.08 mg/L. Iron and manganese concentrations in the IMAA column effluent were 0.06–0.07 and 0.02–0.04 mg/L, respectively. At the first cycle breakthrough, a mass balance showed that 21.86 and 37.69 mg As(III) had been removed by AA and IMAA, respectively, yielding an average mass loading of 0.35 and 0.60 mg As(III) per mL of medium for AA and IMAA, respectively. In comparing the performance of IMAA with that of MAA (Kunzru & Chaudhuri 2005), it was observed that IMAA removed 20% more As(III) per mL of medium. Better performance of IMAA was due presumably to impregnated iron oxide which promoted a higher amount of manganese dioxide impregnation – 61 mg Mn/g in IMAA compared to 42 mg Mn/g in MAA, and the additional role of impregnated iron oxide in adsorption and oxidation of As(III) and adsorption of As(V). The results indicated the promise of IMAA as a more effective medium for use in small drinking water systems or point-of-use treatment for removing arsenic [As(III) and As(V)] from groundwater.

HOME ARSENIC REMOVAL UNIT

Two home arsenic removal units (Figure 3) with IMAA or AA as the medium were operated in parallel to evaluate the performance of IMAA *vis-à-vis* AA in removing arsenic [As(III) and As(V)] from groundwater. Each unit comprised two chambers made of galvanised iron sheet and placed one above the other. The top chamber (200 mm ID × 380 mm) contained 4.2 kg (4 L) of IMAA or 3.3 kg (4 L) of AA medium up to a height of 125 mm and served as the raw water reservoir. The bottom chamber (200 mm ID × 280 mm) was fitted with a tap at the bottom and served as storage for the treated water. A brass disc with a 1.0 mm diameter orifice was fitted to the top chamber, which produced an average flow rate of 6 L/h (empty-bed contact time 40 min).

The units were operated in parallel. In each run, 7 L of the arsenic-bearing [1.0 mg/L of arsenic – 0.6 mg/L of

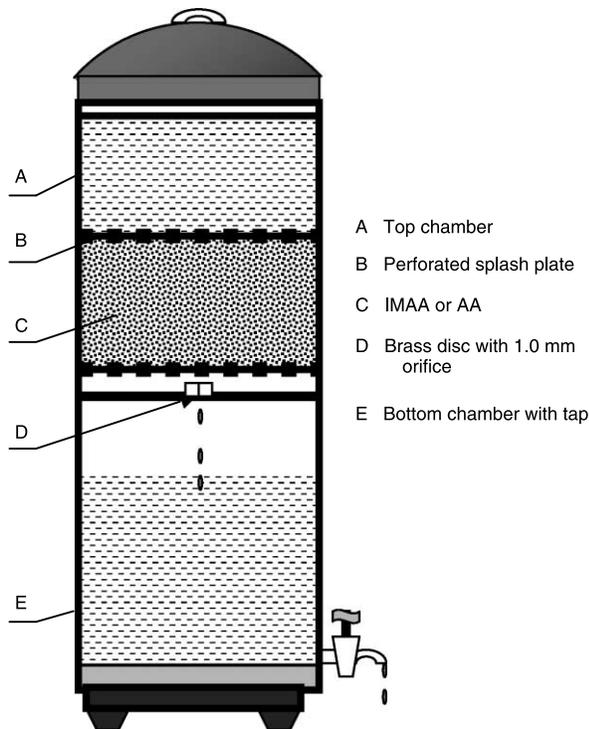


Figure 3 | Home arsenic removal unit.

As(III) and 0.4 mg/L of As(V)] water were placed in the top chamber and allowed to pass into the bottom chamber. Twelve runs were conducted daily, and runs were continued until the effluent arsenic level exceeded the WHO guideline value of 0.01 mg/L for arsenic in drinking water. This constituted one cycle. Before commencing the next cycle of runs, the media were regenerated *in situ*; for the IMAA medium, by passing 10 L of a 1% sodium hydroxide solution; the AA medium, by passing 5 L of a 4% sodium hydroxide solution, followed by passing 5 L of a 0.5 N hydrochloric acid solution. Thereafter, both media were washed with 10 L of water. Periodic sampling of the effluent during regeneration indicated that 10 L of a 1% sodium hydroxide solution and 5 L of a 4% sodium hydroxide solution were adequate for regeneration of IMAA and AA, respectively. The IMAA unit produced 2400 L (600 bed volumes) and 2340 L (585 bed volumes) in the first and second cycles, respectively, whereas the AA unit produced 1392 L (348 bed volumes) and 1320 L (330 bed volumes). During regeneration, 85 and 86% of the removed arsenic was recovered from IMAA and AA, respectively.

CONCLUSIONS AND REMARKS

In the laboratory study, iron and manganese amended activated alumina (IMAA) showed promise as a more effective medium than activated alumina (AA) or manganese amended activated alumina (MAA) for use in small drinking water systems or point-of-use treatment, for removing arsenic [As(III) and As(V)] from groundwater. The IMAA medium should be subjected to field trials to assess the long-term effects on performance, such as loss of medium capacity, attrition of the iron and manganese coating, fouling by organics, and pH and competing ion effects.

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