



Breakthrough studies with mono- and binary-metal ion systems comprising of Fe(II) and As(III) using community prepared wooden charcoal packed columns

Kamal Uddin Ahamad^{a,*}, Mohammad Jawed^b

^a Department of Civil Engineering, Tezpur University, Napaam, 784028, Assam, India

^b Department of Civil Engineering, Indian Institute of Technology Guwahati, Guwahati, 781039, Assam, India

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ABSTRACT

Groundwater of Assam (India) contains excessive amounts of As(III) and Fe(II). The rural and semi-urban population of Assam uses indigenous household iron filters fabricated using community prepared wooden charcoal (CPWC) to reduce Fe(II) concentration, however no efforts are made to reduce As(III) concentrations before use. The present work is directed toward assessing the potential of CPWC for metal removal from mono- and binary-metal ion systems comprising of Fe(II) and As(III) through continuous mode column studies. A decrease in breakthrough throughput volumes (V_B) from mono- and binary-metal ion systems is observed with increase in flow rates and decrease in bed depths. The order of breakthrough of metal ions observed as As(III) followed by Fe(II) from binary-metal ion system and hence the V_B for As(III) is termed as critical V_B as Fe(II) is yet to breakthrough through the beds. An early breakthrough for Fe(II) and As(III) from binary-metal ion system compared to respective mono-metal ion systems is observed for all the cases of flow rates and bed depths. It indicates impact on the uptake of a selected metal ion [either Fe(II) or As(III)] by the presence of the other metal ion [either As(III) or Fe(II)] present in the binary-metal ion system. The minimum and maximum errors involved between the predicted and experimental BDST curves for As(III) uptake till critical V_B from the binary-metal ion system varied between 1.0% and 24.8%.

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1. Introduction

Groundwater is the major source of domestic water for people living in rural and semi-urban areas of Assam — a northeastern hilly province of India. The concentration of arsenic [As(III)] and iron [Fe(II)] in the groundwater has been reported in the range of 0.05–0.2 mg/L and 1–25 mg/L respectively [11,20,28] which are much higher than permissible limits of drinking water [0.01 mg/L for As(III) and 0.3 mg/L for Fe(II) [16,31]]. The iron present in the groundwater causes visible coloration to the water and hence the rural and semi-urban population of Assam uses indigenous household iron filter units to reduce its concentration.

The presence of iron in the groundwater above regulatory limits makes the water unusable mainly from esthetic considerations such as discoloration, metallic taste, odor, turbidity, staining of laundry and plumbing fixtures. Aeration and separation are the most common methods for removal of iron from groundwater in public water supply systems, which are however, not so popular among rural and semi-urban communities lacking piped water supply. Other methods available for iron removal from groundwater are ion-exchange [30], oxidation with oxidizing agents such as chlorine and potassium permanganate [13], adsorption on activated carbon and other adsorbents [21] and treatment with limestone [5]. Intensive research have been undertaken in the last

few decades in developing countries such as Sri Lanka, Ghana, Burkina Faso, Argentina, South Africa, Uganda and India which has yielded many different methods, designs and configurations of iron removal units to be used at the community level [4,9]. But surprisingly none of these methods, designs and configurations of iron removal units so developed have found their place in the rural and semi-urban areas either at community levels or at an individual household level in this region probably due to high capital costs and complicated operation and maintenance requirements of these methods.

The problem associated with the presence of arsenic in the groundwater of Assam is just starting to get highlighted. It has been reported that 20 out of 24 districts of Assam have groundwater with arsenic content exceeding 0.05 mg/L [20]. Arsenic contamination in groundwater of developing countries is posing the greatest threat to human health. WHO drinking water guideline for arsenic was lowered from 0.05 to 0.01 mg/L in 1993 [31] considering epidemiological evidences on arsenic carcinogenicity. A number of household arsenic removal technologies have been developed or still under development such as two bucket treatment unit [27], Sono 3-Kolshi filter [18], BUET activated alumina arsenic removal unit [12], SAFI filter [12], well-head arsenic removal units [29], UNESCO-IHE arsenic removal family filter [25], Kanchan arsenic filter [23] and household sand filters [6]. Some of these technologies have undergone field level trials with encouraging results. The household arsenic removal technologies are yet to find its place in the rural parts of Assam due to (i) poor economic conditions

* Corresponding author. Tel.: +91 9678071266; fax: +91 3612582440.

E-mail addresses: k.ahamad@yahoo.com, kahamad@tezu.ernet.in (K.U. Ahamad).

of rural masses, (ii) non-availability of developed technologies, (iii) costly filtering media used, (iv) complex and tedious operation and maintenance to keep units functional, etc. Since arsenic does not cause any visible coloration to groundwater; no efforts are made to reduce its concentration by rural and semi-urban population.

The rural population of Assam use variants of indigenous household iron filters to reduce excess concentration of iron [Fe(II)] from the groundwater [3]. These indigenous filters have been developed based on experiences of rural population and passed from past few generations. These filters have been fabricated using local materials such as community prepared wooden charcoal (CPWC), river sand and gravel [2]. The rural communities believe that wooden charcoal helps in reducing concentration of the iron from the groundwater. However, very limited scientific studies have been carried out to understand the role of the media used in these filters for removal of Fe(II) [3] as well as not much efforts have been made to improve the performance of these filters. Moreover when the groundwater containing Fe(II) and As(III) treated through these filters, the metal adsorption might be taking place from binary-metal ion system comprising of Fe(II) + As(III) rather than mono-metal ion systems comprising of either Fe(II) alone or As(III) alone. Unfortunately, very sparsely available literature is available directly dealing with removal of Fe(II) + As(III) metal ions as part of binary-metal ion system from the groundwater [1,8]. Therefore the objectives of the present work is to assess the potential of CPWC for metal removal from synthetic water samples of mono- and binary-metal ion systems comprising of Fe(II) and As(III) through continuous mode column studies.

2. Material and methods

2.1. Community prepared wooden charcoal

The community prepared wooden charcoal (CPWC) for the study was obtained from Amingaon — a nearby village situated at a distance of 1 km from IIT Guwahati campus on the northern bank of River Brahmaputra. The CPWC are prepared indigenously from woods specially procured from hilltops (not from plain lands) located in and around the communities. The procured woods are cut into smaller pieces, dried in sun and burnt partially in air (not to ashes), and then cooled and washed with surface water resulting in individual wooden charcoal pieces of $2.5\text{ cm} \times 1.5\text{ cm} \times 1.5\text{ cm}$ to $4\text{ cm} \times 2.5\text{ cm} \times 1.5\text{ cm}$ (Fig. 1). The procured CPWC pieces were oversized for carrying out the study. Therefore the CPWC was washed with de-ionized water prepared using reverse osmosis process (Model: QRP-380 BC, M/S Chemiton SL, Spain), dried at 105°C in a drying hot air oven (Make: PSI, M/S Mahindra Scientific Instrument Co., India), grounded to smaller particles and then sieved [17]. Particles passing through $425\text{ }\mu\text{m}$ sieve openings but retaining over $300\text{ }\mu\text{m}$ sieve openings were selected for the study and termed as processed wooden charcoal (PWC). The relevant physical



Fig. 1. Community prepared wooden charcoal pieces as procured from the local village market.

characteristics of PWC were estimated and presented in Table 1. A specimen of PWC [without interaction with Fe(II) and As(III)] was subjected to scanning electron microscopy (Model: LEO, 1430 VP, M/S Carl Zeiss, Germany) which indicated porous structure with an approximate pore size of $10\text{ }\mu\text{m}$ (Fig. 2). The energy dispersive X-ray (EDX) analysis of PWC specimen indicated absence of Fe(II) and As(III) from the surface of PWC — indicating inaccessibility of Fe(II) and As(III) containing groundwater to the woody-plant whereas indicated presence of following predominant elements on its surface (in weight %): Al-K (24.89), K-K (17.82) and Ca-K (27.28). The specific surface area, pore volumes, pore diameter and pore width of PWC was estimated by nitrogen adsorption/desorption at 77 K using BET method (Model: Coulter SA3100, M/S Beckman Coulter, USA). The Brunauer Emmett Teller (BET) surface area, along with total pore volume and average pore diameter is estimated and also presented in Table 1.

2.2. Stock mono- and binary-metal ion solutions and other reagents

A stock solution of Fe(II) having a concentration of 0.2 mg/mL was prepared by dissolving required amount of analytical grade Fe ($\text{SO}_4\text{)}_2 \cdot 7\text{H}_2\text{O}$ in de-ionized water. A stock solution of As(III) having a concentration of 0.001 mg/mL was prepared by dissolving required amounts of analytical grade As_2O_3 in de-ionized water. The initial pH of the working solution was adjusted in the range of $6.0\text{--}6.5$ by addition of 0.1 N HNO_3 or NaOH solutions as [26]. The working solutions of binary-metal ions were prepared by diluting stock solutions of mono-metal ions with de-ionized water. The initial metal concentrations were 5 and 0.5 mg/L respectively for Fe(II) and As(III) in mono- and binary-metal ion systems. The residual concentration of Fe(II) and As(III) was measured using an atomic absorption spectrophotometer (Model: 55 B, M/S Spectra AA Varian, Australia).

2.3. Continuous mode column studies

A series of continuous mode column studies were carried out to understand the effect of bed depths and the impact of linear flow rates on metal uptakes by PWC beds from mono- and binary-metal ion systems comprising of Fe(II) and As(III) using PVC columns of 3 cm internal diameter (Fig. 3). Beds were compacted by putting PWC in layers and imparting short jerks to the column in order to pack the bed up to the required depths. Cotton plug (1 cm depth) was placed at the bottom of the bed to support PWC particles. PWC particles used to float with submergence of bed due to entrapped air in the voids and hence cotton plug (1 cm depth) also used at the top of the PWC beds to check floatation. The bed depths of 5 , 10 and 15 cm in columns contained 9 , 19 and 31 g of PWC giving void ratio in the range of $0.07\text{--}0.12$. The columns were operated continuously at room temperature ($22 \pm 1^\circ\text{C}$) in down-flow mode using a peristaltic pump (Model: PA-SF, M/S IKA-WERKE, Germany) at a constant linear flow rates of 1.5 , 2.5 and 3.5 mL/min with mono- and binary-metal ion systems having initial metal concentrations of 5 mg/L for Fe(II) and 0.5 mg/L for As(III). Samples from the column were collected at regular intervals till the bed

Table 1
Physical characteristics of processed wooden charcoal (PWC).

Characteristics	PWC
Particle size range (μm)	425–300
Bulk density (kg/m^3)	290
Moisture content (%)	10
Ash (Inert) content (%)	8
BET surface area (m^2/g)	30
Pore volume (m^3/g) #	3.584×10^{-7}
Micro pore volume (m^3/g) #	3.233×10^{-7}
Average pore diameter (\AA) #	23.94
Pore width (mode) (\AA) #	14.75

#: A fresh batch of CPWC used to obtain PWC for analysis.

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