



Adsorption of Arsenite from Water by Rice Husk Silica

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ABSTRACT

Arsenic occurs in groundwater in two valence states, as trivalent arsenite [As(III)] and as pentavalent arsenate [As(V)]. As(III) is more toxic and more difficult to remove from water by adsorption on activated alumina. In this study the ability of rice husk silica to adsorb As(III) from water was examined. Silica was prepared by burning rice husk in a muffle furnace at 500°C. Batch adsorption tests showed that extent of As(III) adsorption depends on pH, initial As(III) concentration and the contact time. Equilibrium adsorption was attained within 180 min, with maximum adsorption occurring at a pH value of 7-8 which is in the pH range for groundwater. The adsorption of As(III) by rice husk silica followed pseudo second-order kinetics. Equilibrium adsorption data were well described by the Langmuir and Freundlich isotherm models. According to the Langmuir isotherm, As(III) adsorption capacity of rice husk silica is 1.897 mg/g which is 10.5x higher than that (0.180 mg/g) of activated alumina. Hence, rice husk silica would be an effective substitute for activated alumina in the removal of As(III) from groundwater at wells or in households.

INTRODUCTION

A number of large aquifers in various parts of the world have been identified with arsenic occurring at high concentrations. The most noteworthy occurrences are in parts of West Bengal (India) and Bangladesh, Taiwan, northern China, Hungary, Mexico, Chile, Argentina and many parts of the USA (Kinniburgh & Smedley 2001). Arsenic contamination of groundwater in Vietnam & Cambodia (Berg et al. 2007), Nepal (Tendulkar et al. 2006), and Pakistan (Nickson et al. 2005) has also been reported. Long-term exposure to arsenic in drinking water causes cancer of the skin, lung, urinary bladder and kidney, as well as skin pigmentation and hyperkeratosis (WHO 2001).

Arsenic occurs in groundwater in two valence states, as trivalent arsenite [As(III)] and as pentavalent arsenate [As(V)] (Cullen & Reimer 1989). As(III) is more toxic and more difficult to remove from water. Adsorption by activated alumina is most commonly used for arsenic removal in small municipal drinking water systems and point-of-use treatment. However, the process is costly and difficult to apply in rural areas (Dang et al. 2009). There is an urgent need for low-cost adsorption medium for removing arsenic from groundwater and to reduce arsenic concentration in food grains.

Arsenic has been observed to accumulate in the root, straw, husk (hull) and grain of the rice plant (*Oryza sativa* L.) grown in arsenic contaminated soil and/or irrigated with arsenic-laden water (Rahman et al. 2007a, 2007b, Bhattacharya et al. 2009, 2010). Ensuring sufficient silicon

availability in the soil was suggested to suppress arsenic accumulation in the rice plant (Ma et al. 2008). Under greenhouse conditions, silicon fertilization decreased the total arsenic concentration in straw and grain by 78 and 16%, respectively (Li et al. 2009). This indicates silica in the root, straw and husk of the rice plant immobilizes arsenic. Silica content of rice husk ash is 90-94% (Das et al. 1986, Bakar et al. 2010), and thus rice husk silica would serve as an excellent adsorption medium for arsenic.

In the present study, silica was prepared from rice husk and its ability to absorb As(III) from water examined.

MATERIALS AND METHODS

Rice husk silica: Rice husk was washed several times with distilled water in order to remove the dust and dried in an oven at 105°C for 24 h. The washed and dried rice husk was then burned in a muffle furnace at 500°C for 30 min. The resulting rice husk silica was ground to a finer size of 212-500 µm and then used in various adsorption studies. The pH of zero point charge (pH_{ZPC}) of the rice husk silica was determined by the solid addition method (Balistriero & Murray 1981) and found to be 6.5. Scanning electron micrographs of rice husk silica are shown in Fig. 1.

Adsorption studies: Batch adsorption studies were carried out by shaking 100 mL of As(III) (sodium arsenite, $NaAsO_2$) solution with 0.5 g of rice husk silica in a stoppered glass bottle at room temperature (22°C) using an orbital shaker at 150 rpm. After a predetermined contact time, the bottle was removed from the shaker and the supernatant filtered through

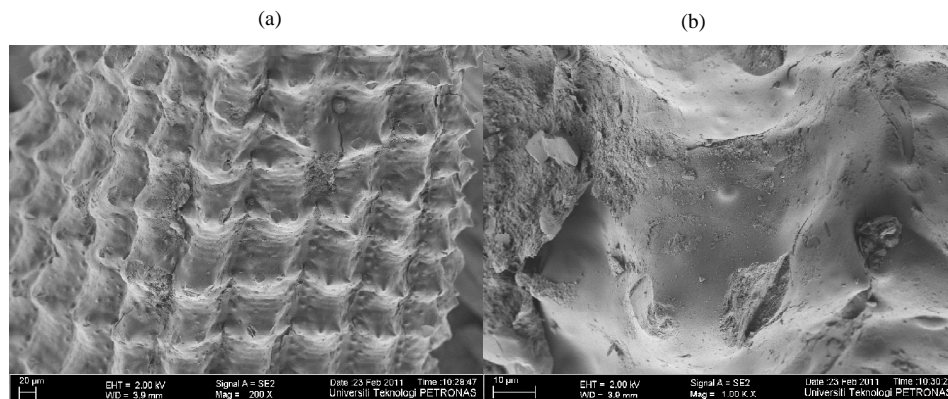


Fig. 1: Scanning electron micrograph of rice husk silica (a) 200x and (b) 1000x magnification.

a 0.45 μm membrane filter and its arsenic concentration analysed by method 3113 B of Standard Methods (APHA 2005). The effects of pH (5-9), contact time (15-240 min), As(III) concentration (0.25 and 0.5 mg/L) and rice husk silica dosage (3-15 g/L) on the adsorption were determined by batch adsorption methods. The adsorption isotherms were determined via batch equilibrium studies using the optimum pH and contact time for As(III) adsorption by rice husk silica, with 100 mL of 0.25-6.0 mg/L of As(III) solution and 0.8 g of rice husk silica.

RESULTS AND DISCUSSION

Effect of pH: The pH value of the As(III) solution influences the adsorption process and adsorption capacity, presumably due to its influence on the surface properties of the adsorbent and ionization of arsenite. The effect of pH on the adsorption of As(III) in 24 h at initial concentration of 0.5 mg/L was studied over the pH range 5-9, with the corresponding results being presented in Fig. 2. Adsorption increased with pH up to 7, with maximum adsorption being achieved at a pH value of 7-8 which is in the pH range (6.5-8.0) for groundwater. Similar observations have been reported for the adsorption of As(III) by activated alumina (Xu et al. 1991, Lin & Wu 2001, Singh & Pant 2004), waste rice husk (Amin et al. 2006), silica ceramic (Salim et al. 2007) and cationic surfactant modified akaganetite (Deliyanni et al. 2007). The trend of As(III) adsorption may be explained by considering the fact that even though below pH 8 the predominant As(III) species is non-ionic H_3AsO_3 , concentration of the anionic H_2AsO_3^- species increases with pH from pH 7 (Xu et al. 1991). At pH above 8, adsorption of As(III) dropped due to repulsion from the rice husk silica surface. A pH value of 8 was used in all subsequent adsorption studies.

Effect of contact time and As(III) concentration: The effect of contact time and As(III) concentration on the adsorp-

tion of As(III) is shown in Fig. 3. The extent of adsorption increased both as the initial As(III) concentration decreased and also as the contact time increased. Equilibrium adsorption was attained within 180 min. A contact time of 180 min was used in all subsequent adsorption studies.

Effect of rice husk silica dosage: The adsorption of As(III) by rice husk silica from a 0.5 and 1.0 mg/L of As(III) solution was studied by varying the rice husk silica dosage over the range 3-15 g/L, employing a pH of 8 and a contact time of 180 min. As shown in Fig. 4, the percentage adsorption increased with rice husk silica dose and maximum adsorption occurred at 8 g/L.

Adsorption kinetics: To identify the kinetics of As(III) adsorption by rice husk silica, two commonly used kinetic models, i.e., the pseudo first-order (Lagergren 1998) and pseudo second-order (Ho et al. 2000) were employed.

$$\frac{dq}{dt} = k_1(q_e - q_t) \quad \dots(1)$$

$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \quad \dots(2)$$

Where, q_e is the amount of solute adsorbed at equilibrium per unit weight of adsorbent (mg/g), q_t is the amount of solute adsorbed at time t per unit weight of adsorbent (mg/g), and k_1 and k_2 are reaction rate constants. The following linearised time dependent functions were obtained by integrating and rearranging Eqs. (1) and (2) for the boundary conditions $t = 0$ to > 0 and $q = 0$ to > 0 .

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad \dots(3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad \dots(4)$$

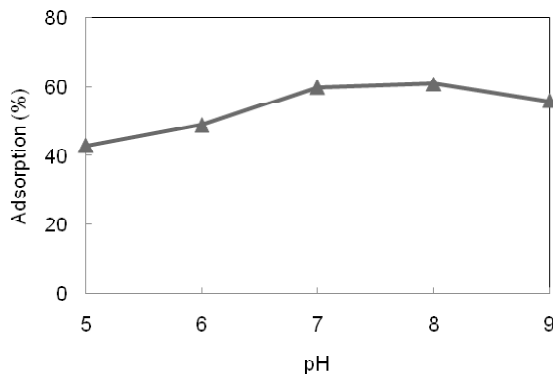


Fig. 2: Effect of pH on adsorption of As(III).

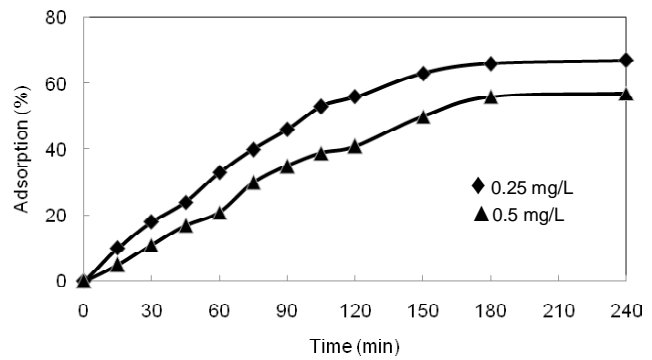


Fig. 3: Effect of contact time and As(III) concentration on adsorption of As(III).

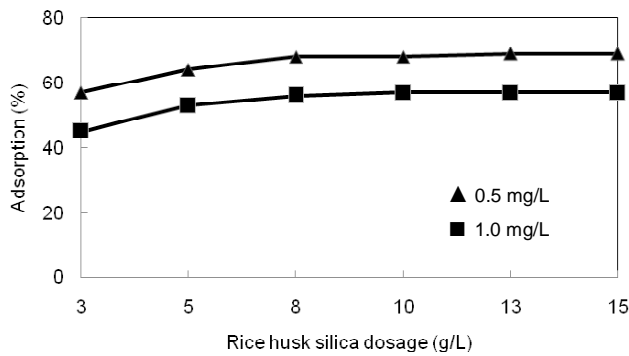


Fig. 4: Effect of rice husk silica dosage on adsorption of As(III).

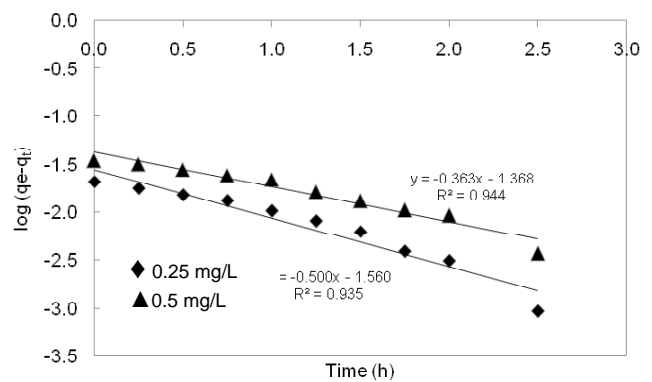


Fig. 5: Application of the pseudo first-order kinetic model to adsorption of As(III).

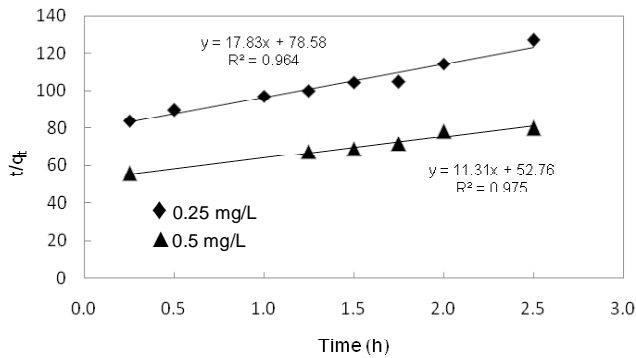


Fig. 6: Application of pseudo second-order kinetic model to adsorption of As(III).

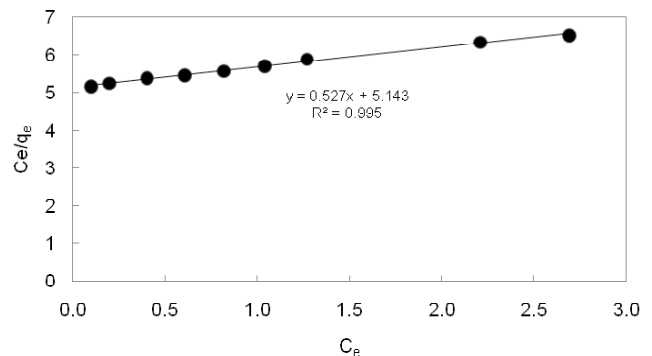


Fig. 7: Langmuir adsorption isotherm for As(III) adsorption.

Plots of $\log (q_e - q_t)$ versus t and of t/q_t versus t are presented in Figs. 5 and 6, respectively. The values of R^2 for the pseudo second-order model were comparatively higher than those for the pseudo first-order kinetic model, indicating that the pseudo second-order kinetic model gave a better fit to the experimental data. Similar observation has been reported for the adsorption of arsenic by iron-modified rice husk carbon (Dang et al. 2009).

Adsorption isotherm: In adsorption in a solid-liquid system, the distribution ratio of the solute between the liquid and the solid phases is a measure of the position of equilibrium. The preferred form of depicting this distribution is to express the quantity q_e as a function of C_e at a fixed temperature, the quantity q_e being the amount of solute adsorbed per unit weight of the solid adsorbent, while C_e the concentration of solute remaining in the solution at equilibrium. An

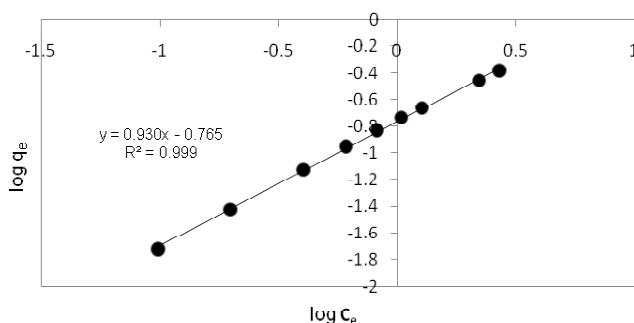


Fig. 8: Freundlich adsorption isotherm for As(III) adsorption.

expression of this type is termed an adsorption isotherm (Weber 1972).

The Langmuir adsorption isotherm is

$$q_e = \frac{Q^o b C_e}{1 + b C_e} \quad \dots(5)$$

where, Q^o is the number of moles of solute adsorbed per unit weight of adsorbent in forming a monolayer on the surface (monolayer adsorption capacity), while b is a constant related to the energy of adsorption. The corresponding linear form of the Langmuir isotherm may be written as:

$$\frac{C_e}{q_e} = \frac{1}{b Q^o} + \frac{C_e}{Q^o} \quad \dots(6)$$

The Freundlich adsorption isotherm is

$$q_e = K_f C_e^{1/n} \quad \dots(7)$$

where, K_f is the Freundlich constant (adsorption capacity), while $1/n$ represents the adsorption intensity. The corresponding linear form of the Freundlich isotherm may be written as:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad \dots(8)$$

Adsorption isotherm for As(III) adsorption was determined by batch equilibrium method employing the optimum pH 8 and contact time of 180 min. The isotherm was fitted to the linear form of the Langmuir isotherm (Fig. 7) and the Freundlich isotherm (Fig. 8) which allowed the values of the various constants to be determined. The corresponding values are listed in Table 1. According to the Langmuir isotherm, compared to the adsorption capacity (0.180 mg/g) of activated alumina for As(III) (Singh & Pant 2004), rice husk silica exhibited 10.5x higher adsorption capacity (1.897 mg/g).

CONCLUSIONS

The As(III) adsorption by rice husk silica followed the

Table 1: Langmuir and Freundlich isotherm constants for As(III) adsorption by rice husk silica.

Langmuir isotherm constants		Freundlich isotherm constants	
Q^o (mg/g)	b (L/g)	K_f	$1/n$
1.897	0.10	0.172	0.930

pseudo second-order kinetic model, with maximum adsorption occurring at a pH value of 7-8 which is in the pH range for groundwater. The adsorption capacity of rice husk silica for As(III) is 10.5x higher than that of activated alumina. Rice husk silica is an effective substitute for activated alumina in the removal of As(III) from groundwater at wells or in households.

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