Arsenic(III) Immobilization on Rice Husk

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Abstract

A number of large aquifers in various parts of the world have been identified with contamination by arsenic. Long-term exposure to arsenic in drinking water causes cancer of the skin, lungs, urinary bladder and kidney, as well as skin pigmentation and hyperkeratosis. Arsenic occurs in groundwater in two valence states, as trivalent arsenite [As(III)] and pentavalent arsenate [As(V)]. As(III) is more toxic and more difficult to remove from water by adsorption on activated alumina. In this study, immobilization (adsorption) of As(III) by quaternized rice husk was examined. Batch adsorption test showed that extent of adsorption was dependent on pH, As (III) concentration, contact time and rice husk dose. Maximum adsorption occurred at pH 7-8, and equilibrium adsorption was attained in 2 h. Equilibrium adsorption data were described by the Langmuir and Freundlich isotherm models. According to the Langmuir isotherm, adsorption capacity of quaternized rice husk is 0.775 mg As(III)/g, which is 4.3x higher than that (0.180 mg As(III)/g) of activated alumina. Quaternized rice husk is a potentially useful adsorbent for removing arsenic from groundwater.

Keywords: arsenic(III); activated alumina; adsorption; immobilization; quaternized rice husk

1. 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 [1]. Arsenic contamination of groundwater in Vietnam and Cambodia [2], Nepal [3] and Pakistan [4] 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 [5].

Arsenic occurs in groundwater in two valence states, as trivalent arsenite [As(III)] and as pentavalent arsenate [As(V)] [6]. 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 system and point-of-use treatment. Arsenic adsorption capacity of activated alumina is 11-24 mg As(V)/g [7] and 0.180 mg As(III)/g [8]. Lee et al. [9] examined quaternized rice husk with high abundance of the quaternary ammonium cation for arsenic adsorption and its arsenic adsorption capacity was found to be 19 mg As(V)/g. In the present study, immobilization (adsorption) of As(III) by quaternized rice husk was examined.

2. MATERIALS AND METHODS

2.1 Quaternized Rice Husk

Quaternized rice husk was prepared according to the method reported by Lee et al. [9] and Lazlo [10]. Rice husk was ground to a size of 212-500 µm and treated with 1% sodium carbonate solution for 45 min to remove color, followed by washing with distilled water and drying at 60-70°C. One hundred grams of the rice husk was treated with 125 mL of 5M sodium hydroxide solution for 30 min. Thereafter, 100 mL of 4M N-(3-chloro-2-hydroxypropyl)-trimethylammonium chloride solution was added to the mixture, thoroughly mixed and kept in an oven at 60-70°C for 4 h with intermittent mixing. The mixture was then rinsed with distilled water, suspended in dilute hydrochloric acid at pH 2, rinsed further with distilled water and dried at 60-70°C.

2.2 Adsorption Test

Batch adsorption test was carried out by shaking 100 mL of sodium arsenite ($NaAsO_2$) solution with 0.75 g of quaternized rice husk in a stoppered glass bottle placed on an orbital shaker at 150 rpm and room temperature (22°C). After a predetermined contact time, the bottle was removed from the shaker and the supernatant was filtered through 0.45 µm membrane filter and analyzed for arsenic concentration by Method 3111 B of Standard Methods [11]. The effect of pH (5-8), contact time (0-4 h), As(III) concentration (0.25-1.0 mg As(III)/ L), and quaternized rice husk dose (2.5-12.5 g/L) on adsorption were evaluated. Adsorption isotherm was determined by batch equilibrium test at the optimum pH and contact time for adsorption with 100 mL of 0.1-1.0 mg As(III) /L arsenic solution and 0.1 g quaternized rice husk.

3. RESULTS AND DISCUSSION

3.1 Effect of pH on Adsorption

Effect of pH on As(III) adsorption from a 0.25 mg As(III)/L arsenic solution in 24 h is shown in Fig. 1. pH higher than 8 was not considered because it is outside the range of groundwater pH.

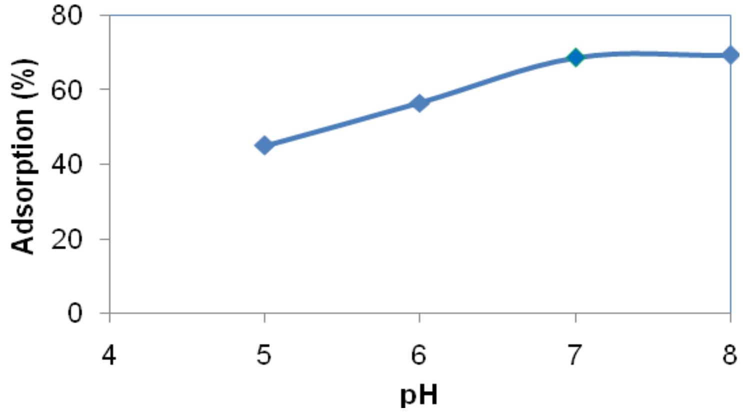

Figure 1: Effect of pH on adsorption.

It is observed that adsorption increased with pH up to pH 7 and maximum adsorption (69%) occurred at pH 7-8, similar to that reported by Singh and Pant [8], Lin and Wu [12] and Xu et al. [13] for adsorption of As(III) by activated alumina and by Deliyanni et al. [14] for adsorption of As(III) by cationic surfactant modified akaganetite. 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 6 [13]. All subsequent adsorption tests were conducted at pH 7.

3.2 Effect of Contact Time and As(III) Concentration on Adsorption

Effect of contact time and As(III) concentration on adsorption are shown in Fig. 2. Extent of adsorption increased with increase in contact time and decrease in As(III) concentration and equilibrium adsorption was attained in 2 h. A contact time of 2 h was used in all subsequent adsorption tests.

3.3 Effect of Quaternized Rice Husk Dose on Adsorption

Effect of quarternized rice husk dose on As(III) adsorption from a 0.25 mg As(III)/L arsenic solution is shown in Fig. 3. Adsorption increased with dose and attained maximum adsorption (73%) at 10 g/l quarternized rice husk dose.

3.4 Adsorption Isotherm

In adsorption in a solid-liquid system, the distribution ratio of the solute between the liquid and the solid phase 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, and C_e the concentration of solute remaining in the solution at equilibrium. An expression of this type is termed an *adsorption isotherm* [15].

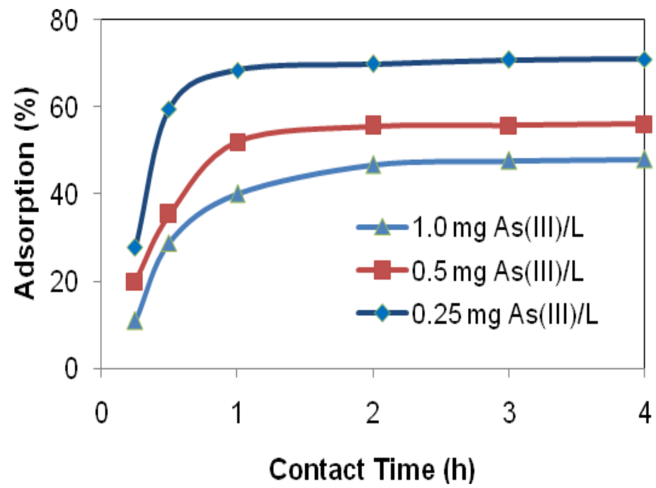

Figure 2: Effect of contact time and As(III**)** rice husk concentration on adsorption

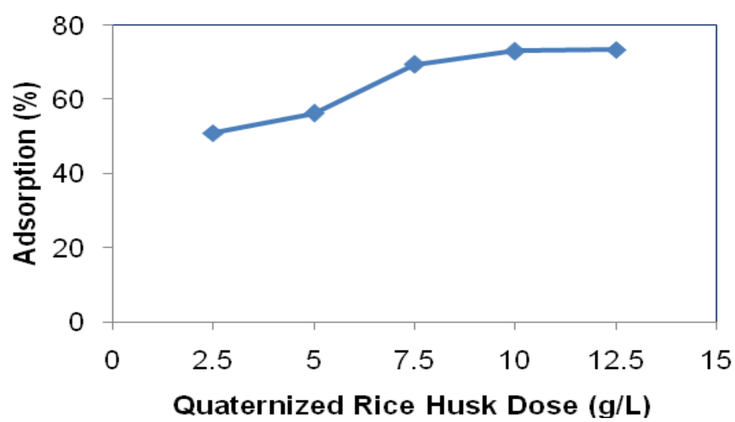

Figure 3: Effect of quarternized dose on adsorption.

The Langmuir adsorption isotherm is

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

where, $Q°$ is the number of moles of solute adsorbed per unit weight of adsorbent in forming a monolayer on the surface (monolayer limiting adsorption capacity) and b is a constant related to the energy of adsorption.

The Freundlich adsorption isotherm is

$$q_e = K_f C_e^{1/n} \quad (2)$$

where, K_f is the Freundlich constant (adsorption capacity) and *1/n* represents the adsorption intensity.

Isotherm for As(III) adsorption was determined by batch equilibrium test using optimum contact time and pH (2 h and pH 7) for adsorption. The isotherm was fitted to the linear form of the Langmuir equation [$1/q_e = 1/Q^o + (1/bQ^o)(1/C_e)$] (Fig. 4) and Freundlich equation [$\log q_e = \log K_f + (1/n)\log C_e$] (Fig. 5). The values of Langmuir constants $Q°$ and b, and Freundlich constants K_f and *1/n* are shown in Table 1. Adsorption capacity of quaternized rice husk (0.775 mg As(III)/g) is 4.3x higher than that (0.180 mg As(III)/g) [8] of activated alumina.

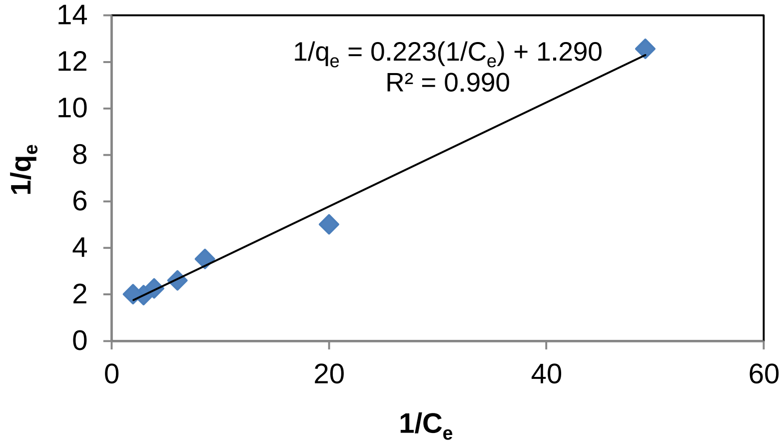

Figure 4: Langmuir adsorption isotherm.

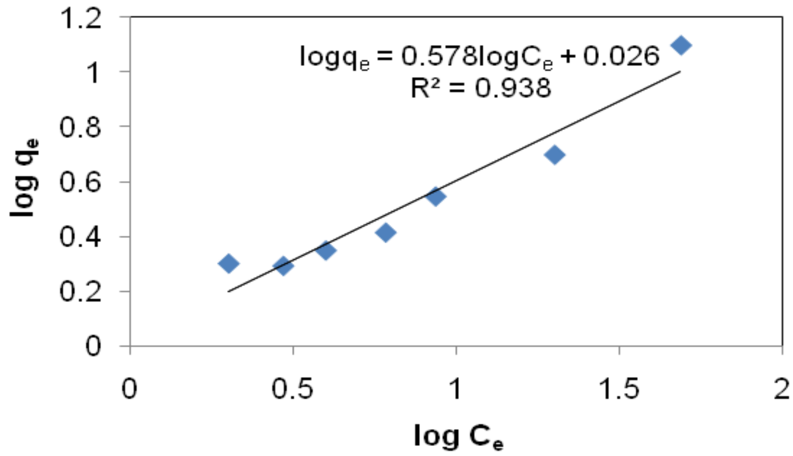

Figure 5: Freundlich adsorption isotherm.

Table 1: Langmuir and Freundlich constants.

Langmuir constant		Freundlich constant	
Q^o	b	K_f	$1/n$
0.775	5.785	1.062	0.578

Arsenic adsorption capacity of quaternized rice husk is 0.775 mg As(III)/g and 19 mg As(V)/g [9] compared to 0.180 mg As(III)/g [8] and 11-24 mg As(V)/g [7] of activated alumina. Thus, quaternized rice husk is a potentially useful adsorbent for removing arsenic (As(III) and As(V)) from groundwater.

4. CONCLUSIONS

Maximum As(III) adsorption by quaternized rice husk occurred at pH 7-8 and equilibrium adsorption was attained in 2 h. The quaternized rice husk showed higher As(III) adsorption capacity compared with activated alumina. The quaternized rice husk is a potentially useful adsorbent for removing arsenic from groundwater.

Acknowledgment

The authors are thankful to the management and authorities of the Universiti Teknologi PETRONAS (UTP) and the Civil Engineering Department, UTP for providing facilities for this research. Research support through grant FRGS/2/2010/TK/UTP/01/6 is gratefully acknowledged.

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