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The treatment of trace As(III) from water by modified spent grains

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ABSTRACT

Trace arsenic influences the safety of drinking water. Using spent grains modified by polyacrylamide (PAM) to adsorb arsenite [As(III)] has broken through the technical bottleneck of the traditional technology that purified water can only be treated using the method of oxidating As(III) to arsenate [As(V)]. When the concentration of the modifier PAM is 1%, adsorbent dosage is 3 g/L, solution pH = 6, contact time is 2 h, the water with As(III) content is 0.1 mg/L can be reduced to 0.01 mg/L, which meet the limit in "Standard for Drinking Water Quality" (GB5749-2006). The adsorption kinetic of the As(III) upon spent grains modified by PAM (PSGs) has been studied and the adsorptional process was fitted to the pseudo-second-order equation. The activity of amide groups at the surface of PSGs has been strengthened through the Fourier transform infrared spectroscopy analysis. The effect of desorption by alkaline solution was better than that of acid solution. Based on the results of leaching toxicity experiment, spent PSGs can be directly landfilled.

Keywords: Spent grains modified by PAM (PSGs); As(III); Adsorption

1. Introduction

Environmental pollution caused by arsenic has been gaining great attention. Especially Bangladesh, Bengal in India, Inner Mongolia in China, and Chile are facing serious arsenic pollution [1–3]. Following various epidemiological evidences on arsenic carcinogenicity and other deleterious effects on humans [4,5], the Department of Health P.R. of China lowered the China drinking water limit from 0.05 to 0.01 mg/L in July 2007 [6].

Generally, arsenic exists in three or five value state. Arsenate [As(V)] is often found in oxidizing environment, while arsenite [As(III)] is in anoxic and reducing environment and is more mobile [7,8]. Furthermore, As(III) is about 60 times more toxic than As(V) [9]. Hence, there is an urgent need for processes to selectively remove As(III) from potable water as well as to cater the needs of people living in small communities in developing countries.

Numerous treatment technologies, such as ions exchange, precipitation, coagulation and filtration, reverse osmosis, and oxidation/filtration [10] have been developed for the removal of arsenic from water. However, adsorption still remains an attractive and promising technology because of its simplicity, ease of operation, sludge free operation, and regeneration capacity [11,12]. Spent grains, generated in the brewing process, are normally utilized as cattle feed in countries where dairy farming is practiced. In many

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regions of world, spent grains are not fully utilized due to the absence of activity. A few studies have been reported using spent grains as an adsorbent of cadmium, lead, and arsenic from aqueous solutions [13,14]. In this work, spent grain modified by amidogent was an adsorbent for the removal of As(III) from water. Factors affecting the sorption of arsenic, such as modifier polyacrylamide (PAM) concentration, pH, and contact time have been studied.

2. Materials and methods

2.1. Adsorbate

All reagents used in this study were of analytical grade. Arsenic standard solution 1 mL (As(III), 1 g/L), obtained from Iron & Steel Research Institute of P.R. China, was placed to a 1,000 mL volumetric flask. Stock solutions (1 mg/L As) were prepared from arsenic standard solution (As(III)) for As(III). Distilled water was added to a constant volume, which followed by 3 mL of 37% hydrochloric acid (HCl). The volumetric flask was stored in a refrigerator.

2.2. Adsorbents

Fresh spent grains were obtained from a local brewery located in Ganzhou, P.R. China. The spent grains were washed by distilled water and dried at 60℃. After ground to pass through a 1 mm sieve and stored dry until use, the product was named as SGs.

The solid-to-liquid ratio of SGs to a certain concentration of PAM solution was 200 g/L. The mixture was mixed evenly and kept for 12 h at room temperature (26 ± 2℃). Finally, distilled water was used to wash the modified spent grains until the pH of the effluent is 7, and followed by dried at 80℃. This product was called PSGs.

2.3. Experimental methods

The effect of modifier PAM concentration on As (III) removal was studied with 3 g/L PSGs and SGs at pH = 7. The mixture was agitated on a gyratory shaker at 150 rpm for 1.5 h. The treating As(III) operations using the same concentration of PAM (3 mL) were also fulfilled at the same experimental conditions. Then, the suspension of the liquid was decanted and filtered through a 0.45 μm cellulose acetate filter and the supernatant was examined to check the concentration of As(III) using an inductively coupled plasma–atomic emission spectrometer (Intrepid II XSP).

The effect of pH on As(III) removal was carried out with 3 g/L PSGs in 100 ml solution of the arsenic ion. The pH of the solution was adjusted with the 0.1 M NaOH and the 0.1 M HCl.

The influence of contact time for the removal has also been investigated. Samples were withdrawn at predetermined intervals and the removal of arsenic was examined.

For each condition, three tests have been performed at room temperature (26 ± 2℃). If the data analyzed are less than 0.01 mg/L, the presented result is 0.01 mg/L in this study.

Scanning electron microscope (SEM) has been used to investigate the morphology of the SGs. The mechanisms of the adsorption process have been investigated using the Fourier transform infrared spectroscopy (FTIR).

3. Results and discussion

3.1. The physical and chemical properties of SGs

The surface of SGs before sorption has been examined using the SEM. From the scanning electron micrographs (Fig. 1), the surface of SGs is uneven and rough with lots of grooves, pits, and pores. The three-dimensional mesh-hole structure at the cross-section is in favor of the adsorption of metals. Table 1 summarized the structure parameters of SGs.

After reacting with the ratio of 1:1 for SGs to dilute aqua regia for 1 h, the element analysis was carried on by inductively coupled plasma spectroscopy instrument (Table 2).

3.2. The effect of modifier PAM concentration on As(III) removal

Fig. 2 shows the effect of different modifier PAM concentrations on As(III) removal. It included SGs (modified by 0% PAM) 3 g/L, 0.5% PSGs (modified by

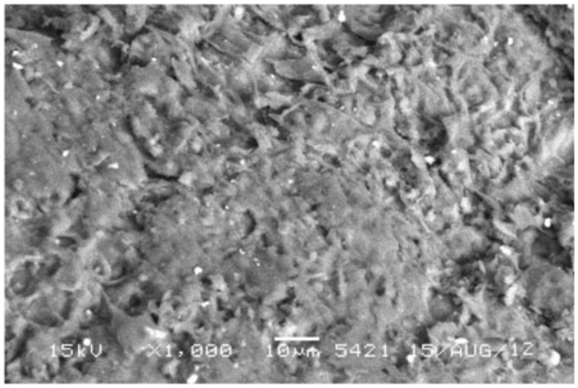

Fig. 1. SEM of SGs before sorption.

Table 1
Structure parameters of SGs

Specific surface area (m^2/g)	Pore volume (mL/g)	Pore diameter (Å)
78.5	0.267	139.9

Table 2
Element analysis of SGs

Element	Wt (%)	Element	Wt (%)
C	62.151	Al	0.079
N	3.702	Ba	0.006
O	32.654	Ca	0.162
Mg	0.403	Cu	0.004
Si	0.296	Na	0.042
P	0.482	Zn	0.009
S	0.334	Pb	0.040

0.5% PAM) 3 g/L, 0.1% PSGs (modified by 1% PAM) 3 g/L, 0.2% PSGs (modified by 2% PAM) 3 g/L, and 0.5% PAM 3 mL/L, 1% PAM 3 mL/L, and 2% PAM 3 mL/L.

In Fig. 2, the effect of PSGs modified by different concentrations of PAM on the As(III) removal has significant improvement compared with the SGs. This is due to strong binding ability with arsenic and amidogent from PAM. Among the different concentrations of PAM, the As(III) removal by 1% PSGs was about 20% higher than that of 0.5% PSGs, which approached to the same removal as 2% PSGs. The uptake of As(III) onto 0.5% PAM, 1% PAM, and 2% PAM became larger with the increase of PAM concentration. But, they are all lower than those three PSGs and higher than the SGs. All subsequent experiments were conducted with 1% PSGs.

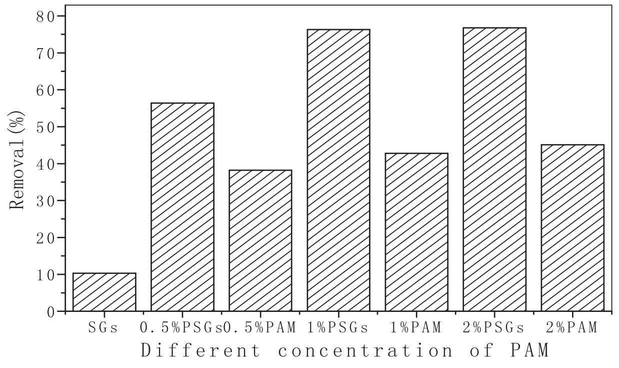

Fig. 2. The effect of modifier PAM concentration on As(III) removal. Initial As(III) 0.1 mg/L, pH 7, and contact time 1.5 h.

3.3. The effect of pH on the As(III) removal

The pH plays an important role in the adsorption process by affecting the surface charge of adsorbent, the degree of ionization, and the speciation of the adsorbate. Thus, the effect of pH in the solutions on the removal efficiency of As(III) was studied at different pH ranging from 4 to 11. The results are shown in Fig. 3.

Little difference can be observed in the As(III) removal from 90.8 to 91.1% at pH 4–6, then a sharp decrease from 91.1 to 73.5% at pH 6–11 was observed. This can be explained on the basis of ionization constant K_a about H_3AsO_3 molecular.

$$H_3AsO_3 + H_2O = H_2AsO_3^- + H^+ \quad pK_1 = 9.20 \quad (K_1' = 6.30 \times 10^{-10}) \tag{1}$$

$$H_2AsO_3^- + H_2O = HAsO_3^{2-} + H^+ \quad pK_2 = 12.13 \quad (K_2' = 7.41 \times 10^{-13}) \tag{2}$$

$$HAsO_3^{2-} + H_2O = AsO_3^{3-} + H^+ \quad pK_3 = 13.40 \quad (K_3' = 3.98 \times 10^{-14}) \tag{3}$$

From Eqs. (1)–(3), the As(III) exists in the H_3AsO_3 molecular at low pH value. With the decrease of solution acidity, the molecular H_3AsO_3 gradually ionized to anion, which in competition between negatively charged OH^- and As(III) anion for the surface sites.

In fact, the effect of pH on the As(III) ion removal rate is also relevant to the functional groups of adsorbent surface. Fig. 4 illustrates that the pH_{ZPC} of 1% PSGs is 6.1. When the solution pH is below 6.1, the surface of adsorbent with positive charge has little effect on the molecular H_3AsO_3. Higher uptake of the As(III) ion at lower pH illustrated the hydrogen bond

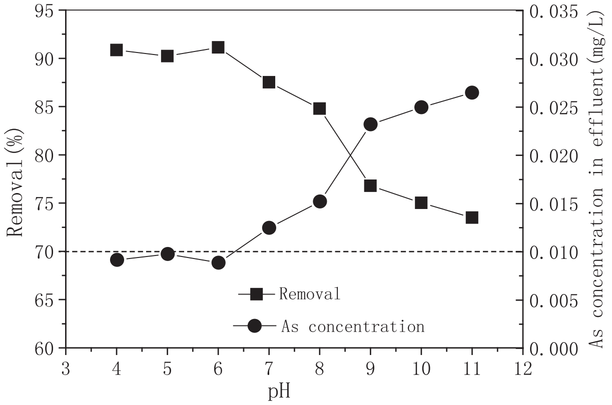

Fig. 3. The effect of pH on As(III) removal. Initial As(III) 0.1 mg/L, 1% PSGs 3 g/L, and contact time 1.5 h.

between –NH_2 in adsorbent and –OH from H_3AsO_3. When the solution pH is above 6.1, negative charge of the surface adsorbent brought electrostatic repulsion between OH^- anion and H_3AsO_3 ionization. This results in the decline of the As(III) removal by PSGs at alkaline environment.

As seen in Fig. 3, the As(III) concentration in effluent are all lower than 0.01 mg/L at pH 4, 5, and 6, which meet the standard 0.01 mg/L in "Standards for Drinking Water Quality" (GB5749-2006). All subsequent experiments are conducted at pH 6.

3.4. Adsorption kinetic study

The rates of the adsorption of As(III) by PSGs are shown in Fig. 5. The adsorption process is rapid in less than 2 h and reached a plateau of 92% in 7 h. Fig. 5 also shows that the As(III) concentration in effluent are all lower than 0.01 mg/L after contacting for 2 h.

Various sorption kinetic models have been used to describe the removal of metals. The Lagergren first-order kinetic process has been used for reversible reaction with an equilibrium being established between liquid and solid phases. The rate equation for the reaction may be represented by the following equation:

$$\lg(q_e - q_t) = \lg q_e - \frac{k_1}{2.303} t \tag{4}$$

where t is the contact time (min), q_t and q_e are the quantities of sorbate sorbed at time t and at equilibrium (mg/g), and k_1 is the sorption rate constant. From Eq. (4), the plot of lg (q_e–q_t) vs. t should give a straight line to confirm the applicability of the first-order kinetic model (Fig. 6).

However, over the past few years, the pseudo-second-order kinetic model has been considered to be the most appropriate among the kinetic models [15].

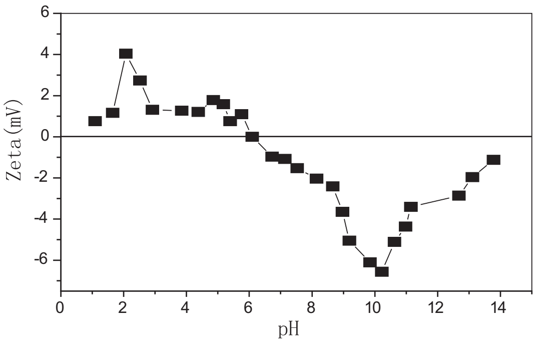

Fig. 4. Effect of pH on ξ-potential of PSGs.

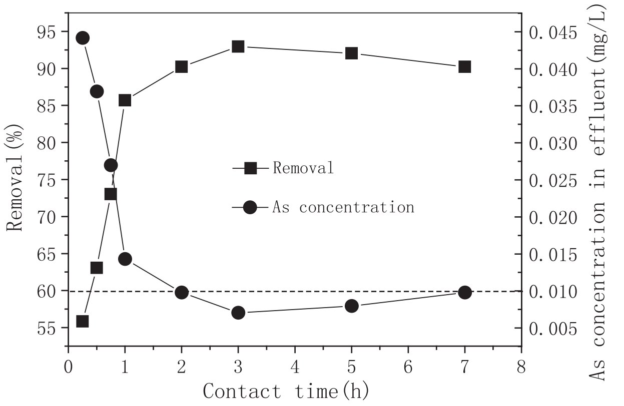

Fig. 5. The effect of contact time on As(III) removal by PSGs. Initial As(III) 0.1 mg/L, 1% PSGs 3 g/L, and pH 6.

According to many authors [16,17] who have studied sorption kinetics applying the pseudo-second-order equation in metal ions using several different adsorbent materials, the rate equation for the reaction may be represented by the following equation:

$$\frac{t}{q_t} = \frac{1}{k_2} - \frac{t}{q_e} \tag{5}$$

where t is the contact time (min), q_t and q_e are the quantities of adsorbate sorbed at time t and at equilibrium (mg/g), and k is the sorption rate constant (mg/(g min)). From Eq. (5), a plot of t/q_t vs. t should give a straight line to confirm the applicability of the second-order kinetic model (Fig. 7).

In comparison with the correlation coefficient (R^2) of the two fitted lines of the two models, the pseudo-second-order kinetic model (R^2 = 0.99) is fitted much better than the Lagergren first-order kinetic model (R^2 = 0.29) for the sorption process. The rate constant

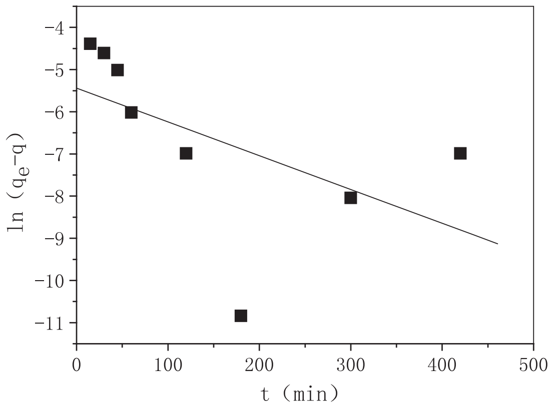

Fig. 6. Lagergren first-order adsorption kinetics of As(III) by PSGs.

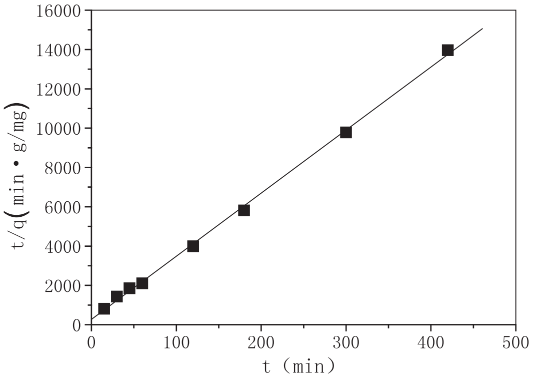

Fig. 7. Pseudo-second-order adsorption kinetics of As(III) by PSGs.

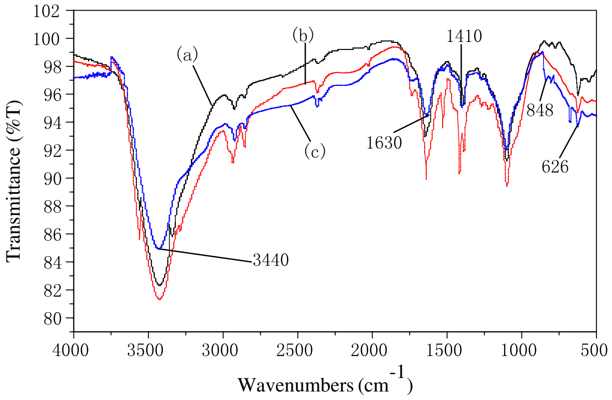

Fig. 8. FTIR spectra of SGs (a), PSGs (b), and PSGs after As(III) sorption (c).

(k) and adsorption at equilibrium (q_e) can be calculated from the intercept and slope, respectively. The results are summarized in Table 3, which illustrate the sorption process for the As(III) on PSGs followed the pseudo-second-order kinetic. The q_e from pseudo-second-order kinetics was 0.0312 mg/g, which is close to the experimental value of 0.0301 mg/g.

3.5. Adsorption mechanism study

The FTIR has been considered as a relatively direct means to investigate the mechanisms of metals adsorption on biomass. FTIR of SGs, PSGs and after As(III) binding sorption on PSGs at pH 6 are shown in Fig. 8.

Two FTIR spectra (Fig. 8(a) and (b)) both have absorption peak from 3,420 to 3,440 cm^{-1}, which represent the extension vibration of hydroxyl group. But, the strength of spectrum of PSGs was augmented compared with that of SGs at that wavenumber range, which implied the activity of hydroxyl group intensifying.

The obvious change of PSGs before and after As(III) adsorption can be observed from spectrum b and c (Fig. 8). The weakening of absorption peak at 3,420–3,440 cm^{-1} suggested that the hydroxyl group is involved in the As(III) adsorption. The weakening and displacement of three absorption peaks at 1,661–1,640 cm^{-1} for C=O stretching vibration, at 1,410–1,420 cm^{-1} for C–N stretching vibration, and at 626 cm^{-1} upon NH_2, the outer rocking bending vibration indicated the amide group is participated in the As(III) adsorption. The appearance of As–O stretching vibration at 848 cm^{-1} and O–As–O bending vibration at 467 cm^{-1} also proved that the As(III) adsorption by PSGs.

3.6. Desorption and leaching toxicity study

Using 0.1 mol/L HCl, H_2SO_4, NaCl, and NaOH solution as desorption agents, desorption experiments were carried out for 3 h with PSGs after the As(III) adsorption at room temperature. Results are shown in Fig. 9.

It is clear from Fig. 9, if the concentration of the desorption agents is the same, the desorption rate of alkali solution is better than that of acid solution and NaCl solution. At a low pH, trivalent arsenic exists in the H_3AsO_3 molecular, while it begins to appear $H_2AsO_3^-$ ionic at pH 9.20. In alkaline conditions, the protonation degree of adsorbent surface would be weakened and the adsorption ability for As(III) will be declined, which makes for the As(III) desorption.

The toxicity characteristic leaching experiment of spent PSGs was conducted for 18 h using the glacial acetic acid as the extractant (pH = 2.88 ± 0.05). The liquid–solid ratio of extractant to PSGs is 20:1. Experimental results showed that the concentration of

Table 3
The adsorption kinetics parameters for As(III) on PSGs

Lagergren first-order kinetic			Pseudo-second-order kinetics		
q_e (mg/g)	k_1 (min^{-1})	R^2	q_e (mg/g)	k_2 (g mg^{-1} min^{-1})	R^2
0.9817	0.0184	0.2982	0.0312	0.0037	0.9993

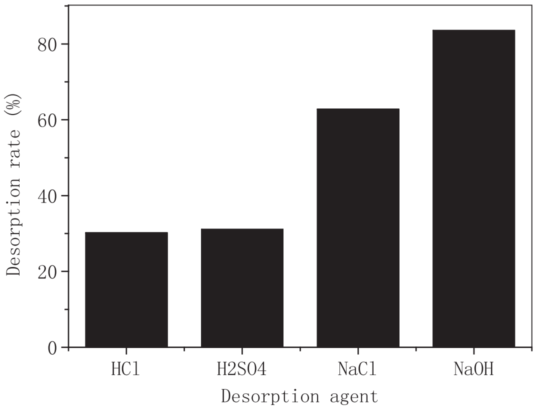

Fig. 9. The effect of desorption agent on PSGs desorption after As(III).

arsenic in leaching solution was 0.11 mg/L, which meet the "Standard for Pollution Control on the landfill Site of Municipal Solid Waste" (GB16889-2008) of arsenic less than 0.3 mg/L. So, the spent PSGs can be disposal in landfill without further operation.

4. Conclusions

Using spent grains modified by PAM to adsorb As (III) is a major breakthrough to the traditional technology that the purified water can only be obtained under the condition of oxidating As(III)–As(V).

(1) When the concentration of the modifier PAM is 1%, sorbent dosage is 3 g/L, solution pH = 6, contact time is 2 h, the water containing As(III) 0.1 mg/L can be treated to meet the limit of 0.01 mg/L in "Standard for Drinking Water Quality" (GB5749-2006).
(2) The kinetics study on the As(III) adsorption onto PSGs determines that the adsorptional process was fitted to the pseudo-second-order equation better than the Lagergren first-order equation.
(3) The activity of amide groups at the surface of PSGs have been strengthened from the FTIR analysis. Arsenic groups appeared after the As (III) adsorpted from the water.
(4) The effect of desorption by alkaline solution was better than that of acid solution and NaCl solution. Based on the results of leaching toxicity experiment, spent PSGs can be directly landfilled.

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