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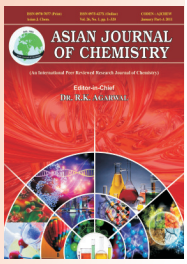

Low-Concentration As(III) Retention from Water on Polyacrylamide Modified Spent Grains

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Human health is concerned by arsenic pollution hazards from water all around the world. The polyacrylamide with acylamino group, whose binding ability with As(III) is strong. Thus polyacrylamide was chosen as sorbent modifier for spent grains (PSGs) to treat water containing low-concentration of As(III) was studied. When PSGs is 5 g/L, initial concentration of As(III) 0.1 mg/L, the equilibrium can be attained after 1.5 h. The As(III) sorption by PSGs had a better relevance to Freundlich isotherm than Langmuir isotherm. Thermodynamics study showed that As(III) retention with PSGs is the exothermic and spontaneous. The co-existing anions of F^-, SO_4^{2-} and PO_4^{3-} can inhibit the As(III) retention. Headwaters containing 0.07 mg/L As(III) can be reduce to 0.01 mg/L after treated by 1.5 g/L PSGs, which meet the provisional guideline value of WHO for arsenic in drinking water.

Keywords: Low-concentration As(III), Spent grains, Polyacrylamide, Sorption, Equilibrium, Thermodynamics.

INTRODUCTION

Many parts of the world has been reported the presence of As(III) in ground water, such as Argentina[1], Bangladesh[2], China[3], Ghana[4], India[5,6], Nepal[7], Pakistan[8,9] and Taiwan[10]. Arsenic(V) predominates in surface waters, while groundwater may contain also relevant concentrations of As(III) that is more mobile and toxic than As(V)[11]. Human health is concerned by arsenic pollution hazards all around the world and water pollution is the most important arsenic pollution issue in relation to public health[12]. Having recognized the enormous health implications, the Department of Health P.R. of China lowered the provisional guideline value for arsenic in drinking water from 0.05 to 0.01 mg/L in July 2006[13]. Hence, it is imperative to selectively remove As(III) from potable water as well as to cater the needs of people living in small communities in developing countries.

Several treatment methods such as ions exchange, precipitation, coagulation and filtration and oxidation/filtration[14-17] have been developed for the removal of As(III) from water. However, adsorption still remains an attractive and promising technology because of its simplicity, ease of operation, sludge free operation and regeneration capacity[18-20]. Spent grains (SGs), generated in the brewing process, are not fully utilized in many regions of world due to the absence of activity. Being containing lots of functional groups, spent grains were used as sorbent of cadmium, lead and arsenic from aqueous solutions[21,22]. In order to increase the sorptional performance of spent grains for As(III) retention from water, chemical reagents are employed to strengthen specific functional groups in this work. Some factors such as modifier, dosage of PSGs, As(III) initial concentration, temperature and co-existing anions which affect the sorptional capability of spent grains have been studied. Meanwhile, one of headwaters containing low-concentration As(III) in Ganzhou, P.R. China is used as object to assess the performance of modified spent grains.

EXPERIMENTAL

Arsenic standard solution 1 mL [As(III), 1 g/L], obtained from Iron & Steel Research Institute of P.R. China, was placed to a 1000 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. The volumetric flask was stored in a refrigerator. All reagents used in this study were analytical grade.

Fresh spent grains sample was obtained from a local brewery located in Ganzhou, P.R. China. The spent grains were washed by distilled water and dried at 60 °C. After ground to pass through a 1 mm sieve and stored dry until use, namely spent grains.

The solid-to-liquid ratio of spent grains to differernt solutions was always 200 g/L. There were two inorganic solutions

as 1 g/L ammonium chloride (NH_4Cl) and concentrated ammonia water ($NH_3 \cdot H_2O$) and one organic 1 % polyacrylamide (PAM) solution. The mixture was mixed evenly and kept for 12 h at room temperature (26 ± 2 °C). Finally distilled water was used to wash the modified spent grains until the pH of effluent was 7 and followed by dried at 80 °C, namely ASGs1, ASGs2 and PSGs, respectively. The three materials were uses as sorbent for solution containing As(III).

General procedure: At room temperature (18 ± 2 °C) the effect of different sorbents was investigated with 3 g/L ASGs1, ASGs2, PSGs and spent grains at pH = 7. The mixture of each sorbent and 0.1 mg/L As(III) simulated water was agitated on a gyratory shaker at 150 rpm for 1.5 h. The treating operations using the same concentration of polyacrylamide (1 %) 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 dosage of PSGs (range from 0.5 to 9 g/L), equilibrium [As(III) initial concentration from 0.05 to 0.5 mg/L] and thermodynamics studies (reaction temperature from 20 to 50 °C) and co-existing anions as F^-, SO_4^{2-}, PO_4^{3-} have also been studied for As(III) retention.

The adjustments of pH were carried out using dilute NaOH and HCl solutions. If the data analyzed is less than 0.01 mg/L, the result present is 0.01 mg/L in this study. All the experiments were carried out at least in triplicate. The results were average of these measurements. The linear regression analysis was carried out for treatment of the data. The relative standard deviation (RSD) was less than 1 %.

RESULTS AND DISCUSSION

Physico-chemical properties of spent grains: The surface of spent grains has been investigated with the scanning electron microscope (SEM). From the scanning electron micrographs (Fig. 1), the surface of spent grains 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 spent grains.

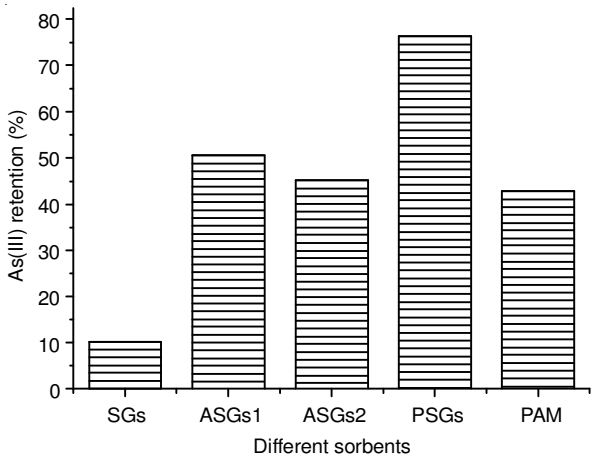

Fig. 1. Effect of different sorbents on As(III) retention

TABLE-1
STRUCTURE PARAMETERS OF SPENT GRAINS

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

Effect of different sorbents on As(III) retention: Fig. 1 showed that the sorptional performance of modified spent grains are all improved compared with spent grains, whose As(III) retention is only 10.3 %. The As(III) retention has a little difference between (45.2 %) and (50.6 %) by ASGs1 and ASGs2, respectively, which are all a bit higher than 1 % polyacrylamide. On the other hand PSGs has a great rise to 76.3 % for As(III) removal, which is seven times for spent grains.

By means of materials studio, which drawing support from Density functional theory (DFT) for module calculation between molecule and material simulation, the frontier orbital energy of combination between different functional groups and arsenic is presented in Table-2.

TABLE-2
FRONTIER ORBITAL ENERGY OF COMBINATION BETWEEN FUNCTIONAL GROUPS AND ARSENIC

Functional groups	E_{LUMO}	E_{HOMO}	ΔE
Hydroxyl	-0.14705	-0.14994	0.00289
Carboxyl	-0.17975	-0.18190	0.00215
Acylamino	-0.15082	-0.18569	0.03487
Amino	-0.11732	-0.12464	0.00732
Sulfydryl	-0.14602	-0.15156	0.00554

It is well known that combination capacity mainly depends on of the stabilized energy of composition, $\Delta E = E_{LUMO} - E_{HOMO}$. The higher the stabilized energy of composition is, the bigger ΔE, which means the lower chemical active and more stabilization. Table-2 showed that the ΔE of traditional modifier hydroxyl is smaller than that of amino compounds. The ΔE of acylamino is the biggest one in this study, which indicates that the combination capacity for arsenic with acylamino is the strongest.The increase for As(III) retention by ASGs1 and ASGs2 may due to the amino group introducing into spent grains which has strong binding ability with As(III). The highest As(III) retention by PSGs is due to the acylamino group from polyacrylamide whose binding ability with As(III) is stronger than that of amino group. All subsequent experiments were conducted with PSGs.

Effect of PSGs dosage on the As(III) retention: The effect of sorbent dosage on As(III) retention is depicted in Fig. 2. It shows that adsorption efficiency of As(III) has a sharp rise by 37.7 to 86.2 % with the dosage of PSGs from 0.5 to 5.0 g/L. A marginal increase is observed on further increasing sorbent dose to 7 and 9 g/L. The increase in the efficient removal may be attributed to the fact that with an increase in the sorbent dosage, more adsorbent surface, or more sorptional sites and also more acylamino group are available for As(III) from solution.

Equilibrium and thermodynamics studies: Equilibrium studies were carried out to determine the conditions for maximum As(III) retention over PSGs. The distribution of As(III) between the liquid phase and the solid sorbent phase is a measure of the position of equilibria at different concentrations in the

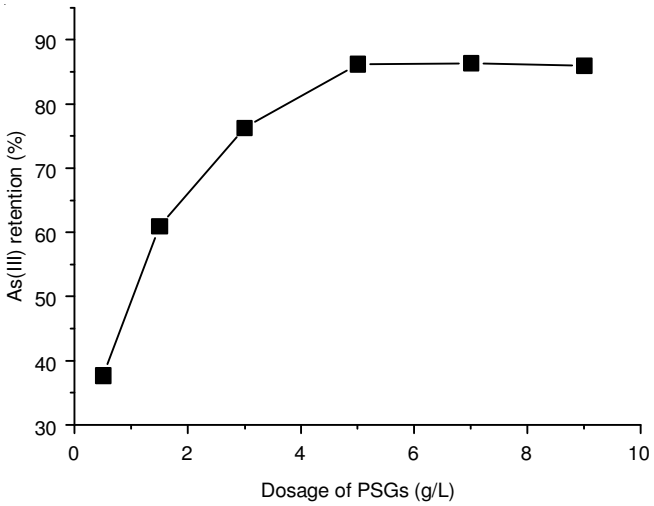

Fig. 2 Effect of PSGs dosage on As(III) retention

sorption process. The equilibrium data was fitted to Langmuir and Freundlich isotherms in the linear form.

Langmuir equation was applied to quantify adsorption capacity and is given as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{q_m b} \quad (1)$$

where C_e is the concentration of the As(III) solution at equilibrium (mg/L), q_e the amount of As(III) sorbed at equilibrium (mg/g), q_m the maximum sorption capacity of the As(III)-PSGs system (mg/g) and b is constant related to the binding energy of the sorption system (L/mg). The linearity of plots for Langmuir is shown in Fig. 3. The values of sorptional isotherm parameters are showed in Table-2.

Freundlich equation has the following form:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (2)$$

where K_F and n are the constants representing the adsorption capacity (mg/g) and intensity of the adsorbent, respectively. The linearity of plots for Freundlich is shown in Fig. 4. The values of K_F and n are obtained from the slope and intercept of the plot between ln q_e and ln C_e and are shown in Table-3. From Tables 3 and 4 can be known that the correlation coefficients of Freundlich are all greater than 0.98 and higher than that of Langmuir.

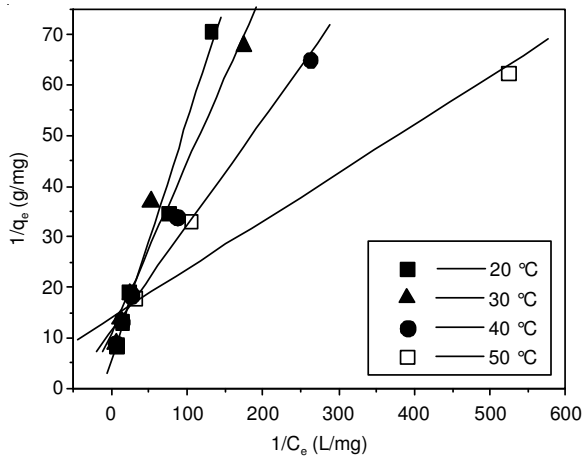

Fig. 3. Langmuir sorptional isotherm for As(III) by PSGs

TABLE-3
LANGMUIR SORPTIONAL ISOTHERM PARAMETERS FOR As(III) BY PSGs

Temperature (°C)	q_m (mg/g)	b (L/mg)	R^2
20	5.369	0.174	0.93
30	3.250	0.091	0.98
40	1.466	0.089	0.98
50	1.218	0.071	0.96

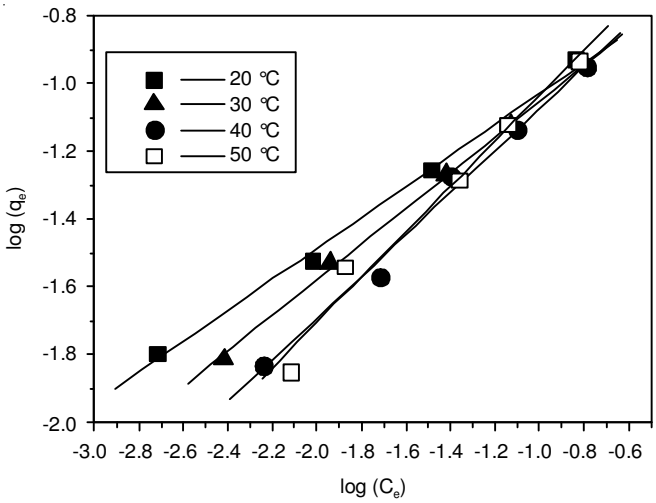

Fig. 4. Freundlich sorptional isotherm for As(III) by PSGs

TABLE-4
FREUNDLICH SORPTIONAL ISOTHERM PARAMETERS FOR As(III) by PSGs

Temperature (°C)	K_F (mg/g)	n	R^2
20	0.432	2.193	0.99
30	0.351	1.902	0.99
40	0.297	1.492	0.98
50	0.267	1.617	0.99

According to thermodynamics, the Gibb's free energy change is also related to the enthalpy change (ΔH) and entropy change (ΔS) at constant temperature by the following van't Hoff equation:

$$\ln K = \frac{-\Delta G}{RT} = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (3)$$

where K is the distribution coefficient of the sorption system defined as the ratio of amount sorbed (mg) to equilibrium concentration of solution (mg/L) and T the temperature (K). Based on some literature[23], the equilibrium constant K can be gained from the extraploted at $q_e = 0$ of plot between ln (q_e/C_e) and q_e at different temperatures (Fig. 5). The values of enthalpy change (ΔH) and entropy change (ΔS) are calculated from the slope and intercept of the plot of ln K *versus* (1/T) (Table-5). The negative value of ΔH and ΔG indicate the exothermic and spontaneous nature of the sorption process, respectively.

TABLE-5
THERMODYNAMICS PARAMETERS FOR As(III) BY PSGs

Temperature (K)	ΔH (kJ/mol)	ΔS (J/mol K)	ΔG (kJ/mol)
293	-20.33	-50.31	-5.48
303			-5.14
313			-4.87
323			-3.87

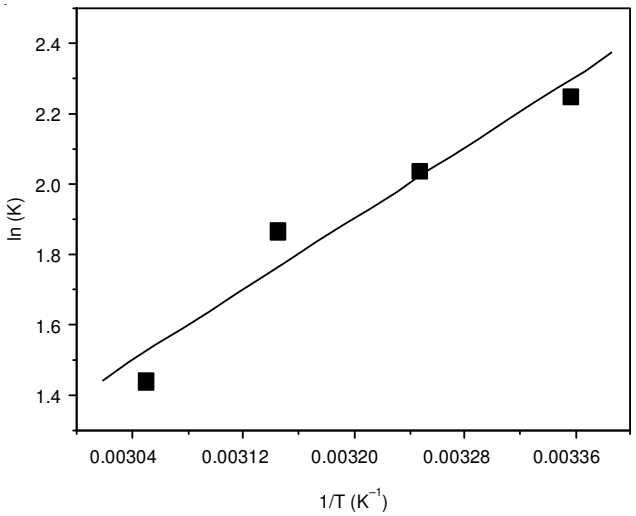

Fig. 5. van't Hoff for As(III) by PSGs

Effect of co-existing anions on the As(III) retention: Potassium fluoride, potassium sulfate and potassium phosphate were added into water containing As(III), respectively. Fig. 6 shows the influence of coexisting anions (F^-, SO_4^{2-}, PO_4^{3-}) upon the sorption removal of As(III). The initial concentration of As(III) in water is 0.1 mg/L and the initial concentration of F^-, SO_4^{2-}, PO_4^{3-} ions varies from zero (no coexisting anions) to 0.8 mg/L.

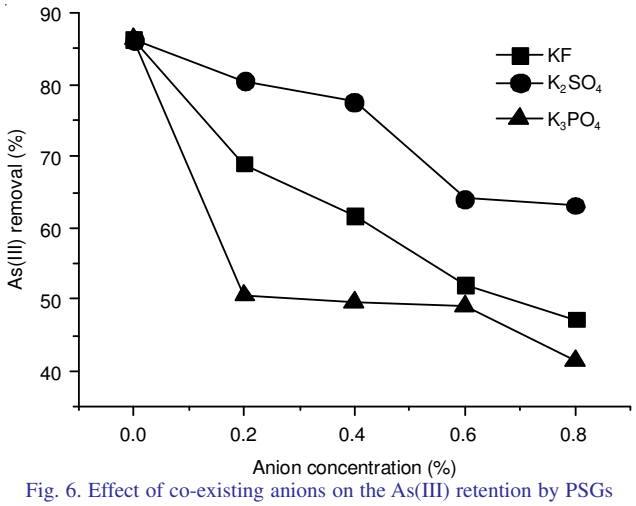

Fig. 6. Effect of co-existing anions on the As(III) retention by PSGs

Fig. 6 shows that the As(III) removal decreases for co-existing anions comparing with only As(III), which indicates that F^-, SO_4^{2-}, PO_4^{3-} can all restrain the sorption for As(III) by PSGs from water. The limited sorptional site of the surface of PSGs, higher concentration of F^-, SO_4^{2-}, PO_4^{3-} competing the sorptional site with As(III) lead to the cutting down of As(III) retention. Meanwhile, phosphor and arsenic are the same main race, which result in the similar electronic structure for PO_4^{3-} and AsO_3^{3-} and the competition of PO_4^{3-} is stronger than that of SO_4^{2-} and F^-. It implies that the water should be pre-treated to increase the As(III) removal if the concentration of PO_4^{3-} is more denseness than AsO_3^{3-}.

Headwaters containing low-concentrations of As(III) retention with PSGs: In order to find out about the As(III) retention with PSGs, one of headwaters containing 0.07 mg/L As(III), pH 6 in Ganzhou, P.R. China is used as an object. After adjusted the pH of water to 6 and 7, 5 g/L PSGs and 5 g/L polymeric aluminium chloride (PAC), which is used to As (III) removal currently, is added to water and contact 1.5 h, respectively. The results are shown in Fig. 7.

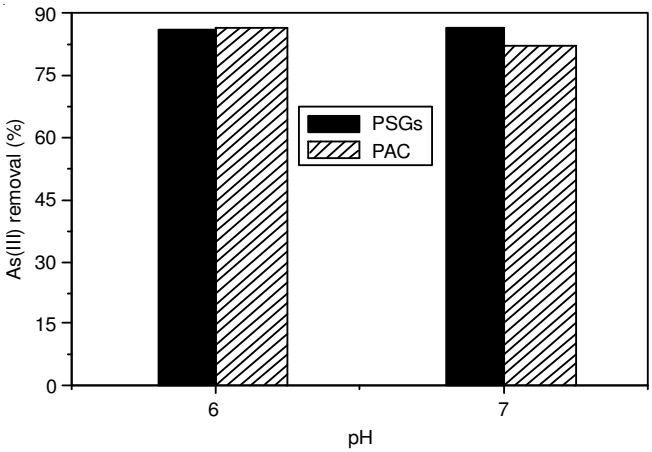

Fig. 7. Headwaters containing As(III) retention by PSGs

Fig. 7 shows that As(III) removal is higher than 85 % at pH 6 and pH 7, by PSGs. It can be calculated that remaining As(III) is lower than 0.01 mg/L. It meets the provisional guideline (value of arsenic in drinking water) prescribed by Department of Health, WHO, P.R. China. At pH 7 the remains of the As(III) is higher than 0.1 mg/L by polymeric aluminium chloride. The PSGs is an efficient sorbnet for As(III) retention.

Conclusion

Due to the polyacrylamide (PAM) with acylamino group, polyacrylamide was chosen as modifier for spent grains (PSGs). When spent grains modified by polyacrylamide (PSGs) is 5 g/L, initial concentration of As (III) 0.1 mg/L, the equilibrium can be attained after 1.5 h. The As(III) sorption by PSGs has a better relevance to Freundlich equation than that of Langmuir. Thermodynamics study shows that As(III) retention with PSGs is the exothermic and spontaneous. The co-existing anions of F^-, SO_4^{2-} and PO_4^{3-} can inhibit the As(III) retention. Headwaters containing 0.07 mg/L As(III) can be reduce to 0.01 mg/L after treated by 1.5 g/L PSGs, which meet the provisional guideline value of WHO for arsenic in drinking water.

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