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Adsorbent prepared from red mud and its adsorption characteristics of As(V)

Zhang Shuwu[a,*], An Wenchao[b]

[a]*School of Environment and Safety Engineering, Qingdao University of Science and Technology, Qingdao 266042, China*
Tel. +86 84022856; Fax: +86 84022617; email: zhangshuwu@126.com
[b]*Environmental Monitoring Station, Qingdao Environmental Protection Agency, Qingdao 266003, China*

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ABSTRACT

A novel method to prepare an activated red mud (activated RM) adsorbent was developed that was mainly produced from RM. The batch adsorption experiments were conducted for the study of the adsorptive performance by activated RM adsorbent. Adsorption of As(V) on activated RM was studied as a function of dosage and time. Results from the batch experiments, conducted at an initial concentration of 0.2 mg/L of As(V), suggest that arsenate removal efficiency was up to 95%. Langmuir and Freundlich isotherms equation were used to fit the adsorption isotherms. Adsorption capacity of activated RM was found to be 127.0, 111.9 and 46.7 mg/g at pH 6, 7, 9, respectively. The results indicate that there is no significant change in the equilibrium concentration after 12 h. The adsorption kinetic curve for the As(V) fit well with the pseudo-second-order equation. The leaching liquid by activated RM after the toxicity characteristic leaching procedure test can reach the Drinking water standards of China (GB 5749-2006). The adsorbent is a safe application.

Keywords: Red mud; Activated red mud; Adsorption; As(V)

1. Introduction

Water pollution has become a serious issue in China, some heavy metals are notorious water pollutants with high toxicity and carcinogenicity. Arsenate is known to cause various ailments to humans ranging from skin rashes to carcinoma and its presence in exceedingly higher concentrations in drinking water poses threat to millions of people in Taiwan, India and Bangladesh [1]. Chronic arsenate poses a serious health problem in China also [2]. In recent years, great effort has been directed to improve the efficiency for arsenate removal. Many methods have been developed to remove excessive arsenate from water, namely, adsorption, coagulation, ion exchange, precipitation, electrolysis, and reverse osmosis [3–6]. Among them, adsorption technology is commonly considered because it is simple to operate. Many kinds of adsorbents have been developed for the removal of arsenic. Arsenate is strongly adsorbed on Fe and Al oxides [5,7], but the cost of the adsorptive removal process is high when pure sorbents (e.g. hydrated Fe and Al oxides) are used.

RM is formed during the digestion in the Bayer Process that is practiced for alumina production from

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*Corresponding author.

bauxite. RM has been used in absorbents, building materials, catalysts, fillers, and pigments. In China, it is estimated that about 10 million tones RM will be produced annually in the future [8–10]. It is widely available in large quantities and is expected to have good affinity for arsenate, as it is rich in Fe and Al oxides and hydroxides. Several studies have used RM or activated RM for adsorbing heavy metals and anionic pollutants from water, including phosphate, cadmium, lead, copper, and arsenic [11–13]. Altundogan et al. activated RM with acid and the maximum removal of As(V) were 96.5% for the initial arsenic concentration of 10 mg/L in dosages 20 g/L [14]. Removal of chlorophenols from wastewater using RM was studied by V.K. Gupta, it shows for all the phenols, 10 g/L is the optimum dosage of the RM for the maximum adsorption [15].

We previously used modified RM (MRM) to remove As(V) from nearly neutral water [16]. Adsorption capacity of MRM was found to be 56.3, 44.2 and 21.7 mg/g at pH 6, 7, 9, respectively. Solution pH significantly affects the adsorption, and the adsorption capacity increases with the decrease in pH. MRM could be regenerated with NaOH, and the regeneration efficiency reached 92.1% when the concentration of NaOH was 0.2 mol/L. Although high removal efficiencies were achieved, the amount of adsorbent required was high. It was therefore suggested that RM could be used for treatment of As(V) and that its adsorption capacity need to be increased.

Here a new method was used to activate the RM. The removal of As(V) from aqueous solution using the activated RM was studied in batch experiments. The influences of dosage and time on the sorption capacity were investigated. The release of metal ions from activated RM during As(V) sorption was also investigated.

2. Materials and methods

2.1. Materials and instrumental

The RM used in the study was obtained from Shandong Aluminum Corporation, China. The raw RM was sieved and the particles below 177 μm were used for activation, 50 g of powder was added to 1 L of 1 M $FeCl_3.6H_2O$ in a beaker, magnetically stirred for 1 h and aged for 24 h. Then 1 M NaOH solution was added drop wise to the mixture while stirring until the pH of the slurry was around 7.0. The slurry was continuously stirred by a magnetic stirrer for 2 h and aged for 24 h. The mixture was centrifuged and the obtained solid was washed with deionized water three times. The obtained solid was dried at 105℃. The activated RM was then sieved again, and particles below 80 mesh screen obtained were used as adsorbent for the experiments. The diagram of activated RM adsorbent preparation was depicted in Fig. 1.

All chemicals were of analytical grade and used without further purification. As(V) was analyzed on Atomic Fluorescence Spectrometer (AF-610A). Zero charge (PZC) for the adsorbent was determined by micro-electrophoresis using a Malven model Zetasizer 2000 zeta potential analyzer. The zeta potentials of the adsorbents suspensions containing 0.02% solid in 0.01 M NaC1 were determined at various pH values. The PZCs were obtained by interpolating the data to zero zeta potential. The specific surface area (SSA) and basal spacing (BS) of the samples was determined by the BET nitrogen gas sorption method using a Micromeritics ASAP2000 V Accelerated Surface Area and Porosimetry. The leachate is filtered through a 0.22 μm cellulose acetate, and analyzed to determine the total solution concentrations of Sb, As, Ba, Be, Cd, Cr, Cu, Pb, Mn, Hg, Ni, Se, Ag, and Zn using a Perkin–Elmer Elan 6000 ICP-MS.

2.2. Adsorption experiments

All glassware and sample bottles were soaked in diluted HCl solution for 24 h and washed three times with deionized water. All experiments were conducted in duplicate and the mean values were considered. Solutions were prepared from $Na_2HAsO_4{\cdot}7H_2O$ for As(V). A 1 g/L As(V) stock solution was prepared by dissolving 4.057 g $Na_2HAsO_4.7H_2O$ in 1 L of distilled water. As(V)-bearing water was prepared by diluting As(V) stock solution to given As concentrations with deionized water. The pH of the solutions was adjusted with either HCl or NaOH solution.

Adsorption studies were carried out by shaking $Na_2HAsO_4{\cdot}7H_2O$ solution at 400 rpm in the bottles for 12 h at 20℃, and a background electrolyte of 0.01 M NaCl was used for all batch experiments. After

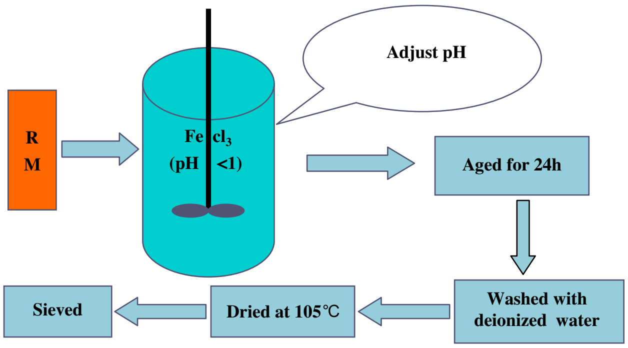

Fig. 1. Schematic diagram of activated RM adsorbent preparation.

equilibrium, the solutions were centrifuged at 5,000 rpm for 10 min and the supernatant was taken and analyzed for As(V). As(V) adsorbed was calculated as follows:

$$q = (C_0 - C_t)V/m \qquad (1)$$

where q is the concentration of the As(V) adsorbed (mg/g), C_0 and C_t are the initial and final concentrations of the As(V) in solution (mg/L), respectively. V is the solution volume (L) and m is the mass of sorbent (g).

2.3. The toxicity characteristic leaching procedure (TCLP)

The possibility that activated RM, which has been used to trap As(V), could become a secondary pollutant is investigated by preparing duplicate samples and using the TCLP developed by the United States Environmental Protection Agency (U.S. EPA) [17]. In this study the TCLP is used to classify the spent activated RM as inert or hazardous in relation to its potential for activated RM to release chemical contaminants. In the TCLP, the spent activated RM (particle size <0.2 mm) is agitated for 20 h in acetic acid at a pH of 3. Finally, the leachate is filtered through a 0.22 μm cellulose acetate, and analyzed to determine the total solution concentrations of Sb, As, Ba, Be, Cd, Cr, Cu, Pb, Mn, Hg, Ni, Se, Ag, and Zn using a Perkin–Elmer Elan 6000 ICP-MS.

3. Results and discussion

3.1. Characterization of activated RM

The zeta potentials of RM and activated RM at various pH values are shown in Fig. 2. As can be seen, in the pH range from 2.0–8.0, activated RM has much higher zeta potentials than RM, which indicates that activated RM is much less negatively charged after activation. The exterior roughened and new cavities appeared during the activation process. Thus, the exchangeable cations are significantly reduced and its zeta potentials increase. The PZC of activated RM occurs at pH 2.8. Zeta potentials of activated RM are positive for pH below 2.8, and decrease slightly with the increase in pH. It indicates that the particles are positively charged and negative for pH over 2.8, which indicates that the particles are negatively charged. Because of its much higher zeta potentials than RM, activated RM can be expected to reduce the repulsion between its particles and negatively charged substances and enhance the removal of these substances from liquid solutions. The SSA and BS of the RM and activated RM are reported in Table 1. As shown in the table, after activation the SSA increases considerably, up to 210.3 m^2/g, which is much larger than that of RM. As SSA increases, adsorption is favored. The BS decreased from 86.5 to 59.7 nm. The new surface area by acidification was generated. Calcium and some other acid-soluble salts were dissolved; some coarse exterior and new cavities appeared during the activation process. So the SSA increased and BS decreased.

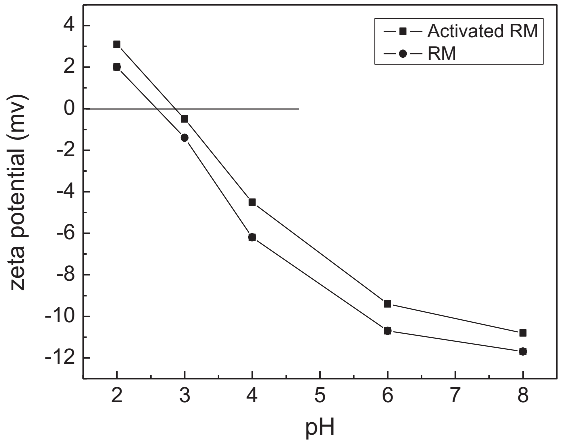

Fig. 2. Zeta potentials of RM and activated RM.

Table 1
The SSA and BS of the RM and activated RM

Sample	BS (nm)	SSA (m^2/g)
RM	86.5	115.7
Activated RM	59.7	210.3

3.2. Adsorption of As(v) to activated RM

3.2.1. The effect of adsorbent dosage

The effect of the adsorbent dosage on the removal has been tested and results are depicted in Fig. 3, where it can be seen that the percentage As(V) removal increases with increasing activated RM dosage. This is consistent with the expectation that higher adsorbent dosages will result in lower q_e values. Here, the percentage of As(V) removed by the activated RM is determined from the ratio of the concentration of As(V) present in the solution. In a previous study on arsenate removal using MRM, it was found that 300 mg/L MRM needs to be applied at pH 6 to achieve the Drinking water standards of China (GB 5749-2006). However, in this study, it was found that an adsorbent dosage of 200 mg /L was sufficient to reach the Drinking water standards of China of ≈ 0.007 mg/L at pH 6,

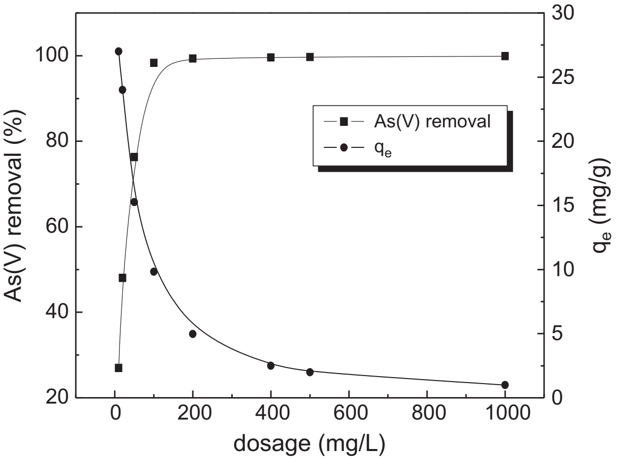

Fig. 3. Effects of adsorbent dosage on As(V) removal efficiency and capacity.

indicating that activated RM has a greater ability than MRM to adsorb As(V). After activation, the content of Fe in RM increased and calcium decreased. As SSA increases, adsorption is favored.

3.2.2. Kinetic study

The effect of time on the removal was investigated as described in sorption studies for increasing periods of time, until equilibrium was achieved. The removal of As(V) vs. time was illustrated in Fig. 4. The results indicate that there is no significant change in the equilibrium concentration after 12 h.

The kinetic data obtained were analyzed by applying the pseudo-first-order and pseudo-second-order kinetic model.

(1) Pseudo-first-order kinetic model

The Pseudo-first-order kinetic model is represented as follows:

$$dq_t/dt = k_1(q_e - q_t) \tag{2}$$

where q_t is amount of adsorbate per unit wt of adsorbent (mg/g) at any time t, q_e adsorption capacity (mg/g) at equilibrium and k_1 (1/min) is the pseudo-first-order rate constant. Integrating Eq. (2) from $t = 0$ to t, and $q_t = 0$ to q_t and rearranging the following equation is obtained:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{3}$$

(2) Pseudo-second-order kinetic model

The pseudo-second-order kinetic model is described as below:

$$dq_t/dt = k_2(q_e - q_t)^2 \tag{4}$$

where q_t and q_e have the usual meaning and k_2 (g/mg/min) is the second-order rate constant. Integrating Eq. (4) from $t = 0$ to t, and $q_t = 0$ to q_t and rearranging the following equation is obtained:

$$t/q_t = 1/k_2 q_e^2 + t/q_e \tag{5}$$

Linearized form of the first-order rate Eq. (3) is fitted with experimental results corresponding to are shown in Figs. 5 and 6, respectively. The values of q_t and k_2 are calculated from intercept and slope of the fitted equations. The values of k_2, R^2 are summarized in Table 2. For each case high correlation coefficient (>0.9) is obtained. However, the values of q_e(model) deviate much from the same corresponding to experimental results. This indicates that the adsorption process does not follow the pseudo-first-order kinetic model. Pseudo-second-order kinetic model therefore is fitted with the same experimental results.

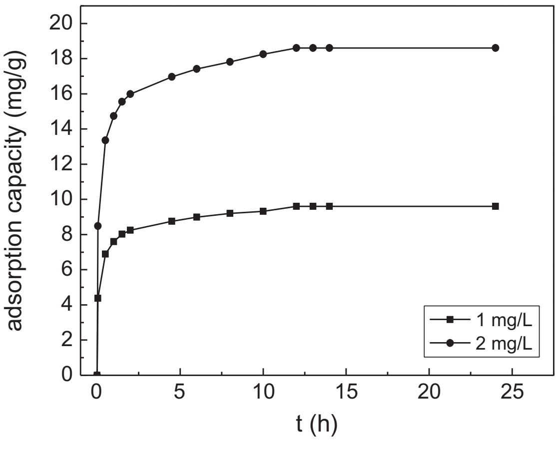

Fig. 4. Effects of time on As(V) removal capacity.

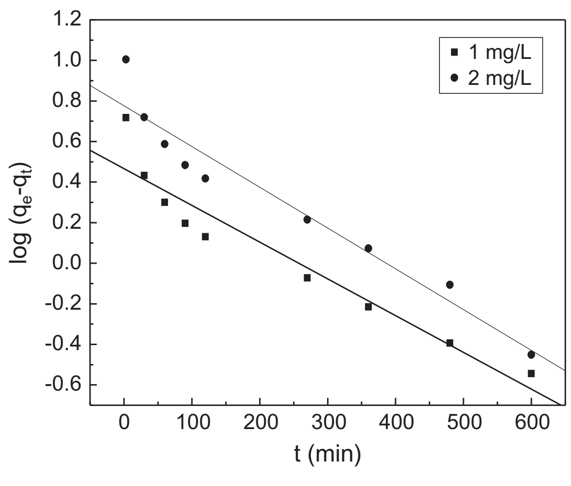

Fig. 5. Pseudo-first-order fit curves of As(V) adsorption.

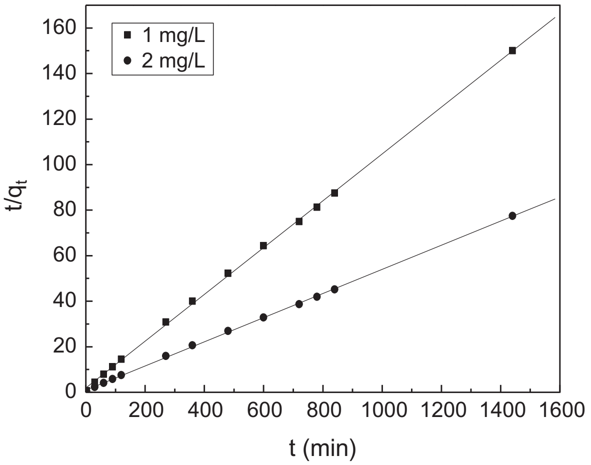

Fig. 6. Pseudo-two-order fit curves of As(V) adsorption.

Table 2
Kinetic constants and related regression coefficients

As(V) (mg/L)	Pseudo-first-order rate equation		Pseudo-second-order rate equation		
	R^2	K_1	q_e	R^2	K_2 (g/(mg min))
1	0.92	0.00417	9.73	0.99	0.0056
2	0.94	0.00462	18.86	0.99	0.0029

3.2.3. Adsorption isotherm

In Fig. 7, the percentage removal of As(V) for different sorbent concentration at pH 6, 7,and 9 was presented, when the initial As(V) content was varied. Two adsorption isotherms, namely the Langmuir and Freundlich isotherm models, were used to analyze adsorption data. The Langmuir equation was applied for adsorption equilibrium as follows:

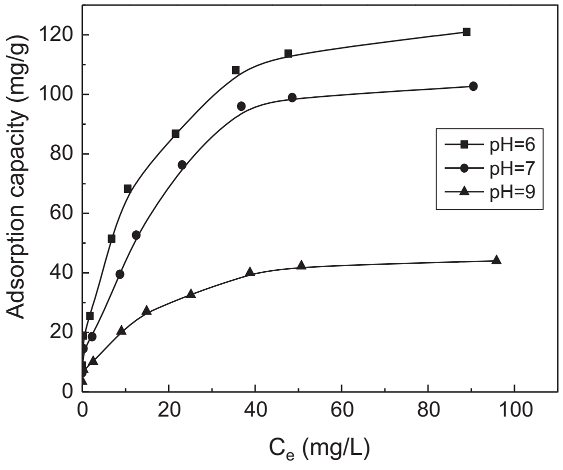

Fig. 7. Effect of equilibrium concentration on arsenate adsorption using the activated RM adsorbent.

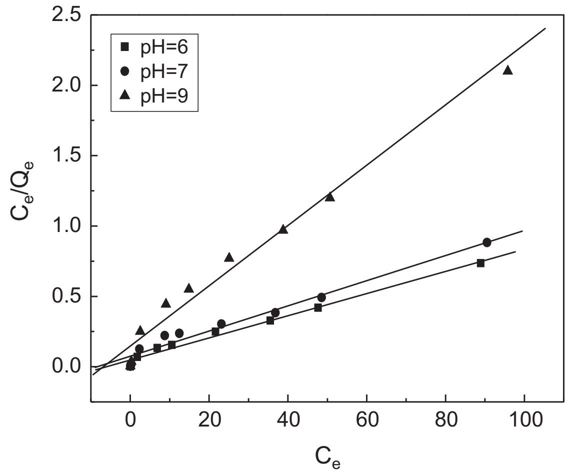

Fig. 8. Langmuir isotherm plots for As(V) adsorption.

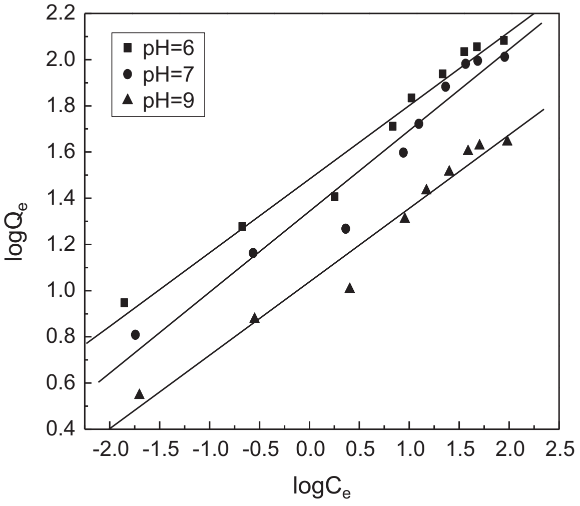

Fig. 9. Freundlich isotherm plots for As(V) adsorption.

Table 3
Langmuir and Freundlich isotherm parameters for As(V) adsorption

pH	Langmuir model			Freundlich model		
	Q_0 (mg/g)	R^2	b (L/mg)	k	R^2	$1/n$
6	127.0	0.99	0.167	30.2	0.97	0.319
7	111.9	0.97	0.119	21.9	0.94	0.35
9	46.7	0.98	0.146	10.9	0.96	0.318

Table 4
The TCLP test results and comparison with China Standards

	Fe (mg/L)	Al (mg/L)	Ti (mg/L)	Cr (mg/L)	Cu (mg/L)	Cd (mg/L)
RM	0.12	8.01	0.023	0.018	0.05	0.003
Activated RM	0.009	0.012	0.004	0.006	0.0025	0.003
Standards	0.3	0.2		0.05	1.0	0.005
	Mn (mg/L)	Hg (mg/L)	Pb (mg/L)	Ca (mg/L)	Mg (mg/L)	Zn (mg/L)
RM	0.03	<0.001	0.004	1.56	0.057	0.021
Activated RM	0.009	<0.001	0.001	0.62	0.025	0.03
Standards	0.1	0.001	0.01	450		1.0

$$\frac{1}{Q_e} = \frac{1}{Q_0 b C_e} + \frac{1}{Q_0} \tag{6}$$

where C_e is equilibrium concentration (mg/L), Q_e is the amount adsorbed under equilibrium (mg/L), Q_0 (mg/g) is the theoretical maximum adsorption capacity, and b (L/mg) is a Langmuir constant related to the enthalpy of adsorption. Q_0 and b were determined from the slope and intercept of the plot. The linear plots of $1/Qe$ vs. $1/Ce$ were obtained with $R^2 = 0.99$ for various pH, indicating that adsorption of As(V) onto activated RM obeys the Langmuir isotherm model. Plots fitted by the Langmuir equation for the three-tested pH were presented in Figs. 3–7. Adsorption capacity of the activated RM was found to be 127.0, 111.9, 46.7 mg/g at pH 6, 7, 9, respectively. In the earlier study, the Langmuir Q_0 values of MRM at pH 6, 7,and 9 was 68.5, 50.6 and 23.2 mg/g. In comparison, it is clear that the Q_0 obtained in this study was much higher (Fig. 8).

On the other hand, the Freundlich isotherm model could be expressed as follows:

$$\ln Q_e = \ln K_f + \frac{1}{n} \ln C_e \tag{7}$$

where k_f and n are constants representing the adsorption capacity and intensity of the adsorption, respectively. Plots fitted by the Freundlich equation for the three-tested pH were presented in Fig. 9. Table 3 lists the calculated Langmuir and Freundlich constants, as well as the correlation coefficients of the respecting straight lines. A linear plot of $\ln Q_e$ versus $\ln C_e$ was also obtained with a $R^2 = 0.97$, 0.94, 0.96, showing that the adsorption follows the Freundlich isotherm model as well.

3.3. The toxicity characteristic leaching procedure (TCLP)

The estimation of the leaching potential of activated RM is important in assessing the possible environmental impacts associated with the activated RM. Here, the TCLP method as developed by the United States. EPA [17] is employed to simulate the leaching of metals from landfill disposal of contaminated materials by organic acid leachates, with the purpose of classifying the spent activated RM as hazardous or nonhazardous waste. The data reported in Table 4 are the average of two duplicate runs with samples prepared in separate vials. When the results are compared with the Standards for drinking water quality of China (GB 5749-2006), it is found that none of the limits are exceeded. This suggests that the spent activated RM is not hazardous; that is, it does not pose a substantial threat to human health and living organisms.

4. Conclusions

Activated RM was successfully prepared and was reported to be an effective adsorbent for the removal of As(V) from water. It was found that an adsorbent dosage of 200 mg/L is sufficient to reach the drinking water standards of China (GB 5749-2006) of $\approx$ 0.007 mg/L at pH 6. Activated RM is effective for the removal of As(V) with a high capacity of 111.9 mg/g at pH 7. It has a much higher adsorption capacity than RM and MRM. The adsorption kinetic curve for the As(V) fit well with the pseudo-second-order equation. The leaching liquid by activated RM after TCLP test can reach the drinking water standards of China (GB 5749-2006). So the activated RM adsorbent is a safe application.

Acknowledgments

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