

Removal of mercury in waste water using activated red mud

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Abstract. Heat activated red mud was used to remove mercury ion (Hg^{2+}) from water in this paper. The removal efficiency of red mud roasted at 400 to 900 °C for 4 to 10 h was measured. The structure of red mud samples which were activated under various temperatures was studied using XRD. The result showed that the samples roasted at 500 °C for 4 h had the highest adsorption capacity, 96.7 ng Hg g⁻¹. Kinetic study showed that the adsorption process followed pseudo second order model while not pseudo first order model. The removal efficiency increased with pH in the range of 3.5 to 6.5 and decreased when pH was over 6.5. As heat could remove almost all of the mercury adsorbed onto activated red mud, the adsorbent could be regenerated times and regeneration did not decrease mercury removal efficiency.

1. Introduction

In the past decades, mercury was widely used in chlorine alkali, plastic and pharmaceutical industry. Much mercury in waste water was discharged into environment, posing an increasing risk to human health through bioconcentration and biomagnification by aquatic organisms[1-2]. Many works were carried out to find methods to treat mercury-containing waste water. Methods such as chemical deposition[3], electrochemical precipitation[4], adsorption[5], ion exchange[6-7] and biological treatment[8] were studied to removal mercury from wastewater before discharged.

Amongst various techniques, adsorption was most common method due to its advantage of high efficient and low cost, especially its better performance in removing low level mercury from water. Activated carbon[9] or sludge[10] and multi-walled carbon nanotubes[8] was used as adsorbent and showed high efficient in removing mercury from wastewater. Red mud was caustic byproduct in alumina industry of Bayer process. Roughly 1.0–1.5 tonnes of red mud residue are produced for each tone of alumina[11]. Over 30 million tons red mud was produced annually and only 4% were utilized in China. Large amount of untreated red mud was rampant disposed and cause serious environmental problems. Studies on proper utilization of red mud are badly needed. Previous studies showed that acid or heat activated red mud[12] could be used as absorbent to remove some heavy metals, e.g., Cd[13], As [11], Cu and Ni[14] from waste water, but there is little research on using activated red mud to treat mercury-containing wastewater. In fact, compared with other heavy metal ions, mercury is much easier to be driven out from red mud at temperature over 400 °C[15] after adsorption. Hence, heat activated red mud was more efficient to be reutilized and has great potential in mercury-containing wastewater treatment.



In this study, the mercury adsorption capacity of heat activated red mud as a function of calcination time and temperature was determined. The influence of reaction factors such as solution pH, contacting time and initial mercury concentration was estimated. In addition, the recyclability of mercury-absorbed red mud by heat was studied.

2. Material and methods

2.1. Activation of red mud

Red mud was sampled randomly from an aluminum plant in Anshun city, Guizhou Province, China. In lab, the samples were mixed, dried at 105 °C, grind and pass through 60 mesh screen in steps. The chemical compositions of red mud samples were investigated using X-Ray fluorescence analysis and presented in Table 1.

Table 1. Chemical compositions of red mud samples (wt %).

Compositions	SiO ₂	Al ₂ O ₃	CaO	Fe ₂ O ₃	Na ₂ O	TiO ₂	SO ₃	K ₂ O	MgO	P ₂ O ₅	ZrO ₂	SrO
Content	19.78	19.78	18.80	11.09	7.00	6.50	2.49	1.85	1.22	0.47	0.29	0.23

The roast temperature gradient of red mud samples was 300, 400, 500, 600, 700, 800, 900 °C for 2, 4, 6, 8, 10 h respectively. Then the prepared samples were tightly sealed and kept in a dry place for the subsequent adsorption experiments.

Trial studies were first conducted and results showed that adsorption process reached equilibrium in 3 h. To estimate influence of roast temperature and time, 1 g red mud roasted at 300-900 °C for 2-8 h reacted with 50 mL of 2 ngHg mL⁻¹ mercury solution respectively. The initial pH was adjusted to be 6.5 with HCl and NaOH.

2.2. Batch adsorption experiments

Stock solution containing 100 ngHg mL⁻¹ was prepared with HgCl₂. It was kept in a refrigerator and diluted to desired concentration before each experiment. Adsorption experiments were conducted in 100 mL sealed erlenmeyer flask. The initial pH of solution was adjusted with HCl and NaOH solution and measured with a microprocessor pH meter. Added 50 mL mercury solution containing 2 ngHg mL⁻¹ (diluted with stock solution) and 1 g prepared red mud sample into the erlenmeyer flask. Then the flasks were immersed in a temperature-controlled water bath and shaken at 200 rpm for 4 h, to ensure sufficient interaction between mercury ion and red mud. The solution was transferred into centrifuge tube and centrifuged at 4000 rpm for 15 mins. The mercury content in supernatant was measured using cold vapor atomic fluorescence spectrometer (ZYG-II, DaCheng Ltd., China). Duplicated experiments were conducted and the results were presented as mean value to ensure accuracy. The initial pH of all react solutions was maintained at 6.5 except for experiments to estimate the influence of pH on adsorption capacity.

All the glassware were thoroughly cleaned by soaking in nitric acid (25% V/V) for 12 h, rinsed with ultrapure water and oven-dried before each experiment in steps. The reagents used in this study are of analytical grade without further purification.

2.3. Data analysis

The adsorption capacity of red mud was calculated using the following equation,

$$Q_e = \frac{C_0 - C_e}{M} \times V \quad (1)$$

where, Q_e (ngHg g⁻¹) is the equilibrium adsorption capacity of red mud, C_0 (ngHg mL⁻¹) and C_e (ngHg mL⁻¹) is the initial and equilibrium concentration respectively, and V is the volume of adsorption solution.

Kinetics relationships of the Hg²⁺ removal were evaluated with pseudo first-order model (Eq. (2)) and pseudo second-order model (Eq. (3))[16].

$$q_t = q_e (1 - e^{-k_1 t}) \quad (2)$$

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (3)$$

Where q_e (ng g^{-1}) and q_t (ng g^{-1}) were the amounts of Hg^{2+} adsorbed per weight unit of adsorbent at equilibrium and at contact time t , respectively. t (min) was contact time. k_1 (min^{-1}) and k_2 ($\text{g ng}^{-1} \text{min}^{-1}$) was the equilibrium rate constant for pseudo first-order model pseudo second-order model respectively. The data were analyzed using excel software.

3. Result and discussion

3.1. Influence of roast temperature and time on adsorption capacity

Figure 1 shows the mercury adsorption capacity of red mud treated under various temperature and time. Mercury adsorption capacity of untreated red mud was measured to be $83.69 \text{ ngHg g}^{-1}$. The result identified that red mud treated with 400 to 700 °C showed higher adsorption capacity on mercury than untreated samples, but when temperature was higher than 800 °C, mercury adsorption capacity decreased rapidly, even lower than untreated red mud.

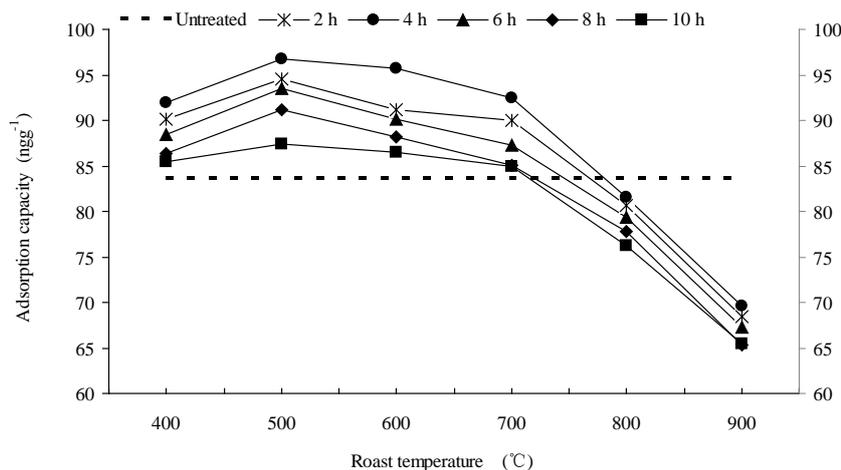


Figure 1. Influence of roast temperature and time on adsorption capacity. Added 1 g activated red mud into 50 mL solution containing 2 ngHg mL^{-1} . Contact time was 3 h and initial pH was 6.5.

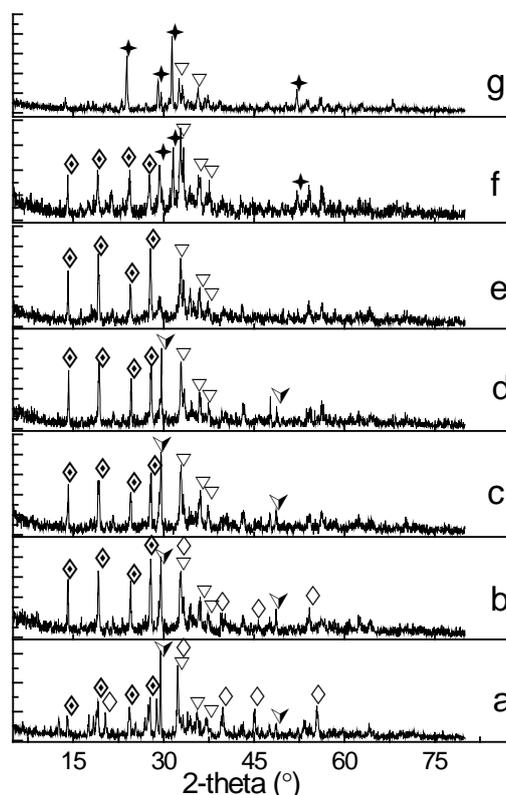


Figure 2. XRD patterns of red mud treated with various temperatures. a for untreated sample, b for 400 °C, c for 500 °C, d for 600 °C, e for 700 °C, f for 800 °C, and g for 900 °C. (◇- $\text{Ca}_3\text{Al}_2(\text{SiO}_4)(\text{OH})_8$ (Katoite, silicatian), ◇- $\text{Na}_6\text{Ca}_2\text{Al}_6(\text{SiO}_4)_6(\text{CO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Cancrinite), ▽- CaCO_3 (Calcite), ▽- Fe_2O_3 (Iron oxide), + - $\text{Ca}_2\text{Al}_2\text{SiO}_7$ (Gehlenite).

Roast time also had influence to adsorption capacity and red mud treated with 500 °C and 4 h gave the highest adsorption capacity ($96.70 \text{ ngHg g}^{-1}$). It meant that 96.7% of mercury in the initial solution was removed and final mercury concentration was $0.066 \text{ ngHg mL}^{-1}$, which was much lower than limited mercury concentration in integrated wastewater discharge standard (GB8978-1996). By comparing the X-ray diffraction patterns (Figure 2) with JCPDS cards, we found that red mud lost surface water, bound water and crystal water gradually with increasing roast temperature from 400 to 500 °C, resulting in much more adsorptive sites for mercury ion and hence adsorption capacity of roasted red mud was enhanced. However, when roast temperature was higher than 700 °C, carbonates (e.g. CaCO_3 , JCPDS 86-0174) in red mud was transformed into gehlenite (JCPDS 87-0969), which was subsequently transformed into cancrinite (JCPDS 48-1862) at 900 °C. It indicated that the skeletal structure of red mud was broken down and some electropositive ion was bonded tightly to skeletal structure, whose ion exchange capacity was decreased significantly. Therefore, roast at temperature over 700 °C decreased adsorption capacity of red mud on mercury[17].

3.2. Kinetic study of mercury adsorption by activated red mud

Kinetic studies were conducted with red mud roasted under 500°C which was added into 50 mL solution containing 2 ngHg L^{-1} . Data of mercury concentration in solution vs time were fitted with pseudo first order equation and second order equation respectively and was shown in Figure 3. It indicated that two stages were involved through the adsorption progress. In the first stage, adsorption rate was very high and about 90% of mercury in solution was removed in 50 mins. Removal rate in the second stage was much lower, and about only 7% of mercury was removed in the left 130 min. The

high adsorption rate on low level mercury is of great importance for application of activated red mud in treatments of mercury containing waste water.

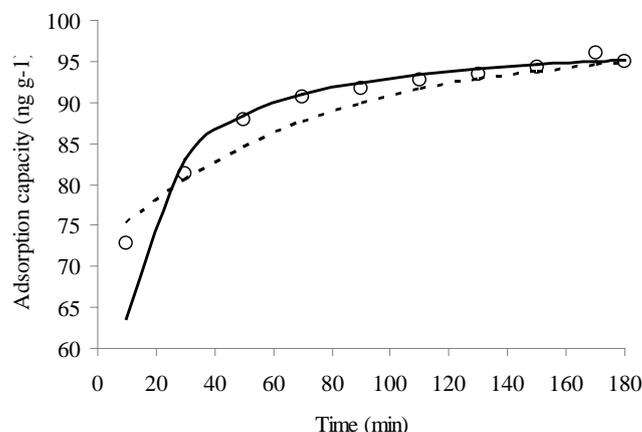


Figure 3. Kinetic fitting of pseudo first-order model and pseudo second-order model for adsorption process of Hg^{2+} onto activated red mud. The circle (\circ) means adsorption capacity measured in this study, dashed line and solid line means calculated results for pseudo first-order model and pseudo second-order model respectively.

Results showed that pseudo second order equation ($R^2 = 0.988$) performed better fitness than first order equation ($R^2 = 0.967$). Using pseudo second order equation, the equilibrium capacity value was estimated to be 95.10 ng g^{-1} ($t = 180 \text{ mins}$), which was closer to the observed value in experiment, 95.06 ng g^{-1} ($t = 180 \text{ mins}$). The equilibrium rate constants and fitting coefficients were calculated and listed in Table 2. Previous research studied adsorption of some cations such as Cd(II) , Cu(II) and Cr(VI) on red mud [13, 18]. Results suggested better fitness of pseudo second order equation displayed compared to pseudo first order equation when fitting the adsorption kinetic data.

Table 2. Kinetic data of the Hg^{2+} adsorption on activated red mud

Kinetic model	equilibrium rate constant	R^2
Pseudo first order	$k_1=0.0144 \text{ (min}^{-1}\text{)}$	0.967
Pseudo second order	$k_2=0.0019 \text{ (g ng}^{-1}\text{min}^{-1}\text{)}$	0.988

3.3. Effect of initial pH

In order to estimate the influence of initial pH of suspension, the adsorption experiments were conducted under at different pH in the range 3.5-8.5, the contacting time was maintained for 3 h, and the results were presented in the Figure 4. It showed that the removal efficiency increased in the range of 3.6-6.5, while decreased when initial pH was over 6.5. The highest removal efficiency 96.7% was observed at pH 6.5. This result suggested that competition between Hg^{2+} and H^+ to adsorption site of surface decreased the removal rate in acidic solution. When initial pH was over 6.5, Hg(OH)^+ or Hg(OH)_2 was dominant species in solution. Since the Hg^{2+} concentration in this study was very low (2 ng mL^{-1}), no mercury precipitate was observed in pH range studied in the work and it was also verified in the solution without red mud.

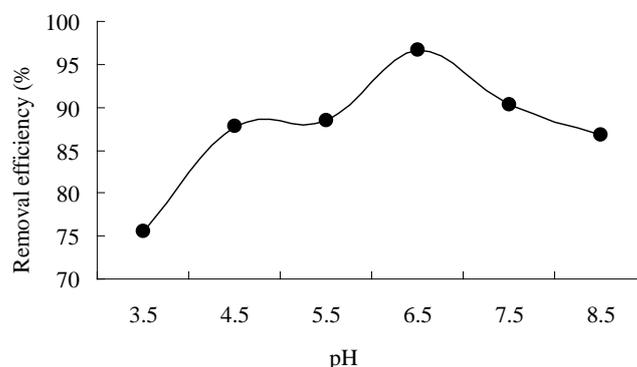


Figure 4. Effect of initial pH on Hg^{2+} removal efficiency by activated red mud. 50 mL solution containing 2 ng mL^{-1} mercury ion, pH was 6.5, contact time was 3 h, and adsorbent dosage was 1 g.

3.4. Regeneration of the adsorbent

To evaluate the adsorption efficiency of regenerated red mud, the solution was filtrated and red mud was collected after adsorption process. Then the collected red mud was dried in the shadow, activated at 500°C for 4 h again and was reused to remove Hg^{2+} from polluted water. The above process was repeated for 3 times. The regenerated adsorbent showed almost the same removal efficiency with the red mud activated one time, since almost all of the adsorbed Hg was emitted at 500°C (this was verified by detecting mercury concentration in the regenerated red mud samples). The result suggested that activated red mud has rather good reproducibility when it was used to remove Hg^{2+} from waste water.

4. Conclusions

This paper aims to use heat activated red mud to remove Hg^{2+} from waste water. The highest removal efficiency (96.7%) was observed with samples roasted at 500°C for 4 h. Kinetic study showed that pseudo second order equation ($R^2 = 0.988$) fitted better than first order equation ($R^2 = 0.967$) to this adsorption process. The removal efficiency increased in the pH range of 3.5 -6.5 and decreased when pH was over 6.5. Regeneration studies showed that removal efficiency did not decrease when the adsorbent was roasted again as most mercury absorbed on red mud was emitted because of high temperature. The result showed that heat activated red mud is a very suitable adsorbent for mercury polluted water because of its high efficiency and cheap price.

Acknowledgement

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