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Removal of cadmium from aqueous solutions using red mud granulated with cement

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Abstract: A novel adsorbent was prepared from granular red mud mixed with cement and its potential to be a suitable adsorbent for the removal of cadmium ions from aqueous solutions was evaluated. The wet red mud was directly mixed up with cement at different mass fractions of 2%−8% and their properties were investigated. Based on the textural characteristics and strength, the granular red mud with 2% addition of cement maintaining for 6 d is identified to have better properties. The batch adsorption experiments for adsorption of Cd^{2+} ions from solution were performed at 30, 40 and 50 °C at different initial concentrations under the condition of constant pH of 6.5. The equilibrium adsorption was found to increase with the increase of temperature during the adsorption process. Langmuir adsorption isotherm model was found to match the experimental adsorption isotherm better. The kinetics of adsorption was modeled using a pseudo second order kinetic model and the model parameters were estimated.

Key words: granular red mud; cadmium; waste water processing; adsorption; aqueous solutions; cement

1 Introduction

Cadmium is an important metal, which can be used in many fields such as the manufacture of paints, plastic stabilizers, phosphors, Ni−Cd battery materials, electric contacts, fusible alloys and control rods for atomic reactor. However, cadmium and its compounds have been found to be very toxic and long-term exposure to cadmium can cause serious damage to human endocrine system, kidney, and bones [1,2]. Although the environmental discharge standards are very strict nowadays, the contamination of Cd in soil, lake and river is still a very serious problem due to the massive mining of zinc-lead [3]. Hence, it is imperative to identify the appropriate technology to control the Cd contamination in the irrigation water ways. One of the effective and time tested treatment techniques for control of water pollution is adsorption [4].

Red mud has been documented well that it can be used as a low cost absorbent for removing heavy metal ions, such as Zn^{2+}[5], CrO_4^{2-} [6], Cd^{2+} [7], Pb^{2+} [8,9], Cu^{2+}[7,10] and Ni^{2+} [11], and having high adsorption capacity for cadmium removal after specific thermal [12,13] or chemical pretreatment [14−16]. However, most of the earlier works pertaining to utilization of red mud employed was only powdered red mud. Powdered red mud, though endowed with a high specific adsorption area, it is not suitable for large scale commercial operation because it requires filtration for removal of the adsorbent.

In the present work, the authors attempt to prepare a novel granular red mud adsorbent (GRM), and assess its ability to remove cadmium(II) ions from aqueous solution using batch tests. In addition, the adsorption isotherm and kinetics of adsorption are investigated.

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2 Experimental

2.1 Preparation of adsorbent

Fresh red mud filter cake, containing 28.24% water with initial pH of about 13.3, was obtained from the Kaiman Aluminum Co. Ltd. in China, and was used as the principal raw materials for granulation. The high quality Portland cement was obtained from a cement plant of the Kunming city. The preparation procedures are described in Fig. 1.

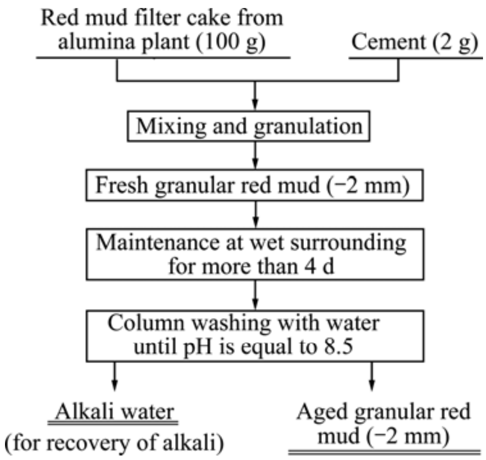

Fig. 1 Preparation procedure of granular red mud (GRM) adsorbent

The specific surface area of granular red mud was analyzed using Quanta Chrome Instruments, AUTOSORB−1.

2.2 Chemicals and reagents

All the chemicals and reagents used in the present work were of analytical grade. The $CdCl_2$ stock solutions with a concentration of 100 mg/L were prepared from $CdCl_2$. The metal ion solutions were subsequently diluted with deionized water to the desired concentration ranging from 1 to 10 mg/L.

2.3 Batch adsorption

Batch adsorption was performed under controlled experimental conditions at a desired concentration of Cd solution and pH. Granular red mud of about 10 g was added to 100 mL of Cd solution in a 250 mL sealed glass conical bottle. The sample bottles were placed in a shaker bath under controlled temperature for 24 h. The adsorption experiments were conducted at 30, 40 and 50 °C. In order to ensure sufficient interaction between Cd^{2+} and granular red mud adsorbent, the agitation speed of the shaker was kept at 100 r/min for all the batch experiments. After completion of adsorption, the solution was filtered directly.

The filtrate was analyzed using an atomic absorption spectrophotometer. The cadmium adsorption experiments were conducted at 5 different initial Cd(II) concentrations (1, 2, 5, 8 and 10 mg/L) added as $CdCl_2$ at 30, 40 and 50 °C, respectively. The pH of solution was maintained at 6.5 for all the experiments.

The adsorption capacity of Cd(II) ions by granular red mud were calculated by the following mass balance equation:

$$q_e = \frac{\rho_0 - \rho_e}{m_s} V \tag{1}$$

where ρ_0 is the initial concentration, ρ_e is the equilibrium concentration, m_s is the mass of adsorbent, and V is the volume of the solution.

3 Results and discussion

3.1 Characterization of adsorbent

The XRD pattern of red mud is shown in Fig. 2.

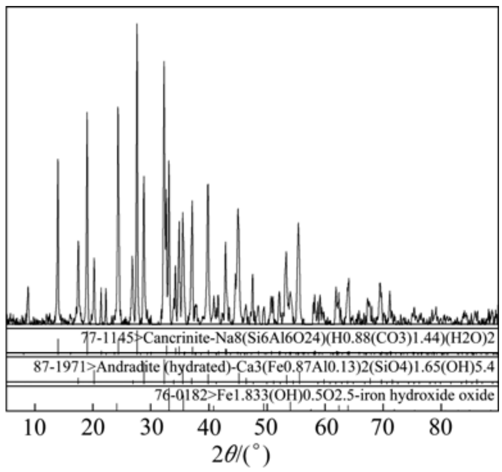

Fig. 2 XRD pattern of granular red mud adsorbent

The nitrogen adsorption isotherm of GRM was performed using surface area analyzer (Quantachrome Instruments AUTOSORB−1).

Table 1 lists the specific surface area and total pore volume of GRM at different cement additions ranging from 2% to 8%. It can be noted that the specific surface area and pore volume do not vary significantly with the increase of cement addition and the 2% addition is considered to be sufficient for the purposes of granulation.

Table 1 Textural characteristics of GRM with different contents of cement addition

Cement addition/%	Particle size/%	Specific surface area/($m^2 \cdot g^{-1}$)	Total pore volume/($m^2 \cdot g^{-1}$)
2	0−5	17.42	0.130
4	0−5	18.54	0.067
8	0−5	23.95	0.133

The strength of GRM was assessed based on the efflorescence rate according to the following procedures: 1) 5 g of GRM with different cement additions were placed into a series of 250 mL conical flasks with water, for different time (either 3 or 6 d); 2) the flasks were placed in the shaker bath and shaken for 1 h; 3) filtering the resultant slurry with a 60 mesh screen; 4) drying the particles with a size 0.25 mm; 5) calculating the mass ratio of material in excess of 0.25 mm particles. The results of efflorescence rate are listed in Table 2.

It can be see from Table 2 that the GRM with a cement addition of 2% (wet base) and after maintaining for 6 d under wet conditions has the highest strength.

The textural characteristics of the GRM with 2% cement addition (wet base) were investigated by SEM and EDS shown in Fig. 3.

It can be seen from Figs. 3 (a−c) that GRM exists on the porous surface. In addition, Fig. 3(b) shows that the pore size of the GRM is in the range of 3.2−6.8 μm. It can be supposed from Figs. 3(d−f) that the GRM prepared by present method has a characteristics of cement existence on the surface, while the red mud exists mainly inside, explaining the reason of minimal amount of 2% cement addition is sufficient to prepare high strength GRM.

Table 2 Efflorescence rates under different conditions

Cement addition (compared with wet red mud)/%	Efflorescence rate/%	
	After 3 d	After 6 d
2	64.10	4.83
4	64.53	24.7
6	44.40	26.15
8	29.38	16.83

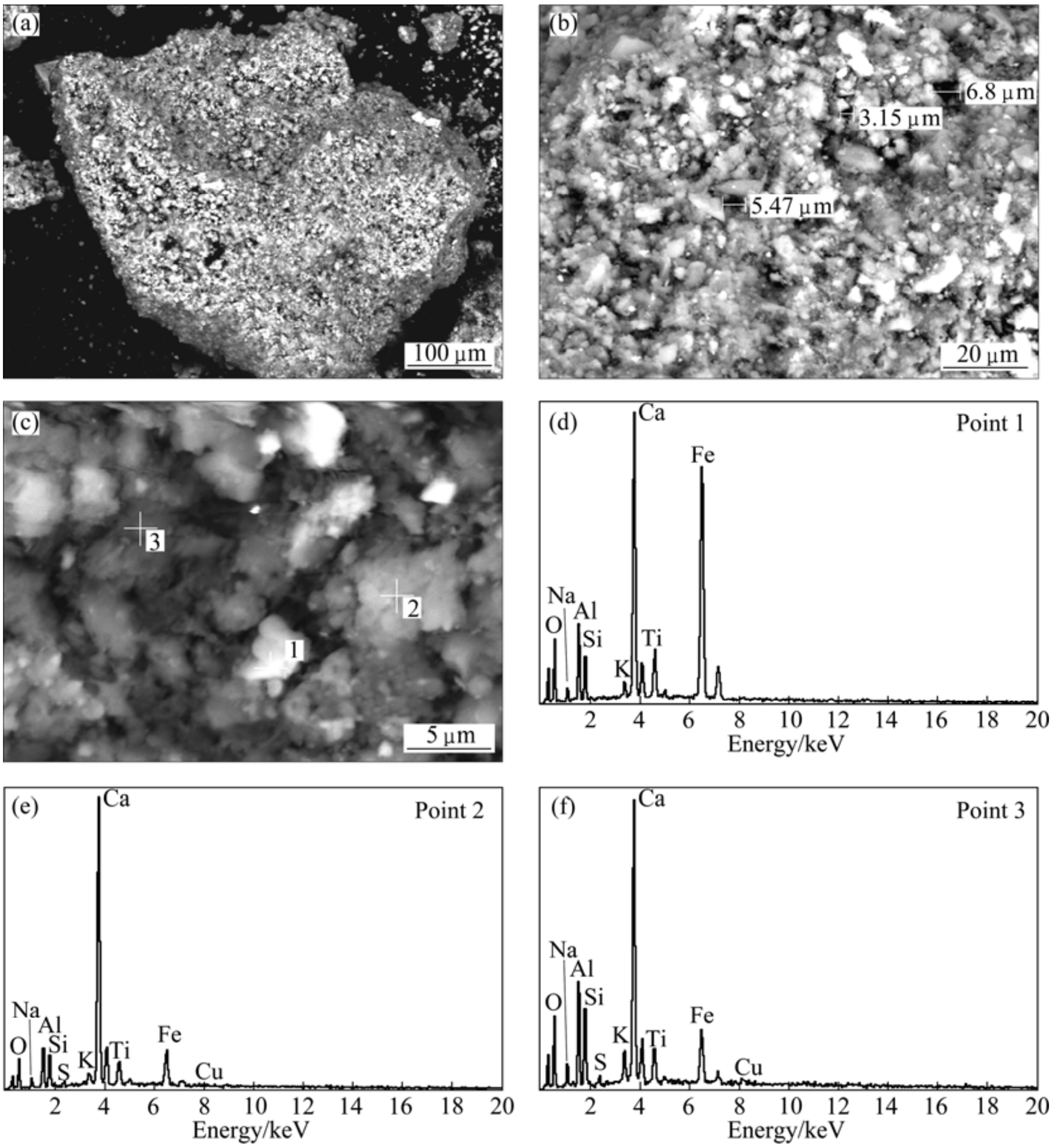

Fig. 3 SEM images and EDS results of cement granular red mud: (a)−(c) SEM images of GRM; (d) EDS result for point 1 in (c); (e) EDS result for point 2 in (c); (f) EDS result for point 3 in (c)

3.2 Effect of contact time on adsorption

Figure 4 shows the effect of contact time on adsorption rate at different initial concentrations of Cd^{2+} solution, using adsorbent dosage of 0.1 g and at temperature of (30±1) °C.

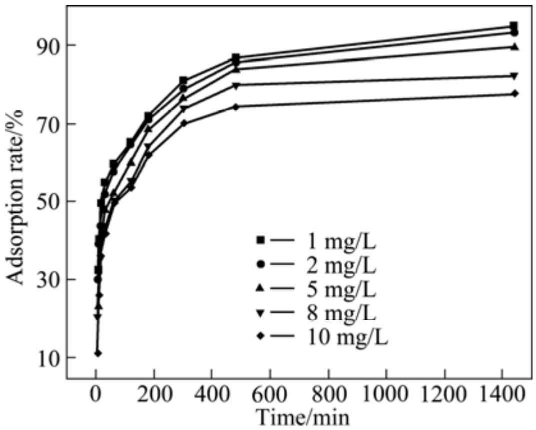

Fig. 4 Effect of contact time on adsorption rate

It is shown in Fig. 4 that the adsorption rate is very high initially, and it decreases when time increases, eventually reaches a steady state. The high initial rate of adsorption is due to the high concentration driving force available for mass transfer from the liquid to the adsorbent active sites. The removal rate of Cd^{2+} from solution decreases with the increase of initial concentration of Cd^{2+}due to the limited availability of the adsorption sites, because the amount of adsorbent is constant in all the experiments.

3.3 Effect of initial Cd^{2+} concentration on batch adsorption

Figure 5 shows the effect of initial concentration of Cd^{2+} on adsorption amount, using adsorbent dosage of 1 g/L at temperature of (30±1) °C.

The removal rate of Cd^{2+} from solution decreases with increase of the Cd^{2+} initial concentration, and the

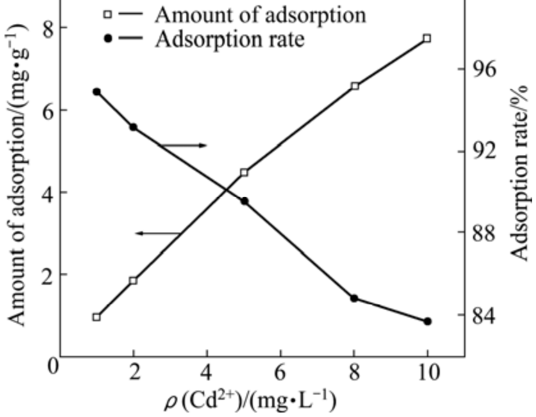

Fig. 5 Effect of initial concentration of cadmium ion on adsorption

reduction was found to be in the range of 95%−84%. The amount of Cd^{2+} adsorbed by the adsorbent increases with increase of the initial concentration of Cd^{2+} in the solution. The higher initial concentration of Cd^{2+} with fixed amount of adsorbent will result in a higher equilibrium concentration of Cd^{2+} in the solution, which contributes to a higher amount of Cd^{2+} adsorbed by the adsorbent.

3.4 Effect of reaction temperature on batch adsorption

Figure 6 shows the effect of solution temperature on the removal of Cd^{2+} from solution at different initial concentrations of Cd^{2+} using adsorbent dosage of 1 g/L.

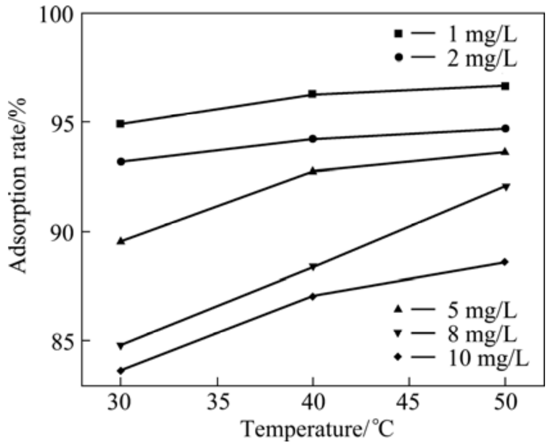

Fig. 6 Effect of reaction temperature on adsorption

It can be seen from Fig. 6 that as the adsorption temperature increases, the removal rate of Cd^{2+} also increases. A higher removal rate of cadmium from solution indicates a higher amount of transfer to the adsorbent phase, resulting in a higher adsorption capacity of the adsorbent. In other words, the adsorption capacity increases with increase in the temperature of the adsorption process. A physical adsorption is generally understood to be exothermic and the equilibrium adsorption will decrease with increase in the temperature of adsorption process. An increase of the adsorption capacity with increase in the temperature indicates a significant adsorption being endothermic reaction.

3.5 Adsorption isotherms and kinetics

The equilibrium adsorption of the Cd^{2+} was tested with the popular adsorption isotherms, Langmuir and Freundlich models. Both models are well detailed in Ref. [17] and hence only the representative model equations are provided. The Langmuir equation is expressed as follows:

$$q_e = \frac{K_L \rho_e}{1 + a_L \rho_e} \tag{2}$$

The linearized form of Eq. (2) is provided as follows:

$$\frac{\rho_e}{q_e}=\frac{1}{K_L}+\frac{a_L\rho z}{K_L} \tag{3}$$

where q_e is the equilibrium adsorption capacity of the adsorbent, ρ_e is liquid phase concentration at equilibrium , and K_L (L/g) and a_L (L/mg) are Langmuir constants. According to Fig. 4 and Eq. (3), a linear relationship between ρ_e and ρ_e/q_e is shown in Fig. 7.

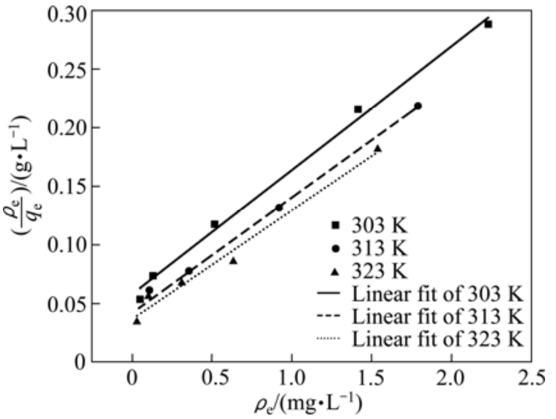

Fig. 7 Langmuir adsorption isotherm for Cd^{2+} onto GRM at different temperatures

From Fig. 7, the model constants, K_L and a_L along with the coefficient of determination (R^2) are calculated and listed in Table 3.

Table 3 Langmuir and Freundlich parameters of GRM adsorbent at different temperatures

T/K	Langmuir constant			Freundlich constant		
	q_{max}/ $(mg\cdot g^{-1})$	a_L/ $(L\cdot mg^{-1})$	R^2	a_f/ $(mg\cdot g^{-1})$	b_f	R^2
303	9.4251	0.0567	0.9933	50.1753	0.5592	0.9810
313	10.1926	0.042	0.9920	84.7540	0.5784	0.9701
323	10.7887	0.0364	0.9779	121.7138	0.6069	0.9560

Freundlich isotherm is the semiempirical equation, with the assumption of multilayer absorption. The equation is expressed as

$$q_e=a_f\rho_e^{b_f} \tag{4}$$

Transfer Eq. (4) into linear form as follows:

$$\ln q_e=\ln a_f+b_f\ln\rho_e \tag{5}$$

where a_f is the constant of Freundlich equation, to a certain extent reflecting the strength of the adsorption ability; b_f is the component factor, which indicates the intensity of adsorption increasing with increase in the concentration and can also indicate the adsorption difficulty.

According to Fig. 4 and Eq. (5), a linear relationship of $\ln\rho_e$ and $\ln q_e$ is shown in Fig. 8. From Fig. 8, the model parameters a_f and b_f along with the R^2 value are listed in Table 3.

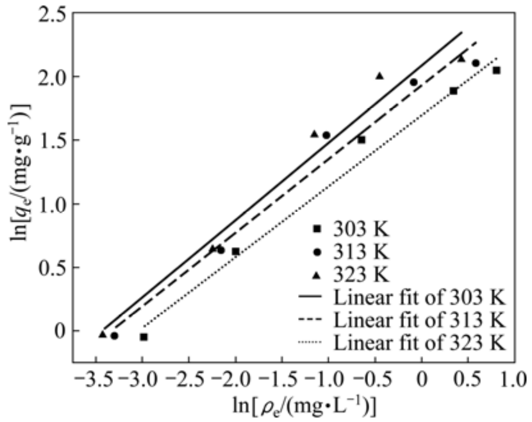

Fig. 8 Freundlich adsorption isotherm for Cd^{2+} onto GRM at different temperatures

The R^2 value listed in Table 3 clearly indicates that the Langmuir mode fits better than the Freundlich model. The value of q_{max} indicates the monolayer adsorption capacity of the GRM, which increases with the increase of the temperature during the adsorption process.

The adsorption kinetics is generally modeled using the pseudo first order or pseudo second order model, while the second order model fits the experimental data better compared with the first order model for the adsorption of metal ions in solution using solid adsorbent [16]. The suitability of the pseudo second order model to match the experimental data was based on the R^2 value. The quasi second order kinetic model is given as

$$\frac{dq}{dt}=k_2(q_e-q)^2 \tag{6}$$

Equation (7) can be linearized to the following form:

$$\frac{t}{q_t}=\frac{1}{k_2q_e^2}+\frac{1}{q_e}t \tag{7}$$

$$h=k_2q_e^2 \tag{8}$$

where h $(mg\cdot g^{-1}\cdot min^{-1})$ is initial adsorption rate, k_2 $(g\cdot mg^{-1}\cdot min^{-1})$ is the quasi second order model of rate constant, and q_t is the amount adsorbed at any given time, while q_e is the equilibrium adsorption capacity.

Figure 9 shows the closeness of the model equation with the experimental data. The R^2 value is presented in Table 4 along with the model kinetic parameters. The microanalysis of the GRM surface after Cd adsorption is shown in Fig. 10.

It can be seen in Fig. 10(a) that the porous surface of GRM after adsorption of Cd still exists, the EDS analysis in Fig.10(b) also clearly indicates the presence of Cd in the GRM.

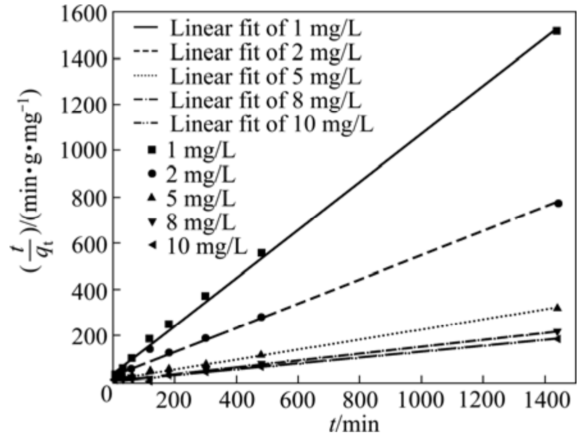

Fig. 9 Fitting curves of pseudo-second-order kinetic model with experimental data

Table 4 Pseudo-second-order model parameters at different concentrations

ρ_0/(mg·L^{-1})	q_e/(mg·g^{-1})	Pseudo-second-order model			
		k_2/(g·mg^{-1}·min^{-1})	h/(mg·g^{-1}·min^{-1})	q_e(cal)/(mg·g^{-1})	R^2
1	0.949	0.0305	0.0282	0.9616	0.9976
2	1.864	0.0113	0.0410	1.9053	0.9903
5	4.477	0.0054	0.1119	4.5714	0.9963
8	6.584	0.0080	0.3527	6.6547	0.9957
10	7.767	0.0091	0.5548	7.8235	0.9894

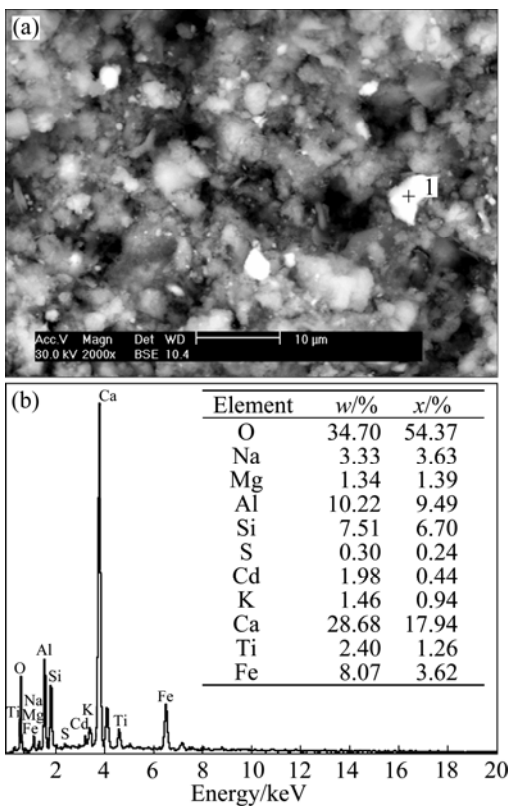

Fig. 10 SEM image of GRM (a) and EDS result (b) for point 1 in (a)

4 Conclusions

1) The wet red mud was directly mixed up with cement at different mass fractions ranging from 2% to 8% and their physical properties were estimated. Based on the textural characteristics and the physical strength, the 2% addition of cement is identified to have better properties.

2) The granular red mud (GRM) mixed with cement has potentials to be a suitable adsorbent for the removal of cadmium ions from aqueous solutions. The batch experiments for adsorption of Cd^{2+} ions with the GRM from solution were performed at 30, 40 and 50 °C at different initial concentrations under the condition of constant pH of 6.5. The results show that the GRM has good adsorption capacities. The equilibrium adsorption increases with the increase of temperature during the adsorption process, indicating the adsorption is an endothermic reaction.

3) The Langmuir adsorption isotherm model matches the experimental adsorption isotherm better. The adsorption capacity of adsorbent for Cd^{2+} is more than 9 mg/g. The pseudo second order model matches the experimental data well. R^2 values are more than 0.99.

4) The SEM and EDS results of the GRM surface after Cd adsorption clearly indicate the presence of Cd in the GRM.

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采用水泥制粒的赤泥脱除水溶液中的镉离子

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摘 要：采用湿赤泥添加水泥作为粘结剂的方法制备出一种新型粒状吸附剂材料，并评价这种粒状赤泥材料脱除水溶液中镉离子的潜力。直接向湿赤泥中添加 2%−8%的水泥，研究不同水泥添加量和保养时间对粒状赤泥基吸附剂材料的粉化率和比表面积的影响。结果表明，在 2%的水泥添加量下保养 6 d 后的粒状赤泥的结构特性和强度等参数达到了较好的水平。在 pH 为 6.5，温度分别为 30、40 和 50 °C 及不同 Cd^{2+}浓度溶液的条件下，进行吸附实验研究。结果表明，随着温度的升高吸附性能提高，并以此采用伪二级动力学模型进行吸附动力学模拟，得到了相关的模型参数。

关键词：粒状赤泥；镉；废水处理；吸附；水溶液；水泥

(Edited by LI Xiang-qun)