

Study on Adsorption for Pb²⁺ of Red Mud Sintering-expanded Haydites

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ABSTRACT

Red mud is discharged as waste during the production of alumina from bauxite. Many approaches were reported to utilize it as a resource for an environmentally friendly application. The aim of the present study was to use Bayer red mud as the main ingredient for the preparation of red mud sintering-expanded haydite (RM-SEH), thereby acting as a kind of adsorbent. The results show that an adsorption efficiency of Pb²⁺ up to 93% can be achieved in static batch adsorption experiments by dosing 2 g/25mL RM-SEH into 50 mg/L Pb(NO₃)₂ aqueous solutions at pH 5.40 with an adsorption time of 6 hours.

Keywords: Red mud, Removal of lead, Sintering-expanded haydit

1. INTRODUCTION

Lead and its compounds, one of the most common toxic metals in the wastewaters, have been known with certain toxicity to be found in peoples nervous, digestive, hematopoietic, renal, cardiovascular and endocrine systems (Wang et al., 2008; Grudic et al., 2013). The physical treatment method is one of the most commonly used methods among them due to its relatively low cost. Adsorbents, flocculants, permeable membrane, ion exchange resin or other materials mainly are used to remove the pollutants from the water (Mhamdi et al., 2013). For example, static adsorption with haydite was used for the removal of lead from wastewater by Wang et al. (2003). The experimental results showed that the removal efficiency of lead ion in the tested wastewater could reach more than 98% in 0~100 mg/L Pb²⁺ and at pH levels between 4.0 and 11.0.

Haydite is a type of ceramic generally with spherical or oval shapes and with particle size at 5~20 mm (Yan and He, 2006). Although haydite is typically used in construction materials, it could also be used as an adsorbent because of its high porosity. Among all types of haydites, the sintering-expanded haydite (SEH) seems to have better adsorption ability because of its evenly distributed interconnected pore

structure and large pore surface area (Xie et al., 2008). SEH is commonly made from fly ash, sludge, clay minerals and shale in which the main chemical compounds are SiO₂ and Al₂O₃. Some organic matters, calcite and other compounds existing in the raw materials can decompose and release large quantities of gases to help the pore formation during SEH preparation at high temperatures (Lei et al., 2013; Gao et al., 2010; He et al., 2012).

Bayer red mud is high in oxides, especially iron, aluminum and silicon oxide. So Bayer red mud may been considered a good source for SEH for the similar chemical composition between it and those common raw materials of SEH. Red mud is an insoluble waste residue with high alkalinity from the alumina production lines. The quantity of red mud is huge (roughly 1~1.5 tonnes per 1 tonne of alumina production). However, currently there is no cost-effective and efficient means to properly handle the red mud in almost all the alumina refineries (Jayasankar et al., 2012). Therefore, research on utilization of red mud to maximize the resource availabilities and minimize the environmental impacts has become popular. As an example, red mud as adsorbent or exchanger for heavy metal removal from aqueous solutions is one of the most interesting research areas, benefiting from its high surface activity (Lopez et al., 1998; Castaldi et al., 2011; Santona et al., 2006). Some research had shown that the adsorption or exchanged capacity of

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the red mud would be enhanced when activated by acid or heat treatment (Huang et al., 2008; Castaldi et al., 2008; Zhu et al., 2007). Rather the red mud could be a potential efficient adsorbent, the adsorbent directly made from red mud waste fines may cause secondary pollution to the environment. Because the adsorbent will become a new sludge, which is very difficult to be recycled. The present research work aims to solve the problem. We used Bayer red mud as main ingredient with additions of pore-forming and fluxing agents to prepare porous RM-SEH with certain particle sizes, mechanical strength, and adsorption properties. To serve the purpose of its applicability as an alternative adsorbent for wastewater treatment, an experimental study of Pb^{2+} removal from aqueous solution was carried out.

2. MATERIALS AND METHODS

2.1 Materials

Red mud was obtained from the Aluminum Corporation of China located in Pingguo county, Guangxi Zhuang Autonomous Region. The main physical and chemical properties are given in Table 1. X-ray diffraction (Using a X'Pert PRO diffractometer with Cu K α radiations generated at 40kV,40mA) was used to determine the mineralogical composition (Figure 1). In the red mud, the major phases are hematite, hydrate garnet, perovskite, calcite and diaspore ore.

Table 1 Properties of the red mud.

Chemical composition (wt.%) (air dried samples)					
Fe ₂ O ₃	Al ₂ O ₃	SiO ₂	CaO	Na ₂ O	
24.92	19.20	7.39	20.12	3.04	
TiO ₂	K ₂ O	MgO	Loss		
6.52	0.09	0.60	15.72		
Mineral composition (wt.%)					
Hematite	Hydrate garnet		Perovskite		
31	30		6		
Calcite	Diaspore ore				
11	7				
Particle size distribution data (wt.%)					
Size(μ m)	> 250	250-120	120-75	75-52	< 52
Dry	6.96	41.81	12.15	23.10	15.98
Wash	3.31	17.91	3.90	4.71	70.18

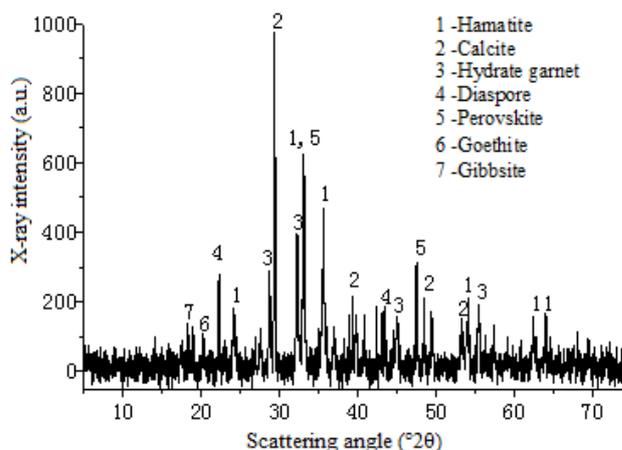


Figure 1 The XRD pattern of the red mud.

2.2 Preparation of RM-SEH

Red mud was used as the main raw material and skeleton agent for the preparation of the sintering-expanded haydite. Limestone was used as the fluxing agent, of which calcium carbonate content was around 98%. Wood sawdust was used for pore-forming. The procedure for the preparation of the RM-SEH from the red mud consisted of the following four steps: (a) Pelletizing: According to the mixing proportion, 71% red mud, 16% limestone, and 13% wood sawdust were first blended evenly. Prior to the pelletizing process, about 20% water was added. The wet mixture was then pelletized (used Φ 800 mm balling disc) into green-balls at 10~15 mm in diameter. (b) Drying: The green-balls were put into a drying oven at 120°C for 2 hours. (c) Roasting: The dried green-balls were roasted in a furnace at temperatures of 1210°C for 10 minutes. (d) Cooling: When the roasting process was done, the RM-SEH samples were moved outside the furnace and cooled in air with natural convection.

The corresponding microstructure was investigated by scanning electron microscope (SEM, S - 4800, Hitachi). The porosity was tested by Archimedes, and the pore structure was tested by mercury intrusion porosimetry (Auto Pore IV9500, America).

2.3 Removal of Pb^{2+} from aqueous solution

Several Pb^{2+} contaminated water samples were prepared using analytical grade $Pb(NO_3)_2$ and home-made distilled water. The total solution volume of batch adsorption experiments was 25 mL. The initial pH value of each samples was tested by PHS-2 acidity meter. The RM-SEH samples, as adsorbent,

were thereafter added into each solution. The mixtures were then put in a HY-4 oscillator for sufficient agitating at room temperature (25 °C) in setting time. Time for several minutes' sedimentation to precipitate the adsorbents was allowed. The supernatant aqueous solutions were obtained by filtration with a 0.2 µm Millipore PTFE filters, and analyzed by dithizone spectrophotometric method (used a UNIC-7200 atomic spectrophotometer) to determine the residual Pb^{2+} concentration for the evaluation of the adsorption efficiency or capacity of Pb^{2+} by the RM-SEH.

All the samples were run in triplicate. First the effects of the adsorption time (from 1 to 6 hours), the adsorbent dosage (from 1 to 5 g) and the Pb^{2+} initial concentration (from 20 to 100 mg/L) on Pb^{2+} adsorption of the RM-SEH samples were completed without adjusting the pH value of each solution samples. Then the effects of the pH (from 3.0 to 8.0) on Pb^{2+} adsorption was carried out. In order to avoid potential saturation with respect to $Pb(OH)_2$ phases, the pH was only run to 8.0. The pH of each sample was adjusted with 0.01 mol/L NaOH and 0.01 mol/L HCl. Last the effects of the adsorbent regeneration cycles (from 1 to 5 times) on Pb^{2+} adsorption of the RM-SEH samples were performed. The desorption experiments were done immediately by 0.1 mol/L HCl after the removal of the supernatant solutions from the previous adsorption. The total desorption reaction time was 24 h. Then the RM-SEH samples were washed by distilled water till the pH was near neutral.

3. RESULTS AND DISCUSSION

3.1 Microstructure and adsorption properties

The appearances and microstructure of the cross-section of the RM-SEH samples (Figure 2) revealed that a large number of non-homogeneously distributed pores with different sizes were found. The formation of these pores resulted from the burning off of the pore-forming agent. The extremely large pores were formed by the gas expansion during the roasting process, in which the gases were trapped by the liquid phases blocking the pathway. Although not all the pores seemed to be interconnected in the SEM image presented here, these pores were generally connected to each other by many micro-channels. The results of the Table 2 showed that the pore surface area and porosity were ideal, especially the pore size distribution was mainly in 500-1000 nm pores. So the RM-SEH samples may fit matter adsorption from the aqueous solutions.

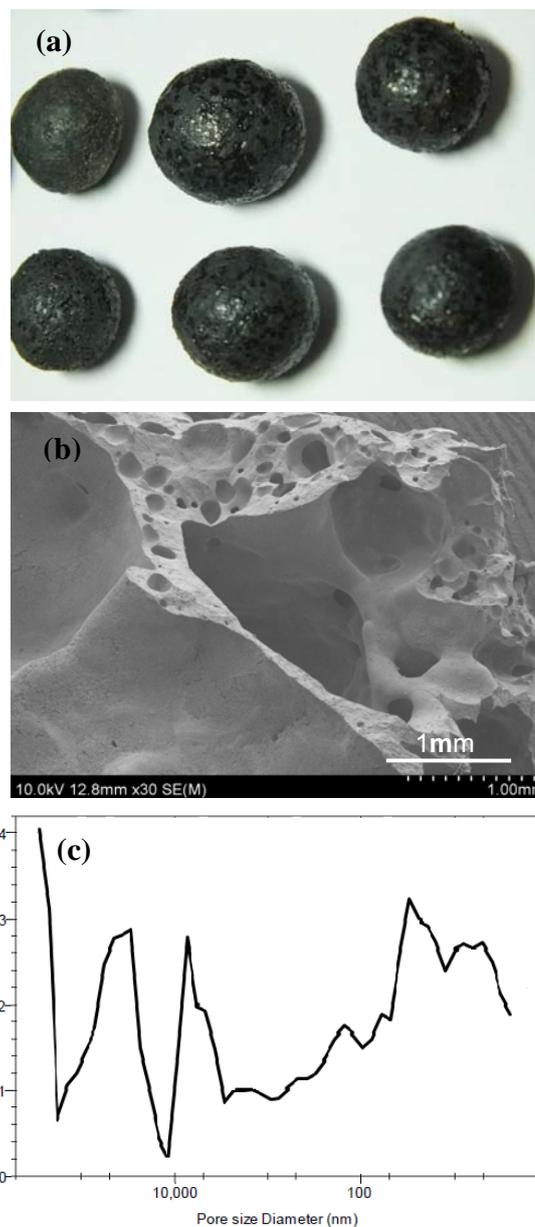


Figure 2 The appearance and cross-section SEM image of the RM-SEH samples, and the corresponding pore size distribution of the samples. (a) appearance; (b) cross-section; (c) pore size distribution.

Table 2. The pore structure of the RM-SEH samples.

Pore surface area (m ² /g)	Pore volume (mL /g)	Average pore size (nm)	Porosity (%)
13.97	0.0974	27.89	23.63

3.2 Removal of lead from aqueous solution

To increase understanding of the Pb^{2+} adsorption with RM-SEH samples, the effects of the adsorption time, the adsorbent dosage, the Pb^{2+} initial concentration and the adsorbent regeneration cycles on Pb^{2+} adsorption were also studied on the RM-SEH sample (Figure 3) without adjusting pH of the solution.

An initial adsorption kinetics study was conducted to determine the optimal adsorption time. The adsorption occurred rapidly within the first hour, but gradually decreased until it reached the equilibrium later (Figure 3a). Although the removal of Pb^{2+} was virtually completed within 3 hours, the final equilibrium was a 6-hour adsorption period. All the following adsorption experiments were then performed at a minimum adsorption time of 6 h.

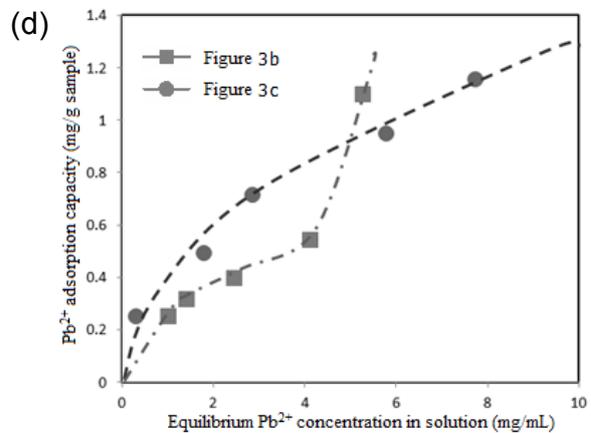
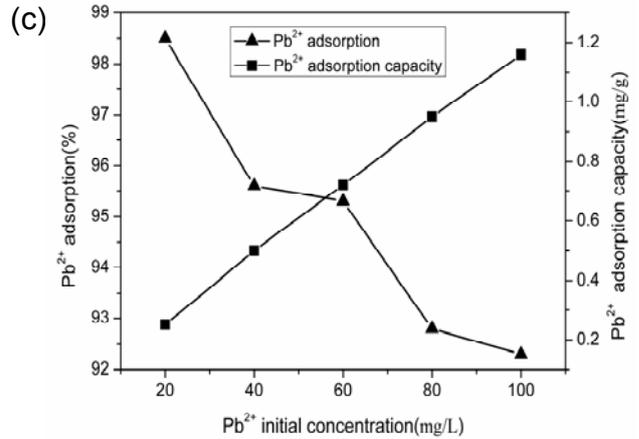
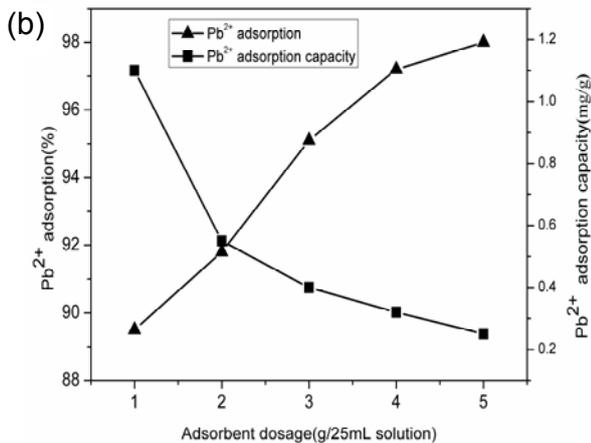
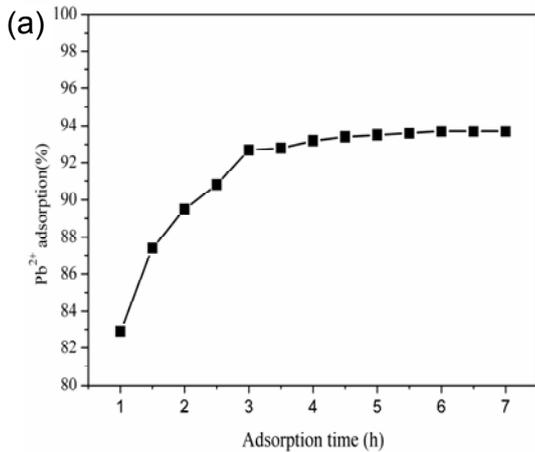


Figure 3 Evolution of Pb^{2+} adsorption with RM-SEH at different (a) adsorption times, (b) adsorbent dosages, (c) Pb^{2+} initial concentrations, and (d) Pb^{2+} adsorption isotherms extracted from Figure 3b-c. Without specific annotation, the adsorption time was 6 h and the initial concentration of the Pb^{2+} solution was 50 mg/L, pH 5.40.

The effect of the adsorbent dosage on the Pb^{2+} adsorption seemed to be significant. With the increase of adsorbent dosage, the Pb^{2+} adsorption increased clearly (Figure 3b). The maximum adsorption efficiency was roughly 98% for 5 g the RM-SEH sample in a 25 mL solution. However, with a continuous increase of the sample dosage, the Pb^{2+} adsorption capacity of the RM-SEH sample decreased gradually. This might be attributed to the limited total lead ion concentration in solution, causing a lower equilibrium Pb^{2+} adsorption capacity at much lower Pb^{2+} concentration in the solution.

The Pb^{2+} adsorption performance of same amount of the RM-SEH sample with different Pb^{2+} initial concentrations (Figure 3c) revealed that the Pb^{2+} adsorption capacity of the RM-SEH sample increased almost linearly with the initial concentration. Because more Pb^{2+} got in contact with the adsorbent with the increase of Pb^{2+} initial concentration, this resulted in the increase of the Pb^{2+} adsorption capacity. Ideally the almost linear increase of the Pb^{2+} adsorption capacity with the initial Pb^{2+} concentration should lead to an almost constant Pb^{2+} adsorption efficiency in the solution with the same amount of adsorbent dosages. However, the real Pb^{2+} adsorption efficiency decreased. This is likely due to both the introduced experimental errors and the nonlinear adsorption isotherm.

Two Pb^{2+} concentration isotherms (Figure 3d) were extracted from Figures 3b-c. However the isotherms obtained from two different experimental approaches seemed to be fairly different. The isotherm data obtained from the experiment with different adsorbent dosages expressed a tendency of Type II adsorption behavior within the experimental Pb^{2+} concentrations, while the other isotherm could be the early part of the Type I, Type II, or Type IV adsorption. However due to the limited data, no conclusion could be drawn on this discrepancy between these two different experimental isotherms.

As pH is influencing the Pb^{2+} chemistry, the effects of the pH on Pb^{2+} adsorption was provided (Figure 4). The results showed that the Pb^{2+} adsorption capacity of the RM-SEH sample was lower at pH <4. While the pH 4-8 was suitable for removing Pb^{2+} from waste water by this method. There was no evidence for precipitation at pH 8, though saturation with respect to $Pb(OH)_2(s)$ was approached at this pH.

A favorable adsorbent should match the requirement so that it could be reused in multiple cycles with no significantly degraded performance after regeneration. For this reason, a preliminary study was performed to check the corresponding RM-SEH's adsorption efficiency with regeneration cycles. In this case, the RM-SEH samples were re-used after desorbing by HCl. The overall Pb^{2+} removal efficiency in a 50 mg/L Pb^{2+} solution with a maximum of 5 cycles (Figure 5) revealed that the Pb^{2+} adsorption remained reasonably efficient after 2 regeneration cycles but dramatically dropped down below 80% for the next following cycles. Although current preliminary results demonstrated the RM-SEHs are not quite favorable for multiple regenerations, because of the abundant availability of the cheap raw materials and the low cost

preparation process, the RM-SEHs could be still considered as an attractive adsorbent candidate. The group is actually launching a new project to further improve the RM-SEH's performance as adsorbents for potential waste water treatment. Different preparation approaches and regeneration methods of various mixes of fluxing agents and pore-forming agents will be investigated.

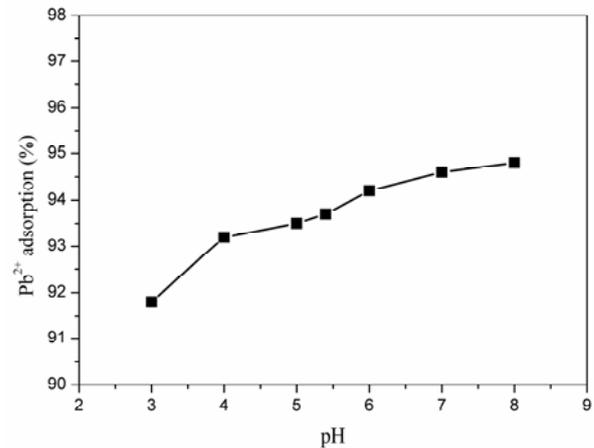


Figure 4 Evolution of Pb^{2+} adsorption with RM-SEH at different pH (2g adsorbent, 50 mg/L Pb^{2+} solution and 6 h adsorption time).

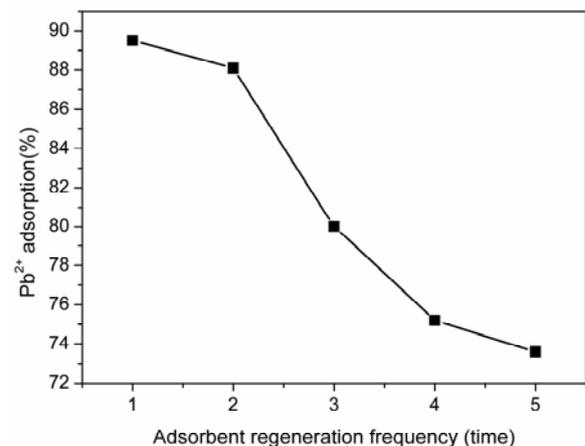


Figure 5 Adsorbent regeneration cycles with RM-SEH (2g adsorbent, 50 mg/L Pb^{2+} solution, 5.40pH and 6 h adsorption time).

4. CONCLUSIONS

This research demonstrated that Bayer red mud could be used to prepare a low-cost, lightweight, highly porous sintering-expanded haydites. The preliminary static batch adsorption experiments also demonstrated the RM-SEHs' capability to remove lead from aqueous solution with acceptable performance. An adsorption efficiency of Pb^{2+} up to 93% could be achieved by dosing 2 g/25mL RM-

SEH into 50 mg/L Pb(NO₃)₂ aqueous solutions at pH 5.40 with an adsorption time of 6 hours. What's more, the RM-SEH can be easily recycled and reused after regeneration. The experiments indicated the RM-SEH might be used for treatment of wastewater containing lead. However, to obtain more promising RM-SEHs, more research such as understanding the adsorption mechanisms, optimizing the regeneration methods, and treating other heavy metals in distilled water are still needed.

REFERENCES

- Gao, X., Ma, F., Tian, D., Wang, S.H., and Jia, H.S. (2010) Preparation of ceramsite based on clay and its static adsorption study for Cd²⁺. *Materials Review*, 24, 488-491.
- Grudic, V.V., Peric, D., Blagojevic, N.Z., Vukasinovic-Pesic, V.L., Brasanac, S., and Mugosa, B. (2013) Pb(II) and Cu(II) sorption from aqueous solutions using activated red mud-evaluation of Kinetic, Equilibrium, and Thermodynamic models. *Polish Journal of Environmental Studies*, 22, 377-385.
- He, H.T., Yue, Q.Y., Gao, B.Y., Zhao, Y.Q., Yu, H., Li, J.Z., Li, Q., and Wang, Y. (2012) The effect of incorporation of red mud on the properties of clay ceramic bodies. *Applied Clay Science*, 70, 67-73.
- Huang, W.W., Wang, S.B., Zhu, Z.H., Li, L., Yao, X.D., Rudolph, V., and Haghseresht, F. (2008) Phosphate removal from wastewater using red mud. *Journal of Hazardous Materials*, 158, 35-42.
- Jayasankar, K., Ray, P.K., Chaubey, A.K., Padhi, A., Satapathy, B.K., and Mukherjee, P.S. (2012) Production of pig iron from red mud waste fines using thermal plasma technology. *International Journal of Minerals, Metallurgy and Materials*, 19, 679-684.
- Lei, G.Y., Wang, D.M., Yang, J.X., and Zhou, M. (2013) Preparation of porous ceramsite by fly ash and its utilization in biological aerated filter reactors. *Journal of Wuhan University of Science and Technology*, 36, 59-63.
- Lopez, E., Soto, B., Arias, M., Nunez, A., Rubinos, D., and Barral, M.T. (1998) Adsorbent properties of red mud and its use for wastewater treatment. *Water Research*, 32, 1314-1322.
- Mhamdi, M., Galai, H., Mnasri, N., Elaloui, E., and Trabelsi-Ayadi, M. (2013) Adsorption of lead onto smectite from aqueous solution. *Environmental Science and Pollution Research International*, 20, 1686-1697.
- Castaldi, P., Silveti, M., Santona, L., Enzo, S., and Melis, P. (2008) XRD, FTIR, and thermal analysis of bauxite ore-processing waste (red mud) exchanged with heavy metals. *Clays and Clay Minerals*, 56, 461-469.
- Castaldi, P., Silveti, M., Enzo, S., and Deiana, S. (2011) X-ray diffraction and thermal analysis of bauxite ore-processing waste (red mud) exchanged with arsenate and phosphate. *Clays and Clay Minerals*, 59, 189-199.
- Santona, L., Castaldi, P., and Melis, P. (2006) Evaluation of the interaction mechanisms between red muds and heavy metals. *Journal of Hazardous Materials*, 136, 324-329.
- Wang, S.G., Gong, W.X., Liu, X.W., Yao, Y.W., Gao, B.Y., and Yue, Q.Y. (2008) Removal of lead(II) from aqueous solution by adsorption onto manganese oxide-coated carbon nanotubes. *Separation and Purification Technology*, 58, 17-23.
- Wang, S.L., Zhang, H., Xie, W.H., and Zheng, L.S. (2003) Treatment of lead-containing wastewater with ceramsite. *Journal of Jinan University (Science and Technology)*, 3, 295-297.
- Xie, X.L., Wang, L.J., Zhao, J.X., and Zhou, J. (2008) Production of sintering-expanded haydite with red mud. *Journal of Guilin University Technology*, 28, 196-199.
- Yan, Z.J. and He, Y.J. (2006) *Practical Technology of Ceramsite Production*, Chemical Industry Press, Beijing.
- Zhu, C.L., Luan, Z.K., Wang, Y.Q., and Shan, X.D. (2007) Removal of cadmium from aqueous solution by adsorption on granular red mud (GRM). *Separation and Purification Technology*, 57, 161-169.