Desalination and Water Treatment
www.deswater.com

1944-3994 / 1944-3986 © 2010 Desalination Publications. All rights reserved.
doi: 10.5004/dwt.2010.1387

20 (2010) 203–208
August

Phosphate removal performance of acid pickling milling wastewater from high-phosphate hematite mineral processing by activated red mud

Zhang Yi, Xia Shibin*, Luo Ji, Zhang Yimin*

School of Resources and Environmental Engineering, Wuhan University of Technology, Wuhan 430070, P.R. China
Tel./Fax +86-27-87212127; email: xiashibin@126.com; zym126135@126.com

Received 28 November 2009; Accepted in revised form 18 January 2010

ABSTRACT

The acid pickling milling wastewater from high-phosphate hematite mineral processing should be treated and comprehensively reused on-line with a low pH value and a high phosphate removal. The absorbents, raw and different activated red mud (RM), named as RM-α, β, γ, δ, and ε, were firstly studied on the phosphate removing performances in this paper. During the treatment of the actual mineral processing wastewater with pH 2.50–2.53, the turbidity 600–800 NTU, and phosphate concentration 98.85 mg/L, the optimum dosage of raw RM, RM-α, β, γ, δ, and ε was 23.00g/L, 22.50 g/L, 22.00 g/L, 23.50 g/L, 28.00 g/L and 20.00 g/L, respectively, and the phosphate removal was 92.47%, 99.39%, 99.32%, 99.42%, 98.56% and 99.66%, respectively, and effluent pH was 8.02, 3.93, 3.06, 3.82, 3.72, and 2.98, respectively. The results indicated that the activated red mud ε, or RM-ε, was the most suitable absorbent with the highest phosphate removal, the lowest dosage and pH value in the effluent.

Keywords: Acid pickling milling wastewater; Activation; High-phosphate hematite; Phosphate removal; Red mud

1. Introduction

The hematite with high amounts of phosphate is one of the most important iron minerals distributed broadly in nature. The acid pickling milling process was usually used for the utilization of their minerals. Then, the acidic wastewater with high phosphate concentration was produced in iron ore. In recent decades, acidic wastewater containing phosphate has been discharged directly into a large number of lakes, rivers, coastal waters and seas without efficient treatment, which caused serious water pollution, increased the nutrients load, destructed the aquatic ecological balance, resulted in the deterioration of sensory properties of the water shed, reduced the self-purification capacity and its quality, raised the cost of water supply, and that had serious affect on the food chain, even poisoned humans, animals, livestock, etc. [1,2].

In order to respond to the demand for lowering the emission of the wastewater into the environment, many technologies for phosphate and other harmful wastes removing have been developed. The current technologies include physical-chemical methods, photochemistry methods and biological methods [3–8]. Biological methods have high removal efficiency and avoid using chemicals, but complex plant configurations and operating conditions are required [9]. Inorganic phosphate acid wastewater is mostly suited to be treated by physical chemical methods which mainly include coagulation, crystalliza-

---

* Corresponding author.

tion, adsorption, electrodialysis, reverse osmosis, and so on [10]. Adsorption is one of the techniques which would be comparatively useful and economical for phosphate removing from the inorganic phosphate acid wastewater. In recent years, considerable attention has been paid to the advantages of adsorption, such as adsorbent recycling, large adsorptive capacity, and low cost. Adsorbents were mainly used to adsorb the components in the wastewater so as to achieve the purpose of the wastewater treatment [11–13]. Nowadays, the research mainly focuses on the improvement of the absorption capacity. The adsorbents widely used contain natural material, waste residue and active alumina as well as its modified material, porous material and synthetic adsorbent. Furthermore, the economic and environmental concerns have been taken into consideration, different types of low-cost sorbents, such as clinoptilolite [14], alum sludge [15], red mud (RM) [16–18] and other waste materials [19–33] were used as alternative adsorbents. RM is a waste by-product during the alkaline leaching of bauxite in the Bayer process, and it causes serious environmental problems due to its high alkalinity and large amount. Owing to the high content of aluminum, iron, and calcium, RM has been used to remove fluoride [34], hexavalent chromium [35], dyes [36], chlorophenols [37], phosphate, Cu^{2+}, Zn^{2+}, Ni^{2+} and Cd^{2+} from aqueous solution, and the RM, neutralized by seawater, can remove arsenate as well [38]. Although red mud was found to be a good phosphate removing medium, the direct use of raw red mud as adsorbent without activation for wastewater treatment is not appropriate due to the high dosage and alkalinity.

Enshi locates in the southwest of Hubei province, China, and it is rich in hematite resources. The acid pickling milling was the main hematite mineral processing, and produced great amounts of acidic wastewater with high phosphate concentration. It must be treated and reused on account of groundwater resources shortage in this area. In our study, red mud was chosen as absorbent due to the adsorption property and tremendous specific surface area, and activated with different methods, and then firstly used for phosphate removing of acid pickling milling wastewater from a high-phosphate hematite mineral in Enshi, aiming to realize the comprehensive reuse of the acidic phosphate wastewater on-line with a low pH value and ultra-high phosphate removal.

2. Materials and methods

2.1. Materials

The acid wastewater tested in the experiment was taken from Enshi Chaoyang Iron Ore, Hubei province, China. The pH value ranged from 2.50 to 2.53, the phosphate concentration was 98.85 mg/L, and the turbidity was 600–800 NTU.

The raw red mud (RM-raw) was obtained from Shandong Aluminium Industry Corporation, Shandong province, China. The particle size was averaged 20 mesh. The preparations of the activated RM, named as RM-α, β, γ, δ, and ε, were mainly described as follows: the raw RM was firstly washed and air dried, then pretreated at 800°C for 2 h or unpretreated and transferred into the glass reactor with HCl at 40–60 g (raw RM)/L(HCl). The mixture was adjusted to pH = 8 or unadjusted along with stirring for 1 h with or without water bathing. Then, the suspended liquids were fully precipitated, and the prepared products were washed, dried, and sieved through a 60 mesh sieve, sealed and preserved. Much preliminary work has been done to illustrate that the RM sieved through 60 mesh sieve was appropriate for the experiment. The phosphate was not fully adsorbed when the particle size was smaller than that while the precipitation after the treatment was not sufficient when the size was a little bigger. The conditions of different activated RM are listed in Table 1.

2.2. Testing

Acid pickling milling wastewater from high-phosphate hematite mineral processing (600 mL, phosphate concentration 98.85 mg/L, pH 2.53) was added into six stirrers, respectively, then RM-raw, α, β, γ, δ and ε were put into the stirrers, respectively, and stirred with the velocity gradient 63.6. The phosphate concentration and pH value of supernate were measured after 4 h settling.

2.3. Analysis methods

The phosphate was measured using the ammonium

Table 1
Conditions of different activated RM

RM	Pretreating	HCl concentration (mol/L)	Additions	Water-bathing
RM-α	Without	2–3	NH_4HCO_3 powder	Without
RM-β	Without	0.5–1	Without	60–100°C 1 h
RM-γ	Without	0.5–1	NH_4HCO_3 powder	60–100°C 1 h
RM-δ	Without	0.5–1	RM powder	60–100°C 1 h
RM-ε	800°C 2 h	0.5–1	Without	60–100°C 1 h

molybdate spectrophotometric method with an ultraviolet spectrophotometer (DR4000/U, Hach Company, USA). A pH meter (PHS-3C, Shanghai LeiCi Instrument Plant, China) was used to measure the pH of the solutions. The specific surface area of RM was determined by the BET nitrogen gas sorption method using a fully automatic specific surface area analyzer (Gemini 2360, Micromeritics, USA). The SEM micrograph of RM was determined using an analytical transmission electron (TEM) (H-600 STEM/EDX PV9100, Hitachi, Japan).

All the chemicals and reagents used in this study were of analytical grade. All glassware and sample bottles were soaked in diluted HCl solution for 12 h, washed and then rinsed three times with deionized water. Deionized water was used for the preparation of solutions. All experiments were conducted in duplicate and the average values were used for data analysis. Each water quality was tested according to Water and Wastewater Monitoring and Analysis Methods (4th ed., in Chinese).

3. Results and discussion

3.1. The characteristics of different activated RM

The components of raw RM and the five modified RM are listed in Table 2. RM–raw consists of a heterogeneous mixture of several minerals, and some metal oxide or metal hydroxide plays an important role in the process of phosphate removal, while some inorganic minerals and metal ions (such as Na^+, K^+, etc.) and other impurities in the components have a bad effect on phosphate removal [7]. In addition, the existence of superficial hydroxyl often brings electronegativity, which could bring about the electrostatic repulsion with phosphate radical ions in solution and consequently results in lower RM adsorption capacity.

The compositions of five modified RM are different from the raw samples. The main compositions were turned to ferric hydroxide and aluminum hydroxide, and some soluble salts were removed, which resulted in different phosphate removal. Besides, the alkalinity of RM reduced greatly after activation treatment. The pH of raw RM was 10.21 (solid/liquid ratio 1:20, dissolved in distilled water), and RM-α, β, γ, δ, and ε were 6.53, 4.46, 6.86, 6.25, and 4.39, respectively.

Scanning electron microscope (SEM) pictures are presented in Fig. 1. The raw RM was relatively smooth and flat, and the activated samples show many new cavities and coarsened exterior, probably due to the removing of some acid-soluble salts. After heat treatment, RM-ε exhibited a morphology similar to the others, but got much more porosity.

The BET surface area of various RM is also given in Table 2. It indicates that the activation treatment increases the surface area of the RM, the BET surface area of the raw RM was 14.79 $m^2 \cdot g^{-1}$ and RM-ε showed the largest one 23.46 $m^2 \cdot g^{-1}$. The membrane clung to the surface of the raw RM, which impeded phosphate removal, was

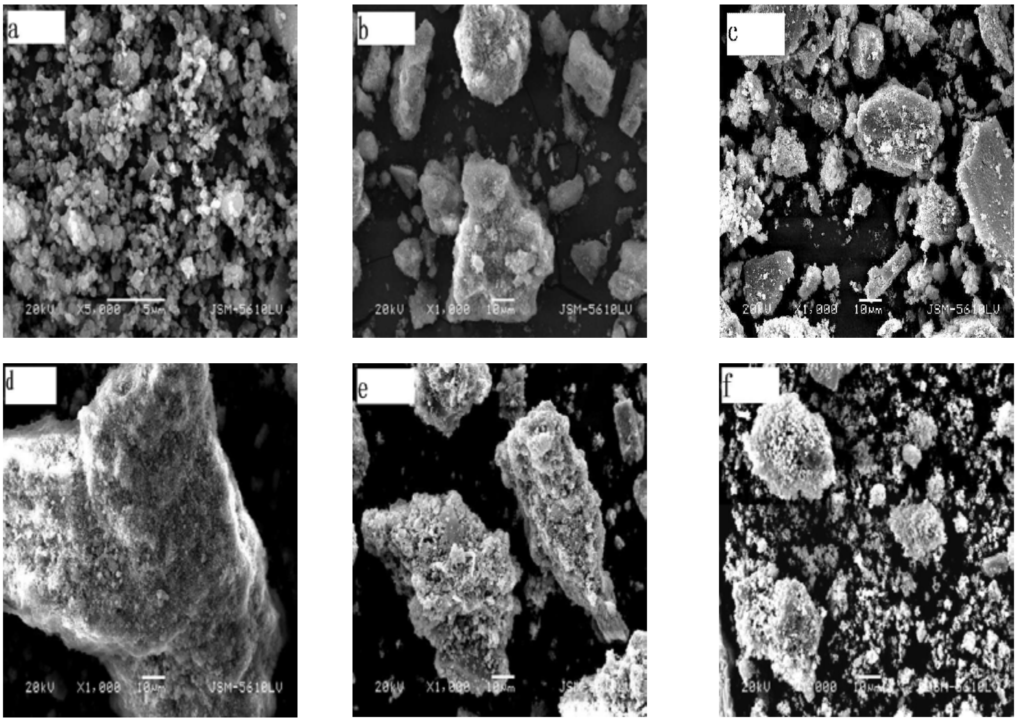

Fig. 1. SEM micrographs of the raw and activated RM: (a) RM-raw, (b) RM-α, (c) RM-β, (d) RM-γ, (e) RM-δ, (f) RM-ε.

Table 2
Composition and properties of different RM

RM	Components (wt.%)								pH	SBET ($m^2 \cdot g^{-1}$)
	Na_2O	Al_2O_3	SiO_2	CaO	TiO_2	Fe_2O_3	MgO	ZnO		
Raw	15.05	26.71	23.57	2.38	1.78	29.46	0.19	0.61	10.21	14.79
α	14.01	27.51	23.85	2.03	2.11	31.52	0.22	0.38	6.53	19.12
β	13.63	29.69	19.26	1.64	2.61	30.68	0.28	0.39	4.46	20.62
γ	13.61	29.72	18.19	1.65	2.66	31.08	0.31	0.42	6.86	20.55
δ	14.35	28.12	20.36	1.97	2.23	30.56	0.23	0.51	6.25	20.67
ε	13.22	28.39	24.33	2.12	2.65	30.43	0.18	0.43	4.39	23.46

washed away in acid activated process, and interior pores were dredged at the same time.

3.2. The phosphate removing performance of different RM

As is known, the influent pH was from 2.50 to 2.53, and the phosphate concentration 98.85 mg/L. The experiment conditions were optimized through batch tests ahead. The optimum conditions were as follows: reaction time was 1 h, and 45 min for RM-raw and five different activated RM, respectively, velocity gradient (G value) 63.6 for all.

3.2.1. Effect of the dosage of RM on the phosphate removal

The effect of the dosage of RM on the removal of phosphate is shown in Fig. 2. From Fig. 2, the optimum dosage of raw RM was 23 g/L, corresponding phosphate removal was 92.47%. When the dosage of raw RM was less than 23 g/L, the phosphate uptake increased with the increase of the dosage of the raw RM. While abnormal phenomenon appeared when the dosage was less than 3.5 g/L, that was because phosphate was adopted by RM to form colloid which could not be deposited adequately, and the liquid–solid was not separated adequately, resulting in a lower phosphate removal. The phosphate removal gradually declined with the increase of the dosage when it was higher than 23 g/L, which may be due to the impact of the increased alkalinity. For activated RM, colloidal phenomena did not appear and liquid–solid was separated quickly. The optimum dosage of activated RM (RM-α, β, γ, δ, and ε) was 22.5 g/L, 22 g/L, 23.5 g/L, 28 g/L and 20 g/L, respectively, corresponding phosphate removal was 99.38%, 99.21%, 99.42%, 98.10% and 99.61%, respectively.

3.2.2. Effect of reaction time on the phosphate removal

Fig. 3 shows the phosphate removal with reaction time 5 min, 15 min, 30 min, 45 min, 60 min and 75 min. As seen from Fig. 3, the raw and activated RM have the similar phosphate removing trends, and the phosphate removals of all the activated RM were higher than that of the raw RM. The phosphate removal achieved the peak value at 60 min for raw RM, and at 45 min for the activated RM. Activated RM could reach higher phosphate removal in a shorter reaction time.

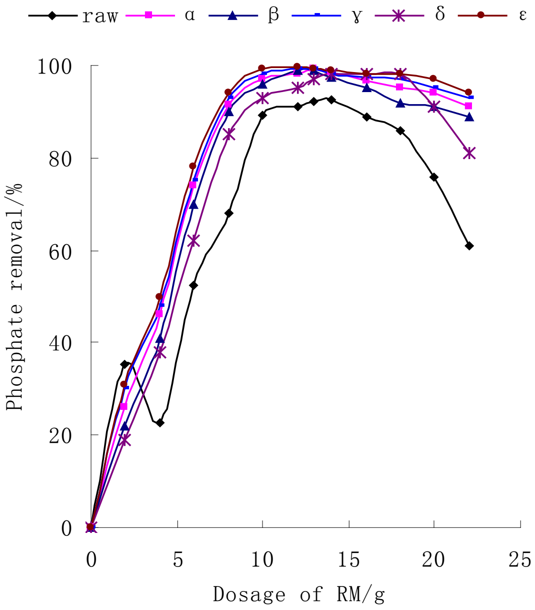

Fig. 2. Effect of dosage on the phosphate removal by raw and activated RM.

3.3. Effect of dosage of RM on the effluent pH

The effect of the dosage of RM on the effluent pH is shown in Fig. 4. All the effluent pHs were increased by varying degrees with the increase of the dosage of RM, while the influence of activated RM was much less. As seen from Fig. 4, when the dosage of RM (raw RM, RM-α, β, γ, δ, and ε) was 23 g/L, the effluent pH was 8.02, 3.99, 3.11, 3.87, 3.78 and 3.06, respectively. The alkalinity of RM reduced obviously after activation, which was more conducive to deal with acidic wastewater. Maintaining the lower pH value is useful for the reuse of acidic wastewater.

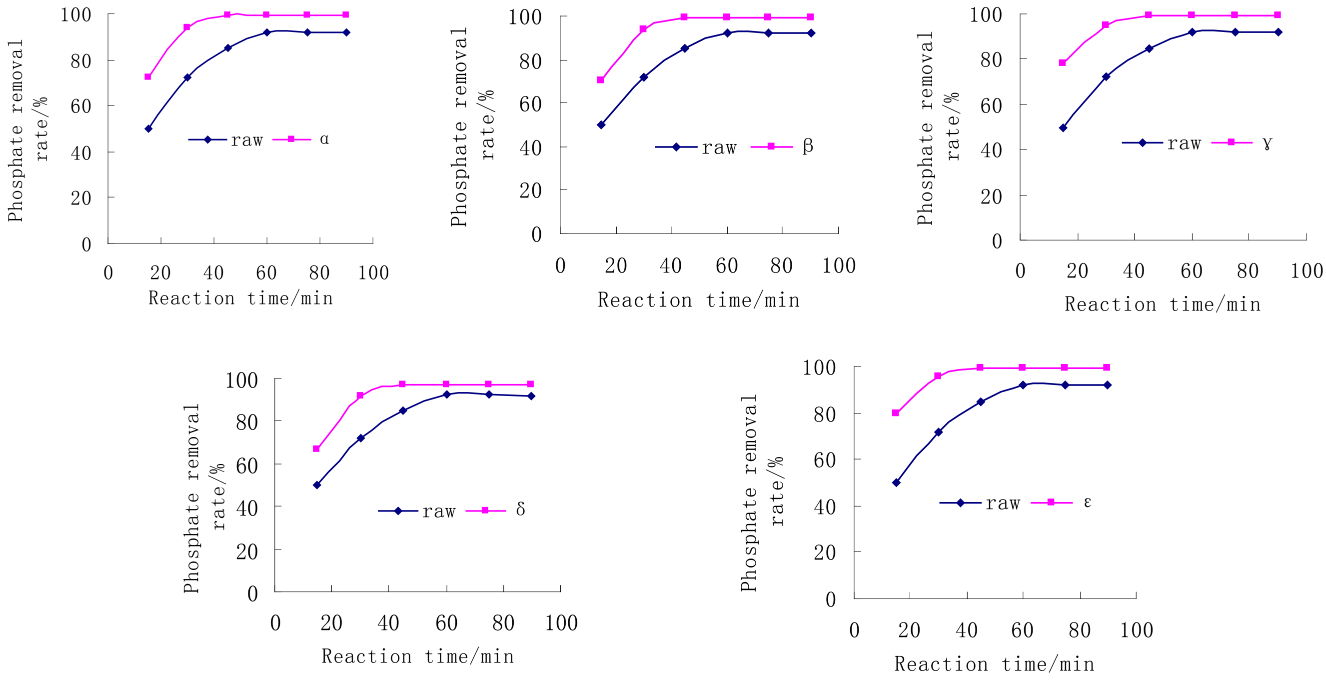

Fig. 3. Effect of reaction time on the phosphate removal with raw and activated RM.

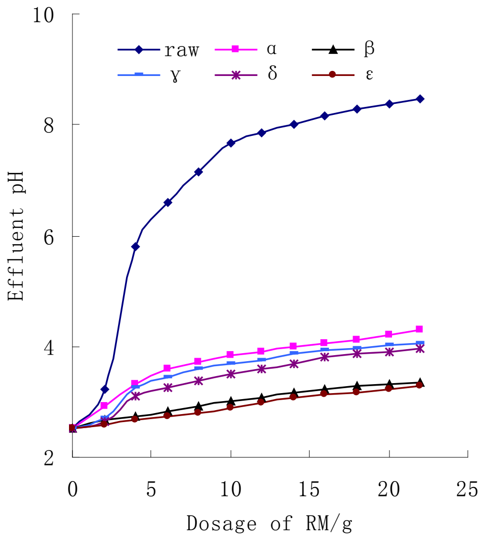

Fig. 4. Effect of the dosage of RM on the effluent pH.

4. Conclusions

Through the experiment study, some conclusions are drawn as follows:

(1) Different red mud activation methods brought about different characteristics: the surface area increased, the adsorption capacity improved, and the alkalinity reduced obviously. The optimum dosage of RM-raw, α, β, γ, δ, and ε was 23 g/L, 22.5 g/L, 22 g/L, 23.5 g/L, 28 g/L and 20 g/L, respectively, corresponding phosphate removal was 92.47%, 99.39%, 99.32%, 99.42%, 98.56% and 99.66%, respectively, and the effluent pH value was 8.02, 3.93, 3.06, 3.82, 3.72, and 2.98, respectively.

(2) The activated red mud ε, or RM-ε, was the most suitable absorbent for the acid pickling milling wastewater treatment and reuse on-line because of its highest phosphate removal and lowest dosage and pH in the effluent. It has great application prospect because of its simple preparation method, low-cost, high rate of phosphate removal and lower effluent pH.

Acknowledgements

This work was supported by the National Key Technology Program during the Eleventh Five-Year Planning, China (2007BAB15B00) and The National Natural Science Foundation of China (50878173).

References

[1] B. Grzmil and J. Wronkowski, Removal of phosphates and fluorides from industrial wastewater, Desalination, 189 (2006) 261–268.

[2] J.Y. Park, H.B. Yun, W.H. Choi and W.H. Kang, Cement paste column for simultaneous removal of fluoride, phosphate, and nitrate in acidic wastewater, Chemosphere, 70 (2008) 1429–1437.

[3] L.L. Blackall, G. Crocetti, A.M. Saunders and P.L. Bond, A review and update of the microbiology of enhanced biological phosphorus removal in wastewater treatment plants, Antonie Van Leeuwenhoek Int. J. Gen. Mol. Microbiol., 81 (2002) 681–691.

[4] E. Yildiz, Phosphate removal from water by fly ash using crossflow microfiltration, Sep. Purif. Technol., 35 (2004) 241–252.

[5] V.K. Gupta, R. Jain and S. Varshney, Electrochemical removal of the hazardous dye Reactofix Red 3 BFN from industrial effluents, J. Colloid Interface Sci., 312 (2007) 292–296.

[6] R. Ganigué, H. López, M.D. Balaguer and J. Colprim, Partial ammonium oxidation to nitrite of high ammonium content urban landfill leachates, Water Res., 41 (2007) 3317–3326.

[7] B. Moreno, M.A. Gomez, J.G. Lopez and E. Hontoria, Inoculation of a submerged filter for biological denitrification of nitrate polluted groundwater: a comparative study. J. Hazard. Materi., 117 (2005) 141–147.

[8] V.K. Gupta, A. Mittal, R. Jain, M. Mathur and S. Sikarwar, Photochemical degradation of hazardous dye — Safaranin-T using TiO_2 catalyst, J. Colloid Interface Sci., 309 (2007) 460–465.

[9] A. Aleboyeh, Y. Moussa and H. Aleboyeh, Kinetics of oxidative decolourisation of Acid Orange 7 in water by ultraviolet radiation in the presence of hydrogen peroxide. Separ. Purif. Technol., 43 (2005) 125–133.

[10] G. Morse, K. Brett, S.W. Guy and J.A. Lester, Review: phosphorus removal and recovery technologies, Sci. Total Environ., 212 (1998) 69–81.

[11] T. Clark, T. Stephenson and P.A. Pearce, Phosphorus removal by chemical precipitation in a biological aerated filter, Water Res., 31 (1997) 2557–2563.

[12] I. Ali and V.K. Gupta, Advances in water treatment by adsorption technology, Nature Protocols, 1 (2007) 2661–2667.

[13] V.K. Gupta, P.J.M. Carrott, M.M.L. Ribeiro Carrott and Suhas, Low cost adsorbents: Growing approach to wastewater treatment – A review, Crit. Rev. Environ. Sci. Technol., 39 (2009) 1–60.

[14] L. Chang-jun, L. Yan-zhong and L. Zhao-kun, Adsorption removal of phosphate from aqueous solution by active red mud, J. Environ. Sci., 19 (2007) 1166–1170.

[15] E. Galarneau and R. Gehr, Phosphorus removal from wastewaters: experimental and theoretical support for alternative mechanisms, Water Res., 31 (1997) 328–338.

[16] L. Yan-zhong, L. Chang-jun and L. Zhao-kun, Phosphate removal from aqueous solutions using raw and activated red mud and fly ash, J. Hazard. Mater., 137 (2006) 374–383.

[17] E. Lopez, B. Soto, M. Arias, A. Nunez, D. Rubinos and T. Barral, Adsorbent properties of RM and its use for wastewater treatment, Water Res., 32 (1998) 1314–1322.

[18] Y. Zhao, W. Jun, L. Zhao-kun, P. Xianjia, L. Zhen and S. Li, Removal of phosphate from aqueous solution by red mud using a factorial design, J. Hazard. Mater., 165 (2009) 1193–1199.

[19] N.M. Agyei, C.A. Strydom and J.H. Potgieter, An investigation of phosphate ion adsorption from aqueous solution by fly ash and slag, Cem. Concr. Res., 30 (2000) 823–826.

[20] N.M. Agyei, C.A. Strydom and J.H. Potgieter, The removal of phosphate ions from aqueous solution by fly ash, slag, ordinary Portland cement and related blends, Cem. Concr. Res., 32 (2002) 1889–1897.

[21] V.K. Gupta, A. Mittal, V. Gajbe and J. Mittal, Adsorption of basic fuchsine using waste materials-bottom ash and deoiled soya as adsorbents. J. Colloid Interface Sci., 319 (2008) 30–39.

[22] V.K. Gupta, I. Ali and V.K. Saini, Adsorption studies on the removal of Vertigo Blue 49 and Orange DNA13 from aqueous solutions using carbon slurry developed from a waste material, J. Colloid Interface Sci., 315 (2007) 87–93.

[23] A.O. Vinka, F. Megan and A.S. James, Simultaneous sorption of benzene and heavy metals onto two organoclays. J. Colloid Interface Sci., 309 (2007) 485–492.

[24] V.K. Gupta, A. Mittal, L. Krishnan and V. Gajbe. Adsorption kinetics and column operations for the removal and recovery of malachite green from wastewater using bottom ash. Separ. Purf. Technol., 40 (2004) 87–96.

[25] V.K. Gupta, C.K. Jain, I. Ali, S. Chandra and S. Agarwal, Removal of lindane and malathion from wastewater using bagasse fly ash — a sugar industry waste, Water Res., 36 (2002) 2483–2490.

[26] V.K. Gupta and I. Ali, Removal of endosulfan and methoxychlor from water on carbon slurry, Environ. Sci. Technol., 42 (2008) 766–770.

[27] V.K. Gupta and Suhas, Application of low cost adsorbents for dye removal — A review, J. Environ. Manage., 90 (2009) 2313–2342.

[28] V.K. Gupta, A. Mittal, L. Kurup and J. Mittal, Process development for removal and recovery of metanil yellow by adsorption on waste materials — bottom ash and de-oiled soya, J. Hazard. Mater., 151 (2008) 834–845.

[29] V.K. Gupta, I. Ali and V.K. Saini, Removal of fluoride from water by adsorption on carbon slurry: a waste material of fertilizer industry, Water Res., 41 (2007) 3317–3326.

[30] V.K. Gupta, A. Mittal, L. Krishnan and V. Gajbe, Removal and recovery of malachite green from wastewater using an agricultural waste material, de-oiled soya, Separ. Purif. Technol., 43 (2005) 125–133.

[31] V.K. Gupta, A. Mittal and L. Krishnan, Use of waste materials, bottom ash and de-oiled soya, as potential adsorbents for the removal of amaranth from aqueous solutions, J. Hazard. Mater., 117 (2005) 171–178.

[32] V.K. Gupta and I. Ali, Removal of DDD and DDE from wastewater using bagasse fly ash, a sugar industry waste, Water Res., 35 (2001) 33–40.

[33] V.K. Gupta, D. Mohan, S. Sharma and K.T. Park, Removal of chromium (VI) from electroplating industry wastewater using bagasse fly ash — a sugar industry waste material, The Environmentalist, 19 (1999) 129–136.

[34] Y. Çengelolu, E. Kır and M. Ersöz, Removal of fluoride from aqueous solution by using RM, Separ. Purif. Technol., 28 (2002) 81–86.

[35] M. Erdem, H.S. Altundogan and F. Tumen, Removal of hexavalent chromium by using heat-activated bauxite, Miner. Eng., 17 (2004) 1045–1052.

[36] S. Wang, Y. Boyjoo, A. Choueib and Z.H. Zhu, Removal of dyes from aqueous solution using fly ash and RM, Water Res., 39 (2005) 129–138.

[37] V.K. Gupta, I. Ali and V.K. Saini, Removal of chlorophenols from wastewater using red mud: an aluminum industry waste, Environ. Sci. Technol., 38 (2004) 4012–4018.

[38] H. Genc, J.C. Tjell, D. McConchie and O. Schuiling, Adsorption of arsenate from water using neutralized RM, J. Colloid Interface Sci., 264 (2003) 327–334.