Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2013.827296

52 (2014) 791–796
January

Taylor & Francis
Taylor & Francis Group

Effective phosphate uptake and inhibition on *M. aeruginosa* by Friedel-based adsorbent

Jun Zhao[a], Yingchun Dai[b], Yongsheng Lu[a], Xiuxiu Ruan[a], Guangren Qian[a], Yunfeng Xu[a,*]

[a]*School of Environmental and Chemical Engineering, Shanghai University, Shanghai 200444, China*
Tel. +86 21 66137745; Fax: +86 21 66137758; email: yfxu@shu.edu.cn
[b]*Shanghai Institute for Design & Research in Environmental Engineering Co. Ltd., Shanghai 200232, China*

Received 20 May 2013; Accepted 24 May 2013

ABSTRACT

Friedel-based adsorbent was successfully prepared by the simple hydration reaction between cement and Cl-bearing salt solution. X-ray diffraction and FTIR spectroscopy were used to characterize the synthesized products and the adsorption behavior of products was examined by adsorption isotherm and kinetics. Furthermore, the inhibitive effect of Friedel-based adsorbents on *Microcystis aeruginosa* (*M. aeruginosa*) was also investigated. The results indicated that the adsorption isotherm could be fit well with Langmuir equations and the adsorption process was followed first-order kinetics. Both the experimental and modeled data indicated that Friedel-based adsorbent had a strong adsorption capacity of phosphate and an effective inhibition on *M. aeruginosa*. A maximum inhibition rate of 99.32% was achieved at the tenth day with an adsorbent dose of 4 g/L.

Keywords: Layered double hydroxides (LDHs); Friedel's salt; Phosphate removal; *M. aeruginosa* inhibition

1. Introduction

Phosphates are widely used in many industries, such as water treatment, corrosion inhibitors, fertilizers and pharmaceuticals, producing the effluents with high concentrations of phosphorus every day. Although phosphate is an essential nutrient for growth of microorganisms in aquatic environments, excess amount of phosphate discharge into surface waters can stimulate plant growth, resulting in eutrophication. In particular, it has been reported that an increase of phosphate in the water column would cause the growth of cyanobacteria blooms in eutrophic lakes [1–3]. Therefore, it is urgent to seek the technology for the effective removal of phosphate from wastewaters.

In the recent years, various methods have been developed to remove phosphate, including biological treatment, chemical precipitation and adsorption. Among these methods, the adsorption technique using various absorbents has been recognized as an effective and potential method. Considerable attentions have been paid on different types of low-cost materials for

---

*Corresponding author.

Presented at the Fifth Annual International Conference on "Challenges in Environmental Science & Engineering—CESE 2012" Melbourne, Australia, 9–13 September 2012

phosphate removal as adsorbents, such as oyster shell [4], modified palygorskites [5], dewatered alum sludge [6], metal-loaded orange waste [7] and modified wheat residue [8]. However, the adsorption capacity of phosphate or the adsorption time, seems not to be ideal. The adsorption amount of phosphate in most cases was less than 0.32 mmol/g. Therefore, it is highly desirable if a low-cost adsorbent can effectively inhibit the algal growth and adsorb phosphate with a high adsorption rate.

Layer double hydroxides (LDHs), with the general chemical formula $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}(A^{n-})_{x/n}{\cdot}mH_2O$, are a family of anionic clay minerals, being composed of cationic brucite layers and exchangeable interlayer anions [9]. Various LDHs have been explored as adsorbents to remove phosphate contaminants in recent years [10–18]. For example, MgAlCl–LDH [12,14] was reported to have a 100% removal of phosphate ($[P] < 2$ ppm) and 1.53 mmol/g adsorption capacity of phosphate. MgMn-3-300 [13], Mg(AlZr)–LDH(CO_3), and Mg(AlZr)–LDH(Cl) [16,18] were proved to be selective toward phosphate ions even in seawater and adsorbed *ca* 0.55 mmol/g of phosphate. These reports demonstrated that LDHs was a good adsorbent for the removal of phosphate. Whereas almost all these LDHs were prepared by coprecipitation method using pure chemicals and this may be a disadvantage for industrial application. Consequently, it is necessary to find a kind of LDHs prepared with cost-effective and easy method.

Friedel's salt ($Ca_4Al_2(OH)_{12}Cl_2(H_2O)_4$ or $3CaO{\cdot}Al_2O_3{\cdot}CaCl_2{\cdot}10H_2O$), also called chloride hydrocalumite, is a major and stable hydration product of cement/concrete subjected to sea water, and thus, it can be easily and cheaply made via the simple cement hydration reaction with Cl-bearing salt solution [19,20]. In our previous research, Friedel's salt was confirmed to have a strong fixation capacity of heavy metals from electronic sludge wastes [21,22]. In particular, it can adsorb almost 1.45 mmol/g of CrO_4^{2-} [23]. Therefore, it was considered to be a low cost and easily available adsorbent material for phosphate, which has the similar structure to CrO_4^{2-}. In this research, Friedel-based adsorbent was prepared by the simple hydration reaction between cement and Cl-bearing salt solution. The structure of adsorbent was analyzed in detail by means of powder X-ray diffraction and FTIR. Then, the adsorption behave of phosphate was characterized with the adsorption kinetics and isotherm. In addition, under the phosphate-deficient condition, the growth of algae was inhibited. It would be expected that Friedel-based adsorbent can effectively inhibit the growth of the algae, the inhibitive effect of the Friedel-based adsorbent on the growth of *Microcystis aeruginosa* was also considered.

2. Materials and methods

2.1. Preparation and characterization of the adsorbent

Friedel-based adsorbent was prepared via the simple hydration reaction between cement and Cl-bearing salt solution. In brief, fondo aluminate cement CA50, NaCl and $Ca(OH)_2$ were mixed with water at a proper proportion. The mixture was aged at cement incubator for 7 days and then dried at 100℃ for 24 h. As a contrast, pure Friedel's salt was synthesized by precipitation method as reported elsewhere [24].

The synthesized Friedel-based adsorbent and pure Friedel's salt were identified with the powder X-ray diffraction pattern recorded on a Dmax/RB diffractometer (Rigaku Co.) with Cu Kα radiation ($\lambda = 0.15418$ nm) at 34 kV and 20 mA, and the FTIR spectrum collected on a Perkin–Elmer 380 FTIR in the range of 4,000–400 cm^{-1} with resolution of 4 cm^{-1} using the KBr pellet technique.

2.2. Adsorption of phosphate

In all adsorption tests, 2.00 g/L of Friedel-based adsorbent was used. To investigate the adsorption equilibrium, a series of phosphate solutions were prepared by dissolving KH_2PO_4 (AR) with the initial phosphate concentration from 4.00 to 9.00 mM and adjusting the initial pH 7.0 with dilute HCl or NaOH solution. In brief, 50 mL of phosphate solution and 0.100 g of Friedel-based adsorbent were added into a 100 mL sealed plastic vial, and then, it was shaken at a speed of 150 rpm in a thermostatic water bath at 25 ± 1℃. After 72 h adsorption, the remaining phosphate concentration was determined.

To examine the adsorption kinetics of phosphate over Friedel-based adsorbent, the initial phosphate concentration of 0.032 and 0.32 mM with the initial pH of 7.0 was selected and the adsorption was conducted under the similar conditions. At the selected time points, the mixture was filtered through a 0.45 μm filter for the phosphate concentration determination. All the experiments were carried out in triplicate. with the reproducibility within ±5%.

The phosphate concentration was determined spectrophotometrically at 700 nm, following the molybdenum blue method [25] in a Unic UV-spectrophotometer (4802 UV/VIS).

2.3. Analytical procedure of algal inhibition

M. aeruginosa was obtained from Wuhan Institute of Hydrology, Chinese Academy of Science. The composition of the BG-11 medium was used in algal growth tests [26]. The algal seeds were cultured in the incubator with illumination (Model GZX-150BS-III) for 10 days under a photon flux density of 2000 lux provided by white lamps with a light/ dark cycle of 14: 10 h at 30 ± 1℃. Flasks were shaken for three times every day by hand during the maintenance and experimental stages.

M. aeruginosa cell were counted on a compound microscope (Nikon 400) using a hemocytometer after preservation in Lugol's iodine. The initial biomass in this experiment indicated the cell numbers immediately counted after treatment (i.e. day 0). Then, all the samples were continuously cultured, and the final biomass showed the cell numbers at the end of the tenth day.

3. Results and discussion

3.1. Structural features of the adsorbent

X-ray powder diffraction patterns of the prepared adsorbents are shown in Fig. 1(A). Sharp and strong diffraction peaks of Friedel's salt appeared at 7.94, 2.87, 3.98, and 3.83 Å on the simple hydration product, similar to the pure Friedel's salt. Some weak reflections of the unreacted $Ca(OH)_2$ and NaCl were also observed in the hydration product. Therefore, the simply prepared adsorbent was a mixture, with Friedel's salts as the main phase and we call it Friedel-based adsorbent. In addition, both the pure and impure materials were confirmed by the FTIR spectrum (Fig. 1(B)). Though, compared with the pure Friedel's salt, there were some vibrations excursion, the pattern of Friedel-based adsorbent showed all the characteristic vibrations of the Friedel's salt, such as 3,630 and 3,500 cm^{-1} (ν_{OH} in structural water), 1,650 cm^{-1} (δ_{H_2O} in interlayer water), and 793 and 536 cm^{-1} (M–O vibrations and M–O–H bending in lattice) [24,27]. Furthermore, the band at 1,420 and 1,470 cm^{-1} due to the stretching vibration of CO_3^{2-} indicated the adsorption of CO_2 from air during the synthesis [28]. As a conclusion, the Friedel-based adsorbent can be successfully prepared by simple cement hydration reaction with Cl-bearing salt solution.

3.2. Removal of phosphate

Synthesized Friedel-based adsorbent exhibited a strong removal capacity on phosphate. The adsorption isotherm and kinetics were conducted to determine the maximum adsorption capacities and rate, respectively.

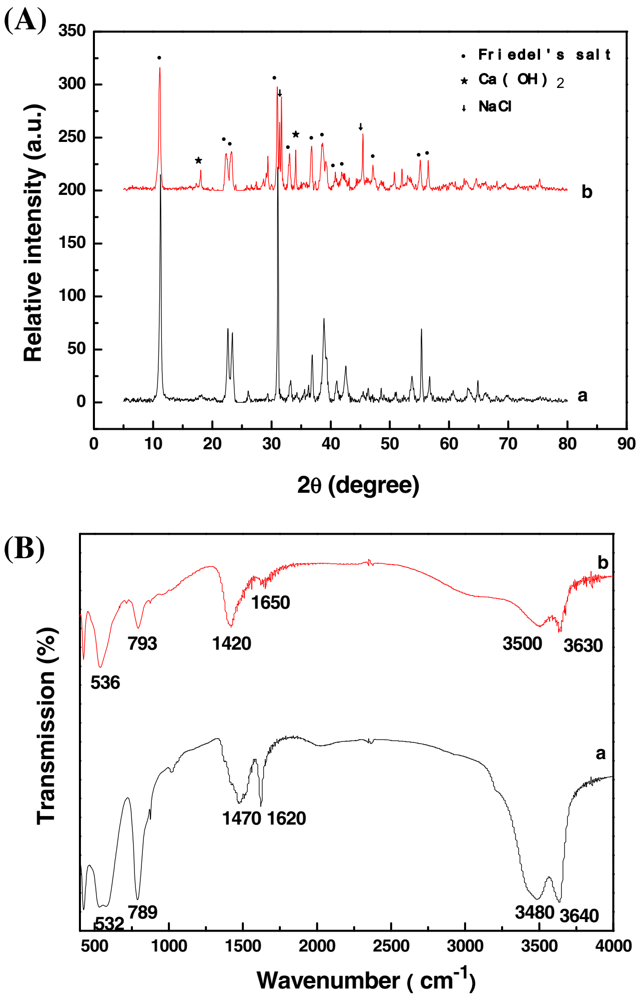

Fig. 1. The XRD pattern (A) and FTIR spectrum (B) of the synthesized adsorbent, where a represent the pure Friedel's salt and the b represent the Friedel-based adsorbent.

3.2.1. Adsorption isotherms

Fig. 2 shows the adsorption isotherm of Friedel-based adsorbent. The equilibrium adsorption amount of phosphate over the mineral (mmol P/g) was increased quickly at the equilibrium phosphate concentration below 0.003 mM. Then, the increase in the adsorption capacity was insignificant, with a further increase of the equilibrium phosphate concentration.

The adsorption data at the equilibrium were analyzed with Langmuir model, and the fitting parameters were listed in Table 1. The higher adsorption capacity was reflected by the Langmuir parameter Q_m (the maximum adsorption amount), which was ca. 3.22 mmol/g. Such an adsorption capacity of Friedel-based adsorbent is also higher than that of most LDH materials and other low-cost absorbents reported elsewhere, as observed in Table 2.

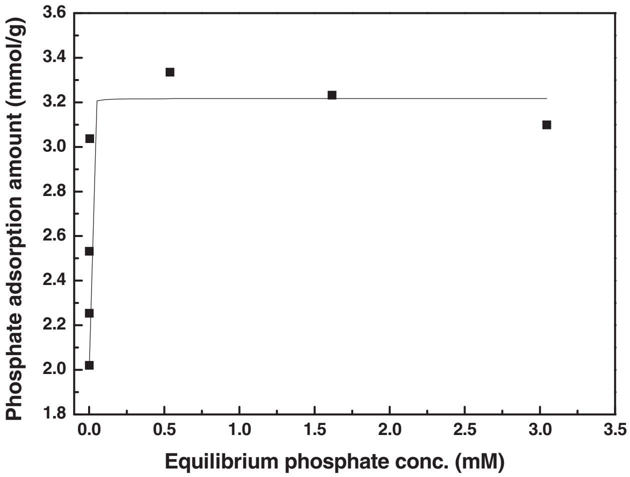

Fig. 2. Phosphate adsorption isotherms over Friedel-based adsorbent.

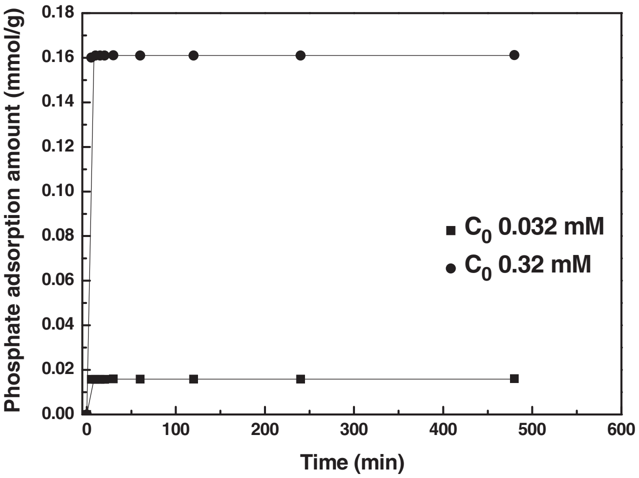

Fig. 3. Phosphate adsorption kinetics over Friedel-based adsorbent.

Table 1
The parameters of adsorption isothermal of phosphate on the Friedel-based adsorbent

Langmuir $Q_e = Q_m C_e/(b + C_e)$			
Fitting parameters	Q_m/(mmol/g)	b	R^2
Value	3.22	5829.57	0.9785

Table 2
The adsorption capacities of phosphate onto different adsorbents

Adsorbents	Capacity (mmol/g)	Reference
$Ca_3Fe–CO_3–LDH$	0.93	[10]
$Mg_2AlCl–LDH$	1.53	[14]
$Mg_2Al–CLDH$	1.43	[15]
$Mg_3(AlZr)–Cl–LDH$	1.84	[16]
$Mg_3(AlZr)–CO_3–LDH$	2.42	[16]
Modified palygorskites	0.27	[5]
Metal-loaded orange waste	0.45	[7]
$HyFeAl–Mt_{0.5}$	0.66	[29]
Furnace slag	1.06	[30]

3.2.2. Adsorption kinetics

As removal efficiency at low phosphate concentration is very important in the processing of the actual wastewater, with markedly low concentration of phosphates. The adsorption kinetics was further investigated at the initial concentration of 0.032 and 0.32 mM. Fig. 3 shows the time-dependent adsorption profile of phosphate at the initial pH = 7.0. Obviously, phosphate adsorption on Friedel-based adsorbent took place within the first 10 min mainly and then reached the saturate plateau. Increasing the adsorption time to more than 10 min seemed to bring no further benefit.

The kinetic data were well fitted to the first-order Lageren equation and the parameters are presented in Table 3. The very similar rate constants (k) at the initial $[P] = 0.032$ and 0.32 mM (1.04–1.13 L/min) indicated the similar adsorption behavior. At the same time, the k values also actually revealed that phosphate adsorption was a very fast process because the calculated adsorption time for the half equilibrium amount was only 0.6–0.7 min (i.e. $t_{1/2} = 0.693/k$ min). In addition, a higher percentage (>97% for $[P] = 0.032$ mM and >99% for $[P] = 0.32$ mM) of phosphate was removed and the equilibrium concentrations were all below 0.0007 mM. Therefore, the Friedel-based adsorbent was a potentially effective adsorbent for phosphate removal, with a large phosphate adsorption capacity and high adsorption rate.

3.3. Algal inhibition

To investigate the effect of inhibitor on the algal growth, one sample was kept as the control, the others

Table 3
The parameters of adsorption kinetic curve of phosphate on the Friedel-based adsorbent

Lageren equation $Q_t = Q_e(1 - \exp(-kt))$			
Conc. (mM)	k/(1/min)	Q_e/(mg/g)	R^2
0.032	1.13	0.016	0.9999
0.32	1.04	0.16	1.0000

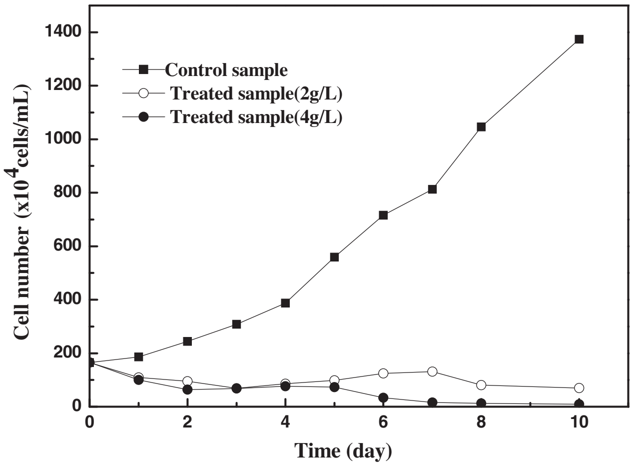

Fig. 4. The changes of cell number with time under the different dosages of inhibitor.

were treated by putting 2 or 4 g/L dosages of inhibitor into the algal solution, respectively. The initial cell numbers was approximately 165.87×10^4 cells/mL. After adsorption, all the samples (control plus treated) were continuously cultured for ten days. Samples from all cultures were collected every day in order to evaluate the inhibition of the growth.

The growth curves of the samples with and without adsorbent are presented in Fig. 4. When the inhibitor was added, the biomass would be changed with the time. The cell numbers of the control sample were gradually rising, the trends of the others were similar, the cell numbers were reduced. The percentage of inhibition increases with increasing amount of adsorbent from 2 to 4 g/L. The maximum inhibition rate of 99.32% was achieved at the tenth day with an adsorbent dose of 4 g/L. This implies that the more the dosages of adsorbent, the higher inhibiting efficiency was obtained. However, it was observed that the effect of adsorbent dosages on inhibiting *M. aeruginosa* is not so significant by comparing two samples. This might be explained that *M. aeruginosa* would be died with the duration time at phosphorus-deficient condition, at the same time, the adsorption of lower doses was also quick and exhausive, so excessive dosage has insignificant influence on the inhibitive effect of *M. aeruginosa*.

4. Conclusions

The present results demonstrated that Friedel-based adsorbent can be used as an effective adsorbent for the removal of phosphate. Some conclusions could be drawn from as follows:

1. The adsorbent can be successfully prepared by the simple hydration reaction between cement and Cl-bearing salt solution, with Friedel's salts as the main phase.
2. The adsorption isotherm could be fitted well with Langmuir equations and the maximum adsorption capacity of 3.22 mmol/g was observed. In addition, a higher percentage (>97%) of phosphate was removed at initial [*P*] = 0.032 and 0.32 mM with a high adsorption rate.
3. Friedel-based adsorbent had an effective inhibition on *M. aeruginosa*. A maximum inhibition rate of 99.32% was achieved at the tenth day with an adsorbent dose of 4 g/L.

Acknowledgements

This project is financially supported by the project of "Method study of developing nutrient criteria in lakes of different areas in China" (No. 2009ZX07106-001) and National Nature Science Foundation of China (Nos. 20477024 and 20677037).

References

[1] L.Q. Xie, P. Xie, Long-term (1956–1999) dynamics of phosphorus in a shallow, subtropical Chinese lake with the possible effects of cyanobacterial blooms, Water Res. 36 (2002) 343–349.

[2] M. Nausch, G. Nausch, H.U. Lass, V. Mohrholz, K. Nagel, H. Siegel, N. Wasmund, Phosphorus input by upwelling in the eastern Gotland Basin (Baltic Sea) in summer and its effects on filamentous cyanobacteria, Estuarine Coastal Shelf Sci. 83 (2009) 434–442.

[3] M.J. Lilover, A. Stips, The variability of parameters controlling the cyanobacteria bloom biomass in the Baltic Sea, J. Mar. Syst. 74 (2008) S108–S115.

[4] C. Namasivayam, A. Sakoda, M. Suzuki, Technical Note. Removal of phosphate by adsorption onto oyster shell powder—kinetic studies, J. Chem. Technol. Biotechnol. 80 (2005) 356–358.

[5] H.P. Ye, F.Z. Chen, Y.Q. Sheng, G.Y. Sheng, J.M. Fu, Adsorption of phosphate from aqueous solution onto modified palygorskites, Sep. Purif. Technol. 50 (2006) 283–290.

[6] Y. Yang, Y.Q. Zhao, A.O. Babatunde, L. Wang, Y.X. Ren, Y. Han, Characteristics and mechanisms of phosphate adsorption on dewatered alum sludge, Sep. Purif. Technol. 51 (2006) 193–200.

[7] B.K. Biswas, K. Inoue, K.N. Ghimire, S. Ohta, H. Harada, K. Ohto, H. Kawakita, The adsorption of phosphate from an aquatic environment using metal-loaded orange waste, J. Colloid Interface Sci. 312 (2007) 214–223.

[8] X. Xu, B.Y. Gao, W.Y. Wang, Q.Y. Yue, Y. Wang, S.Q. Ni, Adsorption of phosphate from aqueous solutions onto modified wheat residue: Characteristics, kinetic and column studies, Colloids Surf. B 70 (2009) 46–52.

[9] P.S. Braterman, Z.P. Xu, F. Yarberry, Handbook of Layered Materials, Marcel Dekker, New York, NY, 2004, pp. 373–474.

[10] Y. Seida, Y. Nakano, Removal of phosphate by layered double hydroxides containing iron, Water Res. 36 (2002) 1306–1312.

[11] N.K. Lazaridis, Sorption removal of anions and cations in single batch systems by uncalcined and calcined Mg–Al–CO_3 hydrotalcite, Water Air Soil Pollut. 146 (2003) 127–139.

[12] R. Nomura, T. Mori, E. Kanezaki, T. Yabutani, Removal of phosphate in water to layered double hydroxide, Int. J. Mod. Phys. B 17 (2003) 1458–1463.

[13] R. Chitrakar, S. Tezuka, A. Sonoda, K. Sakane, K. Ooi, T. Hirotsu, Adsorption of phosphate from seawater on calcined MgMn-layered double hydroxides, J. Colloid Interface Sci. 290 (2005) 45–51.

[14] K. Kuzawa, Y.J. Jung, Y. Kiso, T. Yamada, M. Nagai, T.G. Lee, Phosphate removal and recovery with a synthetic hydrotalcite as an adsorbent, Chemosphere 62 (2006) 45–52.

[15] J. Das, B.S. Patra, N. Baliarsingh, K.M. Parida, Adsorption of phosphate by layered double hydroxides in aqueous solutions, Appl. Clay Sci. 32 (2006) 252–260.

[16] R. Chitrakar, S. Tezuka, A. Sonoda, K. Sakane, K. Ooi, T. Hirotsu, Synthesis and phosphate uptake behavior of Zr^{4+} incorporated MgAl-layered double hydroxides, J. Colloid Interface Sci. 313 (2007) 53–63.

[17] X. Cheng, X.R. Huang, X.Z. Wang, B.Q. Zhao, A.Y. Chen, D. Z. Sun, Phosphate adsorption from sewage sludge filtrate using zinc–aluminum layered double hydroxides, J. Hazard. Mater. 169 (2009) 958–964.

[18] H. Miyauchi, T. Yamamoto, R. Chitrakar, Y. Makita, Z.M. Wang, J. Kawai, T. Hirotsu, Phosphate adsorption site on zirconium ion modified MgAl-layered double hydroxides, Top Catal. 52 (2009) 714–723.

[19] P.W. Brown, A. Doerr, Chemical changes in concrete due to the ingress of aggressive species, Cem. Concr. Res. 30 (2000) 411–418.

[20] F.P. Glasser, A. Kindness, S.A. Stronach, Stability and solubility relationships in AFm phases—Part 1. Chloride, sulfate and hydroxide, Cem. Concrete Res. 29 (1999) 861–866.

[21] G.R. Qian, Y.L. Cao, P. Chui, J. Tay, Utilization of MSWI fly ash for stabilization/solidification of industrial waste sludge, J. Hazard. Mater. 129 (2006) 274–281.

[22] G.R. Qian, J. Shi, Y.L. Cao, Y.F. Xu, P.C. Chui, Properties of MSW fly ash–calcium sulfoaluminate cement matrix and stabilization/solidification on heavy metals, J. Hazard. Mater. 152 (2008) 196–203.

[23] Y.C. Dai, G.R. Qian, Y.L. Cao, Y. Chi, Y.F. Xu, J.Z. Zhou, Q. Liu, Z.P. Xu, S.Z. Qiao, Effective removal and fixation of Cr (VI) from aqueous solution with Friedel's salt, J. Hazard. Mater. 170 (2009) 1086–1092.

[24] U.A. Birnin-Yauri, F.P. Glasser, Friedel's salt $Ca_2Al(OH)_6(Cl, OH)\cdot 2H_2O$: Its solid solution and their role in chloride binding, Cem. Concrete Res. 28 (1998) 1713–1723.

[25] APHA, AWWA, WEF, Standard Methods for the Examination of Water and Wastewater, 20th ed., American Public Health Association, Washington, DC, 1998.

[26] R. Olvera-Ramírez, M. Coria-Cedillo, R.O. Cañizares-Villanueva, F. Martínez-Jerónimo, T. Ponce-Noyola, E. Ríos-Leal, Growth evaluation and bioproducts characterization of Calothrix sp. Bioresour. Technol. 72 (2000) 121–124.

[27] J.V. Bothe, P.W. Brown, PhreeqC modeling of Friedel's salt equilibria at 23 ± 1°C, Cem. Concrete Res. 34 (2004) 1057–1063.

[28] M.Y.A. Mollah, M. Kesmez, D.L. Cocke, An X-ray diffraction (XRD) and Fourier transform infrared spectroscopic (FTIR) investigation of the long-term effect on the solidification/stabilization (S/S) of arsenic (V) in Portland cement, Sci. Total Environ. 325 (2004) 255–262.

[29] M.X. Zhu, K.Y. Ding, S.H. Xu, X. Jiang, Adsorption of phosphate on hydroxyaluminum- and hydroxyiron-montmorillonite complexes, J. Hazard. Mater. 165 (2009) 645–651.

[30] Y.J. Xue, H.B. Hou, S.J. Zhu, Characteristics and mechanisms of phosphate adsorption onto basic oxygen furnace slag, J. Hazard. Mater. 162 (2009) 973–980.