Materials Research Express

PAPER

Zn-Al layered double hydroxide: synthesis, characterization and application for orthophosphates ions adsorption in aqueous medium

Noureddine Rouahna1, Abdelkader Ouakouak1,2, Djamel Barkat3 and Ezzedine Srasra4

1 Faculty of Science and Technology, University of El Oued, PO Box 789, El Oued, 39000, Algeria
2 Research Laboratory in Subterranean and Surface Hydraulics, University of Biskra, PO Box 145 RP, Biskra, 07000, Algeria
3 Faculty of Science and Technology, University of Biskra, PO Box 145, Biskra, 07000, Algéria
4 National Center for Research in Materials Science, Technopole of Borj Cedria (CERTE), 8027 Soliman, Tunisia

E-mail: rouahna2003@yahoo.fr

Keywords: Zn-Al-LDH, orthophosphate, adsorption, kinetic, isotherm

Abstract

This paper aims at studying the preparation of Zn-Al-LDH anionic clay and its adsorption proprieties in removing orthophosphate ions from aqueous medium. The LDH phase was synthesized by coprecipitation method and then calcined at 500 °C. Structural and textural properties of the prepared LDHs were determined by using x-ray diffraction, FTIR, BET, SEM and pHPC analysis. Batch adsorption experiments were carried out under different parameters such as stirring time, pH and initial orthophosphate concentration. Results show that the prepared LDHs are efficient in removing orthophosphate and the maximum uptake was observed after 2 h. Experimental kinetic data are well described by the pseudo-second order model. It was also found that the adsorption process is significantly affected by the pH value. The sorption mechanisms include ion exchange, reconstitution of LDH phase and/or electrostatic attraction. Also, the isotherm study reveals that the Freundlich equation best fit the equilibrium data.

1. Introduction

Phosphorus (P) is an essential compound which is required for all living organisms [1]. This element becomes from natural origin such as the dissolution of soils and decomposition of organic matter [2]. However, the anthropogenic source of P is related to agricultural activities, industrial effluents, detergents, animal excrement and fertilizers [3]. Discharging of elevated amounts of P into aquatic environment generates eutrophication phenomenon and leads to the degradation of aquatic ecosystems [4]. At nowadays, there is a serious regulation for the control of P in wastewaters effluent. The recovery of P from polluted waters would reduce pollution and can present a new source of phosphorus. Therefore, several methods have applied in phosphorus elimination including biological treatments [5], chemical precipitation by calcium, aluminum or magnesium salts [1], phosphate crystallization [6], ion exchange [7], and adsorption [8]. The latter method is considered as a very promising technology for phosphate recovery from wastewater due to its efficiency and simplicity.

Recently, synthetic clays such as layered double hydroxides (LDHs) are demonstrated their high adsorption performance for the removal of organic and inorganic compounds from aqueous solutions. LDHs are anionic clays with a relatively high surface area and important exchange anionic capacity. The general formula of LDH is represented as follow [9]:

\[ \text{[M}^{II}_{1-x}\text{M}^{III}_x(\text{OH})_2\text{]}^{2+}\text{An}^{-x/n}\gamma\text{H}_2\text{O} \]  

(1)

where M^{II} and M^{III} are divalent metallic cation (like Mg^{2+}, Zn^{2+}, Ni^{2+}, Mn^{2+}, ...), trivalent metallic cation (like Al^{3+}, Cr^{3+}, Fe^{3+}, Ga^{3+}, ...), whereas An^{-} is an interlayer anions (such as CO_3^{2-}, Cl^{-}, NO_3^{-}, SO_4^{2-}, ...), x is a ratio between di- and trivalent cations.
The aim of the present work is to prepare Zn-Al-CO$_3$ LDH and its calcined phase (Zn-Al-Cal). The prepared materials are employed as adsorbent to remove orthophosphate ions from aqueous solutions. Various physico-chemical techniques such as XRD, FTIR, BET and pH$_{PZC}$ were used to identify the different proprieties of the synthetized LDH clays. The kinetic and equilibrium studies were investigated to understand the adsorption mechanisms.

2. Experimental

2.1. Materials
ZnCl$_2$, 6H$_2$O and AlCl$_3$,6H$_2$O as reagents have reagent grade and Na$_2$CO$_3$.

2.2. Preparation of Zn-Al-CO$_3$
Zn-Al-CO$_3$, LDH was synthesized by the conventional co-precipitation method [10]. A solution of NaOH (2M) and Na$_2$CO$_3$ (1M) was added dropwise to acid solution containing chlorides of the metal cations (Zn$^{2+}$ and Al$^{3+}$). The solution was agitated at 80 $^\circ$C until crystallization. Then, the slurry was separated by centrifugation and washed with deionized water until chloride free. Finally, the obtained material was dried at 65 $^\circ$C then ground and stored. 2 g of Zn-Al-CO$_3$ was calcined at 500 $^\circ$C which is named Zn-Al-Cal for the rest of this study.

2.3. Characterization of samples
Characterizations of the synthetized LDHs have been studied by x-ray powder diffraction 'PANalytical X’pert HighScore Plus', Infrared spectra (SHIMADZU IR Affinity-1) and N$_2$ adsorption measurements (Micromeritics ASAP 2020 instrument). The pore size distribution was calculated from desorption isotherm using barret-joyner-hallender (BJH) method. The surface morphology adsorbents were studied by scanning electron microscopy (SEM) analysis 'Tescan Vega 3'. Determination of point zero charge (pH$_{PZC}$) was performed according to the method described by Miyah et al [11]. In brief, solutions of 0.01 M NaCl (50 ml) were adjusted to pH range of 2–12 by adding drops of 0.1 M HCl or 0.1 M NaOH. Then, 50 mg of adsorbent was added to each solution. Mixtures were stirred for 24 h at constant speed, and the final pH of solutions was measured. Value of pH$_{PZC}$ was obtained from the plot of ΔpH (pH$_f$–pH$_0$) versus pH$_0$.

2.4. Experiments of orthophosphate adsorption
In this study, the orthophosphate content is expressed in mg/l PO$_4^{3-}$ (1 mg l$^{-1}$ PO$_4^{3-}$ = 0.326 mg l$^{-1}$ P). Stock solution of phosphate was prepared at 1 g l$^{-1}$ by dissolving an accurate amount of Na$_3$HPO$_4$. Adsorption experiments were carried out in batch manner at room temperature (18 ± 1 $^\circ$C). A desired amount of adsorbent was added to phosphate solution (50 ml) at known concentration. The dispersions were stirred at speed of 200 rpm and a constant pH (pH = 6.5). After adsorption, solutions were filtered through a 0.45 µm membrane filter, and the residual concentration of phosphate ions was detected by UV–vis spectrophotometer at a wavelength $\lambda$ = 800 nm [12].

2.5. Analysis of adsorption data
The adsorbed quantity ($q_{ads}$ mg g$^{-1}$) of orthophosphates was determined as follow:

\[
q_{ads} = (C_0 - C_e)V/m
\]

where $C_0$ and $C_e$ are the initial and equilibrium concentration (mg l$^{-1}$), respectively; whereas $V$ is the solution volume (L) and $m$ is the adsorbent mass (g).

In order to investigate the kinetic of orthophosphates ions adsorption onto LDHs, the experimental data were analyzed using the pseudo-first-order [13] and the pseudo-second-order [14] kinetic models. The adsorption mechanism was studied by fitting the isotherm data to the Langmuir [15], Freundlich [16], and [17] models. Table 1 shows the equations and parameters of these models.

The nonlinear coefficient of determination $R^2$ [18] and the residual root mean square error RMSE [19] were used to identify the best-fit model:

\[
R^2 = \frac{\sum (q_{e,exp} - q_{e,cal})^2}{\sum (q_{e,exp} - q_{e,mean})^2},
\]

\[
RMSE = \sqrt{\frac{1}{n-2} \sum (q_{e,exp} - q_{e,cal})^2}
\]
where $q_{e,exp}$ (mg g$^{-1}$) and $q_{e,cal}$ (mg g$^{-1}$) is the experimental and calculated quantity of adsorbed orthophosphates, respectively. $q_{e,mean}$ (mg g$^{-1}$) is the mean of $q_e$ experimental values. $n$ is the number of observations in the adsorption experiment.

3. Results and discussion

3.1. Characterization of samples

X-ray powder diffraction patterns of LDHs phases (Zn-Al-CO$_3$ and Zn-Al-Cal) are depicted in figure 1. The pattern of Zn-Al-CO$_3$ corresponds to typical LDH phase and shows that the prepared powder consists of a single crystalline phase (figure 1(a)). The d-spacing interlamellar value ($d_{003}$) of Zn-Al-CO$_3$ is 7.20 Å, which is close to other values cited in the existing literature [20, 21]. Zn-Al-Cal phase shows a destruction of the crystal lattice by decarbonization and dehydroxylation, consequently leading to the formation of spinel form (ZnAl$_2$O$_4$) as shown in figure 1(b).

FTIR spectrum of Zn-Al-CO$_3$ in figure 2(a) shows absorption bands of LDH containing CO$_3^{2-}$ in the interlayer space [21]. The broad band in the range (3600 to 3100) cm$^{-1}$ corresponds to the vibration mode of the O–H groups of layers and interlayer water molecules [22]. The weak peak at 1630 cm$^{-1}$ is attributed to interlayer water vibrations [23]. The intercalated carbonates anions in the interlayer LDH were observed at 1358 cm$^{-1}$ (ν$_3$),
835 cm\(^{-1}\) (\(\nu_2\)), 667 cm\(^{-1}\) (\(\nu_4\)) \[24\]. Bands at 558 cm\(^{-1}\) and 431 cm\(^{-1}\) can be attributed to the M–O and M–O–M stretching \[25\]. After calcination, all peaks characterizing the Zn–Al–CO\(_3\) phase were decreased considerably (figure 2(b)) \[26, 27\].

The \(\text{N}_2\) adsorption–desorption plots of LDHs samples show type IV isotherm according to IUPAC classification (figure 3). These plots have a hysteresis loops of H\(_3\) indicating a mesoporous structure \[28, 29\]. Results of BET measurements show that the specific surface area increases from 30 to 129.0 m\(^2\) g\(^{-1}\) after calcination of Zn–Al–CO\(_3\). It can be observed also that the loss of CO\(_3^{2-}\) ions leads to develop the total pore volume of mesoporous LDH. All textural characteristics of LDH phases are summarized in table 2.

The morphology of studied LDH phases is provided in figure 4. Results show that the samples consist of relatively uniform hexagonal platelet-like sheets \[27\]. The particles were well-defined and the platelet size is about 400–800 nm. In the Zn–Al-Cal LDH, an increase in the pore diameter was observed, indicating that the interlayer carbonates were disappeared after calcination of the sample. This finding was also confirmed by the increase of pore volume in the BET analysis.
The point of zero charge is defined as the pH value at which the total surface charge of adsorbent is zero [28]. It plays a critical role in studying the surface charge properties of the material and understanding the adsorption mechanisms. Result of experimental determination of pH_{PZC} of Zn-Al-CO_{3} sample is 7.96 (figure 5). When pH of solution >7.96, Zn-Al-CO_{3} reacts as negative surface and as a positive surface when solution pH < 7.96.

### Table 2. Textural proprieties of Zn-Al-CO_{3} and Zn-Al-Cal samples.

| Samples     | BET surface area (m^{2} g^{-1}) | Pore volume (cm^{3} g^{-1}) | Pore size (nm) |
|-------------|---------------------------------|----------------------------|----------------|
| Zn-Al-CO_{3}| Zn-                             | 30                         | 0.21           | 15.16           |
|             | Al-Cal                           | 129                        | 0.75           | 21.58           |

The point of zero charge is defined as the pH value at which the total surface charge of adsorbent is zero [28].

#### 3.2. Kinetic study

The effect of contact time on the adsorbed amount of orthophosphates was examined at initial concentration of 20 mg l^{-1} (figure 6). Results show that the uptake of orthophosphates ions onto LDHs surface is a rapid phenomenon in the first minutes, and becomes slow after stirring time of 60 min. The quantity of
orthophosphates adsorbed per unit mass of clay \((q_t, \text{mg g}^{-1})\) reached its maximum after 2 h. A stirring time of 4 h is chosen for the rest of this study. Using the PSO equation, the correlation coefficients are very important and the calculated \(q_e\) values are very close to the experimental \(q_e\) values. In addition, the RMSE value calculated from PSO equation is significantly inferior to these of PFO equation for all kinetic data (table 3). This finding suggests that the PSO model is more suitable for the adsorption of orthophosphate ions onto Zn-Al-CO\(_3\) and Zn-Al-Cal phases.

### 3.3. Adsorption mechanisms

Adsorption tests were performed at various initial pH values ranging from 2 to 12 to investigate the interaction mechanisms between orthophosphates and LDHs. Depending on the value of pH solution, orthophosphates can exist in several forms \(\text{H}_3\text{PO}_4, \text{H}_2\text{PO}_4^-, \text{HPO}_4^{2-}\), and \(\text{PO}_4^{3-}\) [29]. Results of figure 7 show that the affinity of adsorbent to remove orthophosphates is low at pH \(\leq 3\), this can be explained by the instability of LDHs structure [30]. At \(4 < \text{pH} < \text{pH}_{\text{PZC}}\), the dominant species of orthophosphates could be \(\text{H}_2\text{PO}_4^-\) and \(\text{HPO}_4^{2-}\), and the LDHs surface is positively charged. The adsorption is primarily result of ion exchange between orthophosphate anions and interlayer \(\text{CO}_3^{2-}\) of Zn-Al-CO\(_3\) phase [31], and reconstitution in the case of calcined Zn-Al-LDH (figure 8). At the same time, the electrostatic attraction (surface positive charge-anion) promotes the anionic orthophosphates uptake [32].

As the increase of pH (\(\text{pH}_{\text{PZC}}\) to 12), the amount of orthophosphate anions adsorbed onto LDHs decreased. At this pH range, the LDHs surface becomes negatively charged and the anionic forms of orthophosphate are not favorably attracted by the adsorbent sites. Meanwhile, this decrease of adsorption capacity at higher pH values implies a competition between \(\text{PO}_4^{3-}\) and \(\text{OH}^-\) for the adsorption sites [33].

### 3.4. Equilibrium study

The isotherm of adsorption is represented by the plot of the equilibrium adsorbed amount of orthophosphate \(q_e\) against the equilibrium concentration \(C_e\). The fitting of equilibrium data using the nonlinear Langmuir, Freundlich and Dubinin-Radushkevich models are depicted in figure 9.

Results of isotherm parameters in table 4 show that the Freundlich equation gives the best fit for equilibrium data, which is confirmed by the high value of \(R^2\) and minimum value of RMSE. This finding suggests the multilayer adsorption of orthophosphate ions onto heterogeneous surface of LDHs [34].
**Figure 7.** Effect of pH value on the adsorption efficiency using Zn-Al-CO$_3$ (a) and Zn-Al-Cal (b) ($C_0 = 20$ mg l$^{-1}$, adsorbent mass = 50 mg, $V = 50$ ml).

**Table 4.** Isotherm constant parameters for the orthophosphate adsorption onto Zn-Al-CO$_3$ and Zn-Al-Cal phases.

| Models             | LDH         | $k$ (mg g$^{-1}$) | n   | $R^2$ | RMSE |
|--------------------|-------------|-------------------|-----|------|------|
| Freundlich         | Zn-Al-CO$_3$| 33.43             | 0.292 | 0.96 | 2.46 |
|                    | Zn-Al-cal   | 41.83             | 0.321 | 0.96 | 3.15 |
|                    |             | $Q_{max}$ (mg g$^{-1}$) | $K_L$ (l mg$^{-1}$) | $R^2$ | RMSE |
| Langmuir           | Zn-Al-CO$_3$| 78.93             | 0.909 | 0.92 | 4.56 |
|                    | Zn-Al-cal   | 132.61            | 0.224 | 0.82 | 22.3 |
|                    |             | $q_s$ (mg g$^{-1}$) | $K_{DR}$ (mol$^2$/KJ$^2$) | $R^2$ | RMSE |
| Dubinin–Radushkevich | Zn-Al-CO$_3$| 68.84             | $1.13 \times 10^{-7}$ | 0.80 | 5.13 |
|                    | Zn-Al-cal   | 84.17             | $4.85 \times 10^{-8}$ | 0.67 | 8.08 |

**Figure 8.** Schematic of adsorption mechanism using Zn-Al-CO$_3$ (a) and Zn-Al-Cal (b).
In the present study, Zn-Al-CO₃ LDH was prepared by co-precipitation method and calcined at 500 °C. The synthetized adsorbents were used to remove orthophosphate from aqueous solutions.

The obtained results show that the prepared material corresponds to typical LDH phase with d-spacing of 7.20 Å. The adsorption tests indicate a high efficiency of the used LDHs and the adsorption reaches its maximum after 2 h. It was also found, that the maximum of removal was obtained at pH ranging from 4 to 9. The adsorption of orthophosphate anions can result of ion exchange, reconstitution and/or electrostatic attraction. The Freundlich equation adequately describes the uptake of orthophosphate anions onto LDHs surface.

4. Conclusion

In the present study, Zn-Al-CO₃ LDH was prepared by co-precipitation method and calcined at 500 °C. The synthetized adsorbents were used to remove orthophosphate from aqueous solutions.

The obtained results show that the prepared material corresponds to typical LDH phase with d-spacing of 7.20 Å. The adsorption tests indicate a high efficiency of the used LDHs and the adsorption reaches its maximum after 2 h. It was also found, that the maximum of removal was obtained at pH ranging from 4 to 9. The adsorption of orthophosphate anions can result of ion exchange, reconstitution and/or electrostatic attraction. The Freundlich equation adequately describes the uptake of orthophosphate anions onto LDHs surface.

**References**

[1] Huang H, Liu J and Ding L 2015 Recovery of phosphate and ammonia nitrogen from the anaerobic digestion supernatant of activated sludge by chemical precipitation J. Clean. Prod. 192 437–46

[2] Boeykens S P, Piel M N, Samudio I, Saralegui A B, Aires U D B, De Ingeniera F, De Quimica I. and Heterog D S 2017 Eutrophication decrease: phosphate adsorption processes in presence of nitrates Journal of Environmental Management 203 888–95

[3] Loganathan P, Vigneswaran S, Kandasamy J and Nanthi S 2014 Critical reviews in environmental science and removal and recovery of phosphate from water using Critical Reviews in Environmental Science and Technology 44 847–907

[4] Yang S S, Pang I W, Guo W Q, Yang X Y, Wu Z Y, Ren N Q and Zhao Z Q 2017 Biological phosphorus removal in an extended ASM2 model: roles of extracellular polymeric substances and kinetic modeling Bioresour. Technol. 232 412–6

[5] Sun J et al 2017 Nickel toxicity to the performance and microbial community of enhanced biological phosphorus removal system Chem. Eng. J. 313 115–23

[6] Song Y, Dai Y, Hu Q, Yu X and Qian F 2014 Effects of three kinds of organic acids on phosphorus recovery by magnesium ammonium phosphate (MAP) crystallization from synthetic swine wastewater Chemosphere. 101 41–8

[7] Johir M A H, George J, Vigneswaran S, Kandasamy J and Grasmick A 2011 Removal and recovery of nutrients by ion exchange from high rate membrane bio-reactor (MBR) effluent Desalination 275 197–202

[8] Ouakouak A, Youcef L, Boulouarnour D and Achour S 2017 Adsorptive removal of phosphate from groundwater using granular activated carbon, international Journal of Engineering Research in Africa 32 53–61

[9] Miyata S 1975 The syntheses of hydrotalcite-like compounds and their structures and physico-chemical properties-i: the systems Mg₂⁺–Al³⁺–Cl⁻ and Mg₂⁺–Al³⁺–Cl⁻–ClO₄⁻ J. Am. Chem. Soc. 97 7957–64

[10] Miyata S 1975 The syntheses of hydrotalcite-like compounds and their structures and physico-chemical properties-ii: the systems Mg₂⁺–Al³⁺–Cl⁻–NO₃⁻ J. Am. Chem. Soc. 97 7965–72

[11] Miyata S 1975 The syntheses of hydrotalcite-like compounds and their structures and physico-chemical properties-iii: the systems Mg₂⁺–Al³⁺–Cl⁻–SO₄²⁻ J. Am. Chem. Soc. 97 7973–80

[12] Rodier J, Legube B and Merlet N 2009 Analyse de l’eau Rodier. 9ème edition 9th edn (Paris: Dunod)

[13] Langergren B K S 1898 Zurtheorie der sogenannten adsorption gelösterstoffe Vetenskapaskal Handlingar 24 1–39

[14] Ho Y S and McKay G 1999 The sorption of lead(II) ions on peat Water Res. 33 578–84

[15] Logergeren B K S S 1898 Zurtheorie der sogenannten adsorption gelösterstoffe Vetenskapaskal Handlingar 24 1–39

[16] Freundlich H M F 1906 Uber die adsorption in losungen Zeitschrift Fur Physikalische Chemie (Leipzig) 57A 385–470
[17] Dubinin L V R M M 1947 Radushkevich, equation of the characteristic curve of activated charcoal Proc. Acad. Sci. Phys. Chem. Sect. USSR 55 331–3
[18] Tran H N, Wang Y F, You S J and Chao H P 2017 Insights into the mechanism of cationic dye adsorption on activated charcoal: the importance of II–II interactions Process Safety and Environmental Protection 107 168–80
[19] Kilpimaa S, Runitti H, Kangas T, Lassi U and Kuokkanen T 2015 Physical activation of carbon residue from biomass gasification: novel sorbent for the removal of phosphates and nitrates from aqueous solution J. Ind. Eng. Chem. 21 1354–64
[20] Parida K M, Parija S, Das J and Mukherjee P S 2006 Preparation, Characterisation of Molybdophosphoric and Tungstophosphoric Acid Intercalated Zinc Aluminium Hydrotalcite-like Compounds and their Catalytic Evaluation Towards the Oxidative Bromination of Phenol 7 913–9
[21] Frost R L, Ding Z, Martens T E, Johnson T E and Kloprogge J T 2003 Molecular assembly in synthesised hydrotalcites of formula CuxZnxAl2(OH)16(CO3)4/H2O/* a vibrational spectroscopic study Spectrochim. Acta, Part A 59 321–8
[22] Kloprogge J T, Frost R L and Al M 2002 Infrared and Raman study of interlayer Mg/Al hydrotalcite Am. Mineral. 87 623–9
[23] Zhao D, Sheng G, Hu J, Chen C and Wang X 2011 The adsorption of Pb(II) on Mg2Al layered double hydroxide Chem. Eng. J. 171 167–74
[24] Cavani F, Trifirò F and Vaccari A 1991 Hydrotalcite-type anionic clays: preparation, properties and applications Catal. Today 11 173–301
[25] Rouahna N, Barkat D, Ouakouak A and Sebsra E 2018 Synthesis and characterization of Mg-Al layered double hydroxide intercalated with D2EHPA: application for copper ions removal from aqueous solution Journal of Environmental Chemical Engineering 6 1226–32
[26] Brunauer S 1943 The Adsorption of Gases and Vapors (Physical Adsorption) vol 1 (United States: J. Chem. Educ.)
[27] Wang J, You J, Li Z, Yang P, Jing X, Cao D and Zhang M 2008 Electrochemical performance of Ni/Al hydrotalcite supported on porous nickel electrode in hexacyanoferrate(III) media Solid State Sci. 10 1093–8
[28] Amano Y, Misugi Y and Machida M 2012 Adsorptive behavior of phosphate onto activated carbons varying surface physicochemical properties Separation Science and Technology (Philadelphia) 47 2348–57
[29] Luo X, Wu X, Ren G, Min X, Xiao X and Luo J 2017 Enhancement of phosphate adsorption on zirconium hydroxide by ammonium modification Ind. Eng. Chem. Res. 56 9419–28
[30] Liang X, Zang Y, Xu Y, Tan X, Hou W, Wang L and Sun Y 2013 Sorption of metal cations on layered double hydroxides Colloids Surf. A 433 122–31
[31] Yang K, Yan L G, Yang Y M, Yu S J, Shan R R, Yu H Q, Zhu B C and Du B 2014 Adsorptive removal of phosphate by Mg-Al and Zn-Al layered double hydroxides: kinetics, isotherms and mechanisms Sep. Purif. Technol. 124 36–42
[32] Zhang L, Zhou Q, Liu J, Chang N, Wan L and Junhua C 2012 Phosphate adsorption on hydroxy-iron-lanthanum doped activated carbon fiber Chem. Eng. J. 185–186 160–7
[33] Kumar P, Sudha S, Chand S and Srivastava V C 2010 Phosphate removal from aqueous solution using coir-pith activated carbon Sep. Sci. Technol. 45 1461–70
[34] Heraldy E, Lestari W W, Permatasari D and Arimurti D D 2018 Biosorbent from tomato waste and apple juice residue for lead removal Journal of Environmental Chemical Engineering 6 1201–8