Desalination and Water Treatment
www.deswater.com

29 (2011) 252–257
May

1944-3994 / 1944-3986 © 2011 Desalination Publications. All rights reserved.
doi: 10.5004/dwt.2011.1197

Interaction of Mn^{2+}, Fe^{2+} and Cu^{2+} heavy metal ions from aqueous solution by zaccagnaite, a hydrotalcite-like compound

Amita Jaiswal, M.C. Chattopadhyaya*

Environmental Research Laboratory, Department of Chemistry, University of Allahabad, Allahabad – 211002 (U.P.), India
Tel. + 91 (532) 2461236; Fax +91 (532) 2461997; email: amita_ecsl@rediffmail.com, mcc46@rediffmail.com

Received 1 May 2009; Accepted in revised form 16 December 2010

ABSTRACT

The paper deals with the interaction of heavy metal ions Mn^{2+}, Fe^{2+} and Cu^{2+} with synthesized zaccagnaite, a hydrotalcite like compound, which acts as an adsorbent in aqueous solutions. Zaccagnaite was synthesized by the co-precipitation method and was characterized by XRD. All experiments were carried out by adjusting pH in the range 5.2–5.5. The use of buffer solution was avoided because the net interaction between the adsorbent and the heavy metals could have been destroyed by the components of the buffer solution. The equilibrium adsorption contact time was determined for zaccagnaite. The adsorption rate constants were determined from the kinetic curves which obey the first degree rate constant. Adsorption isotherms of the above said metals on zaccagnaite from aqueous solutions were determined. The adsorption isotherms were seen to be consistent with Freundlich's adsorption isotherm. From this experiment it was found that the zaccagnaite is a better adsorbent for the removal of Cu^{2+} than Fe^{2+} and Mn^{2+}.

Keywords: Heavy metal; Adsorption; Zaccagnaite; Adsorption isotherm; XRD

---

1. Introduction

Heavy metals have densities generally larger than 5 gcm^{-3}. One of the major classes of pollutants in industrial effluents is heavy metals. Their ability to pass easily into the food chain and their poisonous effects need only extremely low levels be allowed to be discharged into the environment. A large number of different industries produce effluents contaminated with heavy metals. Industries such as mineral and metallurgical processing, electroplating and then relating the production of pigments and dyes create heavy metals in aqueous solutions as waste [1]. Adsorption of heavy metals is an attractive option due to the proven efficiency of this process in the treatment of wastewater and removal of large number of different contaminants.

Layered double hydroxides (LDHs) have been extensively researched for many years as host materials for a range of anionic exchange reactions, proving to be beneficial in the removal of anionic impurities in solutions [2–14].They are sometimes referred to as anionic or hydrotalcite-like clays, and are based on the brucite structure, $Mg(OH)_2$ [15–17], where each Mg^{2+} ion is octahedrally surrounded by six OH^- ions and the different octahedral share edges to form infinite sheets [18–21]. The sheets are stacked on one another and are held together by weak interactions through hydrogen bonds [18–20].

LDHs are represented by the general formula, $[M^{2+}_{1-x} M^{3+}_x (OH)_2]^{x+} A^{m-}_{x/m} .nH_2O$, (where $M^{2+} = Mg^{2+}/Zn^{2+}/Ni^{2+}/$

---

* Corresponding author.

CO^{2+}; $M^{3+} = Al^{3+}/Fe^{3+}/Cr^{3+}$ and $A = OH^-/Cl^-/NO_3^-/CO_2^-$); x varies between 0.20 and 0.33 [18].

M^{2+} cations are replaced isomorphously by M^{3+} ones with similar radius, the brucite-like layers becomes positively charged and the electrical neutrality is attained by compensating anions located in the interlayers along with water molecules [18,19].

They can be easily synthesized through different methods [18],the most common being the co-precipitation at constant pH of diluted solutions containing M^{2+} and M^{3+} cations with solutions containing carbonate and hydroxide ions [21–23]. The precipitate is quite amorphous but after ageing by hydrothermal or thermal treatments, the crystallinity is improved [24]. Interest in the study of LDHs continues [25–28].

The unique ability to easily exchange and house a variety of anions have made LDHs very attractive for heavy metal remediation [28] in environmental and industrial settings and that has motivated us to undertake the present study in which a hydrotalcite like compound, zaccagnaite has been synthesised and its activity for metal uptake has been investigated for the first time. Although zaccagnaite has been used as a catalyst but its use as adsorbent of metal ions has not been studied earlier. That is why this is a novel approach in its application towards removal of metal ions. Further, a relative assessment has been made towards its remedial ability for these metals.

The zaccagnaite was synthesized by co-precipitation method and the product was characterized by XRD. The adsorption characteristics of Mn^{2+}, Fe^{2+} and Cu^{2+} on zaccagnaite were also investigated to work out the optimum removal conditions of these metals. The adsorption isotherm studies were also undertaken for these metals.

2. Experimental

2.1. Reagents

The following reagents were used: zinc nitrate (Loba Chemie), aluminium nitrate (B.D.H.), sodium hydroxide (Merck), sodium carbonate (Loba Chemie), hydrochloric acid (Loba Chemie), manganese sulphate (Qualigens), ferrous sulphate (Merck), copper sulphate (Merck).

2.2. Instruments

X-ray diffractometer (Rigaku D/max-2200 PC diffractometer), pH meter (Century CP 901), atomic absorption spectrophotometer (ECIL 4141), orbital shaker (Shivam, ISO 900/ 2000).

2.3. Preparation of adsorbent

Zaccagnaite was prepared by the method described by Miyata [29]. 40 mL of an aqueous solution containing zinc nitrate and aluminium nitrate (3:1) were added in 200 mL of water with stirring (Solution 1). 16 g of NaOH and 2.86 g of Na_2CO_3 were dissolved in 1 L of water (Solution 2). Then Solution 1 was added drop by drop into Solution 2, with vigorous stirring on a magnetic stirrer. The pH was maintained between 11.5 and 12 by addition of NaOH and HCl. The maintenance of pH is critical because if the pH exceeds 12, then dissolution of Al(III) ions can occur and if the value goes below 11.5, a more complex pathway for the precipitation exists and thus the process is not always completed. The mixed suspension was centrifuged to recover the precipitate. The precipitate was washed with deionized water and then dried in an oven for 24 h at 100°C.

3. Methods

The adsorption capacity of zaccagnaite was determined by performing kinetic and isotherm studies. For kinetic studies, 100 mL of a solution containing 200 ppm of initial concentration of the metal ion was taken in a conical flask having 1 g of zaccagnaite. The mixture was shaken in an orbital shaker at different time intervals at 120 rpm. Equilibrium concentration of the metal ion was determined by an atomic absorption spectrophotometer.

For isotherm studies, a series of 100 mL solutions were prepared in which the initial metal ion concentration was varied. Thereafter each solution was brought in contact with 1 g of zaccagnaite kept in different conical flasks followed by shaking in an orbital shaker at 120 rpm, at 30°C for 30–120 min. The equilibrium concentrations of the metal ions were determined by atomic absorption spectrophotometer. The amount adsorbed (Q_e) was calculated from the difference between the initial and equilibrium concentrations.

4. Results and discussion

4.1. Physical characterization

4.1.1. X-ray powder diffraction

The XRD powder pattern of zaccagnaite was obtained by using a Rigaku D/max – 2200 PC diffractometer operated at 40 KV/20 mA using CuKα_1 radiation with wavelength of 1.54 Å and varying 2 θ values from 20° to 80°.

Fig. 1 shows the XRD patterns of the synthesized compound through the co-precipitation method. XRD spectra of zaccagnaite shows peaks at the positions of 11.56°, 23.13°, 29.21°, 35.33°, 39.35° and 62.90°,which are in good agreement with the JCPDS file (JCPDS 38-0486, a = 3.076 Å , b = c = 22.80 Å), and can be indexed as the hexagonal rhomb-centered structure having space group $R\bar{3}m$ (166). All available reflections of the present XRD peaks (i.e. Scherrer's broadening) can be attributes the formation of zaccagnaite, where parameter a corresponds

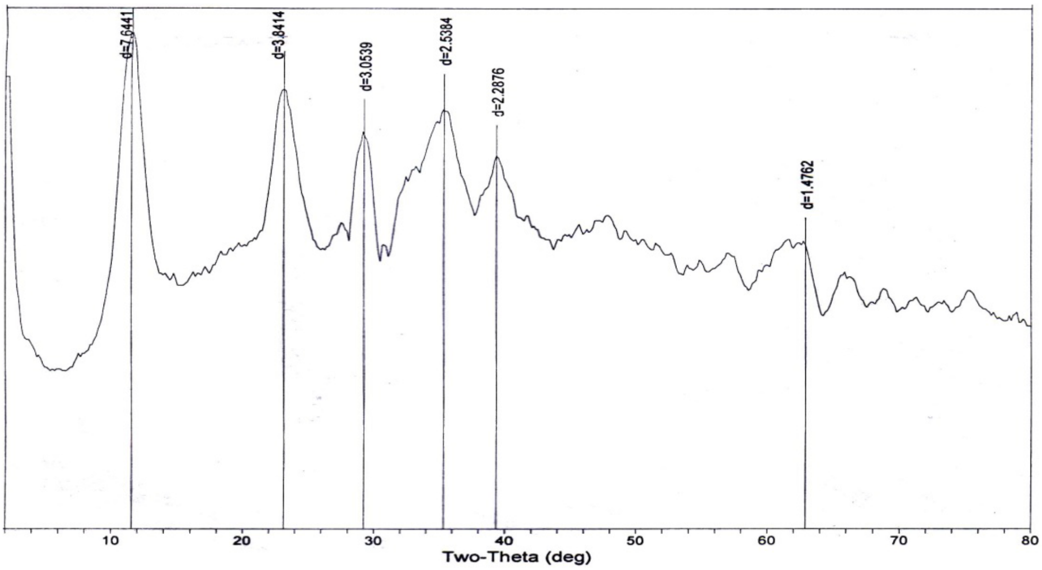

Fig. 1. XRD spectrum of zaccagnaite.

to the cation–cation distance within the cationic layer, while the parameter *c* is related to the total thickness of the brucite –like layer and the interlayer distance [30–32].

The particle size, *d* of zaccagnaite was estimated by Debye–Scherrer's equation:

$$d = \frac{0.9\lambda}{B\cos\theta} \quad (1)$$

where *d* is the particle size, λ is the wavelength of radiation used, θ is the Bragg angle and *B* is the full width at half maxima (FWHM) on 2 θ scale. The particle size of zaccagnaite was found approximately 33 nm.

Fig. 2 displays the kinetic curves related to adsorption of Mn^{2+}, Fe^{2+} and Cu^{2+} on zaccagnaite. Equilibrium contact times from kinetic curves of heavy metals were determined to be 30–120 min, respectively. These findings suggest that adsorption kinetic curves of heavy metals follow the first order (Fig. 3). The high value of adsorption rate constant shows that the adsorbate is adsorbed faster by the adsorbent. The adsorption rate constants follow the order $Mn^{2+} << Fe^{2+} < Cu^{2+}$.

Adsorption rate constants (K_a) were determined by Eq. (2) (Table 1):

$$\ln C / C_1 = -K_a t \quad (2)$$

The hydrolysis constants [33] and ionic diameters [34] of these metals are given in Table 2. Comparing Tables 1 and 2, it is interesting to note that the hydrolysis constants of these metals follow the same order as rate constants. This may be due to the fact that M $[OH]^+$ is formed as the first step. Further, the order of adsorption of these metal ions by zaccagnaite follows the order, $Mn^{2+} << Fe^{2+} < Cu^{2+}$, which is due to the fact that the adsorption event is completed through prompt interaction of these metal ions with negative group of zaccagnaite.

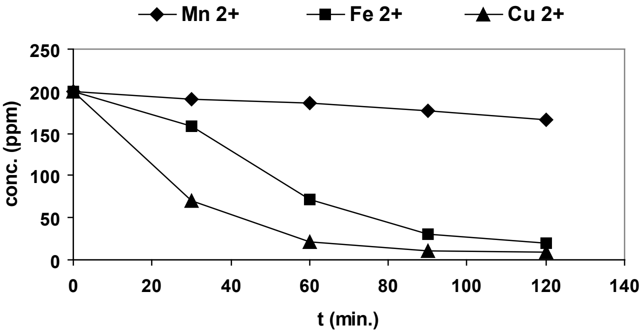

Fig. 2. Kinetic curves related to adsorption of Mn^{2+}, Fe^{2+} and Cu^{2+} from aqueous solution on zaccagnaite.

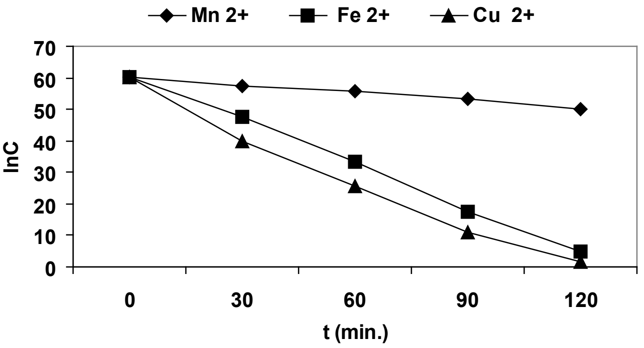

Fig. 3. Kinetic curves of first order related to adsorption of Mn^{2+}, Fe^{2+} and Cu^{2+} from aqueous solution on zaccagnaite.

Table 1
Rate constants related to adsorption of Mn^{2+}, Fe^{2+} and Cu^{2+} from aqueous solution by zaccagnaite

Adsorbate	K_a (time^{-1})
Mn^{2+}	0.6335
Fe^{2+}	3.6138
Cu^{2+}	4.9230

Table 2
Hydrolysis constants and ionic diameters of Mn^{2+}, Fe^{2+} and Cu^{2+}

Heavy metal ions	Mn^{2+}	Fe^{2+}	Cu^{2+}
log K_h	3.4	4.5	6.3
Ionic diameters, pm	80	76	70

Table 3
Percent removal (R%) resulted to Mn^{2+}, Fe^{2+} and Cu^{2+} from aqueous solution onto zaccagnaite

Metal ions	Adsorbent
	Zaccagnaite
Mn^{2+}	16.55
Fe^{2+}	85.00
Cu^{2+}	95.20

The amount of adsorbed Mn^{2+} is very small (Table 3). It can be seen that heavy metal ions are being adsorbed when ionic diameters decreases. The ionic diameters of these metals follow the order of $Mn^{2+} > Fe^{2+} > Cu^{2+}$ (Table 2). Since the zaccagnaite used is a microporous adsorbent, heavy metals penetrate easily into these pores when the ionic diameter becomes small. According to the order above, Mn^{2+} must be the least adsorbed metal while Cu^{2+} the most. This is also experimentally verified.

Table 3 includes the removal percentage [35], calculated according to Eq. (3):

$$R\% = \left[(C_i - C_e)/C_i\right]\cdot 100 \tag{3}$$

where C_i = initial concentration (mg/L) and C_e = equilibrium concentration (mg/L).

The experimental data were fitted into the Freundlich as well as Langmuir equations:

$$\log Q_e = \log K_f + 1/n \log C_e \tag{4}$$

$$C_e / Q_e = 1/Q_{\max} b + C_e / Q_{\max} \tag{5}$$

where C_e = equilibrium concentration (mg/L), Q_e = amount adsorbed (mg g^{-1}), K_f and n = Freundlich's constants, $Q_{\max}$ and b = Langmuir's constants.

Fig. 4 displays the plot of log Q_e vs. log C_e and Fig. 5 displays plots of C_e/Q_e vs. C_e. These two figures display Freundlich's and Langmuir's adsorption isotherm which is followed by zaccagnaite for all the three metals. The adsorption isotherm parameters are tabulated in Table 4.

It can be seen from Table 4 that the correlation coefficient (r^2) for the Langmuir isotherm is much less than 1, whereas the correlation coefficient for the Freundlich isotherm is around 1 for all the metals. It is thus concluded that the Freundlich isotherm is better fitted for these metals with zaccagnaite as an adsorbent.

5. Conclusion

We have compared the adsorption of Mn^{2+}, Fe^{2+} and Cu^{2+} ions on zaccagnaite (Table 3), which shows that Cu^{2+} ions are adsorbed to the extent of 95.20% followed by Fe^{2+} 85.00% and then by Mn^{2+} 16.55%. It can be concluded that novel hydrotalcite-like compound zaccagnaite is a good adsorbent for Cu^{2+} than Fe^{2+} and Mn^{2+}. All the metals follow the Freundlich isotherm rather than the Langmuir isotherm.

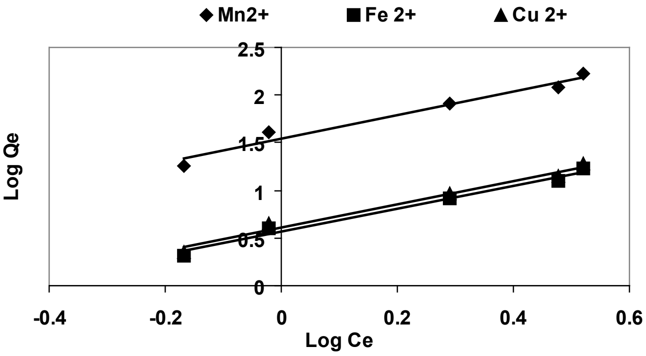

Fig. 4. Freundlich adsorption isotherm related to Mn^{2+}, Fe^{2+} and Cu^{2+} from aqueous solution using zaccagnaite.

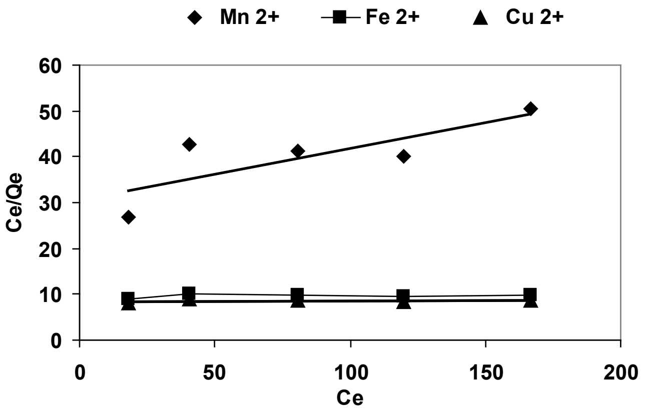

Fig. 5. Langmuir adsorption isotherm related to Mn^{2+}, Fe^{2+} and Cu^{2+} from aqueous solution using zaccagnaite.

Table 4
Freundlich and Langmuir adsorption parameters for the adsorption of Mn^{2+}, Fe^{2+} and Cu^{2+} from aqueous solution by zaccagnaite

	Freundlich parameters				Langmuir parameters		
	Mn^{2+}	Fe^{2+}	Cu^{2+}		Mn^{2+}	Fe^{2+}	Cu^2+
K_f	0.0551	0.3682	2.389	Q_{max}	30.69	9.36	8.40
$1/n$	0.7468	0.4621	0.3878	b	0.11	0.003	0.002
r^2	0.9687	0.9917	0.9801	r^2	0.784	0.388	0.340

Symbols

A^{m-} — An anions with charge m (OH^-, Cl^-, NO_3^-, CO_2^-)
B — Full width at half maxima (FWHM)
C_e — Equilibrium concentration of metal ion in the aqueous phase, mg/L
Ci — Initial concentration of metal ion in the aqueous phase, mg/L
d — Particle size
HTlCs — Hydrotalcite-like compounds
K_a — Rate constants, $time^{-1}$
K_f, $1/n$ — Freundlich's constants
LDHs — Layered double hydroxides
M^{2+} — Divalent cation (Mg^{2+}, Zn^{2+}, Ni^{2+}, CO^{2+}, etc.)
M^{3+} — Trivalent cation (Al^{3+}, Fe^{3+}, Cr^{3+}, V^{3+} etc.)
R — Percentage removal of metal ion from the aqueous phase, %
r^2 — Correlation coefficient
Q_e — Amount adsorbed on adsorbent, mg g^{-1}
Q_{max}, b — Langmuir constants
XRD — X-ray diffractometer
λ — Wavelength of radiation used
θ — Bragg angle

References

[1] S. Dara, Textbook of Environmental Chemistry and Pollution Control, 6th ed., S. Chand and Company Ltd., New Delhi, 2004, pp. 87–109.

[2] A.N. Ay, B. Zuemreoglu-Karan and A. Temel, Boron removal by hydrotalcite-like carbonate free Mg-Al-NO_3-LDH and a rationale on the mechanism. Micropor. Mesopor. Mater., 98 (2007) 1–5.

[3] J. Shibata, N. Murayama, K. Sakai and H. Yamamoto, Removal of toxic metal ions with functional inorganic materials produced from wastes in non-ferrous metal industry, Proc. 7th World Congress of Chemical Engineering, Glasgow, UK 10–14 July 2005.

[4] Y. Kiso, Y.J. Jung, T. Yamada, M. Nagai and K.S. Min, Removal properties of arsenic compounds with synthetic hydrotalcite like compounds. Wat. Sci. Technol.: Wat. Supply, 5 (2005) 75–81.

[5] H. Hirahara, S. Aisawa, H. Sato, S. Takahashi, Y. Umetus and E. Narita, Removal of arsenate and arsenite from aqueous solutions by Mg-Al layered double hydroxides. Nendo Kagaku, 45 (2006) 6–13.

[6] S. Peng, Y. Yang, T. Chen, S. Jiang and H.F. Xu, Adsorption of arsenate anion by Mg-Al anionic clay. Chinese Ceram. Soc., 33 (2005) 1023–1027.

[7] N. Murayama, M. Tanabe, R. Shibata, H. Yamamoto and J. Shibata, Removal of toxic heavy metal ions in aqueous solution with Mg/Al type hydrotalcite derived from wastes. Kagaku Kogaku Ronbunshu, 31 (2005) 285–290.

[8] T. Murakami, H. Oshima, T. Kuwabara, T. Sato and A. Kawamoto, Removal of arsenic and selenium using layer structure inorganic ion exchanger hydrotalcite-like compounds. J. Japan Soc. Wat. Environ., 28 (2005) 269–274.

[9] S. Yapar, P. Klahre and E.K. Lumpp, Hydrotalcite as a potential sorbent for the removal of 2,4 dichlorophenol. Turkish J. Eng. Environ. Sci., 28 (2004) 41–48.

[10] T. Kuwabara, T. Sato, T. Nonaka, H. Yamamoto, M. Aizaki and Y. Fukuda, Phosphorous removal using concrete blocks mixed wlth hydrotalcite compounds. J. Japan Soc. Wat. Environ., 26 (2003) 423–429.

[11] J. Orthman, H.Y. Zhu and G.Q. Lu, Use of anion clay hydrotalcite to remove coloured organics from aqueous solutions. Separ. Purif. Technol., 31 (2003) 53–59.

[12] Y.W. You, H.T. Zhao and G.F. Vance, Removal of arsenite from aqueous solution by anionic clays. Environ. Technol., 22 (2001) 1447–1457.

[13] H.Y. Zhu, J. Orthman and G.Q. Lu, New hydrotalcite sorbents for the removal of coloured organic compounds in aqueous solutions. Sustainable energy and environmental technologies, Proc. 3rd Asia-Pacific Conference, Hong-Kong, China, December 2001, pp. 356–361.

[14] M.A. Ulibarri, I. Pavlovic, C. Barriga, M.C. Hermosin and J. Cornejo, Adsorption of anionic species on hydrotalcite-like compounds: effect of interlayer anion and crystallinity. Appl. Clay Sci., 18 (2001) 17–27.

[15] U. Costantino, F. Marmottini, M. Nocchetti and R. Vivani, New synthetic routes to hydrotalcite-like compounds characterization and properties of the obtained materials. Eur. J. Inorg. Chem., 10 (1998) 1439–1446.

[16] R.L. Frost, M.L. Weier, M.E. Clissold, P.A. Williams and J.T. Kloprogge, Thermal decomposition of the natural hydrotalcites carrboydite and hydrohonessite. Thermochim. Acta, 407 (2003) 1–9.

[17] T. Lopez, P. Bosch, E. Ramos, R. Gomez, O. Novaro, D. Acosta and F. Figueras, Synthesis and characterisation of sol–gel hydrotalcites : Structure and texture. Langmuir, 12 (1996) 189–192.

[18] F. Cavani, F. Trifiro and A. Vaccari, Hydrotalcite type anionic clays: Preparation, properties and applications. Catalysis Today, 11 (1991) 173–301.

[19] W.T. Reichle, Anionic clay minerals. Chemtech., 16 (1986) 58–68.

[20] A.L. McKenzie, C.T. Fishel and R.J. Davis, Investigation of surface structure and basic properties of calcined hydrotalcites. J. Catalysis, 138 (1992) 547–561.

[21] D. Tichit, M.H. Lhouty, A. Guida, B.H. Chiche, F. Figueras, A. Auroux, B. Bartalini and E. Garrone, Textural properties and catalytic activity of hydrotalcites. J. Catalysis, 151 (1995) 50–59.

[22] W.T. Reichle, S.Y. Kang and D.S. Everhardt, The nature of the thermal decomposition of a catalytically active anionic clay mineral. J. Catalysis, 101 (1986) 352–359.

[23] A. Corma, V. Fornes and F. Rey, Hydrotalcites as base catalysts: Influence of the chemical composition and synthesis conditions

on the dehydrogenation of isopropanol. J. Catalysis, 148 (1994) 205–212.

[24] M. Del Arco, C. Martin, I. Martin, V. Rives and R. Trujillano, A FTIR spectroscopic study of surface acidy and basicity of mixed Mg-Al-oxides obtained by thermal decomposition of hydrotalcite. Spectrochim. Acta, 49A (1993) 1575–1582.

[25] Y. You, G.F. Vance and H. Zhao, Selenium adsorption on Mg-Al and Zn-Al double layered hydroxides. Appl. Clay Sci., 20 (2001) 13–25.

[26] L.P. Cardoso and J.B. Valim, Study of acids herbicides removal by calcined Mg-Al-CO_3-LDH. J. Phys. Chem. Solids, 67 (2006) 987–993.

[27] Y. Chao, P. Chen and S. Wang, Adsorption of 2,4-D on Mg/Al-NO_3 layered double hydroxides with varying layer charge density. Appl. Clay Sci., 40 (2008) 193– 200.

[28] S. Wang, C.H. Liu, M.K. Wang, Y.H. Chuang and P.N. Chiang, Arsenate removal from water by Mg/Al-NO_3 layered double hydroxides with varying the Mg/Al ratio. Appl. Clay Sci., 43 (2009) 79–85.

[29] S. Miyata, Physico-chemical properties of synthetic hydrotalcites in relation to compositions. Clays Clay Miner., 28 (1980) 50–56.

[30] T.J.B. Holland and S.A.T. Redfern, Unit cell refinement from powder diffraction data: the use of regression diagnostics. Mineralog. Magazine, 61 (1997) 65–77.

[31] S.M. Auerbache, K.A. Corrado and P.K. Dutta, Handbook of Layered Materials, New York, 2004.

[32] S. Velu, N. Shah, T.M. Jyothi and S. Sivasanker, Effect of manganese substitution on the physic- chemical properties and catalytic toluene oxidation activities of Mg-Al layered double hydroxides. Micropor. Misopor. Mater., 331 (1999) 61–75.

[33] R.M. Smith and A.E. Martell, Critical Stability Constants, London, vol. 4, 1978.

[34] J.E. Huheey, Inorganic Chemistry, Harper Intern. Ed., New York, 1978.

[35] N.A. Adesola Babarinde, O.O. Oyesiku, J. Oyebamiji Babalola and O. Olatunji, Isothermal and thermodynamic studies of the biosorption of zinc (II) ions by *Calymperes erosum*. J. Appl. Sci. Res., 4 (2008) 716–721.