Removal of Methyl Orange from Aqueous Solutions by Using Zn-Al Layered Double Hydroxide as Photocatalyst

Ancuta-Corina Marcu[1], Laura Cocheci[1,*], Paul Barvinschi[2] and Aniela Pop[1]

[1]*Politehnica University of Timisoara, Faculty of Industrial Chemistry and Environmental Engineering, 6 Parvan Blvd, 300223 Timisoara, Romania*

[2]*West University of Timisoara, Faculty of Physics, 4 Parvan Blvd., 300223 Timisoara, Romania*

Abstract: The Zn-Al layered double hydroxide (LDH) was prepared using co-precipitation method at constant pH and characterized from structural point of view. Due to the high concentration of ZnO obtained after LDH calcinations, the material can be used as photocatalyst in removal of organic persistent compounds from water. The photocatalytic activity of the as-synthesized and calcined materials was evaluated for the degradation of Methyl Orange dye under UV irradiation. The influence of calcination temperature, solid: liquid ratio and initial dye concentration on photocatalytic activity of LDH was studied. The increase of calcination temperature and solid: liquid ratio and the decrease of initial dye concentration leads to increasing degradation efficiency.

Keywords: layered double hydroxides, structural characterization, calcination product, photocatalytic activity, dye removal.

1. INTRODUCTION

The layered double hydroxides, also called hydrotalcite-like compounds or anionic clays, have similar structure as hydrotalcite. Hydrotalcite, $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$, first discovered in Sweden around 1842, is a hydroxycarbonate of magnesium and aluminum and it occurs in nature in forms of foliated and contorted plates and/or fibrous masses [1].

The general formula of layered double hydroxides is $[M^{II}_{1-x}\ M^{III}_{x}(OH)_2]^{x+}\ [A^{n-}_{x/n} \cdot mH_2O]^{x-}$, where M^{II} is a divalent cation (Mg^{2+}, Mn^{2+}, Zn^{2+}, Ni^{2+}, Fe^{2+}, Co^{2+}, Cd^{2+}, Cu^{2+} etc.), M^{III} a trivalent cation (Al^{3+}, Fe^{3+}, Ga^{3+}, In^{3+}, Cr^{3+} etc.) and A^{n-} charge compensating anions (NO_3^-, Cl^-, SO_4^{2-}, ClO_4^- etc.).

The decomposition of layered double hydroxides when heated at around 500 °C leads to mixed metal oxides, which are characterized by a high specific surface area and homogeneous dispersion of the metal cations [2]. The mixed metal oxides can take up anions from aqueous solution, resulting in a concomitant reconstruction of the original layered structure, the so-called “memory effect” [3]. Also, the resulting metal oxides have been used as catalysts or catalyst precursors in many processes, such as hydrogenation [1], condensation [4], oxidation reactions [5,6] or polymerization [7,8]. By using this proprieties of layered double hydroxides, a large number of water contaminants can be removed: metal ions (as Cr(VI), Cu^{2+} and Pb^{2+})[9-12], halogenates compounds [13], humic and fulvic acids [14,15], phenolic compounds [16,17], dyes [18-20], resins from pulp industry [21], bacteria and viruses [22].

Azo-dyes constitute the largest dye class being common aquatic pollutants. Normally they are difficult to be removed due to their enhanced non-biodegradability and their presence in aqueous medium. Methyl Orange (MO) is a well known acid-base indicator and can be considered as a model of a series of common azo-dyes used in textile industry.

In this study, a Zn-Al layered double hydroxide was synthesized by co-precipitation under low saturation method and was characterized in order to be used as photocatalyst in removal of persistent organic compounds from water. Due to the high concentration of ZnO obtained after calcinations, the semiconductor property of this oxide has been exploited as catalyst in MO dye removal.

2. EXPERIMENTAL

2.1. Synthesis and Characterization of LDH

The Zn-Al layered double hydroxide was prepared by using a classic procedure, i.e. the co-precipitation method [1]. All used nitrates were commercially purchased from Sigma-Aldrich. A solution of NaOH was slowly added to a 1 mol/L solution of zinc nitrate ($Zn(NO_3)_2 \cdot 6H_2O$), and aluminum nitrate ($Al(NO_3)_3 \cdot 9H_2O$) in distilled water, under magnetic stirring, and that the pH was kept constant by a Hanna HI 991003 pH-meter.

---

*Address correspondence to this author at the Politehnica University of Timisoara, Faculty of Industrial Chemistry and Environmental Engineering, 6 Parvan Blvd., 300223 Timisoara, Romania; Tel: 0040 256 403069;
Fax: 0040 256 403060; E-mail: laura.cocheci@upt.ro

E-ISSN: 2410-3624/14

The mixing step was carried out for 1 h, at room temperature, under stirring conditions, and then for 18 h on an oil bath at 80°C, under reflux and magnetic stirring conditions. The obtained powder was separated by centrifugation and washed several times with demineralized water until pH = 7. This step was followed by drying at 80°C overnight. Then, the dried sample was crushed and sieved and fractions lower than 90 µm were used in experiments. The product was divided in three parts: one was used as-synthesized (Zn-Al-LDH) and the other two were calcined at 300 and 500 °C (Zn-Al-LDH-300 and Zn-Al-LDH-500), with a rate of 5 °C/min for 4 hours.

TG-DSC was performed under an inert atmosphere (nitrogen), from 20 to 500 °C, with a heating rate of 5 °C/min by using a Netzsch analyzer.

Powder X-ray diffraction patterns were recorded on a Bruker D8 Advance diffractometer using MoKα radiation (0.70930 nm).

Surface area and pore volume of the calcined sample (Zn-Al-LDH-500) were determined by N_2 adsorption-desorption at 77 K, using the BET analysis method, with a Micromeritics ASAP 2020 instrument.

2.2. Photocatalytic Experiments

The experiments regarding photocatalysis process were carried out under magnetic stirring at 20 °C into a RS-1 Heraeus photo-catalytic reactor, having a submerged lamp surrounded by a quartz shield. Solutions of 400 mL MO dye at different concentrations containing different catalyst dose were placed in the photoreactor and irradiated with an UV light between 280 and 360 nm. Prior to irradiation, the suspension was stirred in the dark for 30 min to reach the equilibrium. Samples were collected periodically from the reactor, filtered through Milipore filter (pore size of 0.45 µm) and the resulting solutions were analyzed at 460 nm using a Varian Cary 100 UV-Vis Spectrophotometer. A decrease of dye solution absorbance at 460 nm corresponds to degradation of MO polyaromatic rings to create mono substituted aromatics [23]. The pH of all samples was the natural pH of dye solutions (pH = 5 – 6).

3. RESULTS AND DISCUSSION

3.1. Characterization of Zn-Al-LDH Samples

Figure **1** illustrates the XRD pattern for the as-synthesized sample (Zn-Al-LDH) and the calcination products (Zn-Al-300 and Zn-Al-500). The diffractogram shown $Zn_6Al_2(OH)_{16}.4H_2O$ as the main compound of the synthesized material. Besides the layered double hydroxide, impurities coming from the side reactions (ZnO – zincite) were identified. The basal peaks corresponding to (003) and (006) planes, which are typical for layered double hydroxides, were present at low 2θ angle values. In addition, (110) and (113) reflexions occurred at 2θ angles ranging from 25 to 30 °, which is also characteristic of the layered double hydroxides. The diffractogram allowed the calculation of a and c, rhombohedric lattice parameters, where: $a = 2d_{(110)} = 3.08$ Å is cation - cation gap within brucite layer, $c = 3d_{(003)} = 3c' = 23.68$ Å, c' thickness corresponding to one brucite-like layer and one interlayer. By performing calcination at 300 and 500 °C,

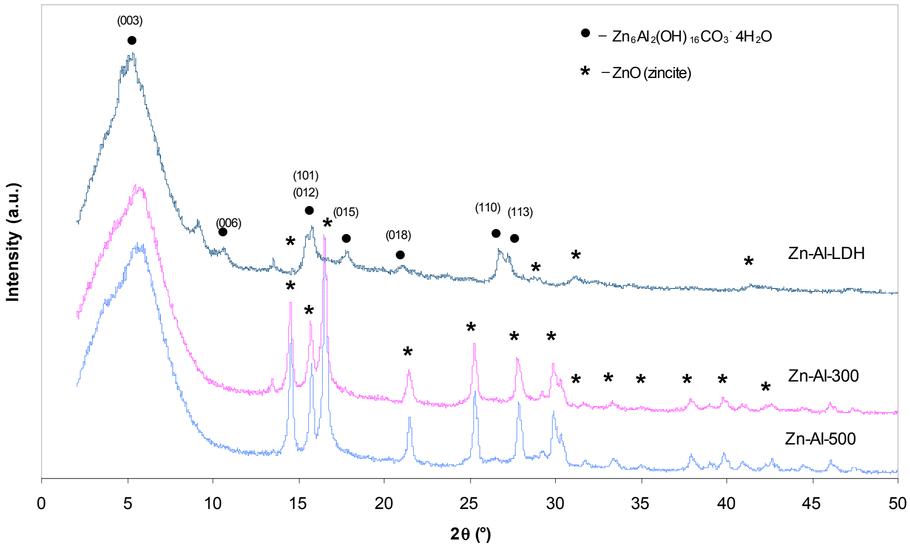

Figure 1: The XRD pattern of the as-synthesized (Zn-Al-LDH) and the calcined samples (Zn-Al-300 and Zn-Al-500).

only a small amount of LDH-like phase remains in the samples, the main compound being ZnO (zincite), crystallised in hexagonal system. The presence of zincite confirms the destroying of the layered structure [17].

During thermal treatment of the material under non-isothermal conditions at a constant rate of 5 °C/min up to 500 °C, two mass loss processes were identified (Figure **2**). The first process occurred within temperatures of 21-200 °C, with maximum rate at 194 °C and mass loss of 20%. The mass loss occurred due to the loss of material humidity and loss of water within the sheets of the layered double hydroxide. The following processes took place at within temperatures of 231 and 500 °C, the mass loss was 10 % and they corresponded to the decarbonatation and dehydroxylation of the material and to the conversion of the double layer into ZnO lattice. Accordingly to the XRD pattern of the calcined products, the ZnO phase has been identified (Figure **1**).

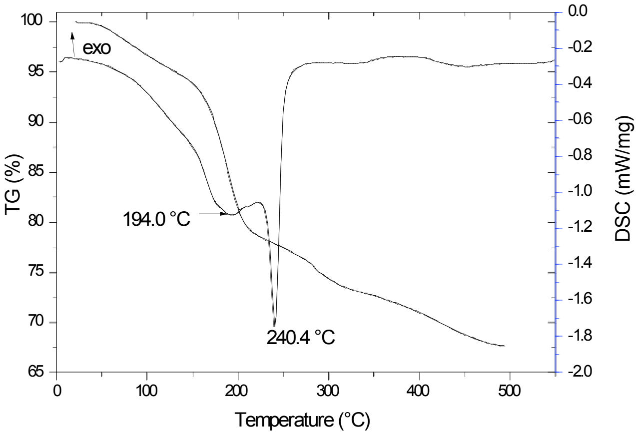

Figure 2: Thermoanalytical curves of the Zn-Al-LDH sample.

The BET surface area of the Zn-Al-500 sample was 32 m^2/g and the pore volume 0.14 cm^3/g. The value of BET surface area are lower that those reported in literature for similar products (mixed metal oxides) obtained by calcination of layered double hydroxides [24], revealing that the calcined products consist mostly of ZnO phase.

3.2. Photocatalytic Degradation

3.2.1. Effect of the LDH Calcination Temperature

The calcination temperature of the layered double hydroxide used as catalyst influences both, the type of process responsible for removing dye from water and process efficiency (Figure **3**).

By applying the as-synthesized (Zn-Al-LDH) material for removing the MO dye from water the main process was adsorption, with 81.9 % efficiency and photocatalysis was inefficient. By using the calcined materials, the adsorption efficiencies were 45.4 % for Zn-Al-300 and 42.0 % for Zn-Al-500 sample, while the photocatalysis efficiencies were 22.1 % for Zn-Al-300 and 37.1 % for Zn-Al-500 sample, respective.

The increased adsorption of the dye on the Zn-Al-LDH surface can be explained by the excellent adsorption properties of layered double hydroxides. The presence of small quantities of ZnO crystals on the surface of the brucite-like layers do not improved the photocatalytic behaviour of the material. By calcination, the efficiency of adsorption process decrease and the efficiency of photocatalysis increase due to the increasing of the quantities of ZnO crystals on the surface of the materials, which have smaller adsorption capacities due to the small surface area. These findings are in contradiction with the literature data [20],

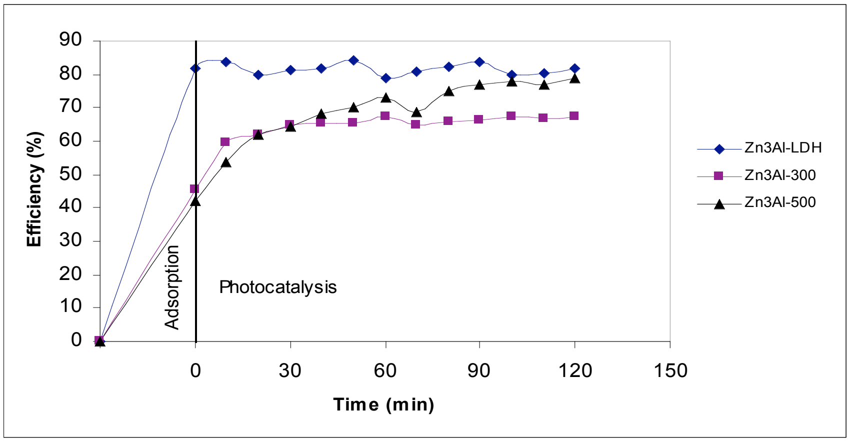

Figure 3: The effect of calcination temperature on dye removal efficiency. Initial dye concentration: 10 mg/L; catalyst dose: 0.5 g/L.

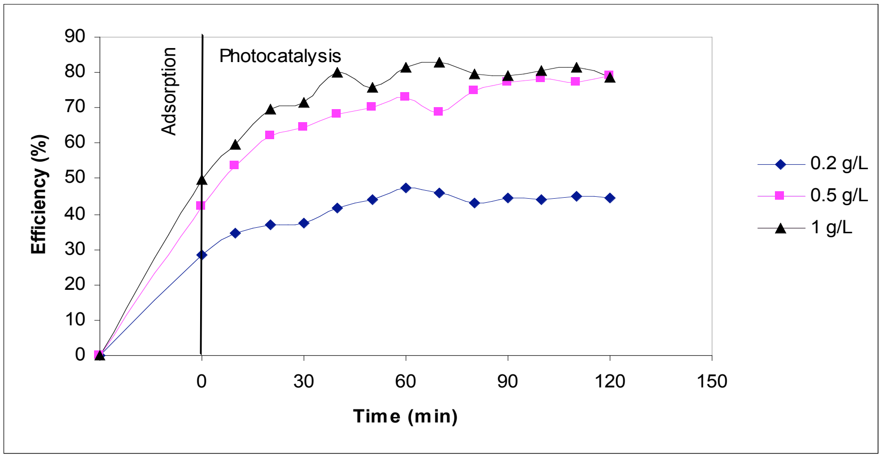

Figure 4: Influence of catalyst dose on MO removal efficiency. Initial MO dye concentration: 10 mg/L.

but are in good agreement with the surface characteristics of the materials used in this study.

3.2.2. Effect of the Catalyst Dose

In order to study the effect of catalyst dose, the degradation of MO was investigated using different catalyst concentration: 0.2 g/L, 0.5 g/L and 1 g/L. The results are presented in Figure **4**. It can be observed that increasing the catalyst concentration from 0.2 to 0.5 g/L, the efficiency of dye removal increased from 44.7 % to 79.1 %. This increasing of efficiency may be attributed to the enhancement of active sites on LDH surface based on increasing of catalyst amount in the dye solution. But doubling the catalyst dose from 0.5 g/L to 1 g/L, after 120 minutes of irradiation, the same efficiency was reached. This behavior may be due to the enhancement of light reflectance by the catalyst and degreasing the light penetration. Other studies reporting similar results under the condition of catalyst excess [25]. Therefore, the catalyst dose of 0.5 g/L was chosen as optimum for an efficient MO removal from water.

3.2.3. Effect of Initial Dye Concentration

The effect of initial dye concentration on dye removal efficiency is presented in Figure **5**. The discoloration efficiency decrease with the increasing of initial dye concentration from 5 mg/L to 50 mg/L.

The photocatalytic efficiency depends on the initial dye concentration based on two aspects: the amount of dye adsorbed on the catalytic surface and the UV light penetrability in the dye solution. The amount of the dye adsorbed on catalyst surface increases with the increasing in dye concentration in relation with the available surface. This behavior enhances the catalytic activity of the photocatalyst. On the other hand, higher concentration of the dye affects negatively the UV light penetrability in the dye solution and the dye molecules may absorb a large amount of light required for the

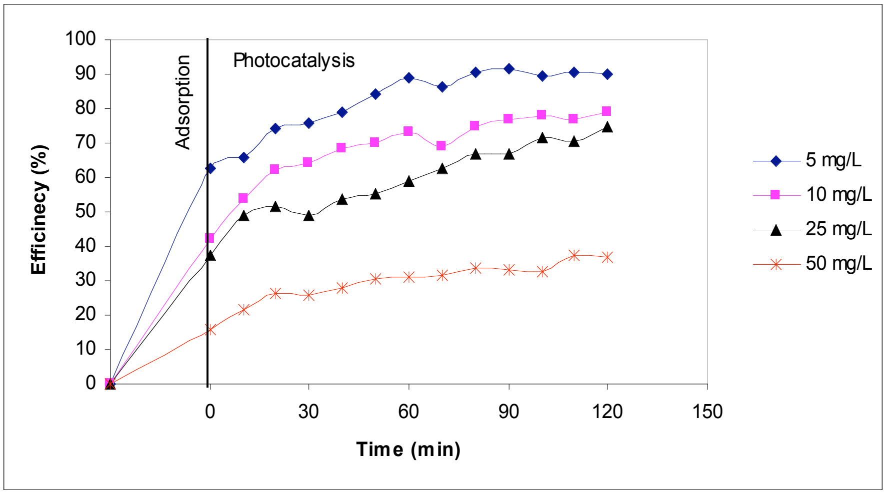

Figure 5: Effect of initial dye concentration on MO removal efficiency.

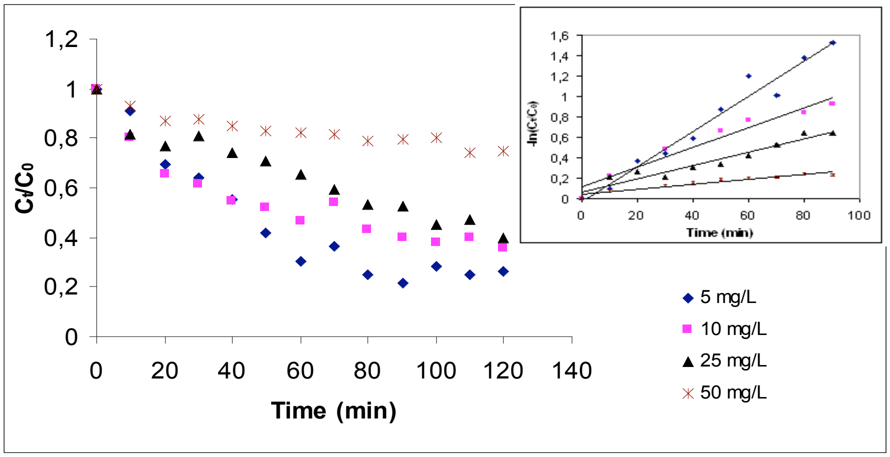

Figure 6: Kinetics of MO dye removal by Zn-Al-500 photocatalyst. Inset: linearization of Eq. (2).

Table 1: Apparent Rate Constants for Different Initial Dye Concentrations

MO Initial Concentration (mg/L)	k_{app} (min^{-1})	R^2
5	0.0172	0.9664
10	0.0097	0.9511
25	0.0065	0.9375
50	0.0024	0.9117

surface of the catalyst irradiation, which reflects in decreasing of dye removal efficiency.

3.2.4. Photodegradation Kinetics

Langmuir–Hinshelwood kinetics is the most commonly used kinetic expression to explain the kinetics of the heterogeneous catalytic processes. The Langmuir–Hinshelwood expression that explains the kinetics of heterogeneous catalytic systems is described by Eq. (1), which can be simplified to a pseudo-first-order equation (Eq. (2)):

$$r = - dC / dt = k \cdot K \cdot C / (1+K \cdot C) \qquad (1)$$

$$\ln (C_0 / C_t) = k \cdot K \cdot t = k_{app} \cdot t \qquad (2)$$

where r is the rate of dye degradation (mg/L·min), k is the limiting rate constant of reaction at maximum coverage under the given experimental conditions, K is the equilibrium constant for adsorption of the substrate onto catalyst, C_0 is the initial dye concentration (mg/L), C_t is the concentration of the dye at time t (mg/L), t is the time of irradiation (min) and k_{app} is the apparent rate constant (min^{-1}).

The apparent rate constant for dye removal, k_{app}, was calculated by linearization the plot of $\ln(C_0/C_t)$ versus time, t, for different initial dye concentration (Figure **6**).

The kinetics results presented in Table **1** shown that the rate of MO dye removal process was better for low initial dye concentration than for higher dye concentrations.

4. CONCLUSIONS

In the present study, a Zn-Al layered double hydroxide was prepared by the co-precipitation method at constant pH and characterized from structural point of view. The structural analysis by X-ray diffraction pointed out that the synthesised material was a layered double hydroxide. By performing calcination at 300 and 500 °C, although the main compound is ZnO (zincite), a small amount of LDH-like phase remains in the samples. The presence of large amounts of zincite allows to use the calcined material as photocatalyst for removal of Methyl Orange dye from water. The photocatalist dose of 0.5 g/L was established as optimal condition for application of the obtained photocatalyst in the MO removal. It has been observed that by decreasing of initial dye concentration, increases the efficiency of the dye removal. The rate of MO dye removal process was better for low initial dye concentration than for higher dye concentrations.

REFERENCES

[1] Cavani F, Trifiro F, Vaccari A. Hydrotalcite-type anionic clays: preparation, properties and applications, Catal. Today 1991; 11: 173-301. http://dx.doi.org/10.1016/0920-5861(91)80068-K

[2] Chang Z, Zhao N, Liu J, Li F, Evans DG, Duan X, Forano C, de Roy M. Cu–Ce–O mixed oxides from Ce-containing layered double hydroxide precursors: Controllable preparation and catalytic performance. J Solid State Chem 2011; 184: 3232-3239. http://dx.doi.org/10.1016/j.jssc.2011.09.035

[3] Lv L, He J, Wei M, Evans DG, Duan X. Uptake of chloride ion from aqueous solution by calcined layered double hydroxides: Equilibrium and kinetic studies. Water Res 2006; 40: 735-743. http://dx.doi.org/10.1016/j.watres.2005.11.043

[4] Kustrowski P, Sulkowska D, Chmielarz L, Olszewski P, Rafalska-Lasocha A, Dziembaj R. Effect of rehydration conditions on the catalytic activity of hydrotalcite-derived Mg-Al oxides in aldilization of acetone. React Kinet Catal Lett 2005; 85: 383-390. http://dx.doi.org/10.1007/s11144-005-0285-3

[5] Takehira K, Shishido T. Preparation of supported metal catalysts starting from hydrotalcites as the precursors and their improvements by adopting memory effect. Catal Surv Asia 2007; 11: 1-30. http://dx.doi.org/10.1007/s10563-007-9016-2

[6] Jimenez-Sanchidrian C, Hidalgo JM, Llamas R, Ruiz JR. Baeyer–Villiger oxidation of cyclohexanone with hydrogen peroxide/benzonitrile over hydrotalcites as catalysts. Appl Catal A 2006; 312: 86-94. http://dx.doi.org/10.1016/j.apcata.2006.06.031

[7] He FA, Zhang LM. New polyethylene nanocomposites prepared by in-situ polymerization method using nickel α-diimine catalyst supported on organo-modified ZnAl layered double hydroxide. Compos Sci Technol 2007; 67: 3226-3232. http://dx.doi.org/10.1016/j.compscitech.2007.04.002

[8] Grafova IA, Grafov AV, Costantino U, Marmottini F, Dias ML. Layered double hydroxides as supports for norbornene addition polymerisation catalysts. Z Naturforsch B: Chem Sci 2003; 58b: 1069-1074.

[9] Carriazo D, del Arco M, Martin C, Rives V. A comparative study between chloride and calcined carbonate hydrotalcites as adsorbents for Cr(VI). Appl Clay Sci 2007; 37: 231-239. http://dx.doi.org/10.1016/j.clay.2007.01.006

[10] Hsu LC, Wang SL, Tzou YM, Lin CF, Chen JH. The removal and recovery of Cr(VI) by Li/Al layered double hydroxide (LDH). J Hazard. Mater 2007; 142: 242-249. http://dx.doi.org/10.1016/j.jhazmat.2006.08.024

[11] Park M, Choi CL, Seo YJ, Yeo SK, Choi J, Komarneni S, *et al*. Reactions of Cu^{2+} and Pb^{2+} with Mg/Al layered double hydroxide. Appl Clay Sci 2007; 37: 143-148. http://dx.doi.org/10.1016/j.clay.2006.12.006

[12] Zhao D, Sheng G, Hu J, Chen C, Wang X. The adsorption of Pb(II) on Mg_2Al layered double hydroxide. Chem Eng J 2011; 171: 167-174. http://dx.doi.org/10.1016/j.cej.2011.03.082

[13] Paredes SP, Fetter G, Bosch P, Bulbulian S. Iodine sorption by microwave irradiated hydrotalcites. J Nuclear Mater 2006; 359: 155-161. http://dx.doi.org/10.1016/j.jnucmat.2006.07.022

[14] Gasser MS, Mohsen HT, Aly HF. Humic acid adsorption onto Mg/Fe layered double hydroxide. Colloids Surf A 2008; 331: 195-201. http://dx.doi.org/10.1016/j.colsurfa.2008.08.002

[15] Vreysen S, Maes A. Adsorption mechanism of humic and fulvic acid onto Mg/Al layered double hydroxides. Appl Clay Sci 2008; 38: 237-249. http://dx.doi.org/10.1016/j.clay.2007.02.010

[16] Pode R, Cocheci L, Popovici E, Seftel EM, Pode V. Degradation of p-Chlorophenol by Advanced Oxidation Processes. Rev Chim 2008; 59: 898-901.

[17] Tzompantzi F, Mendoza-Damian G, Rico JL, Mantilla A. Enhanced photoactivity for the phenol mineralization on ZnAlLamixed oxides prepared from calcined LDHs. Catalysis Today 2014; 220-222: 56-60. http://dx.doi.org/10.1016/j.cattod.2013.07.014

[18] El Gaini L, Lakraimi M, Sebbar E, Meghea A, Bakasse M. Removal of indigo carmine dye from water to Mg–Al–CO_3-calcined layered double hydroxides. J Hazard Mater 2009; 161: 627-632. http://dx.doi.org/10.1016/j.jhazmat.2008.04.089

[19] Auxilio AR, Andrews PC, Junk PC, Spiccia L. The adsorption behavior of C.I. Acid Blue 9 onto calcined Mg–Al layered double hydroxides. Dyes Pigm 2009; 81: 103-112. http://dx.doi.org/10.1016/j.dyepig.2008.09.011

[20] Seftel EM, Popovici E, Mertens M, De Witte K, Van Tendeloo G, Cool P, Vansant EF, Zn–Al layered double hydroxides: Synthesis, characterization and photocatalytic application. Micropor Mesopor Mat 2008; 113: 296-304. http://dx.doi.org/10.1016/j.micromeso.2007.11.029

[21] Michalik A, Serwicka EM, Bahranowski K, Gawel A, Tokarz M, Nilsson J. Mg,Al-hydrotalcite-like compounds as traps for contaminants of paper furnishes. Appl Clay Sci 2008; 39: 86-97. http://dx.doi.org/10.1016/j.clay.2007.04.012

[22] Jin S, Fallgren PH, Morris JM, Chen Q. Removal of bacteria and viruses from waters using layered double hydroxide nanocomposites. Sci Technol Adv Mat 2007; 8: 67-70. http://dx.doi.org/10.1016/j.stam.2006.09.003

[23] Al-Qaradawi S, Salman R. Photocatalytic degradation of methyl orange as a model compound. J Photoch Photobio A: Chem 2002; 148: 161-168. http://dx.doi.org/10.1016/S1010-6030(02)00086-2

[24] Balsamo N, Medieta S, Oliva M, Eimer G, Crivello M. Synthesis and characterization of metal mixed oxides from Layered Double Hydroxides. Procedia Mater Sci 2010; 1: 506-513. http://dx.doi.org/10.1016/j.mspro.2012.06.068

[25] Soutsas K, Karayannis V, Poulios I, Riga A, Ntampegliotis K, Spiliotis X, *et al*. Decolorization and degradation of reactive azo dyes *via* heterogeneous photocatalytic processes. Desalination 2010; 250: 345-350. http://dx.doi.org/10.1016/j.desal.2009.09.054

Received on 26-11-2014 Accepted on 06-12-2014 Published on 10-01-2015

DOI: http://dx.doi.org/10.15377/2410-3624.2014.01.02.1