IRON CONTAINING LAYERED DOUBLE HYDROXIDES: STRUCTURAL, TEXTURAL PROPERTIES AND APPLICATIONS AS CATALYSTS IN DECOLORIZATION OF SOME WATERS BY HETEROGENOUS OXIDATIVE PROCESSES

BY

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Abstract. The paper presents a laboratory study of the structural, textural properties of double layered hydroxides containing iron together with their preliminary experimental applications in some advanced processes of heterogenous catalytic oxidation with hydrogen peroxide applied for water resources loaded with organic Orange 16 dye. The influence of different operational variables (*i.e.* stirring regime, pH, H_2O_2 concentration, concentration of catalyst based on layered double hydroxides containing Fe(III)/Fe(II), dye concentration, oxidation time) was experimentally studied in order to find the best values for high decolorization efficiency. A laboratory scale set-up decolorization experiment was performed for these values of the studied variables in the case on an effluent loaded with 80 mg/L Orange 16 dye. The highest decolorization efficiency (> 70 %) was performed at pH (1.8), continuous stirring regime (50 rpm), temperature of 19-20°C, with 0.176 M H_2O_2, 1.2 g catalyst/L, and after 30 min of advanced heterogenous oxidation.

Key words: layered double hydroxides containing iron (FeLDH), azo dye, decolorization, heterogenous advanced oxidation process.

1. Introduction

The decolorization of the industrial effluent is essential for reuse of dyeing water resources or safe discharge into different receiver basins (*i.e.* different emissaries or urban sewerage system) even when dyes are released in small concentrations. The dye removal from different water resources is an important problem that must be solved with reduced reagents consumption, energy consumption and reduced over-all treatment costs.

Progress in the removal of some industrial dyes considered as important bio-refractory compounds has lead to the development of advanced oxidation processes (AOPs) [1],…,[3]. Among these processes, there can be distinguished the homogenous and heterogenous advanced oxidation processes.

The main disadvantages of homogenous advanced oxidations is the tight range of pH in which the reaction proceeds and also the need for recovering of precipitated catalyst after dyeing water resource treatment. These disadvantages can be resolved if are used some efficient heterogenous materials as catalysts (*i.e.* zeolites, modified zeolites, hydroxides double layered containing iron etc.) [4],…,[6].

Some catalysts based on zeolites with ferrous or ferric ions in composition together with hydrogen peroxide can be efficiently used into the dye decomposition process, based on reaction between Fe(II), Fe(III) and hydrogen peroxide with HO• generation. The mechanism is similar with the action of "Feroxide process" [5], [6]. The decomposition compounds after the catalytic wet hydrogen peroxide dye oxidation were intermediate compounds as amines, organic acids (*i.e.* oxalate acids, etc.) and inorganic compounds as, carbonates, nitrates, sulphates, etc.

The objective of the present work is the evaluation of the catalytic performances of a layered double hydroxide containing iron (FeLDH) into the heterogenous advanced oxidation of some textile Orange 16 dye solutions or synthetic textile effluents containing this type of azo dye. The main laboratory analyses performed for the description of structural and textural properties were presented in order to understand their structure and action mechanism as heterogenous catalyst into a water resource treatment. All experiments were performed at laboratory scale set-up. The pH, H_2O_2 concentration, catalyst concentration and oxidation time are the basic chosen factors that were studied to find their influences against the decolorization efficiency, in condition of delivering the treated effluent into aquatic environment or inside reuse.

2. Experimental

2.1. Materials and Reagents

The layered double hydroxides containing iron (FeLDHs) are represented by the empirical formula $[M^{(II)}_{1-x}M^{(III)}_x(OH)_2]^{x+} (A^{n-})\cdot mH_2O$, and are considered as synthetic anionic clays with brucite $[Mg(OH)_2]$-like layers in which some of the divalent cations (*e.g.*, Fe^{2+}, Mg^{2+}, etc.) have been replaced by trivalent ions (*e.g.*, $Fe^{3+,}$ etc.). These FeLDHs were prepared and characterized as new solid materials, and are not yet as final homologated commercial products. The principal characteristic data of synthesis applied for these LDHs containing iron (FeLDHs) are: (i) use of a synthesis method based on coprecipitation, and (ii) the principal basic used reagents were hydrotalcite -

anionic clay, brucite, ferric nitrate, and ferrous sulphate. The principal structural and textural proprieties were determined using X-ray diffraction (XRD) and scanning electron microscopy (SEM) [7], [8]. There were used between 0.02-5 g FeLDH per each sample of 50 mL containing Orange 16 dye.

The studied azo dye, Orange 16, is a commercially available textile dye used without further purification. The chemical formula of this azo dye is $C_{20}H_{16}N_3O_{11}S_3Na_2$ (C.I. 17757) and has the following properties: molecular weight (MW) of 617.54 g/mol; solubility at 293 K of 70 g/L; maximum absorbance (λ_{max}) at 495 nm and purity of 80.90%. Working solutions (in concentrations of 30-150 mg/L) were prepared by appropriate dilution with bidistilled water of the stock dye solution (600 mg/L).

The hydrogen peroxide (30%) of analytical grade was obtained from S.C. Nordic Invest S.R.L. Company (Cluj Napoca, Romania).

All the other solutions were used for pH adjustment (*i.e.* H_2SO_4 0.5N and NaOH 0.1N).

2.2. Apparatus and Heterogenous Catalytic Advanced Oxidation Procedures

The characterisation of the synthetized FeLDH used in this paper as heterogenous catalyst into some advanced oxidation processes of aqueous systems containing Orange 16 dye was done by different analytical analysis measurements: X-ray diffraction (XRD) with a Shimadzu XRD-6100 diffractometer using monochromatic CuKα radiation, and scanning electron microscopy (SEM) with a Mira II Tescan Emission Scanning Electron Microscope.

The heterogenous advanced oxidation of Orange 16 dye was carried out into a 300 mL glass reactor equipped with magnetic stirrer (AG-2) and thermostatically stabilized. Different quantities of solid tested FeLDH were introduced into 50 mL of aqueous dye solution, under continuous stirring. After temperature stabilization at 19-20°C and correction of pH, different volumes of 30% H_2O_2 solution were added to achieve the selected H_2O_2 concentrations and selected H_2O_2/dye ratio, these being the basic conditions for the experimental tests. The moment when hydrogen peroxide was added into solution was considered the beginning of the heterogenous advanced oxidation experiment (zero time). Samples of ca 5 mL were collected from reactor at different specific time intervals and analysed in order to find the dye and colour removal progress. Into each collected sample, the hydrogen peroxide was removed by increasing pH value to basic interval (pH 9-10) with NaOH 2N solution and adding of solid MnO_2.

The dye absorbance and colour were measured using a SP 830 Plus spectrophotometer, Metertech Inc. The visible light absorbance at the characteristic wavelength of dye, *i.e.* 495 nm, was measured to follow the progress of the dye removal during heterogenous advanced oxidation process

(HeAOP). Colour determination was done by measuring the absorbance at $\lambda = 456$ nm using the distilled water as reference sample or at one of the standard wavelengths (*i.e.* 436, 525 and 620 nm; obligations are for absorbance measurement at 436 nm for all types of wastewaters).

The pH measurements were performed at a HACH One-Laboratory pH-meter (Hach Company, USA).

The decolorization degree or dye removal (*i.e.* AOP treatment degree) was expressed with the general formula of a treatment degree for dye or colour (eq. 1).

$$(1) \qquad\qquad DD = \frac{C_0 - C_t}{C_0} \cdot 100, \ [\%]$$

where: *DD* is the decolorization degree, [%]; C_0 – the initial dye concentration into the initial analyzed sample, [mg/L]; C_t – the dye concentration at *t* oxidation time, [mg/L].

3. Results and Discussions

3.1. The structural and Textural Properties of FeLDHs

The layered double hydroxides (LDHs) are based on hydrotalcite (*i.e.* anionic synthetic clay) and brucite $[Mg(OH)_2]$-like layers in which some of the divalent cations have been replaced by trivalent ions. The cationic layers are bound together by the interlayer counter anions as well as by water molecules (Fig. 1).
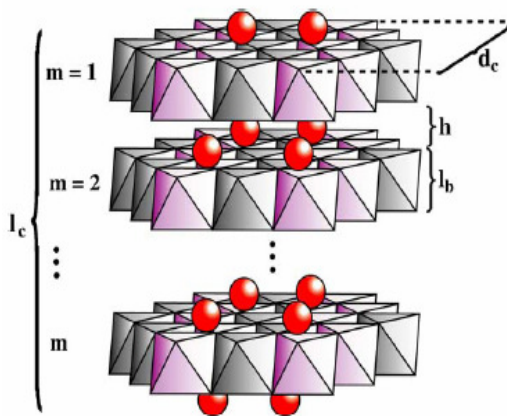

Fig. 1 − Schematic view of the LDH layers.

The Structural and Textural Characterisation of the Tested FeLDHs

X-ray diffraction (XRD) analysis. Fig. 2 presents the XRD pattern of Fe/Fe LDH sample.
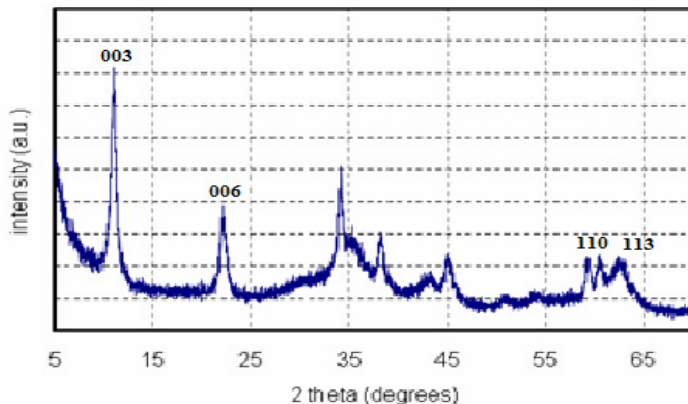

Fig. 2 − XRD patterns of Fe/Fe LDH.

The pattern exhibits sharp and symmetric reflections for the (003), (006) basal planes and for the (110) and (113) non-basal planes. The sharp and intense peaks demonstrate that the sample has a very high crystallinity. The decrease of the parameter *a* (distance between metallic ions) for the FeLDH sample clearly indicates the incorporation of iron into the brucite-like layer, as the ionic radius of Fe^{2+} is 0.61 Å. The decrease of the parameter *c* (interlamelar distance) and the d_{003} (basal spacing) can be attributed to the modified electrostatic interactions between the layer and the interlayer network when another metal is introduced in the LDH layer. The XRD results demonstrate the incorporation of iron in the LDHs network.

Scanning electron microscopy (SEM) analysis. The scanning electron microscopy gives information about the textural properties of the FeLDH sample. The SEM image (Fig. 3) shows that the sample is highly crystalline, the formed particles are hexagonal-shaped and interconnected with each other.

The average value of the particle size is about 70 nm for these FeLDH samples.

The textural properties of the hydrotalcite-like material are strongly influenced by the synthesis conditions.

The different pH values, the distinct nature, the electronegativities of the ions presented in the synthesis medium, and the different concentrations of the starting solutions could be important factors to determine the changes of the textural properties of the Fe/Fe LDH sample.
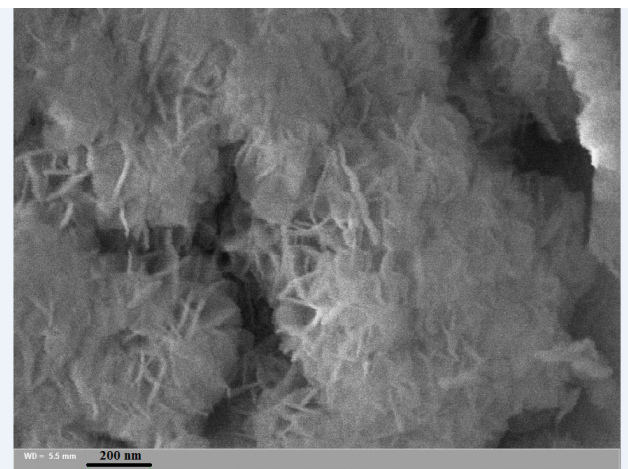
Fig. 3 − SEM micrograph of Fe/Fe LDH.

3.2. Heterogenous Advanced Oxidation Treatments. FeLDH Catalytic Applications Into Treatments of Aqueous Systems Containing Orange 16 Dye

Some kinetic experiments were performed in order to find the performance of FeLDHs as solid catalyst into a HeAOP applied for decomposition of Orange 16 dye from aqueous systems or decolorization of aqueous effluents. It was worked into the same operational conditions concerning the stirring regime (*i.e.* continuous stirring, 50 rpm), temperature (*i.e.* 19-20°C), and order of reagents addition. The main problem is to find the adequate pH value for high dye removal and comparison with the pH of other HeAOPs. In general, the advanced oxidation with hydrogen peroxide of some dyes is accelerated by the catalytic action of some cationic species as Fe^{2+}, Fe^{3+}, Al^{3+}, Cu^{2+}, etc. that can be leached from the solid heterogenous catalyst. There are formed hydroxyl radicals that can react with organics or with cationic species at high acidic pH (1-3) or low acidic pH (5-6) [1],…,[6]. At pH of 7, some active species are presented and able to establish an effective redox system with H_2O_2. The oxidation products are usually low molecular weight oxygenated compounds that are easily biodegradable or, in some instances, the organic compounds reduce to carbon dioxide and water.

Some solid catalysts can leaching into solution some cationic ions from their internal mesoporous structure only at high acidic pH value (1-3) and accelerates the decomposition of colored effluents only into high acidic medium or at low acidic medium with fulfillment of legislative and agreed demands for final effluent discharges or reuse (*i.e.* pH values of 6.5-8.5) [4].

a) *The Influence of pH*

The scientific literature indicates that into the experiments performed with homogenous iron species as catalyst (*i.e.* different types of Fenton processes) the oxidation rate depends strongly of pH value [1],…,[6]. Contrarily, the heterogenous catalyst remains active even at neutral pH, having different behavior comparison with the homogenous ferrous or ferric catalyst because of mesoporous structure with Fe cations inside.

The distribution of iron species in the structure of FeLDH is not completely elucidated, but it is believed that different iron ions appear into solution and act as catalysts into the advanced oxidation with hydrogen peroxide. The performance of this catalyst-FeLDH will depend on the iron or other cationic species released or not in solution, but also on the dye content and hydrogen peroxide concentration added into the aqueous sample.

In the case of Orange 16 dye degradation, the effect of pH is presented in Fig. 4 as a result of the kinetic studies of HeAOP performed into solutions with 80 mg/L dye, 1.2 mg/mL FeLDH, 0.176 mM H_2O_2, under continuous stirring (50 rpm) for 120 min.
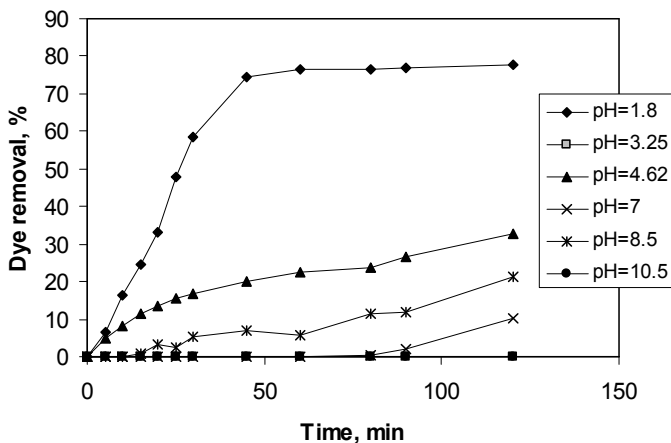

Fig. 4 – The influence of pH on dye HeAOP process.

It is observing that in high acidic conditions (1-2), there were performed the highest HeAOP efficiencies for dye removal (*i.e.* > 74.30% after 45 min of HeAOP, and > 58.60% after only 30 min). The adequate pH range for Orange 16 decomposition by HeAOP with H_2O_2 in the presence of FeLDHs is 1.8, and permits a maximal dye removal of 80% after 120 min (but it is necessary a neutralization step before direct discharge of treated effluent into different receiver basins).

b) *The Influence of H_2O_2 Concentration*

There were performed kinetic experiments of heterogenous advanced oxidation into aqueous systems with 80 mg/L dye, 1.2 mg/mL FeLDH, pH of 1.8, temperature of 19-20°C, under continuous stirring (50 rpm) for 120 min. The experimental results were synthesized into Fig. 5 and indicate that higher H_2O_2 concentrations than 0.353 M H_2O_2 produce no increasing of dye removal and an inhibitory effect can appear.
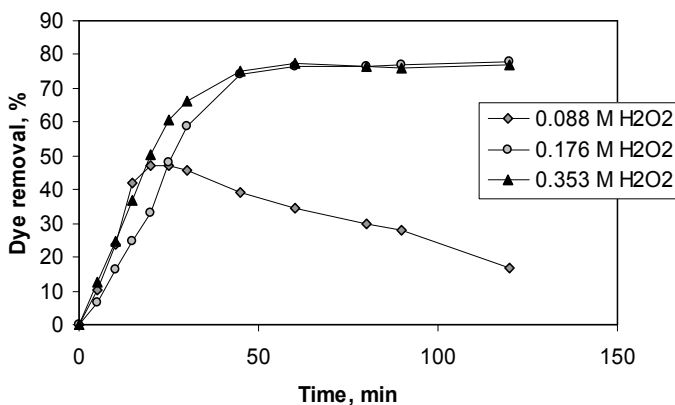

Fig. 5 – The influence of H_2O_2 concentration on dye HeAOP.

The adequate H_2O_2 concentration for Orange 16 decomposition by HeAOP with hydrogen peroxide in the presence of FeLDH must be between 0.176-0.353 M H_2O_2 for an effluent loaded with 80 mg/L dye at pH of 1.8 and normal room temperature (*i.e.* the best value of H_2O_2 concentration was of 0.353 M H_2O_2).

c) *The Influence of FeLDH Concentration*

There were performed kinetic experiments of HeAOP into aqueous solutions with 80 mg/L dye, 0.176 M H_2O_2, pH of 1.8 and 4.62, under continuous stirring (50 rpm) for 120 min.

The experimental results were presented into Figs. 6 and 7 and indicate a reaction rate of dye oxidation that increases with catalyst concentration.

The adequate FeLDH concentration for Orange 16 decomposition by HeAOP after 120 min must be between 1.2 – 2.4 mg/mL for an effluent loaded with 80 mg/L dye at pH of 1.8 and normal room temperature (*i.e.* the best value of FeHDL concentration was of 1.2 mg/mL, and the decolorization degree was of 80% after 120 min of dye HeAOP).
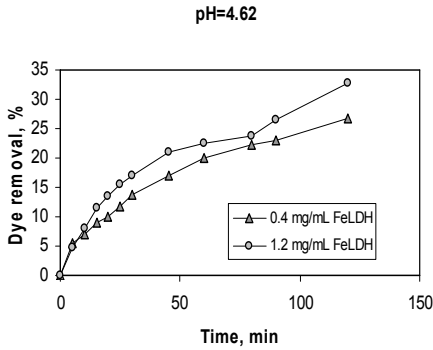
pH=4.62

pH=1.8

Fig. 6 – The influence of FeLDH concentra-
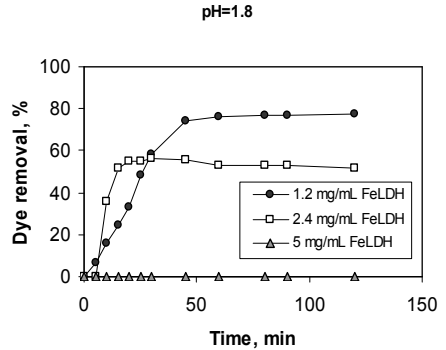tion on dye HeAOP (high acidic pH).

Fig. 7 – The influence of FeLDH concentra-
tion on dye HeAOP (low acidic pH).

The treated effluent is possible and legal admissible into different receiving basins or urban sewerage system having admissible values of total iron concentration < 1 mg/L, but a supplementary step of neutralization is obvious necessary (*i.e.* neutralization with lime or sodium hydroxide or carbonate).

d) *The Influence of Dye Concentration*

The same operational methodology was applied for other kinetic experiments having similar basic operational conditions: pH of 1.8, 0.176 M H_2O_2, 1.2 mg/mL FeLDH, continuous stirring (50 rpm), and final oxidation time of 120 min. The results are presented into Fig. 8.
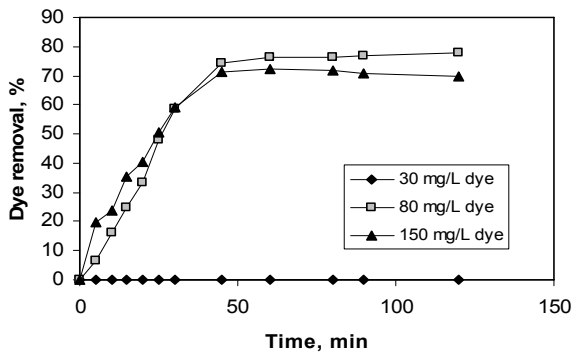

Fig. 8 – The influence of dye concentration on dye FO process.

It is attempt that for constant FeLDH and H_2O_2 concentrations, the dye oxidation degree decreases with the increasing of dye concentration. This HeAOP is better to be applied for relatively high loads of dyeing effluents. The

higher part of dye is rapidly destroyed in the first 60 min.

e) *The Influence of Oxidation Time*

The effect of oxidation time vs. HeAOP efficiency or dye removal can be observed into each of the Figs. 3,…,8. After only 30 min of HeAOP process, there were performed dye oxidation degrees higher than 70% at high acid pH (1.8). The higher part of dye is rapidly destroyed in the first 45 min.

The remained concentration of dye is slowly transformed into the rest oxidation time. In general, can be concluded that the HeAOP process of textile Orange 16 dye degradation takes place with higher efficiency into the first 60 min, and must be monitoring dye decomposition no more than a time period of 120 min.

4. Conclusions

The experimental results of a preliminary laboratory study of some heterogenous advanced oxidation process (HeAOP) with hydrogen peroxide in the presence of layered double hydroxides containing iron (FeLDH) as catalysts was presented for aqueous systems containing Orange 16 dye.

The layered double hydroxides containing iron (FeLDHs) were characterized by X-ray diffraction and scanning electron microscopy (SEM).

The influence of pH, H_2O_2 concentration, FeLDH concentration, dye concentration and oxidation time were analyzed in order to get the optimal variation field for high dye removal efficiencies.

High decolorization efficiencies (*i.e*. 70% after 120 min of HeAOP, temperature of 19-20°C) were performed at pH (1.8), continuous stirring regime (50 rpm), with 0.176 M H_2O_2 and 1.2 mg/mL FeLDH.

Additional laboratory studies will be performed in order to clarify the catalytic action of FeLDHs into heterogenous advanced oxidation processes with H_2O_2 applied for aqueous systems containing Orange 16 dye.

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HIDROXIZI DUBLU LAMELARI PE BAZĂ DE FIER: PROPRIETĂŢI STRUCTURALE, TEXTURALE ŞI APLICAŢII CATALITICE ÎN DECOLORAREA UNOR APE PRIN PROCESE OXIDATIVE ETEROGENE

(Rezumat)

Lucrarea prezintă un studiu de laborator privind proprietăţile structurale, texturale şi aplicaţiile experimentale preliminare ale hidroxizilor dublu lamelari conţinând fier în procese catalitice de oxidare eterogenă avansată cu apă oxigenată a unor ape încărcate cu colorant organic Orange 16. A fost studiată experimental influenţa diferitelor variabile operaţionale (*i.e.* regimul de agitare, pH-ul, concentraţia de H_2O_2, de catalizator pe bază de hidroxizi dublu lamelari conţinând Fe(III)/Fe(II), de colorant, timpul de oxidare) în vederea găsirii celor mai bune valori pentru eficienţe mari de decolorare. Un experiment de decolorare la scară de laborator a fost realizat cu aceste valori propuse în cazul unui efluent încărcat cu o medie de 80 mg/L colorant Orange 16. Cea mai mare eficienţă de decolorare (*i.e.* > 70%) a fost obţinută la pH (1,8), agitare continuă (50 rpm), temperatură de 19-20ºC, cu 0,176 M H_2O_2, 1,2 g catalizator/L şi după 30 minute de oxidare avansată.