

Catalytic Wet Oxidation of Phenol with Hydrogen Peroxide over Modified Clay Minerals

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Phenol oxidation was investigated through Fenton-like reaction, using iron-pillared clay minerals. The influence of the specific surface area was examined using three commercial clay materials: sodium-bentonite (37.5 m²/g), KSF montmorillonite (106 m²/g) and K10 montmorillonite (240 m²/g). Experimental results show that chemically modified clays, bentonite type, presented a higher catalytic activity in Fenton like processes than chemically modified clays type KSF and K10 montmorillonite. By testing the derived catalyst from sodium bentonite, a 100 % phenol conversion was obtained after 50 minutes. The other two catalysts derived from KSF and K10 montmorillonite led to a 98 % respectively 28 % phenol conversions.

Keywords: Iron pillars, montmorillonite, phenol; Fenton, catalytic oxydation

Phenols and derivatives are well known to be hazardous pollutants that produce negative environmental impact via harmful interaction with fauna and flora. Phenols display increased toxicity in media with low oxygen concentration, increased alkalinity and relatively high temperature [1]. Complete elimination of such compounds in wastewaters has become one of today's major issues to be addressed. So far, photocatalytic decomposition process [2,3] have shown limited performances. An essential requirement for an effective oxidation process of such by-products resides in their thorough mineralization into carbon dioxide [4,5].

Promising performances have been obtained by solid catalysts like ion-exchanged montmorillonite [6,7], activated carbon [8], alumina alone [9] or combined with CuO [10], or TiO₂ [2,3]. Y-type zeolite ion-exchanged with transition metals showed appreciable effectiveness in phenol hydroxylation [11] and wastewater oxidative treatment [12]. Fe(II)-Fe(III)/H₂O₂ systems are effective Fenton catalytic combinations in wastewater oxidation, owing to the formation of reactive radicals [13].

In heterogenous oxidation process, the extent of the specific surface, the structure of the solid surface and porosity are expected to play keyroles. When dealing with porosity, clay minerals [14-17] turn out to be more interesting than zeolites, thanks to their expandable structures devoid of pore size limitations. That is why a special interest was devoted to lamellar clay mineral like montmorillonite, which possess lamellae with two reactive faces. When intercalated or pillared with bulky species, montmorillonite could display interesting catalytic features. Intercalation usually occurs through a mere physical impregnation with a solution containing the intercalating species (polyhydroxycations). Pillaring, instead, could be achieved via in-situ or ex-situ procedures. The first route

involves pillar synthesis within the very interlayer space by contacting the clay mineral with the reactants [18]. The second one involves a previous step of pillar synthesis, which will be further contacted with the clay mineral suspension. The in-situ procedure appears to be more interesting, requiring shorter reaction times. Microwave aging allows to shorten the pillaring process [19]. Clays mineral have extensively been used in environmental applications, more particularly as molecular sieves, selective adsorbents [20]. PILCs, instead, have scarcely been employed in similar purposes, and even less as catalysts for removing the organic matter from wastewaters [21]. Clay pillaring with iron based pillars could be a judicious way to achieve similar catalytic activities as those obtained in conventional Fenton processes, or even higher. That is why the present work was undertaken. In this study, montmorillonites K10 and KSF were selected as starting clays for the preparation of PILC catalysts for phenol oxydation. For this purpose, phenol oxidation was studied through Fenton reaction, using iron-pillared clay minerals. The influence of the specific surface area was examined using three commercial clay materials. The catalyst effectiveness was discussed herein in terms of properties and magnitude of the specific surface area.

Experimental part

Materials and solution preparation

Three commercial clay materials provided by Sigma-Aldrich were used in the present study, namely sodium-bentonite (37.5 m²/g), KSF montmorillonite (106 m²/g) and K10 montmorillonite (240 m²/g). KSF and K10 were fully ion-exchanged into Na-forms by repeated impregnations in a fresh 2M NaCl solution in a solid-liquid phase volume ratio of 1:50, at 353 K for 3 hrs. The ion-exchanged samples

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were then filtered through centrifugation, and further air-dried overnight at 333 K. Sodium-bentonite did not require ion-exchange, being already supplied in its original Na-form.

Aqueous solutions containing of Fe polyhydroxycations were prepared by adding dropwise, under vigorous stirring at room temperature, a 0.2 M NaOH solution to a 0.2 M FeCl₃ solution with an OH/Fe mole ratio of 2.2. Besides, an aqueous solution containing 250 mg of phenol (Merck, analytical grade) in 1 liter of distilled water was prepared.

Clay pillaring

Two pillaring methods were used. In the ex-situ procedure, the pillaring agent was previously synthesized by mixing 0.2 M NaOH (A) and 0.2 M FeCl₃ (B) solutions, and the resulting mixture was then added dropwise to a 2 wt % aqueous clay suspension. In the in-situ route, both the 0.2 M NaOH and 0.2 M FeCl₃ solutions were simultaneously added dropwise to a 2 wt % aqueous clay suspension, with a rigorous pH control. (Here, for preventing from iron precipitation it was prepared using a molar ratio OH/Fe of 2.2.) The final mixture containing 4 mmol Fe⁺³/g clay was then stirred for 1 h at room temperature. In both methods, the final step involves the very pillaring process, and was carried out upon heating at 333 K for 3 h. The pillared clay mineral was further separated through decantation, and then aged during 10 minutes under microwave exposure. The final product was repeatedly washed with distilled water till the total disappearance of Cl⁻ anions. The latter were detected by means of a 0.1 M AgNO₃ solution. The clay material was recovered by filtration, and then dried stepwise at a rate of 1 h at each of the following temperatures: 313, 333, 353, 373 and 393 K. The dried powder was calcined during 2 h at 673 K.

Characterization

The final pillared clay samples were fully characterized through X-ray diffraction with a Siemens model D 5000 instrument (Ni filter, CuK α at $\lambda = 0.15401$ nm), thermogravimetry (TG-DTG) by means of a Mettler Toledo TGA-SDTA851e (under nitrogen stream at a 20 mL/min throughput, heating rate of 5K/min, sample weight of 4÷6 mg, temperature range of 293-1273 K, error on temperature of 0,01 K), Fourier transform Infrared spectroscopy (FTIR Bruker Tensor 27) and energy dispersion by X-ray analysis (EDX) using an EDAX device coupled to a Philips XL 30 SEM equipment. The specific surface area was determined through BET method, using nitrogen adsorption at 77K and a Quantachrome Autosorb-1-MP surface area and porosity analyzer.

Phenol oxydation attempts

Batch attempts of phenol oxydation were run in a 500 mL glass reactor under vigorous and continuous stirring at normal pressure and a controlled temperature of 298 K. pH was adjusted accordingly at the required value (2.5; 3.5; 4.5; 5.5; 7), using suitable amounts of 0.1 N HNO₃ and/or 0.1 N NaOH. A hydrogen peroxide (H₂O₂) solution was mixed to a phenol solution (250 mg/L) in stoichiometrical proportions at a H₂O₂/phenol mole ratio of 14:1. Various solid:liquid phase ratios (0; 2.5; 5.0; 10; 15 and 20 g/L) and H₂O₂/phenol ratios (10; 14, 20 mol/mol) were investigated. The evolution time of the oxydation process was studied through periodical measurements of the phenol index by spectrophotometry using a Thermo Spectronic Genesys 20 instrument and 4 - amino - antipyrine (Determination of phenol index in water ISO 6439:1990).

Results and discussions

The higher value of the SiO₂:Al₂O₃ mass ratio for K10 montmorillonite (4.17) as compared to KSF montmorillonite (3.94) is due to Al removal on acid treatment. The contents in the two other major elements, namely K₂O and Fe₂O₃, were of ca. 1.6 and 4.7 wt % for K10 montmorillonite and of 1.0 and 5.0 wt % for KSF montmorillonite, in agreement with other data [22]. Besides, EDX analysis of the all the pillared clay samples revealed a high iron content and a total disappearance of calcium, sodium and potassium. For instance, the iron content raised from 3.22 to ca. 19 wt % after Na bentonite pillaring through the ex-situ procedure.

Specific surface area and clay sheet arrangement

Pillaring is strongly depending on the nature of the initial exchangeable cation of the starting material. Na⁺-exchanged montmorillonite is usually employed in most cases, because of its higher dispersibility in water, facilitating intercalation of the pillaring species by cation exchange. The occurrence of the pillaring process is supported by the broadening of the 001 XRD reflexion (fig. 1). This is a precise index of a transition from an almost uniform face-to-face arrangement to a disordered structure with various orientations of the clay sheets. The residual peak of the 001 reflexion at 9.0 - 9.5 degrees suggests a low ex-situ pillaring grade due a partial delamination the clay mineral.

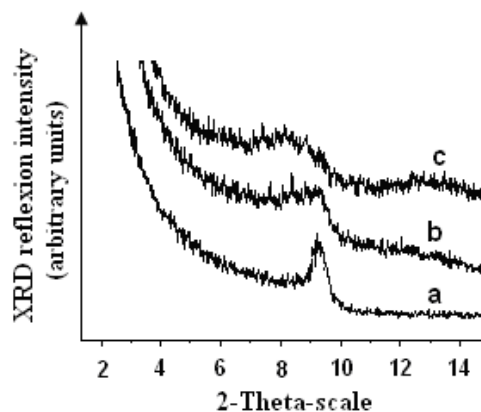


Fig. 1. 001 XRD reflexion of Na-bentonite before (a) and after ex-situ (b) and in-situ (c) pillaring procedure.

The in-situ pillaring gave an even more disordered structure. This random arrangement of the clay sheets and the increase in the basal d_{001} spacing up to 14-16 Å indicate the presence of a wide size variety of intercalated chemical species [23,24]. A first overview of the BET measurements presented herein showed significant improvement of the specific surface area (S_A) by clay pillaring. For Na-bentonite, S_A increased from 37.5 to 70 and even 140 m²/g through the in-situ and ex-situ procedures respectively. Similarly, K10 and KSF samples showed similar behaviour by pillaring, in as much the in-situ pillaring gave lower S_A values (83 and 101.2 m²/g, respectively) as compared to the ex-situ procedure (210 and 232 m²/g, respectively).

This indicates that the presence of compact lamellar structure in the in-situ procedure did not favour the total conversion of Fe⁺³ cations into polyhydroxycations, in agreement with previous data [25]. This must be to a competitive ion-exchange with Fe⁺³ cations, resulting in strong sandwiching effect effect that hinders full clay exfoliation. Unlike KSF, the K10 displayed appreciable specific surface area (240 m²/g), presumably due to its higher microporosity, as reported for saponite [26]. This

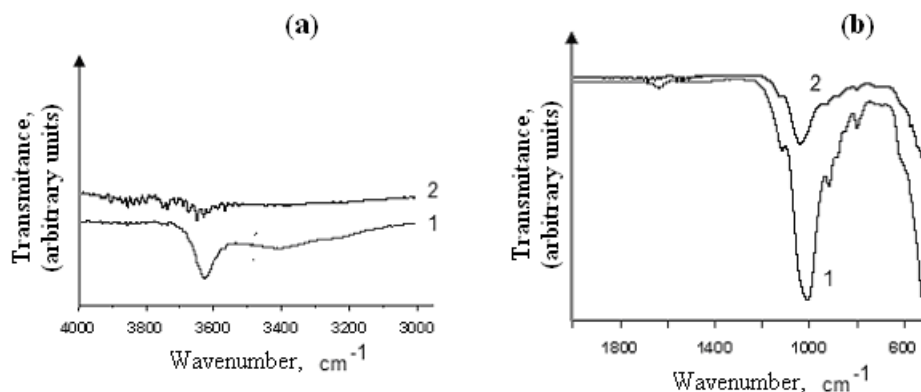


Fig. 2. FTIR spectra of Na-bentonite before (1) and after ex-situ pillaring (2)

value is in the same magnitude as that of 223 m²/g provided by literature [27].

Changes in the surface structure

The pillaring process involves the formation of a rigid cross-linked and non-expandable structure. Many possible mechanism pathways are used to explain how the pillaring process takes place. One of these pathways supposes that the metal oxide pillar binds via oxygen bridges to the atoms of the intermediate octahedral alumina layer. In this regard, FTIR investigations provided clear evidence of the occurrence of the pillaring process, through the dramatic decrease in the 3640 cm⁻¹ band, attributed to the stretching vibration of the clay-OH sites belonging to the octahedral layers. This is presumably due to the formation of Fe-O-clay bridges at the expense of the clay-OH and Fe-OH [28]. As expected, this phenomenon was more visible via the ex-situ procedure (fig. 2-a). The formation of a new band at 3740 - 3770 cm⁻¹ is regarded as being a special feature of pillared clay minerals [28].

This indicates that the presence of compact lamellar structure in the in-situ procedure did not favour the total conversion of Fe⁺³ cations into polyhydroxycations, in agreement with previous data [25]. This must be to a competitive ion-exchange with Fe⁺³ cations, resulting in strong sandwiching effect that hinders full clay exfoliation. As expected [29], the Si-O-Si band at 1033 cm⁻¹ was found to slightly shift towards higher frequencies (fig. 2-b), which suggests a decay in the Si-O-Si group elasticity. This must be due to the formation of next-neighboring covalent bonds, providing additional evidence of the formation of pillared clay minerals. KSF and K10 showed different IR spectra as compared to the untreated Na-bentonite, but similar observations were made for their pillared counterparts (fig. 3-4).

Changes in thermal behavior

Deeper insights through thermal analyses (TG-DTG) showed that pillaring induces significant changes in the thermal behavior of the clay mineral within the investigated temperature range (table 1). At 45 - 145°C, a first mass loss of ca. 6.4 % for Na-bentonite, 10.3 % for KSF and 9 % for K10 was observed (table 1, step 1). This is a common feature of clay based materials, and was attributed to dehydration [18]. The relatively higher values obtained for KSF and K10 as compared to Na-Bentonite must be due to their increased specific surface area and numbers of both terminal Si-OH and Al-OH groups. The latter are supposed to enhance the hydrophilic character of the clay material.

Between 150 and 400°C, only KSF and its ex-situ intercalated counterpart showed an endo peak,

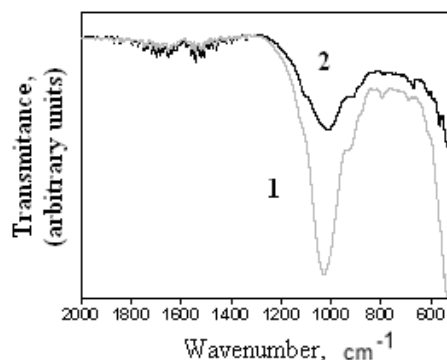


Fig. 3. FTIR spectra of KSF before (1) and after ex-situ pillaring (2)

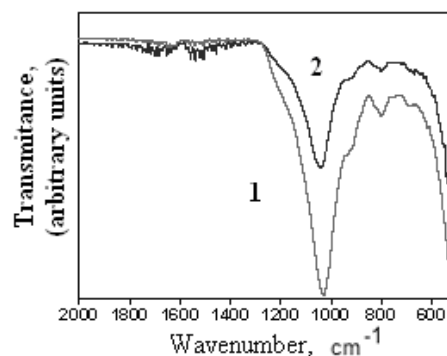


Fig. 4. FTIR spectra of K10 before (1) and after ex-situ pillaring (2)

corresponding to mass loss of approximately 3 - 4 % (table 1). These clay materials showed higher mass losses than Na-Bentonite, i.e. 6.7 % for K10 and 13 % for KSF. Beyond 400°C, Na-bentonite displayed only a one-step mass loss of ca. 5.3 % at 673°C, but multiple thermal processes were observed at 471 and 713°C for K10, and at 577, 700 and 837°C for KSF.

After pillaring, the appearance of other thermal processes must be due to the successive dehydroxylation steps of the Fe polyhydroxycations [30]. As compared to the starting materials, involved mainly in the pillaring process. The first step around 250-350°C is due to water release from the external surface of the clay mineral. Beyond 600°C, the other steps must be due to dehydroxylation water delayed by diffusion hindrance and pillars dehydroxylation via the formation of oxygen bridges [31].

Phenol oxydation

As compared to the starting materials, all pillared clays showed improved catalytic activity in phenol decomposition through a Fenton process (fig.5, fig.6 and table 2). In phenol oxydation attempts using ex-situ catalysts, Be-Na-Fe turned out to be quite effective,

SAMPLE	Pillaring method	D degradation step	Measured temperatures, °C			Mass loss, wt %	
			T _{onset} ^a	T _{peak} ^b	T _{endset} ^c	by step	residue ^d
Na-Bentonite	None	I	47.65	94.32	117.52	6.28	88.42
		II	575.93	673.26	698.74	5.30	
KSF	None	I	51.65	108.13	136.59	10.32	73.68
		II	209.92	234.36	277.96	2.92	
		III	419.83	577.92	606.77	5.82	
		IV	606.77	700.30	720.41	3.65	
		V	778.90	837.95	850.23	3.61	
K10	None	I	47.38	85.50	145.35	9.03	84.2
		II	436.84	471.34	646.21	3.74	
		III	646.21	713.71	850.45	3.03	
Be-Na-Fe	Ex-situ	I	50.51	86.83	131.38	4.19	86.65
		II	131.38	373.77	530.21	4.49	
		III	530.21	642.65	678.92	2.99	
		IV	735.38	766.23	774.83	0.84	
		V	818.37	834.19	850.70	0.84	
KSF -Na-Fe	Ex-situ	I	46.47	73.52	122.64	4.33	89.39
		II	406.33	485.83	512.20	3.53	
		III	512.20	608.99	723.91	2.75	
K10-Na-Fe	Ex-situ	I	47.76	73.58	115.74	3.52	91.40
		II	437.99	468.45	528.74	2.93	
		III	528.74	563.83	703.32	2.15	
Be-Na-Fe	In situ	I	50.55	80.11	125.56	5.15	88.54
		II	394.05	435.48	548.55	2.36	
		III	548.55	626.30	673.03	1.11	
		IV	740.76	763.42	782.51	2.84	
KSF -Na-Fe	In situ	I	50.54	80.83	129.52	4.66	88.29
		II	415.86	490.03	519.58	3.84	
		III	519.58	733.64	850.63	3.21	
K10-Na-Fe	In situ	I	46.41	72.32	11.75	4.65	90.34
		II	378.65	472.91	501.56	2.24	
		III	501.56	562.79	700.24	1.56	
		IV	700.24	755.44	850.23	1.21	

Table 1
THERMOGRAVIMETRIC
FEATURES OF THE
INVESTIGATED CLAY SAMPLES

^a starting temperature of the corresponding thermal process or step;

^b temperature of the maximum mass loss;

^c ending temperature of the corresponding thermal process;

^d amount of the residual clay material after calcination till 900°C.

Table 2
PHENOL CONCENTRATION VALUES AFTER TESTING

Material	Dose (g/L)	Solutions added to the solution of phenol subject tests	Phenol concentration after 4 hours (mg/L)
Catalyst absent	0		100
	0	peroxid 6 % + 4 mmoli Fe (solution FeCl ₃)	0.025
Sodium bentonite raw material	5	-	200
	5	peroxid 6 % + 4 mmoli Fe (solution FeCl ₃)	0.13
Montmorillonite raw material KSF	5	-	180
	5	peroxid 6 % + 4 mmoli Fe (solution FeCl ₃)	0.05
Montmorillonite raw material K10	5	-	200
	5	peroxid 6 % + 4 mmoli Fe (solution FeCl ₃)	190

affording a total decomposition of phenol within less than 20 min. Almost similar behaviour was observed with ex-situ-KSF-Na-Fe, but almost complete phenol oxydation was achieved only after 25-30 min (fig. 5). K10-Na-Fe showed the lowest catalytic activity, since the phenol conversion barely attained 28-30 % even after 60 min of oxydation process.

Similar observations were made for the in-situ PILC catalysts (fig. 6). Indeed, here also, K10-Na-Fe exhibited low activity as compared to the two other catalysts, in as much as the total decomposition of phenol required oxydation times exceeding 4 h. KSF-Na-Fe, instead,

displayed almost similar catalytic activity as its ex-situ pillared counterpart, affording a thorough phenol oxydation in 30-35 min. The appreciable effectiveness of KSF-Na-Fe catalysts must be due to its relatively acidity as compared to that of K10-Na-Fe, notwithstanding the latter is supposed to possess a larger specific surface area [32].

The different performances of KSF and K10 cannot be explained by their specific surface area, but rather by their differences in chemical composition and crystalline structures, as already reported [22]. The type of starting clay mineral is expected to influence the phenol adsorption and reaction with hydrogen peroxide. This different

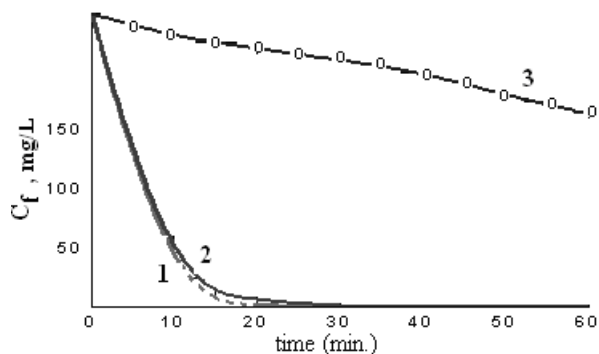


Fig. 5. Evolution in time of phenol concentration in the presence of ex-situ PILCs $T = 298\text{ K}$; C_i (phenol concentration) = 250 mg/L; $\text{pH}_{\text{initial}} = 3.5$; R_1 (rapport solid/liquid) = 5 g/L; R_2 (rapport H_2O_2 /phenol) = 14 mol/mol.

behavior can be related to the different effects of pH on the pillared clay samples. For instance, total decomposition of phenol was made possible at pH 2.5 – 3.5, while only 72 % of phenol was removed at pH = 4.5, and even lower conversion yield of 60 % at neutral pH [19].

However, care should be taken, because, excessively low pH, e.g. below 2.5–3.0, seems to be strongly detrimental, more particularly for low Si: Al ratio inducing changes in the catalyst composition via acid attack and autotransformation the clay structure [33-35]. These data reveal that the specific surface area and H_2O_2 : phenol mole ratio does not play significant roles as compared to pH.

The fact that Na-Fe-bentonite and KSF-Na-Fe showed the highest catalytic activity must be due to their higher acidity. Increased surface acidity is a special feature of the so-called K-catalysts [36,37]. In most reaction involving organic compounds, there exists a pseudoproportionality between the Brönsted acidity and catalytic activity. Acid attack is a suitable route to improve the surface acidity but only up to a certain threshold level, because excessive depletion of the octahedral cations turns out to be detrimental [38-40].

Conclusions

The results provided herein clearly demonstrate the possibility to obtain effective catalysts for a thorough oxydation of phenol with hydrogen peroxide. Na-exchanged bentonite, KSF and K10 showed catalytic activity when pillared with iron-based polyhydroxycations. The type of the starting clay materials played a keyrole, in as smuch complete decomposition of phenol can be achieved with bentonite and KSF based catalysts after 20-30 min. The surface acidity of the catalyst appeared to play a more significant role than the specific surface area. Indeed, K10-catalyst showed relatively low effectiveness notwithstanding its higher specific surface area, affording a phenol conversion yield not exceeding 35% even after 4 h. The pillaring procedure (in-situ and ex-situ) did not seem to play a keyrole, giving rise to comparable catalytic activity regardless to the starting material. Besides, Na-Fe-bentonite showed slightly higher effectiveness as compared to KSF-Na-Fe catalyst. This clearly demonstrates that acid treatment is not an essential requirement for achieving complete oxydation of phenol with hydrogen peroxide. This results opens new prospects for obtaining low-cost and ecofriendly large scale methods for the decomposition toxic and harmful organic pollutants.

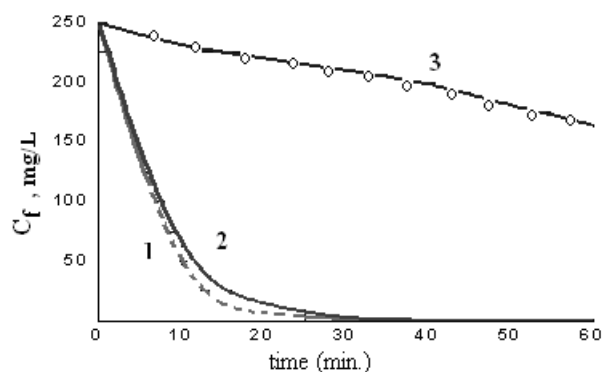


Fig. 6. Evolution in time of phenol concentration in the presence of in-situ PILCs $T = 298\text{ K}$; C_i (phenol concentration) = 250 mg/L; $\text{pH}_{\text{initial}} = 3.5$; R_1 (rapport solid/liquid) = 5 g/L; R_2 (rapport H_2O_2 /phenol) = 14 mol/mol. 1. Be -Na-Fe; 2. KSF -Na-Fe; 3. K10-Na-Fe

Acknowledgement. One of the authors (Silion M.) acknowledges the grant of the Romanian National Authority for Scientific Research, CNCS – UEFISCDI, project number PN-II-ID-PCCE-2011-2-0028 and the European Social Fund “Cristofor I. Simionescu” Postdoctoral Fellowship Program (ID POSDRU/89/1.5/S/55216), Sectoral Operational Program Human Resources Development 2007–2013.

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Manuscript received: 15.07.2013