Fe - pillared Clay as an Efficient Fenton-like Heterogeneous Catalyst for Phenol Degradation

NICOLETA PLATON[1*], ILIE SIMINICEANU[2], ILEANA DENISA NISTOR[1], NECULAI DORU MIRON[1], GABRIELA MUNTIANU[1], ALINA MONICA MARES[3]
[1]"Vasile Alecsandri" University of Bacau, Engineering Faculty, 157 Calea Marasesti, 600115, Bacau, Romania.
[2]"Gh. Asachi" Technical University of Iaşi, Faculty of Chemical Engineering and Environmental Protection, Department of Chemical Engineering, 73 Mangeron Blv., 700050, Iasi, Romania.
[3]" Politechnica University of Bucharest, Faculty of Applied Chemistry and Materials Science, 313 Splaiul Independentei, 060042, Bucharest, Romania

In this paper, we used three catalysts - type of Fe^{3+} *- pillared clay, with different surface areas. We studied the influence of specific surface area on the catalytic activity in the phenol removal by Fenton - like (*Fe^{3+}/H_2O_2*) reaction. The catalysts were obtained using as starting materials clays with different structure and textural properties: Na - bentonite with the surface area of 37.5* m^2/g*, montmorillonite KSF with the surface area of 106* m^2/g *and montmorillonite K10 with the surface area of 240* m^2/g*, all provided by Sigma Aldrich. Catalytic wet peroxide oxidation (CWPO) of phenol (*$C^0_{phenol} = 250$ *mg/L) from process of Fenton-like has been studied at different operating conditions: T = 298 K, pH = 2.5 - 7, the catalyst dose of 0 - 20 g/L aqueous liquid, the ratio* H_2O_2*/phenol = 10 – 20. The catalyst obtained from sodium bentonite presents a high catalytic activity leading to advanced removal of phenol after only 50 minutes of reaction.*

Keywords: iron- containing pillared clays, phenol, Fenton-like, catalysis, CWPO reaction.

Industrial processes generate a wide diversity of wastewaters containing organic pollutants with negative impacts for ecosystems and humans. Such wastewaters had become a major social and economic problem as modern health-quality standards and environmental regulations are gradually being more restrictive. Particularly the phenol (commonly chosen as,"model" molecule for studies on catalytic oxidation of organic compounds in diluted aqueous solutions) is considered as one of the most toxic pollutants [1, 2, 3] harmful to human health and to aquatic fauna, causing an increase in the demand of oxygen in water sources and giving out unpleasant taste and smell in drinking water even when it is found in very small quantities.

According to the literature, the methods of phenol removing from water have generated development of accessible and respectively efficient technologies. Applying one particular technology is strongly dependent on the phenol concentration in the wastewater, copresence of other contaminants and the nature of the installation where this problem was detected. The classic methods such as, adsorption on activated carbons, without need of regeneration necessity, are expensive because of high costs for carbon layers replacement. The adsorption on activated carbons with calcination of the adsorbent and heat recovery is profitable only in case of small dimension plants [4]. Most advanced technologies such as catalytic combustion or high-voltage discharge methods, make certainly the plant more expensive and operations more complex, but these methods might become very successful in the future to abate small concentration of pollutants in small plants.

Several procedures have been developed to eliminate the organic contaminating compounds found in wastewaters, e.g., adsorption processes, biological processes incineration through dry way and wet oxidation (WO) processes, and from these only the WO processes show greater viability and relative efficiency when the contaminants are found in the diluted aqueous phase.

One alternative of special interest is the wet catalytic oxidation with hydrogen peroxide (CWPO), which is framed within the category of the advanced oxidation processes (AOP) which have in common the generation of (•OH) radicals and the use of their oxidizing capacity [6]. These radicals are not very selective and attack the majority of the organic molecules, causing their oxidation up to CO_2 and H_2O. One of the most important process in which are generated hydroxyl (•OH) and perhydroxyl (•HO_2) radicals is achieved with the Fenton system, that uses iron salts and hydrogen peroxide, [Fe(II)-Fe(III)/•H_2O_2]. The use of this system as an oxidizing agent for the treatment of wastewater is very attractive since the iron is an abundant and non-toxic element, and the hydrogen peroxide is not harmful to the environment [7], it is totally miscible in aqueous media and its decomposition products are oxygen and water which does not cause additional contamination. The CWPO could be a more efficient process than the catalytic wet air oxidation (CWAO) since the oxidizing properties of hydrogen peroxide are stronger than those of molecular oxygen.

Moreover, the reaction conditions when hydrogen peroxide is used as oxidant are close to the ambient ones (0.1 - 0.5 Mpa, T < 353 K) allowing the possibility to treat a large amount of polluted water without a too important energy consumption [6,7].

The Fenton (Fenton-like) heterogeneous catalysis processes do not show the disadvantages of the Fenton homogenous processes like, sensibility at various *p*H [8,9] and additionally operation for iron removal from water after treatment is completed.

Among the catalysts used in Fenton (Fenton - like) reactions the pillaring clays presented a high interest in the late years due to their special texture and catalytic properties [10]. This catalyst confers a high catalytic activity for phenol conversion and moreover, it can be reused for

---

* email: nicoleta.platon@ub.ro; nicoleta7platon@yahoo.com

many times, without loosing its catalytic activity. The Fe - pillared mineral clays were proposed in 1988 [11] as an alternative to Al - pillared minerals.

The present research study reports very good results for the decreasing of phenol degradation duration, from a synthetic solution (250 mg/L), by using a low amount (5 g/L) of catalyst (pillared clay with Fe^{3+}). According to the literature, different types of pillared clays (pillared with Fe, Fe-Al, Cu-Al, [12, 13], Fe-Al-Ce [14, 5, 16]) were used in phenol degradation. In this paper, using clays pillared with Fe, an advanced degradation of phenol was obtained in only 50 min compared to 4-5 h found in literature for other pillared clays.

Materials and method

The pillared clays were obtained from three types of clays - starting materials: Na - bentonite, montmorillonite KSF and montmorillonite K10 provided by Sigma Aldrich.

The obtaining method for chemically modified clay by pillaring was detailed in other paper [17]. The ageing stage of the intercalated clay was realized in microwave environment. In table 1 the surface areas of the materials obtained after pillaring with iron are showed.

Table 1
SURFACE AREAS OF THE OBTAINED MATERIALES FOR Fe – PILLARING

No. crt.	Sample	S_{BET} m^2/g
1.	Na – bentonite	37.5
2.	$M_{0\text{-}10}$Be-Na-Fe	139.60
3.	Montmorillonite KSF	106
4.	$M_{0\text{-}10}$KSF -Na-Fe	101.2
5.	Montmorillonite K10	240
6.	$M_{0\text{-}10}$K10-Na-Fe	232

The phenol oxidation reaction in a diluted aqueous medium was carried out in a glass (Pyrex) reactor, with a capacity of 500 mL, open to the atmosphere, at 298 K, with a perfect stirring. The solid catalyst (pillaring clay with iron) was introduced into an aqueous phenol solution (250 mg/L) under continuous stirring. After temperature stabilization at the selected value (room temperature) and *p*H correction (with HNO_3 0.1 N), a solution of 6 % H_2O_2 was added to achieve the selected H_2O_2/ phenol ratio, these being the basic conditions for experimental tests. This time was considered the initial time for the reaction.

The stoichiometric equation is showed in (1):

$$C_6H_5OH + 14\ H_2O_2 = 6\ C0_2 + 17\ H_20 \qquad (1)$$

Phenols concentrations were measured using the 4-aminoantipyrine spectrophotometer method using a Thermo Spectronic Genesys 20 spectrophotometer. The detection limit according to SR ISO 6439 is 0.005 mg/L [18].

The catalytic activity of the pillared clays in the phenol oxidation reaction in diluted aqueous medium is represented by reaction of Fenton-like (Fe^{3+}/H_2O_2) and is evaluated by catalytic coefficient considering the reaction of first order. The mechanism process includes the following reactions:

$$\mathbf{Fe}^{3+} + H_2O_2 \leftrightarrow Fe...OOH^{2+} + H^+ \qquad (2)$$

$$Fe...\ OOH^{2+} \rightarrow HO_2\cdot + Fe^{2+} \qquad (3)$$

$$H_2O_2 + Fe^{2+} \rightarrow \mathbf{OH}\cdot + OH + Fe^{3+} \qquad (4)$$

$$\mathbf{OH}\cdot + RH \rightarrow R\cdot + H_2O \qquad (5)$$

The rate of phenol (RH) consumption in the reaction is:

$$r_{phenol} = k \cdot C_{phenol} \cdot C_{\bullet OH} \qquad (6)$$

where C_{phenol} is the phenol concentration [mg/L].

For a constant concentration of HO, this is:

$$-\frac{dC_{phenol}}{dt} = r_A = k_1 \cdot C_{phenol} \qquad (7)$$

where:

$$k_1 = k \cdot C_{\bullet OH}$$

By integration of the (7) equation, one obtains:

$$\int_{C_A^0}^{C_A} -\frac{dC_{phenol}}{C_{phenol}} = k_1 \int_0^t dt \qquad (8)$$

$$\ln\frac{C^0_{phenol}}{C_{phenol}} = k_1 \cdot t \qquad (9)$$

where:

C^0_{phenol} is the initial concentration of phenol [mg/L];

C_{phenol} represents the final concentration of phenol [mg/L].

The studied parameters that influence the phenol oxidation process were: the type of solid (catalyst), the solid/liquid ratio (catalysts dose), the H_2O_2/phenol ratio and the *p*H solution (table 2).

Table 2
PARAMETERS THAT INFLUENCE THE PHENOL OXIDATION PROCESS THROUGH THE USE OF PILLARING CLAY AS CATALYSTS

No.crt.	Parameter	Values
1.	Type of solid: $M_{0\text{-}10}$Be-Na-Fe $M_{0\text{-}10}$KSF -Na-Fe $M_{0\text{-}10}$K10-Na-Fe *(m^2/g)*	 139.6 101.2 232
2.	Rapport solid/liquid *(R_1)* *(g/L)*	0; 2.5 ; 5; 10; 15; 20
3.	Rapport H_2O_2/phenol *(mol/mol)*	10; 14; 20
4.	pH of the solution	2.5; 3.5; 4.5; 5.5; 7
5	Temperature *(K)*	298
6.	C^0_{fenol} *(mg/L)*	250

Table 3
VALUES OF PHENOL CONCENTRATION (mg/L) IN TIME DEPENDING ON THE CATALYST USED

No. crt	Catalyst	Time (minute)						
		10	20	30	40	50	60	240
1.	$M_{0\text{-}10}$Be-Na-Fe	10	6.5	1	0.05	SLD	SLD	SLD
2.	$M_{0\text{-}10}$KSF-Na-Fe	30	25	22.5	20	17.5	15	SLD
3.	$M_{0\text{-}10}$K10Na-Fe	230	220	210	200	187.5	170	1

Results and discussion

The catalysts performance was studied using a stirring reactor, for 60 min. The values of phenol concentrations in time (starting from 250 mg/L concentration) were determined by a spectrophotometric method and are presented in table 3.

Influence of solid type on phenol degradation

For catalytic process is known that the specific surface plays an important role, thus we have used 3 materials with different specific surface area: sodium bentonite (37.5 m^2/g), montmorillonite KSF (106 m^2/g) and montmorillonite K10 (240 m^2/g). These studies aim is to evaluate the influence of these 3 types of materials for obtaining an efficient catalyst for phenol degradation from aqueous solutions.

In order to illustrate the influence of the catalyst type over phenol conversion degree in graphical form the conversion curves depending on time, were drawn at constant values of the followings parameters: T = 298 K, C^0_{phenol} = 250 mg/L, *p*H = 3.5, R_1 = 5 g/L; R_2 = 14 mol/mol.

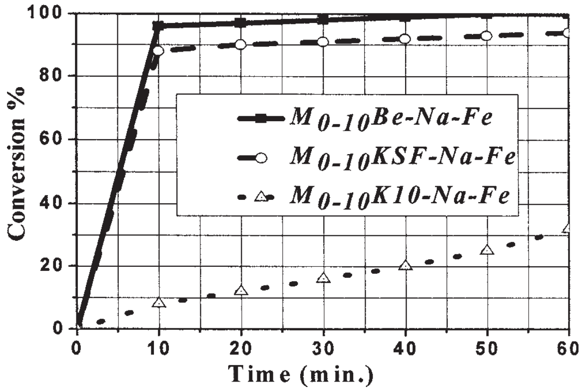

Fig.1. Influence of the solid type on phenol conversion degree

It can be observed (fig. 1) that the three types of clay used as raw material have a different behavior in phenol oxidation reactions. The catalytic activity of catalyst obtained from sodium bentonite shows the most favorable results in the degradation process of phenol. Instead, utilisation of catalysts obtained from KSF and mostly K10 makes more difficult the oxidation process.

An initial starting material with a high specific surface area from which it was obtained the catalyst, did not lead to the higher catalytic activity, on the contrary, a high surface area (montmorillonite K10 case) led to more difficult phenol removing processes. The catalyst obtained from this material, did not lead to an advanced phenol removal not even after 4 h of reaction. Instead the catalyst obtained from sodium bentonite presents a high catalytic activity for phenol oxidation after only 50 min of reaction, leading to phenol removal yield ≥ 99.99 %.

By using the catalyst obtained from KSF, it was obtained a conversion degree of 93 % after 50 min while using the catalyst obtained for K10 the phenol conversion was only 25 %.

The conversion of phenol on the pillared clay obtained from Na-bentonite was achieved in a short time compared to the other two studied clays. Besides, Na-bentonite modification following the proposed method [17] was the fastest and most economically efficient.

Influence of the catalyst dose on phenol degradation

Influence of the catalyst amount on phenol degradation was evaluated by using the most representative catalyst from structural point of view ($M_{0\text{-}10}$Be-Na-Fe).

In figure 2 it can be observed that a minimum amount of 5 g/L was sufficient for the advanced phenol degradation from an aqueous solution (250 mg/L).

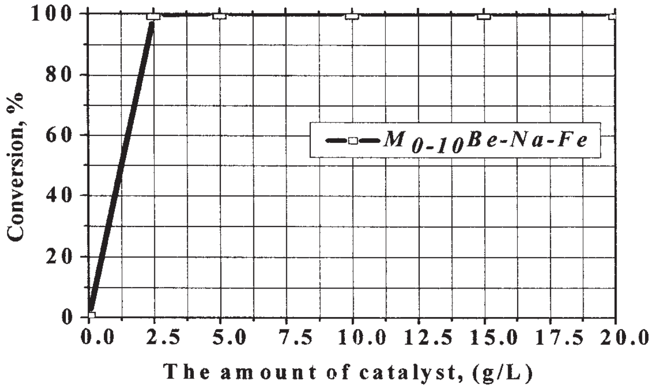

Fig. 2. Influence of the catalyst amount on phenol conversion degree T = 298 K, C^0_{phenol} = 250 mg/L, *p*H = 3.5, R_2 = 14 mol/mol

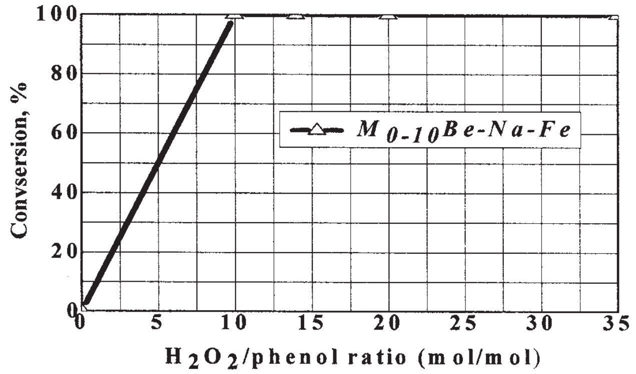

Fig. 3. Influence of H_2O_2/phenol ratio (mol/mol) on phenol conversion degree T = 298 K, C^0_{phenol} = 250 mg/L, *p*H = 3.5, R_1 =5 g/L

Influence of the H_2O_2/phenol ratio (mol/mol) on phenol degradation (R2)

The H_2O_2/phenol ratio (mol/mol) influence on phenol degradation was evaluated for the catalyst obtained from sodium bentonite as the representative material (M_0-$_{10}$Be-Na-Fe) for the phenol removal by Fenton-like processes. The experimental duration was 60 min (fig. 3).

Analysing the experimental results it can be observed that H_2O_2 /phenol ≥ 10 is favorable to the phenol degradation process, this being in accordance with the results presented in literature [1,12,14,]

Influence of pH on phenol degradation

The *p*H influence on phenol degradation was evaluated for the representative catalyst ($M_{0\text{-}10}$Be-Na-Fe) in figure 4.

A characteristic of the Fenton reactions is the fact that the kinetic of the reactions is potentiated by an acid *p*H [2]. The diagram plotted in figure 4 shows that after 60 min

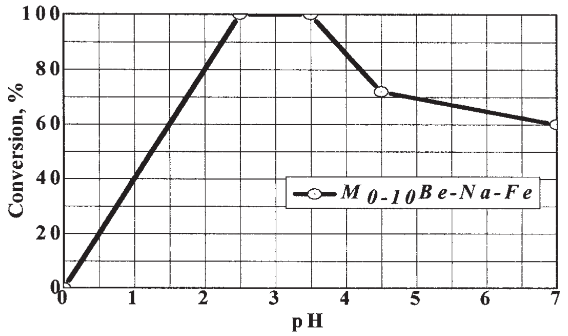

Fig. 4. Influence of pH on phenol conversion degree
T = 298 K, C^0_{phenol} = 250 mg/L, R_1 = 5 g/L; R_2 = 10 mol/mol

there are big differences on the phenol conversion degree achieved for the range of *p*H = 2.5 – 7. A pH value situated between 2.5- 3.5 assures advanced degradation of phenol.

Determination of the rate constant of phenol degradation reaction

In this study the hypothesis that the reaction is of first order has been verified by determination of the constant rate (k = 0.2885min^{-1}) and by the correlation coefficient (R^2 = 0.96) for phenol oxidation in presence of the most representative catalyst (M_{o-10}Be-Na-Fe). The diagram presented in figure 5 validates this hypothesis.

Conclusions

This study presents remarkable results regarding the use of the CWPO method for Fenton - like reaction. Using a small dose of catalyst (5 g/L) obtained from pillaring Na - bentonite with Fe^{3+}, we obtained a total conversion of phenol after only 50 min. The results are spectacular compared with those mentioned in the literature (the minimum time for advanced phenol oxidation using catalysts obtained from pillaring clay was 60 min [1], 90 min [12] and 240 min [15,14,19] respectively.

Regarding the catalyst amount used in the phenol degradation process, the literature mentions generally an amount of 10g catalysts/L solution [1]. The results of our study show that using a minimum amount of catalyst (5 g/ L) we obtain advanced phenol degradation in a short time.

In the given conditions the efficiency of the process allows us to achieve a remanent phenol concentration situated under the limits imposed at the evacuation (max. 0.3 mg/L) for surface waters according to HG 352/2005 [20,21].

References

1.CATRINESCU, C., TEODOSIU, C., MACOVEANU, M., MIEHE-BRENDLE, J., LE DRED, R., Catalytic wet peroxide oxidation of phenoi over Fe-exchanged pillared beidellite, Wat. Res., 37, 2003, p. 1154

2.CRUTESCU, R., UNGUREANU C., Rev. Chim. (Bucharest), **58**, no. 12, 2007, p.1322

3.DUMITRAN, G. E., Rev. Chim. (Bucharest), **61**, no. 2, 2010, p.192

4.URSU, A.V., FABRICE G., NISTOR D.I., DJELVEH G., Rev. Chim. (Bucharest), **59**, no. 10, 2008, p.1067

5. BUSCA, G., BERARDINELLI, S., RESINI, C., ARRIGHI, L., Technologies for the removal of phenol from fluid streams: A short review of recent developments, J Hazard Mater, 160, 2008, p. 265

6. ANDREOZZI, R., CAPRIO, V., INSOLA, A., MORATTA, R. Advanced oxidation processes (AOP) for water purification and recovery , Catal. Today, 53, 1999, p.51

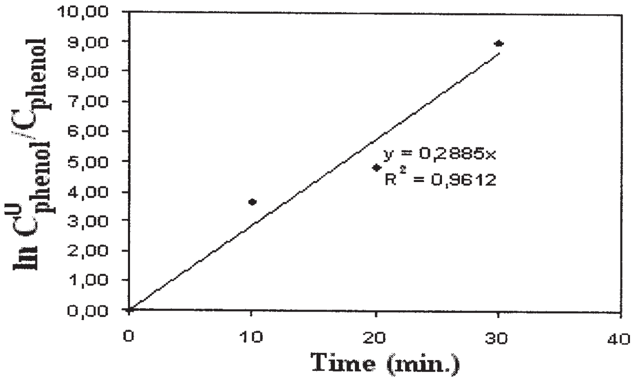

Fig. 5. Determination of the catalytic coefficient for the phenol oxidation reaction in the presence of clay catalyst
T = 298 K, C^0_{phenol} = 250 mg/L, pH = 3.5, R_1 =5 g/L; R_2 = 10 mol/mol

7. JONES, C.W., Application of Hydrogen Peroxide and Derivates, RSC, 1999, p.41

8. PARKHOMCHUK, E.V., VANINA, M.P., PREIS, S., The activation of heterogeneous Fenton-type catalyst Fe-MFI, Catal. Commun., 9, 2008, p. 381

9.CALLEJA, G., MELERO, J.A., MARTINEZ, F., MOLINA, R., Activity and resistance of iron-containing amorphous, zeolitic and mesostructured materials for wet peroxide oxidation of phenol, Water Res., 39, 2005, p.1741

10.YANG, R.T., THARAPPIWATTANANON, N., LONG, R.Q., Ion-exchanged pillared clays for selective catalytic reduction of NO by ethylene in the presence of oxygen, Appl. Catal. B: Environ., 19, 1998, p. 289-304.

11. DOFF, D.H., GANGAS, N.H.J, ALLAN, J.E.M., COEY, J.M.D., Preparation and characterization of iron oxide pillared montmorillonite, Clay Minerals, 23, 1988, p.367

12. TIMOFEEVA, M.N., KHANKHASAEVA, S.T, CHESALOV, YU.A., TSYBULYA, S.V, PANCHENKO, V.N., DASHINAMZHILOVA, E.TS., Synthesis of Fe,Al-pillared clays starting from the Al, Fe-polymeric precursor: Effect of synthesis parameters on textural and catalytic properties, Appl. Catal. B: Environ., 88, 2009, p.127

13. OLAYA, A., BLANCO, G., BERNAL, S., MORENO, S., MOLINA, R., Synthesis of pillared clays with Al-Fe and Al-Fe-Ce starting from concentrated suspension of clay using microwaves or ultrasound, and their catalytic activity in the fenol oxidation reaction, Appl Catal B: Environ, 93, 2009, p. 56

14. CARRIAZO, J.G., GUELOU, E., BARRAULT J., TATIBOUET J.M., MOLINA R., MORENO S., Cataliytic wet peroxide oxidation of phenol by pillared clays containing Al-Ce-Fe., Water Res., 39, 2005, p. 3891

15. SANABRIA, N.R., CENTENO, M.A., MOLINA, R., MORENO, S., Pillared clays with Al-Fe and Al- Ce –Fe in concentrated medium: synthesis and catalytic activity, Appl. Catal., 356, 2009, p. 243

16. TABET, D., SAIDI, M., HOUARI, M., PICHAT, P., KHALAF, H., Fe-pillared clay as a Fenton-type heterogeneous catalyst for cinnamic acid degradation, J. of Environ. Management, 80, 2006, p. 342

17. PLATON, N., DRAGOI, B., DUMITRIU, E., SIMINICEANU, I., NISTOR, D.I., MIRON, N.D., The texture of a iron pillared bentonite catalyst, 4, CISA, 2010, p.352

18. SR ISO 6439, CALITATEA APEI, Determinarea indicelui de fenol. Metode spectrometrice cu 4-aminoantipirină după distilare, 2001

19. BARRAULT, J., TATIBOUET, J.M., PAPAYANNAKOS, N., Catalytic wet peroxide oxidation of phenol over pillared clays containing iron or copper species, C.R. de l'Académie des Sciences - Series IIC – Chem, 3, 2000, p.777

20. NICOLAU M., Implementarea directivelor europene de mediu-probleme şi soluţii, FINMEDIA, Bucureşti. 2005

21. *** HG nr. 352/2005

Manuscript received: 20.12.2010