



## OXIDATIVE TREATMENT OF PHENOLIC WASTEWATERS: DETERMINATION OF THE EFFICIENCY OF FE-CONTAINING CATALYST

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### ABSTRACT

Phenol and substituted phenols are toxic organic pollutants commonly present in industrial water streams, especially in wastewater of chemical and pharmaceutical industries. However, the phenolic compounds in water can be natural origin, especially some Hungarian thermal water contains these materials. The effective removal of these toxic pollutants from wastewater is an important task of the environmental technology.

The treatment of phenol in aqueous solutions has been generally carried out by oxidation of molecular oxygen from the air, at elevated pressure in the presence of catalysts (CWAO: catalytic wet air oxidation). However, the development of CWAO technique is a continuous work to find the proper reaction conditions (oxidant, catalyst, etc.). Our task has been to study the applicability of iron containing materials with different structure in the oxidative treatment of phenolic wastewaters.

The catalyst samples (Fe-ZSM<sub>5</sub> zeolite, Fe-MCM<sub>41</sub> mesoporous silicate, Fe,Mg,Al-mixed oxide and supported Fe<sub>2</sub>O<sub>3</sub>) either were synthesized in our laboratory, or natural materials were used after thermal pretreatment (bauxite ore and red mud). XRD and BET adsorption methods were used for characterization of the catalysts. A recirculating bubble reactor was utilized to perform the oxidation of phenol in different origin waters. The reaction was followed by the determination of chemical oxygen demand (COD).

All the catalyst samples tested have reasonable activity in the air oxidation at ambient temperature, however, the efficiency can be improved by using of ozone. The obtained results proved the enforceability of the cheap mineral catalysts besides the expensive synthetic ones.

### Keywords:

phenol, catalytic wet air oxidation, Fe-MCM-41, Fe-hydrotalcite, red mud

## 1. INTRODUCTION

Increasing interest for the environment is making it necessary to develop effective techniques to treat industrial waste waters containing compounds that are toxic to aquatic life. Phenol and substituted phenols are of particular interest because these toxic organic pollutants commonly present in industrial water streams, especially in wastewater of chemical and pharmaceutical industries. Moreover, phenol and its derivatives are powerful bactericide which prevents them from being treated in classical sewage processing plants even at concentrations as low as 50 mg/l [1]. Thus, phenolic aqueous effluents must be specially decontaminated before being biologically treatment. The effective removal of these pollutants from wastewater is a problem with great practical importance and interest.

In the present years, the treatment of phenol in aqueous solutions has been generally carried out by oxidation of molecular oxygen from the air at elevated pressure [2]. These are the so called "wet air oxidation: WAO" processes. The rate and efficiency of oxidation can be enhanced by the increasing of temperature and by the optimization of pH, however, the solubility of oxygen decreases at higher temperatures. The prosperous solution is decreasing of temperature, however, it could be achieved by application of catalyst. Nowadays, the investigation and development of catalysts, which would have high activity for oxidation of phenols and related compounds in aqueous solutions under mild conditions, are the objective of many studies in the wastewater treatment [3,4].

One of the most promising catalyst families for phenol oxidation is the transition metal containing micro and mesoporous materials [5-7].

The hydrotalcite type materials are layered double hydroxides (LDH) and their structures is very similar to that of the brucite [Mg(OH)<sub>2</sub>]. For LDH-s an isomorphous substitution of Mg<sup>2+</sup> by a trivalent element (generally aluminum) occurs in the brucite-like network and this replacing generates a positive charge in the brucite layer. The positively charged Mg-Al double hydroxide sheets are charge balanced by anions residing in the interlayer sections. During the synthesis of LDH both of magnesium

and aluminum can be changed many bivalent or trivalent cations respectively resulted in materials with different character. LDH and LDH originated materials have many practical applications such as catalysts, adsorbents, anion-exchangers, stabilizers, etc. because of their relatively high surface area, basic properties, high metal dispersion and stability [8].

The MCM-41 material is a well-known member of the recently discovered mesoporous molecular sieves M41S family which possesses a regular hexagonal array of uniform pore openings with a broad spectrum of pore diameters between 1.5 and 10 nm [9]. As oxidation catalyst the  $Fe^{2+} \leftrightarrow Fe^{3+}$  system is well-known in the Fenton type reactions in which  $H_2O_2$  is the oxidation agent [10].

Recently, development of catalysts based on waste materials is an issue of great interest, because of two environmental objectives could be achieved simultaneously: (i) reuse the waste materials and (ii) the saving of raw materials, such as catalyst precursors [11]. After a proper pretreatment as possible waste material the „red mud” can be considered as hydrodechlorination catalyst. The red mud is a by-product in the manufacture of alumina using Bayer-process that contains mainly oxides of iron, aluminum, titanium, silicon, calcium and sodium. In Hungary the annual red mud production is over one million tons in the last decades. The environmental danger of red mud originates from the high alkalinity, and from the very fine-graining. The mixed oxide from red mud could be possible alternative of commercial scale catalysts implied for hydrodechlorination reactions [12].

In this paper we present the study on the preparation and application in air and ozone oxidation of phenol over Fe-containing synthesized (hydrotalcite, MCM-41) or natural origin catalysts (red mud and bauxite after heat treatment) at ambient temperature working on atmospheric pressure.

## 2. EXPERIMENTAL SECTION

### Catalysts

The Al/Fe-mixed oxide was synthesized by coprecipitation from aluminum nitrate and iron nitrate solutions followed by calcination at 500 °C for four hours, and the alumina supported iron oxide was prepared by impregnating  $\gamma-Al_2O_3$  with iron nitrate solution followed by heat treatment at 500 °C. The Fe/Al/Mg-hydrotalcite ( $M^{II}/M^{III} = 2$ , and  $M^{III}$ : 0.9 Al and 0.1 Fe) was prepared by coprecipitation at constant pH =  $10 \pm 0.2$  of an aqueous solution of  $Mg(NO_3)_2$ ,  $Al(NO_3)_3$  and  $Fe(NO_3)_3$  with a solution of NaOH and  $Na_2CO_3$ .

The Fe-ZSM-5 zeolite catalyst was prepared by solid state ion-exchange starting from the synthesized H-ZSM-5 and  $FeCl_3 \cdot 5 H_2O$ . The Fe-MCM-41 specimen was prepared from sodium silicate, CTMA-Br and  $Fe(NO_3)_3$  solution at pH 12. The crystallization was carried out at 373 K for 2 days followed by calcination at 823 K for six hours.

Table 1: The average composition of Hungarian *red mud*

$Al_2O_3$	16-18 wt%	CaO	0,5-3,5 wt%
$Fe_2O_3$	33-48 wt%	$V_2O_5$	0,2-0,3 wt%
$SiO_2$	9-15 wt%	$P_2O_5$	0,5-1 wt%
$TiO_2$	4-6 wt%	$CO_2$	2-3 wt%
$Na_2O$	8-12 wt%	S	0.15-0.30 wt%
MgO	0.3-1 wt%	F	0.10-0.15 wt%

The *red mud* utilized for catalyst preparation was the original waste from the Ajka Aluminum Industry of Hungary. The wet *red mud* was filtered, dried at 100 °C followed by calcination at 500 °C for four hours. The average composition of the Hungarian *red mud* is displayed in Table 1.

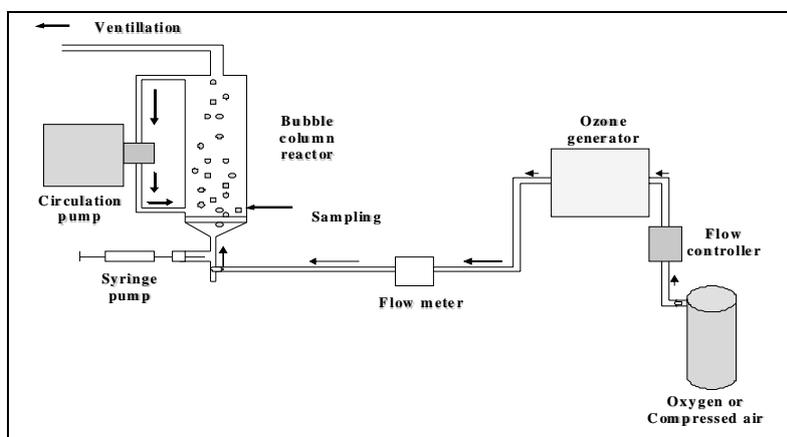


Figure 1: The experimental setup for oxidative treatment of phenol containing waters

used as flowing gas phase. The rate of the gas flow was constant: 50 dm<sup>3</sup>/h, and the reaction was carried out at ambient temperature.

All the catalyst samples were heat treated at 400 °C for two hours before the use in the oxidation reaction. The catalyst samples were characterized by XRD,  $N_2$  adsorption IR-spectroscopy and TEM.

### Methods

The oxidation of phenol was carried out in a recirculating laboratory bubble column reactor (Fig. 1).

In the bubble column reactor air at atmospheric pressure or ozone containing air (also at the same pressure) was

The reaction was followed by the determination of Chemical Oxygen Demand (COD) using the operative Hungarian Standard, No: MSZ 448-20.

### 3. RESULTS AND DISCUSSIONS

#### Characterization of the catalysts

The X-ray diffractograms of the hydrotalcite and the hydrotalcite origin Fe-Mg-Al mixed oxide, Fe-ZSM-5 and Fe-MCM-41 samples prove the expected crystallinity, while the XRD data of bauxite and red mud are very complicated correspond to the complex structure of these materials.

The BET surface areas and pore diameters could be calculated by the evaluation of N<sub>2</sub> adsorption isotherms, the data are presented in Table 2. The Fe content of the catalysts were determined by X-ray fluorescence method.

Table 2: : Characteristics of the catalysts

Catalyst sample	Average pore diameter (Å)	Character of the pore	BET surface area (m <sup>2</sup> /g)	Fe content (w/w%)
Fe/Al/Mg-mixed oxide	180	wide	135	1.0
FeZSM-5	5.5	narrow	335	4.13
Fe-MCM-41	36	wide	964	1.5
Fe <sub>2</sub> O <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub>	-	wide	103	2.5
Bauxite, calcined	-	none	2.5	14.0
red mud, calcined	-	none	37	35.0

#### Oxidation measurements

In the first stage the catalysts were tested in a well determined reaction, namely in the oxidation of phenol solution in distilled water (concentration: 2000 mg/L), at ambient temperature, where the pH of the solution was 4.6. The reactions were run for four hours, with sampling and COD determination hourly. As oxidant air or ozone was applied, the latter was produced using an *OZOMATIC Modular* type ozone equipment. The data can be seen on Figure 1, lines A and B.

Considering the data it could be established, that using air the oxidation efficiency is low (under 5 %), and by charge of ozone the activity could be increased significantly, but the extent is also low.

To regard the catalyst it could be appointed that the efficiency of the cheap, iron oxide base materials near to activity of the synthetic samples, nevertheless their surface area is significantly less.

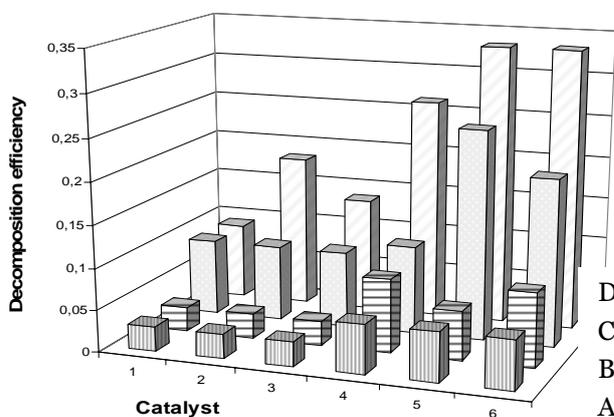


Figure 2: Catalytic oxidation of phenol in water with: a) air, b) ozone, c) air by buffering, d) ozone by buffering; Catalysts: 1. red mud, 2. Fe<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>, 3. bauxite, 4. Fe-ZSM-5, 5. Fe-hydrotalcite, 6. Fe-MCM-41

could be observed. This behavior can be explained by the formation of stable intermediates which oxidation is hindered. The identification of these compounds, as well as the determination of the mechanism of the oxidation is another task.

In the next measurements the solutions were stabilized using a phosphate-borax buffer solution of pH 6.8, and the reactions were run similarly as earlier. The results obtained can be seen in Figure 1, lines C and D.

To summarize the results obtained for synthetic waste water: the demolition of phenol could be achieved with relatively high efficiency. Choosing the optimal pH, the oxidation by ozone is proper, first of all in the presence of the synthetic, porous catalysts. Nevertheless, the activity of the natural origin catalysts with iron oxide content are less, these achievements are enough high to the demolition of the organic pollutants.

In the initial stage the oxidation was fast, however, after four hours a saturation

### 4. CWAO TREATMENT OF PHENOLIC THERMAL WATER

Additional studies were carried out with used (cooled) thermal water from Szentes (southeast Hungary). The pH of this water 8.6 and its COD is 90 mg/dm<sup>3</sup>. The investigations were emphasized to utilize the natural origin catalysts, while for treatment of large amount of water – considering the economical conditions – the application of these materials possesses fundamental importance.

The results obtained can be seen on Fig. 3 and 4. In the reaction by air (Fig. 3) the tendency of efficiency curves is close to saturation for two hours, which indicate the formation of stable intermediates. These compounds could react with the radicals or could inhibit the active centers of the catalyst. To determine of these intermediates or steps is important for the clarifying the mechanism of the reaction, moreover for the optimization of the reaction conditions as well.

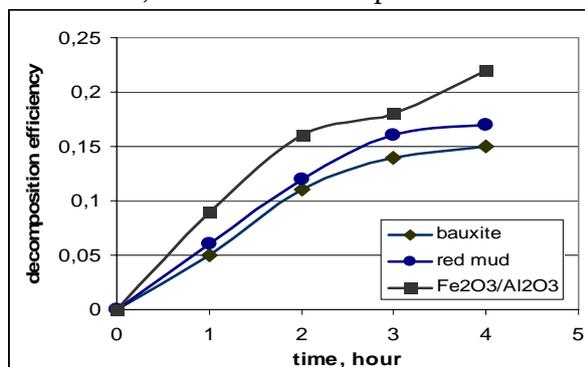


Figure 3: Oxidative treatment of used thermal water (COD: 90 mg/dm<sup>3</sup>) in the presence of iron oxide base catalysts, oxidative agent: air

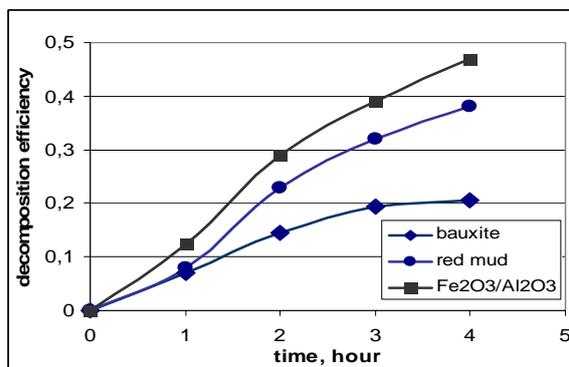


Figure 4: Oxidative treatment of used thermal water (COD: 90 mg/dm<sup>3</sup>) in the presence of iron oxide base catalysts, oxidative agent: ozone

Using ozone as oxidative agent, the decomposition efficiency increased in a large extent, and the saturation character could be observed only in the case of bauxite. Theoretically, this method is proper for removing of organic pollution in industrial scale. Considering the economical aspects, however, the utilization of ozone is too expensive for the treatment of the high amount of thermal water. Therefore, the development of catalytic air oxidation is the important task.

## 5. CONCLUSIONS

The mesoporous Fe-MCM-41, Fe/Al/Mg-mixed oxide and the microporous Fe-ZSM-5 zeolite are promising catalysts for the treatment of toxic wastewater containing phenol or other poisonous organic materials. Highest activity could be produced in the presence of Fe-MCM-41.

Considering the technological aspects the application of Fe-MCM41 would be prosperous because of the higher specific activity, however, from the economic point of view the application of the much less expensive natural catalysts (red mud or bauxite) could be suggested.

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