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IRON DOPED CARBON AEROGEL AS CATALYST FOR PHENOL TOTAL OXIDATION

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ABSTRACT. Two types of iron doped carbon aerogels were prepared by sol-gel polymerization of potassium salt of 2,4-dihydroxybenzoic acid with formaldehyde. This process was followed by an ion-exchange process between K^+ doped wet gel and Fe(II) or Fe(III) ion aqueous solutions. The resulted Fe(II) or Fe(III) doped gels were dried in supercritical conditions with liquid CO_2 and then pyrolyzed when two types of iron carbon aerogels were obtained. These aerogels were morpho-structural investigated by means of transmission electron microscopy (TEM), X-ray diffraction (XRD), specific surface area determination using nitrogen adsorption (BET and BJH methods) and elemental analysis. Iron doped carbon aerogels were tested as catalytic materials in phenol wet air oxidation process (total oxidation). Temperature, air flow, catalyst quantity and phenol concentration over the removal efficiency of the organic compound was studied.

Keywords: *iron doped carbon aerogel, phenol, catalytic wet air oxidation*

INTRODUCTION

Wastewaters containing organic compounds (pollutants) from chemical, petrochemical or pharmaceutical industries can create many problems in choosing an appropriate method to treat them. Many of them, (refractory organic pollutants), are difficult to remove by conventional methods (mechanical and biological treatment), therefore alternative methods have to be developed [1-3]. Because of their toxicity and frequency of their presence in industrial wastewaters, phenol and phenolic compounds have gained increased attention in the last two decades. Moreover, phenol is considered to be an intermediate in the oxidation route of higher molecular weight aromatics and so usually is taken as a model compound in research studies [4,5]. The choice of treatment, in case of wastewaters polluted with phenol and phenolic compounds, depends on the concentration, which can varies from 0.1 to 6800 mg/dm^3 depending on the wastewater source (pulp and paper industry, refineries, coking operations, coal processing) [5], economics, efficiency, easy control and reliability [6].

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Several processes for phenol abatement from wastewaters, which can be included in two large categories, recuperative methods (separation) and destructive methods, were studied.

In the first category, methods such as: steam distillation [5], liquid-liquid extraction (n-hexane, cyclohexane, benzene, toluene, etc.) [5], adsorption (activated carbon, activated bentonite, activated zeolites, perlite, resins, etc.) [5,7,8], adsorption-flocculation [9], membrane pervaporation [5], membrane-based solvent extraction [5,10,11] are included.

In the second category the following methods are included: (a) total oxidation by air or oxygen (non catalytic wet air oxidation – WAO, supercritical water oxidation – SCWO, catalytic wet air oxidation – CWAO, oxidative polymerization with oxygen in presence of enzimes), (b) wet oxidation with chemical oxidants (ozone and H_2O_2 – wet peroxide oxidation WPO – with its alternative, non catalytic oxidation, catalytic homogeneous and heterogeneous Fenton oxidation CWPO, catalytic non iron heterogeneous catalysis, and oxidative polymerization in presence of peroxidases) [5,12-16], (c) oxidation with chlorine, chlorine dioxide, potassium permanganate, ferrate (VI) ion [5], (d) electrochemical treatment (indirect electro-oxidation, direct anodic oxidation) [5,17,18], photocatalytic oxidation [5,19,20], supercritical water gasification – SCWG [5], electrical discharge (electro-hydraulic discharge, pulsed corona discharge, glow discharge electrolysis) [5], sonochemical processes [5,21], biodegradation (microbial or fungi species) [5,22,23].

Chemical oxidation with all its alternatives is widely used for treatment of wastewaters in order to remove organic pollutants, and has as final objective total oxidation (mineralization) of the organic contaminants to CO_2, H_2O and inorganics or, at least at their transformation into harmless products [13]. Also between the oxidation processes the catalytic ones become useful alternative due to the working conditions, which are milder [24]. As catalyst used to destroy organic pollutants, including phenol, we can mention: Ru, Rh, Pt, Ir, Ni, Ag supported on TiO_2, CeO_2, Al_2O_3 [24,25], metal oxides CuO, CoO, Cr_2O_3, NiO, MnO_2, Fe_2O_3, ZnO, CeO_2 [6,24,26,27], activated carbon [28], and iron and copper immobilised on synthetic zeolites [29,30] or pillared clays [31,32].

Due to their controllable and interesting nanostructural properties, such as high surface area, low mass density, high conductivity and continuous porosity, iron doped carbon aerogels [33-36], could be attractive materials for total oxidation of organic compounds.

In this paper two iron doped, Fe(II) and Fe(III) carbon aerogels were prepared, characterized and investigated as catalytic materials in phenol total oxidation process (catalytic wet air oxidation).

RESULTS AND DISCUSSION

Iron doped aerogel morpho-structural characterization

TEM images of the iron doped carbon aerogels presented in figure 1, show metal particles dispersed in the carbon aerogel matrix.

The XRD patterns of $Fe^{(2+)/(3+)}$-DCA shows two broad bands around $2\theta = 22^o$ and 43^o, indicating an amorphous structure of the carbon matrix (figure 2). The thin peaks correspond to the iron/iron oxide phases of metal particles [35].

Specific surface area was determined to be 745 m^2/g for $Fe^{(3+)}$-DCA and 368 m^2/g for $Fe^{(2+)}$-DCA.

The iron content determined using elemental analysis is about 10% (wt) for $Fe^{(3+)}$-DCA and 18% (wt) for $Fe^{(2+)}$-DCA [35]. Because of its high metal content a smaller specific surface area and a higher content of graphitic structures are present in $Fe^{(2+)}$-DCA [35]. A part of these graphitic structures cloud the iron/iron oxide particles.

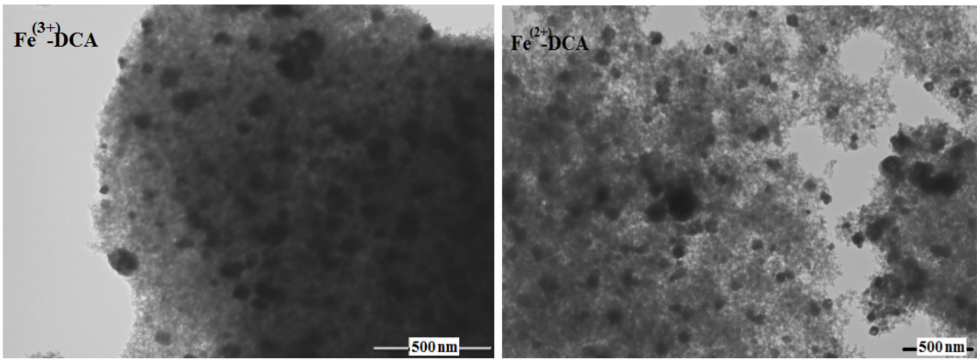


Figure 1. TEM images of iron doped carbon aerogels.

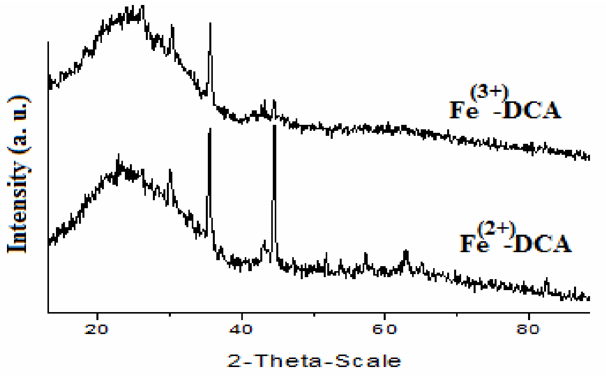
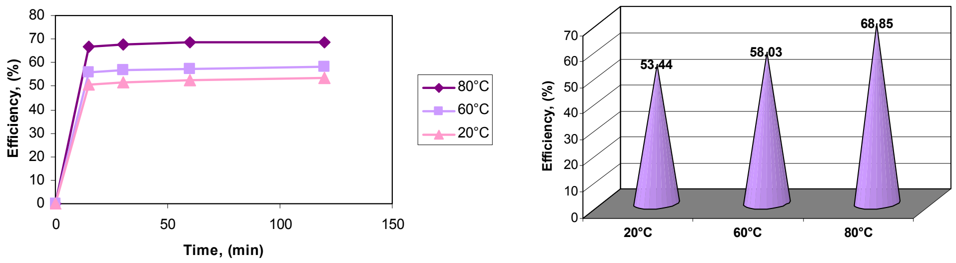


Figure 2. XRD patterns of iron doped carbon aerogels.

Phenol total oxidation results

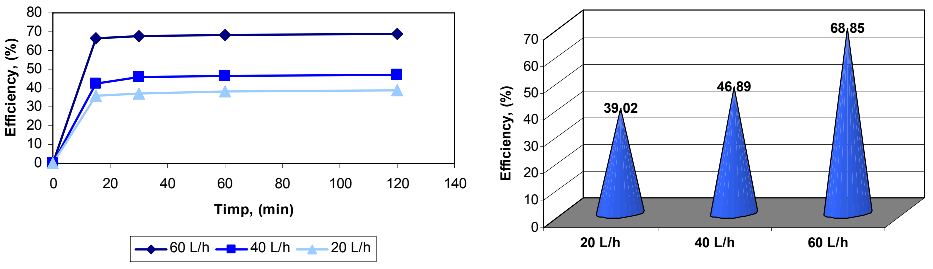
The influence of operating temperature over the evolution of the overall efficiency, air flow 60 L/h, 0.1 g $Fe^{(3+)}$-DCA catalyst and C_i = 1000 mg phenol/dm^3, is presented in figure 3(a). As expected, overall efficiency increased with the increasing of the temperature. In the first 30 minutes, the efficiency increased up to 50.65, 55.74 and 66.56% for an operating temperature of 20, 60 and 80°C respectively. Maximum values for overall efficiency are presented in figure 3(b). The highest value obtained was 68.85% at 80°C.



(a) **(b)**

Figure 3. Variation (a) and maximum values (b) of overall efficiency in the phenol CWAO process, at different temperatures and constant air flow, 60 L/h, for $Fe^{(3+)}$-DCA catalyst (0.1 g catalyst and C_i = 1000 mg phenol/dm^3).

The influence of air flow over the overall efficiency variation in time, for $Fe^{(3+)}$-DCA catalyst, at constant temperature 80°C, 0.1 g catalyst and C_i = 1000 mg phenol/dm^3, is presented in figure 4(a). Maximum increase of the overall efficiency was observed in the first 15 minutes and varies from 36.07 to 66.56% for 20 and 60 l/h respectively. We observed also that the increase of overall efficiency is not as steep as in case of temperature variation, suggesting that oxygen diffusion process could be rate determining step in the catalytic wet air oxidation process. Maximum values obtained for all air flows are presented in figure 4(b).



a **b**

Figure 4. Variation (a) and maximum values (b) of overall efficiency in the phenol CWAO process, at different air flows and constant temperature, 80°C, for $Fe^{(3+)}$-DCA catalyst (0.1 g catalyst and C_i = 1000 mg phenol/dm^3).

We also studied the influence of the catalyst quantity and phenol initial concentration over the overall efficiency in the CWAO process. Results obtained in these cases are presented in figures 5 and 6. If we used a double catalyst quantity (0.2 g instead of 0.1 g) an increase with only 11% of the overall efficiency was observed, figure 5. Also a 10 times decrease of the phenol solution concentration led to an increase of 28% in overall efficiency value (figure 6).

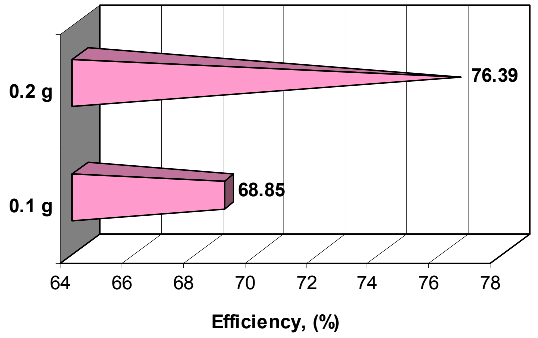


Figure 5. Catalyst quantity influence over the maximum overall efficiencies obtained in the phenol CWAO process, at constant air flow and constant temperature, 60 L/h, 80°C, for Fe$^{(3+)}$-DCA catalyst (C_i = 1000 mg phenol/dm^3).

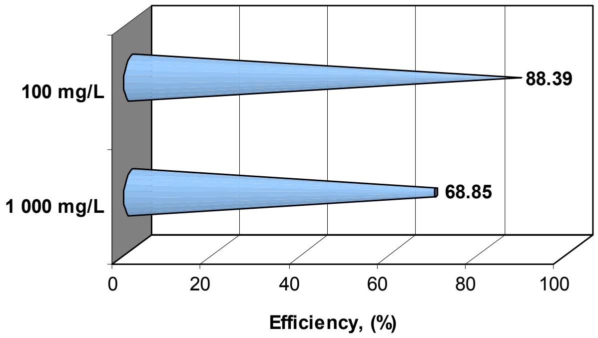


Figure 6. Phenol initial concentration influence over the overall efficiencies in the phenol CWAO process, at constant air flow and constant temperature, 60 L/h, 80°C, for Fe$^{(3+)}$-DCA catalyst (0.1 g catalyst).

In the same working conditions, on the Fe$^{(2+)}$-DCA catalyst we obtained overall efficiency values with 20% smaller than in case of Fe$^{(3+)}$-DCA, fact that can be explained by its smaller surface area and partial coverage of iron/iron oxide particles by graphitic clouds. The blank carbon aerogel sample had no activity in phenol oxidation process.

CONCLUSIONS

The influence of catalyst type and air flow rate over the overall process efficiency was studied. An increase of the temperature and air flow rate led to an increase of the overall efficiency. Total oxidation overall efficiencies up to 88.39% were reached for $Fe^{(3+)}$-DCA catalyst at 80°C and 60 l air/h for 0.1 g catalyst and C_i = 100 mg phenol/dm^3.

$Fe^{(3+)}$-DCA catalyst proved to be more efficient than $Fe^{(2+)}$-DCA catalyst, probably due to its superior morphological properties (higher surface area, iron particles on the DCA surface).

Further studies will be performed in order to establish the optimum working conditions for total oxidation of organic compounds, and catalyst reproducibility and lifetime

EXPERIMENTAL SECTION

Iron doped carbon aerogel preparation

Carbon aerogels doped with Fe were prepared by sol-gel polymerization of potassium salt of 2,4-dihydroxybenzoic acid with formaldehyde, followed by an ionic exchange process between K^+ doped wet gel and Fe(II) or Fe(III) ion aqueous solutions [35,37]. The resulted Fe(II) or Fe(III) doped gels were dried in supercritical conditions with liquid CO_2 and then pyrolyzed in high temperature and inert atmosphere.

K_2CO_3 was added under vigorous stirring to a 2,4-dihidroxybenzoic acid (DHBA) demineralised water suspension (DHBA/K_2CO_3 = 0.5; DHBA/H_2O = 0.0446 g/cm^3), a potassium salt solution resulting. After 30 min, when all the acid was neutralized, the solution became clear and after another 30 min, 37% formaldehyde (F) and then K_2CO_3 (C) (DHBA/F = 2; DHBA/C = 50) were added to the solution. The resulting mixture was placed into tightly closed glass moulds (7 cm – length × 1 cm – internal diameter) and cured in two time intervals: 1 day at room temperature and 4 days at 70°C. The resulting K^+-doped gel rods were cut into 0.5-1 cm pellets and washed with fresh acetone for 1 day. The K^+-loaded wet gels were then soaked for 3 days in 0.1M aqueous solutions of $Fe(NO_3)_3 \cdot 9H_2O$ or $Fe(OAc)_2$ [35]. Iron solutions were renewed daily. Finally, samples were washed once more with fresh acetone and then were subsequently dried with CO_2 in supercritical conditions. The resulting iron doped organic aerogels were pyrolysed at 750°C for 3h in an Ar atmosphere, obtaining iron and iron oxide particles-doped carbon aerogel. The iron doped carbon aerogels prepared using Fe (II) and Fe (III) salts were termed $Fe^{(2+)}$-DCA and $Fe^{(3+)}$-DCA, respectively. By drying and pyrolysis of K^+-doped gels the blank carbon aerogel sample (K-DCA) was obtained.

Iron doped aerogel morpho-structural investigations

Transmission electron microscopy (TEM) of the metal doped carbon aerogels was performed with a Hitachi H-7000 microscope operating at 125 keV.

X-ray diffraction patterns were recorded in a θ–2θ Bragg–Bretano geometry with a Siemens D5000 powder diffractometer with Cu-K_α incident radiation (λ = 1.5406 Å) and a graphite monochromator.

Specific surface area determinations were performed using Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods using an ASAP 2000 surface area analyzer (Micrometrics Instruments Corp.). Prior to determination, samples of approximately 0.03 g were heated to 130°C under vacuum (10^{-5} Torr) for at least 18 h to remove all adsorbed species.

Elemental analyses were performed with an inductively coupled plasma-mass spectroscope (ICP-MS).

Phenol total oxidation – working conditions

Phenol total oxidation or catalytic wet air oxidation (CWAO), was carried out in a thermostated stirred batch reactor (magnetic stirrer) at atmospheric pressure, using different temperatures of 20, 40 and 60°C, air flows (20, 40 and 60 L/h), catalyst quantities (0.1 and 0.2 g) and phenol initial concentrations (100 and 1000 mg/dm^3). The Fe$^{(3+)}$-DCA catalyst, brought at a grain size of d < 250 μm using an appropriate sieve, was contacted with 100 cm^3 phenol solution. During the experiment, determination of the organic compounds in solution was carried out every 15 minutes, (first two determinations), and then every 30 minutes. Taking in account the fact that in this stage of the research we were interested to see how this type of material acts as catalyst for total oxidation of organic compounds we used $KMnO_4$ chemical oxygen demand, CCO-Mn, method in order to establish the final concentration of the organics in solution. This determination is currently used in environmental laboratories for wastewaters characterization (STAS 3002/85, SR ISO 6060/96) according to Romanian legislation [38]. The experiment was carried out for 120 minutes, until no modifications were observed in the organic compound final concentration. We also tested a Fe$^{(2+)}$-DCA catalyst and a blank carbon aerogel sample (K-DCA).

The evolution of phenol oxidation process was followed by means of overall efficiency (calculated using chemical oxygen demand values as CCO-Mn at a moment *t* and the initial CCO-Mn value), eq. (1).

$$\mathbf{X = \frac{C_i - C_t}{C_i} \cdot 100} \tag{1}$$

where,

C_i is the CCO-Mn initial value, in mg $KMnO_4$/dm^3

C_t is the CCO-Mn value at moment *t*, in mg $KMnO_4$/dm^3.

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