BULETINUL INSTITUTULUI POLITEHNIC DIN IAŞI
Publicat de
Universitatea Tehnică „Gheorghe Asachi” din Iaşi
Volumul 63 (67), Numărul 1, 2017
Secţia
CHIMIE şi INGINERIE CHIMICĂ

MAGNETIC ACTIVATED CARBON COMPOSITES USED AS FENTON LIKE CATALYSTS FOR PHOTODEGRADING ORGANIC COMPOUNDS IN AQUEOUS SOLUTIONS

BY

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Received: March 16, 2017
Accepted for publication: April 10, 2017

Abstract. The main goal of the present work consists in investigating the performance of several magnetic activated carbon composites towards the photo-Fenton degradation of Ibuprofen molecule. Three Granular Activated Carbon (GAC) matrices having different pH_{PZC} were employed to prepare the magnetic GACs using the co-precipitation method. UV light irradiation tests were carried out to determine the performance of the prepared magnetic composites towards the degradation of Ibuprofen molecule in aqueous solution in the presence of Hydrogen Peroxide. The photo-Fenton tests were conducted after the adsorption equilibrium has been established. The magnetic GAC composites prepared with acid-surfaced matrix L27 GAC was found to enhance significantly the degradation process of Ibuprofen molecule.

Keywords: Magnetic composites; photocatalysis; Fenton reaction; Ibuprofen; micropollutant.

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1. Introduction

There has been a growing concern about the presence of pharmaceuticals in different types of water bodies. These compounds are commonly referred to as emerging micropollutants. Their presence in water is due to both their use in medicine and the ineffectiveness of water treatment plants (Motoc *et al*., 2013). Up to present, there are no well-established water treatment processes designed to remove micropollutants (Ahmed and Theidan, 2013).

Various physical and chemical treatment techniques such as catalytic oxidation, photocatalytic, membrane separation, biodegradation, solvent extraction and adsorption have been used for the reduce the organic pollutants from water (Martins *et al*., 2016; Sadegh Hassania *et al.*, 2016; Wang *et al*., 2016). One of the traditional technologies for the removal of contaminants in water is based on adsorption process using carbon active (Alzahrani *et al*., 2016; Garcia-Zaleta *et al*., 2016). Inexpensive adsorbents can be can easily be separated from solution using a magnetic constituent. In case of magnetic activated carbon several benefits can be mentioned: micrometer sized particles, very high surface area and microporosity, magnetic particles embedded in carbon matrix; fully dispersivity into water; fast uptake of pollutants; easy reuse and disposal; continuous and semi batch operation (Goscianska *et al*., 2015; Liu *et al*., 2010; Mohd Din *et al*., 2009).

Known as an emergent micropollutant, Ibuprofen is nonsteroidal anti-inflammatory drug and has a wide usage, and is investigated as model micropollutant in the present study. Despite current research in ibuprofen removal, only a few studies approaching the methods effectiveness have been reported. Degradation of ibuprofen by advanced oxidation processes such as ozonation and UV/H_2O_2 have been investigated (Jain *et al*., 2016).

The purpose of this study is to investigate the removal of Ibuprofen molecule from aqueous solutions by photo-Fenton process. Three different granular activated carbon materials (GAC) are selected based on their chemical surface properties to prepare magnetic composites. Their efficiency as Fenton like catalysts towards Ibuprofen removal from aqueous solution is investigated.

2. Experimental Part

2.1. Materials

Activated Carbon materials were obtained from CECA-Jacobi (France). Three ACs, L27, X17 and S21 were employed in this study in order to establish the influence of surface pH_{PZC} onto the performance of Fenton-like catalysts. The ACs were washed with bidistilled water to remove residual acidity of basicity, and dried at 75°C for 24 h. Analytical standard $FeSO_4 * 7H_2O$ (>99%), Ibuprofen Sodium salt, (>98%), and Hydrogen Peroxide (35% w/w sol) were purchased from Sigma Aldrich. All solutions were prepared using bidistilled water.

2.2. Preparation of Acid Treated Fe-Amended Activated Carbon

Magnetic composites were prepared by co-precipitation method. Each of the considered ACs was dried at 75°C for 24 h. The ACs were used as such and in parallel, each one of the considered ACs was oxidized with concentrated HNO_3 in ultrasonic bath for 60 min, washed with bidistilled water and dried. A solution of Fe^{2+} and Fe^{3+} was prepared in 1:2 ratio. The unmodified and oxidized ACs respectively were suspended in Fe2+ and Fe3+ solution. This mixture was sonicated for 15 min. 8 M NH_4OH solution was added dropwise to adjust the pH to 12 in order to co-precipitate Fe_3O_4. This reaction was conducted for 1 h at 50°C under mechanical stirring. Two types of composites, magnetic composites (M-GAC), and pre-oxidized magnetic composites (M-GAC/HNO3) were obtained after washing and drying at 55°C (Bayazit and Kerkez, 2014).

2.3. Characterization Methods

The textural characterization of the supports and catalyst was based on the N_2 adsorption-desorption isotherms, determined at −196°C, which were obtained using a Micromeritics 2020 analyzer. Pore size distribution was determined by Density Functional Theory (DFT) method.

2.4. Fenton and Photo-Fenton Tests

The performance of the synthesized catalysts was evaluated in Fenton and photo-Fenton processes of Ibuprofen degradation. Catalytic degradation experiments were carried out in conical flasks for 2 h on a magnetic stirrer using a catalyst dosage of 0.1 g/250 mL, pH of 3, 100 mg/L H_2O_2. A volume of 4 mL of reaction mixture was systematically sampled, separated by centrifugation and then 1 mL was diluted and analyzed by means of UV–Vis Jasco spectrophotometer following the absorbance at 219 nm. After the analysis, the undiluted solution was added back into the photocatalytic reactor to minimize the loss in total volume and maintain the solid/liquid ratio.

3. Results and Discussion

The raw ACs have different porous properties. The N_2 adsorption-desorption isotherms showed that L27 is microporous but also contain some mesopores which is confirmed by the values of its S_{micro} and S_{ext}. Also, according to the number of surface oxygen groups L27 is acidic. Table 1 exemplifies the textural properties of the L27 materials based on N_2 isotherms. The N_2 adsorption-desorption isotherms for M-L27 (figure not shown) presents an enlarged hysteresis loop compared to L27 indicating an increased mesopore volume, confirmed by the increased pore size. For the oxidized M-L27 the adsorbed volume decreases.

The decreased surface area of the oxidized carbons, may be due to the high amount of oxygen-containing groups introduced on the AC surface with HNO_3 treatment, which possibly block the entry of N_2 molecules inside the small pores (Chen *et al*., 2015).

Table 1

Textural Properties of the Raw and Magnetic L27 GACs

GAC	V_{MICRO} [cm^3g^{-1}]	Pore Size [Å]	S_{EXT} [m^2g^{-1}]	S_{MICRO} [m^2g^{-1}]	S_{TOTAL} [m^2g^{-1}]	S_{BET} [m^2g^{-1}]
L27	0.57	18.5	444	616	1060	1575
M-L27	0.46	25.4	644	362	1006	1336
M-L27/HNO_3	0.38	17.2	492	442	934	1100

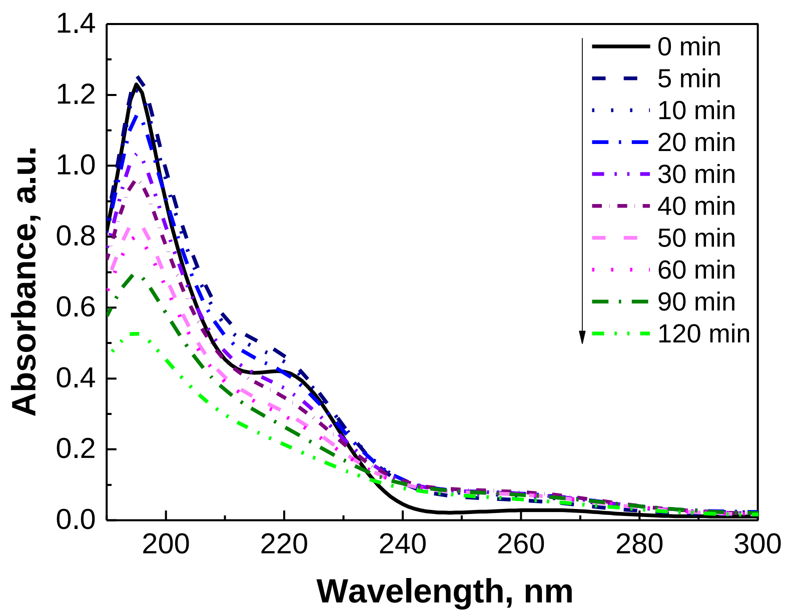

Fig. 1 – Evolution of UV spectra during Ibuprofen degradation by M-L27, pH = 3.

Light irradiation tests were carried out to determine the performance of the prepared Iron-impregnated composites towards the removal of Ibuprofen from aqueous solution. Photo-Fenton tests conducted at near-neutral pH using an UV lamp of 17 W resulted in low values of removal efficiency. Therefore, the experimental runs were also performed at the pH value of 3. These tests were conducted after the adsorption equilibrium was reached. Fig. 1 shows the evolution of Ibuprofen molecule spectra during photo-Fenton degradation in presence of M-L27 and H_2O_2.

Fig. 2 presents the first order kinetics of the photo-Fenton degradation of Ibuprofen molecule in presence of magnetic GACs.

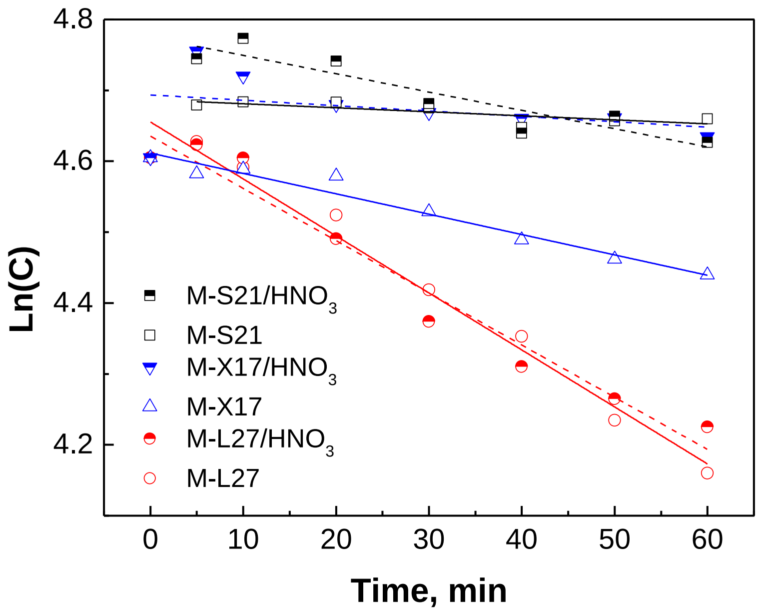

Fig. 2 – First order kinetics of photo-Fenton processes using M-GACs, pH = 3.

Both, the neutral and basic surfaced matrices, S21 and X17, lead to low values of constant rate (Table 2). On the contrary, the composites prepared with acid surfaced matrix L27 resulted in the highest efficiency.

M-S21 and M-S21/HNO_3 show very weak catalytic activity towards Ibuprofen degradation. M-L27 and M-L27/HNO_3 present strong activities as Fenton-like catalysts at pH = 3.

Table 2

Kinetics of Photocatalytic Tests Under UV Light Irradiation (17 W), pH = 3

M-GAC	M-L27	M-L27/HNO_3	M-X17	M-X17/HNO_3	M-S21	M-S21/HNO_3
$10^3 * k_1$	8.2	7.7	2.0	2.1	0.7	2.9
R^2	0.991	0.867	0.983	0.892	0.840	0.861

4. Conclusions

Total iron content in M-GAC was higher than in the pre-oxidized magnetic composites. M-L27 had the highest iron content. HNO_3 preactivation resulted in an increase in hydrophilicity and consequently in a significant decrease in the sorption capacity. N_2 adsorption analysis show a decrease in total surface after Fe embedment.

Photocatalytic degradation tests were conducted under UV light irradiation by using a low pressure lamp of 17 W (312 nm). Photodegradation of Ibuprofen molecule obeys the first order kinetic model. Among the synthetized adsorbents only M-L27 and M-L27/HNO_3 were suitable for Fenton and photo-Fenton reactions. Fe(II) embedment on L27 provides the possibility to regenerate the AC by photo-Fenton.

Acknowledgements. This work was supported by a grant of the Romanian National Authority for Scientific Research and Innovation, CNCS - UEFISCDI, project number PN-II-RU-TE-2014-4-0405.

REFERENCES

Ahmed M.J., Theydan S.K., *Adsorption of p-Chlorophenol onto Microporous Activated Carbon from Albizia Lebbeck Seed Pods by One-Step Microwave Assisted Activation*, J. Anal. Appl. Pyrolysis, **100**, 253-260 (2013).

Alzahrani E., Abo-Dief H.M., Mohamed A.T, *An Investigation Into the Adsorption of Sulphur Compounds Using Iron Oxide/Activated Carbon Magnetic Composite*, Adv. Environ. Biol., **10**, *4*, 204-219 (2016).

Bayazit Ş.S., Kerkez Ö, *Hexavalent Chromium Adsorption on Superparamagnetic Multi-Wall Carbon Nanotubes and Activated Carbon Composites*, Chem. Eng. Res. Des., **92**, *11*, 2725-2733 (2014).

Chen H., Zhang L., Zeng H., Yin D., Zhai Q., Zhao X., Li J., *Highly Active Iron-Containing Silicotungstate Catalyst for Heterogeneous Fenton Oxidation of 4-Chlorophenol*, J. Mol. Catal. A: Chemical, **406**, 72-77 (2015).

García-Zaleta D.S., Torres-Huerta A.M., Domínguez-Crespo M.A., García-Murillo A., Silva-Rodrigo R., López González R., *Influence of Phases Content on Pt/TiO_2, Pd/TiO_2 Catalysts for Degradation of 4-Chlorophenol at Room Temperature*, J. Nanomater, doi: 10.1155/2016/1805169 (2016).

Goscianska J., Ptaszkowska M., Pietrzak R., *Equilibrium and Kinetic Studies of Chromotrope 2R Adsorption onto Ordered Mesoporous Carbons Modified with Lanthanum*, Chem. Eng. J., **270**, 140-149 (2015).

Jain S., Sharma K., Chandrawat U., *Photocatalytic Degradation of Anti-Inflammatory Drug on Ti Doped $BaBiO_3$ Nanocatalyst under Visible Light Irradiation*, Iranica Journal of Energy and Environment, **7**, *1*, 64-71 (2016).

Liu Q.-S., Zheng T., Wang P., Jiang J.-P., Li N., *Adsorption Isotherm, Kinetic and Mechanism Studies of Some Substituted Phenols on Activated Carbon Fibres*, Chem. Eng. J., **157**, 348-356 (2010).

Martins T.F., Marques R.P., Nunes E.S., Moreto J.A., *Synthesis of Metallic Iron Nanoparticles and their Use in 4-Chlorophenol Dehalogenation*, 22º CBECiMat - Congresso Brasileiro de Engenharia e Ciência dos Materiais 06 a 10 de Novembro de 2016, Natal, RN, Brasil.

Mohd Din A.T., Hameed B.H., Ahmad A.L., *Batch Adsorption of Phenol onto Physiochemical-Activated Coconut Shell*, J. Hazard. Mater., **161**, 1522-1529 (2009).

Motoc S., Remes A., Pop A., Manea F., Joop Schoonman J., *Electrochemical Detection and Degradation of Ibuprofen from Water on Multi-Walled Carbon Nanotubes-Epoxy Composite Electrode*, J. Environ. Sci., **25**, *4*, 838-847 (2013).

Sadegh Hassani S., Madannejad S., Tasharrofi S., Samiee L., Rashidi A.M., *Comparable Study of 4-Chlorophenol Removal from Petrochemical Wastewater Using Mesoporous and Microporous Carbons: Equilibrium and Kinetics Investigations*, J. Pet. Environ. Biotechnol., **7**, 289, doi:10.4172/2157-7463.1000289 (2016).

Wang F., Wenzhi Q., Shaolei L., Hui W., Zhaoyong B., *Electrolysis Conditions Optimization of 4-Chlorophenol Degradation with Pd/Graphene Gas-Diffusion Electrode by Response Surface Methodolog*y, Int. J. Electrochem. Sci., **11**, 1172-1183 (2016).

COMPOZITE MAGNETICE PE BAZĂ DE CĂRBUNE ACTIV UTILIZATE DREPT CATALIZATORI DE TIP FENTON PENTRU FOTODEGRADAREA COMPUŞILOR ORGANICI DIN SOLUŢII APOASE

(Rezumat)

Principalul obiectiv al prezentei lucrări constă în investigarea performanţelor unor compozite magnetice de cărbune activ în ceea ce priveşte fotodegradarea moleculei de Ibuprofen din soluţii apoase. Trei suporturi de cărbune activ granular (CAG), având diferite valori ale pH_{PZC}, au fost considerate în vederea preparării de CAG magnetic prin metoda coprecipitării. Teste de iradiere UV au fost efectuate pentru determinarea performanţelor compozitelor magnetice preparate în privinţa degradării moleculei de Ibuprofen din soluţie apoasă, în prezenţa peroxidului de hidrogen. Testele foto-Fenton au fost conduse ulterior stabilirii echilibrului de adsorbţie. S-a determinat faptul că materialele magnetice compozite preparate folosind CAG suport L27, având suprafaţă acidă, conduc la intensificarea semnificativă a procesului de degradare a moleculei de Ibuprofen.