

The Comparative Assessment of Photolysis, Sorption and Photocatalysis Processes to Humic Acids Removal from Water

D. Sonea^{*}, R. Pode^{*}, F. Manea^{*}, C. Ratiu^{**}, C. Lazau^{**}, I. Grozescu^{**} and G. Burtica^{*}

^{*} University "Politehnica" Timisoara, Faculty of Industrial Chemistry and Environmental Engineering, Victoriei Sq. No. 2, 300006 Timisoara, Romania

^{**} National Institute for Research and Development in Electrochemistry and Condensed Matter, Timisoara, Condensed Matter Department, Plautius Andronescu no.1, 300254, Timisoara, Romania

Abstract: Taking into account the photosensitive character of humic acids and the sorption as prerequisite step to reach an effective degradation by photocatalysis application for removal of humic acids from water, the assessment of photolysis and adsorption contribution to overall photocatalysis process using TiO₂-modified zeolite catalyst with 1% TiO₂, w/w (TiO₂-Z) is necessary. The results obtained at low concentration of humic acid (25 mg·L⁻¹) using TiO₂-Z, indicated that in comparison with adsorption process, the photocatalysis application did not improve removed amount of humic acid. Though, the functionalization of zeolite with TiO₂ led to improve the adsorption capacity for humic acid. The best results were achieved for photolysis due to fact that humic acids act as natural photosensitizers. At higher concentrations of humic acids (100 mg·L⁻¹), better results were achieved on TiO₂-Z for photocatalytic process (41.8 mg) than the sorption (28.7 mg) and photolysis (27.3 mg) processes, but no a cumulative effect of sorption and photolysis was noticed. The similar results obtained through application of photocatalysis using both TiO₂-Z and Z-Na catalysts and taking into account the photoinert character of Z-Na and enhanced sorption capacity of TiO₂-Z for HA proved the significant contribution of both photolysis and sorption processes.

Keywords: photolysis, photocatalysis, sorption, TiO₂-zeolite, humic acid

1. Introduction

Humic acids (HA) are natural polymers, formed during degradation of plants and microbial materials, with a high molecular weight, containing aromatic blocks, characterized by a broad molecular weight distribution and high chemical heterogeneity, with acidic character due to carboxylic and phenolic groups. The structure, molar mass and functional groups vary depending on origin and age [1-3]. During drinking water disinfection stage, HA react with chlorine and cause hazardous disinfection by-products, e.g., trihalomethanes, haloacetic acids, haloacetonitriles [4]. Humic acids play an important role as photosensitizer in aquatic processes, form soluble complexes with pesticides and heavy metals, increase the bacteria regrowth potential in water distribution pipelines resulting in pipe corrosion [5]. Many treatment conventional methods, e.g., coagulation and flocculation [6], adsorption [7,8], biofiltration [9,10], electromagnetic treatment followed by electrocoagulation using aluminium electrodes [11] were applied in order to remove humic acids from water. Taking into account the disadvantages of these methods, the heterogenous photocatalysis can be regarded as an effective alternative solution for the elimination of HA from aqueous solution [12-19].

In general, the catalyst type plays a main role of the performance of the heterogenous photocatalytic process. Thus, based on both the importance of sorption capacity of catalyst material in its photocatalytic activity and the potential of the photosensitive character of HA, prior to

practical application of photocatalysis on the HA removal the contribution of each photolysis, sorption and photocatalysis process to humic acids removal from water is required. This study focused on the assessment of the contribution of photolysis and sorption to overall photocatalysis application using TiO₂-Z catalyst for the removal of humic acids from water for two different concentrations of humic acids. In addition, the sorption and photocatalytic capacity of catalyst for humic acids was determined in comparison with monocationic form of clinoptilolitic zeolite (Z-Na).

2. Experimental

All photolytic, sorption and photocatalytic experiments were carried out under magnetic stirring at 20 °C into a RS-1 photocatalytic reactor (Heraeus, Germany), which consisted of a submerged lamp surrounded by a quartz shield. The sorption and photocatalytic activity of TiO₂ (1%, w/w) immobilized on monocationic form of zeolite (TiO₂-Z) synthesized by solid-solid method, was assessed in comparison with monocationic form of clinoptilolitic zeolite (Z-Na). The amount of catalyst was 1g·L⁻¹.

The adsorption experiments were carried out under dark conditions and photolytic experiments under UV irradiation in the absence of catalyst, under the similar conditions of photocatalysis. After the adsorption and photocatalysis application for 120 minutes, the suspension was sampled and filtered through a 0.45 µm Millipore filter. The concentration of humic acid was measured in

terms of absorbance at 254 nm (A_{254}) and 436 nm (A_{436}) with a Carry 100 Varian spectrophotometer.

3. Results and Discussion

Based on the literature data regarding photosensitive character of humic acids and photoinert character of zeolite and its affinity for Has [1], the application of each photolysis, sorption and photocatalysis process on HA removal was tested for two initial HA concentrations, 25 $\text{mg}\cdot\text{L}^{-1}$ and 100 $\text{mg}\cdot\text{L}^{-1}$, respectively.

The sorption and photocatalysis experiments using monocationic form of clinoptilolitic zeolite (Z-Na) and TiO_2 -modified zeolite catalyst (TiO_2 -Z) were carried out for both HA concentrations. The comparative results regarding HA removal by sorption, photolysis and photocatalysis are shown in Figures 1-5.

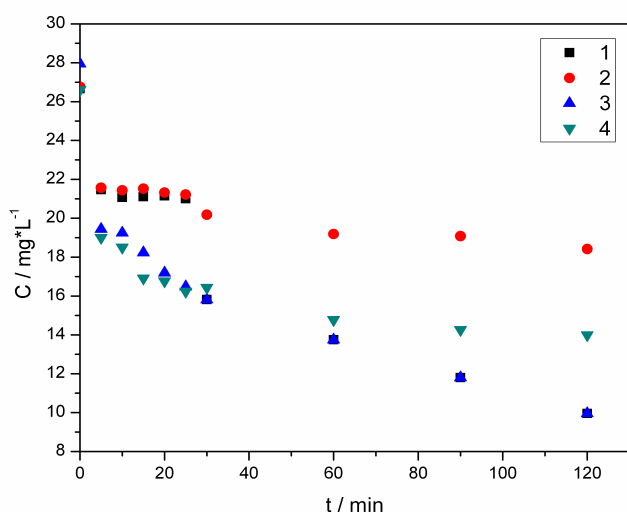


Figure 1. Evolution of HA concentration (UV_{254}) versus time ($C_i=25 \text{ mg}\cdot\text{L}^{-1}$) corresponding to the processes: 1 –sorption on TiO_2 -Z; 2 – sorption on Z-Na; 3 – photocatalysis on TiO_2 -Z; 4 – photocatalysis on Z-Na.

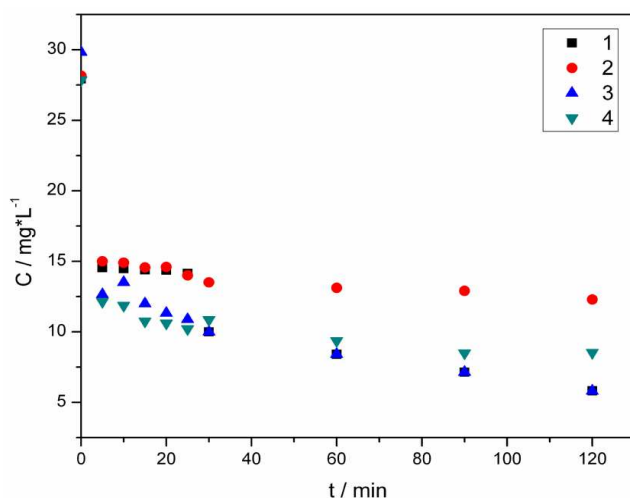


Figure 2. Evolution of HA color (VIS_{436}) versus time ($C_i=25 \text{ mg}\cdot\text{L}^{-1}$) corresponding to the processes: 1 –sorption on TiO_2 -Z; 2 – sorption on Z-Na; 3 – photocatalysis on TiO_2 -Z; 4 – photocatalysis on Z-Na.

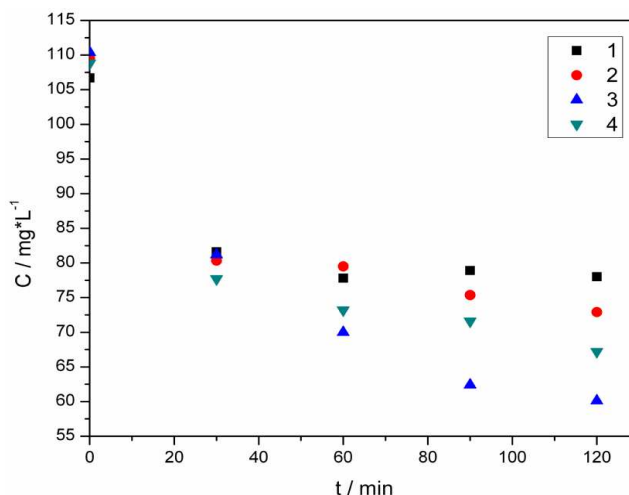


Figure 3. Evolution of HA concentration (UV_{254}) versus time ($C_i=100 \text{ mg}\cdot\text{L}^{-1}$) corresponding to the processes: 1 –sorption on TiO_2 -Z; 2 – sorption on Z-Na; 3 – photocatalysis on TiO_2 -Z; 4 – photocatalysis on Z-Na.

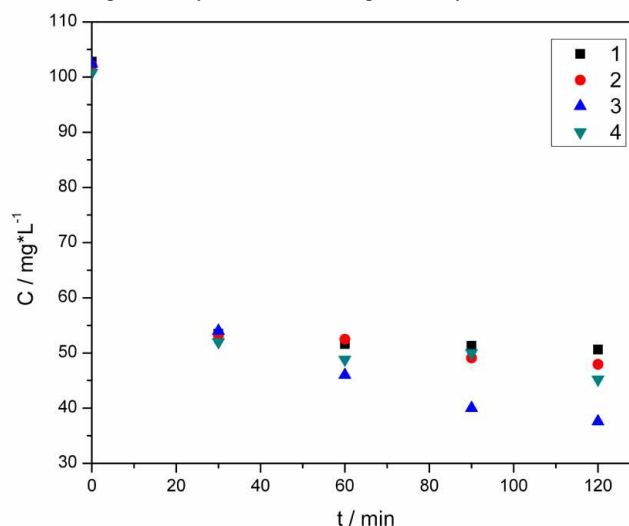


Figure 4. Evolution of HA color (VIS_{436}) versus time ($C_i=100 \text{ mg}\cdot\text{L}^{-1}$) corresponding to the processes: 1 –sorption on TiO_2 -Z; 2 – sorption on Z-Na; 3 – photocatalysis on TiO_2 -Z; 4 – photocatalysis on Z-Na.

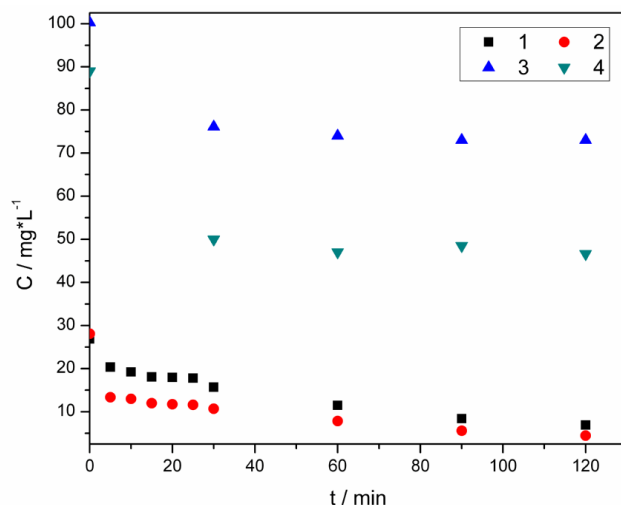


Figure 5. Evolution of HA concentration (UV_{254}) and color (VIS_{436}) versus time corresponding to the photolysis process for two initial HA concentrations: $C_i=25 \text{ mg}\cdot\text{L}^{-1}$ (1 – UV_{254} , 2 – VIS_{436}); $C_i=100 \text{ mg}\cdot\text{L}^{-1}$ (3 – UV_{254} , 4 – VIS_{436}).

Based on the experimental data and balance mass, it was determined the amount of humic acid (mg) reported to 1 Liter of solution that was removed through sorption, photolysis and photocatalysis processes, at two HA initial concentrations (25 and 100 mg·L⁻¹) and the catalyst dose of 1g·L⁻¹ after 120 minutes reaction time. The results obtained for the two HA initial concentrations are gathered in Tables 1 and 2.

TABLE 1. Contribution of different processes to humic acids removal at initial HA concentration of 25 mg·L⁻¹

Process	Catalyst type	A ₂₅₄ [mg]	A ₄₃₆ [mg]
Sorption	TiO ₂ – Z	18.0	24.0
	Z – Na	8.0	14.9
Photocatalysis	TiO ₂ – Z	18.3	23.3
	Z – Na	15.2	21.1
Photolysis	-	22.3	30.9

TABLE 2. Contribution of different processes to humic acids removal at initial HA concentration of 100 mg·L⁻¹

Process	Catalyst type	A ₂₅₄ [mg]	A ₄₃₆ [mg]
Sorption	TiO ₂ – Z	28.7	52.1
	Z – Na	36.6	54.1
Photocatalysis	TiO ₂ – Z	41.8	64.2
	Z – Na	41.6	55.6
Photolysis	-	27.3	42.4

It can be noticed that at lower HA concentration (25 mg·L⁻¹), the amount of HA removed by sorption and photocatalysis on TiO₂ – Z were practical similarly (~18 mg). The photocatalysis inefficiency at low HA concentration could be own the low TiO₂ content of zeolite (1%, w/w). The best results were achieved for photolysis (22.3 mg) due to fact that humic acids act as natural photosensitizers, this property being obviously manifested at low concentrations of HA. The increase of sorption capacity of TiO₂-Z catalyst as the consequence of TiO₂ immobilization on zeolite surface was noticed.

The results regarding the solution discoloration, expressed also removed HA mg reported to 1 L, was almost similarly, 24.0 mg for sorption and 23.3 mg for photocatalysis, respectively. Based on these results, it can be said that at low HA concentrations, the solution decoloration is the result of sorption process and no oxidation of cromophore groups. By comparison HA removal through sorption and photocatalysis process using Z-Na catalyst at low HA concentrations can be noticed a significant difference between the amount of HA removed by the two processes. Thus, 8 mg HA was removed by sorption and 15.2 mg HA was removed by photocatalysis using Z-Na catalyst. Taking into account the photoinert character of zeolite [1] and photosensitive character of HA [5], the increased amount of HA removed by photocatalysis using Z-Na catalyst could be the result of both sorption and photolysis processes, without to reach a cumulative effect.

At higher concentrations of HA (100 mg·L⁻¹), better results were achieved on Z-TiO₂-SS for photocatalytic process (41.8 mg) than the sorption (28.8 mg) and

photolysis (27.3 mg) processes, and no a cumulative effect of sorption and photolysis was noticed. The significant contribution of sorption and photolysis processes on the overall photocatalysis process for the removal of humic acids from water was found, but no satisfactory results of photocatalysis applying was obtained due to the low loading of TiO₂ into zeolitic matrix.

The amount increase of HA adsorbed on TiO₂- Z at HA concentration of 100 mg·L⁻¹ (28.8 mg) compared with initial HA concentration of 25 mg·L⁻¹ (18.0 mg) can be explained by the fact that sorption process is favored by initial concentration increasing. Under high initial HA concentrations, the photocatalysis exhibits a more pronounced effect on the discoloration degree in comparison with sorption application, by the attack of chromophore groups.

The assessment of the contribution of each sorption, photolysis and photocatalysis on Z-Na catalyst under both HA initial concentrations of 25 mg·L⁻¹ and respective, 100 mg·L⁻¹ allowed to notice the affinity of zeolite for HA and photosensitive character of HA. As we expected, higher initial HA concentrations higher HA amount retained on zeolite. Also, it has to be mentioned that the humic acid sorption on zeolite must be regarded as a complex phenomenon, occurring as a compromise between the ability of the cations to form stable bridges with the organic matter and, on the other hand, their specific selective sorption by the zeolite [14]. The better results obtained for photocatalysis could be attributed to photolysis process and no photocatalytic effect of Z-Na, taking into account its photoinert character.

Based on these comparative results, it can be concluded that the sorption and photolysis processes have a significant contribution for HA removal based on the affinity of zeolite for HA and the photosensitive character of HA. The contribution of these processes was proven by the similar results regarding the amount of HA (expressed by A₂₅₄) removed by photocatalysis process using TiO₂-Z and Z – Na for both initial HA concentrations, taking into account the photoinert character of Z-Na.

For all studied situations, the results regarding solution discoloration were better versus aromatic ring removal.

4. Conclusions

The contribution of each photolysis, sorption and photocatalysis process using TiO₂-modified zeolite for HA removal from water was assessed in relation with evolution of A₂₅₄ and A₄₃₆ parameters, chosen for quantitative evaluation of humic acids. In comparison, the application of sorption and photocatalysis processes using monocationic form of clinoptilolitic zeolite was investigated.

At low initial HA concentration, the best results regarding HA removal were achieved by photolysis application, which proved the photosensitive character of HA. The presence of TiO₂ on zeolite surface led to enhance the sorption capacity of zeolite for HA, and the better results regarding HA removal by sorption on TiO₂-Z was reached in comparison with sorption on Z-Na. The

photocatalysis application using $\text{TiO}_2\text{-Z}$ catalyst was ineffectively under low HA initial concentrations, and the sorption step led the overall process of photocatalysis. The better results of HA removal by photocatalysis using Z-Na catalyst obtained in comparison with sorption, could be attributed to photolysis process based on the photoinert character of Z-Na. These results were slight worse in comparison with photocatalysis application using $\text{TiO}_2\text{-Z}$ catalyst.

At high HA concentrations ($100 \text{ mg}\cdot\text{L}^{-1}$) the photocatalysis application led to better results for HA removal in comparison with sorption and photolysis, but no cumulative effect was reached. The similar results obtained through application of photocatalysis using both $\text{TiO}_2\text{-Z}$ and Z-Na catalysts and taking into account the photoinert character of Z-Na and enhanced sorption capacity of $\text{TiO}_2\text{-Z}$ for HA proved the significant contribution of both photolysis and sorption processes.

The photolysis application led to almost similar results for HA removal for both HA initial concentrations. No photocatalytic effect of $\text{TiO}_2\text{-Z}$ was found, which can be explained by low TiO_2 loading on zeolite (1%, w/w).

The future research will be focused on new catalyst material based on zeolitic matrix with higher TiO_2 loading.

REFERENCES

1. Capasso S., Coppola E., Iovino P., Lombardo M., Salvestrini S., and Collella, C., Zeolite '06-7th International Conference on the Occurrence, Properties and Utilization of Natural Zeolites (Bowman R. S. and Delap S. E., Eds.), Socorro, New Mexico USA, 16-21 July 2006, 64.

- Gaffney J.S., Marley N.A., and Clarck, S.B., ACS Symposium Series, Washington (DC): ACS, 651, 1996, 2.
- Corin N., Backlund P., and Kulovaara M., *Chemosphere*, 33(2), 1996, 245-255.
- Li J. W., Yu Z., Gao M., Zhang L., Cai X., and Chao F., *Water Res.*, 30(2), 1996, 347-350.
- Carp O., Huisman C.L., and Reller A., *Progress Solid State Chem.*, 32, 2004, 35-177.
- Wang G. S., Hsieh S. T., and Hong C.S., *Water Res.*, 34(15), 2000, 3882-3828.
- Bansal A., Madhavi S., Yang Tan T., and Lim T.M., *Catal. Today*, 131, 2008, 250-254.
- Doulia D., Leodopoulos Ch., Gimouhopoulos K., and Rigas F., *J. Colloid Interface Sci.*, 340(2), 2009, 131-141.
- Hu C., Yu J.C., Hao Z., and Wong P.K., *Appl. Catal. B: Environ.*, 46, 2003, 35-47.
- Wang Y., *Water Res.*, 34(3), 2000, 990-994.
- Ghernaout D., Ghernaout B., Saiba A., Boucherit A., and Kellil A., *Desalination*, 239(1-3), 2009, 295-308.
- Cho Y., and Choi W., *J. Photochem. Photobiol. A: Chem.*, 148, 2002, 129-135.
- Bekbölet M., and Özkösem G., *Water Sci. Technol.*, 33(6), 1996, 189-194.
- Eggins B.R., and Byrne J.A., *Water Res.*, 31(5), 1997, 1223-1226.
- Al-Rasheed R., and Cardin D.J., *Chemosphere*, 51, 2003, 925-933.
- Al-Rasheed R., and Cardin D.J., *Appl. Catal. A: Gen.*, 246, 2003, 39-48.
- Tsimas E.S., Tyrovolas K., Xekoukoulotakis N.P., Diamadopoulos E., and Mantzavinos D., *J. Hazard. Mat.*, 169(1-3), 2009, 376-385.
- Tercero Espinoza L.A., and Frimmel F.H., *Water Res.*, 43(16), 2009, 3902-3909.
- Portjanskaja E., Stepanova K., Klauson D. and Preis S., *Catal. Today*, 144(1-2), 2009, 26-30.

Received: 17 June 2010

Accepted: 16 November 2010