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Enhancement of Natural Organic Matter Removal from Surface Water Using TiO_2-Modified Zeolite

C. Ratiu*, C. Orha*, P. Sfirloaga*, C. Lazau*, F. Manea**, A. Pacala***, I. Vlaicu***, G. Burtica**, I. Grozescu*

* National Institute of Research-Development for Electrochemistry and Condensed Matter, Condensed Matter Department, Str. Plautius Andronescu, No. 1, Timisoara

** "Politehnica" University of Timisoara, Piata Victoriei, No. 2, 300006, Timisoara

*** S.C. AQUATIM Timisoara AQUATIM" Company, Str. Gheorghe Lazar No. 11 A, 300081 Timisoara, Romania

Abstract: This study aimed to enhance the removal of humic acids as major part of natural organic matter (NOM) from surface water using TiO_2 – modified zeolite (TMZ) suspension. Two types of TMZ granulations were tested, i.e., 315-500 µm and zeolite – powder, which were synthesized by sol-gel method. TMZ materials were characterized by SEM-EDAX and XRD. Their application by Jar-test experiments showed the enhanced efficiency of coagulation related to NOM removal. The concentration of NOM before and after TMZ application was determined as UV_{254} absorbance and non-purgeable organic carbon (NPOC) parameter. Versus simple coagulation, NOM removal was improved with 23.3-47.5 % as NPOC parameter, and with 69.6-74.2 % as UV_{254} absorbance, function of type of material and applied method.

Keywords: natural organic matter, zeolite, TiO_2, photocatalytic oxidation process

1. Introduction

The presence of humic acids (HA), as part of natural organic matters, has been a problem in the water industry due to their water-soluble formation, a wide range of distribution in molecular weight and size, and their non-biodegradability. It has been confirmed that humic substances are precursors of disinfection by-products in chlorination processes [1-3,5]. The structures, molar masses, and functional groups vary depending on origin and age [4]. In addition to causing problems with reverse osmosis (RO), many HAs possess methyl groups, which can lead to the formation of trihalomethanes on treatment with hypochlorite [6]. Hypochlorite is often used in water treatment as a biocide and the formation of trihalomethanes, haloacetic acids, or other chlorinated by-products, some of which are suspected to be carcinogenic is thus highly undesirable. The removal of such organic matter is therefore an important factor in water treatment [7].

In addition to the convential treatments such as coagulation, precipitation, filtration, ion-exchange, use of activated carbon, or biological treatment, advanced photocatalytic methods have been applied to reducing the organic content of water [8,9]. Thus in non-saline waters it has been demonstrated that more than 80% of commercial HA can be removed efficiently by photocatalysis over TiO_2 [10]

Titanium-dioxide (TiO_2)-based photocatalysis has been the focus of numerous investigations in recent years, particularly owing to its application for the complete mineralization of undesirable organic contaminants to CO_2, H_2O and inorganic constituents. Many papers reported that humic substances could be effectively degraded in TiO_2 suspensions under UV irradiation [11,12]. To further improve the photooxidation of organics in aqueous TiO_2 suspension, most efforts have been addressed on the modification of TiO_2-based catalysts by doping different dopants [13,14].

Zeolite seems to be a promising support for TiO_2 photocatalyst because of its regular pores and channel sizes and good adsorption ability. TiO_2 supported on zeolite integrates the photocatalytic activity of TiO_2 with the adsorption properties of zeolite together, which induce a synergistic effect, resulting in the enhancement of photocatalytic efficiency. In recent years, the natural mineral materials, such as natural zeolite [15], have also attracted an increasing interest due to their layered or porous structure, low cost and abundant storage.

2. Experimental

To obtain TiO_2, and TMZ, was used sol-gel method. As precursors for the synthesis, natural zeolites from the Mirşid-Romania area were used, of composition (% wt): 62.20% SiO_2; 11.65% Al_2O_3; 1.30% Fe_2O_3; 3.74% CaO; 0.67% MgO; 3.30% K_2O; 0.72% Na_2O; 0.28% TiO_2. Titanium isopropoxide (Fluka) has been used as TiO_2 precursor.

For a more efficient ion exchange, the zeolite in the natural form (315-500 µm) must be converted in the sodium form (Z-Na); the preparation of the chemically modified zeolite presumes two stages: acid (HCl) and alkaline treatment ($NaNO_3$).

For the sol-gel method, 5 g of natural zeolite in sodium form (Z-Na) were mixed by the magnetic stirrer with 30 mL of ethylic alcohol; afterwards 5 mL of titanium isopropoxide was added dropwise. After a few minutes of stirring, 30 mL of distilled water were added also in drops. The pH was adjusted with nitric acid solution, reaching a value of 2.5. After one hour of continuous stirring the obtained material was filtered, washed and dried at 60ºC for 5 hours. The thermal treatment was realized at 250ºC, for 2 hours.

The morphology and composition of the unmodified/modified zeolite were characterized by X-ray Diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDAX). XRD spectra were recorded at room temperature with a BRUKER D8 ADVANCE X-ray diffractometer using Cu Kα radiation in θ:2θ configuration.. The SEM images were made in an Inspect S scanning electron microscope coupled with EDAX device.

TiO_2-modified zeolite by two types, e.g., powder and with granulation ranged 315-500 µm, was tested by hybrid photooxidation/coagulation experiments using JAR test experiments at doses of $1 g\cdot L^{-1}$ TMZ, performed with 14 $mg\cdot L^{-1}$aluminium sulphate as coagulation agent and applied for two different situations, i.e., preoxidation followed by coagulation and the combination of photooxidation with coagulation process.

The preoxidation time was 10 minutes at 150 rpm. A UV-light source, UVMLS-38 UVP, LLC 8W low-pressure luminescent mercury UV-lamp with emission at 365nm, was positioned horizontally over the samples. For coagulation process and combination of coagulation and oxidation, fast mixing was performed for 2 minutes at 150 rpm. Slow mixing was performed for 15 min at about 45 rpm for floc agglomeration and quiescent settling was about 30 minutes.

The presence of natural organic matter in the water is measured through indicators such as non-purgeable organic carbon (NPOC) and ultraviolet absorbance (UV_{254}). UV absorbance was measured using a UV/VIS spectrophotometer (Jasco V-530) at 254 nm in 1 cm quartz cells. NPOC was determined at TOC-V CPH P/N 638-91026-13, Shimadzu, Japan. Turbidity was measured on a Hach 2100 turbidity meter.

3. Results and discussion

In figure 1 is presented the SEM image of zeolite in sodium form. No major differences were observed in the morphology of the Romanian sodium zeolitic mineral in relation to the natural zeolitic tuff (SEM image of natural zeolite is not presented here).

Figures 2 and 3 shows the SEM and EDAX image of TMZ for both form (315-500µm and powder).

For both TMZs, TiO_2 particles are non-uniformly distributed on the surface of the zeolite due to the complex structure of this natural material. It is noticed that the TiO_2 particles are distributed on the zeolite surface and not inside of the internal pores, because the dimensions of the pores are very small (a few Å). The dimensions of the TiO_2 particles do not allow the entrance in the zeolite's pores. The presence of TiO_2 particles on the zeolite surface is certified by EDAX analysis.

The comparative XRD spectra of TiO_2, Z-Na, TMZ are presented in figure 4.

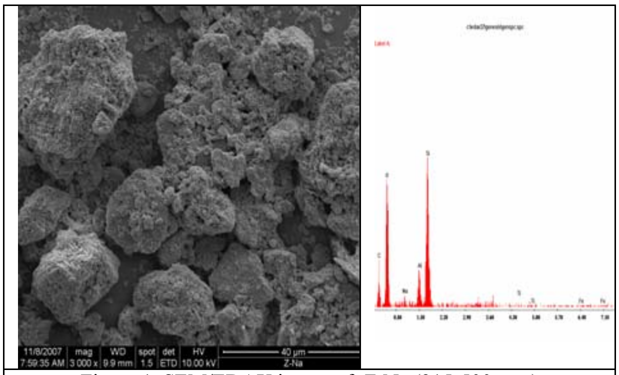

Figure 1. SEM/EDAX image of Z-Na (315-500 µm)

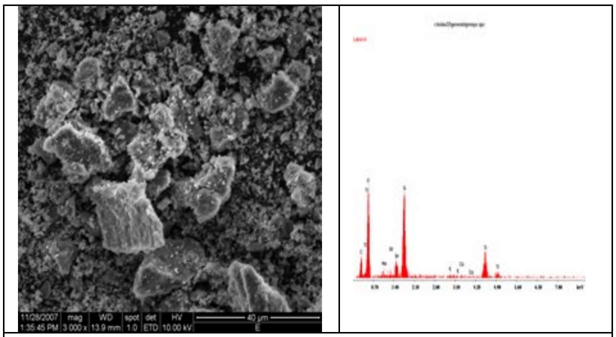

Figure 2. SEM/EDAX image of TMZ (315-500 µm)

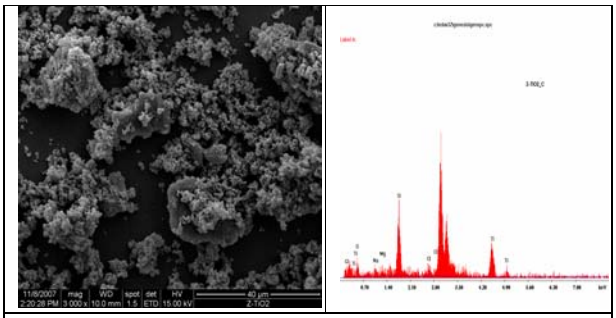

Figure 3. SEM/EDAX image of TMZ powder

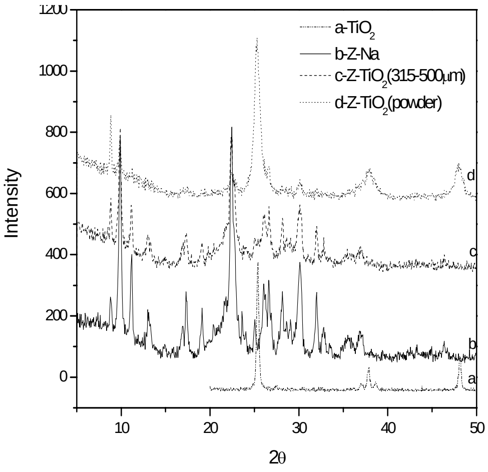

Figure 4. X-Ray diffraction of:a) TiO_2; b) Z-Na; c) TMZ (315-500µm); d)TMZ (powder)

The results reveal that the natural zeolite used in the experiment is mostly clinoptilolite ($2\ \theta \sim 10^{\circ}$; 12°; 22.5°; 30°). The peaks of anatase TiO_2 corresponding to $2\theta \sim 25.2^{\circ}$, 37.87, 48.01, are more predominant in TMZ powder.

TiO_2-modified zeolite application under the two ways, the first of preoxidation followed by coagulation as well as the combination of preoxidation with coagulation were performed on the real surface water from Bega river, with the characteristics gathered in the table 1.

TABLE 1. The initial values of several parameters characteristics to Bega river

Parameter	U.M.	Value
NPOC	$mg\cdot L^{-1}$	3.51
Turbidity	NTU	16.2
$Absorbance_{254}$	-	0.152

In order to compare the effect of the photoactivity and coagulation adjuvant of both types of TMZ applied for two different situations, i.e., preoxidation followed by coagulation and the combination of photooxidation with coagulation process for humic acid removal the Jar-test experiments were performed comparatively only with coagulation process at the similar doses of aluminium sulphate ($14\ mg\cdot L^{-1}$). The results are presented in table 2.

TABLE 2. The water characteristics after Jar-test experiments application, aluminium sulphate dose was $14\ mg\cdot L^{-1}$

Parameter TMZ	NPOC ($mg\cdot L^{-1}$)	$Absorbance_{254}$	T (NTU)	Type of applied method
-	3.35	0.1401	2.01	Coagulation
Powder	1.76	0.0361	2.20	Photooxidation followed by coagulation
315-500 µm	1.94	0.0403	1.62	
Powder	2.57	0.0327	1.58	Combination of photoxidation with coagulation
315-500 µm	1.87	0.0426	1.53	

Based on the results obtained, it can be concluded that the application of TiO_2 -modified zeolite exhibited a significant effect on the removal of non-purgeable organic carbon and natural organic matters expressed as absorbance at 254 nm during the hybrid photooxidation/coagulation for both types of applied method. Under the applied conditions, both TiO_2-modified zeolite gave the similar performances. The reduction degree for the NPOC and NOM versus simple coagulation is gathered in table 3.

TMZ application during Jar-test experiments improved the efficiency of coagulation related to NPOC and NOM removal. The removal of NPOC was enhanced with 23.3-47.5 % of NOM with 69.6-74.2 %, function of type of material and applied method.

TABLE 3. Removal degree of NPOC and NOM versus simple coagulation

TMZ	Removal degree of NPOC (%)	Removal degree of NOM (%)	Type of applied method
Powder	47.5	74.2	Photooxidation followed by coagulation
315-500 µm	42.1	71.3	
Powder	23.3	76.6	Combination of photooxidation with coagulation
315-500 µm	44.2	69.6	

4.Conclusions

TiO_2-modified zeolite by two granulations, e.g., 315-500 µm and zeolite – powder was synthesized by sol-gel method.

The presence of TiO_2 particles on the zeolite surface as anatase form was certified by EDAX and XRD analysis. TiO_2 particles are non-uniformly distributed on the surface of the zeolite due to the complex structure of this natural material.

Involving photoxidation using TiO2-modified zeolite catalyst into coagulation process as hybrid photooxidation/coagulation process related to humic acid removal led to good performance. The removal degree for humic acid expressed as NPOC and NOM reached the values ranged from 23.3 % to 47.5 %, respective 69.6-74.2, related to TiO_2-modified zeolite and type of applied method.

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