THE EFFICIENCY OF TiO_2/ZEOLITES FOR PHOTOCATALYTIC DEGRADATION OF DIFFERENT POLLUTANTS FROM AQUEOUS SOLUTION

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ABSTRACT

This work presents synthesis and characterization of hybrid photocatalysts based on commercial TiO_2 nanoparticles and mixed shape nanocrystals obtained from TiO_2 nanotubes and zeolites, natural (clinoptilolite) and synthetic (ZSM-5 and 13X). Furthermore, their efficiency towards the removal of different contaminates such as atenolol (ATL) and bisphenol A (BPA) from aqueous solution as well as herbicides from pesticide factory's wastewater was investigated using multianalytical approach. Hybrid photocatalysts were made by simple and inexpensive solid-state dispersion method. The prepared materials were characterized by the X-ray powder diffraction, FTIR spectroscopy, UV-Vis diffuse reflectance spectroscopy and SEM-EDS technique. Successful removal of ATL, BPA and herbicides was accomplished in the presence of the prepared materials. The most efficient hybrid photocatalysts proved to be those based on ZSM-5 zeolite: complete ATL removal was achieved after 70 minutes of simulated sun irradiation and removal of over 60 % of detected herbicides was reached after 3 h of simulated sun irradiation.

Key words: TiO_2, photocatalytic degradation, atenolol, bisphenol A, herbicide.

INTRODUCTION

Emerging water contaminants, such as pesticides, personal care products and cosmetics, pharmaceutically active compounds, etc. originating from human and industrial activities pose a global challenge [1]. Their detection in the environment highlights the urgent issue of water pollution and exposes the limitations of conventional water treatment methods for the efficient removal of these harmful substances. In this regard, the heterogeneous photocatalytic oxidation of organic compounds, facilitated by TiO_2 as a well-known photocatalyst, offers a promising solution for water purification [2]. However, there are challenges related to the separation and the recyclability of TiO_2 in aqueous medium as well as to its tendency to agglomerate, leading to decreased activity. To address these issues, a lot of research has been conducted on immobilizing TiO_2 onto various solid surfaces [3]. Materials with high surface area such as zeolites, can be used as TiO_2 supports as they facilitate its separation and reusability. Additionally, their usage reduces the agglomeration of TiO_2 [3]. For wider application, it is preferable to use available and affordable materials for simple and environmentally friendly preparation of TiO_2/zeolites.

This research examines the effectiveness of hybrid photocatalysts composed of zeolites and two differently shaped TiO_2 nanocrystals in removing different contaminants from aqueous solution. They were prepared using simple and economical solid-state dispersion method. The synthesized materials were tested for the removal of contaminants such as the most commonly used beta-blocker atenolol (ATL) and an endocrine-disrupting compound bisphenol A (BPA), but also for the removal of various herbicides from the pesticide factory's wastewater.

EXPERIMENTAL

The commercial P25 TiO_2 nanoparticles (Aldrich) and TiO_2 nanocrystals with mixed shapes, synthetized following the procedure reported in [4], were used in this work. Different zeolitic structures were chosen as carriers for TiO_2. Natural zeolite clinoptilolite (Cli) from Zlatokop mine, Serbia, and two synthetic zeolites: ZSM-5 (Si/Al = 40) from Zeolyst and 13X (Si/Al = 1,2) from Union Carbide were used. Hybrid photocatalysts were prepared with mass ratios TiO_2/zeolite wt%: 20:80 using the solid-state dispersion method described in [5]. They were labelled T-Cli, T-ZSM5, and T-13X or TNT-Cli, TNT-ZSM5, and TNT-13X where T denotes TiO_2 P25, and TNT represents modified TiO_2 nanotubes and Cli, ZSM5, and 13X indicate the type of used zeolite. XRPD patterns of all TiO_2/zeolite hybrid photocatalysts were recorded on a Rigaku Ultima IV diffractometer in Bragg-Brentano geometry, using Cu Kα radiation (λ=1.54178 Å, from 4° to 50° 2θ, 0.020° step, 1°/min). FTIR spectra were collected on Nicolet 6700 FTIR spectrometer using KBr technique. UV-Vis DR spectra were measured on Agilent Cary UV-Vis-NIR 5000 spectrophotometer equipped with an integration sphere. SEM-EDS analyses were performed using Phenom ProX desktop scanning electron microscope equipped with an energy dispersive spectrometer (15 kV was used for analysis).

The experimental conditions for photocatalytic tests and the reusability study are reported in detail by Stojanović et al. [4, 5]. UV-Vis spectrophotometer (Thermo scientific evolution 220) was used for measuring the concentration of ATL (Galenika, Belgrade, Serbia) at λ_{max} = 224 nm and BPA (Sigma Aldrich, ≥ 99%) at λ_{max} = 225 nm. Pesticide wastewater (PWW) was collected in factory Agrosava d.o.o., Belgrade, Serbia and diluted 15 times for photocatalytic experiments. The liquid-liquid extraction of PWW and water aliquots after irradiation was performed three times using 10 ml of dichloromethane (Carlo Erba). Extracts were dehydrated using anhydrous sodium sulfate (Lachner) and evaporated in the stream of nitrogen to dryness. Afterwards, the samples were dissolved in dichloromethane and analyzed using a GC-MS QP2010 Ultra (Shimadzu, Kyoto, Japan) comprehensive two-dimensional gas chromatograph-quadrupole mass spectrometer (GC×GC-MS) with ZX2 thermal modulation system (Zoex Corp.). A RtxR-1 (RESTEK, CrossbondR 100% dimethyl-polysiloxane, 30 m x 0.25 mm, 0.25 μm film thickness) and a BPX50 (SGE Analytical Science, 1 m x 0.1 mm, 0.1 μm film thickness) columns were connected through the GC×GC modulator as the first and second capillary columns, respectively. The oven was initially set to 60 °C for 1 min, then increased at a rate of 8 °C/min until it reached 300 °C, where it remained for 6 min with no modulation. The scan range used for m/z was 20-500 and compounds were identified by comparing them to the NIST library and standards.

RESULTS AND DISCUSSION

XRPD patterns of starting zeolites and hybrid photocatalysts are presented in Fig. 1. Diffractograms of all hybrid photocatalysts show peaks of starting zeolites (Cli, ZSM-5, 13X) and TiO_2 anatase phase at 25.3°, 37.8°, 48.1°. The XRPD results reveal the loading of TiO_2 nanoparticles and the preserved structure of starting zeolites in the case of all prepared materials. Likewise, FTIR and UV-Vis DR spectra, along with SEM-EDS analysis confirm that zeolitic structures were preserved after the preparation procedure as well as successful loading of TiO_2 nanoparticles [4].

All composite materials successfully removed ATL from aqueous solution under solar simulated irradiation. After 70 minutes of irradiation, hybrid photocatalysts based on ZSM-5 zeolite demonstrated the highest removal efficiency for ATL, (T-ZSM5 removed 94%; TNT-ZSM5 88 %), comparable to P25 (92 %), and exhibited higher removal efficiency than TNT (57 %) [4].

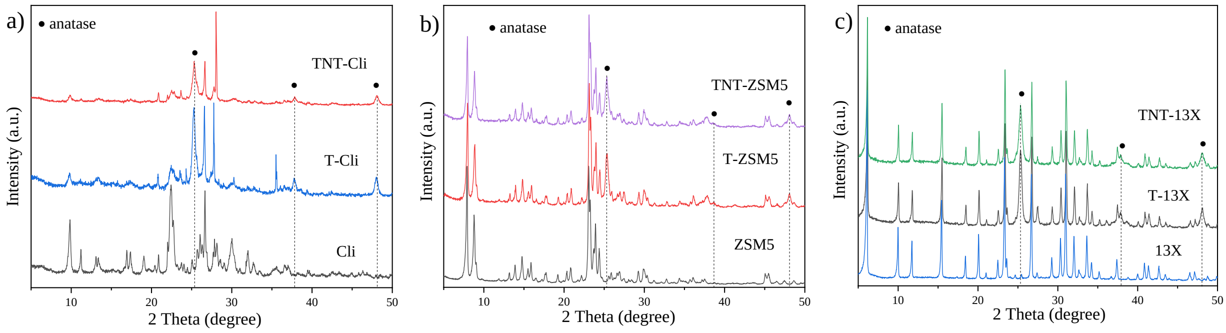

Figure 1. XRPD patterns of starting zeolites and hybrid photocatalysts based on a) Cli, b) ZSM5 and c) 13X zeolite. Vertical dashed lines are at 25.3º, 37.8º and 48.1º 2θ, ● denotes reflections of anatase phase.

Additionally, hybrid photocatalysts based on ZSM-5 zeolite showed significant adsorption of ATL (T-ZSM5 58 %, TNT-ZSM5 50 %). Hence the ATL removal was achieved through combined processes of adsorption and photocatalytic degradation. Hybrid photocatalysts based on 13X and Cli were less effective (T-13X removed 50 %, TNT-13X 50%, T-Cli 45 % and TNT-Cli 56 % of ATL) and a longer irradiation time was necessary for complete ATL degradation [4].

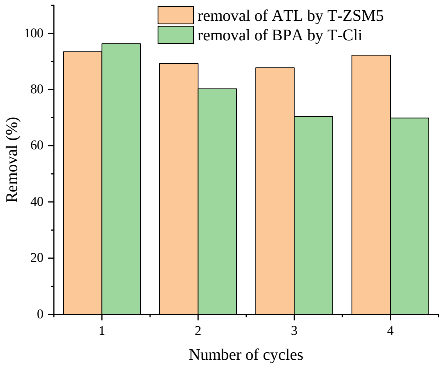

Figure 2. Reusability of hybrid photocatalysts: T-ZSM5 - removal of ATL (C_o = 50 mg/L) and T-Cli - removal of BPA (C_o = 5 mg/L) (modified from [4, 5]).

Considering low cost and the abundance of natural zeolite Cli, and its proven effectiveness in degrading ATL, T-Cli hybrid photocatalyst was tested for BPA removal from aqueous solution. After 180 minutes of irradiation, the complete removal of BPA was achieved using 2 g/L of T-Cli. Furthermore, the complete elimination of BPA was observed after 120 minutes of irradiation with addition of 10 μL H_2O_2 to the experimental suspension [5]. This suggests that using T-Cli and small quantity of H_2O_2 can be a promising approach for the rapid and efficient removal of BPA. The reusability of synthesized T-ZSM5 and T-Cli was tested to assess their practical applicability. The results (Fig. 2) indicate that T-ZSM5 remains effective for ATL removal even after the 4th cycle (photocatalytic activity restored by calcination at 500 ºC for 5 h after the 3rd cycle). However, the photocatalytic activity of T-Cli for the removal of BPA slightly decreased after each cycle, yet even after the 4th cycle, approximately 70% of BPA was removed [4,5].

T-ZSM5 and TNT-ZSM5 were also investigated for herbicides removal from PWW. GC-MS analysis of the PWW revealed the presence of various herbicides (listed in Table 1) and co-formulants (data not shown), typical additives in pesticide formulations. After 3 hours of irradiation, T-ZSM5 showed slightly higher total removal percentage for all detected herbicides (~ 75 %) in comparison to TNT-ZSM5 (~ 66 %). The removal percentages of herbicides metamitron, terbuthylazine, metalaxyl, metribuzin, and clomazone by T-ZSM5 were 96.5 %, 79.5 %, 71.9 %, 51.7 %, and 43.8 %, respectively. The composite material based on TNT exhibited a comparable trend, though with less efficiency in removing the detected herbicides, with removal percentages: 94.2%, 72.4 %, 50.7 %, 44.7 %, and 32.9 %, respectively. Although clomazone and metamitron were the most abundant herbicides, the removal of metamitron in the presence of both composite materials exceeded 90 %, whereas clomazone removal was significantly lower, ranging from 33 % to 44 % for T-ZSM5 and TNT-ZSM5. Haloxyfop-methyl, mefenpyr-diethyl, metolachlor were present in small quantities in PWW and after 3 h of irradiation were completely removed in the case of both hybrid photocatalysts.

Table 1. Detected herbicides from factory's wastewater using GC-MS and the removal percentage using hybrid photocatalysts T-ZSM5 and TNT-ZSM5.

Retention time (min)	Area	Herbicides	m/z (% of relative intensity)	Removal (%)	
				T-ZSM5	TNT-ZSM5
21.6	1 630 050	Clomazone	204 (100), 125 (79), 127 (26)	43.8	32.9
26.9	1 284 602	Metamitron	104 (100), 174 (79), 202 (69), 173 (42), 28(39)	96.5	94.2
21.9	877 069	Terbuthylazine	173 (100), 214 (96), 28 (72), 175 (32), 44 (31)	79.5	72.4
23.1	533 561	Metribuzin	198 (100), 28 (72), 57 (43), 41 (30), 32 (28)	51.7	44.7
23.81	187 696	Metalaxyl	28 (100), 32 (40), 45 (33), 160 (29), 44 (28)	71.9	50.7
26.2	41 757	Haloxyfop-methyl	28 (100), 32 (41), 44 (31)	n. d.*	n. d.
29.6	33 646	Mefenpyr-diethyl**	28 (100), 32 (40), 44 (37)	n. d.	n. d.
24.8	31 545	Metolachlor	28 (100), 32 (40), 44 (29), 162 (24)	n. d.	n. d.
			Total percentage of removal (normalized to 100 %)		
				74.7	**65.9**

*not detected in the sample after treatment, so % of degradation wasn't calculated, **herbicide safener

CONCLUSION

The TiO_2/zeolites hybrid photocatalysts have been successful in removing different organic pollutants such as ATL, BPA and herbicides from aqueous solution. The best efficiency for removing ATL was exhibited by T-ZSM5 and TNT-ZSM5 hybrid photocatalysts. Additionally, complete removal of BPA can be achieved using low-cost T-Cli. Moreover, the GC-MS results showed successful removal of various herbicides from a complex mixture such as pesticides factory' wastewater using T-ZSM5 (removed 74.7 %) and TNT-ZSM5 (removed 65.9 %).

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