

Removal of Pollutants by Zeolite-TiO₂ Systems

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A system able to remove at the same time inorganic and organic pollutants from an aqueous effluent by combining zeolites as ionic exchanger of metals with titanium dioxide in anatase form as catalyst of photodegradation of pesticides and chlorophenols as representatives of organic pollutants is proposed. For practical reasons the system was also applied in form of a catalytic membrane which was optimized for its composition and whose activity was increased by addition of polyaniline.

The worldwide environmental pollution increasingly threatens human and ecological health.

The industrial wastes represent a significative source of pollution. They can contain both organic and inorganic species such as pesticides, halocompounds, surfactants in the first group and heavy metals in the second one. This coexistence complicates the problem of the effluent treatment in order to minimize the environmental impact; as known some techniques are suitable to degrade organic pollutants but are ineffective on metals, some other can remove metals but not organics.

Today the detoxification of an effluent is generally performed by three different approaches to the pollutants: containment, removal, decrease [1], performed by different methods such as chemical precipitation, vaporization, adsorption, inverse osmosis, solvent extraction, electrodialysis, ionic exchange [2, 3], biological, chemical and photochemical degradation [4].

In this paper we present a system able to remove at the same time inorganic and organic pollutants from an aqueous effluent by combining zeolites as ionic exchanger with titanium dioxide in anatase form as catalyst of photodegradation of pesticides and chlorophenols as representative of organic pollutants. In the first step, batch tests were performed in presence of TiO₂ and zeolite on solutions containing heavy metals and organics in order to check, if any, the possible mutual interferences between metal adsorption on zeolite and photodegradation by TiO₂ catalysis. In the second step, in order to bypass the problem of the powder in solution, the two compounds were immobilised, firstly by immobilisation of TiO₂ on zeolite and secondly by immobilising both in a membrane of polyvinylalcohol, polyvinylacetate and polyvinylchloride previously checked as not active as such in both the processes. The catalytic membrane was then optimized for its composition as well as the ex-

perimental conditions, especially pH. Lastly the membrane activity was increased by addition of polyaniline and some intermediates were evidenced.

Experimental

Chemical reagent were from Degussa, Fluka, Carlo Erba, Aldrich, Merck. Polyaniline was obtained in laboratory by letting under stirring for 6 hours a mixture constituted by HCl 1.25 mol/l, KIO₃ and aniline monomer, by filtering, washing and drying. Its nature was verified by conductivity and ESCA analysis [5-7]. The tested mixtures for photodegradation had the compositions shown in Table 1.

Table 1

	Zeolite (mg)	TiO ₂ (mg)	Polyaniline (mg)
1	200	10	6
2	200	10	-
3	-	10	6

Mixture n. 1 was also adopted for the metal adsorption tests. These compositions were chosen according to the literature [7]. The membrane was prepared as previously described [8]. The optimized membrane was 100 µm thick with a surface area of 2.0 cm² and % w/w of TiO₂, PA and zeolite equal to 20, 19 and 61 respectively. The photodegradation experiments were performed by the Q.U.V. Panel Accelerated Weathering Tester supplied by Q-Panel Company, Cleveland, Ohio. The control of the degradation and removal processes was performed by inverse phase HPLC, Perkin Elmer apparatus, with UV detector for organics (studied compounds and intermediates), by a Varian atomic adsorption spectrophotometer for metals.

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Results and discussion

The first experiments in batch conditions were finalised to see if any interference could exist between the two processes, the ionic exchange and the photodegradation, both involved in the resulting methodology.

The mixture 1 was suspended in 50 ml of aqueous solution containing the following heavy metals ions Cd, Zn, Cu, Mn at the concentration $1 \cdot 10^{-4}$ mol/l. The adsorption of the metals was as reported in Table 2 so resulting that already after 2 hrs copper and manganese are completely adsorbed while for Zn and Cd respectively 4 and 8 hrs are requested, according a possible affinity order $Cu=Mn>Zn>Cd$.

Table 2 - Adsorption of Cd, Zn, Cu and Mn ($1 \cdot 10^{-4}$ mol/l) on zeolite-TiO₂-PA (200mg:10mg:6mg), suspended in solution

Time (hrs)	Adsorption, (%) (RSD% \leq 5%)			
	Cd	Zn	Cu	Mn
2	89.3	89.6	100	100
4	98.2	100	100	100
6	98.2	100	100	100
8	100	100	100	100

On the same mixture the possible effect of zeolite on the photocatalytic activity was controlled by comparing it with mixture 2 and 3 (Table 3); the results show that zeolite improves the photocatalytic activity.

Table 3 - Photodegradation of *p*-chlorophenol ($2.5 \cdot 10^{-5}$ mol/l) in presence of zeolite-TiO₂-PA (mixture 1), zeolite-TiO₂ (mixture 2), TiO₂-PA (mixture 3)

Time (hrs)	% photodegradation		
	Mixture 1	Mixture 2	Mixture 3
2	98.3	88.6	80.5
3	99.0	88.6	85.5

Similar results were obtained on pesticide propoxur with increasing differences (from about 10% to about 20%).

As the system TiO₂-zeolite results to be active both as ionic exchanger and as photocatalyst we passed to the immobilised system firstly immobilising TiO₂ on zeolite with different ratios. The results are qualitatively similar to those ones obtained with powered mixtures but the kinetics of the ionic exchange are different as shown by the results in Table 4.

Table 4 - Adsorption of Cu, Cd, and Zn ($1 \cdot 10^{-4}$ mol/l, 50 ml) in presence of suspended zeolite supporting TiO₂ (75% TiO₂)

Time (hrs)	Adsorption, (%) (RSD% \leq 5%)		
	Cu	Cd	Zn
2	98.5	30.6	98.7
4	98.5	57.7	98.7
6	98.5	72.3	98.7

The optimum composition resulted to be 75% TiO₂.

Finally we passed to the polymeric membrane considering different supporting polymers: polyvinylalcohol, polyvinylacetate + dibutylsebacate, polyvinylchloride. The first one was abandoned for solubility problems; the second one resulted not enough active; the third behaved as the best (Figure 1), obviously less than powered compounds but much more suitable for handiness.

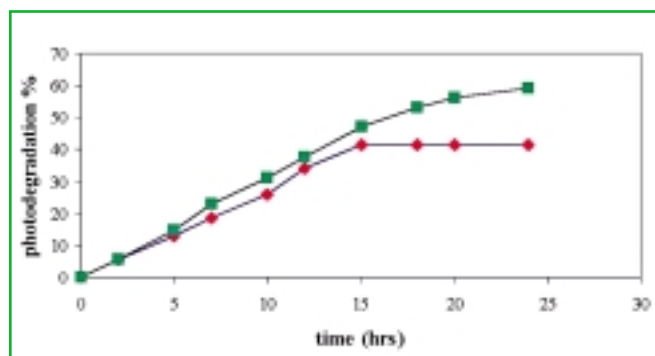


Figure 1 - Photodegradation of propoxur ($4.8 \cdot 10^{-5}$ mol/l, 50 ml) catalysed by polymeric membranes ($A_s = 29.6$ cm², 100 μ m thickness) containing TiO₂(75%)-zeolite. \blacklozenge PVAc+DBF, \blacksquare PVC

The membrane constituted by PVC, TiO₂ and zeolite with the same characteristics was used for adsorption of metal (Cu, Cd, Zn, Mn) ions. The results are shown in Table 5, an affinity order is evidenced $Cu=Mn>Zn>Cd$, with cadmium adsorption largely reduced in comparison with the free in solution compounds system.

Table 5 - Adsorption of Cd, Zn, Cu and Mn ($1 \cdot 10^{-4}$ mol/l, 50 ml) PVC membranes ($A_s = 29.6$ cm², 100 μ m thickness) containing TiO₂(75%)-zeolite

Time (hrs)	Adsorption, (%) (RSD% \leq 5%)			
	Cu	Cd	Mn	Zn
2	58.5	0.73	56.9	6.3
4	89.2	2.2	93.8	30.0
6	96.9	2.2	98.5	65.0
8	96.9	3.0	100	82.5
24	100	3.0	100	100

In order to verify the chance of improving the photodegradation and adsorption processes, PVC membranes were prepared for which, on maintaining the physical characteristics, chemical composition was varied from 3:1 to 1:3 TiO₂:zeolite. The best results were obtained with a membrane containing 50% TiO₂ and 50% zeolite (Figure 2) but mechanical resistance is higher for the 25% TiO₂, 75% zeolite membrane so that only this can remain operating for a time long enough to bring to the full degradation of the considered pollutant.

The membranes were also tested for the metal adsorption properties: on increasing zeolite concentration the efficiency improves (as example behaviour of copper in Table 6).

The following experiments were performed with membrane c (thickness 100 μ m, $A_s = 30$ cm²). Influence of pH was studied both on photodegradation and on metal adsorption. Results are presented in Figure 3 and Table 7; pH was varied starting

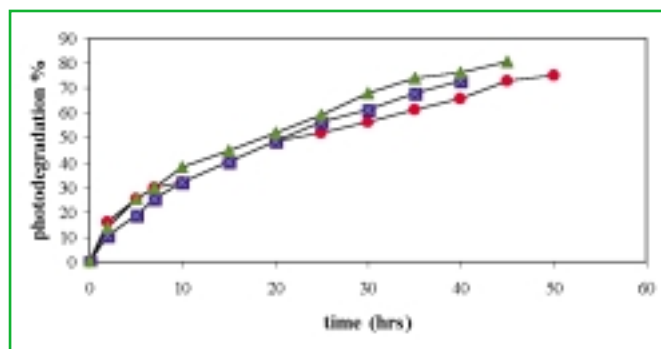


Figure 2 - Photodegradation of *p*-chlorophenol ($2.5 \cdot 10^{-5}$ mol/l, 50 ml) catalysed by polymeric membranes ($A_s = 29.6$ cm², 100 μ m thickness) containing TiO₂-zeolite at different composition.
 ■ 75% TiO₂, ▲ 50% TiO₂, ● 25% TiO₂

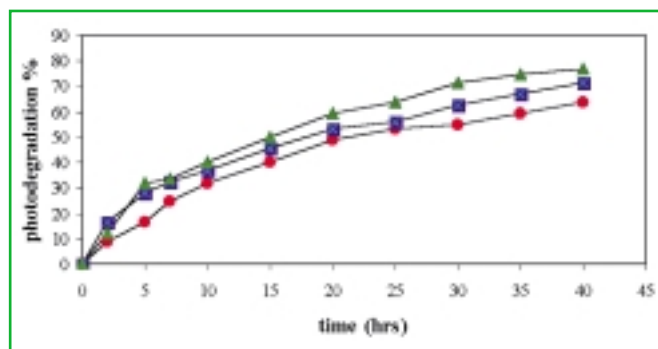


Figure 3 - Photodegradation of *p*-chlorophenol ($2.5 \cdot 10^{-5}$ mol/l, 50 ml) catalysed by polymeric membranes ($A_s = 29.6$ cm², 100 μ m thickness) containing TiO₂(25%)-zeolite at different pH.
 ▲ pH = 3.2, ● pH = 6.7, ■ pH = 9.1

from the initial value (6.7 for the solution of chlorophenol and 3.2 for the solution of the metal ions to be adsorbed) and moving to acid and basic field.

carried out together or successively. Adsorption results to be improved by an in parallel operating procedure while for photodegradation a little increment in efficiency is obtained with an

Table 6 - Adsorption with the passage of time of copper from $1 \cdot 10^{-4}$ mol/l solution on membranes of TiO₂ and zeolite.
 a) TiO₂/zeolite = 3:1, b) TiO₂/zeolite = 1:1, c) TiO₂/zeolite = 1:3

Time (hrs)	Adsorption, (%) (RSD% _≤ 5%)		
	a	b	c
2	58.5	76.5	79.7
4	89.2	92.6	97.1
6	96.9	97.1	98.5
8	98.2	98.7	99.0
24	100	100	100

In Figure 4 the two processes, proceeding during the time are together represented.

At this point polyaniline was considered as additive of membrane according to the results of our previous researches [8, 9]. The polyaniline concentration was optimized at the value of 19%; higher values result in a release of the conducting polymer from the membrane. At this concentration an improvement of the photodegradation efficiency of about 20% was obtained. In order to explore if in series or in parallel system could be better for the efficiency, adsorption and photodegradation were

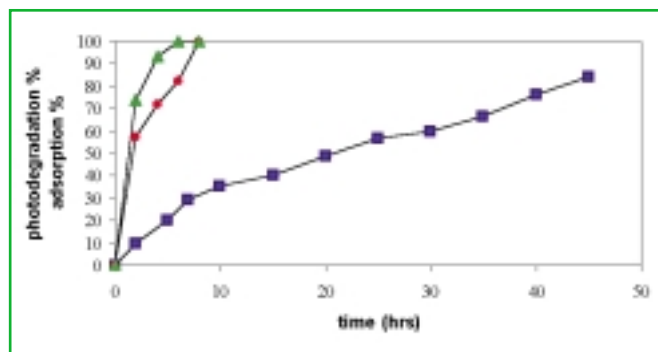


Figure 4 - Photodegradation of *p*-chlorophenol ($2.5 \cdot 10^{-5}$ mol/l, 50 ml) with contemporary adsorption of Cu and Cd obtained with polymeric membranes ($A_s = 29.6$ cm², 100 μ m thickness) containing TiO₂(25%)-zeolite. ▲ Cu adsorption, ● Cd adsorption, ■ *p*-chlorophenol photodegradation

in series procedure. Even if in the case of the pesticide propoxur this increase is higher, the advantage is overbalanced by the more difficult engineering of the operating plant. So in parallel systems seem to be preferred. In any case all the variations induced by the operating procedure are within 25%.

Table 7 - Adsorption of copper and cadmium ($1 \cdot 10^{-4}$ mol/l, 50 ml) on a PVC-TiO₂(25%)-zeolite membrane, at different initial pH. The trend of pH is reported in the square brackets

Initial pH	Time (hrs)	Adsorption, (%) (RSD% _≤ 5%)			
		Cu		Cd	
6.7	2	78.9	[6.5]	52.0	[6.8]
	6	86.3	[6.4]	61.3	[7.0]
	8	86.3	[6.4]	67.4	[6.7]
8.4	2	85.2	[6.0]	58.3	[7.0]
	6	88.9	[6.1]	68.6	[6.6]
	8	92.6	[6.2]	73.0	[6.4]
3.2	2	79.7	[3.9]	63.4	[4.2]
	6	98.5	[6.0]	76.2	[5.9]
	8	98.5	[6.5]	82.3	[6.0]

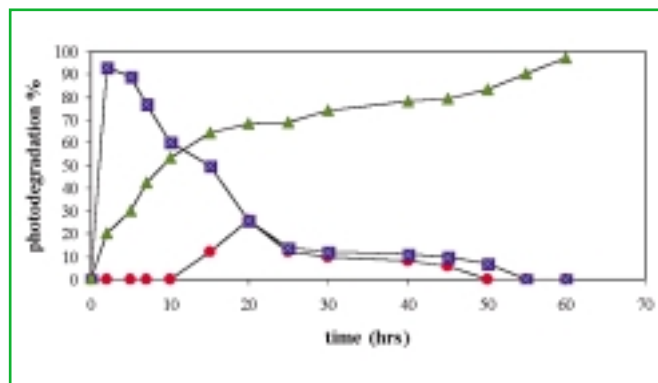


Figure 5 - Trend of the *p*-chlorophenol degradation (initial conditions: $2.5 \cdot 10^{-4}$ mol/l, 50 ml) and of the concentration of two intermediates. ▲ *p*-chlorophenol degradation, ● *p*-benzoquinone, ■ hydroquinone

As last part of the paper the photodegradation reaction was considered in our experimental conditions looking for its characterisation. So on the basis of kinetic theory and Langmuir and Hinshelwood equation, kinetic and adsorption constants were calculated and found to be respectively $3.026 \pm 0.035 \mu\text{mol/h}$ and $0.004 \pm 0.001 \text{ l}/\mu\text{mol}$. Literature data give hydroxyhydroquinone, hydroquinone, p-benzoquinone, chlorohydroquinone, catechol and phenol as possible degradation products. By chromatographic analysis hydroquinone and p-benzoquinone were evidenced during 60 hrs of the photodegradation experiment (Figure 5) with retention time respectively of 7.2 and 8.6 min. Two other unknown species are detected at $t = 6.6$ and 13.2 min.

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