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Photocatalytic Wastewater Treatment Using the Zeolite-Y Entrapped Ruthenium Tris-2,2′-bipyridine Complex

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The zeolite-Y entrapped ruthenium tris-2,2′-bipyridine complex, in 1% wt. metallized with platinum (Z-$[Ru(bpy)_3]^{2+}$/Pt), has been examined as a new photocatalyst for wastewater treatment in flow reactors of the pilot plant at the Plataforma Solar de Almeria, in Spain. The catalyst generated by the template synthesis of $[Ru(bpy)_3]^{2+}$ within the zeolite-Y supercages (with the occupancy of one the $[Ru(bpy)_3]^{2+}$ molecule per five the zeolite supercages), and then platinized of the resulting Ru intrazeolitic complex. The catalytic activity of Z-$[Ru(bpy)_3]^{2+}$/Pt for wastewater treatment has been compared to that of TiO_2, as the standard. For this, phenol (PhOH) and pirimicarb (a pesticide) have been used as models for water pollutants. By kinetic measurements it has been documented that Z-$[Ru(bpy)_3]^{2+}$/Pt decomposes PhOH with the relative photonic efficiency of $\zeta_r = 0.37$, assuming that $\zeta_r = 1.0$ for TiO_2, under the same experimental conditions. To improve the Z-$[Ru(bpy)_3]^{2+}$/Pt photocatalytic activity, all the zeolite supercages have to be occupied by $[Ru(bpy)_3]^{2+}$ molecules, since this might increase the rate of the photoinduced electron transfer reaction. Moreover, it has been revealed that Z-$[Ru(bpy)_3]^{2+}$/ Pt is mostly active at the visible range of the solar radiation, at which TiO_2 is inactive and unable to decompose organic pollutants. This has been supported by the diffuse reflectance spectroscopic measurement exhibiting the electronic absorption of Z-$[Ru(bpy)_3]^{2+}$/Pt at $\lambda_{max} = 454$ nm.

Key words: photocatalysis, zeolite entrapped complex, photonic efficiency, titanium dioxide

The TiO_2 photosensitized oxidation of organic pollutants continues to attract much attention as for their relevance to wastewater treatment plants [1–3]. The crucial in this process is the production of $^{\bullet}OH$ radicals, known as particularly powerful oxidative agents, $E(^{\bullet}OH/OH^-) = 2.31$ V [1,2], readily decomposing all organic compounds. These radicals origin from the oxidation of water molecules by UV-excited TiO_2 catalyst that the valence band oxidation potential is 2.7 V [2].

In this work the zeolite-Y entrapped $[Ru(bpy)_3]^{2+}$ complex (Z-$[Ru(bpy)_3]^{2+}$), as an alternative to TiO_2 for wastewater treatment goals, has been tested. For a schematic representation of Z-$[Ru(bpy)_3]^{2+}$/Pt see Figure 1. It is thought that the complex is a

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sufficient powerful agent to decompose organic pollutants (such as pesticides and phenols) after the optical excitation, since E($[Ru(bpy)_3]^{3+}/[Ru(bpy)_3]^{2+}$) = 1.26 V [6]. It has been recently documented that the zeolite-Y framework efficiently retards the energy wasting processes, as well as increases the photostability of the entrapped catalysts [4–10]. Moreover, in contrast to TiO_2 operating at $\lambda < 350$ nm [2], the intrazeolitic complexes enable to construct catalysts, active in the visible range of solar radiation, since the electronic absorption of $[Ru(bpy)_3]^{2+}$ occurs at $\lambda_{max} = 453$ nm [7,8]. That is why this approach provides the opportunity for a more effective utilization of solar energy for environmental goals.

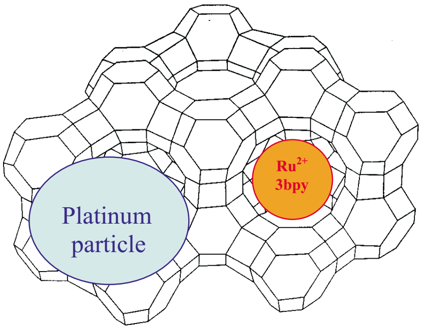


Figure 1. Schematic representation of Z-$[Ru(bpy)_3]^{2+}$/Pt.

The objectives of this work are summarized as follows: for the first, producing of platinized Z-$[Ru(bpy)_3]^{2+}$, and for the second, evaluating of Z-$[Ru(bpy)_3]^{2+}$/Pt zeolite catalytic activity towards organic pollutants photodegradation. For this, such organics as phenol (PhOH), and pirimicarb (an aphicide [11]) have been selected as model pollutants. The reactivity has been compared to that of TiO_2 reference catalyst [3,12,13].

EXPERIMENTAL

Materials: The sample of zeolite-Y (CBV 100) with a surface area of 934 m^2/g, $SiO_2/Al_2O_3 = 5.17$, and a unit cell size of 24.65 Å was purchased from *Zeolyst International*. $RuCl_3 \times 3H_2O$, $PtCl_4$, 2,2′-bipyridyl (2,2′-bpy), pirimicarb (as the standard), phenol (PhOH), and all solvents were purchased from *Aldrich Chemical Co*. The 2,2′-bpy was sublimed prior to use. The samples of the $Ru(NH_3)_6Cl_3$ salt were obtained from Alfa Inorganics. Pirimicarb (as the pollutant) purchased from *Zeneca Agro* was used as granulate *PirimorG* containing of the active ingredient in 50%. The reference photocatalyst was TiO_2 Degussa P-25 (*ca*. 80% anatase, 20% rutile) with a surface area of about 50 m^2/g corresponding to a mean elementary particle size of *ca*. 30 nm. The water used in all solar experiments was obtained from the PSA distillation plant (evaporation by a multi-effect system using solar energy).

Preparation of compounds. Generation of Z-$[Ru(bpy)_3]^{2+}$ and Z-$[Ru(bpy)_3]^{2+}$/Pt samples: In order to prepare the Ru-exchanged (Z-Ru^{3+}) zeolite with an occupancy of one Ru^{3+} cation per 5 supercages (1:5), 0.12 g of $Ru(NH_3)_6Cl_3$) dissolved in 1 dcm^3 deionised (DI) water was mixed with 5.0 g of the Y-zeolite had been calcined at 500°C, washed with 20% aqueous NaCl, and then with DI water [6–8]. It was assumed that 2 g of the Y-zeolite contained 5.556×10^{20} supercages [6,7]. During this ion-exchange operation, the solution was stirred vigorously and kept in the dark at 4°C for 24 hrs. Then, the zeolite was filtered, washed with DI water and air dried. After that, 5.0 g of Z-Ru^{3+} was mixed in a high vacuum reaction vessel (~ 2.5 cm × 12.5 cm) with 0.84 g of 2,2′-bpy dissolved in ethanol and kept overnight at 4°C. Then, the ethanol was evaporated under a stream of dry nitrogen. The solid mixture was evacuated to 0.1 Torr, and held at that pressure for the next 2 hrs. Subsequently, the powder was heated at 180°C for 10 hours, during which time the sample changed colour to orange. After cooling, the crude product was stirred in boiling 10% NaCl for 3 hours, and then extracted with ethanol. In order to facilitate desorption of the unreacted 2,2′-bpy and any residual $Ru(bpy)X_4^{2+}$ from the zeolite, 2–3 g of solid NaCl was placed in the Soxhlet thimble. The extraction was conducted until the total amount of the solid NaCl had been washed out from the Soxhlet thimble, and the UV spectrum of the ethanolic extract did not show typical of absorption the ligand at 254 nm. This operation took around 5 days. Subsequently, the zeolite was washed with DI water (500 ml) to remove from the zeolitic samples any residual NaCl, and then dried in air. The integrity of the Z-$[Ru(bpy)_3]^{2+}$ sample was confirmed as described previously [6–8] by emission spectra, RR and electronic absorption of its HCl extract. In order to prepare a platinized form of the zeolite entrapped ruthenium complex containing 1% (wt.) of Pt, Z-$[Ru(bpy)_3]^{2+}$/Pt, typically 5.0 g of Z-$[Ru(bpy)_3]^{2+}$ was dispersed in 500 cm^3 water containing 0.085 g of $PtCl_4$ (its pH was adjusted to 5.4 using 0.1 N HCl). Then gaseous H_2 passed through it until the suspension changed colour from orange to brown. Subsequently, the brown solid was filtered off, washed with DI water and dried in air.

Photocatalytic experiments: The photocatalytic water decontamination experiments were performed using compound parabolic collectors (CPC) installed at the Plataforma Solar de Almeria (PSA), Tabernas, Spain [1]. The photoreactor consisted of three CPC modules set up in series (total reflective surface 3 m^2), and placed on fixed support inclined at 37° (latitude of the PSA) with respect to the horizontal plane and facing south, in order to maximise the performance. Each CPC module was 1.2 m wide and 1 m long and consisted of eight reflectors with UV-Visible transparent tubular receivers (ID 48 mm). The total volume of the system was *ca*. 40 litres [1,12].

For a typical experiment, around 39 dcm^3 of PSA distillated water containing suspension of selected zeolitic catalyst, at the amount of 0.1 g/dcm^3 (comparing to the optimal amount that had been determined for TiO_2 before [1,12]) and ~0.025 mg/dcm^3 of selected organic substrate (pirimicarb, DCA, or PhOH) was circulated at a CPC with flow of 3.5 m^3/h, the pH of the mixture was adjusted to 4–5 with 0.5 M H_2SO_4. At another CPC, localized in parallel to the first one, was filled with the same amount (volume) of water and selected organic substrate, however, the zeolitic catalyst was replaced with TiO_2, for the reference measurements. The circulated suspensions were maintained in the dark for 0.5 h to reach the adsorption equilibrium of the pollutant. Time zero corresponded to the beginning of solar-irradiation. Following the sun exposure, samples were collected at regular intervals (15 or 30 minutes) from both CPC-s, at their exits and the temperature was monitored (during the measurements the temperature changed in the range of 25–35°C). In all cases, the concentration of pollutants and their main degradation intermediates were determined, using chromatographic (HPLC equipped with a UV detector set at 220 or 245 nm) and total organic carbon (TOC) measurements. Before the chromatographic measurements samples were filtered using syringe-tip filters Millex-GN (pore size 0.2 μm) from Millipore Intertech.

HPLC-UV analysis. Pirimicarb and phenol analyzed by HPLC using reverse-phase liquid chromatography with UV detection (245 nm for pirimicarb, 270 nm for phenol) using a HPLC-UV (Hewlett-Packard, series 1050) with C-18 column (LUNA 5μ-C18, 3 × 150 mm from Phenomenex).

TOC analysis performed by direct injection of the filtered samples into a Shimadzu-5050A TOC analyser calibrated with standard solutions of hydrogen potassium phthalate.

UV-Visible and **Diffuse Reflectance** spectra were collected using a Model UV-2501 PC Shimadzu spectrophotometer equipped with an integrated sphere attachment. The zeolite samples were measured as KBr pellets, where pellets with an identical content of plain zeolite-Y were used as blanks. The spectra were recorded in the transmittance mode and were numerically corrected *via* Kubelka-Munk expression.

Power density data for solar radiation (flux) were collected using KIPP&ZONE sensor, Model CUV3, with a sensitivity of 264 $\mu VW^{-1}m^{-2}$. This radiometer was mounted at a 37° angle, around 10 m from the used CPC reactors.

RESULTS AND DISCUSSION

To evaluate the photocatalytic activity of the zeolite entrapped $[Ru(bpy)_3]^{2+}$ for wastewater treatments gaols, the experiments on PhOH photodegradation by Z-$[Ru(bpy)_3]^{2+}$/Pt have been performed. Similar experiments have been also done for TiO_2, under the same experimental conditions for a comparison (quantitative analysis). The question is how changes the photonic efficiency of phenol degradation if the zeolite has been replaced by TiO_2 standard. The choice of phenol as an organic substrate has been dictated by its regular application as a reference in solar detoxification experiments. For example, Serpone *et al.* [3] selected PhOH as the standard for determining of the relative photonic efficiency (ζ_r) for the heterogeneous photocatalysis. All the photochemical experiments have been performed using two equal CPC flow reactors installed at PSA, identically exposed to sun (irradiated by sun), as described in the Experimental part. Both reactors were filled out with the same amount of water (39 dcm^3) slightly contaminated by phenol (0.027 g/dcm^3). The first CPC contained 0.1 g/dcm^3 of Z-$[Ru(bpy)_3]^{2+}$/Pt with pH = 4.7 adjusted with 0.1 M H_2SO_4. In the second reactor, TiO_2 has been substituted for the zeolite with the same concentration (for reactors at PSA, the most efficient TiO_2 concentration is around 0.2 g/dcm^3 [1]). Up to now, any concentration optimization experiment for the zeolitic catalyst has not been performed yet. However, it is expected that several parameters might affect the reactivity, such as the zeolite-Y supercages occupancy by $[Ru(bpy)_3]^{2+}$, and the percentage of Pt loading. That is why, all reported here photochemical experiments have to be related to the strictly the same concentration of the zeolitic catalyst in the reaction mixture (0.1 g/dcm^3), the zeolite Pt loading (1% wt.), and the Ru complex occupancy (one $[Ru(bpy)_3]^{2+}$ per five supercages, 1:5).

Figure 2 shows the PhOH decay (photodegradation) catalysed by Z-$[Ru(bpy)_3]^{2+}$/Pt and TiO_2, respectively. These experimental points have been obtained based on chro-

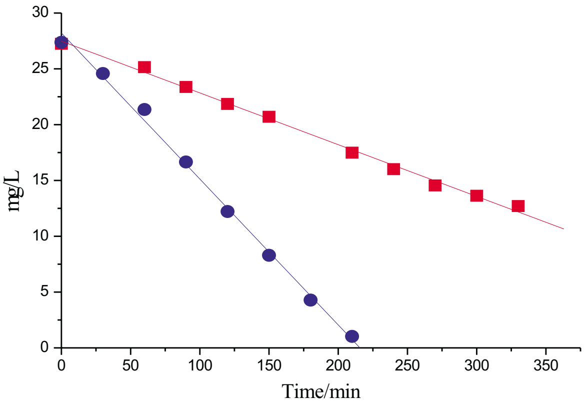


Figure 2. Plots of organic pollutants concentration (in mg/dcm^3) as a function of solar irradiation time (in minutes) for the photodegradation of phenol in the presence of TiO_2 (circles) and Z-$[Ru(bpy)_3]^{2+}$/Pt (squares).

matographic (HPLC) measurements on [PhOH] concentrations for samples regularly collected (*i.e.* every 30 minutes) from both CPC reactors.

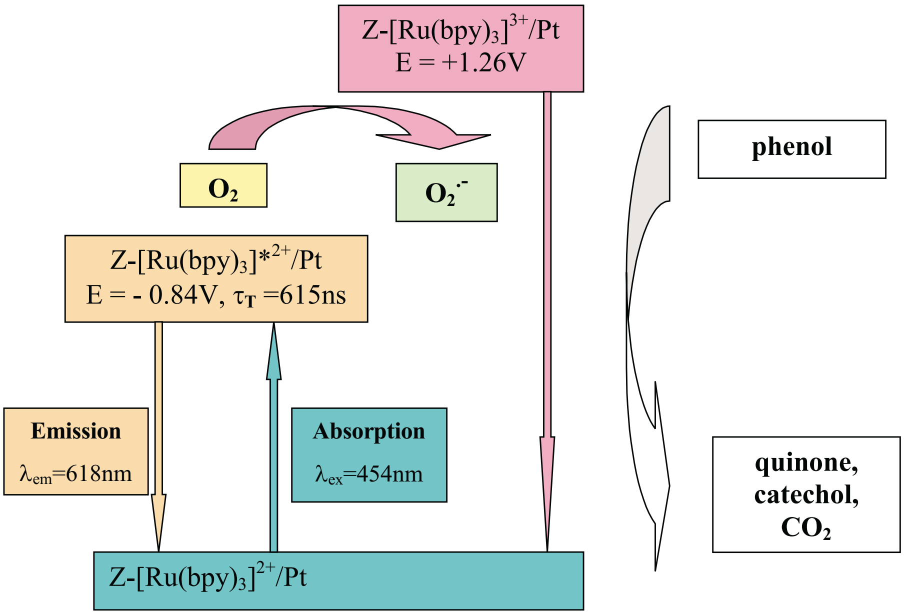
As shown in Fig. 2, the relative photonic efficiency of phenol photodegradation by $[Ru(bpy)_3]^{2+}/Pt$ is $\zeta_r = 0.37$ assuming that $\zeta_r = 1$ for TiO_2, under the same experimental conditions. The ζ_r numbers were evaluated using the expression adopted from that developed by Serpone *et al.* [3])

$$\zeta_r = \frac{R(Z\text{-}[Ru(bpy)_3]^{2+})}{R(TiO_2)}$$

where: R – the rate of PhOH disappearance calculated from graphs.

It is important to note that the photonic efficiency is twice smaller if no platinized zeolite (*i.e.* $Z\text{-}[Ru(bpy)_3]^{2+}$) has been applied. Moreover, the PhOH degradation has been only partial (or does not occur) if the reactors are closed, *i.e.* there is not access to air (oxygen). This can be explained in terms of the photoinduced electron transfer, followed by trapping of free electrons on a reaction with oxygen dissolved in the reaction mixture [1–3]. In the case of TiO_2, the electrons come from the valence band of the optically excited semiconductor, *i.e.* electron-hole pair production. Consequently, PhOH is decomposed either by $^{\bullet}OH$ radicals, generated from water and the holes or directly by the holes. To reach the electronic balance of the reaction system, the "free electrons" from the TiO_2 valence band are consumed on reacting with oxygen soluble in water, and superoxide producing [1–3]. A similar mechanism can be adopted for the PhOH photodegradation in the presence of $Z\text{-}[Ru(bpy)_3]^{2+}/Pt$, see Scheme 1. In this case, the photoinduced electron transfer is probably associated with the photooxidation of $[Ru(bpy)_3]^{2+}$ to $[Ru(bpy)_3]^{3+}$ by dissolved oxygen, and superoxide production in the presence of the Pt redox-catalyst. Therefore, it is necessary to have oxygen in the reaction mixture to keep the process on. On the other hand, the zeolite entrapped $[Ru(bpy)_3]^{3+}$ complexes are enough powerful oxidizing agents (E = 1.26 V [6]) to decompose phenol to its quinone and pyrocatechol derivatives. However, the $Z\text{-}[Ru(bpy)_3]^{3+}$ redox form is apparently less oxidative than $^{\bullet}OH$ (E = 2.31 V [1,2]), therefore, the zeolite is expected to be less active in the PhOH photodegradation with respect to TiO_2, as it has been supported by the experiments.

The difference in the relative photonic efficiency for $Z\text{-}[Ru(bpy)_3]^{2+}/Pt$ *versus* TiO_2 is also attributable to the variation in solar flux in the range absorbed by these catalysts. As shown in Figure 3, the zeolitic complex absorbs visible radiation at λ_{max} = 454 nm that well matches to the absorption maximum of the free $[Ru(bpy)_3]^{2+}$ complex [6–8]. Contrary, TiO_2 is optically activated only by UV-radiation with $\lambda < 350$ nm. If these catalysts operate in different ("incompatible") ranges of solar radiation, a variation in the photonic efficiency is possible. However, the solar flux at $\lambda < 350$ nm absorbed by TiO_2 is lower than that at $\lambda > 400$ nm absorbed by the zeolite. For that reason, the photonic efficiency decrease for the zeolite is due to a lower absorptivity of $Z\text{-}[Ru(bpy)_3]^{2+}/Pt$, rather than the solar flux variation. This might result from a lower concentration of the catalytic centres (*i.e.* $[Ru(bpy)_3]^{2+}$) in the zeolite comparing to



Scheme 1. Schematic representation of the oxidative quenching of electronically excited Z-[Ru(bpy)$_3$]*$^{2+}$/Pt by oxygen followed by it reduction with phenol.

TiO_2 by a factor of 135 (the number of [Ru(bpy)$_3$]$^{2+}$ molecules entrapped in the zeolitic catalyst is around 135 lower corresponding to the number of TiO_2 molecules in the same amount of the semiconductor).

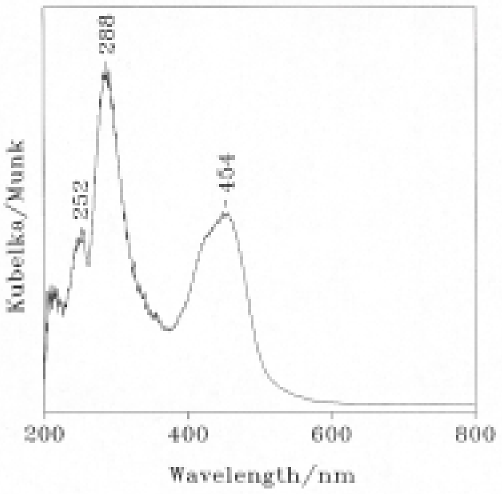


Figure 3. Diffuse reflectance spectrum of Z-[Ru(bpy)$_3$]$^{2+}$/Pt.

The Z-$[Ru(bpy)_3]^{2+}$/Pt photocatalytic activity has been also tested for a selected pesticide (pirimicarb). These results are plotted in Figure 4 together with those obtained for TiO_2. They are presented as a function of the accumulated solar energy (Q_{UV}). The latter has been calculated based on [12]:

$$Q_{UV,n} = Q_{UV,n-1} + \Delta t_n\, UV_{G,n}\, A_r/V_t \qquad \Delta t_n = t_n - t_{n-1}$$

where t_n is the experimental time of each sample, $UV_{G,n}$ the average UV radiation power density during Δt_n time (in W m^{-2}), Q_{UV} the accumulated solar energy per unit of volume (in J/dcm^3), V_t the reactor volume, and A_r the collector surface. The measurements of the solar power density (in W/m^2) have been performed using the radiometer as presented in the Experimental part. The presentation of the kinetic data as a function of Q_{UV} is a more adequate way to present the catalytic activity, since Q_{UV} is independent on weather, as well as photo-optical and geometrical properties of reactor used.

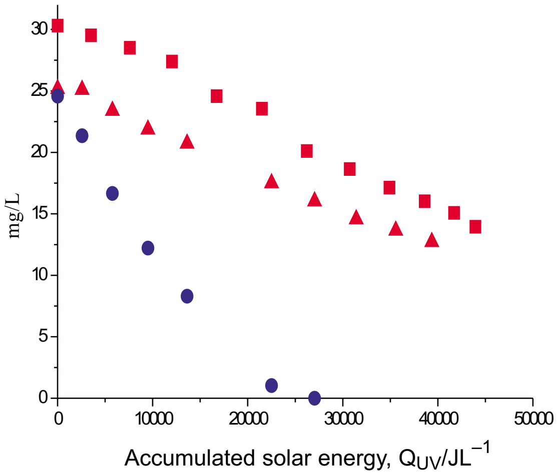


Figure 4. Plot of organic pollutants photodegradation as a function of accumulated solar energy (in J/dcm^3). The line with circles corresponds to phenol/TiO_2, the line with triangles corresponds to phenol/ Z-$[Ru(bpy)_3]^{2+}$/Pt, and line with squares corresponds to pirimicarb/ Z-$[Ru(bpy)_3]^{2+}$/Pt.

As shown in Figure 4, the decrease of [PhOH] concentration and that of [pirimicarb] are similar. This might indicate that the photodegradation of pirimicarb photosensitized by Z-$[Ru(bpy)_3]^{2+}$ proceeds *via* the same mechanism as that of PhOH. In other words, kinetics of both processes is, presumably, controlled by the rate of the same intermediating species generation that is responsible for the substrates photooxidation. The most likely species is the Ru^{3+} redox form of Z-$[Ru(bpy)_3]^{3+}$. Apparently, for all the experiments, a steady state concentration of the intermediates is the same, since the concentration of the zeolite, dissolved oxygen, and pH of the reaction mixture have been identical. Moreover, corresponding to the mechanism of oxidative quenching of electronically excited polypyridine ruthenium complexes [14,15], thermodynamically the Ru^{3+} species is capable to oxidize, such organic compounds as EDTA, TEA and pirimicarb.

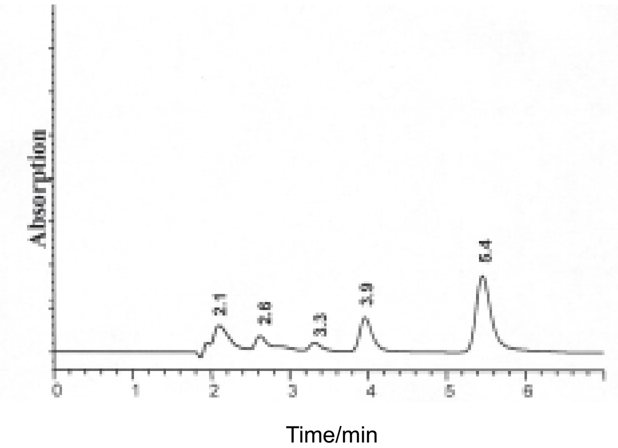


Figure 5. The HPLC pattern acquired after 4 hours of solar irradiation for pirimicarb being photodecomposed by Z-$[Ru(bpy)_3]^{2+}$/Pt.

Figure 5 illustrates a chromatogram acquired during the experiment of pirimicarb photodegradation, after around 4 hours of the solar irradiation. Under these experimental conditions, the peak of pirimicarb appears at t = 5.441 minutes with a hight two times smaller corresponding to that monitored at the beginning of the experiment. Moreover, at the lower range of retention time, four new peaks at t = 2.097, 2.620, 3.314 and 3.961 minutes have been developed. Obviously, they origin from products of the pesticide photodegradation. It is interesting that these peaks have not disappeared completely even after a following solar irradiation, for the next 5 hours. This observation indicates that the pesticide has been transformed to relatively stable photoproducts, those do not mineralize to CO_2 under these experimental conditions. Similar results of a partial degradation/mineralization obtained also for another pesticides, such as imidacloprid, pyrimethanil, *etc*., however with TiO_2 as the photocatalyst [1,13].

CONCLUSIONS

In this work, the use of Z-$[Ru(bpy)_3]^{2+}$/Pt as a new heterogeneous photocatalyst for organic wastewater treatments is reported. Concerning the relative photonic efficiency of phenol and pirimicarb degradations, the commonly used TiO_2 appears to be the most efficient catalyst. This difference in the catalytic activity can be explained in terms of the different nature of the active transient states produced during both photodegradation processes, *i.e.* $^{\bullet}OH$ radicals in the case of TiO_2, and the transient Z-$[Ru(bpy)_3]^{3+}$ redox form in the case of the zeolite (*i.e.* Z-$[Ru(bpy)_3]^{3+}$ is less oxidative than $^{\bullet}OH$ radicals). Moreover, the average concentration of the catalytic centers in the zeolitic catalyst is lower by a factor of 135 corresponding to that of TiO_2.

Therefore, to improve the Z-$[Ru(bpy)_3]^{2+}$/Pt photocatalytic activity, all the zeolite supercages have to be occupied by $[Ru(bpy)_3]^{2+}$ molecules, since this might increase the rate of the photoinduced electron transfer reaction. It is important to note that Z-$[Ru(bpy)_3]^{2+}$ (as a nontoxic zeolite) is resistant against hydrolysis (at $3 < pH < 11$ [6,16]), as well as does not undergo any redox degradation by most organic pollutants (for free $[Ru(bpy)_3]^{2+}$ in acetonitrile: $E^{2+/+3} = 1.26$ V and $E^{2+/1+} = -1.34$ V *vs*. NHE [17,18]), therefore, it appears to be particularly interesting for environmental goals and wastewater treatments.

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