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Kinetic Study of Photocatalytic Degradation of Several Pharmaceuticals Assisted by SiO_2/ TiO_2 Catalyst in Solar Bath System

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ABSTRACT

The photo-catalytic degradation of five pharmaceuticals using TiO_2 modified with SiO_2, and sun light was monitored. The initial concentrations used in the solar bath system were100 µg/L for caffeine, diclofenac, glimepiride and ibuprofen, and 25 µg/L for methotrexate. Kinetic disappearance of caffeine, diclofenac, glimepiride and ibuprofen shows pseudo- first order kinetics, while methotrexate shows a zero order kinetic degradation which was monitored using HPLC/UV at $\lambda = 225$ nm, F = 1ml/min and on a C8 reversed phase column. The rate constants for diclofenac (wastewater 0.3238 sec^{-1}, distilled water 0.4057 sec^{-1}), glimepiride (wastewater 0.2203 sec^{-1}, distilled water 0.2771 sec^{-1}), ibuprofen (wastewater 0.2802 sec^{-1}, distilled water 0.2411 sec^{-1}), caffeine (distilled water 0.416 sec^{-1}) and methotrexate (distilled water 3.1407 mole L^{-1} sec^{-1}). The removal efficiency for the drugs was ranged between 79% and 96%.

Keywords: Kinetics, Photo-catalytic degradation, Pharmaceuticals, SiO_2 / TiO_2, Solar bath.

INTRODUCTION

During the last few years, the presence of pharmaceuticals in the aquatic environment, classified as the so-called emerging contaminants, raised a great concern among the scientific community [1].

Pharmaceutical compounds have been found in aquatic system, sewage treatment plant effluents [1,2], surface waters [3] as well as drinking waters [4], as a result of their growing use.

Sewage treatment plants (STP) have been pointed out as the main source of pharmaceutical discharge into the environment, due to their low efficiency for the elimination resulting in a continuous input into the aquatic environment.Various elimination rates between almost none and almost quantitative elimination have been reported for different substances and different sewage treatment plants [5-9].

Recently chemical treatment methods involving the generation of hydroxyl radicals, known as Advanced Oxidation Processes (AOPs), have been applied successfully for the removal or degradation of pollutants based on the high oxidative power of the HO radical [10].

The AOPs are generally referred to the bleaching of organic pollutants with a combination of ultraviolet light in association with different methods using, ozone [11], photo-Fenton type reactions [12], reduction followed by a photo-oxidation process [13,14], and using catalysts such as titanium dioxide [15,16]. As a result, the organic impurities will be removed by converting them into harmless inorganic end products as CO_2, H_2O, etc.

Major improvement to be achieved is an increase in the degradation efficiency by using TiO_2 /UV. One of the factors to be determined is to increase the adsorption efficiency of the substrate to TiO_2, incorporated with silica [17-18], alumina [20], or zeolite [21-23].

The mechanism of the TiO_2/UV degradation has been

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described using the band-gap model [15]. It is well established that by irradiation of an aqueous TiO_2 suspension with light energy (*hv*) greater than the band gap energy of the semiconductor , electrons (e^-) and valence band holes (h^+) are generated (equation 1). It was demonstrated that most of the TiO_2-covered adsorbents are more efficient than bare TiO_2. These will act as strong oxidizing agents that can easily attack any organic molecule adsorbed on, or located close to, the surface of the catalyst, thus leading to their complete degradation into small inorganic species illustrated as follows [15]:

$$TiO_2 + hv \longrightarrow TiO_2\ (h^+ + e^-)\ (hv \geq E_g = 3.2eV;\ \lambda < 390nm) \quad (1)$$

$$O_2 + e^- \longrightarrow O_2^{\cdot -} \quad (2)$$

$$H_2O + h^+ \longrightarrow H^+ + OH^{\cdot} \quad (3)$$

$$OH^{\cdot} + RH \longrightarrow H_2O + R^{\cdot} \quad (4)$$

$$R^{\cdot} + O_2 \longrightarrow ROO^{\cdot} \longrightarrow \quad \longrightarrow CO_2 \quad (5)$$

It is also important to support TiO_2 on larger adsorbent particle, so that the recovery of photo-catalyst is facilitated. However, the more advantageous is to modify existing highly efficient TiO_2 to a better photo-catalyst [24].

It was reported that silica is a very good medium, which not only facilitates adsorbing organics but also transferring those adsorbed compounds to active sites on TiO_2 [25], and the dispersion of the TiO_2 particles was also getting better [26]. In addition to the better recovery of the photocatalyst from the solution, those supports or mixtures were widely reported as good adsorbents for the organics [27].

The rate and efficiency of the photocatalytic reaction depend on a number of factors. One such important factor is adsorption of the substrate onto the surface of the catalyst. In these reactions, the contaminant substrate is oxidized by the photo-generated holes or by reactive oxygen species such as the OH• and O_2^-• radicals formed on the surface of the catalyst [28,29].

Langmuir–Hinshelwood (L-H) model represents the mechanism required for the contaminant adsorbs on the catalyst surface as a prerequisite for efficient oxidation. The adsorption–desorption process is characterized by the transfer of the reactants in the aqueous phase to the surface; adsorption of the reactants; reaction in the adsorbed phase; desorption of the products; and removal [28-29].

Although the L-H model seems to describe adequately the macroscopic kinetics when dealing with very dilute aqueous solutions of photodegradable contaminants, some of the inherent assumption of the model may not be valid at the microscopic level, which includes its failure to account for simultaneous adsorption (or desorption) [30-32].

L-H model equation is represented in equation 6:

$$r = k\,\theta = -dC\,/\,dt = k\,(KC/1+KC) \ldots\ldots (6)$$

where r is the rate of mineralization, k is the reaction rate constant, C is the concentration, K is the adsorption coefficient and θ is the fractional site coverage for the reactant as KC<<1, the equation became as in 7 or 8:

$$C(t)=C_0\, e^{-krt} \ldots\ldots (7)$$

$$Ln\ C = Ln\ C_0 - k_r t \ldots\ldots (8)$$

where k_r is the first-order photocatalytic reaction rate constant. This first-order rate constant is often determined by observing the relative aqueous concentration changes [33-35].

Five pharmaceutical compounds were chosen according to their most common use in the Jordanian Society and their solubility in water. These compounds are methotrexate,caffeine, diclofenac, glimperide and ibuprofen.

MATERIALS AND METHODS

Chemical and Materials

The solvents: acetonitrile, methanol, ethyl acetate of the gradient grade were purchased from Chromanorm (VWR International bvba, EC). Tetraethoxysilan (TEOS) (98%, GC-grade) was purchased from Sigma Aldrich, Trifluoroacetic acid (TFA) of the synthesis grade was purchased from Scharlau Chemie (S.A.).Titanium dioxide (›99%) was purchased from Merck (Germany).

The standards: caffeine (99%), diclofenac (99%), nifidipen (98%), glimpride (98%), ibuprofen (98%), methotrexate (95%) were purchased from Sigma Aldrich (Germany).

SPE cartridges, three milliliter size, packed with 500 mg C_{18} stationary phase, were purchased from Thermo/USA, membrane filter paper (Nylon), pore size 0.45 mm, diameter 47 mm was purchased from Agela/USA.

Instrumentation

The used High Performance Liquid Chromatograph (HPLC) consisted of a pump model GBC (LC 1110), UV detector type ProStar 325 (Varian/U.K.). The UV detector was controlled by a system controller version 6.41 (ProStar 325 UV.

Chromatographic Conditions

LC separations were performed at ambient temperature on RP-C_8 column (25 cm, 4.6 mm, 5 µm) was purchased from Phenomenex (USA). For routine analyses a mobile phase consisting of a mixture of 1:1 acetonitrile: water with 0.1% TFA at a flow rate of 1 ml/min. The UV detector was set at λ=225 nm.

SiO_2/ TiO_2 Preparation

1.5 g of tetraethoxysilane (TEOS) was dissolved in 20 ml methanol**;** 3 g TiO_2 were added, stirred magnetically until all methanol was evaporated. 100 ml of distilled water was added to the residue, stirred for several seconds, then the mixture was centrifuged for 4 min. at 4000 rpm, and decanted. The solid residue was suspended in 50 ml water again, and stirred for one hour for hydrolyzing the unreacted TEOS. The sample was centrifuged for 4 min. at 4000 rpm, decanted, washed with methanol, dried at 100°C and finally calcinated at 300°C for one hour [24,36].

Solar Bath System

Heterogeneous photocatalytic experiments using SiO_2/ TiO_2-catalyst, were carried out under UV- sunlight in a solar bath-pilot plant of two containers (high-density polyethylene), one on the ground containing the catalyst and spiked water sample and the other one stand two meters up where the contents of the lower container were pumped to it, as shown in Figure 1.

The volume of each container was 20 L. One recirculation pump was used for pumping the sample from the lower container to the upper one, while water goes down through Pyrex tubes by gravity. The pump was connected to a plastic bypass tube of 1 m length to insure mixing and lowering the pressure on the pump.

The suspension was circulating through a Pyrex glass tubes of 828 cm length and 13 mm diameter, while exposed to the UV-sunlight from 10.00 am – 17.00 pm (9 hours totally). The total volume of the Pyrex tube was about 1.1 L

Figure 1: Solar-Bath System

Sampling

For the degradation studies, each time (every1 hour) a sample of 200 ml was taken from the lower container. A total of 8 samples were studied.

All the experiments were performed twice. Spiked experiments were carried out in 20 L distilled water with caffeine alone, methotrexate alone and the mixture of diclofenac, glimepiride and ibuprofen at the concentrations of 100µg/L, 25µg/L and 100µg/L respectively. And the wastewater sample from Baqa'a

STP (not chlorinated) was spiked with the same above concentrations of diclofenac, glimepiride and ibuprofen.

Catalyst mass was fixed in all experiments at 5 g for 20 L water (distilled and wastewater) which is the optimized mass load from previous study [36].

Sample Extraction

Prior to extraction the sample was filtrated through 0.45 µm Nylon filter. Solid phase extraction (SPE) cartridges was conditioned using 6 ml of methanol (2×3) and 6 ml of deionized water (2×3) at a slow flow-rate (ca. 3 ml/min). The spiked sample was transferred to the SPE cartridges through at a very slow flow-rate using a vacuum manifold system connected to a vacuum pump.

The loaded cartridge was rinsed with 3 ml of deionized water; then eluted with 8 ml (2×4) aliquots of ethyl acetate at a slow flow-rate (ca. 3ml/min). The combined aliquots were evaporated to dryness using a gentle stream of nitrogen. The residues were dissolved in 0.3 ml of mobile phase containing a constant concentration or volume of the internal standard (I.S.), sonicated in the ultra sonic bath to insure complete dissolution, then injected into the HPLC system.

Validation of the Analytical Procedure

The range of linearity of the five studied pharmaceuticals were calculated and calibrated with the internal standard (see Figure 2). Six-point calibration curve were established at the concentrations: 3, 6, 10, 20, 30, 50 mg/L with the internal standard (Nifidipen t_R = 8.98 min) using the UV detector. The average of four injections of each concentration was used to calculate the linear equations and correlation coefficient.

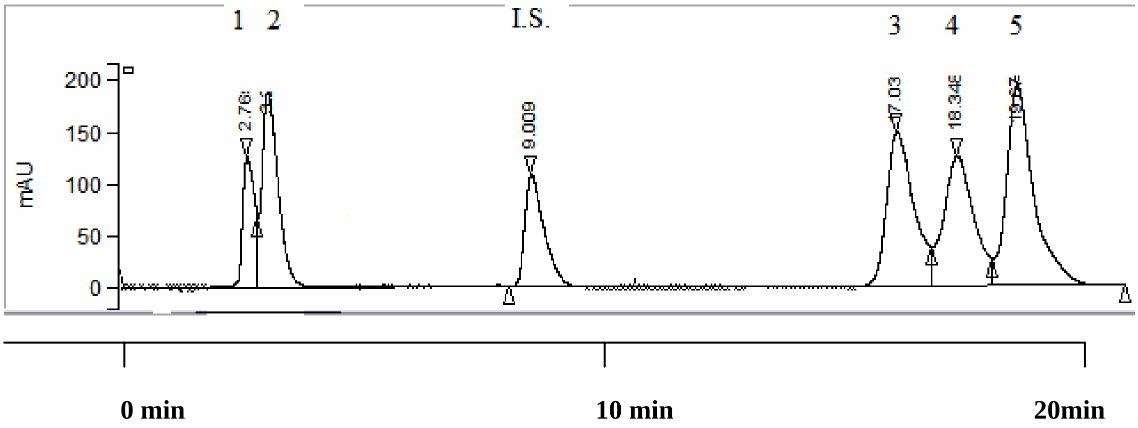

Figure 2: 100 µg /L concentration mixture of each compound, 20 µl was injection under the above mentioned conditions. 1: methotrexate, 2: caffeine, 3: diclofenac, 4: glimpride, 5: ibuprofen.

Experiments in Dark and without using Catalyst

Each experiment was performed twice. The dark experiment was performed in a 2 L Pyrex beaker covered completely with aluminum foil. The same initial concentrations were spiked with 1:4 mass load of the catalyst. The experiment duration was eight hours. Each two hours, a sample of 200 ml was taken.

The experiment without catalyst was performed using the solar-bath system using the same initial concentrations, where eight samples, each of 200 ml volume, were taken every one hour for analysis, the concentration of drugs were caffeine 68.57± 0.15 µg/L, methotrexate 19.89 ± 0.15 µg/L, diclofenac 21.35 ±0.04 µg/L, glimepiride 12.77 ± 0.22 µg/L, and ibuprofen 25.72 ± 0.33 µg/L.

RESULTS AND DISCUSSION

Validation of the Analytical Procedure

Table1 summarizes the calibration results: retention time (t_R), limits of detection (LOD), limits of quantification (LOQ), the linear equation, the correlation coefficient (R^2) and the recovery of three quality control concentrations namely: 3, 10 and 30 mg/L with their standard deviations (STD).

Table 1: Method's Validation parameters (t_R, R^2, LOD, LOQ, Recovery, STD)

%Recovery (x_{av} ± s) for 30 mg/L	%Recovery (x_{av} ± s) for 10 mg/L	%Recovery (x_{av} ± s) for 3 mg/L	R^2	Linear Equation	LOQ µg /L	LOD µg /L	t_R (min.)	Drug
89% ±5.0	103% ±6.0	108% ±15.0	0.997	*Y=0.900x+0.166*	2.55	0.768	2.64	**Methotrexate**
100.8% ±6.0	99.8% ±13.0	100% ±20.0	0.997	*Y=0.0551x+0.0538*	1.27	0.382	3.22	**Caffeine**
99.6% ±3.0	99.4% ±9.0	102.0% ±13.0	0.999	*Y=0.0684x+0.0152*	3.87	1.161	15.89	**Diclofenac**
91.3% ±10.0	94.6% ±13.0	99.1% ±12.0	0.997	*Y=0.0666x+0.0192*	3.03	0.908	17.31	**Glimepiride)**
96.2% ±7.0	92.0% ±5.0	102.4% ±8.0	0.998	*Y=0.0572x+0.0040*	2.53	1.727	18.13	**Ibuprofen**

Kinetics of Disappearance Using Catalytic Solar-Bath System

The present data are consistent with the Langmuir–Hinshelwood model; because when plotting Ln C_t versus time, the results represent a straight line, the slope of which upon linear regression equals the apparent first-order rate constant k with pseudo-first-order kinetics. Table 2 shows the rate constants (k_r) and R^2 for each of the studied pharmaceuticals in both wastewater and distilled water.

The degradation of caffeine in water obeyed the pseudo-first-order Langmuir–Hinshelwood kinetics, where the equation gave a rate constant of 0.416, and the degradation of the high concentrations of caffeine in wastewater can be achieved.

Rosal et al. [37] reported the degradation of caffeine using ozone at different pH values, but the degradation kinetic was found to be of second order.

The degradation kinetics of methotrexate is a zero order which gave R^2 = 0.9763 by plotting the concentration versus time. Removing of methotrexate using the photo-catalytic solar-bath system is efficient even if the concentration in wastewater is high.

The removal of diclofenac, glimepiride and ibuprofen was studied as a mixture at the concentrations of 100 µg/L (distilled water and wastewater).

The degradation rate constant for diclofenac in distilled water is higher than that in wastewater. The lower degradation rate constant in wastewater could be due the scattering phenomena, where active sites on the surface of the catalyst do not bring more e/h^+ generation and therefore a decrease in the degradation rate occur.

Glimepiride degradation also obeys pseudo-first order in both distilled water and wastewater. The degradation rate and the correlation coefficient for both samples were close to each other. The initial concentration was the same, because the concentration in the Baqa'a effluent was below the detection limit.

The degradation rate constants of ibuprofen in wastewater and distilled water were close to each other, while the correlation coefficient in the case of wastewater was higher. The concentration of ibuprofen in Baqa'a effluent was found to be 6 µg/L; therefore the initial concentration in wastewater is a little bit higher.

Figure 3 give the degradation of pharmaceuticals in distilled water by plotting LnC/C0 vs. time.

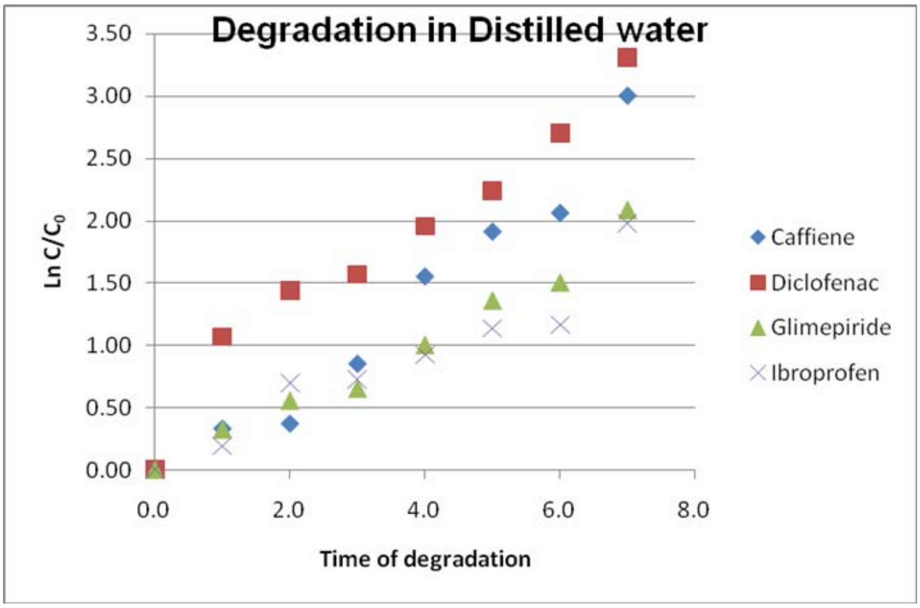

Figure 3: Degradation of caffiene, diclofenac, glimepiride and ibroprofen in distilled water.

Methotrexate degradation gives zero order kinetics' by plotting the concentration vs. time, as shown in Figure 4.

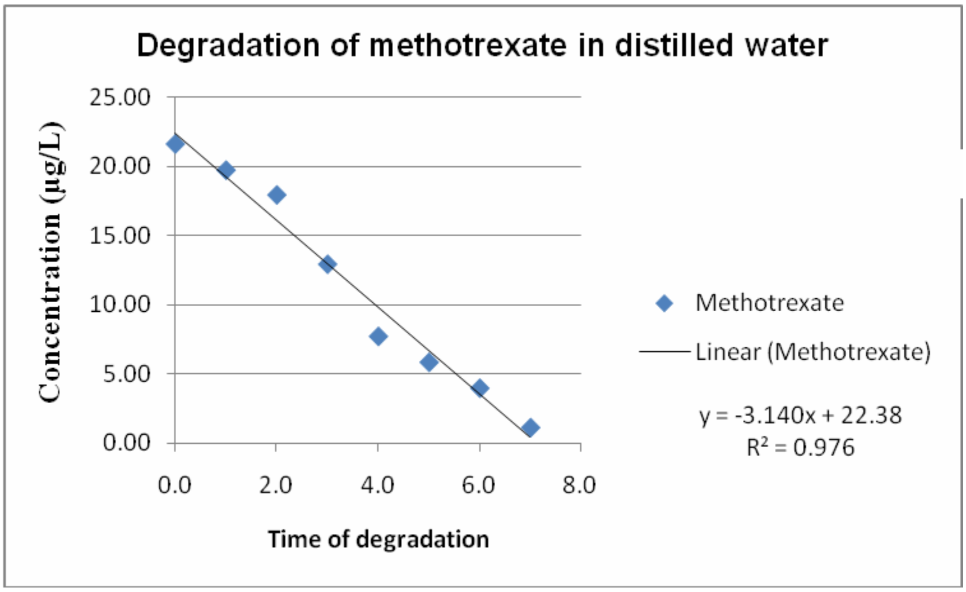

Figure 4: Degradation of methotrexate in distilled water.

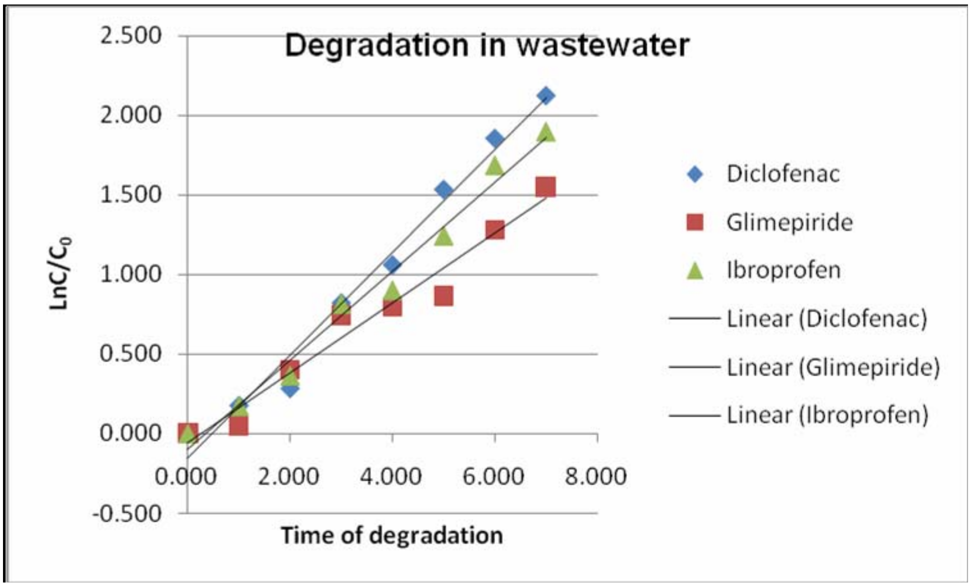

Figure 5: Degradation of pharmacuticales in wastewater.

Table 2: Results of kinetic disappearance of the studied drugs in wastewater and distilled water

Drug	Wastewater		Distilled water	
	Rate constant	R^2	Rate constant	R^2
Diclofenac*	0.3238	0.9815	0.4057	0.9533
Glimepiride *	0.2203	0.9651	0.2771	0.9745
Ibuprofen*	0.2802	0.9837	0.2411	0.9175
Caffeine*	------------------------------		0.416	0.9597
Methotrexate**	------------------------------		3.1407	0.9763

* Pseudo-first-order kinetic; $\text{Ln } C_t = - k_r t + \text{Ln } C_0$, k unit; sec^{-1} .

** Zero order; $C_t = -k_r t + C_0$, k unit; mole L^{-1} sec^{-1}.

Table 3 shows the removal efficiency of the studied drugs in the photocatalytic solar bath system in both spiked wastewater and spiked distilled water samples. The removal (degradation) efficiency from wastewater ranged between 79 and 88% while from distilled water ranged between 86 and 96%. Caffeine and methotrexate were not studied in wastewater because of the high contamination in the chromatograms at t_R between 1.5 to 2.9 min. during degradation process. The lower degradation rate constant in wastewater in general could be due the scattering phenomena, where active sites on the surface of the catalyst do not bring more e/h^+ generation and therefore a decrease in the degradation rate occur.

Table 3: Removal efficiency of the studied drugs using the photo-catalytic solar bath system in both spiked wastewater and spiked distilled water samples.

	Removal Efficiency %	
Drug	**Wastewater**	**Distilled water**
Caffeine	NS*	95.0%
Diclofenac	88.1%	96.2%
Glimepiride	79.2%	87.5%
Ibuprofen	84.8%	86.5%
Methotrexate	NS*	95.0%

*NS: not studied

Removal efficiency= [initial concentration- final concentration] / initial conc.*100%

Dark and Without Catalyst Experiment

In both experiments and for all sampling times, the relative peak area (RPA) was constant all the time, which means that for the degradation of the pharmaceuticals, both UV-sunlight and the catalyst are necessary. Table 4 gives the average RPA for eight samples with standard deviation (±S) for all studied pharmaceuticals in two experiments one the same initial concentrations in dark conditions with catalyst and the other in the solar system without the catalyst.

Table 4: Average RPA±S for the pharmaceuticals in Dark and without catalyst experiments

Drug	**Dark**		**Without Catalyst**	
	RPA	**±S**	**RPA**	**±S**
Diclofenac	3.10	0.04	3.05	0.08
Glimepiride	4.00	0.22	4.34	0.20
Ibuprofen	2.83	0.33	3.31	0.35
Caffeine	3.10	0.15	3.28	0.17
Methotrexate	1.10	0.12	1.15	0.15

CONCLUSION

Photo-catalysis enhanced by UV-sunlight appears to be a promising technology for the degradation of pharmaceuticals in wastewater such as caffeine, methotrexate, diclofenac, glimepiride and ibuprofen, where transformation, deactivation and minimization of the environmental persistent compounds can be achieved. Photocatalysis as a treatment step should enhance the biodegradability of these pollutants, but does not require reaching the complete mineralization.

As a consequence the combination of photocatalysis and a subsequent biological treatment step can be favorably applied for advanced water treatment. On the other hand the identification of possibly formed toxic compounds is essential for a sound assessment of the treated water.

The SiO_2/TiO_2 catalyst has an advantage over TiO_2 alone, as it can be modified in different shapes using nanotechnology which give it the ability of being reused, instead of using TiO_2 powder, which is an economical point of view.

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دراسة كانتيكية التكسر الضوئي لعدد من الأدوية على المحفز ثاني أكسيد التيتانيوم المعدل بثاني أكسيد السيليكون وباستخدام نظام الحمام الشمسي

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ملخص

تمت دراسة تحطم خمسة أدوية تحت تأثير ضوء الشمس واستخدام المحفز ثاني أكسيد التيتانيوم المعدل بثاني أكسيد السيليكون.

كانت التراكيز الابتدائية التي استخدمت في النظام الشمسي لكل من الكافائين، الدايكلوفيناك، جلمبرايد والأيبوبروفين هي 100 مايكروغرام/لتر وللمثوتركسيت هي 25 ميكروغرام/لتر.

الاختفاء الكاينتيكي لكل من الكافائين، الدايكلوفيناك، جلمبرايد والأيبوبروفين كان يتبع حركية "شبه الدرجة الأولى" بينما تكسر الميثوتركسيت كان يتبع حركية "الدرجة الصفرية" والذي روقب باستخدام جهاز الكروماتوغرافيا السائلة ذات الأداء العالي مع المكشاف الفوق بنفسجي عند طول موجة 225 نانومتراً ومعدل تدفق للطور السائل المتحرك 1 مللتر/دقيقة وباستخدام عمود ذي طور معكوس C8 .

كان ثابت سرعة التفكك للدايكلوفيناك 0.3238 ثانية-1 في الماء العادم و 0.4057 ثانية-1 في الماء المقطر، للجلمبرايد 0.2203 ثانية-1 في الماء العادم و 0.2771 ثانية-1 في الماء المقطر، وللكفائين 0.416 ثانية-1 في الماء المقطر وللميثوتركسيت 3.1407 مول. لتر-1 .ثانية-1 في الماء المقطر.

كانت نسبة الكفاءة لإزالة الأدوية بهذا النظام تتراوح بين 79 و 96%.

الكلمات الدالة: كانتيكية، التكسر الضوئي، الأدوية، SiO_2/ TiO_2، الحمام الشمسي.

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