

Porous and Bifunctional ZnO-Hydroxyapatite Nanostructure for Photocatalytic Degradation of Paracetamol and Methylene Blue in Water

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ABSTRACT

Porous ZnO-hydroxyapatite nanocomposite was prepared by dissolution of a rock phosphate ore in an acidic medium followed by alkaline precipitation. Its photocatalytic activity was assessed for the degradation of paracetamol as one of the most commonly prescribed pharmaceutical drugs and methylene blue as dye model. Thanks to its good porosity, the 40ZnHAp nanocomposite adsorbed the selected pollutants better than the individual ZnO and HAp phases. 40ZnHAp calcined at 500° completely degrades the studied pollutants faster than ZnO, although a longer illumination time is required for the degradation of paracetamol. The low-cost 40ZnHAp nanomaterial can be considered as a potential photocatalyst for wastewater treatment due to its high porosity, which facilitates the entrapment of initial pollutants and/or by-products. It leads to a complete mineralization, consequently yielding healthy discharged water.

Keywords: ZnO-Hydroxyapatite, nanocomposite, Photocatalysis, Paracetamol, Methylene blue

1. Introduction

Pollution of the aquatic environment by persistent and non-biodegradable pharmaceuticals and dyes in domestic and industrial wastewaters is a serious environmental problem, due to its harmful effects on human physiological development and the ecosystems functions [1, 2]. Wastewater is a complex system because it comes from different combinations of domestic, industrial, commercial, or agricultural activities and it contains many harmful organic pollutants such as dyes and drugs [3, 4].

Several wastewater treatment processes were considered before releasing into the natural environment or reuse. The treatment of colored pigments or pharmaceutical residues in water is generally inefficient, expensive, and non-destructive or it sometimes just transfers the pollution from water to another phase [5]. Adsorption and heterogeneous photocatalysis were reported as more promising technologies for the

removal of organic micropollutants [6, 7], among which drugs or dyes are abundantly spread into waters. The process is based on the activation of a semiconductor by light. TiO₂ is the most popular photocatalyst used in this respect [8-10], despite some drawbacks which limit its industrial applications [11, 12]. ZnO is considered an alternative for the photodegradation of surrounding pollutants due to a rapid electron transfer [13-15]. However, it is a non-porous material. Its association with a porous matrix is very attractive and got the attention of several researchers [16-20]. The association of ZnO with porous hydroxyapatite (ZnHAp) prepared from Moroccan rock phosphate proved very efficient at degrading antibiotic molecules [21]. In order to more deeply evaluate the ZnO-HAp nanocomposite as photocatalyst, special emphasis is placed on eliminating paracetamol as one of the most commonly prescribed drugs and methylene blue as a dye model. This made it possible to evaluate the catalytic efficiency of the ZnHAp catalyst towards most organic pollutants that are found in the aquatic environment. Its effectiveness in

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trapping pollutants and their by-products is all the more important as the by-products can be even more toxic than the parent drugs. Therefore, the porous nanomaterials of ZnHAp are excellent adsorbents and therefore are more efficient photocatalysts than bulk materials. This provides them with a wide variety of applications for solving environmental problems.

2. Experimental

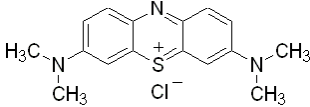
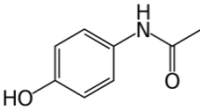
2.1. Preparation of catalysts

The pure hydroxyapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ powder (called HAp) was produced by the simultaneous dissolution/reprecipitation from a Moroccan natural phosphate ore as described in previous work [22]. ZnO powder was prepared by precipitation through alkalization of zinc nitrate dihydrate $\text{Zn}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ by adding concentrated ammonia NH_4OH (25%), paralleling the conditions for the HAp synthesis. Details of the synthesis and structural characterization were described in previous work [21]. For ZnHAp nanocomposite, the Zn^{2+} ions were added to the solution containing Ca^{2+} ions and H_3PO_4 from the ore dissolution followed by neutralization with a concentrated solution of NH_4OH (25%) up to $\text{pH} = 10$ with continuous stirring at room temperature. The quantity of zinc having a final theoretical weight ratio ZnO: HAp $w = 40\%$ was added and the resulting material was named 40ZnHAp. Finally, the powders were dried in an oven at 100°C for 24 hours and heat-treated at 500°C for 3 h.

2.2. Photocatalysis experiments and modeling

The photocatalysis experiments were carried out using a photoreactor equipped with an open two-neck Pyrex cylinder with a capacity of 150 ml, allowing the possibility to introduce solutes and taking samples. Water circulation in a double-walled casing was used for cooling. The inner cavity was placed under a 125W UV A-B-C lamp (200-600 nm). A 0.2 g catalyst sample was first dispersed in 100 mL of contaminated solution and left to react in the dark for 30 min for MB and 60 min for paracetamol. The solution was then exposed to UV light under magnetic stirring. At different reaction times (t), aliquots of the supernatant solution were taken with a 2 mL propylene syringe and centrifuged at 4000 rpm for 20 min, and the residual concentrations of MB

Table 1. Structure and main physico-chemical characteristics of the studied pollutants

	MB	Paracetamol
Structure		
Ab. λ_{max} (nm)	664	240
pK _a	3.14	9.38

and paracetamol were analyzed by UV-visible and controlled by HPLC. Structure and physico-chemical characteristics of the two pollutants are given in **Table 1**. The kinetics data were fitted with the linear form of the Langmuir-Hinshelwood equation [23]: $\text{Ln}C_t/C_0 = -k_{\text{app}} \cdot t$, where C_0 and C_t are the initial and instantaneous concentrations, respectively and k_{app} is the apparent rate constant determined as the slope of the linear plot $\text{Ln}(C_t/C_0)$ against time t .

3. Results and Discussion

3.1. Characterization

The powder dried at 100°C and calcined at 500°C of 40ZnHAp nanocomposite was characterized by XRD and compared to those of HAp and ZnO as references (**Fig. 1a**). The main diffraction peaks of hydroxyapatite and ZnO are identified. This suggests that the association of hydroxyapatite with ZnO particles was effective. The association of HAp with ZnO increases the specific surface of the 40ZnHAp nanocomposite ($250 \text{ m}^2 \text{ g}^{-1}$). Heating the 40ZnHAp powder to 500°C does not significantly reduce the S_{BET} value ($135 \text{ m}^2 \text{ g}^{-1}$), but the ZnO particles are more sensitive to heating (**Table 2**). Whatever the heat treatment, the specific surface of the 40ZnHAp nanocomposite is larger than that of the HAp and ZnO references (**Fig. 1b,b'**). TEM images show that 40ZnHAp and HAp powders are well-defined aggregates of particles with average sizes of 20-30nm, while ZnO powder is dense with 50 nm particles (**Fig. 1c,c'**) such as detailed in our previous work [21].

Table 2. Elemental analysis, specific surface area of the materials dried at 100°C and calcined at 500°C .

Sample	Ca/P	Zn/P	$S_{\text{BET}100} (\text{m}^2 \text{ g}^{-1})$	$S_{\text{BET}500} (\text{m}^2 \text{ g}^{-1})$	$D_p100(\text{nm})$	$D_p500 (\text{nm})$
40ZnHAp	1.65	0.48	250	135	11	11
HAp	1.89	-	165	105	14	12
ZnO	-	-	20	11	4	9

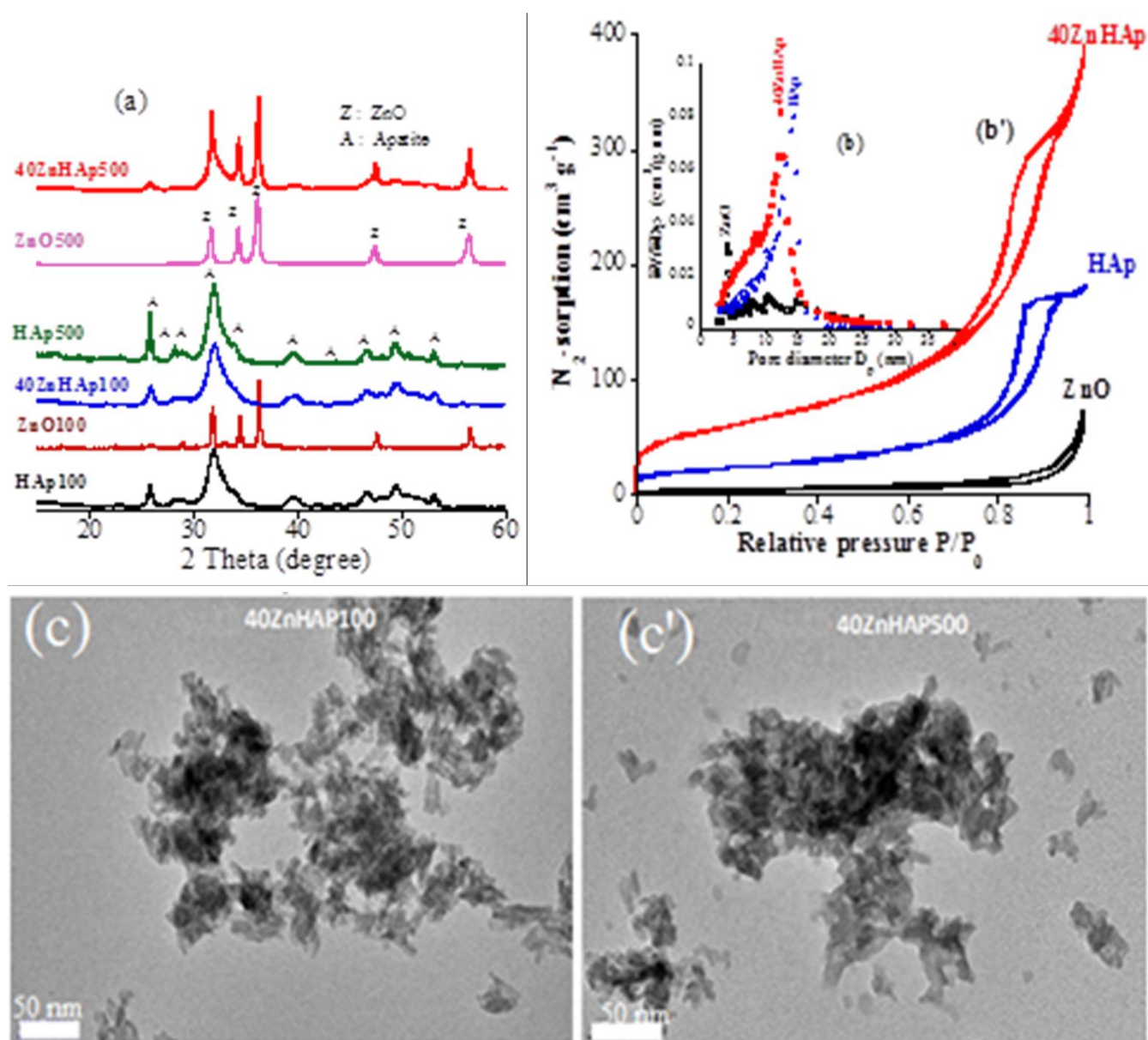


Fig. 1. Structural, textural characteristics of 40ZnHAp nanocomposite compared to individual ZnO and HAp phases. (a) XRD patterns powder, (b, b') N_2 sorption isotherms and (b) pore size distribution, and (c, c') TEM images.

The Ca/P and Zn/Ca molar ratios of the prepared 40ZnHAp and HAp materials were quantified by inductively coupled plasma atomic ICP-AES, showing that the Zn content in this composite agrees with the amount initially introduced (**Table 2**). Results confirm that ZnO was evenly combined with the HAp matrix in the 40ZnHAp nanopowder catalyst, which exhibits a high specific surface area contrary to individual ZnO and HAp powders. Thus, the presence of pores in 40ZnHAp nanocomposite may facilitate the adsorption of paracetamol and methylene blue and afterwards their degradation under UV light.

3.2. Adsorption and photocatalysis

Fig. 2 shows the variation in the adsorbed amount of paracetamol and methylene blue on the 40ZnHAp, HAp, and ZnO powders. In all cases, the adsorption is limited, but 40ZnHAp dried at 100 °C exhibits significant adsorption after 30 min for MB and 60 min for paracetamol as solid/solute contact, which may be related to its high porosity ($S_{BET} = 250 \text{ m}^2\text{g}^{-1}$). In order to completely remove the studied pollutants, the photochemical activity of 40ZnHAp catalyst was evaluated under UV-light and compared to those of individual ZnO and HAp powders. It should be noted that the sorption capacity depends on the specific surface but also on the chemical formulation of the pollutant, in particular the ionic charge and the nature of the chemical functions. Therefore, this adsorption is

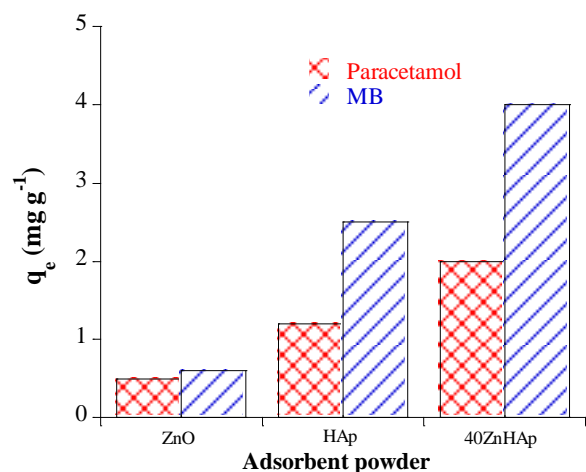


Fig. 2. Preliminary adsorption step before photocatalysis, showing the fixation of pollutants on the surface of the catalysts ($C_0=20 \text{ mg L}^{-1}$, adsorbent dose = 2 g/L , room temperature of 24°C).

related to the diffusion of pollutants into the pores of the solid surface via the electrostatic interactions between adsorbate/adsorbent, both hydrogen bonds and Van der Waals forces. The better adsorption of MB is due to its positive charge supported by the negative apatite surface such as indicated by its pK_a . In fact, the electrostatic attraction between the negatively charged PO_4 groups of the porous hydroxyapatite and the positively charged sulfur group of MB promotes the adsorption [24]. Indeed, the nitrogen atom of MB might interact with Ca^{2+} or Zn^{2+} groups of the nanocomposite 40ZnHAp via Lewis acid-base interaction. For paracetamol, its -OH and -NH functions can be the active sites but in different acido-basic pH domains.

Before proceeding with photocatalysis, the direct photolysis of pollutants in water by UV irradiation without a catalyst was accomplished to evaluate its contribution to the degradation of pollutants under the same operating conditions as for photocatalysis. **Fig. 3** shows that no degradation of the two selected pollutants was achieved under UV light without catalysts. In the presence of catalyst and before UV-irradiation (in the dark), adsorption equilibrium was established by stirring during 30 min for methylene blue and 60 min for paracetamol. For pure apatite HAp, the adsorption step was observed and followed by a very weak change in the photodegradation step, suggesting that the two pollutants were not degraded (**Fig. 3**). However, degradation of the selected pollutants using 40ZnHAp or ZnO catalysts is complete, but it is faster for MB (**Table 3**). Heat treatment of the catalysts at 500°C markedly improves their catalytic efficiency and 40ZnHAp500 shows better degradation efficiency than ZnO500. This strongly suggests that the reduced

fraction of the photoactivity of ZnO in the 40ZnHAp composite is compensated by its high porosity. This shows that trapping is an essential step for the pollutants to be degraded.

The kinetics of the degradation reaction vary with the pollutant formulation and follow a Langmuir-Hinshelwood model based on the linear relation of the $\log(C/C_0)$ versus time. A proper fitting of the experimental data was obtained using this model ($R^2 > 0.99$) (**Fig. 4**). The calculated K_{app} values and the full degradation times are reported in **Table 3**. Based on the correlation coefficients (R^2) relating to the linearity of the Langmuir-Hinshelwood relation, this model is most likely to characterize the degradation kinetics of the target molecules supported on the studied catalysts. It confirms that the reaction follows a first order law. The significant difference in reaction rates might be due to the different structural features and the thermal treatment of catalyst. As shown in **Table 3**, the apparent first order rate constant increases with the combination of ZnO and apatite and with the 500°C heat treatment which is effective.

Results showed that MB degraded faster than paracetamol, depending on the nature of the composite. Good efficiency of the 40ZnHAp nanocomposite is due to coupling of the adsorption and photocatalysis within the same unit operating the degradation of the two organic species. This material transfer coupling is an efficient way to optimize both adsorption and photodegradation operations to obtain a process capable of treating non-negligible volumes and concentrations of organic pollutants without a particular maintenance.

The 40ZnHAp catalyst showed the highest ability to degrade the methylene blue and paracetamol molecules. This suggests that the presence of Zn in 40ZnHAp and its large surface area enhance its photocatalytic efficiency. Our approach has the advantages of using natural sources of calcium and phosphate precursors and requiring a small amount of Zn-precursor, both contributing to the potential decrease of the processing costs. The highly interconnected pore structure and uniform dispersion of ZnO in 40ZnHAp nanocomposite are helpful for administering monolayer homogeneous adsorption of organic molecules and for their photodegradation. Based on our previous experimental results and those published elsewhere [21, 25-27], it turns out that the photogenerated holes and superoxide radicals are the main active species responsible for the photocatalytic degradation of organic matter on 40ZnHAp and ZnO photocatalysts. Unlike ZnO, using the 40ZnHAp500 catalyst, no HPLC peak was found

related to the by-products at the end of the degradation reaction of the two pollutants (4h for paracetamol and 2h for MB). As previously proposed, this can be explained by the attachment of small quantities on the porous surface of the apatite, while the ZnO catalyst is a non-porous material. Therefore, advanced water treatment under UV light can achieve a complete removal of various toxic organic matters owing to adsorption of the by-products by the porous surface of the apatite.

To warrant that the 40ZnHAp catalyst retains its photocatalytic efficiency and test the possibility of its

reuse, successive tests of degradation of MB and paracetamol species were performed after heating the catalyst at 500°C for 3 hours after each photodegradation process of 20 mg L⁻¹ solute. Three additional photodegradation-regeneration cycles were performed. A very small loss of photocatalytic degradation efficiency was observed (1-3%), which may be related to the loss of catalyst weight at each cycle. As a result, the 40ZnHAp500 nanocomposite retains its photocatalytic efficiency without changing its structure and surface properties and it can be reused several times without loss of efficiency.

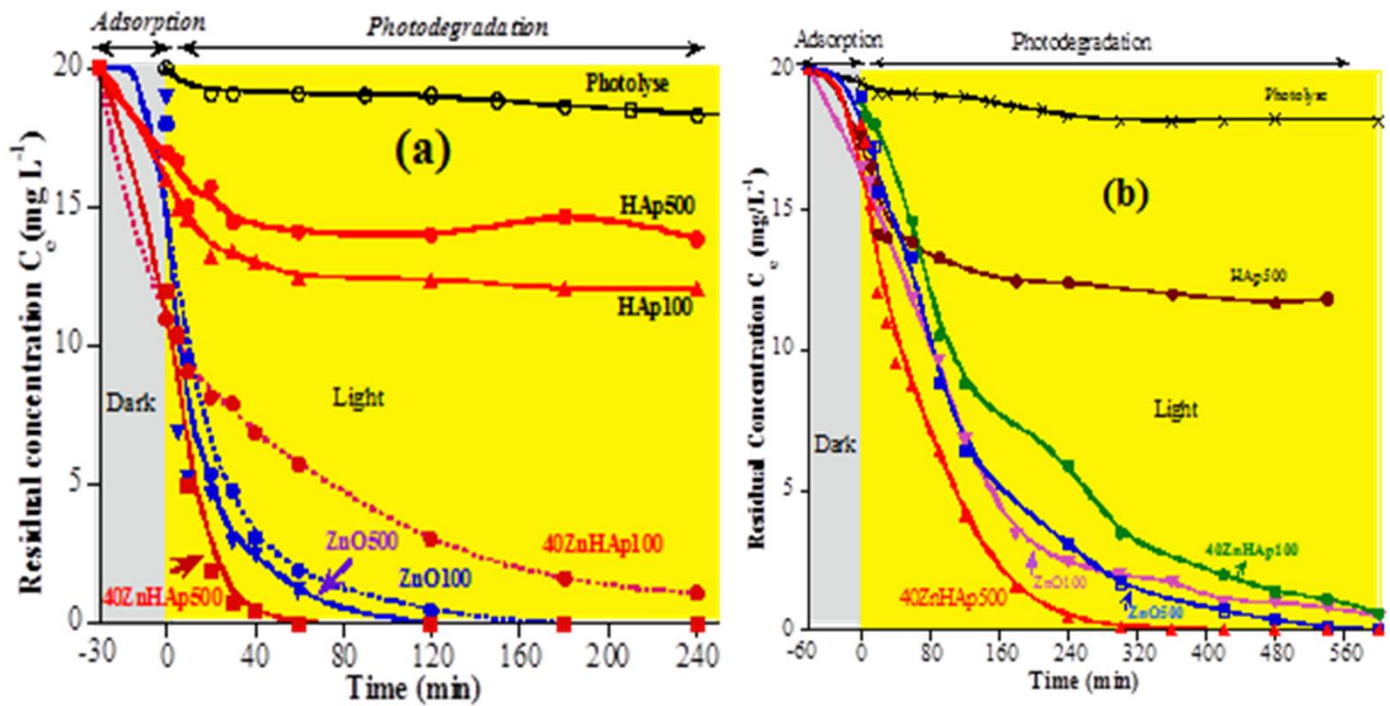


Fig.3. Kinetics of degradation of (a) MB and (b) paracetamol by 40ZnHAp nanocomposite powder dried at 100°C and heated at 500°C compared to pure HAp and ZnO ($C_0 = 20 \text{ mg L}^{-1}$, $T = 24^\circ\text{C}$, dose = 2 g L^{-1}).

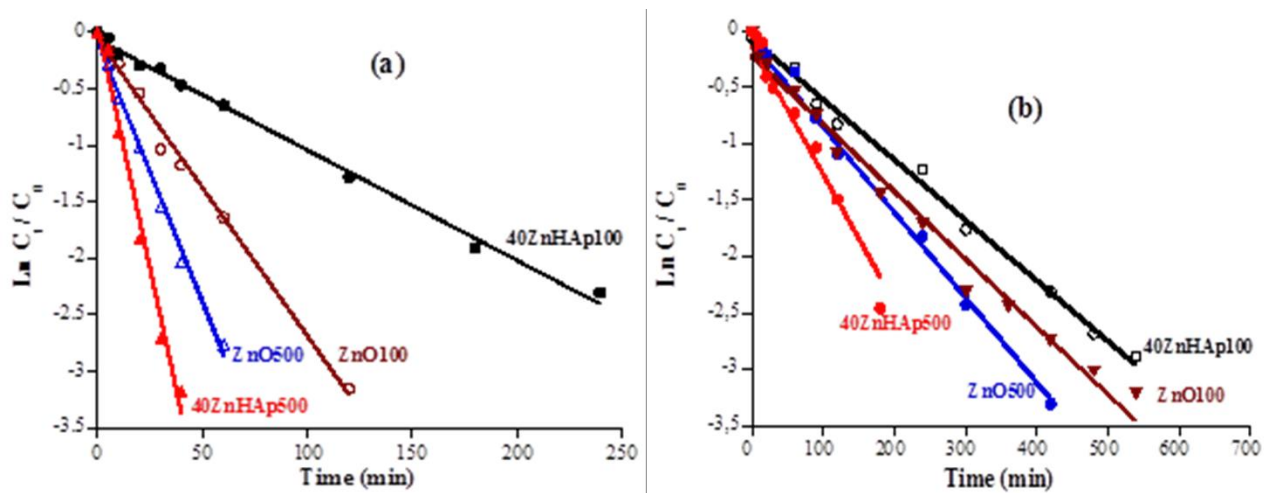


Fig. 4. Plots of $\ln(C_t/C_0)$ versus time for the degradation of (a) MB and (b) paracetamol over ZnO and 40ZnHAp calcined at 500°C.

Table 3. Rate constants (k_{app}) and the required time for complete degradation of paracetamol and MB under UV light ($C_0 = 20 \text{ mg L}^{-1}$, $\text{pH} = 6$, $T = 24^\circ\text{C}$, catalyst dose = 2 g L^{-1}).

		ZnO100	ZnO500	40ZnHAp100	40ZnHAp500
Paracetamol	$k_{app}(\text{min}^{-1})$	0.0059	0.0080	0.0053	0.0130
	R^2	0.9917	0.9943	0.9973	0.9926
	Time (min)	> 600	240	> 600	540
MB	$k_{app}(\text{min}^{-1})$	0.0262	0.0463	0.0097	0.0854
	R^2	0.9967	0.9971	0.9970	0.9907
	Time (min)	160	118	> 240	60

4. Conclusions

The paracetamol and methylene blue pollutants undergo distinct degradation pathways, which appear to be related to their affinity for the studied materials. Decontamination of water using 40ZnHAp500 nanomaterial has various advantages owing to its multiple functions, including by-products trapping after the photodegradation reaction.

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