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# Preparation and characterization of TiO<sub>2</sub> incorporated 13X molecular sieves for photocatalytic removal of acetaminophen from aqueous solutions

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## ABSTRACT

Although stabilizing of nano-particles on porous media is a suitable method in harnessing the agglomeration and inactivation of nano-particles, but still release of particles to the environment remains the most serious challenges facing toward photocatalysis process. Attachment of nanoparticles through ion exchange may be a promising method to solving these defects. In this study TiO<sub>2</sub> was incorporated into the 13X molecular sieves by addition of the titanyl ion through an ion-exchange of ammonium-titanyl-oxalate as well as the decomposition of titanyl oxalate salt, which remained on the zeolite through the impregnation and calcination process. A part of TiO<sub>2</sub> on the zeolite was also bound through a Ti–O–Si bond. The investigation of TiO<sub>2</sub>-HX catalytic potential showed that neutral pH and 500 mg/L catalyst were the optimal conditions for acetaminophen removal (1 mg/L) in the UV/TiO<sub>2</sub>-HX process. The maximum removal efficiency of 95.45% ± 0.8 was attained after 75 min contact time. The acetaminophen degradation during the UV/TiO<sub>2</sub>-HX process was followed a pseudo first order kinetic model with rate constants ( $K_{app}$ ) of 0.8676 h<sup>-1</sup>. Under the optimum conditions, maximum synergistic efficiency of 60.07% was acquired. The experimental data showed that the UV/TiO<sub>2</sub>-HX process is effective in acetaminophen removal from aqueous solutions.

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## 1. Introduction

Pharmaceuticals are becoming a growing environmental problem, known as “emerging contaminants” (Petrovic et al., 2011; Yang et al., 2008). Acetaminophen (paracetamol) is a different type of ibuprofen and naproxen (Muir et al., 1997). It is one of the most used drugs and due to its antipyretic and analgesic properties it is a primary

choice in different emotional and physical discomfort (Antunes et al., 2013). Muir et al. (1997) found that 58–68% of took acetaminophen is excreted from the body. Pharmaceutical compounds cannot be completely destroyed in the wastewater treatment plants (WWTP) using conventional techniques such as biological treatments and physico-chemical treatments including coagulation, volatilization, absorption, sedimentation and filtration (Dixit and Parmar, 2013). Although adsorp-

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tion process has shown good efficiency toward removal of recalcitrant and toxic compounds like heavy metals (Gupta et al., 2015, 1998), dyes (Gupta et al., 2013; Jain et al., 2003; Mittal et al., 2010a,b, 2009) and antibiotic (Braschi et al., 2010; Gao et al., 2012; Rivera-Utrilla et al., 2009) from aqueous solution but the global trend toward this process to overcome recalcitrant and toxic compound pollution ceased due to mass transfer nature of adsorption process. The WWTP effluents containing un-metabolized and metabolized pharmaceutical residues are discharged into the water bodies, mainly rivers, or they are reused for irrigation (Dixit and Parmar, 2013). In a survey, during 1999–2000, in 139 streams in the U.S., acetaminophen was detected with a median concentration of 0.11 ppb, also concentrations as high as 10 ppb being reported (Kolpin et al., 2002; Zhang et al., 2008). Acetaminophen has been detected up to approximately 1–6 ppb in the effluent of a WWTP in Europe (Ternes, 1998), 6.8 ppb in the effluent of a WWTP in Korea (Sim et al., 2010) and more than 65 ppb in the river Tyne in England (Roberts and Thomas, 2006). Toxicity induced by acetaminophen usually occurs by reactive oxygen species and can lead to multiple effects including protein denaturation, lipid peroxidation and DNA damage (Antunes et al., 2013). Acetaminophen has been the subject of many environmental researches, due to its wide usage and potential nefarious chemistry (Bender and Maccrehan William, 2006). Several chemical (Klamerth et al., 2015; Tabassum et al., 2011; Vogna et al., 2002) and electrochemical (Brillas et al., 2005; Sireis et al., 2006) methods have been reported for the treatment of aqueous solutions containing acetaminophen. In some studies, the decomposition of acetaminophen in advanced oxidation systems, such as  $O_3/H_2O_2/UV$  (Andreozzi et al., 2003; Vogna et al., 2002),  $O_3/UV$  with  $Fe^{2+}$  or  $Cu^{2+}$  as a catalyst (Skoumal et al., 2006),  $H_2O_2/UV$  with  $Fe^{2+}$  or  $Cu^{2+}$  as a catalyst (Sireis et al., 2006) and anodic oxidation with boron-doped diamond electrodes were used (Brillas et al., 2005). While acetaminophen is treated using hypochlorite, a considerable decomposition efficiency is achieved after an hour, however, 1,4-benzoquinone and *N*-acetyl-*p*-benzoquinone imine (two quinoidal oxidation products which are more toxic than acetaminophen) form up to 25% and 1.5% of the initial acetaminophen concentration respectively (Bender and Maccrehan William, 2006). Nano materials in the form of powder, sheet, tube and wire have attracted recent interest by providing hollow structure, large surface area, high aspect ratio, light activation and easily modified surfaces (Gupta et al., 2013) and acquired great success in removing toxic and recalcitrant compound, either solely or in combination with other supports (Gupta and Nayak, 2012; Saleh and Gupta, 2012a). It has been found that the nano-powder based photocatalytic can be promising methods to remove pharmaceutical compounds from water (Khetan and Collins, 2007). Titanium dioxide ( $TiO_2$ ) is one of the most effective photocatalysts which is frequently used for the removal of recalcitrant from aqueous solutions (Gupta et al., 2012, 2011; Kim and Yoon, 2001). With regard to its high efficiency, the known defects, recombination, agglomeration and difficulty in suspension mode use, still remain (Kim and Yoon, 2001). Many researchers have therefore studied methods to overcome these defects (Kim and Yoon, 2001; Sabate et al., 1991; Saleh and Gupta, 2012b). Stabilization of  $TiO_2$  nano-powder on appropriate supports can reduce the problem with separation of the catalysts from water (Alwash et al., 2013a). In this type of procedures, some porous supports, such as activated carbon (Sampath, 1994; Zhang et al., 2010), glass fibers (Hofstadler et al., 1994), clay (Yoneyama et al., 1989), and zeolite (Liu and Thomas, 1993), were loaded with  $TiO_2$  through sol-gel methods, wet impregnation (Alwash et al., 2013b; Chen et al., 1999; Kim and Yoon, 2001; Liu et al., 1992; Zendeheidel et al., 2011). Although these methods have good success rates, loose bonds to the structure and release of nano-powders were observed (Chen et al., 1999; Liu et al., 1992; Liu and Thomas, 1993). Incorporation of  $TiO_2$  into the support structure is a promising method to overcome this issue. Some researchers have used zeolite as a basis for the stabilization of semiconductors (Kim and Yoon, 2001). Incorporation of  $TiO_2$  into the structure of zeolite Y was performed by Krueger et al. and Liu et al. for the first time (Krueger et al., 1990; Liu et al., 1992; Liu and Thomas, 1993). Incorporation of  $TiO_2$  into the rigid cavities of the zeolites integrates the photocatalytic activity of  $TiO_2$  with the absorption properties of zeolite, which causes a synergistic effect, leading to an increase in either the photocatalytic activity (Alwash et al., 2013a) or

recovery efficiencies (Kim and Yoon, 2001). This strategy is also a simple way for controlling  $TiO_2$  optical activity and solving the problem of aggregation (Anandan and Yoon, 2003; Chen et al., 1999; Zendeheidel et al., 2011). When  $TiO_2$  nanoparticles are strongly connected to a suitable matrix, they give rise to photodegradation characteristics, which means less environmental risk arise as a result of the reduction in release to the environment (Desrosiers et al., 2006). Chen et al. (1999), Liu et al. (1992), and Zhang et al. (2011), incorporated  $TiO_2$  into the structure of Y zeolite via ion exchange and impregnation methods using ammonium titanyl oxalate. This salt of titanium provides a way for direct entry of Ti species into the zeolite pores using a conventional ion exchange method (Liu et al., 1992). The present study is focuses on the incorporation of 13X-molecular sieves (sodium potassium aluminosilicate) with  $TiO_2$  using an ion exchange method. The catalytic importance of 13X molecular sieves was the reason for choosing this type of zeolite. The 13X molecular sieves are a type of X zeolite, in which the number 13 refers to sodium as the main cation (Shanshool and Sabri, 2009). This zeolite has a good cation exchange capacity and it can easily exchange sodium ions with other cations (Delaude and Laszlo, 1990; Mishra, 2007). After the preparation and characterization of a target catalyst, the photocatalytically removal of acetaminophen, as a model of pharmaceutical recalcitrant, from aqueous solution was determined.

## 2. Material and methods

### 2.1. Preparation of catalyst

The 13X zeolite is sodium modified molecular sieve (NaX) with a pore diameter of ten angstroms with an average particle size of 2  $\mu m$  and a ratio of silicon to aluminum (Si/Al) of 1.3. It was purchased from Sigma–Aldrich (Germany).

Proton type 13X-zeolite (HX) was prepared using cation exchange method from NaX zeolite in an ammonium sulfate solution. Briefly, 1 g of 13X-zeolite was mixed with 1.5 g of anhydrous ammonium sulfate and 7.5 mL of de-ionized water at 367 K for 1 h. It was then filtered and washed with de-ionized water and was calcinated at 810 K for 2 h. After cooling, the prepared powder was blended with 1 g of 13X-zeolite, 2.997 g of ammonium sulfate and 59 mL of de-ionized water at 367 K for 3 h, calcination was then carried out at 810 K for 2 h. The obtained powder was then mixed with 1 g of 13X-zeolite, 1.5 g of ammonium sulfate, and 7.5 mL of de-ionized water at 367 K for 1 h, followed by calcination at 921 K for 4 h. The prepared powder was denoted as HX-zeolite.

$TiO_2$  modified HX-zeolite was prepared by an ion exchange of HX-zeolite with an aqueous solution of ammonium titanyl oxalate monohydrate,  $(NH_4)_2TiO(C_2O_4)_2 \cdot H_2O$  (99.998%, Sigma–Aldrich), in accordance with the procedures of Liu et al. (1992). 1 g of HX-zeolite was immersed in 100 mL of aqueous solution, made up of  $5.5 \times 10^{-2}$  mol/L of monohydrate titanyl ammonium oxalate, at 303 K for 12 h. After the ion exchange process, the catalyst was filtered with a membrane filter (pore size 0.45  $\mu m$ ) and then it was dried in an oven at 333 K. The calcination of the sample was done in a furnace at 773 K for 5 h in air. The temperature of the sample was elevated and cooled down at a rate of 278 K/min. In order to increase the amount of  $TiO_2$  on HX-zeolite, the above procedure was repeated three times. The prepared powder was introduced as  $TiO_2$ -HX.

### 2.2. Catalyst characterization

The 13X, HX and  $TiO_2$ -HX samples were analysed for crystalline phase, surface morphology and elemental analysis. The crystallinity of each sample was evaluated by X-ray diffrac-

tion (XRD). XRD patterns were recorded by use of an automatic powder X-ray diffractometer (Philips X'Pert XRD) at 30 mA and 40 kV using CoK $\alpha$  radiation, ( $\lambda = 1.78897$  nm) for  $2\theta$  between  $5^\circ$  and  $80^\circ$ . The surface morphology, shape and elemental analysis of the zeolites were done with Ziess (Germany) scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (SDD detector, Oxford Instruments). Infrared spectra of samples were measured by Bruker Vertex 70 FTIR spectrometer and the KBr disc technique.

### 2.3. Photocatalysis experiments

The photocatalytic potential of TiO<sub>2</sub>-HX was investigated for the degradation of acetaminophen (98%, Sigma-Aldrich) in aqueous solutions under UV-C irradiation. The effects of different pH levels (5, 7 and 9) on the performance of UV/TiO<sub>2</sub>-HX were examined at a catalyst concentration of 1000 mg/L and an acetaminophen concentration of 10 mg/L. Furthermore, the effects of TiO<sub>2</sub>-HX concentration (50, 500 and 1000 mg/L) were investigated in the degradation of acetaminophen (10 mg/L) under optimal the pH level. Subsequently, removal efficiency of the initial concentrations of 1, 3, 5 and 10 mg of acetaminophen using the target process was determined under optimal conditions.

The experiments were carried out in a batch reactor, consisting of a glass cylinder equipped with a UV-C lamp ( $\lambda = 245$  nm, 15 W, Philips, TUV G5T8, Netherlands; connected in series to a DC power supply). The lamp was located in a quartz sleeve at the center of the cylinder. For each experiment, 100 mL of suspension, containing a predetermined concentration of acetaminophen solution and catalyst, was transferred into the reactor. The slurry was stirred with a magnetic stirrer and was equilibrated in the dark for 30 min before UV exposure. The light source was switched on and the suspension was irradiated for 120 min. During irradiation, nine samples at different time intervals were taken to analyze the acetaminophen concentration. The samples were filtered through a 0.45  $\mu$ m cellulose acetate membrane (Sartorius, German) to remove the catalyst particles prior to analysis. Total volume of the withdrawn sample was less than 5% (by volume) of the stirred solution. The acetaminophen concentrations were determined using HPLC (Shimadzu, C18 column (4.6  $\times$  250 mm, 5  $\mu$ m)) with a flow rate of 1.0 mL min<sup>-1</sup> and UV absorbance detection (Waters 481 detector) of 242 nm. The mobile phase was a CH<sub>3</sub>OH/H<sub>2</sub>O mixture (30/70, v/v). The

injection volume was 20  $\mu$ L. The acetaminophen removal efficiency was calculated as:

$$\text{Degradation efficiency (\%)} = \left( \frac{C_0 - C_t}{C_0} \right) \times 100 \quad (1)$$

where  $C_0$  and  $C_t$  are the acetaminophen concentrations before and after degradation, respectively.

Direct photolysis (no catalyst) of the acetaminophen was determined in the same reactor under similar conditions. By subtracting of the pollutants' removal efficiency of UV/TiO<sub>2</sub>-HX process from the removal efficiency of the direct photolysis (acetaminophen degradation by UV light alone) and dark experiment, synergetic effects of the process, or catalytic potential in the different concentrations of acetaminophen, were obtained.

In the photocatalytic degradation reactions, the Langmuir-Hinshelwood equation has been widely used, and in low concentrations, it converts to the pseudo first order model (Aguilar et al., 2011). Therefore, in this study, the reactions rates were studied using the pseudo first order reaction rate model as follows (Dudukovic, 2005):

$$\ln \left( \frac{C_t}{C_0} \right) = -k_{app}t \quad (2)$$

where  $C_0$  is concentrations of acetaminophen at the beginning of the reaction,  $C_t$  is acetaminophen concentrations at time  $t$  of the reaction, and  $k_{app}$  is the pseudo first order rate constant of degradation of acetaminophen during photocatalysis.

## 3. Results and discussion

### 3.1. Characterization of zeolites

#### 3.1.1. XRD

The XRD patterns of the zeolites before and after ion exchange are shown in Fig. 1. The diffractograms indicate that the crystallinity of the 13X-zeolite decreased after protonation. Although some changes in the peaks can be seen, the ion exchange process with a solution of ammonium titanyl oxalate and the subsequent incorporation of titanium ions into the network did not have significant effect on the structure of the acceptor material (Alwash et al., 2013a; Chen et al., 1999; Kim and Yoon, 2001; Liu et al., 1992; Zendejdel et al., 2011). XRD patterns showed that there are characteristics of

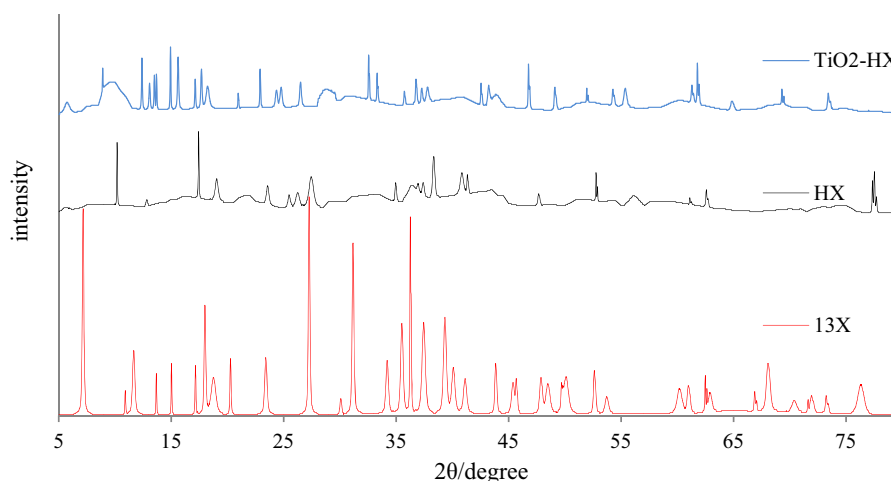


Fig. 1 – XRD patterns of 13X, HX and TiO<sub>2</sub>-HX samples.

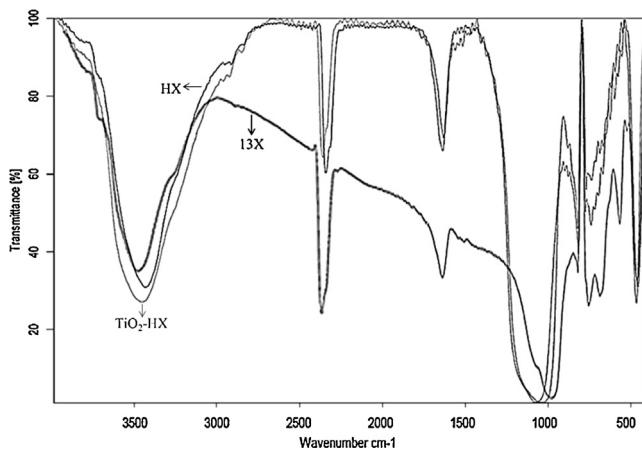


Fig. 2 – FTIR spectra of modified samples.

anatase peaks at  $2\theta$  of  $29.44^\circ$  (*hkl*: 1 0 1),  $44.19^\circ$  (*hkl*: 0 0 4) and  $64.92^\circ$  (*hkl*: 2 1 1) according to JCPDS card No. 1272-21. Furthermore, some brookite peaks were seen at  $2\theta$  of  $29.51^\circ$  (*hkl*: 1 2 0),  $35.93^\circ$  (*hkl*: 1 2 1),  $42.35^\circ$  (*hkl*: 0 2 1),  $43.59^\circ$  (*hkl*: 2 0 1) and  $46.98^\circ$  (*hkl*: 0 2 2) (JCPDS card No. 1360-29). The low intensity of these peaks indicates low levels of anatase microcrystals in the modified samples. It is likely that actual amounts of formed anatase microcrystals in the zeolite structure are greater than the observed levels, as due to their small size they were not detectable in the pores by XRD analysis (Alwash et al., 2013b; Zhang et al., 2011). No specific peak was seen for the rutile phase of  $\text{TiO}_2$ . In the Liu et al. (1992), Chen et al. (1999), and Ratiu et al. (2008) studies, anatase has been the dominant phase of formed  $\text{TiO}_2$  on zeolite. However, in the studies by Chatti et al. (2007), Anandan and Yoon (2003), Lee et al. (2001), Alwash et al. (2013b) and Zendehdel et al. (2011), no peak of anatase has been observed for the modified zeolite. They explained two reasons for this occurrence, including the relatively low  $\text{TiO}_2$  content and its uniform dispersion on zeolite (Anandan and Yoon, 2003; Chatti et al., 2007), and too small a size of titanium species residing in the zeolite cavities or channels that could not be detected by XRD (Alwash et al., 2013b; Lee et al., 2001; Zendehdel et al., 2011).

### 3.1.2. FTIR

Fig. 2 shows the FTIR spectra of 13X, HX and  $\text{TiO}_2$ -HX samples.

Table 1 shows the IR index peaks and their bands in the micrographs of the 13X, HX and  $\text{TiO}_2$ -HX samples.

The acidic treatment of 13X-zeolite has caused an increase in the peak height of  $1642\text{ cm}^{-1}$  from about 13% to 32%. The

peak at  $978\text{ cm}^{-1}$  was transferred to  $1031\text{ cm}^{-1}$ . The peak at around  $1100\text{ cm}^{-1}$  relates to the Si–O–Si bond that the height of this peak increased after acidic treatment. This peak became stronger after the loading of Ti, which shows that the structure has been affected by titanium ions. Bands around  $940\text{ cm}^{-1}$  and  $472\text{ cm}^{-1}$  relate to Si–OH and Si–O–Si bonds that show clearly the height of these peaks increasing after acidic treatment. In addition to the foregoing, the peaks of  $1640\text{ cm}^{-1}$  and  $3450\text{ cm}^{-1}$  relate to adsorbed water molecules, the heights of which decrease after modification of the HX zeolite with Ti and heating. The majority of  $\text{TiO}_2$ -HX index peaks are similar to the peaks of HX zeolite. However, the addition of titanium ions to the HX zeolite structure has led to the creation of three additional peaks around  $1087\text{ cm}^{-1}$ ,  $915\text{ cm}^{-1}$ , and  $894\text{ cm}^{-1}$ . The peaks of around  $910\text{ cm}^{-1}$  are associated with the Ti–O–Si bond. This result was in agreement with those reported in a study by Liu et al. (1992), Anandan and Yoon (2003) and Faghihian and Bahraniard (2011). However, the addition of titanium leads to displacement of the peak of  $1031\text{ cm}^{-1}$  at  $1087\text{ cm}^{-1}$ . According to Beattie and Fawcett (1967), the monomer Ti–O and Ti=O stretching vibrations have frequencies of  $1087$  and  $975\text{ cm}^{-1}$ , respectively, and the Ti–O–Ti linkage vibration is around  $850\text{ cm}^{-1}$ . Therefore, linkage of Ti is confirmed with Si, Ti–O and Ti=O. In the present study, similar to Chen et al. (1999), a part of  $\text{TiO}_2$  was formed on the zeolite through Ti–O–Si bond and another part of it was created by oxidation of  $\text{TiO}^{2+}$ , which was entered into the zeolite using the ion exchange process. Hence, the amount of  $\text{TiO}_2$  has been affected by the ion exchange capacity of zeolite. During the ion exchange process, a divalent cation of  $\text{TiO}^{2+}$  was exchanged by two  $\text{H}^+$  cations and  $\text{TiO}_2$  content has increased by the repetition of the modification steps. In addition to ion exchange, formation of  $\text{TiO}_2$  on HX zeolite has been through the decomposition of titanyl oxalate salt, which remained on the HX by the impregnation and calcination processes (Chen et al., 1999). Chen et al. (1999) suggested that a significant proportion of  $\text{TiO}_2$  particles were formed in zeolite cavities as well as captured in defective parts of the zeolite structure. The present study also is possible (Chen et al., 1999).

### 3.1.3. SEM

The shape and surface morphology of the samples 13X, HX and  $\text{TiO}_2$ -HX are shown in Fig. 3.

As seen in Fig. 3(A), 13X particles have edged and polygonal crystal structures with smooth surfaces. These particles are arbitrarily distributed in an agglomerated fashion (Arslan and Veli, 2012). The observations of Payne and Abdel-Fattah

Table 1 – The IR index peaks and their bands in the micrographs of the 13X, HX and  $\text{TiO}_2$ -HX samples.

Type of band	$\text{TiO}_2$ -HX peak ( $\text{cm}^{-1}$ )	HX peak ( $\text{cm}^{-1}$ )	13X peak ( $\text{cm}^{-1}$ )
–OH (adsorbed water)	3492	3492	3492
Si–H (silane)	2358	2358	2358
–OH	1642	1642	1642
Si–O–Si		1031	
Si–O–Ti	1087		
Si–OH	950	950	978
Ti–O	915		
Ti=O	894		
O–T–O (T=Si or Al)	878	878	
			752
			683
			592
Si–O–Si	461	461	461



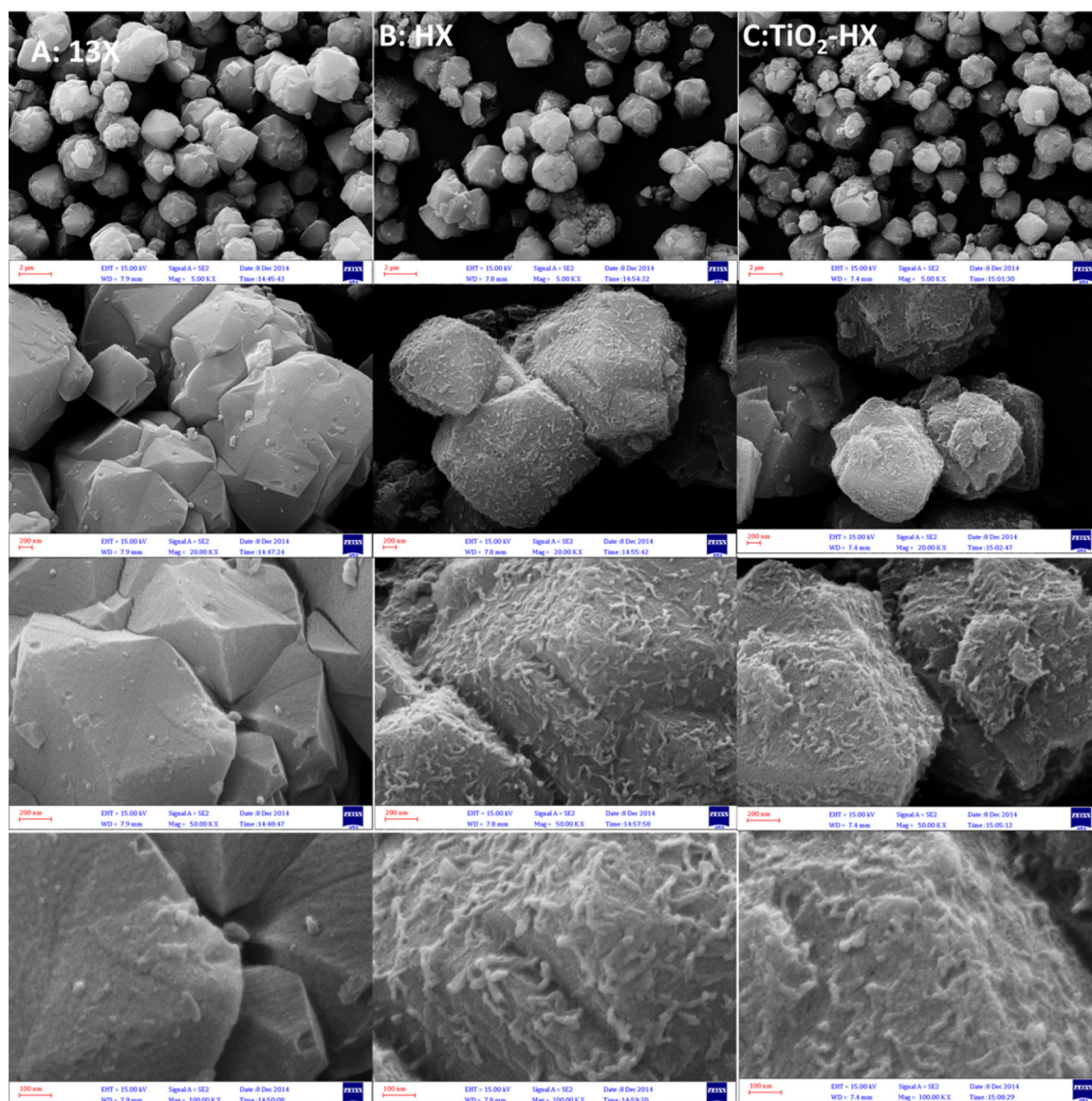


Fig. 3 – SEM images of the 13X (column A), HX (column B) and TiO<sub>2</sub>-HX (column C) on the same scales.

(2004) and Breck (1974) confirm these results. However, as it is obvious from Fig. 3(B), particles' surfaces become rough after the protonation phase. After TiO<sub>2</sub> loading (Fig. 3(C)), no change in the surface morphology of TiO<sub>2</sub>-HX particles relative to HX is observed, but the particle sizes become smaller.

#### 3.1.4. EDAX

The Energy Dispersive X-ray analysis of the 13X, HX and TiO<sub>2</sub>-HX samples is shown in Fig. 4. Wt% of oxygen, silicon,

aluminum, sodium and titanium elements in the samples 13X, HX and TiO<sub>2</sub>-HX is listed in Table 2.

According to data obtained from EDAX analysis, the average of the Si/Al ratio in the 13X, HX and TiO<sub>2</sub>-HX samples was equal to 1.3, which is in line with the results reported by Payne and Abdel-Fattah (2004) and Breck (1974). After the acid treatment step, the weight percentages of sodium cations were greatly reduced; indicating that the protonation phase and hydrogen ions' exchange with sodium were successfully completed. In EDAX of the TiO<sub>2</sub>-HX sample, some signals for the

Table 2 – The percentage weights of O, Si, Al, Na and Ti elements in the 13X, HX and TiO<sub>2</sub>-HX samples.

Elements	Sample					
	13X		HX		TiO <sub>2</sub> -HX	
	Spectrum					
	1	2	3	4	5	6
O (Wt%-σ)	42.0-0.4	42.7-0.5	48.2-0.4	45.9-0.4	42.8-0.5	46.5-0.5
Si (Wt%-σ)	25.9-0.4	25.0-0.4	27.7-0.3	28.9-0.4	34.1-0.4	31.2-0.4
Al (Wt%-σ)	20.0-0.3	19.1-0.4	20.7-0.3	21.7-0.3	16.9-0.3	17.3-0.3
Na (Wt%-σ)	12.0-0.3	13.3-0.3	3.4-0.2	3.6-0.2	3.1-0.1	3.1-0.2
Ti (Wt%-σ)	0	0	0	0	4.9-0.3	3.7-0.3

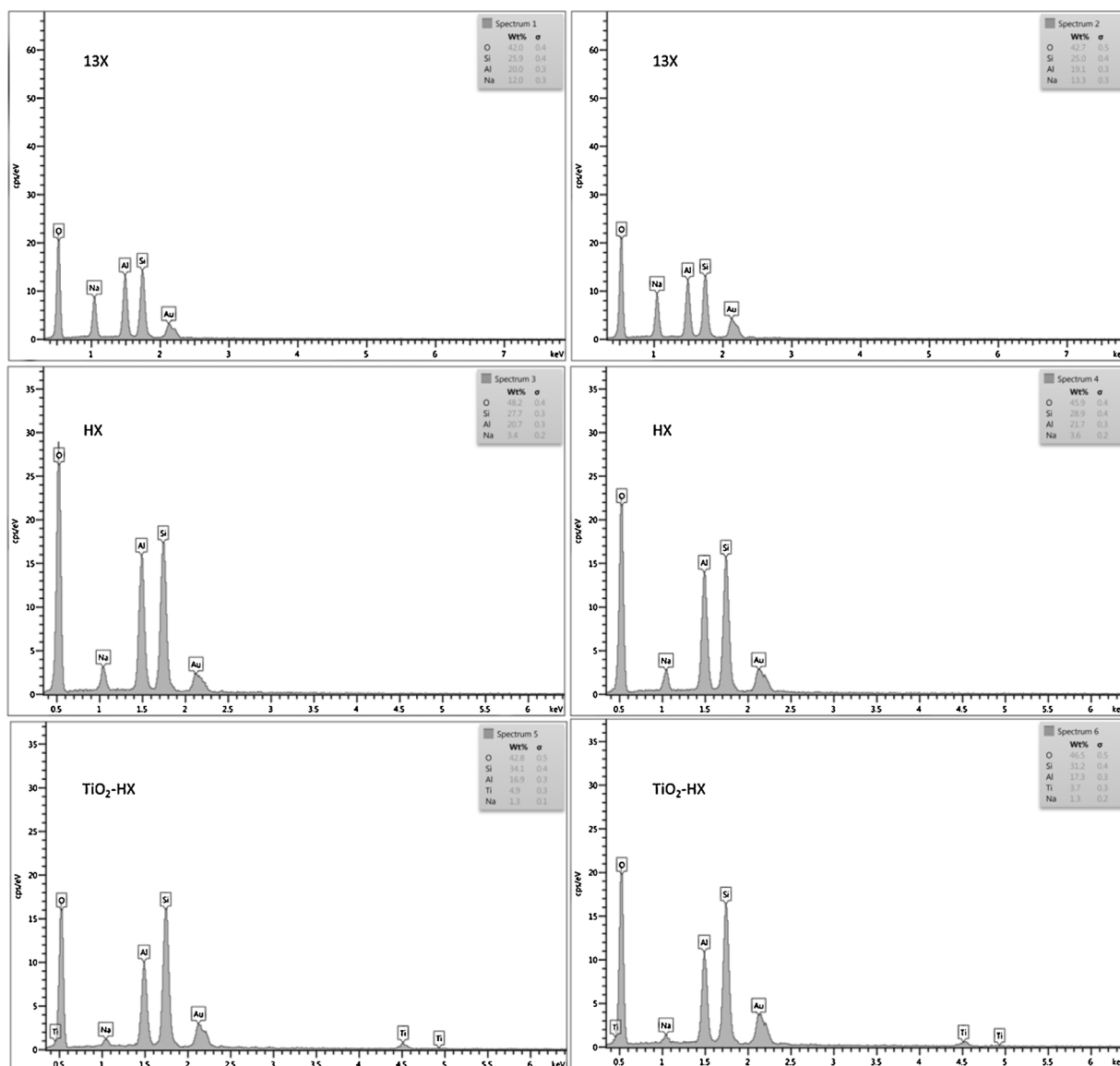


Fig. 4 – Place of receiving spectra of EDAX in the pure and modified zeolites and the corresponding characteristics.

titanium element can be seen on the catalyst's surface, which confirms the presence of Ti in the TiO<sub>2</sub>-HX. However, in the different points of TiO<sub>2</sub>-HX, due to the non-uniform distribution of Ti, varying amounts of this element were obtained. Due to the complex structure of the zeolite, it is possible that TiO<sub>2</sub> particles are distributed heterogeneously on the surface of the TiO<sub>2</sub>-HX sample. The results of EDAS analysis match with the results of XRD and FT-IR analysis (Alwash et al., 2013b).

### 3.2. Photocatalytic activity of TiO<sub>2</sub>-HX

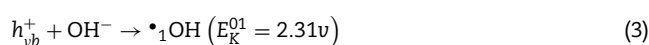
#### 3.2.1. Effect of solution pH

Fig. 5 shows the effects of acidic, neutral, and alkaline conditions (pH of 5, 7 & 9) on the performance of the UV/TiO<sub>2</sub>-HX process for the acetaminophen removal at an initial acetaminophen concentration of 10 mg/L and catalyst loading of 1000 mg/L.

As can be seen in Fig. 5, the acetaminophen removal was strongly affected by the solution's pH level. Accordingly, the removal efficiency was higher in acidic conditions, although at higher contact times, removal efficiency at pH 5 and 7 was equal. At all pH levels, acetaminophen removal efficiency increased with increasing the reaction time. With increasing

the reaction time (after 2 h reaction time) the pH of the solution was dropped 2 units, which is due to the oxidation processes. The acetaminophen removal efficiency was promoted by the pH reduction. The rate constant at different pH levels is shown in Fig. 6, as observed when increasing the pH from 5 to 9, the rate constant decreased from 0.0167 to 0.0137. These results are inconsistent to reports of Young et al. (Yang et al., 2008).

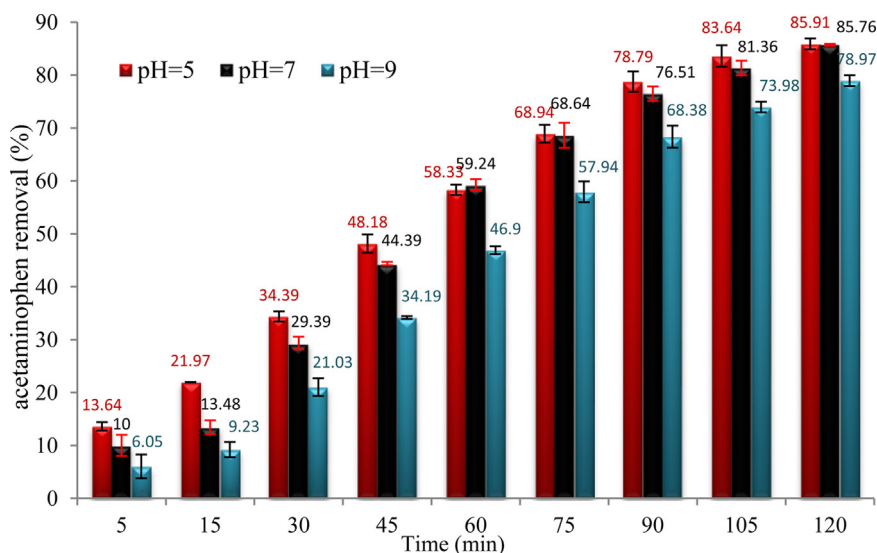
In heterogeneous photocatalysts, there is usually competition between water dissociated ions (H<sup>+</sup> and OH<sup>-</sup>) and pollutants toward the catalyst's surface.



The point of zero charge (pH<sub>ZPC</sub>) of the catalyst is 6.3 and in pHs lower than the pH<sub>ZPC</sub>, the catalyst's surface is positively charged (Eq. (4)).



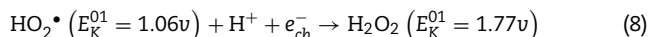
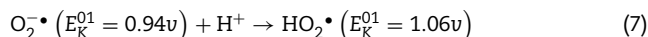
On the other hand, since the pK<sub>a</sub> of acetaminophen (9.71) is higher than the pH ~ 5, acetaminophen will be presented in cationic form, so acetaminophen has a low tendency toward the catalyst's surface and this condition will provide more



**Fig. 5 – Effect of solution pH on acetaminophen removal efficiency by UV/TiO<sub>2</sub>-HX process (concentration of acetaminophen solutions: 10 mg/L; TiO<sub>2</sub>-HX concentration: 1000 mg/L; solution pH: solution pH: 5, 7, 9; lamp power: 15 W; reaction time: 120 min).**

chance for adsorption of OH<sup>-</sup> ions produced from the dissociation of water molecules on the catalyst's surface, which will be finally formed as  $\cdot\text{OH}$  or  $\cdot\text{O}_2^-$  under ultraviolet radiation. In turn, these free radicals will lead to degradation of target pollutants. However, pollutant concentration has shown a significant decrease at pH ~9. In the alkaline condition, formation of  $\cdot\text{OH}$  increases as most of the available hydroxyl ions can be easily oxidized and they produce more hydroxyls (Eq. (5)). As a result, acetaminophen degradation efficiency increases (Brunner et al., 1998; Yang et al., 2008). In alkaline conditions, the surface of the catalyst will be negatively charged (Eq. (6)). Because pK<sub>a</sub> of acetaminophen solution equals 9.71 (Yang et al., 2008), if solution pH is more than acetaminophen pK<sub>a</sub>, acetaminophen will be presented in an anion form. Thus, increase of pH causes a gradual increase in the electrostatic repulsion between the TiO<sub>2</sub> surface and acetaminophen with further reduction in adsorption of acetaminophen to the zeolite surface (Brunner et al., 1998; Yang et al., 2008). Hence, it is not surprising that the degradation rate of acetaminophen decreases at alkaline pH levels. In addition, at a higher pH level, the formation of a superoxide radical anion ( $\cdot\text{O}_2^-$ ) through oxygen reduction by electrons can be prevented (Eq. (7)), and as a result, H<sub>2</sub>O<sub>2</sub> and  $\cdot\text{OH}$  (Eqs.

(8)–(10)) will be formed less. Consequently, the degradation of acetaminophen decreases (Yang et al., 2008).



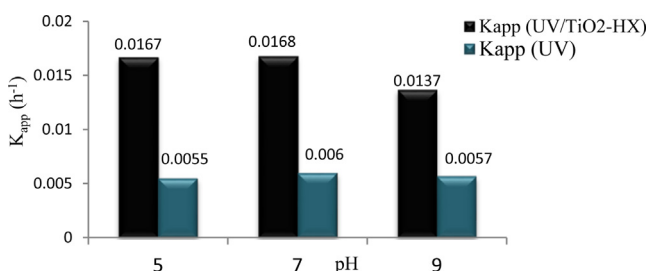
Taken together, while the role of neutral and acidic pHs may be insignificant, under a stronger alkaline condition, effects of pH on the degradation of acetaminophen should be taken into account in order to assess changes in the degradation of acetaminophen. Due to the fact that the majority of the water and wastewater treatment processes are exploited in a range of pH levels from 6.5 to 8.5 and considering the fact that the difference between the efficiency of acetaminophen removal in the acidic and neutral pH levels is negligible, pH ~7 is considered to be the most suitable condition for the UV/TiO<sub>2</sub>-HX process.

### 3.2.2. Effect of TiO<sub>2</sub>-HX dosage on acetaminophen degradation

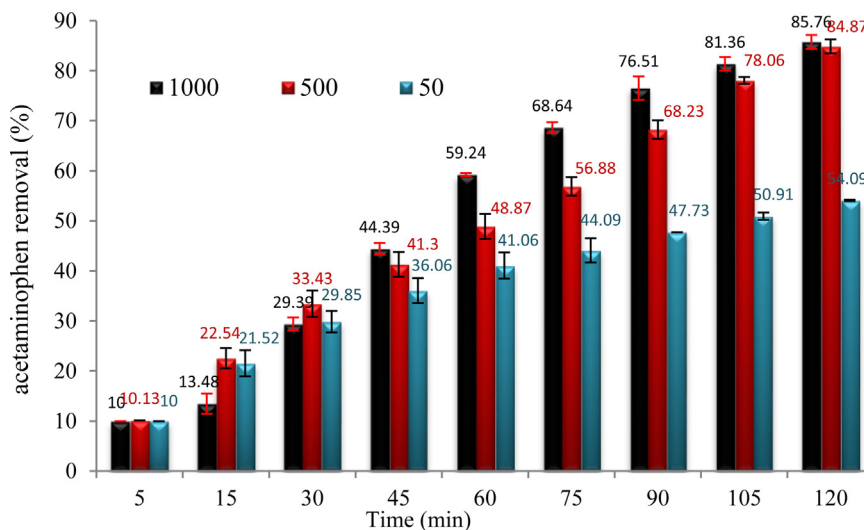
The effects of 50, 500 and 1000 mg/L TiO<sub>2</sub>-HX on the acetaminophen's removal efficiency with initial concentration of 10 mg/L under UV irradiation and pH ~7 is shown in Fig. 7.

By increasing TiO<sub>2</sub>-HX dose, acetaminophen removal efficiency, as well as the pseudo first order reaction rate constant, increased (Fig. 8).

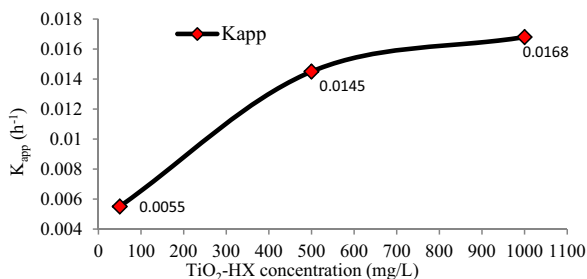
The increase of degradation efficiency is due to the fact that increasing the catalyst's concentration provides more active sites for the photocatalytic reaction and greater production of hydroxyl radicals. In addition, the increasing of catalyst dosage would increase the acetaminophen adsorption. Several studies reported similar results (Wong and Chu,



**Fig. 6 – Effects of pH on the photocatalytic degradation rate constants of acetaminophen by the direct photolysis and UV/TiO<sub>2</sub>-HX process (concentration of acetaminophen solution: 10 mg/L; TiO<sub>2</sub>-HX concentration: 500 mg/L; solutions pH: 5, 7 and 9; Lamp power: 15 W; reaction time: 2 h).**



**Fig. 7 – Effect of the different concentrations of photocatalyst to the acetaminophen removal from aqueous solutions (concentration of acetaminophen solution: 10 mg/L; TiO<sub>2</sub>-HX concentration: 50, 500 and 1000 mg/L; solutions pH: 7; lamp power: 15 W; reaction time: 120 min).**

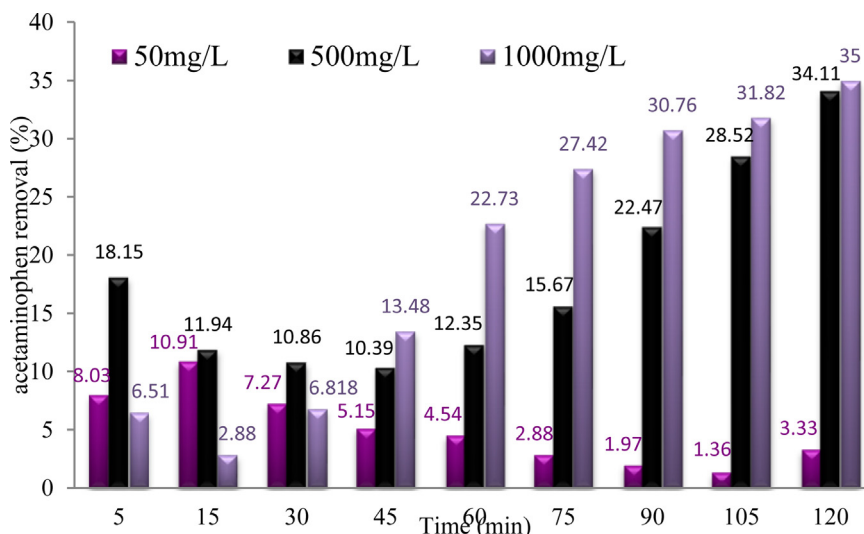


**Fig. 8 – Effects of TiO<sub>2</sub>-HX dosage on acetaminophen degradation rate constants ( $k_{app}$ ) (concentration of acetaminophen solution: 10 mg/L; TiO<sub>2</sub>-HX concentrations: 50, 500 and 1000 mg/L; solutions pH: 7; lamp power: 15 W; reaction time: 120 min).**

2003; Xiong and Hu, 2012; Zhang et al., 2008). As seen in Fig. 8, the acetaminophen degradation rate constant increased from 0.0055 to 0.0145 h<sup>-1</sup> as the catalyst amount increased from 50 to 500 mg/L. However, with further increases in TiO<sub>2</sub>-

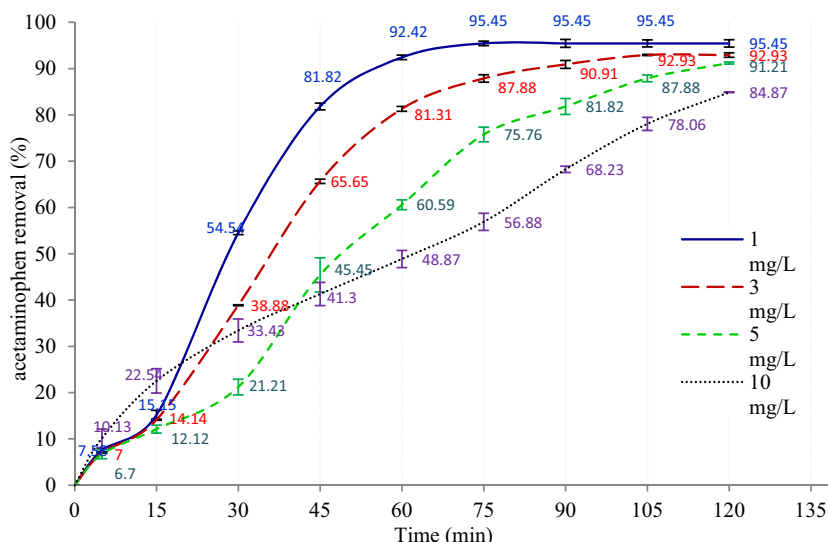
HX loading, little improvement in degradation rate constant (0.0168 h<sup>-1</sup>) was observed. Higher catalyst loading results in more turbidity, which leads to a decrease in access of UV light to particles. Furthermore, increased light scattering and the occasional loss of surface area by agglomeration at a high solid concentration were other important considerations. Above a certain level, the amount of substrate molecules would not be enough to fill the surface’s active sites of the catalyst. Hence further addition of the catalyst did not lead to improvement in the degradation rates. No differences were found between the removal efficiency of pharmaceutical pollutant from 500 and 1000 mg/L of the TiO<sub>2</sub>-HX catalyst. The results were in agreement with previous studies (Evgenidou et al., 2007; Kaur and Singh, 2007; Toor et al., 2006; Wiszniewski et al., 2002; Xiong and Hu, 2012; Yang et al., 2008). In this study, a lower dosage of catalyst, 500 mg/L, was selected as the optimal dose and further experiments used at this catalyst concentration.

Fig. 9 shows the catalytic potential of different concentrations of TiO<sub>2</sub>-HX to remove acetaminophen from aqueous solutions.

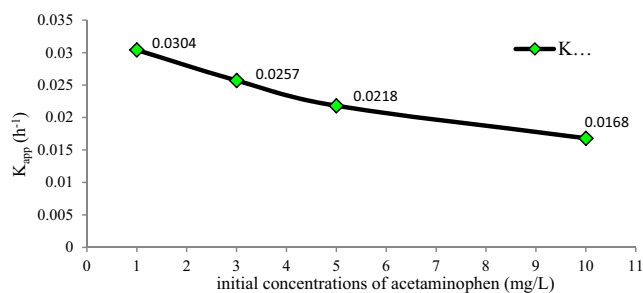


**Fig. 9 – The catalytic potential of different concentrations of TiO<sub>2</sub>-HX during removal of acetaminophen from aqueous solutions (concentration of acetaminophen solutions: 10 mg/L; TiO<sub>2</sub>-HX concentration: 50, 500 and 1000 mg/L; solutions pH: 7; reaction time: 120 min).**





**Fig. 10 – Acetaminophen removal efficiency with different initial concentrations by UV/TiO<sub>2</sub>-HX process (concentration of acetaminophen solutions: 1, 3, 5 and 10 mg/L; TiO<sub>2</sub>-HX concentration: 500 mg/L; solutions pH: 7; lamp power: 15 W; reaction time: 120 min).**

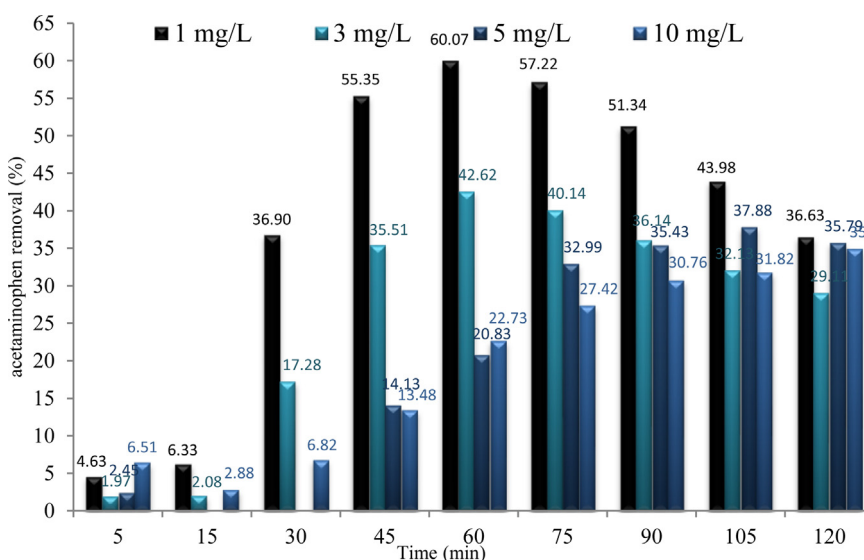


**Fig. 11 – Effects of initial concentrations of acetaminophen on photocatalytic degradation rate constants (k<sub>app</sub>) (concentration of acetaminophen solutions: 1, 3, 5 and 10 mg/L; TiO<sub>2</sub>-HX concentration: 500 mg/L; solutions pH: 7; lamp power: 15 W; reaction time: 120 min, errors were analyzed using linear regression with a 95% confidence level).**

As seen in Fig. 9, synergistic effects of the UV/TiO<sub>2</sub>-HX process were greater at higher concentrations of TiO<sub>2</sub>-HX. The catalytic potential of 500 and 1000 mg/L at 2 h reaction time was 34.11% and 35% respectively.

**3.2.3. Effects of initial concentrations of acetaminophen**  
In this study, the effects of different acetaminophen concentrations (1, 3, 5, 8 & 10) on the removal efficiency of UV/TiO<sub>2</sub>-HX process under optimal conditions were surveyed, results shown in Fig. 10.

The maximum removal efficiency (95.45% ± 0.8) related to the initial concentration of 1 mg/L that occurred after 75 min contact time. By reducing the initial concentrations of acetaminophen, the removal efficiency, using the UV/TiO<sub>2</sub>-HX process, increased. According to Fig. 11, the pseudo first order degradation rate constant of acetaminophen decreased when the initial concentration of acetaminophen increased from 1 to 10 mg/L (R<sup>2</sup> = 0.9526). This result corresponds with findings



**Fig. 12 – The catalytic potential of TiO<sub>2</sub>-HX during removal of acetaminophen with different initial concentrations from aqueous solutions (concentration of acetaminophen solutions: 1, 3, 5 and 10 mg/L; TiO<sub>2</sub>-HX concentration: 500 mg/L; solutions pH: 7; reaction time: 120 min).**

from the studies of Yang et al. (2008), Xiong and Hu (2012), Chen et al. (1999) and Zhang et al. (2008). In the mentioned studies, it was also reported that pseudo first order reaction rate constants for acetaminophen degradation reduces with the increasing of its initial concentrations (Chen et al., 1999; Xiong and Hu, 2012; Yang et al., 2008; Zhang et al., 2008).

In Fig. 12 the catalytic potential of TiO<sub>2</sub>-HX for different concentrations of acetaminophen has been evaluated. Under optimal conditions, the maximum synergistic effect (60.07%) was obtained at 60 min reaction time and 1 mg/L acetaminophen concentration.

#### 4. Conclusion

In this study, 13X-zeolite modified with TiO<sub>2</sub> was obtained via ion-exchange and impregnation methods with ammonium titanyl oxalate solution. Entry of the titanyl ion through an ion-exchange of ammonium titanyl oxalate and decomposition of titanyl oxalate salt, which remained on the zeolite through the impregnation and calcination process and Ti–O–Si bond were the main pathways to incorporating TiO<sub>2</sub> on the 13X molecular sieves.

The loaded TiO<sub>2</sub> was often in the form of brookite micro-crystals. In addition, the anatase phase was observed at lower amounts. The photocatalytic activity of incorporated zeolite was further surveyed to remove acetaminophen from aqueous solution. Experimental data showed that with decreasing concentration of acetaminophen, the removal rates increase. Maximum removal efficiency for the acetaminophen under the optimum conditions (pH: 7, TiO<sub>2</sub>-HX dose: 500 mg/L and acetaminophen concentration: 1 mg/L) was 95.45% ± 0.8, which occurred at 75 min contact time. Study of the kinetic models showed that the acetaminophen degradation kinetic in UV/TiO<sub>2</sub>-HX process followed a pseudo first order reaction with rate constants ( $K_{app}$ ) of 0.8676 h<sup>-1</sup>. Maximum synergistic efficiency of acetaminophen removal under the optimum conditions was 60.07%, which occurred after 60 min after the photo-catalytic reaction.

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