Titanium(IV) Oxide Modified with Activated Carbon and Ultrasounds for Caffeine Photodegradation: Adsorption Isotherm and Kinetics Study

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ABSTRACT

In this paper the adsorption and photodegradation of caffeine (CAF) using modified photocatalysts were studied. The laboratory synthesis method of commercial titanium(IV) oxide, activated carbon and ultrasound was proposed. The adsorption effect of caffeine was described by the Langmuir and Freundlich isotherms. The effectiveness of CAF photocatalytic decomposition was evaluated as well as the parameters of the pseudo-first-order and pseudo-second-order reaction kinetics were estimated. It was determined that the caffeine adsorption fit both the Langmuir and Freundlich isotherms. The value of the experimental maximum adsorption capacity (q_e) was the highest for TiO_2 modified with activated carbon and ultrasounds ($TiO_2/AC/Us$). The highest removal degree (over 99.0%) of CAF was observed for titanium(IV) oxide modified with activated carbon. Both photodegradation kinetics models show good or very good fit; however, the pseudo-first-order model shows better fit to the experimental data ($R^2 = 97–99\%$). After 20 minutes of the photodegradation process, the following efficiency order was determined: $TiO_2 < TiO_2/AC < TiO_2/AC/US$. The results indicate that the combination of TiO_2, activated carbon and ultrasound is an interesting alternative for the efficient degradation of caffeine, comparing to commercial TiO_2.

Keywords: TiO_2; caffeine; photocatalysis; modified photocatalysts; activated carbon; ultrasound; kinetics; adsorption

INTRODUCTION

Micropollutants are a constantly growing group of substances that occur in water and wastewater environment at trace levels (i.e. at the level from ng/l to µg/l). An examplary compound belonging to the group of micropollutants is 1,3,7-trimethylxanthine, commonly known as caffeine (CAF). Caffeine is an alkaloid naturally occurring in over 60 species of plants (beans, leaves and fruits etc.). CAF is mainly consumed with drinks such as coffee, tea and energy drinks. Caffeine belongs to natural psychoactive substances. When it is consumed in moderate doses, it is safe for humans. However, an excessive consumption increases the risk of serious toxicity (Turnbull et al., 2017).

The main sources of caffeine for aquatic ecosystems (both marine and freshwater) are anthropogenic sources. Increasing the consumption of caffeine-containing products contributes to the increase of caffeine concentration in wastewater. This is due to the fact that a small amount of caffeine (0.5–10%) is completely excreted by the urinary system and enters the wastewater treatment plant. The consequence of untreated or inadequately treated wastewater is the increasing concentration of CAF in aquatic ecosystems. Over the last decade, caffeine has been detected in marine ecosystems, estuarine and coastal waters

and water inflows at relatively low levels from < 2.0 ng/l to 5.0 µg/l (Rodriguez et al., 2012).

The presence of micropollutants such as caffeine in the environment determines that the development of new treatment technologies is justified. Advanced oxidation processes (AOPs) are one of such technologies that are of great interest nowadays. AOPs are highly efficient novel methods that accelerate the oxidation and the degradation of a wide range of organic and inorganic substances that are resistant to the conventional treatment methods (Deng & Zhao 2015). The common feature of AOPs is the production of the OH$^{\bullet}$ radicals. The mechanism of generating radicals depends on the sort of AOPs technique. Heterogeneous photocatalysis is an example of the AOPs technology, in which the titanium dioxide (TiO_2) photocatalyst is used. Photocatalytic oxidation process combines UV irradiation at a wavelength of $\lambda \leq 400$ nm with a catalyst (e.g. TiO_2, CdS, ZnO). This study focusing on titanium(IV) oxide. From a practical point of view, improving the properties of semiconductors has gained particular interest. Therefore, many scientific papers are focused on the modification of TiO_2 (Wang et al., 2018; Hunge et al., 2020; Zawadzki, 2020).

Ultrasonic modification technology is a safe, simple and efficient method for potential use in water and wastewater treatment. Ultrasound improves the TiO_2 activity, increases the specific surface area, thus better adsorption of TiO_2 on the activated carbon surface can be achieved (Chu et al., 2017; Lee et al., 2017). In turn, activated carbon is a commonly used adsorbent in water and wastewater technology. It has decent quality for a low price (10–12 \$/kg), it is non-toxic, provides a high specific surface (S_{BET} about 2500 m²/g) and is a support for TiO_2 particles (Pereira et al., 2019). The applied modification method (activated carbon and ultrasound) is not cost consuming and does not require large number of expensive chemical reagents, which is the basis of the principles of green chemistry. Short modification time and simplicity is the advantage of this technology. Due to its simplicity, it can be used in water or wastewater treatment plants.

Titanium(IV) oxide was chosen as the base material for modification. It is non-toxic and stable compared to other catalysts, e.g. ZnO or CdS. However, it still needs to be modified to improve its properties. A modified photocatalyst should be characterized by better performance than the raw material. The advantages of modified photocatalysts include: higher sorption capacity; stability at variable pH; better pollutants degradation; visible light activity; facilitated post-process recovery (Xing et al., 2016).

Therefore, in this study, the adsorption isotherm and reaction kinetics towards caffeine degradation on modified photocatalysts were determined. The assessment of factors affecting the adsorption and photocatalytic degradation was also conducted.

MATERIALS AND TEST METHODOLOGY

Materials

The caffeine model solutions were prepared by dissolving analytical standard of caffeine with >98% of purity purchased from Sigma-Aldrich (Poznań, Poland) in deionized water. The pH of the model solution was adjusted with 0.1 mol/l HCl or 0.1 mol/l NaOH and monitored using the Elmetron CPC-511 pH-meter (Zabrze, Poland). The conductivity of the model solutions was 0.2 mS/cm. In order to maintain constant ionic strength, the model solutions contained 0.01 mol/l of $NaNO_3$.

The commercial titanium dioxide TiO_2-P25 (anatase/rutile = 80/20) was selected as the base material for the modification of photocatalysts. The material was obtained from Evonik Degussa GmbH (Germany). Photocatalysts were modified using commercial, powdered activated carbon CWZ-30 by Gryfskand (Gryfino, Poland). The specification of TiO_2 and activated carbon is shown in Table 1.

Table 1. Physicochemical characteristics of TiO_2 and activated carbon

Symbol	Origin	Surface area S_{BET} [m²/g]	Particle size [nm]	Granulation [%]	Density [g/cm³]
TiO_2-P25	Evonik Degussa GmbH (Germany)	50.0 ± 15.0	21.0	-	4.26
CWZ-30	Gryfskand (Gryfino, Poland)	1134.0	-	90.0	0.28 – 0.36

Synthesis of photocatalysts samples

The photocatalyst samples were prepared based on commercial titanium(IV) oxide and powdery activated carbon (AC). In order to modify the TiO_2 samples, a hybrid method of preparation based on mechanical mixing, calcination and ultrasound irradiation has been applied. In the first stage of preparation, a TiO_2-AC mixture in deionized water (85:15, w/w) was prepared. The suspension was stirred for 30 minutes in a dark at room temperature. The TiO_2/AC photocatalysts (TiO_2 modified with activated carbon) were prepared as follows: the mixture of TiO_2-AC was calcined in a CHEMLAND muffle furnace at 300°C for 8 hours. Hereby, the TiO_2/AC precursors were obtained. The TiO_2/AC/Us photocatalysts (TiO_2 modified with activated carbon and ultrasound) were prepared as follows: the mixture of TiO_2-AC was subjected to ultrasound irradiation in an ultrasonic washer for one hour at 30°C using 50% of the device output power. The process was carried out in the dark. An IS-1K ultrasonic cleaner (InterSonic, Poland) was used with a 50 Hz operating frequency and a power density of 5 W/cm². The device has the ability to work at temperatures up to 80°C and smooth power regulation in the range of 10 to 100%. Then, a TiO_2-AC mixture irradiated with ultrasound was calcined in a CHEMLAND muffle furnace at 300°C for 8 hours. This catalyst was denoted as TiO_2/AC/Us, where 'Us' means modified by ultrasound.

Instruments and analytical methods

Caffeine was determined using GC-MS-EI chromatographic analysis coupled with a mass detector by Perlan Technologies (Warsaw, Poland). The device was equipped with a 5 SLB™ – 5 ms capillary chromatography column with the dimensions of 30.0 m x 0.25 mm x 0.25 μm by Sigma-Aldrich (Poznań, Poland). The column heater was programmed in the temperature range from 80 to 300°C. The stove worked for eight minutes at 80°C. Then, for five minutes, the temperature was increased by 10°C/min to 300°C. Helium (flow 1.1 ml/ min) was used as the carrier phase. The samples of 1 μl volume were injected automatically. The samples with the volume of 20 cm³ were separated from the photocatalyst particles using a filtration apparatus connected to a vacuum pump by AGA Labor (Warsaw, Poland). A chromatographic analysis was preceded by Solid Phase Extraction (SPE). The extraction process was carried out on Supelclean™ ENVI-18 columns. The columns were filled with a silica gel modified with octadecyl groups (C_{18}). For the conditioning of the column bed, 5 cm³ of acetonitrile and methanol were used. The bed was washed with distilled water (5 cm³). The compounds adsorbed on the bed were eluted with 3 cm³ of a mixture of acetonitrile and methanol (60:40, v/v).

Isotherm studies

In order to describe the adsorption effect of caffeine, two adsorption isotherm models, i.e. the Langmuir and Freundlich isotherms were used (Table 2). The Langmuir and Freundlich isotherms were used for the mathematical description of adsorption process (Eqs. 1–4). The Langmuir isotherm model (Eqs. 1–2) assumes that the adsorbate forms a monolayer on the adsorbent's surface and that each site may adsorb a single particle, ignoring interactions between them. The Freundlich isotherm (Eqs. 3–4) describes the adsorption on heterogeneous surfaces and microporous adsorbents.

The isotherm studies were carried out as follows: 0.2 L of a caffeine model solution at a concentration of 0.25–2.0 mg/l was placed in the flask; a catalyst at a concentration of 100.0 mg/l was added and shaken vigorously for 20 minutes. The pH of the model solution was 6.0±0.5 over

Table 2. The equation of isotherms

Model	Equation		Linear form	
Langmuir	$q_e = \dfrac{K_L q_m C_e}{1 + K_L C_e}$	(1)	$\dfrac{C_e}{q_e} = \dfrac{1}{q_m} \cdot \dfrac{1}{K_L} + \dfrac{C_e}{q_m}$	(2)
Freundlich	$q_e = K_F \cdot C_e^{\frac{1}{n}}$	(3)	$\log q_e = \dfrac{1}{n} \cdot \log C_e + \log K_F$	(4)

where: q_e – the mass of the adsorbate per unit weight of adsorbent, mg/g; q_m – the maximum amount of adsorbate required to form monolayer, mg/g; K_L – Langmuir isotherm constant, mg/g; C_e – adsorbate concentration in equilibrium, mg/l; K_F, n – Freundlich isotherm constants

the temperature T = 298 K. The process was carried out in a dark.

Photocatalysis experiments

The photodegradation of caffeine was carried out in a Heraeus reactor with a capacity of 0.7 L. The initial concentration of caffeine in the photodegradation tests was 1.0 mg/l. The batch reactor was equipped with a 150W mercury high-pressure lamp. The lamp emits ultraviolet light in the range of 200–580 nm. The UV lamp was placed in a glass jacket cooled by tap water. Therefore, the temperature of reaction solutions was maintained in the range from 20 to 21°C. The batch reactor was placed on a magnetic stirrer to ensure proper mixing of the reaction mixtures. The reactor was equipped with aeration pump with a capacity of 0.25 cm^3 of air per 1 hour. The dose of the catalysts in the photocatalysis process was 0.1 g/l. Before switching on the radiation source, a 15 minute contact time of adsorption was provided. The adsorption process was carried in the dark. The photodegradation process was carried out continuously for 20 minutes. The samples for the chromatographic analysis were taken at a time intervals of 5 min. All experiments were carried out independently in triplicate.

Kinetics studies

Most of the kinetic studies were performed using the pseudo-first-order kinetics which is fitted to the Langmuir-Hinshelwood (L-H) model. Under ideal conditions, the L-H model can be expressed by Eq. 5 and Eq. 6. Although it is the most commonly used model to describe the rate of pollutants degradation (Asenjo et al., 2013), pseudo-second-order model (Eq. 7 and Eq. 8) were considered. The equation isotherms are shown in Table 3.

RESULTS AND DISCUSSION

Effect of sorption time

Figure 1 presents the effect of caffeine adsorption on catalysts. Caffeine was removed in the range from 25–50% in 20 min. It can be observed that the maximum adsorption was reached in approx. 15 min for all the catalysts tested. The rate of caffeine uptake onto commercial catalyst surface (TiO$_2$) was the most intense in 5 min (17%). In the next minutes (5–15 min) adsorption degree increased slightly to 25%. Over the next 15 to 20 minutes, the increase in the CAF removal was not significant (less than 0.1%). Thus, equilibrium was attained within 15 min. The adsorption on modified catalysts was different. In fact, the most intense rate of caffeine adsorption was observed up to 10–12 min. After 15 minutes, adsorption almost stopped at 39% and 50% for TiO$_2$/AC and TiO$_2$/AC/Us, respectively. Therefore, 15 min was chosen as the optimal adsorption time. The 15 min duration time matches with the studies related to the adsorption of other organic pollutants reported by (Shirsath et al., 2013; Li et al., 2018).

Poor caffeine uptake on commercial TiO$_2$ comparing to modified catalysts is related to its low surface area (S$_{BET}$ = 50.0 ± 15.0 m^2/g) and the physico-chemical properties of CAF. Caffeine is characterized by high solubility in water (21.6 g/l) and a negative logK$_{OW}$ partition coefficient (-0.07). This means that caffeine is poorly adsorbed on adsorbents, which affects its low removal degree.

The TiO$_2$/AC/Us material showed the highest CAF adsorption performance. The influence of activated carbon and ultrasonic modification on modified catalysts potential for adsorption was observed. First of all, activated carbon has a high active surface area (S$_{BET}$ = 1134.0 m^2/g in this study). Bel Hadjltaief et al. (2016) studied

Table 3. The equation of kinetics

Model	Equation		Plot		References
Langmuir-Hinshelwood	$-\ln\left(C_t/C_0\right) = k_1 t$	(5)	$-\ln\left(C_t/C_0\right)$ VS t	(6)	(Armenise et al., 2013)
Pseudo-second-order	$\dfrac{1}{C_t/C_0} = k_2 t + \dfrac{1}{C_0}$	(7)	$\dfrac{1}{C_t/C_0}$ VS t	(8)	(Marcinkowski et al., 2014)

where: C$_t$ – concentration at time t, mg/l; C$_0$ – initial concentration, mg/l; k$_1$ – pseudo-first-order rate constant; k$_2$ – pseudo-second-order rate constant.
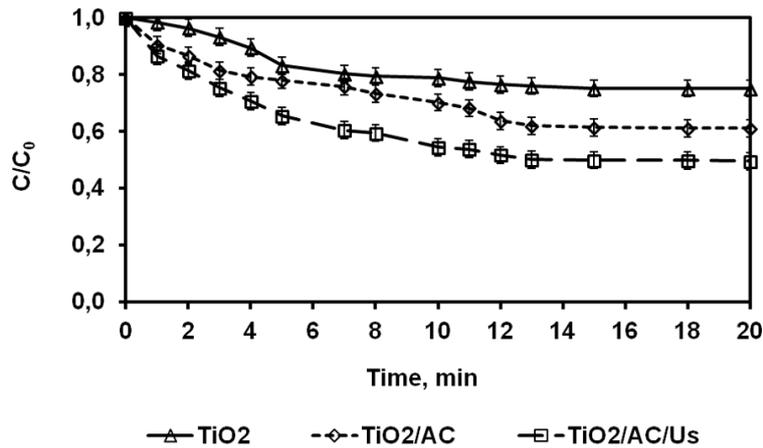
Fig. 1. Influence of sorption time on caffeine removal. Conditions: TiO_2 dosage = 0.1 g/l; caffeine concentration = 1.0 mg/l; pH = 6.0±0.5

the effect of activated carbon on the increase of catalyst surface. The authors modified the surface of titanium(IV) oxide by means of activated carbon, which increased the TiO_2 active surface area to 420 m^2/g. Afterwards, ultrasonic radiation increased the active surface area by dispersing the solid phase of TiO_2. Furthermore, the surface of the modified TiO_2 was activated by ultrasound, leading to higher adsorption potential of pollutants, which was confirmed by Bulychev (2019).

Effect of caffeine concentration

Figure 2 shows the adsorption isotherm of caffeine at 298 K. On the basis of the obtained results, adsorption isotherm was classified by fitting them to the isotherm classification system. The shape of isotherms is the first experimental tool to investigate the nature of a particular adsorption phenomenon. The isotherm classification system presented by Sing (1985) divides the shape of isotherms on six general types. More detailed system of isotherm classification divides all isotherms into four main classes (18 shapes of isotherms) (Giles et al., 1960). A simplified classification system was taken into account. The obtained isotherms are of type I. This means that as the adsorbent pores are filled, the caffeine particles find harder a vacant site to adsorb. Thus, the identified isotherm shapes are the most common, two well-known equations isotherms, i.e. Langmuir and Freundlich could be applied (Ghosh et al., 2019).

Additionally, the values of the experimental maximum adsorption capacity (q_e) were determined (Fig. 2). The maximum adsorption capacity of TiO_2 is similar to those reported by Janus et al. (2011). The modified catalysts showed the highest adsorption capacity compared to commercial titanium dioxide. The adsorption capacity depends, among others on the modification
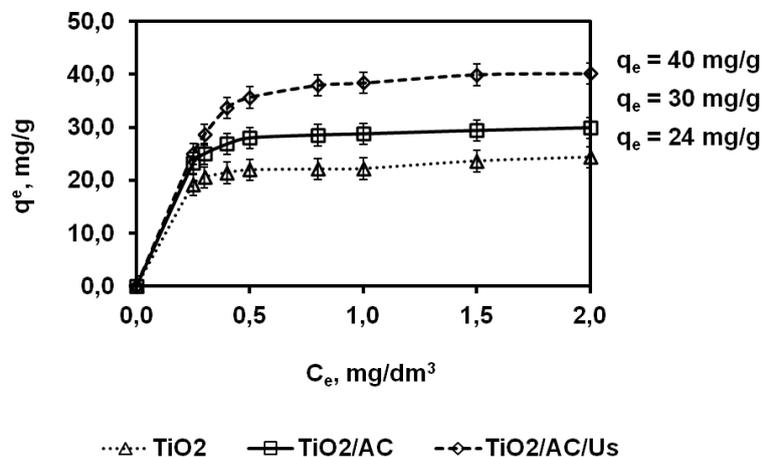

Fig. 2. Effect of caffeine concentration on maximum adsorption capacity. Conditions: TiO_2 dosage = 0.1 g/l; caffeine concentration = 1.0 mg/l; time = 15 min; T = 298 K

Table 4. Langmuir and Freundlich isotherm parameters

Isotherm	Parameter	TiO$_2$	TiO$_2$/AC	TiO$_2$/AC/Us
Langmuir	a_m	0.56±0.04	1.80±0.02	1.67±0.04
	K_L	6.06±0.07	0.91±0.03	0.52±0.02
	R^2	0.90±0.02	0.95±0.02	0.99±0.01
Freundlich	n	0.72±0.03	1.47±0.04	1.04±0.02
	K_F	0.37±0.02	0.73±0.02	0.74±0.02
	R^2	0.94±0.02	0.95±0.03	0.99±0.01

method. For example, Jafari et al. (2016) produced an elemental carbon-modified TiO$_2$ at various temperatures. Carbonization at 300°C caused an increase in the maximum adsorption capacity by more than 4 times. This study found that the activated carbon-ultrasonic-modified titanium dioxide performs better adsorption potential than the commercial TiO$_2$. The TiO$_2$/AC/Us catalyst proved to be the best adsorption material for caffeine (q$_e$ = 40 mg/g).
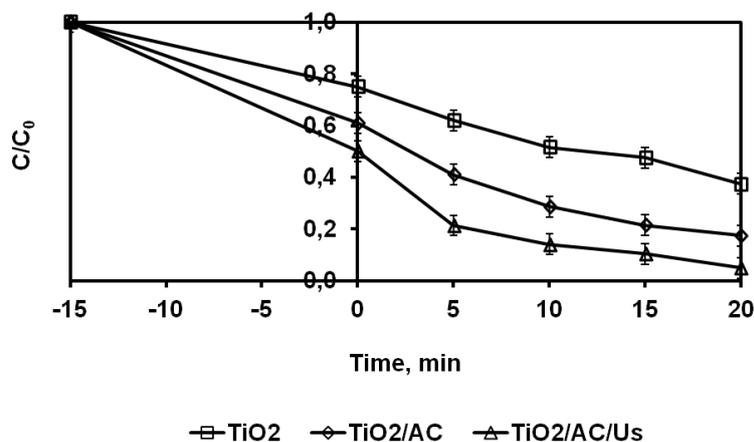
Langmuir and freundlich isotherm studies

Table 4 shows the Langmuir and Freundlich parameters. Langmuir parameter K_L indicates the adsorption conditions: unfavourable when $K_L > 1$, linear when $K_L = 1$, favourable when $0 < K_L < 1$, and irreversible when $K_L = 0$ (Ayawei, 2017). Freundlich parameter n in the range within 1–10 shows favourable adsorption (Fierro et al., 2008). A high correlation was found between experimental data and linear isotherms. The correlation coefficient R^2 showed good or very good fit of the experimental data (R^2 ranged from 90% to 99%). It was found that the Freundlich isotherm fit the caffeine adsorption onto pure TiO$_2$ (R^2 = 94%). Furthermore, the adsorption conditions for Langmuir isotherm are

unfavourable ($K_L > 1$). Both Langmuir and Freundlich isotherms fit the caffeine adsorption data onto modified photocatalysts. The R$_2$ values are very close to 1 (i.e. 99% for TiO$_2$/AC/Us) and adsorption conditions (n) are higher than 1.

Photodegradation study

In order to determine the photocatalytic activity of the prepared catalysts, a photodegradation study and a kinetics study were carried out. As shown in Fig. 3, the removal of caffeine is time-dependent. The time period from -15 to 0 means adsorption process. A 15 min contact time was selected according to preliminary studies (section 3.1). The implementation of UV radiation ("0" time of the process) has started the photodegradation process. The photocatalytic degradation of caffeine was carried out for 20 min. At the end of 20 min of the reaction, the caffeine degradation was approximately 60% for pure TiO$_2$, 82% for TiO$_2$/AC and 95% for TiO$_2$/AC/Us. Thus, this indicates the synergistic effect between activated carbon and ultrasound. Similar results were reported by Khani et al. (2019). The authors synthesized the catalysts modified with ultrasound. These materials were up to 50% more active than conventional TiO$_2$.

Fig. 3. Photodegradation of caffeine. Conditions: TiO$_2$ dosage = 0.1 g/l; sorption time = 15 min; pH = 6.0±0.5; T = 298 K

The results indicated that in TiO_2/AC/Us system caffeine can be remarkably removed to a low level (approx. 80%) within 5 min, whereas in the TiO_2 system in only 35%. Moreover, photocatalysis carried out in the presence of modified photocatalysts requires a shorter degradation time compared to the processes carried out by i.e. Sacco et al. (2019).

Improved photocatalytic performance of modified photocatalysts may be explained in several ways. Enhanced adsorption of caffeine was possible due to the high specific surface area of TiO_2 covered by activated carbon; however, the better performance of the ultrasound modified catalyst is attributed to an acoustic cavitation of ultrasound waves. Ultrasounds alter the surface properties, such as surface area and particle size distribution; therefore, the amount of radicals generated during the process increased (Stucchi et al., 2018; Giannakoudakis et al., 2020). Moreover, ultrasounds limit the phenomenon of blocking active sites. The blocking active sites phenomenon is related with poor specific surface area and the generation of by-products. The identification of intermediates was beyond the scope of this study.

In order to analyze the photodegradation kinetics of caffeine, pseudo-first-order and pseudo second-order reaction were investigated (Fig. 4). Taking into account the relationship between $-ln(C/C_0)$ and reaction time, the two-stage oxidation process, which is a characteristic phenomenon, e.g. for heterogeneous oxidation processes (Covinich et al., 2018) was not found. The two-stage oxidation process is mainly attributed to the indirect reaction of oxygenating species with by-products or decreasing amount of radicals during the reaction.
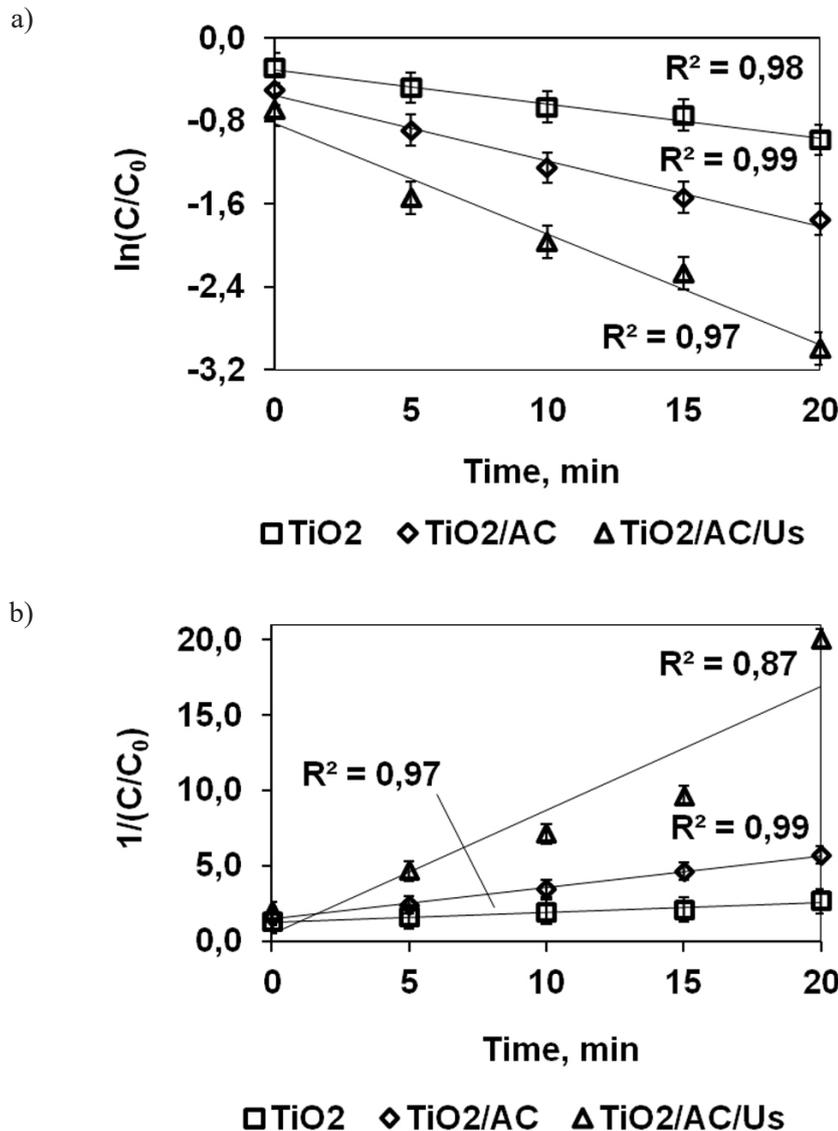
a)

b)

Fig. 4. Kinetics of caffeine photodegradation (a – Langmuir-Hinshelwood; b – pseudo-second-order)

Table 5. Kinetic parameters of the photocatalysis

Model	Parameter	Catalyst		
		TiO_2	TiO_2/AC	$TiO_2/AC/US$
Pseudo-first-order	k, 1/min	0.033	0.063	0.107
	R^2	0.98	0.99	0.97
Pseudo-second-order	k, 1/min	0.063	0.208	0.822
	R^2	0.97	0.99	0.87

The presented parameters were calculated from the slopes of the plots and are presented in Table 5. As it was shown, both models are well fitted and show good or very good fit ($R^2 > 87\%$). However, the pseudo-first-order model shows better fit to the experimental data ($R^2 = 97$–99%). Pseudo-first-order rate constant k becomes twice faster by activated carbon modification and 3.2-fold faster by combination of activated carbon and sonochemical treatment. These changes can be explained by particle size distribution, inhibition of nanoparticles agglomeration and inhibition of electron-hole recombination (Ambati & Gogate, 2018; Prasad et al., 2011).

CONCLUSION

The effectiveness of the commercial titanium(IV) oxide and modified photocatalysts for the photocatalytic degradation of caffeine were studied. Modified catalysts were synthesized by activated carbon and sonochemical method using commercial TiO_2 as a starting material. It was observed that the physicochemical characteristics of caffeine influenced the uptake and photodegradation by photocatalysts. The results showed that the caffeine uptake by a modified catalyst followed both the Langmuir and Freundlich models. The general results of this study showed that TiO_2 modified with activated carbon and ultrasound promotes surface adsorption of caffeine with a maximum adsorption capacity and removal efficiency of 40 mg/g and 95%, respectively. In overall, the photodegradation of caffeine followed the pseudo-first-order kinetics. After 20 minutes of the photodegradation process, the following efficiency order was determined: $TiO_2 < TiO_2/AC < TiO_2/AC/US$.

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