TiO_2 NANOMATERIAL USED AS PHOTOCATALYST FOR DEGRADATION OF BENZALKONIUM CHLORIDES (C14-BAC AND C16-BAC) FROM WASTEWATER

IULIANA PAUN[1,2], CRISTINA ILEANA COVALIU- MIERLA[1]*, EUGENIU VASILE[1]
[1]*University Politehnica of Bucharest, 313 Splaiul Independenței, 060042, Bucharest, Romania*
[2]*INCD ECOIND, 71-73 Drumul Podu Dâmboviței street, 060652, Bucharest, Romania*
[3]*National Centre for Micro and Nanomaterials, University Politehnica of Bucharest, 060042 Bucharest, Romania*

Benzalkonium chlorides are among the active ingredients of the products with biocidal properties used for disinfection of hands and surfaces. After use, a large part of benzalkonium chlorides end up in the wastewater from the treatment plants where they can cause imbalances of the biological treatment step by destroying the bacteria in the activated sludge. Having bactericidal properties, these pollutants are unlikely to be removed by conventional wastewater treatment techniques. In this paper we present an unconventional method for wastewater treatment using TiO_2 nanomaterial with a particle size of 10 nm having the photocatalytic activity for degrading two components of benzalkonium chloride, namely tetradecyldimethyl benzyl ammonium chloride (C14-BAC) and hexadecyldimethylbenzyl ammonium chloride (C16-BAC) from wastewater. The concentration of the two compounds was analyzed using a high-performance liquid chromatograph equipped with a diode array detector (HPLC-DAD). The wastewater treatment yield was 100 %, and the half-life was for C14-BAC of 7.56 h and for C16-BAC of 10.67 h.

Clorurile de benzalconiu se numără printre ingredientele active din produsele cu proprietăți biocide utilizate pentru dezinfectarea mâinilor și a suprafețelor. După utilizare, o mare parte din clorurile de benzalconiu ajung în apele uzate din stațiile de epurare unde pot provoca dezechilibre în etapa de epurare biologică, prin distrugerea bacteriilor din nămolul activ. Având proprietăți bactericide, este puțin probabil ca acești poluanți să fie îndepărtați prin tehnici convenționale de epurare a a apelor. În această lucrare prezentam o metodă neconvențională de epurare a apelor folosind nanomaterialul TiO_2, cu o dimensiune a particulei de 10 nm, având activitate fotocatalitică pentru degradarea a doi compusi din clasa clorurilor de benzalconiu, și anume clorură de tetradecildimetilbenzilamoniu (C14-BAC) și clorură de hexadecildimetilbenzil (amoniu) C16-BAC) din apele uzate. Concentrația celor doi compuși a fost analizată folosind un cromatograf lichid de înaltă performanță echipat cu un detector cu matrice de diode (HPLC-DAD). Randamentul de epurare a apei a fost de 100 %, iar timpul de înjumătățire a fost pentru C14-BAC de 7,56 ore și pentru C16-BAC de 10,67 ore.

Keywords: *benzalkonium chloride, nanomaterial, TiO_2 powder, wastewater treatment*

1.Introduction

The removal of organic substances from wastewater could be achieved by: i) their decomposition with the help of microorganisms, when these substances are not toxic for the microorganisms in the sludge of the sewage treatment plant; ii) their decomposition with the help of photocatalysts when these substances have toxic, even bactericidal effects on the existing microorganisms in wastewater treatment plants.

To prevent the transmission of the Covid-19 coronavirus during the SARS-COV-2 pandemic, chemical products with biocidal properties were used to disinfect the hands and surfaces [1]. Benzalkonium chlorides are among the active ingredients in these products. Benzalkonium chlorides (BAC) represent a class of quaternary ammonium compounds, cationic surfactants. BAC is a mixture of alkyldimethylbenzyl ammonium chloride homologues with alkyl chains ranging from 8 and 18 carbon atoms [2]. The most usually homologues are dodecyldimethylbenzyl ammonium chloride (C12-BAC), tetradecildimethylbenzyl ammonium chloride (C14-BAC) and hexadecil dimethyl benzyl ammonium chloride (C16-BAC).

BAC are present in environment worldwide. Studies on the presence of these compounds in environmental samples (wastewater, surface water) and in the activated sludge of the wastewater treatment plant are relatively few. Studies during the pandemic and after the pandemic show that, wastewater effluent samples from 12 treatment plants around the Minneapolis–Saint Paul metropolitan area (United States of America) had BAC high concentrations. The C14-BAC was detected in all analyzed samples and the highest concentration was 1.386 µg/L, and for C12-BAC the

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* Autor corespondent/*Corresponding author*,
E-mail: cristina_covaliu@yahoo.com

highest concentration was 0.143 µg/L and for C16-BAC was 1.015 µg/L. Concentrations of these compounds were also found in the sediments of the lake where the treated wastewater was discharged. The maximum concentrations determined were for C12-BAC of 127 µg/kg, for C14-BAC of 211 µg/kg and for C16-BAC was 163 µg/kg [3]. This proves that the treated wastewater discharged into the lakes still contains BAC that concentrates in the sediment.

In Germany, benzalkonium chlorides were found in sewage treatment plant sludges that used a mechanical primary stage and a biological secondary stage for wastewater treatment. The concentrations of 12-BAC found in sewage sludge were between 562 ug/kg and 38600 ug/kg, while the concentrations of 14-BAC were between 55 ug/kg and 19940 ug/Kg, and the concentrations of 16-BAC they were lower, being between 10 ug/kg and 3203 ug/kg. [4]. This proves that benzalkonium chlorides do not decompose during wastewater treatment, being concentrated in the sewage treatment plant sludge.

In addition to the disinfectant properties that benzalkonium chlorides had, they were used to inhibit the corrosion of carbon steel in an acidic environment. For carbon steel in the presence of 0.1 M H_2SO_4, the concentration of benzalkonium chloride of 300 mg/L had an excellent corrosion removal efficiency [5], and for the same concentration of benzalkonium chloride the inhibitory effect of steel corrosion in the presence of the strong corrosive substance 1 M HCl was 90.4% [6].

Also, benzalkonium chlorides were used to protect steel from corrosion caused by bacterial algae that form a film on its surface. Thus, the concentration of 30 mg/L of benzalkonium chloride produced a 95% inhibition on steel corrosion for algae of the Chlorella vulgaris type [7] and for bacteria of the Desulfotomaculum nigrificans type, the concentration of benzalkonium chloride used was 80 mg/L and reduced both uniform corrosion and pitting corrosion [8].

After use, a large part of benzalkonium chlorides end up in the wastewater from the treatment plants where they have a negative effect on the biological treatment step by destroying the bacteria in the activated sludge. Having bactericidal properties, these pollutants are unlikely to be removed by conventional wastewater treatment techniques. The development of nonconventional methods for removing these pollutants from waste water is required. The use of photocatalysts in the presence of UV radiation or sunlight could lead to the development of effective methods for the decomposition of these pollutants, in order to remove them from wastewater treatment plants. Titanium dioxide is considered to be the ideal photocatalyst because it is cheap and chemically stable. The most important characteristics of titanium dioxide are the photogenerated holes that are highly oxidizing and the photogenerated electrons that reduce and produce oxygen superoxide [9]. The uses of the TiO_2 photocatalyst are multiple. Benzalkonium chloride together with rutile titanium dioxide nanoparticles were formed a new effective inhibitor for carbon steel in 0.5M sulfuric acid solution [10]. TiO_2 film photocatalysts can also be used to sterilize surfaces. Thus, an experiment was carried out in which Escherichia coli bacteria in contact with a plate covered with TiO_2 under UV radiation for 1 hour determined a 100% inactivation of microorganisms, while without the TiO_2 catalyst and subjected to UV radiation for four hours only 50% were destroyed [11].

Since the beginning of the 1980s, the TiO_2 has been tested and used in the treatment of cancer [12-14].

But the most important use of TiO_2 is the removal of organic substances from water. It is known that the three crystalline structures under which TiO_2 is found are anatase (trigonal structure), rutile (tetragonal structure) and brookite (orthorhombic structure) [15,16,17]. Of these, TiO_2 in the atanase phase is the most used for the photodegradation of wastewater because it has high photocatalytic activity [15]. With the help of the TiO_2 photocatalyst, methods were developed to degrade some organic pollutants such as pesticides, herbicides and dyes from wastewater [16]. The TiO_2 photocatalyst was initially used in powder form. In order to improve the photocatalytic activity of TiO_2, its structure was modified by introducing metals and other compounds into TiO_2, creating hybrid or composites having morphological modification [19]. The properties of TiO_2 photocatalysts are influenced by their structure. Nanomaterials of TiO_2 were manufactured in the form of spheres, nanorods and interconnected structures [20]. TiO_2 spheres are the most used in the removal of organic pollutants from wastewater because they have a large specific surface on which these pollutants can be adsorbed. TiO_2 spheres are usually obtained from titanium tetraisopropoxide or titanium tetraboxide, in the presence of sulfuric acid and a polymer. The methods by which TiO_2 spheres are obtained are sol-gel methods coupled with hydrothermal methods to produce nanocatalysts [21, 22]. TiO_2 materials in the form of fibers and tubes are also used for the photocatalytic decomposition of organic compounds in wastewater. The preparation of these fibers is carried out by electrospinning and electrospray methods [23-25]. TiO_2 nanostructures were prepared in wheel shapes, in the form of flowers, multipods, snowflakes, windmills and dendrites. The methods by which these nanostructures are obtained are particularly simple, namely a simple solvothermal method followed by a calcination process [26].

This paper reports the investigation of the photocatalytic activity of the TiO_2 nanomaterial previously synthesized and characterized on degradation of benzalkonium chloride type (C14- and C16-BAC) from wastewater**.**

2.Materials and methods

2.1. Chemicals and reagents

Benzalkonium chloride used in this study were tetradecyldimethylbenzyl ammonium chloride (C14-BAC) and hexadecyldimethyl benzyl ammonium chloride (C16-BAC). Experimental stock solutions were prepared using ultrapure water. Acetonitrile and ammonium acetate were used for HPLC analyses. Also in this study were used titanium isopropoxide ($C_{12}H_{28}O_4Ti$), NTA ($C_6H_9NO_6$) and ammonia. All reagents were from Sigma Aldrich.

2.2 Preparation and Characterization of TiO_2 nanomaterial

NTA (0.09g) was dissolved in 1 M ammonia water solution (2.5 mL), followed by adding absolute ethanol (40 mL) into it. After 30 min of vigorously stirring at room temperature, into the mixture was drop wise added a solution of titanium isopropoxide (18 mL) and ethylic alcohol (20 mL). After 8 h of stirring, the mixture was maintained stable and the supernatant was removed. The precipitate was dried at 100℃ and the resulted powder was calcined at 450℃.

2.3 Photocatalytic Experiments

The photocatalytic experiment was carried out in four Berzelius glasses of 150 ml. In glasse 1, 100 mL of C14-BAC solution with a concentration of 10 mg/L and 0.1 g of TiO_2 photocatalyst powder was introduced, in glasse 2, 100 mL of C14-BAC solution with a concentration of 10 mg/L was introduced, the glasse 3 was introduced 100 mL of C16-BAC solution with a concentration of 10 mg/L and 0.1 g TiO_2 photocatalyst powder, in glass 4 was introduced 100 mL of C16-BAC solution with a concentration of 10 mg/L. During the experiment, the solutions of C14-BAC and C16-BAC were homogenized by mixing with a magnetic stirrer and the UV lamp was positioned sideways. All experiments were performed at room temperature. During the experiment, samples were taken for measuring the concentration of C14 and C16-BAC. The collected samples were kept at 4°C and analyzed by the HPLC-DAD method.

2.4 Analytical method

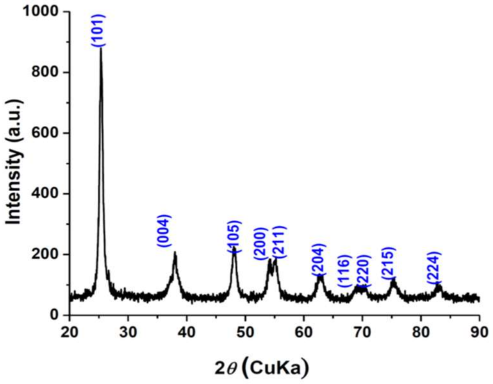
High-performance liquid chromatograph Agilent 1200 equipped with a DAD detector was used to detected the concentration of C14-BAC and C16-BAC. The chromatographic column used was mobile phase was a mixture of acetonitrile and ammonium acetate 0,2 M in a 1:1 ratio. The flow rate was 0.5 mL/min and isocratic conditions at room temperature were employed. The injection volume was 20 µL and peak areas were measured. The wavelength at which the compounds C14-BAC and C16-BAC were detected was at 262 nm. The retention times were 3,1 min for C14-BAC and 4,2 min for C16-BAC. The limits of quantification (LOQ) were 0,06 mg/L for C14-BAC and 0,08 mg/L for C16-BAC.

The X-ray diffraction (XRD) analyses were obtained using a X’PERT PRO MPD with Cu-Kα radiation (λ = 0.15418 nm) and transmission electron microscopy (TEM) investigations were done on FEI Tecnai TMG2F30 S-TWIN with EDAX energy dispersive X-ray spectrometer. The X-ray source was monochromatized Al Kα radiation (1486.6 eV) and the overall energy resolution is estimated at 0.65 eV by the full width at half-maximum (FWHM) of the Au4f7/2 photoelectron line (84eV). Although the charging effect was minimized by using a dual beam (electrons and Ar ions) as neutralizer, the spectra were calibrated using the C1s line (BE = 284.8 eV) of the adsorbed hydrocarbon on the sample surface (C-C or (CH)n bondings). As this spectrum was recorded at the start and the end of each experiment, the energy calibration during experiments was quite reliable.

3.Experimental section

3.1 X-ray diffraction

XRD pattern for powder calcined at 450℃ is presented in Fig.1. The crystal structure is strongly dependent on calcination temperature. Around 400℃, anatase phase appeared whereas the powder calcined at temperature 600℃ still consists of pure anatase type. As described in the literature, the phase transformation from anatase to rutile appeared at about 800 ℃ [19]. Therefore it was expected that TiO_2 obtained by calcinations at 450℃ has the crystalline structure of anatase, having tetragonal symmetry (ICSD 154603). Fig.1. The average crystallite size estimated using Scherrer’s formula for titanium dioxide powder obtained at 450℃ was 5 nm.



Acclaim Surfactant Plus using column (3µm, 3,6x150mm, Thermo Scientific) set a at 30°C. The

Fig. 1 – XRD patterns of TiO_2 powder

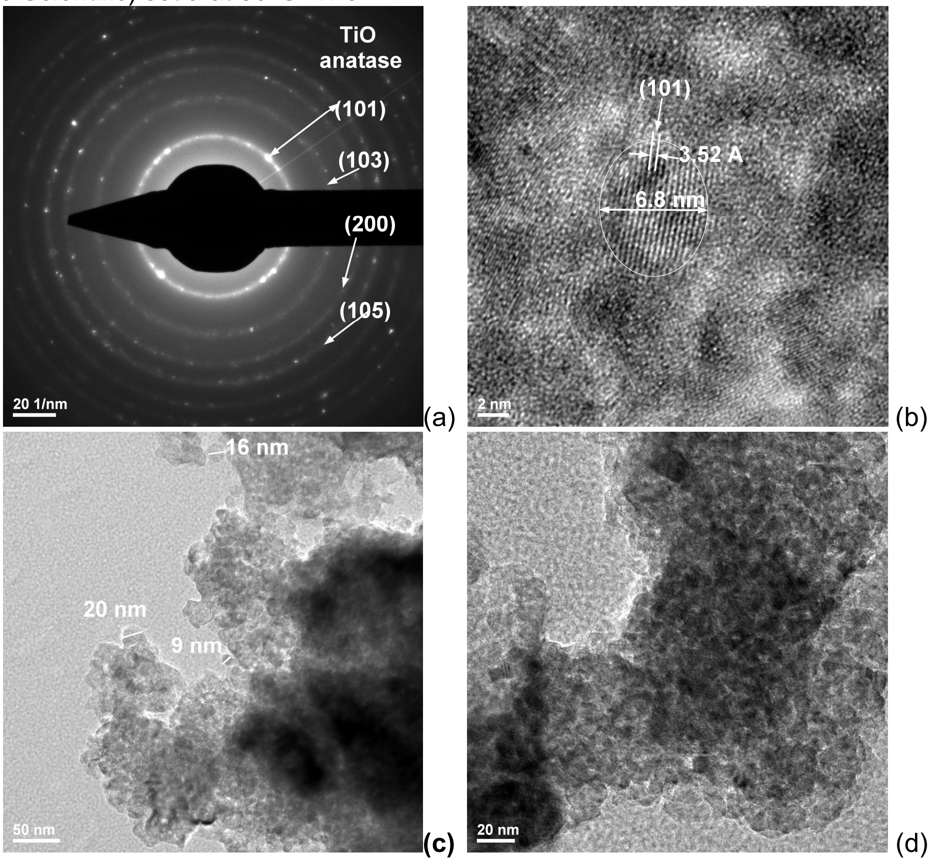


Fig. 2 – SAED image (a), HRTEM (b) and BF-TEM with different scales of measurements: (c) 50 nm, (d) 20 nm of TiO_2

3.2 TEM investigation

Fig. 2a is the SAED image of TiO_2 indexed as a tetragonal structure of anatase and the diffraction rings correspond to the diffraction planes previously identified by XRD analysis.

The BF-TEM (bright field TEM) and high resolution TEM (HRTEM) images sustain the nanometric particles size, with a mean size of 10 nm (Fig.2 b, c and d). The HRTEM shown in Fig. 2b, shows the lattice spacing of 3,52 Å between adjacent lattice planes corresponds to d-spacing of (101) plane of anatase.

The Fig. 2d shows the nearly monodisperse particles having polyhedral shape which have a small tendency of agglomeration.

3.3 Photocatalytic Degradation of Benzalkonium chloride on TiO_2

By removing the concentrations of C14-BAC and C16-BAC, the photocatalytic performance of TiO_2 was demonstrated. The degradation rate was calculated using the formula:

$$\eta\,\% = \frac{c_0 - c_t}{c_0} x\, 100 \qquad (1)$$

Where c_0 and c_t were the concentration value of the solution at 0 and t time, respectively.

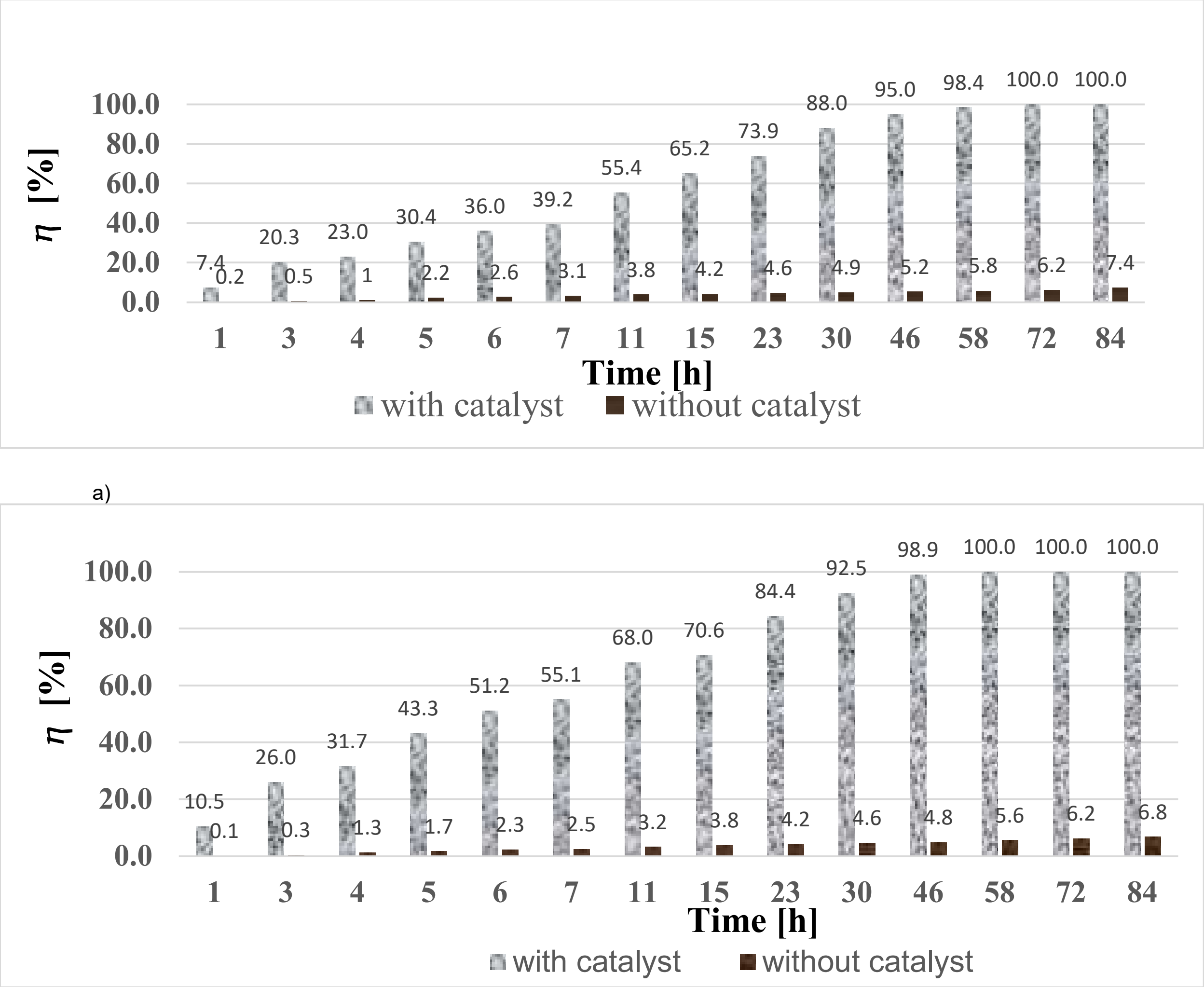
Figure 1 shows the percentage of C14-BAC and C16-BAC removal as a function of time in the absence and presence of TiO_2 powder.

The C14-BAC and C16-BAC may undergo self-degradation under UV-light irradiation. To confirm this, a blank test was performed under UV-light irradiation without using a catalyst. The blank test showed degradation with 5.2% for C14-BAC and with 4.8% C16-BAC respectively, which is a negligible amount. The C14-BAC and C16-BAC degradation in the wastewater treatment process after 46 hours were 95.0% and 98.9 % respectively. After 58 h the efficiencies of the wastewater treatment processes for both compounds tested was 100 %.

The degradation of C14-BAC and C16-BAC is performed according to first order kinetics (Figure 3), defined by the above equation [10]:

$$C_t = C_0 \cdot e^{-kt}$$

where k ($hour^{-1}$) is defined as a constant of the rate of degradation of the compound. This constant (k) can be calculated from the slope of the line obtained by plotting a -ln (C / C0) as a function of the time of the irradiation time (t), as can be seen in Figure 4.



a)

b)

Fig. 3 - Degradation of C14-BAC a) and C16-BAC b) in the absence and presence of TiO_2 under UV-light irradiation.

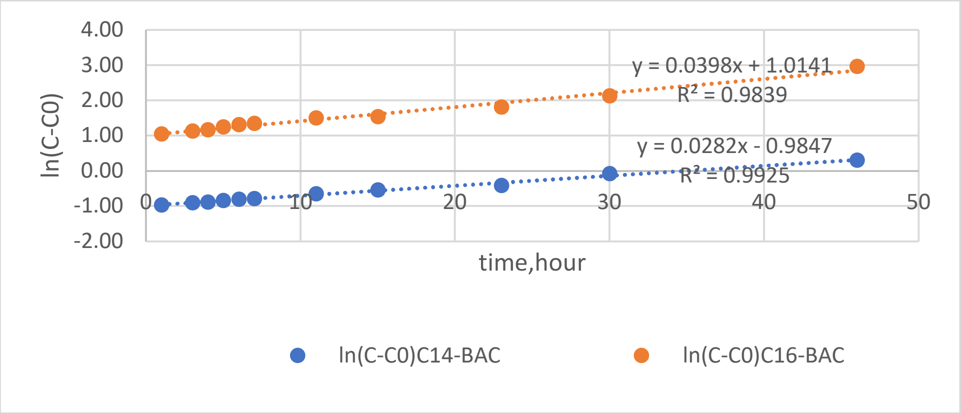


Fig. 4 - First-order plot of C14-BAC and C16-BAC photocatalytic degradation.

The correlation coefficients (R^2) were 0.9839 for C14-BAC and 0.9925 for C16-BAC which indicates

The half-life (t1/2) was determined using the equation below [10]:

that the degradation of this compounds follows the first-order kinetic model.

$$t_{1/2} = \frac{\ln 2}{K}$$

Table 1

The first-order degradation rate constant (k) and half-life ($t_{1/2}$) for C14-BAC and C16-BAC photodegradation by TiO_2.

Cationic surfactant	k, hour^{-1}	$t_{1/2,}$ hour	R^2
C14-BAC	0.0398	7.56	0.9839
C16-BAC	0.0282	10.67	0.9925

The kinetic data resulting from Figure 4 on the degradation rate constant K, and the half-life, t1 / 2, for the photocatalytic degradation of C14-BAC and C16-BAC are listed in Table 1.

The treatment of wastewater by photocatalytic degradation of C14-BAC and C16-BAC after 46 hours were 95.0% and 98.9% respectively, reaching to 100 % at the end of the study.

The half-life ($t_{1/2}$) for C14-BAC was 7,56 hours and for C16-BAC was 10,67 hours.

During irradiation, in the presence of the TiO_2 photocatalyst, for both C14-BAC and C16-BAC, a decrease in concentration was observed compared to irradiation without catalyst.

4. Conclusions

The TiO_2 nanomaterial synthesized having 10 nm was tested based on its photocatalytic activity for the treatment of wastewater containing C14-BAC and C16-BAC. The analyses of C14-BAC and C16-BAC during the investigation were done using HPLC-DAD equipment. The obtained results demonstrate the photocatalytic performances considering that the two compounds degraded with yields of 100 %. It can be concluded that the obtained TiO_2 nanomaterial can also be studied for the removal of other organic pollutants from wastewater.

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