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Photocatalytic activity of TiO_2 nanofibers in simulated and real municipal effluents

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ABSTRACT

Improvement of photo-oxidation efficiency and separation ability of photocatalysts is a challengeable issue for the application of TiO_2-based technology in water treatment. A recently developed H-titanate nanofiber (NF) was proven to be a promising catalyst. In this study, adsorption and degradation performances of the NF and commercial Degussa P25 (P25) catalysts were assessed in a laboratory scale photo-reactor. Matrix effect on the photocatalytic degradation of two different compounds, the anionic azodye Congo Red (CR) and the recalcitrant pharmaceutical Carbamazepine (CBZ), was studied in saline water and real municipal effluent. Dark adsorption of CR appeared to be higher in real effluents than in saline water, while CBZ adsorption was negligible in both the matrixes. The two catalysts showed similar photocatalytic activity in saline water and MBR effluent. Opposite matrix effects were found for the degradation of the two model compounds, and the degradation selectivity strongly depended on the initial adsorption step. A weak influence of different anions, but a strong influence of the divalent calcium was found in the photocatalytic system using NF catalyst. The negative influence of the organic substances in the real effluent was proved to remain stable in repeated tests.

1. Introduction

Titanium based photocatalytic degradation and removal of azodyes and other organic pollutants have been extensively studied during the last 2 decades [1]. However, its full scale application still has not been demonstrated in an industrial process. In reviewing developments and potential for this technology, significant technique and economic challenges are mostly related to separation and recovery of the catalyst powder from slurry reactors, low activity of fixed and composite catalysts and inefficient distribution and/or capture of the light [1–3].

While solar photocatalysis seems to be appealing as a low cost option for small scale treatments [1,4], lamp driven process intensification is mandatory for continuous large scale applications. Although the latter option is not as cheap and environmental friendly as solar based processes, the adoption of mild reaction conditions and the lower use of energy and chemicals still make it promising, compared with other advanced oxidation processes [5].

Among different approaches to facilitate the catalyst post separation, the use of titanium nanofibers has been recently proposed [6–8]. These new materials are characterized by surface area in the same range of commercial powders and good separation ability by settling or filtration, allowing for satisfactory photocatalytic activity and low operational costs.

Characteristics of the catalyst particles, such as pH of zero point charge (pH_{zpc}), mean particle size, settling and fouling propensity, can be variable, depending on the synthesis method and operation parameter of photo-reactor system, which influence its photoactivity. The properties of any new catalyst should be assessed and compared to those of other well studied catalysts in order to provide useful information for their practical applicability. In this view, the main objective of this study was to assess the photodegradation activity of a new titanium based catalysts (H-titanate nanofiber), adopted with the specific aim to overcome the post-separation problems. The performances of the nanofiber catalyst were compared with those of the commercial Degussa P25 powder, which has been extensively studied and is considered one of the most active catalysts.

Previous studies on photo-catalytic degradation and decolouration processes were mainly conducted in deionised water and focussed on the optimization of reaction conditions, such as pH, initial reactant concentration, catalyst load and light intensity. The presence of salinity, specific ions and organic compound in the

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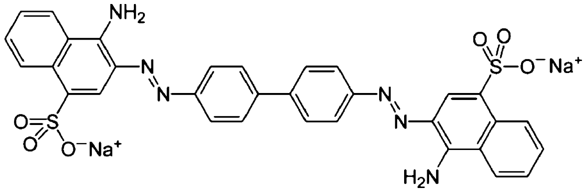
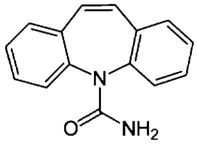
Table 1
Chemical structure of the target compounds.

Compound	Developed structure
Congo Red	
Carbamazepine	

real water can influence the characteristics of the catalyst surface and its interaction with the reactant. A few studies focused on the impact of different anions on photo-oxidation performance [9–15], while the effect of common non-reactive cations (such as Na^+ and Ca^{2+}) has been seldom investigated [13,15,16]. Depending on the nature of the target chemicals (anionic, cationic or neutral) and pH, it has been proposed that inorganic ions have detrimental effects due to competition with the substrate in the initial adsorption step [9,11], formation of ionic double layer [14] and blocking the active sites on the catalyst surface [9,12,13]. At neutral pH, the scavenging of hydroxyl radicals by inorganic anions seems to be negligible [14], while sulphate and phosphate can form reactive radical and promote the oxidation of organic pollutants [17].

These studies typically refer to the matrix effect of different ions in single salt/single target solutions. As pointed out by Gaya and Abdullah [18], although pollutants are typically found in mixtures, only a limited number of studies have been carried out using synthetic mix, natural waters and effluents from biological treatments [among other 10,19–22].

The nanosized catalyst particles tend to aggregate due to van der Waals attractions existing between the particle surfaces [23,24]. It has been demonstrated that the presence of salts promotes this natural aggregation tendency [1,25], with consequent reduction of catalyst surface area and photo-catalytic activity. Despite this, there are very few studies found in the literature which evaluated the effects of ionic strength [25,26], or buffered the salinity while studying the influence of different ions. For these reasons, it is difficult to interpret or compare previously reported results.

Considering possible applications of the TiO_2 catalysts for the treatment of sewage effluents, we experimentally studied the matrix effect on photo-degradation activity of the new catalyst by adopting both synthetic saline solutions and real effluent from a membrane bioreactor (MBR) fed on municipal wastewater. These allowed us to compare the effect of solutions with similar content of sodium chloride, phosphate and pH and to evidence the effect of ions and organic matter. Although pH is a very important parameter in governing the interactions between target compounds and catalyst surface, it could be unlikely to change the pH of a great amount of water before and after the reaction in an industrial process. Therefore, the effect of pH was not investigated in this study and buffered systems have been used in most of the tests. Batch photo-catalytic degradation tests were conducted under UVA illumination. Moreover, a sequencing batch operation mode has been adopted to evaluate the long term performances of the new catalyst and assess possible loss of activity due to irreversible adsorption and surface inactivation in real wastewater.

2. Materials and methods

2.1. Photo-catalysts

Hydrogen titanate nanofibers were synthesized through a hydrothermal reaction between NaOH (10 M) and TiO_2 at 180 °C for 48 h [27]. Then, ion exchange with hydrochloric acid (0.1 M) was performed to convert the sodium titanate nanofibers to their hydrogen form. The fibers were then washed with deionised water until neutral pH, dried at 80 °C and calcined at 700 °C for 3 h. The obtained anatase nanofibers retained the fibril morphology of the sodium titanate, with diameter in the range of 10–50 nm and length in the range of 1–10 μm. The specific surface area and pH_{zpc} of the synthesized catalyst were found to be 15.7 m^2/g and 4.6, respectively. In comparison, higher values of both these parameters have been reported for the commercial TiO_2 Degussa P25 (55 ± 15 m^2/g and 6.4 ± 0.4, respectively).

2.2. Pollutants and matrix

The chemical structures of the two model compounds adopted for this study are reported in Table 1. Congo Red (CR, Labchem Ajax Finechem, Australia) is an anionic azodye and is also used as pH indicator. Its colour changes at pH around 4 ($pK_a = 4.1$), due to the protonation of one of the two amino groups of the molecule. Carbamazepine (CBZ, Sigma–Aldrich) is a widely used antiepileptic. It is a low polar compound ($pK_a = 13.9$ and water solubility <20 mg/L) and is refractory to conventional biological treatments. In all tests the initial target concentration was 10 mg/L, obtained by dilution of a stock solution (CR) or by direct dissolution of the pure compound in the adopted matrix (CBZ).

Three matrixes have been adopted for this study, as described in the following:

1. deionised water (DW);
2. saline water (SW): NaCl 1 g/L, KH_2PO_4 6 mg_P/L, pH adjusted at 7.5 with NaOH 2 M (final electrical conductivity about 1300 μS/cm);
3. MBR effluent (pH 7.5, COD 30 mg/L, NO_3^- 30 mg_N/L, PO_4^{3-} 6 mg_P/L, electrical conductivity about 1700 μS/cm). The effluent was collected from a lab-scale MBR system fed on real municipal primary effluent [28].

2.3. Experimental device

Photo-reactor was set up in a glass cylinder (1 L), which was equipped with an axial quartz tube holding the UV lamp. Aeration from the bottom ensured mixing and oxygen transfer to reach at least 90% of saturation. The cylinder was immersed in a tempera-

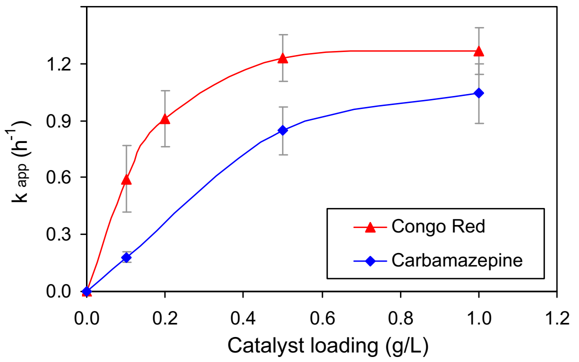


Fig. 1. Effect of titanate nanofibers loading in the degradation of Congo Red and Carbamazepine (both 10 mg/L) in MBR effluent.

ture control system to keep it constantly at 20 ± 1 °C. A 8 W lamp peaked at 360 nm has been used for UVA irradiation (NEC FL8BLB).

Preliminary investigations of adsorption on the catalyst surface have been conducted in small batch (100 mL) under completely mixed condition (magnetic stirrer).

2.4. Analysis

Congo Red concentration was measured using a UV–vis spectrophotometer at 496.5 nm, after removing the catalyst particles by centrifugation at 13,200 rpm (4 min). Carbamazepine concentration was measured using an HPLC equipped with a C-18 column and an UV detector (254 nm), after removing the catalyst by centrifugation and filtration on 0.2 μm. All other analyses were performed according to standard methods.

3. Results and discussion

3.1. Optimization of catalyst loading

It is well known that the photo-degradation rates increase with an increase in catalyst concentration until a constant value is reached [1]. Excess catalyst loading results in unfavourable phenomenon, such as light scattering and reduction of light penetration into the solution [18]. Therefore, to avoid catalyst waste and ensure the total adsorption of efficient photons, the optimum catalyst loading for the adopted system needs to be firstly determined.

As shown in Fig. 1, with the adopted system, only slight improvement can be obtained at a catalyst concentration higher than 0.5 g/L. Hence, the latter was adopted as reference concentration for all of the following tests.

3.2. Comparison of catalyst performances

In comparing the performances of TiO_2 nanofiber (NF) and Degussa P25 (P25), the loading of the commercial powder was chosen to obtain the same dark adsorption and so to better compare the respective photo-degradation activities.

The adopted pH (7.5) is higher than the point of zero charge (pH_{pzc}) of both the catalysts and so their surface is negatively charged according to the following equilibrium:

$$-\mathrm{TiOH} \rightleftharpoons -\mathrm{TiO}^{-} + \mathrm{H}^{+}$$

In the adopted conditions, the adsorption of the low polar Carbamazepine was found to be negligible using both catalysts in both the matrixes (data not shown). Preliminary adsorption test with Congo Red (CR) in deionised water resulted in higher initial adsorption followed by a release until reaching equilibrium values close to that reached in saline water (Fig. 2a). Therefore, it can be assumed that the salinity due to monovalent cations, chloride and phosphate has weak effects on the extent of adsorption, although it appears to favour the equilibrium achievement. This can be explained in terms of balancing opposite effects of the increased ionic strength: the catalyst surface area available for target adsorption can be reduced due to catalyst particle aggregation, while the neutralization of the negative superficial charge of the catalyst results in reducing the repulsion of the anionic dye.

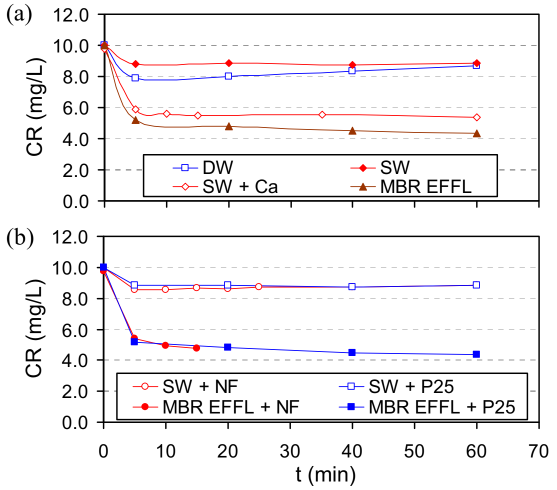


Fig. 2. Adsorption tests with Congo Red and Degussa P25 0.1 g/L in different matrixes (a) and in comparison with titanate nanofiber 0.5 g/L (b).

On the other hand, the increased adsorption of CR in real effluent may be ascribed to the presence of divalent cations (such as Ca^{2+} and Mg^{2+}) and organic substances. As suggested by Li et al. [16], the influence of calcium and magnesium can be explained in terms of ion bridging between the catalyst surface and the anionic dye and between different layers of adsorbant. This was confirmed by our results from testing saline water added with calcium chloride 1 mM (Fig. 2a). Organic compounds that are typically found in real effluents, such as residues of proteins and humic acids, can perform similar functions. Moreover, it has been demonstrated that the natural organic matter can reduce the aggregation tendency of the nanoparticles [29], resulting in enlarging catalyst surface available for interaction with the target compound.

Very similar adsorption trends were found for the two catalysts when changing from saline water to MBR effluent (Fig. 2b), confirming that the hydrated surface of the two catalysts had similar nature and charge and analogous matrix effects took place.

The adoption of different catalysts loading (0.5 and 0.1 g/L for NF and P25, respectively) resulted in different available surfaces, i.e. catalyst concentration multiplied by its specific surface (7.85 and 5.5 m^2/L for NF and P25, respectively). Therefore, the results shown in Fig. 2b suggest that CR was better adsorbed on Degussa P25 than on the nanofiber. The commercial powder had a lower surface charge (because its pH_{zpc} is closer to the pH of the test) and the resulting lower repulsion may explain the better adsorption of Congo Red.

From preliminary degradation tests in real effluent, the photocatalytic activity of the two catalysts appeared to be similar with Congo Red (Fig. 3a), while Carbamazepine was better degraded in presence of the TiO_2 nanofiber (Fig. 3b).

In order to better compare the catalyst performances, the degradation curves can be fitted according to the Langmuir–Hinshelwood model. In case of diluted solutions (i.e. with organics in the range of mM or lower, as in this study), the initial degradation rate typically follows a pseudo-first order kinetic and the apparent rate constant can be obtained by plotting

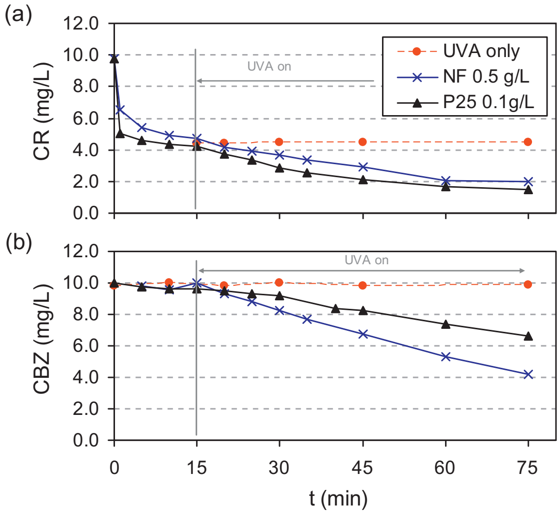


Fig. 3. Degradation of Congo Red (a) and Carbamazepine (b) in real MBR effluent.

the following equation [2]:

$$\ln\left(\frac{C_0}{C}\right) = -k_{\text{app}}t$$

The degradation constants obtained from tests performed with different matrixes/catalysts/targets are resumed in Fig. 4. The matrix effect on the photocatalytic activity appeared to be similar for the two catalysts, with the nanofiber slightly less sensitive to variations of the characteristics of matrix and target compound.

The change from saline water to the real matrix had opposite effects on the degradation rate of CR and CBZ. This opposite trend can be ascribed at the difference in hydrophobicity of the two compounds, leading to different adsorptions and interactions with the catalyst surface. As discussed above, the presence of divalent cations and organic polyelectrolyte can favour the adsorption of ionic compounds, while had no detectable effects on the negligible adsorption of low polar compounds. On the other hand, the aggregation of catalyst particles and blocking of active sites by inorganic ions can also be improved, resulting in reducing the photocatalytic activity. From our results, the positive effect on the adsorption appears to prevail in case of CR, while the degradation of low polar molecules like CBZ seems to be mainly related to the effective active surface.

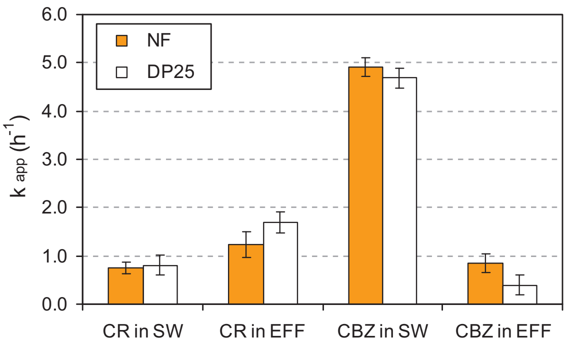


Fig. 4. Observed pseudo-first order constant for photo-degradation of Congo Red and Carbamazepine in saline water (SW) or MBR effluent (EF) and catalyzed by titanate nanofiber (0.5 g/L) or Degussa P25 (0.1 g/L).

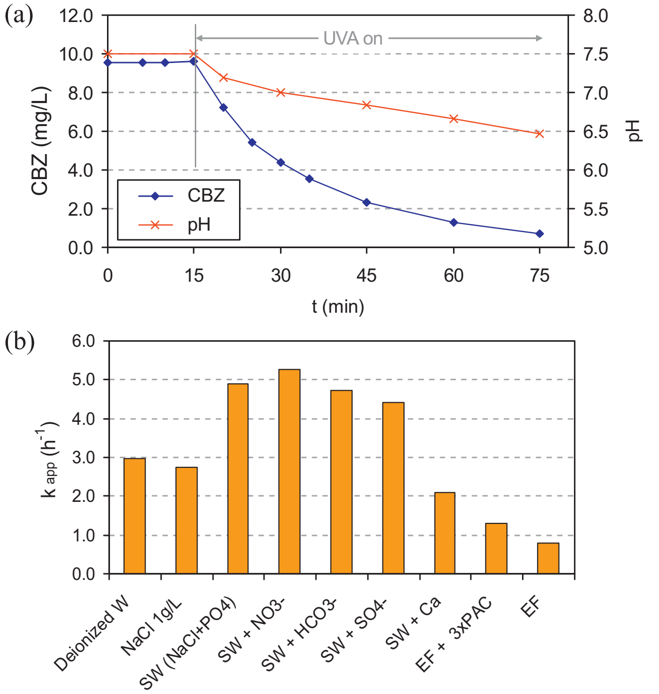


Fig. 5. Degradation of Carbamazepine 10 mg/L in deionised water (a) and comparison of the effect of different ions and real matrix on the photocatalytic activity of titanate nanofibers (b).

3.3. Matrix effect on TiO_2 nanofiber photocatalytic activity

Considering that the adsorption of Carbamazepine was negligible while its degradation was found to be very sensitive to the matrix composition, CBZ was selected as target compound. A set of degradation tests were undertaken in order to evaluate the effect of inorganic ions and natural organic matter on the photocatalytic performance of TiO_2 NF in solutions with similar salinity and buffered pH. To this aim, different salts were added to the saline water (SW) and the added amount was chosen to obtain final anions and cations concentrations within the typical range found in treated wastewaters.

A preliminary degradation test has been performed in deionised water (Fig. 5a). The initial pH was adjusted with NaOH 2M and the system was not buffered. The pH decreased during the reaction, suggesting the formation of organic acids. Similar disappearance curves were obtained for the degradation of CBZ in different saline solutions. These data were fitted according to the pseudo-first order law and the apparent rate constants are compared in Fig. 5b.

As shown in this figure, the addition of sodium chloride (17 mM) to deionised water, despite the considerable increase of electrical conductivity, only resulted in a negligible decrease of the NF photocatalytic activity. Similar results have been generally ascribed at scavenging and interactions with the positive holes formed after the adsorption of photons [5,12,13] or to competitive adsorption on active sites [9]. However, it has been recently suggested that this effect is rather due to the formation of ionic double layer that reduces the target adsorption [14]. As discussed in the previous section, these results can be explained in terms of increase in aggregation of the catalyst particles and decrease in the available active surface due to the increased salinity.

The addition of potassium hydrogen phosphate (0.2 mM) to the same sodium chloride solution resulted in an increased activity of around 40%, while further addition of other anions only resulted in slightly positive (sodium nitrate 2.5 mM) or negative effects (sodium carbonate or sulphate 1 mM). The positive effect of phos-

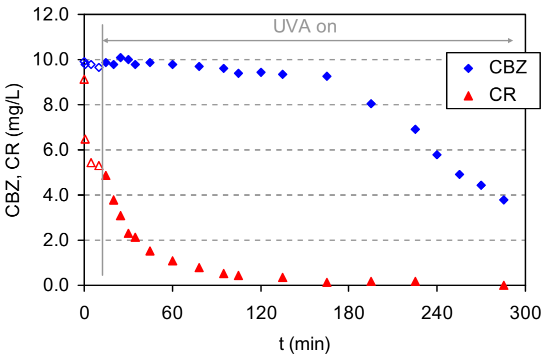


Fig. 6. Simultaneous degradation of Congo Red and Carbamazepine in real MBR effluent.

phate suggests that it could be directly involved in the oxidation of CBZ through the generation of a reactive radical according to the following reaction [17]:

$$h^+ + H_2PO_4^- \rightarrow H_2PO_4^{\bullet}$$

On the other hand, the addition of calcium chloride (1 mM) to the saline water resulted in remarkable decrease in the catalyst activity (Fig. 5b). As suggested in the previous section, the adsorption of divalent cations can increase the aggregation of the catalyst particles. This was obviously detrimental for the photocatalytic degradation of both polar and non/low polar compounds, since it results in reducing the number of active sites. However, in case of the low polar Carbamazepine this is not counterbalanced with increased adsorption, as found for Congo Red. In a similar study on the degradation of phenol at pH 5 [15], it was reported that anions had stronger detrimental effect than cations. This result is only apparently in contrast with our findings, since the titanium dioxide surface is positively charged at pH 5, i.e. below its pH_{zpc}. Therefore, in the latter case the same conclusions can be withdrawn but for anions instead of cations.

The effect of the organic substances in the real matrix have been evaluated by comparing the observed catalytic activity taking place in MBR effluent and in MBR effluent which was treated 3 times with powder activated carbon (final COD below the detection limit of 1 mg/L and unchanged ionic strength). Although a considerable increase in photocatalytic activity can be observed (Fig. 5b), it may be concluded that divalent cations have the greater impact on the photocatalytic performances of the titanate nanofiber.

One of the main advantages of using advanced oxidation processes (including TiO_2/UVA) is that the hydroxyl radicals can demonstrate unselective oxidation performances. The TiO_2 photocatalytic process is also controlled by diffusion and adsorption capability of the catalysts. This can lead to a selectivity towards anionic/cationic and polar/non polar compounds. The contemporary presence of polar and non-polar compounds is common in real treated effluents. Thus, it is important to assess how the selective process can influence the degradation of the target.

In this view, the simultaneous degradation of Congo Red and Carbamazepine in real effluent has been tested. Fig. 6 indicates that NF showed a strong selectivity towards the anionic azodye. The degradation of CBZ only started when all CR was removed from the solution. Moreover, the observed rate constant for the degradation of CBZ was lower than in real MBR effluent without CR, i.e. 0.6 instead of 0.8 h^{-1}. This finding suggests that part of the active sites on the catalyst surface was still occupied in adsorption and reactions with CR and its degradation by-products.

This negative effect needs to be taken into account when the photocatalytic technology is considered of practicable application for water/wastewater treatment and pilot testing is required to assess the effective applicability of the technology.

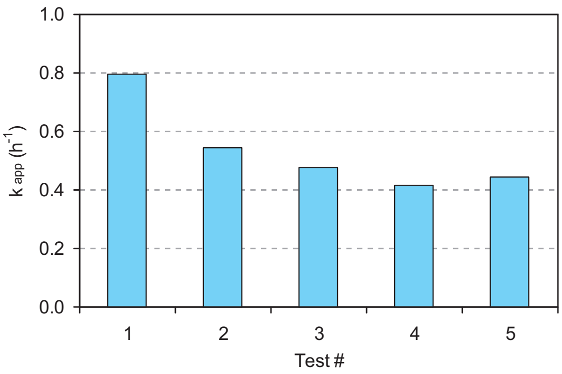


Fig. 7. Repeated test in sequencing batch operation for the degradation of Carbamazepine (10 mg/L) in MBR effluent with titanate nanofibers (0.5 g/L).

3.4. *Repeated tests*

In order to investigate possible de-activation of the catalysts, due to irreversible adsorption on active sites, fouling and catalyst particles aggregation, a long term test was performed in a sequencing batch operation mode, i.e. after every cycle the reacted solution was decanted to allow for discharging the supernatant and feeding fresh solution. From the results of these repeated tests (Fig. 7), it can be concluded that the nanofiber performances in real effluent remained stable after a few cycles. This finding confirms that the NF catalyst could be used in a continuous operation of treatment plant and could be easily recovered based on its good settling properties and filterability.

4. Conclusions

A novel titanate nanofiber has been assessed in terms of its photocatalytic activity and matrix effect of inorganic and organic contaminants.

In comparison with the commercial TiO_2 Degussa P25, the nanofiber performed a similar degradation behaviour, but a lower specific adsorption (per unit of available surface).

Opposite matrix effects were found for the degradation of the two model compounds and, although it is difficult to predict catalyst/target/matrix interactions, it seems clear that the catalyst selectivity strongly depends on the initial adsorption step and that the degradation of low/non polar compound could be strongly hindered.

It was found that monovalent ions slightly affected adsorption and degradation rates. The divalent calcium positively influenced the adsorption of the anionic Congo Red, while it was detrimental for the degradation of the low polar Carbamazepine. This was ascribed to bridging effects that influenced both the interaction with the target compounds and between the catalyst particles (aggregation phenomenon with consequent reduction of the active surface).

The degradation of Carbamazepine in the saline water was found to increase with the addition of phosphate, and resulted scarcely affected by further addition of other reactive anions (nitrate, sulphate and carbonate).

Despite a higher catalyst loading is required to obtain the same performances of TiO_2 Degussa P25, the nanofiber offers the great advantage of being easily separate by settling or microfiltration, allowing for a simpler use in continuous operation. For the full scale applicability of the new material, further investigations are required in order to assess its mechanical resistance, as well as study its selectivity and possible deactivation in long term operations in real effluents.

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