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Reuse of TiO_2-based catalyst for solar driven water treatment; thermal and chemical reactivation

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ABSTRACT

Reuse of photocatalyst and activity-loss in consecutive cycles presents a major hurdle in the environmental application. In this study, thermal and chemical treatments have been investigated as potentially viable methods for photocatalyst reactivation. A composite prepared from titania and iron-exchanged zeolite was used as photocatalyst for diclofenac (DCF) removal under simulated solar irradiation. DCF and total organic carbon (TOC) removal extents, biochemical and chemical oxygen demand were monitored in reuse cycles, for air-dried, and thermally and chemically reactivated photocatalyst. Thermal reactivation yielded higher DCF and TOC removal extents, while chemical reactivation slightly improved photocatalyst stability and biodegradability in reuse cycles.

1. Introduction

The benefits of semiconductor photocatalysis for the treatment of various pollutants in water are well demonstrated and documented in the literature. The advantages of TiO_2 compared to other metallic semiconductors are numerous, including non-toxicity, chemical stability and low cost [1–7]. However, one of the commonly overlooked or vaguely explored aspects of TiO_2 for practical applications is the loss of activity in consecutive usage cycles. Reactivation strategies of the deactivated heterogeneous non-photocatalytic catalysts have been well studied and documented [8]. Photocatalysts are susceptible to the same detrimental effects of activity loss. However, due to substantially lower process temperatures involved in photocatalytic water treatment, compared to commercial heterogeneous catalytic processes such as catalytic hydrogenation, dehydrogenation and hydrocarbon cracking, certain causes of activity loss such as coking and sintering are nonexistent. In photocatalytic water treatment, the mechanism of activity loss usually involves the adsorption of oxidation products on the surface of the catalyst [9]. The magnitude of activity loss during consecutive usage cycles depends on the nature [9–17] and concentration of the pollutant [12]. It should be also noted that inorganic salts, such as sulphates, which may be constituents of model or real wastewater matrix, can hamper the activity of the photocatalyst [15].

Reactivation procedures may involve washing or rinsing with water [14,15] or organic solvents [14], treating with aqueous bases [12,13] or hydrogen peroxide [14], thermal treatment [12–16], UV irradiation [17], and UV photooxidation [13]. Metal cations can be complexed with low molecular weight carboxylic acids, which can be a byproduct of photocatalytic degradation of organics in the aqueous medium, and hence desorbed from the surface of the catalyst thereby restoring activity [10]. The applied strategy for catalyst reactivation strongly depends on the nature of the catalytic poison. Washing with water and aqueous bases is a viable strategy for removing of inorganic compounds or low molecular weight organic acids from the photocatalyst's surface. (Photo)oxidation or treatment just by addition of peroxide can be applied for removal of any adsorbed organic on the TiO_2 surface. The aforementioned methods are most efficient for compounds containing many functional moieties, aromatic rings and unsaturated bonds. Complex organic compounds are most susceptible towards hydroxyl radicals generated in the process. Thermal reactivation poses an all around solution being able to greatly or even fully restore the activity of the deactivated photocatalyst. However, care must be taken in order to avoid morphology changes

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at excessively high temperatures. It is well known that anatase, the most photocatalytically active TiO_2 polymorph, undergoes a crystalline phase change around 700 °C to rutile, which is less photocatalytically active than anatase, while higher temperatures lead to a loss of activity altogether [1,2,5].

In this study we applied and compared two reactivation procedures; thermal, as most common, and chemical, using not so widely studied ozone treatment. Since the effectiveness of reactivation treatment may significantly depend on the conditions applied, we have studied how parameters of applied thermal and chemical reactivation treatment influence the activity of immobilized composite photocatalyst, TiO_2-FeZ, which showed enhanced activity under solar irradiation comparing to AEROXIDE TIO_2 P25 [18]. To this purpose, we applied statistical/empirical approach using response surface modeling in order to study potential interactive effects of investigated parameters of applied reactivation treatment, which can not be effectively enlighten by common "one-parameter-at-a-time" approach [3,18–23]. Upon establishing the optimal conditions within investigated parameters range for each of applied reactivation treatments, we compared the activity of such reactivated TiO_2-FeZ through consecutive cycles with ordinary reused photocatalyst. The activity of fresh, reused and reactivated of TiO_2-FeZ was studied within solar/TiO_2-FeZ/H_2O_2 process for the treatment of diclofenac (DCF), recently added pharmaceutical to the first "watch list" of priority substances in water regulated by EU Water Framework Directive [24]. DCF is selected as a model organic pollutant because is produced and consumed in large quantities worldwide owned to its therapeutic benefits, while conventional (waste)water treatment technologies shown to be insufficiently effective regarding its removal, causing its presence in natural waters exhibiting adverse effects to human health and the environment [25–27].

2. Materials and methods

2.1. Chemicals

The following chemicals were used in the study. Diclofenac sodium salt ($C_{14}H_{10}Cl_2NNaO_2$, p.a., Sigma-Aldrich) was used as a target organic pollutant. The composite photocatalyst was prepared using titanium dioxide (AEROXIDE TiO_2 P25, Evonik; BET surface area 90 $m^2 g^{-1}$ [28]), ZSM5 type zeolite (NH_4ZSM5, CVB8014, Zeolyst International; BET surface area 425 $m^2 g^{-1}$ [29]) and ferrous sulfate ($FeSO_4 \times 7H_2O$, p.a., Kemika, Croatia). The binder for photocatalyst immobilization was prepared using ethanol (CH_3CH_2OH, abs., Sigma-Aldrich), titanium tetraisopropoxide (TTIP, $Ti\{OCH(CH_3)_2\}_4$, 97%, Sigma-Aldrich), perchloric acid ($HClO_4$, 70%, Kemika), tetraethyl orthosilicate (TEOS, $Si(OC_2H_5)_4$), 99% GC grade, Sigma-Aldrich), hydrochloric acid (HCl, 36.5%, Gram-mol), and Levasil® 200/30 (colloidal SiO_2, Obermeier). The oxidation agent was hydrogen peroxide (H_2O_2, 30% v/v, Gram-mol, Croatia). Adjustment of pH was performed using HCl. The remaining oxidant was quenched using sodium sulfite (Na_2SO_3, p.a., Kemika), while the determination of bulk iron was preformed using potassium thiocyanate (KSCN, p.a, Kemika). Constituents of the mobile phases for high performance liquid chromatography (HPLC) were methanol (CH_3OH, HPLC grade, Sigma-Aldrich), *ortho*-phosphoric acid (*o*-H_3PO_4, 85% v/v, Sigma-Aldrich) and ultra-pure water obtained from Millipore Direct-Q UV 3 system, Merck, USA.

2.2. Photocatalysts preparation and immobilization

Iron-exchanged zeolite (FeZ) was prepared by solid-state ion exchange using NH_4ZSM5 and $FeSO_4 \times 7H_2O$ by the modified procedure given by Rauscher et al. [30], described in Juretic Perisic et al. [23]. As-prepared FeZ was mixed with commercial TiO_2 in a mass ratio 25.4:74.6, which is determined as optimal in the previous study [18]. Powder mixture was immobilized on the soda-lime glass plates (r = 37.5 mm) applying the low-temperature method described in Kete et al. [31], forming composite photocatalyst, TiO_2-FeZ. At each Plate 4 layers, determined to be the optimal number in the previous study [18], were coated using spin coating (1500 rpm) technique with KW-4A Spin Coater, Chemat Technology, USA.

2.3. Photocatalytic treatment of diclofenac

All experiments involving the treatment of diclofenac (DCF) aqueous solution (c_0 = 0.1 mM) were performed in a water-jacketed (V = 0.09 L and T = 25.0 ± 0.2 °C) batch photoreactor under simulated solar irradiation. The reactor scheme is provided in a previous paper [32]. The reactor was placed under the irradiation source Oriel Arc source, Newport, USA, with Xe lamp of 450 W. The used apparatus was equipped with an Oriel AM1.5 G air mass filter, correcting the output of arc lamp to approximate the solar spectrum when the sun is at a zenith angle of 48.2°. The light intensity was measured to be 124.78 +/− 0.11 mW cm^{-2} using pyranometer CMP21, Kipp & Zonen, Netherland. The experiments were performed at conditions found as optimal in the previous study [18]. The experimental procedure was as follows: pH of DCF aqueous solution was adjusted at 4, then the glass plates with immobilized photocatalyst (TiO_2: FeZ = 74.6: 25.4, with 4 layers) were placed at the bottom of the reactor and reaction solution was spiked with H_2O_2 aliquot to obtain its concentration of 3.88 mM in the system. The mixing of reaction solution was ensured with orbital shaker DOS-20, Neo-lab, Germany (90 rpms). The experiments were run for 30 min in the dark to reach adsorption equilibrium, and thereafter the reaction solution was exposed to the simulated solar irradiation. Samples (500 μL) were taken at −30 (30 min prior irradiation; dark adsorption test), 0 (starting of irradiation) and 15, 30, 45 and 60 min (during irradiation), filtered using Chromafil XTRA RC (25 mm, 0.45 μm, Macherey Nagel, Germany), quenched with CH_3OH and submitted to HPLC analysis. The samples for other analyses performed: TOC, COD, BOD_5 and spectrophotometric determination of iron concentration, were collected at the end of the treatment (60 min), filtered and then submitted to analyses. All experiments were repeated at least three times and averages are reported, while the reproducibility of the experiments was >96.9%. In desorption tests used plates were immersed in DI water (90 mL, pH 8.00 ± 0.05) and placed in shaker for 30 min; the solution was analyzed according to the above described procedure.

2.4. Catalyst reactivation

The glass plates with the immobilized photocatalyst were thermally reactivated after the performed photocatalytic treatment of DCF aqueous solution. Plates were placed on the custom-made stainless steel holder and treated in the laboratory furnace (LP-08, Instrumentaria, Croatia) at conditions set by applied Design of Experiments (DoE). The temperature was varied from 200 to 400 °C, while the time of reactivation varied from 120 to 240 min. After the reactivation treatment, glass plates were cooled down to the room temperature and submitted to the next cycle of DCF photocatalytic treatment under solar irradiation at above stated conditions.

Chemical reactivation was performed by ozonation in aqueous media. To this purpose, the used glass plates with immobilized TiO_2-FeZ photocatalyst were placed on a custom-made Teflon holder, located at the bottom of the batch reactor. The reactor was filled with 600 mL of DI water. The ozone was generated from pure oxygen (>99.5%) by introducing it into the ozone generator