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Sonophotocatalytic degradation of dye C.I. Acid Orange 7 by TiO_2 and Ag nanoparticles immobilized on corona pretreated polypropylene non-woven fabric

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ABSTRACT

This study discusses the possibility of using corona pre-treated polypropylene (PP) non-woven fabric as a support for immobilization of colloidal TiO_2 and Ag nanoparticles in order to remove dye C.I. Acid Orange 7 from aqueous solution. Dye removal efficiency by sonocatalysis, photocatalysis and sonophotocatalysis was evaluated on corona pre-treated fabric loaded with TiO_2 nanoparticles, corona pre-treated fabric double loaded with TiO_2 nanoparticles and corona pre-treated fabrics loaded with TiO_2 nanoparticles before and after deposition of Ag nanoparticles. In addition, the stability of PP non-woven fabric during these processes was investigated. The substrates were characterized by SEM, EDX and AAS analyses. The change of the dye concentration was evaluated by UV–VIS spectrophotometry. Unlike sonocatalysis and photocatalysis, complete dye removal from both solution and non-woven fabric was obtained already after 240–270 min of sonophotocatalysis. Corona pre-treated PP non-woven fabric loaded with Ag nanoparticles prior to deposition of TiO_2 nanoparticles provided excellent degradation efficiency and superior reusability. Sonophotocatalytic degradation of dye in the presence of all investigated samples was the most prominent in acidic conditions. Although this nanocomposite system ensured fast discoloration of dye solution, TOC values of water measured after sonophotocatalysis were not satisfactory because of PP degradation. Therefore, it is suggested to include TOC evaluation in each case study where different supports for TiO_2 nanoparticles are used since these nanoparticles may guarantee the dye removal from solution but the stability of support could be problematic causing even more serious environmental impact.

1. Introduction

Negative environmental impact of municipal and particularly industrial effluents became the issue of serious global concern. Elimination of the effluent pollution requires efficient and cost effective solutions. Industrial effluents commonly contain various toxic organic compounds that are highly stable and mostly resistant to conventional wastewater treatments [1]. Advanced Oxidation Processes (AOPs) such as heterogeneous photocatalysis, Fenton and photo-Fenton oxidation, ozonation, sonolysis and UV/H_2O_2 treatment are very efficient methods for oxidation and mineralization of many resistant organic contaminants [2–6]. AOPs rely on generation and action of highly reactive hydroxyl radicals ($OH^{\cdot}$) which possess great oxidative potential. Hence, they are able efficiently to oxidize organic pollutants and mineralize them to carbon dioxide, water and mineral acids.

Recently, environmental sonochemistry gained much attention due to its safety, cleanness, high penetration ability through aquatic medium and high degradation efficiency without generation of secondary pollutants [1]. Ultrasound has been utilized for degradation of different pollutants including phenols, pesticides, herbicides, pharmaceuticals, organic dyes and pathogenic bacteria [7]. High cost is the major obstacle for industrial scale application of the ultrasound in wastewater treatment. It has been reported that overall cost of the ultrasound exploitation in phenol, dyes and

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trichloroethylene degradation is significantly higher compared to the one that comes up when ultrasonic treatment is combined with other AOPs. Recent studies revealed that combination of sonolysis and heterogeneous photocatalysis i.e., sonophotocatalysis enhances the degradation rate of some organic compounds [1–8]. In other words, sonophotocatalysis seems to be more efficient than sonolysis or photocatalysis alone [6,8]. Both processes generate OH· radicals but through different reaction mechanisms. Ultrasound cavitations induce splitting of water molecules into the H· and OH· radicals. In the case of photocatalysis, OH· radicals are created in the reaction of positive holes generated on the photocatalyst surface under UV irradiation and water molecules [1,6,9]. Synergistic effect of these processes becomes prominent at low ultrasound frequencies (20–100 kHz) and when the photocatalysts is applied in the form of small particles [10]. Namely, particles of photocatalyst facilitate the cavitation phenomena by breaking up the microbubbles into smaller ones. On the other hand, mechanical effect of ultrasound waves induces deaggregation and cleaning of photocatalyst particles. In addition, it increases the mass transfer of pollutant between the solution phase and photocatalyst surface.

Although very efficient in wastewater treatment, photocatalyst nanoparticles are not convenient for the practical use as they require expensive liquid–solid separation due to formation of milky dispersions after mixing with water. In order to avoid additional post-treatment, the immobilization of nanoparticles on various supports is seen as a reasonable solution [11–15]. A wide range of materials have been evaluated as supports including glass [16], activated carbon [17], silica material [18] and polymeric materials [19]. Boutoumi et al. demonstrated that loading of montmorillonite with TiO_2 nanoparticles (TiO_2 NPs) ensured sonophotocatalytic degradation of dye Rhodamine 6G [11]. It was also reported that TiO_2 NPs immobilized on polypropylene (PP) fibers showed higher stability and photodegradation ability than TiO_2 NPs immobilized on Pyrex glass [14].

This study discusses the possibility of immobilization of colloidal TiO_2 NPs on the PP non-woven fabric in order to provide degradation of synthetic dye C.I. Acid Orange 7 in aqueous medium by sonocatalysis, photocatalysis and sonophotocatalysis. In addition, the stability of PP non-woven fabric as a support during these processes was investigated. The material based on PP fibers was chosen as a substrate for NPs immobilization due to good mechanical properties of PP fibers, their thermal resistance and resistance to alkalis and acids, low cost and recyclability [20–22]. PP fibers are hydrophobic in nature and quite inert. Hence, prior to impregnation with colloidal TiO_2 NPs, non-woven fabric was modified by corona discharge at atmospheric pressure. Introduction of polar groups on the surface of PP fibers would enhance the binding of hydrophilic colloidal TiO_2 NPs. In addition, PP fibers were loaded with small amount of Ag NPs since their presence can facilitate the photocatalytic activity of TiO_2 NPs.

2. Experimental

2.1. Materials

PP non-woven fabric (40 g/m^2) was used as a substrate for immobilization of colloidal TiO_2 and Ag NPs. In order to remove the surface impurities, the sample was immersed in ethyl alcohol (Zorka, Serbia) for 10 min at liquor-to-fabric ratio of 40:1 and rinsed with tap and distilled water.

Corona pre-treatment of the PP material (CPP) was performed at atmospheric pressure using a commercial device Vetaphone CP-Lab MK II. PP samples were placed on the electrode roll, rotating at the minimum speed of 4 m/min. The distance between electrodes was 2.3 mm. The power was 700 W and the number of passages was set to 30.

All the chemicals used for the synthesis of colloidal solution consisting of TiO_2 NPs were analytical grade and used as received without further purification (Aldrich, Fluka). Milli-Q deionized water was used as a solvent. The colloids of TiO_2 NPs were prepared in a manner analogous to the one proposed by Rajh et al. [23]. The solution of $TiCl_4$ cooled up to -20 °C was added dropwise to cooled water (at 4 °C) under vigorous stirring and then kept at this temperature for 30 min. The pH of the solution was in the range 0–1, depending on $TiCl_4$ concentration. Slow growth of the particles was achieved by using dialysis against water at 4 °C until the pH of the solution reached 3.5. The concentration of TiO_2 NPs colloidal solution was determined from the concentration of the peroxide complex obtained after dissolving the particles in concentrated H_2SO_4 [24]. Subsequently the colloid was thermally treated in reflux at 60 °C for 16 h.

$AgNO_3$ (Kemika) and $NaBH_4$ (Fluka) of p.a. grade were used without any further purification for the synthesis of colloid of Ag NPs. Colloidal solution consisting of Ag NPs was prepared as described elsewhere [25]. 1.7 mg of $AgNO_3$ was dissolved in 100 ml of water purged by argon for 30 min. Under vigorous stirring, reducing agent $NaBH_4$ (10 mg) was added to the solution and left for 1 h in argon atmosphere. The concentration of Ag NPs colloidal solution was 10 mg/L. In order to get concentration of 5 mg/L, freshly prepared Ag colloidal solution of 10 mg/L was mixed with deionized water (1:1). 5 mg/L Ag NPs colloidal solution was applied to CPP material.

CPP samples were impregnated with TiO_2 NPs (CPP + TiO_2) according to the following procedure: CPP sample was immersed in TiO_2 NPs colloidal solution (0.1 M) for 5 min at liquor-to-fabric ratio of 40:1, squeezed out through laboratory pad (2 kg/cm^2) and dried at room temperature. After 5 min long curing at 100 °C the samples were rinsed twice (5 min) with deionized water and dried at room temperature. This procedure was repeated one more time for getting CPP material double loaded with colloidal TiO_2 NPs (CPP + $TiO_2 \times 2$).

CPP samples were dipped into the Ag NPs colloidal solution (5 mg/L) for 5 min at liquor-to-fabric ratio 60:1 and dried at room temperature. The liquor-to-fabric ratio in this case was higher compared to impregnation with TiO_2 NPs because the concentration of Ag NPs colloidal solution was very low. After 5 min of curing at 100 °C, the samples were rinsed twice (5 min) with deionized water and dried at room temperature. Afterwards, these samples were treated with 0.1 M TiO_2 colloidal solution (CPP + Ag + TiO_2) according to procedure described in previous paragraph. When colloidal TiO_2 NPs were deposited on the CPP fabrics prior to loading of colloidal Ag NPs (CPP + TiO_2 + Ag), only the order of described procedures was switched.

The photocatalytic activity of TiO_2 NPs deposited on non-woven PP fabric pre-treated with corona discharge was examined in aqueous solution of acid dye C.I. Acid Orange 7 (AO7, Cassella). Chemical structure of AO7 is shown in Fig. 1. AO7 is monoazo dye with one sulfonate group.

HCl (Zorka, Serbia) and NaOH (Zorka, Serbia) were used to adjust pH of dye solution.

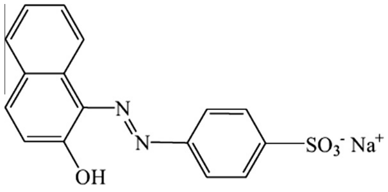

Fig. 1. Chemical structure of dye C.I. Acid Orange 7.