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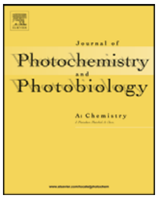

Photocatalytic efficiency of ZnO plates in degradation of azo dye solutions

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ABSTRACT

Tape casting method was used to prepare ZnO plates for photocatalytic degradation of Reactive Orange 16 (RO 16) and Reactive Red 180 (RR 180) textile dyes in aqueous solutions. The plates were sintered at 700 °C and 1050 °C and characterized by using TG-DTA, BET and SEM. The sintering process at 700 °C yields relatively high surface area ZnO plates comparing with the plates sintered at 1050 °C. The photocatalytic activity was enhanced when the high surface area plates were used in photocatalytic degradation processes. Up to 95.7% and 88.6% color removal was obtained in 90 min for the RR 180 and RO 16 aqueous solutions, respectively, when the plates were sintered at 700 °C. Total organic carbon (TOC) removal was 43% at 180 min for RR 180 solution. Photocorrosion tendency was observed to some extend during photocatalysis when multiple tests were performed on the same plate. This corrosive effect was recovered by the memory effect when the plates were subjected to dark interval overnight.

1. Introduction

In recent years, novel heterogeneous metal oxide semiconductor materials such as TiO_2 and ZnO have been developed and attracted considerable attention owing to their photocatalytic ability in the degradation of various environmental pollutants such as dyes, pesticides, detergents, and volatile organic compounds under UV-light irradiation [1–5]. Heterogeneous photocatalysis is a promising new alternative method among advanced oxidation processes (AOPs) which generally includes UV/H_2O_2, UV/O_3 or UV/Fenton's reagent for oxidative removal of organic chemicals [6,7]. Heterogeneous semiconductors in the field of photocatalysis were investigated deeply because of its high efficiency, commercial availability and high chemical stability. When the semiconductor particles are illuminated with UV-light, an electron promotes from the valence band to the conduction band due to photoexcitation, thus leaving an electron deficiency or hole in the valence band; in this way, electron/hole pairs are generated. These electron hole pairs can either recombine or can interact separately with other molecules. Both reductive and oxidative processes can occur at/or near the surface of the photoexcited semiconductor particle [8]. In aerated aqueous suspensions, oxygen adsorbed on the surface of the catalyst acts as an electron trap on the conduction band and electron/hole recombination can be effectively prevented and lifetime of holes is prolonged.

TiO_2 as a semiconductor oxide has been investigated extensively since 1980s and found as very efficient photocatalyst due to its abundant availability, cost-effectiveness and chemical stability. However, current researches show that ZnO can also be used as a very efficient semiconductor photocatalyst when compared with TiO_2 [9,10]. ZnO and TiO_2 have similar band gap energies around 3.2 eV [11,12]. Lower cost and better performance of ZnO in the degradation of organic molecules in both acidic and basic medium have stimulated many researchers to further explore the properties of this oxide in many photocatalytic reactions [13,14]. Therefore, ZnO is very effective as TiO_2 in photocatalytic degradation processes under UV radiation. Some studies have also confirmed that ZnO exhibits a better efficiency than TiO_2 in photocatalytic degradation of some dyes even in aqueous solutions [15–17]. Other advantages of ZnO have also been claimed that it had absorption capacity with larger fraction of solar spectrum than TiO_2 [18]. In some studies it is mentioned that ZnO loses its efficiency because of photocorrosion tendency when it is illuminated with UV-light after test runs more than once [19]. On the other hand, this corrosion tendency can be removed by keeping the catalyst in aqueous solutions in the dark, thereby increasing the efficiency of semiconductor photocatalyst [20]. This process is called memory effect of recovering the catalyst surface which also depends on the time interval.

In many applications, ZnO has been used in the form of fine powders suspended in water. Despite the simplicity of this technique, recovery of the ZnO powders after photocatalytic water treatment is necessary. Due to the cost of recovery operations and the possible powder loss, researchers have used other methods to immobilize ZnO powders on a substrate material [21]. High quality ZnO thin

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films have been prepared by many different techniques such as chemical vapor deposition (CVD) [22], physical vapor deposition (PVD) [23], molecular beam epitaxy (MBE) [24], anodizing [25], sputtering [26] and spray pyrolysis [27]. Considering the simplicity and the costs, these techniques still have disadvantages comparing with the use of powders.

In this study, ZnO powders are shaped into the self-supported plates as an alternative to both powder and costly thin film coating techniques. Tape casting is one of the ceramic processing techniques and is applied to prepare ZnO plates in relatively simple, fast, cost effective and environmentally friendly ways [28–30]. To evaluate the efficiency of the plates in the degradation of model azo dye solutions, commercial azo dyes (namely, Remazol Brilliant Orange 3R (C.I. Reactive Orange 16) and Remazol Brilliant Red F3B (C.I. Reactive Red 180)) were used.

2. Experimental

2.1. Materials

ZnO powder (Fluka) and vinyl-based commercial polymer solution (TC-S1, MSE Teknoloji Ltd. Sti, Turkey) were used for tape casting of the plates. Methyl ethyl ketone/ethanol (MEK/EtOH) was used as a solvent during the processing of the ZnO powders. Remazol Brilliant Orange 3R (C.I. Reactive Orange 16 (RO 16)) and Remazol Brilliant Red F3B (C.I. Reactive Red 180 (RR 180)) dyes were obtained from DyStar and used as-received without further purification. Structures of these dyes were presented in Fig. 1.

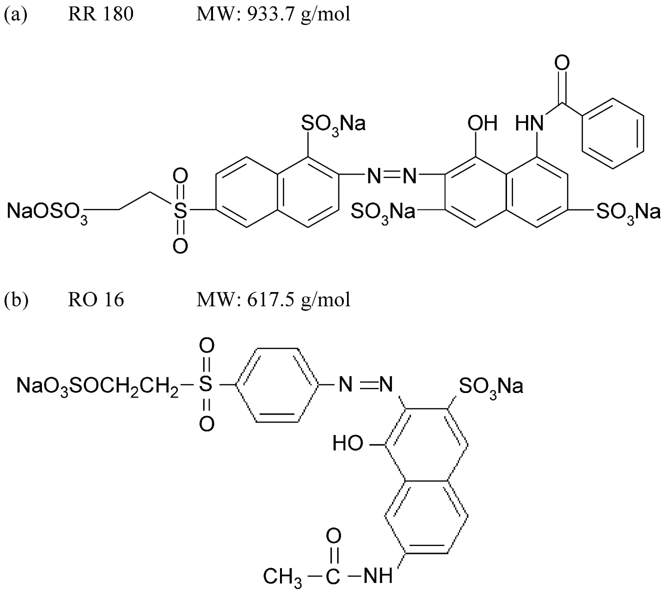

Fig. 1. Structures of Reactive Red 180 (a) and Reactive Orange 16 (b) dyes.

2.2. Preparation of photocatalysts

ZnO powders were mixed with vinyl-based commercial polymer mixture dissolved in MEK/EtOH. The solid content of the mixture was adjusted to 40% by volume. The acquired mixture was then ball milled to obtain a stable slurry. The ball milling was performed for 1 day using zirconia grinding media. After the ball milling, the viscosity of the slurry was adjusted by evaporating some of the excess solvent of the slurry simply by stirring. When the desired viscosity was achieved, the slurry was cast on a flat glass platform with a thickness of 200 μm and at a speed of 10 cm/s by using a doctor blade. The green tapes were cut into a rectangular shape at the dimension of 95 mm × 40 mm. The green plates were prepared using 15 layers of the green tapes and then laminated by applying 8 MPa pressure. Polymer burn-out was carried out by heating samples to 250 °C at 50 °C/h then to 275 °C at 30 °C/h and finally to 600 °C at 45 °C/h. At each step, there was a dwell time of 1 h. The green plates were then sintered at 700 °C and 1050 °C for 1 h to be used in photocatalytic degradation process.

2.3. Characterization of photocatalysts

Before sintering the green plates, thermo-gravimetric/differential thermal analysis (TG-DTA) (NETZSCH STA 409 PC/PG) was performed for binder burn-out process between room temperature and 800 °C at a heating rate of 20 °C/min in air. The microstructures of the sintered samples were observed under scanning electron microscope (SEM) (Philips XL 30SFEG) after the sample surfaces were gold coated by sputtering. The surface area of the plates and ZnO powder were measured by using BET (Quantachrome-Autosorb®-1) technique after the plates were pre-activated for 1 day.

2.4. Photocatalytic reactor setup and degradation procedure

All reactions were performed in a 500 mL capacity batch photoreactor. The laboratory-scale quartz photoreactor was designed in a column shaped in 34-cm height and 4.6-cm diameter. Air

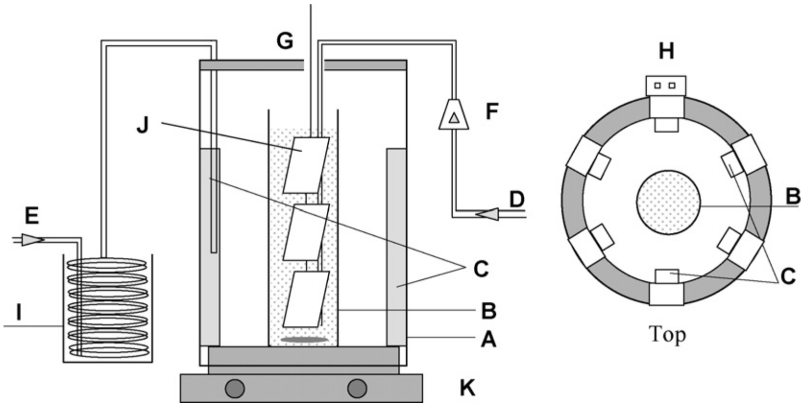

Fig. 2. Reactor used in the photocatalytic experiments: (A) lamp assembly; (B) quartz batch reactor; (C) UV lamps; (D) and (E) air inlet; (F) flow meter; (G) sampling point; (H) switches for lamps; (I) ice bath; (K) stirrer and (J) ZnO plates.

was blown into the reaction solution by an air pump at a flow rate of 150 mL/min to saturate the solution with oxygen during the reaction. Magnetic stirring at a speed of 700 rpm was applied to solution. The reactor assembly was surrounded by six UV-A type lamps which predominantly emit waves at 365 nm (8W, Philips TL 8W/08 F8T5/BLB). The lamps are located equally in an aluminum sealed tube in hexagonal position to enhance the radiation by reflection. Schematic representation is shown in Fig. 2. The light intensity of all six lamps was measured using UV-light meter (Lutron UVA-365) inside the quartz reactor and found as 3.55 mW/cm^2. Blowing cooled air between the lamps and the quartz reactor eliminated heat effect of the lamps and kept the temperature at around 25 °C.

For photocatalytic color removal and degradation process, the dye concentrations were prepared as 500 mg/L and adjusted to desired concentrations. Three ZnO plates were attached to the reactor by immersing them into the solution vertically using a Teflon cord.

2.5. Analytical methods

Color removal efficiency of RO 16 and RR 180 dyes was measured using UV–vis spectrophotometer (Hach-Lange DR 5000) at λ_{max} = 495 nm and λ_{max} = 525 nm, respectively. For mineralization efficiency carbon content of the dye solutions during the process was measured by total organic carbon (TOC) (Hach-Lange IL-550) analyzer.

3. Results and discussion

3.1. Characterization of photocatalysts

3.1.1. TG-DTA analysis of ZnO plates

TG-DTA results showed that all the polymers in the green plates were burned-out completely at 480 °C. Since photocatalysis is a surface phenomenon, the semiconductor surfaces should not contain any polymers left from the ceramic processing step. In order to remove the organic contents of the green plates, they were heated slowly up to 500 °C. The green samples were then sintered at 700 °C and 1050 °C.

3.1.2. SEM analysis of ZnO plates

The microstructures of the ZnO plates were observed using a SEM (Figs. 3 and 4). At 700 °C, although the sintering process is not complete, the neck formation is clearly observed, which gives the plates enough strength for handling during the photocatalytic process. In addition, this type of highly porous structure creates relatively high surface area materials (Fig. 3). On the other hand, the sintering process is much more complete at 1050 °C. The microstructure is homogenous with relatively less porosities than 700 °C (Fig. 4). However, this type of microstructure leads to lower surface area materials.

3.1.3. BET surface area analysis for ZnO plates and powder

The surface areas of the plates sintered at 700 °C and 1050 °C were measured to be 2.02 m^2/g and 0.4 m^2/g, respectively. Parallel to the SEM results, BET results show that the surface area of the samples sintered at 700 °C are higher than that of the samples sintered at 1050 °C. Note that the surface area of the as-received ZnO powders was measured to be 5.5 m^2/g.

3.2. Photocatalytic efficiency of ZnO plates

ZnO plates sintered at 700 °C and 1050 °C reflect the effect of surface area in terms of photocatalytic efficiency. In photocatalytic reactions, large surface area is favored since the incident UV-light can interact with more ZnO surfaces, which leads to faster rate of reactions and improved dye decolorization efficiency. Fig. 5 shows that when the plate sintered at 700 °C was used, dye decolorization efficiency in solution was found to be about 95% for RR 180 and 88% for RO 16 in 90 min. On the other hand, the efficiencies of the plates sintered at 1050 °C reached only to 8% for RR 180 and 10% for RO 16 for the same reaction time. These results indicate that the plates sintered at 700 °C are much more effective than the ones sintered at 1050 °C due to highly porous microstructure of the former. Therefore, the plates sintered at 700 °C were selected for further photocatalytic experiments. However ZnO powder result is also given in Fig. 5. ZnO powder amount was calculated based on the surface areas and weight of the plates sintered at 700 °C. It is clear from Fig. 5 that efficiency of powder is higher such that around 95% color removal takes place within 30 min in ZnO powder as compared to 90 min in ZnO plates (700 °C). This distinctive difference can be attributed to more catalyst surface area and light absorption interaction in the powder. In other words surface area inside the plates are less efficient for light absorption and interaction. It should be kept in mind that recovery and re-use of powders are tedious and time consuming.

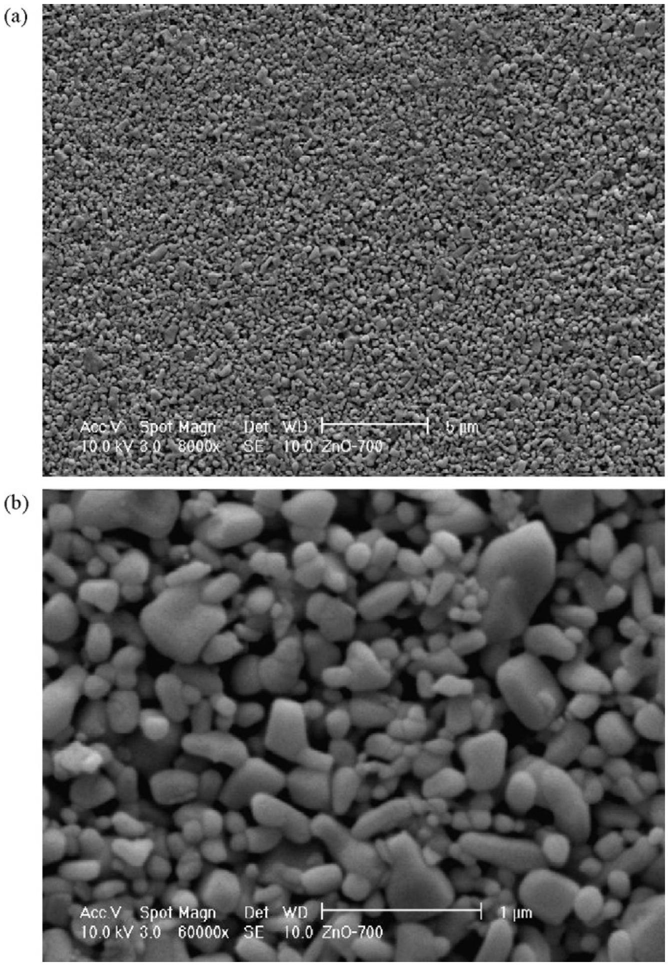

Fig. 3. SEM images of the plates sintered at 700 °C. (a) 8000× magnification and (b) 60,000× magnification.

The effect of the dye concentration on the color removal efficiencies is also investigated for 20 mg/L, 40 mg/L, 50 mg/L and 60 mg/L RR 180 dye concentrations for ZnO plates (Fig. 6). Increasing dye

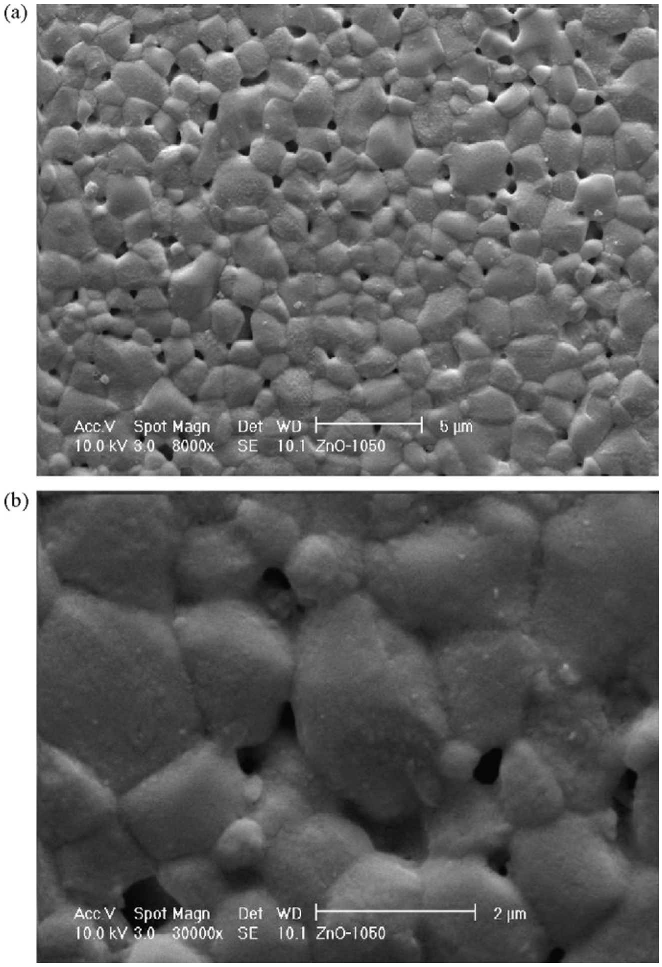

Fig. 4. SEM images of the plates sintered at 1050 °C. (a) 8000× magnification and (b) 30,000× magnification.

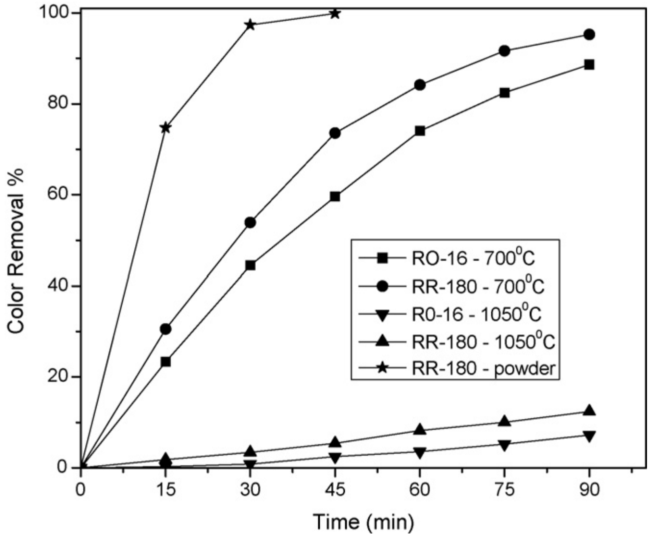

Fig. 5. Color removal efficiency of the plates sintered at 700 °C and 1050 °C for RR 180 and RO 16 dyes and powder ZnO with RR 180 dye only (dye concentration: 20 mg/L).

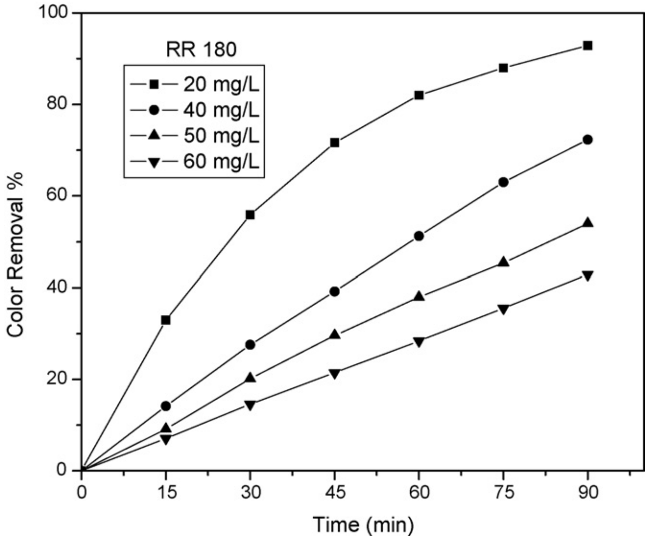

Fig. 6. Color removal efficiency of 700 °C sintered plates with increasing dye concentration.

concentration decreases the photocatalytic efficiency of ZnO plates. The dye concentration affects adsorptive and reactive processes in various manners. The negative effects of the dye concentration depresses the positive ones; the adsorption of dye molecules on the catalyst surface hinders competitive adsorption of OH^- ions, thus, lowering the formation rate of hydroxyl radicals and, consequently, affecting negatively all the steps of the mechanism. Furthermore, as the initial dye concentration increases, the path length of photons entering the solution decreases according to the well-known Beer–Lambert law, resulting in obviously lower photonic absorption on catalyst particles and slower photocatalytic reaction rate [31].

3.3. *Recycling effect of ZnO plates*

The plates sintered at 700 °C are tested for their re-usability effect. The photocatalytic activities of the plates were tested on four runs with 20 mg/L RR 180 dye solutions (Fig. 7). On each

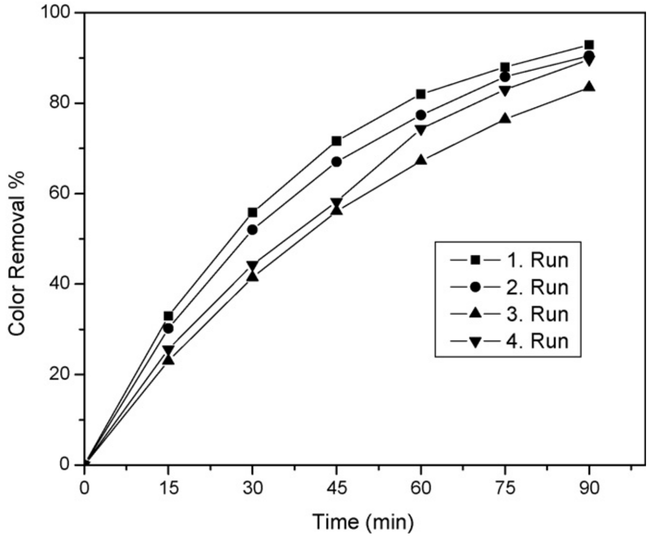

Fig. 7. Color removal efficiency of plates sintered at 700 °C without subjecting the plates to dark interval except for fourth run (dye concentration: 20 mg/L, RR 180).

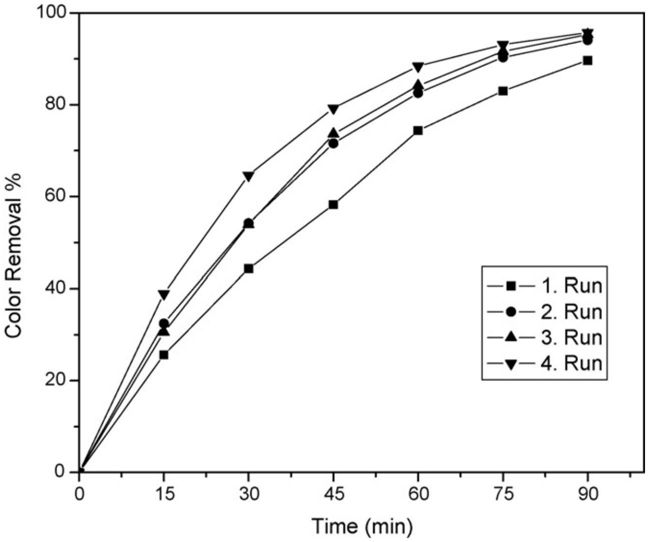

Fig. 8. Color removal efficiency of plates sintered at 700 °C with subjecting the plates to dark interval (dye concentration: 20 mg/L, RR 180).

run after 90 min process time, the plates were subjected to UV-light for 60 min in deionized water in order to remove organic dye molecules remained on the surface. Before the fourth run, however, the plates were additionally kept overnight in the dark in the same deionized water after illumination. The results show that the photocatalytic activity slightly decreases till to the third run. On the other hand, at the fourth run, the efficiency of plates was increased. In order to further investigate the effect of dark interval, this process repeated with next four consecutive runs at the same conditions i.e. between each run, with subjecting the plates to 60 min UV illumination in deionized water and keeping them overnight in the dark. Again the results (Fig. 8) show that the dark interval affects the photocatalytic activity. This activity can be attributed to be a memory effect of the plates when kept under dark interval periods [19,20]. The illuminated surface becomes less negatively charged during the photocatalytic process when the positive holes are drawn to illuminated surface by the space charge layer. On the other hand, when the catalyst is kept under darkness, the crystal gains negative charge. In order to balance the charges when the plates are subjected to UV illumination again, surface diffusion occurs and controls the hole trapping rate, thus leading to the photocatalytic activity to be enhanced.

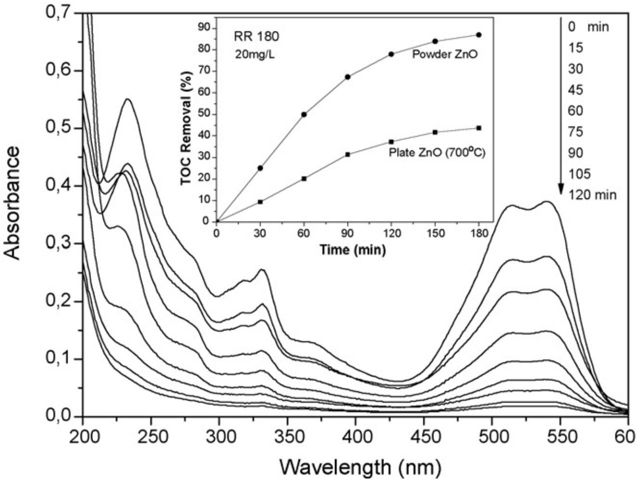

Fig. 9. Absorbance spectrums of the dye solution and TOC removal efficiency during the course of the reaction (inset).

3.4. Mineralization

Apart from decolorization effect of sintered plates, mineralization effect of dye solutions, i.e. degradation of dye molecules to CO_2, water and mineral ions were studied by measuring TOC value of the solution as a function of time. Meanwhile, the progress in the absorbance spectrum of the dye solution was also monitored between 200 nm and 600 nm wavelengths. For both performances, 20 mg/L dye solution concentration was used. Results in Fig. 9 show that reductions in the absorbance peaks indicate the degradation of the dye molecules to smaller intermediates. All absorption peaks were also progressively decreased and no new absorption peaks appeared during the reaction. Intermediate products formed during the dye degradation were also successfully degraded towards to a complete mineralization. However, it is clear from the TOC results (inset in Fig. 9) that a total mineralization needs a longer reaction time.

4. Conclusions

Self-supported ZnO semiconductor photocatalysts in the form of plates were successfully prepared by tape casting method. It was found that the photocatalytic activities strongly depended on the surface area of the plates. Therefore, the specific surface area of the plates was controlled by changing the sintering temperature. Lowering the sintering temperature to 700 °C has not only given the plates enough strength for handling purposes but also the relatively high surface area. It was found that the efficiency of the plates sintered at 700 °C was higher in terms of color removal due to the relatively higher surface areas than that of the plates sintered at 1050 °C (e.g., 2.02 m^2/g vs. 0.4 m^2/g). The other important aspect of making the photocatalysts in form of a self-supported plate is the re-usability of the plates in consecutive multiple photo-degradation processes. Although it was found that the photocatalytic activity of the plates was decreased to some extent after the first run, it could be recovered when the plates were subjected to a dark interval overnight. Therefore, use of semiconductor plates prevented the costly and time consuming removal and recycling processes of the powders after the treatment, and also given the advantage of re-use of the plates repeatedly.

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