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Microwave-assisted degradation of acid orange using a conjugated polymer, polyaniline, as catalyst

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Abstract Microwave-assisted photocatalytic degradation of dyes is one of the emerging technologies for waste water remediation. Microwave effectively accelerates photocatalytic degradation, when microwave electrodeless lamp (MEL) substitutes traditional UV lamp as light source. This setup can be extremely simplified if MEL and photocatalyst can be replaced by a catalyst which can work under microwave irradiation in the absence of any light source. The present work reports for the first time degradation of acid orange 7 (AO) under microwave irradiation using polyaniline (PANI) as catalyst in the absence of any UV lamp as light source. The degradation/decolourization was carried out in neutral acidic and basic media and was monitored spectrophotometrically to evaluate the ability of microwave irradiation to degrade AO. Microwave irradiation showed excellent performance as it completely decolourizes AO dye solution in 10 min. With the advantages of low cost and rapid processing, this novel catalyst is expected to gain promising application in the treatment of various dyestuff wastewaters on a large scale.

1. Introduction

Lately, the use of alternative degradation processes and newer technologies are typically considered to minimize the quantities of pollutants discharged in waste effluents (Lei et al., 2005, 2007; Liu et al., 2007; Bo et al., 2006; Chen et al., 2004). Novel methods of water purification have been used for chemical and photochemical destruction of contaminants (Han et al., 2004; Horihoshi et al., 2002, 2003a). Among the wide variety of green earth and renewable energy projects underway, semiconductor photocatalysis has emerged as one of the most promising technologies because it represents an easy way to utilize the energy of either natural sunlight or artificial indoor illumination (Horihoshi et al., 2003b, 2004).

Microwave heating has been shown to dramatically reduce reaction times, increase product yields, and enhance product purities by reducing unwanted side reactions compared to conventional heating methods. The advantages of this enabling technology have more recently been exploited in the context of multi-step total synthesis (Baxendale et al., 2002), medicinal chemistry (Kappe and Dallinger, 2006), polymer synthesis (Bogdal et al., 2003), material sciences (Perelaer et al., 2006;

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Jhung et al., 2007), nanotechnology (Tsuji et al., 2005) and biochemical processes (Collins and Leadbeater, 2007; Lill et al., 2007). The use of microwave irradiation in chemistry is thus gaining immense popularity in the scientific community (Glasnov and Kappe, 2007).

In the field of catalysis, microwave enhanced photocatalytic technology, has been adopted in combination with electrodeless discharge mercury lamp (EDML) to generate ultraviolet (UV) radiation which can excite TiO_2 for photocatalysis, but also can significantly improve the photocatalytic activity of TiO_2 for removing pollutants (Horikoshi, 2002). In the recent years, microwave enhanced photocatalysis using EDML was considered as an efficiently advanced coupling technology, which has been used to treat organic wastewater (Gao et al., 2007; Zhang et al., 2007).

TiO_2 has drawn much attention of researchers over the past decades due to its excellent photocatalytic activity and long-term chemical stability (Chen et al., 2011; Guttel et al., 2011; Ou et al., 2011; Zarezade et al., 2011) .However, its large band gap of 3.2 eV, has limited its use as an ideal photocatalyst because it is not efficient to absorb visible light with photon energy ~1.7–3.1 eV. To improve its efficiency, conducting polymers such as polyaniline (PANI) and its derivatives have been widely used as photo-sensitizers (Li et al., 2008; MacDiarmid et al., 1985). Conducting polymers have high electron mobility and get easily excited under visible-light illumination. The electrons generated in the π^* orbital of conjugated polymers transfer into the CB of TiO_2, and subsequently react with molecular oxygen and with H_2O to yield superoxide radicals $O^{2\cdot-}$ and OH**.** radicals respectively which enhances the degradation efficiency of TiO_2 (Zhang et al., 2006). Conjugated polymers themselves possess VB and CB similar to that of TiO_2, but microwave energy is of 10^{-5} eV which is enormously less to excite electrons from valence band to conduction band and to produce electron and hole pairs in PANI. PANI is therefore expected to accelerate the degradation of the dye by a different mechanism. Since PANI is easily synthesizable, is much cheaper than TiO_2, and is also environmentally stable, it can replace an UV lamp-TiO_2 combination in the degradation of the dyes. So far no report is available which shows the microwave degradation of the dye solution, in particular Acid Orange 7 (AO) dye, in the absence of a photocatalyst and conventional or electrodeless UV lamp. We have applied microwave irradiation without any electrodeless lamp to degrade AO dye in the presence and absence of a conducting polymer – polyaniline (PANI). This approach has not yet been applied. Microwave irradiation has been variously attributed with nonthermal effect to account for the exceptionally fast organic reactions and higher yield. The unique feature of our system is that microwave irradiation provides a very simple, economic and efficient method for the degradation of dyes using PANI as catalyst in the absence of a photocatalyst and UV–visible radiation.

2. Experimental

2.1. Materials

2.1.1. Experimental

Acid Orange 7 (AO) dye (Sigma–Aldrich, USA) was used as received. All solutions were prepared in deionized distilled water. PANI was prepared as per the reported method (Zhang et al., 2004). Solutions of AO dye of concentrations 100 and 50 mg/L were prepared by dilution of a stock solution of 500 mg/L and were labeled as AO-100 and AO-50 respectively. The solutions were irradiated under microwave in a Ladd Research Microwave oven model LBP-250, USA. The oven was fitted with a factory programed temperature controller, time of heating controller, and a controller for the rate of heating up to the desired temperature of heating, ramp controller, with dimensions as shown in Fig. 1. The temperature was controlled at 30 °C .This microwave read the sample temperature and controlled the same by an 'off' and 'on' mechanism of microwave source. The standard thermocouple was a type "K" and was field replaceable. The solutions were stirred by bubbling O_2 through them and were exposed to microwave irradiation in a batch process for 2, 4, 6, 8 and 10 min.

All the experiments were repeated by adding 200 mg of the conducting polymer, PANI in each solution of AO-100, and AO-50 (50 ml). The solutions were marked serially as PANI-AO-100, and PANI-AO-50 and were shaken for one hour in the dark for establishing equilibrium and then were irradiated at 30 °C in the microwave oven used above under continuous bubbling of O_2. 10 ml supernatant of the PANI-AO dye solution was taken and centrifuged for 10 min at a speed of 5000 rpm and analyzed as the dye solutions without PANI.

3. Characterization

The concentration of the dye was found out by measuring absorbance of the solutions on a spectrophotometer model Shimadzu-UV-1800, Japan, and reading the concentration from a calibration curve. Transmission electron micrographs (TEM) were taken on Morgagni 268-D TEM, FEI, USA. Brunauer, Emmett and Teller (BET) surface area of PANI was obtained using Micromeritics ASAP 2100 with N_2 adsorption at temperature of 77.40 K.

Mineralization of the dye was determined by measuring the total organic content (TOC) of the degraded dye at 10, 20, 30 and 40 min on a Shimadzu TOC-5000A total organic carbon analyzer. For confirming the formation of HO**.** radicals, isopropyl alcohol (PrOH) was added to the dye solution at the rate of 5 and 0.1 mmol/L and decolourization was monitored as in the earlier experiments. Formation of H_2O_2 was confirmed spectrophotometrically (Strylidi et al., 2003).

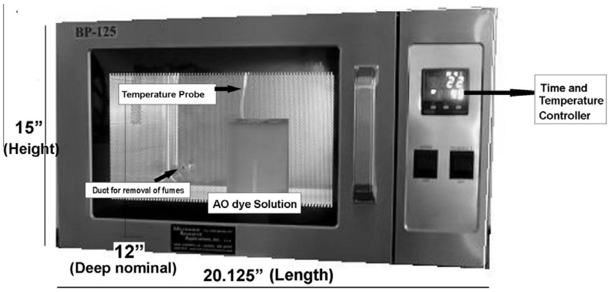

Figure 1 Photograph of the experimental setup of LBP 125 Microwave Oven Reactor.

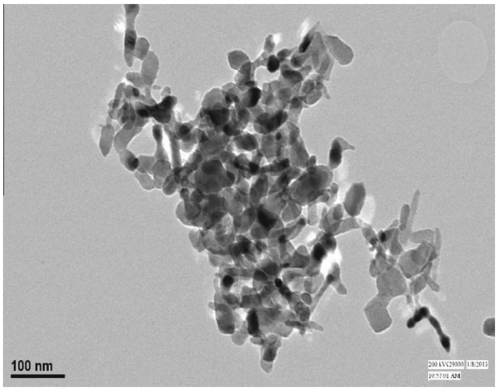

Figure 2 TEM of PANI.

4. Results and discussion

4.1. TEM analysis

The TEM micrograph of PANI, Fig. 2, shows large clusters of elongated PANI nanoparticles of size 35–40 nm. The particles are longitudinally shaped forming a dense self-assembled nanostructure. The resulting particle appears to be interconnected and nearly of the same size. TEM thus confirms the nanosize of PANI synthesized by the template method (Zhang et al., 2006). PANI exhibited considerably high surface area of 90 m^2/g which provides a large surface for dye adsorption and degradation. This is discussed in the proceeding sections.

4.2. UV–vis spectral changes of AO neutral solution with microwave irradiation time in the presence and absence of PANI

AO exhibits a peak at 480 nm in the visible region, corresponding to the azo form (Strylidi et al., 2003). The peak in the ultraviolet region, located at 310 nm corresponds to the naphthalene and benzene rings of AO, respectively (Strylidi et al., 2003; Wu et al., 2000).The UV–visible spectra of the AO-100 and PANI-AO-100 solutions at different times are shown in Fig. 3(a) and (b) respectively. The UV–visible spectra of AO-100 corresponding to the 100 ppm dye solution of AO in neutral medium, Fig. 3(a) show the characteristic absorbance peaks at 330 and 480 nm. The peak at 330 nm is assigned to π–π^* transitions of conjugated double bonds while the peak at 480 nm is typical of a substituted azobenzene. As

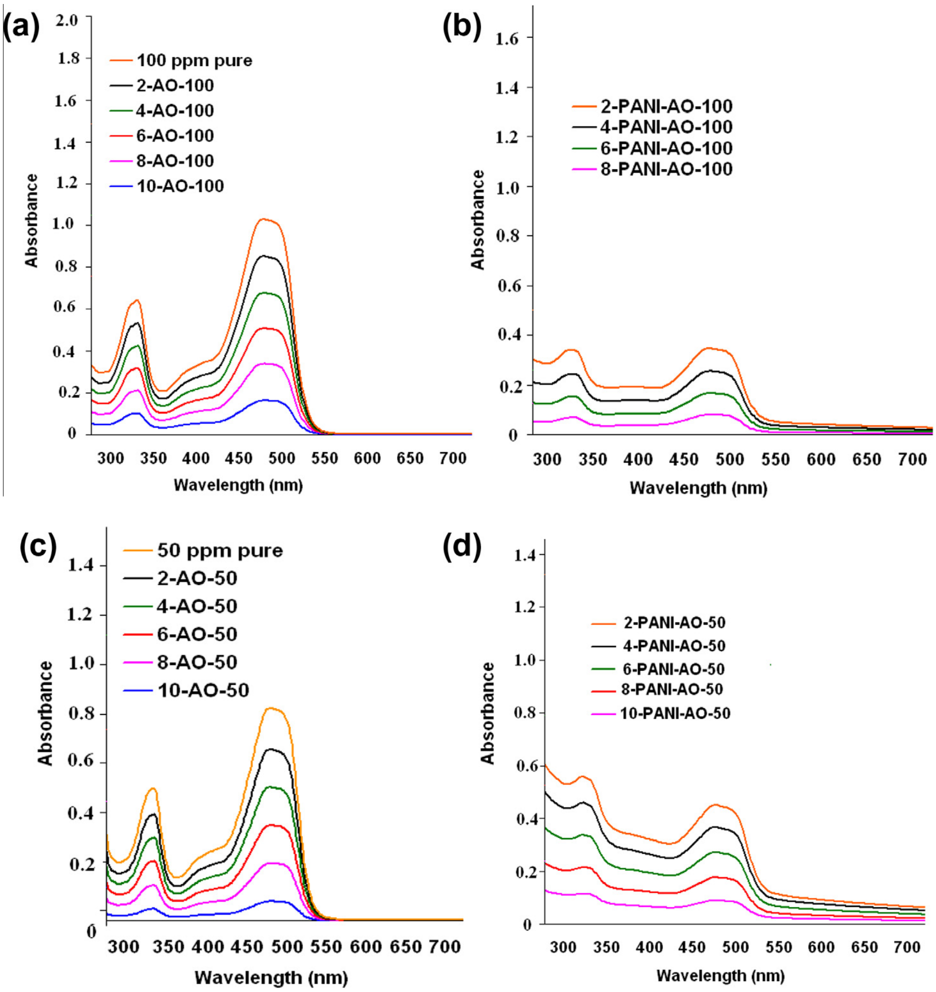

Figure 3 UV–Visible spectra of AO-100 and AO-50 in neutral medium exposed to microwave radiation (a) AO-100 (b) PANI-AO-100 (c) AO-50 and (d) PANI-AO-50.

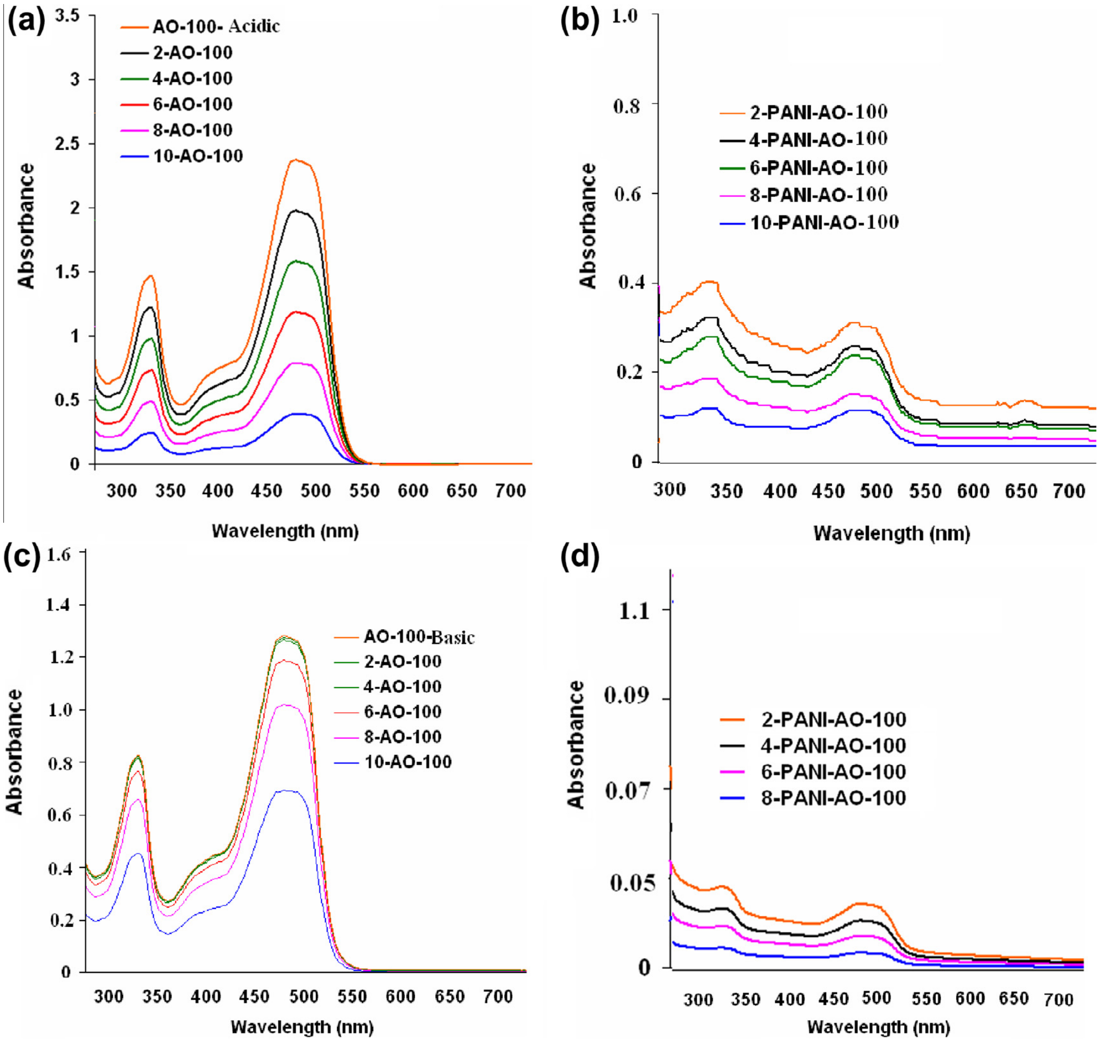

Figure 4 UV–Visible spectra of (a) AO-100 (in acidic medium) (b) PANI-AO-100 (in acidic medium) (c) AO-100 (in basic medium) (d) PANI-AO-100 (in basic medium).

the exposure time is increased from 2 to 10 min, the absorbance maxima decrease in both the peaks. The peak at 330 nm shows a decrease in the absorbance value from 0.5 in 2 min to 0.12 in 10 min while the peak at 480 nm shows a decrease from 0.8 in 2 min to 0.13 in 10 min. The peak in the visible region shows a higher decrease in the absorbance intensity as compared to the peak in the UV region. The UV–visible spectra of PANI-AO-100, Fig. 3(b), show a decrease in the absorbance value from 0.38 in 2 min to 0.10 in 10 min incase of the peak observed at 330 nm while the peak at 480 nm shows a decrease from 0.4 in 2 min to 0.10 in 10 min. The decrease in the absorbance intensity of the peaks in the UV and visible regions confirms the degradation of the AO dye. It appears that upon the addition of PANI, the decrease in the absorbance intensity of the peak in the visible region is enhanced. The decrease in the absorbance intensity of the 480 nm is caused by the chemical modification of the azo group. The decrease in the absorbance intensity of the peak at 330 nm results from elimination of the azo group and modification of the naphthalene ring. It is observed that the absorbance intensity at both λ = 480 nm and λ = 330 nm decreases with time which respectively shows the decolourization and degradation of the dye with time.

4.3. Effect of acidic and basic pH on UV–vis spectra of AO in the presence and absence of PANI

The UV–visible spectra of AO-100 corresponding to the 100 ppm dye solution of AO in acidic medium are shown in Fig. 4(a). As the exposure time is increased from 2 to 10 min, the absorbance maxima decrease in both the peaks. The peak at 330 nm shows a decrease in the absorbance value from 1.3 in 2 min to 0.22 in 10 min. Likewise the peak at 480 nm shows a decrease from 2.0 in 2 min to 0.25 in 10 min. The peak in the visible region shows a higher decrease in the absorbance intensity as compared to the peak in the UV region. The UV–visible spectra of PANI-AO-100, Fig. 4(b), show a decrease in the absorbance value from 0.42 in 2 min to 0.11 in 10 min incase of the peak observed at 330 nm while the peak at 480 nm shows a decrease from 0.35 in 2 min to 0.12 in 10 min. The absorbance intensity of the peaks is found to drastically decrease upon the addition of PANI. The decrease

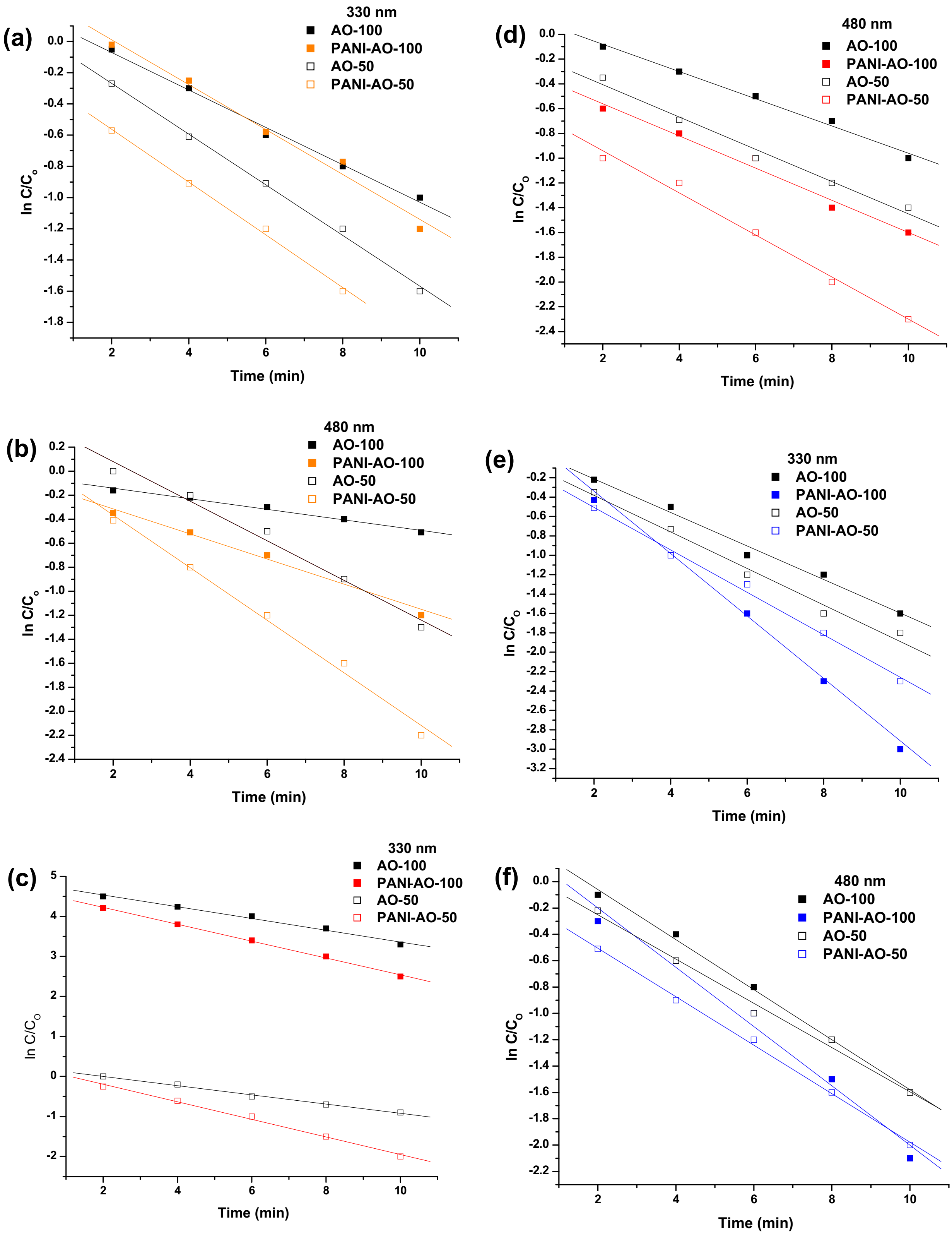

Figure 5 ln C/Co vs. time plot for AO-100, PANI-AO-100, AO-50 and PANI-AO-50 at (a) 330 nm (neutral medium), (b) 480 nm (neutral medium), (c) 330 nm (acid medium), (d) 480 nm (acid medium), (e) 330 nm (basic medium), (f) 480 nm (basic medium).

in the absorbance intensity of the peaks in the UV and visible regions is higher as compared to the neutral media which confirms rapid degradation of the AO dye in acidic medium.

The UV–visible spectra of AO-100 corresponding to the 100 ppm dye solution of AO in basic medium are shown in Fig. 4(c). The increase in the exposure time from 2 to 10 min

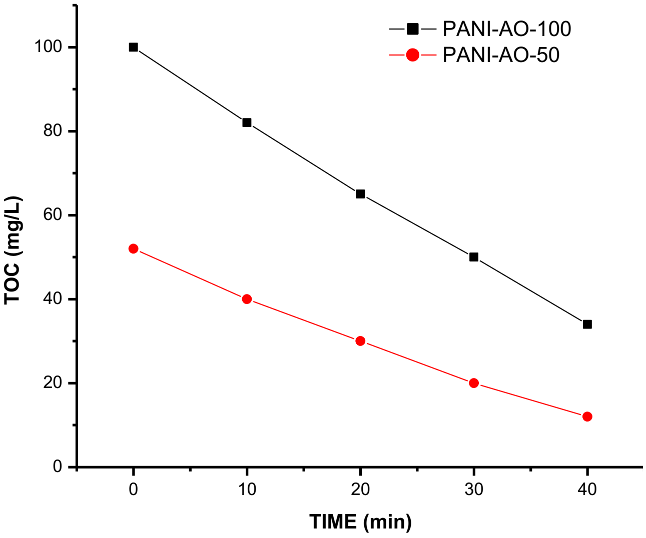

Figure 6 TOC of PANI-AO-100 and PANI-AO-50.

showed a decrease in the absorbance value of the peak at 330 nm from 0.8 in 2 min to 0.4 in 10 min. Likewise the peak at 480 nm shows a decrease from 1.2 in 2 min to 0.6 in 10 min. The UV–visible spectra of PANI-AO-100, Fig. 4(d), show a decrease in the absorbance value of the peak observed at 330 nm from 0.05 in 2 min to 0.03 in 8 min at which the dye solution undergoes complete decolourization. Similarly incase of the peak at 480 nm we observe a decrease in the absorbance value from 0.048 in 2 min to 0.02 in 8 min.

4.4. ln *C*/*Co* vs. time plot

Fig. 5(a) and (b) show ln *C*/*C*o vs. time plot for AO-100, AO-50, PANI-AO-100 and PANI-AO-50 at 330 and 480 nm respectively in neutral medium. The plot shows straight lines for all the dye solutions. The straight lines indicate first order rate kinetics. The *k* values for degradation at λ = 330 nm are slightly different than at λ = 470 nm which shows that the rate of degradation in the two cases differs slightly. The rate constant (*k*) values at λ = 330 nm for AO-100 and PANI-AO-100 were found to be 0.12 and 0.14 respectively and at λ = 480 nm the *k* values were observed to be 0.044 and 0.104 for AO-100 and PANI-AO-100 respectively. Likewise, rate constant values at λ = 330 nm for AO-50 and PANI-AO-50 were found to be 0.16 and 0.17 respectively and at λ = 480 nm, the *k* values were observed to be 0.17 and 0.21 for AO-50 and PANI-AO-50 respectively.

The plots of ln *C*/*C*o vs. time, Fig. 5(c) and (d) reveal the degradation kinetics of AO and PANI-AO under microwave irradiation in acidic medium .The kinetics was found to be of first order in all the cases. The rate constant (*k*) values at λ = 330 nm and λ = 480 nm for AO-100 and PANI-AO-100 were found to be 0.14, 0.21, 0.11 and 0.13 respectively. Likewise, rate constant values at λ = 330 nm for AO-50 and PANI-AO-50 were found to be 0.11 and 0.21 respectively and at λ = 480 nm the *k* values were observed to be 0.13 and 0.17 for AO-50 and PANI-AO-50 respectively.

The plots of ln *C*/*C*o vs. time, Fig. 5(e) and (f) reveal the degradation kinetics of AO and PANI-AO in basic medium. The rate constant (*k*) values at λ = 330 nm for AO-100 and PANI-AO-100 were found to be 0.17 and 0.32 respectively and at λ = 480 nm the *k* values were observed to be 0.19 and 0.22 for AO-100 and PANI-AO-100 respectively. Likewise, rate constant values at λ = 330 nm for AO-50 and PANI-AO-50 were found to be 0.18 and 0.21 respectively and at λ = 480 nm, the k values were observed to be 0.16 and 0.18 for AO-50 and PANI-AO-50 respectively.

The rate of degradation is found to be higher in the solution of 50 ppm AO dye concentration in the presence and absence of PANI. Also the peak in the visible region i.e., 480 nm shows higher degradation as compared to the peak in the UV region. The decolourization/degradation of the dye alone solution in the presence of PANI, therefore, follows the first order kinetics as a similar mechanism of degradation is involved in both the cases. This confirms that the degradation of the azo group occurs faster as compared to the degradation of the naphthalene ring. It is noteworthy that the decolourization/degradation of OG dye in a Ladd Research Microwave oven at 30 °C occurs without conventional catalyst and/or UV–visible light exposure.

4.5. TOC analysis

Fig. 6 shows that AO is progressively mineralized by microwave irradiation in the conditions in the Ladd Research Microwave Oven at 30 °C. PANI-AO-100 mineralized to 65% by 40 min of microwave irradiation; while PANI-AO-50 mineralized to 70% in the same time. PANI provides the surface for the adsorption of the dye, the intermediates, and the oxy free radicals and lowers the interaction energies involved in the degradation of the dye and intermediates that results into mineralization. The presence of hydroxyl free radicals and its participation in the degradation of the dye molecules was confirmed through a scavenger. i-PrOH has been used as a scavenger of the OH free radical. When isopropyl alcohol (5 mmol/L) was added in 100 ml of AO-100 solution and exposed to microwave irradiation, the degradation was completely stopped as no decrease in the intensity of 480 and 330 nm peaks takes place. When isopropyl alcohol (0.1 mmol/L) is added similarly in the dye solutions and exposed to microwave irradiation at 30 °C, dye degraded slowly and intensity of both 480 and 330 nm peaks decreased. H_2O_2 is detected spectrophotometrically (Wu et al., 2000). It is generated by recombination of two OH**.** free radicals or the recombination of an OH**.** and OOH**.** free radicals.

4.6. Change in pH before and after exposure

The pH of the AO dye solutions, Fig. 7(a–c), before and after exposure was monitored to study the change in pH upon microwave irradiation. In case of neutral medium, the AO dye solutions showed a decrease in the pH after exposure, while PANI-AO exposed solutions revealed much lower pH as compared to AO dye solutions. Likewise, in case of the AO acidic dye solutions, the pH was found to increase from 3 to around 5 for AO-dye solutions and to 5.5 for PANI-AO dye solutions. The pH of basic solutions exposed to microwave irradiation was found to be around 7.3 for AO-dye solutions and 6.5 for AO-PANI dye solutions. The change in the pH can be attributed to the generation of H^+ and OH^- ions

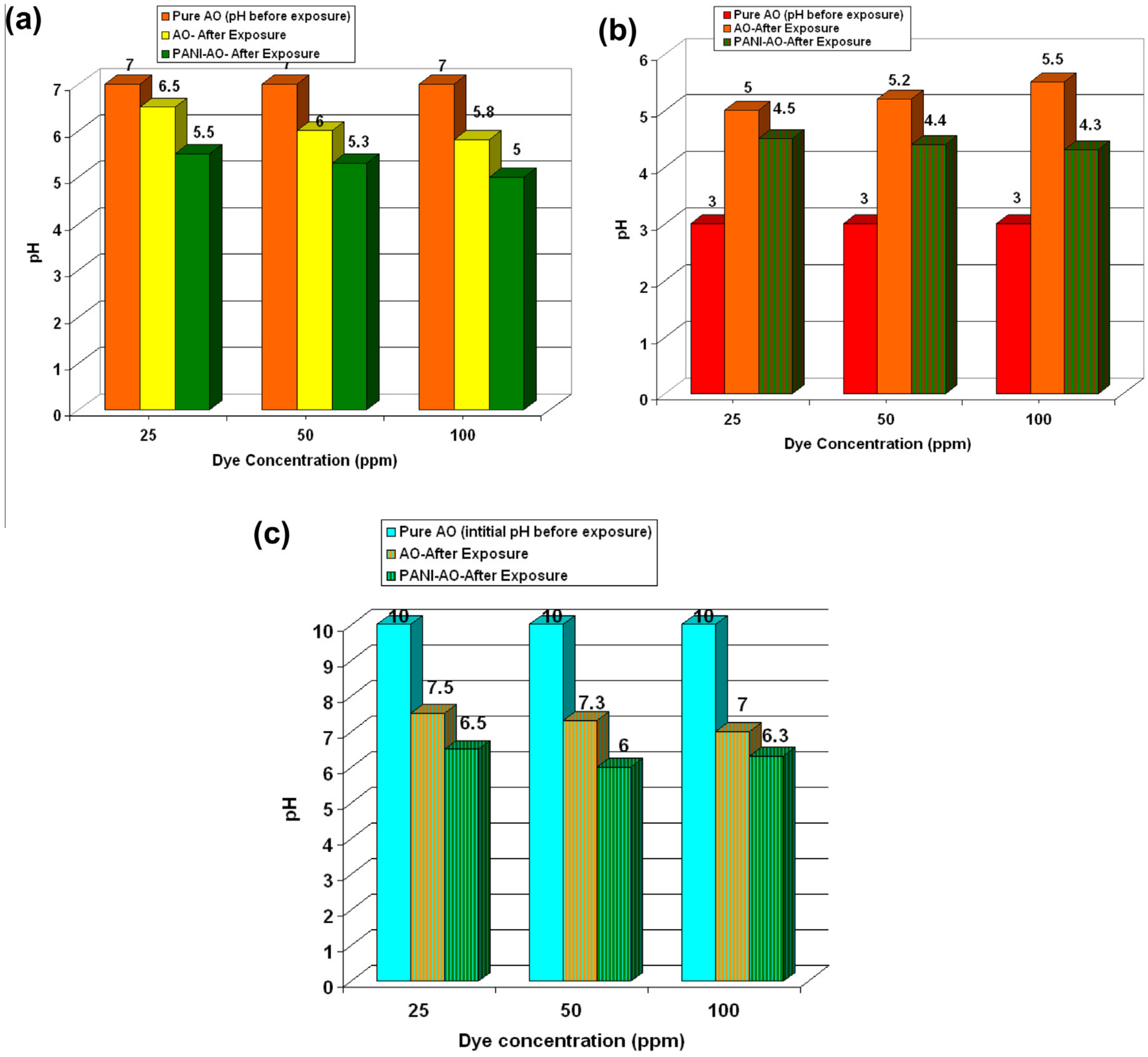

Figure 7 Change in pH upon exposure to microwave irradiation.

consequent to the generation of OH**.** and H**.** free radicals by nonthermal effects of microwave irradiation. These ions lead to the increase in the pH incase of acidic solutions and decrease in the pH incase of neutral and basic solutions. Formation of intermediates during degradation of the dye also contributes in the increase and decrease of the pH.

It has been observed by several authors that nonthermal effect of microwave irradiation enhances the generation of $OH^{\bullet}$ free radicals in microwave assisted photocatalytic degradation of the dyes (Horikoshi, 2002). The microwave degradation of the dye in the absence of UV radiation and a photocatalyst leads to the conclusion that microwave alone also produces OH**.** free radicals by splitting water molecules through nonthermal effect. PANI is a good adsorbent of dye and water molecules. The OH**.** free radicals require low energy to degrade the dye adsorbed on the PANI catalyst surface. This enhances the degradation of the dye. PANI thus behaves as a conventional catalyst in the degradation of the dye. PANI can be regenerated after the mineralization of the dye. We have found that PANI shows same efficiency of mineralization up to 4 cycles. We have not checked the efficiency further.

5. Conclusion

Microwave irradiation shows remarkable decolorization/degradation of AO7 dye. Complete decolorization/degradation of 100 mg/L dye solution was achieved in 10 min. 65% of OG-PNA-100 dye solution mineralized in 40 min under microwave irradiation. The degradation and mineralization of AO7 at 30 °C in the presence of PANI by microwave irradiation show better performance than other reported methods. A large amount of **.**OH free radicals are generated in AO dye solution under microwave irradiation to degrade AO7 dyes effectively. Detailed investigations on the degradation pathway are under progress in our laboratory and will be published soon.

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