

Application of polyaniline/manganese dioxide composites for degradation of acid blue 25 by hydrogen peroxide in aqueous media

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MS received 25 January 2011; revised 1 June 2011

Abstract. The kinetics of catalytic degradation of acid blue 25 dye (AB-25) by hydrogen peroxide using polyaniline/manganese dioxide (PANI/MnO₂) composites was investigated. To optimize the degradation kinetics of the dye, several parameters have been varied: (i) parameters varied during the preparation of PANI/MnO₂ composites include: aniline concentration, acid concentration, acid type, amount of β-MnO₂, stirring time and polymerization temperature and (ii) kinetic variables include: [H₂O₂], dye concentration, amount of composite, pH, addition of salt, and UV-light irradiation. The catalytic activity of the composite is obtained when it has (i) high % PANI content, (ii) high degree of crystallinity, and (iii) high doping ratio. The reaction obeyed second-order kinetics with respect to [H₂O₂], attains a maximum, and decreases thereafter. The degradation decreased when the dye concentration increased. Additionally, the effect of salts on the degradation rate was also studied. The rate of reaction decreases with increasing pH of the medium due to (i) the conversion of ES form of PANI into EB form and (ii) protonated form of the dye is more facial to be oxidized than the deprotonated form. Degradation rate was increased in the presence of UV/H₂O₂ compared to H₂O₂ alone. Mechanism was proposed for the catalytic degradation reaction which is in agreement with the experimental data.

Keywords. Polyaniline/manganese dioxide composite; hydrogen peroxide; degradation; acid blue 25.

1. Introduction

Conducting polymers have become one of the most attractive subjects of investigations in the last few decades (Olad and Nabavi 2007). Their unique properties such as electrical conductivity and electrochemical properties (like metals), mechanical strength and ease of processing (like polymers) and possibility of both chemical and electrochemical synthesis, make them useful in a wide area of applications. Polyaniline (PANI) is one of the most investigated conducting polymers (Šeděnková *et al* 2008). It has been studied frequently because of its low cost, its ease in preparation, good thermal and environmental stabilities, and its versatile applications (Salaneck *et al* 1986; Mac Diarmid *et al* 1987a; Cao *et al* 1992; Ng *et al* 2001).

PANI exists in three oxidation states, such as leucoemeraldine (reduced form), emeraldine (the stable intermediate form), and pernigraniline (oxidized form) (Stejskal *et al* 2009). It has been observed that emeraldine can reduce noble metals compounds to corresponding metals. This fact has been illustrated especially for silver, gold, palladium, platinum and rhodium. The process can be used for the noble metals recovery. Polyaniline has been used as a reductant for the generation of metallic silver from the corresponding silver salts (Dimeska *et al* 2006; Wang *et al* 2007).

Hirao and co-workers demonstrated that polyaniline serves as synthetic metal catalysts in dehydrogenative oxidation under oxygen bubbling (Higuchi *et al* 1997). In addition, Punniyamurthy and co-workers reported that polyaniline supported metal catalyzed aerobic oxidation of alcohols to aldehydes and ketones (Reddy *et al* 2004). Also, the nanoporous conjugate polyaniline with high surface area is effectively used for the dehydrogenative oxidation reaction of benzylamine and benzyl alcohol with or without oxygen (Chi *et al* 2009). The catalytic activity can be controlled by various oxidation states of PANI. After oxidation, the resulting structure of PANI-ES is transformed into pernigraniline base (PB). This result suggests the involvement of radical mechanism by the reversible redox properties of conjugated polyaniline.

Composites of polyaniline with different metal oxides have been investigated and it has been found to improve thermal stability and conductivity properties of PANI (Majid *et al* 2007). Many studies are reported on the preparation of conducting composites such as TiO₂/PANI, ZrO₂/PANI, Fe₃O₄/PANI, zeolite/PANI, MoO₃/PANI, MnO₂/PANI, WO₃/PANI, and Mn₃O₄/PANI (Posudiersky *et al* 2002; Deng *et al* 2003; Chuapradit *et al* 2005; Gemeay *et al* 2005; Xu *et al* 2005; Parvatikar *et al* 2006; Wang *et al* 2006).

Dyes are an abundant class of coloured organic compounds that represent an increasing environmental danger (Khataee *et al* 2009). There are many different classes of dyes such

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as azo, anthraquinone, metal complex and phthalocyanine (Abbasi and Asl 2008). Decolourization of these dyes by physical or chemical methods is financially and often also methodologically demanding, time-consuming and mostly not very effective (Ghodbane and Hamdaoui 2009). Recently, there has been increasing interest in the application of advanced oxidation process (AOPs) as attractive alternative treatments for the degradation of dyes in wastewater. The sonolytic degradation of an anthraquinonic dye, acid blue 25 (AB25), in aqueous phase using high frequency ultrasound waves (1700 KHz) for an acoustic powder of 14 W was investigated (Ghodbane and Hamdaoui 2009). The rate of acid blue 25 degradation was dependent on initial dye concentration, pH and temperature. To increase the efficacy of AB25 degradation, experiments combining ultrasound with Fe (II) or H₂O₂ were conducted. Fe(II) induced the dissociation of ultrasonically produced hydrogen peroxide, leading to additional OH radicals which enhance degradation of the dye.

The objective of this work is to understand the effect of preparation conditions of PANI/MnO₂ composites on the kinetics of oxidative degradation of AB25 with hydrogen peroxide. AB25 was chosen because of its known wide applications (wool, nylon, silk, paper, ink, aluminum, detergent, wood, fur, cosmetics, biological stain) and it often is used as model compound for removing anthraquinonic dyes from aqueous solutions (Ghodbane and Hamdaoui 2010).

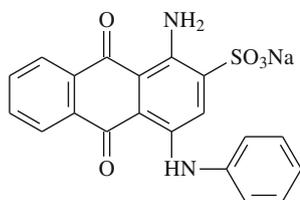
2. Experimental

2.1 Materials

Aniline was distilled under reduced pressure and stored in dark below 4°C. Pure β-MnO₂ (99%, Riedel de Haen) having a specific surface area of 20 m² g⁻¹ was used as received. Hydrogen peroxide (30% w/v, Merck) was used. The initial concentration of H₂O₂ was determined iodometrically using standard Na₂S₂O₃ solution. The desired concentration of H₂O₂ was obtained by successive dilution from the standard stock solution. Acid blue 25 {1-amino-9,10-dihydro-9,10-dioxo-4-(phenylamino)-2-anthracenesulfonic acid, monosodium salt} was supplied from Aldrich. The structural formula of this dye is shown in scheme 1.

2.2 Preparation of composites

Polyaniline/manganese dioxide composites (PANI/MnO₂) were prepared according to the procedure reported in our previ-



Scheme 1. Structure of acid blue 25.

ous works (Gemeay et al 2005, 2007). The composites were characterized using SEM, X-ray, FT-IR, TA, zero point of charge, and magnetic susceptibility

2.3 Kinetic measurements

The kinetic measurements were carried out spectrophotometrically using a UV/visible Shimadzu-2100S recording spectrophotometer. It was equipped with a thermoelectrically temperature controlled cell holder (TCC-260) at high accuracy over a 7–60°C range of temperature. The spectrophotometer operating via a data acquisition system was interfaced to a computer for data storage and processing. The UV-lamp (Vilber Lourmat, 2 × 6 w-254 nm tube) was used as a UV-light source.

In a typical heterogeneous kinetic run, a number of flasks (volume, 100 cm³) containing a definite quantity of the catalyst (PANI/MnO₂ composite) together with doubly distilled H₂O were placed in shaker thermostat to attain the desired temperature. To each flask one ml of separated thermostatted dye and H₂O₂ solutions were added within about 3 s by micropipette and zero time was noted at half the addition point. At regular time intervals, aliquot of each flask was withdrawn and the absorbance was recorded at the corresponding λ_{max} = 603 nm of the dye. Generally, the dye/H₂O₂ mixture was stable for several hours without any noticeable change in the absorbance of dye, which indicates that there is no reaction taking place between dye and H₂O₂ in the absence of the composite.

2.4 Stoichiometry

In CO₂ free doubly distilled H₂O, 10⁻³ M of each dye was allowed to react with 0.5 M of H₂O₂ in the presence of 0.5 g of the composite. After complete colour removal the mixture was filtered off and the unreacted H₂O₂ was determined iodometrically. The complete oxidative degradation of the dye led to the conversion of organic carbon into gaseous CO₂ where the results revealed that about 60% of the dye carbon were degraded and transformed to CO₂. The difference between the observed and the expected quantities of CO₂ was probably due to the persistence of some intermediate products and to loss of volatile one. The sulfate ions were determined gravimetrically by precipitating it as BaSO₄ using BaCl₂ solution (Spadaro et al 1994). The total acid concentration in the mixture was determined by titration with sodium hydroxide and the concentration of HNO₃ was estimated by difference.

3. Results and discussion

Acid blue 25 dye was chosen as a model to study the catalytic activity of PANI/MnO₂ composites. The dye has an absorption maximum at 603 nm. Figure 1 depicts the change

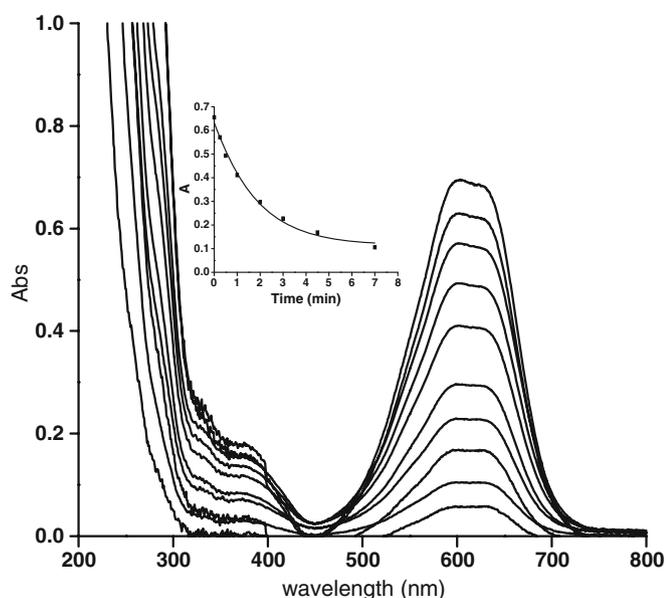


Figure 1. Time resolved absorption spectra during reaction of 2×10^{-4} M of AB-25 with 0.007 M of H_2O_2 in presence of 0.02 g of composite (III) at 30°C .

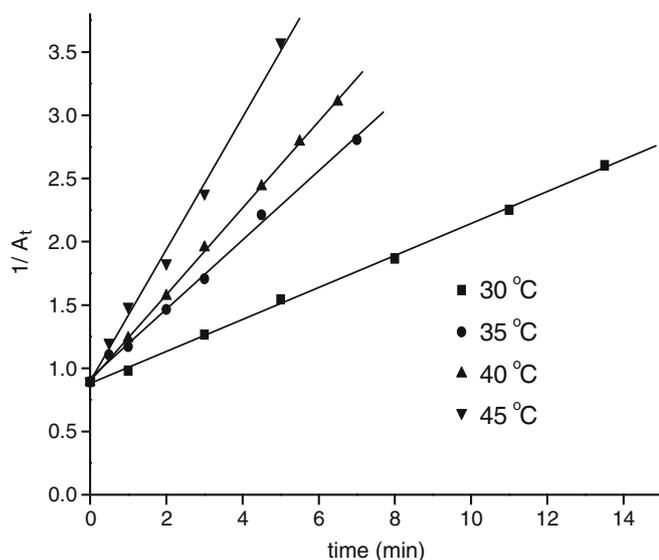


Figure 2. Illustration of first-order plot for reaction of AB-25 (2.0×10^{-4} M) with H_2O_2 (0.007 M) in presence of 0.02 g of composite (III) at different temperatures.

in the absorption maxima of dye solution. Initially, experiments were carried out in the absence and presence of either PANI/ MnO_2 composites or H_2O_2 alone. The results showed no degradation in such individual cases. However, when the two reagents were mixed together in the dye solution, rapid dye degradation was observed. Absorbance-time data gives a best fitting relationship of a second order kinetics (figure 2) with respect to the dye concentration according to (1)

$$1/C_t - 1/C_0 = k_0 t, \quad (1)$$

where $k_0 = Kw$. C_0 is the concentration at time, $t = 0$, C_t the concentration at a given time t , k the second order rate constant, w the mass of the composite. The rate constant k/g of dry composite ($pgdc$) was determined and listed in table 1.

3.1 Variation of PANI/ MnO_2 composites

Several parameters have been varied during the preparation of PANI/ MnO_2 composites in order to establish the optimum conditions to obtain composites having high catalytic activity toward the oxidative degradation of the above dyes. These parameters include: (i) aniline concentration, (ii) acid concentration, (iii) acid type, (iv) amount of $\beta\text{-MnO}_2$, (v) stirring time and (vi) polymerization temperature. The

Table 1. Preparation conditions of PANI/ MnO_2 composites and their abbreviations cited in text.

Preparation conditions	Varied parameter	Composite number	* k ($\text{mol}^{-1} \text{L s}^{-1}$)
$\beta\text{-MnO}_2 = 2 \text{ g}$ $[\text{H}_2\text{SO}_4] = 1.15 \text{ M}$ $t = 25^\circ\text{C}$ Stirring time = 1h	[ANI] M		
	0.43	I	6.87
	0.54	II	9.51
	0.64	III	11.3
	0.76	IV	20.3
	0.87	V	23.9
	0.96	VI	30.6
$[\text{ANI}] = 0.64 \text{ M}$ $[\text{H}_2\text{SO}_4] = 1.15 \text{ M}$ $t = 25^\circ\text{C}$ Stirring time = 1h	$\beta\text{-MnO}_2 \text{ g}$		
	1.0	VII	5.73
	1.5	VIII	8.89
	2.5	VIII	17.2
	3.0	X	23.1
	4.0	XI	29.4
$[\text{ANI}] = 0.64 \text{ M}$ $\beta\text{-MnO}_2 = 2 \text{ g}$ $t = 25^\circ\text{C}$ Stirring time = 1h	$[\text{H}_2\text{SO}_4] \text{ M}$		
	0.57	XII	12.9
	0.64	XIII	15.7
	0.76	XIV	19.1
	0.95	XV	17.6
	1.33	XVI	9.63
	1.52	XVII	8.44
$[\text{ANI}] = 0.64 \text{ M}$ $\beta\text{-MnO}_2 = 2 \text{ g}$ $[\text{acid}] = 1.15 \text{ M}$ $t = 25^\circ\text{C}$ Stirring time = 1h	H_3PO_4	XVIII	0.29
	HCl	XVIII	16.9
$[\text{ANI}] = 0.64 \text{ M}$ $\beta\text{-MnO}_2 = 2 \text{ g}$ $[\text{H}_2\text{SO}_4] = 1.15 \text{ M}$ $t = 25^\circ\text{C}$	HNO_3	XX	45.7
	4 h	XXI	15.9
	10 h	XXII	20.0
	17 h	XXIII	24.3
	24 h	XXIV	28.3
$[\text{ANI}] = 0.64 \text{ M}$ $\beta\text{-MnO}_2 = 2 \text{ g}$ $[\text{H}_2\text{SO}_4] = 1.15 \text{ M}$ Stirring time = 1h	$t = 5^\circ\text{C}$	XXV	40.5

* k_0 is determined for reaction carried out using 0.007 M H_2O_2 , $[\text{dye}] = 2 \times 10^{-4}$ M, 0.02 g of composite.

parameters and abbreviation numbers of the prepared composites are listed in table 1.

The catalytic activity of PANI/MnO₂ composites (I–VI) prepared with variable aniline concentrations has been investigated. Degradation of the dye was carried out at a dye concentration = 2×10^{-4} M, [H₂O₂] = 0.007 M at 30°C using 0.02 g of the composites. Values of k_0 were determined from the corresponding second-order plots and are listed in table 1. The relationship between k_0 and aniline concentration exhibited two characteristic stages as shown in figure 3. This figure demonstrates that k_0 is directly proportional to [ANI] in both stages. At [ANI] < 0.65 M, the slope has a value of 0.232 while at [ANI] > 0.65 M the slope has a value of 0.638. These results can be ascribed to the following aspects: (i) increasing the PANI content in the resulting composites with increasing [ANI]. As we have mentioned before (Gemeay *et al* 2005, 2007), the PANI content increased by about 13% when [ANI] increased from 0.58 M to 0.85 M, (ii) increasing the molecular weight of PANI, the PANI formed at [ANI] > 0.64 M has a higher molecular weight, compared with PANI formed at [ANI] < 0.64 M, (iii) it is well known that the general formula of PANI is $[(-B-NH-B-NH)_y(-B-N=Q=N-)]_{1-y}_x$ in which B and Q denote the C₆H₄ rings in the benzenoid and quinoid forms, respectively (Ayad *et al* 2003). The conducting and oxidized forms of PANI (emeraldine salt, (ES)), can be achieved by protonation of nitrogen in its 50% oxidized emeraldine state ($y = 0.5$, emeraldine base), where x is the degree of polymerization. Thus, increasing the [ANI] can increase the value of x and consequently the doping ratio of PANI. Therefore, the rate constant is increased. To confirm which form of PANI (EB or ES) is the active catalyst in our system, a kinetic run was carried out using PANI/MnO₂ composite which is previously treated with NH₄OH, i.e. the formation of deprotonated form (EB). The run showed no catalytic reaction. This is good evidence that the active form of PANI in our system is the

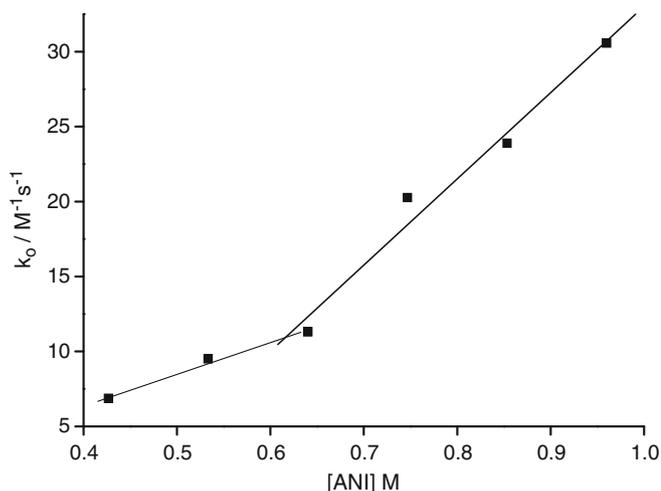


Figure 3. Relationship between [ANI] and rate constant for reaction of AB-25 dye (2.0×10^{-4} M) with H₂O₂ (0.007 M) in presence of 0.02 g of composites (I–VI) at 30°C.

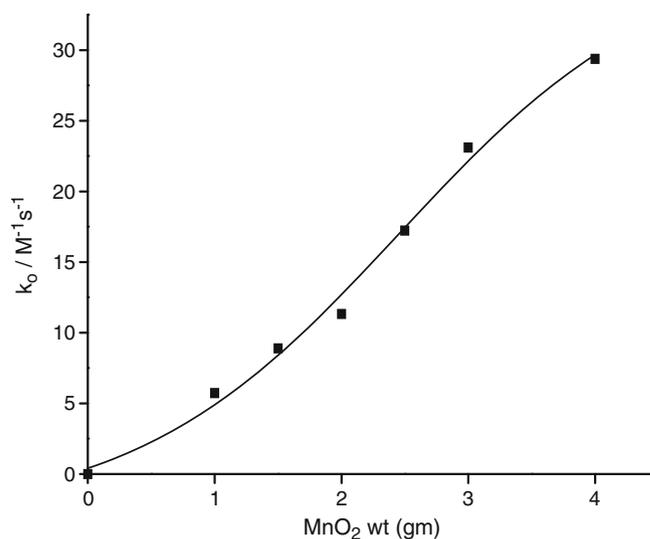


Figure 4. Relationship between amount of MnO₂ and rate constant for reaction of AB-25 dye (2.0×10^{-4} M) with H₂O₂ (0.007 M) in presence of 0.02 g of composites (III and VII–XI) at 30°C.

protonated form of PANI (ES) and (iv) the highly crystalline composite is formed at high [ANI]. This confirms that the catalytic activity of the composites depends on the doping ratio and degree of crystallinity.

The influence of the amount of β -MnO₂ used during the preparation of PANI/MnO₂ composites has also been studied. The kinetic measurements were carried out using composites prepared with different amounts of β -MnO₂ in the (1–4 g) range. The relationship between k_0 and the amount of β -MnO₂ is shown in figure 4, and are listed in table 1. It is clear that the k_0 values increased with increasing amount of β -MnO₂. These results can be ascribed to the following: (i) the composites prepared at high amounts of oxide have high acidic characters due to (a) adsorption of H⁺ on the surface of the oxide, (b) formation of H-bonding between the hydroxyl groups on the surface and amine, imines nitrogen of the PANI, (c) transformation of MnO₂ into MnOOH and (ii) increasing the MnO₂ leads to an increase in the degree of crystallinity of the produced composites, this is attributed to the increase in the PANI content and the doping ratio. Therefore, the catalytic activity of the composite is obtained when it has (i) high % PANI content, (ii) high degree of crystallinity and (iii) high doping ratio.

The effect of initial [H₂SO₄] used as dopant acid during the polymerization reaction has been investigated. As shown in figure 5, the rate constant increased with increasing [H₂SO₄] attaining a maximum at [H₂SO₄] \approx 0.76 M and thereafter decreased. This indicates that the most active composite is that synthesized with 0.76 M H₂SO₄ in the medium polymerization process. It is well known that the acid has an effect on the growth rate and yield of PANI. It was reported that, the higher acid concentration leads to higher extent of the anilinium cations formation as intermediates which play a significant role in favouring rapid transformation of ANI

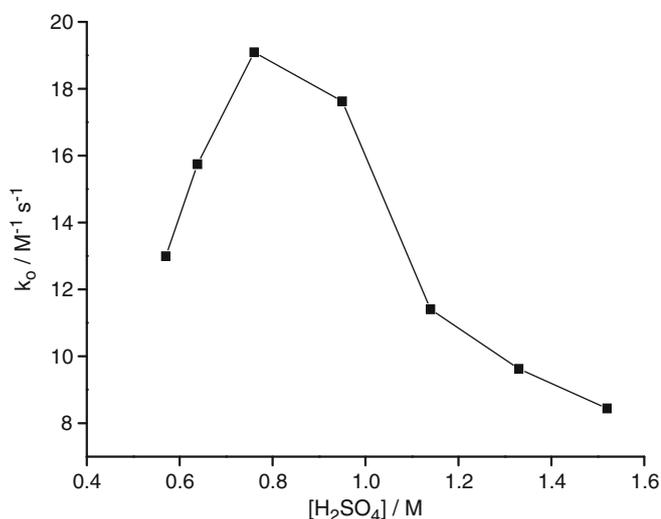


Figure 5. Variation of rate constant, k_0 , with $[\text{H}_2\text{SO}_4]$ for reaction of AB-25 dye (2.0×10^{-4} M) with H_2O_2 (0.007 M) in presence of 0.02 g of composites (XII–XVII) at 30°C .

into PANI (Ghosh *et al* 2001), so the yield of PANI increased with increasing $[\text{H}_2\text{SO}_4]$ until *ca* 0.76 M. While for solutions of $[\text{H}_2\text{SO}_4] > 0.76$ M, increase in concentration of acid leads to the degradation of PANI and consequently low yield of the polymer was obtained (Gemeay *et al* 2005). As reported elsewhere, concentrated sulfuric acid has been used for the dissolution of PANI for the spinning of fibres (Andreatta and Heeger 1991; Hsu *et al* 1999; Brožová *et al* 2008).

It has been proposed that multivalent anions like phosphate can act as a kind of cross-linking centres, because they can simultaneously protonate the imine units in different chains. It has been proposed and proved that PANI protonated with sulfuric acids comprises monovalent hydrogen sulfate anions HSO_4^- , rather than bivalent sulfate anions SO_4^{2-} , also PANI protonated with H_3PO_4 comprises H_2PO_4^- counter ions rather than PO_4^{3-} , and HPO_4^{2-} (Neoh *et al* 1990; Yue *et al* 1992; Prokš and Stejskal 2004). It was found that the composites prepared in the presence of H_2SO_4 , HNO_3 , HCl and H_3PO_4 have different characters. To test these characters, each composite was subjected to the dye solution with H_2O_2 in the medium. The reactivity order of PANI/ MnO_2 composites towards the oxidation of the dye was found to be $\text{NO}_3^- > \text{Cl}^- > \text{HSO}_4^- > \text{H}_2\text{PO}_4^-$. The catalytic order of the composites is in good agreement with (i) strong acid which is beneficial for high yield of PANI while the weak acid has an opposite behaviour and (ii) the reported conductivity of PANI prepared in the presence of different acids follows the order: PANI/ $\text{Cl}^- > \text{PANI}/\text{HSO}_4^- > \text{PANI}/\text{H}_2\text{PO}_4^-$ (Zhang *et al* 2002).

The influence of stirring time during the preparation of PANI/ MnO_2 composites on their reactivity has been considered. It is clear that by increasing the stirring time the catalytic activity of the concerned composites increases (figure 6). It has been reported that the % PANI content increased with increasing polymerization time. It has been

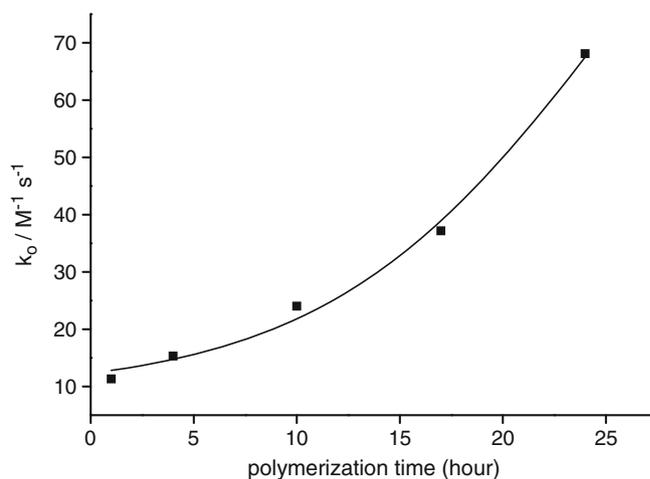


Figure 6. Variation of rate constant, k_0 , with polymerization time for reaction of AB-25 dye (2.0×10^{-4} M) with H_2O_2 (0.007 M) in presence of 0.02 g of composites (XXI–XXIV) at 30°C .

reported that long polymerization time is essential to obtain high molecular weight PANI (Vilenik *et al* 1998). Also, Jin *et al* (2000), reported that the stability of PANI significantly improved by increasing the polymerization time (Jin *et al* 2000).

The polymerization temperature is crucial to obtain PANI which has the morphology of honey combed clews. Most studies have been performed on PANI chemically synthesized at $1\text{--}5^\circ\text{C}$ according to Mac Diarmid *et al* (1987b). This standard PANI in the form of EB is only partly soluble in 1-methyl-2-pyrrolidinone (NMP) (Beadle *et al* 1998). And the soluble part has a low molecular weight, $M_w = 30\text{--}60$ g/mol and large polydispersity, 2.5–3. It has been reported that decreasing the synthesis temperature below -3°C increases M_w of EB to $M_w = 160$ g/mol and a large polydispersity of ≈ 7 . To verify this phenomenon, two composites were prepared at 25°C and 5°C and their catalytic activity toward the oxidative reaction of the chosen dye is investigated. Table 1 clearly indicates a greater enhancement in the reaction rate constant for reaction containing the composite previously prepared at 5°C more than that prepared at 25°C . The enhancement reaches 73.9%. It has been reported that the molecular weight of PANI increased with decreasing polymerization temperature.

The effect of a mild thermal treatment of composite (III) at ($100\text{--}200^\circ\text{C}$) on the reaction rate was investigated. Figure 7 shows decrease in the reaction rate with increasing annealing temperature. The heat treatment of PANI/ MnO_2 composites at elevated temperature leads to destruction of crystal structure (Bhadra and Khastgir 2008). Polymer chain scission, cross-linking quinoid to benzenoid ring conversion and *vice versa* along with doping and dedoping process depended on the heat treatment temperature. All these changes due to heat treatment of PANI are reflected in its change in conductivity and solubility. The heat treatment decreases the crystallinity. Also, it is found that when PANI is heated at 150°C , the

conductivity is decreased to some extent due to the partial oxidation and hence loss of emeraldine sequence and decrease in crystallinity. A large drop of conductivity is observed when PANI is heat treated at 200 °C due to chain scission and/or crosslink formation and hence loss of emeraldine sequence (Boyle *et al* 1992; Bhadra *et al* 2006, 2007). The former causes decrease in the catalytic activity of the annealed composites.

3.2 Effect of kinetic variables

To optimize degradation kinetics of the dye, a systematic study varying the concentration of H₂O₂ was conducted. The degradation rate of AB25 at different H₂O₂ concentrations in presence of PANI/MnO₂ composites is shown in

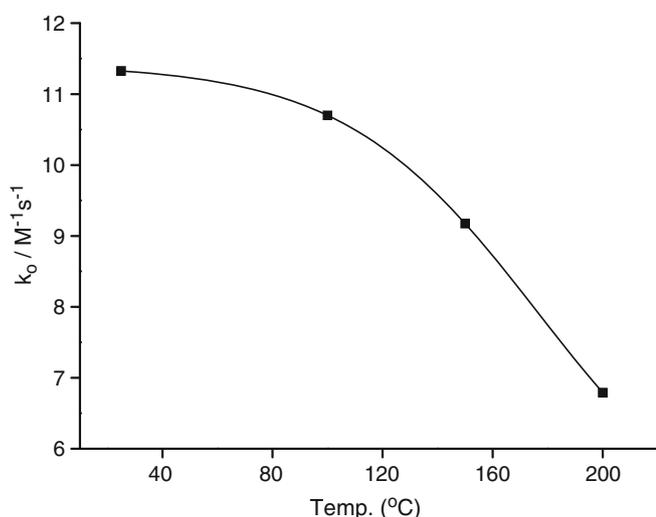


Figure 7. Dependence of rate constant on annealing temperature for reaction of AB-25 dye (2.0×10^{-4} M) with H₂O₂ (0.007 M) in presence of 0.02 g of annealed composite (III) at 30°C.

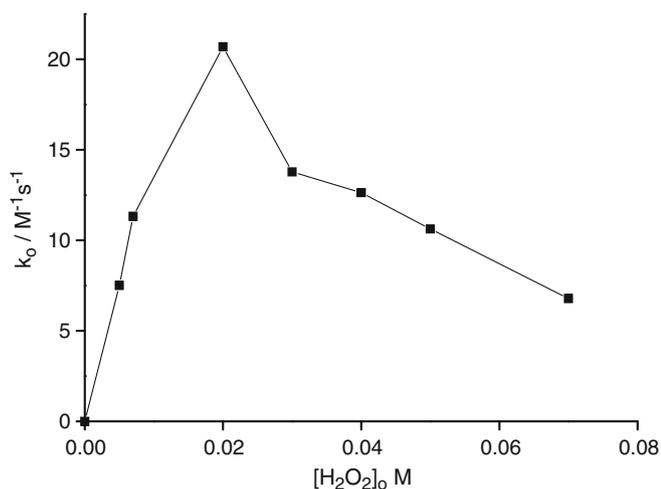
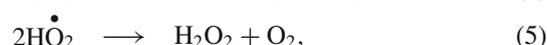
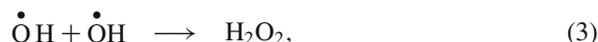
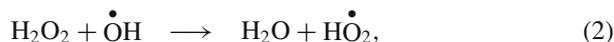


Figure 8. Dependence of reaction rate on $[H_2O_2]_0$ for oxidative reaction of AB-25 dye (2.0×10^{-4} M) with different concentrations of H₂O₂ in presence of 0.02 g of composite (III) at 30°C.

figure 8. The reaction rate constant attained a maximum at ~ 0.02 mol/l and after that it decreased. This behaviour can be explained on the basis that at $[H_2O_2] < 0.02$ M, the rate of generation of hydroxyl radicals is higher, which leads to a higher rate of decolourization of AB25 (Ghodbane and Hamdaoui 2010). At $[H_2O_2] > 0.02$ M, the solution undergoes self-quenching of $\cdot OH$ radicals by added amounts of H₂O₂ to produce HO₂ radicals (Šeděnková *et al* 2008). Additionally, $\cdot OH$ radicals generated at high concentration, dimerize to H₂O₂ (Salaneck *et al* 1986). The peroxy radicals produced as a result of reaction (2) can also enter in other reaction pathways (4–6).



Dilute solution of H₂O₂ is the key factor for the method to be more efficient in the removal of organic from wastewaters.

The effect of dye concentration on the degradation rate was studied by keeping the mass of composite constant while the concentration of the dye varies in the $(0.5\text{--}3.0) \times 10^{-4}$ M range. Figure 9 represents the rate constant which decreased with increase in dye concentration. This can be attributed to: (i) as the initial concentration of the dye increases, more molecules are adsorbed on the surface of composite. The large amount of adsorbed dye has an inhibitive effect on the reaction with $\cdot OH$ due to lack of possible contact between them and (ii) since the initial $[H_2O_2]$ is fixed, the increase in dye concentration increases the number of dye molecules in the medium and not the hydroxyl radicals. Hence, the additional dye molecules will not participate in degradation.

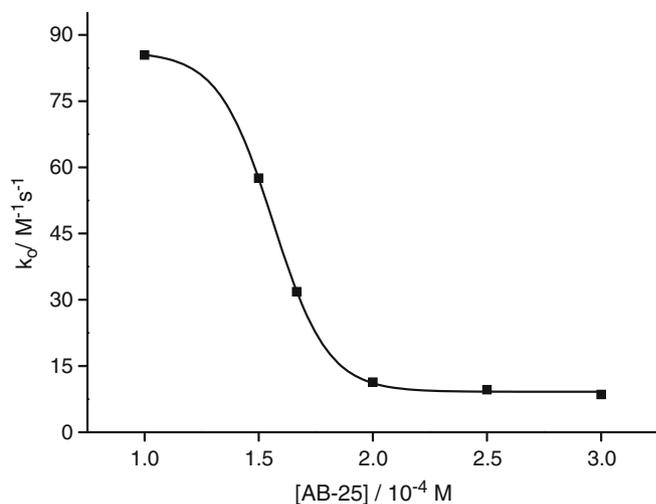


Figure 9. Dependence of reaction rate constant on $[AB-25]_0$ for its reaction with H₂O₂ (0.007 M) in presence of 0.02 g of composite (III) at 30°C.

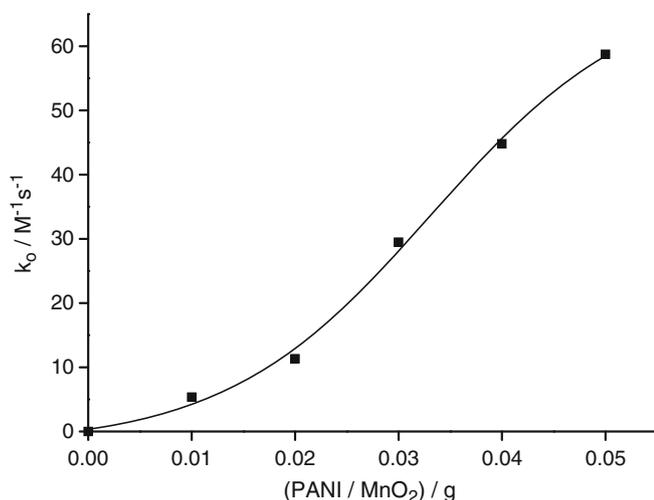


Figure 10. Variation of rate constant, k_0 , with amount of composite (III) for reaction of AB-25 dye (2.0×10^{-4} M) with H_2O_2 (0.007 M) in presence of different amounts of composite (III) at 30°C .

Table 2. Rate constants and activation parameters for decolourization of AB-25 with composite (III). [AB-25] = 2.0×10^{-4} M, Composite mass = 0.02g, [H_2O_2] = 0.007 M.

t ($^\circ\text{C}$)	k (pgdc)* ($\text{mol}^{-1} \text{Ls}^{-1}$)	E (kJ/mol)	ΔH^\ddagger (kJ/mol)	ΔG^\ddagger (kJ/mol)	ΔS^\ddagger (J/mol.K)
30	11.33	75.87	73.29	57.48	50.92
35	24.65				
40	30.86				
45	47.12				

*(pgdc) denotes per gram dry composite.

The effect of amount of the composite on the degradation efficiency was studied at constants [H_2O_2] = 0.007 M, [AB25] = 2×10^{-4} M at 30°C while amount of the composite varied in the range 0.01–0.05 g. As shown in figure 10, the rate constant increased with increasing mass of the composite.

Catalytic degradation of AB25 was carried out under different temperatures ranging from 30– 45°C and the corresponding rate constant per gram dry composite (pgdc) was determined (table 2). The k values are used in arrhenius plot (figure 11), to determine the activation energy, E . The values of the other activation parameters are depicted in table 2.

The pH studied was conducted to determine the optimum pH at which maximum colour removal could be achieved for AB25 dye. The effect of pH was observed by studying the degradation of dye over a broad pH range (3–12) using a phosphate buffer of 0.067 mol/L and a few drops of NaOH were added to obtain higher pH values. As shown from figure 12, the rate constant of the reaction decreases with increasing pH getting a plateau at higher pH. This trend may be ascribed to the following aspects: (i) the conversion of ES form of PANI into EB form (deprotonation) with

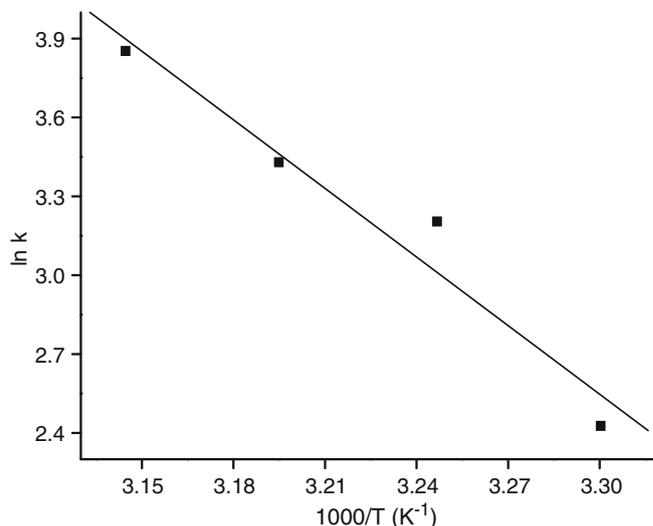


Figure 11. Arrhenius plot for reaction of AB-25 with H_2O_2 in presence of composite III.

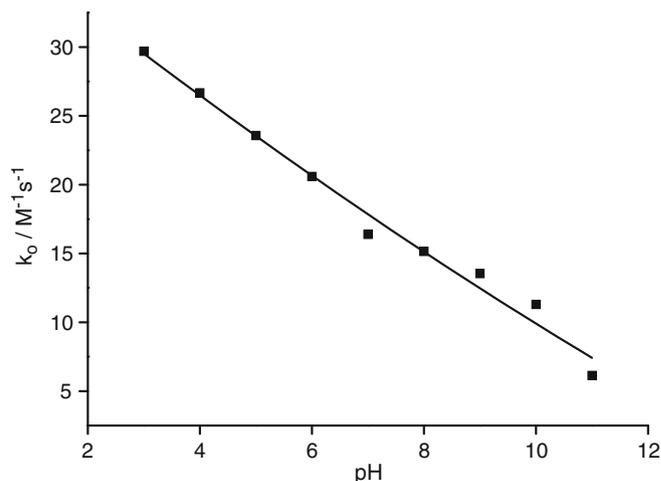


Figure 12. Variation of reaction constant rate with pH for reaction of AB-25 (2×10^{-4} M) with H_2O_2 (0.007 M) in presence of 0.02 g of composite (III) at 30°C .

increasing pH. The EB form of PANI has been reported to be an inactive catalyst in other oxidation systems (Gemeay *et al* 2008) and (ii) the protonated form of the dye is more facial to be oxidized than the deprotonated form. It has been reported that PANI is stable in strongly alkaline or acidic aqueous media, i.e. no degradation on the polymer skeleton has been detected after immersion of PANI in 9 M KOH or 5 M H_2SO_4 (Brožová *et al* 2008).

The effect of various salts on the catalytic degradation of AB-25 by H_2O_2 using PANI/ MnO_2 composites were examined for an initial dye concentration = 2×10^{-4} M and [H_2O_2] = 0.007 M at 30°C in the presence of 0.02 g of composite (III), while [K_2SO_4] and [KNO_3] was varied in 0.01–0.20 M and 0.05–0.30 M range, respectively. As shown in figure 13, the rate of reaction increases with increasing

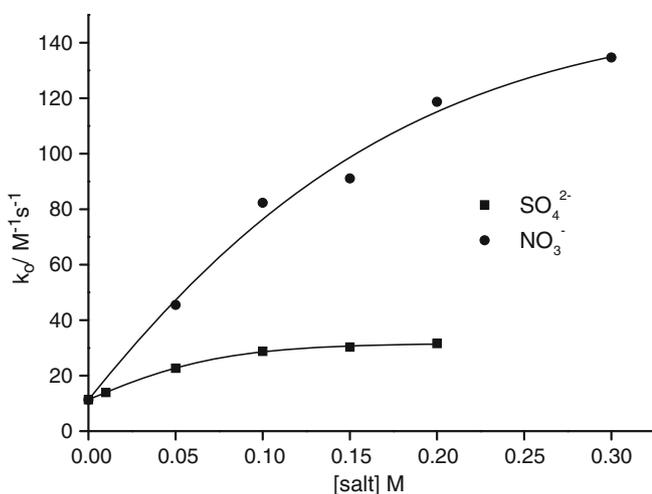


Figure 13. Variation of reaction rate constant with $[\text{NO}_3^-]$, $[\text{SO}_4^{2-}]$ for oxidation of AB-25 dye with H_2O_2 (0.007 M) in presence of 0.02 g of composite (III) at 30°C .

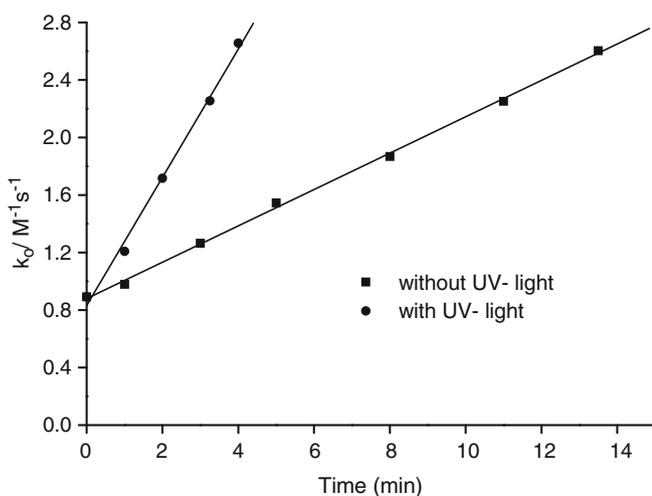


Figure 14. Effect of UV-light irradiation, $\lambda = 254$ nm, on reaction of AB-25 (2×10^{-4} M) with H_2O_2 (0.007M) in presence of 0.02 g of composite (III) at 30°C .

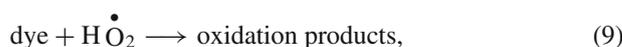
salt concentration. This enhancement of rate may be ascribed to the following: (i) addition of salts to dye aqueous solution pushes AB25 molecules from the bulk aqueous phase to the bulk-bubble interface (Ghodbane and Hamdaoui 2009). The presence of salts may increase the hydrophilicity, (ii) increase in the concentration of hydroxyl radicals as well as to the increase in NO_2 radical (Truong *et al* 2004). The formation of nitrite radical (NO_2) in the presence of H_2O_2 was reported (Hamlin *et al* 1999) and (iii) adsorption of NO_3^- on the surface of composite was revealed from the TG analysis (Gemeay *et al* 2005). The adsorbed NO_3^- can work as dopant anions for PANI, which increases the reaction rate. The intercept shown in figure 13 is in good agreement with the value

of rate constant determined in absence of NO_3^- and SO_4^{2-} ions under comparable conditions.

It is well established that the irradiation of H_2O_2 by UV-light source leads to generation of hydroxyl radicals (Gemeay *et al* 2003). Therefore, when our reaction mixture was irradiated by UV-light of $\lambda = 254$ nm, an enhancement of the rate constant of ca 80.8% in the reaction rate was observed (figure 14). The conclusion can be drawn that the irradiation of reaction increased the amount of hydroxyl radicals species and thus increase the reaction rate.

3.3 Reaction mechanism

Based on the above experimental findings and observations, the reaction mechanism has been suggested utilizing the redox properties of H_2O_2 . These properties involve a cyclic electron transfer process and initiated by transfer of an electron from the catalyst to H_2O_2 to produce HO^\bullet radicals or transfer of an electron from H_2O_2 to the catalyst to produce HO_2^\bullet radicals (DeLaat and Le 2006; Flox *et al* 2006). The redox mechanism of PANI is also established based on the thermodynamics of redox processes in homogeneous solutions (Lei and Kocherginsky 2000; Duic and Grigic 2001; Duic *et al* 2004). Nevertheless, the limitation of this system is that its redox activity is important only at $\text{pH} < 4$ (DeLaat and Le 2006). Two possible reaction types for the oxidation of the polymer have been proposed: (i) PANI oxidation without degradation of the polymer chains due to reversible amine-imine-type transformation and (ii) redox reaction, which directly modifies the polymer skeleton and then ruptures the chain with its subsequent hydrolysis (Genies *et al* 1990). With respect to MnO_2 counterpart of the composite, in addition of its main role as oxidant in the preparation of the composite, its presence in the composite offer two important functions during the oxidative reaction of the target dyes: (i) the adsorbed anions, NO_3^- , Cl^- , SO_4^{2-} , or PO_4^{3-} , can compensate the excess positive charges which may be generated in the PANI chains during the oxidative reactions and (ii) moreover, the adsorbed H^+ on its surface adjusted pH of the reaction medium in $3 \approx 4.5$ range, which is close to the value reported for the Fenton-like reaction of H_2O_2 to generate the HO^\bullet radical. Thus, the proposed mechanism involves catalytic action of the composite towards H_2O_2 , which leads to the generation of HO^\bullet radicals. A reaction mechanism involving free radical species can be proposed as



where (PANI)_{ox} and (PANI)_{red} are the ES and EB forms of the polymer. The first step of reaction mechanism is the adsorption of H₂O₂ on the oxidized sites of the polymer (7), which is followed by the reduction of oxidized PANI with H₂O₂ to form HO₂ radical species (8). The generated radicals will attack the dye molecules (9), to form the reaction products. It is well known that the conversion between EB and ES forms of PANI can occur by protonation, thus (10) involves the regeneration of oxidized form of PANI. Identification of the oxidation products is out of the scope of this work.

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