Oxidative degradation of dyes in water using Co^{2+}/H_2O_2 and $Co^{2+}/$peroxymonosulfate

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ABSTRACT

Dye degradation using advanced oxidation processes with Co^{2+}/H_2O_2 and $Co^{2+}/$peroxymonosulfate (PMS) systems has been investigated. Two types of dyes, basic blue 9 and acid red 183, were employed. Several parameters affecting dye degradation such as Co^{2+}, PMS, H_2O_2, and dye concentrations were investigated. The optimal ratio of oxidant (PMS, H_2O_2)/Co^{2+} for the degradation of two dyes was determined. It is found that dye decomposition is much faster in $Co^{2+}/$PMS system than in Co^{2+}/H_2O_2. For Co^{2+}/H_2O_2, an optimal ratio of H_2O_2 to Co^{2+} at 6 is required for the maximum decomposition of the dyes. For $Co^{2+}/$PMS, higher concentrations of Co^{2+} and PMS will increase dye degradation rate with an optimal ratio of 3, achieving 95% decolourisation. For basic blue 9, a complete decolourisation can be achieved in 5 min at 0.13 mM Co^{2+}, 0.40 mM PMS and 7 mg/l basic blue 9 while the complete degradation of acid red 183 will be achieved at 30 min at 0.13 mM Co^{2+}, 0.40 mM PMS and 160 mg/l of acid red 183. The degradation of acid red 183 follows the second-order kinetics.

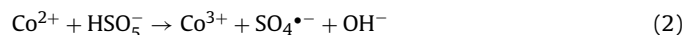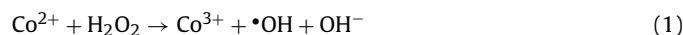## 1. Introduction

Wastewaters from textile, printing, and leather processing industries usually contain high concentration of various dyes, which will produce adverse effects on the eco-environments due to their non-biodegradability, toxicity, potential carcinogenic and mutagenic nature. In the past decades, some techniques such as adsorption, membrane separation, coagulation, chemical oxidation, and electrochemical degradation have been investigated to treat dyeing wastewater. However, low removal efficiency or high cost in operation often limit their application [1].

Advanced oxidation processes using highly reactive radicals, such as $^\bullet OH$, $^\bullet OOH$, $O_2^{\bullet -}$ and $SO_4^{\bullet -}$, are excellent methods for degradation of organic pollutants in water. In the past years, Fenton-type oxidation (Fe^{2+}/H_2O_2) using hydroxyl radicals has been comprehensively investigated [2–4]. In recent years, chemical oxidation using peroxymonosulfate (PMS) conjunction with cobalt ions to generate sulfate radicals has raised an interest and is found as a very promising technique. Compared with hydroxyl radical reaction with standard reduction potential of 1.8–2.7 V, sulfate radicals demonstrate higher reduction potential of 2.5–3.1 V at neutral pH and are more selective for oxidation [5]. For Fenton-type oxi-

dation, Fe ion is found to be the most effective and is commonly used. However, this type of Fenton oxidation suffers from several drawbacks such as low pH (pH at 3) and large sludge residues. Other metal ions such as Co^{2+} and Cu^{2+} are also active for hydroxyl radical generation while few investigations have been reported. Co/H_2O_2 and Co/PMS systems producing hydroxyl (Eq. (1)) and sulfate radicals (Eq. (2)) are presented in the following reactions.

$$Co^{2+} + H_2O_2 \rightarrow Co^{3+} + {}^\bullet OH + OH^- \tag{1}$$

$$Co^{2+} + HSO_5^- \rightarrow Co^{3+} + SO_4^{\bullet -} + OH^- \tag{2}$$

In the past a few years, some investigations have been reported in using $SO_4^{\bullet -}$ radicals for oxidation of organics in water [6–13]. For dye containing wastewater, few investigations have been reported while focusing on the effect of photo-assisted decolourisation. Fernandez et al. [10] investigated photobleaching and mineralisation of orange II in $Co^{2+}/$oxone reagent under visible light. Chen et al. reported photoassisted decolourisation and mineralisation of acid orange 7 in Co^{2+}-catalysed PMS and nano-Co_3O_4/PMS systems under UV radiation [8,9]. Madhavan et al. [13] studied the kinetics of degradation of acid red 88 in the presence of Cu^{2+} and Fe^{3+} ions coupled oxone reagent assisted by visible light. In this study, we will compare the effectiveness of Co/H_2O_2 and Co/PMS in oxidative decomposition of different dyes at neutral pH range and investigate the effects of several operation parameters on dye degradation efficiency.

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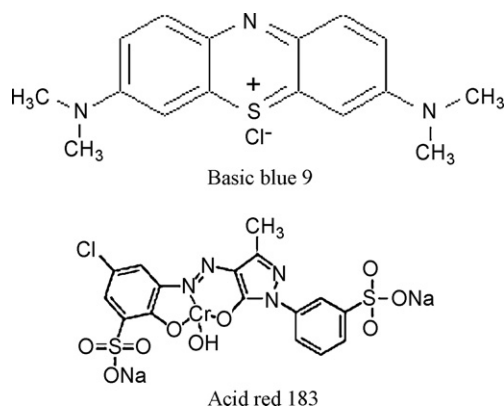
Basic blue 9

Acid red 183

Fig. 1. Chemical structure of the two tested dyes.

2. Experimental

2.1. Chemicals and reagents

Cobalt nitrate hexahydrous (Co(NO$_3$)$_2$·6H$_2$O), oxone (2KHSO$_5$ KHSO$_4$ K$_2$SO$_4$), hydrogen peroxide (H$_2$O$_2$, 30%), and two dyes, basic blue 9 (C.I. 52015, C$_{16}$H$_{18}$N$_3$ClS) and acid red 183 (C.I. 18800, C$_{16}$H$_{11}$ClN$_4$Na$_2$O$_8$S$_2$), were supplied by Aldrich. Fig. 1 shows the chemical structure of the two dyes. They were used as received without further purification. For preparation of dye solutions deionised and distilled water was used.

2.2. Experimental procedure and analysis

The degradation experiments were carried out in erlenmeyer flasks. Dye solution with 200 ml was filled into the flasks and reacted at room temperature (26 °C, with water bath) and 700 rpm stirring speed. The initial concentrations of basic blue 9 and acid red 183 were kept at 7 and 165 mg/l, respectively, in most of tests, unless indicated. For Co^{2+}/H$_2$O$_2$ reaction, 1.30 × 10^{-2} M of Co^{2+} was used with varying concentrations of H$_2$O$_2$ while for Co^{2+}/PMS reaction, 1.30 × 10^{-4} M of Co^{2+} was used to activate different concentrations of PMS, unless otherwise indicated. During the homogeneous Co^{2+}/H$_2$O$_2$ and Co^{2+}/PMS reactions, a small quantity of the solution was withdrawn from the reactor at selected time intervals for spectrophotometric analysis of dye concentration at 663 and 494 nm for basic blue 9 and acid red 183, respectively. For some tests, total organic content (TOC) was also determined using a Shimadzu TOC-5000 CE analyser. For the measurement of TOC, 5 ml sample was drawn at an interval of 1 h and quenched with 5 ml of 3 M sodium nitrite and then analysed on the TOC analyser.

3. Results and discussion

3.1. Basic blue 9 decomposition in Co^{2+}/H$_2$O$_2$

Fig. 2 shows the degradation of basic blue 9 under different concentrations of H$_2$O$_2$. It is seen that decomposition of basic blue 9 is dependent on H$_2$O$_2$ concentration. Without Co^{2+}, H$_2$O$_2$ itself cannot effectively induce dye degradation. For Co^{2+}/H$_2$O$_2$ system, a low degradation of 26% can be observed after 60 min at 2 × 10^{-3} M H$_2$O$_2$. With the increase in H$_2$O$_2$ concentration, decomposition rate of basic blue 9 is increasing. At 8 × 10^{-2} M H$_2$O$_2$, 100% of basic blue 9 is decomposed at 30 min. However, if H$_2$O$_2$ concentration is continued to increase, the decomposition rate is reduced. At 1 × 10^{-1} M H$_2$O$_2$ decomposition rate will be less than that at 8 × 10^{-2} M H$_2$O$_2$. At 1.2 × 10^{-1} M H$_2$O$_2$ the degradation rate is significant slower and it takes 180 min for a complete degradation.
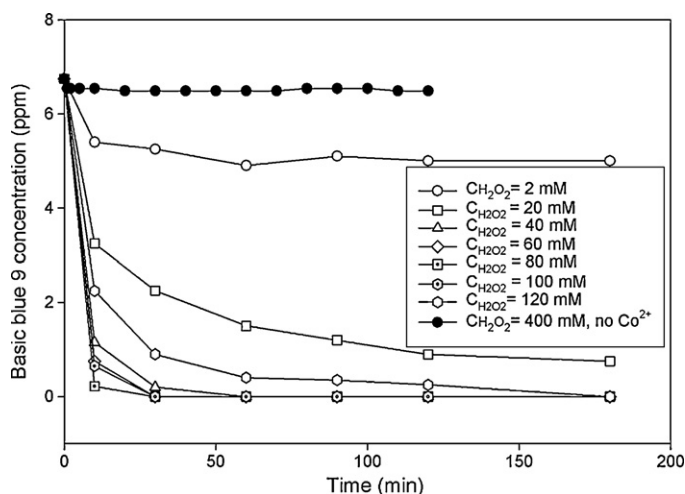

Fig. 2. Effect of H$_2$O$_2$ concentration on dynamic degradation of basic blue 9 in Co^{2+}/H$_2$O$_2$. Reaction conditions [basic blue 9] = 7 ppm, [Co^{2+}] = 1.3 × 10^{-2} M.

It has been found that H$_2$O$_2$/Fe^{2+} ratio is more important in Fenton type oxidation. Fig. 3 presents the effect of H$_2$O$_2$/Co^{2+} ratio on dye degradation. As shown, there is an optimum ratio (H$_2$O$_2$/Co^{2+} = 6) for achieving the highest degradation rate. When H$_2$O$_2$/Co^{2+} is higher than 6, the degradation rate is much reduced. The decreasing rate of dye decolourisation is attributed to unreacted H$_2$O$_2$ acting as a scavenger of •OH and producing a less potent perhydroxyl radicals (Eq. (3)). Several investigations of wastewater decolourisation using Fenton oxidation have been conducted and the similar observation was reported [1].

$$H_2O_2 + {}^\bullet OH \rightarrow H_2O + HO_2{}^\bullet \qquad (3)$$

3.2. Basic blue 9 decomposition in Co^{2+}/PMS

Compared with the decomposition of basic blue 9 in Co^{2+}/H$_2$O$_2$, dye degradation is much faster in Co^{2+}/PMS system. Thus, the concentrations of Co^{2+} and PMS used in this investigation are much lower. The dynamic degradation of basic blue 9 under different concentrations of PMS is shown in Fig. 4. As seen, without Co^{2+}, PMS exhibits quite low oxidation rate for dye degradation, suggesting minor activation of PMS for sulfate radical generation occurs. In Co^{2+}/PMS, nearly 47.4% of basic blue 9 was decomposed after 5 min at 5 × 10^{-5} M PMS, much faster than Co^{2+}/H$_2$O$_2$. When PMS con-
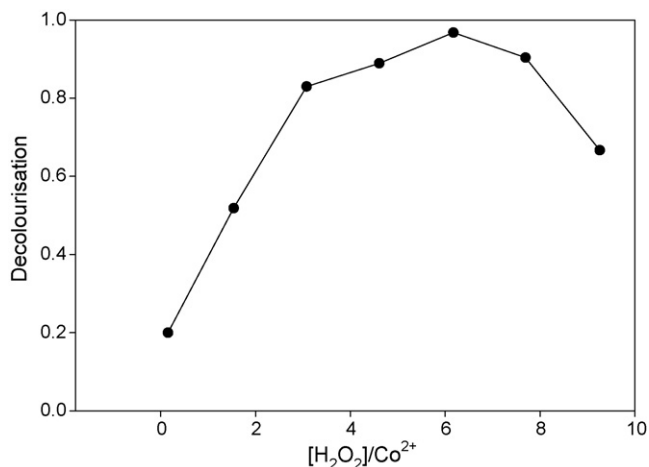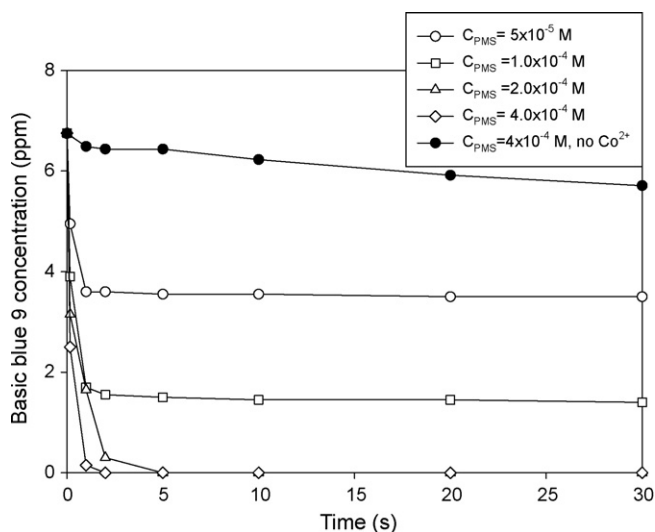

Fig. 3. Effect of [H$_2$O$_2$]/[Co^{2+}] on degradation efficiency of basic blue 9. Reaction conditions [basic blue 9] = 7 ppm.

Fig. 4. Effect of PMS concentration on dynamic degradation of basic blue 9 in Co^{2+}/PMS. Reaction conditions [basic blue 9] = 7 ppm, $[Co^{2+}] = 1.3 \times 10^{-4}$ M.

Fig. 5. Effect of PMS concentration on dynamic degradation of acid red 183 in Co^{2+}/PMS. Reaction conditions [acid red 183] = 165 ppm, $[Co^{2+}] = 1.3 \times 10^{-4}$ M.

centration is increased, degradation rate of basic blue 9 will also increase. At 4×10^{-4} M PMS, 100% of basic blue 9 degradation is achieved in 2 min.

As stated before, sulfate radicals have higher reduction potential, making it more reactive than hydroxyl radicals. Anipsitakis and Dionysiou [7] have investigated the transformation of chlorophenol using Co^{2+}/H_2O_2, Co^{2+}/persulfate, and Co^{2+}/PMS and found that Co^{2+}/PMS showed very high reactivity and 98% of chlorophenol was transformed in less than 1 min. However, other two oxidant systems (Co^{2+}/H_2O_2 and Co^{2+}/persulfate) did not show any activity in degrading the chlorophenol due to the low efficiency of Co^{2+} to activate the oxidants to produce hydroxyl and sulfate radicals, respectively.

Table 1 presents an estimation of the cost for Co^{2+}/PMS and Co^{2+}/H_2O_2 systems based on the above degradation of basic blue 9. It is seen that Co^{2+}/PMS shows not only faster dye degradation rate but also lower cost than Co^{2+}/H_2O_2.

3.3. Acid red 183 decomposition in Co^{2+}/PMS

Fig. 5 showed the degradation of acid red 183 under varying PMS concentration at Co^{2+} concentration of 1.3×10^{-4} M. At 5×10^{-5} M PMS, only 29.1% of acid red 183 is removed after 10 min. When PMS concentration is increased, higher degradation rate of acid red 183 will be achieved. At 4×10^{-4} M PMS, nearly 96.4% of acid red 183 will be degraded after 60 min. However, the degradation rate is slowed at higher concentration of PMS of 5.2×10^{-4} M and the degradation efficiency will be 95% after 60 min.

The oxidation rate was negatively affected when the concentration of oxone was further increased which may be due to the scavenging of sulfate radicals by HSO_5^- and the formation of less reactive $SO_5^{\bullet-}$ based on Eq. (4) [13].

$$HSO_5^- + SO_4^{\bullet-} \rightarrow SO_5^{\bullet-} + SO_4^{2-} + H^+ \qquad (4)$$
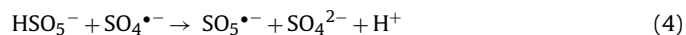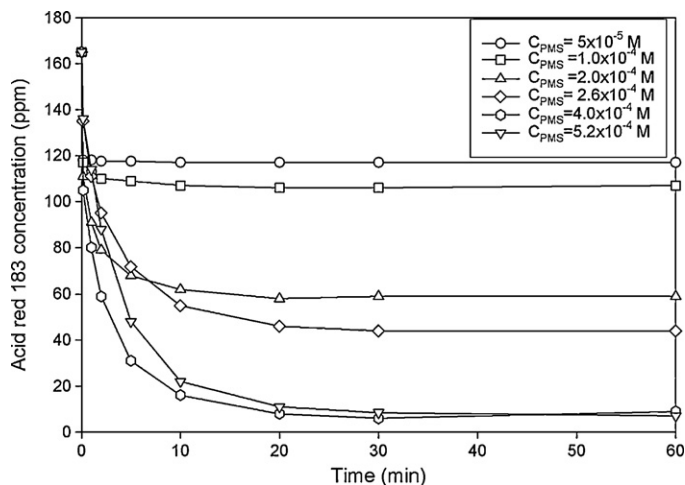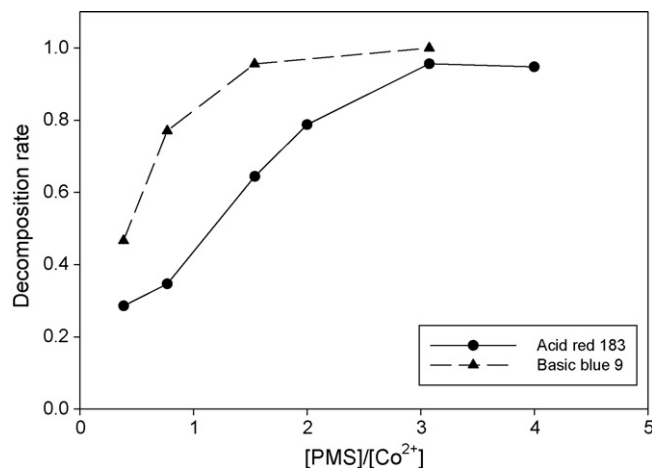
Fig. 6 shows the effect of concentration ratio of PMS/Co^{2+} on dye degradation efficiency for basic blue 9 and acid red 183. It is

Fig. 6. Effect of PMS/Co^{2+} on degradation efficiency of two dyes.

seen that high ratio will increase dye degradation efficiency and the degradation efficiency will reach the maximum at the ratio around 3 for the two dyes. Compared with Co^{2+}/H_2O_2 system for dye degradation, the ratio is much lower, suggesting the less loading of oxidant PMS in the reaction.

Fig. 7 illustrates the degradation of acid red 183 at varying Co^{2+} concentration with PMS concentration of 4×10^{-4} M and the relationship between degradation efficiency and PMS/Co^{2+}. It is seen that acid red 183 decomposition is also increased with increasing Co^{2+} concentration. At 6.51×10^{-5} M of Co^{2+}, acid red 183 decomposition can reach 50% in 10 min. After 60 min, 90% decomposition will be achieved. If Co^{2+} concentration is at 1.30×10^{-4} M, the initial rate of decomposition will be increased and 80% decomposition will be obtained in 10 min. While further increase in Co^{2+} concentration to 8.59×10^{-4} M, acid red 183 decomposition rate will be similar at 10 min and nearly 95.1% of the dye was removed after 60 min. Based on the relationship of degradation efficiency and PMS/Co^{2+}, one can see that degradation efficiency will reach the maximum

Table 1
Cost estimation of Co^{2+}/PMS and Co^{2+}/H_2O_2 for degradation of basic blue 9 in 200 ml solution.

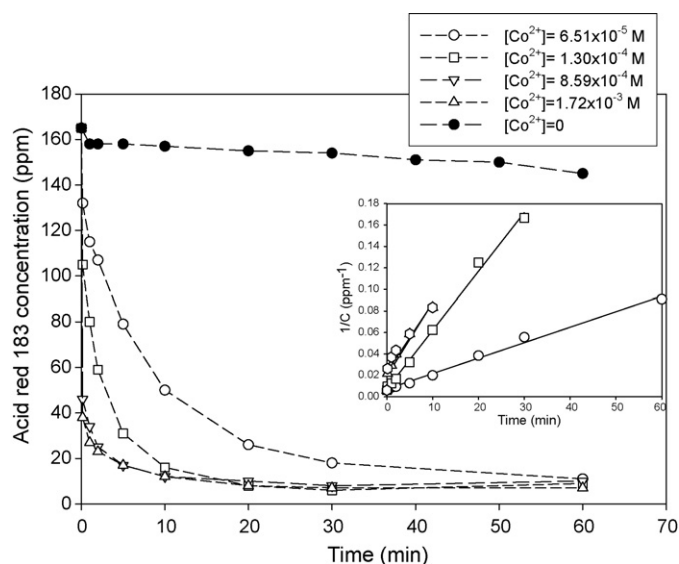| Process	$[Co^{2+}]$ (A\$)	[PMS] (A\$)	$[H_2O_2]$ (A\$)	Total cost (A\$)
Co^{2+}/H_2O_2	1.3×10^{-2} M (\$11.34)	–	8×10^{-2} M (\$0.32)	11.66
Co^{2+}/PMS	1.3×10^{-4} M (\$0.11)	4×10^{-4} M (\$0.02)	–	0.13

Fig. 7. Effect of Co^{2+} concentration on dynamic degradation of acid red 183 in Co^{2+}/PMS. Inset: relationship between $1/C$ and time. Reaction conditions [acid red 183] = 165 ppm, [PMS] = 4×10^{-4} M.

at PMS/Co^{2+} of 2–4, which is similar to the results obtained above based on the change of PMS concentration while at fixed Co^{2+} concentration.

For degradation of acid red 183, the kinetics was investigated using two models, the first-order and second-order kinetics. The integral equations for the two models are presented in Eqs. (5) and (6).

$$C = C_0 e^{-K_1 t} \qquad (5)$$

$$C = \frac{1}{1 + K_2 C_0 t} \qquad (6)$$

where C_0 and C are dye concentrations at time $t = 0$ and t, K_1 and K_2 are the rate constants for the first-order and second-order kinetics, respectively.

Fig. 8 presents a comparison of the first-order and second-order kinetics in fitting the experimental results. The parameters obtained based on the models are given in Table 2. As shown, the second-order kinetics exhibits better fitting results in terms of initial concentration and regression coefficient, suggesting the dye degradation may follow the second-order kinetics. Further investigation using different dye initial concentrations confirms the second-order kinetics as shown later.

Fernandez et al. [10] conducted bleaching reaction of acid orange 7 (AO7) in Co^{2+}/PMS system and found zero-order kinetics. Chen et al. [9] also carried out kinetic studies of AO7 degradation in aqueous solution induced by Co^{2+}/PMS and proposed a pseudo first-order decolourisation. They believed the PMS/[AO7] ratio caused the change of kinetic order. In Fernandez et al. experiments, PMS/[AO7] ratio ranged from 20 to 400, whereas the range was 1–20 in Chen et al. investigation. The higher dye concentration in solution played an important role in limiting the reaction rate. In another investigation by Madhavan et al. [13], the kinetics of decolourisation of acid red 88 (AR88) in Cu^{2+}/oxone system was found to follow zero-order kinetics with respect to the dye
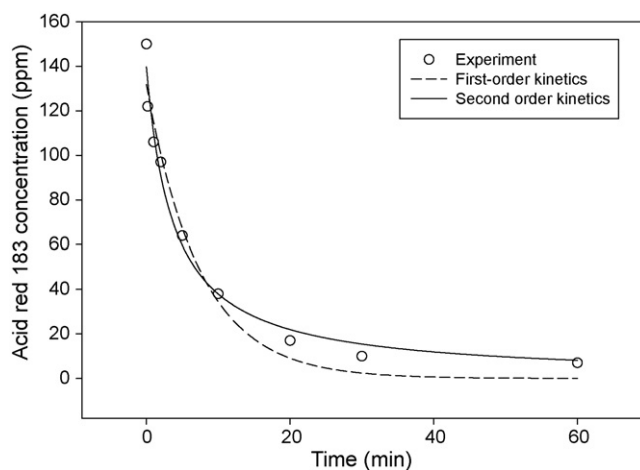

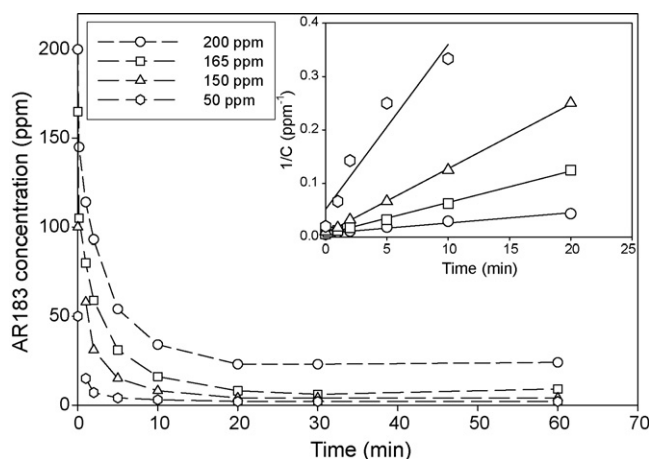**Fig. 8.** Comparison of kinetic models for degradation of acid red 183 in Co^{2+}/PMS.

Fig. 9. The kinetics of degradation of acid red 183 at varying concentrations in Co^{2+}/PMS. Inset: relationship between $1/C$ and time. Reaction conditions [PMS] = 4×10^{-4} M, [Co^{2+}] = 1.3×10^{-4} M.

and first-order kinetics when Fe^{3+}/oxone system was employed. Therefore, it seems that kinetics of dye degradation in metal/PMS depends on dye concentration and metal ion. The second-order kinetics observed in this investigation is probably due to the higher concentration of dye and much lower PMS/AR183 ratio, which is at 1–4.

Fig. 9 shows the decomposition of acid red 183 at varying initial concentration. As seen, acid red 183 decomposition rate is increased with decreased initial concentration. For 200 ppm, the decomposition efficiency can be obtained at 88% after 60 min. At 50 ppm, the decomposition efficiency will be at 96%. TOC measurements were conducted and the results are shown in Table 3. It is found that removal efficiency of TOC was significant. The reduction of TOC was 87, 55, 40 and 25% at initial concentration of 50, 100, 165 and 200 ppm, respectively, after 1 h reaction.

Based on the second-order kinetics, the apparent reaction rates at each concentration was obtained and presented in Table 3. As shown, the estimated initial concentration using the second-order

Table 2
Parameters of acid red 183 degradation kinetics.

C_0 (Exp, ppm)	First-order kinetics			Second-order kinetics		
	C_0 (ppm)	K_1 (min^{-1})	R^2	C_0 (ppm)	K_2 (ppm^{-1} min^{-1})	R^2
150	131.9	0.134	0.970	139.8	1.92×10^{-3}	0.983

Table 3
Dye degradation rate constant for AR183 at varying dye concentrations.

Concentration (ppm)	Estimated concentration (ppm)	Rate constant (K_2) (ppm^{-1} min^{-1})	R^2	TOC reduction (%)
200	179	2.37×10^{-3}	0.982	25
165	148	5.87×10^{-3}	0.998	40
100	101	0.0121	0.999	55
50	50	0.0460	0.928	87
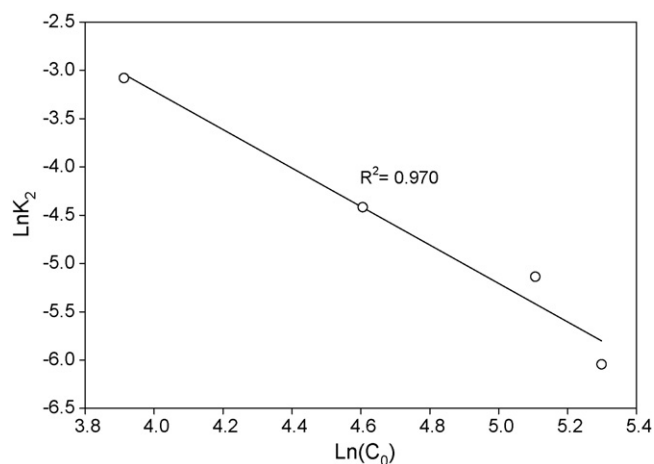
Fig. 10. Relationship between $\ln K_2$ and $\ln C_0$.

kinetics is close to the value of experiment and degradation rate constant is increasing with decreasing dye concentration.

The apparent rate constant of the reaction is then correlated to the initial dye concentration by a simple power law as follows.

$$K_2 = kC_{0,\text{dye}}^n \tag{7}$$

Fig. 10 shows the relationship between $\ln K_2$ and $\ln C_0$. It is determined that the order (n) respective to dye concentration is 1.99 and rate constant (k) is 156 ppm^{-3} min^{-1}, thus confirming the second-order kinetics.

4. Conclusion

Co^{2+}/PMS exhibits a better efficiency in dye degradation than Fenton-type Co^{2+}/H_2O_2. For basic blue 9 and acid red 183, the degradation can be achieved in very short time. The ratio of oxidant (PMS, H_2O_2) to Co^{2+} is important and the maximum degradation of dye would be achieved at the optimum ratio, which is 6 and 3 for Co^{2+}/H_2O_2 and Co^{2+}/PMS, respectively. Co^{2+}/PMS requires less oxidant than Co^{2+}/H_2O_2. The kinetics of acid red 183 follows the second-order reaction.

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