



Online Spectrometric Decolorization of Rhodamine B and Acid Yellow G by Homogeneous Cobalt-Activated Peroxymonosulphate Reaction

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ABSTRACT

Homogeneous cobalt-activated peroxymonosulphate reaction (Co^{2+} /PMS) was applied to decolorize Rhodamine B (RhB) and Acid Yellow G (AYG) and the main experimental parameters (nitrate cobalt concentration, PMS dosage, pH) were investigated. At the optical condition (1 mg/L $\text{Co}(\text{NO}_3)_2$, 20 mg/L PMS and pH=7 for RhB; 10 mg/L $\text{Co}(\text{NO}_3)_2$, 65 mg/L PMS and pH=9 for AYG), the colour removal of RhB and AYG were 99.5% and 98% respectively. Plus, M^{n+} /PMS process (Cu^{2+} /PMS, Mn^{2+} /PMS, Ni^{2+} /PMS, Fe^{3+} /PMS, Fe^{2+} /PMS) was carried out to study the catalytic effect of similar activators with same molar concentration. The evidence indicates that Fe^{2+} and Cu^{2+} ion are more reactive compared to other ions, while that catalysis is still incomparable to cobalt ion. Furthermore, in Co^{2+} /PMS process, the acid dyes (Acid Red 6B, Acid Yellow G, Acid Blue) were found to become more degradable at alkaline condition (pH 9) than neutral solution.

INTRODUCTION

In recent years, another advanced oxidization process via divalent cobalt ion activating Peroxymonosulphate (Co^{2+} /PMS) induced heated investigations once more due to its advantages such as lower metal ion dosage, highly efficient and wider pH range. In mechanism, Co^{2+} /PMS is similar to $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ Fenton process, a kind of transition metal ion catalysing oxide and generating highly oxidative free radicals ($\cdot\text{OH}$ (1.8-2.7eV), $\text{SO}_4^{\cdot-}$ (2.5-3.1eV), $\text{HSO}_5^{\cdot-}$ (1.82eV), H_2O_2 (1.76eV)) (Yu et al. 2013). What is well accepted is that the sulphate radical decompose the target via electron transfer, while the hydroxyl radical through directly oxidization of oxygen (Ji et al. 2015). Additionally, in Co^{2+} /PMS process, the sulphate radical and hydroxyl radical are believed to exist at the same time. When the model substances added, radicals attack them and various by-products, that are even more hazardous, generated along with mother molecule breakdown. Therefore, enough redox potential is necessary for complete mineralization and total detoxication. The sulphate radical is more selective for decomposing organics than hydroxyl radical and has higher oxidation-reduction potential (Zou et al. 2013). Compared to Fenton process, the Co^{2+} /PMS reaction not only has a remarkable pollution removal, but also overcomes the drawbacks of the Fenton process (i.e. strong acidic media, unstable reagent, lower mineralization, secondary ferric pollution).

According to the present publications, Sie King Ling (Ling et al. 2010) reported the oxidative degradation of

basic blue 9 and acid red 183 with $\text{Co}^{2+}/\text{H}_2\text{O}_2$ and Co^{2+} /PMS process. It was found that the Co^{2+} /PMS process decomposed target dye more quickly than $\text{Co}^{2+}/\text{H}_2\text{O}_2$ with complete decolorization. Plus, the researchers believed the acid red 183 degradation follows second order kinetics. Yao-Hui Huang (Huang et al. 2009) explored the degradation of reactive black B at near neutral condition with extremely low dosages, especially ppb level of catalyst cobalt ions. The results demonstrate that the reactive black B was decolorized completely and no residual cobalt ion was detected by atomic absorption after process.

The dyeing wastewater is generally acknowledged as a kind of troublesome pollution and need to be treated seriously. In our study, the Acid Yellow G and Rhodamine B which act as the representative of azo-dye (-N=N-) and xanthone-dye respectively, are used as the decolorization probe in Co^{2+} /PMS process. Based on our former researches about dyeing wastewater degradation with Fenton or Fenton-like process (Xu et al. 2015), here, the online spectrometric system was also determined as the decolorization analysis method. Other than the conventional measurement, online spectrometry that involves less manual operation is an advanced, fast, and successive detecting method result in minimum system error, more accurate and abundant experimental data. And instantaneously the objective decolorization was vividly reflected in the monitor screen and quantized at selected recording frequency (minimize to 1 s^{-1}). The whole reaction kinetics can be analyzed in smaller time ranges such as several hundred seconds. Plus, there is a novelty

discovery that the acid dyestuffs have better removal in weak alkaline solution (pH = 9) compared at the neutral which has been hardly reported. Most researchers concluded that the neutral solution is the optimum operative condition for their model compound in Co²⁺/PMS process (Yavuz et al. 2009).

EXPERIMENT

Chemical reagents: Oxone (KHSO₅·0.5KHSO₄·0.5K₂SO₄, ≥ 47% KHSO₅ basis) was used as the source of Peroxymonosulphate (PMS). Cobalt nitrate hexahydrate (Co(NO₃)₂·6H₂O), copper nitrate trihydrate (Cu(NO₃)₂·3H₂O), nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O), manganese nitrate hexahydrate (Mn(NO₃)₂·6H₂O), iron nitrate nonahydrate, (Fe(NO₃)₃·9H₂O), ferrous sulphate heptahydrate (FeSO₄·7H₂O), sulphuric acid and sodium hydroxide were analytical pure and purchased at e-store of Aladdin. Four dyes Rhodamine B, Acid Yellow G, Acid Red 6B, Acid Blue 9 were chemically pure and directly used without further purification. Moreover, the whole experimental dissolutions were operated with distilled water.

Procedure: The simulated dyeing wastewater was prepared by dissolving Rhodamine B and Acid Yellow G in advance. According to the single factor experiment demanding, nitrate cobalt concentrations, PMS concentrations and solution pH were adjusted properly. The homogeneous reaction takes place at a beaker which is fixed on a magnetic stirrer. First of all, a certain amount of dyeing wastewater was added into the beaker with an adjusted pH. Then, nitrate cobalt and PMS were added in sequence to initiate the reaction. As soon as the PMS was added, in substantively, the reaction began due to the tremendous reaction rate constant (Avetta et al. 2014). In the mean time, the online spectro-metric system monitored the whole degradation process and recorded the absorbance of the target. Here, the recording frequency was selected as 1 s⁻¹. Therefore, with the application of online technology, more authentic and accurate degradation details can be noted down and analysed adequately. The probe compound decolorized efficiency was characterized as Eq. 1:

$$\text{Color removal}(R) = A_t / A_0, \quad \dots(1)$$

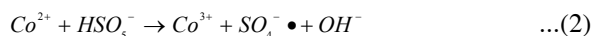
Where the A_t is the absorbance of probe at time t and A_0 is the absorbance at time 0.

Apparatus: The online reaction and spectrophotometric analysis system is illustrated in Fig. 1. This system consists of a reaction container, a digital display thermostat magnetic stirrer (85-2 Shanghai instrument manufactory), a digital pH meter (PHS-3C-01 experimental pH meter Hangzhou instrument limited corporation), a UV-Vis spectrophotometer

(SP-756PC Shanghai spectrometric instrument manufactory), a peristaltic pump (HL-1D Beijing instrument manufactory) and a computer. A plastic hose with an inner diameter of 2 mm links the reactive solution with the flowing cell cuvette within the spectrophotometer with the solution pumped by the peristaltic pump. The return liquid is sent back to beaker to form the cycle. UV-Vis spectrophotometry was used to monitor the colour change in the flowing cell cuvette at 1 s⁻¹.

RESULTS AND DISCUSSION

The effect of cobalt nitrate concentration and different metal ion activators: Similar to Fe²⁺/H₂O₂ process, divalent cobalt ion acts as a catalyst and takes the responsibility of initiating the reaction to generate sulfate radicals. Co²⁺ ion also has a circle during the reactions as shown in Eqs. 2 and 3:



In Fig. 2 and Fig. 3, different nitrate cobalt concentrations were investigated in RhB and AYG degradation. A general tendency can be concluded that the colour removal increases sharply with adding larger amount of nitrate cobalt and tends to be balanced. At the minimal dosages (0.05 mg/L for RhB and 1 mg/L for AYG) the colour removals are 55% and 50% respectively, due to lack of adequate oxidative radicals. Along with Co²⁺ continuing to increase there is no evident scavenging effect observed. Higher dosage results in better colour removal and cut down the necessary time to reach the maximal decolorized percentage. Chemically speaking, cobalt ion is a kind of transition metal and its ionic form can be accumulated naturally in a contaminated area resulting in heavy metal poison. Therefore, the amount of cobalt ion should be controlled strictly. Comprehensively, 1 mg/L and 10 mg/L can be selected as the appropriate nitrate cobalt concentration in RhB and AYG decolorization with respective 99.5%, 98% balanced colour removals.

There are some papers that reported the similar transition metal ion equips certain ability to activate PMS (Madhavan et al. 2008). Therefore, the Co²⁺/PMS, Fe³⁺/PMS, Fe²⁺/PMS, Cu²⁺/PMS, Ni²⁺/PMS, Mn²⁺/PMS processes were tested for RhB decolorization. As shown in Fig. 4, at the same molar concentration of metal ions, cobalt ion shows the best catalytic effect with 93.4% colour removal. As the sole PMS has about 5% colour removal, the Ni²⁺ (6.15%), Mn²⁺ (8.68%) and Fe³⁺ (7.43%) can be assumed as bare effective. The left Cu²⁺ and Fe²⁺ have slightly better catalytic function with 10.92% and 13.88% removal. Consequently, in this study, all the other metal ions are not competent for RhB decolorization with such small dosage. From the mini-

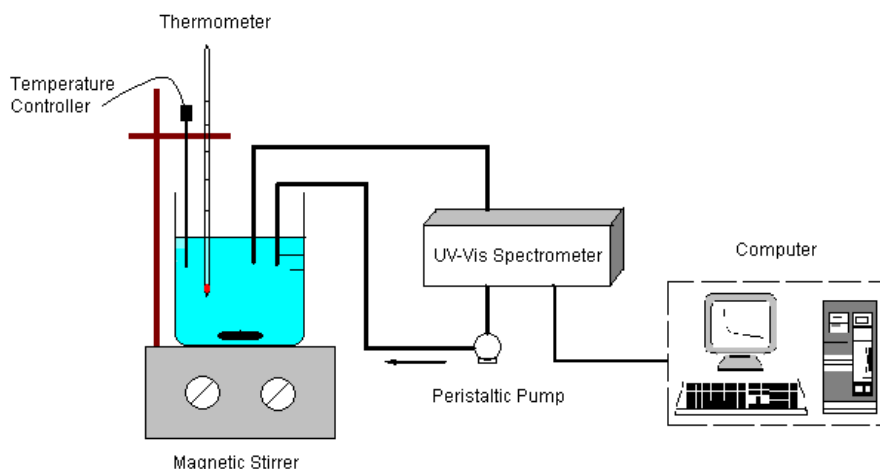
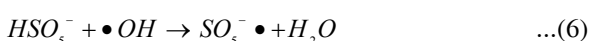
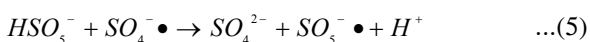
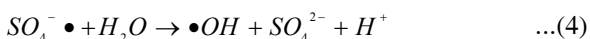


Fig. 1: Online spectrophotometric system.

ature in Fig. 4, the first order kinetics reaction constant of cobalt ion is about 35 times bigger than the others average.

The effect of PMS concentration on decolorization of RhB and AYG: Through the basic reaction (Eq. 2) in Co^{2+} /PMS process, large amount of sulfate radicals were generated. And according to some reports, it is reasonable that the hydroxyl radical and sulfate radical co-exist due to water oxidation of sulfate radical (Eq. 4) (Madhavan et al. 2015). Therefore, the PMS is considered as another necessary component and its dosage should be studied seriously due to excessive inhibition of PMS.



On the one hand, sulfate radical was transformed into less reactive persulphate radical (Eq. 5). While on the other hand, the excessive PMS could also scavenge the hydroxyl radical (Eq. 6). Consequently, an optimum concentration of PMS is vital for excellent performance of Co^{2+} /PMS process. Figs. 5-6 reveal the effect of different PMS dosages on colour removal of RhB and AYG. The amount of nitrate cobalt was fixed as 0.5 mg/L and 5 mg/L respectively, in RhB and AYG degradation. First of all, both images show that inadequate PMS results in inferior colour removal, in detail, 3 mg/L PMS for about 20% RhB colour removal and 20 mg/L PMS for 40% AYG colour removal. Moreover, the upgraded degradation efficiency is proportional to PMS dosages before it reaches the optimum PMS concentration. The best PMS dosage could not be found in this experimental condition. But, in the higher PMS dosage, the ending reaction

time was only 400s. It was a very fast reaction rate. The detailed information can be more clearly reflected by latter discussion about kinetics. At this point, the Co^{2+} /PMS reaction is more applicable and the excessive PMS do not undermine final removal. Yet, in order to avoid waste, the optimum dosages of PMS in RhB and AYG decolorization are 20 mg/L and 65 mg/L respectively.

The effect of solution pH: For homogenous reaction, solution pH is very important so the optimum value should be investigated. Zou et al. (2014) investigated the effect of initial solution pH on methyl orange decolorization. The study indicated that the colour removal maintains high at pH range of 4 to 8, and the removal drops at pH 9. Anipsitakis et al. (2003) proved that the Co^{2+} /PMS process is very effective for degradation of 2,4-dichlorophenol and naphthalene in water without buffer at neutral condition. In mechanism, in strong acidic media, large amount of hydrogen ions scavenge sulfate radicals, hydroxyl radicals or Peroxymonosulphate (Eqs. 7-9) leading to removal deficiency directly. On the contrary, when solution pH surpasses neutral, cobalt ion begins hydrolysis and generate cobalt precipitation which leads to lack of catalyst and indirectly affect the reaction.



In Figs. 7-8, the solution was adjusted for different pH demands except neutral one (distilled water is the solvent directly and immediately without buffer). For RhB degradation, obviously the neutral condition is the most appropriate. At the most acidic circumstance (pH=2.8 which

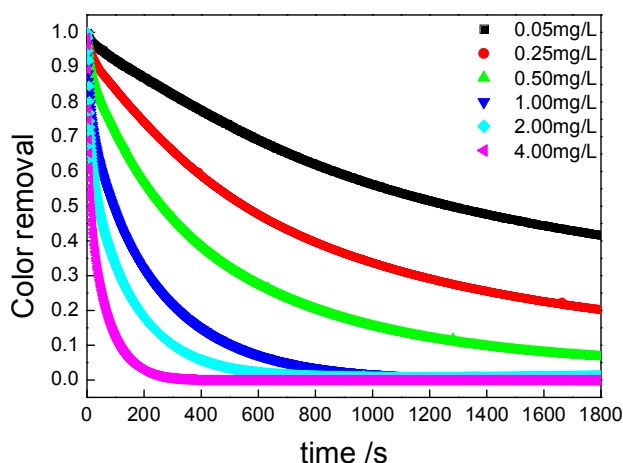


Fig. 2: Decolorization of RhB at different cobalt nitrate concentrations. Conditions: Near neutral solution (distilled water is the solvent without pH adjusting), $T=25^{\circ}\text{C}$ and $\text{PMS}=26\text{ mg/L}$, $\text{RhB}=4\text{ mg/L}$.

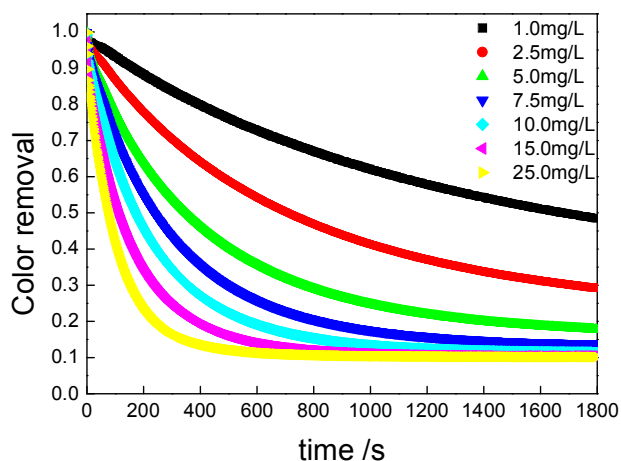


Fig. 3: Decolorization of AYG at different cobalt nitrate concentrations. Conditions: Near neutral solution (distilled water is the solvent without pH adjusting), $T=25^{\circ}\text{C}$ and $\text{PMS}=50\text{ mg/L}$, $\text{AYG}=20\text{ mg/L}$.

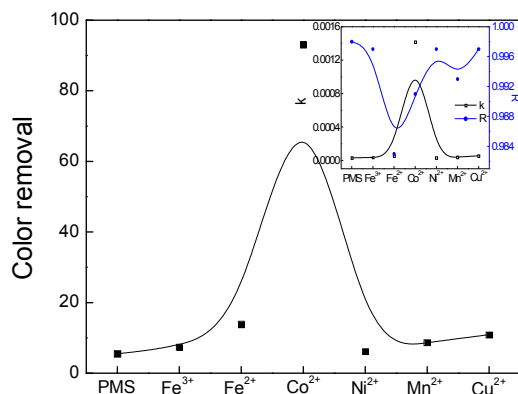


Fig. 4: Decolorization of RhB in M^{n+}/PMS process. Conditions: Near neutral solution (distilled water is the solvent without pH adjusting), $T=25^{\circ}\text{C}$ and $\text{PMS}=20\text{ mg/L}$, $\text{RhB}=4\text{ mg/L}$, $n_{\text{M}^{n+}}=2.73 \times 10^{-3}\text{ mmol/L}$ ($\text{Co}(\text{NO}_3)_2=0.5\text{ mg/L}$, $\text{Cu}(\text{NO}_3)_2=0.66\text{ mg/L}$, $\text{Ni}(\text{NO}_3)_2=0.79\text{ mg/L}$, $\text{Mn}(\text{NO}_3)_2=0.78\text{ mg/L}$, $\text{Fe}(\text{NO}_3)_3=1.1\text{ mg/L}$, $\text{FeSO}_4=0.76\text{ mg/L}$). Inset: the first order kinetics information of M^{n+}/PMS process.

is a considerable pH for Fenton process) the corresponding colour removal is 15% and it changes dramatically as the solution pH increases. At alkaline environment (pH 9 or 10), the colour removal decreases remarkably to 55% and even around 10%. However, for AYG decolorization, the optimum pH lies at alkaline side. Additionally, the corresponding colour removal drops down 40% when the solution pH further rises to 11. The phenomenon seems abnormal and could be explained by that the Acid Yellow G belongs to acid dye, its molecule is easier to break at alkaline condition. As the decomposition of this dye takes place, more acid intermediate is generated and inhibit cobalt ion hydrolysis in certain degree. Moreover, the HSO_5^- is more stable at alkaline condition. Consequently the $\text{Co}^{2+}/$

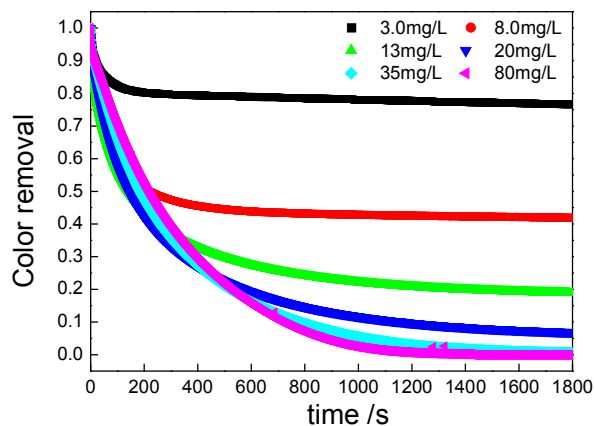


Fig. 5: Decolorization of RhB at different PMS concentrations. Conditions: Near neutral solution (distilled water is the solvent without pH adjusting), $T=25^{\circ}\text{C}$ $\text{Co}(\text{NO}_3)_2=0.5\text{ mg/L}$, $\text{RhB}=4\text{ mg/L}$.

PMS process works more efficiently at weak alkaline condition than neutral. Hence, an assumption can be proposed that the acid dyestuff is more degradable with $\text{Co}^{2+}/\text{PMS}$ process at weak alkaline or around neutral condition, which is a marvellous advantage for special wastewater treatment without pH adjusting.

In order to testify this hypothesis, acid red 6B and acid blue 9 were degraded similarly as depicted in Fig. 9. There is a common character that all the three acid dyes have superior decolorization performance at pH 9 compared to the neutral condition. Their final removals are nearly approaching (pH 7 and pH 9) and main discrepancy is reflected in the reaction rate. Basically, within 300s the colour removal tends to be balanced at pH 9 condition. According to Fig. 9, the reaction rate of the three dyes degradation at pH 9 is about triple times

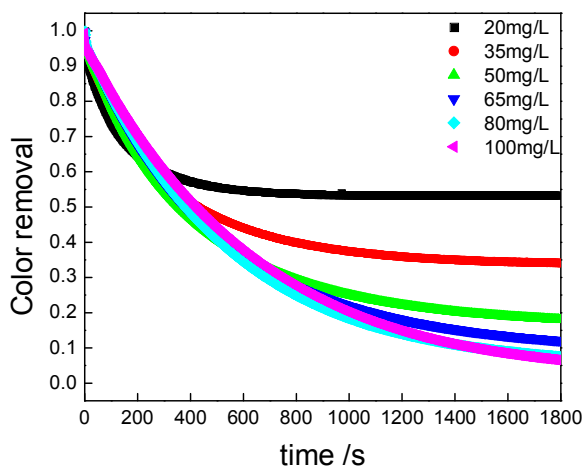


Fig. 6: Decolorization of AYG at different PMS concentrations. Conditions: Near neutral solution (distilled water is the solvent without pH adjusting), T=25°C Co(NO₃)₂=5 mg/L, AYG=20 mg/L.

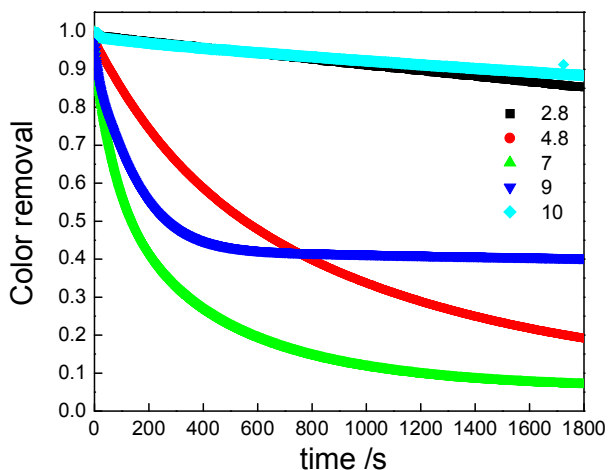


Fig. 7: Decolorization of RhB at different solution pH Conditions: T=25°C, and Co(NO₃)₂=0.5 mg/L, PMS=20 mg/L, RhB=4 mg/L

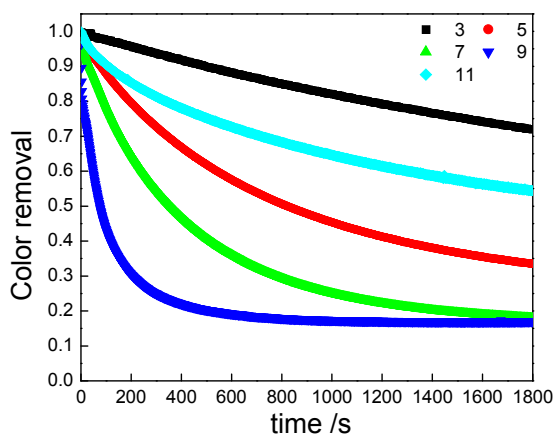


Fig. 8: Decolorization of AYG at different pH solution. Conditions: T=25°C, Co(NO₃)₂=5 mg/L, PMS=50 mg/L, AYG=20 mg/L.

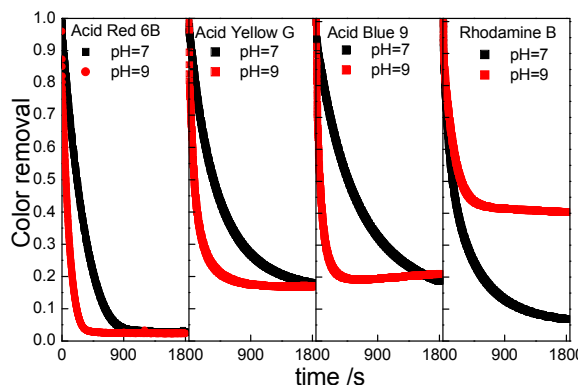


Fig. 9: Decolorization of AR6B, AYG, AB9, RhB at different pH. Conditions: T=25°C, AR6B=20 mg/L, AYG=20 mg/L, AB9=50 mg/L, RhB=4 mg/L.

higher than that at pH 7. Therefore theoretically, at same disposal time, the treatment ability of acid dye wastewater can be tripled at pH 9. While at the neutral condition, the colour removal increases gradually along with the degradation. By contrast, the degradation percentage of RhB reduces 35% once the pH rises to 9. In sum, the Co²⁺/PMS process is a reliable dyeing wastewater remediation, especially for the acid dyestuffs because of the wider pH range (4-9).

CONCLUSION

The Rhodamine B and Acid Yellow G were successfully decolorized by Co²⁺/PMS process with online spectrometric system. The effect of various nitrate cobalt dosages, PMS concentrations and pH on probe compound colour removal was investigated.

1. The results demonstrated that with the preferred respective condition (1 mg/L Co(NO₃)₂, 20 mg/L PMS and pH 7; 10 mg/L Co(NO₃)₂, 65 mg/L PMS and pH 9) the Xanthone Rhodamine B and Azo Acid Yellow G can be degraded thoroughly with nearly 100% colour removal.
2. Moreover, the solution pH has pronounced effect on the Co²⁺/PMS process. For Rhodamine B, neutral pH is the optical reaction condition, however, weak alkaline condition is beneficial to Acid Yellow G decolorization. And then a hypothesis was proposed that alkaline condition is favourable to acid dye decomposition with Co²⁺/PMS process. Additionally, Acid Red 6B and Acid Blue 9 were also used as probe contamination to verify this assumption. According to the evidence that each acid dye conformably has a superior deterioration performance at pH 9 compared to the neutral environment. And through kinetic analysis, the change of pH (from 7

to 9) tripled the reaction rate at the first 300s.

3. Furthermore, at the same molar concentration of metal ion, $\text{Cu}^{2+}/\text{PMS}$, $\text{Mn}^{2+}/\text{PMS}$, $\text{Ni}^{2+}/\text{PMS}$, $\text{Fe}^{3+}/\text{PMS}$, $\text{Fe}^{2+}/\text{PMS}$ and $\text{Co}^{2+}/\text{PMS}$ processes were studied for catalytic effect of similar activators, the outcome demonstrated that the cobalt ion is the most reactive one at the same molar concentration to activate PMS.

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