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Catalytic oxidation of Rhodamine B in aqueous solutions with sulphate radicals over Co_3O_4/MgO and $CoFe_2O_4$/MgO

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The oxidative degradation of Rhodamine B (RhB) in aqueous solutions with peroxymonosulphate (PMS) was studied using Co_3O_4/MgO and $CoFe_2O_4$/MgO as catalysts. The as-prepared samples demonstrated strong PMS-activating ability despite low active phase loading percentage (5 wt%) and very low catalysts concentration (0.15 g dm^{-3}). The performance of the supported catalysts was found much better than that of their bulk analogues and mechanical mixtures of corresponding bulk oxide and bare MgO due to the crucial role of basic support for facilitating decomposition of PMS into highly reactive radicals. RhB degradation was found to follow the first order kinetics. The effect of catalyst dosage, PMS concentration, and pH on the rate of RhB oxidation was investigated. The radical species generated from the catalytic decomposition of PMS were identified by quenching studies.

Keywords: Rhodamine B degradation; Sulphate radicals; Co_3O_4/MgO; $CoFe_2O_4$/MgO; Peroxymonosulphate activation.

INTRODUCTION

Dyestuffs represent one of the largest groups of organic pollutants in wastewaters, generally released from textile finishing, dye manufacturing, leather dyeing, pulp and paper production, Kraft bleaching and tannery industries [1]. Dyes are considered hazardous to the environment and could cause significant health concerns due to their non-biodegradability, toxicity, potential carcinogenic and mutagenic nature [2]. Therefore, the removal of dyes from industrial effluents prior to their discharge into natural water bodies has attracted much interest and is an important practical problem.

Advanced oxidation processes (AOPs) based on the activation of environmental friendly oxidants to generate highly reactive radicals are recognized as effective technologies for degradation of refractory organic pollutants in water at ambient conditions [3-5]. Over the past few years, sulphate radical based-AOPs are attracting considerable attention in the area of wastewater treatment because, compared to hydroxyl radicals, sulphate radicals ($SO_4^{\bullet-}$) have higher oxidizing strength, longer half-life and are more selective for the oxidation of contaminants in industrial effluents, thus overcoming some limitations of the conventional Fenton processes [5,6]. An efficient route for production of $SO_4^{\bullet-}$ is the homogeneous activation of peroxymonosulphate (PMS) with transition metal ions, cobalt ions being the best activator [7]. However, cobalt is recognized as a priority pollutant in water and the adverse effect of dissolved cobalt ions on animals and human beings might result in environmental concern [8]. Several researchers have found that heterogeneous cobalt-based catalysts - bulk and immobilized on various supports such as TiO_2, Al_2O_3, SiO_2, activated carbon, etc., coupled with PMS exhibited a good performance on the degradation of 2,4- dichlorophenol and phenol [8-10]. However, few studies have been conducted on cobalt oxides and supported Co oxides for degradation of organic dyes using PMS as oxidant [11-13]. Considering the environmentally friendly nature, relative low cost and abundance of iron, Su *et al.* [14] have investigated the catalytic activity of a series of $Co_xFe_{3-x}O_4$ nanoparticles for activation of PMS for heterogeneous degradation of RhB dye and found that the increase in cobalt content in the catalyst resulted in higher degradation efficiency. In our previous study cobalt and mixed iron–cobalt oxides immobilized on MgO were synthesized and were proven to be very effective heterogeneous catalysts for Acid Orange 7 oxidation in aqueous solution by using PMS as oxidant [15]. To date, few studies have reported the heterogeneous degradation of RhB in aqueous solution through sulphate radical approach [13, 14, 16].

This study reports the oxidative degradation of the refractory dye Rhodamine B in aqueous solutions using Co_3O_4 and $CoFe_2O_4$ supported on MgO as catalysts for heterogeneous activation of PMS. The kinetics of the oxidation process and the effect of some important factors such as catalyst dosage, PMS concentration, and initial solution pH on the RhB degradation efficiency were investigated. Furthermore, quenching experiments were conducted for identifying the dominating reactive

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radicals generated from the catalyst-mediated decomposition of PMS.

EXPERIMENTAL

MgO supported catalysts with 5 wt. % Co_3O_4 or $CoFe_2O_4$ loading were prepared by incipient wetness impregnation [15]. Bulk Co_3O_4 and $CoFe_2O_4$ were prepared by a precipitation/co-precipitation method.

XRD patterns of the samples were obtained on a TUR M62 powder X-ray diffractometer (XRD) using Co-Kα radiation (λ= 1.789 Å) at 40 kV and 20 mA. The morphology of the catalysts was characterized on a JEOL JEM 2100 high resolution transmission electron microscope (TEM) using an accelerating voltage of 200 kV. Two basic regimes of microscope mode were used – bright field transmission microscopy (TEM) and selected area electron diffraction (SAED). The pH of the point of zero charge (pH_{PZC}) of the catalysts was determined by the pH drift method [17]. The amount of cobalt and iron in the prepared samples, as well as the concentrations of leached Co and Fe in the solution were measured by atomic absorption spectrometry (AAS, Perkin-Elmer).

Catalytic oxidation of RhB with PMS was carried out in a 400 cm^3 glass reactor at 293 K with constant stirring at around 400 rpm. In a typical experimental procedure, a fixed amount of catalyst was added to a 200 cm^3 solution containing 50 mg dm^{-3} of RhB and the suspension was stirred for 30 min to achieve adsorption-desorption equilibrium. The reaction was initiated by addition of oxidant to attain the predefined PMS/RhB molar ratio. Aliquots of 4.0 cm^3 withdrawn from the mixture at given time intervals were immediately mixed with 1 mL of methanol to quench the reaction. The RhB concentration in the aqueous solution was determined by means of UV–Vis spectrophotometry (Cintra 101, GBS) at 554 nm. All tests were conducted in triplicate to ensure the reproducibility of experimental results.

RESULTS AND DISCUSSION

The crystal structure of the synthesized supported catalysts was investigated by XRD and compared with those of the MgO support and bulk cobalt and iron-cobalt oxides (Fig. 1). The spectra of unsupported samples showed distinct peaks, which match well with cubic spinel-type Co_3O_4 (JCPDS 42-1467, lattice parameter a=8.08 Å) and $CoFe_2O_4$ (JCPDS 22-1086, lattice parameter a=8.37 Å), respectively. The average crystallite size of bulk Co_3O_4 and $CoFe_2O_4$, calculated according to the Debye-Scherrer equation, was found to be 34.7 and 11.3 nm, respectively. As seen in Fig.1, the XRD patterns of Co_3O_4/MgO and $CoFe_2O_4$/MgO are similar to that of bare MgO and no obvious reflections typical of the corresponding spinel oxide phases could be observed. This suggests a high dispersion of cobalt and iron particles on MgO because the Fe and/or Co levels on supported catalysts were close to preparation settings as revealed from the AAS analysis.

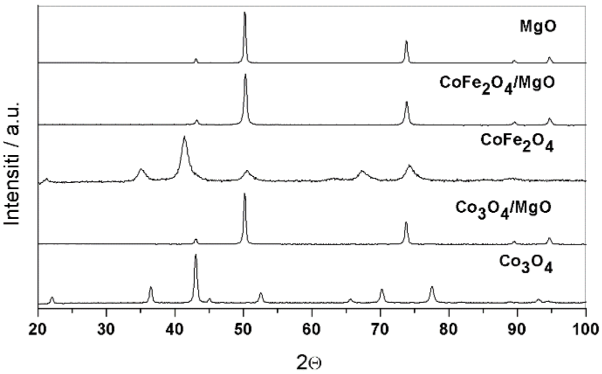

Fig. 1. XRD patterns of bulk and MgO supported Co_3O_4 and $CoFe_2O_4$

The presence of spinel structured oxide phases on MgO was evidenced by using TEM (Fig. 2). The bright field TEM images (Fig.2a) show that the immobilized spinel oxide nanoparticles (the small dark spots) are well dispersed on the surface of the MgO support and their size is in the range of about 10-20 nm. The diffraction patterns (SAED) obtained from the TEM (Fig. 2b) show spinel phases Co_3O_4 and $CoFe_2O_4$, respectively, with the diffraction rings corresponding to reflections from the crystal planes of the expected phases marked on the figure.

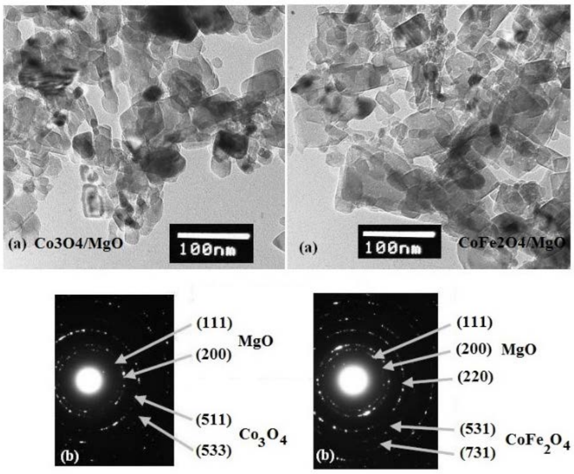

Fig. 2. (a) Bright field TEM (60 kX) and (b) SAED patterns of the synthesized supported catalysts.

The temporal spectral changes of RhB in solution during oxidative degradation on the Co_3O_4/MgO sample are depicted in Fig. 3. It is seen that the characteristic RhB absorption peak at 554 nm rapidly decreases throughout the reaction and finally disappears, indicating the facile break-up of the conjugated xanthene structure. Meanwhile, no hypsochromic shift in the maximum absorption band of RhB was observed during oxidation, implying that no N-de-ethylation of the dye takes place in competition with the degradation of the RhB chromophore ring. Furthermore, a simultaneous reduction in the absorption peak at 259 nm attributed to the π–π^* transition in the aromatic ring group was also registered, indicating concomitant degradation of the aromatic part of the RhB dye. Since there are no additional peaks appearing in the UV–Vis spectra in the course of the experiment, it could be speculated that no other products detectable by UV–Vis spectroscopy are left in the reaction mixture.

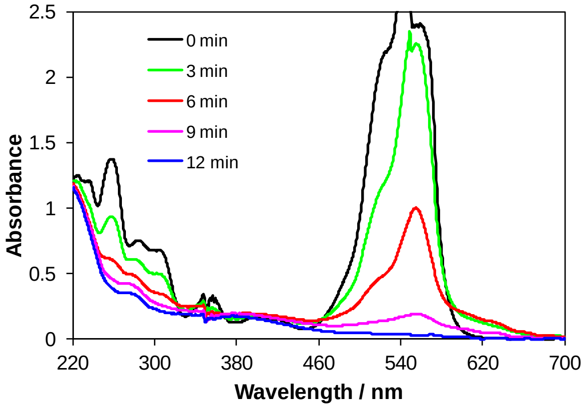

Fig. 3. UV–vis spectral changes of RhB in the Co_3O_4/MgO-PMS process.

The representative data for degradation of RhB in different systems are presented in Fig. 4.

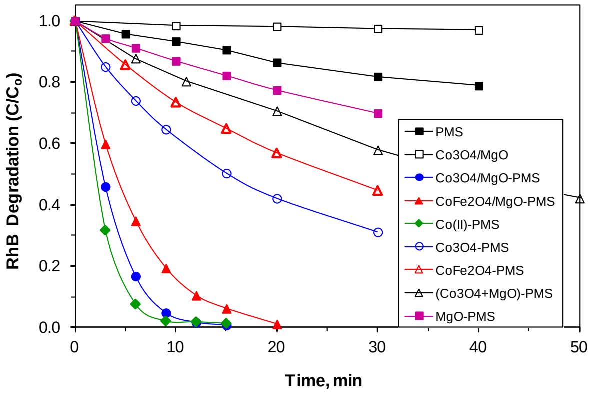

Fig. 4. RhB degradation with time in different systems. Reaction conditions: $[RhB]^o$ = 50 mg dm^{-3}, catalyst loading = 0.15 g dm^{-3}, PMS/RhB=20:1.

In the control experiment without PMS a negligible decay of nearly 2.5% in RhB concentration was noticed within 30 min, which could be attributed to physical adsorption of dye molecules on the surface of the supported catalysts. PMS alone brought about only 22% RhB removal after 30 min, indicating that the oxidant itself could not induce significant RhB oxidation. A limited RhB degradation was also observed in the presence of bare MgO coupled with PMS. After 30 min, the RhB reduction was less than 30%, implying that PMS could be activated by MgO to produce peroxymonosulphate radicals ($SO_5^{\bullet -}$) probably due to the following reaction,

$$MgO + HSO_5^- \rightarrow Mg^{2+} + {}^{\bullet}OH + SO_5^{-\bullet} \qquad (1)$$

However, the RhB oxidation over bare MgO slightly differs from that of PMS self-oxidation, suggesting that generation of radical species in the given case takes place at a very low rate. Besides, the observed linear RhB removal profile in the MgO–PMS mixture further evidences that activation of oxidant is the rate-limiting step of the oxidation process rather than the destruction of the dye molecules by radicals formed.

The catalytic performance of unsupported Co_3O_4 and $CoFe_2O_4$ oxides was also explored. The results reported in Fig. 4 revealed that the RhB degradation rate has reached less than 60% and 43 % within 20 min in the Co_3O_4–PMS and $CoFe_2O_4$–PMS systems, respectively. However, when Co_3O_4 and $CoFe_2O_4$ nanoparticles immobilized on MgO were used as catalysts for PMS activation, RhB underwent rapid and almost complete degradation. More than 99% of RhB was eliminated in 12 min using Co_3O_4/MgO, whereas $CoFe_2O_4$/MgO displayed lower activity, with complete dye removal after 20 min. Moreover, the performance of the supported catalyst was found only slightly inferior to that of the homogeneous Co(II)/PMS reagent. A very low extent of cobalt and iron leaching from Co_3O_4/MgO, and $CoFe_2O_4$/MgO catalysts (less than 3%) during the reaction suggests that the RhB degradation is not influenced by the homogeneous reaction taking place due to the leached metal ions. These results strongly suggested that the spinel structured oxide supported on MgO has strong PMS activation functionalities. The relatively slower RhB degradation kinetics assisted by supported cobalt ferrite could be attributed to the lower cobalt content in this catalyst. Moreover, our previous Mössbauer studies showed that Fe ions in the synthesized $CoFe_2O_4$/MgO are in 3+ oxidation state and occupy both tetrahedral and octahedral sites in a face- centered cubic crystalline structure [15]. Unlike Co (II), Fe (III) is an electron acceptor and decomposes PMS by generating $SO_5^{\bullet -}$. These radicals are much less reactive than sulphate radicals and hence their contribution to the oxidative destruction of the dye is insignificant.

Meanwhile, Co species in Co_3O_4 are also a mixture of Co(II) and Co(III) with Co(III) being predominant (the molar ratio of Co(III)/Co(II) is 2 as it is the Fe(III)/Co(II) ratio in $CoFe_2O_4$). It could be speculated that the better catalytic activity of Co_3O_4/MgO resulted from the more intimate interactions between Co(III) and Co(II) at the molecular level (i.e. Co–Co linkages) than Fe–Co interactions in $CoFe_2O_4$/MgO. As a result, the cobalt redox cycling in Co_3O_4 could take place faster thus facilitating the radical generation. Although the Co_3O_4/MgO catalyst exhibited higher catalytic effect on RhB degradation than supported cobalt ferrite, the latter is a more relevant catalyst considering environmental and practical aspects (non-toxicity and abundance of iron).

The observed enhancement in the catalytic activity of MgO loaded Co_3O_4 and $CoFe_2O_4$ could be attributed to two factors: (i) the hydroxyl groups on the surface of MgO facilitate the formation of functional Co(II)–OH complexes through direct interaction of surface cobalt species with the nearby surface OH groups on the support, which are crucial for radical generation in the subsequent step of PMS activation [18]; (ii) the basic surface of MgO ensures good dispersion of the active phase, leading to more intimate interaction of cobalt species with the surface hydroxyl groups of the support. Hence, more active sites for PMS activation were produced on Co_3O_4/MgO and $CoFe_2O_4$/MgO compared to their bulk analogues, which led to the accelerated generation of active radicals and thus to the higher RhB degradation efficiency. The much weaker catalytic performance exhibited by the mechanical mixture of Co_3O_4 and MgO confirms the crucial role of the close contact between the support and the active oxide phase for the efficient PMS activation.

Experimental data revealed that RhB oxidation over bulk and MgO supported catalysts follows the first order kinetics. The reaction rate constants (k) and regression coefficients (R^2) of the model fitting are given in Table 1.

Table 1. Kinetic parameters of RhB degradation in different catalyst – PMS systems

Catalyst	Rate constant (min^{-1})	R^2
Co_3O_4	0.0428	0.992
$CoFe_2O_4$	0.0274	0.994
Co_3O_4/MgO	0.3243	0.994
$CoFe_2O_4$/MgO	0.2212	0.991

Further assessment of the efficiency of the as-prepared supported catalysts for RhB degradation was done by studying the influence of several operating parameters, including catalyst dosage, PMS concentration, and initial solution pH.

The RhB degradation efficiency was enhanced with the increase in catalyst dosage regardless the nature of the supported active phase (Fig. 5). The increased reaction rate with catalyst loading is evidently due to the availability of more active sites on the catalyst surface for activation of PMS, resulting in faster generation of more reactive radicals. In fact, complete RhB removal could be reached within 12 min at Co_3O_4/MgO loading of 0.15 g dm^{-3}, whereas catalyst concentration at 0.5 g dm^{-3} resulted in 100% dye degradation within very short duration of 3 min. Accordingly, upon the same increase in the amount of $CoFe_2O_4$/MgO catalyst, the time required for full discoloration of dye solution was reduced 2.5 times.

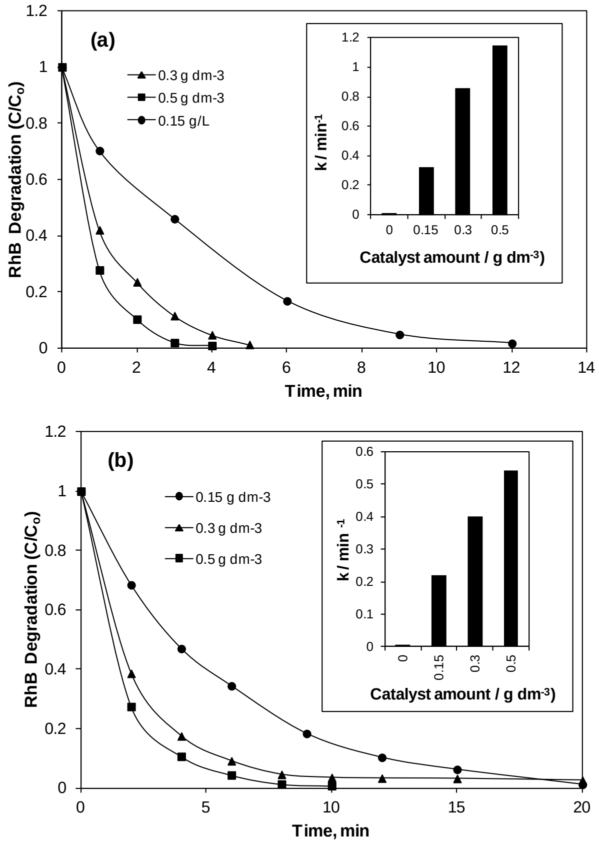

Fig. 5. Effect of catalyst amount on the RhB degradation rate. (a) Co_3O_4/MgO; (b) $CoFe_2O_4$/MgO (0.15 g dm^{-3}). Reaction conditions: $[RhB]^o$ = 50 mg dm^{-3}, PMS/RhB=20:1.

However, a less pronounced increase of the rate constants with catalyst amount increasing from 0.3 to 0.5 g dm^{-3} was found (inset of Fig. 5), which could be due to the self-quenching of a rapidly generated large amount of radicals by PMS instead of reacting with target molecules. Another reason could be the formation of aggregates between catalyst particles which resulted in a reduced number of available sites for PMS activation. It should be emphasized that although a difference in the degradation rate of RhB was observed, the final removal efficiencies were similar due to the same concentration of oxidant.

Fig. 6 presents RhB degradation kinetics in the presence of Co_3O_4/MgO at different PMS concentrations (in terms of molar ratio of

PMS/RhB). As can be seen, faster RhB decay rate and higher removal efficiency are achieved by increasing the PMS/RhB molar ratio due to the production of more radicals to degrade RhB dye. At a molar ratio of 2/1, RhB was slowly and not completely degraded with a final removal of 51.8 % after 20 min, while for the same duration at a five-fold higher PMS concentration, the removal efficiency was near 100%. Incomplete degradation of the dye was also registered using a molar ratio of 6/1, attributed to the depletion of oxidant, which dosage was much less than the required stoichiometric dosage for complete RhB mineralization [13].

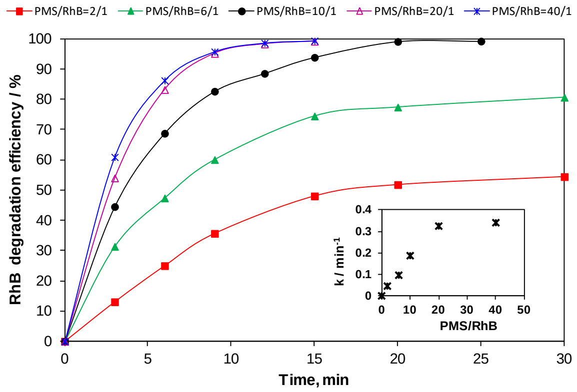

Fig. 6. RhB degradation over Co_3O_4/MgO at different PMS concentrations. Reaction conditions: [RhB]° = 50 mg dm^{-3}, catalyst loading = 0.15 g dm^{-3}.

The RhB removal rate, as characterized by the pseudo-first order rate constant, increased almost linearly with increasing PMS/RhB ratio up to 20/1, implying that the active sites on the catalyst surface were still not totally occupied by PMS, but no significant change in the removal efficiency was observed at further increasing the PMS dosage (inset of Fig. 6).The observed trend might be attributed to the fixed number of surface active sites, which gradually became the limiting factor controlling the yield of radicals at high PMS concentration, so that the radical yield was almost independent of PMS. Less pronounced enhancement of the RhB removal efficiency when the molar ratio of PMS/RhB was higher than 20/1 could also be explained by the increased competition of the higher number of PMS molecules for absorption and consequent activation on the finite number of surface sites.

Since the dye-containing effluents are discharged at various pH, the ability of a heterogeneous catalyst to operate efficiently under different pH conditions is highly desirable. The effect of initial pH on the RhB degradation over supported catalysts was studied at pH 4.1, 6.98 and 9.2 and the results are presented in Fig. 7. It is obvious that acidic medium is more suitable for the catalytic degradation reaction and an evident decrease in the RhB degradation efficiency can be observed in neutral-alkaline conditions. At the initial pH of 6.98, 100% RhB removal was achieved after 40 min using the $CoFe_2O_4$/MgO catalyst, while the dye was fully degraded for a twice shorter period when pH was decreased to 4.1. It is worthy to note that even under alkaline conditions, a complete discoloration of the RhB solution could be achieved in about one hour, implying that the catalysts prepared still exhibited a good catalytic activity at high pH values.

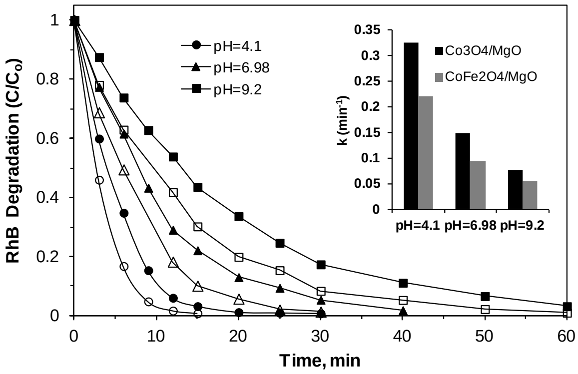

Fig. 7. Effect of pH on RhB degradation over Co3O4/MgO (open symbols) and $CoFe_2O_4$/MgO (closed symbols). Reaction conditions: [RhB]° = 50 mg dm^{-3}, catalyst loading = 0.15 g dm^{-3}, PMS/RhB=20:1.

The decrease in dye removal rate with increasing pH (inset of Fig. 7) might be explained considering that the solution pH significantly affects the surface charge of the catalysts and the speciation of RhB and PMS in solution. Hence, the adsorption of dye molecules and the effectiveness of oxidant activation on the catalyst surfaces could change at different pH and thus influence the degradation efficiency. Since the pH_{PZC} of the MgO supported catalysts was found about 9.8 – 10.1, the surface of the catalyst particles was positively charged in the entire pH range studied. On the other hand, at pH values higher than pKa of RhB (3.7), the carboxyl group of the cationic form of the dye is deprotonated and the zwitterionic form of RhB is formed [19]. Accordingly, due to the electrostatic interaction, RhB species tend to adsorb on the positively charged surface sites of the catalyst *via* the negatively charged carboxyl group. However, the positively charged surface sites decrease with increasing pH, while the fraction of zwitterionic form increases. The latter would favor the aggregation of RhB by forming dimers due to the electrostatic interactions between the xanthenes and the carboxyl groups of the RhB monomers. The adsorption of large dimers is hindered and under such conditions the RhB removal might be inhibited. Furthermore, the observed decreasing trend could also be due to the radical scavenging effect of bicarbonate anions used to adjust pH, as well as to the inefficient self-decomposition of PMS through a non-radical pathway at high pH values [20]. Thus, these could be possible reasons for the lower RhB degradation rates observed at neutral-alkaline conditions.

The activation of PMS by heat, UV, metal ions or metal oxides usually generates two major kinds of radicals, *viz.*, hydroxyl radicals ($^{\bullet}OH$) and sulphate radicals ($SO_4^{\bullet-}$) [3, 9, 21]. To confirm that RhB degradation resulted from radical attack and to identify the dominant radical species generated by catalyst/PMS couples, quenching tests were conducted with the addition of EtOH and TBA as radical scavengers. Ethanol acts as a scavenger of both $^{\bullet}OH$ and $SO_4^{\bullet-}$, while TBA is often used as an effective $^{\bullet}OH$ quenching agent because the rate constant of TBA with $^{\bullet}OH$ is approximately 1000 times greater than that with $SO_4^{\bullet-}$ [3]. The effect of both quenching agents on the rate and efficiency of RhB catalytic oxidation over Co_3O_4/MgO is shown in Fig. 8.

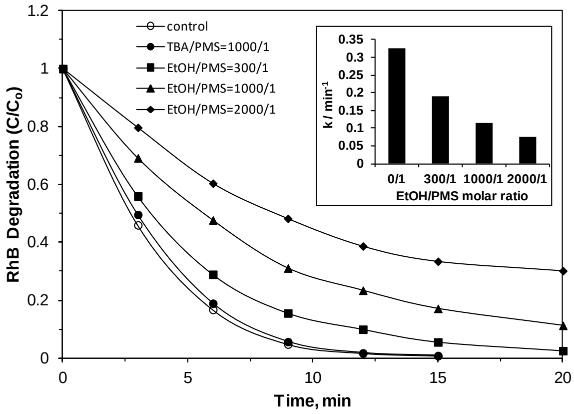

Fig. 8. Effect of different radical scavengers on RhB degradation in the Co_3O_4/MgO – PMS system. Reaction conditions: $[RhB]^o$ = 50 mg dm^{-3}, catalyst loading = 0.15 g dm^{-3}, PMS/RhB=20:1.

Results showed that there was no distinct difference in the rate and efficiency of RhB removal when TBA was added to the reaction mixture even at very high dosage. However, addition of ethanol suppressed the oxidation process and the inhibition was enhanced with increasing EtOH concentration (inset of Fig. 8). In fact, only 10% drop in RhB degradation efficiency with rate constant decreasing from 0.3243 to 0.1897 min^{-1} at lower EtOH/PMS molar ratio (300/1) was observed despite the fact that ethanol is a strong quencher of both sulphate and hydroxyl radicals. The RhB degradation was more significantly inhibited on further increase in the ethanol dosage (EtOH/PMS =2000/1), attaining only 70.6% oxidation upon exhaustion of the oxidant. The same effect of both scavenging agents was also observed in the PMS–$CoFe_2O_4$/MgO oxidation system. The results provided evidence that sulphate radicals appeared to be the major radical species generated during the activation of PMS by the catalysts prepared in this work and controlling the oxidation reaction.

CONCLUSIONS

In this study, sulphate radical-based degradation of RhB in aqueous solutions was studied. Reactive radicals were produced through heterogeneous activation of PMS mediated by Co_3O_4 and $CoFe_2O_4$ supported on MgO. Deposition of Co_3O_4 and $CoFe_2O_4$ nanoparticles on a basic MgO support led to considerable enhancement of their PMS activation functionality. MgO-supported catalysts produced fast and complete degradation of RhB (50 mg dm^{-3}) the apparent rate constants being almost eight-fold of that over corresponding bulk analogues. More than 99% of RhB was degraded in 12 min using Co_3O_4/MgO, while a slightly inferior catalytic performance was presented by the $CoFe_2O_4$/MgO catalyst with complete dye removal after 20 min. The higher catalytic activity of supported catalysts compared to bulk oxides is attributed to the increased basicity of the catalyst surfaces, which facilitates decomposition of oxidant and thus favors radical generation. Increasing the catalyst amount and PMS concentration enhanced the RhB degradation rate, while removal efficiency decreased as solution pH rose. Quenching studies showed that the destruction of RhB is due to the generated sulphate radicals.

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КАТАЛИТИЧНО ОКИСЛЕНИЕ НА РОДАМИН В ВЪВ ВОДНИ РАЗТВОРИ СЪС СУЛФАТНИ РАДИКАЛИ ВЪРХУ Co_3O_4/MgO И $CoFe_2O_4$/MgO

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(Резюме)

Изследвано е окислителното разграждане на Родамин В във водни разтвори с пероксимоносулфат (PMS) с използване на Co_3O_4/MgO and $CoFe_2O_4$/MgO като катализатори. Синтезираните образци показват висока PMS-активационна способност, независимо от ниското съдържание на нанесената активна фаза (5wt%) и много ниската концентрация на катализатора (0.15 g dm^{-3}). Активността на нанесените катализатори е значително по-висока от тази на масивните им аналози и на физични смеси на шпинелните оксиди и MgO, дължащо се на определящата роля на базичния носител за подпомагане разлагането на PMS до силно реактивоспособни радикали. Разграждането на RhB се подчинява на кинетичните закономерности на реакции от първи порядък. Изследвано е влиянието на количеството на катализатора, концентрацията на PMS и pH върху скоростта на окислителния процес. Чрез експерименти с добавяне на радикал-улавящи агенти са идентифицирани радикаловите частици, образувани при каталитичното разлагане на окислителя.