

Enhancing the PMS activation ability of Co₃O₄ by doping with Bi and Mg

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A series of Co-Bi and Co-Mg composite oxides were prepared by co-precipitation method and their catalytic activity for heterogeneous peroxymonosulphate (PMS) activation was investigated through Acid Orange 7 (AO7) degradation in aqueous solutions. The as-prepared catalysts were characterized by XRD, XPS, TEM, and ICP-OES. A significant increase in catalytic activity of Co₃O₄ by modifying with Bi and Mg oxides was registered. Composites with 50 wt.% Co₃O₄ content displayed the best catalytic activity by achieving complete removal of 50 mg dm⁻³ AO7 within 12–15 minutes under the reaction conditions of 0.1 g dm⁻³ catalyst and PMS/AO7 molar ratio of 6:1. The enhanced PMS activation functionality of the composite catalysts was ascribed to an increased amount of surface hydroxyl groups because of modifying with the basic oxides. Surface hydroxyls favoured the formation of a surface Co(II)-OH intermediate and thus the generation of sulphate radicals (SRs) from PMS was accelerated. AO7 degradation was found to follow first order kinetics. The quenching study clearly indicated that oxidative degradation of AO7 is a radical-involved process with SRs being the dominant radical species. The Co-Bi and Co-Mg composite oxides presented stable performance with minor cobalt leaching even under acidic conditions.

Key words: composite oxides, Co₃O₄, Bi₂O₃, MgO, peroxymonosulphate, AO7 degradation.

INTRODUCTION

In recent decades, advanced oxidation processes (AOPs) based on *in situ* generation of highly reactive radical species by activation of inorganic peroxides have emerged as a promising technology for degradation of refractory organic compounds to harmless products in water at ambient conditions [1–3]. Despite promising performance and cost-effectiveness of the conventional Fenton process, several significant drawbacks limit its practical applications such as a low pH range (2–4), a large catalyst dosage, and large amount of iron sludge produced [4]. Sulphate radical induced AOPs are regarded as a more feasible and effective alternative to the Fenton process, owing to comparative standard reduction potential, longer half-life, and better selectivity of SRs than hydroxyl radicals, to remove or even mineralize organic pollutants [5,6].

Homogeneous activation of unsymmetrical peroxide PMS by transition metal ions is proven an efficient route for production of SRs with cobalt ions being the best activator [7]. However, the adverse effect of dissolved cobalt ions on animals and human beings raise a great concern. Hence, the development of cobalt-based heterogeneous catalysts of high PMS activating ability to conduct catalytic oxidation of organic pollutants is highly desirable. For the first time Anipsitakis *et al.*

explored the possibilities of CoO and Co₃O₄ in activation of PMS for 2,4-dichlorophenol degradation in replacing homogeneous Co(II)/PMS [8]. Nano-sized Co₃O₄ catalyst was found to exhibit an excellent long-term stability and low dissolved Co ions, especially under neutral conditions in degradation of AO7 by PMS activation [9]. Although Co₃O₄ nanoparticles present good catalytic performance, they can easily agglomerate during catalytic reaction to cause a drop of the catalytic efficiency. To tune the surface properties, and therefore improve the catalytic activity, various supports such as TiO₂, Al₂O₃, SiO₂, carbon materials, MgO, etc. have been used to prepare supported cobalt catalysts [10–12]. Among these, metal oxides with abundant surface basic sites such as MgO and TiO₂ were reported to lead to a relative high catalytic activity. Besides, supports can also act as components with synergistic and hybrid property dramatically boosting the catalytic efficiency [13]. Mixed metal catalysts have improved stability (reduced leaching), multifunctionality (e.g. photoactive, magnetically separable, etc.), high redox activity, and better catalytic activity compared to single metal [14]. Many cobalt composite catalysts that have been used as PMS activators including CoFe₂O₄ [15], CoMn₂O₄ [16], CuFe₂O₄ [17], and CuBi₂O₄ [18] were found to exhibit a much stronger catalytic activity in PMS oxidation process than Co₃O₄. As PMS activation is favoured on a basic surface, modification of the Co₃O₄ with basic metal oxides would have a promotional effect on its PMS

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activation ability. AO7 is a representative azo dye widely used for the dyeing of textiles, food, and cosmetics. It is reported that AO7 shows good resistance to biodegradation, thus it is normally not amenable for the conventional wastewater treatment process [19].

The aim of the present work was to examine the effect of Bi and Mg oxides addition to Co_3O_4 on the catalytic performance in PMS activation for degrading Acid Orange 7 as a model water pollutant.

EXPERIMENTAL

Co_3O_4 -MgO and Co_3O_4 - Bi_2O_3 composite catalysts of various Co_3O_4 content (20, 50, and 80 wt.%) were synthesised by co-precipitation method using NaOH as a precipitation agent and subsequent annealing of the precursor at 773 K. In a typical procedure, 0.8 mol l^{-1} NaOH were added dropwise at 333 K into a certain volume of aqueous solution containing fixed amounts of cobalt nitrate and magnesium or bismuth nitrate under vigorous stirring until solution pH reached 10. The obtained precipitate was further aged at 333 K for 30 minutes under continuous stirring. The solid product was collected by filtration, washed with deionised water and ethanol several times to neutral pH, dried at 378 K overnight, and finally calcined at 773 K for 3 h in static air. For comparative purposes, pristine Co_3O_4 , MgO, and Bi_2O_3 were also prepared by the same synthesis procedure.

The amount of Co, Bi, and Mg in the prepared samples as well as the concentration of leached cobalt ions after the reaction were measured by ICP-OES analysis (iCAP 6300 Thermo Scientific). XRD analysis was performed using Bruker D8 Advance diffractometer with Cu $K\alpha$ radiation and LynxEye detector. Phase identification was accomplished by *DiffraPlus* EVA using ICDD-PDF2 Database. Catalyst morphology was determined on a JEOL JEM 2100 high-resolution transmission electron microscope 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). X-ray photoelectron spectroscopy (XPS) measurements were carried out on an AXIS Supra photoelectron spectrometer (Kratos Analytical Ltd.) using monochromatic Al $K\alpha$ radiation with photon energy of 1486.6 eV. The binding energies (BEs) were determined with an accuracy of ± 0.1 eV utilising the C1s line of adventitious carbon as a reference with energy of 285.0 eV. The pH of the point of zero charge (pH_{PZC}) of the catalysts was determined by pH drift method [20].

Degradation experiments were carried out in a 400- cm^3 glass reactor at 293 K under constant stirring at around 400 rpm. In a typical run, a fixed amount of PMS (in the form of Oxone, $2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$) was added into a 200- cm^3 aqueous solution (50 mg dm^{-3} AO7) to attain a pre-defined PMS/AO7 molar ratio and stirred until dissolved. Degradation reaction was initiated by adding a specified amount of catalyst. Aliquots of 4.0 cm^3 were taken at given time intervals, immediately mixed with 1 ml methanol to quench the reaction, and centrifuged at 4000 rpm for 1 min to remove the catalyst. The AO7 concentration was determined by measuring the absorbance at a fixed wavelength of 486 nm using UV-Vis spectrophotometer (Cintra 101, GBS). All tests were conducted in triplicate to ensure the reproducibility of experimental results. For quenching experiments, prior to addition of oxidant and catalyst, a known amount of the alcohol quencher (ethanol or tert-butyl alcohol) was added into the AO7 solution to obtain a required molar ratio of alcohol to PMS.

RESULTS AND DISCUSSION

Calculated Co_3O_4 content in the synthesised composite materials based on ICP-OES results and XRD characterisation is given in Table 1 along with preparation parameters for comparison.

Table 1. ICP-OES results for Co, Bi, and Mg content in synthesised catalysts

Catalyst	Co_3O_4 content (wt.%)	
	Preparation	ICP-OES
X% Co_3O_4 -MgO	20	21.6
	50	47.1
	80	74.3
X% Co_3O_4 - Bi_2O_3	20	23.8
	50	45.1
	80	79.2

Fig. 1 shows XRD pattern of the 20% Co_3O_4 - Bi_2O_3 catalyst in comparison with Bi_2O_3 and Co_3O_4 as reference compounds. The diffraction peaks of the pristine metal oxides can be indexed to single-phase monoclinic α - Bi_2O_3 , (JCPDS 41-1449) and cubic spinel-type Co_3O_4 (JCPDS 42-1467), respectively. Reflexes typical of the two individual metal oxides were observed in the spectrum of the composite sample, which indicated the presence of Co_3O_4 and Bi_2O_3 in the catalyst. Notably, the intensity of peaks associated with cobalt species was very weak, suggesting good dispersion of the Co_3O_4 particles in the resulting product. Similarly, the peaks corresponding to the MgO were clearly observed and domi-

nant for the 20% Co_3O_4 -MgO sample (not shown).

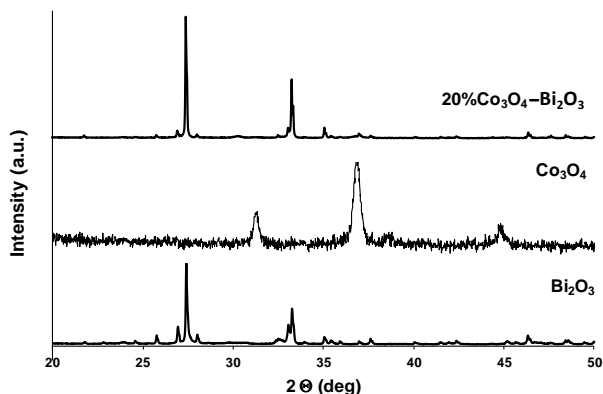


Fig. 1. XRD patterns of 20% Co_3O_4 - Bi_2O_3 , Co_3O_4 , and Bi_2O_3 .

Bright field TEM images (Fig. 2a) of the 20% Co_3O_4 -MgO and 20% Co_3O_4 - Bi_2O_3 catalysts indicate that the particles in both samples are predominantly flat with a near-rectangular shape. Particles with elongated rod-like shape were also observed. The diffraction patterns of both samples (Fig. 2b) reveal their polycrystalline nature with a good degree of crystallisation. Indexations of the SAED patterns confirm the presence of two metal oxide phases in each catalyst, indicated by arrows in Fig. 2b.

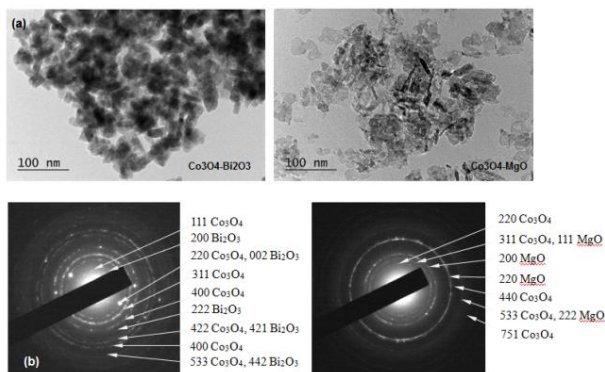


Fig. 2. (a) Bright field TEM (50k) and (b) SAED patterns of 20% Co_3O_4 -MgO and 20% Co_3O_4 - Bi_2O_3 .

The particle size distribution of both composite catalysts was close to normal (Gaussian), but being more homogeneous in the 20% Co_3O_4 -MgO sample (not shown). Particle sizes in both samples were mainly concentrated in the range of 7–20 nm. The average crystallite size of 20% Co_3O_4 -MgO and 20% Co_3O_4 - Bi_2O_3 was estimated to be 10.1 and 13.7 nm, respectively.

Wide-scan XPS spectra of the composite catalysts show that both Co and Mg or Bi elements are present on the surface (Fig. 3a). Deconvolution of the Co (2p) envelopes (not shown) indicated that the cobalt species were present in Co(II) and Co(III) oxidation states at atomic ratio close to 2, which is typical of Co_3O_4 . A pronounced asymmetry of the

O1s spectra implies for simultaneous presence of two types of oxide particles in the composite catalysts. Two subpeaks could be resolved with BE of 529.4 and 531.1 eV, which were assigned to lattice oxygen and surface hydroxyl species, respectively (Fig. 3b). Based on both peak areas, the ratio of hydroxyl to oxide groups in the Co-Mg composite was calculated to be 62:38 indicating that OH groups dominantly covered the catalyst surface. The relative content of the surface hydroxyl oxygen in the Co-Bi composite was lower (*ca.* 21% of total oxygen), but was twice higher than estimated for Co_3O_4 (11%). A higher extent of surface hydroxylation of the composite catalysts compared to the Co_3O_4 could be due to a higher pH_{zpc} of MgO (11.8) and Bi_2O_3 (9.2) than that of non-modified cobalt oxide (7.3). More surface basic sites available of in composite catalysts can promote the formation of surface Co(II)-OH complexes that was considered crucial for radical generation in the subsequent step of PMS activation [11].

Control experiments were conducted to compare AO7 removal efficiencies by various processes. As shown in Fig. 4a, no obvious degradation of AO7 by PMS alone was observed in the investigated time scale although PMS is a strong oxidizing agent ($\varphi^0 = +1.82$ V). Less than 1% colour removal was reached after 8 h to imply that chemical oxidation process is most likely to occur through a non-radical mechanism. In the presence of composite catalysts without PMS addition *ca.* 5% extent of decolourisation of the solution was attained in 10 min pointing out that AO7 adsorption on the catalysts was less effective to remove it from the water. Similar decolourisation efficiency was observed with the Bi_2O_3 /PMS system showing that the pure Bi_2O_3 could not activate the PMS to degrade the dye. However, AO7 degradation was found more significant for the MgO/PMS system under the same conditions with around 63% extent of oxidation suggesting that bare MgO can decompose PMS into active radicals. There was still 55% of AO7 remaining after 15 min, when pure Co_3O_4 was used as the PMS activating catalyst, and a complete decolouration of the solution was achieved for 90 min. However, when the composite oxides even with lowest MgO or Bi_2O_3 content (20 wt.%) were added as a catalyst, the dye pollutant was oxidised rapidly achieving up to 99% colour removal in 15 min even at a very low catalyst concentration of 0.10 g/l. These results confirmed that the degradation process was a radical-involved process and the active radical species were generated much faster in the presence of hybrid catalysts than bare Co_3O_4 (100% active phase).

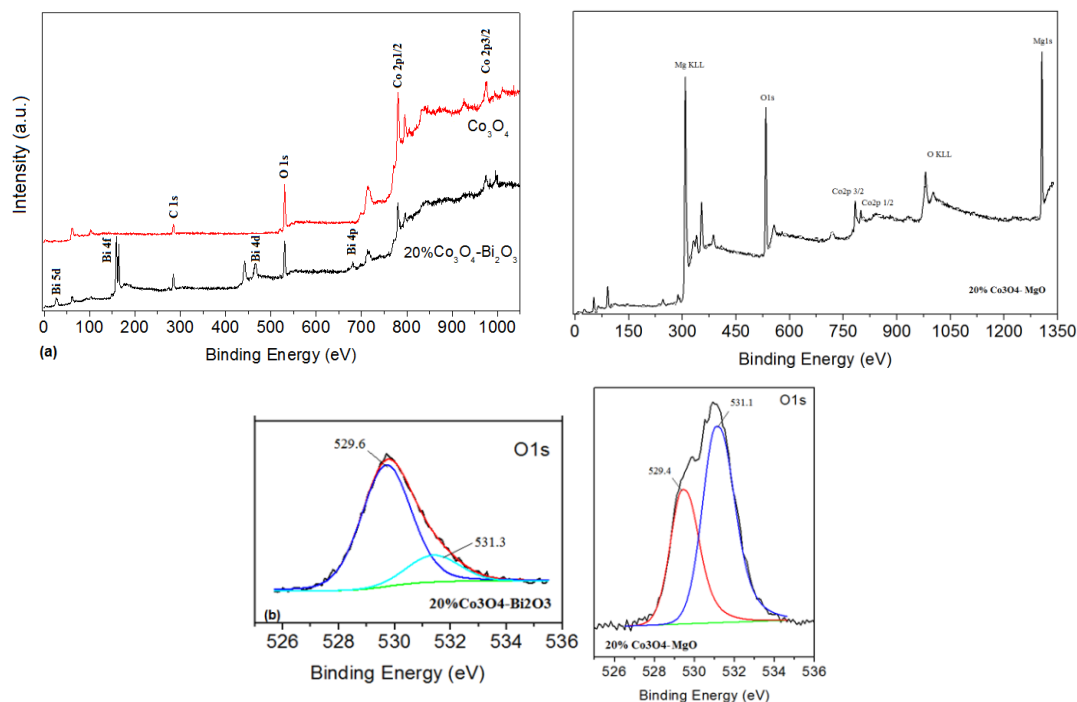


Fig. 3. (a) Wide scan XPS spectra of the 20% $\text{Co}_3\text{O}_4\text{-Bi}_2\text{O}_3$ and 20% $\text{Co}_3\text{O}_4\text{-MgO}$ catalysts and (b) their O1s envelopes (with deconvolution).

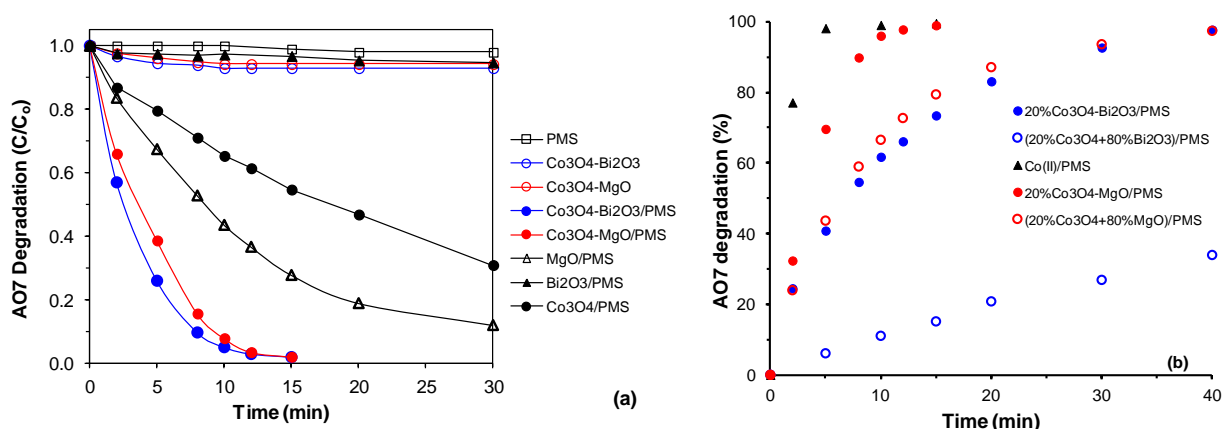


Fig. 4. AO7 degradation with time in different systems. Reaction conditions: 50 mg dm^{-3} AO7; 0.1 g dm^{-3} catalyst loading; $\text{PMS}/\text{AO7} = 6/1$; $\text{pH} = 4.0$. Co_3O_4 content in composite catalysts was 80 wt. %.

A much higher catalytic activity presented by Co-Bi and Co-Mg composite oxides for AO7 degradation suggests a synergistic effect of both oxide components in the catalysts. The observed synergism supports a hypothesis of the important role of the basic dopants (Bi_2O_3 and MgO) in facilitating the formation of functional Co(II)-OH complexes through direct interaction of surface cobalt species with the nearby surface of dopant OH groups. Besides, a better dispersion of the Co_3O_4 active species in the composites because of their smaller size ensures more effective sites on the surface to generate radicals.

The key role of close contact between metal oxide components of the composite catalysts was con-firmed by a much weaker catalytic performance exhibited by mechanical mixture of bismuth oxide/magnesium oxide and Co_3O_4 (Fig. 4b). In fact, in the presence of 20% $\text{Co}_3\text{O}_4\text{-MgO}$ complete AO7 degradation was achieved in 10 min, while for the same reaction period around 40% of dye did not undergo conversion under the catalytic action of matching mechanical mixture despite the same amount of Co_3O_4 . The decrease in activity was more pronounced for the mechanical mixture of 20% Co_3O_4 and 80% Bi_2O_3 due to inability of the

Bi_2O_3 to induce PMS activation to produce radicals. For the 20% $\text{Co}_3\text{O}_4\text{-Bi}_2\text{O}_3/\text{PMS}$ system, 50 min were required for complete discoloration of the dye solution while for the same time only 43% removal efficiency was attained using a mixture of both oxides. Besides, a linear rate of AO7 decay over mechanical mixture suggests that the rate-limiting step of the oxidation process is decomposition of PMS to radical species rather than destruction of the dye molecules by the radicals formed.

It should be noted that the homogeneous Co(II)/PMS system showed faster oxidation kinetics. At a concentration of Co(II) ions equivalent to the cobalt content in composites, complete discoloration of dye solution was achieved within 5 min. Although the homogeneous approach is more efficient for destroying dye molecules, its practical application is restricted due to potential health hazards caused by cobalt ions released in water as well as to the inability to separate the catalyst from the solution and reuse. The registered difference in degradation kinetics of AO7 under homogeneous and heterogeneous oxidation mode as well as negligible cobalt leaching into the solution (less than 1%) suggests that the activation of PMS is heterogeneously conducted on the catalyst surface.

Figure 5a shows the change in the UV-Vis absorption spectra of the AO7 solution during 80% $\text{Co}_3\text{O}_4\text{-Bi}_2\text{O}_3$ -mediated catalytic oxidation with PMS as a function of reaction time. As the reaction progressed the intensity of the absorption peak at 486 nm decreased due to degradation of the chromophore azo bond. In addition, a simultaneous decrease of the absorbance at 230 and 310 nm, ascribed to $\pi\text{-}\pi^*$ transitions in the benzene and naphthalene rings of dye, respectively, is considered evidence of a break-up of the conjugated π -system of the dye molecule. In the meantime, a new

absorbance band at about 255 nm appeared in the ultraviolet region at the very beginning of reaction (even at 2 min) and then started to drop slowly. This indicates that a new structure unit was formed from chromophore cleavage, which further was also degraded. 1,2-Naphthoquinone was identified to contribute to the peak by comparing spectra of the reaction mixture and a standard solution containing the expected degradation intermediates (Fig. 5b). Similar UV-vis spectra profiles were observed also in experiments carried out in the presence of other composite catalysts.

Catalytic oxidation of AO7 over synthesised composite catalysts follows first-order kinetics model, thereby implying that the oxidation process was not controlled by the radicals generation step. Table 2 gives reaction rate constants (k) and corresponding regression coefficients (R^2) of the model fitting.

Table 2. Kinetic parameters of AO7 degradation in different catalyst – PMS systems

Catalyst	Co_3O_4 (wt.%)	k (min^{-1})	R^2
Co_3O_4	100	0.039	0.992
$\text{Co}_3\text{O}_4\text{-MgO}$	20	0.315	0.991
	50	0.334	0.989
	80	0.237	0.991
$\text{Co}_3\text{O}_4\text{-Bi}_2\text{O}_3$	20	0.091	0.984
	50	0.374	0.992
	80	0.257	0.996

Because Co_3O_4 is the component of the composite catalysts that basically determines their PMS activation functionality, the lowest AO7 degradation rate was observed for the samples with lowest Co_3O_4 content. However, the 20% $\text{Co}_3\text{O}_4\text{-MgO}$ catalyst produced faster and complete AO7 degradation with a rate constant being more three-fold that using Co-Bi analogue.

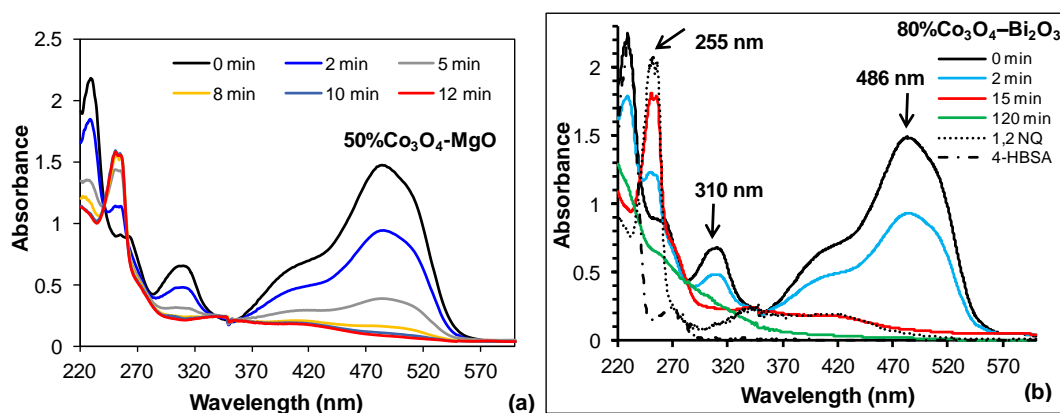


Fig. 5. (a) The UV-Vis spectral changes of AO7 in 50% $\text{Co}_3\text{O}_4\text{-MgO}/\text{PMS}$ process. (b) Comparative UV-Vis spectra of the AO7 solution during oxidation over 80% $\text{Co}_3\text{O}_4\text{-Bi}_2\text{O}_3$ and standard solutions of 1,2-naphthoquinone (NQ), and 4-hydroxybenzenesulphonic acid (4HBSA). Reaction conditions were the same as those indicated in Fig. 4.

The difference in activity could be explained by a stronger basic surface of MgO than Bi_2O_3 , which provides formation of more Co(II)-OH complexes and consequently generation of more active radicals for a shorter time. The increase of Co_3O_4 content up to 50 wt.% favoured the AO7 degradation rate, which was contributed to the higher activation rate of PMS. A further increase of the Co_3O_4 amount caused a decrease in degradation activity that could be attributed to a lesser amount of hydroxyl groups on the catalyst surface as well as to aggregation of Co_3O_4 particles resulting in less active sites for PMS activation.

Catalytic activation of PMS mediated by transition metals or metal oxides could generate three main types of reactive radicals, viz., sulphate ($\text{SO}_4^{\cdot-}$), hydroxyl ($\cdot\text{OH}$), and peroxymonosulphate ($\text{SO}_5^{\cdot-}$) [1,11]. Due to $\text{SO}_5^{\cdot-}$ very low redox potential, sulphate radicals and hydroxyl radicals were regarded as active species in the catalytic PMS oxidation.

Ethanol (EtOH) and *tert*-butyl alcohol (TBA) were used as radical scavengers to evaluate the contribution of $\text{SO}_4^{\cdot-}$ and $\cdot\text{OH}$ in the oxidation. According to the literature, EtOH readily reacts with both hydroxyl and sulphate radicals at high and comparable rates whereas TBA mainly reacts with hydroxyl radical and about 1000-fold slower with sulphate radicals [1]. The inhibition of the degradation process brought by the two quenching agents is shown in Fig. 6. It is obvious that addition of EtOH to the reaction mixture inhibited AO7 degradation, whereas the process was negligibly affected in the presence of TBA. Based on the results it may be concluded that sulphate radicals played a major role throughout the AO7 degradation process on the composite catalysts. The retarding effect of EtOH can be explained by competitive reactions of generated radicals with AO7 and radical quenching agent.

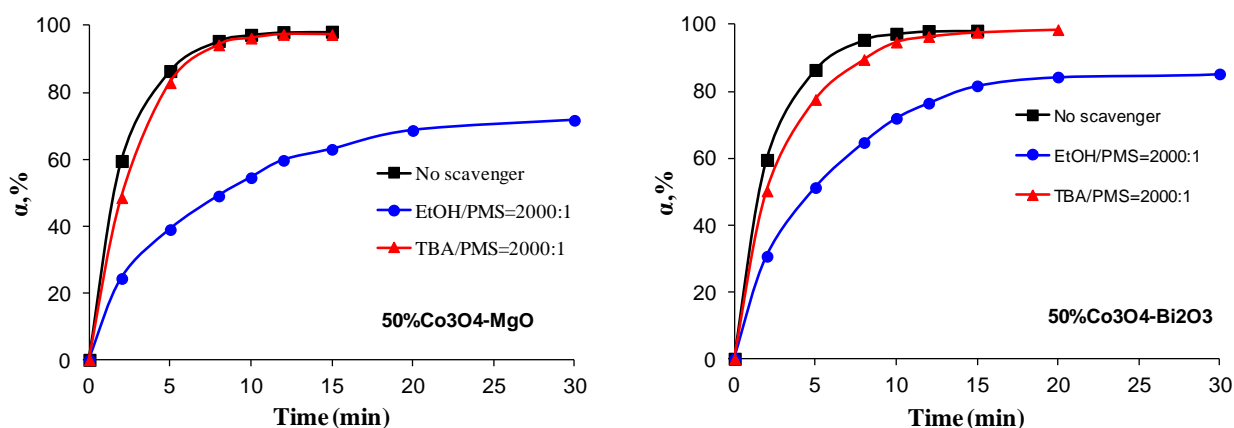


Fig. 6. Influence of ethanol and TBA addition on the AO7 degradation efficiency in composite catalyst-PMS system.

CONCLUSIONS

In this study, $\text{Co}_3\text{O}_4\text{-Bi}_2\text{O}_3$ and $\text{Co}_3\text{O}_4\text{-MgO}$ composite oxides with different Co_3O_4 content were synthesised and used as heterogeneous catalysts to activate PMS for degrading AO7 in aqueous solution. The formation of the composites was confirmed by XRD and TEM characterisation. It was found that the as-prepared catalysts manifested a superior catalytic activity toward PMS than pristine Co_3O_4 . Composites containing 50 wt.% Co_3O_4 exhibited the best catalytic performance. In the presence of PMS, they induced fast and complete degradation of AO7 (50 mg dm^{-3}) with the rate constant being 8 times higher than that over unmodified Co_3O_4 . The presence of Mg and Bi was found to be beneficial for enhancing the content of

hydroxyl groups on the catalyst surface that form Co(II)-OH complexes critical for heterogeneous PMS activation. Radical quenching studies demonstrated that sulphate radicals are the dominating species formed by the catalyst-PMS interaction, and hence those that are responsible for effective AO7 degradation.

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ПОВИШАВАНЕ НА PMS-АКТИВАЦИОННАТА СПОСОБНОСТ НА Co_3O_4 ЧРЕЗ ДОТИРАНЕ С Bi И Mg

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(Резюме)

Синтезирани са серия от композитни Co-Bi и Co-Mg оксиди чрез метод на съутаяване и е изследвана каталитичната им активност за хетерогенно активиране на пероксимоносулфат (PMS) за разграждане на Кисело Оранжево 7 (AO7) във водни разтвори. Катализаторите са охарактеризирани чрез XRD, XPS, TEM, и ICP-OES. Установено е съществено увеличаване на каталитичната активност на Co_3O_4 чрез модифициране с Bi_2O_3 и MgO . Композитите с 50% теглово съдържание на Co_3O_4 показват най-висока каталитична активност, постигайки пълно разграждане на 50 mg dm^{-3} AO7 в рамките на 12–15 минути при концентрация на катализатора 0.1 g dm^{-3} и молно съотношение PMS/AO7 = 6:1. Повишената PMS-активационна функционалност на композитните катализатори се дължи на по-високото съдържание на повърхностни хидроксилни групи вследствие модифицирането с базичните оксиди. Хидроксилните групи върху катализаторната повърхност благоприятстват образуването на повърхностни Co(II)-OH комплекси, което ускорява генерирането на сулфатни радикали (SRs) от PMS. Разграждането на AO7 се подчинява на кинетичните закономерности на реакции от първи порядък. Експериментите с добавяне на радикал-улавящи агенти показват, че окислителното разграждане на AO7 е радикалов процес, като SRs са доминиращите радикалови частици. Co-Bi и Co-Mg композитните оксиди демонстрират устойчива активност с ниска разтворимост на Co дори в кисела среда.