Journal of International Scientific Publications: Ecology and Safety

Volume 8, ISSN 1314-7234 (Online), Published at: http://www.scientific-publications.net

STUDY ON THE CATALYTIC ACTIVITY OF COBALT AND IRON-COBALT MIXED OXIDES FOR THE OXIDATIVE DEGRADATION OF ACID ORANGE 7 IN AQUEOUS SOLUTION

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Abstract

The oxidative degradation of Acid Orange 7 (AO7) by nanosized cobalt and iron-cobalt spinel oxides activated Oxone has been performed in this study. It was found that the as-prepared catalysts could effectively catalyze decomposition of oxidant to generate sulfate radicals to degrade AOR in aqueous solution. Co_3O_4 catalyst exhibited better catalytic activity than cobalt ferrites; however the latter are more relevant catalysts considering environmental and practical aspects. Kinetic studies showed that heterogeneous oxidation of AO7 in catalyst/Oxone systems followed first order kinetics. The effects of several parameters on the degradation efficiency of the process were investigated. Furthermore, the scavenging effect was examined by using ethanol and tert-butyl alcohol which indicated that sulfate radicals were the dominating reactive species responsible for the degradation process.

Key words: *Cobalt and iron-cobalt mixed oxides, Acid Orange 7 degradation, advanced oxidation, Oxone, wastewater treatment*

1. INTRODUCTION

Dyes are widely used in textile, leather, pharmaceutical, plastic, paint, and food industries. Over 15% of the synthetic textile dyes used are lost during manufacturing or processing operations and released as effluents (Wang & Chu 2011). Most of dyes are chemically and photolytically stable and highly persistent in natural environment due to their complex structure and high chemical stability. The discharge of untreated dye-containing effluents in the natural water resources not only creates aesthetic concerns, but far more importantly, it could produce adverse effects on the environment because some of them are even toxic, carcinogenic and mutagenic (Jin et al. 2008; Bouhent et al. 2011). Therefore, treatment of wastewaters containing dyes prior their disposal into waterways is obligatory but at the same time a complicated process.

The typical treatment techniques used to treat dye-containing wastewater are physical, biological and chemical processes (Sun et al. 2002; Lourenco et al. 2001; Qada et al. 2008). The commonly applied physical or physicochemical methods such as adsorption, sedimentation, flotation, flocculation effectively remove certain dyes from water (Harrelkas et al. 2009; Sengil & Ozacar 2009; Zidane et al. 2008). However, these techniques are non-destructive and merely transfer the dye from one form of waste to another, thus generating secondary pollutants requiring further treatment (Arslan-Alaton & Ferry 2002; Slokar & Le Marechal 1998; Brown et al. 1993). In biological treatment methods degradation of dyes occurs by means of living microorganisms (e.g., bacteria or fungi) (Ge & Qu 2004; Azmi et al. 1998; Casas et al. 2007; Tavares et al. 2009). Usually these techniques comprise combined anaerobic and aerobic treatment to ensure efficient dye removal. Biological processes are generally cheap and capable of removing dyes from large volumes of wastewater. However, most textile wastewaters cannot be readily degraded by biological treatment because many dyes are non-biodegradable and toxic to the organisms used in the processes. Chemical oxidation methods such as chlorination (Zeng et al. 2009), ozonation (Constapel et al. 2009; Zhang et al. 2007), wet air oxidation (Lei et al. 2007; Gözmen et al. 2009), etc are traditionally accepted as the most promising alternative for the degradation of persistent pollutants with limited biodegradability and tendency to accumulate in the environment. Chemical oxidation is the only destructive technology that has the potential to completely transform harmful organic contaminants in water into biodegradable substrates, harmless end products, or even carbon dioxide and water (total mineralization) (Rivas et al. 2005). However, most of these processes have essential drawbacks (high operation costs and/or the need for the special equipment), which limit the practical application.

In the past few decades, advanced oxidation processes (AOPs) have attracted extensive attention as innovative wastewater treatment technologies for the degradation of organic pollutants in water as they operate at temperature near ambient and atmospheric pressure (Rajeshwar et al. 2008; Espugas et al. 2002; Papic et al.

2006). These processes involve in situ generation of strongly oxidizing radicals which can readily attack organic pollutants in water, thereby transforming them into harmless end products ((Yang et al. 2010; Madhavan et al. 2009; Zhang et al. 2009). Recently, the sulfate radicals-based advanced oxidation processes has been the subject of interest in the field of wastewater treatment due to their high oxidative capacity and applicability to a wide pH range (Anipsitakis & Dionysiou 2003, 2006; Rastogi et al. 2009). Sulfate radicals (SRs), with reduction potential of +2.6 V vs. NHE, can be produced by the activation of sulfate-based oxidants (peroxydisulfate or peroxymonosulfate) with heat, ultraviolet, microwave, ultrasound irradiation and/or transition metal ions. Commercial Oxone ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$), the source providing peroxymonosulfate (HSO_5^-) is reported to be a more efficient oxidant than hydrogen peroxide or persulfate (Lei et al. 2007). A series of experimental evidences have proved that Co (II) ions are the best homogeneous catalysts for the activation of Oxone to produce SRs for complete degradation of persistent organic compounds in water (Madhavan et al. 2009; Ling et al. 2010; Chen et al. 2007). Nevertheless, 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. Therefore, the activation of Oxone *by* heterogeneous cobalt sources is highly demanded and has been given great attention recently. Several researchers have found that heterogeneous cobalt oxide catalysts - bulk and immobilized on various supports such as TiO_2, Al_2O_3, SiO_2, activated carbon, etc. in combination with Oxone exhibited a good performance on degradation of 2,4- dichlorophenol and phenol (Anipsitakis et al. 2005; Yang et al. 2007, 2008; Shukla et al. 2010, 2011). However, few investigations have been reported in Co oxides (Chen et al. 2008) and supported Co oxides (Zhang et al. 2010; Shi et al. 2012) for degradation of organic dyes using Oxone as oxidant. It is reported that the coupling of Fe_3O_4 with a suitable amount of cobalt ions might be the efficient way to attain efficient nanoscale catalyst for activating Oxone (Su et al. 2013). The application of iron-cobalt mixed oxide nanocatalysts with different Fe/Co ratios for the activation of Oxone for degradation of 2,4-dichlorophenol was investigated (Yang et al. 2009). Results showed that Fe–Co catalysts are more effective than the bulk Co_3O_4 and concluded that $CoFe_2O_4$ is the most environmentally friendly of the catalytic materials tested. In contrast, authors (Su et al. 2013) investigated a series of $Co_xFe_{3-x}O_4$ nanoparticles on the activation of Oxone for heterogeneous degradation of Rhodamine B and found that the higher cobalt content in the catalyst, the better removal performance was achieved.

The aim of this study was to evaluate the performances of cobalt and iron-cobalt spinel oxides on the activation of Oxone and then degrading monoazo-dye Acid Orange 7 (AO7) in aqueous solution. The kinetics of the oxidation process and the effect of catalyst loading and concentration of oxidant on the AO7 removal efficiency were investigated. Quenching experiments were conducted with the addition of ethanol and *tert*-butyl alcohol for identifying the dominating reactive radicals generated from the catalyst-mediated decomposition of Oxone.

2. EXPERIMENTAL PART

2.1. Chemicals

Acid Orange 7 dye ($C_{16}H_{11}N_2O_4SNa$, C.I. 15510) and the oxidant Oxone ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$, 95%) were purchased from Sigma–Aldrich Company and used as received. AO7 is anionic monoazo dye, which belongs to the hydrosoluble phenylazonaphthol dyes and was chosen as a model compound because it is a widely used in the dyeing of textiles, food, and cosmetics dying, in weaving, tanning and paper industries and resistant to photodegradation and biodegradation (Stylidi et al. 2004; Chen et al. 2008). Other reagents including $Co(NO_3)_2 \times 6H_2O$, ethanol, *tert*-butyl alcohol (TBA), and $NaHCO_3$ were all analytical grade.

2.2. Catalyst preparation

Co_3O_4 and cobalt ferrites with Fe/Co molar ratio of 2 and 0.5 (hereafter denoted as $CoFe_2O_4$ and Co_2FeO_4, respectively), were prepared by precipitation/ co-precipitation method. In this, a 1M Na_2CO_3 solution was added dropwise to a 0.5M aqueous solution of cobalt nitrate or mixed Co and Fe salts (taken in the desired Fe/Co molar ratio) until the solution pH reach 9. The precipitates, thus obtained, were digested under continuous stirring for 1 h at room temperature. After washing with distilled water and drying at 105◦C overnight, the as-obtained powders were finally transformed into the desired oxides by thermal decomposition at 500◦C for 3 h in static air.

2.3. Experimental procedure

The catalytic oxidation of AO7 were conducted at room temperature (20±2◦C) in a jacketed glass reactor of 400 mL capacity at batch mode with constant stirring at around 400 rpm. In a typical run, 200 ml 50 mg/L aqueous solution of an AO7 was transferred into the vessel and then a fixed amount of catalysts was added. The suspension was stirred for 30 min to achieve adsorption equilibrium. The degradation reaction was initiated by adding appropriate amount of oxidant into solution with the fixed Oxone/AO7 molar ratio. At given intervals,

samples of 4 ml were withdrawn from the suspension and were mixed immediately with 1 mL methanol as a quenching reagent to prevent further reaction. Then the samples were centrifuged at 4000 rpm for 1 min to remove the catalyst. The concentration of AO7 in the filtrate was determined by monitoring decrease in absorbance at the maximum wavelength (486 nm) with UV–Vis spectroscopy using a UV-Vis spectrophotometer (Cintra model 101). The AO7 degradation efficiency at time t was calculated according to the formula:

$$\alpha_t = \frac{C_o - C_t}{C_o} 100, \%$$

where C_o and C_t are the initial and the dye concentration at time t (mg/L), respectively.

For the quenching experiments, prior to the 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 Oxone.

3. RESULTS AND DISCUSSION

In the course of liquid phase catalytic oxidation of AO7 with Oxone, three simultaneously proceeding processes could contribute to the overall degree of its removal from solution: adsorption of the dye on the catalyst surface, chemical oxidation with oxone alone, and heterogeneous catalytic oxidation. Therefore, prior to evaluate the catalytic performance of the prepared samples in the studied reaction, it is important to clarify the role of non-catalytic oxidation and physical adsorption for the dye removal from solution.

The first control experiment was designed to evaluate the effectiveness of the oxidant - oxone for the AO7 degradation without the addition of catalyst (homogeneous or heterogeneous) in the reaction mixture. Oxone is a strong oxidizing agent, whose standard oxidation–reduction potential is slightly higher than that of hydrogen peroxide ($\varphi^o_{HSO_5^- / HSO_4^-} = 1.82V$; $\varphi^o_{H_2O_2 / H_2O} = 1.76V$ vs.HBE). It is reported that although oxone is a strong electron acceptor, it present limited ability to oxidize organics independently (Yang et al. 2010). In order to confirm the advisability of the oxidant activation by addition of a catalyst in the system, an oxidation of AO7 with oxone alone was performed. The results obtained showed that the degradation reaction proceeds at an extremely low rate under ambient conditions and less than 1% removal efficiency was reached after 8 hours. Moreover, there was still 23% of dye remaining unchanged in the solution after 20 days. The long reaction period required for a noticeable reduction in the AO7 concentration suggests that oxone itself is unable to generate active radical species through self decomposition and most probably chemical oxidation occurs through non radical pathway. Furthermore, the relatively high stability of the Oxone in the acidic medium may further reduce its effectiveness ((Anipsitakis & Dionysiou 2003).

To assess the contribution of adsorption process on the extent of AO7 solution discoloration another control test with as-prepared catalysts but without Oxone addition was performed. The adsorption kinetics of AO7 on Co_3O_4 is illustrated in Fig.1.

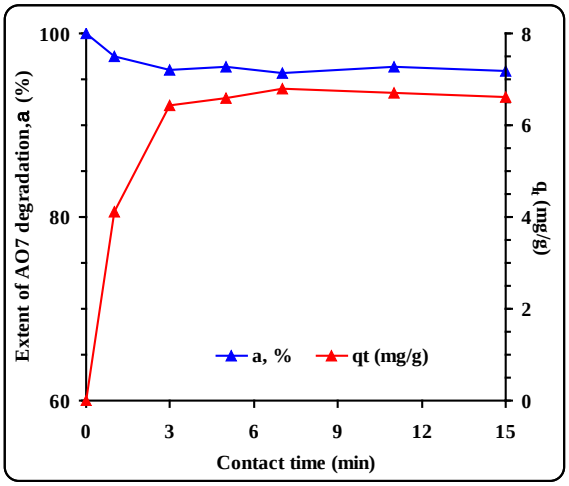


Fig.1.Kinetics of Acid Orange 7 adsorption on Co_3O_4

(50 mg/L AO7; 0.15 g/L catalyst loading; pH=4.0; 20 ^oC)

Data reveals that Co_3O_4 exhibits inferior capacity in adsorption of AO7 and only about 2% of AO7 was removed in 15 min. The catalyst presented fast adsorption and approached equilibrium in 5 min. After that minor variation in AO7 concentration was registered. Similar adsorption behavior of AO7 dye was observed during experiments carried out with the mixed Co-Fe spinel oxides pointing out that adsorption of dye molecules on the surface of the solids is negligible.

The degradation profiles of AO7 in the presence of cobalt and iron-cobalt oxides as well as those obtained from the homogeneous catalytic oxidation using Co(II) ions or a mixture of Co(II) and Fe(III) ions are shown in Fig.2. The amount of metal ions (from corresponding dissolved nitrate salts) in the homogeneous catalytic experiments was equivalent to that in the solid catalysts used for the heterogeneous reactions.

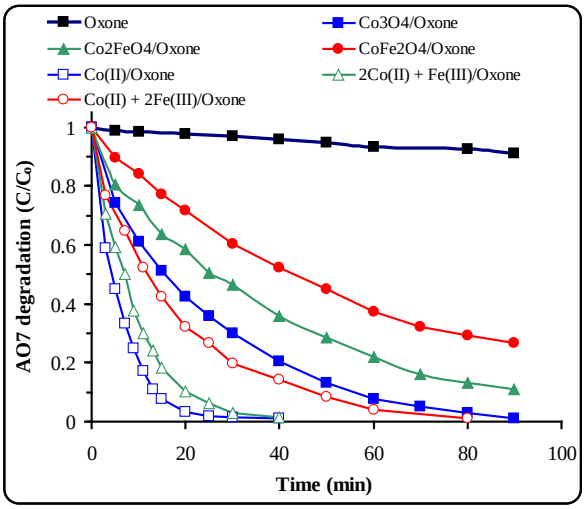


Fig.2. Degradation kinetics of AO7 during chemical and catalytic oxidation

(50 mg/L AO7; 0.15 g/L catalyst loading; Oxone/AO7= 5/1; pH=4.0; 20 ^oC)

It can be seen from the Fig.2 that when heterogeneous catalyst and oxidant simultaneously were presented in the solution a significant enhancement of the AO7 degradation rate is achieved as compared to the adsorption and oxidation with Oxone alone. Despite very low catalysts concentration of 0.15 g/L used in reaction, complete discoloration of the AO7 solution on Co_3O_4 could be attained within 90 min, which was higher than the AO7 removal of 89% and 73% achieved by adding Co_2FeO_4 and $CoFe_2O_4$ particles as the catalyst, respectively. Considering the minor dye adsorption on as-prepared catalysts, as well as the negligible separate contribution of oxidation by Oxone alone, the degradation behavior in the case of the co-existence of catalyst and Oxone could be predominantly ascribed to the catalytic transformation of dye molecules by sulfate radicals rather than the adsorption. Furthermore, an insignificant degree of dye degradation was observed for the same reaction period using Fe_3O_4. Less than 9% AO7 was reduced in the Fe_3O_4/Oxone mixture. Obviously, the presence of Fe in the cobaltite spinel structure did not favor the AO7 decomposition. As seen from Fig.2 the reaction rate decreased with the increase of iron content in the catalysts, which is most probably due to the lower activation rate of Oxone caused by of iron presence. Preliminary Mössbauer studies of cobalt ferrites showed that all Fe ions in the synthesized Fe-Co mixed oxides are in 3+ oxidation state. Reaction of ferric ions with oxone generates peroxymonosulfate radicals ($SO_5^{-\bullet}$) which are less reactive compared to sulfate radicals ($SO_4^{-\bullet}$):

$$Fe^{3+} + HSO_5^- \rightarrow Fe^{2+} + SO_5^{-\bullet} + H^+$$

By this reaction ferric ions are reduced to ferrous ions, which further reacts with oxone and generate highly active SRs. However, in Fe(III)/Oxone system electron transfer takes place from Fe(III) to oxone and is a much slower process compared to that taking place in Fe(II)/Oxone system (in reverse direction). Thus, the rate limiting reduction of Fe(III) resulted in a slow generation of sulfate radicals and could be a probable cause of the observed slower kinetics in the presence of cobalt ferrite oxides. Although Co_3O_4 catalyst exhibited better catalytic activity than cobalt ferrites the latter are more relevant catalysts considering environmental and practical aspects (Fe is cheap, less toxic, and naturally abundant in soil and sediment).

Results depicted in Fig.2 also show that the rate of homogeneous catalytic oxidation of AO7 was faster under the same operating conditions. In fact, complete discoloration of the dye solutions in the presence of Co(II) was reached in about 30 min whereas there was still 30% of AO7 remaining unchanged in the solution after the same reaction time when Co_3O_4 was used as catalyst. However, due to the potential harmful effects on human health and environment caused by discharged cobalt ions in water as well as an inability to recover catalyst from the reaction mixture, practical application of this homogeneous approach is limited.

Fig. 3 illustrates that the rate of AO7 degradation followed first order kinetic model $\ln C_o/C=kt$, where C_o and C are the AOR concentration at time (t) and t=0, respectively, and k is the reaction rate constant. These results imply that the AO7 oxidation rate is controlled by the reaction of dye molecules with active radicals rather than their generation by surface reaction between catalyst and oxidant.The reaction rate constants and correlation coefficients (R^2) were given in Table 2. The high values of regression coefficients proved that a pseudo first order kinetics indeed fit to dye discoloration.

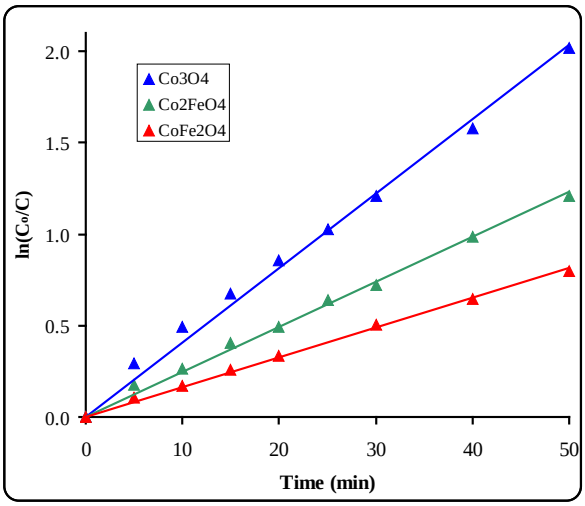


Fig. 3. Linear transformation of the kinetic curves of AO7 catalytic oxidation with Oxone

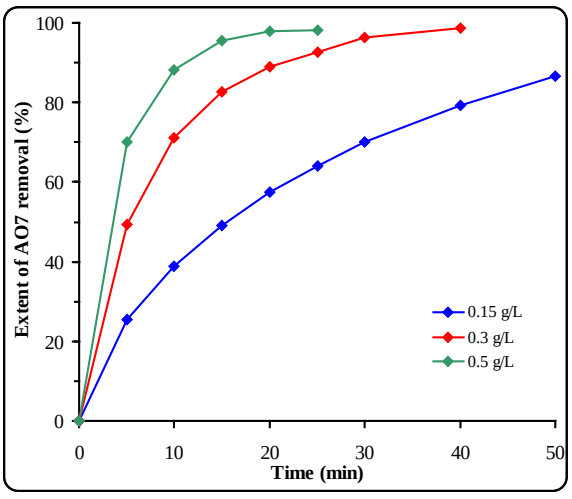


Fig. 4. The effect of Co_3O_4 amount on the AO7 degradation rate and efficiency

(50 mg/L AO7; Oxone/AO7= 5/1; pH=4.0; 20 ^oC)

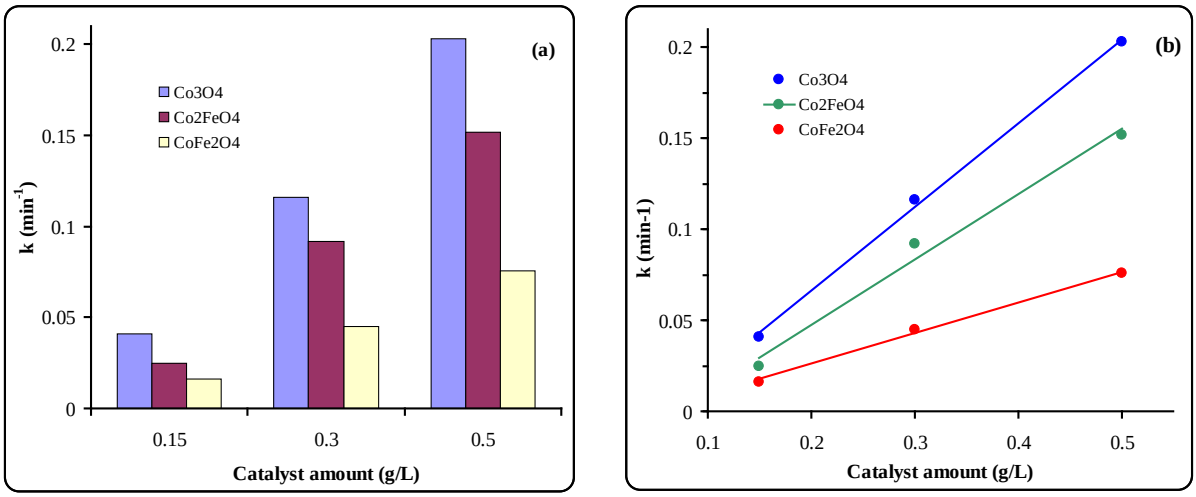


Fig. 5. Correlation of the apparent first-order rate constant with amount of catalyst

The effect of catalyst and oxidant amount on the AO7 degradation rate and efficiency was investigated. The influence of catalyst amount on the AO7 conversion was studied by varying the concentration of catalysts from 0.15 g/l to 0.5 g/l keeping the oxidant/dye molar ratio constant (Oxone/AO7=5/1). Higher catalyst loading in solution would result in higher dye removal efficiency. As the amount of catalyst is increased, the number of active sites for the activation of oxidant molecules increases thereby resulting in an enhancement in generation of active radical species, which in turn increases the rate of oxidation. For example, at 0.15 g/L Co_3O_4 AO7 removal was 64 % at 25 min while it was 100% for the same reaction period at 0.5 g/L catalyst loading (Fig.4). Experiments carried out using iron-cobalt mixed oxides showed a similar trend and about five-fold enhancement of AO7 removal rate is observed (Fig.5a). Results also showed that the rate constant is linearly dependent on the catalyst loading (Fig.5b), thereby implying that the reaction rate constants are the first order with respect to the concentration of catalyst.

The effect of Oxone concentration on AO7 degradation is shown in Fig.6. When the catalyst amount was fixed at 0.15 g/L, the increase of initial oxidant concentration also accelerated the removal of AO7. It was found that at Oxone/AO7 molar ratio of 1/1 complete removal of AO7 was not attained - only 66 % of dye was degraded within 70 min in the presence of Co_3O_4 due to lack of sufficient oxidant amount, whereas five-fold increase in Oxone concentration led to nearly 98% extent of dye decolorization in about 90 min. A minimal change in the rate of reaction with further increase in the oxidant amount was observed. This is justified because the rate of radical generation is limited by the fixed amount of catalyst used for the reaction as well as the oxidant is inactive by itself.

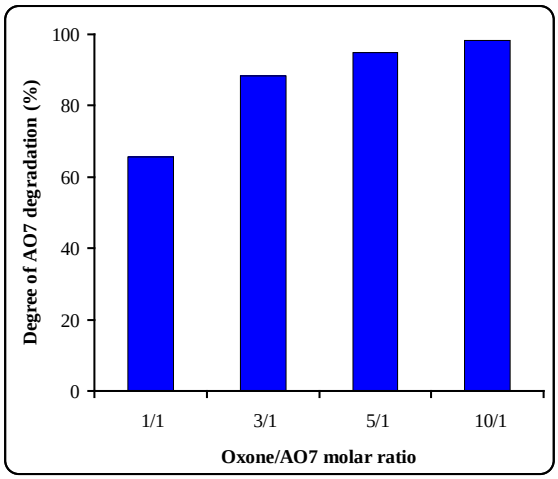


Fig.6. Effect of Oxone concentration on the AO7 removal efficiency over Co_3O_4 at 70 min

(50 mg/L AO7; 0.15 g/L catalyst loading; pH=4.0; 20 ^oC)

It is well documented in the literature that Oxone could generate sulfate $SO_4^{\bullet-}$ and/or hydroxyl $^{\bullet}OH$ radicals by homogeneous or heterogeneous activation (Anipsitakis & Dionysiou 2004). Peroxomonosulfate radicals $SO_5^{\bullet-}$ could also be formed, but due to their much lower redox potential would not contribute to dye degradation. Radical quenching tests using ethanol (EtOH) and *tert*-butyl alcohol (TBA) as radical scavengers were performed to identify the dominant radical species formed from the catalyst/Oxone interaction and to evaluate their contribution to the process. Ethanol (containing α-H atom) is capable of quenching both sulfate and hydroxyl radicals as it readily reacts with both radicals at high and comparable rates, whereas TBA (without α-H atom) is effective quenching agent for hydroxyl radicals and reacts about 1000-fold slower with sulfate radicals (Anipsitakis & Dionysiou 2003). Fig. 7 illustrate the effect of both quenching reagents on the AO7 degradation efficiency over Co_2FeO_4 at different alcohol/Oxone molar ratio.

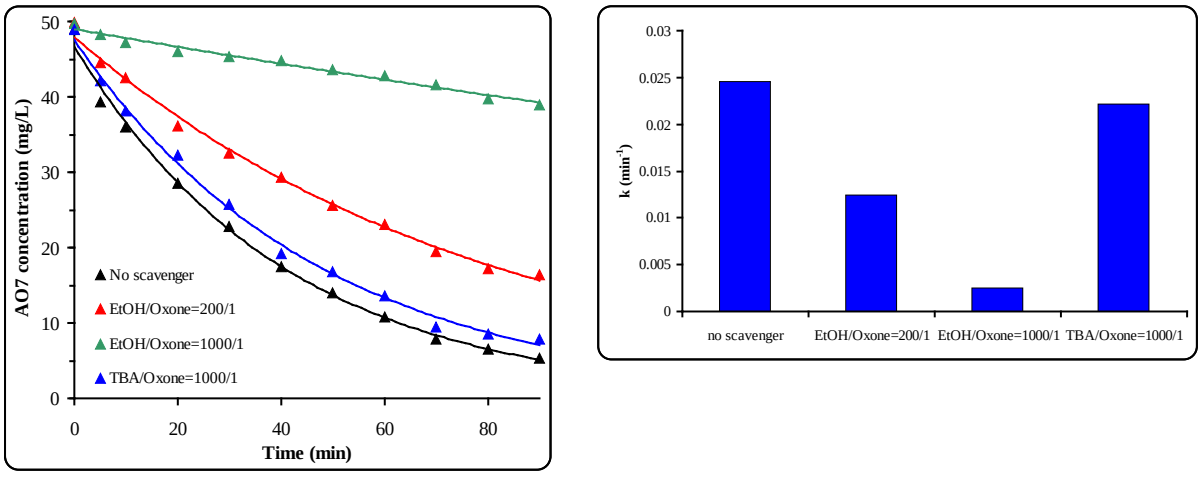


Fig.7. Effect of ethanol and tert-butyl alcohol addition on AO7 degradation in Co_2FeO_4 – PMS system (50 mg/L AO7; 0.15 g/L catalyst loading; Oxone/AO7= 5/; pH=4.0; 20 ^{o}C)

It is seen that the addition of ethanol at EtOH/Oxone molar ratio of 200:1 reduced AO7 degradation from 78 to 54 % in the reaction period of 1 h. Further increase in the concentration of ethanol to EtOH/Oxone=1000/1 significantly inhibits the system performance, showing 64 % AO7 removal drop within the same reaction time. Nevertheless, the AO7 was not fully quenched and upon exhaustion of the oxidant about 22% dye was still degraded. The reaction carried out under the similar TBA/Oxone molar ratio shows a very slight reduction in the rate of dye oxidation. Similar behavior was also demonstrated by Co_3O_4 and $CoFe_2O_4$ catalysts after addition of both alcohols. Based on these results it may be concluded that the oxidative degradation of AO7 in the studied catalyst/Oxone systems is dominated by radical based mechanisms and the main radical species generated during the catalytic activation of Oxone were sulfate radicals.

CONCLUSIONS

Nanosized cobalt and iron-cobalt spinel oxides were synthesized by precipitation/ co-precipitation method and their catalytic activity for oxidative degradation of a textile monoazo-dye Acid Orange 7 in aqueous solution through sulfate radicals (SRs) approach has been studied. The as-prepared catalysts exhibited good efficiency for heterogeneous activation of Oxone to provide sulfate radicals for degrading AO7. Complete discoloration of the AO7 solution on Co_3O_4 could be achieved within 90 min using very low catalysts concentration of 0.15 g/L, which was higher than the AO7 removal of 89% and 73% attained by adding Co_2FeO_4 and $CoFe_2O_4$ particles as the catalyst, respectively. Despite the better catalytic performance of cobalt spinel oxide, the replacement of cobalt with iron is an advantage because Fe is cheap, less toxic, and naturally abundant in soil and sediment. The degradation reaction of AO7 obeys the pseudo-first order kinetics in the catalyst/Oxone process. Increasing catalyst amount and Oxone concentration promoted AO7 degradation. The quenching studies confirmed that sulfate radicals are indeed the primary species produced during the catalytic decomposition of Oxone by the catalysts prepared in this work and are responsible for the AO7 degradation.

Authors gratefully acknowledge financial support by the National Science Fund (Projects DFNI-E01/7) and by the University of Plovdiv Research Fund (Project NI HF-2013).

REFERENCES

Anipsitakis, GP & Dionysiou, DD 2004, 'Transition metal/UV-based advanced oxidation technologies for water decontamination', *Applied Catalysis B: Environmental*, vol. 54, pp. 155–163.

Anipsitakis, GP, E. Stathatos, E & Dionysiou, DD 2005, 'Heterogeneous activation of oxone using Co_3O_4, *Journal of Physical Chemistry B*, vol. 109, pp. 13052–13055.

Anipsitakis, GP & Dionysiou, DD 2003, 'Degradation of Organic Contaminants in Water with Sulfate Radicals Generated by the Conjunction of Peroxymonosulfate with Cobalt', *Environmental Science & Technology*, vol. 37, pp. 4790-4797.

Anipsitakis, GP, Dionysiou, DD & Gonzalez, MA 2006, 'Cobalt-Mediated Activation of Peroxymonosulfate and Sulfate Radical Attack on Phenolic Compounds. Implications of Chloride Ions', *Environmental Science & Technology*, vol. 40, pp. 1000-1007.

Arslan-Alaton, I & Ferry, JL 2002, 'Application of polyoxotungstates as environmental catalysts: wet air oxidation of acid dye Orange II', *Dyes and Pigments*, vol. 54, pp. 25–36.

Azmi, W, Sani, RK & Banerjee, UC 1998, 'Biodegradation of triphenylmethane dyes', *Enzyme* and *Microbial Technology*, vol. 22, pp.185-191.

Bouhent, MM, Derriche, Z, Denoyel, R & Prevot, V 2011, 'Thermodynamical and structural insights of orange II adsorption by Mg_RAlNO_3 layered double hydroxides', *Journal of Solid State Chemistry*, vol. 184, pp. 1016-1024.

Brown, D, Mark, A & De Vito, SC 1993, 'Predicting azo dye toxicity', *Critical Reviews in Environmental Science and Technology*

Casas, N, Blánquez, P, Gabarrell, X, Vicent, T, Caminal, G & Sarrá, M 2007 'Degradation of Orange G by laccase: Fungal versus enzymatic process', *Environmental Technology*, vol. 28, pp. 1103-1100.

Chen, X, Qiao, X, Wang, D, Lin, J & Chen, J 2007, 'Kinetics of oxidative decolorization and mineralization of Acid Orange 7 by dark and photoassisted Co^{2+}-catalyzed peroxymonosulfate system', *Chemosphere*, vol. 67, pp. 802-808.

Chen, X, Chen, J, Qiao, X, Wang, D & Chai, X 2008, 'Performance of nano-Co3O4/peroxymonosulfate system: Kinetics and mechanism study using Acid Orange 7 as a model compound', *Applied Catalysis B: Environmental*, vol. 80, pp. 116-121.

Constapel, M, Schellanträger, M, Marzinkowski, JM & Gäb, S 2009, 'Degradation of reactive dyes in wastewater from the textile industry by ozone: Analysis of the products by accurate masses', *Water Research*, vol. 43, pp. 733–743.

El Qada, EN, Allen, SJ & Walker, GA 2008, 'Adsorption of basic dyes from aqueous solution onto activated carbons', *Chemical Engineering Journal*, vol. 135, pp. 174–447.

Esplugas, S, Giménez, J., Contreras, S, Pascual, E & Rodriguez, M 2002, 'Comparison of different advanced oxidation processes for phenol degradation', *Water Research*, vol. 36, pp.1034-1042.

Ge, J & Qu, J 2004,'Ultrasonic irradiation enhanced degradation of azo dye on MnO_2', *Applied Catalysis B:Environmental*, vol. 47, pp. 133-140.

Gözmen, B, Kayan, B, Gizir, AM & Hesenov, A 2009, 'Oxidative degradations of reactive blue 4 dye by different advanced oxidation methods', *Journal of Hazardous Materials*, vol. 168, pp. 129-136.

Harrelkas, F, Azizi, A, Yaacoubi, A, Benhammou, A & Pons, MN 2009, 'Treatment of textile dye effluents using coagulation–flocculation coupled with membrane processes or adsorption on powdered activated carbon', *Desalination*, vol. 235, pp. 330-339.

Jin, X, Jiang, M, Shan, X, Pei, Z & Chen, Z 2008, 'Adsorption of methylene blue and orange II onto unmodified and surfactant-modified zeolite', *Journal of Colloid and Interface Science*, vol. 328, pp. 243-247.

Lei, L, Dai, Q, Zhou, M & Zhang, X 2007, 'Decolorization of cationic red X-GRL by wet air oxidation: Performance optimization and degradation mechanism', *Chemosphere*, vol. 68, pp. 1135-1142.

Ling, SK, Wang, Sh & Peng, Y 2010, 'Oxidative degradation of dyes in water using Co2+/H2O2 and Co2+/peroxymonosulfate' *Journal of Hazardous Materials*, vol. 1178, pp. 385–389.

Lourenco, ND, Novais, JM & Pinheiro, HM 2001, 'Effect of some operational parameters on textile dye biodegradation in a sequential batch reactor', *Journal of Biotechology*, vol. 89, pp. 163-174.

Madhavan, J, Maruthamuthu, P, Murugesan, S & Ashokkumar, M 2009, 'Kinetics of degradation of acid red 88 in the presence of Co^{2+}-ion/peroxomonosulphate reagent', *Applied Catalysis A:General*, vol. 368, pp. 35-39.

Papic, S, Koprivanac, N, Božic, AL, Vujevic, D, Dragicevic, SK, Kušic, H & Peternel, I 2006, 'Advanced Oxidation Processes in Azo Dye Wastewater Treatment', *Water Environment Research*, vol. 78, pp. 572-579.

Rajeshwar, K, Osugi, ME, Chanmanee, W, Chenthamarakshan, CR, Zanoni, MVB, Kajitvichyanukul, P & Krishnan-Ayer, R 2008, 'Heterogeneous photocatalytic treatment of organic dyes in air and aqueous media', *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, vol. 9, pp. 171–192.

Rastogi, A, Ai-Abed, SR & Dionysiou, DD 2009, 'Sulfate radical-based ferrous peroxymonosulfate oxidative system for PCBs degradation in aqueous and sediment systems', *Applied Catalysis B: Environmental*, vol. 85, pp. 171–179.

Rivas, FJ, Beltra´n, FJ , Carvalho, F & Alvarez, PM 2005, 'Oxone promoted wet air oxidation of landfill leachates', *Industrial & Engineering Chemistry Research*, vol. 44, pp. 749-758.

Sengil, IA, Ozacar, M 2009, 'The decolorization of C.I. Reactive Black 5 in aqueous solution by electrocoagulation using sacrificial iron electrodes', *Journal of Hazardous Materials*, vol. 161, pp. 1369–1376.

Shi, P, Su, R, Zhu, S, Zhu, M, Li, D & Xu, S 2012a, 'Supported cobalt oxide on graphene oxide: Highly efficient catalysts for the removal of Orange II from water', *Journal of Hazardous Materials*, vol. 229-230, pp. 331–339.

Shukla, P, Wang, S, Sun, H, Ang, HM & Tade, M 2010, 'Activated carbon supported cobalt catalysts for advanced oxidation of organic contaminants in aqueous solution', *Applied Catalysis B: Environmental*, vol. 100, pp. 529-534.

Shukla, P, Wang, S, Sun, H, Ang, HM & Tade, M 2011, 'Nanosized Co_3O_4/SiO_2 for heterogeneous oxidation of phenolic contaminants in waste water', *Separation and Purification Technology*, vol. 77, pp. 230-236.

Slokar, YM & Le Marechal, AM 1998, 'Methods of decoloration of textile wastewaters', *Dyes and Pigments*, vol. 37, pp. 335–356.

Su, S, Guo, W, Leng, Yi, IC & Ma, M 2013, 'Heterogeneous activation of Oxone by $Co_xFe_{3-x}O_4$ nanocatalysts for degradation of rhodamine B', *Journal of Hazardous Materials*, vol. 244-245, pp. 736–742.

Sun, Z, Chen Y, Ke, Q, Yang, Y, Yuan, Y 2002, 'Photocatalytic degradation of a cationic azo dye by TiO_2/bentonite nanocomposite', *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 149, pp. 169-174.

Tavares, APM, Cristovao, RO, Loureiro, JM, Boaventura, RAR & Macedo, EA 2009, Application of statistical experimental methodology to optimize reactive dye decolourization by commercial laccase', *Journal of Hazardous Materials*, vol. 162, pp. 1255-1260.

Wang, YR & Chu, W 2011, 'Degradation of a xanthene dye by Fe(II)-mediated activation of Oxone process', *Journal of Hazardous Materials*, vol. 186, pp. 1455–1461.

Yang, Q, Choi, H & Dionysiou, DD 2007, 'Nanocrystalline cobalt oxide immobilized on titanium dioxide nanoparticles for the heterogeneous activation of peroxymonosulfate', *Applied Catalysis B:Environmental*, vol. 74, pp. 170-178.

Yang, Q, Choi, H, Al-Abed, SR & Dionysiou, DD 2009, 'Iron-cobalt mixed oxide nanocatalysts: Heterogeneous peroxymonosulfate activation, cobalt leaching, and ferromagnetic properties for environmental applications**',** *Applied Catalysis B:Environmental*, vol. 88, pp. 462-469.

Yang, Q, Choi, H, Chen, Y & Dionysiou, DD 2008, 'Heterogeneous activation of peroxymonosulfate by supported cobalt catalysts for the degradation of 2,4-dichlorophenol in water: The effect of support, cobalt precursor, and UV radiation', *Applied Catalysis B: Environmental*, vol. 77, pp. 300-307.

Yang, S, Wang, P,Yang, X, Shan, L, Zhang, W, Shao, X & Niu, R 2010, 'Degradation efficiencies of azo dye Acid Orange 7 by the interaction of heat, UV and anions with common oxidants: Persulfate, peroxymonosulfate and hydrogen peroxide', *Journal of Hazardous Materials*, vol. 179, pp. 552–558.

Zeng, Q, Fu, J, Shi, Y & Zhu, H 2009, 'Degradation of C.I. Disperse Blue 56 by Ultraviolet Radiation/Sodium Hypochlorite

Zhang, H, Choi, HJ, Canazo, P & Huang, CP 2009, 'Multivariate approach to the Fenton process for the treatment of landfill leachate', *Journal of Hazardous Materials*, vol. 161, pp. 1306–1312.

Zhang, W, Tay, HL, Lim, SS, Wang, Y, Zhong, Z & Xu, R 2010, 'Supported cobalt oxide on MgO: Highly efficient catalysts for degradation of organic dyes in dilute solutions', *Applied Catalysis B: Environmental*, vol. 95, pp. 93-99.

Zhang, F, Yediler, A & Liang, X. 2007, 'Decomposition pathways and reaction intermediate formation of the purified, hydrolyzed azo reactive dye C.I. Reactive Red 120 during ozonation', *Chemosphere*, vol. 67, pp. 712-717.

Zidane, F, Drogui, P, Lekhlif, B, Bensaid, J, Blais, JF, Belcadi, S & El Kacemi, K 2008, 'Decolourization of dye-containing effluent using mineral coagulants produced by electrocoagulation' *Journal of Hazardous Materials*, vol. 155, pp. 153-163.