HETEROGENEOUS Co_3O_4-MgO COMPOSITE CATALYSTS FOR OXIDATIVE DEGRADATION OF ACID ORANGE 7 IN WATER BY SULFATE RADICALS BASED ADVANCED OXIDATION TECHNOLOGY

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Abstract

A series of Co_3O_4–MgO nanocomposite oxides were prepared by a conventional reverse co-precipitation method and post-calcination and tested as heterogeneous catalysts for activation of Oxone for degradation of azo dye Acid Orange 7 (AO7) in aqueous solution. The as-prepared catalysts demonstrated to be very efficient for heterogeneous decomposition of oxidant producing sulfate radicals for the oxidation of AO7 in solution. Typically, 50 mg/L of AO7 could be completely degraded by the combination of 0.10 g/L of 40% Co_3O_4–MgO and 0.25 g/L of PMS within 12 min at 20 ^oC. The composite catalysts exhibited much higher catalytic activity than bare Co_3O_4 under similar conditions. Hence, it is suggested that the presence of Mg increased the content of surface hydroxyl oxygen, thus favoring the formation of Co(II)–OH complexes, which are vital for heterogeneous activation of Oxone. Kinetic studies confirmed that AO7 degradation catalyzed by Co_3O_4–MgO catalysts followed the first order kinetics model. The effects of several parameters such as catalyst and oxidant concentration, pH, and solution ionic strength on the AO7 degradation efficiency were assessed. 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: *Co_3O_4–MgO composite catalysts, AO7degradation, Oxone, wastewater treatment*

1. INTRODUCTION

Water treatment of organic contaminants is one of the major problems in the last few years. Azo dyes are a large class of industrial colorants constituting about 70% of the commercially available dyes. They are not only used in the textile, plastics, paints, inks and lacquers, but also as components in high-tech applications as optical data storage, display devices, dye-sensitized solar cells etc.(Kamaljit and Sucharita 2011). These industries annually generate huge amounts of highly colored wastewater, uncontrolled emmiting of that in natural waters presents a serious risk for aquatic life and human health due to the high toxicity, chemical and photostability of azo dyes, determining of their complex aromatic structure and synthetic. The latter will require treatment of wastewater prior to their discharge in natural water bodies (Bharathi and Ramesh 2013). Conventional methods of water treatment such as biological methods are not effective to remove the azo dyes because these methods use populations of microorganisms for which, however, most of the contaminants are proving toxic (Franco 2008). Another disadvantage of biological processes is the large amount of sludge, which require a subsequent step of the reduction of their volume and their subsequent landfill, which in turn is the source of secondary contamination (Bertanza, Collivignarelli and Pedrazzani 2001). Physical methods such as adsorption are effective for the removal of various organic contaminants from water, but often the adsorbents such as activated charcoal are not cost-effective for water treatment and the saturated carbon is a hazardous waste, requiring either discharge of adsorbed toxic dyes.

Towards chemical methods fall coagulation, flotation, conventional oxidation processes using strong oxidants such as ozone, ultraviolet treatment or electrochemical processes et al. These techniques are effective and rapid but are not generally employed due to the high chemical and operational costs as well as complex sludge generation (Ghoreishi and Haghighi 2003, Sirianuntapiboon, Chairattanawan and Jungphungsukpanich 2006).

An alternative to the conventional processes are the so-called Advanced Oxidation Processes (AOPs). They have received increasing attention in the research and development of wastewater treatment technologies in the last decades due to their low-cost and destructive character.

These methods are based on the generation of hydroxyl radicals, which are extremely strong and non-selective oxidants. Among the conventional AOP's is the Fenton process in which Fe^{2+}-ions decompose hydrogen peroxide to hydroxyl radicals. Although Fenton reagent has a number of industrial applications and is highly powerfull oxidant there are also disadvantages. Fenton reagent is effective only in a limitted pH range (2-6), under alkaline conditions hydrogen peroxide is unstable and rapidly decomposes into water and oxygen, as a result of precipitation of iron at pH > 6, in the most cases, the mineralization of organic substances does not exceed 60% (Anipsitakis 2005).

Over the past years, the sulfate radicals-based advanced oxidation processes (SR-AOPs) have been recognized as the most effective approaches for the degradation of toxic, persistant and non-biodegradable organic pollutants in wastewaters (Madhavan et al. 2008, Y.-S. M, C.-F. S, J.-G. L, 2010). Sulfate radicals have a number of advantages over the hydroxyl such as higher oxidation potential (2.5-3.1 V), higher stability and longer "lifetime" because of their selectivity with respect to the substrate to attack(Rastogi, Al-Abed and Dionysiou 2009, Xu et al. 2013)

Sulfate radicals can be generated by the combination of Oxone ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) whose active component is $KHSO_5$ - peroxymonosulfate (PMS) , with radiation excitation, heating and ultrasound irradiation (Huang, Couttenye and Hoag 2002, Oh et al. 2009, Yang et al. 2009, Su et al. 2012). These techniques are often accompanied by a number of disadvantages as a very high price. The latter leads to the development of low-cost methods for decomposition of PMS to generate sulfate radicals. Such a method is a homogeneous catalytic oxidation, wherein the action of suitable transition metal ions catalysts Oxone is destroyed with the preparation of highly reactive sulfate radicals. The ability of various transition metals Co(II), Fe(II), Cu(II), Mn(II), and Ti(III) for the activation of the PMS were studied (Rivas et al. 2009). The results showed that cobalt ions exhibit the highest activity and selectivity to the decomposition of the oxidant to obtain sulfate radicals. A number of other studies, also show that cobalt ions are the best catalyst for the decomposition of Oxone to highly reactive radicals (Anipsitakis 2005, Anipsitakis and Dionysiou 2003). The catalyzed activation of PMS by Co (II) –ions proceeds as follows (Anipsitakis and Dionysiou 2003):

$$Co^{2+} + H_2O \leftrightarrow CoOH^+ + H^+ \quad (1)$$

$$CoOH^+ + HSO_5^- \rightarrow CoO^+ + SO_4\text{•}^- + H_2O \quad (2)$$

$$CoO^+ + 2H^+ \leftrightarrow Co^{3+} + H_2O \quad (3)$$

$$Co^{3+} + HSO_5^- \rightarrow Co^{2+} + SO_5\text{•}^- + H^+ \quad (4)$$

$$SO_4\text{•}^- + \text{organics} \rightarrow [\text{stable and unstable intermediate products}] \rightarrow CO_2 + H_2O \quad (5)$$

It has been found that the rate limiting step of cobalt assisted activation of peroxymonosulfate is the formation of $CoOH^+$ complexes by dissociation of H_2O with Co(II) ions flowing equation (1) but these complexes are difficult to regenerate after interaction with PMS (Anipsitakis and Dionisiou 2003, 2004).On the other hand the use of cobalt ions in homogeneous form is unacceptable due to their toxity and risk of secondary contamination. Cobalt ions are recognized as priority metal pollutants (Shi et al. 2012). US EPA recommended limit concentration of cobalt in drinking water of $1mg.l^{-1}$. Therefore, development of cobalt-containing heterogeneous catalysts characterized by high activity and stability is the subject of increasing interest from researchers.

It was found that Co_3O_4 nanoparticles are highly effective in heterogeneous activation of peroxymonosulfate to produce sulfate radicals for degradation of AO7 and are promising alternative to toxic Co^{2+} ions but bulk Co_3O_4 is not stable under acidic conditions. The amount of leached cobalt ions is 0.61 mg/l in acidic conditions (Chen et al. 2008). The latter determines the immobilization of Co_3O_4 active phase on various metal oxide supports. Zhang et al. 2010 investigate the catalytic performance of Co_3O_4 immobilized on various metal oxide supports such as MgO, ZnO, Al_2O_3, ZrO_2, P25, SBA-15 for degradation of organic dyes in aqueous solutions. The results obtained showed that Co_3O_4/MgO is

found to be more efficient catalyst than bulk Co_3O_4 and homogeneous cobalt ions due to the higher dispersion of Co_3O_4 onto MgO surface. Liang et al. 2012 reported that with the use of Co_3O_4/MnO_2-PMS system phenol is degraded completely in 20 min. Yang et al. 2009 studied heterogeneous peroxymonosulfate activation by Fe-Co mixed oxides for decomposition of 2,4-dichlorophenol. They found that $CoFe_2O_4$ is the most promissing catalyst for activation of peroxymonosulfate and report that cobalt leaching is significantly reduced due to strong Fe-Co interactions. In addition, immobilization of Fe-Co catalyst on TiO_2 support showed very high cobalt leaching as titanium dioxide prevents the formation of close Fe-Co interaction.

Much lower catalytic activity to the bulk Co_3O_4 compared to the supported or the mixed catalysts could be explained by kinetically limited stage of regeneration of the surface Co(II)-OH^+ functional complexes on the surface of bulk Co_3O_4, the formation of which is vital for the activation of peroxymonosulfate. So immobilization of Co_3O_4 active phase on basic metal oxides surface assists modifying the surface properties of cobalt oxide by creating basic centers - surface OH groups on the catalyst surface, facilitating the formation of surface Co (II) -OH complexes (Yang et al. 2009).

Another technique for improving the stability and the surface properties of the catalysts is their preparation as nanocomposite materials. Ding et al. 2012 synthesized $Co_3O_4 – Bi_2O_3$ nanocomposite oxides as a heterogeneous catalyst for activation of peroxymonosulfate to generate sulfate radicals for oxidative degradation of methylene blue dye, rhodamine B, 2,4-dichlorophenol and phenol. The results obtained indicated that $Co_3O_4 – Bi_2O_3$ catalyst produced 8.6 fold higher rate constant in degradation of methylene blue rather that over bulk Co_3O_4 due to presence of Bi which result in increasing content of surface hydroxyl oxygen and favoured the formation of surface Co (II) -OH complexes. In addition, cobalt leaching was reduced to 43µg/L, being much less than that from bulk catalyst (158 µg/L). The high stability of these nanocomposite catalyst is a result from incorporated Co_3O_4 at the monoclinic structure of Bi_2O_3 resulting in strong interactions between Co and Bi components. Higher stability and catalityc activity of Co_3O_4 active phase modified by Bi_2O_3 is reported by a number of other investigations (Peng-bo et al. 2004, Hai-Sheng et al. 2004).

In our previous study we examined the catalytic behavior of Co_3O_4 and mixed Fe–Co spinel oxides active phases immobilized on MgO for activation of peroxymonosulfate to produce sulfate radicals for oxidative degradation of AO7 dye in aqueous solutions. The results obtained showed Co_3O_4/MgO catalyst exhibited much better catalytic performance than supported cobalt ferrities but there was low cobalt leaching (Stoyanova et al. 2014). To combine the high catalytic activity of Co_3O_4 and promoting effect of MgO with a maximum stability in a final product in this work we prepared Co_3O_4-MgO composite catalysts with different content of catalytically active phase of Co_3O_4 by reverse co-precipitation method and post-calcination. To our best knowledge, this is the first attempt to synthesize such catalysts with different weight ratios and to examine their catalytic activity in oxidative degradation of monoazo-dye AO7 in aqueous solutions. The kinetics of the oxidation process as well as the effects of the content of doped Co_3O_4, catalyst loading, Oxone concentration, pH, and ionic strength on the AO7 removal efficiency was investigated. Quenching experiments with specific alcohols were also conducted to identify the main radicals generated from the catalyst/Oxone interactions

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, which is a commercially important and readily available anionic textile dye, was chosen as a target compound due to its resistance to biological degradation. AO7 dye is 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 $Co(NO_3)_2 \times 6H_2O$, $Mg(NO_3)_2 \times 7H_2O$, ethanol, *tert*-butyl alcohol (TBA), and NaOH were all analytical grade.

2.2. Catalyst preparation

Co_3O_4-MgO composite catalysts with Co_3O_4 loading of 20wt.%, 40wt.%, 60wt.%, and 80wt.%, respectively, were synthesized by reverse co-precipitation method using NaOH. In a typical procedure, fixed amounts of cobalt nitrate and magnesium nitrate were dissolved into 20 ml water. 0.8M NaOH solution heated at 60◦C was then added dropwise into the above solution prepared under vigorous stirring until the solution pH reach 10. Thus obtained precipitate was further aged at 60◦C for 30 minutes under continuous stirring and then was washed with deionized water and ethanol several times After filtering the solid powder obtained was dried at 105◦C overnight, and finally calcined at 500◦C for 3 h in static air to obtain cobalt /bismuth oxide composite. For comparison, pristine Co_3O_4 and MgO were also prepared by the same synthetic procedure.

The amount of cobalt and magnesium in the prepared samples as well as the concentrations of leached Co and Mg after the reaction was completed were measured by ICP-OES analysis (iCAP 6300 Thermo Scientific).

2.3. Experimental procedure

The degradation of AO7 was carried out at room temperature (20±2◦C) in 400 mL reactor at batch mode with constant stirring throughout the reaction at around 400 rpm to ensure continuous contact between the solution and catalyst. In a typical run, a fixed amount of oxidant was added to the 200 ml 50 mg/L AO7 aqueous solution to achieve the predefined Oxone/AO7 molar ratio and stirred until dissolved. The experiment was initiated by the addition of a fixed amount of catalyst. At specific reaction time interval, samples of 4 ml were withdrawn from the suspension and immediately quenched with 1 mL methanol to prevent further reaction. Tamples 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.

All experiments have been repeated four times and the reproducibility was confirmed.

3. RESULTS AND DISCUSSION

The phase compositions of the as-prepared catalysts as determined by ICP-OES are given in Table 1. Results showed that the Co and Mg levels on nanocomposites were close to the preparation settings.

Table1. The content of Co and Mg in the as-prepared catalysts

Catalyst	***Oxide phase content (wt.%)***	
	Co_3O_4	***MgO***
20%Co_3O_4-MgO	21.6	78.4
40%Co_3O_4-MgO	42.1	57.9
60%Co_3O_4-MgO	54.3	45.7
80%Co_3O_4-MgO	74.3	25.7

The residual concentration of AO7 left in the solution during its oxidative degradation was monitored by measuring its absorption at 486 nm, which corresponding to the n–π* transitions of the hydrazone form of AO7. Fig. 1 displays the changes of temporal UV-Vis absorbance spectra of AO7 recorded at different reaction times during the 40%Co_3O_4-MgO - mediated catalytic oxidation of AO7. According to the results, a steady decrease of the main absorbance at 486 nm occurred with the progress of the reaction and disappeared after 10 min, indicating the destruction of azo chromophore. Meanwhile, a concomitant decrease in intensity of other two bands in the ultraviolet region, located at 230 and 310 nm and ascribed to the π–π* transitions in the benzene and naphthalene rings of dye, respectively, was also occurred. This indicates that the conjugated π-system of dye is also destroyed during the reaction, as well as that intermediates with benzoic- and naphthalene-type rings are not generated from chromophore cleavage. However, a new absorbance peak at about 255 nm appears even at 2 min of oxidation, reaches strongest absorbance intensity at about 8 min and then starts to drop slowly. The appearance of the band at 255 nm implies that a new structure unit is formed from the cleavage of AO7 chromophore structure which further is also degraded. 1,2-naphthoquinone, which is primary degradation intermediate accompanying AO7 cleavage in the vicinity of the azo bond, was speculated to contribute to the aforementioned absorbance peak. This suggestion was confirmed by comparing UV-Vis spectra of 50 mg/L AO7 before and after 80%Co_3O_4-MgO/Oxone treatment for 10 min with a spectrum of a standard solution, containing 1,2-naphthoquinone (Fig. 2).

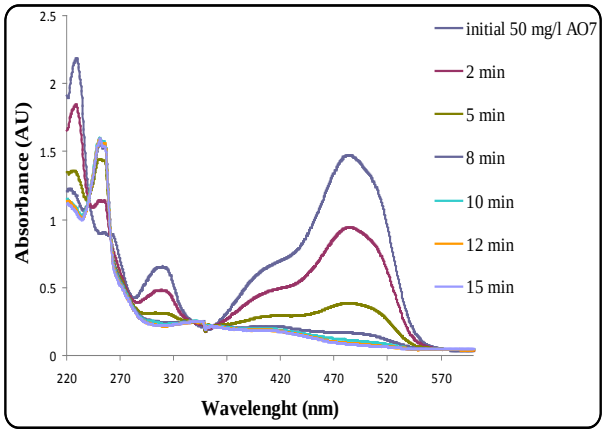

Fig.1. UV–Vis spectral changes of AO7 in aqueous solution after catalytic degradation over 40%Co_3O_4-MgO

(50 mg/L Orange II; 0.10 g/L catalyst loading; Oxone/ Orange II molar ratio= 3/1; pH=3.0; 20 ^oC)

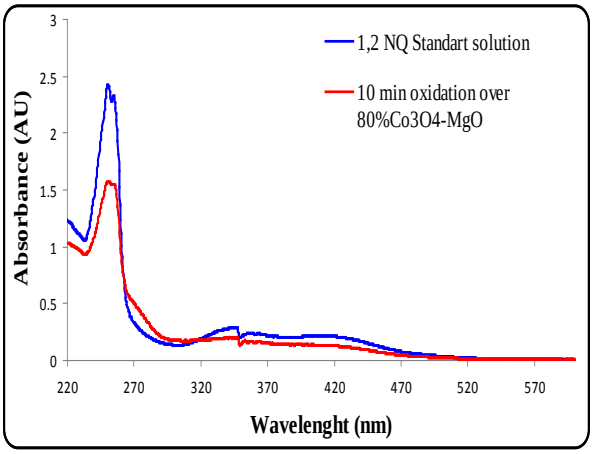

Fig.2. UV-Vis spectra of standard solution of 1,2-naphthoquinone and AO7 dye solution after catalytic oxidation over 80%Co_3O_4-MgO *for 10 min*

Fig. 3 represents the kinetics curves of AO7 removal from the solution in different systems. To verify the catalytic ability of Co_3O_4-MgO composite materials to effective activate PMS for degrading AO7, control experiments were conducted in the presence of catalyst without addition of oxidant and using of PMS alone (without any catalyst) under the same experimental conditions. According to Fig. 3, negligible dye degradation (less than 1 %) was observed even after 8 hours in the presence of oxidant without adding catalyst, indicating that Oxone could not degrade AO7 dye directly. In blank experiments where no oxidant was added to the reaction mixture containing AO7, between 5-15% of dye was removed in 30 min, probably due to the adsorption of dye molecule on the surface of the catalysts (data not shown). The extent of AO7 adsorption was found to increase with increasing the content of MgO oxide in the composites. However, when using Co_3O_4-MgO composites as catalysts, a remarkable improvement in AO7 degradation efficiency was observed with almost 100 % AO7 occurring within 12-15 min depending on the Co_3O_4 content in the catalytic samples. This indicates a fast generation of active radical species once Oxone is in contact with the as-prepared catalysts. It is observed that the composite catalysts with different cobalt loading do not display distinctly different catalytic activity, represented by final AO7 removal efficiency.

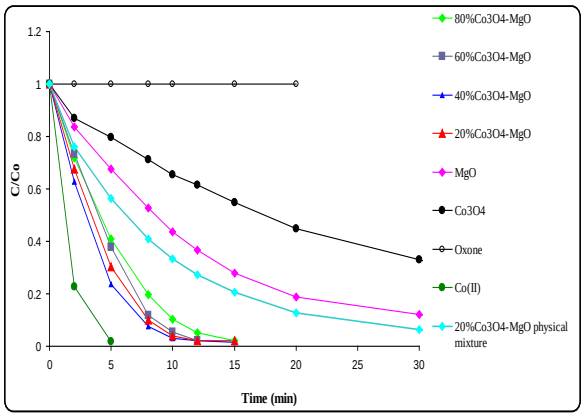

Fig. 3. Degradation kinetics of AO7 in different systems

(50 mg/L AO7; 0.10 g/L catalyst loading; Oxone/AO7= 3/1; pH=3.0; 20^oC)

There is only slight decrease in the rate constant of AO7 degradation if the relative amount of Co_3O_4 is higher than 40 wt.% (Fig. 4). Increasing the amount of catalytically active spinel phase would favor aggregation of Co_3O_4 particles, which leads to reduced number of available active sites on the catalyst surface (Shi et al. 2014). As a result, the formation of Co–OH complexes, which allow the activation of PMS, is prevented and hence a lower rate of AO7 degradation is attained. Moreover, the surface of MgO, due to its high point of zero charge of 11.8, is covered by the hydroxyl groups, which facilitates the formation of hydroxylated cobalt complexes through the direct interaction of cobalt species by nearby OH groups. Thus, reducing the MgO content in the hybrids also results in a lesser amount of hydroxyl groups on the MgO surface and hence a lower rate of formation of Co–OH complexes is attained.

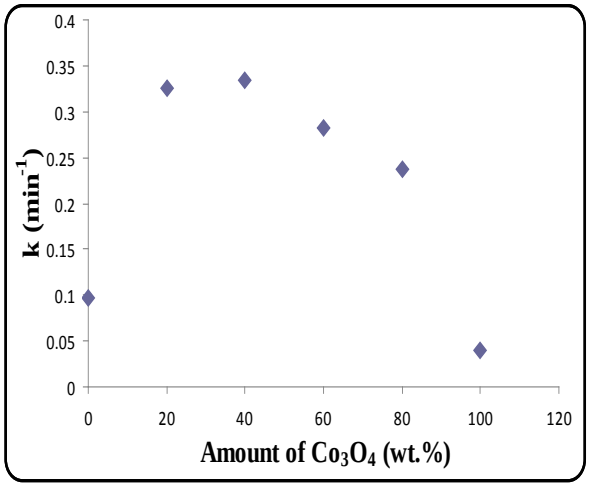

Fig. 4. Variation of the first-order degradation rate of AO7 with Co_3O_4 amount in the Co_3O_4-MgO composites

Bare Co_3O_4 exhibited a much lower degradation activity than Co_3O_4-MgO composites with only about 39% AO7 removal efficiency after 12 min. However, AO7 degradation was found more significant for pure MgO/ Oxone system with a removal of approximately 63% for the same time period. The results suggest that oxidant could also be activated by bare MgO to generate active radicals for degrading of AO7, but at much lower rate compared to that attained in the presence of MgO doped Co_3O_4 materials. Therefore, a synergistic effect by the conjunction of Co_3O_4 and MgO was thought to occur in the studied reaction, thus confirming the existence of strong Co-Bi interaction in the composite catalysts, leading to accelerated activation of Oxone. This suggestion was confirmed by the much better catalytic performance of Co_3O_4-MgO composites than that exhibited by corresponding physical mixture of Co_3O_4 and MgO, the latter being slightly higher that of MgO. It should be noted that the homogeneous Co^{2+}/Oxone system showed faster oxidation kinetics - complete discoloration of dye solution catalyzed by Co^{2+} ions was reached in 5 min. Although the homogeneous approach is more efficient for destroying dye molecule, its practical application is restricted due to the 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 suggests that the activation of oxidant is heterogeneously conducted on the catalyst surface. The ICP-OES results indicate that Co_3O_4-MgO composites showed minor and acceptable Co leaching during oxidation, which is less pronounced in alkaline medium (Fig. 5) thus confirming that catalytic degradation of AO7 was mainly through the heterogeneous pathway.

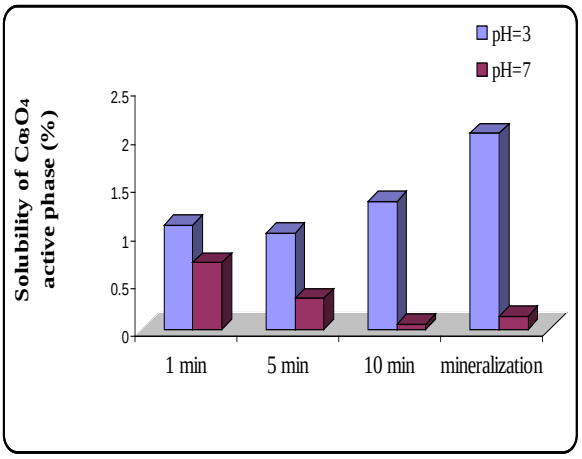

Fig.5. Co leaching of 40%Co3O4-MgO catalyst during AO7 catalytic oxidation at pH=3 and pH=7.

The experimental data were found to be best fitted the first-order kinetics with respect to AO7 concentration (Fig. 6), thereby implying that in the studied heterogeneous systems the reaction rate and AO7 degradation efficiency were not controlled by the generation of the radicals. The rate constant for the most active catalysts Co_3O_4-MgO was determined as 0.330 min^{-1}, being 8.4 times higher than that for bare Co_3O_4.

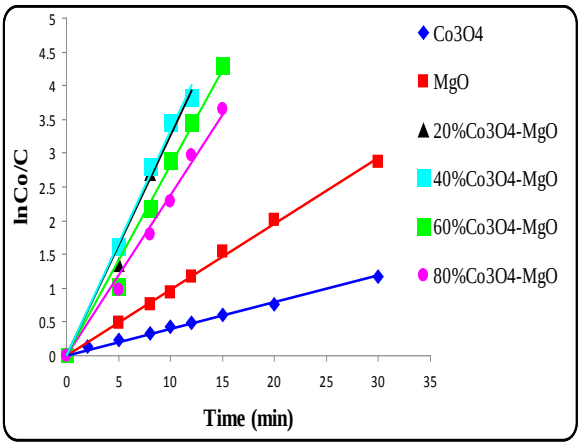

Fig. 6. Linear transformation of the kinetic curves of AO7 catalytic oxidation with Oxone.

According to the literature data, homogeneous or heterogeneous activation of Oxone could generate three main types' radicals including sulfate $SO_4^{\bullet-}$, hydroxyl $^{\bullet}OH$, and peroxymonosulfate $SO_5^{\bullet-}$ (Anipsitakis et al. 2005; Shukla et al. 2011). Sulfate and hydroxyl radicals could attack and effectively destroy the organic molecules due to their high oxidation efficiencies. In contrast, $SO_5^{\bullet-}$ has a much lower redox potential and is usually considered not responsible for the degradation of organics. In order to understand the role of these radicals in the Co_3O_4-MgO /Oxone system, effects of quenching agents, namely ethanol and *tert*-butyl alcohol (TBA) on the rate of AO7 decolorization were examined. Ethanol is capable of quenching both sulfate and hydroxyl radicals at comparable rates, whereas TBA mainly reacts with hydroxyl radical and much slowly with that of sulfate radical (Anipsitakis & Dionysiou 2003; Zhao et al. 2010). Fig. 7 represents the effect of both quenching agents on the rate and efficiency of AO7 catalytic oxidation over 40%Co_3O_4-MgO.

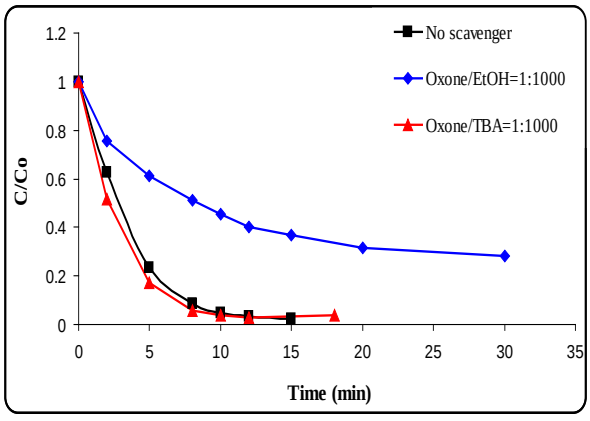

Fig.7. Effect of ethanol and TBA addition on AO7 degradation in 40%Co3O4-60%MgO/Oxone system. (50 mg/L AO7; 0.10 g/L catalyst loading; Oxone/AO7= 3/1; pH=3.0; 20°C)

As seen from the results, the AO7 degradation is strongly inhibited by addition of ethanol into the reaction mixture, leading to 29% drop in dye removal extent, whereas the reaction was negligibly affected by the presence of TBA. These results implied that sulfate radicals were the main active species, generated during the heterogeneous activation of Oxone and controlling the oxidation reaction in the Co_3O_4-MgO/Oxone system. The high oxidation efficiencies of $SO_4^{\bullet -}$ radicals, in combination with the slow rate of consumption of precursor oxidant Oxone (due to its stability), make sulfate radical based processes very effective for the degradation of recalcitrant organic compounds.

To elucidate the efficiency of as prepared catalysts for AO7 degradation, the effect of different operating parameters, including the concentrations of catalyst and Oxone, initial solution pH, and ionic strenght and was investigated. The experiments were performed by using the most active catalyst in this study - 40%Co_3O_4-MgO.

Fig. 8 depicted the degradation kinetics of AO7 by Oxone in the presence of 40%Co_3O_4-MgO at different catalyst loading.

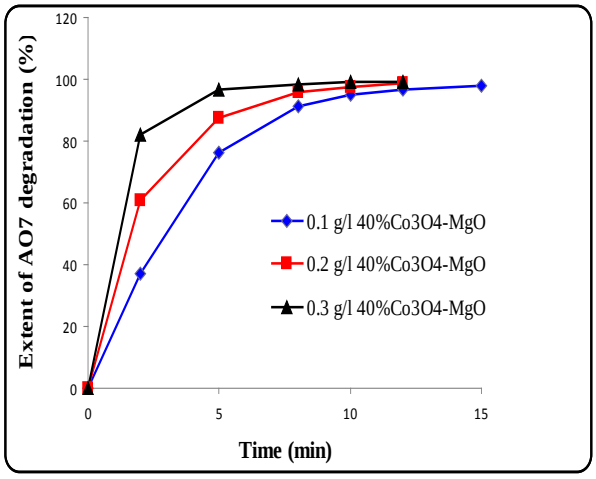

Fig.8. The effect of 40%Co3O4-MgO amount on the AO7 degradation efficiency.

(50 mg/L AO7; Oxone/AO7= 3/1; pH=3.0; 20°C)

As seen from the figure, higher rate of AO7 degradation was observed with increasing catalyst dosage from 0.1 to 0.3 g/l. Almost complete removal of dye could be reached within 5 min at 0.3 g/L catalyst concentration while in the same duration there was still about 24% of AO7 remaining unchanged in the solution. The positive effect of increasing catalyst dosage can be attributed to the increased number of active sites for Oxone activation and hence the production of radical species could be accelerated. Besides, the values of rate constants, expressed per unit mass of catalysts, do not differ significantly, which indicates that the reaction is not controlled by external diffusion and moreover that the process runs on the surface of the catalysts.

Fig. 9 presents the AO7 degradation (in terms of reaction rate constant) by 40%Co_3O_4-MgO activated Oxone at varying Oxone/AO7 molar ratios from 1/1 to 3/1. It is evident that increasing initial Oxone concentration at fixed catalyst dosage of 0.1 g/L could promote the AO7 degradation. Two-fold increase in oxidant concentration led to increase of the rate constant from 0.177 to 0.334 min^{-1}, indicating that the rate is controlled by radical generation under low concentration of oxidant. However, at further increase in Oxone concentration a slower enhancement of the degradation efficiency was registered. Since the number of active sites on the catalyst surface is finite at fixed dosage of catalyst in the solution, it gradually became the limiting factor under a high concentration of Oxone, and consequently the radical yield was more slightly dependent on Oxone. Furthermore, it was found that Oxone is inactive by itself under experimental conditions. However, increased

concentration of Oxone is beneficial to achieve higher extent of dye mineralization as evidenced by a gradual degradation of the formed intermediate absorbing in the UV region. It should be noted that a complete degradation of AO7 was not achieved at molar ratio of 1/1 due to depletion of oxidant (insufficient PMS amount).

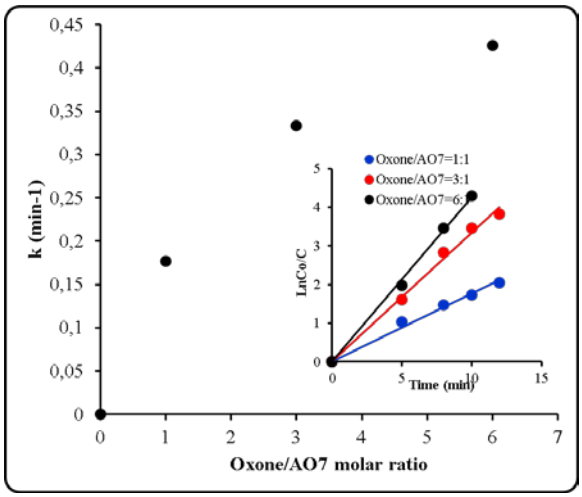

Fig.9. AO7 degradation on 40%Co3O4-MgO at different Oxone concentration.

(50 mg/L AO7; 0.10 g/L catalyst loading; pH=3.0; 20°C)

The effect of pH on the degradation efficiency of the dye is very important, because it affects not only the surface charge of the catalysts but also the speciation of Oxone in the solution. Therefore, the influence of initial solution pH on AO7 removal was also studied at three different pH values. As shown in Fig. 10, the rate of AO7 degradation became slower as the pH rose from 3 to 7. In acidic medium, the dye could be nearly complete degraded within 12 min using 40%Co_3O_4-MgO catalyst, while at neutral conditions the decolorization rate was 67% within the same reaction time. However, a final removal of 96 % could still be achieved after 60 min at pH=7, implying that the catalyst still exhibited a good catalytic activity under neutral condition. Given that the second p*K*a of PMS is 9.4, the oxidant will exists mainly in its monoanion form (HSO_5^-) at acid-neutral condition, while the fraction of its dianion form (SO_5^{2-}) would sharply increased at pH > pKa_2 (Guan et al. 2011**)**. On the other hand, the surface of the catalyst particles was positively charged in the entire pH range studied. Therefore, the electrostatic attraction between negatively charged peroxymonosulfate species and catalyst surfaces is not significantly affected at rising pH from 3 to 7, so that could not be a reason for the decrease of dye degradation efficiency. It could be speculated that the observed decreasing trend is due to the radical scavenging effect of phosphate anions coming in the solution from the phosphate buffer used to adjust pH to 7 (Yang et al. 2010**)**. However, the oxidation of AO7 was quite significant at further increase in pH to 10 and the degradation efficiency was almost comparable to that attained in an acidic medium. This result could be explained because of two reasons. First, at alkaline pH $SO_4^{\bullet -}$ reacted with hydroxyl anions and transform into $^{\bullet}OH$ radical, which has a relatively stronger oxidizing power than sulfate radicals (Guan et al. 2011). Another reason is that at pH=10 adjusted by bicarbonate, Oxone could be homogeneously activated by HCO_3^- to generate active species for degrading AO7, as well as a possible generation of percarbonate from interaction between bicarbonate species and Oxone could be assumed (Chen et al. 2008). In fact, when the oxidation was carried out at pH=10 without catalyst, the concentration of AO7 was reduced by 95% in 30 min. However, there is a significant difference in the profile of the UV-Vis spectra of the solution registered at different pH 3 and 10. In contrast to the results obtained at acidic medium, the appearance of band at 255 nm was not observed during the degradation of dye at pH=10. Meanwhile, noticeable residual absorbance in the

wavelength range of 300 – 350 nm was observed in the spectrum after complete destruction of the azo linkage, implying that naphthalene intermediates are generated. The observed difference in the selectivity of the oxidation process imply for different pathway of AO7 degradation at alkaline pH. Further investigations of end products of AO7 degradation under alkaline pH are underway.

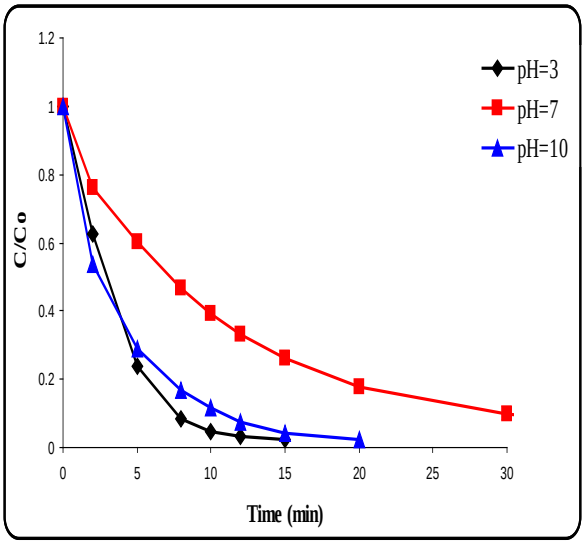

Fig.10. Influence of pH on AO7 degradation on 40%Co3O4-MgO.

(50 mg/L AO7; 0.10 g/L catalyst loading; Oxone/AO7= 3/1; 20°C)

The presence of a certain quantity of different additives, including inorganic salts, is common in textile effluents. These compounds have been utilized in the dyeing process and dyehouse effluents often contain salt at concentrations as high as 100 g/L, which imposed a significant influence on its treatment (Wang and Chu 2011). As an example, NaCl, is used to promote the transfer of dyestuff to the fabric. The addition of such ionic compounds in solution led to the increase of the ionic strength, which on turn significantly influences electrostatic bonding (outer-sphere interactions) between the oxide surface and solute. However, inner-sphere complexation (covalent bonding or a combination of covalent and ionic bonding) is not affected (Stumm 1992). Thus, a study of the effect of solution ionic strength on the AO7 oxidative degradation in the 40%Co_3O_4-MgO/PMS system was carried out, and the results are shown in Fig. 11.

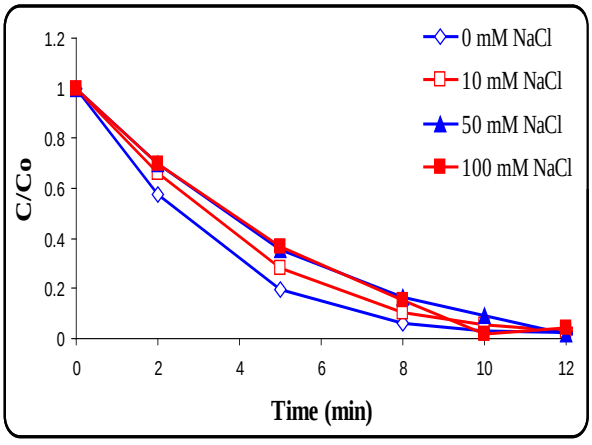

Fig.11. Effect of solution ionic strength (represented as NaCl concentration) on AO7 oxidative degradation over 40%Co3O4-MgO.

(50 mg/L AO7; 0.10 g/L catalyst loading; Oxone/AO7= 3/1; pH=3.0; 20°C)

It can be noted that the AO7 degradation was negligible delayed with increasing NaCl concentration (used to adjust the ionic strength) in the reaction solution from 10 to 100 mM. Even at 100 mM NaCl concentration (corresponding to about 6 g/L), as high as 98% AO7 removal after 15 min was achieved, implying that generation of powerful sulfate radicals is not inhibited by the high ionic strength of the solution. Based on this result it could be suggested that activation of Oxone resulted from the strong binding or complexation of negatively charged PMS ions with the surface Co(II) sites and the reaction rate is not affected substantially by the electrostatic attraction between the positively charged catalyst surface and HSO_5^- (Zhang, Zhu and Croué 2013).

CONCLUSIONS

The catalytic performances of series of Co_3O_4–MgO composite oxides on the activation of Oxone for oxidative degradation of Acid Orange 7 were explored in this study. Doping of Co_3O_4 with Mg oxide induced remarkable increase in the Oxone decomposition and AO7 oxidation. The coupling of Oxone with the most active 40% Co_3O_4–MgO catalyst led to almost 100% decolorization of the AO7 solution within 12 min at ambient conditions, while using bare Co_3O_4 only XXX % of dye was degraded whithin the same reaction period. The enhanced catalytic activity of Co_3O_4–MgO composites is attributed to the increased basicity of the catalyst surfaces, which facilitates the formation of surface Co–OH complex and thus favoring the sulfate radical generation. The first order kinetics was observed to fit the Co_3O_4–MgO/Oxone process. The addition of methanol and TBA as radical scavengers proved the generation of sulfate radicals in the Co_3O_4–MgO/Oxone reaction system. Increasing the catalyst amount and Oxone concentration promoted the AO7 degradation, while the reaction efficiency decreased at neutral medium. In particular, common salt found in textile wastewater such NaCl has no influence on the AO7 degradation rate.

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