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Synthesis of Supported Ruthenium Catalyst for Phenol Degradation in the Presence of Peroxymonosulfate

Mansoor Anbia · Marzie Rezaie

Abstract Industrial synthesis processes produce high concentration of hazardous organic pollutants into water body, which must be removed before being discharged. Advanced oxidation processes (AOPs) using heterogeneous catalysts has been widely utilized for wastewater treatment. Here, RuO_2-based catalyst was synthesized by a general impregnation method and used to oxidize phenol by peroxymonosulfate (PMS) as an oxidant in aqueous solution. The properties of this supported catalyst were characterized by SEM (scanning electron microscopy), XRD (powder X-ray diffraction), and nitrogen adsorption-desorption. The mesoporous Al_2O_3 support had large surface area and high thermal stability. It is found that ruthenium oxide-based catalyst is highly effective to activate PMS to related sulfate radicals. The effects of catalyst loading, phenol concentration, PMS concentration, reaction temperature, and reusability of the as-prepared catalyst on phenol degradation have been investigated. Overall, our findings demonstrate that in RuO_2/Al_2O_3 mesoporous catalyst, Oxone (PMS) is effectively activated, and 100% phenol degradation occurs in 60 min. To regenerate the deactivated catalyst and improve its catalytic properties, three different methods involving annealing in air, washing with water, and applying ultrasonics were used. The catalyst was recovered thoroughly by heating treatment.

1 Introduction

Many organic contaminants in polluted water are toxic and extremely refractory to natural degradation causing significant problems to public health and ecological system (Shukla et al. 2010b; P. R. Shukla et al. 2010; Lu et al. 2015). Several methods such as adsorption, flocculation, membrane separation, and chemical oxidation can be used to remove the organic toxins. Among these methods, advanced oxidation process (AOP) such as wet air oxidation, thermal destruction, ozonation, and homogeneous/heterogeneous oxidation can achieve complete degradation of organic contaminants in wastewater to water and carbon dioxide as final products (Wang 2008; Cao et al. 2009; Agustina et al. 2005; M Anbia and Amirmahmoodi 2011; Mansoor Anbia and Ghaffari 2009). Fenton oxidation using OH radical in the presence of Fe^{2+} ions is a typical AOP. However, they suffer from disadvantages such as low pH range, metal leaching, and generation of large quantity of sludge (Melero et al. 2007). In order to eliminate this drawback, another oxidant such as peroxymonosulfate has been proposed. The high oxidation potential of sulfate radicals has caused them to be suggested as an alternative recently (Anipsitakis and Dionysiou 2003; Muhammad et al. 2013). For the oxidation of organic

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pollutants, conjunction of heavy metals such as cobalt, ruthenium, and iron with PMS to produce sulfate radicals has been proposed. The radical generation process can be described as shown below (Anipsitakis and Dionysiou 2003).

$$Co^{2+} + HSO_5{}^- \rightarrow Co^{3+} + SO_4{}^- + OH^- \qquad (1)$$

$$Co^{3+} + HSO_5{}^- \rightarrow Co^{2+} + SO_5{}^- + H^+ \qquad (2)$$
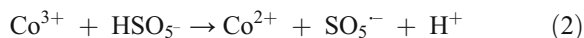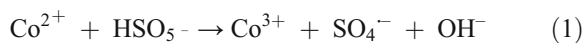
The main issue, in the use of metal ions as catalysts, is their toxicity causing health problems to humans. Therefore, heterogeneous catalysts operating at room temperature with normal pressure and low energy have been proposed recently to overcome the disadvantages of the homogeneous process (Anipsitakis et al. 2005; Shukla et al. 2011b; Chen et al. 2008; Zhang et al. 2010). Heterogeneous catalysts are usually synthesized using cheap materials as supports which bring excellent catalyst performance and practicability (Saputra et al. 2012). Among the various supports such as metal oxides, silica, and zeolite, Al_2O_3 is an important one that widely used in the chemical and petrochemical industries owing to its diverse merits featuring the acid-base characteristics, having high specific surface area, high mechanical strength, excellent chemical stability, and low price (Rao et al. 2005; Gao et al. 2009; Khalil 2007; Li et al. 2014). In addition, many reports show that ruthenium is one of the best transition metal catalysts that it can be used in oxidation of organic compounds such as aniline, acetic acid, chlorophenols, and phenol (Gallezot et al. 1997; Carrier et al. 2009; Liu et al. 2010; Minh et al. 2006). However, the utilization of this heavy metal-based catalysts with peroxymonosulfate (PMS or Oxone) for phenol degradation has been less developed so far (Muhammad et al. 2012). Therefore, this paper investigates the use of ruthenium heterogeneous catalyst with PMS for chemical oxidation of phenol in aqueous solution. In order to prepare of ruthenium-based catalyst, firstly, mesoporous Al_2O_3 supports with different surface area were synthesized via precipitation method, and then during impregnation treatment, RuO_2 was loaded on the surface of as-prepared alumina supports.

2 Materials and Methods

2.1 Mesoporous Al_2O_3 Preparation

At first, 27.5 g of aluminum sulfate octadecahydrate ($Al_2(SO_4)_3$, Aldrich) was dissolved in deionized water under constant stirring. Then, $NH_3 \cdot H_2O$ solution (1.56 wt. %) was added dropwisely so that the pH of the solution reached 8.0; the solution was heated at 40 °C. After the completion of reaction, the white product was isolated and washed with deionized water until the precipitate became free of $SO_4{}^{2-}$ and then heated at 90 °C for 3 h by water bath method. After that, the precipitate was washed with anhydrous ethanol (Merck) to remove water and then
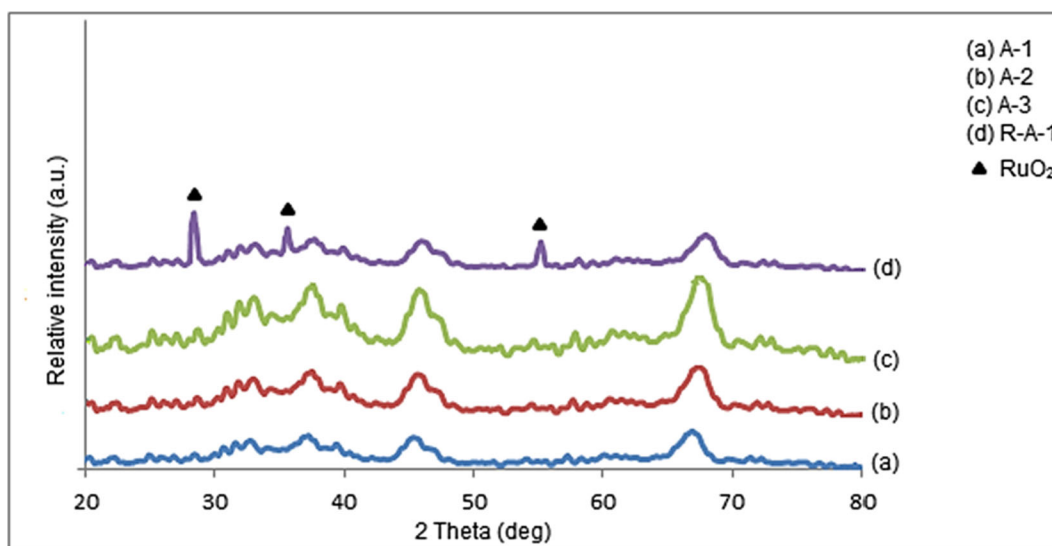

Fig. 1 XRD patterns of A-1, A-2, A-3, and R-A-1

dispersed in a solution containing 1.0 g cetyltrimethylammonium bromide (CTAB, Aldrich) and 50 mL anhydrous ethanol for 4 h. In the next step, the vessel was transferred in an oven to be heated at 120 °C for 12 h and finally calcined in the air at 600, 800, and 1000 °C for 6 h, respectively, at a heating rate of 1 °C/min.

2.2 Preparation of RuO_2/Al_2O_3 Catalyst

A general impregnation method was used for the synthesis of RuO_2/Al_2O_3 catalyst. At first, 5 g Al_2O_3 was dispersed in 90 mL of ethanol for 15 min. Next, ruthenium chloride (Aldrich) and 50 mL ethanol were added into the solution and kept stirring vigorously for 16 h, and then dried at 100 °C. The resultant solid was heated at 200 °C for 2 h, and finally calcined at 550 °C for 6 h. The loading of Ru on the support was maintained at 5 wt. %.

2.3 Characterization

The characterization of the obtained catalyst was performed by SEM (scanning electron microscopy), XRD (X-ray diffraction), and nitrogen adsorption-desorption. The mineralogy and the structural features of the support and catalyst were studied by XRD patterns. These experiments were carried out on a Philips 1830 diffractometer with Cu-Kα ($\lambda = 0.154$) radiation at a current of 30 mA and voltage of 30 kV. The textural and morphological information of the mesoporous Al_2O_3 support were obtained using scanning electron microscopy (SEM, Philips XL 30). The specific surface areas were identified by N_2 adsorption-desorption experiments performed at 77 K on micromeritics model ASAP 2010 sorptometer. The support and catalyst were degassed at 120 °C for 12 h prior to the analysis.

2.4 Experimental Procedure

To perform the catalytic oxidative examinations, 500 mL of phenol solution with initial concentration of 50 mg/L was poured into a glass beaker and stirred constantly to obtain a homogeneous mixture at 25 °C. Next, a certain amount of catalyst was added to the mixture, and then, it was allowed to reach adsorption equilibrium between phenol molecules and the catalyst during reaction time. The next step of the experiment was to blend an amount of Oxone as an initial reactant. The reaction proceeded for 3 h. Then, during appropriate time interval namely 0 to 160 min, 50 mL of the
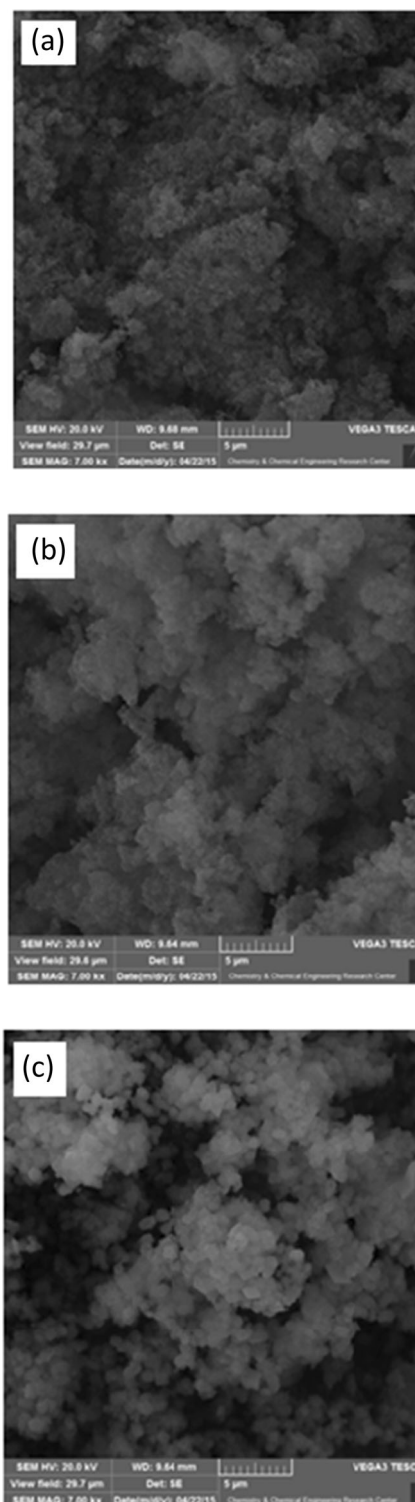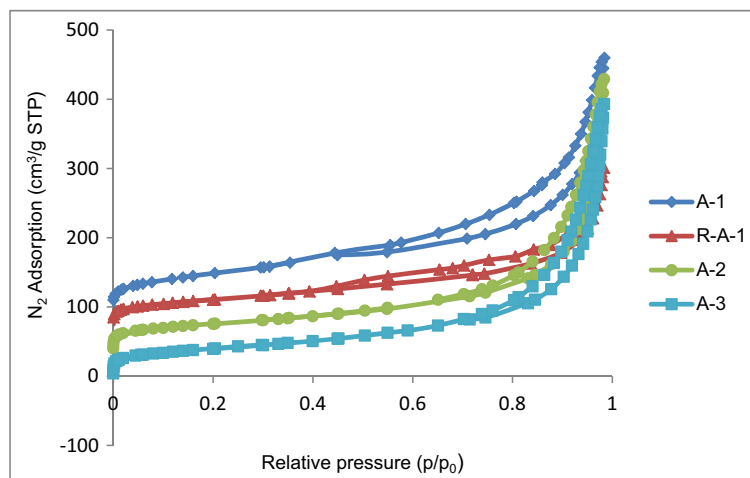

Fig. 2 SEM images of A-1 (**a**), A-2 (**b**), and A-3 (**c**)

solution was separated, and an excess of sodium nitrite as a quenching reagent was added to the sample. After

Fig. 3 N₂ adsorption-desorption isotherms of A-1, A-2, A-3, and R-A-1

that, the solution was filtered with filter paper. Next, phenol concentrations were determined using spectro-photometric measurements (UV/Vis mini 1240 Shimadzu) by standard method employed 4-aminoantipyrine at maximum wavelength of phenol i.e., 500 nm. The same procedures were performed for other initial concentration of phenol (20, 70, and 100 ppm).

3 Results and Discussion

3.1 Characterization of Ru Impregnated Al₂O₃ Catalyst

XRD patterns of mesoporous Al_2O_3 calcined at 600 °C (A-1), 800 °C (A-2), 1000 °C (A-3), and RuO_2/Al_2O_3 (R-A-1) are presented in Fig. 1. It seems very week diffraction peaks in the XRD patterns of A-1, when the

calcination temperature increased from 600 to 1000 °C, the diffraction peaks became stronger, which corresponded to the γ-Al_2O_3 phase. It can be seen that ruthenium species are found in the form of RuO_2 on RuO_2/Al_2O_3 at 2θ coordinate of 28°, 35°, and 54.3°.

In Fig. 2, SEM images of the synthesized Al_2O_3 particles are shown. The samples are composed of very tiny spherical particles. Homogeneous particle size distributions are perceived in all samples.

The N_2 adsorption-desorption isotherms of A-1, A-2, A-3 as supports and R-A-1 as catalyst sample are shown in Fig. 3. The specific surface area of A-1, A-2, A-3, and R-A-1 was determined to be 222.05, 140.97, 82.1, and 143.37, respectively. Since the specific surface area of A-1 is larger than A-2 and A-3, it was utilized as the catalyst support. After the RuO_2 loading on the support, the specific surface area of catalyst became lower than support. The

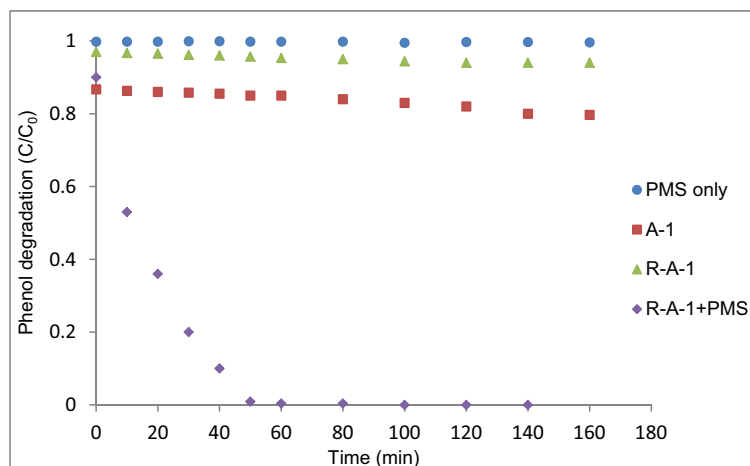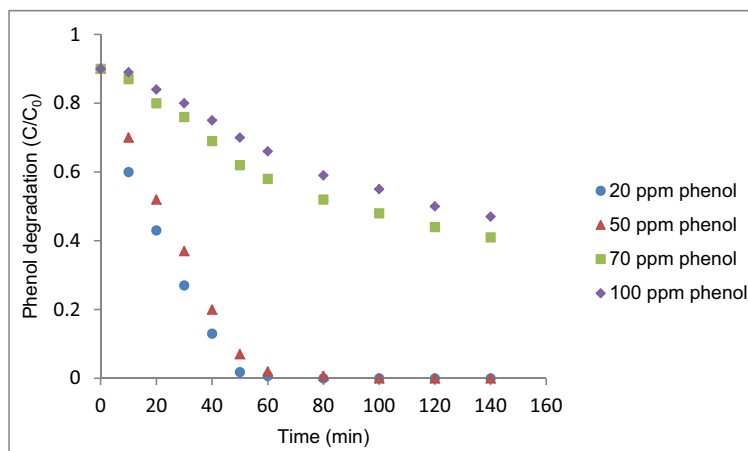**Fig. 4** Phenol removal in various reaction conditions

Fig. 5 Effect of phenol concentration on phenol removal. *R-A-1* RuO$_2$/Al$_2$O$_3$. Reaction conditions: 1 g Oxone, 0.2 g catalyst, 25 °C
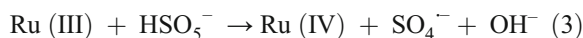
hysteresis loop indicated the mesoporous structure of Al$_2$O$_3$ and RuO$_2$/Al$_2$O$_3$ samples.

3.2 Preliminary Study of Phenol Degradation Using Catalyst

Figure 4 shows preliminary tests of adsorption and phenol degradation in aqueous solution on A-1 and R-A-1 under various experimental conditions. Generally, phenol can adsorb on the surface of A-1 and R-A-1 even at low efficiency. The adsorption efficiency on A-1 and R-A-1 is 8 and 3 % in 2 h, respectively. The results indicate that the surface area of support decreases by loading ruthenium on the surface of the support. In oxidation tests, the Oxone without a solid catalyst could not oxidize phenol. Phenol degradation would occur when catalyst and oxidant (PMS) simultaneously were present in the solution. In RuO$_2$/Al$_2$O$_3$-Oxone, phenol could be removed completely from solution in 60 min.

Anipsitakis and Dionysiou (Anipsitakis and Dionysiou 2004) have reported that Co (II) and Ru (III) are the best transition metal catalysts for the activation of PMS. The reaction of Ru (III) with PMS can be described as following:

$$Ru\ (III)\ +\ HSO_5^-\ \rightarrow\ Ru\ (IV)\ +\ SO_4^{\cdot-}\ +\ OH^- \quad (3)$$

The oxidation process is proposed as below.

$$S\text{-}Ru\ (IV)\ +\ HSO_5^-\ \rightarrow\ S\text{-}Ru\ (III)\ +\ SO_5^{\cdot-}$$
$$+\ H^+\ (S\ :\ solid\ surface) \quad (4)$$

$$S\text{-}Ru\ (III)\ +\ HSO_5^-\ \rightarrow\ S\text{-}Ru\ (IV)\ +\ SO_4^{\cdot-}$$
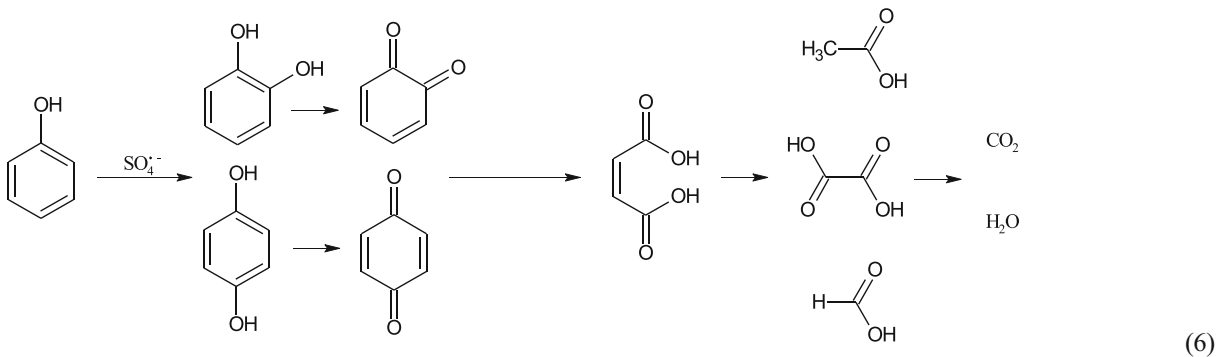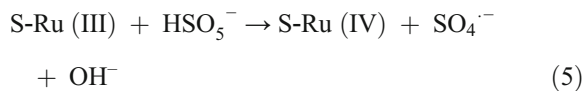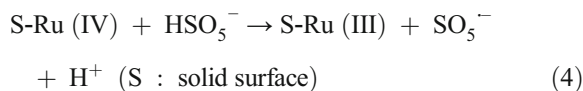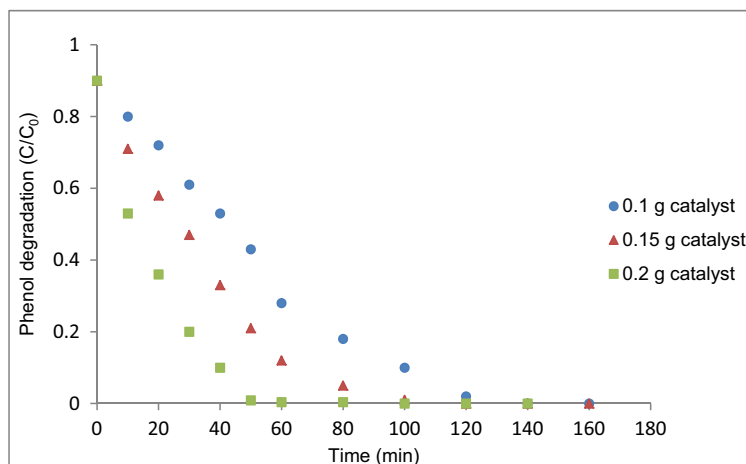$$+\ OH^- \quad (5)$$

(6)

Fig. 6 Effect of catalyst loading on phenol removal. *R-A-1* RuO$_2$/Al$_2$O$_3$. Reaction conditions: 50 ppm, 1 g Oxone, 25 °C

At first, catechol was produced in the presence of sulfate radicals and then converted to hydroquinone and benzoquinone (Anipsitakis et al. 2006; Mijangos et al. 2006; Yalfani et al. 2009). Maleic acid, oxalic acid, and acetic acid, as the latter intermediates, were finally mineralized to CO$_2$ and H$_2$O (Hu et al. 2011).

3.3 Effects of Reaction Parameters on Phenol Degradation

Several variables such as phenol concentration, catalyst loading, Oxone concentration, and reaction temperature can influence phenol degradation in aqueous solution. These variables were investigated here.

Figure 5 shows various concentrations of phenol (between 20 and 100 ppm) on the phenol degradation. Phenol degradation efficiency decreased with increasing phenol concentration. At low phenol concentrations (20–50 ppm), 100 % phenol degradation could be achieved within 60 min. At phenol concentration of 100 ppm, degradation efficiency was only 50 % within 140 min.

In phenol degradation, production of sulfate radicals is the main reaction, which depends on supported ruthenium catalyst and Oxone. Due to the same concentration of RuO$_2$/Al$_2$O$_3$ and Oxone, sulfate radical concentration produced in solution will be the same. Thus, a high amount of phenol in solution will require more time to achieve the same removal rate, thus lowering phenol degradation efficiency.

Degradation of phenol in the solution depends on the amount of the RuO$_2$/Al$_2$O$_3$ (R-A-1) catalyst (Fig. 6). Phenol oxidation efficiency is enhanced by increasing catalyst dosage in the solution. At 0.1 g RuO$_2$/Al$_2$O$_3$, phenol degradation would be 88 % at 100 min, while RuO$_2$/Al$_2$O$_3$ loading of 0.2 g, oxidation of phenol would reach 100 % at 60 min. It was noticed that the highest degradation efficiency was achieved at the

Fig. 7 Effect of Oxone concentration on phenol removal. *R-A-1* RuO$_2$/Al$_2$O$_3$. Reaction conditions: 50 ppm, 0.2 g catalyst, 25 °C
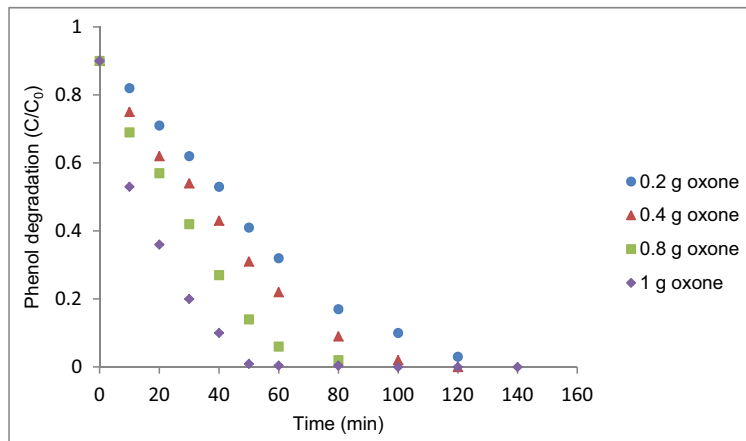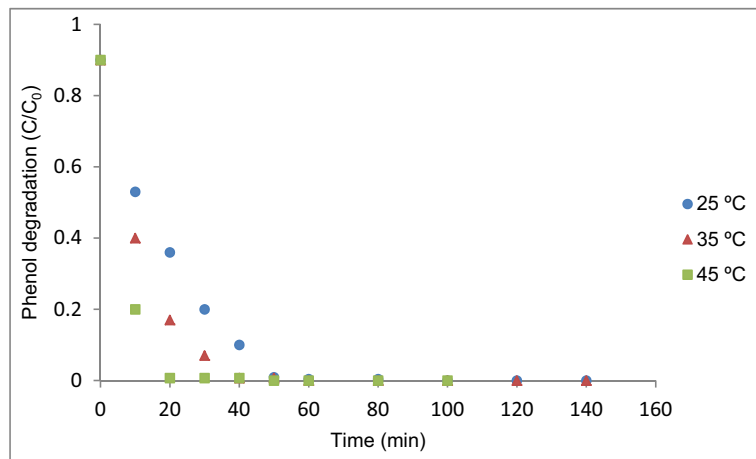
highest Ru-based catalyst dosage, mainly because increasing catalyst dosage could increase the active sites.

Figure 7 indicates that degradation of phenol depends on the Oxone amount. It was reasonable that higher Oxone concentration led to more degradation of phenol, because Oxone was the origin of driving force for the forming of SO$_4^{\cdot-}$. At 0.2 g Oxone, 88 % removal of phenol could be achieved in about 100 min. When concentration of oxidant component is increased to 1 g, phenol could be fully removed within 60 min. Degradation efficiency would decrease, at extra Oxone loading. It has been reported that self-quenching phenomenon of hydroxyl and sulfate ions by PMS are possible as shown below (P. Shukla et al. 2010a).

$$HSO_5^- + OH^{\cdot} \rightarrow SO_5^{\cdot-} + H2O \qquad (7)$$

$$HSO_5^- + SO_4^{\cdot-} \rightarrow SO_5^{\cdot-} + H^+ \qquad (8)$$
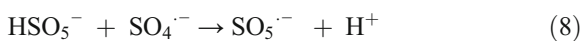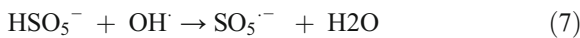
The reduction potential of SO$_5^{\cdot-}$/HSO$_5^-$ is 0.95 V at pH 7. Meanwhile, SO$_4^{\cdot-}$/SO$_4^{2-}$ has an oxidation potential of [2.5–3.1 V] (Shukla et al. 2011a), which makes it possible that extra amounts of HSO$_5^-$ from Oxone would consume the active SO$_4^{\cdot-}$, resulting in a lower degradation rate.

The reaction temperature effect on phenol degradation is shown in Fig. 8. As can be seen, the rate of reaction would increase considerably with increase in temperature owing to accelerating the formation of SO$_4^{\cdot-}$. Complete phenol degradation at temperature of 25 °C would be achieved in 60 min. When the temperature is raised to 35 °C, 100 % degradation efficiency of phenol would be achieved in about 40 min. At 45 °C, complete removal could be achieved in about 20 min. Taking into account the practical application of the system, the optimal condition for the following experiments was ambient temperature.

Fig. 9 Regeneration studies of the used catalyst
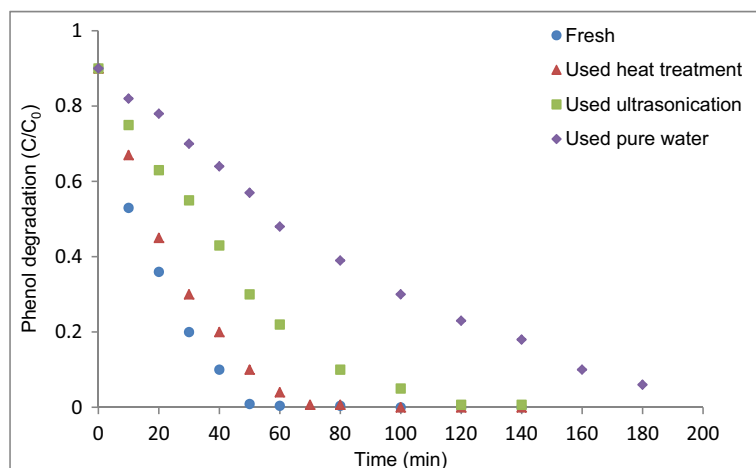
Based on the results, it can be concluded that supported ruthenium catalyst has accelerated the phenol degradation due to physicochemical properties of catalyst. The catalyst was used once before the regeneration process, and then, it was tested after its regeneration by annealing in air, using ultrasonication and washing with water. The deactivation of catalyst occurs probably due to adsorption of intermediates and a fraction of loose ruthenium leaching from the support. One hundred percent phenol removal was achieved after 70 min for the catalyst regenerated by annealing in air. This shows that the catalytic activity of the catalyst was recovered thoroughly by heating treatment, and surface-attached intermediates were removed, whereas regeneration of the used catalyst by applying ultrasonic and washing with water partially eliminated the intermediates presented on the surface of the catalysts (Fig. 9).

4 Conclusions

This study provided a feasible approach for applying the mesoporous alumina as appropriate support for synthesizing of based catalyst. Heterogeneous oxidative degradation of phenol using RuO_2/Al_2O_3-Oxone is effective methods for waste water treatment. Investigations indicated that RuO_2/Al_2O_3 is a good catalyst for generating sulfate radicals in the presence of Oxone to degrade phenol under atmospheric pressure and close to ambient temperature. Performance of phenol oxidation was dramatically influenced by operating parameters, such as catalyst dosage, oxidant and phenol concentration, and reaction temperature. Our findings demonstrate that in this catalyst, Oxone effectively activated, and 100 % phenol degradation occurs in 60 min. Regeneration by heat treatment could fully recover the catalyst activity.

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