Removal of Phenol Using Sulphate Radicals Activated by Natural Zeolite Supported Cobalt Catalysts

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Abstract

Two Co oxide catalysts supported on natural zeolites from Indonesia (INZ) and Australia (ANZ) were prepared and used to activate peroxymonosulphate for degradation of aqueous phenol. The two catalysts were characterized by several techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), and N_2 adsorption. It was found that Co/INZ and Co/ANZ are effective in activation of peroxymonosulphate to produce sulphate radicals for phenol degradation. Co/INZ and Co/ANZ could remove phenol up to 100% and 70%, respectively, at the conditions of 25 ppm phenol (500 mL), 0.2 g catalyst, 1 g oxone, and 25 ºC. Several parameters such as amount of catalyst loading, phenol concentration, oxidant concentration and temperature were found to be the key factors influencing phenol degradation. A pseudo first order would fit to phenol degradation kinetics and the activation energies on Co/INZ and Co/ANZ were obtained as 52.4 and 61.3 kJ/mol, respectively.

Key words: Heterogeneous oxidation; sulphate radical; phenol degradation; natural zeolite; Co oxide

1. Introduction

Phenolic compounds are important organic pollutants in wastewater, which can be produced in chemical, petrochemical, and pharmaceutical industries (Ahmaruzzaman, 2008, Busca, et al., 2008). This type of organic contaminants can not be easily removed in primary and secondary treatment processes. Therefore, it is essential to adopt a tertiary treatment such as thermal oxidation, chemical oxidation, wet air oxidation, catalytic oxidation etc, which are generally known as advanced oxidation processes (AOPs) (Parmeggiani and Cardona, 2012, Wang and Xu, 2012, Shukla, et al., 2010). In principle, the AOPs will produce harmless compounds to the environment such as CO_2 and H_2O. Among the AOPs, heterogeneous catalytic oxidation usually has some advantages such as operating at room temperature with normal pressure and low energy. Furthermore, heterogeneous catalysts can be synthesized using cheap materials as supports such as activated carbon, silica, alumina and zeolites (Saputra, et al., 2012). Among the materials, zeolites are important heterogeneous catalysts used in industry. Their key properties are size and shape selectivity, together with the potential for strong acidity. Zeolites also have ion exchangeable sites and highly hydrothermal stability, making them widely used for many applications in separation, ion exchange and adsorption. Natural zeolites are much cheaper than synthetic zeolites due to their wide availability in the world (Wang and Peng, 2010). However, few investigations have been reported in use of natural zeolites for AOPs (Valdes, et al., 2009).

Currently, most of AOPs are based on the generation of very reactive species, such as hydroxyl radicals (OH•), which will oxidize many pollutants quickly and non selectively (Wang and Xu, 2012, Dhakshinamoorthy, et al., 2012, Wang, 2008). Recently, sulphate radicals have also been proposed as alternative active oxidants due to their higher oxidation potential (Zhou, et al., 2011, Ling, et al., 2010). For sulphate radical production, peroxymonosulphate (PMS, HSO_5^-) reaction with Co ions has been found to be an effective route (Anipsitakis and Dionysiou, 2003, Anipsitakis and Dionysiou, 2004).

However, the use of Co metal ion as a catalyst to activate PMS for generation of sulphate radicals raises an issue of toxicity of the cobalt ions in water, because Co is one of heavy metals which can cause diseases to animals and human beings. Thus, employing Co^{2+}/PMS for oxidation of aqueous pollutants and minimizing the discharge of cobalt in wastewater require development of an efficient heterogeneous catalytic system by incorporating cobalt ions in a substrate. In addition, it is easy to recover the used catalysts after simple separation process. In the past years, several types of heterogeneous cobalt catalyst including cobalt oxides (Anipsitakis, et al., 2005, Chen, et al., 2008), cobalt composite (Yang, et al., 2009) and supported cobalt catalysts have been investigated (Yang, et al., 2008, Hu, et al., 2011, Shukla, et al., 2010, Shukla, et al., 2010, Shukla, et al., 2011, Shukla, et al., 2011, Hardjono, et al., 2011).

In the previous investigations, synthetic materials were employed and they are usually expensive. Moreover, some of the supported catalysts did not show good activity. Natural zeolites are cheaper porous aluminosilicate materials and have been used for adsorbents and catalyst supports. However, no work has been reported for natural zeolite supported Co catalysts in PMS activation water treatment. In this research, we investigate cobalt based catalysts supported on Indonesian natural zeolite (INZ) and Australian natural zeolite (ANZ) for heterogeneous generation of sulphate radicals for chemical mineralization of phenol in the solution. Several key parameters in the kinetic study such as phenol concentration, catalyst loading, oxone concentration and temperature were investigated.

2. Materials and Methods

2.1 Synthesis of natural zeolite supported cobalt catalysts

Cobalt/Indonesian-natural-zeolite (Co/INZ) and cobalt/Australian-natural-zeolite (Co/ANZ) were synthesized using an impregnation method. INZ and ANZ samples were crushed in particle size of 60-100 µm. Cobalt nitrate ($Co(NO_3)_2 \bullet 6H_2O$, Sigma-Aldrich) was dissolved into 200 mL ultrapure water. Then, INZ or ANZ was added into the solution and kept stirring for 24 h. The solid was dried in an oven at 120 ºC for 6 h. Calcination of the catalysts was conducted in a furnace at 550 ºC for 6 h. For the two catalysts, Co loading was kept at 5 wt%.

2.2 Characterization of catalysts

The synthesized catalysts were characterized by XRD, SEM combined with EDS, and N_2 adsorption. Crystalline structure of the materials was analyzed by a X-ray diffractometer (Bruker D8 Advance equipped with a Lynx eye detector, Bruker-AXS, Karlsruhe, Germany) operated at 40 kV and 30 mA. SEM (Philips XL30) with secondary and backscatter electron detectors at 15 kV and 7 mm distance was used to obtain a visual image of the samples to show the texture and morphology of the catalysts with magnification up to 8000 times. The catalysts were also characterized by EDS (Energy Dispersive X-ray spectroscopy) to identify the structural features and the mineralogy. Furthermore, nitrogen adsorption (Micromeritics Gemini 2360) was used to obtain the BET surface area (S_{BET}). Prior to the analysis, the catalyst samples were degassed under vacuum at 200 ºC for 12 h.

2.3 Kinetic study of phenol oxidation

Catalytic oxidation of phenol was conducted in 500 mL phenol solutions with concentrations of 25 - 100 ppm. A reactor attached to a stand was dipped into a water bath with a temperature control. The solution was stirred constantly at 400 rpm to maintain a homogeneous solution. A fixed amount of

oxidant of peroxymonosulphate (using oxone, DuPont's triple salt $2KHSO_5 \bullet KHSO_4 \bullet K_2SO_4$, Aldrich) was added to the mixture until completely dissolved. Then, a fixed amount of catalysts (Co/INZ or Co/ANZ) was added into the reactor for running of 3-5 h. At the fixed time interval, 0.5 mL of solution sample was withdrawn and filtered using a HPLC standard filter of 0.45 μm and mixed with 0.5 mL methanol as a quenching reagent to stop the reaction. Phenol was then analyzed on a HPLC with a UV detector at wavelength of 270 nm. The column is C18 with mobile phase of 70% acetonitrile and 30% ultrapure water.

3 Results and Discussion

3.1 Characterization of natural zeolite supported cobalt catalysts

XRD patterns of Co/INZ and Co/ANZ are presented in Fig.1. Co_3O_4 peaks were identified on both catalysts, however, the peaks are weaker and broad on Co/INZ. This suggested that dispersion of Co_3O_4 crystallites on INZ was higher and thus more active sites (Co_3O_4) were produced on Co/INZ, which could enhance reaction rate. N_2 adsorption showed that the BET surface areas of INZ and ANZ are 30.5 and 16.0 m^2/g, respectively, while the BET surface areas of Co/INZ and Co/ANZ are 17.9 and 8.1 m^2/g, respectively. In general, high surface area of a support will result in high dispersion of active metal on the support.

[Insert Fig.1]

SEM images and EDS spectra of Co/INZ and Co/ANZ catalysts are shown in Fig. 2 and Fig. 3. Both secondary electron (SE) and backscattered (BSE) detectors were adopted to observe the dispersion of active cobalt on the catalyst support. From Fig. 2A and 2B, it can be seen that the BSE detector produces the brighter image than the SE detector at the same observed area. This brighter area refers to the presence of cobalt specks on Co/INZ particles. It also implies that cobalt was well dispersed and coated on the natural zeolite support. The presence of cobalt in the catalyst was also confirmed by EDS spectra (Fig. 2C).

[Insert Figure 2]

A similar observation was also obtained on Co/ANZ catalyst (Fig. 3). However, the particle size of Co/ANZ seems to be larger than Co/INZ. BSE image also shows a good dispersion of cobalt on Co/ANZ surface confirmed by EDS spectra. Thus, compared with Co/INZ, Co/ANZ presents larger particle size but low Co dispersion.

[Insert Figure 3]

3.2 Phenol oxidation

Adsorption and oxidation of phenol on Co/INZ and Co/ANZ are presented in Fig. 4. In the presence of only oxone in phenol solution, no phenol degradation occurred, indicating that oxone itself could not produce sulphate radicals to induce phenol oxidation. Both Co/INZ and Co/ANZ presented low adsorption of phenol at less than 10% in 5 h. However, Co/INZ presented a slight higher phenol adsorption than Co/ANZ, which can be ascribed to higher surface area of Co/INZ.

[Insert Figure 4]

In oxidation tests, Co/INZ with the presence of PMS could degrade phenol up to 100% in 5 h. Meanwhile, Co/ANZ could reach around 70% phenol removal. Significant degradation of phenol in the systems confirms that cobalt in both catalysts could activate PMS to generate sulphate radicals ($SO_4^{-\bullet}$ and $SO_5^{-\bullet}$) for phenol decomposition in solution. XRD analyses showed that Co_3O_4 is major Co species in both catalysts, which will play the role for oxone activation. The reaction mechanism can be listed as below.

$$NZ–Co^{3+} + HSO_5^- \rightarrow NZ–Co^{2+} + SO_5^{-\bullet} + H^+ \qquad (1)$$

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

Adsorption tests showed that Co/INZ presented higher phenol adsorption than Co/ANZ. XRD also indicated that Co dispersion on Co/INZ is higher than that on Co/ANZ. SEM images show smaller particle size of the catalyst, Co/INZ. For heterogeneous oxidation, high surface adsorption of phenol and more active Co oxide on surface will promote catalytic activity. Thus, Co/INZ exhibits higher activity than Co/ANZ, achieving 100% phenol removal in less time. Some investigations using different supported Co catalysts have been reported. It was reported that Co/ZSM5 could achieve complete degradation of phenol in 6 h (Shukla, et al., 2010) and that Co/SiO_2 could make 100% phenol degradation at 350 min (Shukla, et al., 2011). Therefore, Co/INZ is better than Co/ZSM5 and Co/SiO_2.

Several variables influencing phenol degradations were also investigated. The effect of initial phenol concentration at 25, 50, 75 and 100 mg/L on phenol degradation is shown in Fig. 5. Phenol degradation efficiency decreased with increasing phenol concentration. The 100% phenol removal could be achieved at phenol concentration of 25 mg/L in 5 h by using Co/INZ catalyst. While in the same duration at phenol concentrations of 50, 75 and 100 mg/L, removal efficiency obtained are 50, 40 and 30%, respectively. For phenol degradation in Co/INZ-oxone, phenol degradation rate is dependent on the concentration of sulphate radicals. Due to the same concentrations of Co/INZ and

PMS, sulphate radical concentration produced in solution will be the same. Thus, high amount of phenol in solution will require more time to achieve the same removal rate, thus lowering phenol degradation efficiency.

[Insert Figure 5]

Phenol removal efficiency is also affected by catalyst loading in the system as shown in Fig. 6. A complete removal of phenol could be reached within 5 h at 0.4 g/L Co/INZ loading. While 70% and 40% removals could be reached at Co/INZ loading of 0.2 and 0.1 g/L, respectively. For phenol degradation, increased catalyst loading would enhance phenol adsorption and Co oxide to activate PMS, resulting in high phenol degradation.

[Insert Figure 6]

The effect of oxone concentration on the removal efficiency of phenol is presented in Fig. 7. For both catalysts, higher oxone concentration resulted in higher phenol removal. At reaction time of 3 h, the highest removal efficiency of phenol was obtained at 2 g/L oxone and the lowest was at 0.5 g/L oxone on Co/ANZ. However, phenol degradation would reach a similar level after oxone loading higher than 1 g/L on Co/INZ, suggesting the optimal loading at 1 g/L.

[Insert Figure 7]

In addition, temperature is also a key factor influencing catalyst activity and phenol degradation. Fig.8 shows the effect of temperature on phenol degradation. Higher phenol removal was obtained at increased temperature. For instance, at reaction time of 3 h, removal efficiencies of phenol on Co/ANZ at 25, 35, and 45 ^{o}C were 45, 75 and 100%, respectively (Fig. 8B). A similar trend is also obtained on Co/INZ catalyst and the removal efficiencies increased from 80% at 25 ^{o}C to 100% at 35 and 45 ^{o}C.

[Insert Figure 8]

For variation of phenol degradation with time, a first order model as shown in equation below was used to fit kinetics.

$$C = C_0 e^{(-k \bullet t)} \quad (3)$$

Where k is the first order rate constant of phenol removal, C is the concentration of phenol at various time (t), C_o is the initial concentration of phenol.

Fig.8 also shows the curves of phenol degradation kinetics from the first order model and it is seen that phenol degradation on Co/INZ and Co/ANZ catalysts could be well fitted by the model. The rate constant and regression coefficients are presented in Table 1. Several heterogeneous Co catalysts have been tested in PMS activation for phenol degradation. It was found that phenol degradation on Co/SiO_2 (Shukla, et al., 2011) and Co/ZSM5 (Shukla, et al., 2010) presented zero order kinetics while Co/AC showed the first order kinetics (Shukla, et al., 2010). Chen et al. (Chen, et al., 2007) also found the pseudo first-order for decolourization of acid orange 7 (AO7) in aqueous Co^{2+}/oxone system.

[Insert Table 1]

Fig.9 shows the relationship between rate constants *(k)* and temperatures by the Arrhenius correlation. It can be seen that a good relationship for both catalysts was achieved and activation energies for phenol degradation on Co/ANZ and Co/INZ were obtained at 52.4 and 61.3 kJ/mol, respectively.

[Insert Figure 9]

4 Conclusions

Co/INZ and Co/ANZ are effective catalysts for generating sulphate radicals in the presence of PMS to degrade phenol. Co/INZ has better activity in removing phenol than Co/ANZ. Phenol removal is a combination of oxidation and adsorption processes. The concentration of phenol, catalyst loading, concentration of oxone, and temperature are key parameters affecting the reaction rate in phenol degradation. Kinetic studies show that phenol oxidation on the Co/INZ and Co/ANZ follows the first order reaction with the activation energies of 52.4 and 61.3 kJ/mol, respectively.

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List of Tables

Table 1 Rate constants at different temperatures for Co/INZ and CCo/ANZ.

Catalyst	Temperature (ºC)	Rate constant (min^{-1})	R^2
Co/INZ	25	7.08 x10^{-3}	0.972
	35	0.0116	0.952
	45	0.0269	0.989
Co/ANZ	25	3.19 x10^{-3}	0.991
	35	6.42 x10^{-3}	0.963
	45	0.0151	0.985

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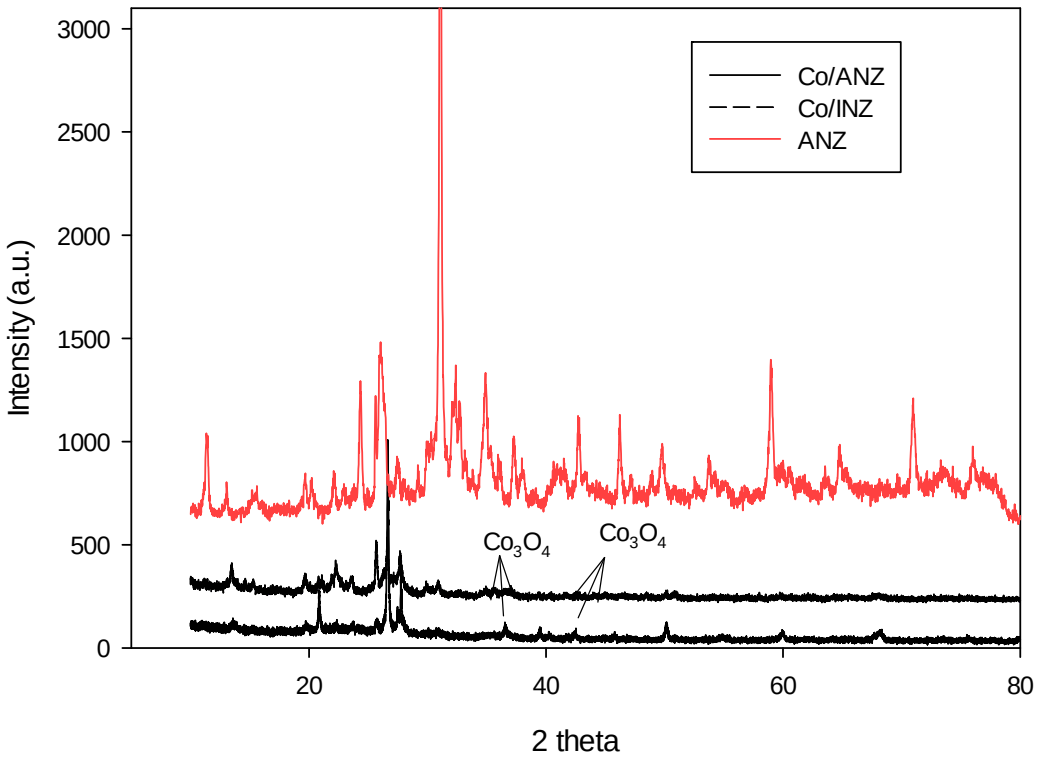


Fig.1 XRD patterns of Co/ANZ and Co/INZ.

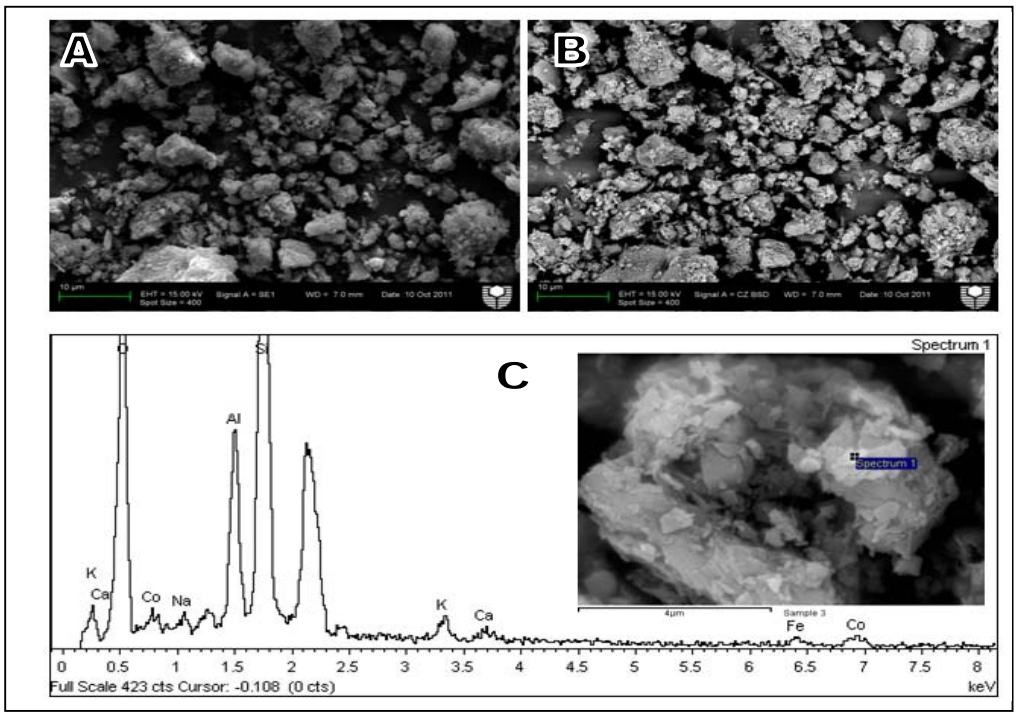


Figure 2. SEM images and EDS spectra of Co/INZ, (A) SE Detector, (B) BSE Detector, (C) EDS spectra with inset of spectrum image source

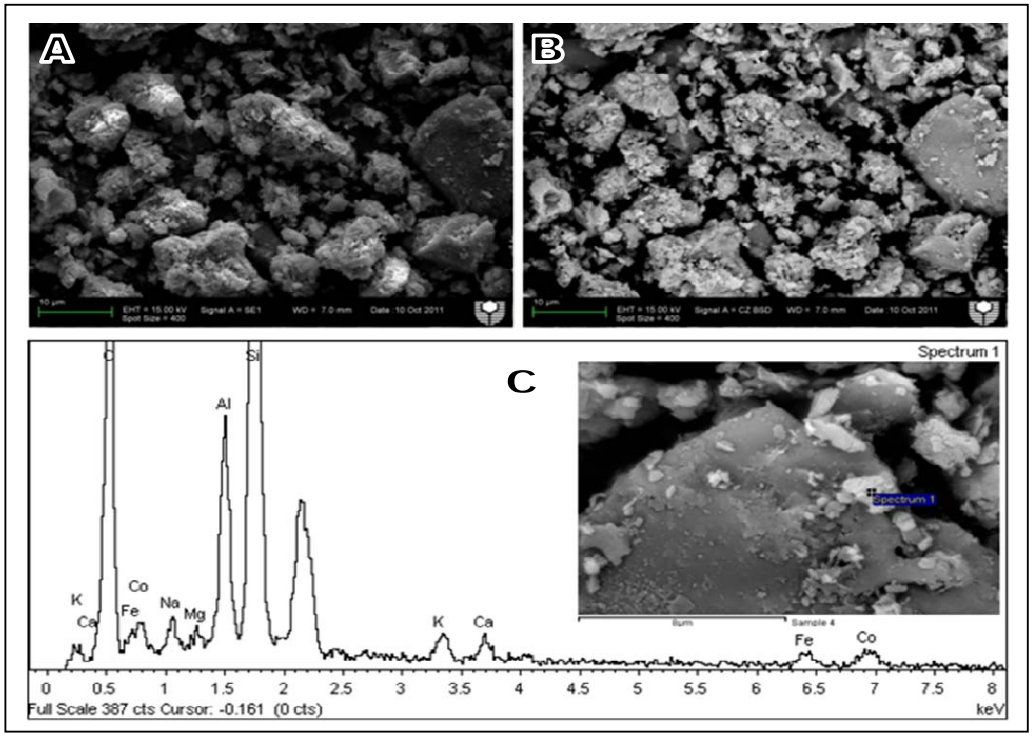


Figure 3. SEM images and EDS spectra of Co/ANZ, (A) SE Detector, (B) BSE Detector, (C) EDS spectra with inset of spectrum image source

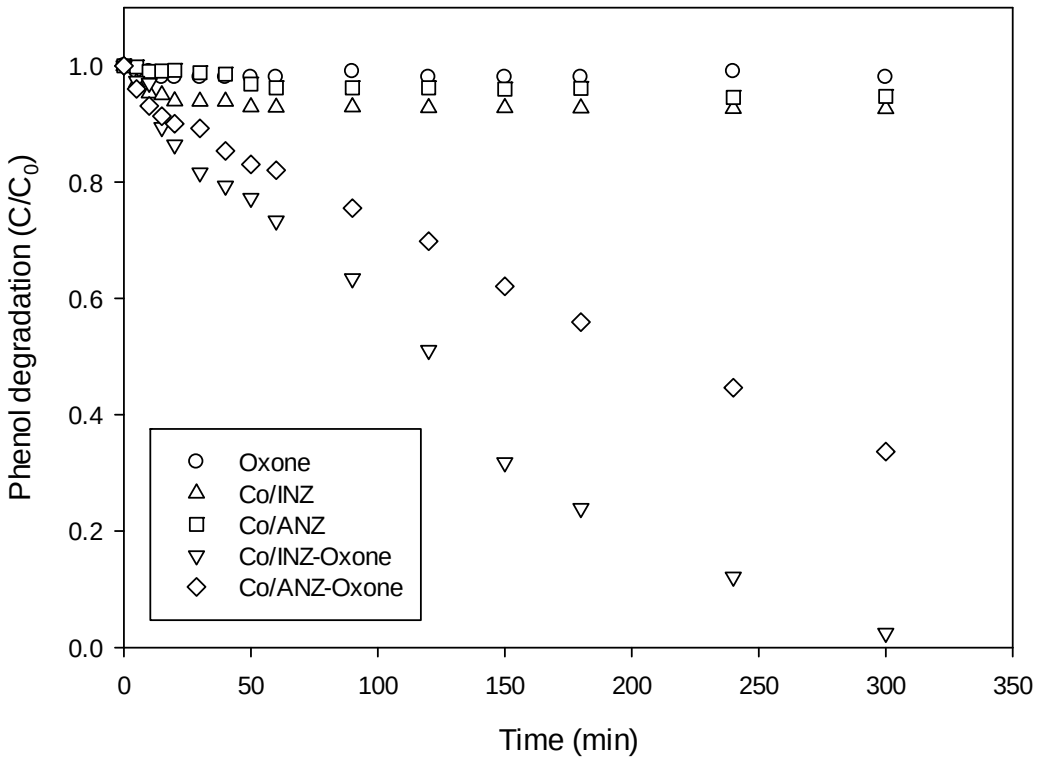


Figure 4. Phenol reduction with time in adsorption and catalytic oxidation. Reaction condition: 0.4 g/L catalyst, 2 g/L oxone, 25 ppm phenol, 25°C and stirring speed of 400 rpm.

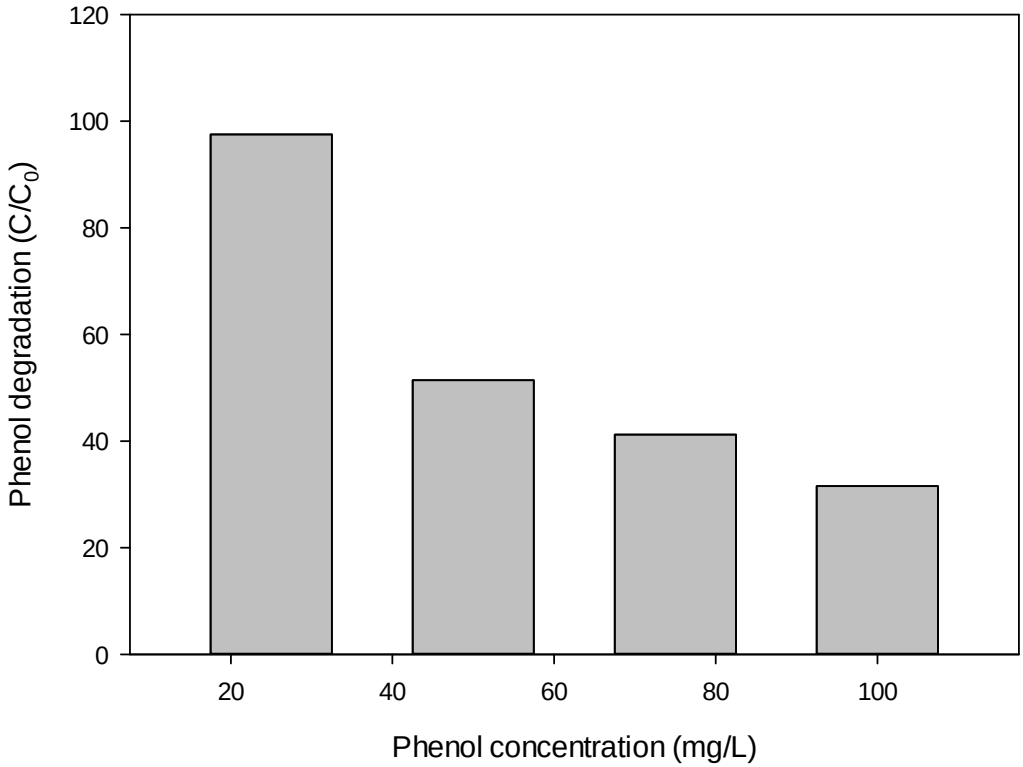


Figure 5. Effect of phenol concentration on phenol degradation using Co/INZ catalyst. Reaction condition: 0.4 g/L catalyst, 2 g/L oxone, 25°C and stirring speed of 400 rpm.

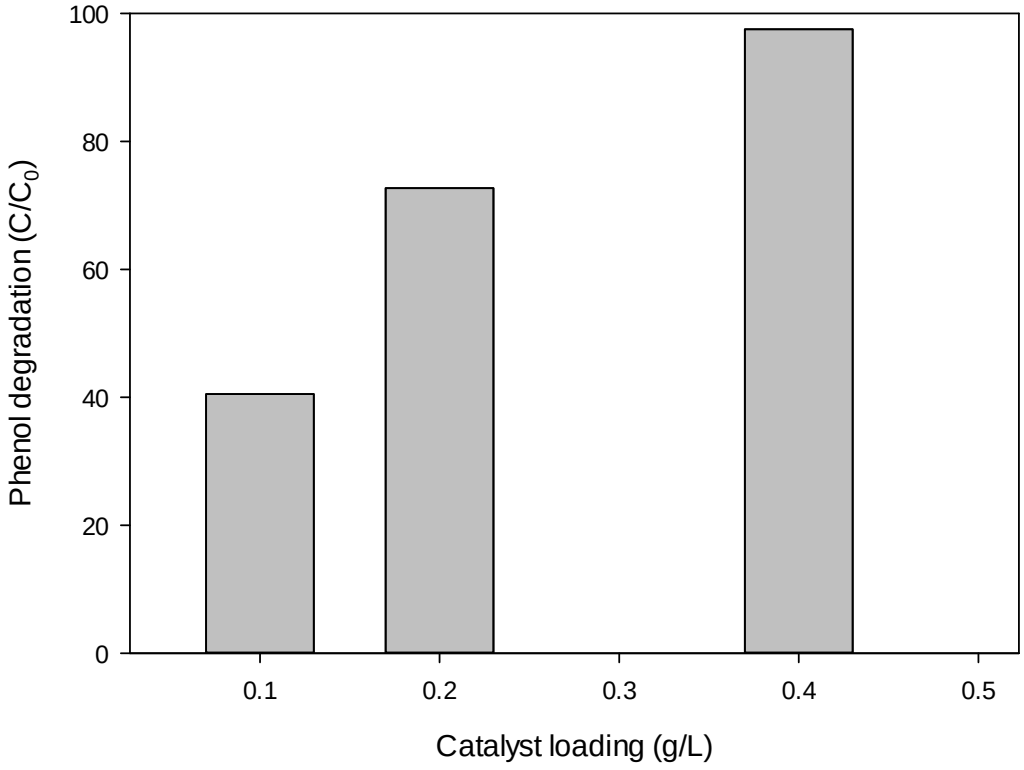


Figure 6. Effect of catalyst loading on phenol degradation using Co/INZ catalyst. Reaction condition: 2 g/L oxone, 25 ppm phenol, 25°C and stirring speed of 400 rpm.

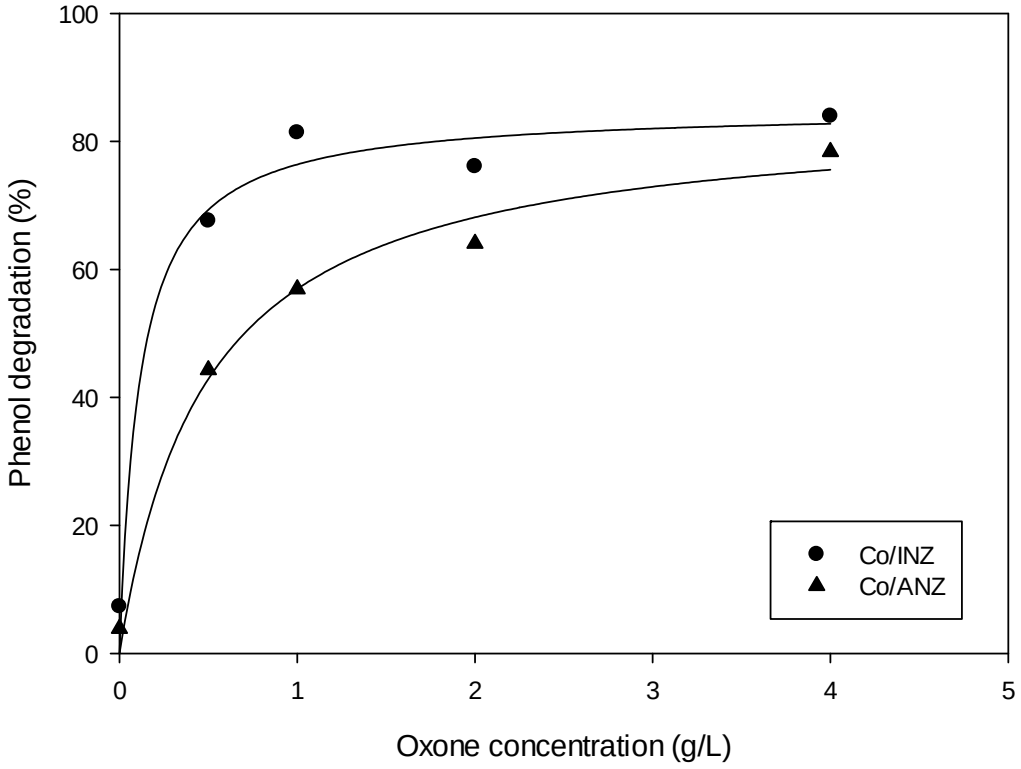
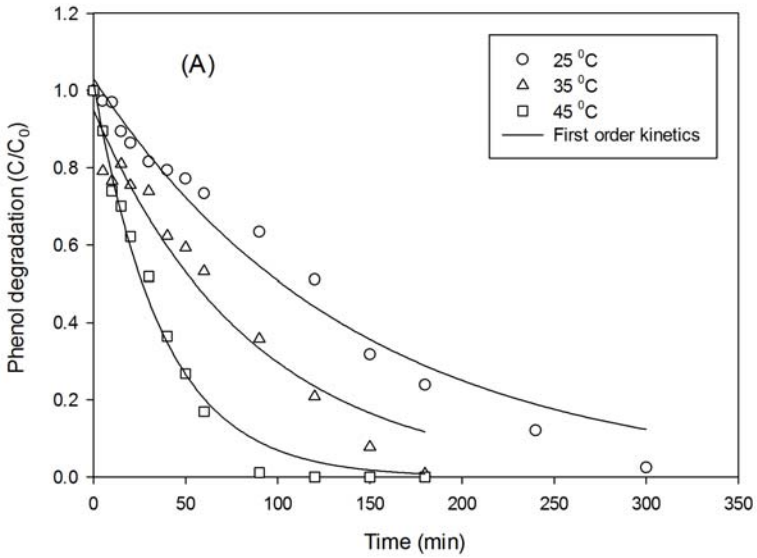


Figure 7. Effect of oxone concentration in phenol reduction using Co/INZ catalyst. Reaction condition : 0.4 g/L catalyst, 25 ppm phenol solution, 25°C and stirring speed of 400 rpm.



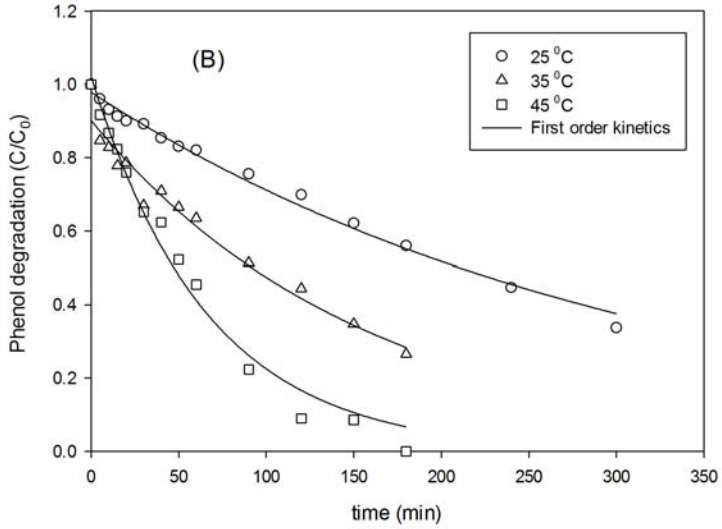


Figure 8. Effect of temperature in phenol reduction, (A) Co/INZ catalyst, (B) Co/ANZ catalyst. Reaction condition : 0.4 g/L catalyst, 2 g/L oxone, 25 ppm phenol, and stirring speed of 400 rpm.

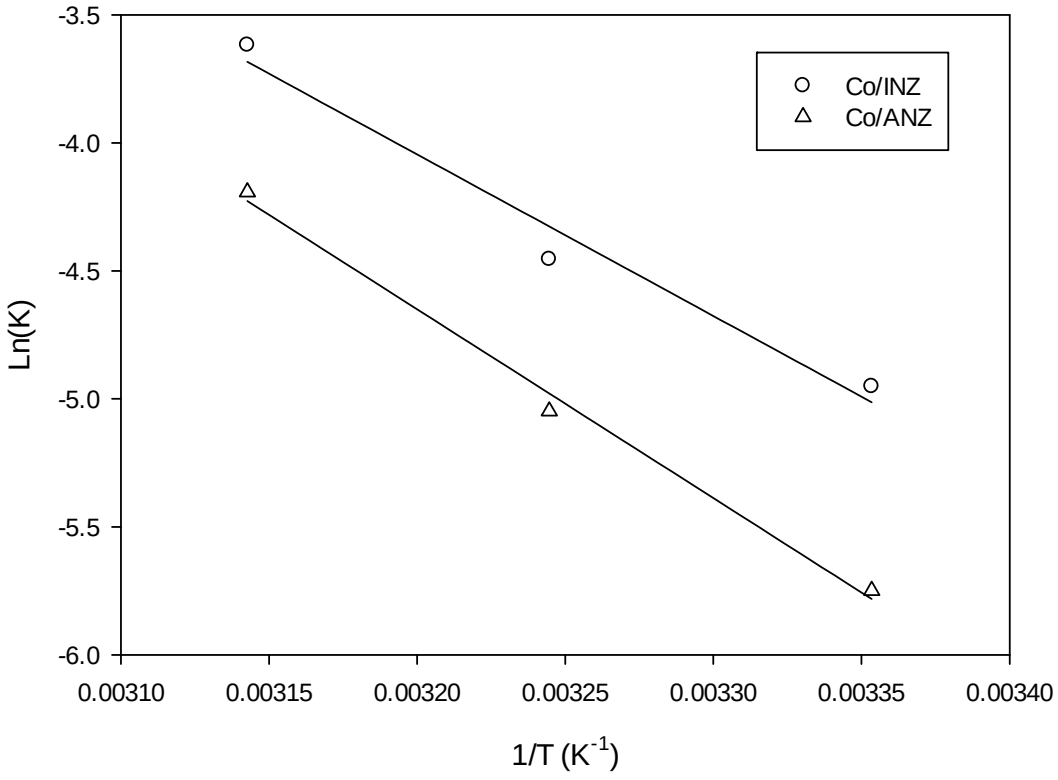


Figure 9. Arrhenius plots of phenol degradation on Co/ANZ and Co/INZ.