Phenol degradation on heterogeneous catalytic oxidation by using cobalt-natural zeolite catalyst

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Abstract. Two types of catalysts based on Indonesia Natural Zeolite (INZ) and Australia Natural Zeolite (ANZ) were prepared by impregnation of 5 % of active metal cobalt. The synthesized catalysts were calcined in air at 550^0C for 6 hours. The catalysts were then used to degrade phenol concentration in heterogeneous catalytic oxidation with the presence of oxone as peroxymonosulphate source. The catalysts were also characterized by several techniques such as SEM, EDS and N_2 adsorption. It was found that Co-INZ and Co-ANZ are effective catalyst in activation of peroxymonosulphate to produce sulphate radicals to degrade phenol concentration. In reaction test of 5 hours, with condition of 25 ppm phenol, 0.2 g catalyst loading, 1 gram oxone, 25^0C and stirring speed of 400 rpm, Co-INZ and Co-ANZ could reduce phenol up to 100% and 70% respectively. Further, several parameters such as amount of catalyst loading, phenol concentration, oxidant concentration and temperature are found as key factors in phenol degradation. Moreover, based on the trend of phenol degradation following by kinetic study, it was proved that the pseudo first order kinetics would fit to phenol oxidation with the rate constants of 0.0106 and for 0.0033 Co-INZ and Co-ANZ respevtively.

Keywords: Impregnation; heterogeneous catalytic oxidation; sulphate radical; phenol degradation

Introduction

One of common organic pollutant in wastewater, which generally produced by Industry such as chemical, petrochemical, and pharmaceutical, is phenol (Fortuny et al.. 1998). This organic contaminant will not be easily removed by using primary and secondary treatment processes. Therefore, it is essential to be adopted the tertiary treatment such as thermal oxidation, chemical oxidation, wet air oxidation, catalytic oxidation etc, which are generally known as advanced oxidation processes (AOPs) (Shukla et al.. 2010). In principle, the AOPs method will produce the harmless compound to environment such as CO_2 and H_2O (Chiron et al.. 2000). Among the methods, heterogeneous catalytic oxidation usually has some advantages such as can be operated at room temperature with normal pressure and high energy efficiency. Furthermore, heterogeneous catalysts can be synthesized by using cheap materials as supports such as activated carbon, silica, alumina and zeolite (Camporro et al.. 1994). Among the materials, zeolites are one of the most important heterogeneous acid 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 such as separation, catalysis, ion exchange and adsorption (Erdem et al., 2004 & Song et al., 2004). Therefore, zeolite will be worthy to be tested as catalyst support in AOPs.

Currently, most of AOPs are based on the generation of very reactive species, such as hydroxyl radicals (OH•) which oxidize many pollutants quickly and non selectively (Pignatello et al.. 2006, Wang, 2008 and Pera-Titus et al., 2004). Beside hydroxyl radical, sulphate radical has also been proposed as an alternative active oxidant due to its higher oxidation potential. For sulphate radical production, peroxymonosulphate (PMS, HSO_5^-) reaction with Co ions has been found to be an effective route (Anipsitakis & Dionysiou, 2003).

However, the use of cobalt metal as a catalyst to activate PMS and generate sulphate radical raises an issue of toxicity of the cobalt ions in water, because Co is one of heavy metals which causing 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 reaction by

incorporating cobalt ions in a substrate. In addition, it is easy to recover the used catalysts simply by separation of the heterogeneous catalysts. In the past years, several types of heterogeneous cobalt catalysts including cobalt oxides (Anipsitakis et al.. 2005 & Chen et al.. 2008), cobalt composite (Yang et al.. 2009) and supported cobalt catalysts have been investigated (Zhang et al.. 2010, Shukla et al.. 2011 & Shukla et al.. 2010).

This research is investigating the use of cobalt based catalysts supported on Indonesia natural zeolite (INZ and Australia Natural Zeolite (ANZ) by impregnation in heterogeneous catalytic oxidation process with the presence of peroxymonosulphte (using oxone) as an oxidant to generate sulphate radical for chemical mineralizing of phenol in the solution. Several key parameters in the kinetic study such as phenol concentration, catalyst loading, oxone concentration and temperature were also investigated.

Materials and Methods
Synthesis of Cobalt impregnated natural zeolite
Cobalt-Indonesia Natural Zeolite (Co/INZ) and Cobalt-Australia Natural Zeolite (Co/ANZ) were synthesised using an impregnation method. INZ and ANZ were crushed in range of 60-100 micron meter of particle size. Then, 5% of cobalt from cobalt nitrate (Co(NO3)2•6H2O, Sigma-Aldrich), relative to zeolite amount was added into 200 ml ultrapure water until the cobalt compound was dissolved. Next, INZ or ANZ were added into the solution and kept stirring for 24 hours. The solid was then recovered and dried in an oven at 120^0C for 6 hours. Calcination of catalyst was conducted in a furnace at 550^0C for 6 hours. The catalyst was stored in a desiccator until used.

Characterisation of Catalyst
The synthesised catalysts were characterised by SEM combined with EDS and N_2 adsorption. SEM (Philips XL30) with secondary and backscatter electron detector 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 characterised by EDS (Energy Dispersive X-ray spectroscopy) to identify the structural features and the mineralogy of the catalysts. Further, nitrogen adsorption (Micromeritics Gemini 2360) was used to identify the pore size, pore volume and surface area (S_{BET}). Prior to the analysis, the catalyst samples were degassed under vacuum at 200^0C for 12 hours.

Kinetic study of phenol oxidation
Catalytic oxidation of phenol was conducted in 500 ml phenol solution with concentration of 25, 50, 75 and 100 ppm. A reactor attached to a stand was dipped into a water bath with temperature control. The solution was stirred constantly at 400 rpm to maintain homogeneous solution. Next, a fixed amount of oxidant of peroxymonosulphate (oxone, DuPont's triple salt $2KHSO_5.KHSO_4.K_2SO_4$, 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 starting the oxidation of phenol. The reaction was run for 3-5 hours and at the fixed interval time, 0.5 ml of sample was withdrawn from the solution and filtered using HPLC standard filter of 0.45 μm and mixed with 0.5 ml methanol as a quenching reagent to stop the reaction. Phenol was 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.

Results and Discussion
Characterisation of cobalt impregnated activated natural zeolite
The Co/INZ and Co/ANZ catalyst were characterized by using SEM and EDS where the result can be seen in Fig. 1 and Fig. 2. Both secondary electron (SE) and backscattered (BSE) detector were adopted to observe the dispersion of active metal on the catalyst support. By comparing between Fig. 1A and 1B, it can be seen that BSE detector produces the brighter image than SE detector at the same observed area. This brighter area refers to the presence of cobalt specks on Co/INZ particle as a catalyst support. It also implies that cobalt is well dispersed and coated on the natural zeolite. The presence of cobalt in the

catalyst was also confirmed by EDS spectra as seen in Fig. 1C. However, several ESD spectra in the same sample with different spectrum source show that the active metal of cobalt dispersion was not full covering on the zeolite surface. Some spectrums confirm that there is no cobalt on the support surface particularly on the big particle size of zeolite. Supposedly, the big particle of zeolite and the less of cobalt loading in the system are the main reason on this. Similar phenomenon is also occured on Co/ANZ catalyst as seen in Fig. 2. In the same magnification, the particle size of Co/INZ seems to be smaller than Co/ANZ.

The catalyst samples were also characterised by N_2 adsorption to identify pore size distribution and surface area (S_{BET}). As seen in Fig. 3, the Co/INZ has 17.948 m^2/g, 0.009041 cm^3/g and 20.1504 Å of surface area, pore volume and pore size, respectively. All of them are higher than that 8.1176 m^2/g, 0.003053 cm^3/g and 15.0457 Å for Co/ANZ. Both catalysts have the pore radius around 20 Å, which means they are microporous materials (Mintova, 2003). Detail of pore size distribution and N_2 isotherm analysis can be seen in Figure 3.
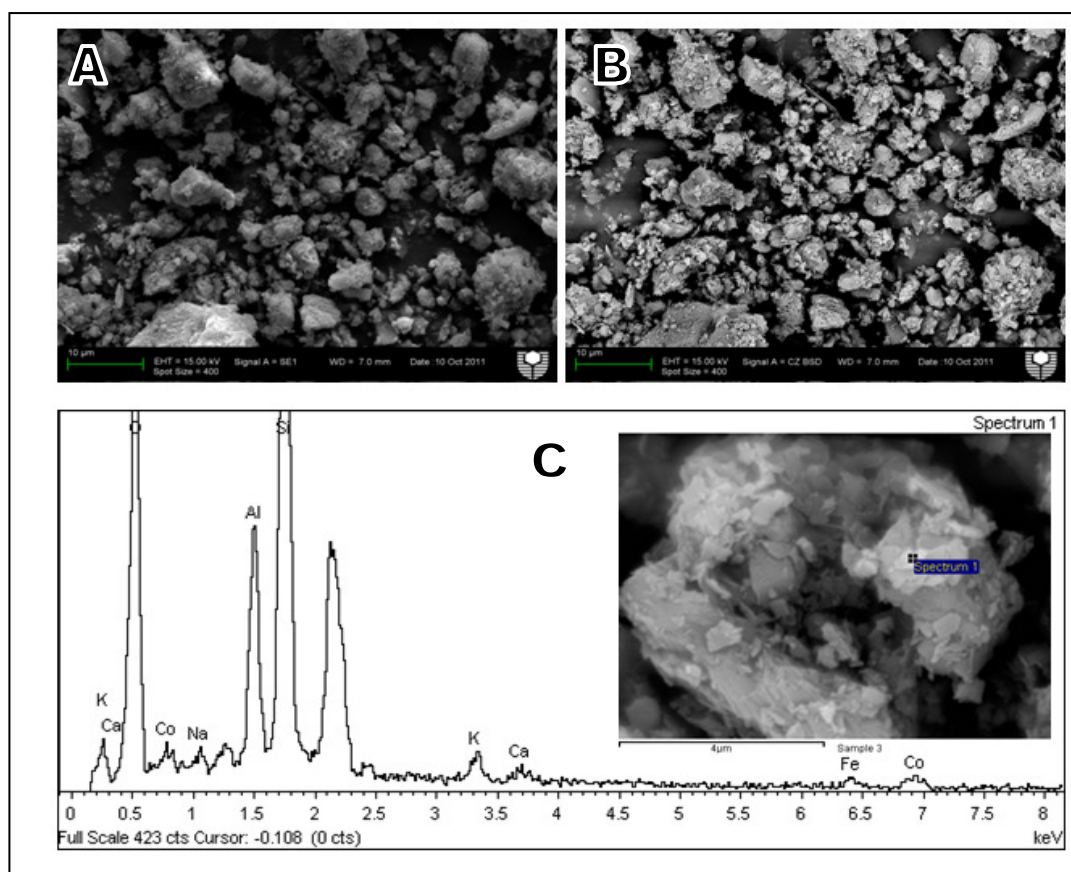

Figure 1. SEM Image and EDS Spectra of Co/INZ, (A) SE Detector, (B) BSE Detector, (C) EDS Spectra with insert of spectrum image source.
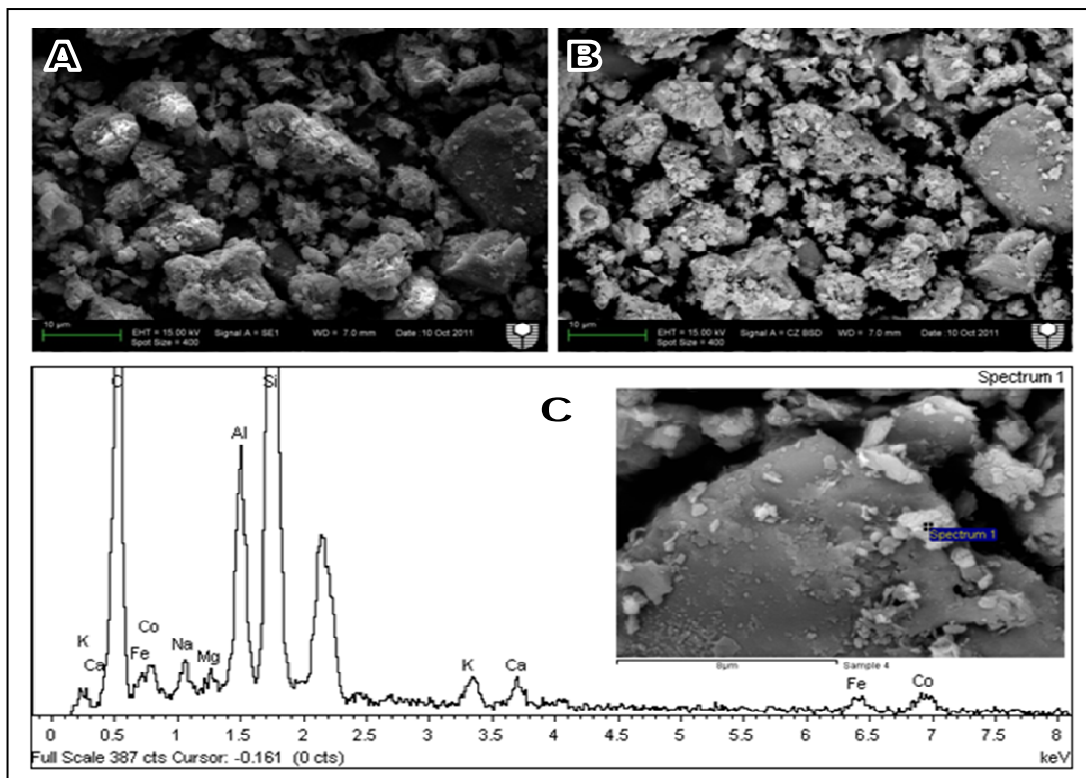
Figure 2. SEM Image and EDS Spectra of Co/ANZ, (A) SE Detector, (B) BSE Detector, (C) EDS Spectra with insert of spectrum image source
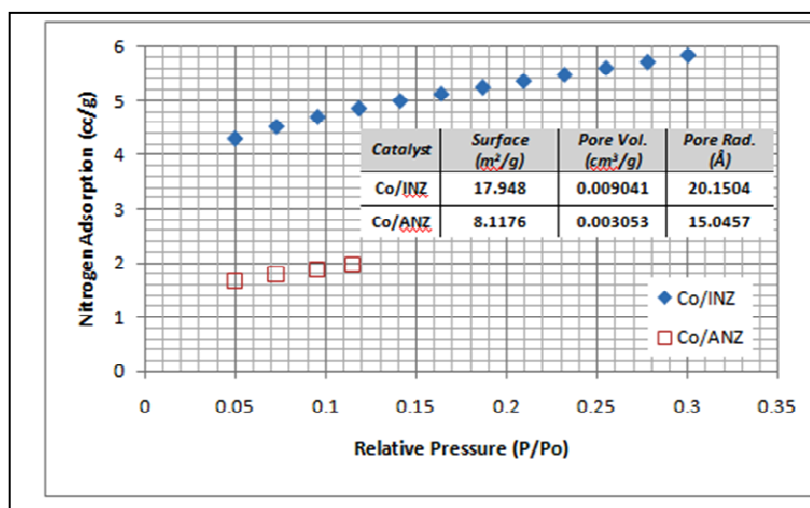

Figure 3. N_2 adsorption isotherm of Co/INZ and Co/ANZ

Preliminary study of phenol oxidation

Preliminary test of Co/INZ and Co/ANZ by adsorption and oxidation are presented in Fig. 4. The aqueous solution system conditions are 0.2 g catalyst loading, 1 g oxone in 500 ml phenol solution of 50 ppm, temperature of 25^0C and stirring speed of 400 rpm. It can be seen that both Co/INZ and Co/ANZ can adsorb organic compound of phenol despite at low concentration, less than 10% in 5 hours test. In adsorption process, Co/INZ and Co/ANZ exhibit similar efficiency, although Co/INZ slightly better than Co/ANZ. It seems the adsorption test result is well correlated with pore characteristic of zeolite where Co/INZ has

bigger pore and surface area than Co/ANZ (Fig. 3). It is well known that the bigger pore (volume/diameter) and surface area of the particle, the higher adsorption efficiency is.
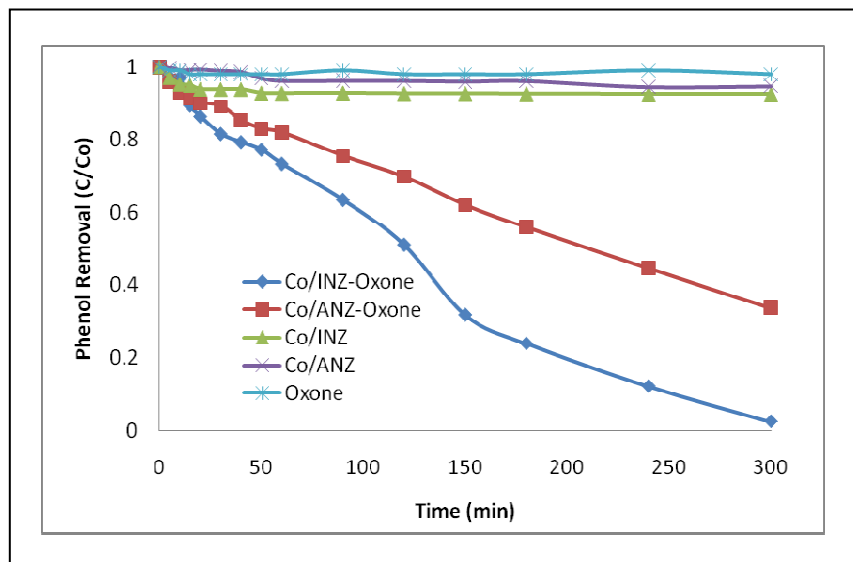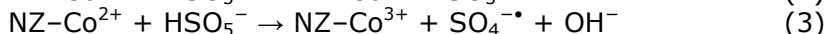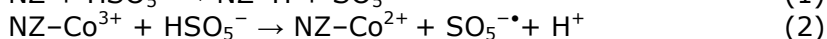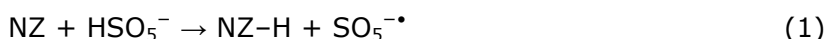

Figure 4. Phenol reduction with time in adsorption and catalytic oxidation. Reaction condition: 0.2g catalyst loading, 1 g oxone, 25 ppm phenol solution, $25^{o}C$ and stirring speed of 400 rpm.

It also can be seen in Fig.4 that Co/INZ and Co/ANZ do not be able to oxidize phenol in the solution without the presence of oxone as a source of pereoximonosulphate (PMS). This can be proved by a fact that phenol reduction in this system is minimal. Similar to this, oxone it self also could not induce a reaction in the system. Therefore, it is supposed that the oxidation of phenol is done by the presence of active metal cobalt together with PMS in the system.

In oxidation tests, Co/INZ with the presence of PMS could degrade phenol up to 100% in 5 hours reaction time. Further, in the same interval time, Co/ANZ could reach around 70% in removal efficiency of phenol. Hence, the Co/INZ gave batter result than Co/ANZ in removing phenol. Significant degradation of phenol in the system confirms that cobalt in both catalysts can activate PMS to generate sulphate radicals ($SO_5^{-\bullet}$) for removing phenol from solution (Anipsitakis et al.., 2005). The supposed reaction mechanism can be seen below.

$$NZ + HSO_5^- \rightarrow NZ-H + SO_5^{-\bullet} \hspace{2cm} (1)$$
$$NZ-Co^{3+} + HSO_5^- \rightarrow NZ-Co^{2+} + SO_5^{-\bullet} + H^+ \hspace{1cm} (2)$$
$$NZ-Co^{2+} + HSO_5^- \rightarrow NZ-Co^{3+} + SO_4^{-\bullet} + OH^- \hspace{1cm} (3)$$

Furthermore, this research also confirms that supporting noble metal on support material such as metal oxide, activated carbon, zeolite and other surface material will increase activity the catalysts as reported by many researchers (Matatov-Meytal and Sheintuch, 1998). However, Co/INZ and Co/ANZ still have lower removal efficiency of phenol than Co/Activated Carbon (Shukla et al., 2010).

Effects of reaction parameters on phenol removal

Phenol concentration of 25, 50, 75 and 100 ppm are the first parameters measured in this experimental work. As can be seen in Fig. 5A, removal efficiency of phenol decreases with increasing phenol concentration. The 100% phenol removal can only reach at phenol concentration of 25 ppm in 5 hours by using Co/INZ catalyst. While in same duration at

phenol concentration of 50, 75 and 100 ppm, removal efficiency obtained are 50, 40 and 30 %, respectively. The increase of phenol concentration, from 25 to 50 ppm, would decrease removal efficiency of 50%. The removal efficiency is also affected by amount of catalyst loading in the system. According to this research as shown by Fig. 5B, the complete removal of phenol can be reached within 5 hours with 0.2 g Co/INZ loading. While the 70% and 40% removal can be reached using 0.1 and 0.05 g Co/INZ. It means, by decreasing the catalyst amount of 2 times, the removal efficiency will decrease around 30%. The greater of catalyst amount used, the higher of phenol degradation efficiency is. Because by increase amount of catalyst loading, adsorption will increase and the availability of active site of metal to activate PMS also will increase. Similar trend would also be applied for Co/ANZ catalyst.
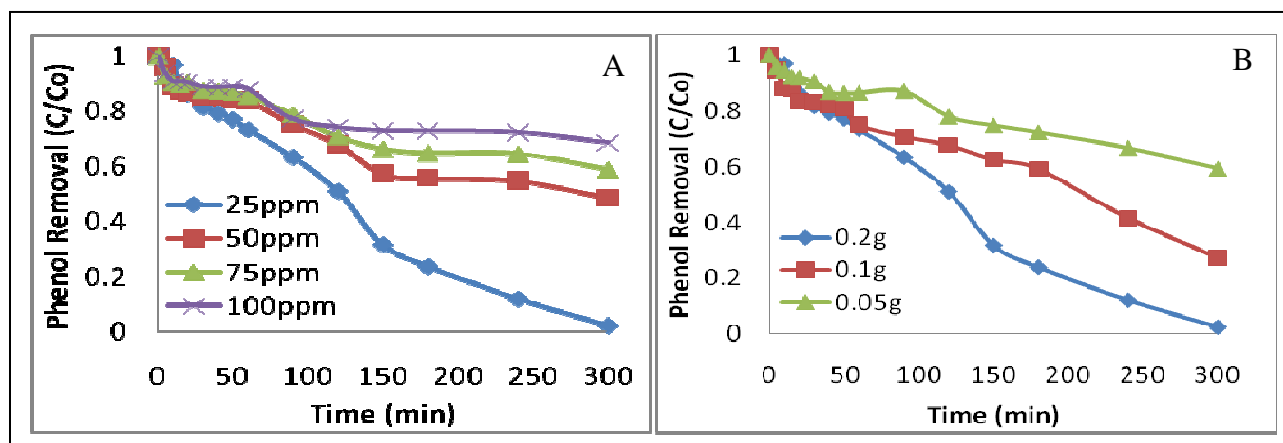

Figure 5. Phenol reduction with time in catalytic oxidation, (A) Effect of phenol concentration and (B) Effect of catalyst loading. Reaction condition: 1 g oxone, $25^{o}C$ and stirring speed of 400 rpm

The other important parameters affected the removal efficiency of phenol are oxone concentration and temperature as presented in Fig. 6 and Fig 7. As commonly known that oxone contains pereoximonosulphate (PMS) compound as oxidant in the heterogeneous catalytic oxidation of phenol. Further, in the presence of Co/INZ or Co/ANZ, PMS will generate sulphate radicals ($SO_5^{-\bullet}$) followed by phenol reduction. Referring to Fig.6, it can be seen at reaction time of 3 hours, the highest removal efficiency of phenol obtained at 2g oxone and the lowest at 0.25g oxone. From this, looks the higher oxone concentration, the greater phenol removal is. However, the 0.5g oxone give better result than 1 g oxone. Moreover, by using Co/INZ catalyst, the 0.5g oxone has similar result with 2 g oxone. Based on these experimental works, the optimal amount of oxone for removing phenol by using Co/INZ and Co/ANZ catalyst is 0.5 g.

Further, temperature is also key factor in organic compound oxidation. It also well known that the higher temperature, the faster of reaction rate is. Fig.7 shows the effect of temperature on phenol degradation. Significant effect on phenol removal was obtained by increasing temperature. For instance, at reaction time of 3 hours, removal efficiency of phenol removal using Co/ANZ from $25^{o}C$ to $35^{o}C$ and $45^{o}C$, increase from 45% to 75% and 100%, respectively (Fig. 7B). Similar trend is also obtained in Fig. 7A using Co/INZ catalyst, the removal efficiency increase from 80% at $25^{o}C$ to 100% at 35 and $45^{o}C$.
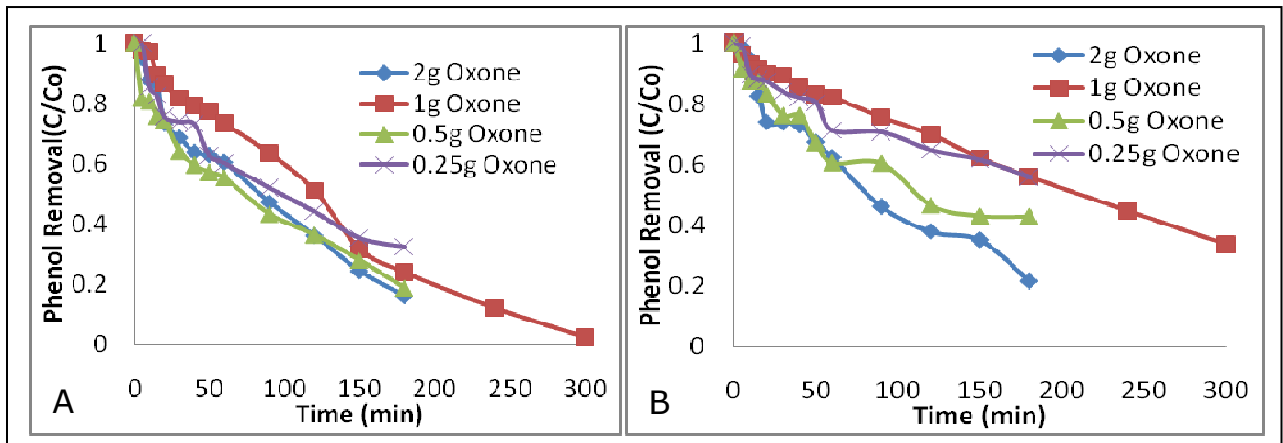
Figure 6. Effect of oxone concentration in phenol reduction, (A) Co/INZ and (B) Co/ANZ. Reaction condition: 0.2g catalyst loading, 25 ppm phenol solution, 25°C and stirring speed of 400 rpm.
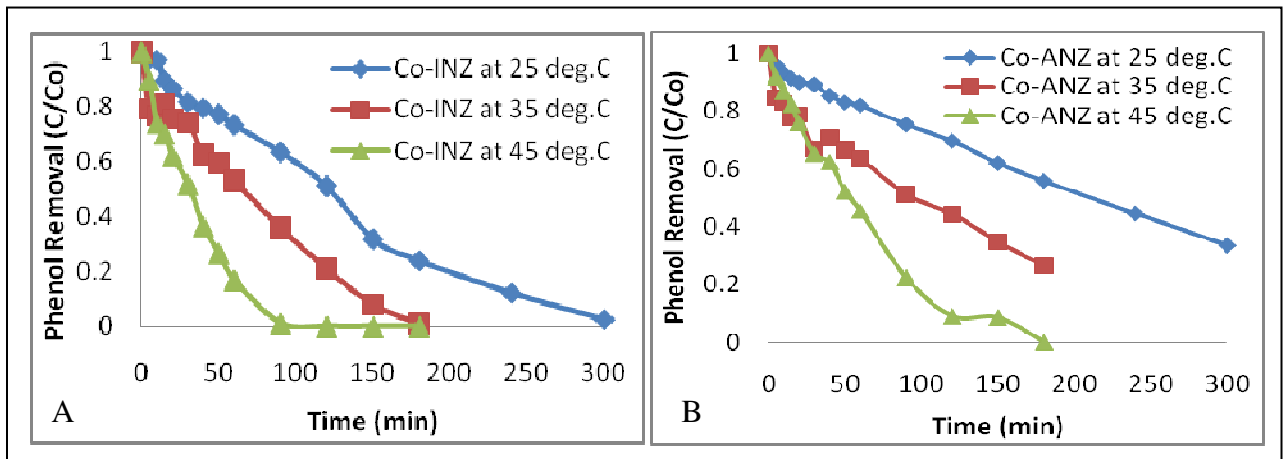

Figure 7. Effect of temperature in phenol reduction, (A) Co/INZ catalyst, (B) Co/ANZ catalyst. Reaction condition : 0.2g catalyst loading, 1 g oxone, 25 ppm phenol solution, and stirring speed of 400 rpm.

Oxidation kinetics

For kinetics study, a general equation of the pseudo first order kinetics was used, as shown in equation below.

$$\frac{dC}{dt} = -(k.C) \qquad (3)$$

Where *k* is the first order rate constant of phenol removal, *C* is the concentration of phenol at various time, *Co* is the initial concentration of phenol. By integrating the equation above, the profile decrease in phenol concentration can be further elaborated in the following equation (Shukla et al.. 2010).

$$C = Co.e^{-k.t} \qquad (4)$$

From data fitting as seen in Fig.8, it is obtained that phenol degradation using Co/INZ and Co/ANZ catalyst can be represented by the pseudo first order kinetics. This can be validated from the values of R^2, which are 0.9236 and 0.9892 for Co/INZ and Co/ANZ respectively. The rate constant *(k)* shows that the value of *k* for Co/INZ of 0.0106 is higher than Co/ANZ of 0.0033, which means the Co/INZ is able to degrade phenol more rapidly.
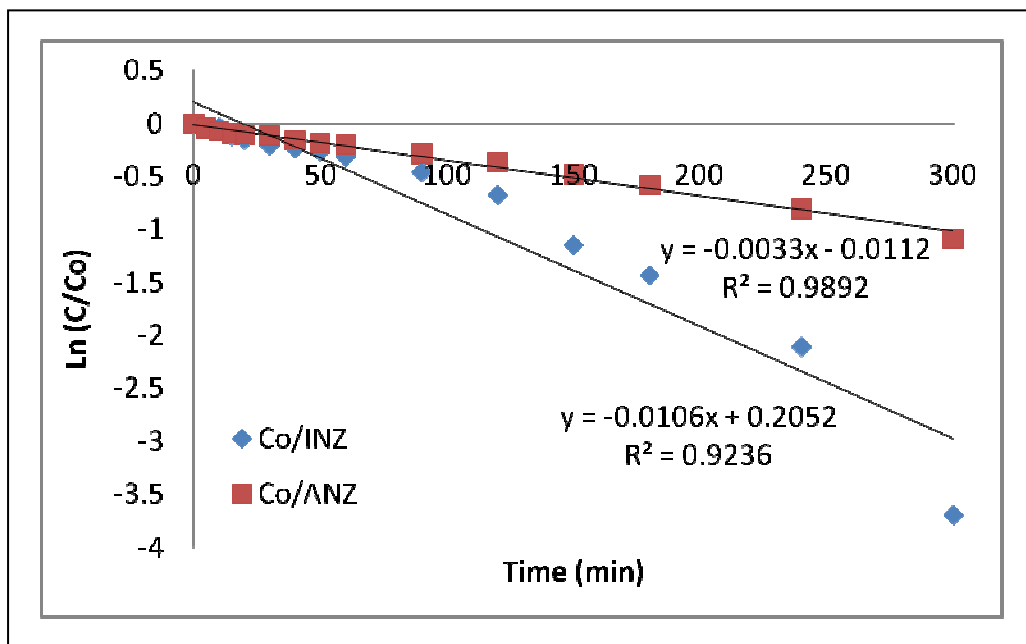
Figure 8. Data fitting using pseudo first order kinetic

Conclusions

Co/INZ and Co/ANZ were successfully synthesized by impregnated 5% active metal of cobalt on natural zeolite surface. The active metal was well coated on natural zeolite surface although not all zeolite surfaces were covered by cobalt due to large size of zeolite particle. However, this research proves that Co/INZ and Co/ANZ are effective catalysts for degrading phenol in the presence of PMS which generating sulphate radical. Further, Co/INZ has better ability of removing phenols than Co/ANZ. Phenol removal is a combination of oxidation and adsorption processes. This research also confirmed that the concentration of phenol, catalyst loading, concentration of oxidant (oxone) and temperature are key parameters that affect the reaction rate in removing phenol. Kinetic studies show that phenol oxidation on the Co/INZ and Co/ANZ follows the first order reaction with the rate constants of 0.0106 and 0.0033, respectively.

Acknowledgements

References

Anipsitakis G.P. and Dionysiou D.D. 2003. Degradation of Organic Contaminants in Water with Sulfate Radicals Generated by the Conjunction of Peroxymonosulfate with Cobalt, Environmental Sciences and Technology 37: 4790-4797.

Anipsitakis G.P., Stathatos E. and Dionysiou D.D. 2005. Heterogeneous Activation of Oxone Using Co_3O_4, Journal of Physical Chemistry B 109: 13052-13055.

Camporro A., Camporro M.J., Coca J. and Sastre H. 1994. Regeneration of an activated carbon bed exhausted by industrial phenolic wastewater. Journal of Hazardous Material 37: 207-214.

Chen X.Y., Chen J.W., Qiao X.L., Wang D.G. and Cai X.Y. 2008. Performance of nano-Co_3O_4/peroxymonosulfate system: Kinetics and mechanism study using Acid Orange 7 as a model compound, Applied Catalysis B Environmental 80: 116-121.

Chiron S., Fernandez-Alba A., Rodriguez A. and Garcia-Calvo E. 2000. Pesticide chemical

oxidation: state-of-the-art. Water Research 34: 366–377.

Erdem E., Karapinar N. and Donat R. 2004. The removal heavy metal cations by natural zeolites. Journal of Colloid Interface Science, 280: 309-314.

Fortuny A., Font J. and Fabregat A. 1998. Wet air oxidation of phenol using active carbon as catalyst, Journal of Applied Catalyst B: Environmental 19: 165-173.

Mintova S. 2003. Nanosized Molecular Sieves. Journal of the Chemical Society Chemical Communications, 68: 2032-2054

Pera-Titus M., Garcia-Molina V., Banos M.A., Gimenez J. and Esplugas S. 2004. Degradation of chlorophenols by means of advanced oxidation processes: a general review, Applied Catalysis B-Environmental 47: 219-256.

Pignatello J.J., Oliveros E. and MacKay A. 2006. Advanced Oxidation Processes for Organic Contaminant Destruction Based on the Fenton Reaction and Related Chemistry, Critical Review Environmental Science and Technology, 36: 1-84.

Shukla, P.R., Wang S., Ang H.M and Tade M.O. 2010. Photocatalytic oxidation of phenolic compounds using zinc oxide and sulphate radicals under artificial solar light. Separation and Purification Technology 70(3): p. 338-344.

Song W., Justice R.E., Jones C.A., Grassian V.H. and Larsen S.C. 2004. Synthesis, Characterization, and adsorption Properties of Nanocrystalline ZSM-5. Langmuir 20: 8301-8306.

Shukla P., Sun H.Q., Wang S.B., Ang H.M. and Tade M.O. 2011. Nanosized Co_3O_4/SiO_2 for heterogeneous oxidation of phenolic contaminants in waste water, Separation and Purification Technology 77: 230-236.

Shukla P., Wang S.B., Singh K., Ang H.M. and Tade M.O. 2010. Cobalt exchanged zeolites for heterogeneous catalytic oxidation of phenol in the presence of peroxymonosulphate, Applied Catalysis B-Environmental 99: 163-169.

Shukla P.R., Wang S.B., Sun H.Q., Ang H.M. and Tade M.O, 2010. Activated carbon supported cobalt catalysts for advanced oxidation of organic contaminants in aqueous solution, Applied Catalysis B-Environmental 100: 529-534.

Wang S. 2008. A Comparative study of Fenton and Fenton-like reaction kinetics in decolourisation of wastewater, Dyes and Pigments 76: 714-720.

Yang, Q., Choi H., Al-Abed S.R. and Dionysiou D.D. 2009. Iron–cobalt mixed oxide nanocatalysts: Heterogeneous peroxymonosulfate activation, cobalt leaching, and ferromagnetic properties for environmental applications, Applied Catalysis B-Environmental 88: 462-469.

Zhang W., Tay H.L., Lim S.S., Wang Y.S., Zhong Z.Y. and Xu R. 2010. Supported cobalt oxide on MgO: Highly efficient catalysts for degradation of organic dyes in dilute solutions. Applied Catalysis B Environmental 95: 93-99.