

Research Projects 491 - 492

Semester 1 - 2 2009

Wastewater treatment-Heterogeneous catalytic oxidation of phenol

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Executive Summary

The catalytic oxidation of phenol is studied in this research. Phenolic compound is exceptionally common in the petrochemical, chemical and pharmaceutical industries which produce wastewater containing large amounts of organics perilous to humans and the environment as some of the derivatives are carcinogenic and not biodegradable. The main objective is to study the feasibility of new cobalt based activated carbon catalyst for the degradation of the phenol pollutant. Various factors affecting the feasibility of cobalt impregnated activated carbon catalyst and its reusability were studied.

Similar research methodology as previous work was maintained; however the aid of analytical tools for high resolution microscopic imaging was hereby integrated into the research. These additional analytical studies were incorporated into Extension Studies 1-3, serving the purpose of providing insight on catalyst morphology hence explanations on various phenomena. The experiment was carried out by first preparing 500 mL of 25 ppm phenol solution by diluting 2.5 mL of 5000 ppm phenol stock solution with ultrapure water. The prepared phenol solution was poured into a 500 mL conical flask, which was then clamped and immersed in a water bath set at 25°C. The solution was stirred using an overhead stirrer with a constant speed of 400 rpm for a continuous of $2\frac{1}{2}$ hours to ensure uniformity of solution. For standardisation purposes, 0.5 mL of phenol solution before adding any catalyst and oxidant, and 0.5 mL of methanol were added to a vial bottle using a 1000 μ L auto-pipette. The stopwatch was started right after the oxidant and catalyst were added to the solution. Samples were taken at every 10 minutes. The stirrer was stopped for one minute before taking the sample to let the small particles of catalyst settle. Since the catalyst particles are too small, the sample was pipetted from the reactor using a syringe and filtered through a syringe filter to a small bottle. 0.5 mL of sample was then taken from the small bottle by a 1000 μ L auto-pipette and the remaining sample in the small bottle was then immediately returned to the reactor. This extra step of filtration is carried out to avoid the removal of tiny catalyst particles from the reaction and also to provide full protection of the HPLC instrument, as the presence of these particles is harmful towards the column. 0.5 mL of methanol was added for reaction quenching purposes. At the end of the experiment, for the purpose of catalyst reusability test, the catalysts were filtered using a vacuum pump and washed thoroughly with 250 mL of ultrapure water for five times to wash off any impurities or oxidants adsorb onto the catalyst surface. After filtering, the catalysts were left in the oven to dry before using in the next reusability experiment.

In comparison of pure activated carbon with cobalt based activated carbon catalyst, despite the performance of pure adsorption activity of activated carbon better than cobalt based activated carbon catalyst, cobalt based activated carbon catalyst is further examined on various parameters as this research focused solely on effective catalytic oxidation technique. The results provided by comparing the difference in phenol removal rates show promising catalyst potential.

First-order reaction rate has been proven from the exponentially decay of normalised concentration profile. Thus, the first-order model was used for obtaining individual rate data

from the slope of the $\frac{\ln[\text{Phenol}]_t}{[\text{Phenol}]_0}$ versus time graph. Quantitative benchmarking values of reaction rates associated with different parameters can then be graphed and analysed. The experiment was repeated with 25 ppm, 50 ppm, 75 ppm and 100 ppm concentration of phenol to examine the effect of initial phenol concentration on the reaction rate. The reaction rates responded in a linearly decreasing manner with respect to the effect of increasing initial phenol concentration. This may due to the tendency of high phenol concentration to obstruct the pores or the catalyst support. The catalyst amount is varied from 0.025 g to 0.1 g to examine the effect on the degradation reaction rate. It is observed that with a constant initial concentration of phenol and oxidant, the degradation of phenol increases as the amount of catalyst increases. To examine the effect of oxidant amount, the oxidant amount is varied from 0.25 g to 1 g. The experimental results show that the phenol oxidation reaction rates exhibit a linear increment with the increase in oxidant amount. The experiments again were repeated at different temperatures of 40°C and 50°C to inspect the effect of temperature on the reaction rates. The effect of increased temperature, however, showed an exponential increase in the reaction rates which can be reasonably deduced from the famous Arrhenius equation. The activation energy of the phenol degradation can also be determined from the Arrhenius equation to be $-66.13 \frac{\text{kJ}}{\text{mol}}$ of phenol reacted.

Catalyst reusability tests showed satisfactory performance for all test apart from the second reusability tests. A third reusability test was carried out to obtain validations. Further discussion is provided in the actual report.

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1.0 Introduction

1.1 Project Background

Anthropogenic water pollution has been a lurking predicament since the mushrooming of industrial activities in today's globalised world. Water is a fundamental universal solvent. Its unavailability in appropriate quantities and qualities will impede life of all forms. Associated environmental and societal impacts have proven to be detrimental and a new direction towards remediation is favoured. Toxic wastewater production is inevitable, owing to heavy water consumptions in major industries and subsequent massive discharges of water with dissolved hazards. A vicious cycle is formed between the source and sink of the pollutants; between surface and groundwater.

The existing methods of wastewater treatment sufficiently handle the demand of stringent regulations, but may not act as fully efficient processes. The favourable characteristics regarding a wastewater treatment method are effectiveness and economical feasibility. Current wastewater treatment can incur a hefty cost over the life of an industrial plant, hence the reluctance of relevant parties to comply with regulations. This demands the need of an effective catalyst that can facilitate faster degradation of wastewater pollutants.

Catalysts are generally known as the core driving force of a reaction; their absence would lead to unfavourably sluggish reaction rates that would in turn greatly reduce feasibility of an industrial reaction. As a direct consequence of the swift and rapid emergence of industrial activities, massive quantities of wastewater require thorough treatment on a daily basis.

As per the devising of all reactions, the development of catalysts is the key to successful industrial environmental remediation. Extensive research has been carried out in this area, however due to the long and tedious nature of such work, on-going research is imperative for possible breakthrough in this field that will contribute drastically towards successful wastewater treatment in this sustainable-based industrial era.

Handling issues, together with regeneration and disposal concerns have proven to be burning topics in related industries which form the driving force of continuous innovative research over the span of many years (Ruiz and Thyron 1993).

1.2 Objectives

The model wastewater pollutant of concern is phenol. The ultimate objectives of this research is to quantify reaction rate constants and study the sensitivity of phenol oxidation rates with respect to various affecting parameters including initial concentration of phenol, concentration of cobalt impregnated activated carbon catalysts, concentration of

peroxymonosulphate as the oxidant, and temperature. The performance of catalyst regeneration is also desired to be confirmed with the purpose of identifying its true performance.

It is desired to understand the reaction kinetics of the catalytic oxidation process, where the final and major outcome will be the reaction rates and constants which directly describe the reaction processes. The documented results will aid future research aimed at developing suitable technology based on the catalytic oxidation on a larger scale to treat phenolic wastewaters. All related investigations are done in order to assist the advancement of future process design of this wastewater treatment technology. Moreover, the compiled findings can provide essential design parameters and serve a basis of comparisons for peer research.

1.3 Expected Outcomes

The concentration of phenol is to be completely eliminated upon the completion of each reaction. The hypothetical time required for the reaction to complete is approximately two and a half hours. Separate studies on cobalt-activated carbon and activated carbon are carried out to test their effectiveness in the phenol oxidation reaction. The rate of phenol oxidation is affected by several parameters, which include the types of catalysts used, the reaction temperature, initial concentration of phenol, and the amount of oxidant and catalyst. The rate of reaction was expected to increase with the amount of oxidants and catalysts used and the reaction temperature. The research will allow the documentation of these optimum concentrations, depending on their performance. The High Performance Liquid Chromatography (HPLC) instrument will aid in obtaining a clear determination of the initial and final concentrations of all important compounds, as well as their formation and disappearance behaviours throughout the experiment.

1.4 Significance of Research

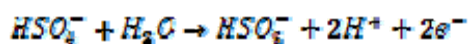
Emphasis on sustainable development issues have developed greatly over the years, and there is no reason to doubt that scrutiny on these issues will continuously intensify.

Catalytic oxidation of phenolic wastewater has been receiving extensive attention. Apart from studying the effect of catalyst concentration and other common affecting parameters such as temperature; the phenomenon of catalyst degradation needs to be studied before a catalyst can be concluded to be truly feasible and effective.

2.0 Literature Review

2.1 Potassium Peroxymonosulphate as Oxidant

Potassium peroxymonosulphate (also known as oxone) is widely used as an oxidizing agent because of the versatility and strong reactivity. It is the potassium salt of peroxymonosulphuric acid and a component of a triple salt with the formula of $2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$. The half reaction generating the hydrogen sulfate is as follow:



2.2 Heterogeneous Catalysis and Catalyst Preparation

A heterogeneous catalytic process involves more than one phase; usually the catalyst is a solid and the reactants and products are in liquid or gaseous form. These types of catalysts are typically insoluble solids or catalyst immobilized on an insoluble support such as silica, activated carbon, zeolite and synthetic or natural polymers. Heterogeneous reactions are widely imperative towards the development of industrial based catalysts due to the strengths that they exhibit as opposed to homogeneous systems. The important advantages heterogeneous catalysis offers to chemical process include improved selectivity and the ease of separation of the catalyst from reaction mixture, reducing processing intensity and waste. Thus, notwithstanding the relative faster reaction kinetics and simplicity homogeneous reactions can offer, these systems are not viable due to the following reasons. Firstly, the nature of the substances used for catalyst preparation is toxic; hence under a homogeneous reaction the dissolved perilous remnants will be discharged together with the treated solution. Therefore, although the phenolic solution can be successfully oxidised, another hazard is introduced into the waste stream. Secondly, the option of recovery and reuse of catalyst would greatly boost the economical feasibility of a treatment technique. In homogeneous reactions, catalysts tend to be loss in solution. This disadvantage is amplified by the costly nature of cobalt.

The support structure often acts to control the orientation of substrate into the pore mouth of the catalyst and thus potentially control the reaction selectivity or by helping to activate the catalyst. Moreover, the support structure such as pore sizes and surface characteristics in the porous solids can help create a physical and chemical environment that will aid the reaction (Green Chemistry Centre of Excellence for Industry). The simple and complete separation of the end-product reaction mixture from the solid catalyst makes heterogeneous catalysis commercially attractive, especially because many catalysts are quite valuable and their reuse is demanded. Heterogeneous catalysis eliminates the need for additional separation operation

of catalyst from the homogeneous solution, which can often be expensive and can lead to generation of large volumes of waste, which is often toxic. Besides, heterogeneous catalysis minimizes metal leaching, improves handling and process control, and it is cheaper than homogenous catalysis (McMorn and Hutchings 2004).

Catalyst immobilization is the transformation of a homogeneous catalyst into a heterogeneous one, which is able to be separated easily from the reaction mixture and preferably be reused for multiple times. There are few different techniques for immobilization of catalyst onto a support, including adsorption, encapsulation, tethering using a covalent bond and electrostatic interaction (McMorn and Hutchings 2004). Catalyst immobilized by adsorption has been one of the major pathways to achieve a heterogeneous catalyst. It can sometimes rely only on weak interaction of van der Waals interaction between the catalyst and the support, causes the catalyst readily leaches into solution as the catalyst will reach equilibrium between the surface absorbed species and solution species (McMorn and Hutchings 2004). One general requirement for the reusability of the supported catalyst is that both the support material and the catalytic sites must have sufficient mechanical, thermal and chemical stability to maintain the catalytic activity during the recycling process and withstand the reaction conditions used in the catalytic process (Ding and Uozumi 2008, 3). The instability of the linkage between the catalyst and support will cause leaching of metal into the solution. In addition, limited accessibility of the active site of catalyst will reduce the reaction rate.

In order to apply the immobilized catalyst in this experiment, it is necessary to make a critical evaluation in terms of its activity, stability, ease of recovery and reusability. An ideal immobilized catalyst should not only exhibit activity and selectivity comparable or superior to the homogeneous catalyst, but also be easily recoverable from the reaction stream without metal leaching, and reusable for many runs without any loss of catalytic performance (Skukla 2009).

In this research, the catalyst of profound interest is cobalt based activated carbon catalyst. Cobalt is impregnated onto the activated carbon support which is very accommodating..

3.0 Experimental Setup and Procedure

3.1 Materials

The chemicals used in this experiment were phenol from Sigma Aldrich, ultrapure water, 99.9% methanol from Biolab and peroxymonosulphate. Phenol was used as the contaminant to prepare the artificial wastewater. The required concentration of phenol in this experiment was diluted to 25ppm from the stock solution of phenol with 5000ppm prepared and stored earlier. Ultrapure water was used to dilute the stock solution of phenol to prepare 500mL of 25ppm phenol wastewater. Methanol was used as the quenching agent for each sample taken in the experiment to stop the reaction in the vial bottle for later HPLC test. Peroxymonosulphate in powder form was used as an oxidant in the reaction. The catalysts used in this experiment are the pure activated carbon and cobalt-activated carbon.

3.2 Equipments

The equipments used in this experiment were an electronic weighing balance, a stopwatch, autopipettes, sample vials, water bath with heating and cooling system, stirred batch reactor, and HPLC. HPLC was used to test samples to analyse the initial concentration and disappearance of phenols throughout the experiment. Sample vials were inserted into the HPLC unit, then by utilizing the integrated user-interface, samples were tested and data was extracted into Microsoft Excel spreadsheets. The reaction took place inside the stirred batch reactor, which was a 500mL Pyrex conical flask (inert towards reacting components). The solution was stirred with an overhead plastic stirrer with constant stirring speed of 400rpm. The heating and cooling system was used to maintain the temperature of the water bath, which the stirred batch reactor was immersed in, to keep the reaction at the desired temperature. 1000 μ L auto-pipette was used to transfer 0.5mL of the sample at every sampling interval and 0.5mL of methanol to quench the reaction in the vial bottle. Electronic weighing balance was used to weigh the amount of the catalyst and oxidant used in the experiment.

3.3 Experiment Methodology

25ppm phenol solution was prepared by pipetting 2.5mL of the 5000ppm phenol stock solution into a 500mL measuring cylinder and diluting the solution to 500mL by adding ultrapure water. The phenol stock solution is mix properly before pipetting to ensure homogeneous concentration of phenol stock. Prudence is provided towards this preparation to ensure consistency in the experimental results and to obtain the true effects of varying parameters to be studied. The volume of phenol should be withdrawn from the 5000ppm

phenol stock solution for a 500mL 25ppm phenol was calculated from a simple mole balance as shown:

$$M_1V_1 = M_2V_2 \quad (1)$$

$$25 \times 500 = 5000 \times 2.5 \quad (2)$$

The prepared phenol solution was poured into a 500mL conical flask, which was then clamped and immersed in a water bath set to the desired reaction temperature of 25°C by the heating system. The solution was stirred using an overhead stirrer with a constant speed of 400rpm for a continuous of $2\frac{1}{2}$ hours to ensure uniformity of solution. The top of the reactor was closed by a rubber stopper to avoid spillage. Two experiments were conducted simultaneously.

First sample for the HPLC test was taken before any catalyst and oxidant were added to check the initial concentration of phenol. 0.5mL of phenol solution was taken by a 1000μL auto-pipette from the phenol solution and 0.5mL of methanol was added to the vial bottle as a standard for the experiment.

After taking the first sample, different amounts of oxidants (ranging from 0.25g to 1g) and catalysts (from 0.025g to 0.1g) were measured using the electronic weighing balance and added to the solution after switching on the stirrer of the reactor. The stopwatch was started right after the oxidant and catalyst were added to the solution. Visual examination is carried out to check whether the catalyst dissolved in the solution to avoid homogeneous reaction.

Samples were taken at every 10 minutes. The stirrer was stopped for one minute before taking the sample to let the small particles of catalyst to settle to avoid the catalyst being pipetted out from the solution, which will further affect the reaction rate. Since the catalyst particles are too small, the sample was pipetted from the reactor using a syringe and filtered through a syringe filter to a small bottle. 0.5 mL of sample was then taken from the small bottle by a 1000 μL auto-pipette and the remaining sample in the small bottle was then immediately returned to the reactor to avoid volume loss. This extra step of filtration is carried out to avoid the removal of tiny catalyst particles from the reaction and also to provide full protection of the HPLC instrument. Keeping a constant volume of the reaction is also imperative for a successful experiment. 0.5 mL of methanol was added for reaction quenching purposes. This is to prevent the reaction from progressing further inside the vial during the period before HPLC analysis is commenced. Samples were collected every 10 minutes for the

first hour and every 15 minutes for the remaining half an hour. Depending on circumstances, sometimes sampling times are more frequent. Samples were labelled according to the time interval and kept aside for HPLC testing and result analysis to check the phenol concentration in each sample for each sampling interval. It is important to note that methanol correction factors will need to be included when analysing experimental results. Methanol also acts as a diluting agent to halve the concentration of the phenolic sample. Thus, the final concentration of phenol obtained from HPLC is multiplied by two to obtain the actual concentration of phenol in the reaction.

At the end of the experiment, for the purpose of catalyst reusability test, the catalysts were filtered using a vacuum pump and washed thoroughly with 250 mL of ultrapure water for five times to wash off any impurities or oxidants adsorb onto the catalyst surface. After filtering, the catalysts were left in the oven to dry before using in the next reusability experiment.

The experiment was repeated with 50 ppm, 75 ppm and 100 ppm concentration of phenol to examine the effect of initial phenol concentration on the reaction rate. To prepare different concentration of phenol, 5 mL, 7.5 mL and 10 mL of 5000 ppm phenol stock solution was pipetted. To check the effect of amount of oxidant on the reaction rate, the experiment was repeated with 0.25 g, 0.5 g, and 1 g of oxidants whereas 0.025 g, 0.05 g, 0.075 g, and 0.1 g of catalyst were added at different experiments to observe the effect of catalyst amount. The water bath was set to 25°C , 40°C , and 50°C to observe how the temperature affects the reaction rate.

A very crucial aspect is the vigilant pipetting of the samples and methanol. Autopipettes are used for the purpose of result consistency, however proper pipette settings on the required solution volume and careful usage are essential. An example error would be the over-addition of quenching methanol into the sample vial, which will cause over-dilution and lead to unusual concentration curves. The experimental results are therefore subjected to a certain level of human errors which will be briefly demonstrated in the data discussion section.

4.0 Results and Discussions

4.1 Preliminary Kinetic Study of the Catalytic Activity

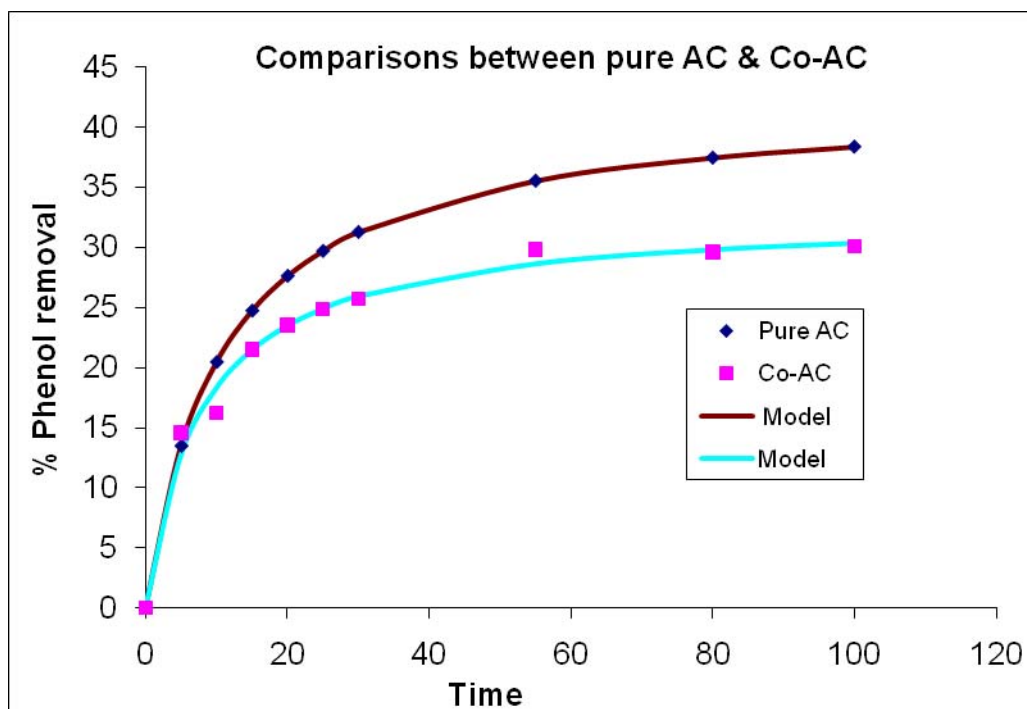


Figure 1: Comparisons between pure activated carbon and cobalt-activated carbon

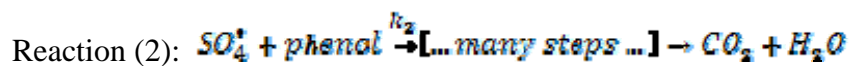
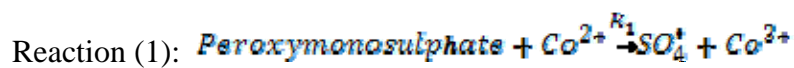
The figure above illustrates the differences between phenol elimination rates between the pure adsorptive ability of activated carbon and the catalytic oxidation reaction driven by the cobalt based catalyst. It can be observed that phenol was removed at a much higher rate by pure activated carbon. Activated carbon is a universal adsorbent that has gained wide popularity among industries, hence it can be logically deduced that the associated phenol degradation rates are high. Notwithstanding the performance of cobalt based activated carbon catalyst being less superior compared to the pure adsorption activity of activated carbon, this research is focused solely on an effective tertiary wastewater treatment technique. Compared to secondary methods, such techniques can achieve complete mineralisation of phenol towards the end of each experiment. Adsorption related secondary wastewater treatment methods are not of interest in this research because such techniques are merely capable of removing the pollutant from the solution; however this does not truly eliminate the problem, however presents further issues of demolishing those adsorbed quantities on the adsorbent. On the other hand, the effect of cobalt based catalyst truly eradicates the presence of the model pollutant.

Moreover, by comparing the difference in phenol removal rates with those of activated carbon adsorption, the promising potential of the catalyst can be observed. This further

justifies the reason to proceed with the research with hope of achieving all experimental objectives.

4.2 Reaction Mechanism and Pathway

As per reaction kinetics explained in Semester 1 Research report, the heterogeneous catalytic degradation of phenol follows a sequence of individual steps, which include mass transfer and adsorption of oxidant from bulk solution to the pore mouth of the catalyst and react with cobalt ions to form active sulphate radicals and desorption of sulphate radicals from the catalyst to oxidize phenol presence in the solution. The two simple elementary rate equation for both of the homogeneous and heterogeneous reactions are conducted over the experimental reaction system, wherein the phenol degradation takes place in the homogeneous system in the presence of sulphate radicals (generated from the heterogeneous reaction) to produce carbon dioxide and water as per the following reactions:



Peroxymonosulphate is a triple salt with proven oxidising potential whereas the sulphate radicals generated are high-energy molecules that react virtually as fast as it is formed. Thus, the precise role of the mechanism it involves in is relatively intricate. As a result, the many steps involved in the homogeneous reaction are assumed to be very fast compared to the rate of generation of sulphate radical. This has been justified through the experiment in Semester 1 that the heterogeneous reaction step of sulphate radicals' generation is extremely slow as compared to the homogeneous reaction rate, and thus it will be the degradation kinetics rate-determining step. It is also assumed that the sulphate radicals present in a very small concentration and is in equilibrium at any instant. Because the sulphate radical reacts virtually as fast as it is formed, the net concentration of the sulphate radical is zero, which is $C_{\text{SO}_4^{\bullet-}} = 0$.

The corresponding rate laws for the sulphate radicals in reaction (1) and (2) are:

$$r_{1,\text{SO}_4^{\bullet-}} = k_1[\text{Peroxymonosulphate}][\text{Co}^{2+}]$$

$$-r_{2,\text{SO}_4^{\bullet-}} = k_2[\text{Phenol}][\text{SO}_4^{\bullet-}]$$

The net rate of sulphate radicals can be summed up as:

$$r_{\text{SO}_4^{\bullet-}} = r_{1,\text{SO}_4^{\bullet-}} + (-r_{2,\text{SO}_4^{\bullet-}})$$

$$r_{SO_4} = k_1[\text{Peroxymonosulphate}][\text{Co}^{2+}] - k_2[\text{Phenol}][\text{SO}_4^{\cdot-}]$$

The net rate of degradation of phenol is as follow:

$$-r_{\text{phenol}} = -r_{\text{SO}_4} = k_2[\text{Phenol}][\text{SO}_4^{\cdot-}]$$

Since the homogeneous reaction is assumed to be very fast compared to the rate of generation of sulphate radical, it is suggested that at any instant, the amount of sulphate radical is very small compared to the moles of phenol ($C_{\text{phenol}} \gg C_{\text{SO}_4}$). Thus, the degradation rate of phenol will be first-order with respect to phenol concentration:

$$-r_{\text{phenol}} = k_2[\text{Phenol}][\text{SO}_4^{\cdot-}] = k_2[\text{Phenol}]$$

A first-order reaction is a reaction whose rate depends on the reactant concentration raised to the first power. Due to negligible concentration of sulphate radical as compared to phenol concentration, the reaction rate is

$$\text{rate} = -\frac{\Delta[\text{Phenol}]}{\Delta t} \approx -\frac{d[\text{Phenol}]}{dt}$$

(3)

$$\text{Thus, } -r_{\text{phenol}} = k_2[\text{Phenol}] = \frac{d[\text{Phenol}]}{dt}$$

(4)

Integrating between $t = 0$ and $t = t$ gives:

$$\int_{[\text{Phenol}]_0}^{[\text{Phenol}]_t} \frac{d[\text{Phenol}]}{[\text{Phenol}]} = -k \int_0^t dt$$

(5)

$$\frac{\ln[\text{Phenol}]_t}{[\text{Phenol}]_0} = -kt$$

(6)

Thus, this first-order reaction rate can be proven from the experiments on the degradation of phenol carried out and the rate constant can be determined from the slope of the

$\frac{\ln[\text{Phenol}]_t}{[\text{Phenol}]_0}$ versus time graph.

4.3 Effect of Initial Concentration of Phenol

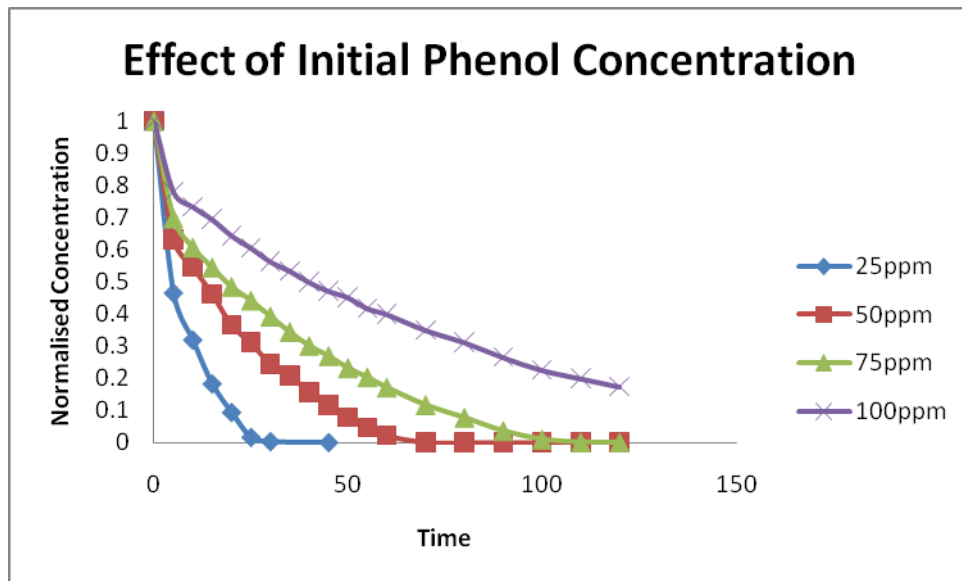


Figure 2: Effect of initial phenol concentration with respect to time

It can be observed from Figure 2 that the concentration of phenol decreases in a first-order manner. The rate constant can thus be identified from the slope of the $\frac{\ln[\text{Phenol}]_t}{[\text{Phenol}]_0}$ versus time graph (Figure 3) and tabulated in Table 1.

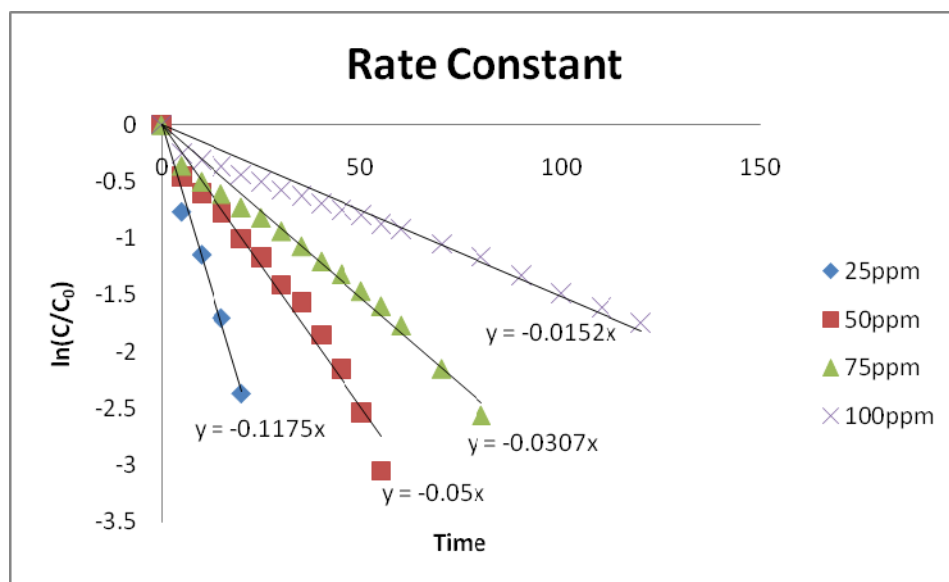


Figure 3: First order model method of obtaining rate constants for different initial concentration of phenol

Table 1: Rate constants for different initial phenol concentrations

Initial concentration of phenol (ppm)	Rate constant, k (min^{-1})
28.16	0.1175
53.14	0.0500
76.84	0.0307
108.34	0.0152

To analyse the trend of rate with respect to the different initial concentration of phenol, Figure 4 is plotted. Because the concentration of phenol within the system is negligible as the reaction approaches completion, the data used for obtaining all rate constant versus phenol concentration graphs only incorporated data up to approximately 95% phenol conversion.

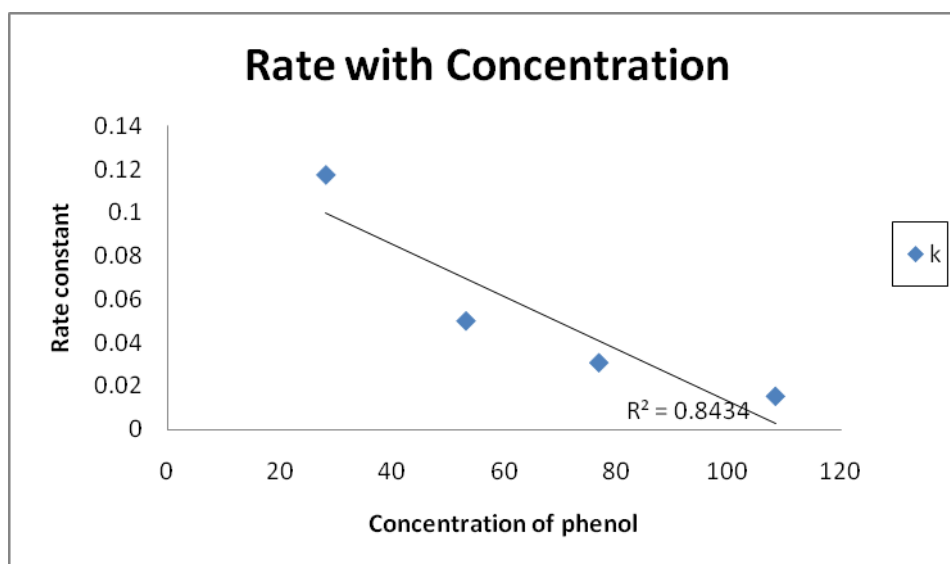


Figure 4: Relationship between initial phenol concentrations and rate constant

It is observed from Figure 4 that the relationship between rate constant and initial phenol concentration merely approaches linearity. As a linear correlation was expected, further work is required to confirm this non-linear relationship. Furthermore, it was initially hypothesised that the rate constant would increase in accordance to increasing initial phenol concentration. However, the results of this section show otherwise. This may be due to the nature of activated carbon which exhibits strong adsorption capacity. Because both oxidation reaction and adsorption contribute to the degradation of phenol, a higher initial phenol concentration would potentially lead to pore blockage or saturation, hence reducing the performance of the oxidation counterpart of the entire phenol degradation mechanism.

4.4 Effect of Concentration of Catalyst

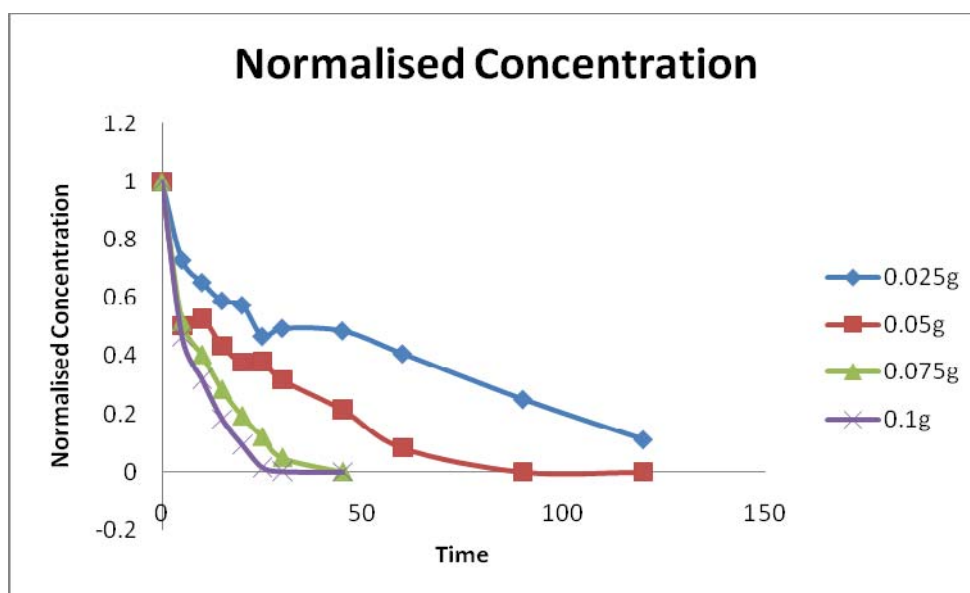


Figure 5: Effect of catalyst amount with respect to time

It can be observed from Figure 5 that the concentration of phenol decreases in a first-order manner with the increase of catalyst. It is also noted that with 0.025g of catalyst, the reaction is not complete after two hours. The rate constant can thus be identified from the slope of the $\frac{\ln[\text{Phenol}]_t}{[\text{Phenol}]_0}$ versus time graph (Figure 6) and tabulated in Table 2.

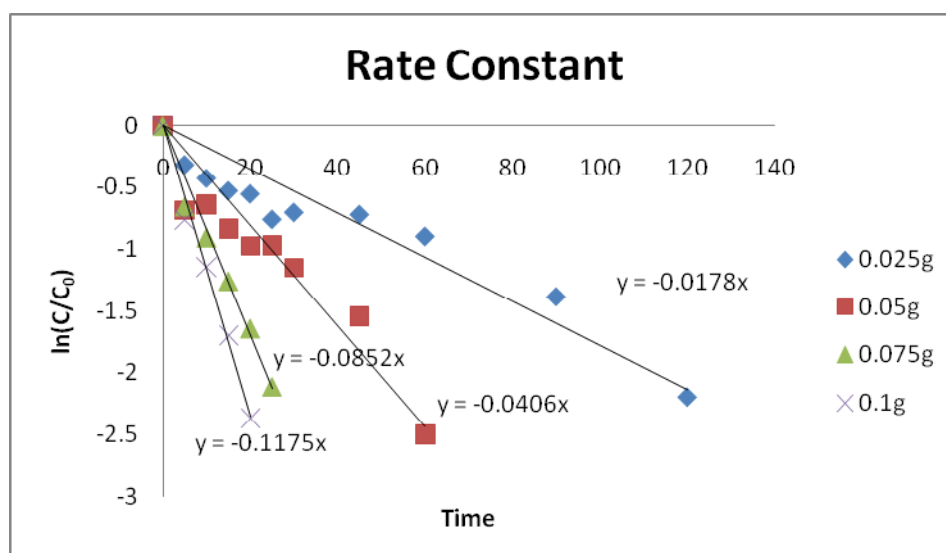


Figure 6: First order model method of obtaining rate constants for different catalyst amount

Table 2: Rate constants for different catalyst amounts

Amount of catalyst (g)	Rate constant, k (min^{-1})
0.025	0.0178
0.050	0.0406
0.075	0.0852
0.100	0.1175

To analyse the trend of rate with respect to the different amount of catalyst, Figure 7 is plotted.

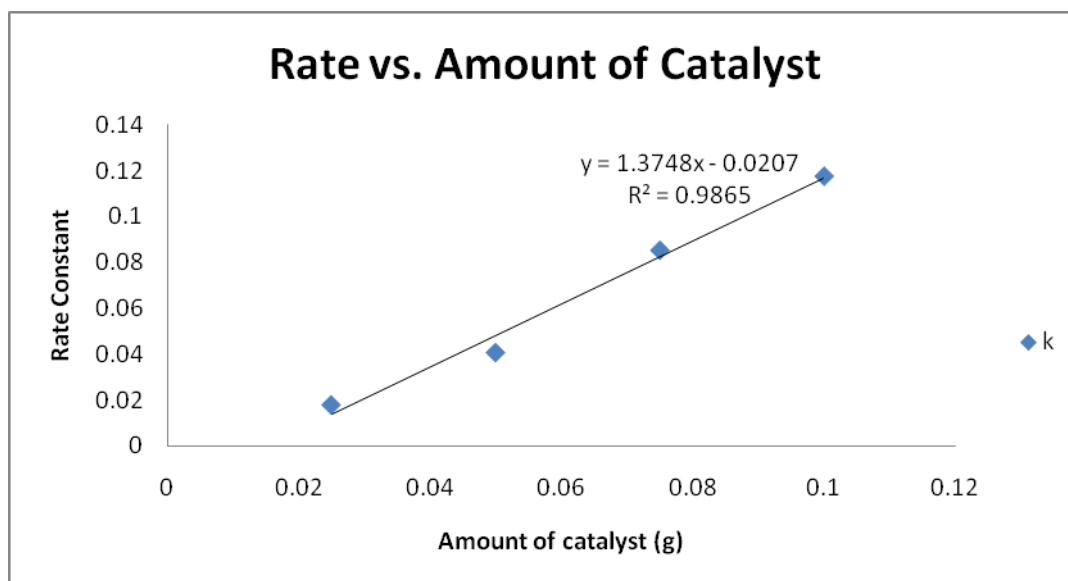


Figure 7: Relationship between catalyst amount and rate constant

It can be observed from the Figure 7 that with a constant initial concentration of phenol and oxidant, the degradation of phenol increases as the amount of catalyst increases. The reaction can be sped up with the addition of more catalyst. This can be explained that with higher amount of catalyst present, there will be more catalytic surface for the oxidant to react with for generating more active sulphate radicals. Thus, the rate of the heterogeneous reaction will increase which further increases the overall reaction rate. This can be proven from the reaction as follows:



It can be seen from Reaction 1 that if the amount of catalyst continues to increase until a certain level, the amount of peroxymonosulphate present will limit the reaction as sulphate radicals are required to react with phenol in the catalytic oxidation reaction. Therefore, in an attempt to manipulate the reaction rate by increasing the amount of catalyst, the oxidant

amounts should be increased accordingly because the reaction rate will only increase if there is enough oxidant to adsorb on the surface of the available catalyst.

4.5 Effect of Concentration of Oxidant

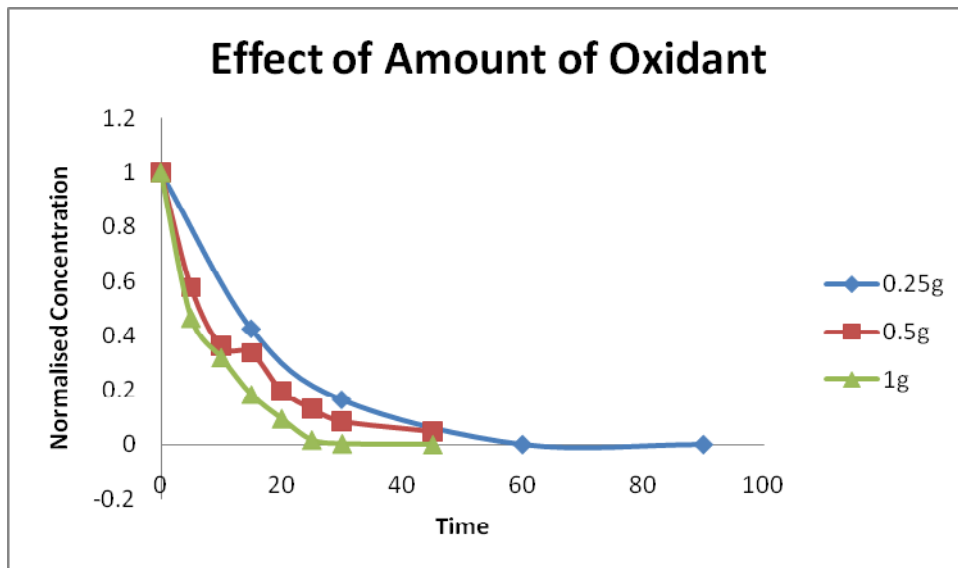


Figure 8: Effect of oxidant amount with respect to time

It can be observed from Figure 8 that the concentration of phenol decreases in a first-order manner with an increase in oxidant. With 1g of oxidant, the reaction is complete within half an hour. However, the reaction only completes after an hour with 0.25g of oxidant used. As per the other studies, the first order model was used to proceed to plot the rate constant as in Figure 9.

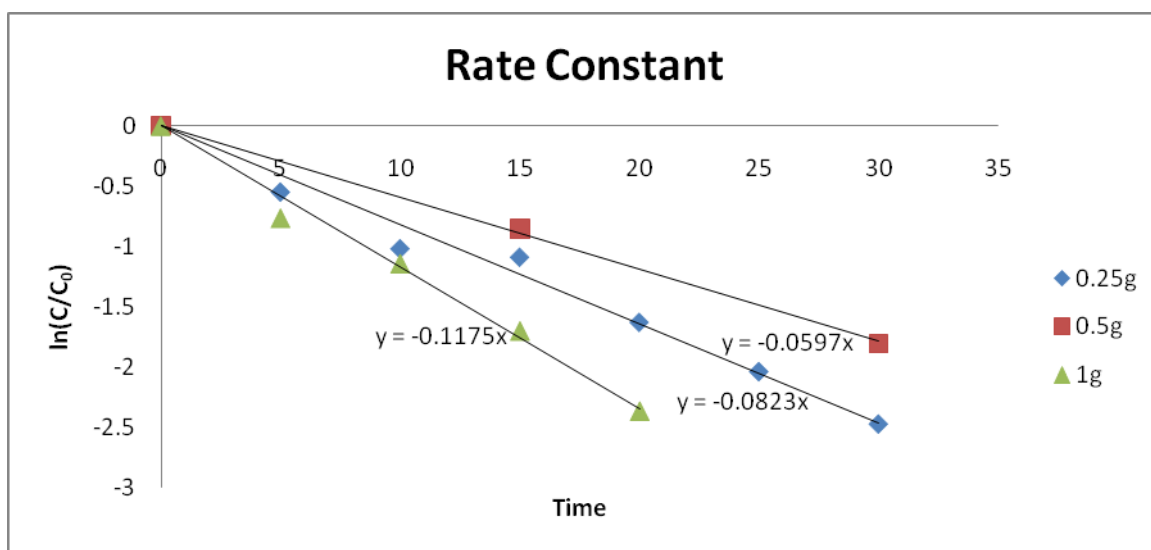


Figure 9: First order model method of obtaining rate constants for different oxidant amount

Table 3: Rate constants for different oxidant amounts

Amount of oxidant (g)	Rate constant, k (min^{-1})
0.25	0.0597
0.50	0.0823
1.00	0.1175

To analyse the trend of rate with respect to the different amount of oxidant, Figure 10 is plotted.

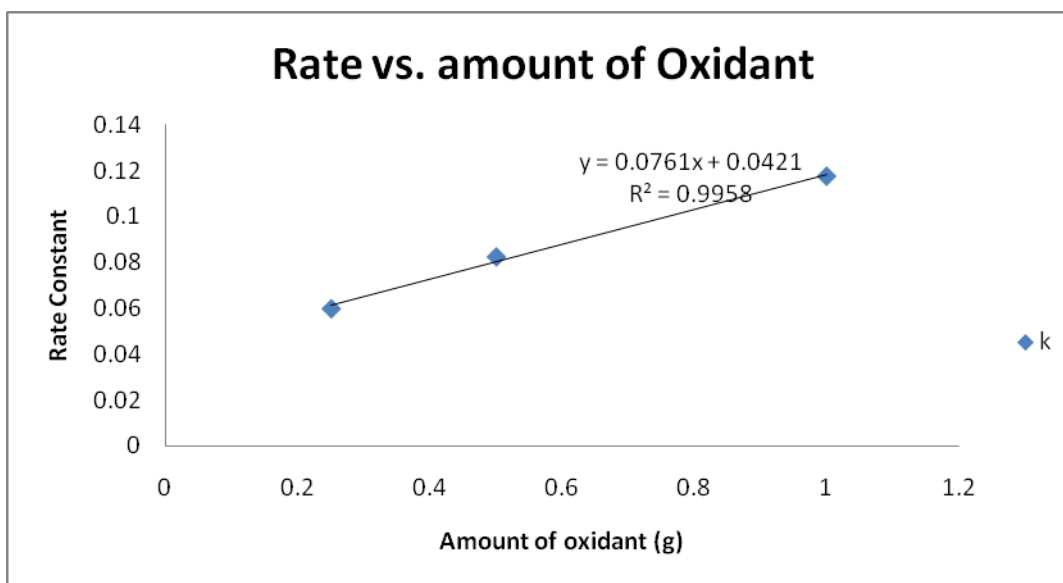


Figure 10: Relationship between oxidant amount and rate constant

The effect of concentration on the reaction rates performed as expected, with an increase in the reaction rate each time the amount of peroxymonosulphate added was doubled.

It is worth noting that the possibility occurrence of crossover if an excessive amount of oxidant was added, therefore it is recommended that the amount of peroxymonosulphate addition be increased up to 5 grams to validate this phenomenon.

4.6 Effect of Reaction Temperature

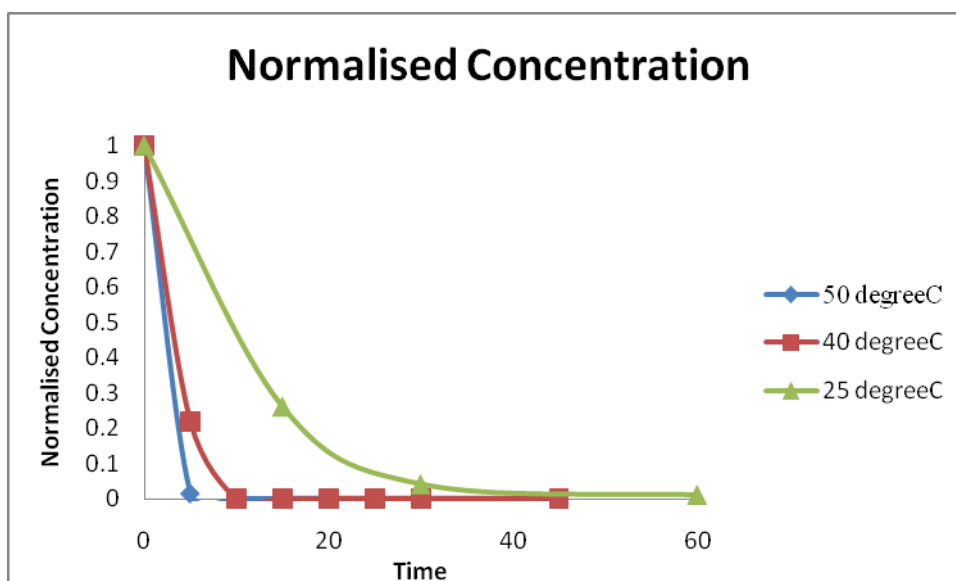


Figure 11: Effect of reaction temperature with respect to time

Figure 11 shows that upon the collection of the first experimental sample at 50°C, the concentration of phenol had been oxidised to negligible amounts. Furthermore, because the initial sample had been withdrawn upon 5 minutes, it can be reasonably inferred that the reaction rates were even more superior to that able to be captured on the graph.

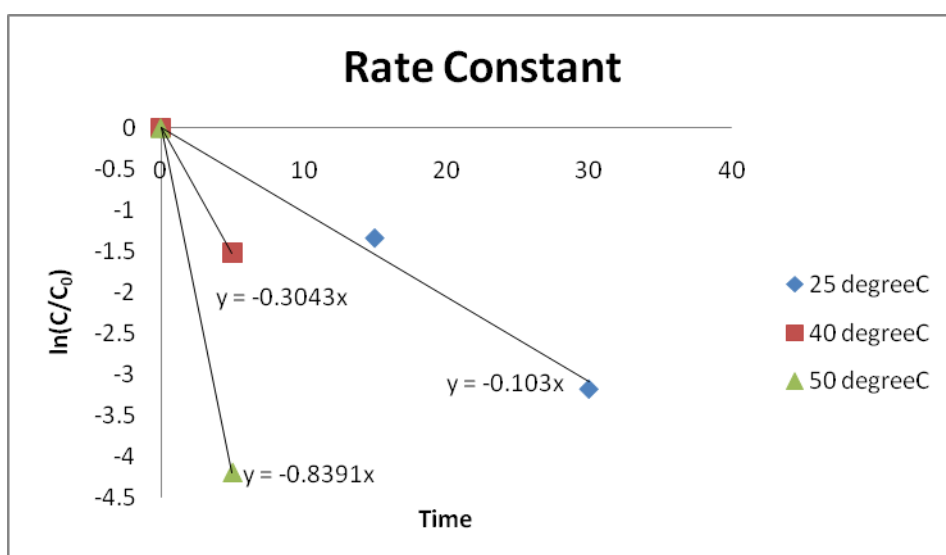


Figure 1: First order model method of obtaining rate constants for different reaction temperatures

Table 4: Rate constants for different reaction temperatures

Reaction temperature (°C)	Rate constant, k (min ⁻¹)
25	0.1030
40	0.3043
50	0.8391

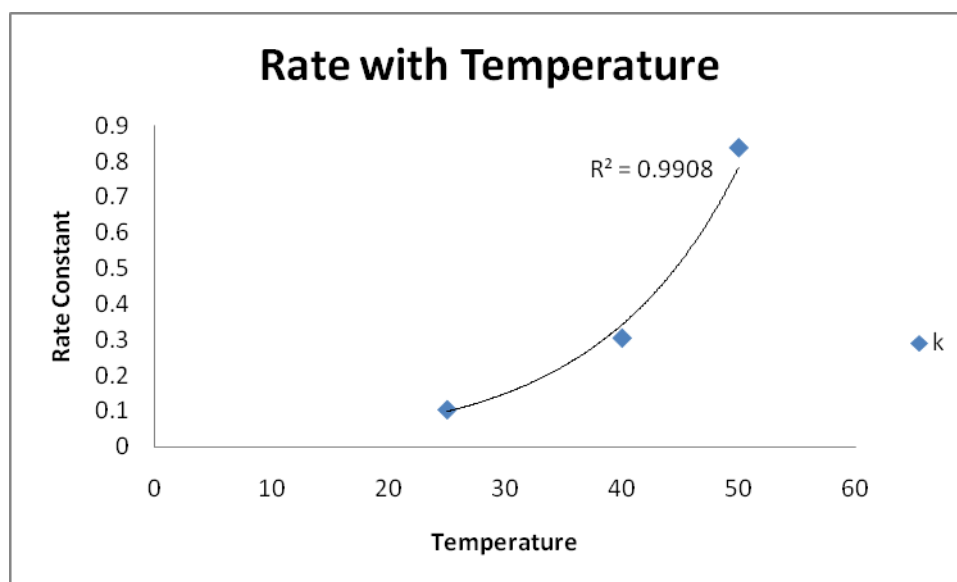


Figure 2: Relationship between reaction temperature and rate constant

As per all reactions, temperature induces significant effects on the rate and kinetics behaviour. Studying the effect of the catalyst or oxidant concentration, higher values of such parameters induce an approximate linearly increasing relationship with the phenol oxidation reaction rates. However, according to Figure 13, the moderate increase in temperature resulted in a substantial boost in terms of the phenol oxidation kinetics. A practical explanation is provided by referring to the famous Arrhenius equation: $k(T) = A e^{-\frac{E}{RT}}$ which shows that the reaction rate constant, k is inherently related to reaction temperature by an exponential relationship. Therefore, this explains the rapid rates of phenol oxidation associated with each temperature increase. As shown in above sections, the degradation rate of phenol is associated with the formation of sulphate radicals, which occurs more rapidly at higher temperatures. The faster generation of sulphate radicals will in turn lead to a quicker oxidation of phenol due to a larger amount of radicals available for reaction at a given time.

Another important understanding from this study is that the cobalt based catalyst could successfully withstand higher temperatures, without exhibiting any abnormal behaviour in the

catalytic activity. Hence it can be induced that there was no undesired damage on catalyst structure.

However, it is important to acknowledge the limitations of this research. Experiments have only been conducted up to 50°C; beyond this temperature there exists further possibility of discovering more superior reaction rates which may be however compromised by a negative modification of the catalyst structure. Thus, a trade-off needs to be made between the catalytic activity and the catalyst structure in determining the optimum temperature for the phenol degradation reaction.

The reaction rate follows the Arrhenius temperature dependence, which can be correlated by the equation of:

$$k(T) = A e^{-\frac{E}{RT}}$$

$$\ln k(T) = \ln A - \frac{E}{R} \left(\frac{1}{T} \right)$$

Where $k(T)$ is the specific rate constant at temperature T

A is the pre-exponential factor or frequency factor

E is the activation energy

The reaction rate constant obtained for the first-order reaction can be used to plot the $\ln k$ versus $\frac{1}{T}$ graph to identify the activation energy and the pre-exponential factor in Figure

14.

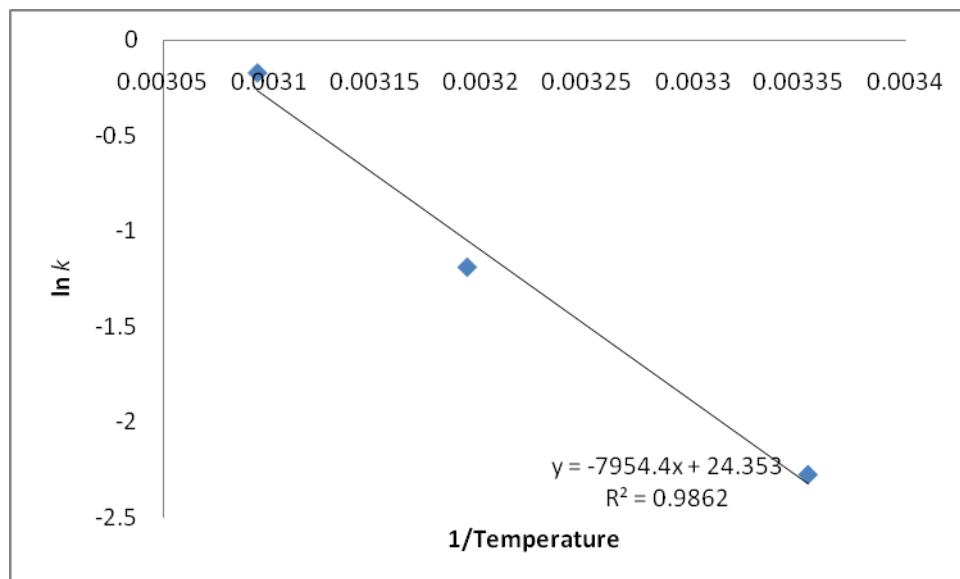


Figure 14: Arrhenius temperature dependence of the reaction

From Figure 14, the frequency factor can be calculated from the y-intercept as follow:

$$\ln A = 24.353$$

$$A = 3.77 \times 10^{10}$$

Activation energy can be calculated from the slope of Figure 14 as follow:

$$-\frac{E}{R} = 7954.4$$

$$-E = 7954.4 \times 8.314 \text{ J/mol}$$

$$-E = 66133 \text{ J/mol}$$

4.7 Catalyst Reusability

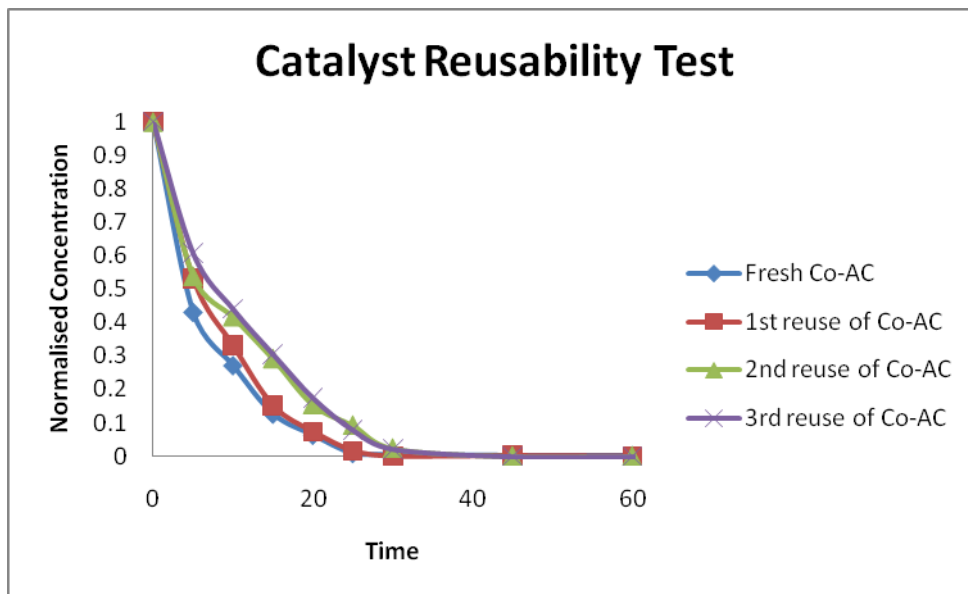


Figure 15: Catalyst reusability test

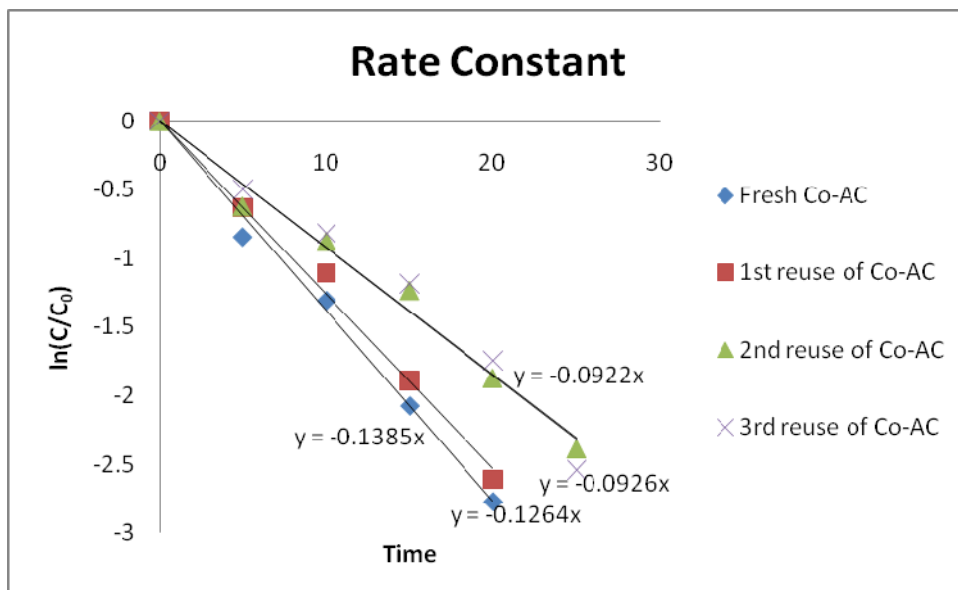


Figure 16: First order model method of obtaining rate constants for the catalyst use frequency

Table 5: Reaction constants for the catalyst use frequency

Condition of catalyst	Rate constant, k (min^{-1})
Fresh	0.1385
First reuse	0.1264
Second reuse	0.0926
Third reuse	0.0922

It is worth re-highlighting the objective of researching into the pros and cons associated with the catalyst. An effective catalyst would still be deemed unfavourable from an economical point of view if it exhibits poor performance in reusability tests. Reusability performance is generally benchmarked in terms of the occurrence of catalyst leaching, decay, and fouling. Therefore, in order to justify the viability of the cobalt based catalyst, reusability tests were carried on both fresh and once-used catalysts. As shown in Figure 15, the first reusability test showed promising results and a high potential for catalyst recycling. However, upon the second reusability test, a significant reduction in phenol oxidation rate was observed. This may be due to loss of catalyst contributed by the catalyst leaching effect. Moreover, the catalyst regeneration step which involves prolonged heating in the oven may have contributed to undesired catalyst decay. This raises concern over certain experimental procedures in the catalyst regeneration section. The absence of a specific constant drying time of each catalyst in the oven could be used to explain the increasingly serious loss in catalytic activity upon the second reusability test. Extended heating times have been determined to have negative effects on the well-being of the catalysts. In short, a myriad of other explanations may be used to explain the above phenomenon however no concrete conclusions can be drawn until further tests are commenced.

Upon the conduction of the third reusability test, results showed a similar phenol degradation rate as the second reusability test. This proves to some extent that the Cobalt based catalyst performs reasonably well in terms of its reusability potential. The remarkable loss in performance during the second reusability test may well be due to the aforementioned reasons of prolonged heating in the oven. There is also the possibility of experimental errors during the weighing process of the second reusability test. In short, further research is encouraged to confirm the suitability of catalyst reuse.

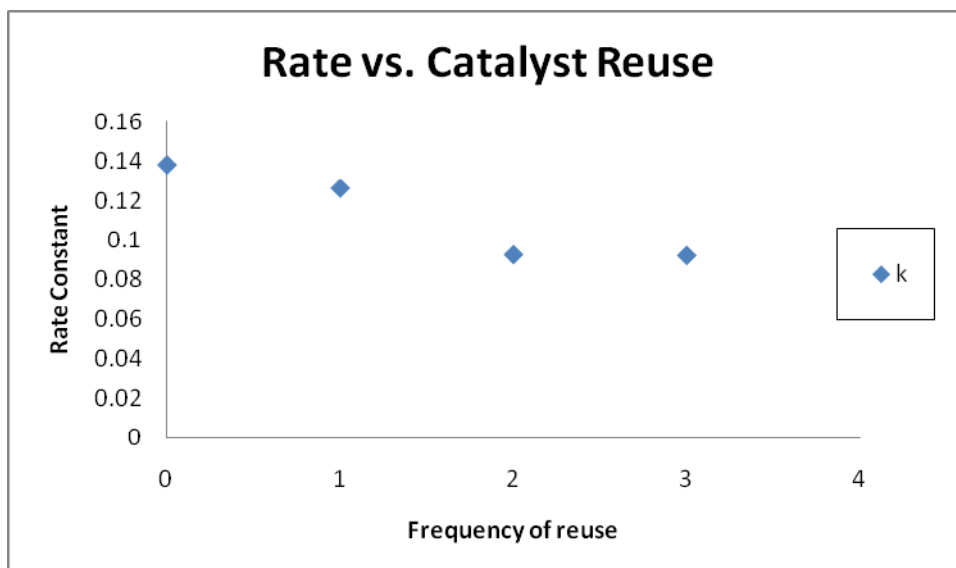


Figure 17: Relationship between catalyst use frequency and rate constant

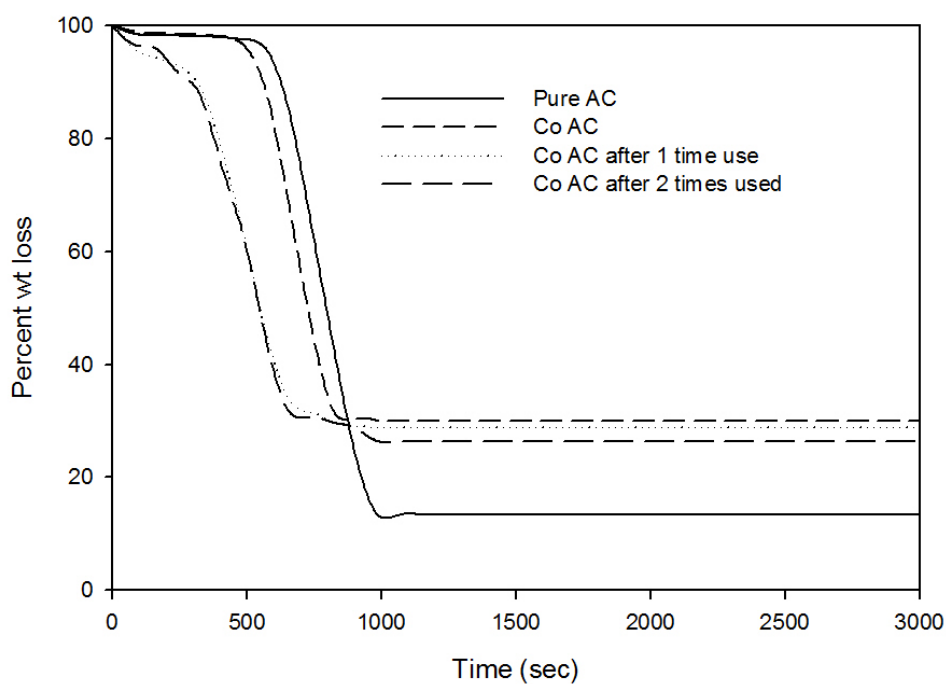


Figure 38: Thermal gravimetric analysis result

Further Thermal Gravimetric Analysis was carried out to identify the changes in catalyst weight with respect to temperature. The analysis was carried out by burning the catalyst and measuring the weight of the slag left behind. Figure 17 conveys similar information as figure 18, which both illustrates a considerable decay in catalyst function upon the second attempt of reusability.

This supplemented the justification of concern over catalyst long-term robustness which deserves attention for further research and justification.

Overall, the catalyst is able to enhance the phenol oxidation rate following similar trends during reusability tests. However, the exhibited degradation is deemed unsatisfactory, especially at early stages of reusability tests. A successful catalyst cannot tolerate vulnerability towards extensive leaching, fouling, or decay; these characteristics would reduce its application worth on a larger scale.

5.0 Extension Studies

5.1 Analysis by Energy Dispersive X-ray Technologies

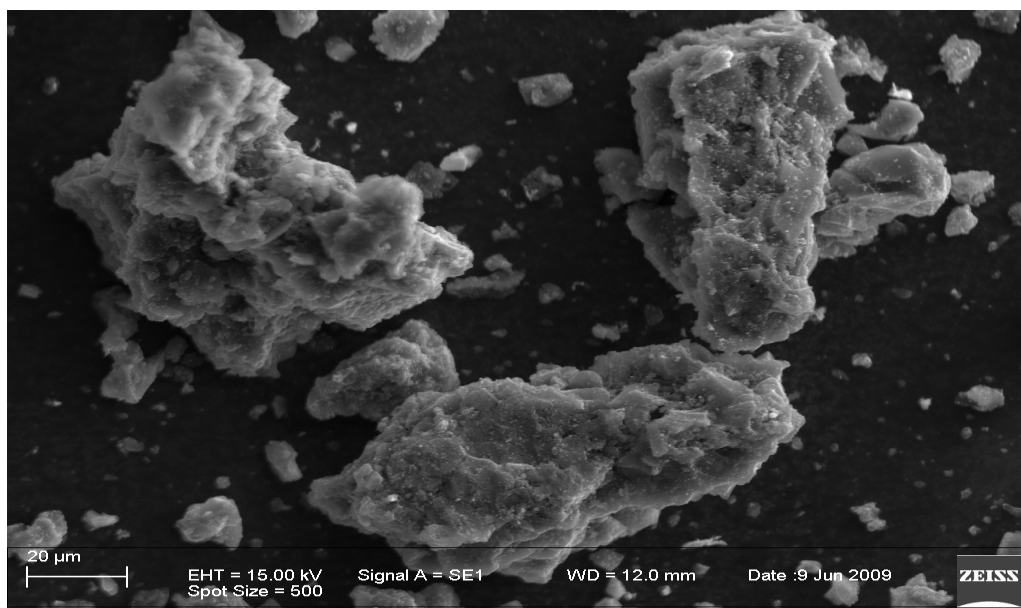


Figure 19: Secondary Electron Detector image

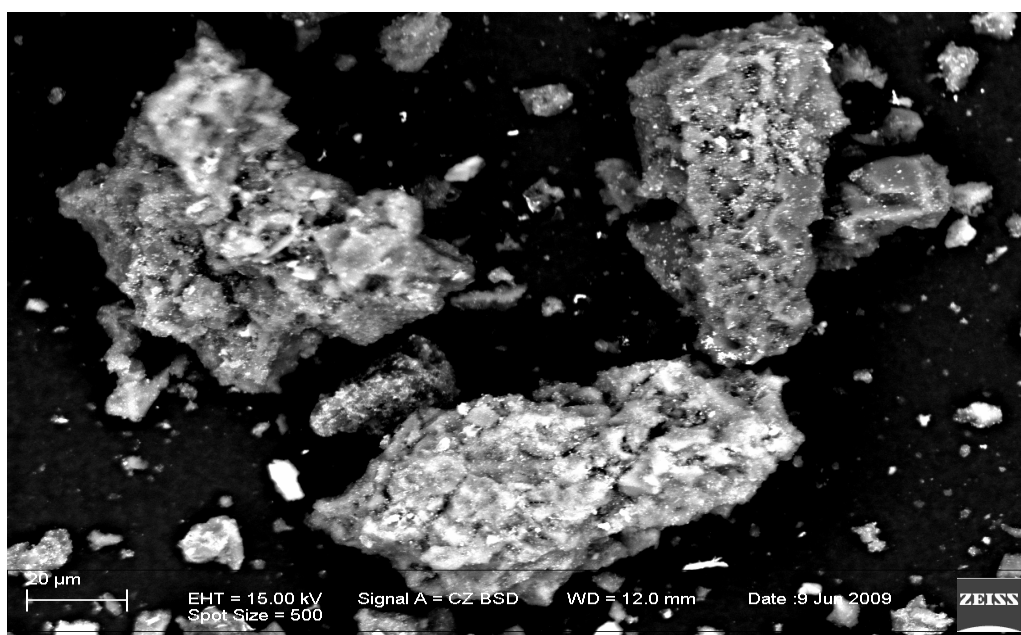


Figure 20: Back-scatter Detector image

To enhance more in-depth understanding within this area of research, it is imperative to utilise contemporary analytical tools which can provide insight on the catalyst's morphology and topography. The current research is very much dependent upon the structure of individual catalysts therefore such further analysis is deemed necessary. These analyses provide magnified images of the catalysts thus overcoming limitations of the human eye.

A good combination of analytical tools greatly enhanced the ability to justify the catalyst nature hence behaviour of various reactions as illustrated by each graphical representation of the results in the following sections. Such discussion is furthered by extension studies in which Scanning Electron Microscopy (SEM) facilitated the semi-quantitative analysis of catalysts that allows the determination of elements that make up the substance. Other functions and modes of the instrument include Energy Dispersive Spectroscopy (EDS) and detectors of back-scattered electrons (BSE). The capability of superior magnification of each image facilitated understanding obtained by pictorial images of specific areas or points on the sample. Clear spectrographs could be produced, where individual peaks convey information regarding the elements presence in a sample.

5.2 *Extension Study 1 – The Nature of Cobalt Impregnation on Activated Carbon*

As per the discussion on catalyst preparation in section 2.2, it is imperative to validate the results of such procedures before arriving at any research conclusions.

Scanning Electron Microscopy (SEM) tools provided different pictorial images of the catalyst. The Dispersive X-ray technologies discussed above provided images shown in figure 19 to figure 20, where the cobalt particles which have higher molecular weights with respect to activated carbon will appear as bright spots; these show strong contrast in relative to activated carbon which appears as dark solid images. Secondary Electron Imaging (SEI) illustrated the morphology of the catalyst while the BSE (Back-scatter Detector) showed the presence and relative location of cobalt on the catalyst. When Secondary Electron Imaging and Back-scatter Detection was carried out, it was provided extra attention to focus on the exact identical position for imaging.

The original intention during catalyst preparation was to allow the cobalt particles to enter via the pores on activated carbon and subsequently become trapped within. However, this did not occur, justified by the almost uniform bright image on the entire catalyst particle. It was found that cobalt exists as cobalt (III) oxide, forming a coated layer around the activated carbon particle. This coating effect would in turn lead to a lower adsorption ability of the catalyst due to a great reduction in available adsorptive surface area. However, albeit the lower adsorptive capability, catalyst function is still proven due to the oxidation reaction mechanisms as discussed in earlier sections.

Therefore, these findings highlight the importance of validating the true nature of any prepared catalysts to determine any variance from the initially envisaged phenomena. Similar approach is recommended for future research of new catalysts.

5.3 Extension Study 2 – Justifying the Presence of Cobalt (III) Oxide in the Catalyst

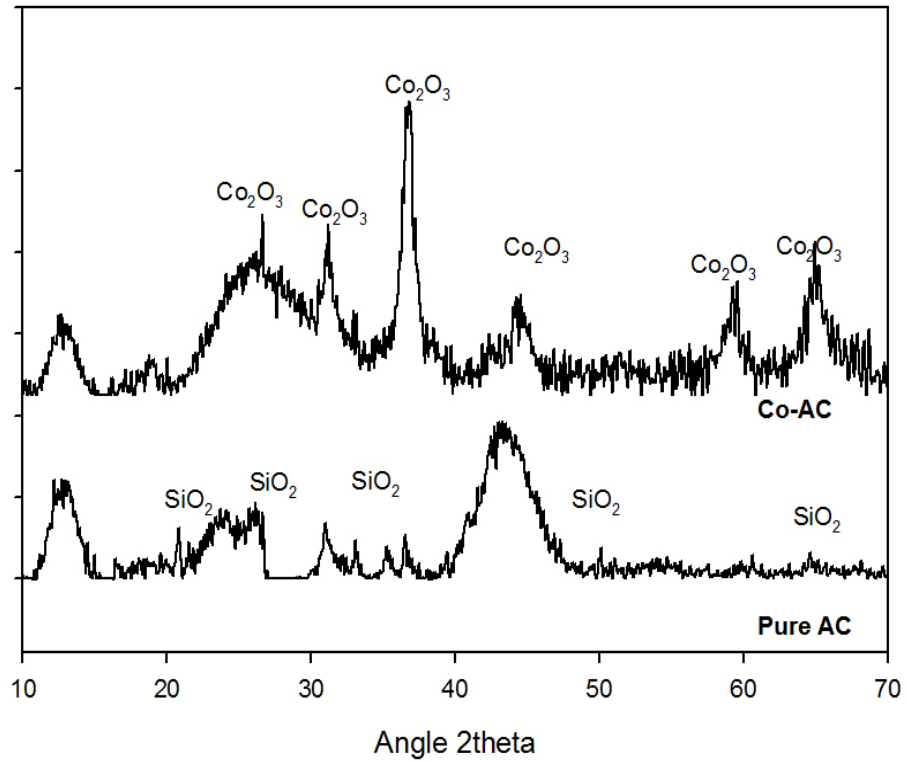


Figure 214: X-ray diffraction analysis

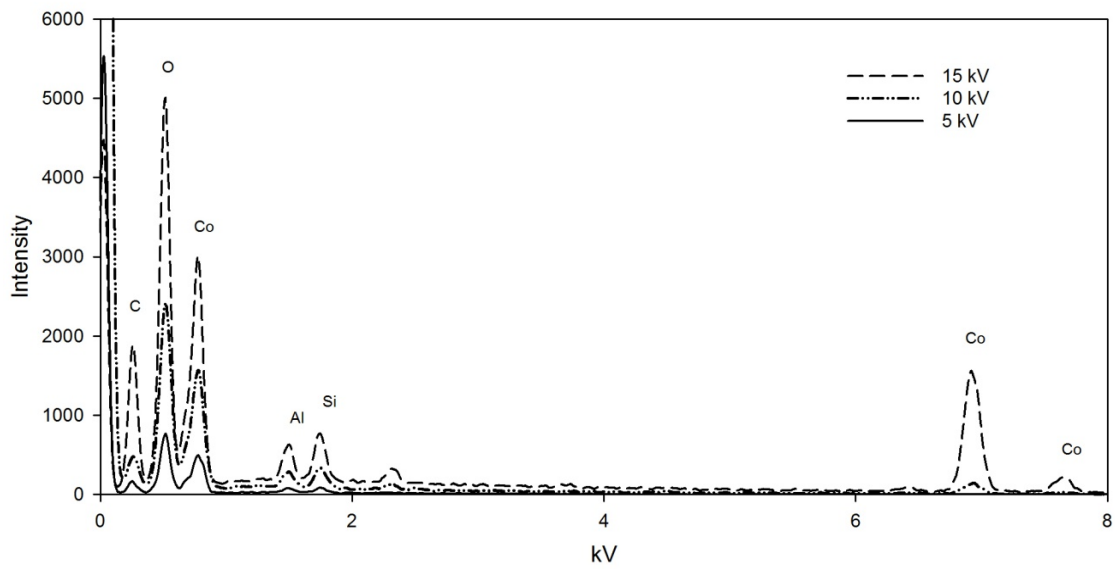


Figure 5 Energy Dispersive Spectroscopy analysis

X-Ray Diffraction analysis and the famous Bragg's Law provided insight on the crystallographic structure of the catalyst. Energy Dispersive Spectroscopy analysis provided full justifications of the presence of cobalt (III) oxide in the catalyst, based on the fact that all elements exhibit a unique atomic structure. Logically speaking, the presence of pure cobalt in the catalyst is very unlikely due to the non-inert nature of such a substance; however this assumption required means of justifying before conclusions were to be drawn. The above figures allowed the identification of the true elements that make up the catalyst. As per the different peaks in figure 22, it can be verified that the cobalt exists as cobalt (III) oxide within the catalyst. This also explains the phenomenon in Extension Study 1 where the impregnated cobalt was seen to form a coated layer around the surface of the activated carbon support.

5.4 *Extension Study 3 – Silver Impregnated Activated Carbon*

A silver based activated carbon catalyst sample was tested in a similar way as per the cobalt based catalyst in Extension Study 1. Discussion on the varying morphology between cobalt and silver based catalysts is provided as follows.

As mentioned in Extension Study 1, the understanding of catalyst morphology was greatly facilitated by SEM images which proved that the original intention of preparing a cobalt Impregnated activated carbon catalyst did not produce results as planned because of the crystalline structure of cobalt that resulted in an almost full coating around the carbon particle.

On the other hand, silver impregnated activated carbon appears because similar analysis as per the above discussion showed that silver is successfully penetrated into the activated carbon particle in an almost orderly manner (Shukla 2009). It can be reasonably deduced that the Silver based catalyst is likely to provide fresh insight due to the nature of the dot-like impregnated silver within the activated carbon pores. This nature of impregnation seemingly provides a larger available surface area for pure adsorption to occur, giving a good compromise between the combined mechanism of adsorption and oxidation to achieve the complete mineralisation of phenolic pollutants. This provides promising potential for the development of a more superior catalyst for the treatment of phenolic wastewater.

6.0 Conclusions

In a nutshell, the research objectives have been achieved and useful recommendations have been drawn. The combination of an oxidant (peroxymonosulphate), catalyst (cobalt impregnated activated carbon) and effective catalyst support (activated carbon) exhibit reasonably good performance towards the degradation of phenol. The research has proven the effect of various parameters on the reaction rates of phenol oxidation. These parameters include concentrations of phenol, catalyst, and oxidant; where catalyst and oxidant concentration have been proven to affect the rates following a well-justified linear relationship. The linear relationship between phenol concentration and reaction rate requires further validation. Moreover, the effect of temperature was proven to drive the reaction rates in an exponential manner.

The reusability tests presented certain ambiguity, however the results provided great insight regarding experimental methodology, and opened new doors of potential for further research into this phenomena shown.

7.0 Recommendations

As it is generally known that reaction rates are strongly influenced by the basic operating parameters such as temperature of pH, more research within these areas is recommended. Higher temperatures denote benefits in terms of faster reaction kinetics as per the Arrhenius equation; however there is the possibility of abnormal catalyst structure deviations at these more extreme conditions. In broader terms, a higher temperature would also incur a significantly higher operating cost. Therefore, not only should the feasibility of such conditions be tested, associated economical viability should also be studied. When conducting the experiments for studying the effect of temperature, it is recommended that samples be drawn at very small intervals especially when high reaction temperatures are applied. This recommendation is drawn from section 4.6 where the rapid oxidation rates lead to a complete reaction upon sample collection upon 5 minutes. However, due to the complicated nature of sample collection which involves syringing, filtering, and autopipetting at one go, it is recommended that the experiments should be carried out by simultaneously by more than one researcher. Any human error related experimental flaws will strongly affect the results due to the extremely fast oxidation kinetics associated with high temperature.

As per section 4.7, the phenomenon of higher degradation of catalyst activity exhibited by the second reusability test requires further justifications. An improved catalyst regeneration methodology is also proposed to avoid any uncertainties during results analysis caused by catalyst regeneration related inaccuracies. Heating periods in the oven should be optimised and kept constant. Subsequently, the reusability tests need to be repeated to arrive at validations and conclusions over the actually reusability behaviour of the catalyst.

The effect of stirring speed on reaction rates can be studied. This effect has so far been maintained constant at 400 rpm; it has been assumed that increasing the speed beyond this level would have negligible effects upon phenol oxidation. Further research focused on more detailed studies of this assumption is recommended, because although faster stirring enhances mixing hence drives the oxidation rates, stirring power consumption is directly increased by a higher speed. Operating cost is a significant contribution towards the feasibility of a catalyst and it generally dictates the long-term industrial success of such a catalyst, hence such considerations need to be included in all research.

Moreover, Energy Dispersive X-ray Technologies enhanced understanding of morphology and topography of the catalyst. Therefore, it is strongly recommended that similar examinations should be carried out on new catalysts to clearly identify their structures.

It is also recommended towards future researchers that extra care needs to be provided in order to keep other parameters strictly constant when the effect of another is being studied.

Due to the intimate relationship between catalyst and temperature, Differential Scanning Calorimetry (DSC) studies are recommended to gain insight on the thermal stability of the catalyst. This can facilitate trade off between more superior reaction kinetics associated with higher temperatures; and the protection of the catalyst's well-being at these more extreme conditions.

Nomenclature

A	Dimensionless	Pre-exponential factor or frequency factor
E	[J/mol]	Activation energy
k_1	[ppm ⁻¹ min ⁻¹]	Rate constant for first reaction
k_2	[ppm ⁻¹ min ⁻¹]	Rate constant for second reaction
$k(T)$	[ppm ⁻¹ min ⁻¹]	Specific rate constant at temperature T
M	[ppm]	Molarity of phenol
r_{1SO_4}	[min ⁻¹]	Generation rate of sulphate radical at first reaction
r_{SO_4}	[min ⁻¹]	Net rate of sulphate radical
r_{phenol}	[min ⁻¹]	Net rate of degradation of phenol
$-r_{2SO_4}$	[min ⁻¹]	Consumption rate of sulphate radical at second reaction
R	[J/mol]	Ideal gas constant
t	[min]	Time
V	[mL]	Volume of phenol
BSE		Back-scatter Detector
EDS		Energy Dispersive Spectroscopy
ppm		Parts per million
SEI		Secondary Electron Imaging
SEM		Scanning Electron Microscopy
TGA		Thermal Gravimetric Analysis
XRD		X-Ray Diffraction

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