

Research Projects 491 - 492

Semester 1 - 2 2009

Cobalt-containing Metal-organic Framework and Cobalt (II)

**Nitrate [Hexahydrous] Studies on The Degradation of
methylene blue, acid red 183 and reactive blue 4 in the
presence of Hydrogen Peroxide and Peroxymonosulfate**

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Declaration

“I declare that this report is my own work except where referenced to other sources, and all statements of fact in this report are true and correct to my best knowledge”.

Signature,

Sie King, Ling

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Dr. Shaobin Wang is greatly acknowledged for assisting and guiding throughout the research period.

Extended Abstract

Introduction

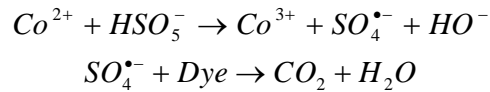
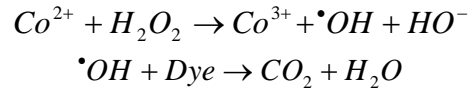
The dyes such as methylene blue, acid red 183 and reactive blue 4 are widely used in textile dyeing and printing industries. They pollute the water source and also cause serious environmental problems. Therefore, decolourization studies are required in order to degrade the polluted solution effectively. Most of the traditional treatment methods available in the market are inefficiency toward these dyes due to the large degree of aromatics presented (Wang, 2007). Therefore, alternative treatment must be discovered in order to solve the increasing pollution problems happening nowadays. There are currently a wide range of advanced oxidation processes (AOPs) developed for the treatment on aqueous waste streams and single treatment processes or combinations of ozonation, UV, Fenton processes, hydrogen peroxide and catalysts such as TiO_2 , WAO and WPO have all been widely investigated (Alsheyab, 2005). Advanced oxidation technologies involved highly reactive radicals, such as $\bullet OH$, $\bullet OOH$, $O_2^{\bullet -}$ and $SO_4^{\bullet -}$, is an excellent methods for degradation of organic pollutants (Chen et al. 2007).

The degradation of methylene blue, acid red 183 and reactive blue 4 are studied. The oxidizing agent involved in this research project was hydrogen peroxide (H_2O_2) and peroxymonosulfate, $KHSO_5$ (PMS). Both of the oxidizing agents have powerful oxidizing potential and can degrade numerous pollutants. Oxone ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) can be used to generate PMS, and 614.7 g/L of Oxone is necessary for release of 2 M PMS (Chen et al. 2007). The catalysts involved in this research project were cobalt-containing metal-organic framework (Co-MOF) and cobalt (II) nitrate [hexahydrous]. Both homogenous and heterogeneous cobalt-mediated activation of H_2O_2 and PMS (Co-MOF/ H_2O_2 , Co-MOF/PMS and Co^{2+}/ H_2O_2 , Co^{2+}/PMS) are studied.

MOF have attracted increasing academic and industrial interest in the last few years. The possible applications of MOFs are gas purification, gas separation, catalysts and sensors. A cobalt-containing metal-organic framework (Co-MOF) was anticipated to exhibit interesting catalytic activity. The objective of this research is to perform a cobalt-containing metal-organic framework (Co-MOF) in order to involve into the degradation of methylene blue, acid red 183 and reactive blue 4 with the presence of oxidizing agent. Apart from that, Co^{2+} (from cobalt (II)

nitrate [hexahydrous]) will also be involved into the degradation activities act as an alternative catalyst.

All the systems used cobalt ions to react with H_2O_2 and PMS respectively, producing sulfate radicals with powerful oxidizing ability to degrade organic pollutants according to the following reactions.



The degradation rate by using PMS as an oxidizing agent was expected to be faster than using H_2O_2 as an oxidizing agent. This is due to PMS higher powerful oxidizing potential compare to H_2O_2 . In addition, according to Chan (2009), the best combination for the generation of $SO_4^{\cdot-}$ is the coupling of Co (II) with PMS due to its much higher degradation efficiencies than others reaction such as Fenton. Therefore, it led to large reduction in treatment time.

Methodology

Method used to prepare cobalt-containing metal-organic framework was quoted from Mueller et al. (2005). The method used by this article is basically a multi-solvent recrystallization. Co-MOF particles were prepared by dissolving 4.22g of terephthalic acid and 14.79g of cobalt (II) nitrate [hexahydrous] into 300g of dimethyl-formamide. Dissolved solution was heated up to $130^\circ C$ for 4 hour. About 7.8g of sample was produced after 4 hour.

Methylene blue, acid red 183 and reactive blue 4 were prepared by dissolving into 1L of distillation water. The amount of methylene blue, acid red 183 and reactive blue 4 used were 6.5 mg, 165 mg and 165 mg respectively. The solutions were shake well and leaved for approximately one days before proceed to any experiment. Apart from that, hydrogen peroxide and oxone were dissolved into distilled water in order to obtain desired concentration. The amount of hydrogen peroxide and oxone are scaled up in order to obtain more accurate data.

An analytical method was carried out by withdrawing small quantity of the solution from the reactor at selected intervals for spectrophotometric analysis. However, for heterogeneous Co-MOF/H₂O₂ and Co-MOF/PMS reactions, 5 mL of the solution was withdrawn from the reactor. Solid in the solution was filtered out by using centrifuge before running the spectrophotometric analysis.

Results and Discussion

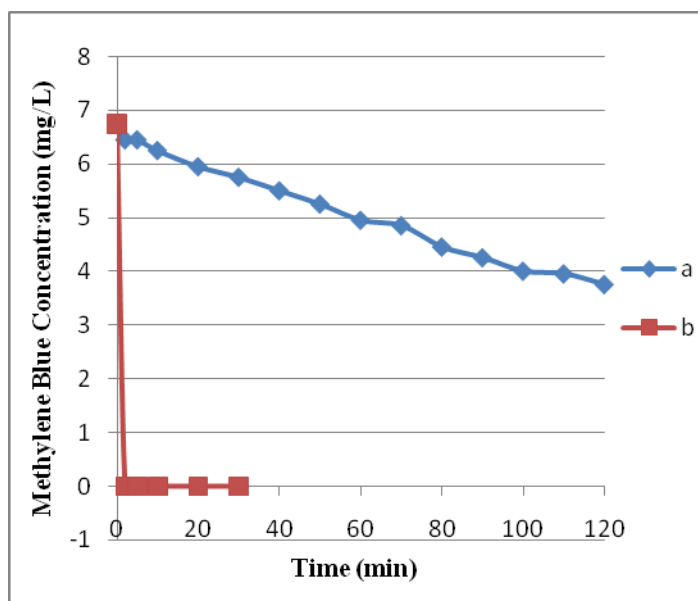


Figure 1: Degradation of 6.75 mg/L Methylene Blue by reacting 0.4g ($1.303 \times 10^{-2} M$) Co-MOF: (a) $4 \times 10^{-4} M$ PMS without Co-MOF, (b) $5 \times 10^{-5} M$ PMS, (c) $2 \times 10^{-4} M$ PMS

Curve (a) only involves $4 \times 10^{-4} M$ PMS in the process of degradation methylene blue solution. It shows that the degradation rate is very slow. 44.4% of methylene blue was degraded upon 120 minutes. The pH of

the solution at the end of the experiment was 3.67. Based on the curve, the degradation process has not reached its constant point. The degradation of PMS in 6.75 mg/L methylene blue solution with the presence of 0.1g ($3.258 \times 10^{-3} M$) Co-MOF under $2 \times 10^{-4} M$ PMS showed a very fast reaction. Methylene Blue took 2 minutes to reach 99.6% degradation. Further degradation does not happen significantly after 2 minutes.

Three recycling runs of the Co-MOF catalyst on methylene blue were carried out. As shown in **Fig. 2**, the regenerated catalyst exhibits excellence and stable performance. The degradation rate of methylene blue remains almost unchanged compare to the initial process. The weight of Co-MOF after initial, 1st recycling and 2nd recycling process were still remained almost the same as before react. This indicates that the catalyst has an excellent long-term stability by using PMS as an oxidizing agent.

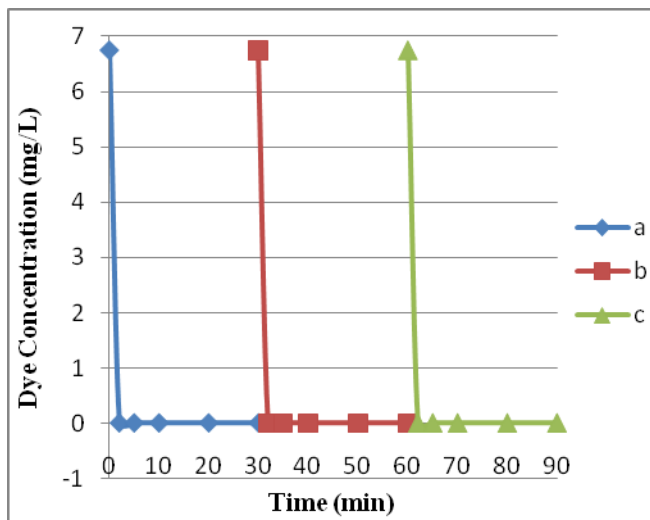


Figure 21: Cyclic degradation of 6.75 mg/L methylene blue by reacting 0.4g ($1.3029 \times 10^{-2} M$) of Co-MOF with $2 \times 10^{-4} M$ PMS : (a) Initial, (b) 1st recycling, (c) 2nd recycling

The results support the initial view that this Co-MOF/PMS can be reused and recovered for the catalytic oxidation of methylene blue without obvious decrease of catalytic activity.

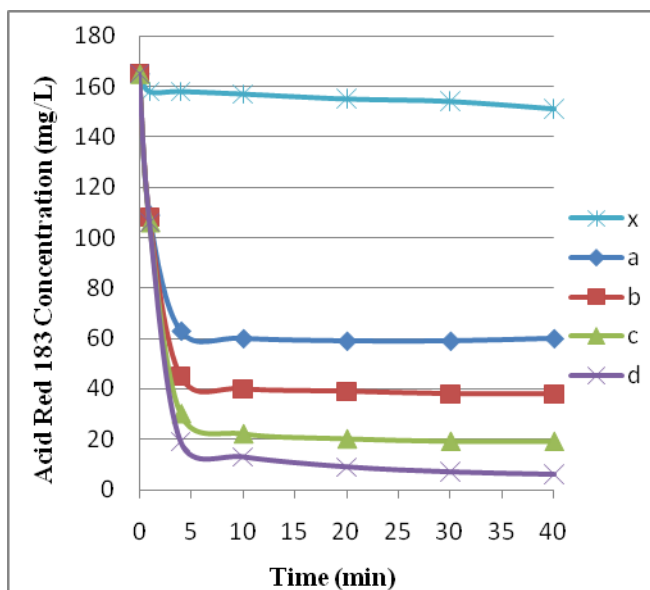


Figure 3: Degradation of 165 mg/L acid red 183 by reacting 0.1g ($3.258 \times 10^{-3} M$) of Co-MOF with different concentration of PMS: (x) $4 \times 10^{-4} M$ PMS without Co-MOF, (a) $2 \times 10^{-4} M$ PMS, (b) $2.6 \times 10^{-4} M$ PMS, (c) $4 \times 10^{-4} M$ PMS, (d) $8 \times 10^{-4} M$ PMS

The result is getting better by increasing the concentration of PMS. However, it results in higher Co-MOF lost. Co-MOF was dissolved into the solution for primary judgments.

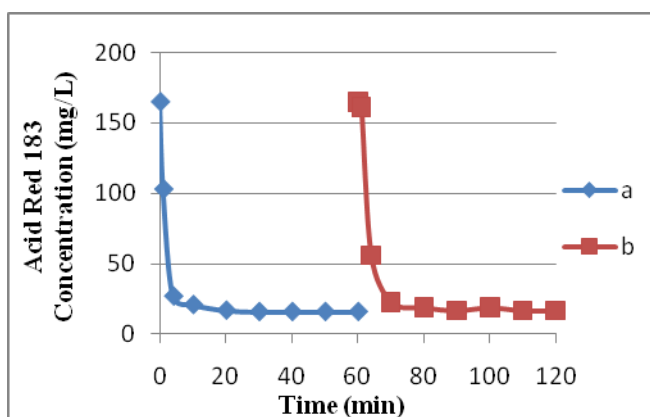


Figure 4: Cyclic degradation of 165 mg/L acid red 183 by reacting 0.1g ($3.258 \times 10^{-3} M$) of Co-MOF with $4 \times 10^{-4} M$ PMS : (a) Initial, (b) 1st recycling

Three recycling runs of the Co-MOF catalyst on acid red 183 were carried out. As shown in **Fig. 4**, the regenerated catalyst

exhibits excellence and stable performance. The degradation rate of acid red 183 is only slightly slower at 1st recycling compare to the initial. The weight of Co-MOF after initial and 1st recycling process was 0.068g, 0.066g.

This indicated that the lost of Co-MOFs are quite significant. Preliminary surmise is that, some Co-MOF gets dissolved during the degradation. However, as overall, the performance still showing the catalyst has an excellent long-term stability by using PMS as an oxidizing agent. The results support the initial view that this Co-MOF/PMS can be reused and recovered for the catalytic oxidation of methylene blue without obvious decrease of catalytic activity.

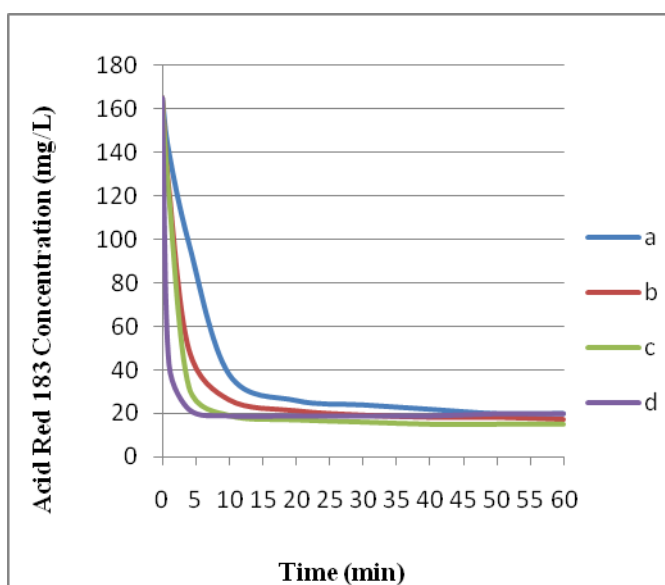


Figure 5: Degradation of 165 mg/L acid red 183 by reacting $4 \times 10^{-4} M$ PMS 0.1g Co-MOF: (a) 8°C, (b) 15°C, (c) 25°C, (d) 40°C

The degradation of acid red 183 under different temperatures is showed in *Fig. 5*. Based on the results, the reaction rate gets faster when temperature of solution increases. At 40°C, degradation was completed (88.5%) within 10 minutes. However, with the same amount of

degradation conditions, 8°C solution required 50 minutes to achieve.

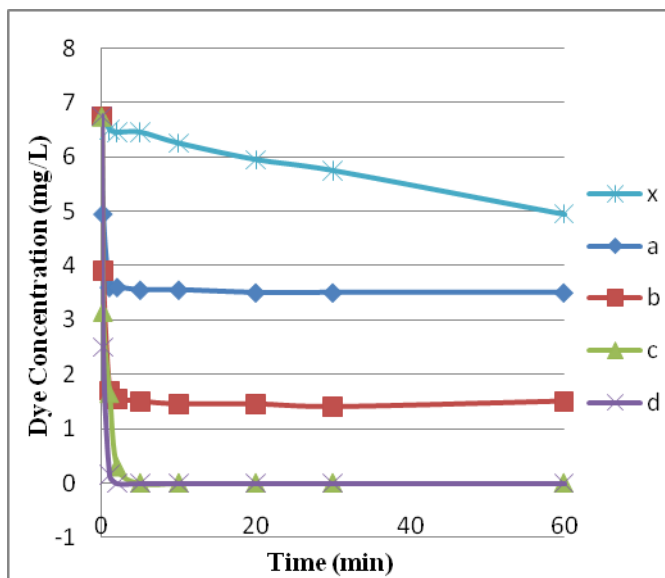


Figure 6: Degradation of 6.75 mg/L methylene blue by reacting $1.303 \times 10^{-4} M$ of Co^{2+} with different concentration of PMS: (x) $4 \times 10^{-4} M$ PMS without Co^{2+} (a) $5 \times 10^{-5} M$ PMS, (b) $1 \times 10^{-4} M$ PMS, (c) $2 \times 10^{-4} M$ PMS, (d) $4 \times 10^{-4} M$ PMS.

It can be easily observed that, the degradation result is getting better by

increasing the concentration of PMS. Apart from that, the degradation rate also increases sharply with the increase of PMS concentration.

Executive Summary

A cobalt-containing metal-organic framework (Co-MOF) was investigated and the decolourization of methylene blue, acid red 183 and reactive blue 4 were studied using Co-MOF and Co^{2+} with hydrogen peroxide and peroxymonosulfate as an oxidizing agent were studied. Apart from that, the degradation of acid red 183 under different temperatures was carried out. Dyes degradation in homogeneous $\text{Co}^{2+}/\text{H}_2\text{O}_2$ was faster than using heterogeneous Co-MOF/ H_2O_2 systems. However, both of the catalysts gave similar results when PMS was used as the oxidizing agent. Besides that, without the presence of any catalysts in methylene blue and acid red 183, H_2O_2 and PMS gave a poor degradation rate. Based on the results, H_2O_2 is totally unable to degrade the dyes without catalysts. However, PMS still have an ability to degrade dyes by itself but much longer time is required. Furthermore, all the degradation on methylene blue either by homogeneous or heterogeneous systems was faster than the solution of acid red 183 and reactive blue 4. This indicated that basic dye is easier to degrade. Regenerated catalyst by using PMS as an oxidizing agent exhibits excellence and stable performance. Thus, Co-MOF can be reused and recovered for the catalytic oxidation of methylene blue and acid red 183 without obvious decrease of catalytic activity. However, Co-MOF/ H_2O_2 system gave poor recycling results. The degradation rate of methylene blue was degenerated compare to the initial process. On the other hand, at 40°C , degradation of 165 mg/L acid red 183 with the presence of Co-MOF/PMS was completed (88.5%) within 10 minutes. However, with the same amount of degradation conditions, 8°C solution required 50 minutes to achieve. This indicated that the reaction rate gets faster when temperature of solution increases. The concentration of reactive blue 4 in the water getting increases rather than keep at the constant point after it was degraded to its maximum point by using Co-MOF/PMS. This shown that the catalysts are unable effectively degrades the dye of reactive blue 4.

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1 Introduction

1.1 Project Background

In this project, the degradation of methylene blue, acid red 183 and reactive blue 4 are studied. A cobalt-containing metal-organic framework (Co-MOF) and cobalt (II) nitrate [hexahydrate] are the catalysts used with hydrogen peroxide and peroxydisulfate as an oxidizing agent.

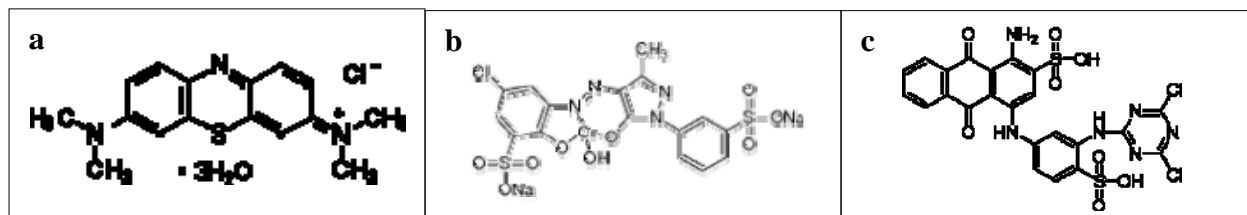


Figure 2: Chemical structure: a) Methylene blue, b) Acid red 183, c) Reactive blue 4 (source: *Sigma Aldrich Co.* 2009)

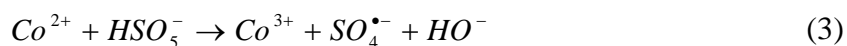
The dyes such as methylene blue, acid red 183 and reactive blue 4 shown in *Fig. 1* above are widely used in textile dyeing and printing industries. These dyes can be easily dissolved into water to form a colour solution. Thus, they pollute the water source and also cause serious environmental problems. The presence of even minute amount of coloring substance makes it unsuitable for drinking or other recreational purposes. Therefore, decolourization studies are required in order to degrade the polluted solution effectively. Most of the traditional treatment methods available in the market are inefficiency toward these dyes due to the large degree of aromatics presented (Wang, 2007). Therefore, alternative treatment must be discovered in order to solve the increasing pollution problems happening nowadays. There are currently a wide range of advanced oxidation processes (AOPs) developed for the treatment on aqueous waste streams and single treatment processes or combinations of ozonation, UV, Fenton processes, hydrogen peroxide and catalysts such as TiO_2 , WAO and WPO have all been widely investigated (Alsheyab, 2005). Advanced oxidation technologies involved highly reactive radicals, such as $\cdot\text{OH}$, $\cdot\text{OOH}$, $\text{O}_2^{\cdot-}$ and $\text{SO}_4^{\cdot-}$, is an excellent methods for degradation of organic pollutants (Chen et al. 2007).

The oxidizing agent involved in this research project was hydrogen peroxide (H₂O₂) and peroxymonosulfate, KHSO₅ (PMS). Both of the oxidizing agents have powerful oxidizing potential and can degrade numerous pollutants. Oxone (2KHSO₅ · KHSO₄ · K₂SO₄) can be used to generate PMS, and 614.7 g/L of Oxone is necessary for release of 2 M PMS (Chen et al. 2007).

The catalysts involved in this research project were Co-MOF and cobalt (II) nitrate [hexahydrate]. Both homogenous and heterogeneous cobalt-mediated activation of H₂O₂ and PMS (Co-MOF/ H₂O₂, Co-MOF/PMS and Co²⁺/ H₂O₂, Co²⁺/PMS) are studied.

Metal-organic frameworks (MOFs) in heterogeneous process are a new class of crystalline porous inorganic-organic hybrid compounds that having a cage structure of metal ions coordinated to organic compounds. MOF have aroused several studies regarding the characterization of known structures and the design of new systems due to their large crystalline pore spaces, surface area as well as the flexibility of pore design characteristic (Biemmi 2007). Thus, MOF have attracted increasing academic and industrial interest in the last few years. The possible applications of MOFs are gas purification, gas separation, catalysts and sensors. A cobalt-containing metal-organic framework (Co-MOF) was anticipated to exhibit interesting catalytic activity.

All the systems used cobalt ions to react with H₂O₂ and PMS respectively, producing sulfate radicals with powerful oxidizing ability to degrade organic pollutants according to the following reactions.



Chemical reaction (1) and (2) illustrate Co-MOF/ H₂O₂ and Co²⁺/ H₂O₂ reaction. While the reaction of Co-MOF/ PMS and Co²⁺/ PMS are show in chemical reaction (3) and (4).

1.2 Objectives

The objective of this research is to perform a cobalt-containing metal-organic framework (Co-MOF) in order to involve into the degradation of methylene blue, acid red 183 and reactive blue 4 with the presence of oxidizing agent. Apart from that, Co^{2+} (from cobalt (II) nitrate [hexahydrate]) will also be involved into the degradation activities act as an alternative catalyst.

1.3 Expected Outcomes

The degradation rate of Co-MOF/PMS on methylene blue was expected to be faster than using H_2O_2 as an oxidizing agent. This is due to PMS higher powerful oxidizing potential compare to H_2O_2 . In addition, according to Chan (2009), the best combination for the generation of $\text{SO}_4^{\bullet-}$ is the coupling of Co (II) with PMS due to its much higher degradation efficiencies than others reaction such as Fenton. Therefore, it led to large reduction in treatment time.

Besides that, the degradation rate of Co-MOF/ H_2O_2 and Co-MOF/ PMS on methylene blue was expected to be faster than using acid red 183 and reactive blue 4. This is due to basic dye easier to degrade compared to the rest. Besides that, recycling of Co-MOFs is expected to have similar degrade ability toward all the dyes compared to its first use.

The homogeneous $\text{Co}^{2+}/\text{H}_2\text{O}_2$ and $\text{Co}^{2+}/\text{PMS}$ reagent were expected to have excellence performance as Co-MOF/ H_2O_2 and Co-MOF/PMS systems in degradation of methylene blue, acid red 183 and reactive blue 4. Apart from that, degradation rate of $\text{Co}^{2+}/\text{PMS}$ on methylene blue is also believed to be faster than using H_2O_2 as an oxidizing agent. The degradation rate of $\text{Co}^{2+}/\text{H}_2\text{O}_2$ and $\text{Co}^{2+}/\text{PMS}$ on methylene blue was also expected to be faster than using acid red 183 and reactive blue 4.

1.4 Significance

Dyes are widely used in our daily life and also in some companies such as, textile dyeing and printing industries. These types of company are always produce huge amount of wastewater and colour into the water sources (Wang, 2007). Therefore, this research will be useful not only to chemical industries but also to the society & environment. It will help to breathe new hope to our society.

Due to textile industrial create high water pollutants and consumes a huge amount of water, degradation technique can be applied to textile industrial wastewater in order to save a huge amount of water. Treated water not only save our environment but it also can be recycled or reused in other applications that required less quality water. This is an excellent means for saving huge amount of water, especially in the countries which are suffered with water deficiency (Abbas, 2008).

2 Materials

All the materials used were supplied by Department of Chemical Engineering, Curtin University of Technology. The lists of the materials used in this experiment are shown below.

2.1 Cobalt-containing Metal-organic Framework, Co-MOF

Co-MOF, a light brown particle was used as a catalyst to react with oxidizing agent in order to perform degradation of methylene blue, acid red 183 and reactive blue 4. Co-MOF was prepared by Sie King, Ling. The materials involved in the preparation are terephthalic acid, dimethyl-formamide and cobalt (II) nitrate [hexahydrous].

2.2 Cobalt (II) Nitrate [Hexahydrous], $Co(NO_3)_2 \cdot 6H_2O$

$Co(NO_3)_2 \cdot 6H_2O$ was used as a catalysts to react with oxidizing agent in order to perform degradation of methylene blue and acid red 183. The material is in dark orange colour and it gives purple colour when dissolved into solution.

2.3 Hydrogen Peroxide, H_2O_2

H_2O_2 30%, a water-like liquid was used as an oxidizing agent of Co-MOF and Co^{2+} throughout the degradation process. It is stored in dark container to prevent any oxidation from light. H_2O_2 is a weak acid with strong oxidizing properties. Its oxidation potential is equal to 1.8 (Lennotech Water treatment & purification Holding 2009).

2.4 Oxone, $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$

Oxone ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) can be used to generate Peroxymonosulfate (PMS). A 614.7 g/L of Oxone is necessary for release of 2 M PMS (Chen et al. 2007). PMS has powerful oxidizing potential and can degrade many pollutants. The use of oxone has increased rapidly. This is due to the stability, simple handling, non-toxic nature, versatility of the reagent and low costs (*Organic Chemistry Portal* 2003). PMS will be used as an oxidizing agent of Co-MOF and Co^{2+} throughout the degradation process.

2.5 Methylene Blue Dye

Methylene blue is a very commonly used basic dye and is widely used in a range of chemistry and biology fields (**Fig.1**). It is heterocyclic aromatic chemical compounds with molecular formula of $C_{16}H_{18}ClN_3S$ for methylene blue (*Mallinckrodt Baker*, 2008). The dye can be easily dissolved into water to form a blue colour solution. Thus, it pollutes the water source and also causes environmental problems. Methylene blue was used as a chemical compound for Co-MOF and Co^{2+} in this project. The maximum UV absorption is 663.85. The concentration used throughout the experiment is 6.5 mg/L.

2.6 Acid Red 183 Dye

Acid Red 183 is another type of dye used in chemistry field (**Fig. 1**). It has a molecular formula of $C_{16}H_{11}ClN_4Na_2O_8S_2 \cdot xCr$ (*Sigma Aldrich* 2009). The dye can also be easily dissolved into water to form a dark orange colour solution. Acid red 183 was used as a chemical compound for Co-MOF and Co^{2+} throughout the project. The maximum UV absorption is 493.62. The concentration used throughout the experiment is 165 mg/L.

2.7 Reactive Blue 4 Dye

Reactive blue 4 dye is an anthraquinone-base chlorotriazine dye. It is very important in cellulosic fabrics and textile industry (**Fig.1**). It has a molecular formula of $C_{23}H_{14}Cl_2N_6O_8S_2$ (*Sigma Aldrich* 2009). The indigo colour solution is form when reactive Blue 4 dissolved in to water. It strong colour of discharged dyes has a harmful influence on our environment due to its turbidity and high pollution strength. The maximum UV absorption of this synthetic dye is 602.09 and the concentration used throughout the experiment is 165 mg/L.

2.8 Distillated Water

Distillated water is necessary throughout the experiment. It was used to prepare model compound solutions and used to wash Co-MOF for recycling purpose. Apart from that, all the equipments were washed by distillated water before and after use.

3 Methodologies

Method used to prepare cobalt-containing metal-organic framework was quoted from Mueller et al. (2005). The method used by this article is basically a multi-solvent recrystallization. The recipe was repeatedly checked and scaled-up to the order of kg. While the ratio of each compound involved was provided by vice-supervisor, Dr. Peng. Therefore, this method is believed to be able to generate high quality of product. *Fig. 2* below illustrates the typical principle flowsheet scheme of a semi-technical process.

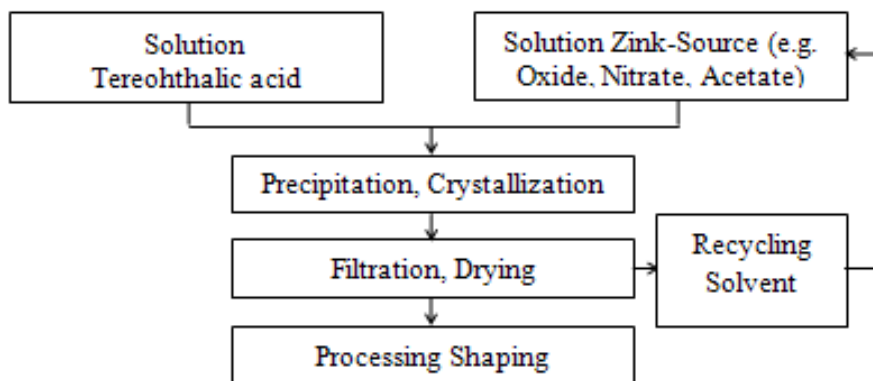


Figure 3: Principle flowsheet scheme of MOF synthesis procedure (source: Mueller et al. 2005)

Methylene blue, acid red 183 and reactive blue 4 were prepared by dissolving into 1L of distillation water. The amount of methylene blue, acid red 183 and reactive blue 4 used were 6.5 mg, 165 mg and 165 mg respectively. The solutions were shake well and leaved for approximately one days before proceed to any experiment.

Hydrogen peroxide and oxone were dissolved into distillated water in order to obtain desired concentration. The amount of hydrogen peroxide and oxone are scaled up in order to obtain more accurate data. Let say 0.02459g of oxone is required to produce $4 \times 10^{-4} M$ PMS. So, the amount

of oxone will be scaled up to 0.2459g, which is 10 times larger. After that, filling the distilled water into 0.2459g of oxone until the total weight equals to 10g. Scale back to the desired concentration by dividing 10. Therefore, 1g of the solution is able to produce $4 \times 10^{-4} M$ PMS. Same procedure was applied to obtain the rest of the oxidizing agent's concentration. The calculation of concentration was illustrated in *Appendices*.

Co-MOF was filtered by using centrifuge after the reaction and washed three times by using distilled water. After that, it was pour into a beaker and dry up in an oven. The weight of the remaining particles was obtained by dividing the weight of the beaker containing dry Co-MOF with the empty beaker.

4 Experimental

4.1 Cobalt-containing Metal-organic Framework Preparation

Co-MOF particles were prepared by dissolving 4.22g of terephthalic acid and 14.79g of cobalt (II) nitrate [hexahydrous] into 300g of dimethyl-formamide. Dissolved solution was heated up to $130^{\circ}C$ for 4 hour. After about 45 minutes, purple crystallization started to form. After 2 hours later, purple crystallization progressively changed into brown colour. Following a total of 4 hours, the reaction product was cooled down to room temperature. The solid was filtered out by using centrifuge and washed three times with DMF. Finally about 7.8g of sample was produced after dried up in the oven at $120^{\circ}C$ for 10 hour.

4.2 Heterogeneous Co-MOF/ H_2O_2 and Co-MOF/PMS Reactions

The degradation experiments were carried out in a 200 mL erlenmeyer flash. Dye with 200 mL volume was filled into the erlenmeyer flash with 700 rpm stirring speed at room temperatures which is approximately $26^{\circ}C$. 0.4 g ($1.303 \times 10^{-2} M$) of Co-MOF was used to activate different concentration of H_2O_2 and PMS. Those solutions were added into 200 mL of dye solution. Methylene blue, acid red 183 and reactive blue 4 were used as the dye solutions in this degradation experiment. During the recycling section, catalyst was separated and thoroughly washed with distilled water after each cycle and then the catalyst was dried at $100^{\circ}C$ for 10 hour

in order to remove the water. Experiment was repeated with different loading of Co-MOF as well as carried out under temperature variation conditions, which is 8°C, 15°C and 40°C.

4.3 Homogeneous $\text{Co}^{2+}/\text{H}_2\text{O}_2$ and $\text{Co}^{2+}/\text{PMS}$ Reactions

The degradation experiments were carried out in a 200 mL erlenmeyer flash. Dye with 200 mL volume was filled into the erlenmeyer flash with 700 rpm stirring speed at room temperature which is approximately 26°C. $1.303 \times 10^{-2} \text{ M}$ of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was used to activate different concentration of H_2O_2 and $1.303 \times 10^{-4} \text{ M}$ of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was used to activate different concentration of PMS. Those solutions were added into 200 mL of dye solution. Methylene blue & acid red 183 were used as dye solutions in this degradation experiment.

4.4 Analytical Methods

For homogeneous $\text{Co}^{2+}/\text{H}_2\text{O}_2$ and $\text{Co}^{2+}/\text{PMS}$ reactions, a small quantity of the solution was withdrawn from the reactor at selected intervals for spectrophotometric analysis. However, for heterogeneous Co-MOF/ H_2O_2 and Co-MOF/PMS reactions, 5 mL of the solution was withdrawn from the reactor. Solid in the solution was filtered out by using centrifuge before running the spectrophotometric analysis. The obtained absorbance and adsorption was converted into concentration of particular dyes by using calibration curve.

5 Results & Discussions

5.1 Calibration Curve

Calibration Curve of Methylene Blue

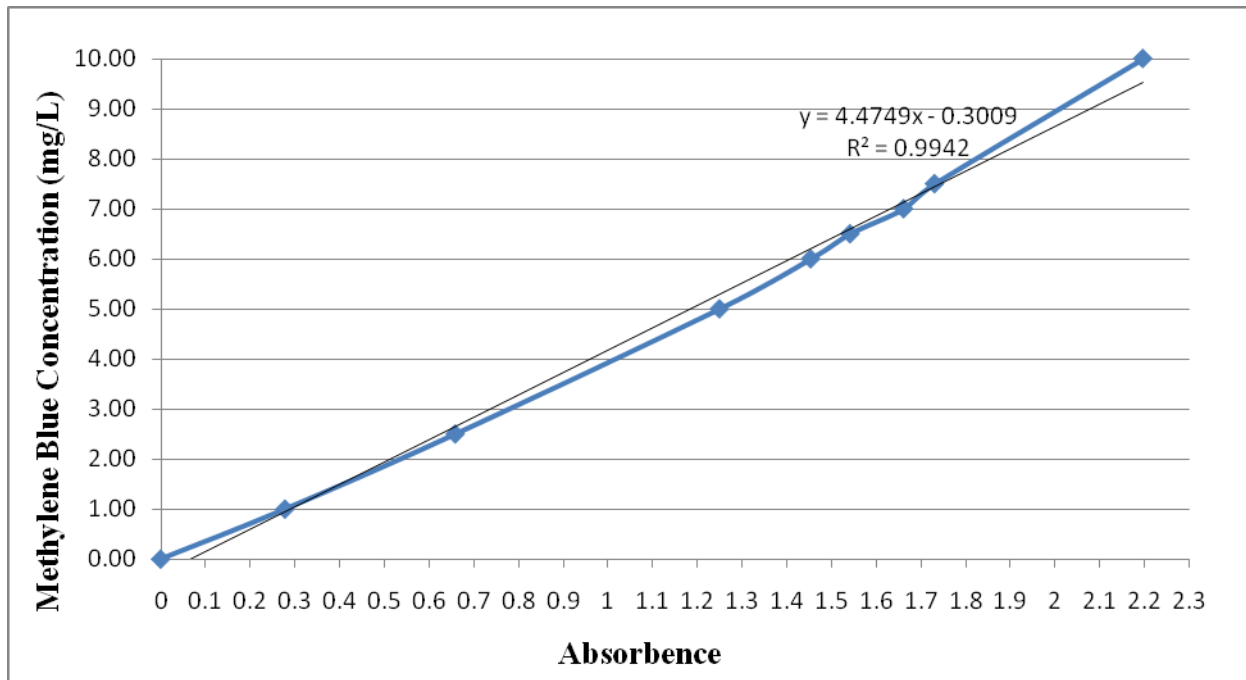


Figure 4: Calibration curve of methylene blue

Calibration Curve of Acid Red 183

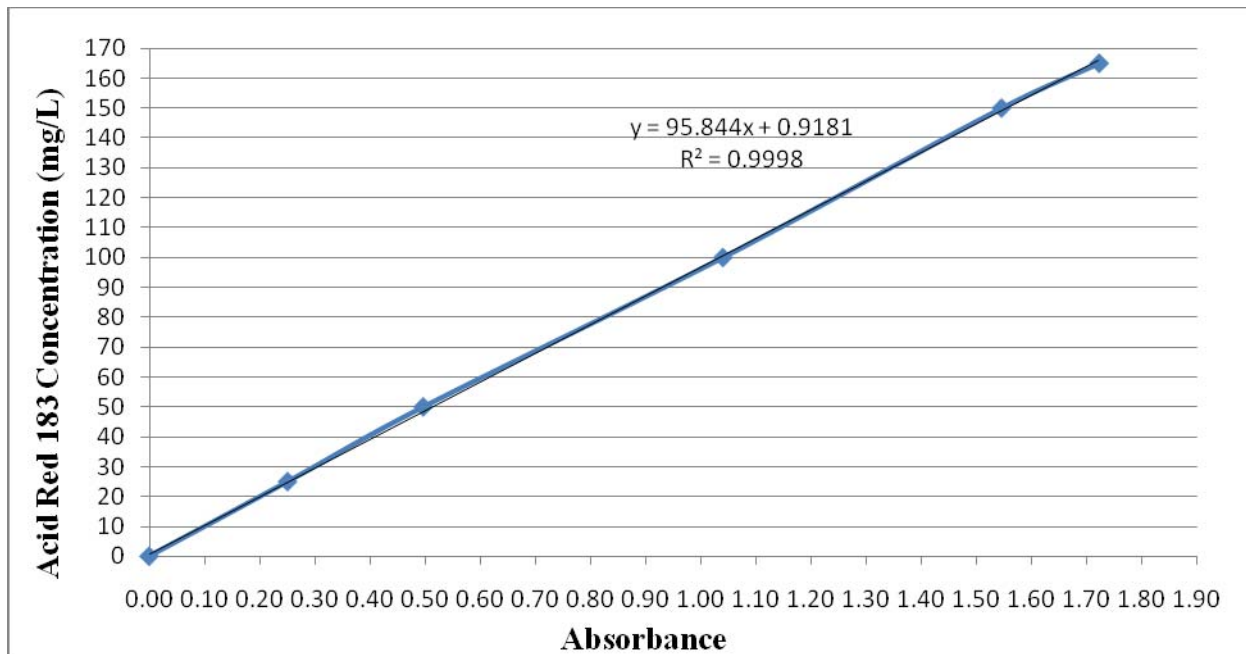


Figure 5: Calibration curve of acid red 183

Calibration Curve of Reactive Blue 4

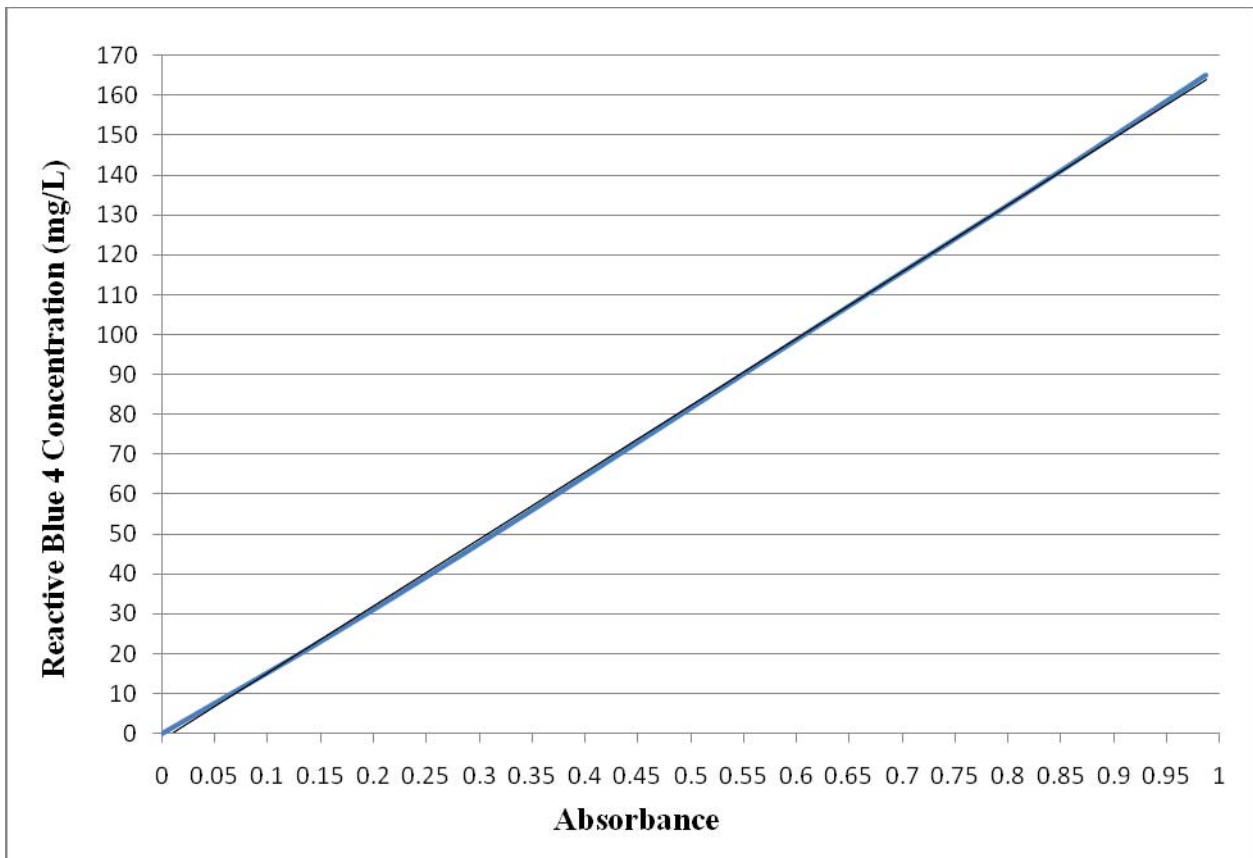


Figure 6: Calibration curve of reactive blue 4

5.2 Catalytic Activity of Co-MOF (Methylene Blue Degradation)

Effect of H_2O_2 Concentrations on Methylene Blue

The degradation of methylene blue under different concentration of H_2O_2 is showed in **Fig. 6**. Experiment was carried out by varying the concentration of H_2O_2 in 6.75 mg/L methylene blue solution with the presence of 0.4g ($1.303 \times 10^{-2} M$) Co-MOF.

Curve (x) presented in **Fig. 6** was carried out without the presence of Co-MOF. With the presence of just $4 \times 10^{-2} M H_2O_2$, only 3.7% of methylene blue degraded after 10 minutes. Further degradation does not happen after 10 minutes. The pH of solution after reaction was 6.4.

For the presence of 0.4g ($1.303 \times 10^{-2} M$) Co-MOF without any oxidizing agent inside methylene blue solution, only 22.2% of methylene blue degraded after 10 minutes. Further degradation does not happen significantly after 10 minutes. Degradation happened at the beginning with the absent of oxidizing agent most probably due to the adsorption ability of Co-MOF (**curve y**). The pH of solution after reaction was 7.8. There were 0.38g of Co-MOF remained after experiment.

However, with the presence of $6 \times 10^{-2} M H_2O_2$, nearly 37% of methylene blue was removed after 10 minutes and the degradation keep constant at 48.9% after 90 minutes (curve a). For $8 \times 10^{-2} M H_2O_2$, nearly 36.3% of methylene blue was removed after 10 minutes and the degradation keep constant at 58.5% after 90 minutes (curve b). Co-MOF remained after experiment was 0.38g for both curve (a) and (b).

For the presence of $1 \times 10^{-1} M H_2O_2$, nearly 39.3% of methylene blue was removed after 10 minutes and the degradation reach its constant point at 71.9% after 90 minutes (curve c). For $1.2 \times 10^{-1} M H_2O_2$, nearly 44.4% of methylene blue was removed after 10 minutes and the degradation reach its constant point at 83.7% after 90 minutes (curve d). Co-MOF remained after experiment were 0.38g and 0.37g for curve (c) and (d) respectively. The pH for curve (a) to (d) was more or less fall at 7.6. It can be easily observed that, the result is getting better by increasing the concentration of H_2O_2 .

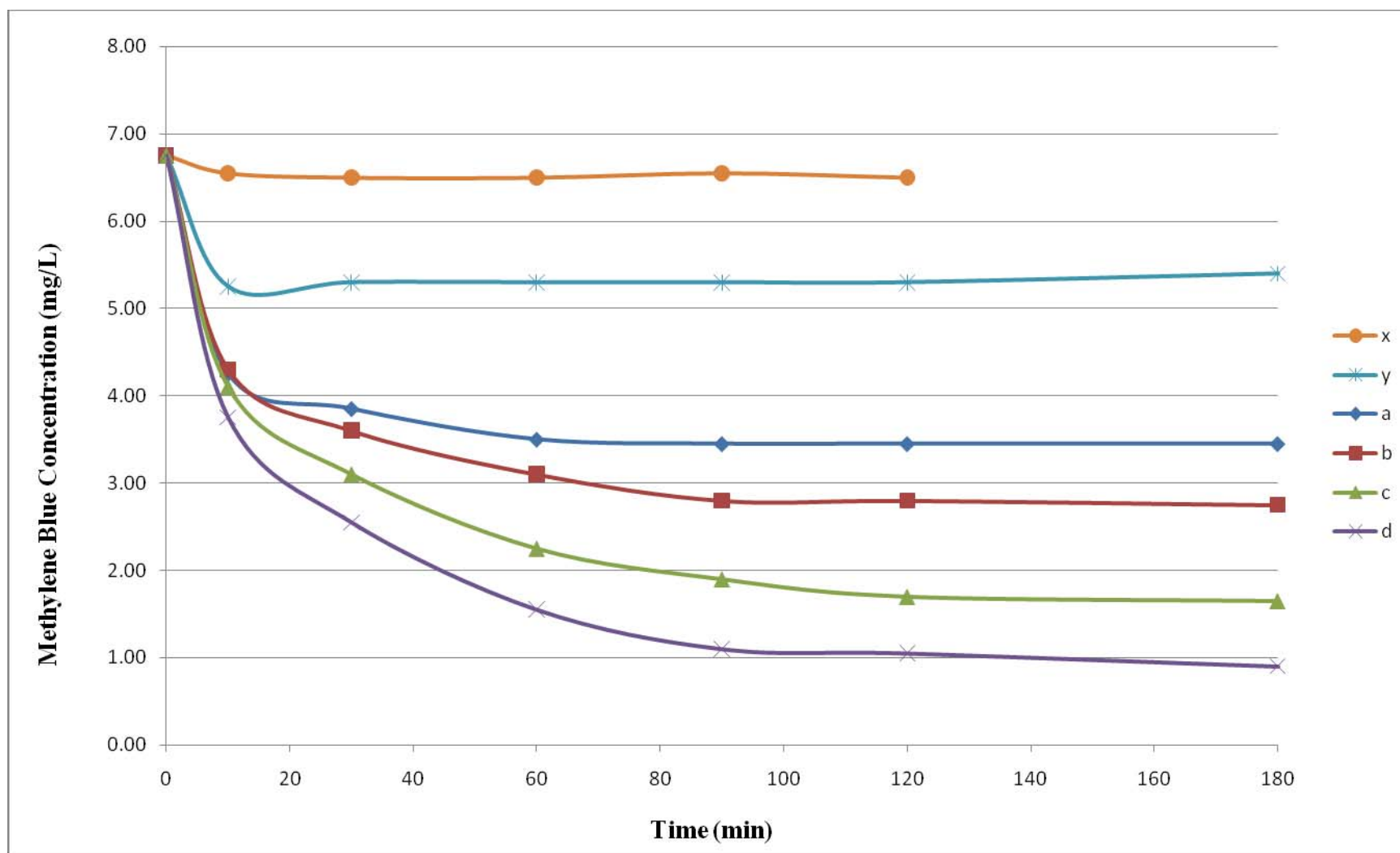


Figure 7: Degradation of 6.75 mg/L methylene blue by reacting 0.4g ($1.303 \times 10^{-2} M$) of Co-MOF with different concentration of H_2O_2 : (x) $4 \times 10^{-2} M H_2O_2$ without Co-MOF (y) no H_2O_2 , (a) $6 \times 10^{-2} M H_2O_2$, (b) $8 \times 10^{-2} M H_2O_2$, (c) $1 \times 10^{-1} M H_2O_2$, (d) $1.2 \times 10^{-1} M H_2O_2$.

Effect of PMS Concentrations on Methylene Blue

The degradation of methylene blue under different concentration of PMS is showed in **Fig. 7**. Experiment was carried out only in two aspects. Curve (a) only involves $4 \times 10^{-4} M$ PMS in the process of degradation methylene blue solution. It shows that the degradation rate is very slow. 44.4% of methylene blue was degraded upon 120 minutes. The pH of the solution at the end of the experiment was 3.67. Based on the curve, the degradation process has not reached its constant point. Therefore, longer time required for it to further degrade the methylene blue presented in water.

On the other hand, the degradation of PMS in 6.75 mg/L methylene blue solution with the presence of 0.1g ($3.258 \times 10^{-3} M$) Co-MOF was too fast. The best and only readable data is showed in **Fig. 7**, curve (b). It can be easily observed that the degradation of methylene blue under $2 \times 10^{-4} M$ PMS showed a very fast reaction. Methylene Blue took 2 minutes to reach 99.6% degradation. Further degradation does not happen significantly after 2 minutes.

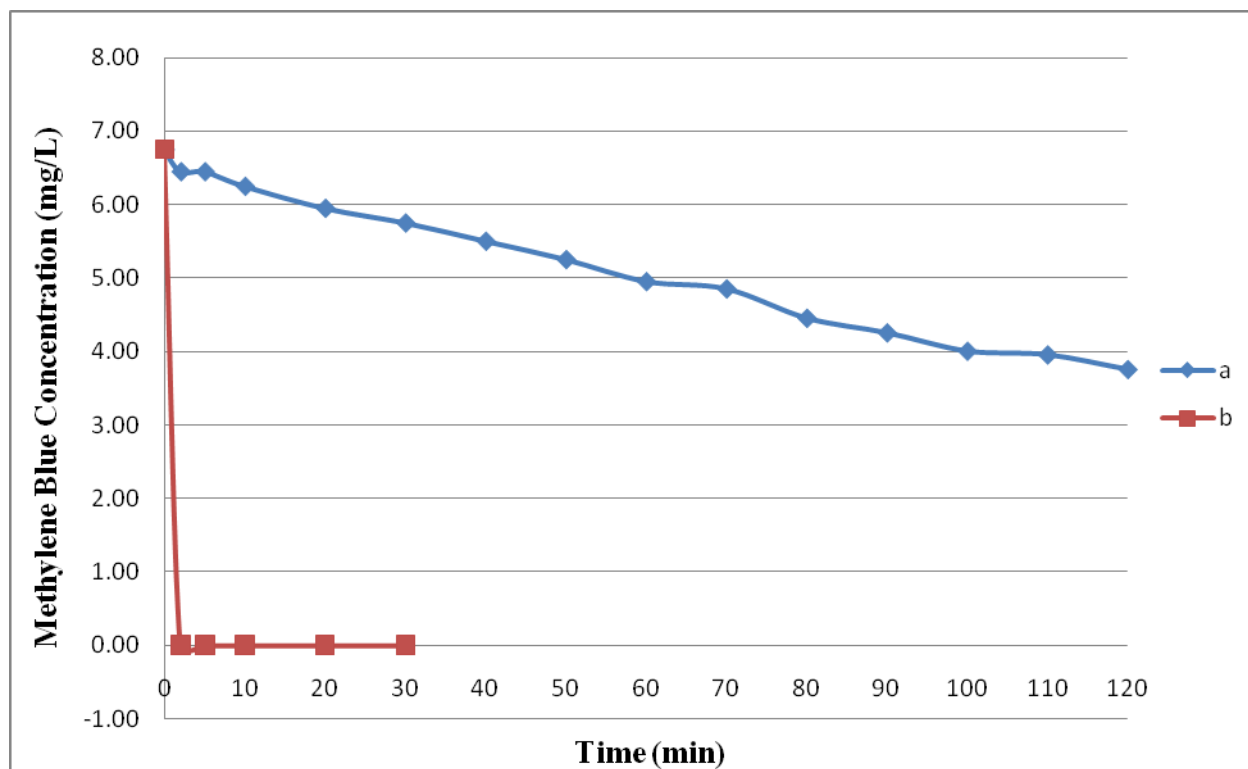


Figure 8: Degradation of 6.75 mg/L Methylene Blue by reacting 0.4g ($1.303 \times 10^{-2} M$) Co-MOF: (a) $4 \times 10^{-4} M$ PMS without Co-MOF, (b) $5 \times 10^{-5} M$ PMS, (c) $2 \times 10^{-4} M$ PMS

5.3 Catalytic Activity of Co-MOF (Acid Red 183 Degradation)

Effect of PMS Concentrations on Acid Red 183

The degradation of acid red 183 under different concentration of PMS is showed in **Fig. 8**. Experiment was carried out by varying the concentration of PMS in 165 mg/L acid red 183 solution with the presence of 0.1g ($3.258 \times 10^{-3} M$) Co-MOF.

Curve (x) presented in **Fig. 3** was carried out without the presence of Co-MOF. With the presence of just $4 \times 10^{-4} M$ PMS, it shows that the degradation rate is extremely slow. A total of 12.1% of acid red 183 was degraded after 40 minutes. The pH of the solution at the end of the experiment was 3.62. Based on the curve, the degradation process has not reached its constant point. Therefore, longer time required for it to further degrade the acid red 183 presented in water.

With the presence of $2 \times 10^{-4} M$ PMS, nearly 63.6% of acid red 183 was removed after 10 minutes. Further degradation does not happen after 10 minutes (curve a). The pH of solution after reaction was 6.78. There was 0.061g of Co-MOF remained after experiment. For $2.6 \times 10^{-4} M$ PMS, nearly 75.8% of acid red 183 was removed after 10 minutes and the degradation does not happen significantly after 10 minutes (curve b). The pH of solution after reaction was 6.77. Co-MOF remained after experiment was 0.079g.

For the presence of $4 \times 10^{-4} M$ PMS, nearly 86.7% of acid red 183 was removed after 10 minutes and further degradation does not happen significantly after that (curve c). For $8 \times 10^{-4} M$ PMS, nearly 92.1% of acid red 183 was removed after 10 minutes and the degradation reach its constant at 95.8% after 30 minutes (curve d). Co-MOF remained after experiment were 0.074g and 0.047g for curve (c) and (d) respectively. The pH for curve (c) and (d) was 6.55 and 5.99 correspondingly.

It can be easily observed that, the result is getting better by increasing the concentration of PMS. However, it results in higher Co-MOF lost. Co-MOF was dissolved into the solution for primary judgments.

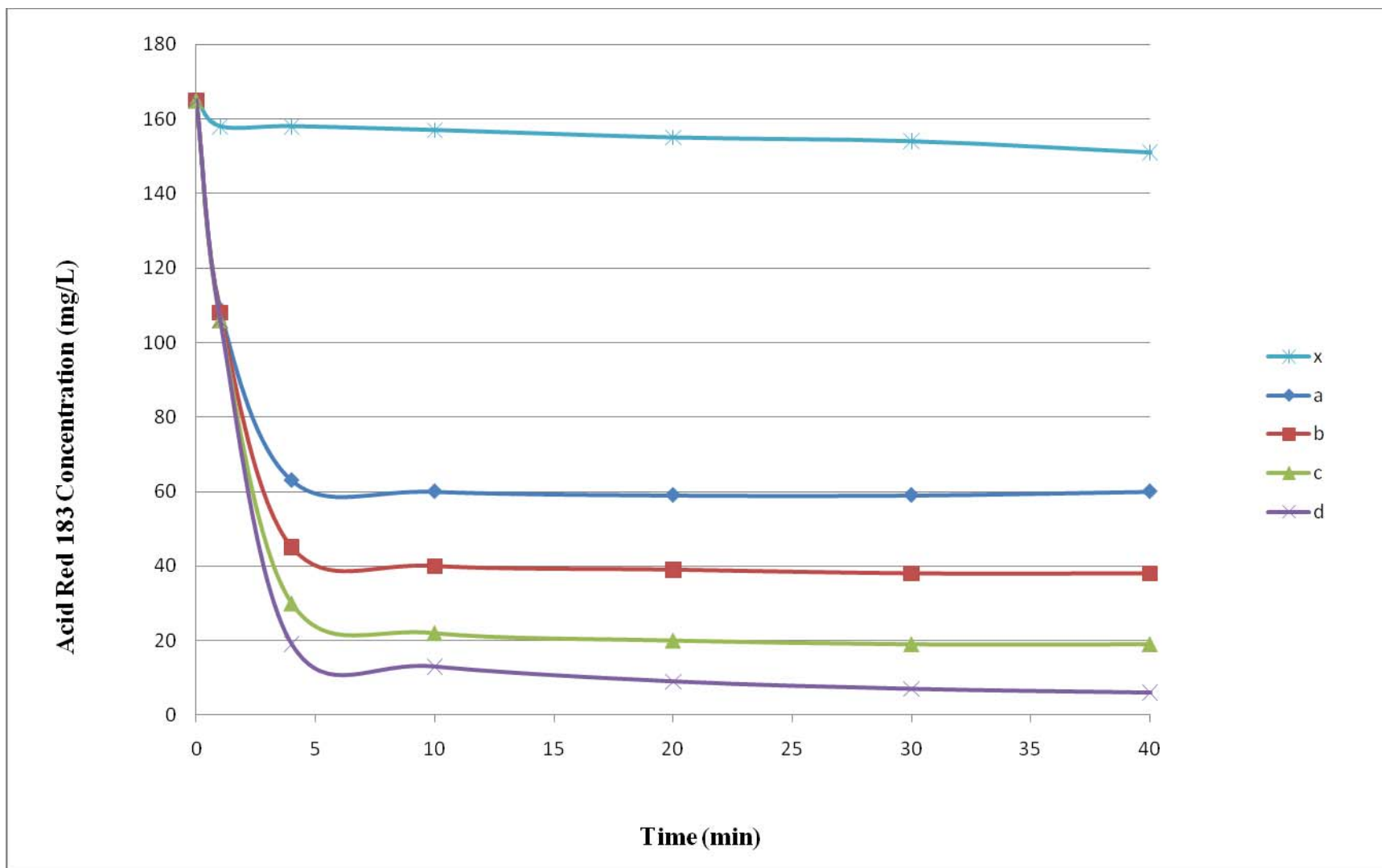


Figure 9: Degradation of 165 mg/L acid red 183 by reacting 0.1g ($3.258 \times 10^{-3} M$) of Co-MOF with different concentration of PMS: (x) $4 \times 10^{-4} M$ PMS without Co-MOF, (a) $2 \times 10^{-4} M$ PMS, (b) $2.6 \times 10^{-4} M$ PMS, (c) $4 \times 10^{-4} M$ PMS, (d) $8 \times 10^{-4} M$ PMS

Effect of Co-MOF Loadings on Acid Red 183

The degradation of acid red 183 under different loading of PMS is showed in **Fig. 9**. Experiment was carried out by varying the loading of PMS in 165 mg/L acid red 183 solution with the presence of $4 \times 10^{-4} M$ PMS .

The degradation rate for 0.05g of Co-MOF is significantly slower than the rest. Nearly 85.5% of acid red 183 was removed after 10 minutes and the degradation keep constant at 90.3% after 30 minutes (curve a). The pH of solution after reaction was 5.92. There was 0.021g of Co-MOF remained after experiment. For 0.1g of Co-MOF, nearly 86.7% of acid red 183 was removed after 10 minutes and further degradation does not happen significantly after that (curve b). The pH of solution after reaction was 6.55. Co-MOF remained after experiment was 0.074g.

For the presence of 0.2g Co-MOF, nearly 86.1 % of acid red 183 was removed after 10 minutes and further degradation does not happen significantly after that (curve c). For 0.3g of Co-MOF, nearly 84.8% of acid red 183 was removed after 10 minutes and further degradation does not happen significantly after that (curve d). Co-MOF remained after experiment were 0.16g and 0.26g for curve (c) and (d) respectively. The pH for curve (c) and (d) was 6.60 and 6.00 correspondingly.

Few samples in this experiment were tested by using total organic carbon (TOC) analysis in order to study the total carbon presence in the solution. For 165 mg/L of acid red 183, it consists of 18.9 ppm carbon. While, after reacted with 0.05g of Co-MOF/ $4 \times 10^{-4} M$ PMS , total carbon presence was increased to 49.2 ppm. Besides that, for 0.2g Co-MOF/ $4 \times 10^{-4} M$ PMS , total carbon presence was 58.1 ppm. Apart from that, for the reaction of 0.1g Co-MOF/ $8 \times 10^{-4} M$ PMS , which is obtained from previous experiment, the carbon consists after the reaction was 78.3 ppm.

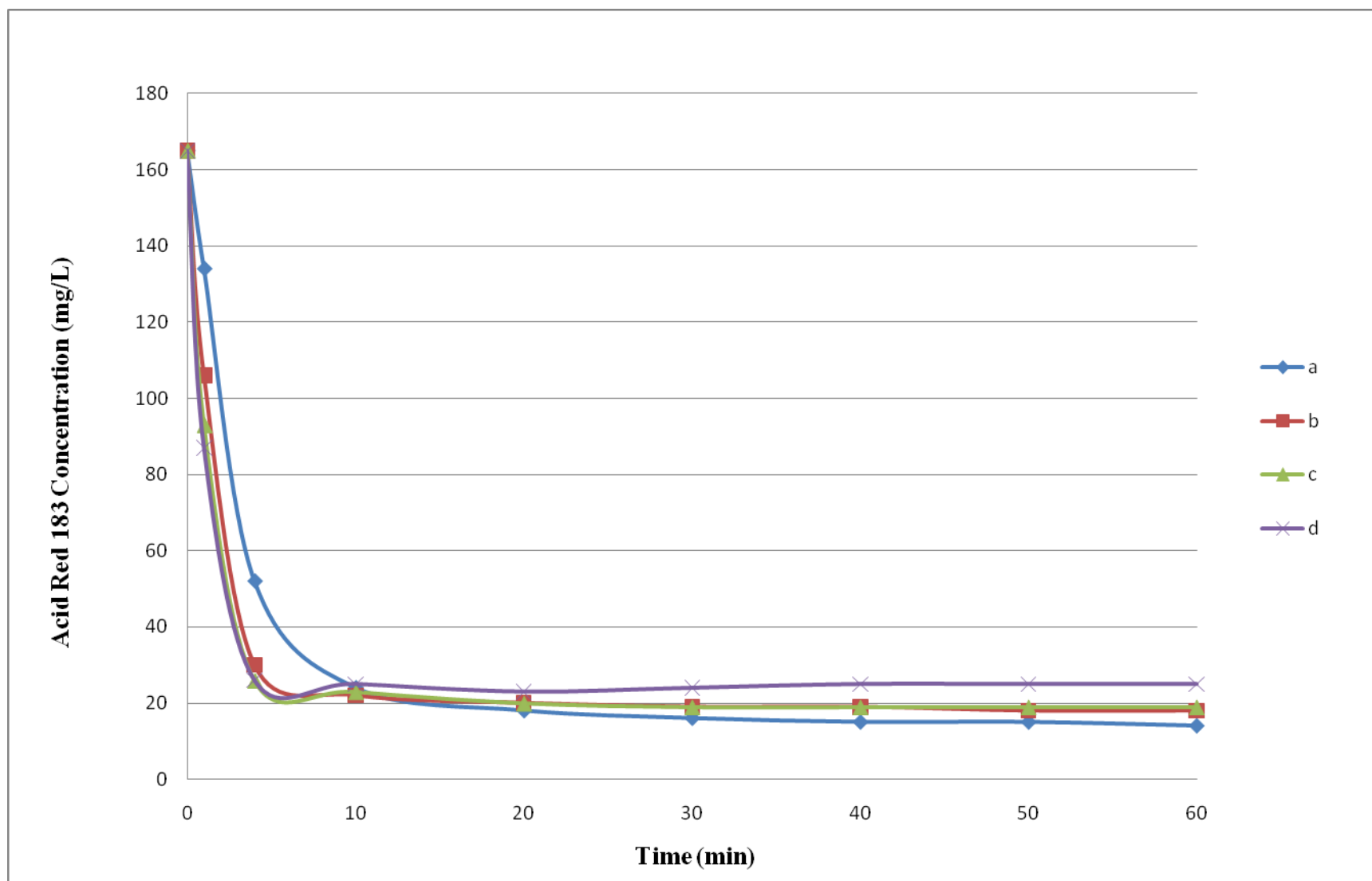


Figure 10: Degradation of 165 mg/L acid red 183 by reacting $4 \times 10^{-4} M$ PMS with different loading of Co-MOF: (a) 0.05g ($1.629 \times 10^{-3} M$), (b) 0.1g ($3.258 \times 10^{-3} M$), (c) 0.2g ($6.515 \times 10^{-3} M$), (d) 0.3g ($9.773 \times 10^{-3} M$)

Effect of Temperature on Acid Red 183

The degradation of acid red 183 under different temperatures is showed in **Fig. 10**. Experiment was carried out by varying the temperature of 165 mg/L acid red 183 solution with the presence of 0.1g ($3.258 \times 10^{-3} M$) Co-MOF and $4 \times 10^{-4} M$ PMS. For the reaction reacted under 8°C, it is obvious that the degradation rate is slower. About 77% of acid red 183 was degraded at the first 10 minutes and the degradation keep constant at 88% after 50 minutes (curve a). For 15°C environment, about 84.2% of acid red 183 was degraded upon 10 minutes and the degradation keep constant at 89.1% after 40 minutes (curve b). After reaction, the pH of the solutions was 6.23 and 6.18 for curve (a) and (b) respectively and the Co-MOF remained was 0.073g and 0.062g. At 25°C, nearly 88.5% of acid red 183 was degraded at the first 10 minutes and the degradation keep constant at 91% after 40 minutes (curve c). The pH after the reaction was 6.22 and Co-MOF remained weight 0.064g. For 40°C environment, nearly 88.5% of acid red 183 was degraded at the first 10 minutes. Further degradation does not happen after 10 minutes. The pH of solution after reaction was 5.93. Co-MOF remained after experiment was 0.067g.

Based on the results, the reaction rate gets faster when temperature of solution increases. At 40°C, degradation was completed (88.5%) within 10 minutes. However, with the same amount of degradation conditions, 8°C solution required 50 minutes to achieve.

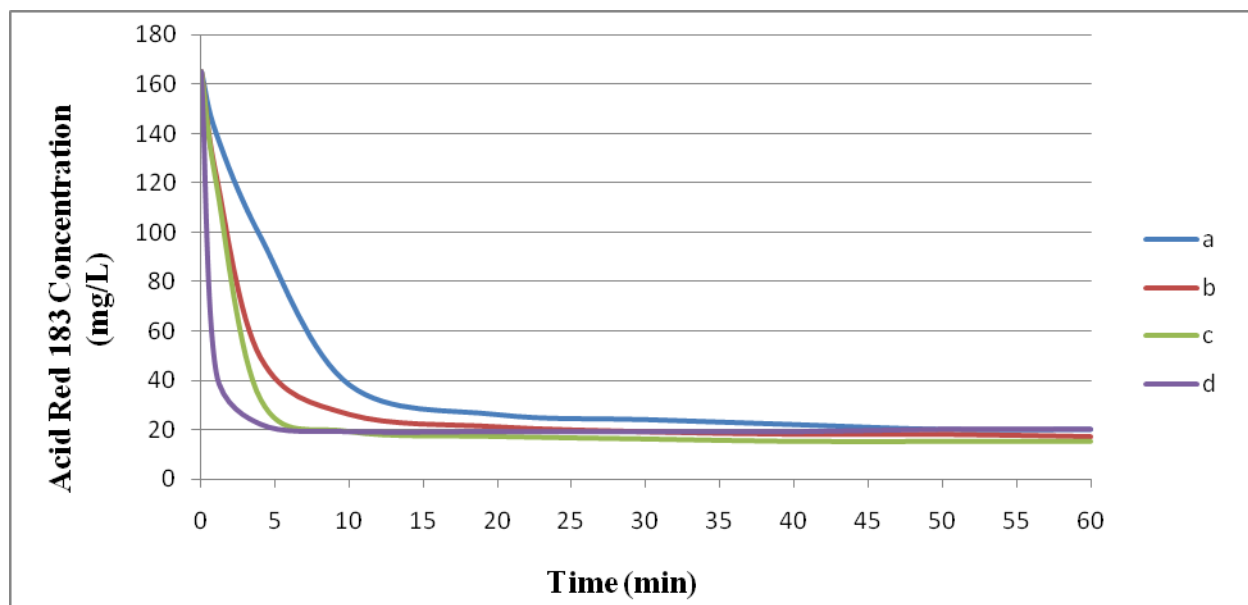


Figure 11: Degradation of 165 mg/L acid red 183 by reacting $4 \times 10^{-4} M$ PMS 0.1g Co-MOF: (a) 8°C, (b) 15°C, (c) 25°C, (d) 40°C

5.4 Catalytic Activity of Co-MOF (Reactive Blue 4 Degradation)

Effect of PMS Concentrations on Reactive Blue 4

The degradation of reactive blue 4 under different concentration of PMS is showed in *Fig. 11*. Experiment was carried out by varying the concentration of PMS in 165 mg/L reactive blue 4 solution with the presence of 0.1g ($3.258 \times 10^{-3} M$) Co-MOF.

With the presence of $2 \times 10^{-4} M$ PMS, the maximum amount of reactive blue get degraded was about 77% upon 4 minutes. However, as the time pass, concentration of reactive blue 4 in the water getting increases rather than keep at the constant point. There was about 4.3% increase upon 10 minutes and there was about 14.6% increase in the concentration of reactive blue 4 after 30 minutes. The result does not happen significantly after this. Therefore, the maximum degradation after 30 minutes was 62.4% (curve a). Solution pH after the reaction was 7.82. Co-MOF remained after experiment was 0.068g.

With the presence of $4 \times 10^{-4} M$ PMS, the maximum amount of reactive blue get degraded was about 85.45% upon 10 minutes. However, as the time pass, concentration of reactive blue 4 in the water getting increases rather than keep at the constant point. There was about 4.8% increase in the concentration of reactive blue 4 after 30 minutes. The result does not happen significantly after this. Therefore, the maximum degradation after 30 minutes was 80.6% (curve b). Solution pH after the reaction was 7.63. Co-MOF remained after experiment was 0.060g.

With the presence of $8 \times 10^{-4} M$ PMS, the maximum amount of reactive blue get degraded was about 98.2% upon 10 minutes. However, as the time pass, concentration of reactive blue 4 in the water getting increases rather than keep at the constant point. There was about 9.1% increase in the concentration of reactive blue 4 after 60 minutes. From the curve, it seems the concentration of reactive blue 4 will still keep increasing after 60 minutes. Thus, longer time required to obtain the final degraded amount. Total reactive blue 4 get degraded after 30 minutes was 89.1% (curve c). Solution pH after the reaction was 7.17. Co-MOF remained after experiment was 0.042g. Increase in the concentration of PMS results in higher Co-MOF lost. Co-MOF was dissolved into the solution for primary judgments.

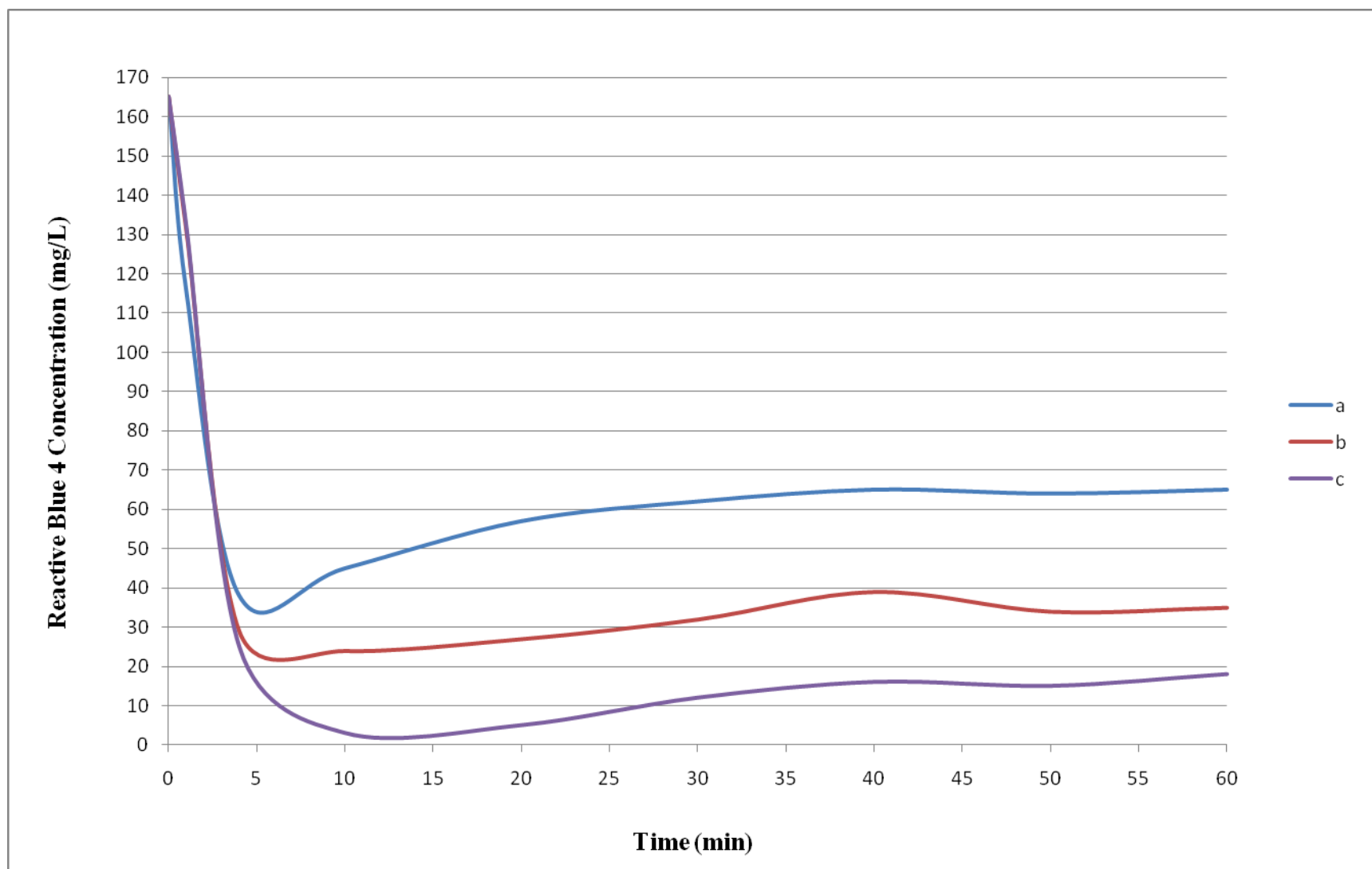


Figure 12: Degradation of 165 mg/L reactive blue 4 by reacting 0.1g ($3.258 \times 10^{-3} M$) of Co-MOF with different concentration of PMS: (a) $2 \times 10^{-4} M$ PMS, (b) $4 \times 10^{-4} M$ PMS, (c) $8 \times 10^{-4} M$ PMS

5.5 Stability of Co-MOF Catalyst in multiple runs

H₂O₂ as an Oxidizing Agent on Methylene Blue

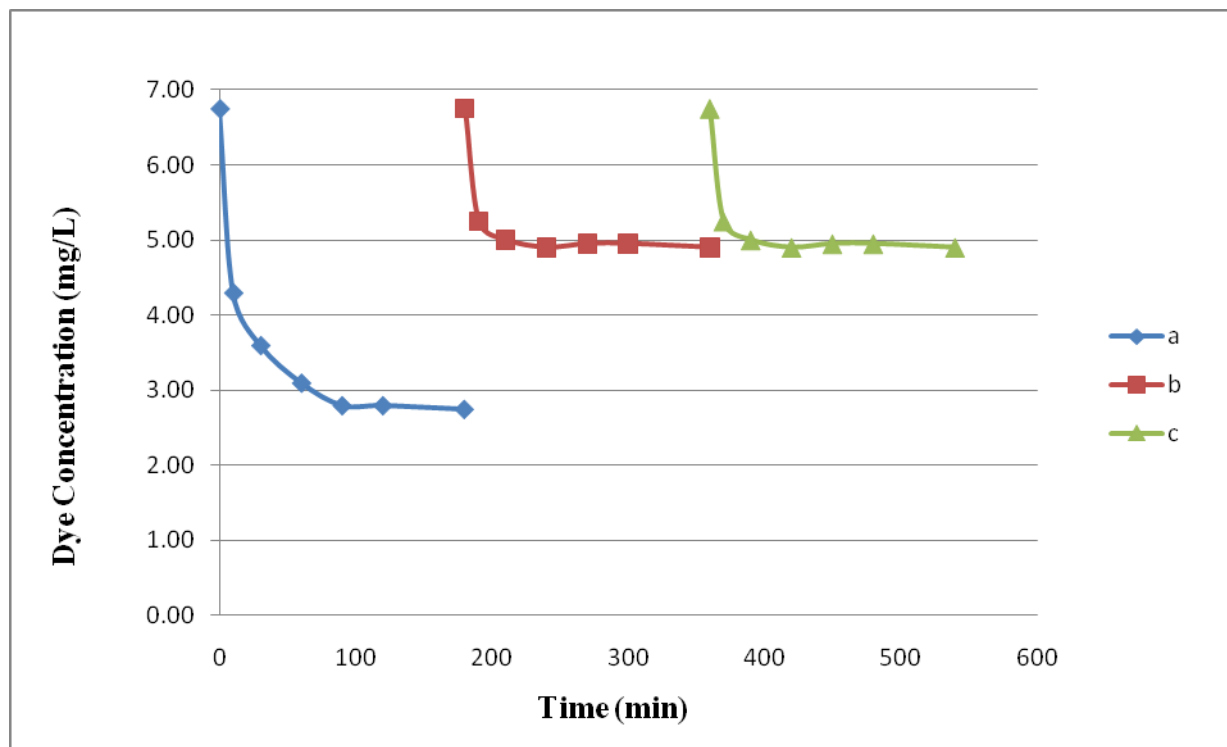


Figure 13: Cyclic degradation of 6.75 mg/L methylene blue by reacting 0.4g ($1.3029 \times 10^{-2} M$) of Co-MOF with $8 \times 10^{-2} M$ H_2O_2 : (a) Initial, (b) 1st recycling, (c) 2nd recycling

Three recycling runs of the Co-MOF catalyst were carried out. As showed in *Fig. 12*, the regenerated catalyst exhibits poor and unstable performance. The degradation rate of methylene blue was degenerated compare to the initial process. Weight of Co-MOF after initial, 1st recycling and 2nd recycling process were still remained almost the same as before react. The results do not support the initial view that this Co-MOF/ H_2O_2 can be reused and recovered for the catalytic oxidation of methylene blue without obvious decrease of catalytic activity.

PMS as an Oxidizing Agent on Methylene Blue

Three recycling runs of the Co-MOF catalyst were carried out. As shown in *Fig. 13*, the regenerated catalyst exhibits excellence and stable performance. The degradation rate of methylene blue remains almost unchanged compare to the initial process. Weight of Co-MOF after initial, 1st recycling and 2nd recycling process were still remained almost the same as before

react. This indicates that the catalyst has an excellent long-term stability by using PMS as an oxidizing agent. The results support the initial view that this Co-MOF/PMS can be reused and recovered for the catalytic oxidation of methylene blue without obvious decrease of catalytic activity.

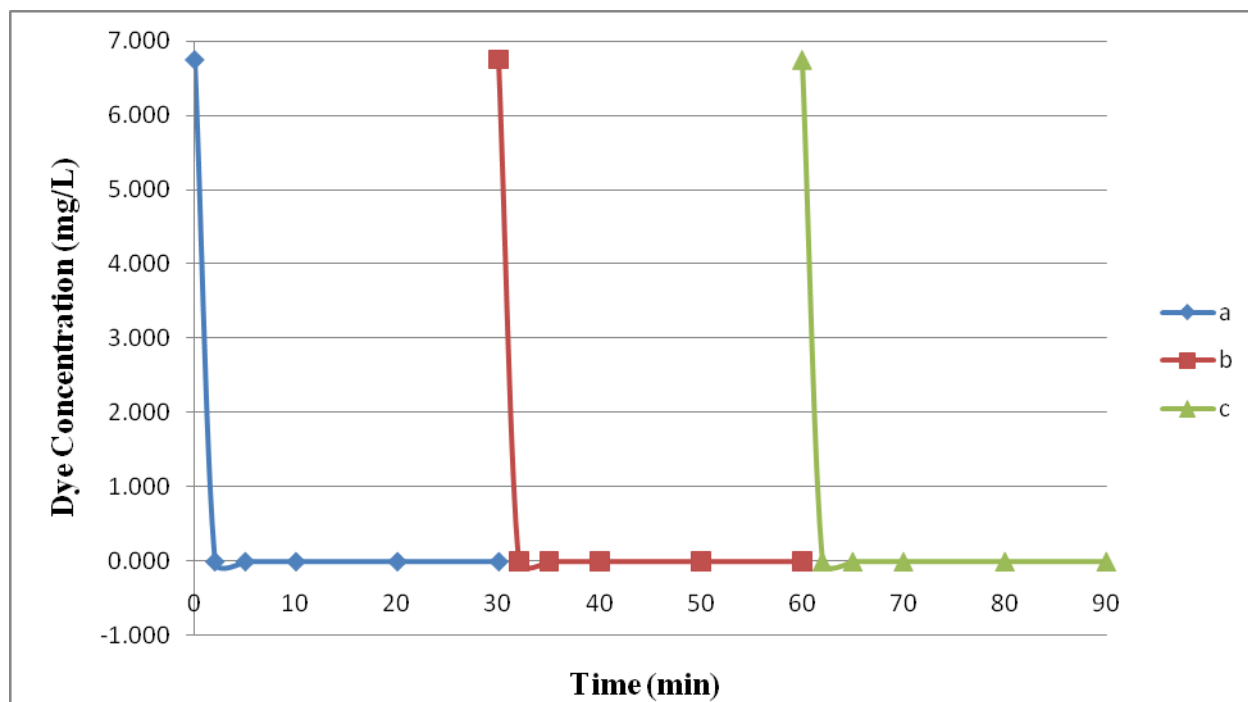


Figure 14: Cyclic degradation of 6.75 mg/L methylene blue by reacting 0.4g ($1.3029 \times 10^{-2} M$) of Co-MOF with $2 \times 10^{-4} M$ PMS : (a) Initial, (b) 1st recycling, (c) 2nd recycling

PMS as an Oxidizing Agent on Acid Red 183

Three recycling runs of the Co-MOF catalyst were carried out. As shown in *Fig. 14*, the regenerated catalyst exhibits excellence and stable performance. The degradation rate of acid red 183 is only slightly slower at 1st recycling compare to the initial. The weight of Co-MOF after initial and 1st recycling process was 0.068g, 0.066g. This indicated that the lost of Co-MOFs are quite significant. Preliminary surmise is that, some Co-MOF gets dissolved during the degradation. However, as overall, the performance still showing the catalyst has an excellent long-term stability by using PMS as an oxidizing agent. The results support the initial view that this Co-MOF/PMS can be reused and recovered for the catalytic oxidation of methylene blue

without obvious decrease of catalytic activity. After experiment, the pH of initial and recycling run was 6.38 and 6.36, respectively.

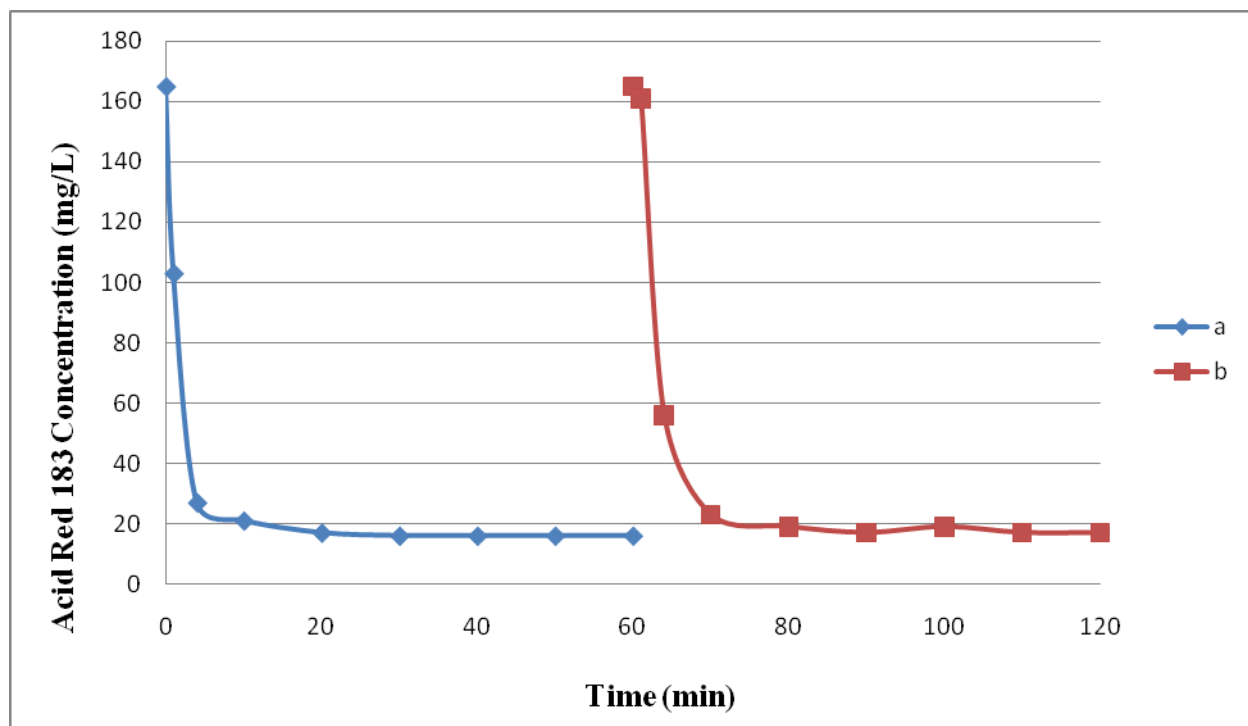


Figure 15: Cyclic degradation of 165 mg/L acid red 183 by reacting 0.1g ($3.258 \times 10^{-3} M$) of Co-MOF with $4 \times 10^{-4} M$ PMS : (a) Initial, (b) 1st recycling

5.6 Catalytic activity of Co^{2+} (Methylene Blue Degradation)

Effect of H_2O_2 Concentrations on Methylene Blue

The degradation of Methylene Blue under different concentration of H_2O_2 is showed in **Fig. 15**. Throughout the experiment, the concentration of Co^{2+} was remained at $1.3029 \times 10^{-2} M$. Curve (x) presented in **Fig. 15** was carried out without the presence of Co^{2+} . With the presence of just $4 \times 10^{-2} M \text{H}_2\text{O}_2$, only 3.7% of methylene blue was degraded after 10 minutes. Further degradation does not happen after 10 minutes. The pH of solution after reaction was 6.4.

In the presence of only $2 \times 10^{-3} M \text{H}_2\text{O}_2$, a very low performance of degradation can be observed. Only about 20% of methylene blue was removed after 10 minutes and it reaches its maximum point of degradation at 27.4% after 30 minutes (curve a). The concentration of methylene blue does not have significant reduction for further reaction. With $2 \times 10^{-2} M \text{H}_2\text{O}_2$ showed in **Fig. 15** curve (b), nearly 51.9% of methylene blue was removed upon 10 minutes and the removal of methylene blue still continue to proceed slowly after 180 minutes. About 88.9% of methylene blue removed upon 180 minutes.

With the presence of $4 \times 10^{-2} M \text{H}_2\text{O}_2$, 83% of methylene blue was removed upon 10 minutes and 100% was removed after 60 minutes (curve c). For $6 \times 10^{-2} M \text{H}_2\text{O}_2$ and $1 \times 10^{-1} M \text{H}_2\text{O}_2$, both of them showed a quite similar results. Nearly 88.9% and 90.4% of methylene blue was removed upon 10 minutes and 100% was removed after 30 minute for curve (d) and (f) respectively.

Compared to other results in **Fig. 15**, $8 \times 10^{-2} M \text{H}_2\text{O}_2$ showed the best outcome among the rest. About 96.8% of methylene blue was removed upon 10 minutes and 100% of methylene blue was removed after 30 min (curve e). Based on the figure, it gave a faster degradation rate compare to curve d & f. Compare to other results of degradation in **Fig. 15**, $8 \times 10^{-2} M \text{H}_2\text{O}_2$ showed the best result that not only 100% of Methylene blue was removed after 30 min (curve e) but also with a faster degradation rate compare to curve d & f.

For $1.2 \times 10^{-1} M H_2O_2$, only 66.7% of methylene blue was removed upon 10 minutes and the removal of methylene blue still continues to proceed slowly after that. Finally it took 180 min to complete the degradation (curve g) and the degradation rate was significant slower compared to curve c, d, e & f. This indicated that, excess H_2O_2 does not help in degradation. Excess H_2O_2 might require higher concentration of Co^{2+} to show the higher degradation rate. However, with $8 \times 10^{-2} M H_2O_2$, the result shown in **Fig. 15** is good enough. Extra catalyst and oxidizing agent could be a waste.

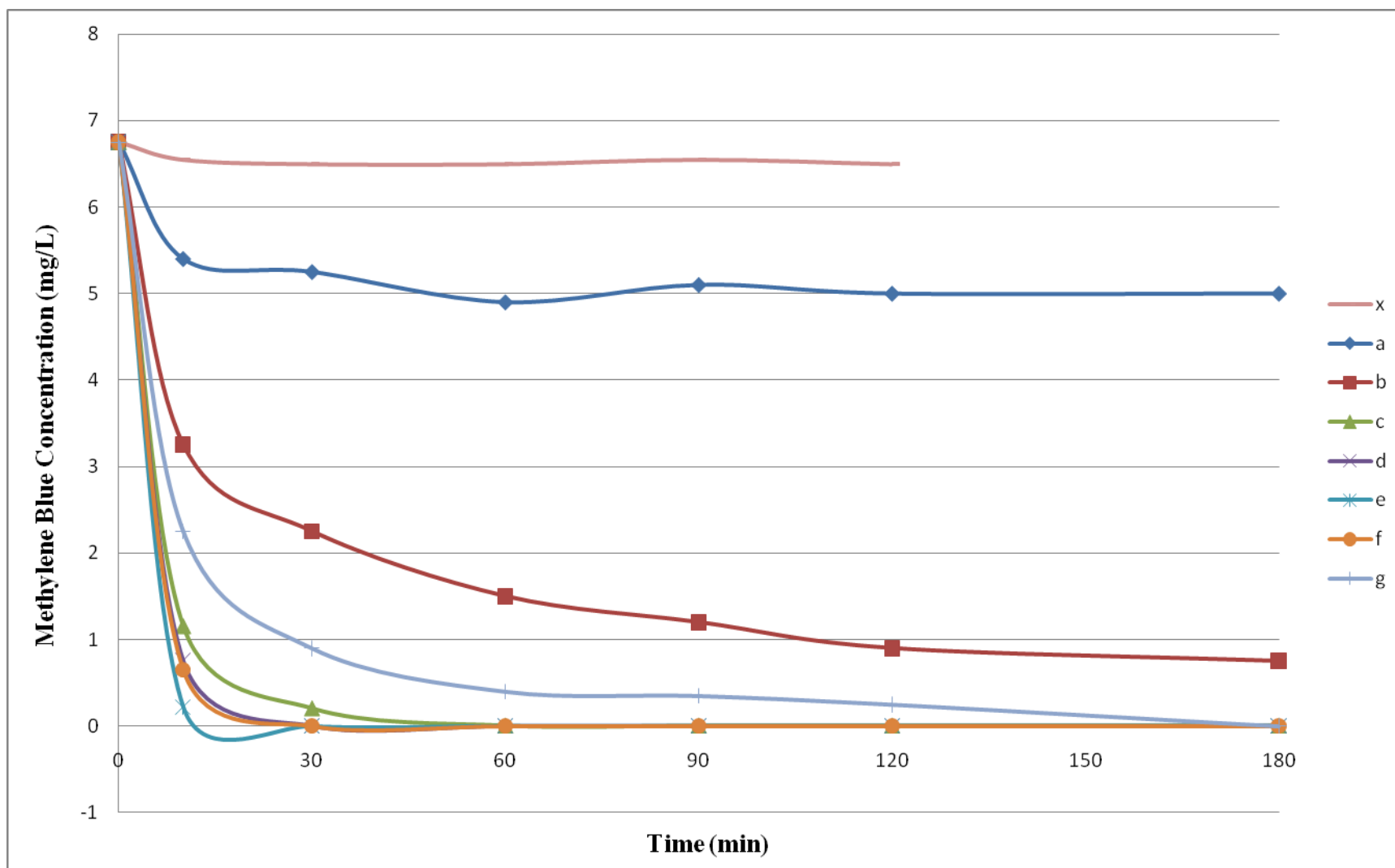


Figure 16: Degradation of 6.75 mg/L methylene blue by reacting $1.3029 \times 10^{-2} M$ of Co^{2+} with different concentration of H_2O_2 : (x) $4 \times 10^{-2} M H_2O_2$ without Co^{2+} (a) $2 \times 10^{-3} M H_2O_2$, (b) $2 \times 10^{-2} M H_2O_2$, (c) $4 \times 10^{-2} M H_2O_2$, (d) $6 \times 10^{-2} M H_2O_2$, (e) $8 \times 10^{-2} M H_2O_2$, (f) $1 \times 10^{-1} M H_2O_2$, (g) $1.2 \times 10^{-1} M H_2O_2$.

Effect of PMS Concentrations on Methylene Blue

The degradation of methylene blue under different concentration of PMS is shown in **Fig. 16**. The concentration of Co^{2+} was remained at $1.3029 \times 10^{-4} \text{ M}$ throughout the experiment. The reaction shows that it is faster than using H_2O_2 as the oxidizing agent.

Curve (x) only involves $4 \times 10^{-4} \text{ M PMS}$ in the process of degradation methylene blue solution. It shows that the degradation rate is very slow. 26.7% of methylene blue was degraded upon 60 minutes. The pH of the solution at the end of the experiment was 3.67. Based on the curve, the degradation process has not reached its constant point. Therefore, longer time required for it to further degrade the methylene blue presented in water.

In the presence of $5 \times 10^{-5} \text{ M PMS}$, nearly 46.7% of methylene blue was removed upon 1 minute. The maximum amount of methylene blue get degraded was 47.4% after 5 minutes (curve a). This indicated that the amount of PMS is not enough for $1.3029 \times 10^{-4} \text{ M Co}^{2+}$. For $1 \times 10^{-4} \text{ M PMS}$, nearly 74.8 % of methylene blue was removed after 1 minute. The maximum amount of methylene blue get degraded was 77.8% after 5 minutes (curve b).

For $2 \times 10^{-4} \text{ M PMS}$, 75.6% of methylene blue was removed upon 1 minute. The maximum amount of methylene blue get degraded was 100 % after 5 minutes (curve c). With the amount of $4 \times 10^{-4} \text{ M PMS}$, about 97.8% of methylene blue was removed upon 1 minute. The maximum amount of methylene blue get degraded was 100% at the second minutes (curve d). It can be easily observed that, the degradation result is getting better by increasing the concentration of PMS. Apart from that, the degradation rate also increases sharply with the increase of PMS concentration.

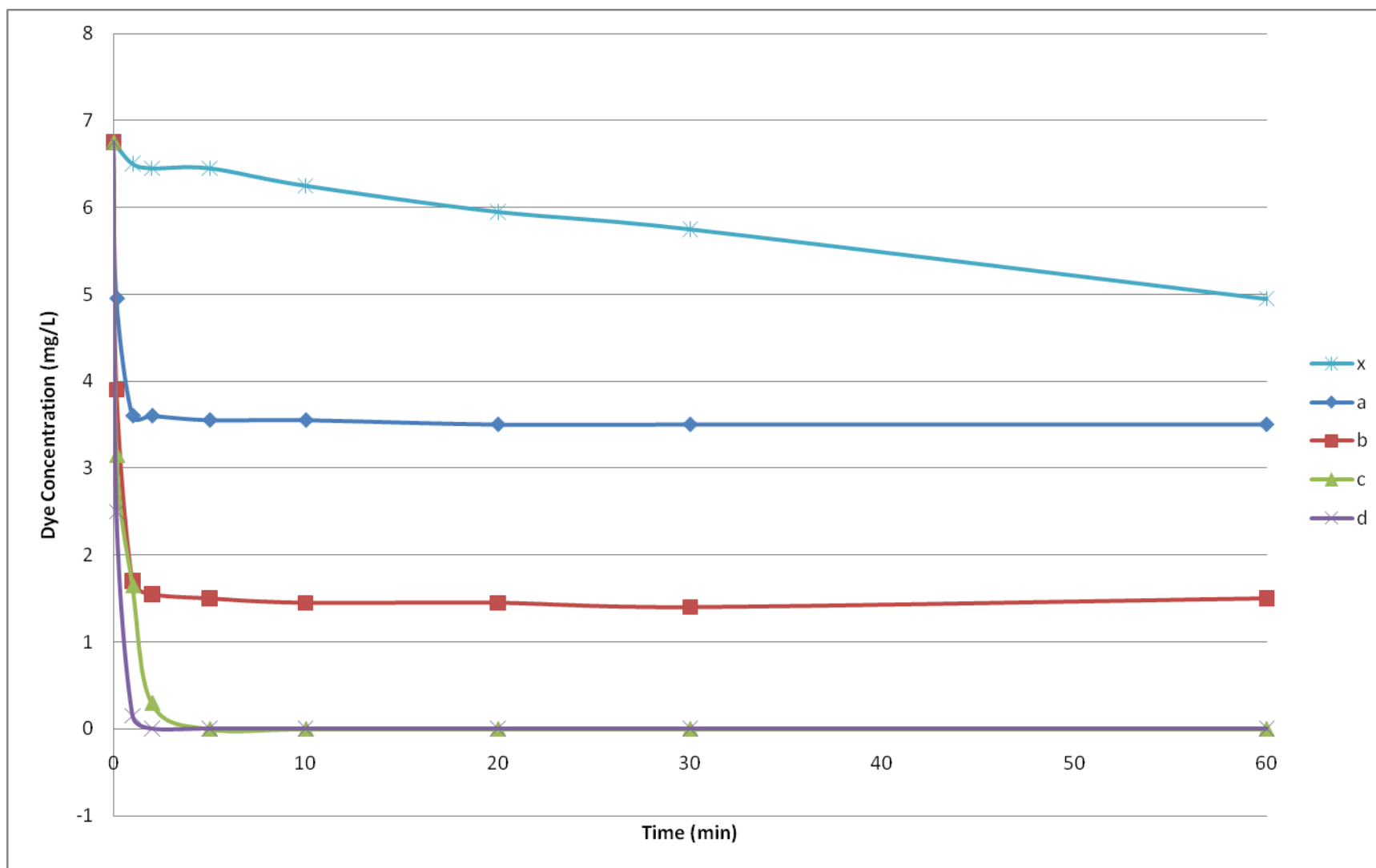


Figure 17: Degradation of 6.75 mg/L methylene blue by reacting $1.303 \times 10^{-4} M$ of Co^{2+} with different concentration of PMS: (x) $4 \times 10^{-4} M$ PMS without Co^{2+} (a) $5 \times 10^{-5} M$ PMS, (b) $1 \times 10^{-4} M$ PMS, (c) $2 \times 10^{-4} M$ PMS, (d) $4 \times 10^{-4} M$ PMS.

5.7 Catalytic activity of Co^{2+} (Acid Red 183 Degradation)

Effect of PMS Concentrations on Acid Red 183

The degradation of acid red 183 under different concentration of PMS is shown in **Fig. 17**. The concentration of Co^{2+} was remained on $1.3029 \times 10^{-4} \text{ M}$ throughout the experiment. Curve (x) presented in **Fig. 17** was carried out without the presence of Co^{2+} . With the presence of just $4 \times 10^{-4} \text{ M PMS}$, it shows that the degradation rate is extremely slow. A total of 14.5% of acid red 183 was degraded after 80 minutes. The pH of the solution at the end of the experiment was 3.62. Based on the curve, the degradation process has not reached its constant point. Therefore, longer time required for it to further degrade the acid red 183 presented in water.

With the presence of $5 \times 10^{-5} \text{ M PMS}$, nearly 26.7% of acid red 183 was removed upon 10 minutes. Further degradation does not happen after 10 minutes (curve a). The pH of solution after reaction was 7.18. For $1 \times 10^{-4} \text{ M PMS}$, nearly 38.8% of acid red 183 was removed upon 10 minutes. It took total 20 minutes to complete the degradation. Overall degradation of acid red 183 was 41.8%. The pH of solution after reaction was 5.64. For the presence of $2 \times 10^{-4} \text{ M PMS}$, nearly 55.8% of acid red 183 was removed after 10 minutes. It took total 40 minutes to complete the degradation. Overall degradation of acid red 183 was 65.5%. The pH of solution after reaction was 5.08. For $2.6 \times 10^{-4} \text{ M PMS}$, nearly 63.6% of acid red 183 was removed after 10 minutes. It took total 40 minutes to complete the degradation. Overall degradation of acid red 183 was 78.8%. The pH of solution after reaction was 4.94.

For the presence of $4 \times 10^{-4} \text{ M PMS}$, nearly 72.1% of acid red 183 was removed after 10 minutes. It took total 40 minutes to complete the degradation. Overall degradation of acid red 183 was 93.3%. The pH of solution after reaction was 4.76. For $5.2 \times 10^{-4} \text{ M PMS}$, nearly 77% of acid red 183 was removed after 10 minutes. It took total 40 minutes to complete the degradation. Overall degradation of acid red 183 was 95.2%.

It can be easily observed that, the result is getting better by increasing the concentration of PMS. However, the pH decreases as the amount of PMS increase.

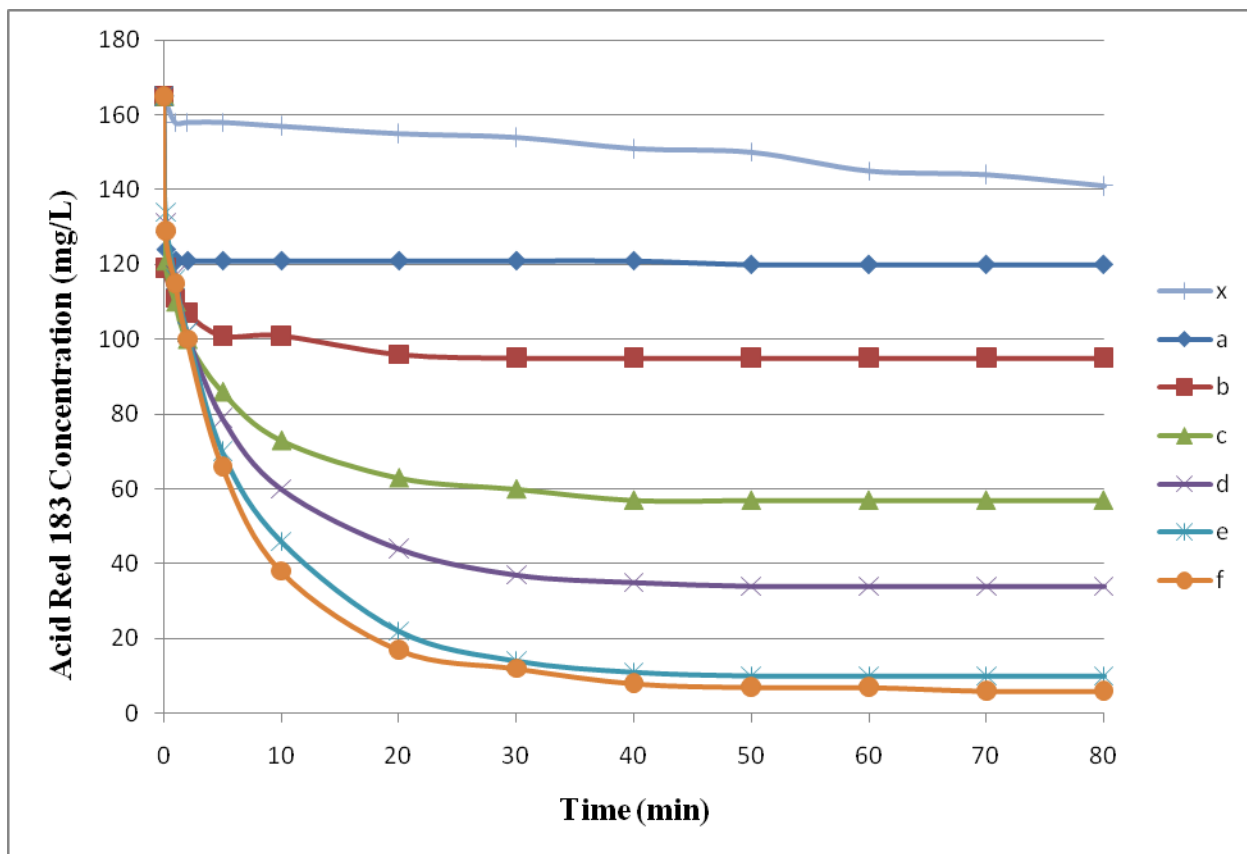


Figure 18: Degradation of 165 mg/L acid red 183 by reacting $1.303 \times 10^{-4} M$ of Co^{2+} with different concentration of PMS: (x) $4 \times 10^{-4} M$ PMS without Co^{2+} (a) $5 \times 10^{-5} M$ PMS, (b) $1 \times 10^{-4} M$ PMS, (c) $2 \times 10^{-4} M$ PMS, (d) $2.6 \times 10^{-4} M$ PMS (e) $4 \times 10^{-4} M$ PMS (f) $5.2 \times 10^{-4} M$ PMS

Effect of Co^{2+} Concentration on Acid Red 183

The degradation of Acid Red 183 under different concentration of Co^{2+} was shown in **Fig. 18**. Throughout the experiment, the concentration of PMS was remained at $4 \times 10^{-4} M$. In the presence of $6.515 \times 10^{-5} M Co^{2+}$, nearly 69.7% of acid red 183 was removed upon 10 minutes. It took total 60 minutes to complete the degradation. Overall degradation of acid red 183 was 93.3 % (curve a). The pH of solution after reaction was 3.26. For $1.3029 \times 10^{-4} M Co^{2+}$, about 90.3% of acid red 183 was removed upon 10 minutes. It took total 30 minutes to complete the degradation. Overall degradation of acid red 183 was 96.4 % (curve b). With the presence of $8.59 \times 10^{-4} M Co^{2+}$, nearly 92.7% of acid red 183 was removed after 10 minutes. It took total 30 minutes to complete the degradation. Overall degradation of acid red 183 was 95.2 % (curve c). With the presence of $1.718 \times 10^{-3} M Co^{2+}$, nearly 92.7% of acid red 183 was removed after 10 minutes. It took total 30 minutes to complete the degradation. Overall degradation of acid red 183 was 95.8 % (curve d).

It can be easily observed that, the performance is getting better by increasing the concentration of Co^{2+} . The extent of acid red 183 degradation of $1.3029 \times 10^{-4} M Co^{2+}$, $8.59 \times 10^{-4} M Co^{2+}$ and $1.718 \times 10^{-3} M Co^{2+}$ was similar after 30 min. however, the degradation exhibited different rates for the three systems. The degradation rate in $1.718 \times 10^{-3} M Co^{2+}$ was faster than that of $8.59 \times 10^{-4} M Co^{2+}$ and the degradation rate in $8.59 \times 10^{-4} M Co^{2+}$ is much faster than that of $1.3029 \times 10^{-4} M Co^{2+}$.

The reaction rates of $1.718 \times 10^{-3} M Co^{2+}$ and $8.59 \times 10^{-4} M Co^{2+}$ was actually very close to each other. This might indicated that the presence of PMS was run out. Extra PMS might help to 100% degrade the concentration of acid red 183.

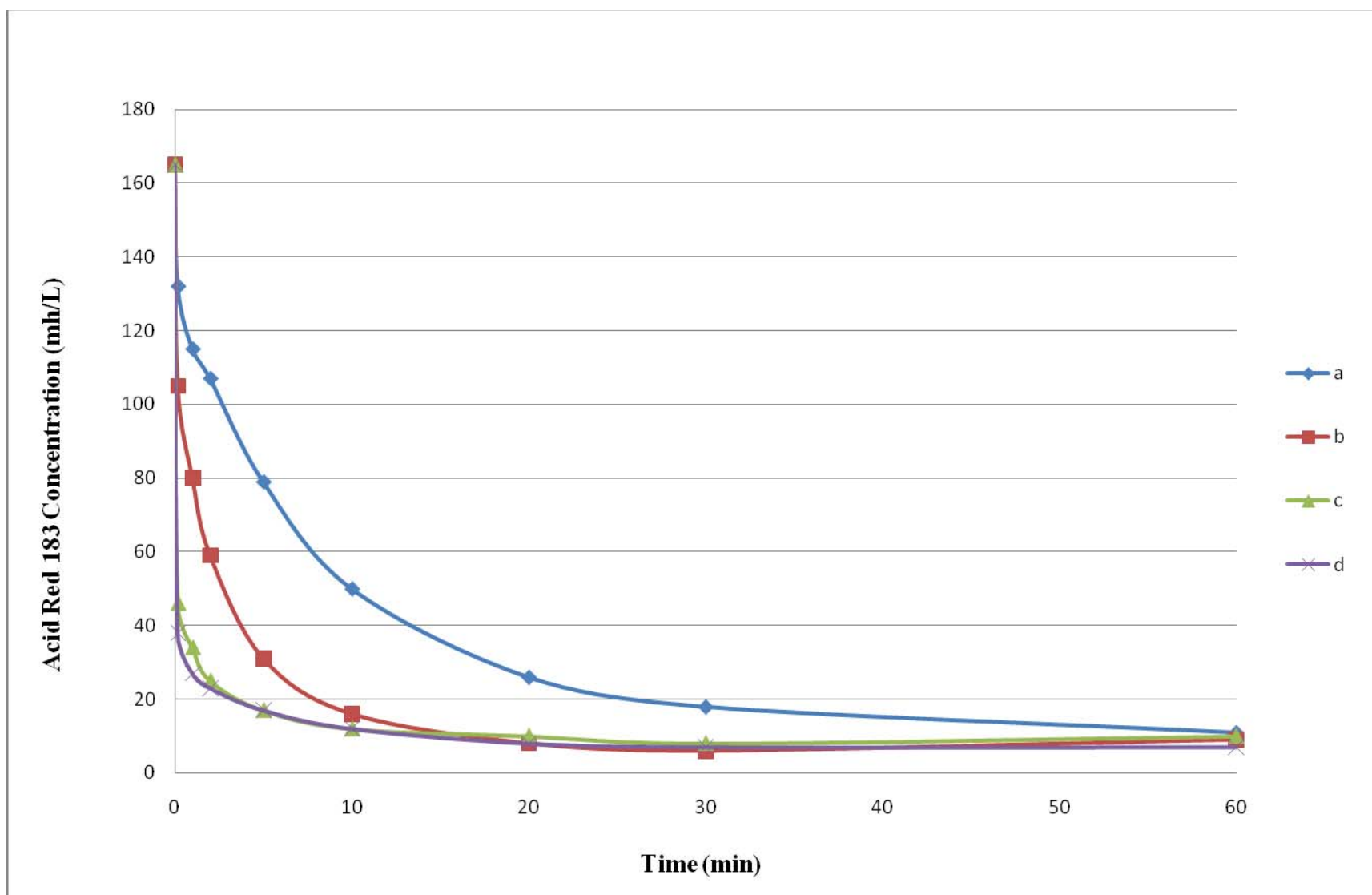


Figure 19: Degradation of 165 mg/L Acid Red 183 by reacting different concentration of Co^{2+} with $4 \times 10^{-4} M PMS$.

(a) $6.5154 \times 10^{-5} M Co^{2+}$, (b) $1.3029 \times 10^{-4} M Co^{2+}$, (c) $8.59 \times 10^{-4} M Co^{2+}$, (d) $1.718 \times 10^{-3} M Co^{2+}$

Effect of Acid Red 183 Concentration on Co^{2+} /PMS

As showed in **Fig. 19**, the degradation was carried out under different concentration of acid red 183 solution dye. Throughout the experiment, the concentration of Co^{2+} and PMS was remained on $1.3029 \times 10^{-4} \text{ M}$ and $4 \times 10^{-4} \text{ M}$ correspondingly. For 200 mg/L Acid Red 183, 83% was degraded in 10 minutes. It took total 20 minutes to complete the degradation. Overall degradation of acid red 183 was 88.5 %. For 100 mg/L Acid Red 183, 92% was degraded in 10 minutes. It took total 20 minutes to complete the degradation. Overall degradation of acid red 183 was 96 %. For 50 mg/L Acid Red 183, 94% was degraded in 10 minutes. It took total 20 minutes to complete the degradation. Overall degradation of acid red 183 was 96 %.

Since same concentration of Co^{2+} and PMS are used, the reaction rate will be the same. However, due to the different in dye concentrations, the degrade level will vary. Lesser dye concentration has higher degradation level and shorter degradation time. On the other hand, higher dye concentration will cause degradation level lower and consumed longer time.

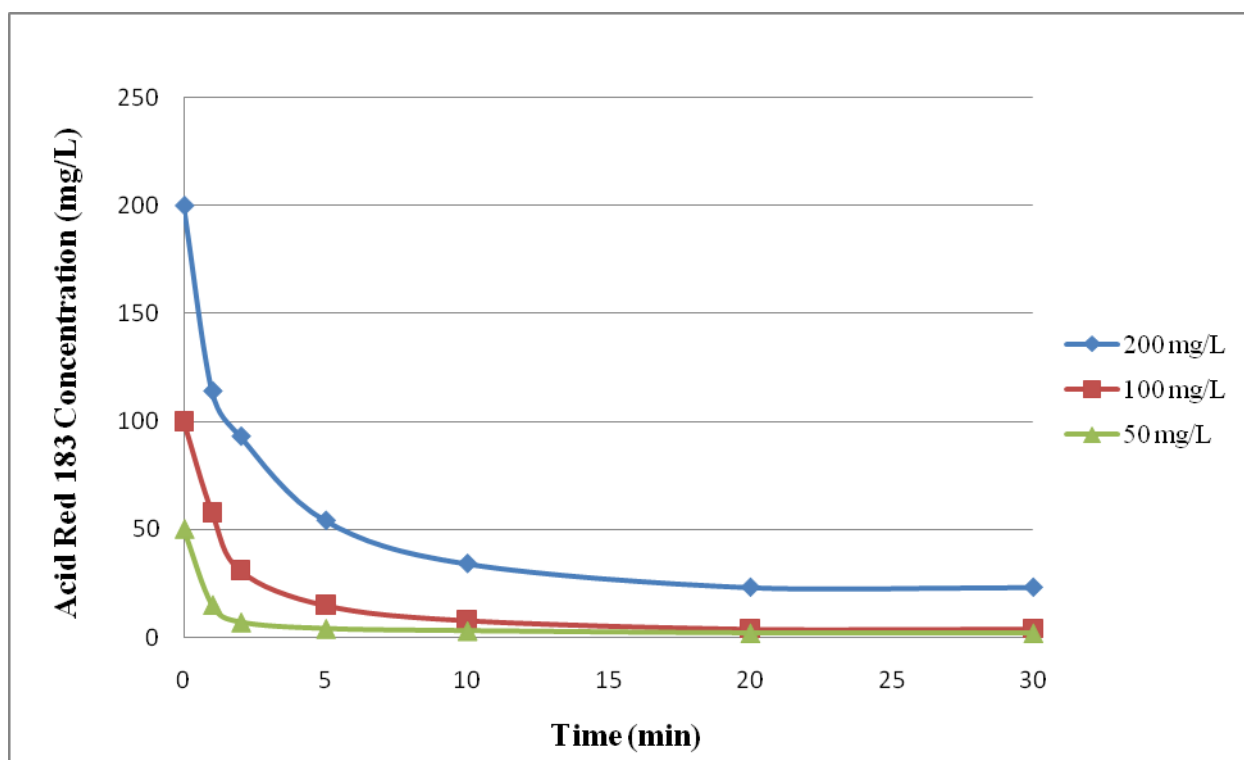


Figure 20: Degradation of different acid red 183 concentrations by reacting $1.3029 \times 10^{-4} \text{ M}$ Co^{2+} and $4 \times 10^{-4} \text{ M}$ PMS

5.8 Oxidizing activity on Methylene Blue

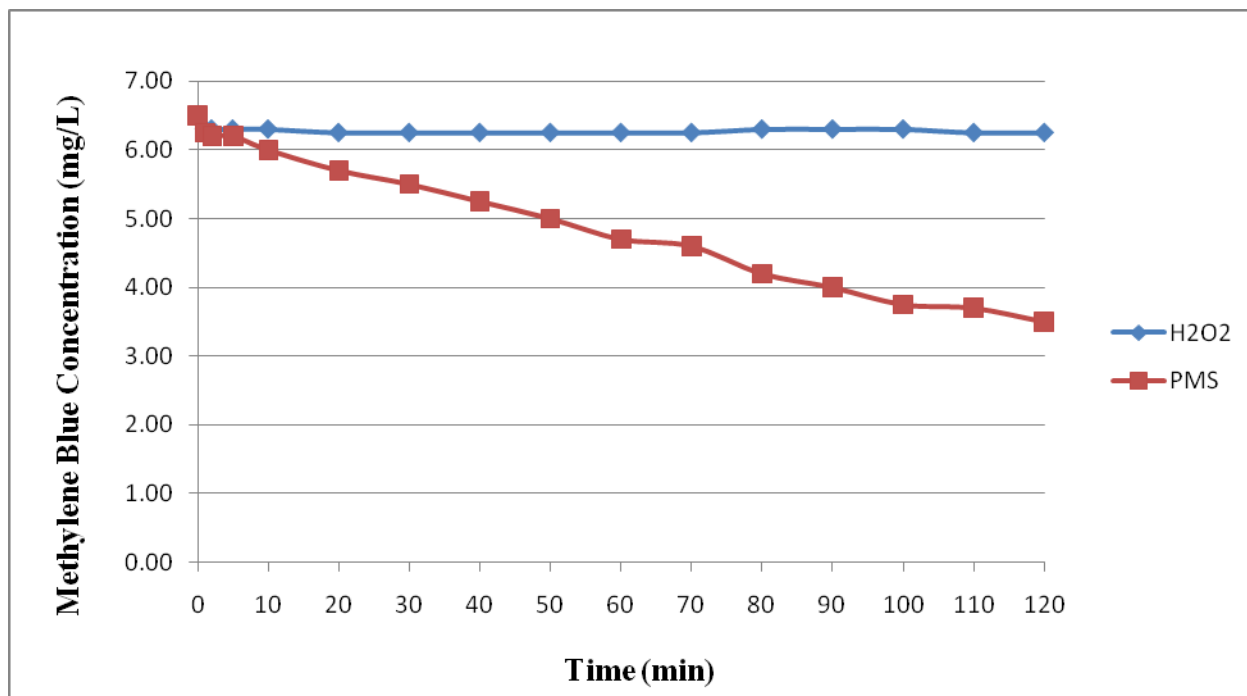


Figure 21: Degradation of different methylene blue concentration by using $4 \times 10^{-2} M H_2O_2$ and $4 \times 10^{-4} M PMS$

Fig. 20 shown above illustrated the reaction of H_2O_2 and PMS toward methylene blue without any catalyst presence in the reaction. The results support the initial view that PMS have a higher powerful oxidizing potential compare to H_2O_2 . This phenomenon has shown in Fig. 6, 7, 15 and 16 before.

5.9 Oxidizing activity on Acid Red 183

Fig. 21 shown above illustrated the reaction of H_2O_2 and PMS toward acid red 183 without any catalyst presence in the reaction. The results support the initial view that PMS have a higher powerful oxidizing potential compare to H_2O_2 . This phenomenon has shown in Fig. 8 and 17 before. Apart from that, it can be easily observed that the total degradation rate for $4 \times 10^{-2} M H_2O_2$ in methylene blue was 3.7% while in acid read 183 was only 1.8%. Besides that, the total degradation rate for $4 \times 10^{-4} M PMS$ in methylene blue was 44.4% while in acid read 183 was only 19.4%. This indicated that methylene blue as a basic dye is easier to degrade compare to acid red 183.

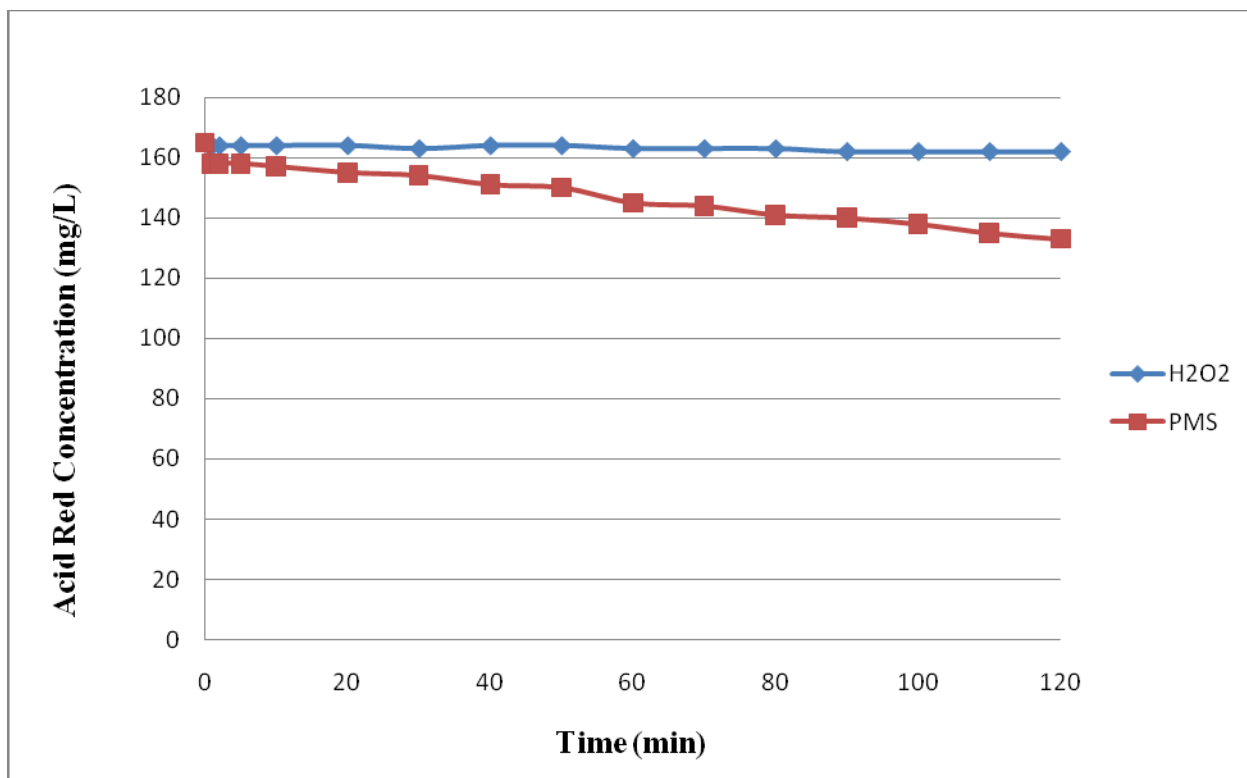


Figure 22: Degradation of different acid red 183 concentrations by using $4 \times 10^{-2} M H_2O_2$ and $4 \times 10^{-4} M PMS$

5.10 Kinetics of Co-MOF and Co^{2+} oxidations

The Co-MOF oxidation of dye and Co^{2+} oxidation of dyes can be represented by the following reaction kinetics.

$$\frac{dC}{dt} = -kC^n \quad (5)$$

Where, C = dye concentration, n = order of the reaction, k = reaction rate coefficient, t = time

Sulphate radicals and hydroxyl radicals are powerful oxidizing agent. Thus, they have high ability of oxidizing Co-MOF and Co^{2+} . This leads to the selection of first order rate equation. It is believed have adequate accuracy in modeling the reaction kinetics. For the first order reaction, the above equation after integration becomes,

$$C = C_o \exp(-kt) \quad (6)$$

Where, C_o = initial dye concentration.

Table 1 and **Table 2** shown below indicated the kinetics of Co-MOF and Co^{2+} oxidation on methylene blue and acid red 183.

Table 1: Kinetics of Co-MOF oxidation

Reaction	First-order	
	K (min^{-1})	R ²
<i>Methylene Blue</i>		
$1.303 \times 10^{-2} \text{ M Co-MOF} / 6 \times 10^{-2} \text{ M H}_2\text{O}_2$	0.0025	0.4491
$1.303 \times 10^{-2} \text{ M Co-MOF} / 8 \times 10^{-2} \text{ M H}_2\text{O}_2$	0.0040	0.6190
$1.303 \times 10^{-2} \text{ M Co-MOF} / 1 \times 10^{-1} \text{ M H}_2\text{O}_2$	0.0070	0.7571
$1.303 \times 10^{-2} \text{ M Co-MOF} / 1.2 \times 10^{-1} \text{ M H}_2\text{O}_2$	0.0104	0.8008
<i>Acid Red 183</i>		
$1.629 \times 10^{-3} \text{ M Co-MOF} / 4 \times 10^{-4} \text{ M PMS}$	0.0355	0.6537
$3.258 \times 10^{-3} \text{ M Co-MOF} / 4 \times 10^{-4} \text{ M PMS}$	0.0265	0.4931
$6.515 \times 10^{-3} \text{ M Co-MOF} / 4 \times 10^{-4} \text{ M PMS}$	0.0244	0.4490
$9.773 \times 10^{-3} \text{ M Co-MOF} / 4 \times 10^{-4} \text{ M PMS}$	0.0187	0.3390

Table 2: Kinetics of Co^{2+} oxidation

Reaction	First-order	
	K (min^{-1})	R ²
<i>Methylene Blue</i>		
$1.303 \times 10^{-4} \text{ M Co}^{2+} / 4 \times 10^{-4} \text{ M PMS}$	3.6678	0.9904
$1.303 \times 10^{-4} \text{ M Co}^{2+} / 4 \times 10^{-2} \text{ M H}_2\text{O}_2$	0.1130	0.9630
<i>Acid Red 183</i>		
$6.5154 \times 10^{-5} \text{ M Co}^{2+} / 4 \times 10^{-4} \text{ M PMS}$	0.0451	0.8677
$1.303 \times 10^{-4} \text{ M Co}^{2+} / 4 \times 10^{-4} \text{ M PMS}$	0.0465	0.5727
$8.59 \times 10^{-4} \text{ M Co}^{2+} / 4 \times 10^{-4} \text{ M PMS}$	0.0306	0.3992
$1.718 \times 10^{-3} \text{ M Co}^{2+} / 4 \times 10^{-4} \text{ M PMS}$	0.0346	0.4641

6 Conclusion

It can be concluded that, both Co-MOF and Co^{2+} catalysts studies provides good performance in the degradation of methylene blue acid red 183 and reactive blue 4 that presented in water. The reaction rate is faster by using PMS as an oxidizing agent compared to H_2O_2 . This is due to PMS has higher powerful oxidizing potential compare to H_2O_2 . Co catalysts coupling with PMS can lead to much higher degradation efficiencies. Methylene blue due to its basic dye characteristic is easier to degrade then acid red 183. Although there was some increase in reactive blue 4 concentration after 10 minutes, Co-MOF/PMS still performs very well for the first 10 minutes as reactive blue 4 is highly degraded. All of the degradation methods presented in this research are a good resource for any degradation project in the future. It is not only benefit to chemical industries but also to the society & environment. The observations of these investigations clearly demonstrated the importance of choosing the best degradation catalyst to obtain a highest reaction rate.

7 Recommendations

The reaction rate can be enhanced by running the experiment under lower pH condition. It is believed that certain catalysis, acidic condition gives better degradation rate. Further increase in the reaction temperature might give a better result. However, exorbitant temperatures might cause catalysis or oxidizing agent decomposed. Furthermore, increase the stirrer speed also another options to increase the reaction rate in order to achieve higher degradation rate. Besides that, use alternative catalyst or oxidizing might give different results on reactive blue 4. Lastly, different ways to produce Co-MOF, such as using autoclave might gives a better results on the degradation of methylene blue, acid red 183 and reactive blue 4.

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Nomenclature

Co-MOF	Cobalt-containing metal-organic framework
PMS	Peroxymonosulfate
rpm	Revolutions per minute

Appendices

Calculation for Cobalt (II) Nitrate [Hexahydrous] Cocentration

Molecular weight : 291.035g/mol

Amounts : 0.7584g

$$\begin{aligned} \text{Molarity} &= \frac{\text{moles of solute}}{\text{volume of solution (L)}} && (7) \\ &= \frac{0.7584\text{g}}{291.035\text{g/mol}} \\ &= \frac{0.2\text{L}}{0.2\text{L}} \\ &= 1.303 \times 10^{-2} M \end{aligned}$$

Molecular weight : 291.035g/mol

Amounts : 0.007584g

$$\begin{aligned} \text{Molarity} &= \frac{\text{moles of solute}}{\text{volume of solution (L)}} \\ &= \frac{0.007584\text{g}}{291.035\text{g/mol}} \\ &= \frac{0.2\text{L}}{0.2\text{L}} \\ &= 1.303 \times 10^{-4} M \end{aligned}$$

Calculation for Co-MOF Cocentrations

Molecular weight of cobalt (II) nitrate [hexahydrous]	: 291.035g/mol
Amounts of cobalt (II) nitrate [hexahydrous] used	: 14.79g
Amounts of Co-MOF produced	: 7.8g
Amounts of Co-MOF used in experiment	: 0.1g

$$\begin{aligned} \text{Molarity} &= \frac{\text{moles of solute}}{\text{volume of solution (L)}} \\ &= \frac{(0.1\text{g}/7.8\text{g}) \times 14.79\text{g}}{291.035\text{g/mol}} \\ &= \frac{\quad}{0.2\text{L}} \\ &= 3.258 \times 10^{-3} M \end{aligned}$$

Molecular weight of cobalt (II) nitrate [hexahydrous]	: 291.035g/mol
Amounts of cobalt (II) nitrate [hexahydrous] used	: 14.79g
Amounts of Co-MOF produced	: 7.8g
Amounts of Co-MOF used in experiment	: 0.4g

$$\begin{aligned} \text{Molarity} &= \frac{\text{moles of solute}}{\text{volume of solution (L)}} \\ &= \frac{(0.4\text{g}/7.8\text{g}) \times 14.79\text{g}}{291.035\text{g/mol}} \\ &= \frac{\quad}{0.2\text{L}} \\ &= 1.303 \times 10^{-2} M \end{aligned}$$

Calculation for PMS Cocentration

Amounts : 0.0030735g O₃

Known: 614 g/L O₃ = 2M PMS

$$\text{Thus, Concentration of PMS} = \frac{\text{mass of } O_3}{\text{volume of solution (L)}} \times 2M \text{ PMS}$$
$$= \frac{0.0030735g}{614.7g/L} \times 2M \text{ PMS}$$

$$= \frac{0.0030735g}{614.7g/L} \times 2M \text{ PMS}$$
$$= \frac{0.2L}{614.7g/L} \times 2M \text{ PMS}$$
$$= 5 \times 10^{-5} M \text{ PMS}$$

Amounts : 0.024588g O₃

Known: 614 g/L O₃ = 2M PMS

$$\text{Thus, Concentration of PMS} = \frac{\text{mass of } O_3}{\text{volume of solution (L)}} \times 2M \text{ PMS}$$
$$= \frac{0.024588g}{614.7g/L} \times 2M \text{ PMS}$$

$$= \frac{0.024588g}{614.7g/L} \times 2M \text{ PMS}$$
$$= \frac{0.2L}{614.7g/L} \times 2M \text{ PMS}$$
$$= 4 \times 10^{-4} M \text{ PMS}$$

Project Log Book

