Degradation of methylene blue utilizing cobalt-impregnated zeolite beta via sulfate radical-based advanced oxidation process

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Abstract. Sulfate radical-based oxidation process (SRAOP) is an efficient way to completely degrade toxic dyes from wastewater. The purpose of this study is to utilize zeolite beta to support cobalt ions as a catalyst for such application. Zeolite beta was synthesized hydrothermally with SiO2/Al2O3 ratio of 30. Cobalt was impregnated into zeolite beta via wet impregnation method, with cobalt loading of 2wt% and 5wt% Co2+/zeolite beta. Catalyst characterization was done by XRD, ICP, SEM-EDS, FT-IR, BET, and TPD. Methylene blue was used as model dye to investigate the catalytic capability of the catalyst. The set up for the batch reaction was a 500 mL beaker containing 200 mL of 100 ppm dye mechanically stirred at 300 rpm. Oxone concentration was 2mM and the catalyst loading was varied with concentrations of 0.1, 0.5 and 1 g/L. UV-vis was employed to determine the concentration of dye remaining in the solution. Catalyst particle size ranged from 150 to 300 nm with BET surface area of 576.2 m2/g. The dye exhibited adsorption activity to the zeolite, where 92.4% of the dye were adsorbed after 2 hours. Degradation capability of the catalyst was satisfactory, reaching 100% removal after 45 minutes. The study showed that utilization of zeolite beta as a support for cobalt shows promising results for SRAOP application.

1. Introduction
Removal of dyes in wastewater prior to discharge is necessary due to more stringent regulations, and the carcinogenic and toxic nature of organic dyes [1]. Sulfate radical-based advanced oxidation process (SR-AOP) is one of the most promising technologies for the total degradation of most organic compounds, including dyes. Oxone® (peroxymonosulfate, PMS, as the active component) is an environmentally friendly oxidant and is the usual choice for the source of sulfate radicals (SR). SR generation has been reported to be accelerated by coupling PMS with Co2+ [2]. However, the usage of homogeneous cobalt ions raises a potential hazard regarding the cobalt content and toxicity in the effluent, thus heterogeneous sources of Co2+ using supported cobalt oxide have been given a lot of attention lately. To obtain a good catalyst for this heterogeneous catalyzed oxidation process, it is important for the active metal (Co2+) to be well dispersed on the surface of a support material with high surface area. In this regard, zeolites, owing to their microporous structures with regular array of channels (high surface area) and high hydrothermal stability, is chosen to be the support material for cobalt [3].
SRAOP has been shown to be a promising alternative to the traditional AOP methods involving methods involving the hydroxyl radical (OH·) attributable to a series of properties of the sulfate radical (SO₄²⁻): (a) SO₄²⁻ has a higher oxidation potential versus OH·, (b) SO₄²⁻ reacts more selectively and with organic compounds (c) the half-life period of SO₄²⁻ is generally 30–40 μs, which enables SO₄²⁻ to have more stable mass transfer and better contact with target compounds [4]. One of the ways to generate sulfate radicals is from the chemical activation of peroxymonosulfate (PMS, HSO₅²⁻) or persulfate (PS, S₂O₅²⁻). Oxone®, a commercial name for potassium permonosulfate (KHSO₅·0.5KHSO₅·0.5K₂SO₄), has been widely used as an environmentally friendly oxidant and source of PMS. PMS can be activated by various transition metal ions, such as Mn²⁺, Ce³⁺, Ni²⁺, Fe³⁺, and so forth, to produce the sulfate radicals. Among them, Co³⁺/PMS system displays the best performance and is shown to be better than the traditional Fenton reaction [5]. Homogeneous activation of PMS by transition metals has its disadvantages due to the difficulty of removing the metals from the effluent, which pose environmental threats from the toxicity of the metals, hence the need for the catalyst to be in solid phase for ease of separation from the liquid phase [2]. For this purpose and in the case of cobalt, several methods have been done such as cobalt oxide nanoparticles, metal oxide supports, zeolites, and carbon-derived supports [5].

The most studied materials for supporting cobalt for SRAOP application have been metal oxides, such as TiO₂, MgO, Al₂O₃, SiO₂, MnO₂, and ZnO [2]. Zeolites possess important properties for catalysis, such as high surface area, porosity, thermal stability, which are superior to that of metal oxides. Studies show that zeolites having high Si/Al ratio has shown favorable results for the incorporation of cobalt, and for this reason, zeolite beta was chosen for this study.

The aim of this paper is to synthesize and characterize a catalyst using zeolite beta as a support for cobalt for the activation of peroxymonosulfate (PMS) to generate sulfate radicals (sulfate radical activation by various transition metal ions, such as Mn²⁺, Ce³⁺, Ni²⁺, Fe³⁺, and so forth, to produce the sulfate radicals. Among them, Co³⁺/PMS system displays the best performance and is shown to be better than the traditional Fenton reaction [5]. Homogeneous activation of PMS by transition metals has its disadvantages due to the difficulty of removing the metals from the effluent, which pose environmental threats from the toxicity of the metals, hence the need for the catalyst to be in solid phase for ease of separation from the liquid phase [2]. For this purpose and in the case of cobalt, several methods have been done such as cobalt oxide nanoparticles, metal oxide supports, zeolites, and carbon-derived supports [5].

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The aim of this paper is to synthesize and characterize a catalyst using zeolite beta as a support for cobalt for the activation of peroxymonosulfate (PMS) to generate sulfate radicals (sulfate radical-based advanced oxidation process, SR-AOP) for the degradation of textile dyes. Characterization methods include powder X-ray diffraction (XRD), fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy with energy dispersive x-ray spectroscopy (SEM-EDS), Brunauer-Emmett-Teller surface area (BET), and temperature-programmed desorption (TPD). Catalytic activity of the catalyst was studied by investigating the effects of catalyst loading, cobalt loading, as well as adsorption due to the porous nature of zeolite beta. UV-visible spectroscopy was employed in determining the concentration of the dye after reaction.

2. Experimental

2.1. Chemicals and reagents
For the synthesis of zeolite beta, Ludox® AS-40 colloidal silica (SiO₂, 40wt.% suspension in H₂O) was purchased from Sigma-Aldrich, sodium aluminum oxide (Al₂O₃·Na₃O) and tetraethylammonium hydroxide (TEAOH, 35% w/w aq.) were from Alfa Aesar. Cobalt sulfate heptahydrate (CoSO₄·7H₂O) was from Showa Chem Co. Ltd. The dye used was methylene blue trihydrate from Alfa Aesar. Oxone® was purchased from Sigma-Aldrich. Sodium nitrite (≥99%) from Sigma-Aldrich was used to quench the reaction in the samples.

2.2. Synthesis of cobalt-impregnated zeolite beta (Co/Beta)
Zeolite Beta (BEA) was synthesized by hydrothermal synthesis using SiO₂, Al₂O₃·Na₃O, and TEAOH. Reactants were weighed with SiO₂: Al₂O₃·Na₃O:TEAOH mole ratio of 30: 1:15. TEAOH and Al₂O₃·Na₃O were mixed (300 rpm) first and allowed to age for 5 minutes. Silica was subsequently added and allowed to age for another 5 minutes. Afterwards, the solution was transferred to a Teflon-lined autoclave and reacted hydrothermally in an oven at 170°C for 24 hours to undergo crystallization. The resulting mixture was centrifuged, washed with deionized water, and dried at 60°C. The dried white powder was ground and then calcined at 500°C for 6 hours. Finally, the zeolite was ground again and stored for later use.

Impregnation of cobalt ions to the zeolite beta was done by mixing 3 mL of cobalt solution with 1 g
of BEA. Cobalt solutions of 0.283 M CoSO₄·7H₂O and 0.113M CoSO₄·7H₂O were prepared, which would correspond to Co/Beta mass ratio of 0.05 and 0.02, respectively and will be denoted as 5% Co/Beta and 2% Co/Beta throughout the study. Similarly, unimpregnated BEA would be denoted as 0% Co/Beta. The resulting mixture was dried at 60°C, ground, and calcined at 600°C for 6 hours. The powder was washed to remove loosely attached cobalt ions and other impurities. Finally, the Co/Beta was dried and ground.

2.3. Characterization of Co/Beta

XRD analyses were recorded in the 2θ range of 5° to 65° with a scan step of 0.01° (2θ). Inductively coupled plasma optical emission spectrometry (ICP-OES) was utilized to determine the amount of cobalt ions impregnated into BEA. Cobalt leaching was also measured using ICP-OES. The morphology of the catalysts was observed using a SEM equipped with energy-dispersive spectrometer (EDS). The FT-IR spectra of catalyst samples were recorded in the 4000 to 400 cm⁻¹. The BET specific surface area of the catalysts was characterized using N₂ at 77K as the adsorbate. Temperature-programmed desorption of CO₂ and NH₃ to measure the basicity and acidity of the catalysts, respectively.

2.4. Catalytic activity

Dye degradation was conducted at a room temperature in a 500 mL glass beaker. Typically, 200 mg (1 g/L) of the catalyst and 123 mg (2 mM) of Oxone® were added to 200 mL of 100 ppm of dye with a constant stirring rate of 300 rpm. 1 mL of the suspension was withdrawn from the beaker at certain time intervals and was quickly quenched with 1 mL of 0.1 M NaNO₂. The samples were further diluted with 8 mL deionized water (dilution factor = 10) and centrifuged to separate the solid catalyst from the supernatant, which subsequently underwent UV-vis spectroscopy to measure the absorbance of the dye.

3. Results and discussion

3.1. Characterization

![Figure 1. XRD patterns of Co/Beta with different cobalt loading.](image-url)

3.1.1. Powder X-ray diffraction (XRD). XRD pattern of the synthesized zeolite (0% Co/Beta) shown in figure 1 possesses the characteristic peaks of the BEA (IZA) standard, which confirms that the synthesized zeolite was indeed zeolite beta. The results also suggest that zeolite retained its structure after impregnation and calcination. The standards for CoO or Co₃O₄ were also obtained and compared with Co/Beta. However, no new peaks appeared, suggesting cobalt ions were highly dispersed in the surface or there is a low amount of cobalt impregnated into the zeolite, both of which would result to
low XRD signals and subsequently be drowned out by the strong signals of zeolite beta [6].

3.1.2. Cobalt loading. The amounts of cobalt in the solution used for the impregnation of Co$^{2+}$ are 50 mg/g beta and 20 mg/g beta for 5% Co/Beta and 2% Co/Beta, respectively. Through ICP analysis, the actual amount of cobalt impregnated into the zeolite beta was determined with 16.585 and 13.539 mg Co$^{2+}$/g beta for 5% and 2% Co/Beta, respectively.

3.1.3. Scanning electron microscopy. SEM analysis (figure 2) shows that zeolite beta is spheroidal with particle size range from 150 to 300 nm. After impregnation, no significant change was observed in the morphology and size. However, square-shaped crystals can be seen which could be Co$_3$O$_4$.

![Figure 2. SEM micrographs of (a) 0% Co/Beta, and (b) 5% Co/Beta at x30000 magnification.](image)

3.1.4. Fourier transform infrared spectroscopy. Figure 3 shows that there is no discernible difference in the IR spectra of the catalyst even after cobalt impregnation and reaction with methylene blue with the presence of Oxone, suggesting that the catalyst retained its functional groups. Moreover, despite having a strong adsorption activity for methylene blue, as observed in dye degradation, no peaks corresponding to methylene blue appeared in the spectra of the catalyst after the reaction. It is likely that the sulfate radicals also degraded any methylene blue that adsorbed into the catalyst.

![Figure 3. FT-IR spectra of (a) Zeolite Beta, (b) 5% Co/Beta, (c) 5% Co/Beta after reaction with methylene blue and Oxone.](image)
3.1.5. Brunauer-emmett-teller analysis. BET surface areas for 0% and 5% Co/beta were determined to be 665.9 and 576.2 m$^2$/g, respectively. The reduction in the surface area after impregnation of cobalt can be attributed to the cobalt molecules clogging the pores of the zeolite. The N$_2$ sorption isotherms of zeolite Beta and cobalt-impregnated Beta are shown in figure 4. Both seem to follow Type IV isotherm. The steep rise uptake at low P/P$_0$ is typical of microporous materials, while the hysteresis loop observed at P/P$_0$ between 0.6 and 1.0 can be explained by interparticle capillary condensation because of small particle sizes [7].

![Figure 4. N$_2$ sorption isotherm of 0% Co/Beta and 5% Co/Beta.](image)

3.1.6. Temperature-programmed Desorption. As shown in figure 5, the peak at 300°C, attributed to strong basic sites [8,9], is only present in the profile of 5% Co/Beta. The appearance of this peak suggests that basic sites have been formed after the impregnation process. Furthermore, the slight shifting of the first and second peak to a higher temperature implies that the sites became more basic [8,9]. While it was shown that both 0% Co/Beta and 5% Co/Beta possess very strong basic sites, the low amount of desorbed CO$_2$ shown in table 1 implies that the number of basic sites is very low.

![Figure 5. TPD – CO$_2$ profile of Beta zeolite and cobalt-impregnated beta zeolite.](image)  
![Figure 6. TPD – NH$_3$ profile of Beta zeolite and cobalt-impregnated beta zeolite. Perforated lines are deconvoluted peaks of TPD – NH$_3$ profile of Beta zeolite by Gaussian function.](image)

The TPD-NH$_3$ profile for 0% Co/Beta was deconvoluted using the Gaussian function to reveal the overlapping peaks, as shown in figure 6. The peaks centered on 75 to 150°C are associated with weak acid sites, the one on 330°C is strong acid site, while the one on 600°C corresponds to very strong acid site [8,9]. The peaks of 0% Co/Beta on 76.83°C and 154.3°C have combined in a larger peak after impregnation. The increase of these peaks can be ascribed to the Co$^{2+}$ being a Lewis acid [10], therefore increasing the number of acid sites of the catalyst. Further, the peak on 326.9°C seem to have
shifted very far to 604.8°C, indicating a significant increase in acid site strength.

**Table 1.** CO₂ and NH₃ desorbed per gram of catalyst at peak temperatures in the TPD – CO₂ and TPD – NH₃ profiles, respectively.

| Temp. (°C) | CO₂ (cm³/g cat STP) | Temp. (°C) | CO₂ (cm³/g cat STP) | Temp. (°C) | NH₃ (cm³/g cat STP) | Temp. (°C) | NH₃ (cm³/g cat STP) |
|------------|---------------------|------------|---------------------|------------|---------------------|------------|---------------------|
| 28.4       | 0.6882              | 56.7       | 1.11276             | 76.83      | 24.12911            | 85         | 70.90536            |
| 156.9      | 2.1984              | 189.7      | 1.94051             | 154.3      | 24.90029            | 604.8      | 5.23603             |
| 645.4      | 1.0105              | 301.1      | 1.88587             | 326.9      | 9.86388             |            |                     |
|            |                     | 617.1      |                     |            |                     |            |                     |
| Total      | 3.8971              |            |                     |            | 6.83176             | 58.89328   | 76.14139            |

3.2. **Dye degradation**

Methylene blue was used as model dye to investigate the catalytic capability of cobalt-impregnated beta zeolite and Oxone. Dye degradation is achieved by oxidizing the dye molecules with sulfate radicals generated from Oxone using cobalt-impregnated zeolite beta.

The mechanism of generation of sulfate radicals and degradation of organic compounds has been suggested as follows [5]:

\[
\begin{align*}
\text{Co}^{2+} + \text{H}_2\text{O} & \rightarrow \text{CoOH}^+ + \text{H}^+ \\
\text{CoOH}^+ + \text{HSO}_5^- & \rightarrow \text{SO}_4^\cdot + \text{CoO}^+ + \text{H}_2\text{O} \\
\text{CoO}^+ + 2\text{H}^+ & \rightarrow \text{Co}^{3+} + \text{H}_2\text{O} \\
\text{Co}^{3+} + \text{HSO}_5^- & \rightarrow \text{SO}_4^\cdot + \text{Co}^{2+} + \text{H}^+ \\
\text{SO}_4^\cdot + \text{organic dyes} & \rightarrow \text{intermediate products} \rightarrow \text{CO}_2 + \text{H}_2\text{O}
\end{align*}
\]

The potential for the catalyst to be reused is implied in equation (4), where Co³⁺ reverts to Co²⁺ thus being able to restart the catalysis for sulfate radical formation.

![Figure 7. Degradation profile of MB – control experiments. Reaction conditions: 300 rpm stirring rate, ambient temperature, 200 mL 100 ppm MB, 2 mM Oxone.](image-url)

3.2.1. **Control experiments.** In order to see whether the degradation of methylene blue can be ascribed solely to sulfate radical oxidation, experiments with only the (1) beta zeolite, (2) cobalt-impregnated
beta zeolite, and (3) Oxone only, as shown in Figure 7. The profile of these three controls were compared to the degradation profiles of the beta zeolite and cobalt-impregnated zeolite when reacted together with Oxone. The relative concentration of MB significantly decreased when the beta zeolite and cobalt-impregnated beta zeolite were used, leaving only 7.4% and 4.3% of MB in the solution after 2 hours implying that both catalysts exhibit strong adsorption activity for MB due to MB being a basic dye and the catalyst has strong acid sites, as discussed in the TPD-NH₃ analysis. On the other hand, Oxone, when used alone, degraded MB very slowly, leaving 71.2% of MB after 2 hours of reaction. This is due to the slow auto-activation of Oxone, as compared to the cobalt-mediated activation to generate sulfate radicals. As a reference throughout the study, the reaction with 1 g/L 5% Co/Beta with Oxone will be used for further comparison.

3.2.2. Effect of catalyst loading. As seen in Figure 8, higher amounts of the catalyst (Co/Beta) greatly enhances the degradation of MB. The reference reaction (1 g/L 5% Co/Beta with Oxone) degraded 100% of the dye after 45 minutes of reaction, while the reactions having 0.5, 0.1, and 0 g/L of catalyst degraded only 86.6%, 49.6%, and 22.9% of the dye during the same period. The amount of cobalt introduced into the system is proportional to the amount of the catalyst and subsequently, a higher amount of cobalt will favor the generation of sulfate radicals, hence, the improved degradation of MB. However, it should be noted that excess amounts of catalyst will cause an aggregation of particles and inhibition of the reaction [2,4].

3.2.3. Effect of cobalt loading. The amount of cobalt impregnated into the catalyst was varied. It is shown in Figure 9 that 2% Co/Beta enhances the degradation greatly versus using zeolite beta alone with Oxone. This is because the generation of sulfate radicals via activation of PMS require only a small dosage of metal ions, in this case, cobalt ions [2,4]. Additionally, an increase of cobalt loading to 5% does not seem to improve the degradation significantly (100% degradation vs 97.1% degradation after 45 mins, for 5% Co/Beta and 2% Co/Beta, respectively). The reason for this is the difference between the actual amounts of cobalt impregnated into the two catalysts is not much (16.585 mg Co²⁺/g beta and 13.539 mg Co²⁺/g beta for 5% and 2% Co/Beta, respectively). This suggests that simply increasing further the cobalt loading will not be an effective way to improve the catalytic activity of the catalyst.

4. Conclusion
Hydrothermal synthesis of zeolite beta and utilizing the zeolite as a support for cobalt was done successfully. The actual amount of cobalt impregnated into the zeolite beta support (16.585 mg Co²⁺/g
beta). The catalyst was seen to be spherical in shape with particle size ranging from 150 to 300 nm. BET surface area of the catalyst was determined to be 665.9 m$^2$/g and was reduced to 576.2 m$^2$/g after subsequent impregnation method. The catalyst was highly acidic and there were strong basic sites albeit very few. MB displayed strong adsorption to the catalyst due to MB’s basicity interacting with the acidic zeolite beta. However, despite MB being strongly adsorbed into the catalyst, it is suggested that the adsorbed MB was also degraded since Oxone was present to produce sulfate radicals. 5% Co/Beta reached 100% degradation of MB after 45 minutes. Increasing the catalyst loading enhanced the degradation of MB. Similarly, increasing the cobalt loading on the catalyst greatly enhanced the degradation compared to using Oxone alone, even with a relatively low cobalt loading (2% Co/Beta). An increase to 5% Co/Beta improved the degradation but not as much, suggesting that further increase in cobalt loading will not be an efficient way to increase catalytic activity.

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