

*Original Research Article*

# Utilization of Sidoarjo Volcanic Mud as Heterogeneous Catalyst in Persulfate Oxidation Process for Congo Red Dye Removal: A Preliminary Study

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## Abstract

Advanced Oxidation Processes (AOP), such as persulfate oxidation is a promising contaminant removal agent for treating wastewater. In this study, Sidoarjo volcanic mud (VM) was applied as heterogeneous catalyst to support the persulfate oxidation process for Congo Red (CR) dye removal. The Sidoarjo volcanic mud is known to have a high iron content, making it a potential catalyst in AOP. This study was conducted under conditions of pH 2, CR 50 mg/L, and catalyst dosage 0.5 g/L and effective reaction volume of 300 mL. This experiment was conducted by comparing three types of catalysts: unmodified volcanic mud (UVM), impregnated volcanic mud (Fe-IVM), and calcined volcanic mud (CVM). The methods were carried out by comparing two methods, namely simultaneous and sequential. The obtained CR removal values for UVM, Fe-IVM, and CVM catalysts were 83.73%, 78.86%, 51.96% for simultaneous and 84.75%, 81.72%, and 87.69% for sequential method. Whereas the UVM catalyst has the highest CR removal value with a lower adsorption value of 16.89%. The production of sulfate radical analyzed by comparing the oxidation process of homogeneous and heterogeneous catalysts. It was shown that the application of VM catalyst as heterogeneous catalyst is very promising for dye removal in wastewater treatment.

**Keywords:** Persulfate Oxidation; congo red; volcanic mud; heterogeneous catalyst

## 1. Introduction

The production growth of industrial and social sectors is growing rapidly, whereby the waste generated from these activities continues to increase. Industrial wastewater is one of the impacts caused by these events which has harmful traits to the local environment, the majority of the waste is toxic and non-biodegradable (González-Labrada et al., 2019). The textile industries discharge a wide range of multicolored synthetic dyes directly into the water system, which are toxic, mutagenic, and non-biodegradable (Moulick et al., 2023).

Dyes are commonly used in many industries such as paper, textile, screen printing, and food industries. Approximately 10 - 15% of dyes can be found in wastewater. These effluents potentially block the penetration of sunlight and oxygen which interferes with aquatic ecosystem functions (Al-Tohamy et al., 2022). Synthetic dyes commonly used in the textile industry are azo dyes, which contain azo chains, namely nitrogen groups double bonded with nitrogen (Komala et al., 2007). A commonly used azo dye is CR, with properties that are resistant to smears and not easily removed by physical treatments or chemical treatments (Dio et al., 2021).

Several studies developed methods to remove these dyes such as adsorption, coagulation, ozonation, ion exchange filtration, and others (Vignesh and Shanmugam, 2023). Such treatment methods are proven to be ineffectively removing the dyes (Rubeena et al., 2018; Deng, Yang, et al., 2023). Nowadays, renewable technologies such as the AOP have become a hot topic for researchers and have been known to interfere the stability of dye contaminants. AOP is essentially a process that produces hydroxy radical groups ( $\cdot\text{OH}$ ) and sulfate radical groups ( $\text{SO}_4^{\cdot-}$ ) (Ahmadi et al., 2019). These persulfate oxidizers contain an oxidizing value ( $E_0 = 2.01 \text{ V}$ ) close to the value of ozone ( $E_0 = 2.07 \text{ V}$ ) and higher than the peroxide oxidizer ( $E_0 = 1.77 \text{ V}$ ). Likewise, the redox potential value of the radical compound  $\text{SO}_4^{\cdot-}$  ( $E_0 = 2.5\text{-}3.1 \text{ V}$ ) is higher than the value of  $\text{OH}^-$  ( $E_0 = 1.8\text{-}2.7 \text{ V}$ ) which becomes an advantage of persulfate (Xia et al., 2020). This allows sulfate radical group-based AOP to have a high selectivity compared to hydroxyl radical groups (Wang and Wang, 2018).

Sidoarjo VM was formed as a residue of the 2006 volcanic explosion that occurred in Sidoarjo, East Java, Indonesia. These muds are increasingly reaching 50,000 to 120,000  $\text{m}^3$  per day from a hole that has a diameter of  $\pm 50 \text{ m}$  (Putri et al., 2019). Several studies have been undertaken on the characteristics of the mud, where the mud is known to contain a large percentage of iron around 34-36% (Ciptawati et al., 2022). The overflowing of Sidoarjo lapindo mud, which is known to contain heavy metals, may cause pollution to the environment such as contamination to the nearby Porong and Aloo rivers (Sa'diyah et al., 2017). Therefore, the utilization of Lapindo mud, particularly on an industrial scale, may benefit both environmental and economic aspects (Ulfindrayani et al., 2019). Some utilization of iron content in sludge has been done in many processes, such as adsorption (Zhou et al., 2024); electroplating (Gao et al., 2024), anaerobic digestion (Jin et al., 2024), AOP (Luo et al., 2021), and other processes. AOP with persulfate oxidizer (PS) has been shown to be activated with iron catalysts and has been proven to aid in the activation of persulfate to produce sulfate radical groups as done by several studies (Zheng et al., 2022).

Modification of heterogeneous iron catalysts such as the addition of heat, light, electric field, ultrasound, magnetic field, impregnation, and calcination had been applied in the persulfate activation system (Li et al., 2021). Those modifications were successful in generating the radical and nonradical activation in the removal of aqueous organic. Based on previous studies, impregnation and calcination methods of catalyst activation are chosen in this study due to cost-effectiveness, simplicity, easy scale, and reduced energy consumption (Hussain et al., 2021; Moccia et al., 2021; Lama et al., 2022;). The application of iron catalysts requires research on catalyst activation with the aim of increasing the effectiveness and selectivity of the oxidation reaction. The studies were carried out by modifying the surface properties and structure of the catalysts, with the aim of enhancing their stabilization and ability to activate persulfate (Zhi et al., 2021; Tian et al., 2022; Zheng et al., 2022).

In the past few years, researchers have been investigating the treatment of textile industry effluents and the treatment technology continues to develop each year. Some studies have applied the persulfate oxidation process with the iron catalyst in textile effluent treatment (Cifci et al., 2020; Kusic et al., 2011; Wang et al., 2017). This process achieves >90% dye removal, but it requires an economic evaluation of the use of iron catalysts. Considering this, several studies have utilized iron-containing in the sludge as a catalyst for the persulfate oxidation process (Ioannidi et al., 2020; Matthaïou et al., 2018; Soubh et al., 2018; Deng et al., 2023). The catalyst is considered a low-cost and effective catalyst. The study of the utilization of Sidoarjo VM as a catalyst in the oxidation process has never been done, hence this study of Sidoarjo VM is carried out as a novelty alternative catalyst in the persulfate oxidation process in degrading dyes. The main objective of this study is to analyze the effectiveness of utilizing Sidoarjo VM as heterogeneous catalyst to remove CR dye in the persulfate oxidation process. This experiment was observed by comparing three types of catalyst activation to the removal of CR dye, namely unmodified mud or raw mud, calcined, and impregnated.

## 2. Methods

### 2.1. Materials

The volcanic mud samples were obtained from Sidoarjo, East Java, Indonesia. Sidoarjo volcanic VM was gathered within 500 m of the mudflow site in Porong District, Sidoarjo Regency, East Java. Then the mud was dried at 100°C for 24 hours. The preparation of VM prior use is explained in detail in the next section. CR dye, sodium persulfate (PS) ( $\text{Na}_2\text{S}_2\text{O}_8$ , 98%),  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , sulfuric acid ( $\text{H}_2\text{SO}_4$ ), sodium hydroxide, sodium bicarbonate, potassium iodide were all analytical grade compounds purchased from Merck (Germany). All of the work solutions were prepared using distilled water. The pH of each solution was adjusted by using  $\text{H}_2\text{SO}_4$  or NaOH solution.

### 2.2. Catalyst Preparation

The preparation of unmodified catalyst Sidoarjo VM was made by grinding the volcanic mud sample and sieving it with a 100 mesh sieve using a sieve shaker. Then these samples were heated at 60°C for 3 hours. This unmodified volcanic mud called as UVM catalyst.

The modification of the catalyst by impregnation was performed by a method that has been carried out by Laib et al (2019). Iron used for impregnation was 4.4 grams of iron salt ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) dissolved in distilled water. Impregnation was carried out in a glass beaker where 8 grams of UVM catalyst was mixed with iron salt solution and then agitated with a magnetic stirrer at 80°C until the water evaporated. The catalyst then heated at 105°C for 24 hours and continued with drying at 300°C for 2 hours. The result of the impregnation called as Fe-IVM catalyst.

The modification of the catalyst by calcination using the calcination method undertaken by research Talib et al (2016). The method was performed by preparing the UVM catalyst with heating at 550°C for 3 hours in order to eliminate the impurities. The result of the calcination method called as CVM catalyst.

### 2.3. Experimental Procedures

The CR standard solution was prepared by adding 0.5 grams of CR powder with distilled water to a concentration of 500 mg/L. A working solution of 50 mg/L CR was prepared by measuring a defined volume of CR standard solution to achieve the desired concentration. The pH was adjusted with  $\text{H}_2\text{SO}_4$  or NaOH solution to achieve the desired pH of 2. Then catalyst was added to the working solution. Each experiment used 300 mL reaction volume and a magnetic stirrer set at 300 rpm for constant mixing. The reaction was carried out for 60 minutes at ambient temperature of 25°C. The following reactions can be produced in the oxidation process by sulfate radical groups in this experiment following equation 1-6 (Ahmadi et al., 2019; Ioannidi et al., 2020):



Each experiment was performed in duplo. The effect of the activation type of VM catalyst, namely without modification or UVM, activation by impregnation (Fe-IVM) using  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and by calcination (CVM) on the removal of CR was evaluated. A comparative experiment between homogeneous ( $\text{FeCl}_3$  and  $\text{FeSO}_4$ ) and heterogeneous catalysts (UVM) was also proposed in this study.

### 2.4. Analytical Methods

The initial concentration through to residual CR was determined by spectrometric method ( $\lambda = 499 \text{ nm}$ ) using a DR 1900 Spectrophotometric instrument. Fe leached from the working solution was determined by measuring the absorbance using HACH FerroVer® iron reagent and DR 1900

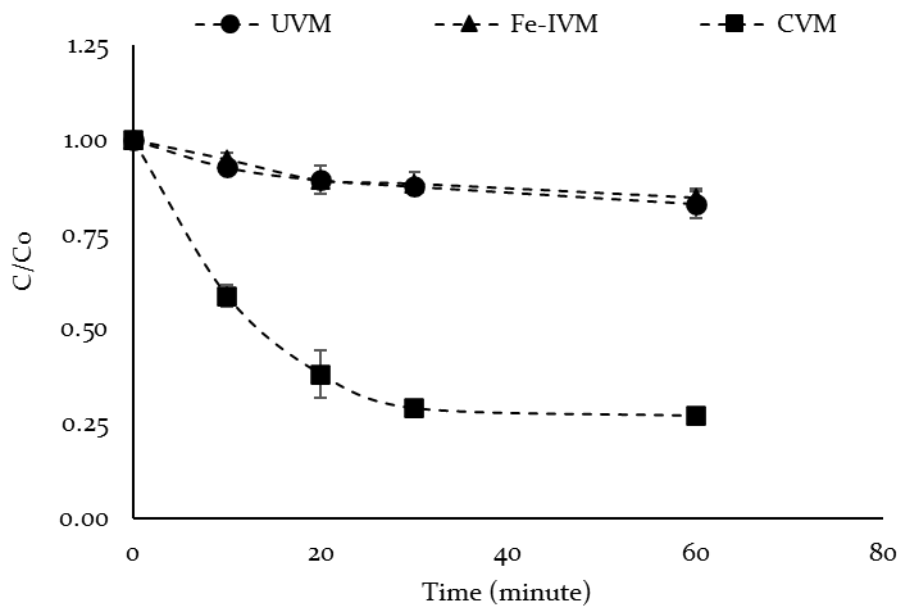
Spectrophotometric instrument at 510 nm wavelength. The residual of PS was determined by titration method using the Thiosulfate standard (0.01 N) from previous research by Kolthoff and Stenger (1947). To determine the success of a catalyst on CR removal, a graph plotting the effectiveness of CR removal ( $C/C_0$ ) against reaction time was formed. The calculation of CR removal effectiveness is based on the equation (7) (Xia et al., 2020).

$$\text{Effectivity of CR} = \frac{C_t}{C_0} \quad (7)$$

### 3. Results and Discussion

#### 3.1. Analysis the Contribution of Adsorption Mechanism

The performance comparison of catalysts was carried out on three types of catalysts: UVM, Fe-IVM, and CVM.



**Figure 1.** Comparison of three catalysts performance on adsorption. reaction conditions:  $[CR]_0 = 50$  mg/L,  $[PS:COD]_0 = 1:1$ ,  $pH = 2$ , and agitation speed = 300 rpm.

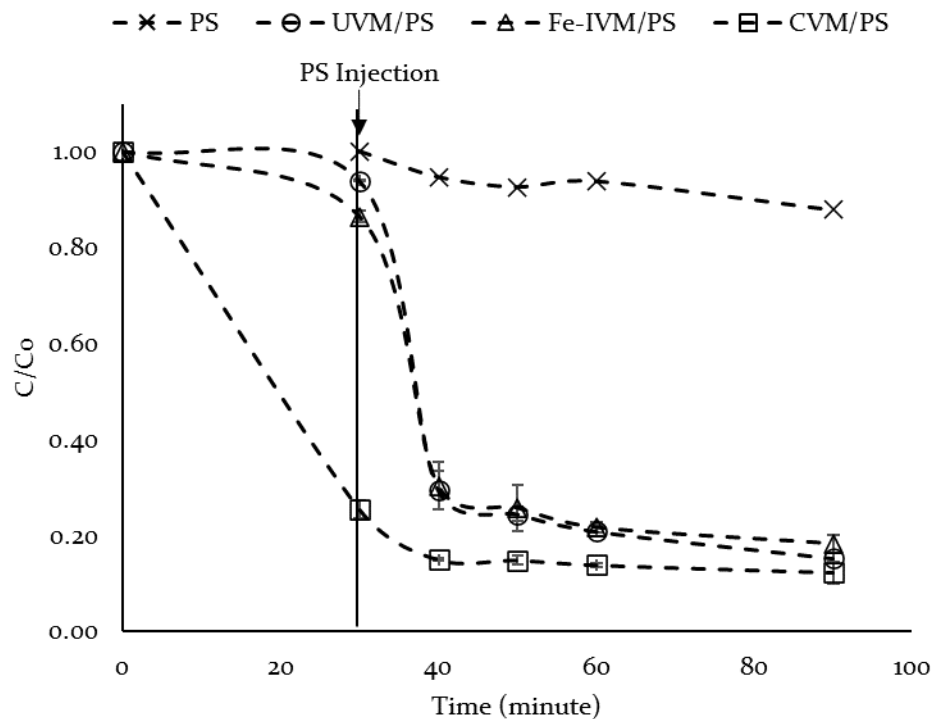
The adsorption experiments towards the removal of CR synthetic solution were carried out under pH 2, CR concentration 50 mg/L, and catalyst dosage 0.5 g/L. It can be seen in Figure 1 that removals of CR for UVM, Fe-IVM, and CVM catalysts reached 16.89%, 15.26%, and 73.05%, respectively, in 60 minutes. The adsorption result on CR removal for the CVM catalyst was higher than UVM and Fe-IVM. The high value of CR adsorption of CVM catalyst is due to the calcination up to 550°C within 3 hours. Whereas the effect of high-temperature heating can identify the volatile organic matter as impurities on the surface of the catalyst are removed, thus increasing the surface area (Jalil et al., 2010; Kumar et al., 2020). This also can be seen in a similar study by Talib et al. (2016), there is an increment in surface area and pore diameter before and after catalyst high-temperature heating, from a surface area of 7.478 m<sup>2</sup>/g to 14.291 m<sup>2</sup>/g and a pore diameter of 6.45 nm to 22.15 nm.

Meanwhile, the adsorption of CR for catalysts UVM and Fe-IVM are insignificantly different. These results are opposite to research on impregnation methods in general, where the results of catalysts activated by these methods have promising results (Shah et al., 2015; Tarekegn et al., 2021; Kyrii et al., 2023). This variation of result could be due to physical and chemical changes to the adsorbent such as surface area and pore diameter. In the study by Park et al (2015), it was found that catalyst impregnation decreased the surface area from 631 m<sup>2</sup>/g to 323 m<sup>2</sup>/g. The impregnation method resulted in a significant surface area decrease, most likely as a result of its highest Fe loading and comparatively large amorphous structures (Park et al., 2015). The amorphous structure can limit the activation of the catalyst which in

turn affects the color removal, this structure can also reduce the number of active sites for the reaction (Luo et al., 2022). The same result was also obtained in the experiment by Maicaneanu et al (2022), that the adsorption value of crystal violet dye natural catalyst and impregnated catalyst had no significant change, namely 58.8% and 76.2% (Maicaneanu et al., 2022).

### 3.2. Oxidation Persulfate Process

This experiment was performed on the persulfate oxidation process to remove CR dye by comparing the decomposition of PS itself and the use of three modified catalysts as UVM/PS, Fe-IVM/PS, and CVM/PS. The two methods used in the experiment were the sequential and simultaneous method. The sequential method was carried out where the PS oxidant injected at  $t = 30$  min, whereby the adsorption process in the reaction was estimated to reach equilibrium. The objective of the sequential method was to optimize the reaction between adsorption and persulfate oxidation (Weng and Tao, 2018; Wang et al., 2021; Lv et al., 2022). The simultaneous method provides advantages such as reduced reaction time with high effectiveness and a simplified process of treating various contaminants (Hajalifard et al., 2023). The simultaneous method was performed where the PS oxidant was injected at  $t = 0$  min.

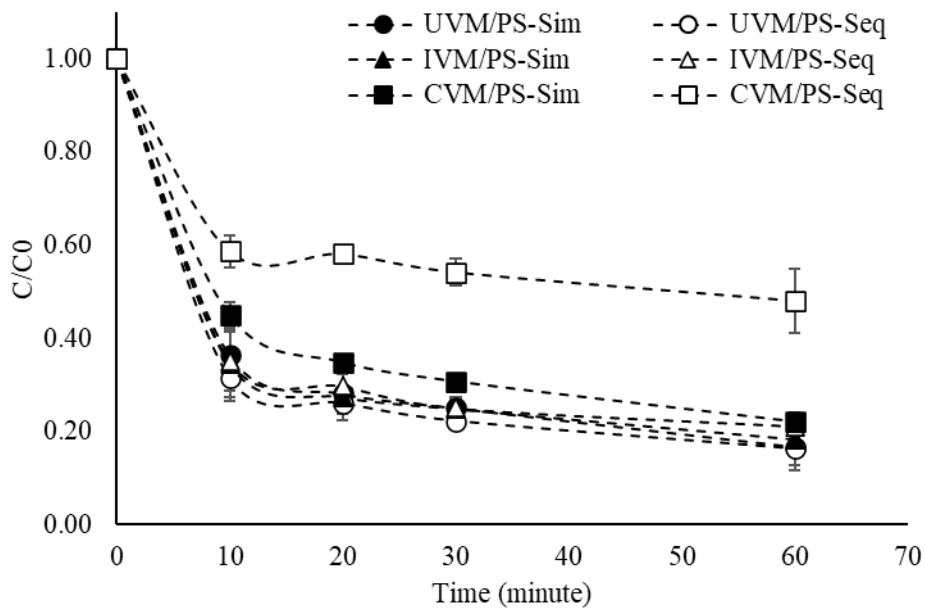


**Figure 2.** Persulfate oxidation process with sequential method (PS injected at  $t=30$  min). Reaction Conditions:  $[CR]_0 = 50$  mg/L,  $[PS:COD]_0 = 1:1$ ,  $pH = 2$ , and agitation speed = 300 rpm.

The influence of persulfate oxidation process experiments with sequential method can be seen in Figure 2. During treatment with PS oxidant without catalyst, a very small removal result of 12.08% was obtained within 60 minutes. The CR removal obtained for UVM/PS, Fe-IVM/PS, and CVM/PS catalysts were 84.75%, 81.72%, and 87.69%, respectively. Based on the obtained data, it can be seen that the adsorption process with the CVM catalyst obtained the highest removal rate followed by UVM and Fe-IVM. Nevertheless, when the percentage of adsorption in the first 30 minutes reached about 6.05%, 13.5%, and 74.5% for UVM/PS, Fe-IVM/PS, and CVM/PS catalysts, respectively. Based on these data, the CR removal rate on the CVM/PS catalyst was reached the highest removal due to fast adsorption rate.

The graph in Figure 3 was formed as a comparison of CR removal results with initial point of PS injection at  $t = 30$  minutes, which is the persulfate oxidation process in the sequential method, and the simultaneous method with initial point of PS injection at  $t = 0$  minutes. The graph aims to determine the activity of persulfate oxidant in the reaction. According to the comparison of both sequential and

simultaneous methods in Figure 3, there was a significant change in the graph of each data. This was due to the sequential method that applied, the reaction between adsorption and persulfate oxidation process can be identified more precisely.



**Figure 3.** The comparison of the persulfate oxidation effect with three catalyst modifications of sequential method at  $t = 30$  min of PS injection and simultaneous method. Reaction Conditions:  $[CR]_0 = 50$  mg/L,  $[PS:COD]_0 = 1:1$ ,  $pH = 2$ , and agitation speed = 300 rpm.

In the simultaneous method, both adsorption and persulfate oxidation processes were carried out at one time, which made difficult to know the results of the contribution of the oxidation process to CR removal. This can be seen from the CR removal results of UVM/PS-Sim, Fe-IVM/PS-Sim, and CVM/PS-Sim catalysts, which are 83.15%, 81.79%, and 77.90%. Based on the results, the catalyst that has the highest removal rate is UVM/PS-Sim catalyst followed by Fe-IVM/PS-Sim and CVM/PS-Sim. However, because the process is carried out simultaneously, it can't be determined which adsorption or oxidation mechanism dominates for each type of catalyst.

Meanwhile, in the sequential method, contribution of persulfate oxidation process (at  $t = 30$  to  $t = 90$  minutes) in the CR removal can be known. During 60 minutes of reaction, CR removal was reached 83.73%, 78.86%, and 51.96% for UVM/PS-seq, Fe-IVM/PS-seq, and CVM/PS-seq catalysts, respectively. It was found that the UVM/PS-seq catalyst has the highest removal rate compared to the other two catalysts. The same condition was reported in Laib et.al (2019), where the unmodified sludge that used as a catalyst had a high iron leaching rate along with large removal value (Laib et al., 2019). Contrary to the results obtained, this study by Tarekegn et al (2021) catalyst showed promising results for iron impregnated clay on methylene blue dye removal via persulfate oxidation (Tarekegn et al., 2021). Based on these results, it can be concluded that the oxidation process is dominating in CR removal compared to the adsorption process for each catalyst.

Leaching of iron catalysts in the reaction period of 90 minutes was also observed, and it was found that the amount of iron leaching from the use of UVM, Fe-IVM, and CVM catalysts were about 1.95 mg/L, 3.45 mg/L, and 2.2 mg/L, respectively. Several previous studies indicate that there is a significant contribution of iron leaching to the persulfate oxidation process at iron leaching concentrations  $>10$  mg/L (Domingues et al., 2021; Ye et al., 2023). However, in this study, the relationship between the amount of iron leaching and CR removal was evaluated as not being directly contributing. The lowest rate of iron leaching was on the UVM catalyst, and the highest rate of iron leaching by the Fe-IVM catalyst has an insignificant comparison to the CR removal performance about 83.73% and 78.86%, respectively. This was also found in the previous study of Mustafa and Hama (2023), where there was no significant change

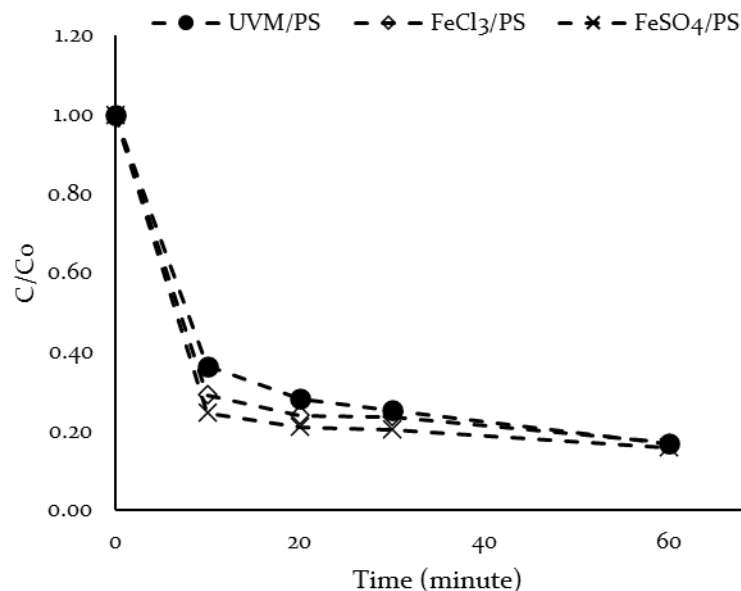
from the value of iron leaching to the oxidation reaction. The low concentration of leached iron in the solution suggests that CR removal is effective, due to the iron on catalyst surfaces, which exhibits strong chemical stability (Rubeena et al., 2018).

Based on data results from experiments that have been carried out, the contribution of VM catalyst to the persulfate oxidation process has the highest CR removal outcome. The CR removal of VM in the persulfate oxidation process reached 83.73%, which was higher than the contribution of the catalyst to the adsorption process at 16.89%. The selection of the catalyst also has a positive impact on the economy because no additional activation bonds were needed such as Fe. In addition, in terms of energy usage where it does not required very high temperatures such as 300°C for IVM and CVM catalysts. Thus, the selected heterogeneous catalyst for the persulfate oxidation process in degrading CR was the VM catalyst.

### 3.3. Homogeneous Vs Heterogeneous Oxidation Persulfate

Homogeneous and heterogeneous persulfate oxidation experiments were designed to investigate the comparison of the two systems for CR dye removal. The comparison is based on the performance of UVM catalyst and commercial homogeneous catalysts. Objective of this experiment is to determine the applicability of persulfate activation with iron, which is the main source of sulfate radical production (Domingues et al., 2021). Whereas, if the removal performance of UVM can approach commercial homogeneous catalysts, it certainly makes UVM catalyst a promising heterogeneous catalyst for its application.

The experiment was conducted using FeCl<sub>3</sub> and FeSO<sub>4</sub> catalysts for a homogeneous system and UVM catalyst (sequential method) as the selected catalyst for a heterogeneous system. The selection of FeCl<sub>3</sub> and FeSO<sub>4</sub> homogeneous catalysts was based on the unknown iron species of Sidoarjo VM in the heterogeneous persulfate oxidation process, hence both Fe<sup>3+</sup> and Fe<sup>2+</sup> ions were obtained. Iron content characterization of UVM, Fe-IVM, and VM catalysts has been carried out, and the results obtained were 19 mg/g, 81 mg/g, and 6 mg/g. The catalyst concentration in this experiment was determined by characterizing the iron content of the VM catalyst which is 19 mg/g.



**Figure 4.** Comparison of homogeneous (FeCl<sub>3</sub> and FeSO<sub>4</sub>) and heterogeneous (UVM) Persulfate Oxidation Process.

Figure 4 represents the results of CR removal showing the comparison between homogeneous and heterogeneous systems of the persulfate oxidation process, the observed results revealed the removal performance of UVM, FeCl<sub>3</sub>, and FeSO<sub>4</sub> catalysts in 60 minutes namely 83.15%, 83.07%, and 84.15%,

respectively. Based on these results by optimizing the Fe concentration, the results of CR removal by the two systems have an insignificant comparison. By the time  $t = 10$  minutes, the dye removal results for catalysts UVM,  $\text{FeCl}_3$ , and  $\text{FeSO}_4$  reached 63.67%, 70.91%, and 75.46%, respectively. The homogeneous process was obtained faster dye removal than heterogenous process, due lower mass-transfer barriers between phases than heterogenous ones (Xiao et al., 2020). Heterogeneous catalysts need time to produce sulfate radicals while homogeneous catalysts dissolve at one time thus can activate PS in a short time (Pulicharla et al., 2018). A similar case was also found in the research of Domingues et al (2023), both homogeneous and heterogeneous iron-mediated oxidation of PS was able to achieve substantial removal of the main components of dyes in wastewater (Domingues et al., 2021).

In the context of dye removal performance, heterogeneous catalysts illustrate a competitive advantage. Particularly, employing a heterogeneous catalyst accomplished 83.15% dye removal efficiency within 60 minutes. This performance is closely comparable to that homogeneous catalysts, such as within the same time period. The identical dye removal rates recommend that heterogeneous catalysts are viable with homogeneous catalysts usage for dye removal. Heterogeneous catalysts offer economic benefits such as reusability, lower consumption, and reduced sludge formation, reducing costs and environmental impact in large-scale applications, as they can be easily separated from the reaction mixture and reused (Samir et al., 2021). Heterogeneous catalysts propose practical advantages such as scalability, stability, durability, and versatility, making them ideal for large-scale industrial applications. Their ease of separation, reusability, and ability to be tailored for specific processes make them highly adaptable (Lee et al., 2020; Pervez et al., 2020).

#### 4. Conclusion

The performance of heterogeneous catalysts from Sidoarjo VM was investigated for the removal of synthetic CR (CR) dye. The VM has been successfully utilized as heterogeneous catalyst for the persulfate oxidation process, with 1 g/L VM, ratio of PS:COD 1:1, under pH 2. The experiment was conducted comparing three types of catalysts: UVM, IVM, and CVM. Under these conditions, the removal of CR with UVM catalyst for sequential method was achieved at 6.05% by adsorption and 83.73% by oxidation within 90 min of reaction time. Meanwhile, under simultaneous method the removal of CR with UVM catalyst achieved 83.15%. UVM catalyst has been proven to be the most superior heterogeneous catalyst for CR removal. The catalyst also had the lowest Fe leaching rate of 1.95 mg/L. These characteristics lead to the possibility of maintaining high stability in the reaction and not generating any secondary contaminant. Future studies are essential to optimize and model the research to build integrated reliability for industry-scale implementation.

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