Original Research Article

Utilization of Sidoarjo Volcanic Mud as Heterogeneous Catalyst in Persulfate Oxidation Process

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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; vulcanic 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 are harmful to the local environment, and 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, textiles, screen printing, and food. 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). CR is a commonly used azo dye, which is resistant to smears and is not easily removed by physical or chemical treatments (Dio et al., 2021).

Several methods have been developed to remove these dyes, such as adsorption, coagulation, ozonation, and ion exchange filtration (Vignesh and Shanmugam, 2023). Such treatment methods have proven ineffective in removing dyes (Rubeena et al., 2018; Deng, Yang, et al., 2023). Nowadays, renewable technologies such as AOP have become a hot topic for researchers and are known to interfere with the stability of dye contaminants. AOP is essentially a process that produces hydroxy radical groups ($\cdot$OH) and sulfate radical groups ($SO_4\cdot-$) (Ahmadi et al., 2019). These persulfate oxidizers contain an oxidizing value (E_0 = 2.01 V) close to the value of ozone (E_0 = 2.07 V) and higher than the peroxide oxidizer (E_0 = 1.77 V). Likewise, the redox potential value of the radical compound SO_4- (E_0 = 2.5-3.1 V) is higher than the value of OH- (E_0 = 1.8-2.7 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 increasingly reach 50,000–120,000 m^3 per day from a hole with a diameter of $\pm$ 50 m (Putri et al., 2019). Several studies have been undertaken on the characteristics of mud, which is known to contain a large percentage of iron at approximately 34-36% (Ciptawati et al., 2022). The overflow of Sidoarjo lapindo mud, which is known to contain heavy metals, may cause environmental pollution, such as contamination of 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). The iron content in sludge has been utilized in many processes, such as adsorption (Zhou et al., 2024), electroplating (Gao et al., 2024), anaerobic digestion (Jin et al., 2024), and AOP (Luo et al., 2021). 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. Several studies have utilized iron-containing sludge as a catalyst for the persulfate oxidation process (Ioannidi et al., 2020; Matthaiou 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 was to analyze the effectiveness of utilizing Sidoarjo VM as a heterogeneous catalyst for the removal of 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

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 the VM prior to its use is explained in detail in the next section. CR dye, sodium persulfate (PS) ($Na_2S_2O_8$, 98%), $Fe(NO_3)_3.9H_2O$, sulfuric acid (H_2SO_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 H_2SO_4 or NaOH solution.
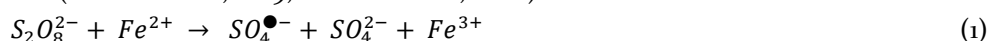
2.2.   Catalyst Preparation

The unmodified catalyst, Sidoarjo VM, was prepared by grinding the volcanic mud sample and sieving it through a 100 mesh sieve using a sieve shaker. The samples were then heated to 60°C for 3 h. This unmodified vulcanic mud called as UVM catalyst.

The modification of the catalyst by impregnation was performed using the method described by Laib et al. (2019). Iron used for impregnation was 4.4 grams of iron salt ($Fe(NO3)3.9H2O$) 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 prepared by heating the UVM catalyst with heating at 550 °C for 3 h to eliminate impurities. The result of the calcination method is referred to as the CVM catalyst.

2.3.   Experimental Procedures

The CR standard solution was prepared by adding CR powder (0.5 g) to 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 using H2SO4 or NaOH solution to achieve the desired pH of 2. Subsequently, the 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):

$$S_2O_8^{2-} + Fe^{2+} \rightarrow SO_4^{\bullet-} + SO_4^{2-} + Fe^{3+} \tag{1}$$
$$S_2O_8^{2-} + Fe^{3+} \rightarrow S_2O_8^{\bullet-} + Fe^{2+} \tag{2}$$
$$SO_4^{\bullet-} + H_2O \rightarrow SO_4^{2-} + \bullet OH + H^+ \tag{3}$$
$$SO_4^{\bullet-} + OH^{\bullet-} \rightarrow SO_4^{2-} + \bullet OH \tag{4}$$
$$2OH^{\bullet} \rightarrow H_2O_2 \tag{5}$$
$$H_2O_2 \rightarrow 2OH \tag{6}$$

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 $Fe(NO3)3.9H2O$ and by calcination (CVM) on the removal of CR was evaluated. A comparative experiment between homogeneous (FeCl3 and FeSO4) 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 (λ = 499 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 a DR 1900 Spectrophotometric instrument at a wavelength of 510 nm. The residual PS was determined by the

titration method using the thiosulfate standard (0.01 N) from a previous study by Kolthoff and Stenger (1947). To determine the success of the catalyst for CR removal, a graph plotting the effectiveness of CR removal (C/Co) against reaction time was obtained. The calculation of CR removal effectiveness is based on the equation (7) (Xia et al., 2020).

$$\text{Effectivity of } CR = \frac{c_t}{c_0} \tag{7}$$

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.
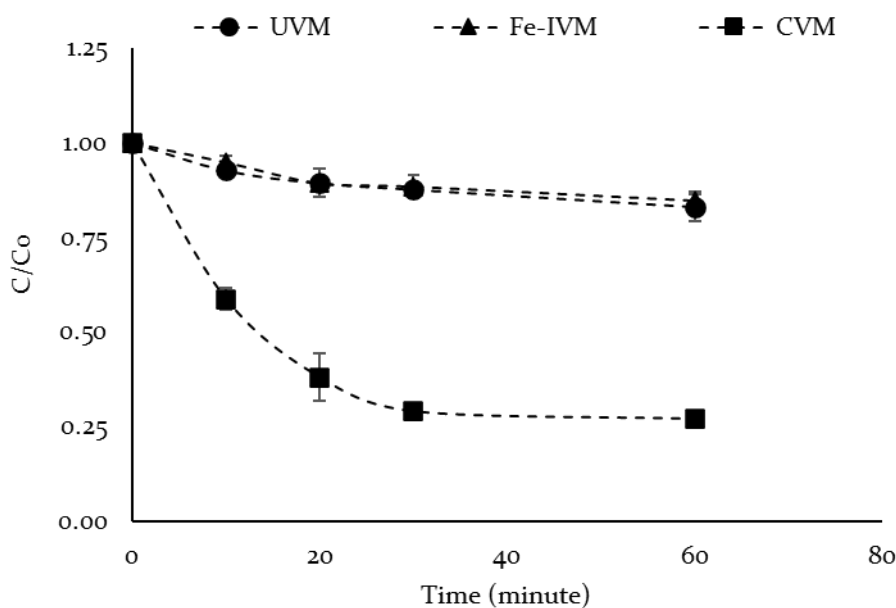

Figure 1. Comparison of the adsorption performance of the three catalysts Reaction conditions: $[CR]_0 =$ 50 mg/L, $[PS:COD]_0 = 1:1$, pH = 2, agitation speed = 300 rpm.

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 results for CR removal by the CVM catalyst were higher than those for 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. The effect of high-temperature heating can identify volatile organic matter as impurities on the surface of the catalyst, thus increasing its surface area (Jalil et al., 2010; Kumar et al., 2020). This can also be seen in a similar study by Talib et al. (2016), where there was an increase in surface area and pore diameter before and after catalyst high-temperature heating, from a surface area of 7.478 m²/g to 14.291 m²/g and a pore diameter of 6.45 nm to 22.15 nm.

Meanwhile, the adsorption of CR on the UVM and Fe-IVM catalysts was insignificantly different. These results are contrary to research on impregnation methods in general, where the results of catalysts activated by these methods are promising (Shah et al., 2015; Tarekegn et al., 2021; Kyrii et al., 2023). This variation in the results could be due to physical and chemical changes in the adsorbent, such as surface area and pore diameter. Park et al. (2015) found that catalyst impregnation decreased the surface area from 631 m²/g to 323 m²/g. The impregnation method resulted in a significant decrease in the surface area, most likely as a result of its high 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), where the adsorption values of the crystal violet dye natural catalyst and impregnated catalyst showed no significant change, namely 58.8% and 76.2%, respectively (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. In the sequential method, the PS oxidant was 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). A simultaneous method was performed, in which the PS oxidant was injected at t = 0 min.
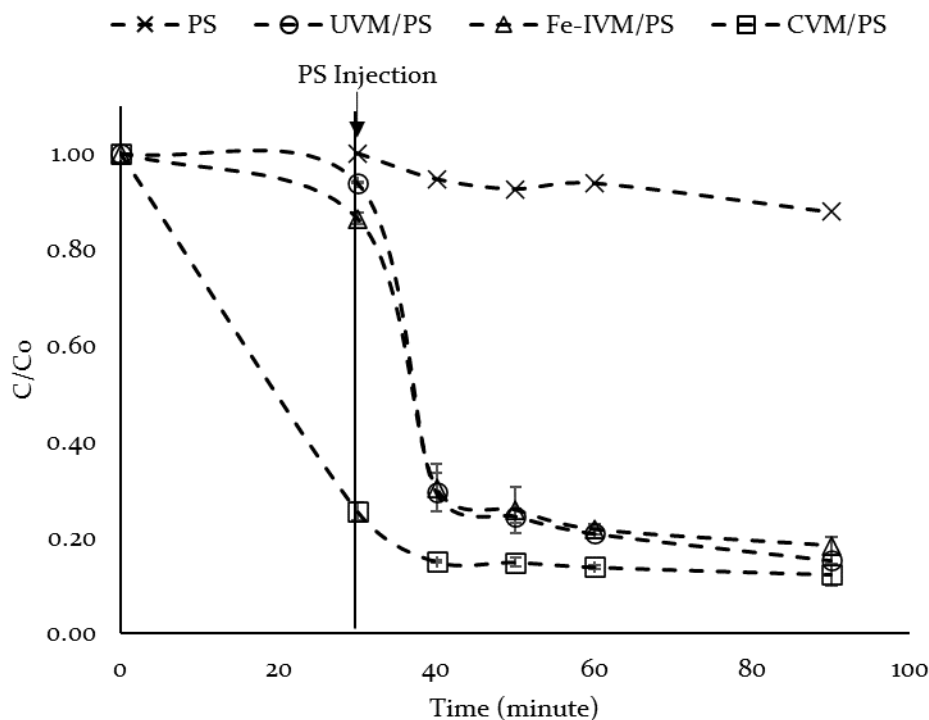

Figure 2. Persulfate oxidation process with a sequential method (PS injected at t=30 min). Reaction Conditions: $[CR]_o$ = 50 mg/L, $[PS:COD]_o$ = 1:1, pH = 2, and agitation speed = 300 rpm.

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, the adsorption process with the CVM catalyst achieved the highest removal rate, followed by UVM and Fe-IVM. Nevertheless, the percentage of adsorption in the first 30 min reached approximately 6.05%, 13.5%, and 74.5% for the UVM/PS, Fe-IVM/PS, and CVM/PS catalysts, respectively. Based on these data, the CR removal rate on the CVM/PS catalyst reached the highest value owing to the fast adsorption rate.

The graph in Figure 3 was formed by comparing the CR removal results with the initial point of PS injection at t = 30 min, which is the persulfate oxidation process in the sequential method, and the simultaneous method with the initial point of PS injection at t = 0 min. 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

because of the sequential method applied, and the reaction between adsorption and the persulfate oxidation process could be identified more precisely.
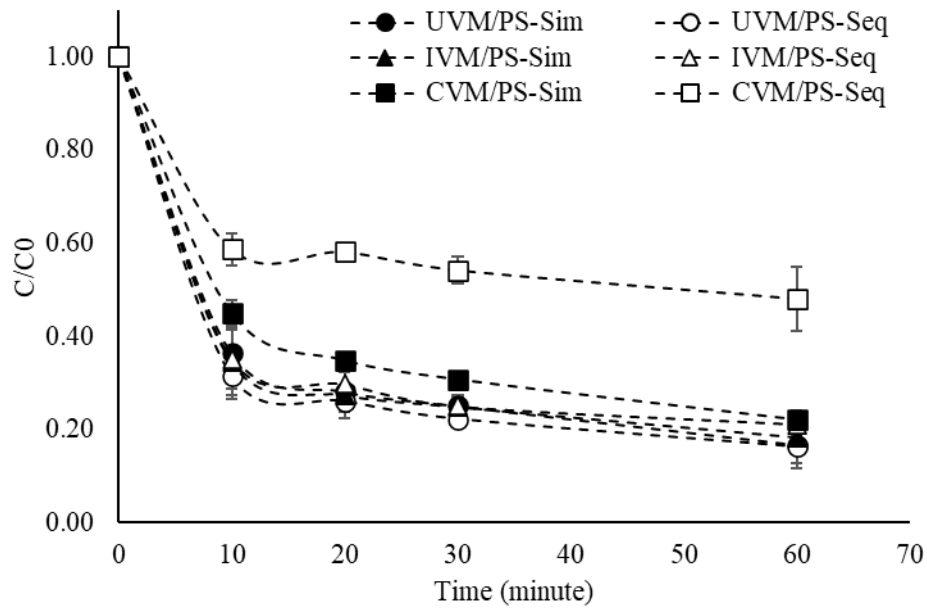

Figure 3. Comparison of the persulfate oxidation effect with three catalyst modifications of the sequential method at t = 30 min of PS injection and the simultaneous method. Reaction Conditions: [CR]$_0$ = 50 mg/L, [PS:COD]$_0$ = 1:1, pH = 2, and agitation speed = 300 rpm.

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

Meanwhile, in the sequential method, the contribution of the persulfate oxidation process (at t = 30 to t = 90 min) to CR removal can be determined. After 60 min of reaction, the CR removal reached 83.73%, 78.86%, and 51.96% for the UVM/PS-seq, Fe-IVM/PS-seq, and CVM/PS-seq catalysts, respectively. The UVM/PS-seq catalyst had the highest removal rate compared to the other two catalysts. The same conditions were reported by Laib et al. (2019), where unmodified sludge used as a catalyst had a high iron leaching rate along with a large removal value (Laib et al., 2019). Contrary to the results obtained, this study by Tarekegn et al. (2021) showed promising results for the removal of methylene blue 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 have indicated that iron leaching significantly contributes 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 16.89% contribution of the catalyst to the adsorption process. The selection of the catalyst also has a positive impact on the economy because no additional activation bonds, such as Fe, are needed. 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 VM catalyst was selected as the heterogeneous catalyst for the persulfate oxidation process for degrading CR.

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 $FeCl_3$ and $FeSO_4$ catalysts for a homogeneous system and UVM catalyst (sequential method) as the selected catalyst for a heterogeneous system. The selection of $FeCl_3$ and $FeSO_4$ homogeneous catalysts was based on the unknown iron species of Sidoarjo VM in the heterogeneous persulfate oxidation process, hence both Fe^{3+} and Fe^{2+} 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.
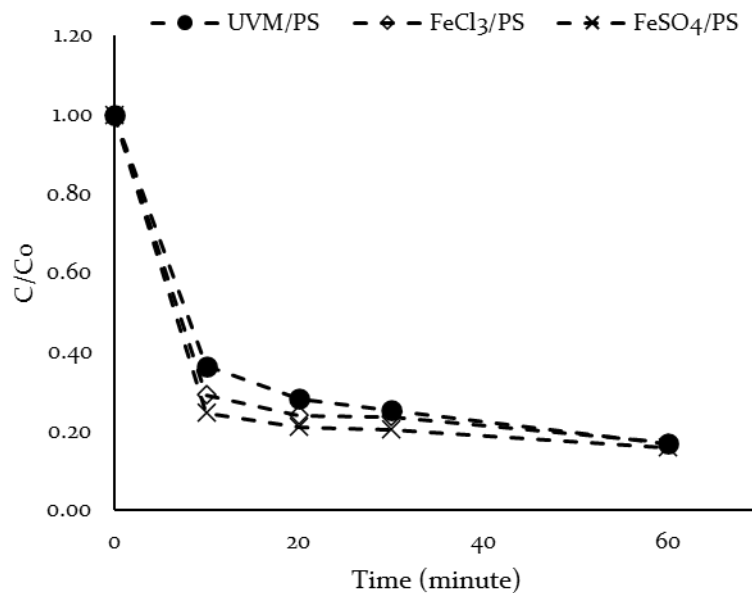
Figure 4. Comparison of homogeneous ($FeCl_3$ and $FeSO_4$) and heterogeneous (UVM) Persulfate oxidation processes

Figure 4 shows the results of CR removal, showing the comparison between homogeneous and heterogeneous systems of the persulfate oxidation process, revealing the removal performances of UVM, $FeCl_3$, and $FeSO_4$ catalysts in 60 min, namely 83.15%, 83.07%, and 84.15%, respectively. Based on these results, by optimizing the Fe concentration, the CR removal results by the two systems were not

significantly different. By the time t = 10 minutes, the dye removal results for catalysts UVM, FeCl3, and FeSO4 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 heterogeneous 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).

Heterogeneous catalysts have a competitive advantage in the context of dye removal performance. Particularly, employing a heterogeneous catalyst accomplished 83.15% dye removal efficiency within 60 minutes. This performance is comparable to that of homogeneous catalysts 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.

Acknowledgment

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