Sulphated Electric Arc Furnace Slag Asfenton-Like Catalyst for Degradation of Reactive Black 5

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Abstract. Sulphated electric arc furnace slag (S-EAFS) was obtained through a facile chemical and thermal treatment method. The S-EAFS was evaluated as a Fenton-like catalyst for the oxidative degradation of reactive black 5 (RB5). The S-EAFS was characterized by XRD, SEM-EDX and nitrogen adsorption analysis. The highest RB5 degradation efficiency obtained in this study was above 90\% which was maintained across seven successive cycles with minimum iron leaching. This was achieved at a RB5 concentration of 0.15 gL\textsuperscript{-1} (50 ppm) with 8 mM of H\textsubscript{2}O\textsubscript{2} and a pH of 4.5. Characterization revealed that the presence of sulphated groups (SO\textsubscript{4}\textsuperscript{2-}) within the EAFS improved the surface acidity of the material and corresponded to an increase in the catalytic activity for the degradation of RB5 at mild pH.

1. Introduction

The presence of low concentrations of certain toxic, carcinogenic and mutagenic pollutantsenable to change the colour of receiving water. Thus, colour of water has been included in water quality standards due to the potential for these pollutants to impart plausible negative impact towards public health and the hydrosphere [1]. Among the typical types of coloured pollutant; reactive and acidic cationic dyes are responsible for the majority of physical, chemical and microbial damage to the environment. Hence, it is imperative to put in place for effective treatment technologies in removing these pollutants prior to discharge into natural water bodies. Among the available technologies, advanced oxidation processes (AOPs) are known to be highly effective in removing these pollutants from waterways. Thus, an investigation into these processes, particularly to Fenton process, is warranted to improve environmental outcomes in this context.

The development of AOP catalysts have been plagued with deactivation issues under the acidic environment of the Fenton reaction. Of the catalysts tested, the iron oxide-silica oxide [2,3] is reported as promising catalyst to overcome this key limitation. In fact, a recent study [4] found that an iron oxide-silica oxide heterogeneous catalyst derived from steel waste electric arc furnace slag (EAFS) is highly stable under Fenton reaction conditions. The generation of this catalyst from waste product, coupled with its high stability make it a high performing and environmentally friendly alternative to the other catalysts in this area. Interestingly, the synergistic effect of multiple iron phases, mainly maghemite and magnetite, played a dominant role in accelerating the redox cycles of active sites in the generation of Fe\textsuperscript{3+}. This allows a continuous oxidative degradation of RB5 to be achieved. However,
the performance of activated electric arc furnace slag (A-EAFS) in the degradation of RB5, AB29 and MB were only excellent under acidic pH reaction (pH 3), even when assisted by visible light [5].

Due to the limited range of high performance of the EAFS catalyst, there is a gap in improving its performance under different reaction conditions. This is particular towards the treatment of dye contaminated wastewater which is often less acidic than the previously reported conditions [4,5]. In this study, it is hypothesized that by improving the surface acidity of the EAFS will subsequently increases its catalytic activity under mild pH reaction conditions. The attachment of a sulphated group (SO$_4^{2-}$) on the surface of catalysts has attracted much attention in academic literature due to their strong acidity, nontoxicity and high catalytic activity [6]. Li et. al., 2016[7], reported that the acidic sites on the catalyst surface formed by the sulphated functional groups were highly active in the photo reduction of pollutants. Therefore, this study will focus on the performance of sulphated--EAFS for degradation of RB5 under mild pH conditions.

2. Materials and methods

2.1 Materials

All materials that were used in this study were purchased from Merck and were used without further alteration. The three purchased materials are: high-quality (98%) RB5, sulfuric acid (95%) and hydrogen peroxide (30%). The Electric Arc Furnace Slag (EAFS) was collected from a local steel factory in Penang, Malaysia. Acidic (0.1M HCl) and basic (0.1M NaOH) solutions were used to regulate pH.

2.2 Catalyst preparation and characterization

Preparation of sulphated electric arc furnace slag (S-EAFS) catalyst. Raw EAFS (R-EAFS) collected from site was ground and sieved into the 40–50 µm size range. The R-EAFS particles were then soaked in 20 wt% H$_2$SO$_4$ for 4 h and washed with distilled water until the pH of the supernatant was neutral. This washing process was performed to remove adhering dust and fine materials. The resulting samples were centrifuged at 500 rpm for 10 minutes, filtered, and dried at 100°C for 24 h. The last stage of preparation involved the calcination of the dried samples at 400 °C for 2 h. Samples that have been prepared up to this step are termed as S-EAFS.

Characterization of catalysts. The structure and crystal phase of S-EAFS catalyst were recorded by X-ray diffraction (XRD) patterns in a D/max-2500/PC X-ray diffractometer (Rigaku, Japan) using Cu Kα radiation, operated at 40 KV and 30mA from 10 to 90°. The morphologies of samples were observed by scanning electron microscope (SEM) equipped with energy dispersive X-ray (EDX). The Brunauer–Emmet–Teller (BET) specific surface area of S-EAFS was determined at liquid-nitrogen temperature (77 K) using Micromeritics ASAP 2020 system. The total pore volumes were calculated based on N$_2$ adsorption at a relative pressure of 0.99. Pore-size distributions were calculated from the adsorption branch of the isotherm, according to the Barrett–Joyner–Halenda (BJH) model.

2.3 Catalytic activity

The oxidative degradation of RB5 was performed in a 250 mL conical flask with 200 mL of solution. The solution pH (2-7) and initial RB5 concentration (25–150 mg L$^{-1}$) were varied in accordance to the study performed by Nasuha et al., 2016 [4]. To initiate each test a certain amount of H$_2$O$_2$ (2–12 mM) was added to the aqueous solution. The adsorption experiments were performed in dark conditions for half an hour to obtain the equilibrium adsorption of RB5. Samples were taken at regular intervals to be analyzed by UV–vis spectrometry (UV-1700 PharmaspecShimadzu). The RB5 concentrations was determined by measuring the absorbance intensity of the solution at $\lambda_{max}$ 599 nm.

2.4 Reusability and leaching test

Oxidative degradation of each solution was carried out for 180 minutes. At the conclusion of the run, spent S-EAFS catalyst was separated, washed with distilled water, and dried at 60 °C before being used in the next cycle. Each of the seven cycles were operated at the same optimal conditions using a
pH of 5. After the completion of all cycles the EAFS sample was designated as used SEAFS (US-EAFS). S-EAFS stability in degrading RB5 over each cycle was monitored using UV–vis spectroscopy. Meanwhile, the filtrate solution was tested for the presence of homogeneous Fe ions. The filtrate solution was submitted for leaching tests performed by an inductively coupled plasma (ICP-OES), Optima 7000 DV, Perkin Elmer.

3. Results and discussions
3.1 S-EAFS characterization
3.1.1. XRD. Figure 1 exhibits the X-Ray Diffraction (XRD) pattern of the optimized S-EAFS sample. It can be seen from the intensity of the peaks that the sample is highly crystalline. The XRD pattern of the S-EAFS sample contains a variety of crystalline phases such as magnetite, maghemite, hematite and calcium sulphate. Crystalline larnite, anorthite and calcium ferrate phases are also present in the sample but at much reduced intensities. It is hypothesized that the CaO compound (highest element) reacted with H₂SO₄ during the synthesis resulting in the formation of new crystalline phases i.e. larnite anorthite.

![XRD pattern for S-EAFS](image)

**Figure 1.** XRD pattern for S-EAFS. L=Larnite (2CaO₄SiO₂), A=Anorthite (Al₂Ca₁O₈Si₂), M=Magnetite (Fe₃O₄), Ma=Maghemite (γ-Fe₂O₃), H=Hematite (α-Fe₂O₃), CF=Calcium Ferrate (IV) (Ca₁Fe₁O₃), CS=Calcium sulphate (IV) (CaO₄S₁).

3.1.2. SEM-EDX. The physical structure of the S-EAFS sample is displayed in Figure 2. It has been shown that the fresh EAFS (R-EAFS) sample has a combination of cluster shapes which include fractured and amorphous particles [4]. Meanwhile, upon exposure to chemical and thermal treatment, the structure significantly changes into bulk breaking particles with some pores presence on the surface of catalyst. It can clearly be seen that the structure of S-EAFS changed markedly after the chemical and thermal treatment. The S-EAFS sample exhibits crushed crystal and rod like shaped particles with a width in the range of 10-20 μm. The S-EAFS sample is also seen to consist of fractured bulk particle agglomerates. Furthermore, EDX analysis confirmed that the S-EAFS sample contains the elements Iron (Fe), Oxygen (O), Calcium (Ca), Silica (Si) and Sulfur (S).
3.1.3. Nitrogen sorption analysis. Nitrogen adsorption and desorption isotherms of S-EAFS sample before and after calcination are shown in Figure 3a. The isotherms in Figure 3a conform to a type IV classification under IUPAC, which represents the characteristics of mesopores materials (2-50 nm). Interestingly, the S-EAFS isotherm that has been calcined adsorbs more nitrogen than the sample that hasn’t been calcined. This result agrees with Figure 3b which shows that the calcined sample has a higher pore volume. Moreover, the pore size distribution, illustrated in Figure 3b, revealed that acid treatment resulted in a narrower pore size distribution between 6.5-7 nm and between 18 – 120nm compared to the previously reported pore size distribution [4, 5, 15]. It can be seen that the surface area of the S-EAFS increases during the calcination process (100 vs 81 m$^2$/g). The increase in surface area is further evidence that acid modification increases sample porosity. The same phenomenon was reported by Ayodele et al., 2012 [8]. Moreover, the pore width of S-EAFS was slightly reduced after undergoing calcination. Mantri et al., 2013 [9] postulated that decreasing pore width was likely due to formation of micro channels after calcination.

Figure 3. (a) Nitrogen adsorption-desorption isotherm and (b) pore distribution of S-EAFS before calcined and after calcined.
3.2. Catalytic activity

3.2.1 Effect of catalyst dosage. Figure 4 shows the effect of catalyst dosage on RB5 degradation. It can be clearly seen in this figure that the dosage of S-EAFS positively influences the performance efficiency of RB5 degradation under mild pH conditions (pH 4.5). Degradation of RB5 was increased from 80 % to 94 % with an increase in catalyst dosage from 0.01 g to 0.03 g under dark Fenton-like conditions. The results suggest that an increase in catalyst dosage results in more adsorption due to the presence of more active sites. This behavior leads towards accelerated decomposition of H2O2 into •OH radicals as report by Wan et al., [10], even though this only occurs up to a certain range of catalyst dosage [16]. Once the optimized dosage is reached, further addition results in possible scavenging of excess generation of •OH radicals. Therefore, the performance of degradation of dyes remained relatively constant at higher catalyst dosages.

3.2.2 Effect of H2O2 dosage. The dosage of H2O2 was varied to understand the impact of oxidant on RB5 degradation in the presence of S-EAFS catalyst. The effect of H2O2 was studied by varying the dosage (2 - 12 mM) while keeping all other parameters constant. The degradation of RB5 gradually increases with H2O2 dosage from 2 mM to 8 mM. Further increases in H2O2 dosage above 8mM resulted in a negligible change of RB5 degradation. It is thought that the hydroxyl radicals generated at H2O2 concentrations in excess of 8mM producing hydroperoxyl radicals, HOO•. Hydroperoxyl radicals are less reactive compared to the hydroxyl radicals and only slightly contributed towards oxidative degradation of organic pollutants [11, 12].

3.2.3 Effect of pH solution. The effect of pH solution on the degradation of RB5 under dark conditions was tested between pH 2 and pH 7 (Figure 5a). It can be seen that a pH of 2 – 5 gives this highest degradation of RB5. Interestingly, the degradation performance was maintained from acidic until mild pH solution. Such findings is suggested due to the nature of acidic surface sites of the sulphated catalyst which confer micro acidic environment within the active sites during the catalysis even at neutral pH solution [6]. The colour removal of RB5 at pH 6 decreased significantly afterwards. This phenomenon can be explained by decomposition of more H2O2 into molecular oxygen and water on the active sites without the formation of appreciable amounts of HO• radicals [13].

3.2.4 Effect of initial concentration. The effect of RB5 degradation on RB5 initial concentration was studied and the results are shown in Figure 5b. It can be seen that degradation performance reduces with an increase in the initial concentration of RB5. At a low RB5 initial concentration (25 mg L−1),

Figure 4. Effect of (a) catalyst dosage and (b) H2O2 dosage on the oxidative degradation of RB5.

(a)  
(b)
complete degradation was achieved while at high initial concentration (150 mg L\(^{-1}\)) approximately half of the RB5 was degraded. The reduction in degradation performance can be attributed to an insufficient amount of •OH radicals which is required for the degradation of dyes. Further, as RB5 initial concentration is increased, the ratio of catalyst dosage to RB5 concentration decreases. This is mainly due to the fact that competitive adsorption may occur in the presence of adsorbed dyes molecules and oxidant molecules (H\(_2\)O\(_2\)) [14].

![Figure 5](image_url)

**Figure 5.** Effect of (a) pH solution and (b) initial dye concentration on the oxidative degradation of RB5.

3.2.5 Catalyst stability

The S-EAFS catalyst has shown high degradation efficiencies, reusability and stability as presented in Figure 6. The catalyst was able to sustain its’ catalytic activity with more than 90% of RB5 degradation over seven successive cycles of reactions. It is anticipated that this high performance can be attributed to the strong interaction and combination between the oxidative radical species and the acid treated surface of the S-EAFS catalyst. The maximum iron leaching concentration after seven cycles was approximately 0.15 mgL\(^{-1}\), which can be neglected because it was below the European Union directives value (<2 ppm) [6].

![Figure 6](image_url)

**Figure 6.** Reusability of S-EAFS for degradation of RB5.
4. Conclusions
This study has shown that S-EAFS as an effective Fenton-like catalyst for degradation of RB5. The collective findings of characterization analysis and catalytic studies have proven that the presence of sulphated sulphated group on the EAFS catalyst surface able to enhance the resultant catalytic performance. The modified S-EAFS catalyst provided with higher degradation of RB5 at mildly acidic pH than any other studies. Such finding is plausible due to the nature of acidic surface sites of the sulphated catalyst which confer micro acidic environment within the actives sites during the catalysis. Interestingly, the resultant catalyst have shown modest catalytic stability of more than 90% RB5 degradation in seven successive cycles at optimised reaction conditions (50ppm, 8 mM of H2O2 and pH 4.5).

5. References
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Acknowledgements
The authors gratefully acknowledges the Ministry of Higher Education Malaysia (MOHE) and UniversitiTeknologi MARA (UiTM) for financial support under Fundamental Research Grant Scheme (600-IRMI/FRGS 5/3 (110/2016)).