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## Development of High Entropy Alloy (HEA) as Catalyst for Azo Dye Degradation in Fenton Process

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**Abstract.** Azo dye is widely used in the textile industry since it is cost effective and simple to use. However, it becomes a continuous source of environmental pollution due to its carcinogenicity and toxicity. Various methods had been used to remove the azo dye in solution. One of the famous and repeatedly used is Fenton process. The Fenton's process is one of the advanced oxidation process where iron catalysed hydrogen peroxide to generate hydroxyl radical. Treating azo dyes in solution requires a catalyst to enhance the process of degradation. Herein, high entropy alloy (HEA) has been proposed as a catalytic material to enhance the performance of Fenton process for azo dye degradation. HEA has been reported as a promising catalyst due to its high surface area. The higher the number of active sites, the higher the rate of azo dye degradation as more active sites are available for adsorption of azo dyes. The results have shown that HEA can be used as a catalyst to fasten the Fenton's reaction since the degradation time is proven to be shorter in the presence of HEA. The method derived from the result of this study will contribute in treating azo dyes for wastewater management in Fenton process.

### 1. Introduction

Textile industry is one of the fastest growing industries and significantly contributes to the economic growth in Malaysia especially in man-made textile fiber. Malaysia produced close to 400 000 tons of man-made fiber and contributed about 1.03% of the world's production [1]. In the last 15 years, from 2000 to 2015, world wide's production of the textile industry has approximately doubled due to the growing middle-class production and increased per capita sales in the mature economy [2]. However, 22% of the total volume of waste water in Malaysia is generated by the textile industry. Besides, according to the United Nations Environment Programme (UNEP) and the Ellen MacArthur Foundation, the release of dyes into the environment during textile fiber dyeing, treatment and finishing process are responsible for about 20% of the global water pollution.

Dyes is colored substances that chemically bond to the substrate to which it is being applied. Azo dyes are the dyes containing azo group (N=N) in chemical constitution [3]. Azo dyes represent the most important class of textile dyes [4]. On top of that, azo dyes are cost effective and simple to use, making them the most popular synthetic dye [5]. This is the reason why azo dyes are widely used in



the textile industry. On one hand, azo dyes are insoluble in water, causing water pollution that can harm humans and the environment due to its toxicity and carcinogenicity [6].

Various methods had been used to remove azo dye in solution such as physical adsorption, chemical treatment, chemical oxidation and biological treatment [7]. Among these methodologies, Fenton method is reported as an effective technology for the degradation of a large number of hazardous and organic pollutants because of the lack of toxicity of the reagents, which makes it environmentally safe [8]. Fenton method is one of the advanced oxidation processes (AOP) where ions catalyze hydrogen peroxide to generate hydroxyl radical. Then, hydroxyl radicals react and oxidize pollutants. However, the disadvantages of the conventional Fenton's method include the high operating cost, limited optimum pH range, the volume of iron sludge is largely produced, and it is difficult to recycle the homogenous catalyst,  $\text{Fe}^{2+}$  [9]. Electro-Fenton method is a good alternative to overcome these problems which according to Matyszczyk [10], Electro-Fenton method uses the electrolysis in quickening the process and increase the efficiency of the Fenton process as the production of hydroxyl radicals will also be increased. If this is applied in treating azo dyes, time and cost could be saved and reduced.

Treating azo dyes in Fenton process requires a catalyst to enhance the process of degradation. Then, several types of catalyst such as iron activated carbon, ferrite bismuth, two electron catalysts and zero valent metal had been discovered, studied and experimented and improved on based on the conventional treatment [6,10-12]. Nevertheless, the catalytic activity is slow and time consuming. Therefore, it is important to develop another catalytic material to fasten the degradation process of azo dye without producing any secondary product that requires further process.

High entropy alloys (HEAs) is defined as a blend of five or more elemental concentrations between 5% and 35%. In HEAs, all elements are concentrated and no obvious base elements [13]. HEAs have been reported as a promising catalyst due to its highly complex atomic structure and highly distorted crystal structure. HEAs have a great potential for tuning adsorption properties and possess higher potential energy thus it produce more catalytic active sites [14]. Herein, high entropy alloys (HEAs) are proposed as a catalytic material to enhance the performance of Fenton's process. The catalytic mechanism or properties of the HEA as catalysis has not been yet widely studied and there are only a few literary studies done by the researchers. They managed to do a study on predicting the catalytic activity of the HEAs [15-16]. Thus, this study compared the performance of High Entropy Alloy as a catalysis to the conventional Fenton process. The characterizations of the dyes before and after the Fenton process as well as the catalytic mechanism during the process was conducted.

## 2. Materials and Methods

### 2.1 Materials

Materials used in this study are solid FeCoNiAlBSi high entropy alloys with the size of 1cm x 1 cm, 35% hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) solution, ferrous sulphate heptahydrate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ), graphite rods, sulphuric acid ( $\text{H}_2\text{SO}_4$ ), sodium hydroxide (NaOH) and methyl orange dye. The high entropy alloys (HEA) were synthesized by arc melting Edmund Buhler GmbH. Materials were purchased from Sigma Aldrich Malaysia with purity of 99%.

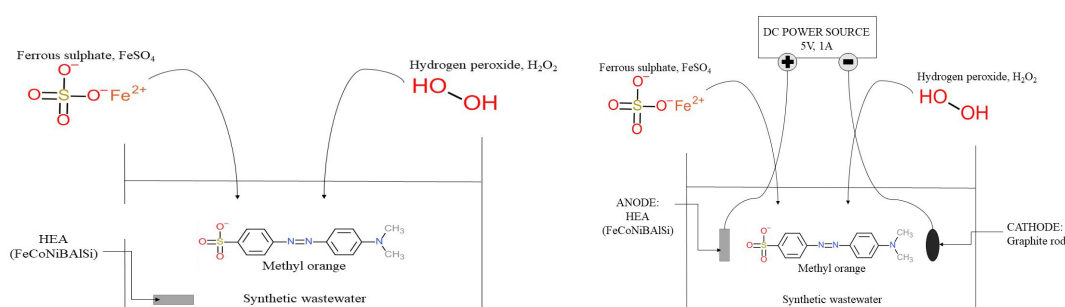
### 2.2 Experimental Setup

The electrochemical experiments were set up for electro-Fenton and the conventional Fenton method as shown in figure 1 and figure 2. Fenton's reagent is the reaction between hydrogen peroxide and ferrous ion,  $\text{Fe}^{2+}$ . Therefore, the ferrous (II) sulphate heptahydrate salt,  $\text{FeSO}_4 \cdot \text{H}_2\text{SO}_4$  is used to react with the hydrogen peroxide in solution. Synthetic wastewater was prepared by adding 2.5 ml of methyl orange dye into 100 ml of water and was put into a 500ml beaker for every run to ensure the equality in comparison between the runs carried out. The solution was then stirred and the pH was monitored with the diluted sulphuric acid/sodium hydroxide. The high entropy alloys sample were grind before every run to ensure there are no oxide layers interfering during the reaction.

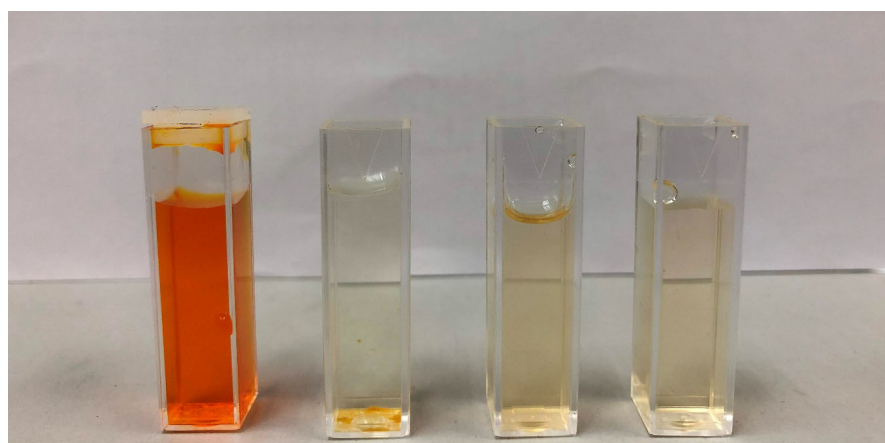
For the conventional Fenton method, 5 ml of ferrous sulphate heptahydrate ( $\text{FeSO}_4$ ) and 50 ml of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) are mixed into 101.25 ml of methyl orange dye solution in the 500 ml beaker.

A DC power source was used to carry out the electro-Fenton process. In this process, the HEA is used as anode and graphite as cathode. Then, both of the anode and the cathode are connected to the DC power source that was set to 5V and 1A. The electrolyte that contain 102.5ml of methyl orange dye ,5 ml of ferrous sulphate heptahydrate ( $\text{FeSO}_4$ ) and 50 ml of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) were mixed together in a 500ml beaker.

Results obtained were characterized using Fourier-transform Infrared Spectroscopy and Ultraviolet Visible Spectroscopy. Conductivity test and Total Dissolved Solid (TDS) was carried out while the discoloration of the dye was observed.



**Figure 1.** (From left) Schematic diagram of the conventional method of Fenton's reagent and electro-Fenton setup with HEA anode and graphite cathode connected to the DC power source set to 5V and 1A of output



**Figure 2.** (From left) Dye, conventional Fenton method, electro-Fenton (graphite anode and cathode) method and electro-Fenton (HEA anode and graphite cathode), respectively.

### 3. Result and Discussion

#### 3.1 Comparison between Coventional Fenton and Electro-Fenton Method

From figure 3, it is shown that conventional Fenton method provides decolorization of the dye and the solution has turned clear after some time but there are very little sludge contained in the cuvette. According to table 1, the electro-Fenton with graphite rods as anode and cathode took a slightly longer time for the decoloration than the electro- Fenton method with HEA anode and graphite cathode. The

conductivity of the run with HEA as anode is 1152  $\mu\text{s}/\text{cm}$  while the TDS value is 6580 ppm. Meanwhile, the electrical conductivity of the sample with HEA anode is lower compared to the electro-Fenton with graphite anode. From the same table, the time taken for the reaction to end in the conventional Fenton method is 14 minutes, the EC value is 5932  $\mu\text{s}/\text{cm}$  and the TDS value is 2143 ppm. In comparison with the electro-Fenton method, the time taken was longer for conventional Fenton's method. Moreover, the electrical conductivity is higher. However, the TDS value is lower compared to the electro-Fenton. From this comparison, we could note that the electrolysis reaction has fastened the process of Fenton reagent by providing the ion charges into the reaction by the power source.

**Table 1.** Result of sample undergone electro-Fenton method with different anode and cathodes and conventional Fenton method (without HEA).

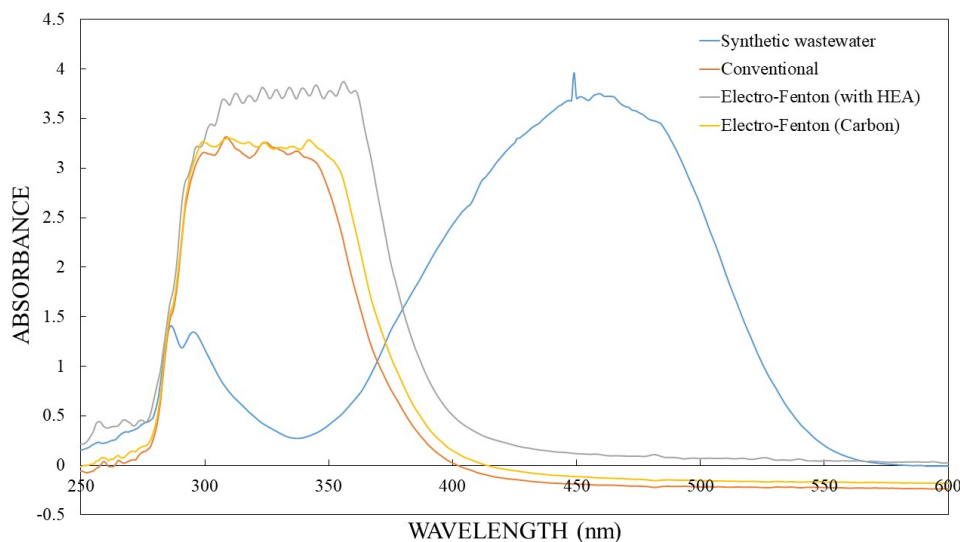
Controlled	Manipulated	Time Taken (min)	Electrical Conductivity ( $\mu\text{s}$ )	Total Dissolved Solid (ppm)
50 ml $\text{H}_2\text{O}_2$ 5 ml (0.35g) $\text{FeSO}_4$	Anode: HEA Cathode: Graphite rod	4	1152	6580
50 ml $\text{H}_2\text{O}_2$ 5 ml (0.35g) $\text{FeSO}_4$	Anode: Graphite rod Cathode: Graphite rod	6	2400	1200
50 ml $\text{H}_2\text{O}_2$ 5 ml (0.35g) $\text{FeSO}_4$	Conventional method	14	5932	2143

Conductivity test measures the capability of water to pass the electrical flow that indicates the presence of ions in the solution. Presence of certain elements such as chloride, nitrate, sulfate, phosphate, sodium, magnesium, calcium, iron and aluminum increases the conductivity of solution (or water). However, the organic substances lower the conductivity of the water. According to the result, the conductivity value was higher in conventional Fenton method which indicates that there is a source of dissolved ions in the solution since there is presence of azo dye sludge in the cuvette. The remain formation of main chromophore “-N=N-”,  $\text{Fe}^{2+}$  and oxidized  $\text{Fe}^{3+}$  as coagulants as well as the formation of other mineralization products such as  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$  are the factors that increase the conductivity of the conventional Fenton method [17].

### 3.2 Characterization

According to the UV-Vis spectra shown below, the conventional Fenton method curve is the lowest among the other two runs. The curves above show that the colour of the methyl orange dye has been degraded since the range 400 to 500 nm wavelength indicates the presence of methyl orange dye that caused by the azo bond “N=N”. However, after the Fenton reagent has been carried out (both conventional and electro-Fenton method), the curves are in sight within the 300 to 350 nm wavelength range, indicating that the molecules from the Fenton reagent are left in the solution. The increase of the reaction of time, decrease the intensity of absorption peak which is proportional to the concentration of azo dye solution. This shows that the azo bond “N=N” breaks into “-NH” as the degradation process proceeds which is always observed in degrading azo dye by zero valent and metallic glasses. Then, the degradation of azo dye in conventional Fenton method show that the azo dye was completely degraded in solution without any detectable characteristic peak at the range of 400 to 500 nm wavelength after 14 minutes. However, it can be observed from Figure 3, there is very little

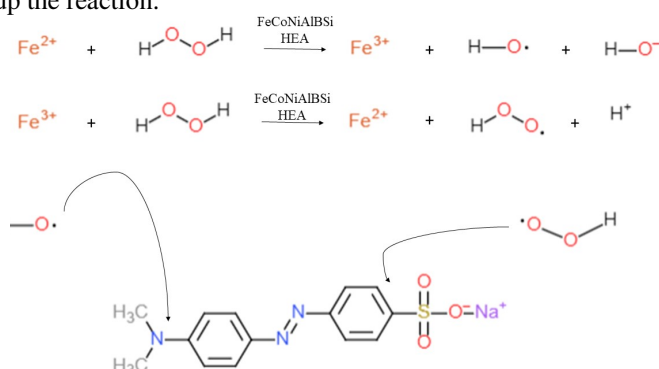
sludge of azo dye contained in the cuvette where this is the main disadvantages of conventional Fenton method.



**Figure 3.** UV-Vis Spectra of four samples: synthetic wastewater, conventional Fenton method, electro-Fenton method (with HEA anode and graphite cathode), and electro-Fenton method (with graphite rods).

### 3.3 Mechanism of HEA as Catalyst on the Reaction Rate in Fenton Process

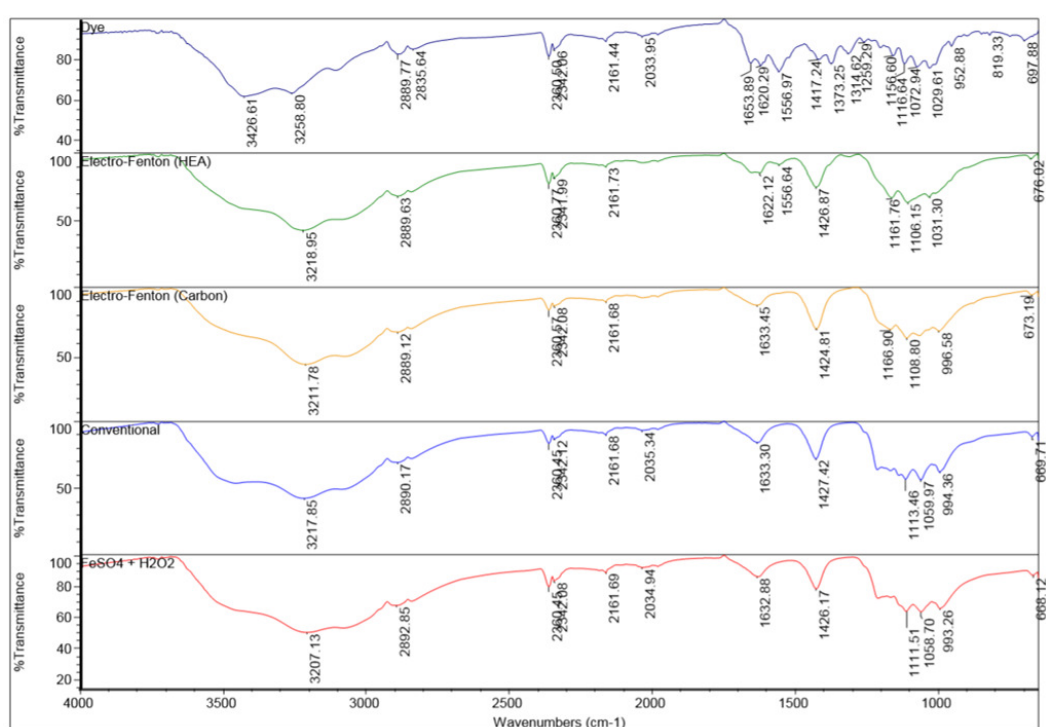
Fenton process is strongly influenced by two reagents which are ferrous (II) sulphate,  $\text{FeSO}_4$  and hydrogen peroxide,  $\text{H}_2\text{O}_2$ . The reaction between these two reagents produce ferric ions and hydroxyl radicals. Hydroxyl radical plays an important role in Fenton reagent to attack the molecule of methyl orange dye and degrades the amine bond which helps the decolorization dye in the solution which can be seen in the figure 4. Then, the presence of HEA as a catalyst its fastened the process due to high surface catalytic properties. HEA provides a more active site for the molecules of Fenton 's reagent to react hence speed up the reaction.



**Figure 4.** Mechanism of Fenton's reagent with HEA as catalyst.

To give additional evidence and further confirm the efficiency of HEA as catalyst, the FTIR characterization was performed. The infrared spectroscopy of dye, electro-Fenton (with HEA anode), electro-Fenton (graphite anode and cathode), conventional Fenton method and Fenton's reagent

( $\text{FeSO}_4 + \text{H}_2\text{O}_2$ ) are presented in figure 5 below. The characteristic IR absorption peaks at  $3200 \text{ cm}^{-1}$ ,  $2890 \text{ cm}^{-1}$ ,  $2360 \text{ cm}^{-1}$ ,  $2161 \text{ cm}^{-1}$  were observed in all samples. The wide bands at  $3200 \text{ cm}^{-1}$  are resultant from O-H banding of absorbed water molecules while  $2890 \text{ cm}^{-1}$  is corresponding  $-\text{NH}$  stretching vibration which can be found in the methyl orange structure. It is noteworthy that the intensity of peaks from the dye have become weaker as Fenton reaction is introduced in the decolourising treatment process. The FTIR spectra of dye showed significant band at  $3426 \text{ cm}^{-1}$  and  $1653 \text{ cm}^{-1}$  which could be assigned as  $-\text{NH}$  group. After the reaction, the intensity of these bands was reduced and the peak was found to be broader. At  $2033 \text{ cm}^{-1}$  is visible in the dye and conventional Fenton method which represents the  $\text{HCN-NH}$  group. However, this peak is invisible both in the electro-Fenton process. It is possible that the electrolysis process can degrade this molecule group compared to the conventional method which failed to do the same.



**Figure 5.** FTIR Spectra of methyl orange dye, electro-Fenton (with HEA as anode), electro-Fenton (with graphite rods as anode and cathode), conventional Fenton method and Fenton reagent.

#### 4. Conclusion

This work was devoted to assess the capability of and mechanism of high entropy alloy (HEA) as a catalyst in degradation of azo dye degradation efficiency in Fenton process. High entropy alloy as catalyst can speed up the Fenton reaction by accelerating the development of hydroxyl radicals due to the active catalytic sites of HEA. Then, the time taken for the reaction to complete is reduced into half of the conventional Fenton method due to the presence of the ionic charge that derived from the presence of ferrous sulphate with hydrogen peroxide and allows the ions move faster. Compared to conventional Fenton method, the sludge generated in Electro-Fenton method is smaller and the UV-Vis absorbance with HEA is lower. This shows that the dye has been degraded more efficiently as the water samples are clearer. This is because the presence of HEA as a catalyst enhances the performance of Fenton reaction. The result of study can be applied in treating azo dye in solution for waste water management especially in the textile industry and fulfil SDG number 9, clean water and sanitation.

## References

- [1] Pang, Yean L Abdullah, Ahmad Z 2013 *Clean Soil, Air and Water* 41 **751**
- [2] Information on: [https://www.ellenmacarthurfoundation.org/assets/downloads/publications/A-New-Textiles-Economy\\_Full-Report.pdf](https://www.ellenmacarthurfoundation.org/assets/downloads/publications/A-New-Textiles-Economy_Full-Report.pdf)
- [3] Gordon P Fand Gregory P 2012 *Organic chemistry in colour (Springer Science & Business Media)*
- [4] Brüschweiler, Beat J, Merlot, Cédric. 2017 *Regul. Toxicol. Pharmacol.* **88** 214
- [5] Jamee, Radia, Siddique, Romana 2019 *Microbiol. Immunol.* **9** 114
- [6] Matyszcak, Grzegorz, Krzyczkowska, Katarzyna, Fidler, Aleksandra 2020 *J. Water Process. Eng.* **36** 101242
- [7] Wu, Shikai, Pan, Ye, Wang, Ning, Dai, Weiji, Lu, Jie, Lu, Tao 2018 *RSC Advances* **8** 41347
- [8] P V Nidheesh, R Gandhimathi 2012 *Desalination* **299** 1
- [9] Sabhi S and Kiwi J 2001 *Water Res.* **35** 1994
- [10] Matyszcak, Grzegorz, Sędkowska, Agata, Kuś, Stanisław 2019 *Dyes and Pigments* **174** 108076
- [11] Abu Bakar Muhammad, Ahmed Lawal Mash 2020 *International Journal of Innovative Science and Research Technology* **5** 479
- [12] Da Cruz Severo, Eric, Dotto, Guilherme Luiz, Silvestri, Siara, dos Santos Nunes, Isaac, da Silveira Salla, Julia, Martinez-de la Cruz, Azael, da Boit Martinello, Katia, Foletto and Edson Luiz 2020 *J. Environ. Chem. Eng.* **8** 103853 (2020)
- [13] Miracle D B 2019 *Nat. Commun.* **10** 1805
- [14] Cui X, Zhang B, Zeng C, Guo S 2018 *MRS Commun.* **8** 1230
- [15] Wang S and Xin H 2019 *Chem* **5** 502
- [16] Tsai M H and Yeh J W 2014 *Materials Research Letters* **2** 107
- [17] Sopaj, Flamur, Oturan, Nihal, Podvorica, Fetah, Oturan, Mehmet 2016 *Appl. Catal. B.* **199** 331

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