N.H.A. HASSAN©[1], N.S.M. NASIR©[1], S.N.A. RAHMAN©[1], A.R. IRFAN©[2,3], N.H. NORDIN©[1*]

DEVELOPMENT OF HIGH ENTROPY ALLOY AS CATALYST FOR AZO DYE DEGRADATION IN FENTON PROCESS

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 frequently used is the Fenton process. The Fenton process is one of the advanced oxidation processes 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 alloys (HEAs) have been proposed as a catalytic material to enhance the performance of Fenton process for azo dye degradation. HEAs have 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 HEAs can be used as a catalyst to fasten the Fenton reaction since the degradation time is proven to be shorter in the presence of HEAs. The method derived from the result of this study will contribute in treating azo dyes for wastewater management in the Fenton process.

Keywords: Azo Dye; Catalyst; Fenton Process; High Entropy Alloys (HEAs)

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 MacAthur 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 coloured 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, mak-

ing 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 iron catalyse hydrogen peroxide to generate hydroxyl radical. Then, hydroxyl radicals react and oxidize pollutants. However, the disadvantages of the conventional Fenton 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, Fe^{2+} [9]. Electro-Fenton method is a good alternative to overcome these problems which according to Matyszczak et al. [10], Electron-Fenton method uses electrochemical process

1 INTERNATIONAL ISLAMIC UNIVERSITY MALAYSIA, DEPARTMENT OF MANUFACTURING AND MATERIALS ENGINEERING, JALAN GOMBAK, 53100 KUALA LUMPUR, MALAYSIA
2 UNIVERSITI MALAYSIA PERLIS, FACULTY OF MECHANICAL ENGINEERING TECHNOLOGY, PERLIS, MALAYSIA.
3 UNIVERSITI MALAYSIA PERLIS, CENTER OF EXCELLENCE GEOPOLYMER AND GREEN TECHNOLOGY (CEGEOGTECH), PERLIS, MALAYSIA

* Corresponding author: norhudahidayah@iium.edu.my

in quickening the process and increase the efficiency of the Fenton process as the production of hydroxyl radicals will also be increased. Thus, this production causes an increase in the efficiency of organic pollutants degradation.

Treating azo dyes in the 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, experimented and improved 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 produces more catalytic active sites [14]. Herein, high entropy alloys (HEAs) are proposed as a catalytic material to enhance the performance of the Fenton process. The catalytic mechanism or properties of the HEAs as a catalyst 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 catalyst 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. Methodology

2.1. Materials

Materials used in this study are solid FeCoNiAlBSi high entropy alloys with the size of 1 cm × 1 cm, 35% hydrogen peroxide (H_2O_2) solution, ferrous sulphate heptahydrate ($FeSO_4 \cdot 7H_2O$), graphite rods, sulphuric acid (H_2SO_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 Fig. 1. Fenton reagent is the reaction between hydrogen peroxide and ferrous ion, Fe^{2+}. Therefore, the ferrous (II) sulphate heptahydrate salt, $FeSO_4 \cdot H_2SO_4$ 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 500 ml 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 samples 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 ($FeSO_4$) and 50 ml of hydrogen peroxide (H_2O_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 5 V and 1 A. The electrolyte that contains 102.5 ml of methyl orange dye, 5 ml of ferrous sulphate heptahydrate ($FeSO_4$) and 50 ml of hydrogen peroxide (H_2O_2) were mixed together in a 500 ml 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.

3. Results and discussion

3.1. Comparison between Conventional Fenton and Electro-Fenton Method

From Fig. 2, it is shown that conventional Fenton method provides degradation of the dye and the solution has turned clear after some time but there is very little sludge contained in the
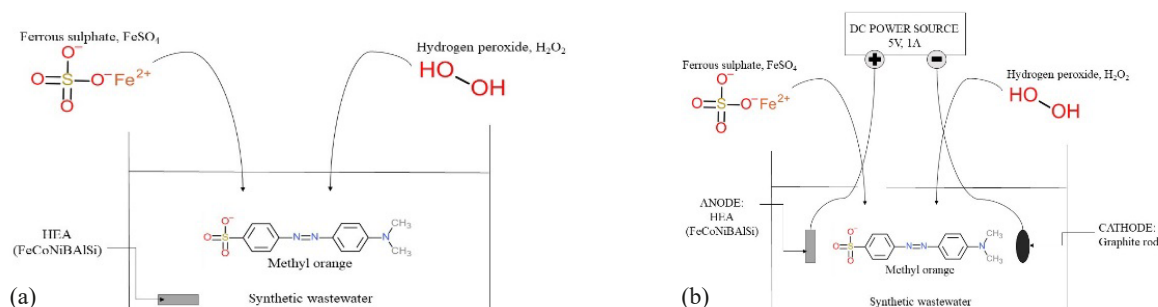

Fig. 1. Schematic diagram of the (a) conventional method of Fenton reagent and (b) electro-Fenton setup with HEA anode and graphite cathode connected to the DC power source set to 5 V and 1 A of output

cuvette. This is proven that higher volume of sludge production is the main drawback of the conventional Fenton method [17]. According to TABLE 1, the electro-Fenton with graphite rods as anode and cathode took a slightly longer time for the discoloration than the electro-Fenton method with HEA as anode and graphite as cathode. The conductivity of the run with HEA as anode is 1152 µs/cm while the TDS value is 6580 ppm. Meanwhile, the electrical conductivity of the sample with HEA as anode is lower compared to the electro-Fenton with graphite as 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 µs/cm and the TDS value is 2143 ppm. In comparison with the electro-Fenton method, conventional Fenton method took a longer time to degrade the azo dye. 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 more hydroxyl radical into the reaction by the power source [18].
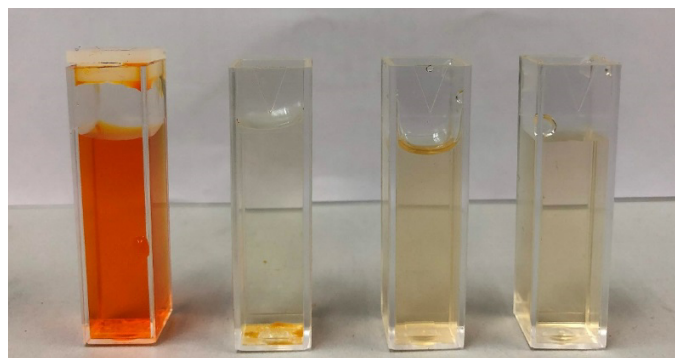

Fig. 2. (From left) Dye, conventional Fenton method, electro-Fenton (graphite anode and cathode) method and electro-Fenton (HEA anode and graphite cathode), respectively

Conductivity test measures the capability of water to pass the electrical flow that indicates the presence of ions in the

TABLE 1

Result of sample undergone electro-Fenton method with different anodes and cathodes and conventional Fenton method (without HEA)

Controlled	Manipulated	Time Taken (min)	Electrical Conductivity (µ/s)	Total Dissolved Solid (ppm)
50 ml H_2O_2 5 ml (0.35g) $FeSO_4$	Anode: HEA Cathode: Graphite rod	4	1152	6580
50 ml H_2O_2 5 ml (0.35g) $FeSO_4$	Anode: Graphite rod Cathode: Graphite rod	6	2400	1200
50 ml H_2O_2 5 ml (0.35g) $FeSO_4$	Conventional method	14	5932	2143

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 "$-N = N-$", Fe^{2+} and oxidized Fe^{3+} as coagulants as well as the formation of other mineralization products such as NH_4^+, NO_3^- and SO_4^{2-} are the factors that increase the conductivity of the conventional Fenton method [19,20].

3.2. Characterization

According to the UV-Vis spectra shown in Fig. 3, the conventional Fenton method curve is the lowest among the other two runs. The curves above show that the color of the methyl orange dye has been degraded since the range 400 to 500 nm wavelength indicates the presence of methyl orange dye that is
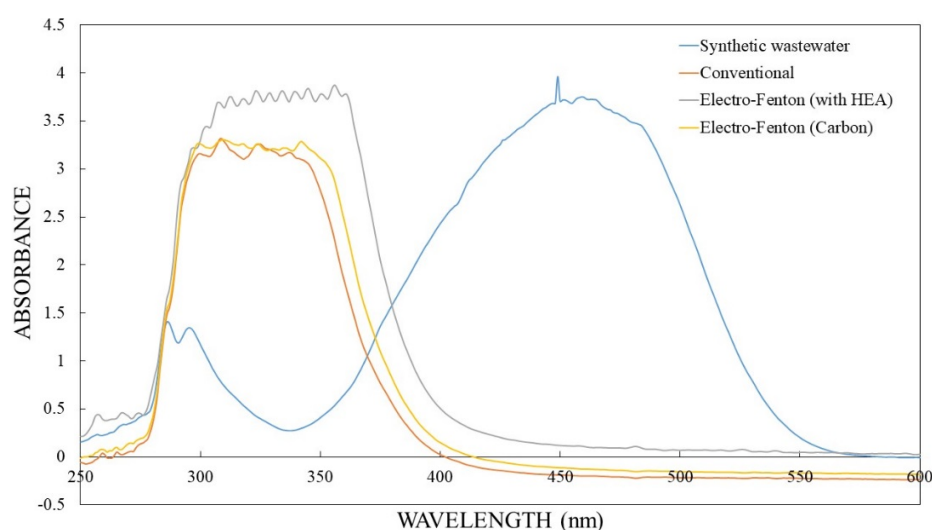

Fig. 3. UV-Vis Spectra of four samples: synthetic wastewater, conventional Fenton method, electro-Fenton method (with HEA anode and graphite cathode), and electro-Fenton method (with graphite rods)

caused by the azo bond "N = N" [21,24]. The increase of the reaction of time would 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 metals and metallic glasses [22]. Then, the degradation of azo dye in conventional Fenton method shows 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, after the Fenton reagent has been carried out (both conventional and electro-Fenton method), the curves are in sight within the 270 to 350 nm wavelength range, indicating that the formation of degradation products. As reported by Feng et al. [23], spectral range between 260 nm-320 nm was attributed to multisubstituted benzene. The aromatic intermediates are formed during the degradation process with the addition of hydroxyl radical to azo bond leading to breaking of azo bond [18]. Thus, this scenario suggested that the first step of azo dye degradation is the azo bond cleavage and followed by the addition of hydroxyl radical on the aromatic ring which resulted in the formation of azobenzene [18].

4. Mechanism of HEAs as a Catalyst on the Reaction Rate in Fenton Process

Fenton process is strongly influenced by two reagents which are ferrous (II) sulphate, $FeSO_4$ and hydrogen peroxide, H_2O_2. The reaction between these two reagents produce ferric ions and hydroxyl radicals. Hydroxyl radical plays an important role in the Fenton reagent to attack the molecule of methyl orange dye and degrades the amine bond which helps the dye decolorization in the solution which can be seen in the Fig. 4. Then, the presence of HEAs as a catalyst speed up the process since HEAs provide more active site for the molecules of Fenton reagent to react hence speed up the reaction [22,24].

To give additional evidence and further confirm the efficiency of HEAs as a catalyst, the FTIR characterization was performed. The infrared spectroscopy of dye, electro-Fenton (with HEAs anode), electro-Fenton (graphite anode and cathode), con-

ventional Fenton method and Fenton's reagent ($FeSO_4 + H_2O_2$) are presented in Fig. 5 below. The characteristic IR absorption peaks at 3200 cm^{-1}, 2890 cm^{-1}, 2360 cm^{-1}, 2161 cm^{-1} were observed in all samples. The wide bands at 3200 cm^{-1} are resultant from O-H banding of absorbed water molecules while 2890 cm^{-1} is corresponding –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 degradation treatment process. The FTIR spectra of dye showed significant bands at 3426 cm^{-1} and 1653 cm^{-1} which could be assigned as –NH group. After the reaction, the intensity of these bands was reduced and the peak was found to be broader. At 2033 cm^{-1} is visible in the dye and conventional Fenton method which represents the 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. This suggested that the electro-Fenton process is an efficient process for azo dye degradation. This is also supported by Elias et al. [24], the continuous electro-generation of Fenton reagent enhances the production of hydroxyl radical and fastens the degradation process. Besides, according to Wu et al. [25], the reaction between different metal elements in HEA and dye solution cause the formation of large amounts of nano-galvanic cells occupying the surface HEA and generate a large number of hydroxyl radicals. Thus, the presence of HEA as a catalyst in the electro-Fenton process will increase the degradation performance due to more hydroxyl radical being produced to break the azo bond.

5. Conclusion

This work was devoted to assess the capability of and mechanism of high entropy alloys (HEAs) as a catalyst in degradation of azo dye degradation efficiency in Fenton process. HEAs as a catalyst can speed up the Fenton reaction by accelerating the development of hydroxyl radicals due to the active catalytic sites of HEAs. 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 is derived from the pres-
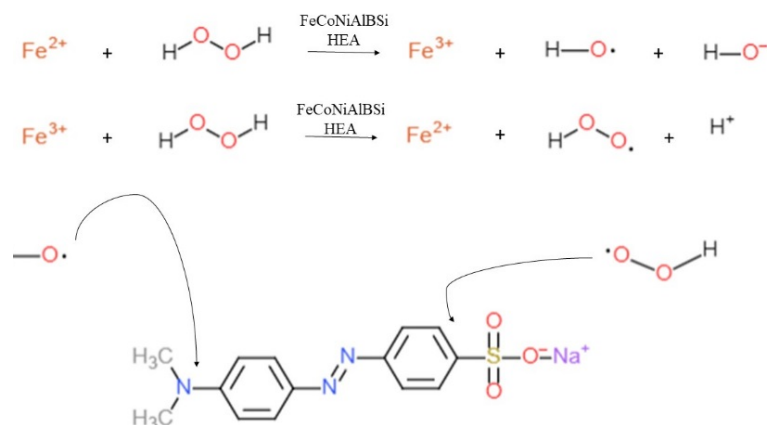

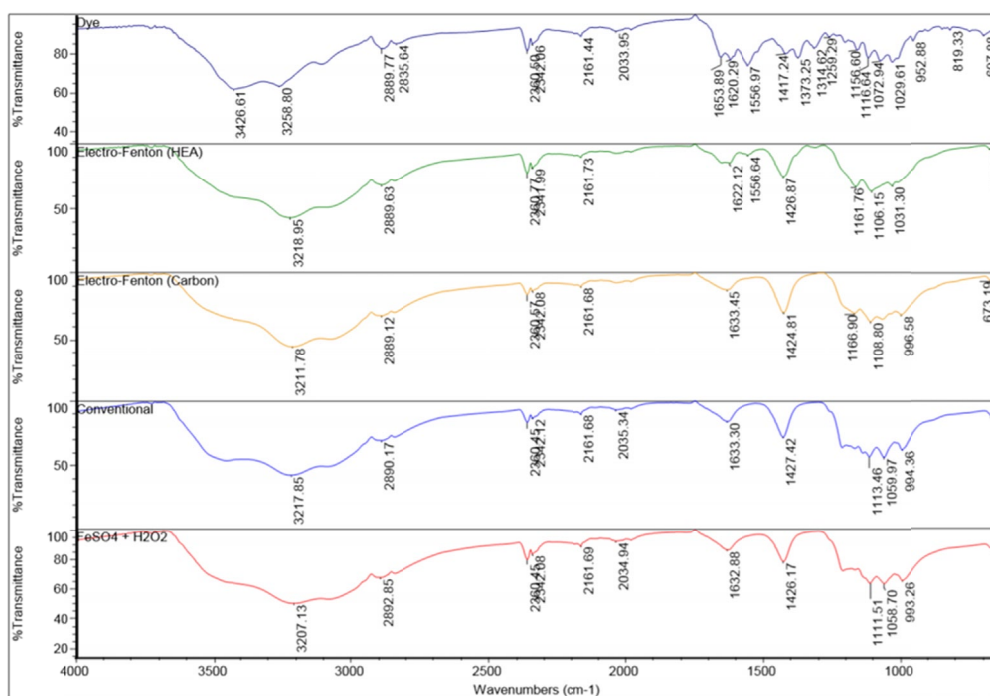Fig. 4. Mechanism of Fenton reagent with HEA as a catalyst

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

ence of ferrous sulphate with hydrogen peroxide and allows the ions to move faster. Compared to conventional Fenton method, the sludge generated in Electro-Fenton method is smaller and the UV-Vis absorbance with HEAs is lower. This shows that the dye has been degraded more efficiently as the water samples are clearer. This is because the presence of HEAs as a catalyst enhances the performance of Fenton reactions. The result of this 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] Y.L. Pang. A.Z. Abdullah, Clean Soil, Air and Water **41** (8), 751-764 (2013).

[2] https://www.ellenmacarthurfoundation.org/publications/a-new-textiles-economy-redesigning-fashions-future, accessed: 17.01.2021

[3] P.F. Gordon, P. Gregory, Organic chemistry in colour, Springer Science & Business Media (2012).

[4] B.J. Brüschweiler, C. Merlot, Regulatory Toxicology and Pharmacology **88**, 214-226 (2017).

[5] R. Jamee, R. Siddique, European Journal of Microbiology and Immunology **9** (4), 114-118 (2019).

[6] G. Matyszczak, K. Krzyczkowska, A. Fidler, Journal of Water Process Engineering **36**, 101242 (2020).

[7] S.K. Wu, Y. Pan, N. Wang, W. Dai, J. Lu, T. Lu, RSC Adv. **8** (72), 41347-41354 (2018).

[8] P.V. Nidheesh, R. Gandhimathi, Desalination **299**, 1-15 (2012).

[9] S. Sabhi, J. Kiwi, Water Res. **35**, 1994 (2001).

[10] G. Matyszczak, A. Sędkowska, S. Kuś, Dyes and Pigments **174**, 108076 (2020).

[11] M. Azami, M. Bahram, S. Nouri, Current Chemistry Letters **2** (2), 57-68 (2013).

[12] E. Severo, G.L. Dotto, S. Silvestri, I. Nunes, J.S. Salla, A. Martinez, K. Martinello, E.L. Foletto, Journal of Environmental Chemical Engineering **8**, 103853 (2020).

[13] D.B. Miracle, Nature Communications **10** (1), 1805 (2019).

[14] X. Cui, B. Zhang, C. Zeng, S. Guo, MRS Communications **1** (2018).

[15] S. Wang, H. Xin, Chem. **5** (3), 502-504 (2019).

[16] M.H. Tsai, J.W. Yeh, Materials Research Letters **2** (3), 107-123 (2014).

[17] M. Xu, C. Wu, Y. Zhou, Advanced Oxidation Processes – Applications, Trends, and Prospect **4** (2020).

[18] E. Guivarch, S. Trevin, C. Lahitte, M.A. Oturan, Environ. Chem. Lett. **1**, 38-44 (2003).

[19] F. Sopaj, N. Oturan, J. Pinson, F. Podvorica, M. Oturan, Applied Catalysis B: Environmental **199**, 331-341 (2016).

[20] M. Nabiałek, M. Szota, M. Dośpiał, P. Pietrusiewicz, S. Walters, Journal of Magnetism and Magnetic Materials **322** (21), 3377-3380 (2010).

[21] H. Jiang, Y. Sun, J. Feng, J. Wang, Water Science and Technology **74** (5), 1116-1126 (2016).

[22] Z. Lv, X. Liu, B. Jia, Sci Rep **6**, 34213 (2016).

[23] W. Feng, D. Nansheng, H. Helin, Chemosphere **41** (8), 1233-8 (2000).

[24] B. Elias, L. Guihard, S. Nicolas, F. Fourcade, A. Amrane, Environmental Progress and Sustainable Energy **30** (2), 160-167 (2011).

[25] S.K. Wu, Y. Pan, N. Wang, T. Lu, W.J. Dai, International Journal of Minerals, Metallurgy, and Materials **26** (1), 124-132 (2019).