Study Of Hematite Ore As A Source Of Iron For The Degradation Of Ether Amines Contained In Mining Wastewaters By The Fenton Reaction

Isabela Brandolis Alves Falconi*[0000-0001-7685-0827], Marcela dos Passos Galluzzi Baltazar, Jorge Alberto Soares Tenório[0000-0002-7849-7470]
Polytechnic School of the University of Sao Paulo
Lago St., 250, second floor, Sao Paulo, Brazil
*isabela_falconi@usp.br

Abstract. In 2015 and 2019, Brazil witnessed two accidents of rupture of iron mining dams (in the Brumadinho and Mariana districts), causing environmental and social damages. Among the principal causes of ruptures, are dams where the water volume accumulates in these systems. Water accumulated in tailings dams can be recuperated to reuse or discharged on rivers, but for this, it is necessary for previous treatment. The current methods developed to degrade ether amine flotation reactants consume additional reactants as Fe ions or yet can take 28 days to achieve satisfactory results as in biodegradation. The heterogeneous Fenton can be an alternative that uses the iron already available in mining wastewaters This study used Fenton heterogeneous to investigate the degradation of an ether amine flotation reactant present in wastewaters from iron mining operations. For this, Fe ore from the mining industry was used as the catalyst. The catalyst was characterized by x-ray diffraction (XRD), and Fenton tests were conducted to evaluate the influence of H_2O_2 ($0.5g.L^{-1}$ – $6.3g.L^{-1}$) and ore concentrations ($0.7g.L^{-1}$ – $14g.L^{-1}$) on degradation. The influence of Fe leached on the solution was also evaluated. The monitorization of the reaction was done by total organic concentration (TOC), iron concentration with atomic absorption (AA), and ether amine by bromocresol green method. The results showed that Fe ore could be used as Fenton heterogeneous catalyst degrading 96% of ether amine in 240 minutes, and with this, the technique could be explored to be applied to real wastewater treatments in mining operations.

Keywords: Ether amine degradation; Heterogeneous Fenton; Iron ore; Flotation reactants; Mining Wastewater, Wastewater Treatment.

1   Introduction

The treatment of iron ores is a process that generates thousands of residues and consumes thousands of tons of water. For example, the Yuanjiacun iron mine generates 400 thousand m^3 of wastewater [1]. The result of the generation of this waste is tailings dams. A preoccupation with dams only increased over the years but was intensified after the accidents of dam ruptures in Mariana (2015) (discharging 50-60 million m^3 of mud in Doce River) and in Brumadinho (2019) (15 million of m^3 of mud), in Brazil. Now efforts have been made to eliminate them [2,3]. The flotation process is an ore concentration step, which requires using around 50-85% of water in the feed pulp. With that, it becomes a step that consumes hundreds of m^3 of water[4,5]. An alternative to turning this process more environmental and in line with the circular economy is the reuse of internal water in the process and from tailings dams [6,7].
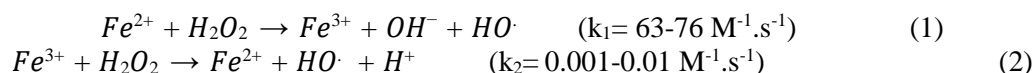
Water recycling and reuse may involve complications such as, for example, carrying organics reminiscent of partially degraded originating from the flotation stage that will impact the recovery and concentration of certain ores. Some researchers observed this effect in beneficiation plants to separate copper, zinc, iron, quartz, potassium, and lead ores [8]. With that, an alternative for continuous reuse of this water would be the use of pre-treatment. Several studies in the literature explore this performance drop in concentration by flotation, where, for example, residual xanthates that increase the hydrophobicity of fsulfide minerals [9–11], residual sulfides (used as depressants) which can depress unwanted minerals [12], metal ions and alkaline earth metals that cause deactivation or activation of unwanted minerals phases [5]. Other effects are observed in non-sulfidesulfidesulfide ores; residuals from carboxylated collectors and alkyl sulfates that increase the surface activity of ores in flotation, activating non-sulfidesulfide and sulfide ores, making separation impossible; residuals from primary amines that activate mud, reducing the grade of the concentrated ore, residuals of oleate (used in the flotation of carbonates) that cause the flotation of silicates with pyrochlore [7,13–15].

On the other hand, wastewater contaminated with these reagents must meet standards for the water to be returned to nature, whereas in Canada, it may be required that the effluent be contaminated below LC_{50} for *Daphnia Magna* and *Rainbow Trout* [16] which can be pretty low levels. For example, the ether amine surfactant has an LC_{50} of 6.8mg.L^{-1} for the first[17]. Therefore, treating effluents is necessary to remove toxic species that pose a risk to the environment. Numerous studies in literature view biodegradation[18], adsorption[19], ozonization[20], Fenton, and photo-Fenton[21,22], photolysis[23] and electrolysis[24] are effectives in treat this type of contaminants.

Ether amines surfactants can degrade completely through bioprocess with bacteria that have naturally in iron dams, but this process takes 28 days[18,25,26]. Still, there are no studies that prove that they are led to complete degradation and achieve a mineralization state (reduce organic substances to CO_2, water, and inert salts)[18,27,28] requires in situ generation of ozone gas which requires electricity and operation expenses, and the adsorption mitigates the pollutant to a secondary source contaminated requiring properly discharge.[26,29]

The advanced oxidative processes/technologies (AOP/AOTs) as ozonation have attracted the attention considering their high kinetic degradation rate better than biological processes, and their capacity to remove traces of recalcitrant organics. AOPs are based on redox reactions that generate hydroxyl radical (HO·) and reactive oxygen species (ROS) as oxidants, and the generation of secondary wastes is mitigated using proper settings (Miklos et al., 2018; Zhang et al., 2019).

The Fenton is a type of AOP process are based (Equation 1 and 2) that consists of the interaction of iron ions and hydrogen peroxide in an acid medium. The Fenton reaction was observed by Henry J. Fenton in 1894, and it has been employed in water treatment processes over the years to remove recalcitrant organic substances. This process has been improved continuously, and it is currently not limited to the use of Fe, but other transition metals and materials as catalysts such as Al, Ce, Ru, Co, Cu, Cr, metal oxides, materials as polyoxometalates [30].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + HO^· \qquad (k_1 = 63\text{-}76 \text{ M}^{-1}.s^{-1}) \qquad (1)$$
$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO^· + H^+ \qquad (k_2 = 0.001\text{-}0.01 \text{ M}^{-1}.s^{-1}) \qquad (2)$$

The utilization of a variety of metals as a catalyst to degrade surfactants or contaminants confers an advantage to the utilization of the Fenton process to treat mining wastewater due to the high metal content present in these effluents. In this way, the additional cost of catalysts is avoided. The homogeneous Fenton reaction occurs only with one soluble phase, but the sludge formation is a problem that is necessary to remediate which requires additional treatments to remove the solid. This occurs due to the Fe^{2+} that is oxidized to Fe^{3+}[31]. Through this, alternatives such as the utilization of solid catalysts with heterogeneous route an effort done by researchers. The solids used as catalysts have a large variety and various degrees of development, such as zeolites, composites[32], graphene, clays, pillaredclays[33], nanoparticules[22], metal oxides, and natural minerals[34]. The exact mechanism of heterogeneous Fenton reactions is not completely understood, and in most cases, the homogeneous Fenton confers higher mineralization[35]. Although some authors defend that the reaction occurs only on the surface of the catalysts, there are those defend that the reaction occurs only due to the metal leaching observed. Still, it is currently attributed that the most stable catalysts or those that do not have any leaching are the most indicated [36].

Therefore, the present study aims at evaluating the utilization of ore from a mining company as a Fe source in a heterogeneous Fenton reaction to degrade the ether amine collector.

2 Materials And Methods

The reagents used were acid oxalic dihydrate (98%, Sigma Aldrich), H_2O_2 (29%, Sigma Aldrich), flotation ether amine commercial surfactant (Flotigam EDA-C, Clariant). Solutions of NaOH 8M (98%, Synth) and H_2SO_4 2M (98%, Synth) were used for pH control. Potential and pH were measured using pH and ORP equipment at Hanna Instruments. The Fe ore was acquired from Brazilian mining located in Minas Gerais state, Quadrilatero Ferrifero region. The study was divided into three parts: characterization, control tests, and Fenton reaction.

The ore was characterized by x-ray diffraction (XRD) using Rigaku MiniFlex300 with Cu-Kα incident radiation (λ=1,54 Å) and equipped with a graphite monochromator and nickel filter. On tests, the degradation was monitored quantifying the concentrations of iron leach every 30 minutes through Atomic Absorption Spectrophotometer Shimadzu, and the total organic carbon (TOC) was measured using TOC-L Shimadzu equipment. The ether amine concentration was determined by the bromocresol green method [37].

All tests were conducted in an orbital shaker in Erlenmeyer's, using 250mL of solution at 240 rpm, 21°C, pH controlled and adjusted in 2.8. The control tests evaluated the influence of adsorption of Ox and ether amine molecules by ore using the concentrations of 180mg.L^{-1} of Flotigam, 18.8 g.L^{-1} of Ox with 1.4 g.L^{-1} and 14 g.L^{-1} of ore. The same conditions were used to evaluate the degradation on Fenton tests in different concentrations of H_2O_2 (0.5 g.L^{-1} - 6.3g.L^{-1}) and Fe ore (0.7 g.L^{-1}, 1.4 g.L^{-1}, and 14g.L^{-1}). Lastly, a comparison was done using the same proportions of pure hematite reactant and $FeSO_4.7H_2O$ (II) (both from Sigma Aldrich) in place of real ore.

3   Results and discussions

3.1   Iron characterization

The iron ore sample used in this study is composed of fractions of hematite and goethite confirmed in the diffractogram of Fig. 1 with the characteristic peaks obtained. Hematite has a structure of the Fe^{3+} oxide (α-Fe2O3) and goethite are a hydrated oxide (α-FeOOH). It could be noted that the phases of both iron oxides presented relativelythe same proportion.
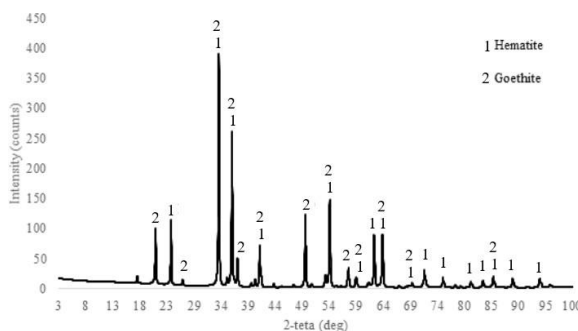

Fig. 1: X-ray diffractogram of the iron ore concentrate sample.

3.2   Control Tests

The control tests evaluated the iron that was leached to the solution by the iron ore and the adsorption in Fig. 2 and **Error! Reference source not found.**.
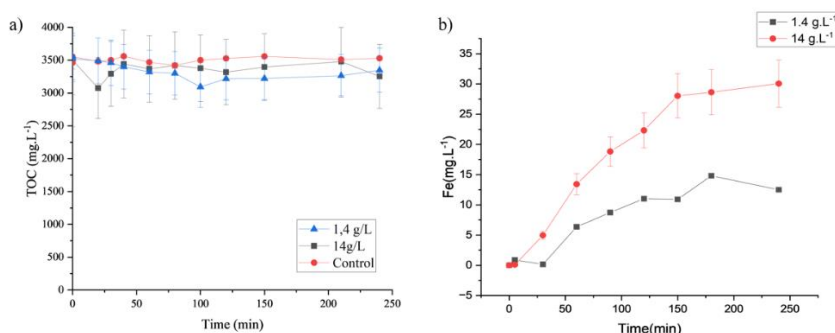

Fig. 2: TOC and Fe leached concentration in control tests that used 1.4g.L^{-1} iron ore and 18.8 g.L^{-1} of Ox.

The results show that the iron ore concentration influences the TOC and the Fe in the solution. The $C_2O_4H_2$ (Ox) in pH between 2.5-4 will be predominant at the specie $HC_2O_4^-$ interacting with the solid surface ore forming $Fe^{3+}Ox_3^{3-}$ and $Fe^{2+}Ox_2^{2-}$ species where the Ox was higher than 0.1 M. However, as far as the Fe species goes to the solution, the pH decreases turning more acid, and the Ox below pH 1.2 turns out to be stable stopping the leaching reaction. These occur after 150 minutes in Fig.1 b) where the Fe leaching achieves more stability [38].

The TOC was not present a significant difference when the ore concentration in the solution was increased.

3.3 Fenton tests

The influence of H_2O_2 and Fe ore concentration on degradation are presented in Fig. 3. The increase on the concentrations of H_2O_2 on the Fenton reaction does not represent a significative difference on mineralization results, but it was noted the growth of TOC removal from solution achieved the higher result in 3.5 g.L^{-1} H_2O_2 concentration and amounts above of this decrease the efficiency. Comparatively, the increase in Fe ore concentration was more significative in degradation.
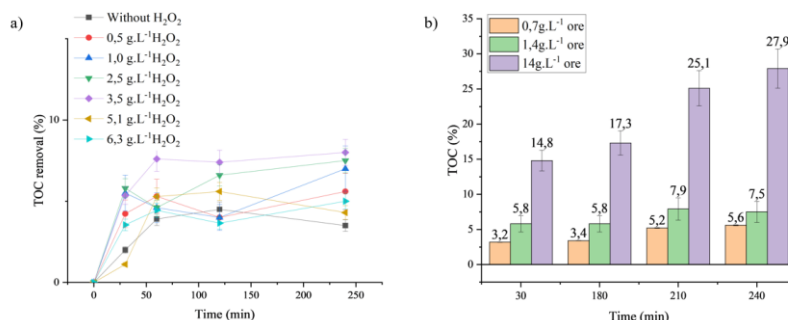

Fig. 3: Influence of mineralization in different a) H_2O_2 (using 1.4 mg.L^{-1} iron ore) and b) Fe ore (with 2.5 g.L^{-1} H_2O_2) and 18.8mg.L^{-1} Ox.

The difference observed in TOC removal is evidence that the Fenton reaction occurred producing HO. radicals capable to promote oxidation of the organic matrix of the solution. The absence of significative influence of the H_2O_2 concentration is appointed by various studies of the Fenton process that reinforce the scavenger effect that occurred when this reactant is present in excess. The H_2O_2 can react with HO. species on a solution faster than with Fe ions available (Equations 4 and 5) decreasing the degradation efficiency [31,39]. On the other side, the 1:1 stoichiometry of mineralization is not always obeyed considering that the radicals' species on Fenton reactions can also be originated by other mechanisms that occur in parallel (Equations 6) [21].

$$\cdot OH + H_2O_2 \rightarrow HOO\cdot + H_2O \tag{4}$$
$$\cdot OH + HOO\cdot \rightarrow H_2O + O_2 \tag{5}$$
$$\cdot OH + \cdot OH \rightarrow H_2O_2 \tag{6}$$

The heterogeneous Fenton can follow different mechanisms to occur; on the mineral catalyst surface depending on the H_2O_2 capable to be adsorbed and can be governed by the homogeneous route. Yet, the process can start on the catalyst surface and continue in the bulk solution. Although the hematite species has been considered thermodynamically stable, it was seen that the Fe leaching to solution occurs in the presence of Ox, then the Fenton reaction could be occurred by mainly the homogeneous route. The concentration of the Fe leached to the solution with the H_2O_2 concentration increase is in

Fig. **4**.

During the heterogeneous reaction, the Fe was leached to the reaction until 60 minutes when the 2.5 g.L^{-1} of H$_2$O$_2$ was used, but in higher H$_2$O$_2$ concentrations minimal Fe concentrations were obtained reflecting that when the Fe achieve maximum concentrations in solution, higher TOC removal rates were obtained[36].
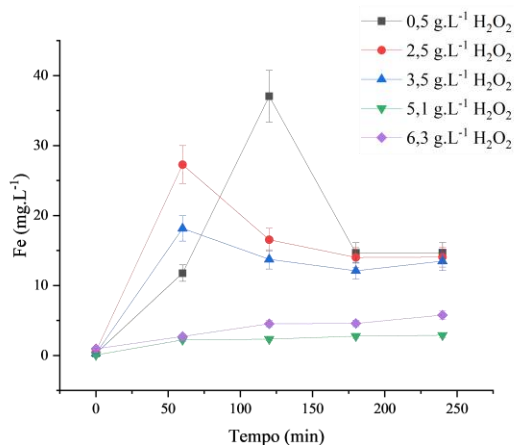

Fig. 4: Fe leached from ore in different concentrations of H$_2$O$_2$ and using 1.4 g.L^{-1} of catalyst and 18.8 g.L^{-1} Ox.

3.4   Fenton degradation compared different Fe sources.

The degradation results when different sources of iron were used are in Fig. 5. The utilization of pure hematite presented a low difference in the ore utilized with could be attributed to the structure differences when a pure reactant is used as the same granulometry size and the absence of various Fe phases that can interfere on the interaction between molecules presents on the solution [34].
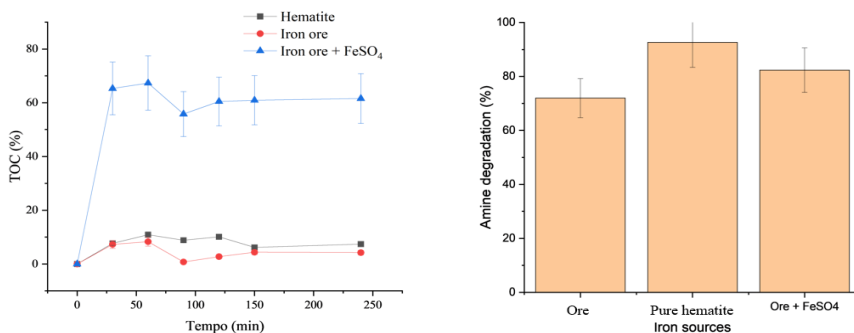

Fig. 5: TOC removal and amine degradation in different iron sources (iron ore, pure hematite, and the same concentration of ore with FeSO$_4$) in 2.5 g.L^{-1} H$_2$O$_2$ and 18.8 g.L^{-1}Ox.

The utilization of the mixture of FeSO$_4$ with Fe ore resulted in a difference from 12% of mineralization to 64% which indicates again that the main process occurs via a homogenous phase. However, the amine degradation on all tests obtained more than 70% amine degradation, and 96% of the amine collector was degraded in the presence of the pure hematite reactant. This shows that the amine has preference by the heterogeneous degradation indicative that the reaction occurred by both routes. The mixture of FeSO$_4$ with Fe ore can decrease the FeSO$_4$ reactant consumption in future studies. It could be observed through an ether amine degradation study by homogenous Fenton that uses FeSO$_4$ alone on the tests, in this research the better result was 30% TOC removal using 2.23g.L^{-1} of Fe^{2+} and 2.7 g.L^{-1} of H$_2$O$_2$. In this

way, the heterogenous dopped with $FeSO_4$ achieve a higher result of mineralization using lower concentrations of catalyst.

On the other side, the degradation of amine in the heterogeneous Fenton which takes 240 minutes to achieve 96% is faster than the biodegradation process which takes 1 day to achieve a similar result to degrade a solution with 10mg.L^{-1} of the contaminant[18]. In the view to transform the process of amine degradation faster mainly in tailings dams the combination of both wastewater treatments could be an alternative.

4   Conclusion

After analyzed the results and discussions obtained were possible to conclude that the heterogeneous Fenton reaction could be applied to degrade ether amine flotation surfactant using Fe ore as a catalyst. Around this, the better mineralization result was obtained using 18.8g.L^{-1} Ox, 2.5 g.L^{-1}, 2.5 g.L^{-1} H_2O_2 and 1.4 g.L^{-1} $FeSO_4$ with 11.4g.L^{-1} of Fe ore resulting in 64% TOC removal and 86% amine degradation. For ether amine degradation the better result was 96% and 12% TOC removal. The Fenton reaction occurred on the catalyst surface, but mainly by the Fe leached to the solution. Also, the results of degradation obtained were higher than the other treatments studied such as biodegradation. As future studies are recommended to investigate the degradation of amine using a combination of $FeSO_4$ and Fe ore with the finality to decrease the reactants consumption and the association of Fenton with biodegradation.

References

[1] W.L. Jiang, H.F. Xu, Treatment and Recycling of the Process Water in Iron Ore Flotation of Yuanjiacun Iron Mine, J. Chem. 2017 (2017) 1–8. https://doi.org/10.1155/2017/9187436.

[2] F. Bottino, J.A.M. Milan, M.B. Cunha-Santino, I. Bianchini, Influence of the residue from an iron mining dam in the growth of two macrophyte species, Chemosphere. 186 (2017) 488–494. https://doi.org/10.1016/j.chemosphere.2017.08.030.

[3] C. dos S. Vergilio, D. Lacerda, B.C.V. de Oliveira, E. Sartori, G.M. Campos, A.L. de S. Pereira, D.B. de Aguiar, T. da S. Souza, M.G. de Almeida, F. Thompson, C.E. de Rezende, Metal concentrations and biological effects from one of the largest mining disasters in the world (Brumadinho, Minas Gerais, Brazil), Sci. Rep. 10 (2020) 1–12. https://doi.org/10.1038/s41598-020-62700-w.

[4] E. Muzenda, An Investigation into the Effect of Water Quality on Flotation Performance, World Acad. Sci. Eng. Technol. Int. J. Chem. Mol. Nucl. Mater. Metall. Eng. 4 (2010) 562–566. https://doi.org/doi.org/10.5281/zenodo.1077880.

[5] Y. Li, S. Xie, Y. Zhao, L. Xia, H. Li, S. Song, The Life Cycle of Water Used in Flotation: a Review, Mining, Metall. Explor. 36 (2019) 385–397. https://doi.org/10.1007/s42461-018-0004-z.

[6] S. Lin, R. Liu, M. Wu, Y. Hu, W. Sun, Z. Shi, H. Han, W. Li, Minimizing beneficiation wastewater through internal reuse of process water in flotation circuit, J. Clean. Prod. 245 (2020) 118898. https://doi.org/10.1016/j.jclepro.2019.118898.

[7] S.R. Rao, J.A. Finch, A review of water re-use in flotation, Miner. Eng. 2 (1989) 65–85. https://doi.org/10.1016/0892-6875(89)90066-6.

[8] N.P. Lima, T.C. de Souza Pinto, A.C. Tavares, J. Sweet, The entrainment effect on the performance of iron ore reverse flotation, Miner. Eng. 96–97 (2016) 53–58. https://doi.org/10.1016/j.mineng.2016.05.018.

[9] M.D. Seke, P.C. Pistorius, Effect of cuprous cyanide, dry and wet milling on the selective flotation of galena and sphalerite, Miner. Eng. 19 (2006) 1–11. https://doi.org/10.1016/J.MINENG.2005.03.005.

[10] I. Muzinda, N. Schreithofer, Water quality effects on flotation: Impacts and control of residual xanthates, Miner. Eng. 125 (2018) 34–41. https://doi.org/10.1016/j.mineng.2018.03.032.

[11] Y. Ozturk, O. Bicak, Z. Ekmekci, Effects of Residual Xanthate on Flotation Efficiency of a Cu-Zn Sulfide Ore, Minerals. 12 (2022). https://doi.org/10.3390/min12030279.

[12] M. Sinche-Gonzalez, D. Fornasiero, Understanding the effect of sulphate in mining-process water on sulfide flotation, Miner. Eng. 165 (2021) 106865. https://doi.org/10.1016/j.mineng.2021.106865.

[13] A. Bahmani-Ghaedi, A. Hassanzadeh, A. Sam, A. Entezari-Zarandi, The effect of residual flocculants in the circulating water on dewatering of Gol-e-Gohar iron ore, Miner. Eng. 179 (2022) 107440. https://doi.org/10.1016/j.mineng.2022.107440.

[14] N.P. Lima, G.E.S. Valadão, A.E.C. Peres, Effect of amine and starch dosages on the reverse cationic flotation of an iron ore, Miner. Eng. 45 (2013) 180–184. https://doi.org/10.1016/j.mineng.2013.03.001.

[15] K. Shrimali, X. Yin, X. Wang, J.D. Miller, Fundamental issues on the influence of starch in amine adsorption by quartz, Colloids Surfaces A Physicochem. Eng. Asp. 522 (2017) 642–651. https://doi.org/10.1016/j.colsurfa.2017.03.031.

[16] O.W.R. Act, Environmental Protection Act, Canada, 2021. https://www.ontario.ca/laws/statute/90e19.

[17] A. Peres, N. Agarwal, N. Bartalini, D. Beda, Environmental impact of an etheramine utilized as flotation collector., 7th Int. Mine Water Assoc. Congr. (2000) 464–471.

[18] D.M. Araujo, M.I. Yoshida, J.A. Takahashi, C.F. Carvalho, F. Stapelfeldt, Biodegradation studies on fatty amines used for reverse flotation of iron ore, Int. Biodeterior. Biodegradation. 64 (2010) 151–155. https://doi.org/10.1016/J.IBIOD.2010.01.004.

[19] R.F. Resende, P.V.B. Leal, D.H. Pereira, R.M. Papini, Z.M. Magriotis, Removal of fatty acid by natural and modified bentonites: Elucidation of adsorption mechanism, Colloids Surfaces A Physicochem. Eng. Asp. 605 (2020) 125340. https://doi.org/https://doi.org/10.1016/j.colsurfa.2020.125340.

[20] P. Fu, X. Lin, L. Wang, Y. Ma, Catalytic ozonation of refractory O-isopropyl-N-ethylthionocarbamate collector with coexisted kaolinite in sulfide flotation wastewaters, Appl. Clay Sci. 198 (2020) 105834. https://doi.org/10.1016/j.clay.2020.105834.

[21] I.B.A. Falconi, M. dos P.G. Baltazar, D.C.R. Espinosa, J.A.S. Tenório, Degradation of surfactant used in iron mining by oxidation technique: Fenton, photo-Fenton, and H 2 O 2 /UV—A comparative study, Can. J. Chem. Eng. 98 (2020) 1069–1083. https://doi.org/10.1002/cjce.23705.

[22] T.A.G. Martins, I.B.A. Falconi, G. Pavoski, V.T. de Moraes, M. dos P. Galluzzi Baltazar, D.C.R. Espinosa, Green synthesis, characterization, and application of copper nanoparticles obtained from printed circuit boards to degrade mining surfactant by Fenton process, J. Environ. Chem. Eng. 9 (2021) 106576. https://doi.org/10.1016/j.jece.2021.106576.

[23] P. Fu, J. Feng, H. Yang, T. Yang, Degradation of sodium n-butyl xanthate by vacuum UV-ozone (VUV/O3) in comparison with ozone and VUV photolysis, Process Saf. Environ. Prot. 102 (2016) 64–70. https://doi.org/https://doi.org/10.1016/j.psep.2016.02.010.

[24] A.G. Merma, B.F. Santos, A.S.C. Rego, R.R. Hacha, M.L. Torem, Treatment of oily wastewater from mining industry using electrocoagulation: Fundamentals and process optimization, J. Mater. Res. Technol. 9 (2020) 15164–15176. https://doi.org/https://doi.org/10.1016/j.jmrt.2020.10.107.

[25] M.T. García, E. Campos, I. Ribosa, Biodegradability and ecotoxicity of amine oxide based surfactants, Chemosphere. 69 (2007) 1574–1578. https://doi.org/10.1016/j.chemosphere.2007.05.089.

[26] Z.M. Magriotis, P.V.B. Leal, P.F. Sales, R.M. Papini, P.R.M. Viana, Adsorption of etheramine on kaolinite: A cheap alternative for the treatment of mining effluents, J. Hazard. Mater. 184 (2010) 465–471. https://doi.org/10.1016/j.jhazmat.2010.08.057.

[27] G.M.B. Batisteli, A.E.C. Peres, Residual amine in iron ore flotation, Miner. Eng. 21 (2008) 873–876. https://doi.org/10.1016/j.mineng.2008.04.002.

[28] A. V. Vorontsov, Advancing Fenton and photo-Fenton water treatment through the catalyst design, J. Hazard. Mater. (2019) 103–112. https://doi.org/10.1016/j.jhazmat.2018.04.033.

[29] S. Ramachandra Rao, Chapter 11 Recycling of water and reagents, in: Waste Manag. Ser., 1st ed., Elsevier Science Publishers B.V, 2006: pp. 459–481. https://doi.org/10.1016/S0713-2743(06)80096-6.

[30] A.D. Bokare, W. Choi, Review of iron-free Fenton-like systems for activating H2O2 in advanced oxidation processes, J. Hazard. Mater. 275 (2014) 121–135. https://doi.org/10.1016/j.jhazmat.2014.04.054.

[31] J.J. Pignatello, E. Oliveros, A. MacKay, Advanced oxidation processes for organic contaminant destruction based on the fenton reaction and related chemistry, Crit. Rev. Environ. Sci. Technol. 36 (2006) 1–84. https://doi.org/10.1080/10643380500326564.

[32] S. Rahim Pouran, A.R.R. Abdul Aziz, W.M.A. Wan Daud, Review on the main advances in photo-Fenton oxidation system for recalcitrant wastewaters, J. Ind. Eng. Chem. 21 (2015) 53–69. https://doi.org/10.1016/j.jiec.2014.05.005.

[33] J. Herney-Ramirez, M.A. Vicente, L.M. Madeira, Heterogeneous photo-Fenton oxidation with pillared clay-based catalysts for wastewater treatment: A review, Appl. Catal. B Environ. 98 (2010) 10–26. https://doi.org/10.1016/j.apcatb.2010.05.004.

[34] T.D.M. Augusto, P. Chagas, D.L. Sangiorge, T.C.D.O. Mac Leod, L.C.A. Oliveira, C.S. De Castro, Iron ore tailings as catalysts for oxidation of the drug paracetamol and dyes by heterogeneous Fenton, J. Environ. Chem. Eng. 6 (2018) 6545–6553. https://doi.org/10.1016/j.jece.2018.09.052.

[35] Y. Zhu, R. Zhu, Y. Xi, J. Zhu, G. Zhu, H. He, Strategies for Enhancing the Heterogeneous Fenton Catalytic Reactivity: A review, Appl. Catal. B Environ. (2019). https://doi.org/10.1016/j.apcatb.2019.05.041.

[36] F.V.F. Araujo, L. Yokoyama, L.A.C. Teixeira, J.C. Campos, Heterogeneous Fenton process using the mineral hematite for the discolouration of a reactive dye solution, Brazilian J. Chem. Eng. 28 (2011) 605–616. www.abeq.org.br/bjche (accessed May 23, 2019).

[37] D.M. Araujo, M.I. Yoshida, C.F. Carvalho, Colorimetric Determination of Ether Amine Greases Utilized in the Flotation of Iron Ore, J. Biol. Chem. 64 (2009) 390–392. https://doi.org/10.1134/S1061934809040121.

[38] S.O. Lee, T. Tran, Y.Y. Park, S.J. Kim, M.J. Kim, Study on the kinetics of iron oxide leaching by oxalic acid, Int. J. Miner. Process. 80 (2006) 144–152. https://doi.org/10.1016/j.minpro.2006.03.012.

[39] D. Ghime, P. Ghosh, Heterogeneous Fenton degradation of oxalic acid by using silica supported iron catalysts prepared from raw rice husk, J. Water Process Eng. 19 (2017) 156–163. https://doi.org/10.1016/j.jwpe.2017.07.025.