Environmental Science and Pollution Research (2022) 29:77071–77080
https://doi.org/10.1007/s11356-022-21306-7

RESEARCH ARTICLE

Iron-loaded leonardite powder for Fenton oxidation of Reactive Red 180 dye removal

Hudaverdi Arslan[1] · Raouf Bouchareb[2] · Ezgi Bezirhan Arikan[1] · Nadir Dizge[1]

Received: 16 December 2021 / Accepted: 1 June 2022 / Published online: 8 June 2022

Abstract
Fenton oxidation is an effective and valuable method for wastewater treatment. To inhibit environmental impacts and increase overall reaction efficiencies, it is important to develop advanced catalysts. This paper illustrates an experimental study on the elimination of RR180 dye from synthetic aqueous solutions with raw leonardite and different iron-loaded leonardite powders, Fe(0)-loaded leonardite, and Fe(II)-loaded leonardite. The effect of solution pH (2.0–6.0), catalyst amount (0.10–1.5 g/L), H_2O_2 concentration (10–50 µL/L), and dye concentration (10–30 ppm) was tested to achieve maximum color removal efficiency using the three catalysts. At $pH=2$, color removal efficiencies were higher and more suitable. Initial experiments showed the advantage of using Fe(II)-loaded leonardite on using Fe(0)-loaded leonardite. Fe(II)-loaded leonardite catalyst was the most efficient in RR180 color removal compared to the other tested reagents. Color removal in function of solution pH did not decrease much when Fe(II)-loaded leonardite was used (100 to 96%) when pH was increased from 2.0 to 6.0. In the other hand, dye removal has been significantly affected in the case of using raw leonardite, Fe(0)-loaded leonardite (93 to 0%), and (100 to 13%) in the same pH range, respectively. At optimum experimental conditions, catalyst amount: 0.75 g/L for Fe(II) and Fe(0)-loaded leonardite and 1.5 g/L for raw leonardite; dye concentration: 10 ppm; solution pH: 2.0; H_2O_2 concentration: 50 µL/L; volume: 100 mL and reaction time: 60 min, RR180 dye removal efficiencies were 91%, 100%, and 100% by raw leonardite, Fe(0)-loaded leonardite and Fe(II)-loaded leonardite, respectively. The stability and reusability of the tested catalyst was investigated up to ten cycles. The experimental results revealed that both Fe(0)-loaded leonardite and Fe(II)-loaded leonardite can be used in Fenton reaction up to four cycles without decreasing their efficiency in RR180 color removal. The characterization of the catalysts was established using scanning electron microscope with energy dispersive X-ray spectroscopy (SEM–EDX). The synthesized catalyst can be used at large scale in any textile industry to effectively remove dyes resulting in high elimination rates at the optimal determined and studied conditions.

Keywords Leonardite · Fenton oxidation · RR180 removal · Recycling · Reusability

Introduction

Water pollution caused by synthetic dyes has come to be one of the most significant environmental issues in the last years. Dyes are involved in the aquatic pollution considerably as a result of numerous industrial resources (Gökku et al. 2013). Various dyes are known to be dangerous and toxic to the human being and to the environment. These toxic materials occurrence in the environment may be detrimental even at low concentrations (Deniz and Kepekci 2016). The elimination of dyes from wastewater is important in order to protect the environment and human health.

Wastewaters comprising dyes are known to be very challenging to treat because of stable nature, resistant, and recalcitrant of these contaminants (Kousha et al. 2015). Several physicochemical processes are presented to remove dyes from aqueous solution, namely coagulation (Demissie et al. 2021; Gökkuş and Yıldız 2014), floculation (Januário et al. 2021), photo-catalytic (Bilici et al. 2021), and membrane filtration(Bouchareb et al. 2020). Long treatment duration,

Responsible Editor: Ricardo A. Torres-Palma

✉ Nadir Dizge
ndizge@mersin.edu.tr

[1] Department of Environmental Engineering, Mersin University, Mersin 33343, Turkey

[2] Department of Environmental Engineering, Process Engineering Faculty, Saleh Boubnider University, 25000 Constantine, Algeria

high-cost, high amounts of produced sludge, poor efficiency, and in some cases toxic by-products creation make these techniques unfeasible and expensive to operate (Albadarin and Mangwandi 2015).

To provide a proper treatment technique for the removal of a specific dye is not only difficult; however, expensive too. Therefore, it is important to develop a new or modified technology which overcomes the challenges of the conventional methods. Biotechnological techniques are efficient and cost-effective alternatives to eliminate dyes in wastewaters as compared to the above processes. In this context, advanced oxidation processes (AOP) are effective techniques for persistent toxic pollutants removal in dyes wastewater (Abukhadra et al. 2019). AOP is established based on chemical oxidation of organic contaminants by various reaction mechanisms using electrocatalysis, ozonation, photocatalysis, electrocatalytic oxidation, and Fenton-like processes (Sievers 2011). The main reaction mechanism of these methods is based on the generation of reactive oxygen species ($^{\bullet}OH$, $^{\bullet}OOH$, and $^{\bullet}O^{2-}$) characterized by high oxidation potential (+ 1.8 to 2.8 V) (Ivanets et al. 2019). This process includes principally hydroxyl radicals ($OH^{\bullet}$) (+ 2.80 V) that are highly reactive and non-selective for degradation of main contaminants to secondary contaminants, H_2O and CO_2 (Babuponnusami and Muthukumar 2014). Along with these processes, Fenton process is the most effective technique for hydroxyl radicals generation which are able to increase the reaction rate and decrease reaction time for dyes removal (Çiner and Gökkuş 2012; Karthikeyan et al. 2011). The different advantages of Fenton reagent compared to other approaches are summarized in Table 1 (Pani et al. 2020).

Equations (1) and (2) represent the main reactions of the process:

$$H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2 \quad (1)$$

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + OH^{\bullet} \quad (2)$$

Organic species reaction with ($OH^{\bullet}$) radical is symbolized in Eq. (3):

$$RH + OH^{\bullet} \rightarrow RH^{\bullet} + OH \quad (3)$$

The efficiency of adsorption-based methods varies, mainly, on the used catalyst. Up to now, several catalysts either from synthetic or natural origin have been used for dyes removal. These include modified activated carbons, industrial, and agricultural by-products, minerals, clay, and biosorbents (Solé-Sardans et al. 2016). Among these catalysts, natural materials containing iron and modified catalysts loaded with iron species are particularly efficient to remove different pollutants from contaminated wastewater. It seems that electrostatic interaction, specific adsorption, and surface complexation are the main mechanisms for dyes removal by iron-loaded materials.

Leonardite is a low-cost substance which has demonstrated a good ability to eliminate dyes and heavy metal (Martínez et al. 2013; Terdputtakun et al. 2017; Sayjumpa et al. 2019; Arslan et al. 2022a, b) from aqueous solutions. Leonardite is an immature coal with high humic acid content containing oxygen functional groups (phenol, carboxyl, and hydroxyl) which allow to remove different contaminants. According to the stated above, the aim of this research study was the preparation of an effective catalyst for RR180 dye from a synthetic aqueous solution. The effects of solution pH, catalyst concentration, and initial dye concentration were investigated for wastewater treatment by Fenton oxidation process.

Material and methods

Materials

The used anionic (RR180) dye was obtained from Alfa Chemistry (USA). Ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$, ACS reagent, ≥ 99.0%), ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, ACS reagent, 97%), sodium tetrahydridoborate ($NaBH_4$, powder, ≥ 98.0%), and hydrogen peroxide solution (H_2O_2, 30% (w/w) in H_2O, contains stabilizer) were purchased from Merck (Germany). The

Table 1 Fenton reagent advantages

Advantages	References
They are capable of oxidizing organic pollutants and metals, providing their transformation and degradation	(Moussavi and Matavos-Aramyan 2016)
They have a complete destruction of pollutants capability to harmless materials (CO_2, H_2O and inorganic salts)	(Nidheesh and Gandhimathi 2012)
Fenton reagent permits high mineralization degree at room temperature and pressure conditions	(Tony et al. 2016)
Energy provision is not necessary to activate hydrogen peroxide	(Bautista et al. 2007)
Cost-effective source of hydroxyl radicals, employing easy-to-handle reagents and generally involves a relatively short reaction time	(Zhang et al. 2016)
Reasonably priced, and the process is easy to operate	(Singa et al. 2018)

molecular structure and fundamentals properties of the dye are shown in Table 2. The surface morphological description and chemical composition of the catalysts were determined by Scanning Electron Microscopy combined with energy dispersive X-ray analysis using Zeiss Supra 55, Germany.

Fe(II) and Fe(0) loaded leonardite preparation

For Fe(II)-loaded leonardite preparation, 5 g of leonardite was added to 100 mL of 0.1 M $FeSO_4$ solution. After shaking in the mixer for 2 h, it was dried in an oven at 60 °C for overnight. A schematic diagram of the procedure is shown in Fig. 1A for Fe(II) loading on leonardite powder.

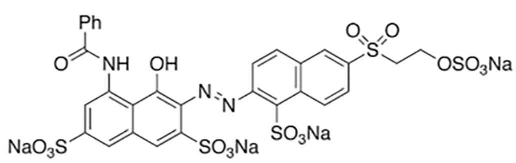
For Fe(0)-loaded leonardite preparation, 5 g of leonardite was added to 100 mL of 0.1 M $FeCl_3$ solution. A 50 mL of 0.1 M sodium borohydride was added to the $FeCl_3$ solution while stirring at 150 rpm in the shaker. After mixing in a shaker at 150 rpm for 2 h, it was dried in the oven at 60 °C overnight. A schematic diagram of the procedure is shown in Fig. 1B for Fe(0) loading on leonardite powder.

Distilled water (500 mL) was added to the Fe(II) and Fe(0)-loaded leonardite (10 g) in the beaker and the content was turbulently stirred until the pH of the leached solution became invariant with time. The leached solutions were filtered through a 0.45-μm cellulose acetate filter and the samples were analyzed for iron analysis using AAS.

Fenton oxidation experiments

Experiments were carried out separately for raw leonardite, Fe(II), and Fe(0)-loaded leonardite powders. RR180 stock dye solution was prepared as 100 ppm. Experiments were carried out in a volume of 100 mL. pH, leonardite amount, H_2O_2 concentration, and kinetic studies were performed sequentially. The main parameters considered were pH (2, 2.5, 3, 4, 5, and 6), the dose of leonardite (0.1, 0.25, 0.5, 0.75, 1, 1.25, and 1.5 g/L), H_2O_2 concentration (10, 25, and

Table 2 Molecular structure and fundamentals properties of RR180 dye

Chemical name	Chemical structure	Molecular formula	UV absorption λ_{max} (nm)
Reactive Red 180 (RR180)		$C_{29}H_{19}N_3Na_4O_{17}S_5$	542

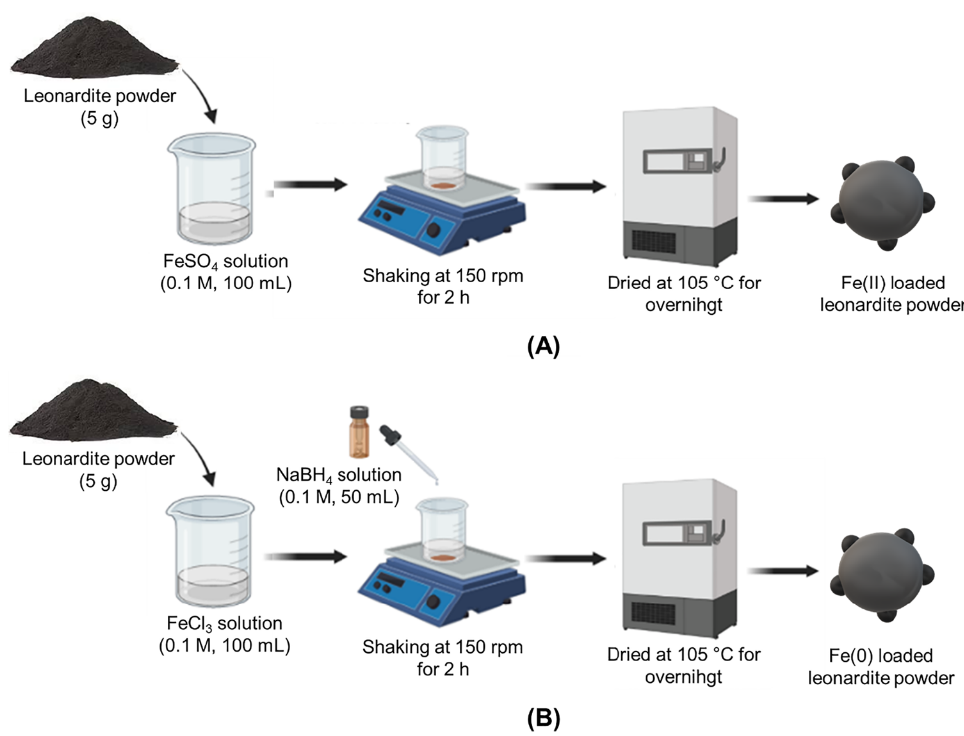


Fig. 1 A schematic representation of the Fe(II) and Fe(0) loading procedure on leonardite powder

50 µL/L), and dye concentration (10, 20, and 30 mg/L). The removal efficiency of RR180 dye was calculated by measuring absorbance at a wavelength of 520 nm using a UV–vis spectrophotometer (T90 + UV/VIS spectrometer, PG Instruments Ltd.).

Kinetic studies

The relationship between the adsorption performance of leonardite and time was investigated by the experiments of adsorption kinetics. Firstly, 50 mL of dye solutions in different concentrations (10, 20, 30 mg/L) was added to 100 mL conical flasks, adjusting the pH of the solution to optimum pH by HCl or NaOH. Then, to each solution, in optimum conditions, Fe-Np-coated ACC was added and agitated for 1 h. Following, a sample was taken at regular times (5, 10, 15, 30, 45, 60 min) to measure the dye content and the concentration of dyes was measured in a UV–vis spectrophotometer.

Results and discussion

SEM–EDX analysis

Raw and iron-loaded leonardite powders were characterized to explore the distinctions between the different tested samples. The morphological definition and chemical composition of the catalysts were observed by a scanning electron microscopy (Fig. 2). It is clearly observed from the SEM image represented in Fig. 2A that leonardite raw material has sheet morphology. Figure 2B and C illustrate the distribution of Fe(II)-loaded and Fe(0)-loaded on leonardite material. Both iron-loaded materials revealed a good dispersion on the leonardite surface. Such dispersion would increase the active material surface area and enhance the redox reaction of iron and improving catalyst effectiveness.

The elemental analysis was further conducted by the EDX attached to SEM analysis. EDX results of the three studied materials: raw leonardite, Fe(II)-loaded leonardite, and Fe(0)-loaded leonardite are depicted in Fig. 3A–C, respectively. Based on the obtained EDX spectrum illustrated in Fig. 3B and C, iron element (Fe) percentage increased revealing the amount of metal that was loaded on the leonardite surface.

Effect of pH

It was reported that solution pH has a significant effect on the dye molecules adsorptive uptake because of its influence on the binding-sites of catalyst surface and on the dye molecule ionization process (Sathishkumar et al. 2012). Fenton oxidation is not appropriate to alkaline solutions (when $pH > 8$). In an alkaline environment, iron ions tend to form flocs and precipitate. In addition, H_2O_2 is unstable and may possibly decompose to form water and oxygen and eventually loses its oxidation ability. Therefore, this study was conducted at pH between 2 and 6 to investigate the effectiveness of the Fenton oxidation reactions. The experimental results are demonstrated in Fig. 4 which shows the RR180 dye removal efficiency as a function of solution pH and type of catalyst. The rest of experimental conditions were kept constant during the reaction time of 60 min, i.e., dye concentration: 10 mg/L; leonardite amount: 1 g/L; H_2O_2

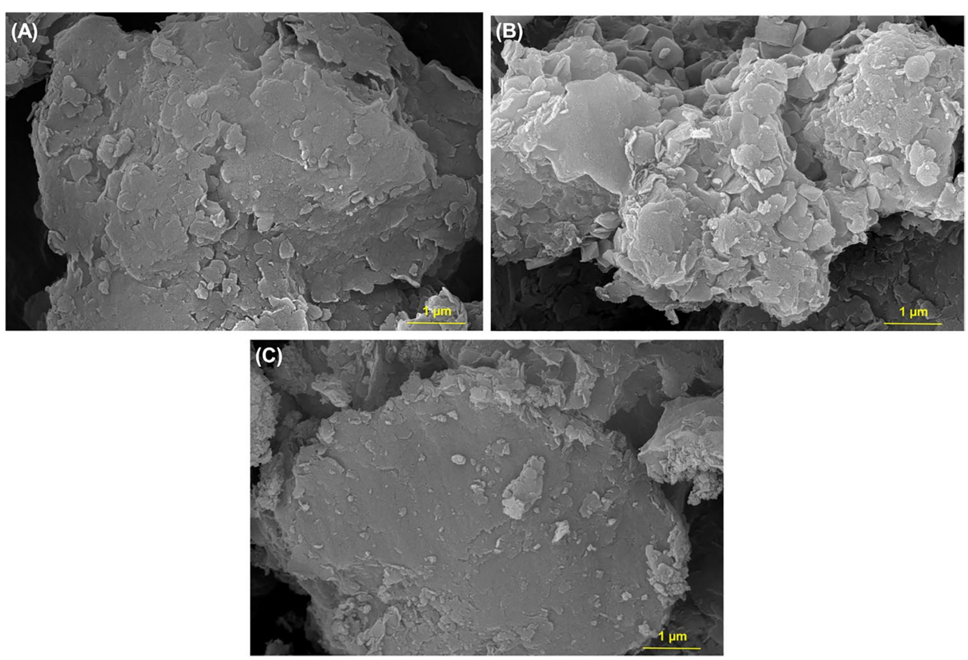


Fig. 2 SEM images of **A** raw leonardite, **B** Fe(II)-loaded leonardite, **C** Fe(0)-loaded leonardite

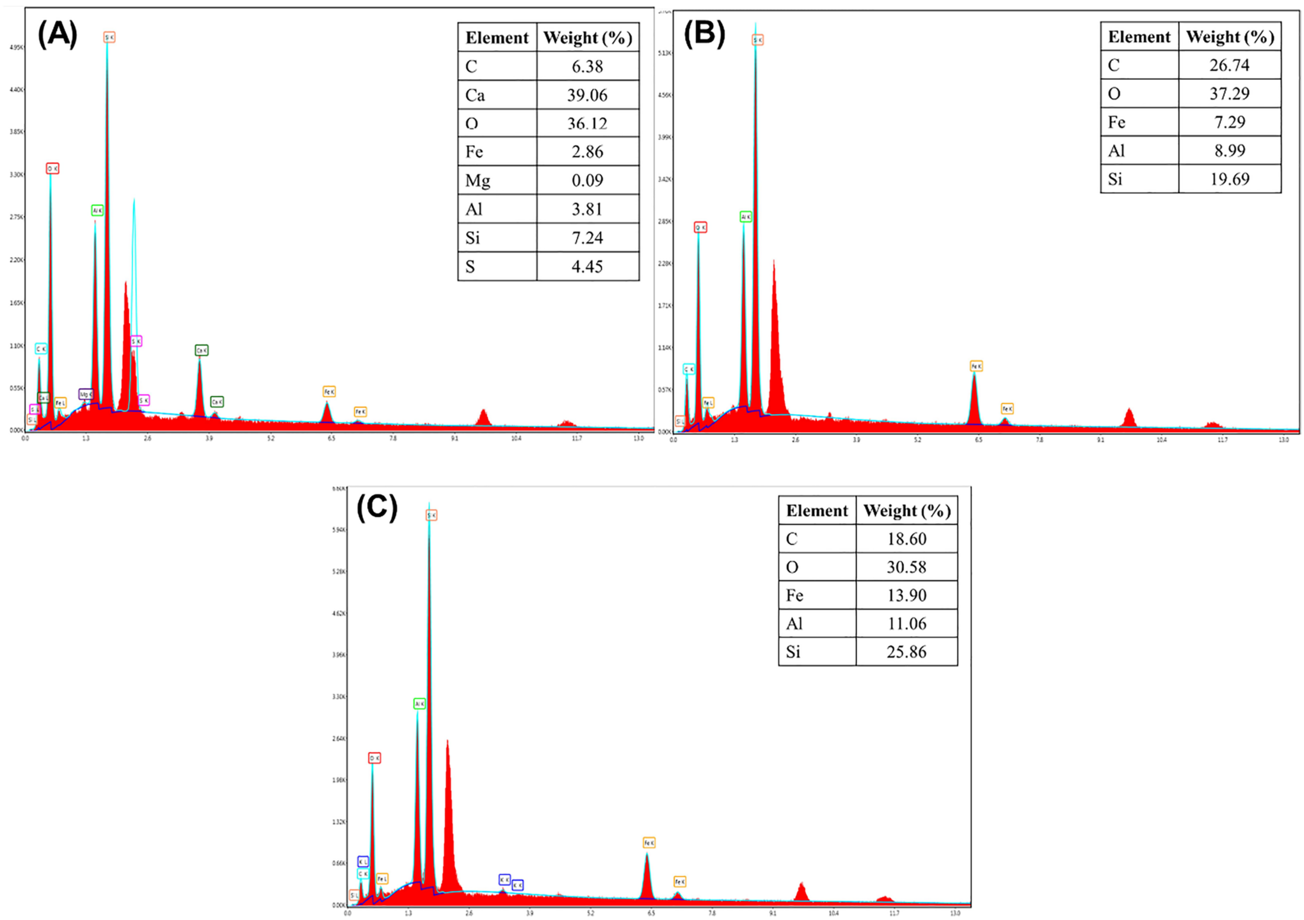


Fig. 3 SEM–EDX of **A** raw leonardite, **B** Fe(II)-loaded leonardite, **C** Fe(0)-loaded leonardite

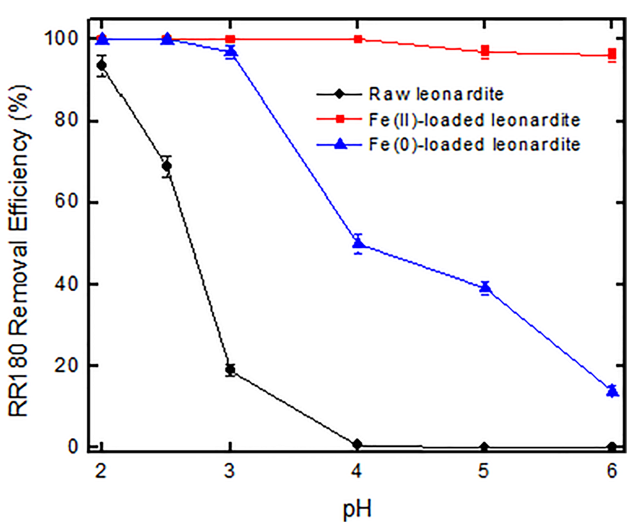


Fig. 4 The effect of pH on RR180 dye removal efficiency (experimental conditions: dye concentration: 10 mg/L; leonardite amount: 1 g/L; H_2O_2 concentration: 50 µL/L; volume: 100 mL; reaction time: 60 min)

concentration: 50 µL/L and sample volume of 100 mL. The trend of dye removal according to pH, when raw leonardite was used as catalyst, is similar with the one when Fe(0)-loaded leonardite is used as shown in Fig. 3. As noticed, the RR180 removal efficiency decreased sharply when aqueous solution pH was increased. Raw leonardite as Fenton oxidation reagent was ineffective when solution pH overcome 3 recording a removal efficiency of RR180 of less than 20% and no dye removal was observed when pH was in the range of 4 to 6. Contrarily, Fenton oxidation using Fe(II)-loaded leonardite as catalyst showed higher and better removal efficiencies in all the investigated pH range. Experimental results showed a total RR180 dye removal for pH values of 2, 2.5, 3, and 4. Thus, RR180 dye was more easily removed by Fenton oxidation using Fe(II)-loaded leonardite than using raw leonardite or Fe(0)-loaded leonardite.

As reported in previous studies, the best dye removal efficiencies were obtained at acidic solution pH (Raji et al. 2021; Sathishkumar et al. 2012; Yang et al. 2018). Treatment efficiency was very low when raw leonardite material was used, and this could be due to the unavailability of ferrous ion for hydrogen peroxide decomposition and eventually no hydroxyl radical is produced. Thus, RR180 dye is hardly decomposed due to the absence of hydroxyl radical. The significant decrease in treatment efficiency when Fe(0)-loaded leonardite was used is probably due to the decrease and precipitation of free iron species in the solution which obstruct the reaction between ferric ion and hydrogen peroxide. Subsequently, the regeneration of ferrous ion was inhibited. Moreover, $Fe(OH)_3$ may form which is able to catalyze the decomposition of hydrogen peroxide to water and oxygen in which outcomes in low production of hydroxyl radical. On the other hand, the best treatment was achieved with Fe(II)-loaded leonardite, where there is abundance of ferrous ion (Fe^{2+}). The ionization conditions of the functional groups on both catalyst surface and dye molecule influence the degree of interaction between the dye and catalyst (Gusain et al. 2020). The best dye removal at acidic pH can be explained by the good electrostatic interactions between the catalyst and the investigated adsorbate (RR180 dye). At acidic pH, more hydroxyl radicals are generated in Fenton oxidation reaction; as result, more dye removal occurs. At higher pH, iron hydroxides precipitation inhibits the ferrous ions regeneration leading hydroxyl groups ($OH^{\bullet}$) formation for further oxidation (El-Desoky et al. 2010; Raji et al. 2021).

Effect of catalyst amount

The effect of catalyst concentration was studied by varying the catalyst amount from 0.125 to 1.50 g/L, while other parameters were fixed, dye concentration: 10 mg/L; H_2O_2 concentration: 50 µL/L; sample volume of 100 mL; solution pH = 2 and reaction time 60 min. Figure 5 illustrates the RR180 color removal vs. different investigated catalysts' dosages. The three studied Fenton reagents have shown a similar trend of dye removal in function of catalyst concentration. Relatively low treatment efficiencies were found at low catalyst dosage. Raw leonardite has shown the least effectiveness of RR180 color removal at the interval of (0.10–0.75 g/L), which only achieved 34–70% of color removal. It was necessary to use up to 1.5 g/L of raw leonardite material to achieve complete RR180 dye removal. In the other hand, both catalysts, Fe(II)-loaded leonardite and Fe(0)-loaded leonardite, showed similar dye removal efficiency against catalyst amount with a slight advantage of Fe(II)-loaded leonardite. When catalyst amount was enhanced from 0.10 to 0.25 g/L, color removal increased from 81 to 96% and from 83 to 99% for Fe(0)-loaded leonardite and Fe(II)-loaded leonardite, respectively. This is explained by the increase of iron concentration leached in the aqueous solution resulting in oxidation effectiveness improvement and eventually better dye removal occurs (Yang et al. 2018). When the optimal catalyst amount was exceeded (more

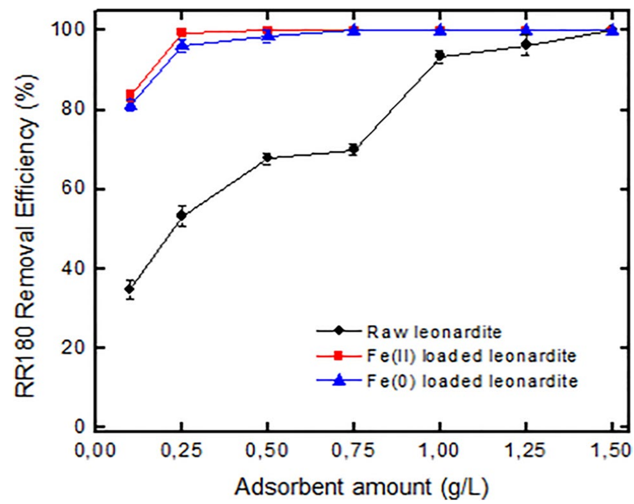


Fig. 5 The effect of catalyst amount on RR180 dye removal efficiency (experimental conditions: dye concentration: 10 mg/L; pH:2.0; H_2O_2 concentration: 50 µL/L; volume: 100 mL; reaction time: 60 min)

than 0.25 g/L), the oxidation activity of the catalyst did not improve as given by results represented in in Fig. 5. Similar results were obtained in previous studies (Bouras et al. 2017; Yang et al. 2018; Zhong et al. 2021).

Effect of H_2O_2 concentration

The main cost of Fenton reaction process is related to the cost of H_2O_2. Therefore, it is critical to optimize H_2O_2 amount involved in the Fenton oxidation reaction (Kim et al. 2004). For optimum H_2O_2 concentration determination, experiments were conducted by varying H_2O_2 concentrations from 10 to 50 µL/L, keeping the rest of parameters fixed at optimal values as determined in the above sections. The dye removal as a function of $[H_2O_2]$ is presented in Fig. 6. The results indicated good removal of RR180 dye for all tested $[H_2O_2]$; however, the removal efficiency did not increase much with the increase in the H_2O_2 concentrations for the three tested materials. Then, it shows that the fractional degradations of RR180 dye were 91%, 95%, and 100% at 10 µL/L of H_2O_2 concentration for raw leonardite, Fe(0)-loaded leonardite, and Fe(II)-loaded leonardite, respectively. When H_2O_2 concentration was increased to 50 µL/L, all the tested catalyst resulted in a complete or nearly complete color removal. The lower performance of dye removal obtained with 10 µL/L H_2O_2 indicates an insufficient amount of hydroxyl radicals for the treatment of 10-ppm RR180 dye concentration. Then, the stoichiometric weight ratio of H_2O_2 should be investigated according to the treated water pollutants content (Bautista et al. 2007; Baycan and Can 2019).

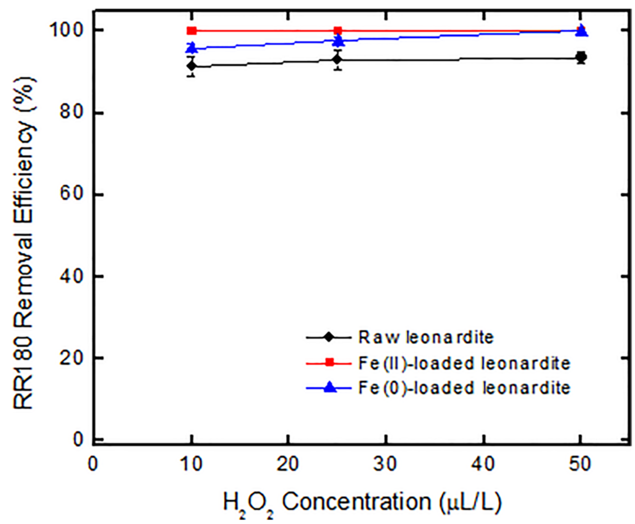
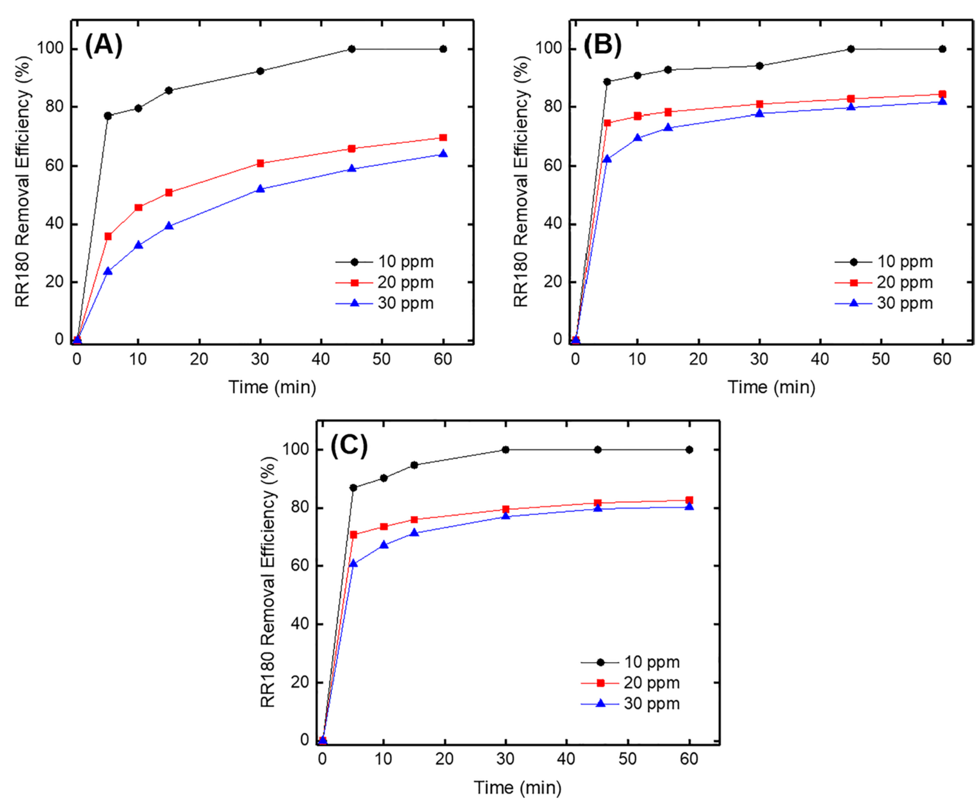


Fig. 6 The effect of H_2O_2 concentration on RR180 dye removal efficiency (experimental conditions: dye concentration: 10 mg/L; leonardite powder: 0.75 g/L for Fe(II) and Fe(0)-loaded leonardite and 1.5 g/L for raw leonardite; pH:2.0; volume: 100 mL; reaction time: 60 min)

Effect of initial dye concentration

Figure 7 demonstrates the impact of the initial RR180 color concentration on Fenton oxidation reactions using the three tested materials at the following optimal experimental conditions: amount of catalyst: 0.75 g/L for Fe(II) and Fe(0) loaded leonardite and 1.5 g/L for raw leonardite; solution pH: 2.0; amount of H_2O_2: 50 µL/L and reaction time of 60 min. The following initial dye concentrations (10, 20, and 30 ppm) were investigated in this study. As can be noticed in Fig. 7, the dye removal trends have known two distinct behaviors, namely a rapid dye removal in the first 5 min, followed by a slowing down of the removal rate in the rest of the reaction time. The fast adsorption rate during the first 5 min of Fenton oxidation reaction indicates the significance of the specific surface on the adsorption process. The experimental results show that the removal efficiency of RR180 dye decreased with increasing initial dye concentration. The rate and the mechanism of a color removal are a function of dyes solubility and their chemical properties (Shen et al. 2001). For example, RR180 color removal when Fe(II)-loaded leonardite was used as catalyst (Fig. 7C) decreased from 100 to 81% when initial dye concentration was increased from 10 to 30 ppm. It can be attributed to the saturation of the available adsorption sites on the catalyst as the different dye aqueous solutions were subject to similar experimental conditions of catalyst amount, H_20_2 concentration, pH, and reaction time. Pelosi et al. (2014) reported that the color removal performance declines with the increase of the initial dye concentration ending to the saturation at higher dye concentrations (Pelosi

Fig. 7 The effect of initial dye concentration on RR180 dye removal efficiency using **A** raw leonardite, **B** Fe(0)-loaded leonardite, and **C** Fe(II)-loaded leonardite (experimental conditions: leonardite powder: 0.75 g/L for Fe(II) and Fe(0)-loaded leonardite and 1.5 g/L for raw leonardite; pH: 2.0; H_2O_2 concentration: 50 µL/L; volume: 100 mL; reaction time: 60 min)



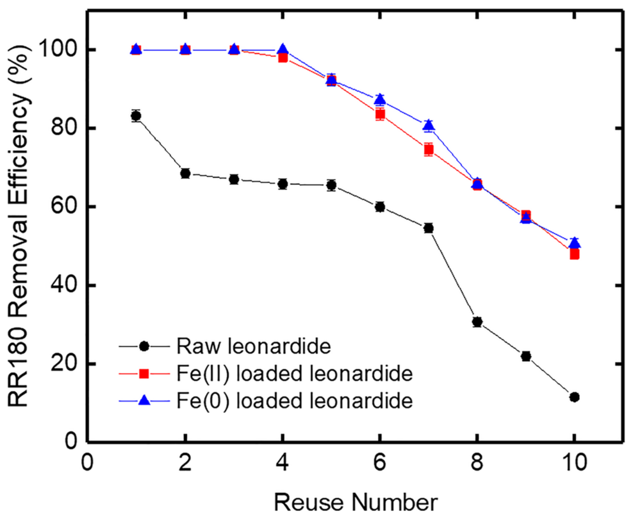


Fig. 8 Stability and reusability of raw leonardite, Fe(0)-loaded leonardite, and Fe(II)-loaded leonardite for RR180 dye removal Fenton oxidation (experimental conditions: leonardite powder: 0.75 g/L for Fe(II) and Fe(0)-loaded leonardite and 1.5 g/L for raw leonardite; dye concentration: 10 ppm; solution pH: 2.0; H_2O_2 concentration: 50 μL/L; volume: 100 mL; reaction time: 60 min)

et al. 2014). Since all experiments for the same catalyst were performed at similar experimental conditions, the amount of catalyst and formed hydroxyl radicals was not enough to degrade greater amounts of RR180 color concentrations. Correspondingly, the number of active catalyst sites was not enough to adsorb higher quantity of dyes (Es'haghzade et al. 2017; Hassani et al. 2018). In addition, the quantity of effective hydroxyl radicals can be reduced because of the adsorption of high concentrations of dye molecules onto the active sites of the catalyst (Acisli et al. 2017).

Reuse number

To test the stability and reusability of the three tested catalysts, ten cycles were performed at optimal operating conditions determined in this study for RR180 dye removal. After each cycle, the catalyst was separated and washed with deionized water for next cycle. Dye removal efficiencies of the ten cycles are shown in Fig. 8. For Fe(0)-loaded leonardite and Fe(II)-loaded leonardite, the color removal efficiency remained stable and the catalyst performance did not decrease for the first four cycles. Then, color removal decreased gradually from 100% to lower levels around 58% after ten cycles. However, the removal efficiency decreased from 82% to less than 10% using raw leonardite.

It was observed that the stability of iron loaded leonardite was higher than raw leonardite material. The reason might be explained since the active sites of the loaded iron species on leonardite were more open because of the agglomeration prevention and color molecules could be adsorbed more easily to the open active sites. Hence, more dye molecules were adsorbed by open active areas and there were occupied during the next cycles. However, reusability of the catalyst for RR180 dye removal declined after four cycles because of the insufficient adsorption sites. Furthermore, iron leaching could lead to a decrease in the removal performance by Fenton oxidation for the next cycles (Ramirez et al. 2007). As a conclusion, experiments showed the importance of iron-loaded leonardite to be used several times in Fenton oxidation for RR180 color removal. The results showed that iron leached into the solution was also insignificant which indicated that the iron was tightly adsorbed and loaded onto the loenardite surface.

Conclusion

In this research study, the activity of raw leonardite, Fe(0)-loaded leonardite, and Fe(II)-loaded leonardite for RR180 dye removal efficiencies was investigated by Fenton oxidation treatment process. It was found that pH was a significant parameter in Fenton oxidation. Acidic $pH = 2$ was more suitable for the color removal. Fe(II)-loaded leonardite as Fenton reagent was the most efficient in RR180 color removal. The molecular interactions between the reactive dye and the tested catalyst including the amount of reactive oxygen species involved in Fenton reaction were affected by solution pH. Only H_2O_2 concentration did not show much effect on color removal efficiency in the Fenton oxidation. However, its optimization is a must since it is a cost-effective parameter. At optimum experimental conditions, catalyst amount: 0.75 g/L for Fe(II) and Fe(0)-loaded leonardite and 1.5 g/L for raw leonardite; dye concentration: 10 ppm; solution pH: 2.0; H_2O_2 concentration: 50 μL/L; volume: 100 mL and reaction time: 60 min, RR180 dye removal efficiencies were 91%, 100%, and 100% by raw leonardite, Fe(0)-loaded leonardite, and Fe(II)-loaded leonardite, respectively. The stability and reusability of the tested catalyst showed that both Fe(0)-loaded leonardite and Fe(II)-loaded leonardite can be used in Fenton reaction up to four cycles without decreasing their efficiency in RR180 color removal.

The results of this study confirmed the importance of iron loaded on leonardite which was low-cost and easily accessible catalyst for textile dyes removal from aqueous solution by Fenton oxidation reaction. A technical and economic study might be suggested as a complementary and additional value to the current research.

Author contributions ZB carried out the methodology. HA and ND found leonardite powder for Fenton oxidation and they had the main idea. RB and ND were a major contributor in writing the manuscript. All authors read and approved the final manuscript.

Data availability The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Ethics approval Not applicable.

Consent to participate Not applicable.

Consent for publication Not applicable.

Competing interests The authors declare no competing interests.

References

Abukhadra MR, Adlii A, MohamedBakry B (2019) Green fabrication of bentonite/chitosan@cobalt oxide composite (BE/ CH@Co) of enhanced adsorption and advanced oxidation removal of Congo red dye and Cr (VI) from water. Int J Biol Macromol 126:402–413

Acisli O, Khataee A, Karaca S, Karimi A, Dogan E (2017) Combination of ultrasonic and Fenton processes in the presence of magnetite nanostructures prepared by high energy planetary ball mill. Ultrason Sonochem 34:754–762. https://doi.org/10.1016/j.ultsonch.2016.07.011

Albadarin AB, Mangwandi C (2015) Mechanisms of Alizarin Red S and Methylene blue biosorption onto olive stone by-product: isotherm study in single and binary systems. J Environ Manage 164:86–93. https://doi.org/10.1016/j.jenvman.2015.08.040

Arslan H, Saleh M, Bilici Z, Dizge N (2022a) Leonardite powder as an efficient adsorbent for cationic and anionic dyes. Water Environ Res 94(5):e10719. https://doi.org/10.1002/wer.10719

Arslan H, Eskikaya O, Bilici Z, Dizge N, Balakrishnan D (2022b) Comparison of Cr(VI) adsorption and photocatalytic reduction efficiency using leonardite powder. Chemosphere 300:134492. https://doi.org/10.1016/j.chemosphere.2022.134492

Babuponnusami A, Muthukumar K (2014) A review on Fenton and improvements to the Fenton process for wastewater treatment. J Environ Chem Eng 2(1):557–572. https://doi.org/10.1016/j.jece.2013.10.011

Bautista P, Mohedano AF, Gilarranz MA, Casas JA, Rodriguez JJ (2007) Application of Fenton oxidation to cosmetic wastewaters treatment. J Hazard Mater 143(1–2):128–134. https://doi.org/10.1016/j.jhazmat.2006.09.004

Baycan N, Can B (2019) Color removal from yeast production industry wastewater using photo-Fenton process. Pamukkale Univ J Eng Sci 25(3):292–296. https://doi.org/10.5505/pajes.2018.78872

Bilici Z, Bouchareb R, Sacak T, Yatmaz HC, Dizge N (2021) Recycling of TiO2-containing waste and utilization by photocatalytic degradation of a reactive dye solution. Water Sci Technol 83(5):1242–1249. https://doi.org/10.2166/wst.2020.606

Bouchareb R, Derbal K, Özay Y, Bilici Z, Dizge N (2020) Combined natural/chemical coagulation and membrane filtration for wood processing wastewater treatment. J Water Process Eng 37(July):101521. https://doi.org/10.1016/j.jwpe.2020.101521

Bouras HD, Yeddou AR, Bouras N, Hellel D, Holtz MD, Sabaou N, Chergui A, Nadjemi B (2017) Biosorption of Congo red dye by Aspergillus carbonarius M333 and Penicillium glabrum Pg1: kinetics, equilibrium and thermodynamic studies. J Taiwan Inst Chem Eng 80:915–923. https://doi.org/10.1016/j.jtice.2017.08.002

Çiner F, Gökkuş Ö (2012) Treatability of dye solutions containing disperse dyes by Fenton and Fenton-solar light oxidation processes. Clean Soil Air Water 41(1):80–85. https://doi.org/10.1002/clen.201000500

Demissie H, An G, Jiao R, Ritigala T, Lu S, Wang D (2021) Modification of high content nanocluster-based coagulation for rapid removal of dye from water and the mechanism. Sep Purif Technol 259(March):117845. https://doi.org/10.1016/j.seppur.2020.117845

Deniz F, Kepekci RA (2016) Dye biosorption onto pistachio by-product: a green environmental engineering approach. J Mol Liq 219:194–200. https://doi.org/10.1016/j.molliq.2016.03.018

El-Desoky HS, Ghoneim MM, El-Sheikh R, Zidan NM (2010) Oxidation of Levafix CA reactive azo-dyes in industrial wastewater of textile dyeing by electro-generated Fenton's reagent. J Hazard Mater 175(1–3):858–865. https://doi.org/10.1016/j.jhazmat.2009.10.089

Es'haghzade Z, Pajootan E, Bahrami H, Arami M (2017) Facile synthesis of Fe3O4 nanoparticles via aqueous based electro chemical route for heterogeneous electro-Fenton removal of azo dyes. J Taiwan Inst Chem Eng 71:91–105. https://doi.org/10.1016/j.jtice.2016.11.015

Gökkuş Ö, Yıldız YŞ (2014) Investigation of the effect of process parameters on the coagulation- investigation of the effect of process parameters on the coagulation flocculation treatment of textile wastewater using the Taguchi experimental method. Fresenius Environ Bull 23(02):463–470

Gökku Ö, Ço F, Kocaoglu M, Yıldız YŞ (2013) Determination of optimum conditions for color and COD removal of Reactive Blue 19 by Fenton oxidation process. Desalin Water Treat:37–41. https://doi.org/10.1080/19443994.2013.812523

Gusain R, Kumar N, Ray SS (2020) Recent advances in carbon nanomaterial-based adsorbents for water purification. Coord Chem Rev 405:213111. https://doi.org/10.1016/j.ccr.2019.213111

Hassani A, Karaca C, Karaca S, Khataee A, Açışlı Ö, Yılmaz B (2018) Enhanced removal of basic violet 10 by heterogeneous sono-Fenton process using magnetite nanoparticles. Ultrason Sonochem 42:390–402. https://doi.org/10.1016/j.ultsonch.2017.11.036

Ivanets A, Roshchina M, Srivastava V, Prozorovich V, Dontsova T, Nahirniak S, Pankov V, Hosseini-Bandegharaei A, Nguyen Tran H, Sillanpää M (2019) Effect of metal ions adsorption on the efficiency of methylene blue degradation onto MgFe 2 O 4 as Fenton-like catalysts. Colloids Surf A Physicochem Eng Asp 571:17–26. https://doi.org/10.1016/j.colsurfa.2019.03.071

Januário EFD, Vidovix TB, Bergamasco R, Vieira AMS (2021) Performance of a hybrid coagulation/flocculation process followed by modified microfiltration membranes for the removal of solophenyl blue dye. Chem Eng Process Process Intensif 168(March). https://doi.org/10.1016/j.cep.2021.108577

Karthikeyan S, Titus A, Gnanamani A, Mandal AB, Sekaran G (2011) Treatment of textile wastewater by homogeneous and heterogeneous Fenton oxidation processes. Desalination 281(1):438–445. https://doi.org/10.1016/j.desal.2011.08.019

Kim TH, Park C, Yang J, Kim S (2004) Comparison of disperse and reactive dye removals by chemical coagulation and Fenton oxidation. J Hazard Mater 112(1–2):95–103. https://doi.org/10.1016/j.jhazmat.2004.04.008

Kousha M, Tavakoli S, Daneshvar E, Vazirzadeh A, Bhatnagar A (2015) Central composite design optimization of Acid Blue 25 dye biosorption using shrimp shell biomass. J Mol Liq 207:266–273. https://doi.org/10.1016/j.molliq.2015.03.046

Martínez CM, Celis LB, Cervantes FJ (2013) Immobilized humic substances as redox mediator for the simultaneous removal of phenol and Reactive Red 2 in a UASB reactor. Appl Microbiol Biotechnol 97(22):9897–9905. https://doi.org/10.1007/s00253-013-5190-5

Moussavi M, Matavos-Aramyan S (2016) Chelate-modified fenton treatment of sulfidic spent caustic. Korean J Chem Eng 33(8):2384–2391. https://doi.org/10.1007/s11814-016-0080-z

Nidheesh PV, Gandhimathi R (2012) Trends in electro-Fenton process for water and wastewater treatment: an overview. Desalination 299:1–15. https://doi.org/10.1016/j.desal.2012.05.011

Pani N, Tejani V, Anantha-Singh TS, Kandya A (2020) Simultaneous removal of COD and ammoniacal nitrogen from dye intermediate manufacturing Industrial Wastewater using Fenton oxidation method. Appl Water Sci 10(2):1–7. https://doi.org/10.1007/s13201-020-1151-1

Pelosi BT, Lima LKS, Vieira MGA (2014) Removal of the synthetic dye remazol brilliant blue r from textile industry wastewaters by biosorption on the macrophyte Salvinia natans. Braz J Chem Eng 31(4):1035–1045. https://doi.org/10.1590/0104-6632.20140314s00002568

Raji M, Mirbagheri SA, Ye F, Dutta J (2021) Nano zero-valent iron on activated carbon cloth support as Fenton-like catalyst for efficient color and COD removal from melanoidin wastewater. Chemosphere 263:127945. https://doi.org/10.1016/j.chemosphere.2020.127945

Ramirez JH, Maldonado-Hodar FJ, Pérez-Cadenas AF, Moreno-castilla C, Costa CA, Madeira LM (2007) Azo-dye Orange II degradation by heterogeneous Fenton-like reaction using carbon-Fe catalysts. Appl Catal B 75:312–323. https://doi.org/10.1016/j.apcatb.2007.05.003

Sathishkumar P, Arulkumar M, Palvannan T (2012) Utilization of agro-industrial waste Jatropha curcas pods as an activated carbon for the adsorption of reactive dye Remazol Brilliant Blue R (RBBR). J Clean Prod 22(1):67–75. https://doi.org/10.1016/j.jclepro.2011.09.017

Sayjumpa J, Jomhataikool B, Faungnawakij K, Kuboon S, Kraithong W, Fuji M, Eiad-Ua A (2019) Porous carbon adsorbent from humin derived from thai leonardite for methylene blue dye adsorption. Curr Appl Sci Technol 19(1):1–8. https://doi.org/10.14456/cast.2019.1

Shen Z, Wang W, Jia J, Ye J, Feng X, Peng A (2001) Degradation of dye solution by an activated carbon fiber electrode electrolysis system. J Hazard Mater 84(1):107–116. https://doi.org/10.1016/S0304-3894(01)00201-1

Sievers M (2011) 4.13 - Advanced oxidation processes. In: Wilderer P (ed) Treatise on water science. Elsevier, pp 377–408. https://doi.org/10.1016/B978-0-444-53199-5.00093-2, https://www.sciencedirect.com/science/article/pii/B9780444531995000932

Singa PK, Isa MH, Ho YC, Lim JW (2018) Treatment of hazardous waste landfill leachate using Fenton oxidation process. E3S Web Conf 34:4–9. https://doi.org/10.1051/e3sconf/20183402034

Solé-Sardans M, Gamisans X, Dorado AD, Lao-Luque C (2016) Exploring arsenic adsorption at low concentration onto modified leonardite. Water Air Soil Pollut 227(4). https://doi.org/10.1007/s11270-016-2827-x

Terdputtakun A, Arqueropanyo O. anong, Sooksamiti P, Janhom S, Naksata W (2017) Adsorption isotherm models and error analysis for single and binary adsorption of Cd(II) and Zn(II) using leonardite as adsorbent. Environ Earth Sci 76(22):1–11. https://doi.org/10.1007/s12665-017-7110-y

Tony MA, Parker HL, Clark JH (2016) Treatment of laundrette wastewater using Starbon and Fenton's reagent. J Environ Sci Health A Tox Hazard Subst Environ Eng 51(11):974–979. https://doi.org/10.1080/10934529.2016.1191817

Yang H, Shi B, Wang S (2018) Fe oxides loaded on carbon cloth by hydrothermal process as an effective and reusable heterogenous Fenton catalyst. Catalysts, 8(5). https://doi.org/10.3390/catal8050207

Zhang MF, Qin YH, Ma JY, Yang L, Wu ZK, Wang TL, Wang WG, Wang CW (2016) Depolymerization of microcrystalline cellulose by the combination of ultrasound and Fenton reagent. Ultrason Sonochem 31:404–408. https://doi.org/10.1016/j.ultsonch.2016.01.027

Zhong J, Yang B, Feng Y, Chen Y, Wang LG, You WD, Ying GG (2021) Enhanced photo-fenton removal efficiency with core-shell magnetic resin catalyst for textile dyeing wastewater treatment. Water (Switzerland) 13(7). https://doi.org/10.3390/w13070968