Photocatalytic performance and photodegradation kinetics of Fenton-like process based on haematite nanocrystals for basic dye removal

Shehab A. Mansour¹ · Maha A. Tony¹ · Aghareed M. Tayeb²

© Springer Nature Switzerland AG 2019

Abstract

Photo-Fenton's reagent based on haematite nanocrystals was investigated to oxidize simulated textile wastewater streams loaded with methylene blue (MB) dye to signify the role of nanocrystals in the Fenton system. Various oxidation systems were compared such as UV photocatalysis, H_2O_2 , dark Fenton's reagent and nano-haematite photo-Fenton reaction. Different operating parameters were investigated, and the maximum oxidation rate reached 70% at the optimal experimental conditions of 40 mg/L nano-haematite, 400 mg/L H_2O_2 and initial pH at 3.0 within 90 min of reaction time. Furthermore, temperature increases showed increment in the reaction rate. Also, the reaction kinetics was studied and the system followed the pseudo-second-order model. Finally, thermodynamic parameters, i.e., $\Delta G'$, $\Delta H'$ and $\Delta S'$, for MB oxidation with photo-Fenton system were investigated and the data illustrated that the reaction was exothermic with non-spontaneous nature.

Keywords Methylene blue · Wastewater · Photo-Fenton · Nanomaterial · Haematite

1 Introduction

A huge amount of dye-containing wastewater is produced during the dyeing processes in different industries, for example, textile and dyeing, leather, food processing, cosmetics, plastic and paper industries. Discharge of those colored wastewater is a major problem for environmental management particularly in developing countries. [1, 2] The textile industry is one of the major sources, which discharges large amounts of industrial wastewater. In industrial use, there are nearly 10,000 of different dyes and pigments. Once dyes are released into environment, it causes coloration of natural water bodies, since it is synthetic aromatic water-soluble and dispersible organic compounds. Among the different types of dyes, methylene blue (MB), which is considered as a cationic dye, is used in dyeing, paint production and wool dyeing [1–3].

The discharges from dyeing factories including dyes effluents are hazardous chemicals. It is well recognized that dyes effluents undergo water pollution because they are highly toxic and carcinogenic. Those dyes cause damage to the aquatic environment by chemical changes as well as biological changes. The dissolved O_2 is consumed and thus disturbs the aquatic ecosystem. Subsequently, there will be a challenge for the existence of fishes and other lives in wide spread [4].

There are various conventional chemical and biological methods to remove dyes from the water. However, high expenses make these methods limited and unfavorable in developing countries. However, these processes result in concentrated sludges which require further processing and disposal. In addition, conventional treatment processes have difficulty in fully removing the pollutants

✉ Shehab A. Mansour, shehab_mansour@yahoo.com | ¹Advanced Materials/Solar Energy and Environmental Sustainability (AMSEES) Laboratory, Basic Engineering Science Department, Faculty of Engineering, Menoufia University, Shebin El-Kom 32511, Egypt. ²Chemical Engineering Department, Faculty of Engineering, Minia University, Minia, Egypt.

from such wastewater. Moreover, it is not favorable for low efficiency and low reaction rate [5].

Abundant research and investigations have been carried out in different part of the world for the search of different methods for treatment suitable to remove dyes from wastewater in a reliable cost. Such methods may include the chemical oxidation processes such as the oxidation by ozone or combination of UV illumination and ozone and H_2O_2 , but they are expensive for treating such raw textile wastewater. Furthermore, it is hard to remove color [6, 7]. In this context, the development of new processes for wastewater treatment in order to degrade these compounds in textile industry effluents is very important. An extensively studied alternative is the use of advanced oxidation process (AOP). Fenton's reagent is one of AOPs which is based on the formation of high active groups, namely hydroxyl radicals, which are responsible for oxidizing pollutants to smaller and less contaminating molecules or even mineralizing them by turning them into CO_2 , H_2O and inorganic ions from atoms [8–14].

Fenton's reagent process is one of the methods that are applied to significantly reduce the concentration of dye in wastewater. For instance, Rahman et al. [5] applied such reagent for the treatment of commercial textile dye named malachite green. The oxidation of methylene blue by Fenton's reagent was achieved by Liu et al. [15]. El Haddad et al. [6] treated azo dye (Reactive Yellow 84) using Fenton's reagent. Also, Fenton-like reagent was used in treating the Amaranth Red [16]. However, Khan et al. [7] investigated the photocatalytic degradation of MB in wastewater. The process is a radical reaction, which generates hydroxyl radicals that are capable of oxidizing even the most resistant pollutants present in the wastewater. The main advantages of the method include high oxidation efficiency, inexpensive and easily available substrates and simple procedure. The major reaction in this process includes Fenton reaction, photolysis of hydrogen peroxide and photoreduction of ferric ion in order to produce $\cdot\text{OH}$ radical as illustrated in the following equation [17]:

Novelty in the oxidation of pollutants by the Fenton method is running it with the participation of iron nanocompounds. The presence of nanoparticles has an influence on the oxidation of many compounds present in water. With the use of iron nanocompounds, the removal of trichloroethylene [18], phenol [19], olefins [20], humic acids [21], antibiotics [22] and chlorophenols [23] was investigated. The presence of nanoparticles affects also the oxidation of dyestuff in water solutions, namely AB24 dye and industrial wastewater [24]. However, according to the literature, there is a lack in applying it for MB dyestuff wastewater effluents.

In the present investigation, haematite ($\alpha\text{-Fe}_2\text{O}_3$) nanocrystalline powder was synthesized using low-cost simple sol–gel technique. Based on such nanopowder as photocatalysis, UV light augmented with nano-haematite Fenton's reagent (NHFR) was used to treat MB dye-containing wastewater. The NHFR parameters were investigated, and the process was compared with other treatment processes.

2 Materials and methods

Nanocrystalline Fe_2O_3 powder was synthesized using sol–gel route. The used procedure was reported elsewhere [25] by using ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), methanol alcohol and diethanolamine [$\text{HN}(\text{CH}_2\text{CH}_2\text{OH})_2$, DEA] as a precursor salt, solvent and chelating agent, respectively. Furthermore, the final product of Fe_2O_3 nanopowder was examined and confirmed by X-ray diffraction (XRD), high-resolution transmission electron microscope and Fourier transform infrared (FTIR) according to a preliminary investigation. The characterization of the synthesized powder confirmed the formation of $\alpha\text{-Fe}_2\text{O}_3$ in nanosize with rhombohedral structure [25].

Methylene blue (MB) degradation was studied in the presence of haematite nanocrystals under UV irradiation. The photo-Fenton's reagents were prepared by adding different doses of hydrogen peroxide (30%) into the synthesized haematite nanopowder. The photocatalytic activity of the prepared photo-Fenton was carried by the degradation of MB aqueous solution. The pH values of (500 mL) water dye solutions were adjusted to the desired value by means of 5 N solution of sulfuric acid using a digital pH meter model type pH2005. Prior to the UV irradiation, the desired amount of the nano-Fenton's reagent was dispersed in the MB aqueous solution in dark at RT for 2 min to reach adsorption–desorption equilibrium using magnetic stirrer. Thereafter, the reaction is subjected to the UV illumination using UV-A, 15-W lamp, enclosed in a transparent glass tube for UV light, and protected in a cover from a stainless steel. The solution is passed through the UV light during the tubular reactor, as shown in Fig. 1. The reaction mixture in that tubular reactor was circulated using a variable speed-dosing pump. At different time intervals, the treated water dye solutions were centrifuged by TDL 16B centrifuge type, to remove the remaining nanopowder. The experiments with the collected solutions were conducted using spectrophotometer (UV-1601, Shimadzu, Model TCC-240A, Japan) to monitor the absorption of the maximum absorbance peak of MB at 664 nm.

Fig. 1 Schematic representation of a treatment steps

3 Results and discussions

3.1 Methylene blue degradation

3.1.1 Comparison of different degradation systems

Firstly, preliminary experiments were conducted to check the H_2O_2 /UV treatment using H_2O_2 different doses in a wide range from 100 to 2000 mg/L. It was found that the removal rate is very low and increases with increasing the reagent doses up to 200 mg/L. The obtained removal percentage are 2 and 10% for 100 and 200 mg/L, respectively. In contrary, the decrease in the removal was achieved which reached 3 and 6% for 400 and 1000 mg/L, respectively. In addition, the 2000 mg/L of the peroxide shows no removal at all. This occurrence could be explained as follows: (1) At low initial H_2O_2 concentration relatively $\cdot\text{OH}$ radicals were formed for dye oxidation and thus the reduction in the removal rate. Though, by increasing peroxide concentration, more $\cdot\text{OH}$ radicals were generated upon its photodissociation; (2) photolysis of H_2O_2 produces $\cdot\text{OH}$ radicals which react with the dye molecules; however, excess H_2O_2 and high $\cdot\text{OH}$ concentration result in a competitive reaction resulting a reduction in the dye removal. In other words, the generated $\cdot\text{OH}$ mostly reacts with the excess peroxide and produces HO_2 , which are less reactive than $\cdot\text{OH}$ and decreasing the overall reaction rate [26].

For the object of investigating and comparing the performances of the photo-Fenton system and different degradation processes, four experiments were separately conducted in the treatment of wastewater contaminated with MB. Figure 2 gives the comparison of

Fig. 2 Comparison of different degradation systems on MB removal

different degradation systems with the performance of NHFR using the UV illumination. Fenton's reagent doses used were: $[\text{Fe}^{3+}] = 40 \text{ mg/L}$; $[\text{H}_2\text{O}_2] = 400 \text{ mg/L}$, and the starting pH value of the MB wastewater was adjusted at 3 for 10 ppm MB dye solution concentration. Investigation of the results illustrates that the UV photolysis without the Fenton's reagent addition only completed a 26% reduction after more than 2 h in the MB concentration. Nevertheless, the sole use of Fenton's reagent achieved a MB reduction of 37%. However, when H_2O_2 was used for treatment (400 mg/L), only 3% of removal was reached. Obviously, the OH radicals are generated through the reaction between the Fe^{2+} and H_2O_2 which plays a vital role in the MB degradation process [27, 28].

As reported in the literature [3], MB dye consists of aromatic compound and Fenton's reagent is proved to be an efficient method in the destruction of such those aromatic compounds. The destruction is summarized as follows: The hydroxyl radicals are attacking those aromatic rings, thus opening the rings and producing reaction intermediates, which are eventually transformed to harmless end products such as CO_2 and H_2O . Additionally, augmentation of the UV radiation the Fenton's reagent (namely photo-Fenton process) led to more pronounced degradation of MB about 84%. However, the processes that use UV radiation in conjunction with the nanocrystals as the source of chemical reagents obtain better results since higher hydroxyl radicals were generated which are mainly responsible for organics oxidation. These remarks are in agreement with that presented by Galvao et al. [29], Moraes et al. [30] and Tony and Mansour [10].

3.1.2 Effect of Fenton's reagent parameters

Photo-Fenton's process is highly sensitive to the initial H_2O_2 , iron catalyst concentration and pH value. This reagent is extremely producer of $\cdot\text{OH}$ radicals, and the reaction rate is limited by the $\cdot\text{OH}$ generation. Traditionally, hydroxyl radical has been viewed as the workhorse of hydrogen peroxide oxidation systems. Thus, the main source of OH radicals and oxygen depends on the hydrogen peroxide. Figure 3a shows the effect of hydrogen peroxide increase on the MB removal at constant pH 3 and Fe^{3+} of 40 mg/L. The results show that the degradation rate of MB increases with an increase in initial H_2O_2 concentration from 100 to 400 mg/L, but in excess of about 400 mg/L, the H_2O_2 dose of 1000 mg/L, plot of the reaction rate curve is almost horizontal. This could be illustrated that the presence of H_2O_2 beyond the ratio with Fe^{3+} does not improve the MB degradation. According to Murry and Parson [31], hydrogen peroxide may also serve as a scavenger of OH radicals when it will be in excess. These results of effect of increasing H_2O_2 on the degradation system are in accordance with the previous results obtained by Tony et al. [13] in the treatment of oily wastewater.

The production of OH radicals from H_2O_2 is catalyzed by Fe^{3+} and thus depends on the concentration of the

catalyst as shown in Fig. 3b. Photo-Fenton treatment was carried out at different Fe^{3+} dosages (20–80 mg/L) while the pH (3.0) and the H_2O_2 dosage (400 mg/L) were maintained constant. The influence of the Fe^{3+} dosage has a positive effect on degradation of MB, while above 40 mg/L the excess of Fe^{3+} renders the reaction rate. Indeed, the UV radiation proved to be very efficient in the H_2O_2 utilization so that the addition of ferrous ion did not lead to a further improvement. The limiting reagent for photo-Fenton's process corresponds to the ferrous ions, and it is present in much lower concentration than hydrogen peroxide. The catalyst is most efficiently used in the system. These results clearly demonstrate the advantage of the photo-Fenton process. Due to the low of Fe^{3+} , the addition of Fe^{3+} is strongly reduced in the produced iron sludge [7, 13]. Therefore, nanoheamatite is significantly applied as the catalyst source to substitute the classic iron source in the Fenton system for decreasing the iron amount used with a high surface area reagent.

Fenton process has a typically sharp, preferred pH region in which it is optimally operated. The pH value influences the generation of OH radicals and thus the activity of oxidation, the speciation of iron, and hydrogen peroxide decomposition. Moreover, the oxidation potential of OH radicals decreases with increasing pH.

Figure 3c illustrates the pH effect on MB removal in the presence of NHFR. It is observed that, by increasing the pH of the dye solution from 2 to 3, there is an increase in the removal percent. This phenomenon of the increasing trend of MB removal with increasing the initial pH of the solution is dependent on the nature of the adsorbent. However, at lower pH, the % removal of MB was 64%. Interestingly, there is an increased trend in the removal rate at higher pH 3.0. More significant enhancement in the % removal of MB is achieved at pH 3.0 (97.5%). For pH values above 3 such as 4 and 8, the degradation strongly decreases as Fe^{3+} -complexes precipitate. This is quite similar to the previous reports in which it was an optimum pH of 3 [32, 33].

As reported in the literature [34], the production yield of the OH radicals in the pH range of 2–4 is highest. This could be explained by reduction in the reaction rate. Organometallic complex is produced which helps in the regeneration of H_2O_2 rather than the production of the hydroxyl radicals. Besides, the presence of inorganic carbon in wastewater also scavenges the hydroxyl radical production [35]. Therefore, controlling the pH in the Fenton's system to the acidic conditions increases the OH radicals production. Thus, the optimum Fenton's reagent conditions are pH 3.0, H_2O_2 400 mg/L and Fe^{3+} 40 mg/L. However, further research should be conducted to overcome the acidic pH effluents after the Fenton's reaction to reach a commercial application.

Fig. 3 Effect of photo-Fenton's parameters on MB degradation (operating parameters [MB concentration]=10 mg/L; flow rate=25 mL/min), **a** effect of H_2O_2 , **b** effect of Fe^{3+} , **c** effect of pH

3.1.3 Effect of initial dye concentration

Removal efficiency greatly depends on the initial concentration of solution of pollutant. For estimating the effect of initial dye concentration on the reaction rate, different 500 mL solution of including different initial MB concentrations was treated under UV radiation after the pH was adjusted at 3.0 and then 40 mg/L of haematite nanopowder was added; subsequently, the Fenton's reaction was initiated with the addition of 400 mg/L H_2O_2 taking flow rate 25 mL/min as constant values. The graph in Fig. 4 shows the comparison of different degradation levels from 5 mg/L to 40 mg/L. It shows the decrease in the removal efficiency with increasing initial concentrations, and it is observed the removal rate of MB is 93, 84, 48 and 20% for initial MB concentrations of 5, 10, 20 and 40 mg/L, respectively. Increasing removal % of MB with decreasing initial MB concentration can be attributed to the enhancement of UV light penetration, resulting in enhanced concentration removal. This observation of the increase in the pollutant removal rate with decreasing the initial pollutant concentration in the photocatalytic oxidation reactions was previously described by Najjar et al. [36] in the photocatalytic treatment of the nitrophenol.

3.1.4 Effect of flow rate

In order to investigate the flow rate on the removal of MB, different flow rates were applied and the results are presented in Fig. 5. The results in the figure reveal that the reduction efficiency decreases with increase in the flow rate of the dye solution. Almost 13% of MB was removed at flow rate 15 mL/min, and then, it is increased to 75% for

Fig. 4 Effect of initial MB concentration (operating parameters $[\text{Fe}^{3+}] = 40 \text{ mg/L}$; $[\text{H}_2\text{O}_2] = 400 \text{ mg/L}$; $\text{pH} = 3$, flow rate = 25 mL/min)

Fig. 5 Effect of flow rate on the NHFR process (operating parameters $[\text{Fe}^{3+}] = 40 \text{ mg/L}$; $[\text{H}_2\text{O}_2] = 400 \text{ mg/L}$; $\text{pH} = 3$)

flow rate 25 mL/min, whereas 33% and 20% of MB were removed at flow rate 40 and 70 mL/min, respectively. The role in increasing the degradation rate of pollutant with increasing the flow rate is valid up to a certain limit, and then, the reaction becomes slower. These phenomena could be illustrated by the fact that once the flow rate was slow, MB in the sample solution got more contact time with UV radiation induced. However, the flow rate of 25 mL/min was chosen to be the optimum because it makes the removal process higher. These results accord with the findings of [37], who investigated the photo-Fenton treatment of a petroleum refinery wastewater.

3.1.5 Effect of temperature

The effect of the treatment temperature on the mineralization of MB was examined. Four different temperatures between 25 and 80 °C were tested on the removal rate of MB. Other experimental conditions except temperature were kept same. It could be understood from the results in Fig. 6 that the removal efficiencies increased as the temperature increased. As temperature increased from 25 to 80 °C, the reduction rate increased and showed 44, 49, 94 and 97%, at only 30 min of reaction time for temperatures 25, 40, 50 and 80 °C, respectively. Thus, higher temperature was most favorable for pollutant removal. The increase in rate with the increase in the solution temperature is illustrated by the increase in the collision frequency of molecules in solution as the temperature increased [38]. This investigation confirms the importance of the solar NHFR when using direct photolysis of solar radiation as the efficiency will be increased.

Fig. 6 Effect of temperature on the NHFR process (operating parameters $[\text{Fe}^{3+}] = 40 \text{ mg/L}$; $[\text{H}_2\text{O}_2] = 400 \text{ mg/L}$; $\text{pH} = 3$)

3.2 Kinetics and thermodynamic investigation

To follow the kinetic MB dye removal using photo-Fenton reaction, different contact time ranges from 0 to 60 min under isothermal condition at various temperatures (25, 40 and 50 °C) were studied. According to the literature, the most common following reaction rates in wastewater treatment are zero, first and second reaction orders as shown in Eqs. (1–3), respectively [39–41].

$$\left(\frac{dc}{dt}\right) = -k_0 \quad (2)$$

$$\left(\frac{dc}{dt}\right) = -k_1 C \quad (3)$$

$$\left(\frac{dc}{dt}\right) = -k_2 C^2 \quad (4)$$

where C is the concentration of MB, C_t is the concentration of MB at time t , C_0 is MB initial concentration, and t is the reaction time. Additionally, k_0 , k_1 and k_2 represent the pseudo-kinetic rate constants of zero-, first- and second-order reaction kinetics, respectively.

Thus, those three models were checked for MB degradation using the photo-Fenton's reagent by plotting the linear regression analysis of the integration of Eqs. (2–3) to investigate the order of reaction. The results given in Table 1 indicate the regression coefficient, R^2 , is higher for the pseudo-second order of reaction. Furthermore, pseudo-second-order kinetic reaction constant, k_2 , is sensitively affected by temperature which is increased from 0.0023 to 0.042 $\text{L mg}^{-1} \text{ min}^{-1}$ by the temperature increase. This could be illustrated by the increase of hydroxyl radicals yield by increasing temperature [42]. Moreover, the reaction half-time, $t_{1/2}$ [43], is affected also by the temperature increase.

Ultimately, it is concluded that MB removal by nano-Fenton's reagent is following the second-order reaction model under various investigated temperatures. This findings in accordance with Samet et al. [44], El Haddad et al. [6] and Youssef et al. [45] in the treatment of contaminated wastewater. However, Bounab et al. [41] found the reaction follows the first-order kinetics on the treatment using electro-Fenton treatment process.

To further understand the nano-Fenton's reagent on MB degradation, thermodynamic parameters were estimated. In this point, activation energy (E_a) of MB degradation can be calculated from the Arrhenius equation [46, 47] ($k_2 = Ae^{\frac{-E_a}{RT}}$), where R is the gas constant, T is the temperature, and A is the pre-exponential factor that is considered to be constant with respect to temperature. Plotting $\ln k_2$ versus $1/T$ gives a straight line whose slope is $-E_a/R$. Figure 7 shows such a relation for the MB photodegradation process under the investigated temperatures. The obtained activation energy of the process was found to be 79.01 KJ mol^{-1} . Additional thermodynamic parameters such as the enthalpy of activation ($\Delta H'$), the entropy of activation ($\Delta S'$) and the free energy of activation ($\Delta G'$) [47] were estimated and are listed in Table 2. The positive values of $\Delta H'$ throughout this investigation indicate that reaction is exothermic. Besides, $\Delta G'$ exhibited positive values; this means at high temperature the reaction is non-spontaneous with a negative entropy of activation [47].

Table 1 Kinetic parameters of MB photodegradation by nano-Fenton's reagent under various temperatures

$T/^\circ\text{C}$	Pseudo-zero order			Pseudo-first order			Pseudo-second order			% Removal
	k_0/min^{-1}	$t_{1/2}/\text{min}$	R^2	$k_1/\text{mg L}^{-1} \text{ min}^{-1}$	$t_{1/2}/\text{min}$	R^2	$k_2/\text{mg}^{-1} \text{ L min}^{-1}$	$t_{1/2}/\text{min}$	R^2	
25	0.089	0.45	0.76	0.014	49.50	0.88	0.0023	43.48	0.94	62.0
40	0.092	0.46	0.76	0.015	46.51	0.86	0.0026	38.46	0.93	96.0
50	0.129	0.63	0.51	0.044	15.64	0.61	0.0346	2.89	0.82	96.7

Fig. 7 Plot of $\ln k_2$ versus $1000/T$ for the investigated photodegradation reaction. The solid lines represent least-squares fitting

Table 2 Thermodynamic parameters of MB photodegradation by nano-Fenton's reagent

$T/^{\circ}\text{C}$	$\ln k_2$	$E_a/\text{kJ mol}^{-1}$	$\Delta G^{\circ}/\text{kJ mol}^{-1}$	$\Delta H^{\circ}/\text{kJ mol}^{-1}$	$\Delta S^{\circ}/\text{J mol}^{-1}$
25	-6.07		88.03	48.79	-131.68
40	-5.95	79.01	92.27	48.67	-139.31
50	-3.36		88.35	48.59	-123.12

4 Conclusion

Haematite nanocrystalline powder can be readily prepared using sol-gel technique. NHFR is achieved by applying haematite nanoparticles rich in hydrogen peroxide shows high efficiency in MB degradation. Furthermore, the effect of reaction Fenton's reagent parameters such as pH effect, Fe^{3+} and hydrogen peroxide concentrations is achieved. The optimum pH value has been found to be 3, while the reaction rate increased with increases in the Fe^{3+} and hydrogen peroxide reagent doses until a certain limit of 40 and 400 mg/L, respectively. The effect of initial MB, flow rate and temperature was also monitored. The obtained results of the investigated NHFR confirm the important role of nanoparticles in photo-oxidation of organic pollutants. Moreover, the study of photo-oxidation reaction under various temperatures referred to that the reaction is non-spontaneous and the used reagent could be more efficient under direct solar radiation.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

References

- Rahman MA, Ruhul ASM, Shafiquel AAM (2012) Removal of methylene blue from waste water using activated carbon prepared from rice husk. *Dhaka Univ J Sci* 60(2):185–189
- Sareen D, Garg R, Grover N (2014) A study on removal of methylene blue dye from waste water by adsorption technique using fly ash briquette. *Int J Eng Res Technol* 3(7):278–281
- Ehrampoush MH, Moussavi GH, Ghaneian MT, Rahimi S, Ahmadian M (2011) Removal of methylene blue dye from textile simulated sample using tubular reactor and TiO_2 /UV-C photocatalytic process. *Iran J Environ Health Sci Eng* 8(1):35–40
- Rizoo L, Agovino T, Nahim-Granados S, Castro-Alferez M, Fernandez-Ibanez P, Polo-Lopez MI (2019) Tertiary treatment of urban wastewater by solar and UV-C driven advanced oxidation with peracetic acid: effect on contaminants of emerging concern and antibiotic resistance. *Water Res* 149:272–281
- Rahman MM, Hasna MA, Kazuaki S (2009) Degradation of commercial textile dye by Fenton's reagent under xenon beam irradiation in aqueous medium. *J Sci Res* 1(1):108–120
- El Haddad M, Regti A, Laamari MR, Mamouni R, Saffaj N (2014) Use of Fenton reagent as advanced oxidative process for removing textile dyes from aqueous solutions. *J Mater Environ Sci* 5(3):667–674
- Khan MR, Kurny A, Gulsha F (2016) Photocatalytic degradation of methylene blue by magnetite + H_2O_2 + UV process. *Int J Environ Sci Dev* 7(5):325–329
- Bauer R, Fallmann H (1997) The photo-Fenton oxidation—a cheap and efficient wastewater treatment method. *Res Chem Intermed* 23(4):341–354
- Serna-Galvis EA, Botero-Coy M, Martinez-Pachon D, Moncayo-Lasso A, Ibanez M, Hernandez F, Torres-Palm RF (2019) Degradation of seventeen contaminants of emerging concern in municipal wastewater effluents by sonochemical advanced oxidation processes. *Water Res*. <https://doi.org/10.1016/j.watres.2019.01.045>
- Tony MA, Mansour SA (2019) Removal of the commercial reactive dye Procion Blue MX-7RX from real textile wastewater using the synthesized Fe_2O_3 nanoparticles at different particle sizes as a source of Fenton's reagent. *Nanoscale Adv*. <https://doi.org/10.1039/c8na00129d>
- Tony MA, Zhao YQ, El-Sherbiny MF (2011) Fenton and Fenton-like AOPs for alum sludge conditioning: effectiveness comparison with different Fe^{2+} and Fe^{3+} salts. *Chem Eng Commun* 98(3):442–452
- Oller I, Malato S, Sanchez-Perez JA (2011) Combination of advanced oxidation processes and biological treatments for wastewater decontamination—a review. *Sci Total Environ* 409(20):4141–4166
- Tony MA, Purcell PJ, Zhao YQ, Tayeb AM, El-Sherbiny MF (2015) Kinetic modeling of diesel oil wastewater degradation using photo-Fenton process. *Environ Eng Manag* 14(1):11–16
- Tony MA, Parker HL, Clark JH (2016) Treatment of Laundrette wastewater using Starbon and Fenton's Reagent. *J Environ Sci Health A* 23(11):974–979
- Liu TJ, Gao H, Liu SJ (2011) Decolorization of methylene blue dye wastewater by Fenton's reagent. *Adv Mater Res* 295–297:1447–1450
- Abou-Gamra ZM (2014) Kinetic and thermodynamic study for Fenton-like oxidation of amaranth red dye. *Adv Chem Eng Sci* 4:285–291
- Fenton HJ (1984) Oxidation of tartaric acid in the presence of iron. *Chem Soc J Lond* 65:899–910

18. Choi K, Lee W (2012) Enhanced degradation of trichloroethylene in nano-scale zero-valent iron Fenton system with Cu(II). *J Hazard Mater* 211:146–151
19. Prucek R, Hermanek M, Zboril R (2002) An effect of iron(III) oxides crystallinity on their catalytic efficiency and applicability in phenol degradation—a competition between homogeneous and heterogeneous catalysis. *Appl Catal A* 366:325–332
20. Dutta B, Jana S, Bhattacharjee A, Gutlich P, Iijima S, Koner S (2010) γ -Fe₂O₃ nanoparticle in NaY-zeolite matrix: preparation, characterization and heterogeneous catalytic epoxidation of olefins. *Inorg Chim Acta* 363:696–704
21. Nie Y, Hu C, Zhou L, Qu J, Wei Q, Wang D (2010) Degradation characteristics of humic acid over iron oxides/FeO core–shell nanoparticles with UVA/H₂O₂. *J Hazard Mater* 173:474–479
22. Chen J, Qiu X, Fang Z, Yang M, Pokeung T, Gu F, Cheng W, Lan B (2012) Removal mechanism of antibiotic metronidazole from aquatic solutions by using nanoscale zero-valent iron particles. *Chem Eng J* 181:113–119
23. Vinita M, Dorathi R, Palanivelu K (2010) Degradation of 2,4,6-trichlorophenol by photo Fenton's like method using nano heterogeneous catalytic ferric ion. *Sol Energy* 84:1613–1618
24. Lin Y, Weng C, Chen F (2008) Effective removal of AB24 dye by nano/micro-size zero-valent iron. *Sep Purif Technol* 64:26–30
25. Mansour SA, Ibrahim MM (2017) Electrical investigation of nano-structured Fe₂O₃/p-Si heterojunction diode fabricated using the sol–gel technique. *J Electron Mater* 46:6502
26. Hamed FH, Rauf MA, Ashraf SS (2009) Degradation studies of Rhodamine B in the presence of UV/H₂O₂. *Desalination* 239:159–166
27. Martinz NS, Fernandez JF, Segura XFF, Ferrer AS (2003) Pre-oxidation of an extremely polluted industrial wastewater by the Fenton's reagent. *J Hazard Mater B* 101:315–322
28. Wang X, Wang J, Cui Z, Wang S, Cao M (2014) Facet effect of α -Fe₂O₃ crystals on photocatalytic performance in the photo-Fenton reaction. *RSC Adv* 4:34387–34394
29. Galvao S, Mota A, Silva D, Moraes J, Nascimento C, Chiavone-Filho O (2006) Application of the photo-Fenton process to the treatment of wastewaters contaminated with diesel. *Sci Total Environ* 367:42–49
30. Moraes J, Quina F, Nascimento C, Silva D, Filho O (2004) Treatment of saline wastewater contaminated with hydrocarbons by the photo-Fenton process. *Environ Sci Technol* 38:1183–1187
31. Murry CA, Parson SA (2004) Removal of NOM from drinking water: Fenton's and photo-Fenton's processes. *Chemosphere* 54:1017–1023
32. Tamimi M, Qourzal S, Barka N, Assabbane A, Ait-Ichou Y (2008) Methomyl degradation in aqueous solutions by Fenton's reagent and the photo-Fenton system. *Sep Purif Technol* 61(1):103–108
33. Emami F, Tehrani-Bagha AR, Gharanjig K, Menger FM (2010) Kinetic study of the factors controlling Fenton -promoted destruction of a non-biodegradable dye. *Desalination* 257(1–3):124–128
34. Sedlak DL, Andren AW (1991) Oxidation of chlorobenzene with Fenton's reagent. *Environ Sci Technol* 25:777–782
35. Buxton GV, Greenstock CL, Helman WP, Ross AB (1988) Critical review of rate constants for reaction of hydrated electrons, hydrogen atoms and hydroxyl radicals ($\cdot\text{OH}/\cdot\text{O}^-$) in aqueous solution. *J Phys Chem Ref Data* 17:513–886
36. Najjar W, Chirchi L, Santosb E, Ghorhel A (2001) Kinetic study of 2-nitrophenol photodegradation on Al-pillared montmorillonite doped with copper. *J Environ Monit* 3:697–701
37. Coelho A, Castro AV, Dezotti M, Sant'Anna GL (2006) Treatment of petroleum refinery sourwater by advanced oxidation processes. *J Hazard Mater B* 137:178–184
38. Zhang H, Choi HJ, Huang C (2006) Treatment of landfill leachate by Fenton's reagent in a continuous stirred tank reactor. *J Hazard Mater B* 136:618–623
39. Silva AMT, Nouli E, Carmo-Apolinario AC, Xekoukoulotakis NP, Mantzavinos D (2007) Sonophotocatalytic/H₂O₂ degradation of phenolic compounds in agro-industrial effluents. *Catal Today* 124:232–239
40. Buthiyappan A, Abdul Raman A, Daud WMAW (2016) Development of an advanced chemical oxidation wastewater treatment system for the batik industry in Malaysia. *RSC Adv* 6:25222–25241
41. Bounab L, Iglesias O, González-Romero E, Pazos M, Sanromán MA (2015) Effective heterogeneous electro-Fenton process of m-cresol with iron loaded activated carbon. *RSC Adv* 5:31049–31056
42. Xu H, Lu G (2013) On-line spectrophotometric method for decolorizing reaction kinetics of reactive black 5 by Fenton oxidation. *Asian J Chem* 25(14):7989–7992
43. Pollard TD, DLC EM (2013) Take advantage of time in your experiments: a guide to simple, informative kinetics assays. *Mol Biol Cell* 24(8):1103–1110
44. Samet Y, Hmani E, Abdelhédi R (2012) Fenton and solar photo-Fenton processes for the removal of chlorpyrifos insecticide in wastewater. *Water SA* 38(4):537–542
45. Youssef NA, Shaban SA, Ibrahim FA, Mahmoud AS (2016) Degradation of methyl orange using Fenton catalytic reaction. *Egypt J Pet* 25:317–321
46. Lonhienne T, Gerday C, Feller G (2000) Psychrophilic enzymes, revisiting the thermodynamic parameters of activation may explain local flexibility. *Biochim Biophys Acta* 1543(1):1–10
47. Chen D, Ray AK (1998) Photodegradation kinetics of 4-nitrophenol in TiO₂ suspension. *Water Res* 32:3223–3234

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.