Journal of Ultrafine Grained and Nanostructured Materials
https://jufgnsm.ut.ac.ir
Vol. 57, No.2, December 2024, pp. 190-202
Print ISSN: 2423-6845 Online ISSN: 2423-6837
DOI: 10.22059/jufgnsm.2024.02.09

Development of heterogeneous nano-zeolite catalyzing Fenton-like oxidation processes for metalworking fluid wastewater treatment: A comparison with conventional methods

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Recieved: 30 June 2024; Accepted: 15 October 2024

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ABSTRACT

To preserve environmental and human health, remediation of the produced wastewater from various industries such as textile and metalworking is of prime significance. The present investigation strives to draw a meaningful comparison between the metalworking fluid (MWF) wastewater chemical oxygen demand (COD) removal ability of three different methods, including coagulation-flocculation, Fenton oxidation, and heterogeneous nano-zeolite catalyzing Fenton-like oxidation processes. The results illustrated that the highest COD removal efficiency achieves through the application of a heterogeneous Fenton-like oxidation process. Also, the influence of nanocatalyst dosage and solution pH on COD removal efficiency of the heterogeneous Fenton-like process is addressed. The concentration of the used catalyst in this method plays a crucial role in its removal ability, wherein COD removal efficiency increases with an increase in the catalyst amount. Besides, the COD removal efficiency of this process is not affected by the pH value of the treated solution. Moreover, the sludge production rate as well as affecting parameters of each method is evaluated. The heterogeneous Fenton-like process provides the lowest sludge production rate, while the maximum sludge production rate is encountered with the coagulation-flocculation route. Therefore, the heterogeneous Fenton-like process overcomes the common challenges facing the successful industrial use of the conventional Fenton process.

Keywords: *Metalworking fluid; Fenton oxidation; Coagulation-flocculation; heterogeneous nano-zeolite catalyzing Fenton-like oxidation processes; Wastewater treatment.*

1. Introduction

The various components involved in machining processes may experience severe friction during the service condition. The application of metalworking fluids (MWFs) and metal cutting fluids (MCFs) are found to be strongly effective in the reduction of such frictions. They can also be employed as coolant agents. Nevertheless, these fluids may drastically pollute the environment by introducing a large amount of oil and other organic/inorganic compounds into the wastewater. MWFs and MCFs are chemically complex compounds containing performance tailoring additives, various kinds of surfactants, complex components, corrosion inhibitors, alkaline reverse compounds, and anti-weld agents, which may result in the high COD content [1-5]. In general, there are two major types of MWFs as follows: (i) water-based and

(ii) oil-based MWFs [6,7]. The drinking water, groundwater, human health, etc. are deeply affected by incorporation of un-treated MWFs and MCFs wastewaters into the environment. Albeit there are several approaches to treat the MWFs wastewaters, more researches should be performed to fulfill the complete removal of their harmful elements and components. Considering the annual incorporation of several million liters of these fluids into the wastewater, it is essential to assess different approaches to achieve the highest performance [8-15]. Generally, three methods, namely physicochemical, physicomechanical, and biological treatments, have been developed for treating MWFs wastewater. Solvent extraction, catalytic oxidation, and chemical flocculation are some of the frequently employed physicochemical treatments. Since most of the physicochemical methods are expensive and technically difficult to be utilized, they have often been used as a pre-treatment step in wastewater remediation. Thermal splitting, incineration, evaporation, and ultrafiltration fall under the classification of physicomechanical approaches. Biological routes include membrane separation, advanced oxidation process, and etc. Nevertheless, these methods are not able to fully remove the oil and other effluents from MWFs wastewater. A significant challenge in these systems is the disposal of the residual sludge, which increases overall costs [16-24]. To overcome the disability of the aforementioned methods in terms of complete removal of effluents from MWFs wastewater, one practical approach is the simultaneous use of two or more methods, namely hybrid methods [25-28]. Furthermore, it is possible to improve the efficiency of MWFs wastewater treatment through the application of post-treatment [3].

Generally, advanced oxidative degradation processes (AOPs) such as Fenton oxidation are employed to diminish and even fully remove the organic contaminations of various wastewaters through oxidation reactions. The processes may proceed via the transformation of such contaminations to CO_2 and inorganic ions. Fenton oxidation method possesses several advantages, as follows: (i) low cost, (ii) acceptable safety, (iii) providing desirable mineralization of the organic matter, and (iv) providing a suitable platform for performing post-biological treatments [29-32].

Coagulation flocculation is an appropriate chemical treatment for remediation of different types of industrial wastewaters, and it can satisfactorily remove the organic materials, thereby decreasing the COD. Similar to Fenton oxidation, coagulation-flocculation is a simple and cost-effective route. Additionally, it can separate various kinds of particles from MWFs wastewaters [33-36]. Among various AOPs, the application of H_2O_2 and Fenton main reagent, i.e., homogeneous Fenton process, has been widely reported as a homogeneous catalytic process for the removal of the various pollutants, especially dyes [37]. However, the so-called "homogeneous Fenton process" has some potential drawbacks, including the need to be operated in a strongly acidic conditions, the production of iron-containing sludge as a by-product to be further removed, and the catalyst deactivation by some produced intermediates in complex matrices encountered in real industrial applications [38]. These drawbacks can be overcome through the development and use of heterogeneous Fenton-type catalysts such as iron-substituted synthetic and natural minerals such as natural and synthetic zeolites [39], laponite [40], pyrite [41], magnetite [42], goethite [43], and pillared clays [44] catalyze the production of $OH^{\cdot}$ radicals. Among them, iron-substituted zeolites have been efficiently used within heterogeneous Fenton-type processes because of their unique physical and chemical properties, including crystallinity and stability in harsh chemical and thermal environments [43-50].

The present work, for the first time, deals with the evaluation of the influence of processing parameters on the performance of heterogeneous nano-zeolite catalyzing Fenton-like oxidation processes. It also attempts to make a comparison between the efficiency of three different methods, including coagulation-flocculation, Fenton oxidation, and heterogeneous Fenton-like oxidation processes in treating wastewater of a locally developed MWF.

2. Materials and methods

2.1. Raw wastewater characteristics

In the present investigation, 1.2 wt.% mineral oil-containing MWF wastewater was used to study the efficiency of the various treatment methods. Inorganic and organic corrosion inhibitors, stabilizers, and anionic surfactant agents are among the other existing compounds in the studied MWF composition. The main organic ingredients of the MWF are Triethanolamine (TEA) and some sodium salts of sulfonated petroleum cuts. Water-soluble MWF was developed locally in our laboratory and used successfully in small-scale local industries during the past decade. Table 1 outlines the physicochemical characteristics of the used MWF wastewater.

All of the other used chemicals were supplied by Merck & Co., Inc. with the analytical grade. Notably, the as-received chemicals were employed without any further treatment and/or purification. During the experiments, the volumetric concentration of H_2O_2 was adjusted at 27% by the titration method.

2.2. Coagulation-flocculation

The major goal of the coagulation-flocculation process is aggregating the present small particles within the colloid to form the big flocculent particles. Iron (III) chloride ($FeCl_3$) is known as a favorable coagulant. $FeCl_3$ can strongly adsorb the present particles when it is being incorporated into the colloid. To perform the coagulation-flocculation process, firstly, 500 ml of MWF wastewater was added to a 1000 ml beaker. In the next step, $FeCl_3$ at various dosages was incorporated into the existing MWF wastewater in the beaker to determine the optimum concentration of $FeCl_3$. Then, a two-step successive blending process was carried out, as follows: (i) rapid blending (150 rpm for 7 min); and (ii) slow blending (30 rpm for 25 min). Then, the mixing process stopped for 45 min in order to obtain the jelly-like deposit. Colloid pH was controlled at 8.20.4 by the incorporation of H_2SO_4 and/or NaOH. Fig. 1 shows the schematic illustration of the employed setup for the coagulation-flocculation process in the present study.

2.3. Fenton oxidation process

Four sequential steps are involved in Fenton oxidation as: (i) oxidation, (ii) neutralization, (iii) coagulation/flocculation, and (iv) separation of solid-liquid. The major chemical compound used in this process is hydrogen peroxide (H_2O_2), an oxidant that is usually employed for the treatment of the different organic and inorganic effluents. Hydrogen peroxide firstly reduces to hydroxyl radicals during the Fenton oxidation process. The chemical reactions that governed this reduction process are reported elsewhere [2, 29].

Table 1- The physicochemical characteristics of the used MWF wastewater.

Physicochemical characteristics	Value
pH	8.6
Temperature	27 ºC
Color	Pale yellow-colorless
COD	Approx. 32000 mg/L
BOD_5	Approx. 2500 mg/L
BOD_5 /COD	0.078

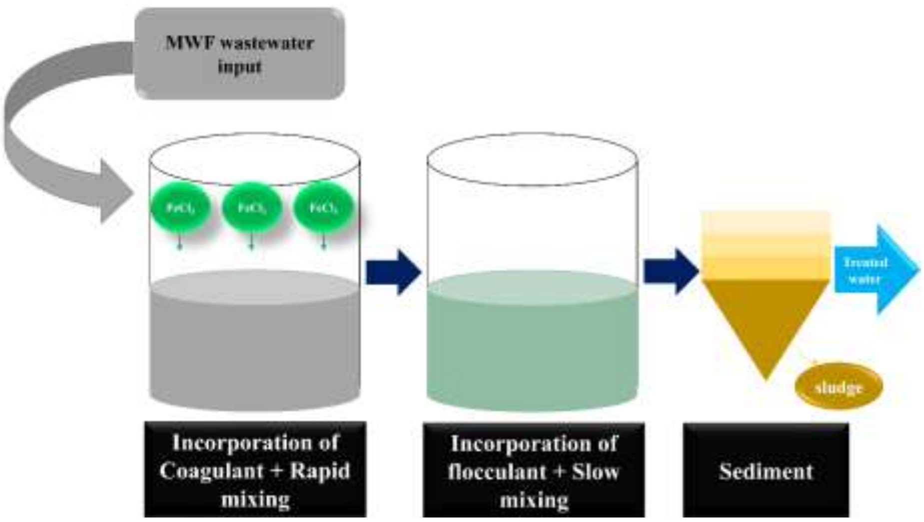


Fig. 1- The schematic illustration of the employed setup for the coagulation-flocculation process.

In the present work, the Fenton oxidation process was performed via a conventional jar test apparatus, where 500 ml of MWF wastewater was injected into the 1000 ml individual beakers at room temperature. MWF wastewater pH was adjusted at 3.60.3 by adding the specified amounts of H_2SO_4 (99% purity). Then, ferrous sulfate ($FeSO_4.7H_2O$) and hydrogen peroxide were incorporated into the beakers, respectively. Similar to Fenton oxidation, the prepared mixture underwent a two-step mixing process as: (i) rapid mixing (150 rpm for 7 min) and (ii) slow mixing (30 rpm for 25 min). Then, the blending process stopped and the mixture was heated to 55 °C to remove the excess hydrogen peroxide. Finally, NaOH was incorporated into the mixture to finish the oxidation process of the hydrogen peroxide. It is to be noted that significant amounts of the iron sludge originated from the conversion of Fe^{3+} to hydroxo complexes formed during this process. Fig. 2 indicates the schematic demonstration of the used setup for the Fenton oxidation process in the present study.

2.4. Heterogeneous Fenton-like oxidation process

Although this process is similar to the conventional Fenton oxidation in terms of the experimental procedure, the recently developed Fe-substituted zeolite-based nanocatalyst is used within the heterogeneous Fenton-like process along with a much lower dosage of hydrogen peroxide with no further ferrous sulfate required. The synthesis method and characteristics of the used Fe-substituted zeolite have been reported previously [46]. The heterogeneous Fenton-like oxidation is able to eliminate the entire present chemicals, which is considered as an outstanding advantage from both economic and environmental perspectives. The results reported the acceptable performance of the abovementioned nanocatalyst in removing the pollutant organic dyes from the wastewaters through a heterogeneous Fenton-like oxidation process [46]. All experimental runs were performed in the batch mode (1000 ml beaker) under constant magnetic stirring at 180 rpm. 500 mL MWF wastewater solutions were treated for 30 min using a variety of catalyst dosages, i.e., 1-6 g/L. The pH of the solution was adjusted by the addition of 1M H_2SO_4 and/or NaOH solutions. Fig. 3 schematically indicates the setup used for heterogeneous Fenton-like oxidation process in the present study.

2.5. COD determination

After completion of the Fenton oxidation process within 1 hour, the colloidal medium divides into two parts of supernatant and sludge including. To study the reduction in COD, the supernatant solutions were filtered using a conventional ultra-fine filter paper followed by dilution using distilled water. The dichromate reflux standard route was employed to measure the COD values. The reported values are the average of three separate measurements.

2.6. Characterization

The surface morphology and chemical composition of the Fe-substituted zeolite powder were evaluated using a field-emission scanning electron microscopy (FESEM, MIRA 3 Tescan, Czech Republic) equipped with energy dispersive spectroscopy (EDS), respectively.

The phase composition of the powder was studied by the X-ray diffraction (XRD, Tongda, TD-3700, China) in the 2θ range of 10-80°.

3. Results

3.1. Microstructural characteristics

The FESEM photograph and EDS elemental mapping images of the Fe-substituted zeolite powder are displayed in Fig. 4. The nano-scaled pores are seen in the FESEM image of the powder. The primary morphology of the powder is cuboctahedron-shaped. The similar morphology has been reported in the already published literature [51]. Fiber-like grains can also be observed in the FESEM image. Fig. 5 shows a high-magnification FESEM image of the powder to provide a clear view of the “fiber-like” grains. The nanopores are shown by arrows in the figure. The EDS elemental mapping images illustrate the presence of Si, Al, O, Ca, Fe, Na, and K elements that uniformly dispersed in the microstructure of the powder.

Fig. 6 shows the XRD pattern of the Fe-substituted zeolite powder. The phase composition of the powder is made of clinoptilolite phase according to the JCPDS 01-079-1461 reference card. Clinoptilolite is the precursor of the zeolite. The main peak is appeared at $2\Theta \approx 22°$. Scherrer equation was used to calculate the crystallite size of the powder [52]. The crystallite size of the powder is 38 nm, which approves that the powder used is a nanostructured material.

3.2. COD removal efficiency

Table 2 summarizes the COD removal efficiency and volume of the produced sludge for three different methods, including coagulation-flocculation, Fenton oxidation, and heterogeneous nano zeolite catalyzing Fenton-like oxidation processes.

The heterogeneous nano zeolite catalyzing Fenton-like oxidation process exhibits the highest COD removal efficiency. Furthermore, this method provides the lowest sludge volume, which leads to a dramatic decrease in the overall cost of the MWF wastewater remediation process. The application of

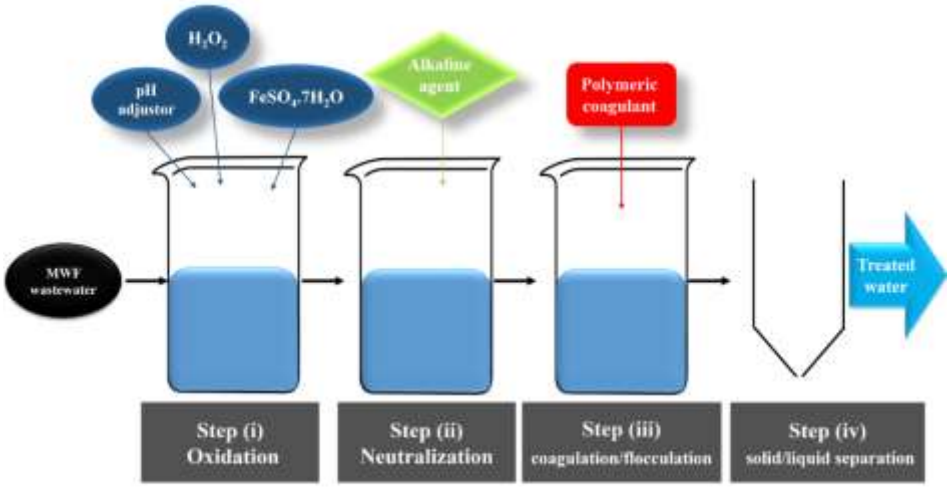


Fig. 2- The schematic demonstration of the used setup for the Fenton oxidation process.

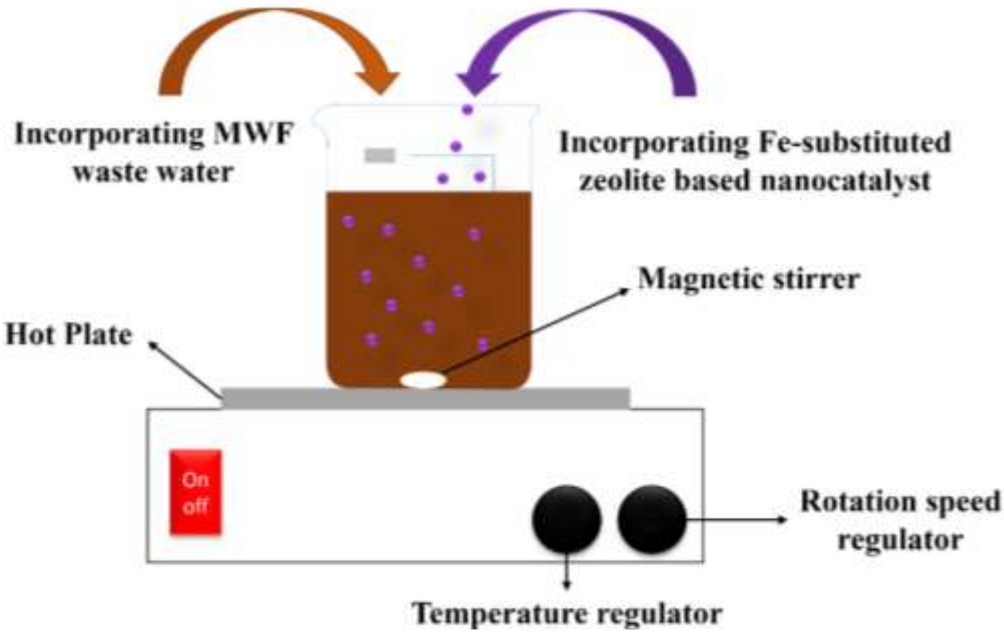


Fig. 3- The schematic demonstration of the used setup for heterogeneous Fenton-like oxidation process.

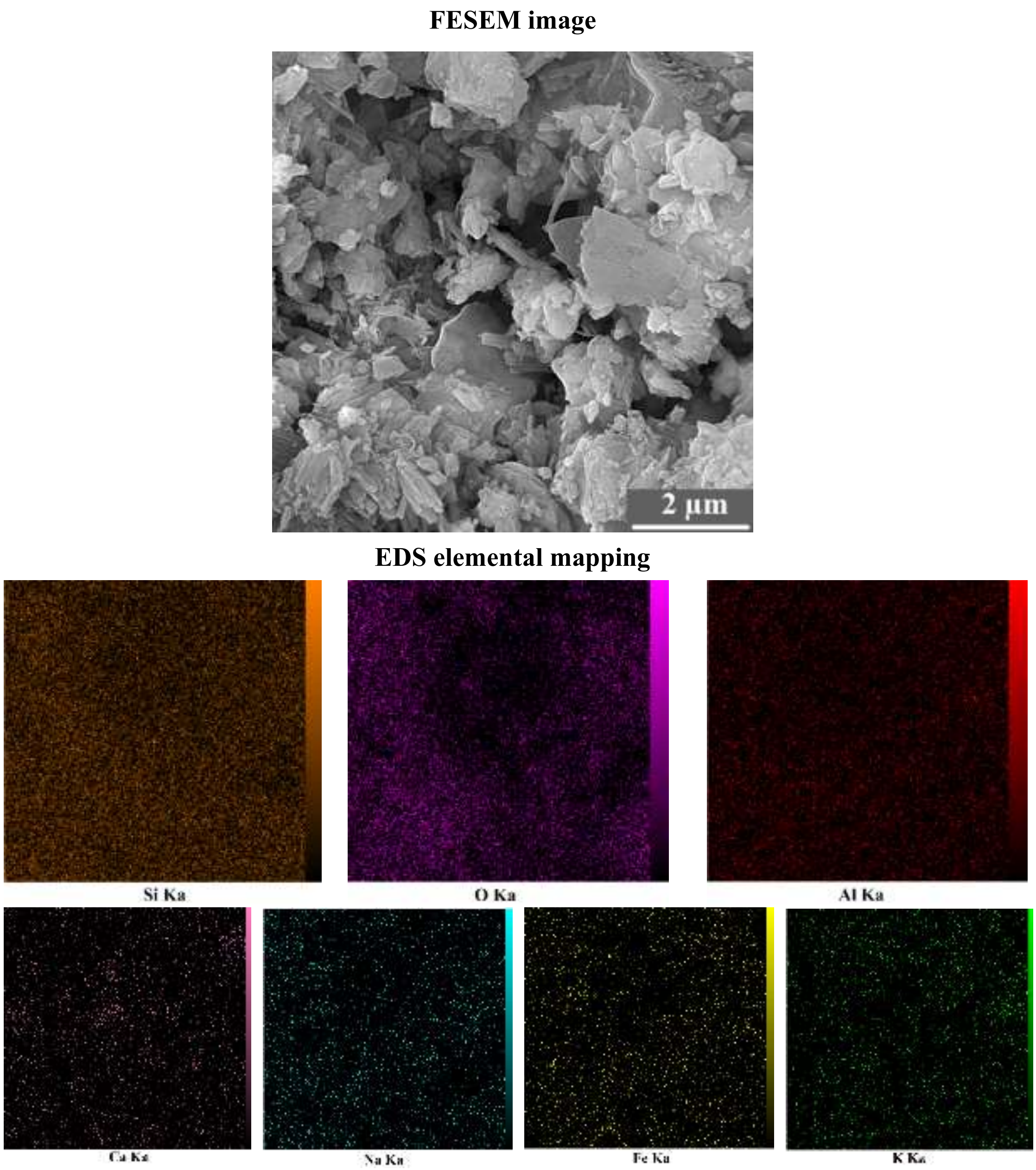


Fig. 4- The FESEM photograph and EDS elemental mapping images of the Fe-substituted zeolite powder.

the nanocatalyst decreases the need for hydrogen peroxide, resulting in decreased final cost of the procedure. Moreover, it can be easily seen that the processing parameters can noticeably alter the COD removal efficiency and sludge production in all of the studied methods. The effect of these parameters will be comprehensively discussed in the following sections.

3.3. Influence of Iron (III) chloride dosage within the coagulation-flocculation process

As can be seen from Table 2, increasing the amount of $FeCl_3$ in C.F process from 10 to 50 g/L increases the COD removal efficiency and totally produced sludge volume by 12 % and 150 ml/L, respectively. The improved COD removal efficiency may be attributed to the higher concentration of the available Fe^{3+} active sites for the organic materials to be neutralized and adsorbed within C.F process. On the other hand, a high volume of the produced sludge in this case which leads to a need for subsequent treatments, prevails over the mentioned advantage.

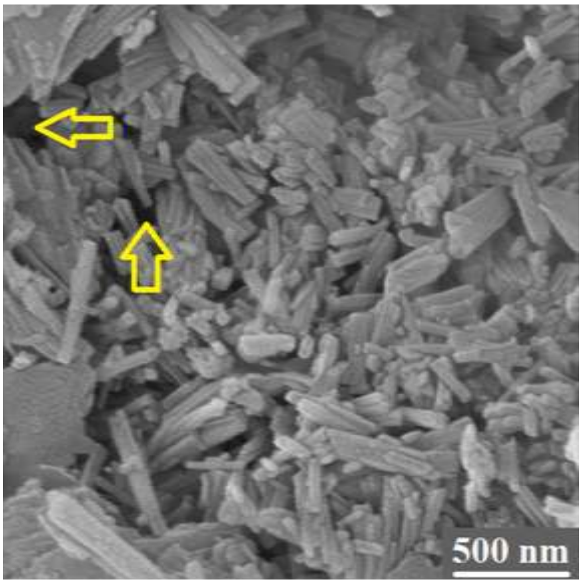


Fig. 5- High-magnification FESEM image of the Fe-substituted zeolite powder.

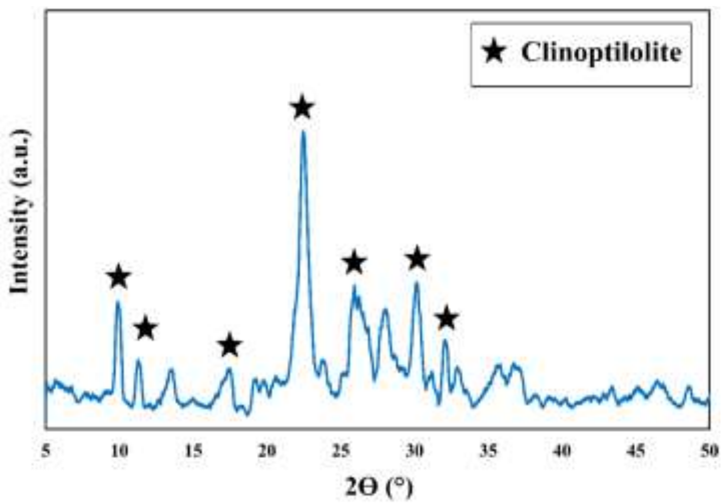


Fig. 6- XRD pattern of the Fe-substituted zeolite powder.

3.4. Influence of ferrous sulfate dosage within the Fenton oxidation process

As is evident in Table 2, at an optimum hydrogen peroxide concentration of 50g/L, ferrous sulfate dosage variation from 10 to 50g/L has no profound effect on both COD removal and produced sludge volume. While COD removal efficiency in this method is comparable to that of C.F, a considerable drop in sludge volume production is observable in F.O, as its main superiority over the C.F process.

3.5. Influence of nanocatalyst dosage within the heterogeneous Fenton-like oxidation process

It is worth mentioning that all of the measurements were carried out at the constant solution pH of 5. The increase in nanocatalyst dosage from 1 to 6 g/L can result in the COD removal efficiency enhancement by 6%. Also, the produced sludge volume is in the range of 35-45 ml/L in this method which is about an order of magnitude less than that of the aforementioned processes. Higher COD removal efficiency, together with quite low sludge volume, make this approach as an industrially promising method for MWF wastewater treatment. To the best of our knowledge, there is no study reporting the efficiency of the zeolite-based nanocatalysts in MWF wastewater treatment; however, the application of such a nanocatalyst has been demonstrated to yield promising outcomes in wastewater treatment. For instance, Yang et al. [53] have employed Fe_2O_3 nanoparticles-reinforced zeolite Y matrix composite catalysts to remove organics in particular phenol. They reported that the degradation rate is varied in a range of 45-90% depending on the Fe content, time, and size of the Fe_2O_3 nanoparticles. Comparing with results of the present work, it is not difficult to recognize that the employed heterogeneous nano zeolite catalyzing Fenton-like oxidation process results in acceptable efficiency.

3.6. Influence of pH value

The MWF wastewater with a wide range of pH values can be released due to several reasons such as the composition of the treated metal, chemical composition of the used fluid, and etc. Therefore, it is crucial to assess whether the developed heterogeneous nano zeolite catalyzing Fenton-like oxidation process is able to preserve its COD efficiency over the wide pH range. To meet this issue, the effect of MWF solution pH on the COD removal efficiency of this process at the constant nanocatalyst dosage of 6 g/L, i.e., the optimum nanocatalyst concentration is evaluated. In this case, MWF solution pH was controlled by the addition of H_2SO_4 and/or NaOH 1M solutions in

Table 2- COD removal efficiency and volume of the produced sludge for three different methods, including coagulation-flocculation (C.F), Fenton oxidation (F.O), and heterogeneous nano zeolite catalyzing Fenton-like oxidation (H.N.F) processes.

Process Type	H_2O_2 (g/L)	$FeSO_4.7H_2O$ (g/L)	$FeCl_3$ (g/L)	Fe-substituted zeolite-based nanocatalyst (g/L)	COD removal efficiency (%)	Produced Sludge Volume (ml/L)
C.F	-	-	10	-	75	420
C.F	-	-	25	-	83	480
C.F	-	-	35	-	85	510
C.F	-	-	50	-	87	570
F.O	50	10	-	-	83	240
F.O	50	25	-	-	85	260
F.O	50	35	-	-	87	270
F.O	50	50	-	-	87	290
H.N.F	5	-	-	1	87	35
H.N.F	5	-	-	2	89	42
H.N.F	5	-	-	3	91	43
H.N.F	5	-	-	6	93	45

the range of 5-9. The correlation between the MWF solution pH and COD removal is presented in Fig.7.

As seen, pH value has a negligible effect on the COD removal efficiency of the process, which is associated with the published results [54]. The results pave the way for the designing a high-efficiency heterogeneous Fenton-like procedure which is not restricted to a limited range of acidic pH values and can be applied over a wide range of pH.

3.7. Catalyst stability and cycleability

There is a tremendous need for the application of catalysts that offer long-term stability along with a high level of reusability in wastewater treatment. Complementary experiments in the batch mode were performed at a nanocatalyst dosage of 6 g/L to investigate the stability and cycleability of the nanocatalyst applied in H.N.F process. All COD removal efficiencies remained higher than 90% after 21 batches of treatment. The COD removal efficiency was declined sharply beyond 35 batch

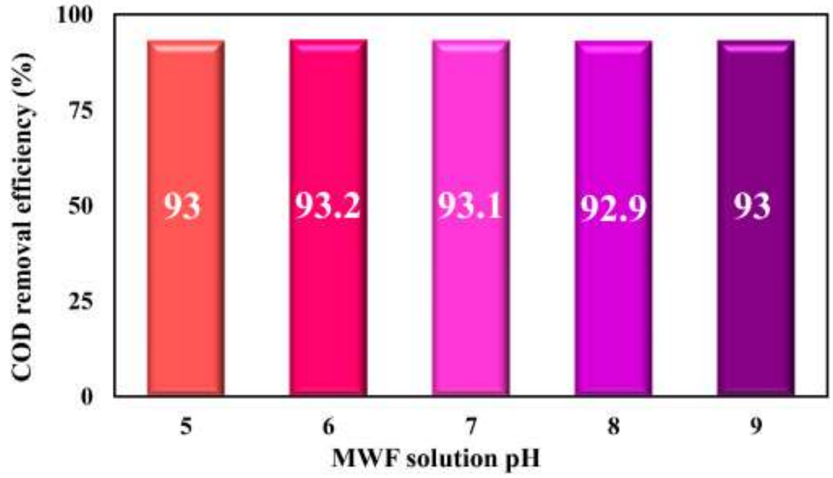


Fig. 7- The correlation between the MWF solution pH and COD removal efficiency of the process at constant nanocatalyst dosage of 6 g/L.

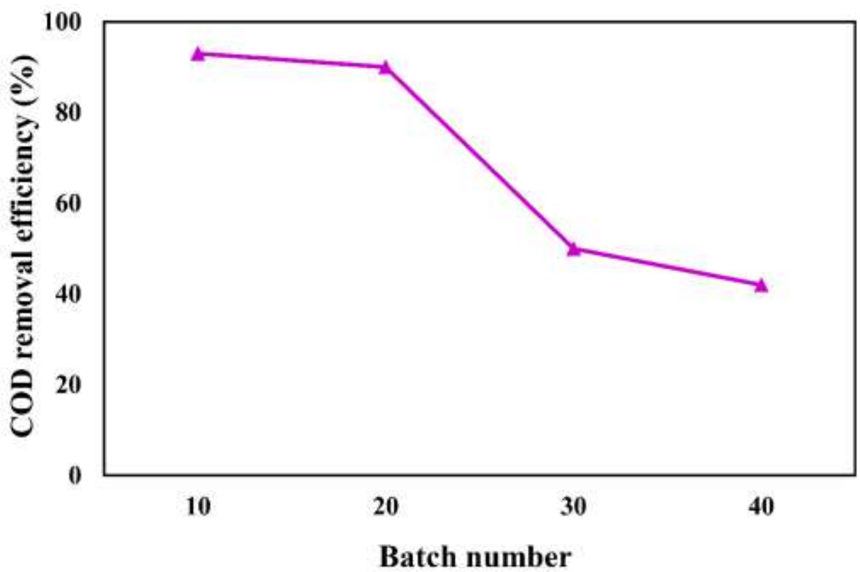


Fig. 8- COD removal efficiency variation of nanocatalyst with the optimum dosage, i.e., 6 g/L as a function of batch numbers.

operations and reached a value of 46%. As a result, the maximum useful life of the nanocatalyst can be considered to be about 20 batches of treatment. Fig. 8 shows the COD removal efficiency variation of the nanocatalyst with the optimum dosage, i.e., 6 g/L as a function of batch numbers.

4. Discussion

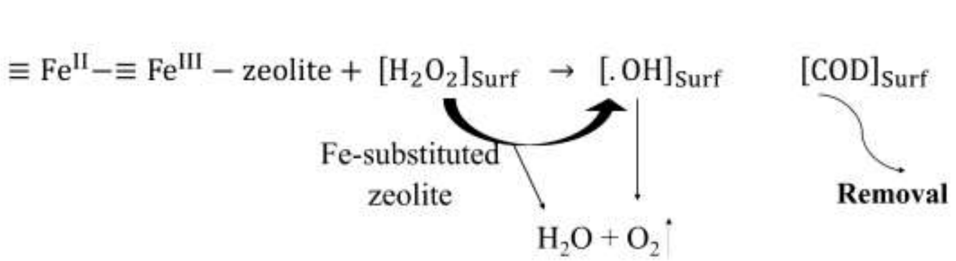
In general, a catalyst can enhance the reaction speed through three mechanisms, as follows: (i) providing a facilitated substrate for reacting species to react more efficiently; (ii) decreasing the activation energy needed for reaction initiation; and (iii) increasing the yield of one specific product when there would be two or more products. However, the thermodynamic aspects of the reaction remain almost unchanged. To date, scholars have benefited from a broad spectrum of nanocatalysts such as carbon nanotubes (CNTs), zero-valent iron, zeolite, Fe_3O_4, and TiO_2 for purification and treatment of wastewater released from various industries. The application of nano-scale materials as catalyst bears two major advantages over the conventional (micron-scaled) catalysts as: (i) emerging some specific properties when a material gets smaller to nano-scale and (ii) profound increment in the surface area-volume ratio which contributes to the improved catalyst efficiency [55-58]. Besides, the unique characteristics offered by nanocatalysts, including surface catalysis, high surface area, fast ion exchange, etc., open up new horizons in the successful use of nano-catalysts in wastewater treatment [59].

Overall, there are two potential challenges, namely the need for a low pH and the production of noticeable sludge content that commonly faces during the conventional Fenton oxidation, which is believed to be bypassed through the application of the appropriate nanocatalyst [60]. Depending on the employed catalyst, the Fenton oxidation process can be categorized into two main groups: homogeneous and heterogeneous. The reaction proceeds on the active sites that exist over the surface of the catalyst within the heterogeneous Fenton-like process. This is shown to drastically limit leaching during the process. The heterogeneous Fenton-like oxidation exhibits several advantages over the homogenous one. The most highlighted superiority of the heterogeneous Fenton oxidation is that there is no need for an acidic medium for reaction initiation & proceeding. Recently, the application of various nanocatalysts for heterogeneous Fenton-like degradation of the various pollutants from industrial wastewaters has received great attention [61-70].

The volume fraction of incorporated nanocatalyst plays a key role in determining the final efficiency. For instance, Sun et al. [54] addressed the influence of nano-Fe_3O_4 catalyst concentration in a Fe_3O_4/H_2O_2 system. They have reported the tremendous role of nano-Fe_3O_4 catalyst concentration during the homogeneous Fenton-like degradation of compound carbamazepine (CBZ) from the polluted wastewater, where the degradation efficiency increases with increasing the Fe_3O_4 concentration, followed by reaching a steady state. Besides, the influence of the amount of H_2O_2 should not be neglected since a similar trend in degradation efficiency by changing the Fe_3O_4 content has been attained for H_2O_2 dosage. In the present survey, it can be seen a direct relation between Fe-substituted zeolite nanocatalyst concentration and COD removal efficiency (see Table 2). Scheme 1 illustrates the proposed mechanism of COD removal by means of a heterogeneous nano-Fenton-like oxidation process.

According to the literature, the surface which serves as a platform for a heterogeneous Fenton-like process can contribute to the formation of hydroxyl radicals via a chelating agent, thereby improving the removal performance of the reaction [71].

Apart from homogenous Fenton process, H_2O_2 concentration can also determine the overall performance of the employed heterogeneous Fenton-like process, where Li et al. [72] reported that COD removal efficiency using heterogeneous UV-Fenton technique increases with an increase in H_2O_2 concentration followed by a descending trend with further increment in H_2O_2 concentration. Moreover, solution pH affects the concentration of H_2O_2 needed for COD removal. For example,



Scheme. 1- The proposed mechanism of COD removal by means of a heterogeneous nano-Fenton-like oxidation process.

a low dosage of H_2O_2 would be needed if solution pH is adjusted at 7, which is a favorable industrial condition in terms of cost management. Notably, the heterogeneous Fenton-like process that benefits nanocatalysts profoundly decreases the dosage of H_2O_2 compared to the conventional Fenton process. [73, 74].

5. Conclusions

The present investigation strives to draw a meaningful comparison between the metalworking fluid (MWF) wastewater chemical oxygen demand (COD) removal ability of three different methods, including coagulation-flocculation, Fenton oxidation, and heterogeneous nano-zeolite catalyzing Fenton-like oxidation processes.

The results indicated that a heterogeneous Fenton-like oxidation process benefiting easy-to-made low-cost nanocatalyst gives the highest COD removal efficiency. This method ends up in the lowest sludge volume, while the coagulation-flocculation route produced maximum sludge production.

A survey on the effects of nanocatalyst dosage and solution pH on COD removal efficiency revealed that a superior COD removal performance is achieved with an increase in nanocatalyst dosage, while the removal efficiency is not related to the solution pH. Moreover, this method preserves its high efficiency up to 20 batches. The use of nano Fe-substituted zeolite catalyzing heterogeneous Fenton-like process not only eliminates the requirement for decreasing the pH value of the treated solution to strongly acidic amounts but also decreases the volume fraction of the produced sludge. Therefore, it overcomes two potential challenges facing the conventional Fenton process. It seems that the heterogeneous Fenton-like oxidation process is a promising approach for remediation of MWF wastewater from the economic, technical, and environmental points of view.

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