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Degradation of tetracycline in Fenton and heterogeneous Fenton like processes by using $FeNi_3$ and $FeNi_3/SiO_2$ catalysts

Behnam Barikbin[a,b], Fatemeh Sadat Arghavan[c], Amina Othmani[d], Ayat Hossein Panahi[e], Negin Nasseh[a,*]

[a]*Social Determinants of Health Research Center, Birjand University of Medical Sciences, Birjand, Iran, emails: negin_nasseh@yahoo.com (N. Nasseh), b_barikbin@yahoo.com (B. Barikbin)*
[b]*Social Determinants of Health Research Center, Mashhad University of Medical Sciences, Mashhad, Iran*
[c]*Student Research Committee, Faculty of Health, Mashhad University of Medical Sciences, Mashhad, Iran, email: fatemeh.arghavna71@mail.com (F.S. Arghavan)*
[d]*Department of chemistry, Faculty of Sciences of Monastir, University of Monastir, Avenue of the Environment, 5019 Monastir, Tunisia, Tel. +21626554812; email: othmaniamina@gmail.com (A. Othamani)*
[e]*Social Determinants of Health Research Center, Birjand University of Medical Science, Birjand, Iran, email: ayatpanahi@yahoo.com (A. Hossein Panahi)*
[f]*Social Determinants of Health Research Center, Faculty of Health, Environmental Health Engineering Department, Birjand University of Medical Sciences, Birjand, Iran,*

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ABSTRACT

This paper aims to investigate the efficiency of Fenton ($FeNi_3/H_2O_2$) and heterogeneous Fenton-like ($FeNi_3/SiO_2/H_2O_2$) catalytic processes in the degradation of tetracycline from simulated wastewater. The effect of pH, initial concentration, catalyst dosage, hydrogen peroxide concentration, and time were evaluated. Results showed an increase in the percentage of degradation of tetracycline following the increase of the dose of catalysts and the concentration of hydrogen peroxide. The highest removal efficiency of tetracycline was obtained at neutral pH, in presence of 0.1 g/L of catalyst and 200 mg/L of hydrogen peroxide after 180 min. Furthermore, the kinetics of degradation reactions followed the first-order model. Results demonstrated the efficiency of the used nanocatalysts $FeNi_3$ and $FeNi_3/SiO_2$ on the degradation of the sewage containing antibiotic tetracycline by Fenton and heterogeneous-like Fenton processes. Furthermore, they confirmed the possibility of their recycling. Scanning electron microscopy, transmission electron microscopy, X-ray diffraction, and vibration sampling magnetometer were used for the characterization of the synthesized nanocatalysts.

Keywords: Tetracycline; Removal; Fenton; Heterogeneous Fenton-like process; Kinetics

1. Introduction

The presence of compounds and drug residues in the environment, especially in water resources, presents a major issue due to their persistence and degradability [1]. Antibiotics along with household (domestic) wastewater, pharmaceutical industries wastewater, hospital waste, veterinary clinics, agricultural products, and fish farming ponds significantly enter into water resources and environment [2,3]. Tetracyclines are the second most common group of antibiotics in terms of production and consumption worldwide [4]. The presence of these antibiotics in the environment, such as the aqueous environment, causes various reactions from simple allergies to direct toxicity in some cases. Moreover,

* Corresponding author.

tetracycline has destructive effects on microbial respiration, the nitrification process, and the recovery of iron 3 in the soil environment [4–7]. Therefore, due to the high consumption of antibiotics, their concentrations increase and therefore threaten the water quality. So far, physical, chemical, and biological methods have been used to minimize the harmful effect of these toxic pollutants from aqueous environment. Adsorption methods, electric coagulation process, membrane process, chlorination, chemical coagulation, and ion exchange are massively used for the removal of these compounds [8]. However, because of low efficiency, investment cost, difficult management, and maintenance, these methods are not economical. Furthermore, some of these methods have disadvantages such as producing a lot of sludge, high consumption of chemicals [9], destroying antibiotics only in a low concentration and long-time requirement to remove pollutants [10]. The advanced oxidation process (AOPS) has attracted great attention in recent decades due to the production of active radicals such as hydroxyl to oxidize organic compounds and purification of drinking waters [11,12]. The traditional Fenton system is one of the processes that have been used since its discovery. This process does not require special equipment, the use of iron salts and hydrogen peroxide (H_2O_2) is economical and environmentally friendly [13]. However, they have some disadvantages that should not be overlooked; for example, the homogeneous Fenton catalytic process requires many iron ions. Moreover, the catalysts used in the homogeneous Fenton process are difficult to be isolated and the hydroxyl radicals produced in the process increase the concentration of iron ions rapidly, somehow considered as secondary pollutants and, thus, high chemical material is wasted [14]. Being limited to acidic pH is the main limitation of the homogeneous Fenton process. Furthermore, in many cases, homogenous catalysts in the Fenton process require additional energy from external sources such as electricity, sonication, ultraviolet light, etc. for speeding up the process, which accordingly will increase costs [15,16]. Nowadays, studies have mostly focused on Fenton and heterogeneous Fenton-like processes, where solid catalysts with metal base are used instead of iron ions in the homogeneous Fenton processes [17]. The amount of sludge produced by this process is adjustable and does not need purification. Most Fenton and Fenton-like heterogeneous catalysts are porous materials (in nano or micro size); therefore, due to their porous nature, the pollutants may be adsorbed onto the catalyst surface [18]. Moreover, catalyst recovery is among the other advantages of heterogeneous Fenton-like processes so that they can remain stable even when used several times. Recently, new materials and solutions have been introduced for wastewater treatment with the introduction of new technologies such as nanotechnology [17–19]. Important reagents in the oxidation of antibiotics are high-capacity metals, non-metal oxidants, mineral salts, and organic peroxides [16]. However, despite these benefits, these compounds have some drawbacks such as high solubility in polar solvents and low effective surface area. Many efforts have been made to put these compounds on porous solid surfaces such as zeolite, silica, and alumina, etc., aimed at overcoming these limitations. Although these levels increase the catalyst efficiency, the problem of recycling and reusing them is still not fully solved, and the traditional filtering and centrifuging methods must still be used and due to trapping the reactants and the product in the cavities of these preservatives, after several times of use, their catalytic activity decreases [14]. The use of magnetic nanoparticles catalytic systems has been considered to solve this problem, as magnetic nanoparticles, in addition of providing a large surface for reactive molecules, it is easy to separate and reuse with the aid of an external magnet after the termination of the reaction. It should be noted that it is necessary to make certain modifications on their surface to increase their applicability in different conditions [17]. Surface cover acts not only to protect magnetic nanoparticles against oxidation and degradation but also to further functionalization with specific compounds such as catalytic active materials [20]. Due to some properties such as relative ease of preparation, good environmental sustainability, and compatibility with other materials, silica is an appropriate option for coating nanoparticles. Silica coating not only protects the magnetic core but also prevents direct contact with the compounds attached to the silica surface, as well as unwanted combinations [12]. The coating of $FeNi_3$ nanoparticles with SiO_2 can effectively improve the electrical resistance of materials in high-frequency operations [21,22]. So far, various methods have been used for preparing nanoparticles of magnetic alloys and their nanocomposites. However, many of them require severe and inappropriate conditions, such as high pressure, high temperature, vacuum, or H_2. In fact, much concern is related to evaluating the hazards of Fe nanoparticles. Although Nickel nanoparticles cause allergies and dermatitis, no report has been made on the harmfulness of $FeNi_3$ nanoparticles. In this study, $FeNi_3$ nanoparticles were prepared with hierarchical structures using polyethylene glycol (PEG) [20]. Therefore, the purpose of the present study is to evaluate and compare the efficiency of $FeNi_3$ and $FeNi_3$/SiO_2 nanoparticles in the degradation of tetracycline antibiotics in the processes of Fenton ($FeNi_3/H_2O_2$) and heterogeneous Fenton-like ($FeNi_3/SiO_2/H_2O_2$), respectively.

2. Materials and methods

2.1. Chemicals

For the synthesis of $FeNi_3$ nanoparticles and $FeNi_3/SiO_2$ magnetic nanocomposite, materials such as PEG (1.0 g MW 6000), $NiCl_2$ ($6H_2O$) nickel chloride, bivalent $FeCl_4$ ($4H_2O$), sodium hydroxide (NaOH), hydrazine hydrate ($N_2H_4{\cdot}H_2O$) with a purity of 80%, tetraethyl orthosilicate (TEOS) with molecular formula ($SiC_8H_{20}O_4$), ammonia (NH_3) were used, all of which the products of Merck GmbH pharmaceutical company (Germany).

Different concentrations of contaminated solutions were made from an antibiotic solution. The specifications of tetracycline powder used in this study are presented in Table 1. It should be noted that deionized water was used to prepare solutions at all stages.

2.2. Characterization of the catalyst

The morphological characterizations of samples were determined by transmission electron microscopy (TEM) device Zeiss-EM10C-100 KV model (Germany) with a high resolution made in Germany with higher resolution and magnification. The determination of the shape, medium diameter, details of the surface of the nanocomposite, and

Table 1
Chemical characteristics of tetracycline used

Tetracycline	Molecular formula	Molecular weight (g/mol)	Solubility (mol/L)	pKa_1	pKa_2	pKa_3
TC	$C_{22}H_{24}N_2O_8$·HCL	480.9	0.041	3.2 ± 0.3	7.78 ± 0.05	9.6 ± 0.3

the synthesized nanoparticle were performed using the field scanning electron microscopy (FESEM) with SIGMA VP-500 made by ZEISS, Germany. The determination of the composition and characteristics of the nanocomposite crystalline structure were done by X-ray diffraction (XRD) characterizations using an X-ray diffractometer Panalytical's X model device made by Pert Pro Company (Cambodia). The determination of the magnetic rate of the synthesized magnetic nanoparticle was carried out by magnetometer device with oscillating sample with a vibration sampling magnetometer (VSM) 7400 model.

2.3. Synthesis of $FeNi_3$ nanoparticle

The nanoparticles were synthesized according to Nasseh et al. [23]. First, 1 g of PEG 6000 was dissolved in 300 mL of deionized water. Then, 1.4 g of nickel chloride and 0.6 g of iron chloride were dissolved in two containers containing 30 mL of deionized water separately and added to the first solution. After perfect mixing, using sodium hydroxide 1 normal, the pH of the solution in an alkaline limitation was adjusted from 12 to 13, and then 27 mL of hydrazine hydrate (N_2H_4·H_2O) was added to the prepared suspension. The reaction was carried out for 24 h at room temperature and during this time the pH was regularly monitored to maintain the desired range [24].

2.4. Synthesis of $FeNi_3/SiO_2$ nanocomposite

$FeNi_3$ alloy is a magnetic material widely used due to its high saturation magnetism, high permeability, high temperature, and low energy losses. However, these nanoadsorbents are easily oxidized and rust, thus, the researchers generally used functionalized polymers, antioxidants materials, or metal oxides. Silica coating prevents iron oxidation. Moreover, the silica coating can provide the context for corrections in the nanoparticle surface by creating Si–OH groups. For this purpose, after the synthesis of $FeNi_3$, this magnetic nano-core was core shelled with SiO_2 [20,24]. Then, 0.5 g of synthesized $FeNi_3$ magnetic nanoparticles in a mixture containing 80 mL of ethanol and 20 mL of deionized water and 2 mL of ammonia of 28% was dispersed. Then, 1 mL of TEOS was added to the previous solution and was stirred at 300 rpm for 24 h at room temperature. Finally, the $FeNi_3/SiO_2$ magnetic nanoparticle obtained was washed several times with water and ethanol. The synthesized nanocomposite was dried in a vacuum oven at 353.15 K for 8 h after separation by an external magnetic field [25].

2.5. Experiments of adsorption and degradation of TC

The stoke solution used in this study was prepared by solubilizing tetracycline hydrochloride salt ($C_{22}H_{24}O_8N_2$·HCL;

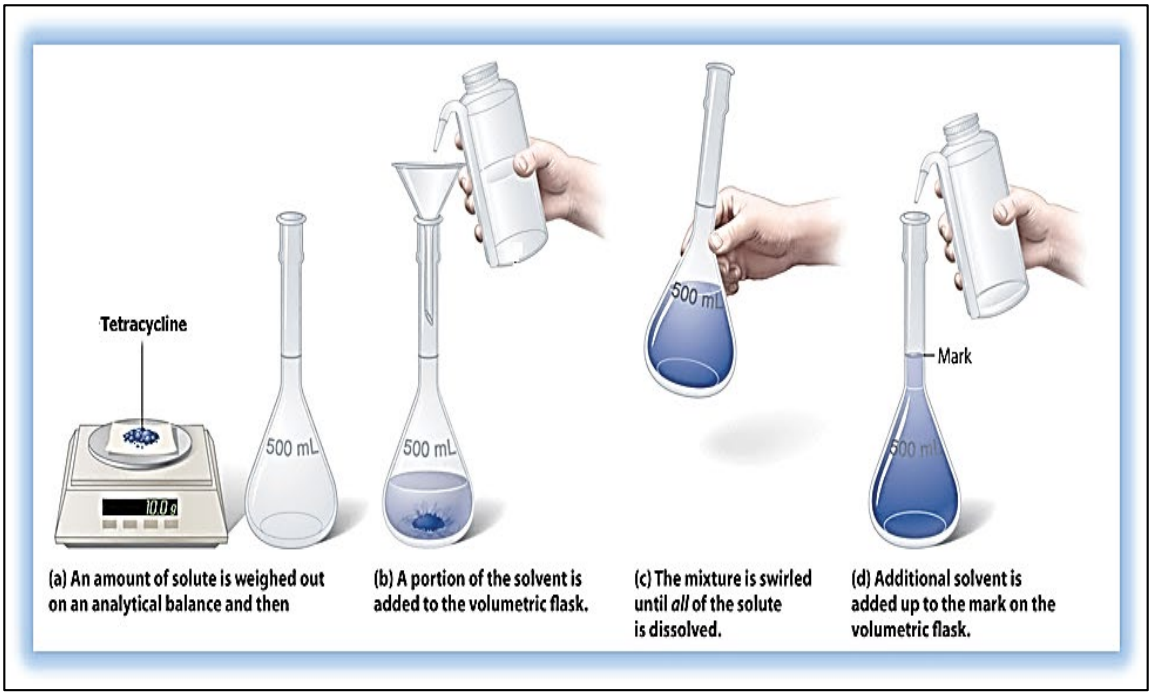

Fig. 1. Experimental method used for the preparation of tetracycline acetone solution.

purity higher than 95% and obtained from the Sigma Aldrich Company, United Kingdom) in deionized water. This solution was made weekly and was stored in the dark at 277.15 K in the refrigerator.

The variables studied were pH (3, 5, 7, and 9), initial concentration of tetracycline (10, 15, 20, 25, and 30 mg/L), contact time (5, 10, 15, 30, 60, 90, and 200 min), the value of magnetic nanocomposite (0.005, 0.01, 0.02, 0.03, 0.04, 0.05, and 0.1 g/L), and hydrogen peroxide concentration (50, 100, 150, and 200 mg/L). It should be noted that a magnetic stirrer (COMBI-Shaker, NB-101MT, France) at 350 rpm was used to mix the samples and pH meter model (Knick, Calimatic) was used for the adjustment of pH with NaCl and NaOH (0.1 Na). All experiments were carried out in a discontinuous system at room temperature (273.15 K) on 400 mL specimens. In the next step, these synthetic materials were used as a catalyst in the presence of hydrogen peroxide for the degradation and removal of this antibiotic. It should be noted that in the samples containing hydrogen peroxide immediately after sampling, 200 μL of $Na_2S_2O_3$ 0.2% solution was used to minimize the interference effect of H_2O_2 in the results [26]. All experiments were done in a discontinuous system at room temperature (273.15 K). The samples were extracted from the reactor at specified intervals using a sampling tap.

After separating the nano-composite by a magnet, the remaining tetracycline concentration was measured using a spectrophotometer device (T80 + UV/visible) at λ = 358 nm [27] verifying the law of the Beer–Lambert with a correlation coefficient (R^2) equal to 0.999.

$$R\% = \left[\frac{\left(C_0 - C\left(t\right)\right)}{C_0}\right] \times 100 \tag{1}$$

where C_0 and C_t, respectively, are the initial concentration and the final concentration of mg/L [28,29].

$$q_e = \frac{V}{M} \times \left(C_0 - C_t\right) \tag{2}$$

where q_e is the adsorbent equilibrium capacity in mg/g; V is the volume of solution in L, M is the adsorbent mass in g, C_0 and C_t, respectively, the initial concentrations and final concentration in mg/L [30,31].

2.6. Effect of kinetic study

The determination of the kinetics of reaction rate was performed in order to investigate the catalytic processes for treating wastewater, especially pharmaceutical wastewater.

Based on results obtained, the pseudo-first-order model described well the photocatalytic degradation of various organic compounds, especially antibiotics. Generally, the reaction rate for the removal of pollutants, such as heterogeneous catalytic processes, as well as photocatalytic processes, are described by Langmuir–Hinshelwood (L–H) under the conditions of the kinetic model illustrated in Eq. (3).

$$r = k'\theta = -\frac{dC}{dt} = k'\left(\frac{KC}{1+KC}\right) \tag{3}$$

where r is the oxidation reaction rate (mg/L/min), k' is the of the reaction rate constant (1/min), C is the pollutant concentration (mg/L), K is the adsorption coefficient of reactant (mg/L), and θ equals the reactor site. For solutions with very low concentrations (such as drugs in water) with $K << 1$, the L–H [Eq. (1)] is simplified into a first-order kinetics law (PFO) as illustrated in Eqs. (4) and (5).

$$\frac{dC}{dt} = k_{obs}C \tag{4}$$

$$\ln\left(\frac{C}{C_0}\right) = -k_{obs}t \tag{5}$$

where k_{obs} is the constant pseudo-first-order reaction observed (1/min), t is the time for reaction (min), C is the remaining concentration after the given time, and C_0 is the initial concentration of the pollutant in terms of (mg/L) [32].

3. Results

3.1. Characterization of catalyst

Fig. 3a presents the FESEM images obtained for the surface morphology of the synthesized nanoparticles $FeNi_3$ and $FeNi_3/SiO_2$. The micrographs obtained from the synthesized materials are well defined and showed an increase in the particle size from the beginning of synthesis to the end. The average particles sizes is 45.02 and 47.31 nm,

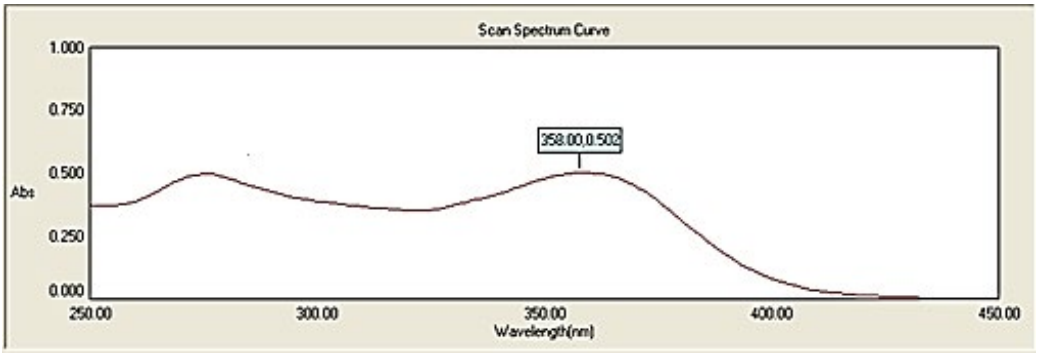

Fig. 2. UV spectrum of 20 mg/L of tetracycline solution at the wavelength λ = 358 nm.

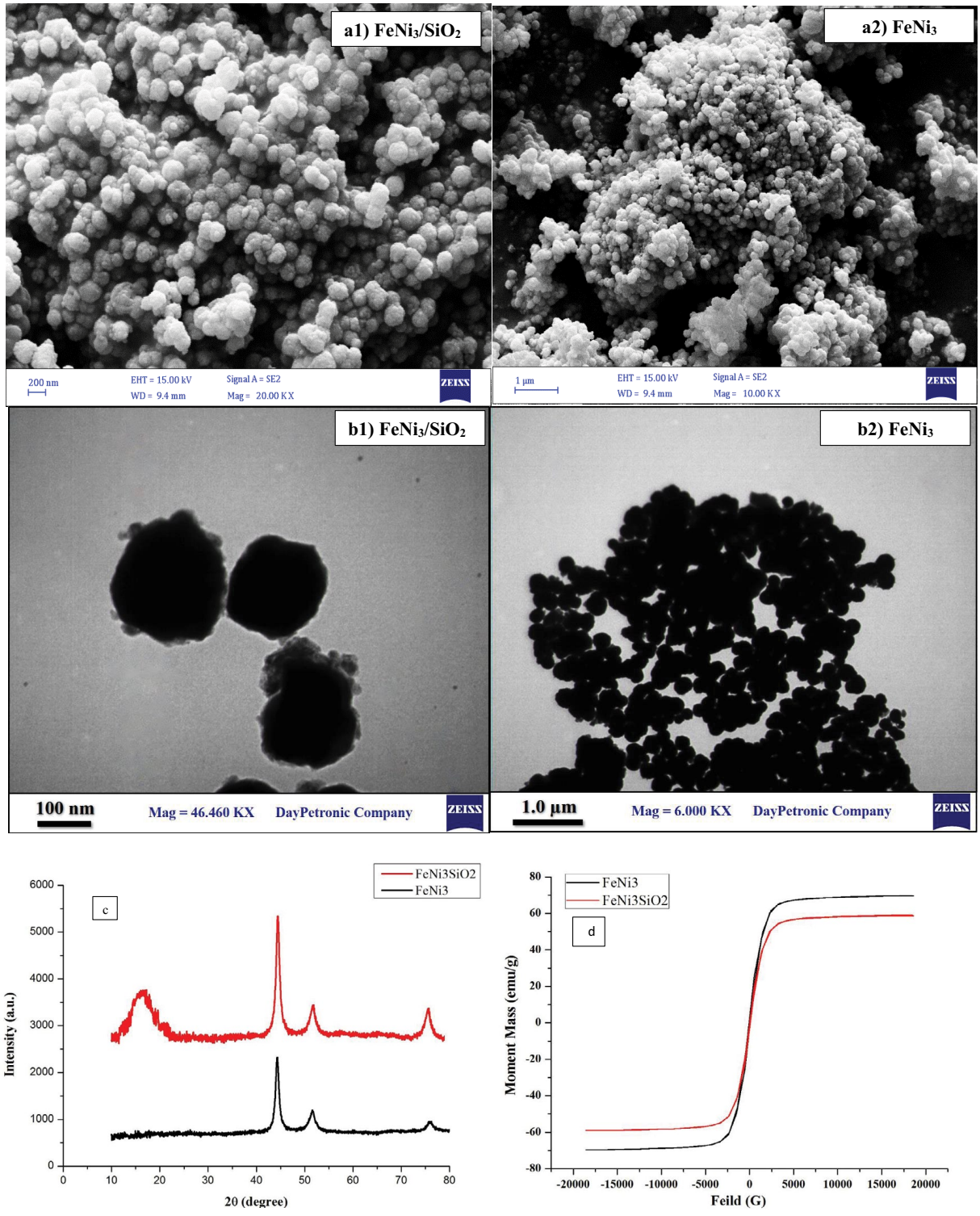

Fig. 3. Specifications of nanoparticles synthesized in the present study (a) FESEM ((a1) $FeNi_3/SiO_2$ and (a2) $FeNi_3$), (b) TEM ((b1) $FeNi_3/SiO_2$ and (b2) $FeNi_3$), (c) XRD, and (d) VSM.

respectively the $FeNi_3$ (Fig. 3a$_2$) and $FeNi_3/SiO_2$ (Fig. 3a$_1$). Based on these observations, it is clear that the materials have a massive property that tends to an accumulation or an aggregation. This agglomeration mode can be related to their magnetic property; which facilitated the adsorption of different pieces or particles of matter and allowed their placement side by side.

As for Fig. 3b, it presents the TEM images of $FeNi_3$ and $FeNi_3/SiO_2$ nanoparticles with different magnifications of 6,000 and 46,460 kx (the image of the samples are taken

from a closed surface and the shape of their materials do not change). Results obtained indicated that the magnetic nanoparticles synthesized are formless or amorphous. Therefore, a regular structure is not recommended for them. In addition, it can be clearly seen that the texture of the materials is densely packed and has a high density in terms of compressibility.

Fig. 3c, presents the XRD pattern of the crystal structure of $FeNi_3$ obtained at 2θ equal to 75.5°, 51.7°, and 44.5°, respectively, for the 10°–20° wide peaks confirmed the presence of amorphous silica, in the $FeNi_3/SiO_2$ nanoparticle. The size of the synthesized nanoparticles was determined by Scherrer's equation, where the most intense peak of diffraction was obtained at 23 and 31 nm in terms of full width in half the maximum (FWHM). Since results obtained FESEM analysis are more precise, the resulting nanoparticles tend to accumulate due to their magnetic properties, therefore, the size of the particle is larger than the one calculated by Scherrer's equation.

The magnetic properties of nanoparticles synthesized are also studied using vibrating sample magnetometer (VSM) at room temperature. Fig. 3d presents the main results obtained. The curves indicated that the synthesized magnetic nanoparticles and nano-composite from the beginning to the end of synthesis have reduced the magnetic saturation, as the amount for $FeNi_3$ and $FeNi_3/SiO_2$ is 68.52 emu/g, 99.58. However, the reduction of the final material has acceptable magnetic properties. Accordingly, one can conclude that the nanoparticles studied are dispersed in water and can be easily collected by means of an external magnetic field within a short time, and then can be separated again with a slight flicker.

3.2. Degradation of tetracycline experiments

3.2.1. Effect of pH

pH is usually considered as one of the important factors in oxidation processes. In the present study, the degradation of tetracycline pollutant was done in the pH range of 3–9 using $FeNi_3/H_2O_2$ and $FeNi_3/SiO_2/H_2O_2$ processes. It should be noted that the use of hydrogen peroxide alone did not have a significant effect on the removal of pollutants under study. For tetracycline pollutant, it showed an efficiency of about 25%–30%. Therefore, the pH of the solution has an important role in the dissolution rate of the catalyst as well as its surface load and can have a great effect on the degradation of these antibiotics from aqueous environments in the Fenton catalytic and heterogeneous Fenton-like processes [33]. The efficacy of removing 20 mg/L of tetracycline at pH = 7 (for both processes $FeNi_3/H_2O_2$ Fenton and heterogeneous Fenton like $FeNi_3/SiO_2/H_2O_2$) using a catalyst dose of 0.02 g/L and 60 min was obtained 53.72% and 68.72%, respectively (Fig. 4). Consequently, the results show that the value of pollutant removal by the magnetic nano-catalysts in the Fenton and heterogeneous Fenton-like systems in the presence of hydrogen peroxide at pH = 3 is less than neutral activity. In addition, the pH of the solution can affect the properties of the surface of the catalysts. The pH_{zpc} of $FeNi_3$ and $FeNi_3/SiO_2$ magnetic nanoparticle in the neutral range reached respectively 6.64 and 7.5.

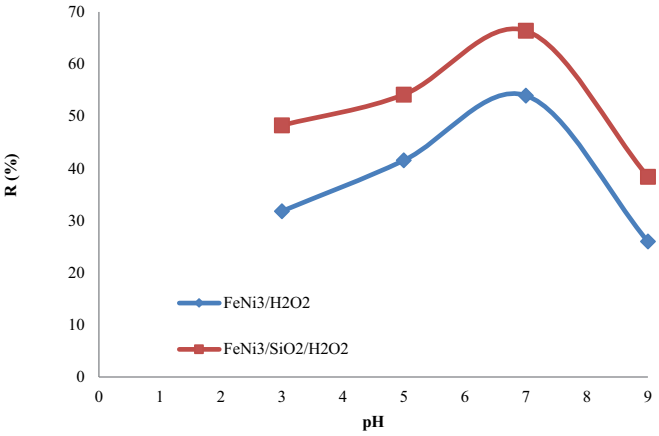

Fig. 4. Effect of pH on removal of tetracycline using Fenton and heterogeneous pseudo-Fenton processes (Tetracycline concentration 20 mg/L, catalyst mass 0.02 g/L, room temperature, and hydrogen peroxide concentration 150 mg/L).

At pH above the isoelectric point, the surfaces of nano-catalysts are negative and the hydroxyl groups available on nano-catalysts lose their positive charge and produce OH^- [34]. The ionized iron in these structures may be combined with OH^- groups and create the formation of iron hydroxide deposits, thus preventing the adsorption of sites. Therefore, at high pH, the proton deficiency will stop Fenton and Fenton-like reactions. When the pH of the solution is close to the pH_{zpc} of the $FeNi_3/SiO_2$ catalyst, the surface load of the nano-catalysts is completely zero [33]. This means that the adsorption or degradation of the contaminant on their surface is not carried out by electrostatic forces. Under these conditions, the activity of hydroxyl groups is more stable and thus, the elimination and degradation of tetracycline contamination is enhanced [34]. This mechanism can be a good reason for explaining the percentage of removal of tetracycline at neutral pH in the Heterogeneous Fenton-like processes. It should be noted that, at optimal pH, near to pH_{zpc} in $FeNi_3/SiO_2$ nanoparticle, OH^- groups could produce chelate (hybrid bands). Additionally, at pH lower than pH_{zpc}, a load level of catalysts is positive. In these conditions, the combined H^+ in water increases the hydroxyl groups of the desired catalysts levels and thus, hydrate increases their surface [16]. Additionally, reduction of pH produces OH^{2+} which causes the surface charge to be positive that results in a repulsive effect. The loose of positive charge at the catalysts level occurs when the pH of the solution is higher than pH_{zpc}, this behavior can be related to the decrease of their catalytic ability due to the reduction of radical hydroxyl. Therefore, the percentage of removal at this pH is due to the adsorption of pollutants onto the surface of the desired nano-catalysts. In acidic pH, the protonation occurs due to the increase of radical hydroxyl onto the surface of $FeNi_3$ and $FeNi_3/SiO_2$ nanoparticles [35]. Moreover, some previous studies specific to the catalytic heterogeneous Fenton-like processes with silica coating have revealed optimum pH in the neutral region related to the SiO_2 coating on the catalyst used in those studies [33].

Besides, in the catalytic systems of Fenton and heterogeneous Fenton-like $FeNi_3/SiO_2/H_2O_2$, a solid–liquid contact

surface will be created and will result in high adsorption of these two. It should be noted that the catalytic decomposition of H_2O_2 occurs onto the surface of the catalysts and the product of this degradation is OH radical with a great ability to oxidize contaminants. Many studies have been carried out on the removal of tetracycline in desired process, most of results showed that the highest removal efficiency was observed at neutral pH. In this regard, we can mention the studies by Hou et al. [6] and Zheng et al. [36].

3.2.2. Effect of $FeNi_3$ and $FeNi_3/SiO_2$ nano-catalyst dose

Experiments were conducted at pH = 7, a concentration of H_2O_2 concentration = 150 mg/L and a concentration of tetracycline concentration = 20 mg/L. In order to investigate the effect of doses of synthesized magnetic nano-catalysts on the value of desired pollutant degradation in Fenton and heterogeneous Fenton-like systems, the doses were varied from 0.005 to 0.1 g/L. Fig. 5 shows the percentage of catalytic degradation of tetracycline in the $FeNi_3/H_2O_2$ Fenton system and heterogeneous Fenton-like $FeNi_3/SiO_2/H_2O_2$ in different doses of nano-catalysts. As shown in these graphs, increasing the dose of nano-catalysts used in the catalyst processes leads to an increase in the percentage of pollutant removal, so that at a dose of 0.005 and 0.1 g/L $FeNi_3$ and $FeNi_3/SiO_2$ nano-catalysts the removal efficiency of tetracycline were obtained 45.91% and 50.21%, and 61.98% and 79.43%, respectively, after 180 min. Therefore, for a concentration of 150 mg/L of catalyst, there is an increase in the percentage of removal of tetracycline pollutants. This increase can be related to the presence of a hydrogen peroxide coupled catalyst. This behavior can explain the increase of the value of active sites available for the decomposition of hydrogen peroxide, which increased, in turn, the dose of nano-catalyst and the reactive oxidants such as radical hydroxyl [37].

Yang et al. [17] have studied the removal of methylene blue color using the catalytic nanoparticle Fe_3O_4/SiO_2 and reported similar results. This comparison well shows that the SiO_2 coating is vital for the catalytic process. Based on the literature, results achieved for the removal of various pollutants using a Fenton-like heterogeneous process have confirmed the obtained results of the present study [8,38]. Furthermore, Hou et al. [6] and Zheng et al. [36] have confirmed the results obtained for the degradation of tetracycline using the described process.

3.2.3. Effect of initial concentration and contact time

The effect of initial concentration of tetracycline contamination in Fenton and heterogeneous Fenton-like processes was investigated. Optimal conditions were chosen for this study; neutral pH, concentration range between 10 and 30 mg/L, catalytic dose = 0.1 g/L and concentration of hydrogen peroxide = 150 mg/L. Fig. 6 presents the effect of the variation of initial concentration of tetracycline in Fenton and heterogeneous Fenton–like processes. Based on the results shown in Fig. 6, there is an inversely proportional relationship between the initial concentration and the removal rate. The increase of the initial concentration of drug from 10 to 30 mg/L has caused the decrease of the removal rate with $FeNi_3/H_2O_2$ and $FeNi_3/SiO_2/H_2O_2$

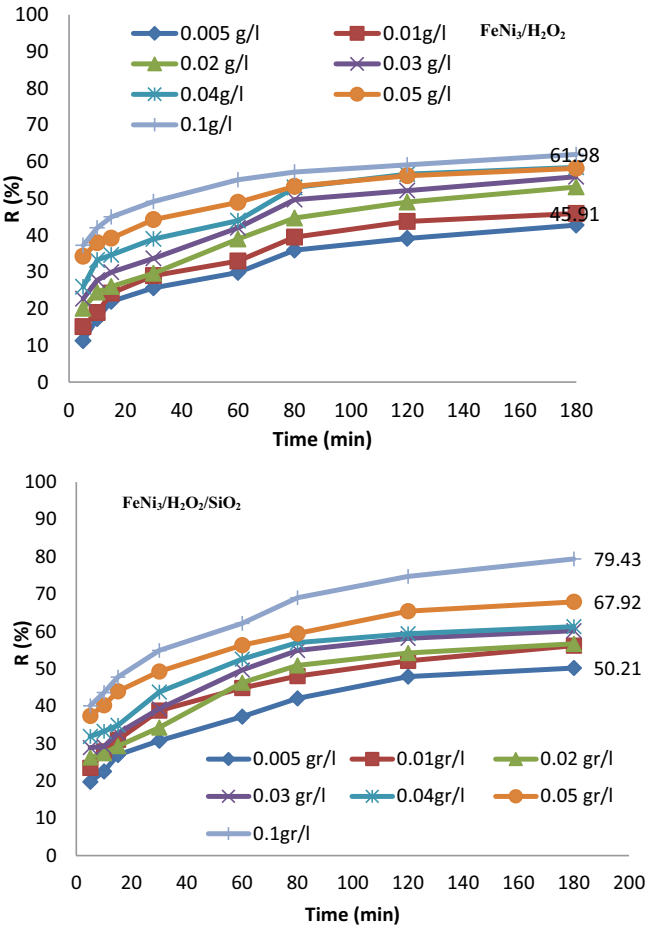

Fig. 5. Effect of nano-catalysts dose on tetracycline removal using Fenton and Heterogeneous Fenton-like processes (pH = 7, concentration of polluant = 20 mg/L, T = 273.15 K, and hydrogen peroxide concentration = 150 mg/L).

processes after 180 min of experimentations. The rate of removals passed from 85.26% to 52.1 % and from 36.94% to 64.53%, respectively for the Fenton and heterogeneous Fenton-like processes. This behavior can be explained by the fact that in all concentrations the value of catalyst ($FeNi_3$, $FeNi_3/SiO_2$), contact time, pH and H_2O_2 concentration is the same. Therefore, the same amount of produced radical of hydroxyl for degradation of pollutant was for all concentrations tested. Thus, the high percentage of removal of tetracycline will be obtained at low concentrations [15]. Additionally, for high concentrations, the presence of more pollutant molecules which can be adsorbed onto the surface of the nano-catalyst will increase in the adsorption of these antibiotics. Therefore, these last can play an inhibitory effect on their reaction with hydroxyl radicals, due to the reduction of direct time between them [39,40].

3.2.4. Effect of hydrogen peroxide concentration

The addition of hydrogen peroxide to heterogeneous Fenton-like catalytic process in most cases leads to an increase in catalytic oxidation rate. In order to maintain the efficiency of the added H_2O_2, the choice of H_2O_2

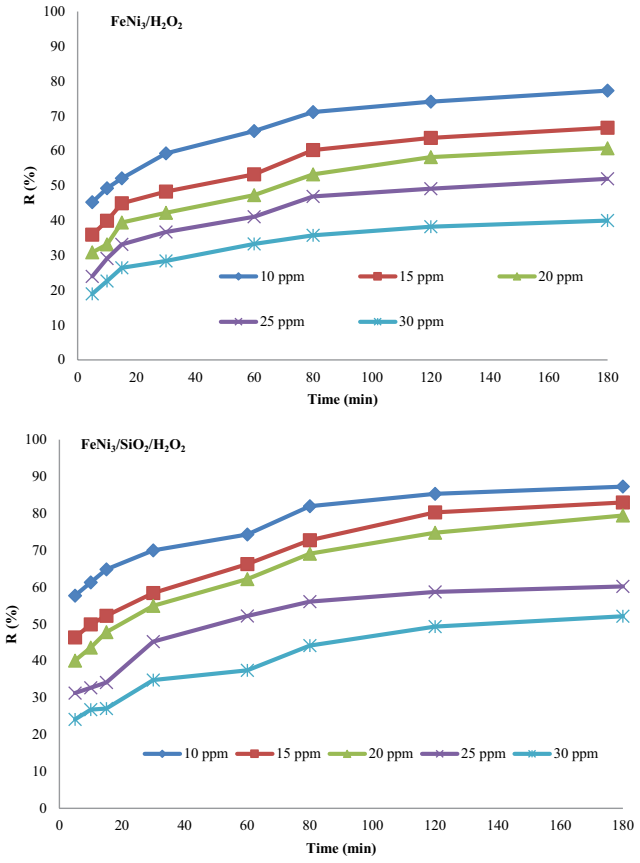

Fig. 6. Effect of initial concentration on the removal of tetracycline by Fenton and heterogeneous Fenton-like processes (pH = 7, concentration of nano-catalysts = 0.1 g/L, T = 273.15 K, and concentration of hydrogen peroxide = 150 mg/L).

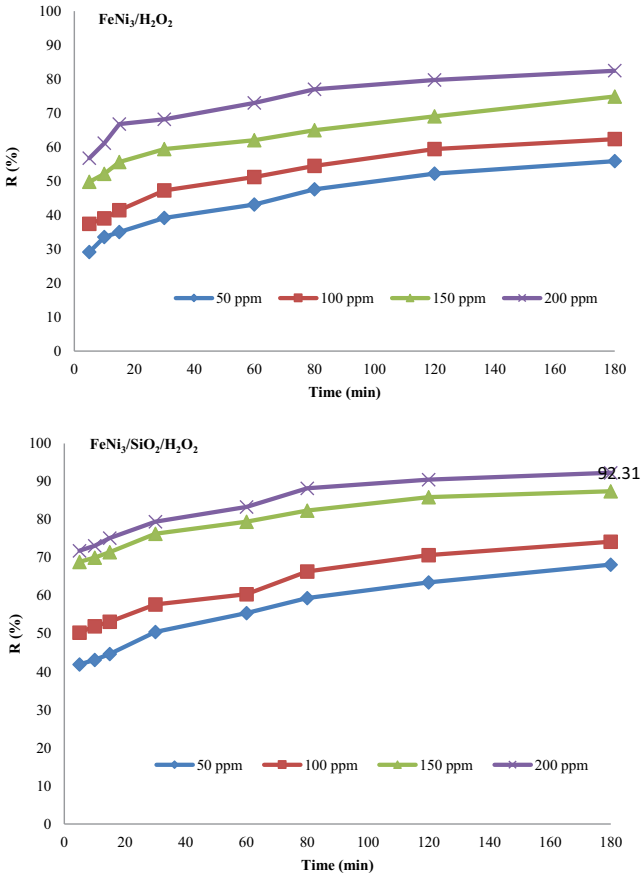

Fig. 7. Effect of hydrogen peroxide concentration on the removal of tetracycline by Fenton and heterogeneous Fenton-like processes (pH = 7, concentration of nano-catalyst value = 0.1 g/L, T = 273.15 K, and pollutant concentration = 20 mg/L).

concentration must be appropriate to the type and concentration of the contaminant. To examine the effect of H_2O_2 in the Fenton-like catalysis system of heterogeneous $FeNi_3/H_2O_2$ and $FeNi_3/SiO_2/H_2O_2$ on the removal of tetracycline; optimal conditions were fixed as follows: the dose of the nano-catalysts, $FeNi_3$, and $FeNi_3/SiO_2$ = 0.1 g/L, optimal pH, initial concentration = 20 mg/L and H_2O_2 pollutant varied from (200 and 150, 100, and 50 mg/L). As shown in Fig. 7 for the tetracycline contaminant, the percentage of removal has increased with the increase in the concentration of hydrogen peroxide. Therefore, the best dose of H_2O_2 was obtained for 200 mg/L of tetracycline. The increase in the percentage of removal of the pollutant can be explained by the increase in the concentration of hydroxyl radicals and the increase of the concentration of H_2O_2 from 50 mg/L upward. Therefore, the determination of the optimal value of hydrogen peroxide in the catalytic heterogeneous Fenton-like process is necessary for many reasons as mentioned below [15,37,38,41].

- An economical aspect related to the increase of the cost following the increase of the used concentration of hydrogen peroxide.
- Radical hydroxyl production decreases with the increase of H_2O_2 concentration (H_2O_2 which acts as a hydroxyl scavenger agent).
- The increase of chemical oxygen demand (COD) in the tested samples due to the presence of the remaining H_2O_2.
- Similar results were obtained in the previous researches [38,34].

3.3. Kinetics study

In order to study the kinetics of degradation of various antibiotic concentrations of tetracycline in the Fenton and Fenton-like processes; experiments were carried out under optimal conditions (nano-catalyst dosage = 0.1 g/L, contact time = 180 min, optimal pH, and hydrogen peroxide concentration = 200 mg/L). Results illustrated in Fig. 8 and Table 2 show that the pseudo-first-order kinetics model described well both reactions rates; it showed excellent results with acceptable expression coefficient (R^2) for all concentrations of pollutants tested. The constant reaction rate of both processes has increased with the increase in the used concentration of tetracycline. This can be due to the increase of the concentrations of intermediate products, reactive hydroxyl radicals. Chen et al. [2] and Eslami et al. [32] have calculated their reaction rate in different kinetic-degradation reactions in accordance with the pseudo-first-order model.

Table 2
First-order pseudo-kinetic parameters for the destruction of tetracycline at different concentrations in the $FeNi_3/H_2O_2$ Fenton and Fenton like $FeNi_3/SiO_2/H_2O_2$ processes

Concentration (mg/L)	Equation	K_0 (1/min)	R^2	$t_{1/2}$ (min)
$FeNi_3/H_2O_2$				
2	$Y = 0.0776x + 2.02$	77.6×10^{-3}	0.9766	8.93
5	$Y = 0.0553x + 1.7347$	55.3×10^{-3}	0.9954	12.53
10	$Y = 0.0237x + 1.601$	23.7×10^{-3}	0.9575	29.24
15	$Y = 0.0223x + 1.3188$	22.3×10^{-3}	0.9831	31.07
$t_{1/2} = 0.693/K_0$				
Concentration (mg/L)	Equation	K_0 (1/min)	R^2	$t_{1/2}$ (min)
$FeNi_3/SiO_2/H_2O_2$				
10	$Y = 0.0081x + 0.7645$	8.1×10^{-3}	0.9241	85.55
15	$Y = 0.0057x + 0.616$	5.7×10^{-3}	0.956	121.57
20	$Y = 0.0049x + 0.0.53$	4.9×10^{-3}	0.9171	141.42
25	$Y = 0.0034x + 0.4296$	3.4×10^{-3}	0.9347	203.82
30	$Y = 0.0027x + 0.3$	2.7×10^{-3}	0.9312	256.6

$t_{1/2} = 0.693/K_0$

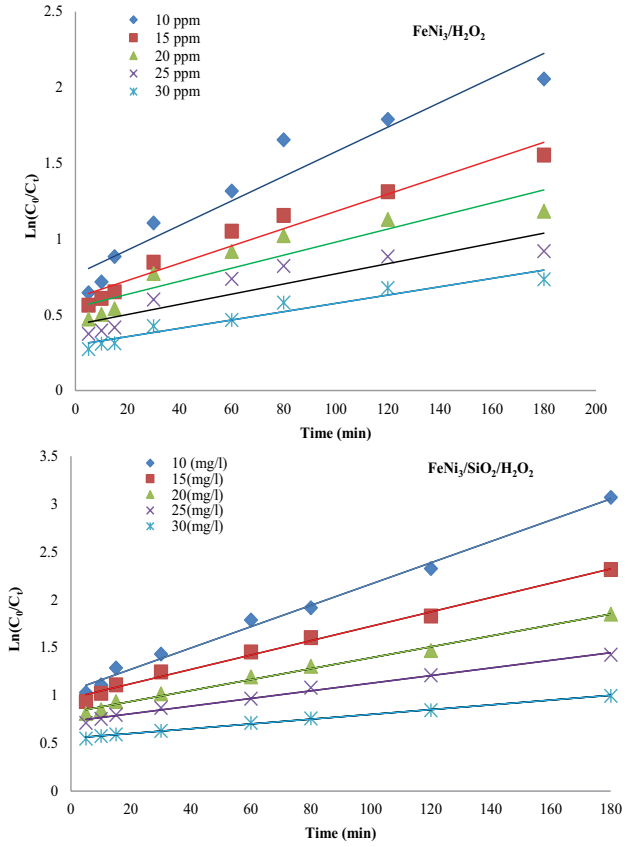

Fig. 8. Kinetic curves of the pseudo-first-order equation for the destruction of tetracycline at various concentrations in $FeNi_3/H_2O_2$ Fenton and pseudo-Fenton $FeNi_3/SiO_2/H_2O_2$ processes.

3.4. Sustainability and reuse of $FeNi_3$ and $FeNi_3/SiO_2$ nano-particles

Measuring the activity, stability, and reuse of solid catalysts is among the important and reviewed parameters [42]. Thus, some experiments were carried out to study the reuse of $FeNi_3$ and $FeNi_3/SiO_2$ synthesized nanoparticles as a catalyst in the presence of hydrogen peroxide in the degradation of tetracycline in 4 alternative cycles; and under conditions (tetracycline concentration = 20 mg/L, catalyst dose = 0.1 g/L, contact time = 180 min, and optimal pH). The desired nano-catalysts in each cycle were separated from the solution using N42 magnet and washed several times with deionized water and dried at 353.15 K in the vacuum oven and must be removed again in the next cycle. The synthesized nanoparticles were used as a catalyst in the presence of hydrogen peroxide during Fenton and heterogeneous Fenton-like processes to destroy tetracycline. The residual contaminant concentration was measured separately after each cycle, the results of which are shown in Fig. 9. According to the obtained results, it has been found that the catalysts used in the present study can be reused and recoverable. Therefore, after four cycles, their efficiency in tetracycline degradation did not significantly reduce. Furthermore, the removal efficiency has decreased slightly from the first cycle to the last cycle for the catalysts $FeNi_3$ and $FeNi_3/SiO_2$. The rates reached respectively were 7.7% and 6.14% which could be due to the reduction of nanoparticle mass over cycles. According to the obtained results, $FeNi_3$ and $FeNi_3/SiO_2$ can be considered as suitable catalysts in the elimination of pollutants in presence of hydrogen peroxide (Fenton process), thanks to their affordable use in terms of cost of operation and due to their high re-usability and good stability [43].

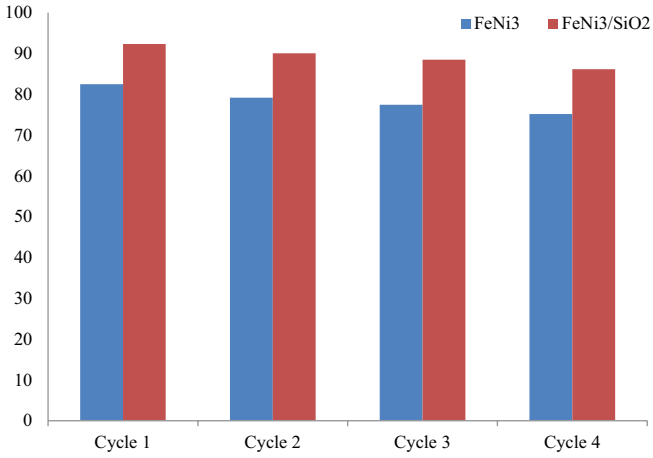

Fig. 9. Number of reusing cycles of $FeNi_3$ and $FeNi_3/SiO_2$ synthesized nano-particles in the destruction of tetracycline in the presence of hydrogen peroxide (pH = 7, concentration of nano-catalyst value = 0.1 g/L, T = 273.15 K, and pollutant concentration = 20 mg/L).

3.5. Removal of COD and TOC in optimal conditions

Fig. 10 shows the removal efficiency of total oxygen carbon (TOC) and COD of tetracycline synthetic contaminant over different times and under the optimal conditions (contaminant concentration = 20 mg/L, catalyst dose = 0.1 g/L, pH = 7, hydrogen peroxide concentration = 200 mg/L, and room temperature). As seen, the removal of tetracycline in the above conditions, respectively, in $FeNi_3/H_2O_2$ and $FeNi_3/SiO_2/H_2O_2$ processes reached about 82.46% and 92.31%, and the % of COD and TOC removals reached, respectively, 68.3% and 79.46%, 45.97% and 58.76%. The determination of TOC and COD were carried out using the methods 5310 B and 5220 D of the Standard Methods for water and wastewater tests. Following the Fenton and heterogeneous Fenton-like processes, the present study does not fully analyze the part of the antibiotic to be considered and it has reduced the removal efficiency of COD and TOC compared to the antibiotic removal efficiency of tetracycline by becoming organic intermediate products. In other words, one can state that the amount of antibiotics has been completely decomposed into the expected inorganic compounds of H_2O and CO_2, and in contrast, it has been transferred to the organic sub-products. In order to identify the intermediates, the GC device was used to analyze the samples. As shown in Fig. 11a, as using $FeNi_3$/SiO2 (heterogeneous Fenton-like)

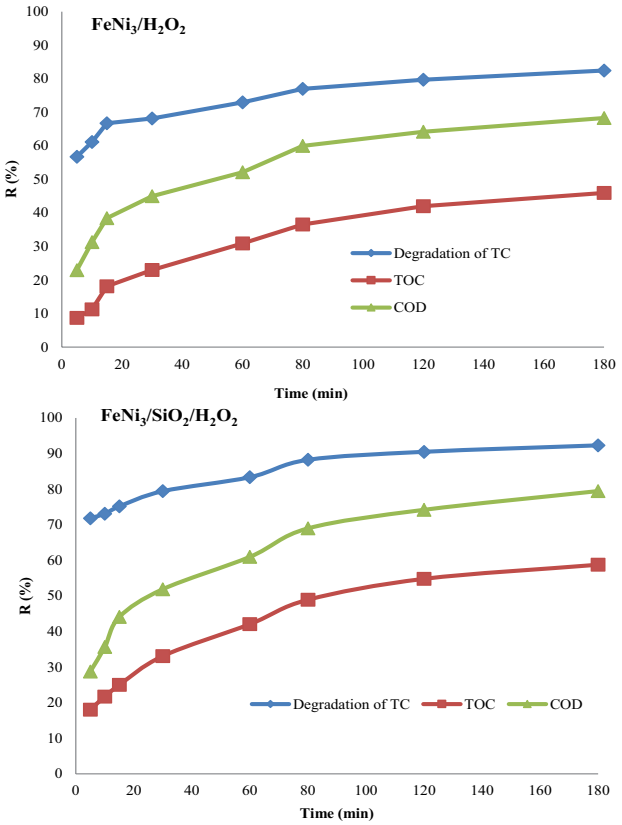

Fig. 10. Evolution of the % of removal of tetracycline, COD, and TOC as a function of Comparison reaction time (tetracycline concentration = 20 mg/L, catalyst dose = 0.1 g/L, pH 7, and 200 mg on liter hydrogen peroxide concentration).

four distinct peaks were generated which were corresponding to ((5-hydroxy-2-methylimidazol-1-yl)), nitroacetic acid methyl ester, 2-methyl-2-pentenal and, 4-methyl-2-pentenal. According to Fig. 11b, the results of TC degradation using $FeNi_3$ (Fenton process) showed four distinct peaks were generated which were related to 1,2-benzenedicarboxylic acid, 3,4-dimethyl-6 (2-methypropyl) decane, 2-methyl-3-ethyl-2-pentene and, 2-methyl-1-pentanol, respectively.

3.6. Mechanism for Fenton and heterogeneous Fenton-like processes

Based on results obtained during this study, a possible mechanism is proposed for Fenton-like degradation of tetracycline using $FeNi_3$ and $FeNi_3/SiO_2$ Catalysts

Table 3
Comparison of tetracycline removal efficiency with different catalysts

Used catalysts	pH	Dosage (g/L)	Tetracycline concentration (mg/L)	Time (min)	% of tetracycline removal	References
$Fe_3O_4/Na_2S_2O_8$/US	3.7	1	100	90	89	[45]
Fe/Co	7	0.6	30	180	86	[46]
Fe_3O_4@MSC	–	–	–	40	99.2	[47]
Fe_3O_4				60	93.6	[6]
$FeNi_3/SiO_2/H_2O_2$	7	0.1	20	180	92.3	Present study

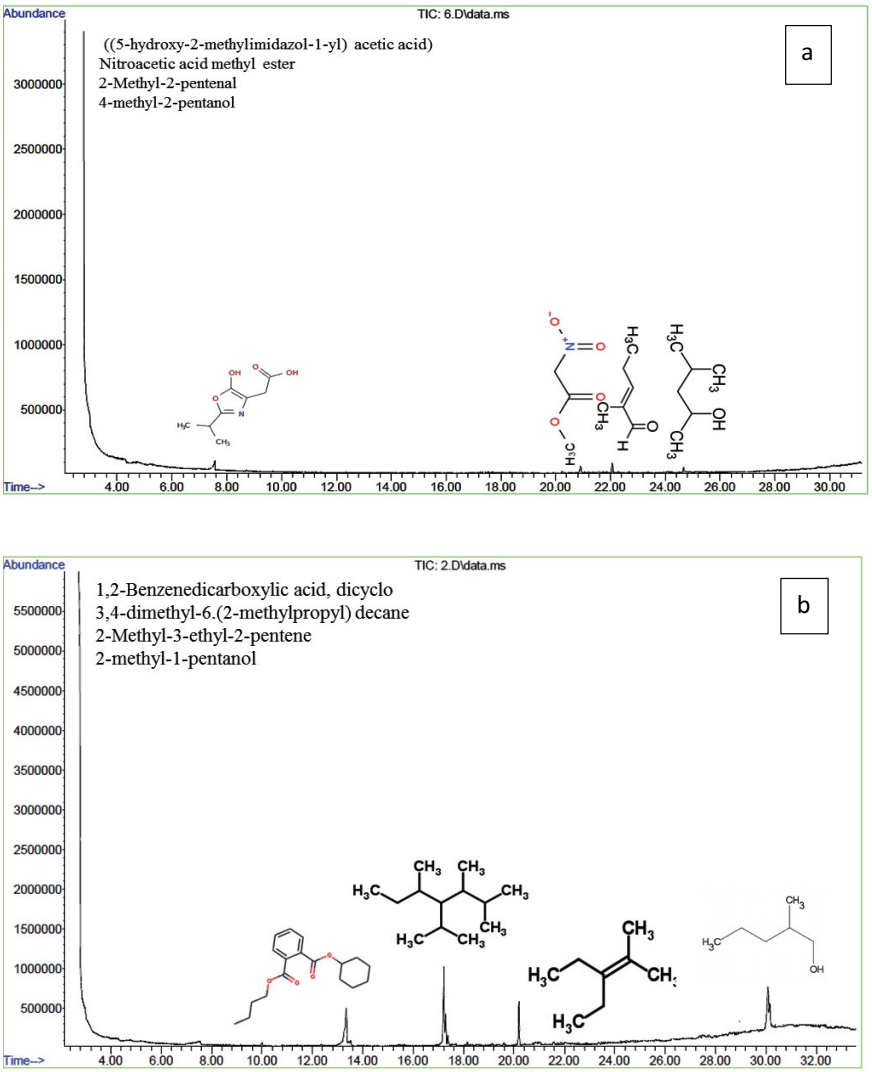

Fig. 11. Results of GC analysis of identification of intermediate compounds using $FeNi_3/SiO_2$ (a) and $FeNi_3$ (b) for TC degradation.

[Eqs. (6)–(9)]. At first, tetracycline adsorbs onto the surface of Fe nanoparticles. The presence of Fe^{3+} causes the decomposition of H_2O_2 and produces large numbers of OH radicals when Fe^{2+} was oxidized into Fe^{3+} by H_2O_2 [44].

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{3+}H_2O_2 \quad (6)$$

$$Fe^{3+}H_2O_2 \rightarrow Fe^{3+} + HO_2 + H^+ \quad (7)$$

$$Fe^{3+} + HO_2 \rightarrow Fe^{2+} + O_2 + H^+ \quad (8)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH + OH^- \quad (9)$$

Table 3 presents the comparison of tetracycline removal efficiency with different catalysts.

4. Conclusion

In the present study, we tried to synthesize $FeNi_3$ and $FeNi_3/SiO_2$ magnetic nanoparticles and evaluate their efficacy in the presence of hydrogen peroxide in antibiotic removal of tetracycline regarding the disadvantages of the homogenous Fenton system and the advantages of the Fenton and heterogeneous catheter Fenton-like systems. Several parameters were studied in order to determine the optimal conditions for the best removal efficiency of tetracycline by Fenton and heterogeneous Fenton processes. One of the desired goals was the decrease in the economic dose of the chemicals used during experimentations. Results confirmed the efficiency of the synthesized catalyst for ten removals for tetracycline. Moreover, the combined effect of synthesized magnetic nanoparticles in the presence of hydrogen peroxide during Fenton and heterogeneous Fenton-like processes can effectively eliminate tetracycline antibiotics under optimum conditions and can be used to remove antibiotics with similar structure and increase their biodegradability.

Therefore, this combined process can be used as a useful way to remove these emerging and severely degradable pollutants from water and sewage. Thanks to the super paramagnetic properties and uniform distribution of the

synthesized magnetic nano-catalysts encouraging results were achieved. Finally, experiments confirmed that the synthesized nanoparticles have the potential for high recycle and reuse.

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