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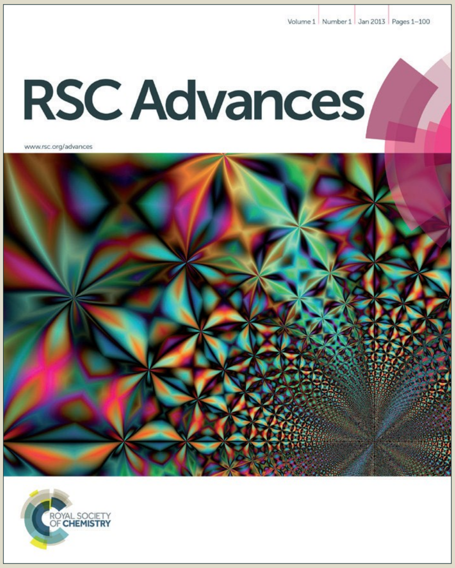

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Powder activated carbon/Fe_3O_4 hybrid composite as a highly efficient heterogeneous catalyst for Fenton oxidation of tetracycline: Degradation mechanism and kinetic

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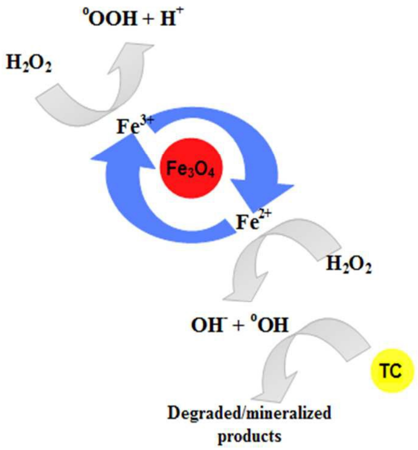
Graphical abstract



Abstract

In this work, we prepared and used a composite of powder activate carbon/Fe_3O_4 magnetic nanoparticles (PAC/Fe_3O_4 MNPs) as a heterogeneous catalyst to remove tetracycline (TC) from aqueous solution. By using XRD, BET, VSM, SEM, TEM and EDX techniques, also, we tried to characterize the catalyst. The effects of pH, H_2O_2, catalyst dosages and also initial TC concentration on the degradation process were assessed. Based on the results, it was indicated that at low pH values and initial TC concentrations, the efficiency of the process is higher than the other values and concentrations studied in this work. Under the ambient conditions and setting the initial pH value and TC concentration at respectively 3.0±0.2 and 10 mg/L, the optimal dosage of reagents were recorded to be 0.3 g/L catalyst and 80.0 mM H_2O_2. The values of observed rate constants, k_{obs}, increased by increasing the catalyst loading in the system; however, these values decreases when the initial TC concentration was increased. Our findings indicated that all of TC concentration was nearly degraded during the 180 min reaction. Regarding the reusability of PAC/Fe_3O_4 MNPs, the results showed that TC and TOC removal efficiencies of 94.5% and 32.3%, respectively, can be achieved after four consecutive runs. By conducting the stability experiments, it was confirmed that PAC/Fe_3O_4

MNPs is a promising and effective catalyst in Fenton reactions and can be used to treat TC-contaminated water with very low loss of catalytic activity.

Keywords: Fe_3O_4 MNPs; Heterogeneous catalysts; Kinetic, Tetracycline; Magnetic carbon; Reusability and stability

1. Introduction

Over the last decade, the pharmaceutical compounds have become an emerging group of organic pollutants. These products which are being used in human and veterinary medicine are now of environmental concern. The presence of these compounds, antibiotics in particular, in water resources can be considered as a serious threat to the public health and the environment. It should be noted that the antibiotics are of low biodegradability as well as high toxicity towards other organisms; and also, these compounds are highly soluble in water [1]. In addition, antibiotics, even at very low concentrations, adversely affect living organisms (i. e. algae and bacteria) [2]. Therefore, removing this compounds from aquatic media is highly important and necessary. Among the widely used antibiotics, tetracycline (TC) has been reported to be among the highest produced and used antibiotics around the world. TC has being widely used as veterinary medicine in treating infectious disease in relation to the gram-positive and gram-negative bacteria in human and animal [3, 4]. Furthermore, various concentrations of TC has been detected in wastewater, surface water and groundwater resources [5].

Several treatment methods, including adsorption/bioadsorption[1], coagulation-sedimentation[6], ozonation and biodegradation [7, 8] and advanced oxidation processes (AOPs) [3, 4] have been applied to remove TC from contaminated water resources. It should be noted that some of these processes have their own drawbacks, including high cost, inefficient removal, toxic byproducts, and excessive sludge production. In fact, most of these methods require further treatment to meet the standard level set for wastewater effluents [9-11]. AOPs involve the generation of highly active oxidizing species which attack and decompose organic components; in other words, the ability to generate such highly oxidizing species makes these processes more efficient, in comparison with other physically-based techniques (e. g. adsorption and flocculation) [12]. In this regard, Fenton and Fenton-like oxidation consisting of catalyst (Fe^{2+}/Fe^{3+}) and hydrogen peroxide (H_2O_2) have been reported to be one of the most effective techniques for degrading and mineralizing organic contaminants in wastewater [13, 14]. Fenton process, according to the following equations (1) and (2), is a way of producing hydroxide radicals, HO•, by a reaction between H_2O_2 as an oxidant and Fe^{2+}/Fe^{3+} ions as a catalyst[15]:

$$\mathrm{Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\bullet} + OH^{-}} \qquad (1)$$

$$\mathrm{Fe^{3+} + H_2O_2 \leftrightarrow Fe^{2+} + HOO^{\bullet} + H^{+}} \qquad (2)$$

The generated free radicals, HO•, are robust oxidant species reacting unselectively with organic compounds which results in the mineralization of these compounds into inorganic ions, CO_2 and H_2O [4, 15].

However, there are specific limitations regarding the application of Fenton processes. In other words, the homogeneous type operates in a narrow range of pH (2-4); besides, this type is uneconomical, and has particular problem regarding the separation and recovery of the ions after the catalyst treatment. It has also been reported that this process could generate secondary pollution (e. g. acid or metal ions) as well as metal hydroxide sludge [12, 13, 16]. In order to overcome previously mentioned problems, heterogeneous Fenton system can be applied. This method is based on using iron-containing solids (Fe_2O_3, Fe_3O_4, Fe^o, FeOOH etc.) and/or incorporating Fenton's catalyst onto surfaces of different carriers (e. g. activated carbon, zeolite, clay, multi-walled carbon nanotubes and polymer) [13, 15, 17-19].

Among iron oxide minerals, based on the reports of previously conducted studies, Fe_3O_4 magnetic nanoparticles (MNPs) are the most effective heterogeneous Fenton catalyst [20, 21]. Fe_3O_4 MNPs can decompose H_2O_2 which results in the formation of HO• as mentioned in Eq. (1). However, the Fe_3O_4 MNPs have a strong tendency to agglomerate due to intra-particle interactions (e. g. van der Waals and intrinsic magnetic interactions). This could decrease the surface/volume ratio of MNPs, and disperse their stability in the solution; in other words, when they become agglomerated, their catalytic activity reduces as well [22, 23]. Therefore, the agglomerated particles show a relatively lower catalytic capability, compared to their normal form in the solution. On one hand, the use of ultrasonic or UV light irradiation has been proposed to improve the rate of catalytic degradation reaction by other authors [24, 25]. On the other hand, these techniques require external energy input and additional equipment [24]. Powder activated carbon (PAC) as a supporting for Fenton catalysts can be considered as a promising and economical method due to its wide availability, low cost and high specific surface area and porosity [17]. By applying PAC, the performance of Fenton catalytic process regarding the adsorption of pollutants can be increased; and also, the separation of catalyst from aquatic media can be facilitated. In fact, this method has a greater flexibility for environmental applications, in comparison with the other methods.

Over the years, the magnetic composites have been considerably studied on to be used as heterogeneous catalyst in the Fenton and Fenton-like processes due to their highly acceptable reusability and stability, low toxicity and easy separation. Xu et al., [26] evaluated the catalytic activity of Fe_3O_4/CeO_2 composite for Fenton oxidation of 4-cholorophenol. Niu et al., [9] synthesized Fe_3O_4 NPs and used it as an effective heterogeneous photo Fenton catalyst for the oxidation of sulfathiazole. The authors found that humic acid coated Fe_3O_4 NPs are highly active and can effectively decompose H_2O_2 into HO• radicals. For Fe_3O_4-based catalyst systems, several heterogeneous catalysts have been applied, including Fe_3O_4-MWCNTs [27-29], Fe_3O_4/mesocellular carbon foam [30], Fe_3O_4-activated carbons [17], $Fe_3O_4@SiO_2$ [31] and Fe_3O_4/graphite oxide [32]. In several reviews, the main aspects and applications of magnetic catalysts regarding the heterogeneous catalytic reactions for the degradation of organic pollutants have been reported [18, 21].

According to these reports, magnetic carbon composites have unique catalytic properties and magnetism. These composites can improve electron transfer, and have higher surface areas as well as active sites, in comparison with the single magnetic catalysts [33, 34]. Regarding the magnetism property of these composites, this property enables these catalysts to be easily separated from the solution by using a magnetic field. Furthermore, they can be reused by dispersing them in the solution. Hence, the present work was aimed to load Fe_3O_4 MNPs on the outer surface of PAC (PAC/Fe_3O_4 MNPs) and apply this composite as a heterogeneous catalyst for removing TC from aqueous solution. Fenton heterogeneous catalyst was synthesized and then characterized by using SEM, TEM, BET, XRD and VSM techniques. The effect of various operational parameters on the removal efficiency of TC by PAC/Fe_3O_4 MNPs was assessed. It is noteworthy that these tests were conducted in a batch system. Moreover, the kinetics of TC removal as well as stability and reusability of the catalyst were also evaluated.

2. Materials and methods

2.1. Chemicals

All chemicals were of analytical grade. Ferric nitrate ($Fe(NO_3)_3.9H_2O$), nitric acid (65% HNO_3) and powder activated carbon (PAC) were used to prepare PAC-Fe_3O_4 MNPs catalyst. TC powder with 98% purity was purchased from Sigma-Aldrich and applied to prepare stock solution in DI-water. Other chemicals, including hydrogen peroxide 33% (w/v), oxalic acid, acetonitrile and methanol, were provided from Merck Co. (Merck, Darmstadt, Germany). All used solutions were prepared with highly pure DI-water. In order to adjust the pH of the solutions, hydrochloric acid 0.1 M (HCl) and sodium hydroxide 0.1 M (NaOH) (i. e. purchased from Merck CO.) were used.

2.2. Catalyst synthesis and properties

In this study, we synthesized PAC/Fe_3O_4 MNPs catalyst according to a chemical co-precipitation method; the procedure can be found in details in our previous work [35]. The specific surface area, pores volume and size of the catalyst were measured by Brunaeur, Emmett and Teller method (BET, Quantachrome, NOVA 2000); in this method, N_2 adsorption-desorption isotherms at 77.3 ^oK was used. The surface morphology of PAC/Fe_3O_4 MNPs and Fe_3O_4 distribution within the activated carbon were evaluated using a scanning electron microscopy (SEM, PHILIPS, XL-30) in 25 keV. In addition, the shape and size of Fe_3O_4 MNPs supported on the PAC were also evaluated by transmission electron microscopy (TEM) (PHILIPS, EM, 208), in 100 keV. An X-ray diffractometer (Quantachrome, NOVA 2000) was applied to assess the X-ray diffraction (XRD) pattern of PAC/Fe_3O_4 MNPs by using graphite monochromatic copper radiation (Cu Kα, λ=1.54 A^o) in the region of 10^o to 70^o at 25°C. Vibrating Sample Magnetometer (VSM, 7400, Lakeshare, USA) was also used to determine the magnetic property of catalyst in a magnetic field with ±10 kOe at 25°C.

2.3. Adsorption and degradation experiments

All the experiments regarding the adsorption and degradation of TC by synthesized catalyst were conducted in a batch system and under the ambient lab conditions ($T=25\pm1^oC$), using a cylindrical Pyrex vessel (500 mL) contained with 200 mL of TC solution. Certain amounts of catalyst was added into solution and placed on a shaker to achieve the adsorption/desorption equilibrium with an agitation speed of 250 rpm under the atmospheric pressure. After reaching to the equilibrium state, Fenton reaction was started by adding H_2O_2 to the solutions. It is noteworthy that before adding the H_2O_2 Fenton reagent, the initial pH of the solution had been adjusted to 5.5±0.3. Fenton oxidation experiments were carried out for a period of 180 min. At selected time intervals and during the reaction, 2mL of the sample from solution was extracted and then the catalyst was magnetically separated from the supernatant using an external magnetic field. Afterwards, in order to analyze the solution, 4 mL of 0.2 mol/L sodium thiosulfate ($Na_2S_2O_3$) solution was added immediately to the supernatant so as to prevent further reaction [36]. The samples were finally filtered using a 0.22 μm syringe filter before injection to high-performance liquid chromatography (HPLC) for measurement the residue of TC. The removal percentage of TC was calculated using Eq. (3). As a function of pH and various concentrations of catalyst, H_2O_2 and TC, we also studied the efficiency of Fenton process. Furthermore, stability and reusability of catalyst under obtained optimal conditions were investigated. The kinetics of TC degradation by PAC/Fe_3O_4 MNPs was also studied. It should be mentioned that the control experiments in which the catalyst was not added were conducted in parallel with the main ones. Each experiment was carried out in triplicate; and, the mean value of these tests was taken as the final result. It is noteworthy that the error bars in the figures were omitted for graphic simplicity except for the cases where they were necessary.

2.4. Analytic method

The concentration of TC in the supernatant was analyzed by using HPLC (model KNAUER) equipped with Ultimate variable wavelength UV detector. The mobile phase was a mixture of 70% 0.01 M oxalic acid, 20% acetonitrile and 10% methanol with a flow rate of 1.0 mL/min. The chromatographic column was a 5 μm 4.6 mm×250 mm 100-5 C18. The temperature of the column and the wavelength of UV detection 2500 were set at 25°C and 360 nm, respectively. The samples were injected into a 20 μL loop by a manual injector. The retention time of TC was 5 minutes. The calibration curve was produced at seven-levels (range 1-50 mg/L) for TC quantification. The mineralization of TC was evaluated by measuring the decay of the total organic carbon (TOC) using a TOC analyzer (model Shimadzu $V_{CHS/CSN}$, Japan). The mineralization percentage was calculated according to Eq. (4). In order to investigate the stability of catalyst, an atomic absorption spectrophotometer (AAS, Analytik jena vario 6, Germany) according to ASTM D1068-90 was used to measure the residual concentration of Fe in the samples [37].

$$\text{TC (re \%)} = \left(\frac{\text{TC}_i - \text{TC}_t}{\text{TC}_i}\right) \times 100 \qquad (3)$$

$$\text{TOC (re \%)} = \left(1 - \frac{\text{TOC}_f}{\text{TOC}_i}\right) \times 100 \qquad (4)$$

Where, TC_t and TC_0 are the concentrations of TC at reaction time t and 0 (mg/L), respectively; and also, TOC_i and TOC_f are respectively the TOC values at initial and final reactions of the heterogeneous Fenton process.

3. Results and discussion

3.1. Characterization of catalyst

The specific surface area of the catalyst and also its pores volume and size were measured using BET method with N_2 adsorption-desorption isotherms of 77.3 °K and $p/p_0 = 0.99$. As shown in Table 1, the specific surface area of the PAC/Fe_3O_4 MNPs was 671.2 m^2/g, which is lower than that of PAC (936 m^2/g). This difference can be due to the filling of the pores of PAC; in other words, Fe_3O_4 MNPs can fill the pores. The average size and pore volume of

PAC/Fe_3O_4 MNPs were around 3.5nm and 0.487 cm^3/g, respectively. According to IUPAC classification, the average size of 3.5 nm belongs to the mesopores groups [38, 39]. In addition, N_2 adsorption/desorption isotherm was between type II and type IV for prepared catalyst according to classification of the IUPAC, indicating that the structure PAC/Fe_3O_4 MNPs is typically porous (see Fig. 1(a)) [40].

In order to characterize crystal phase of iron oxide particles, we applied XRD in 2θ in the region of 10-80° at 25°C (λ=1.54 Å) to analyze the catalyst. Figure 1(b) indicates a broad diffraction peak at 2θ=22.5°, which can be attributed to the characteristic reflection of carbon amorphous nature. Six characteristic peaks for Fe_3O_4 (2θ =30.07°, 35.44°, 43.15°, 54.6°, 56.99°, and 62.6° marked respectively by (220), (311), (400), (422), (511), and (440) indices), were observed for both Fe_3O_4 MNPs and PAC/Fe_3O_4 MNPs patterns. Based on shown XRD pattern for Fe_3O_4 MNPs, the relative position and intensity of all peaks were in good agreement with the standard Fe_3O_4 diffraction data (JCPDS, Card No. 19- 0629). As it can be seen from Fig. 1 (b), all peaks which belong to carbon and Fe_3O_4 MNPs exist in the PAC/Fe_3O_4 MNPs pattern, indicating successful synthesis of Fe_3O_4 MNPs crystals in PAC.

Figure 2(a) shows the SEM image of PAC/Fe_3O_4 MNPs at 25 keV; and also, the TEM image of Fe_3O_4 at 100 keV is shown in Figure 2(b). The SEM image shows uniform distribution of the pores on the PAC surface and also appropriate porosity of the synthesized adsorbent. It also indicates that pores are relatively distributed in a uniform trend on the catalyst surface. The TEM micrograph of catalyst depicts the iron oxide particles with the average diameter of 30-80 nm and cubic structure, which is consistent with the results of the XRD analysis. Based on this result, it can be implied that Fe_3O_4 MNPs were successfully synthesized with nano-size.

The VSM magnetization curve of PAC/Fe_3O_4 MNPs at 25°C and in the magnetic field of ±10 kOe is shown in Fig. 2(c). The highest saturation magnetization which was obtained for catalyst before and after the process was 6.94 and 5.97emu/g, respectively. Figure 2 (c) shows typical S-type hysteresis loops with no residual magnetism or coercivity, suggesting that the PAC/Fe_3O_4 MNPs were super-paramagnetic. At the first run of using the catalyst, a 16% decrease was observed in the saturation magnetization of the catalyst, implying that there was not any remarkable change in the magnetic properties of PAC/Fe_3O_4 MNPs catalyst after the Fenton reaction. Considering this, the catalyst can be used for several times before its magnetization property become saturated. In addition, it should be noted that due to this property, the catalyst has a good magnetic response to the magnetic field (see Fig. 2(d)). Therefore, based on these results, it can be implied that the PAC/Fe_3O_4 MNPs can be easily and rapidly separated from solutions and potentially applied as a magnetic catalyst to remove contaminants from the aqueous environment.

3.2. TC removal

The percentage of TC removal by different materials was studied under identical experimental conditions. The experiments were carried out at neutral pH (pH=5.5±0.5) with initial concentration of 20 mg/L TC within 4 h at 25±1^{o}C. The results are shown in Fig. 3. We observed that after 180 min reaction, 6.2, 12.5, 36.3, 59 and 79.9 % TC were removed by H_2O_2, Fe_3O_4, Fe_3O_4+H_2O_2, PAC/Fe_3O_4 MNPs and PAC/Fe_3O_4 MNPs+H_2O_2, respectively. The removal percentage of TC by H_2O_2 was only similar to the blank sample during the reaction. This shows that TC cannot be degraded by H_2O_2 alone; in other words, H_2O_2 can only be applied as a reagent in the Fenton-like process. A slight removal of TC in presence of H_2O_2 can be explained by the lower oxidation potential of H_2O_2, compared with the oxidation potentials of HO• and HO_2• radicals [29]. The removal efficiency achieved by Fe_3O_4 MNPs was higher than that of H_2O_2 alone, which is mainly due to surface adsorption. These results suggest that the direct oxidation of TC by H_2O_2 and its adsorption by Fe_3O_4 MNPs is very limited. By using Fe_3O_4 MNPs and at the presence of H_2O_2, the removal percentage of TC was significantly more efficient than using Fe_3O_4 MNPs alone; in fact, it indicates that the catalytic activity was improved by adding H_2O_2 to the reaction. Under these conditions, the degradation of TC could be resulted from ferrous ions at the surface of Fe3O4 MNPs [41].

As shown in Fig. 3, 44.4% TC removal was obtained during 180 min by adding PAC to the TC solution; this is attributed to the adsorption of TC on the PAC. High TC adsorption percentages by PAC/Fe_3O_4 MNPs could be due to porous structure and high surface area of PAC/Fe_3O_4 MNPs [42-44]. However, applying only PAC/Fe_3O_4 MNPs resulted in a high percentage of TC removal, compared with using H_2O_2, Fe_3O_4 MNPs, Fe_3O_4 MNPs+H_2O_2 and PAC processes; it should be noted that this is primarily caused by the surface adsorption. Although the specific surface area of PAC/Fe_3O_4 MNPs composite was lower than that of PAC (see Table 1), it should be considered that the percentages of TC adsorbed on PAC/Fe_3O_4 MNPs were higher than the corresponding amount adsorbed on PAC. Considering this, it can be implied that depositing Fe_3O_4 MNPs onto PAC contributed to having additional adsorption sites for TC. These results also indicate the synergistic effect between the Fe_3O_4 MNPs and PAC which could result in an increase in TC removal by the PAC/Fe_3O_4 MNPs composite. The same result has been reported by other researchers [41, 45].

As it can be seen from the Fig. 3, there was not any significant change in the adsorption of TC by PAC/Fe_3O_4 MNPs for the next 60 min; therefore, we chose this point as the equilibrium time. In fact, it was at this point (60 min) when we added H_2O_2 into solution and then the Fenton reaction was started. As shown in Fig. 3, it is clear that using PAC/Fe_3O_4 MNPs and H_2O_2 together (Fenton-like process) significantly enhanced the removal efficiency of TC, compared to other studied processes. The removal rate of TC was faster at initial times of starting the process, and it reached 61.8% after 90 min in the PAC/Fe_3O_4 MNPs+H_2O_2 system. When Fe_3O_4 MNPs and H_2O_2 were both added into the solution, the removal percentage of TC quickly increased to 79.9%. In this condition, the proportion of TC adsorption on the PAC/Fe_3O_4 MNPs was around 52 %. This shows that both adsorption and Fenton oxidation processes have been simultaneously contributed to the removal of TC. Furthermore, as the heterogeneous Fenton reactions has been previously studied, the activated carbon and graphite could generate free radicals (e. g. superoxide ion and activate hydrogen peroxide) [46]. Considering these results, it can be implied that the PAC/Fe_3O_4 MNPs catalyst has a high catalytic ability for degrading TC in the presence of H_2O_2. In this process, H_2O_2 activating ability and catalytic activity increased via Fe_3O_4 MNPs distribution on the PAC surface, which could also avoid the agglomeration of Fe_3O_4 MNPs. Therefore, in the current study, we used the PAC/Fe_3O_4 MNPs catalyst along with H_2O_2 oxidant as a Fenton heterogeneous process for further experiments.

3.3. Experimental parameters affecting Fenton catalysis

3.3.1. Effect of initial pH of solution

One of the highly effective parameters in a Fenton process is the pH of solution. This parameter can affect the activity of the oxidant and the substrate, and also H_2O_2 stability [47]. The effect of various ranges of pH on TC degradation in a Fenton reaction (i. e. PAC/Fe_3O_4 MNPs+H_2O_2) is shown in Fig. 4(a). The removal efficiency decreased when the initial pH of the solution increased from 3 to 7. It can be seen from Fig. 4(a) that after 240 min of reaction time, 89.5, 69.7 and 61.4% of TC were degraded at pH 3, 5 and 7, respectively. The decreased degradation rate at higher pH values can be attributed to the lower oxidation potential of HO• radicals, decomposition of H_2O_2 and deactivation of the catalyst due to the formation of ferric hydroxide complexes [47, 48]. Martinez-Huitle et al.,[49] reported that the pH values which are around 2.8 are the optimal values for maximum HO• production in the Fenton oxidation process, which is in line with the results of the present study. In a number of previous studies, it has been reported that the conventional Fenton process has high catalytic activity under acidic conditions with pH in the range of 2 to 4 [4]. At acidic conditions, there are more dissolved fraction of iron species which could result in an increase in the oxidation rate of TC [48]. These observations are in line with the reports of the previous studies [4].

3.3.2. Effect of H_2O_2 concentration

Hydrogen peroxide, H_2O_2, is directly related to the number of produced HO• radicals, therefore, it can play the role of an oxidizing agent in Fenton-like process [50]. The removal of TC in the PAC/Fe_3O_4 MNPs+H_2O_2 system with different concentrations of H_2O_2, pH: 3.0±0.2, initial TC concentration of 20 mg/L and catalyst dosage of 0.2 g/L was evaluated (Fig. 4(b)). It was found that the removal efficiency of TC increases from 76.5 to 94% within 240 min reaction when the H_2O_2 concentration increases from 20 mM to 80 mM. This is mainly due to higher concentration of HO• radicals [17, 47]. It shows that TC removal is directly related to the concentration of HO• produced by the catalytic decomposition of H_2O_2. These findings are in good agreement with those of previously conducted studies [27, 31]. However, when the concentrations of H_2O_2 is low, an adequate number of HO• radicals cannot be produced; and also, it can contributes to lowering the oxidation rate and subsequently reducing the removal efficiency [29]. As shown in Fig. 4(b), 94% of TC is removed in the presence of 80 mM H_2O_2 within 240 min reaction time. Therefore, the optimal initial concentration of H_2O_2 (80 mM) was deemed for the effective oxidative degradation of TC (20 mg/L) in the present work.

It has been widely reported that excessive concentrations of H_2O_2 does not improved the removal efficiency of contaminants. This can be explained by considering the scavenging effect of HO• radicals at the presence of excessive H_2O_2, which results in a decrease in the number of HO• radicals in the solution (Eqs. 5 and 6) [17, 27]. In a study conducted by Hua et al., [32] it was reported that a competitive reaction forms between H_2O_2 and contaminant when there is high H_2O_2 concentration in the solution; besides, in this condition, HO• radicals react with H_2O_2 to produce $HO_2•$ radical which is less effective in the degradation of contaminant compared with the effectiveness of HO•. This, in fact, could then reduce the rate of degradation. Therefore, in the current study, it was necessary to investigate the scavenging effect of HO• radicals at >80 mM concentrations of H_2O_2 in the heterogeneous Fenton oxidation of TC using PAC/Fe_3O_4 MNPs+H_2O_2.

$HO• + H_2O_2 \rightarrow H_2O + HOO•$ (5)

$HOO• + HO• \rightarrow H_2O + O_2$ (6)

3.3.3. Effect of catalyst dosage

The effects of different dosage of PAC/Fe_3O_4 MNPs (i. e. ranging from 0.1 to 0.3 g/L) on the degradation of TC in the Fenton-like system was evaluated with initial TC concentration of 20 mg/L and H_2O_2 dosage of 80 mM at pH 3.0. The corresponding results are presented in Fig. 5(a). During the adsorption phase, it was found that by increasing the amount of PAC/Fe_3O_4 MNPs catalyst, the amount of TC which can be adsorbed on the catalyst surface increases as well. About 65.4% of TC concentration was removed at 0.1 g/L dosage of catalyst within 240 min; and, by increasing the dosage to 0.2 g/L, the removal efficiency reached 92.7%. During the Fenton phase, as shown in Fig. 5(a), TC was completely removed; in other words, we could remove 99.1% of TC at the presence of 0.3 g/L of the catalyst after 240 min. The removal efficiency of TC from 78.7% at adsorption equilibrium point was increased to 99.1% during 240 min of reaction time. Increasing the number of active sites and also improving the decomposition of H_2O_2 which results in generating more HO• radicals could be the reasons of high removal efficiency of TC in this condition. These are in line with the results of a previously conducted study [41]. Kuang et al.,[47] and Shukla et al.,[51] demonstrated that the higher amounts of heterogeneous catalyst provides additional surface area for the adsorption, and also additional amount of iron species for the formation of HO• radicals.

In a study conducted by Hua et al., [32] on the heterogeneous Fenton degradation of bisphenol by Fe_3O_4/graphite oxide nanocomposite, it was founded that the amount of active sites for the formation of HO• and probably bisphenol adsorption improved when the dosage of the catalyst was increased. Similar results were also reported by other authors [9, 47]. However, it is possible that the removal efficiency of TC deceased with further increase of catalyst concentration from 0.3 g/L; it could be due to scavenging role of HO• radicals at the presence of iron species, as demonstrated in previous studies [17, 47, 48]. This is, in fact, a hypothesis requiring further experimental and theoretical studies. Therefore, we set the dosage of catalyst at 0.3 g/L for the following experiments.

3.3.4. Effect of initial TC concentration

The effect of various initial concentrations of TC, which were in the range of 10 to 50 mg/L, on its degradation efficiency was evaluated. The results indicated that the degradation efficiency decreases when the initial TC concentrations in the solution increases (Fig. 5(b)). Therefore, when the TC concentration changed from 10 to 50 mg/L, the degradation efficiency decreased from 99.8 to 78 % during 240 min. This could be due to the increase of the number of TC molecules and their competition with the number of H_2O_2 molecules in the solution for the active sites, resulting in the decrease of H_2O_2 decomposition on the catalyst surface [17, 52]. It can also be caused by constant dosages of catalyst and H_2O_2 against the increase in the initial concentrations of TC. Xu et al., [53] demonstrated that degradation efficiency of 4-chloro-3-methyl phenol in heterogeneous Fenton system by nZVI decreased when the initial concentration was increased. This could be because of occupying the active sites on the nZVI surface by contaminant molecules and the lower production of HO• radicals.

It can be seen from the Fig. 5(b) that complete removal of TC concentrations of 10 and 20 mg/L can be approximately obtained within 240 min reaction, while a more reaction time for complete degradation of TC needs when the initial concentration of TC increased from 20 to 50 mg/L. This is in line with the observations made in a number of previous studies on the degradation of contaminants by heterogeneous Fenton process [17, 54].

3.4. Degradation kinetic of TC by PAC-Fe_3O_4 MNPs/H_2O_2

According to the reports of previous studies, the hetrogeneous Fenton-like process can be described by a pseudo firs-order kinetic model [47, 55]. In the present study, we described the kinetics of TC degradation at different concentrations of catalyst using pseudo firs-order model. This model was applied in order to have a comparision between the results of model estimation and experimental data. This model can be expressed according to the following equations:

$$\ln\frac{[C]}{[C_0]} = -k_{obs}t \qquad (7)$$

where, C=$[TC]_t$ is the TC concentrations at time t; and, C=$[TC]_0$ is the TC initial concentration (mg/L). Also, t is degradation time (min). k_{obs} is the observed rate constant of psuedo first-order reaction(min^{-1}), which can be determined from the slope of the linear region of the curve of $\ln[TC]_t/[TC]_0$ versus t.

The kinetics of TC degradation at pH 3.0±0.2 was assessed in a 4 h period and 80 mM H_2O_2 under room temperature (25±1°C). The values of kinetic parameters along with correlation coefficients of pseudo first-order kinetic model for various concentrations of catalyst and TC are shown in Table 1. Fig. 6 (a) shows the degradation kinetic of TC by PAC/Fe_3O_4 MNPs+H_2O_2 system at different dosages of the catalyst. The values of the observed rate constants (k_{obs}) increased when catalyst loading in the system was increased. It shows that when the catalyst loading increases from 0.1 to 0.3 g/L, the value of k_{obs} increases from 4×10^{-3} to 1.9×10^{-2} (min^{-1}). This finding suggests that increasing the surface of fresh iron (initial catalyst addition) could accelerate the reactions of iron dissolution and H_2O_2 decomposition [52]. Niu et al., [9] reported that the degradation efficiency of sulfathiazole increased from 0.0073 to 0.0603 min^{-1} with the increase of Fe_3O_4/Humic Acid dosage from 1 to 5 g/L.

However, Fig. 6(b) indicates that the values of k_{obs} decreased from 0.03 to 0.005 min^{-1} when the initial concentration of TC increased from 10 to 50 mg/L. According to Table 2, k_{obs} of 10, 20 and 50 mg/L of TC were found to be 3×10^{-2}, 1.9×10^{-2} and 5×10^{-3} (mim^{-1}), respectively. In this regard, it can be implied that by increasing the initial TC concentration, reaction rate constants decreases. In other word, low concentrations of TC offer a faster degradation rate, compared to high concentration of this compound. This could be due to limited dosages of catalyst and H_2O_2 for higher concentration of TC. Ferrag-Siagh et al.,[56] reported that when the initial concentration increases, the amount of byproducts increases as well, causing an additional consumption of $HO_2\bullet$ radicals.

Based on the obtained correlation coefficients of pseudo first-order kinetic model for TC degradation using heterogeneous Fenton system (PAC/Fe_3O_4 MNPs+H_2O_2), it can be concluded that the degradation process follows the pseudo first-order model with a fairly good correlation coefficients. As shown in Table 2, the values of correlation coefficients were more than $R^2>0.95$ through all the experiments. This model suggests the production of steady-state concentration of $HO_2\bullet$ radicals. This result is in line with the reports of previously conducted studies [4, 56].

The changes in TC concentration in the degradation process by the heterogeneous Fenton system (PAC/Fe_3O_4 MNPs+H_2O_2) are shown in Fig. 7. It can be seen from the figure that TC peak (retention times, 5.7 min) decreases when the reaction time under obtained optimal conditions increases. Our experiments indicated that TC was degraded completely during 240 min of reaction time. This suggests that the PAC/Fe_3O_4 MNPs+H_2O_2 system has an excellent potential to remove TC from the aqueous solutions.

3.5. Oxidation mechanism of TC by PAC/Fe_3O_4 MNPs+H_2O_2 system

Based on the results, 6.2 and 74.8% of TC were respectively removed by H_2O_2 and PAC/Fe_3O_4 MNPs. This demonstrates that the removal of TC was not mainly based on adsorption by PAC/Fe_3O_4 MNPs or direct oxidation by H_2O_2. Therefore, it can be concluded that the effective removal of TC is resulted from using heterogeneous Fenton system (PAC/Fe_3O_4 MNPs+H_2O_2). In heterogeneous Fenton type process, the reaction between ferrous or ferric ions and hydrogen peroxide takes place on the surface of solid catalyst; and also, this reaction depends on the specific surface area of the catalyst [57]. In this study, the reaction was possibility initiated by adsorption on the PAC surface. In fact, this can help the degradation process.

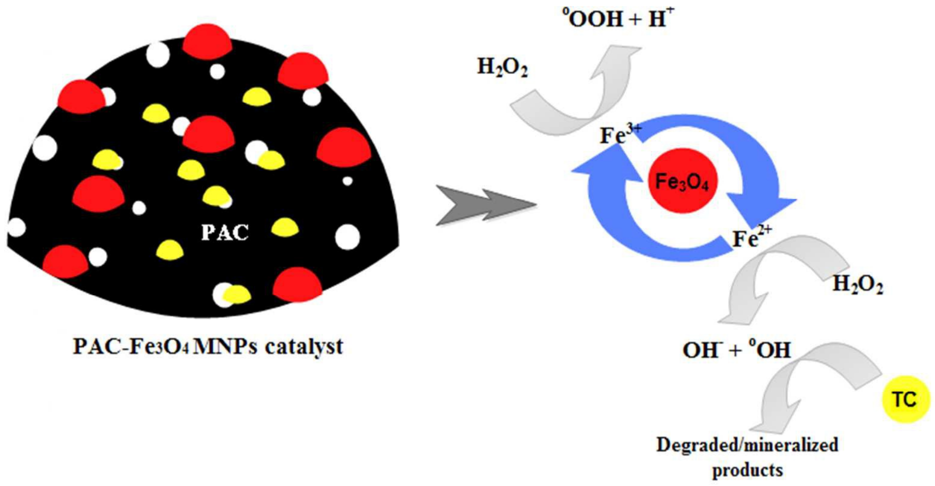
Wang et al., [25] reported that the Fe_3O_4 MNPs could easily adsorb H_2O_2 molecules; and also, the surface properties and chemical compositions of Fe_3O_4 MNPs play a critical role in the peroxidase-like catalysis in the removal of organic pollutants. It was also founded that the Fe_3O_4 catalyst requires having a large specific surface and high dispersion ability to effectively interact with H_2O_2. The possible mechanism of H_2O_2 activation by PAC/Fe_3O_4 MNPs catalyst can be proposed according to Scheme 1. This scheme depicts the route of TC adsorption onto PAC/Fe_3O_4 MNPs and its degradation by the catalyst in the presence of H_2O_2.

The initial molecules of H_2O_2, which were adsorbed on the surface of catalyst, were catalyzed by Fe_3O_4 MNPs nanoparticles coated on PAC surface to produce HO• and HO_2• (Eq. (7)). The HO• radicals are responsible for the degradation and mineralization of TC molecules and converting these molecules into H_2O and CO_2 as described in Eq. (8). The same observation has been reported in a study on Fe_3O_4/graphite oxide nanocomposite applied for removal of bisphenol [32]. According to Eq. (7), Fe^{2+} ions were oxidized to Fe^{3+} ions and then regenerated via the reduction of Fe^{3+} by H_2O_2 (Eq. (9)). Fe^{3+} species also can produce HO_2•, which is less reactive than HO• radicals [9, 13, 24].

$$\mathrm{Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\bullet} + OH^{-}} \qquad (7)$$

$$\mathrm{CC_{22}H_{24}N_2O_8 + \ HO^{\bullet} \rightarrow 22CO_2 + 12H_2O + N_2} \qquad (8)$$

$$\mathrm{Fe^{3+} + H_2O_2 \rightarrow HO_2{}^{\bullet} + Fe^{3+}_{magnetite}} \qquad (9)$$



Scheme 1. The possible mechanism of H_2O_2 activation by PAC/Fe_3O_4 MNPs catalyst in the degradation of organic contaminant.

3.6. Stability and reusability of the PAC/Fe_3O_4 MNPs catalyst

The possibility of reusing the catalyst is an important parameter in evaluating its potential for commercial applications. In the present work, we examined the reusability of PAC/Fe_3O_4 MNPs catalyst under obtained optimal conditions for four consecutive runs. We assessed the removal percentages of TC, mineralization percentage and the iron concentrations leached into the reaction solutions. Between each run of use, the catalyst was separated from the solution by using an external magnetic field. After the reaction time (180 min), the catalyst was washed using DI-water for at least 4 times, and then it was dried in an oven at 100 ^{o}C for 60 min to be ready for the next batch experiment. The solution was analyzed in order to determine the concentrations of TC and Fe after each recycling.

As shown in Fig. 8, initial catalyst activity of PAC/Fe_3O_4 MNPs decreased gradually during four reaction runs. It can be seen from the figure that the degradation percentage of TC in a heterogeneous Fenton reaction decreased from 98.9 % (the first run) to 94.5% (the last run). This suggests that the PAC/Fe_3O_4 MNPs catalyst is durable and has a high stability and reusability. Hence, using this catalyst can results in a significant reduction of the operational cost.

Figure 8 shows the mineralization efficiency of TC using the PAC/Fe_3O_4 MNPs+H_2O_2 process during four reaction runs. It can be seen from the figure that the mineralization efficiency of TC decreased from 46.6 to 32.3% after four runs. This loss of activity is related to the decay of active catalytic sites which are caused by low amount of leached iron from the catalyst surface. Deactivation of the catalyst can also be due to the difficulty in the complete removal of residual by-products and reactants from the active catalytic sites in the following washing and drying procedures. In addition, we observed a TOC removal efficiency of 32.3% after the fifth run, indicating that the reused catalyst retains its excellent catalytic activity. Incomplete removal of TOC suggests that significant amounts of intermediates were still in the solution.

The stability of catalytic activity is an important parameter to evaluate a heterogeneous catalyst. To investigate the catalyst activity of PAC/Fe_3O_4 MNPs, the Fe ions concentration in the TC solution for four reaction runs was analyzed under optimal conditions (pH=3.0±0.2, H_2O_2=80 Mm, dosage=0.3 g/L). Our observations showed that the concentrations of dissolved Fe ions in the solution (i. e. in all studied runs) were negligible and found to be less than 0.1 mg/L, which is below the maximum acceptable drinking water concentration for iron (0.3mg/L) set by the WHO [58]. This indicates that leaching of iron from PAC/Fe_3O_4 MNPs might not cause metal pollution in the water, even under acidic conditions. It also demonstrated that the iron ion is bonded strongly within the PAC structure, making its performance quite stable in the reaction. The results of stability evaluation are consistent with the findings from VSM analysis of catalyst from before and after the reaction time. Therefore, we concluded that PAC/Fe_3O_4 MNPs catalyst indicates acceptable catalytic stability and durability; and also, it can be applied as a promising heterogeneous catalyst to remove TC from wastewater with very low loss of catalytic activity.

4. Conclusion

Based on the results, it was found that both processes of adsorption and degradation are involved in heterogeneous Fenton oxidation of TC using powder activated carbon-supported magnetite nanoparticles (PAC/Fe_3O_4 MNPs). The removal of TC was most efficient at pH 3 and when the loading of catalyst and the concentration of H_2O_2 were high; and also, low concentration of TC was in the solution. Initial concentration of 10 mg/L TC was almost completely removed under optimum conditions which are mentioned in the following: pH=3.0±0.2, 80 mM of H_2O_2, 0.3 g/L of catalyst in 180 min reaction. The kinetic of the experimental data from TC degradation follows the pseudo first-order model. The results from reusability tests of PAC/Fe_3O_4 MNPs indicate that 98.7% degradation of TC can be achieved after four runs. Moreover, we found that the iron ion was bonded strongly within the PAC structure, making its performance quite stable in the reaction. Analysis of the findings demonstrated that the synthesized catalyst has a high reusability and activity during the four sequential runs; besides, using this catalyst could significantly reduce the operational cost of running this system in full-scale practical applications.

Acknowledgment

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Figures:

Fig.1 N_2 adsorptin/desorption isotherm of PAC/Fe_3O_4 MNPs (a) and XRD patterns of PAC, Fe_3O_4 MNPs and PAC/Fe_3O_4 MNPs (b).

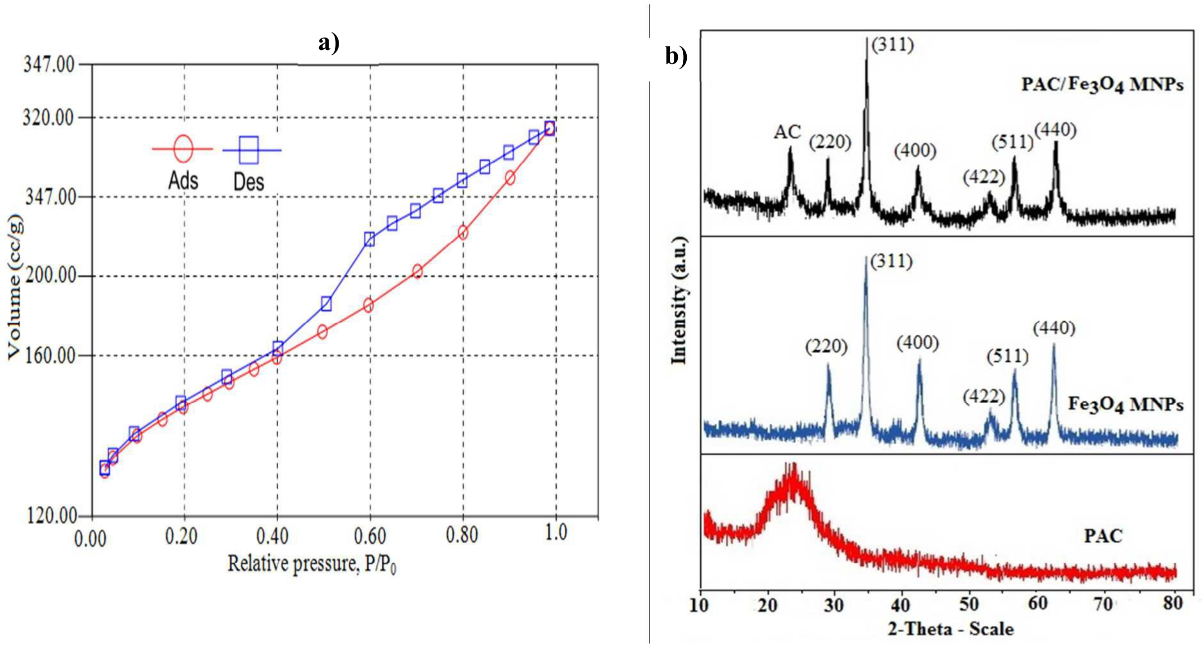
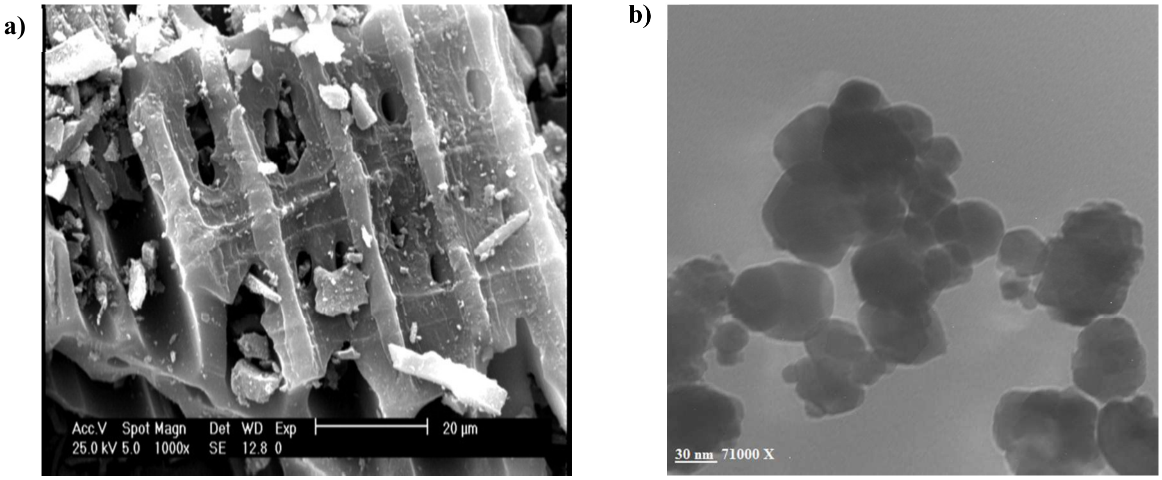


Fig. 2. SEM (a) and TEM (b) images of PAC/Fe_3O_4 MNPs, magnetization curves measured at room temperature for PAC/Fe_3O_4 MNPs before and after reaction (c) and magnetic separation of catalyst from the solution using external magnetic field (d).



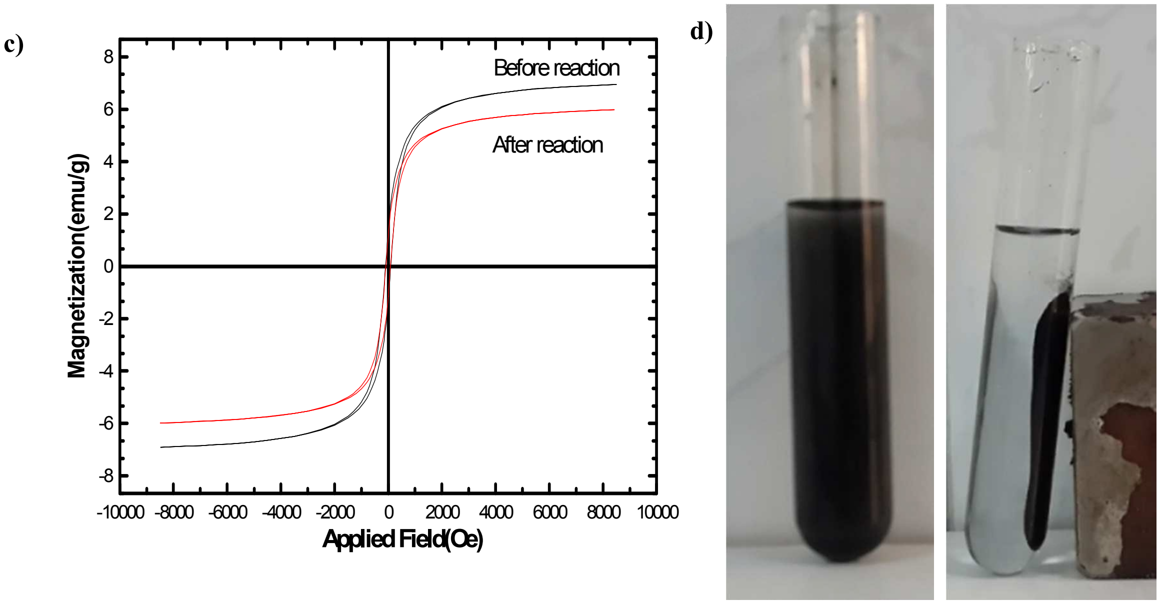


Fig. 3. Comparison of removal efficiency of TC using different processes: (a) 60 mM H_2O_2; (b) 0.2 g/L Fe_3O_4 MNPs; (c) 0.2 g/L Fe_3O_4 MNPs and 60 mM H_2O_2; (d) 0.2 g/L PAC; (e) 0.2 g/L PAC/Fe_3O_4 MNPs; (f) 0.2 g/L PAC/Fe_3O_4 MNPs and 60 mM H_2O_2. Other experimental conditions were C_0=20 mg/L, pH=5.5±0.2 and T=25±1°C.

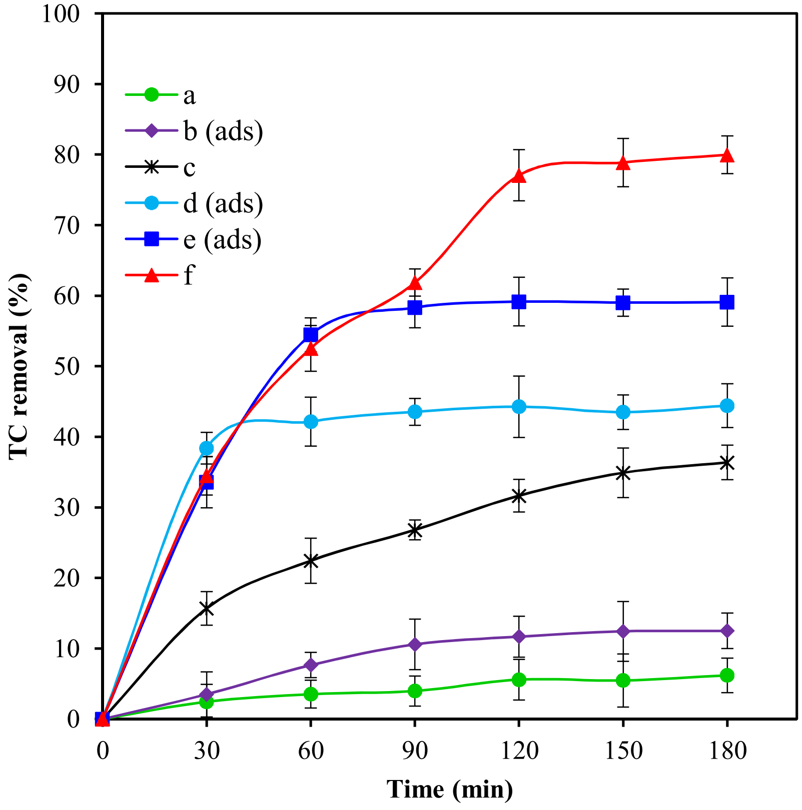


Fig. 4. The influence of initial pH of solution (a) and H_2O_2 concentration (b) on the removal of TC in PAC/Fe_3O_4 MNPs+H_2O_2 system. C_0=20 mg/L, catalyst loading=0.2 g/L, T=25±1°C, (a) H_2O_2= 60 mM; (b) pH=3.0±0.2.

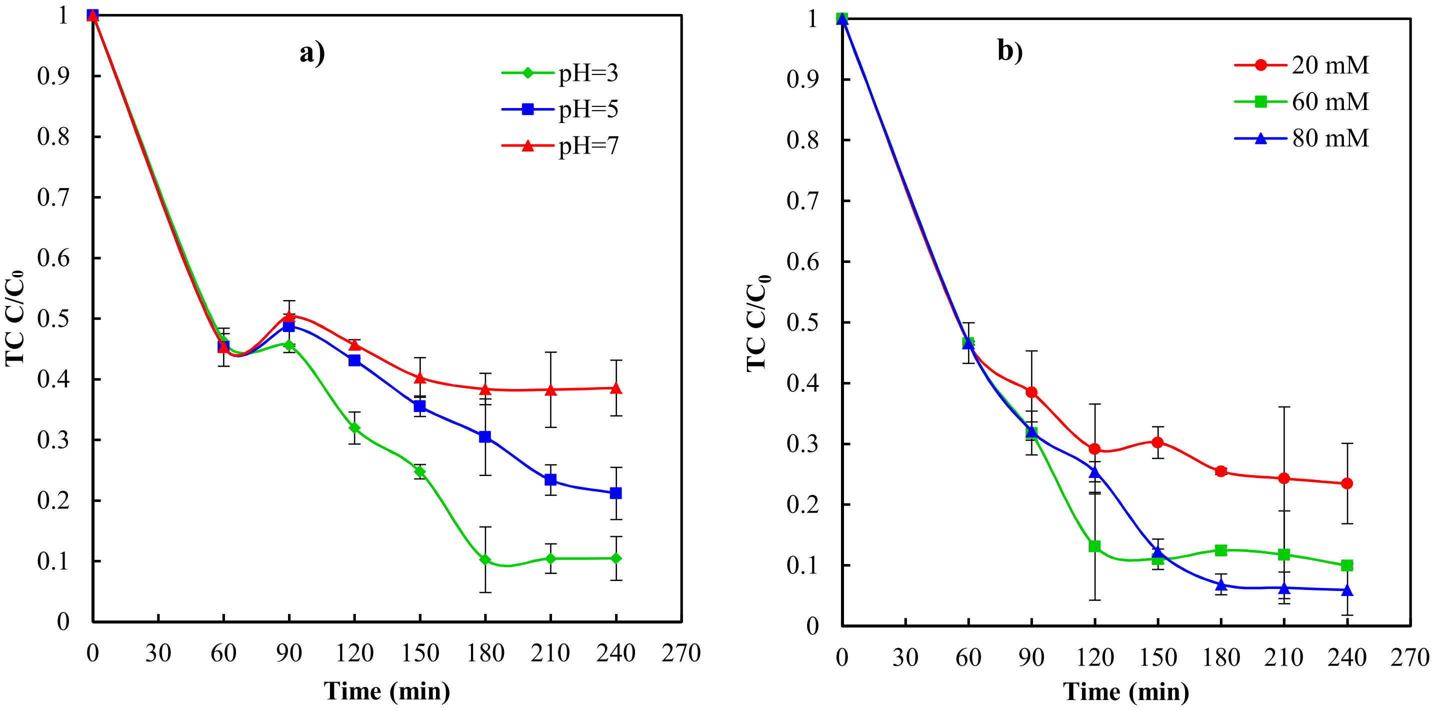


Fig. 5. Effect of loading catalyst (a) and initial TC concentration (b) on the removal TC by PAC/Fe_3O_4 MNPs+H_2O_2 system. pH=3.0±0.2, H_2O_2= 80 mM, T=25±1°C, (a) C_0=20 mg/L; (b) Catalyst loading=0.3 g/L.

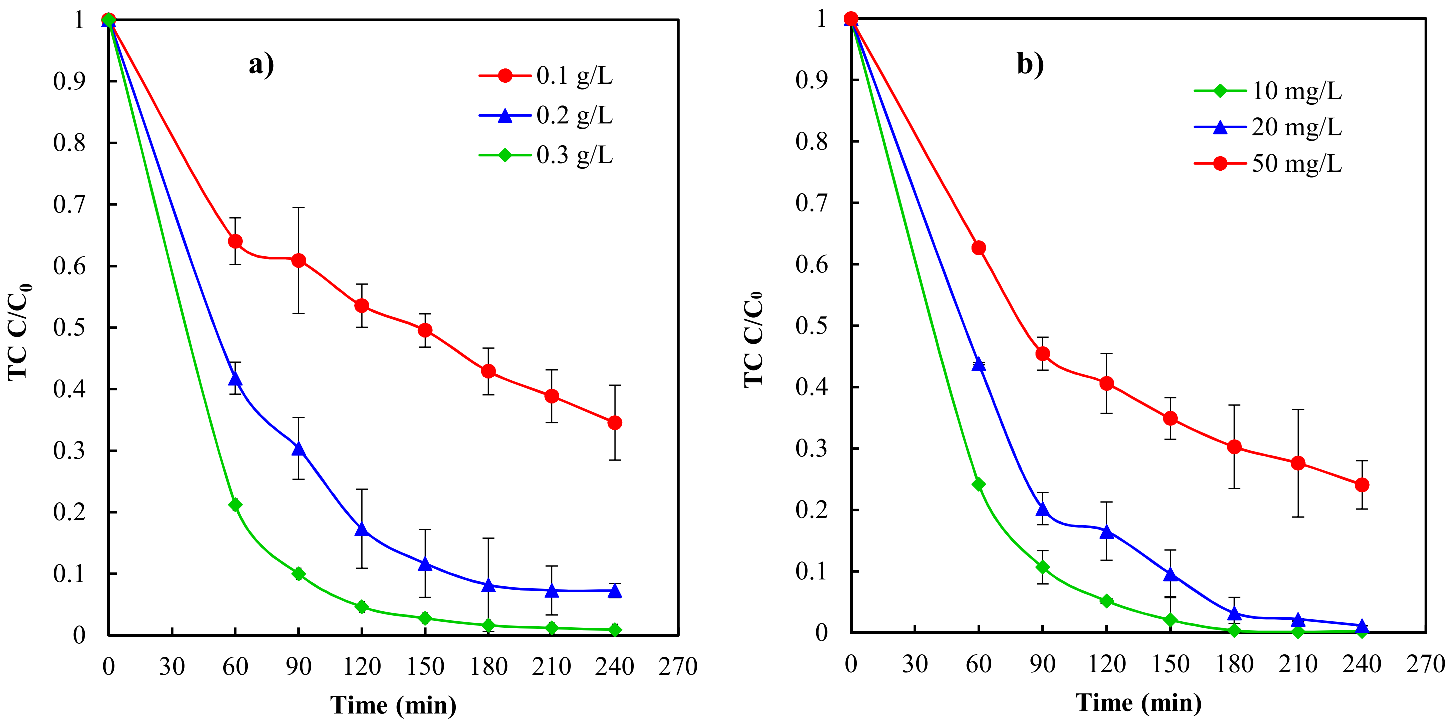


Fig. 6. Degradation kinetic of TC by PAC/Fe_3O_4 MNPs+H_2O_2 system at different dosages of catalyst (a) and initial TC concentrations (b). pH=3.0±0.2, T=25±1°C, H_2O_2= 80 mM, (a) C_0=20 mg/L; (b) Catalyst loading=0.3 g/L.

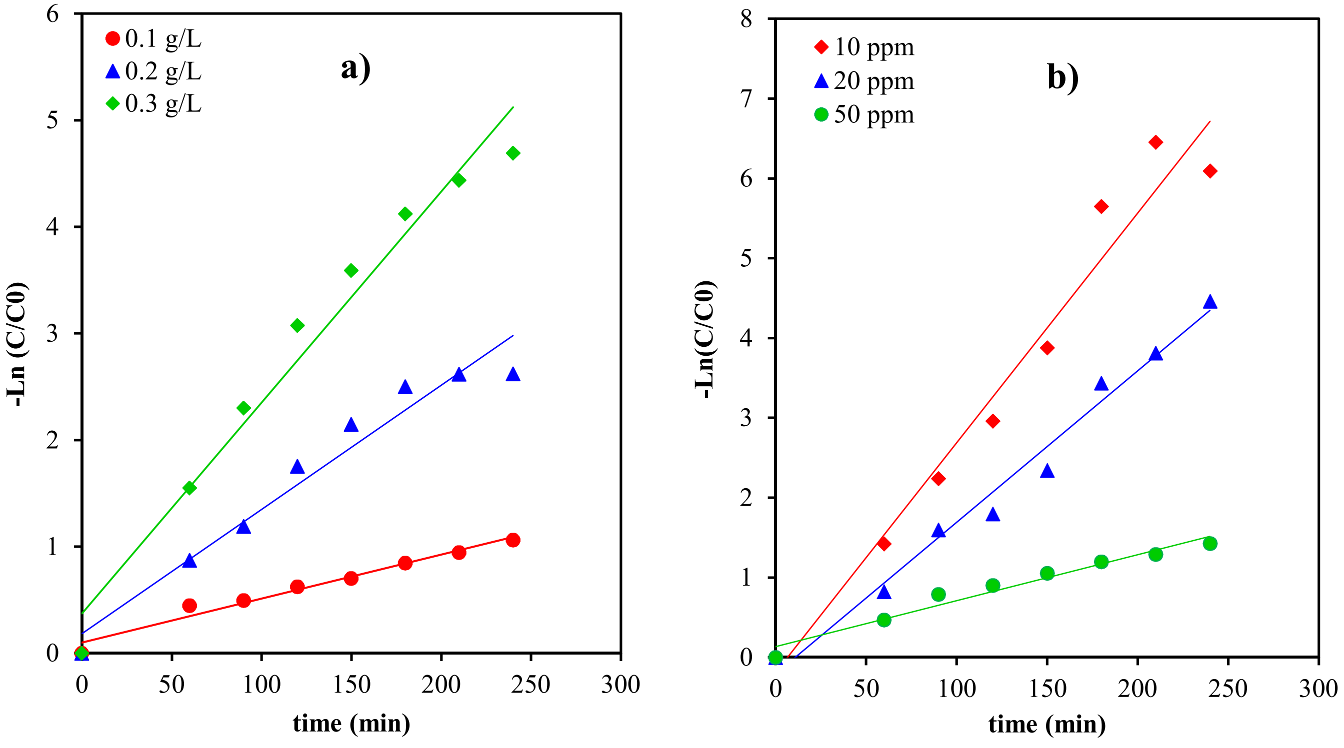


Fig. 7. HPLC spectra of tetracycline during degradation in the heterogeneous Fenton system with PAC/Fe_3O_4 MNPs. pH=3.0±0.2, Catalyst loading=0.3 g/L, C_0=10 mg/L, H_2O_2=80 mM and T=25±1°C.

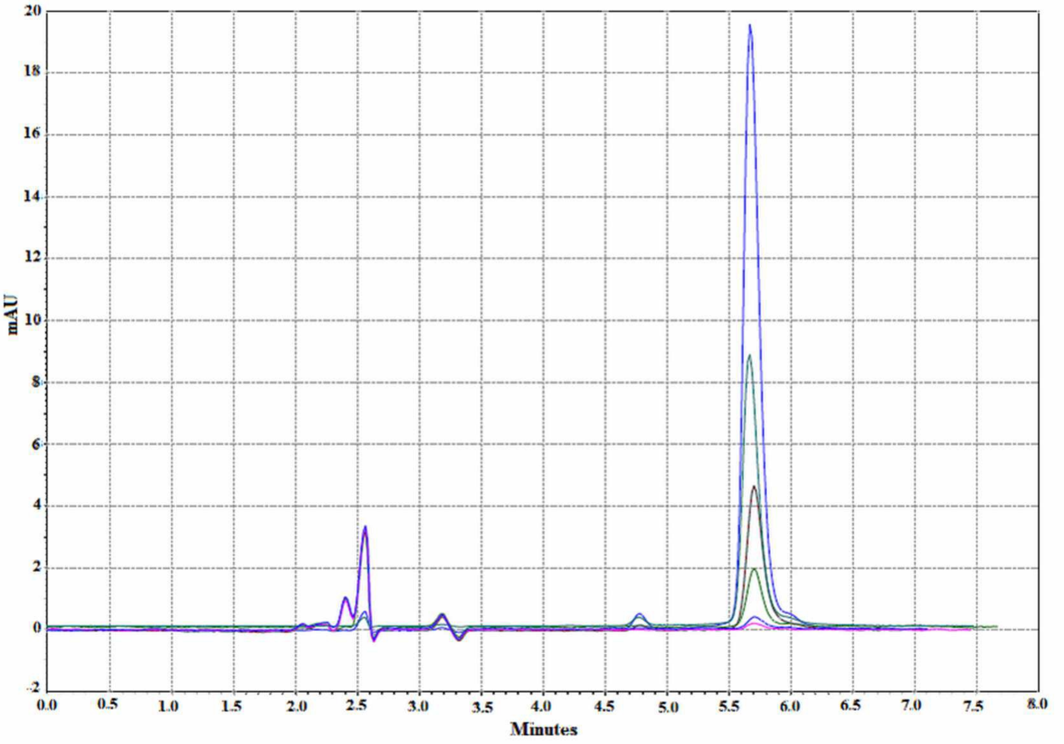
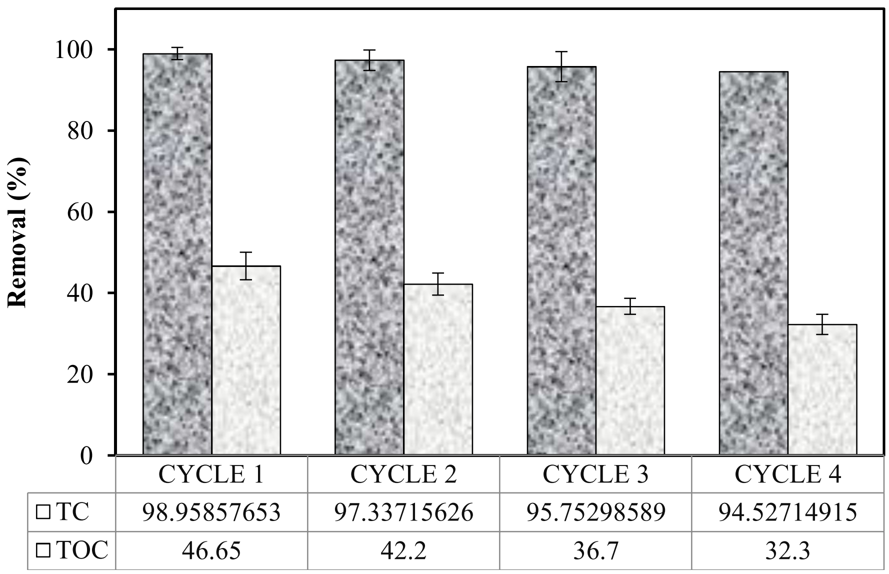


Fig. 8. TC removal over 4 catalytic cycles. pH=3.0±0.2, Catalyst loading=0.3 g/L, C_0=10 mg/L, H_2O_2=80 mM and T=25±1°C.



	CYCLE 1	CYCLE 2	CYCLE 3	CYCLE 4
□ TC	98.95857653	97.33715626	95.75298589	94.52714915
□ TOC	46.65	42.2	36.7	32.3

Tables:

Table 1.
Physicochemical properties of Fe_3O_4 MNPs, PAC and PAC- Fe_3O_4 MNPs.

Parameter	**Sample**		
	Fe_3O_4 MNPs	**PAC**	**PAC- Fe_3O_4 MNPs**
Average pore diameter (nm)	3.6	5.24	3.5
Pore volume (cm^3/g)	0.006	0.753	0.487
Specific surface area (BET) (m^2/g)	63.26	936	671.2
Pore structure	Mesopore	Micropore	Mesopore
Color	Black	Black	Black

Table 2.
Degradation kinetics (pseudo first-order model) constants of TC removal by PAC/Fe_3O_4 MNPs+H_2O_2 system.

Kinetic parameters	**Loading catalyst (g/L)**			**Initial TC concentration (mg/L)**		
	0.1	**0.2**	**0.3**	**10**	**20**	**50**
k_{obs} (min^{-1})	0.004	0.011	0.019	0.028	0.019	0.005
R^2	0.969	0.954	0.971	0.963	0.982	0.962