Investigating the effectiveness of 2-4 dichlorophenoxyacetic acid toxin removal using the combined method of ultrasonic and N-TiO2@SiO2@Fe3O4 magnetic nanocatalyst from aqueous environments

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Abstract:

The herbicide 2,4 dichlorophenoxyacetic acid can cause diseases such as neurotoxicity, hepatotoxicity, immunotoxicity, teratogenicity, endocrine disruption, hepatotoxicity in the human body. Also, due to their polar properties and relatively good solubility in water, they easily enter water sources after use and pollute water and soil. The use of magnetic nanocomposites is due to their selectivity in absorption, environmental friendliness, stability in environmental conditions, low manufacturing cost, high manufacturing speed, regeneration and reuse capability, and high efficiency of these compounds. This study was conducted with the aim of synthesizing N-TiO2@SiO2@Fe3O4 nanocomposite as a catalyst with ultrasonication to remove 2-4 dichlorophenoxyacetic acid from aqueous solutions. In this study, the effect of pH variables, pollutant concentration, stirrer speed, doscatalyst and contact time on the removal efficiency and determining the optimal conditions using the One factor at the time method was used. The catalyst was synthesized by co-precipitation and sol-gel method. The morphology of the synthesized N-TiO2@SiO2@Fe3O4 catalyst was determined using XRD, FT-IR, SEM, EDX, and BET devices. The results of this research showed

that the highest percentage of 2-4 dichlorophenoxyacetic acid removal was obtained at pH= 6, initial concentration=5 mg/L, stirring speed of 300 rpm, duration of 90 minutes and dose catalysts, 0.3 g/L, 88.49% using nano catalyst. Modified titanium dioxide magnetization in the visible range with ultrasonic can be an effective method to remove organic and inorganic pollutants from aqueous solutions.

Keywords: 2- 4 dichlorophenoxyacetic acid, ultrasonic, N-Tio2@SiO2@Fe3O4

Introduction

According to the report of the International Agency for Research on Cancer (IARC, 2- 4 dichlorophenoxyacetic acid herbicide is classified as carcinogenic in group 2B, which has the possibility of causing cancer to humans (1). This herbicide can cause diseases such as neurotoxicity, hepatotoxicity, immunotoxicity, teratogenicity, endocrine disruption, hepatotoxicity in the human body. Also, due to their polar properties and relatively good solubility in water, they easily enter water sources after use and cause water and soil pollution (2). Usually, to increase the photocatalyst efficiency, three methods of doping metal ions on the semiconductor, doping non-metals on the semiconductor and using sensitizing dyes on the semiconductor are used. The energy difference of titanium oxide layers is large, so it is active only in the ultraviolet wavelength region, which contains less than ten percent of the intensity of sunlight. In other words, the only problem in using titanium oxide is its lack of activity in visible light and requires ultraviolet radiation. In addition, most people are aware of the effects of ultraviolet radiation in causing skin problems. An efficient method in modifying the titanium oxide photocatalyst and activating it under visible light is to replace the oxygen ion with anions such as N3+, C4+, S4+, F-, Cl-, Br-, which leads to the narrowing of its energy layer. Nitrogen is important due to its low ionization energy, similar to that of oxygen, and high stability, and it reduces the combined electron/hole characteristic of the photocatalyst (3). Currently, the focus of technology in the field of removing pollutants, especially antibiotics, organic pollutants is centered on magnetic nanocomposites. This method has more advantages than absorbent and common catalysts because they have selectivity in adsorption, strong magnetic responses, environmental friendliness, stability in environmental conditions, low manufacturing cost, high manufacturing speed, regeneration and reuse capability, high efficiency and easier separation of these compounds(4).Increasing the rate of decomposition of organic compounds by adding suspended particles (catalyst) is another possibility to increase the efficiency of the ultrasonic decomposition process, and this is the advantage of this process over some processes (for example, ultraviolet) where the turbidity of suspended particles reduces their efficiency. (5).

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Material and Methods:

In the implementation of the plan, one factor at the time method was used to determine the optimal values of 5 parameters, pH, initial 2- 4 dichlorophenoxyacetic concentration in mg/L, stirring speed in rpm, catalyst dose in g/L and containe time (min). used. The average of the data was used for their analysis. Raw materials included ferric chloride salt ($FeCl_3.6H_2O$) and ferric chloride salt ($FeCl_2.4H_2O$), tetraethyl orthosilicate (TEOS), ammonia, ethanol made by Merck and 2,4 dichlorophenoxyacetic acid herbicide 95% made by Sigma China. The synthesis of N-TiO2@SiO2@Fe3O4 nanoparticles was carried out in the following three steps:

Synthesis of Fe3O4 magnetic nanoparticles

The preparation method of Fe3O4 nanoparticles is co-precipitation. First, 15 ml of ammonia is dissolved in 35 ml of water and kept at a temperature of 60°. Then 0.54 grams of $FeCl_3.6H_2O$ and 0.2 grams of $FeCl_2.4H_2O$ are mixed in 25 ml of water and added drop by drop to the initial solution. The obtained solution is vigorously mixed for 5 hours and then the obtained nanoparticles are separated by a super magnet and washed with water and dried in a vacuum for 24 hours (6).

Synthesis of SiO2@Fe3O4 nanoparticles

SiO2@Fe3O4 is prepared by sol-gel method. In this step, dissolve 1 gram of Fe3O4 and 100 ml (deionized water and 98% ethanol) along with 3 ml of tetraethyl orthosilicate (TEOS) and 3 ml of ammonia and place it in an ultrasonic device for 20 minutes, then place it on a low speed stirrer for 24 hours. It will be given. Next, it is washed several times with deionized water and 70% ethanol. The formed material is separated with a super magnet and dried at 60° for 12 hours and then transferred to a desiccator (7).

Synthesis of N-TiO2@SiO2@Fe3O4 nanoparticles

N-TiO2@SiO2@Fe3O4 nanoparticles are prepared by sol-gel method. 0.25 grams of nanoparticles prepared in the previous step are mixed in 25 ml of ethanol at room temperature for 30 minutes by sonication. Then 5 ml of titanium butoxide is added to the solution. 3.6 grams of urea solution in 2 ml of NH4OH is added drop by drop to the resulting solution and vigorously mixed at 80°. After heating for 16 hours, the obtained powder is dried in an oven at 100° for 1 hour. Then it is calcined in the oven at 500° for 2 hours. Then it is cooled to room temperature and spread in water by sonication. Then it is separated by a magnet until the solution becomes clear. Again, the nanoparticles were dried in an oven at 100° for 6 hours and stored in a desiccator (6).

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Determining the characteristics of the synthesized catalyst

The phase structure and crystal size of the prepared samples were determined by X-ray diffraction (XRD: X-ray diffractometry) using an XRD analyzer model 1730PW made in the Netherlands. The morphology and microstructure of the prepared samples were examined by scanning electron SEM (microscope) model 2000Quantum made in the United States and visible light spectrum (FTIR: Fourier-transform infrared spectroscopy) model Spectrum1 made in the United States. Also, analysis (EDX: Energy-dispersive X-ray spectroscopy) was used to determine the elements present in nanoparticles using a device model 2085EM made in the Netherlands. To determine the specific surface area of nanoparticles (BET: Brunauer-Emmett-Teller), a measuring device model 20Mini made in Japan was used. The pH drift method was used to calculate the pHzpc of the magnetized nanocomposite. In this study, the effect of each parameter on the removal efficiency was investigated by keeping other variables constant. Experiments were carried out in besher 200 cc. The pH of the samples was adjusted to 3, 6 and 9 using 0.1M hydrochloric acid and 0.1M soda. Then the samples with different concentrations of 5, 10, 15, 20 and 25 mg/liter of 2- 4 dichlorophenoxyacetic acid herbicide poison in absorbent doses of 0.1, 0.2 and 0.3 g/liter in times of 10, 15, 30, 60 and 90 minutes at speeds of 200 , 250, and 300 rpm were tested in the presence of visible light and with nanoparticles and ultrasonic. The adsorbent was separated from the solution by magnetic method with the help of a super iron. 2- 4 dichlorophenoxyacetic acid herbicide toxin concentrations before and after were analyzed using a high-performance liquid chromatography device .

Results:

XRD analysis results
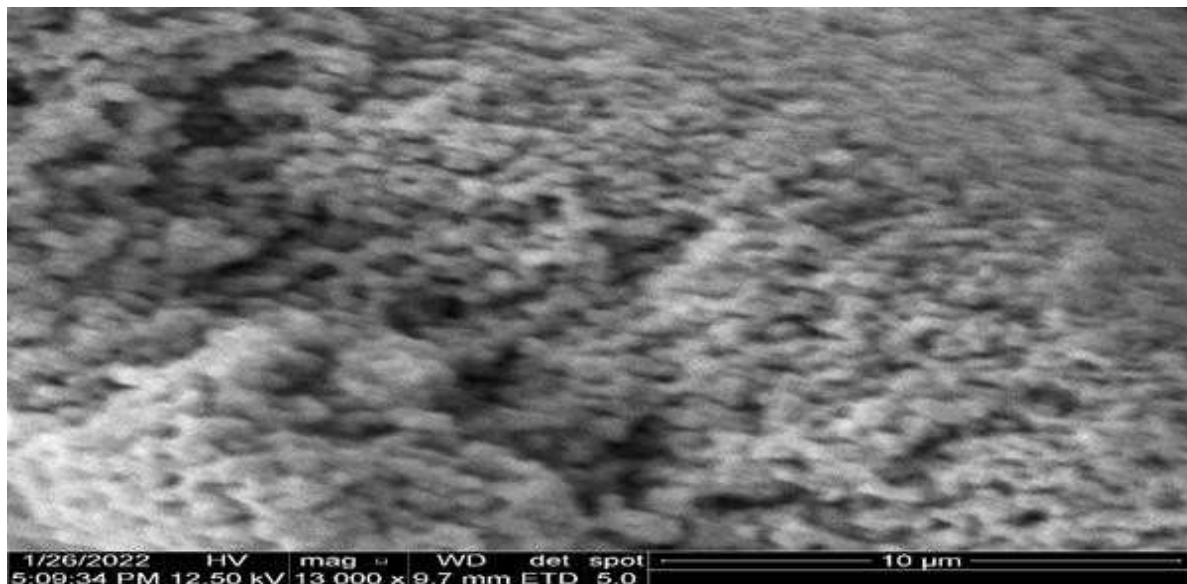
The XRD pattern for N-TiO2@SiO2@Fe3O4 nanoparticles is shown in Figure 1-a. CuKα X-rays with a wavelength of 1.54 angstroms were used in the experiments. The results of XRD analysis at the frequencies created at angles of 23.55, 35.86, 45.04, 54.8, and 53.61 degrees corresponding to crystal planes (206), (004), (471) and (60) respectively. related to Fe3O4 and the peaks created at the angles of 25/34 and 48/37 correspond to the (682) and (244) crystal planes of titanium dioxide, respectively.
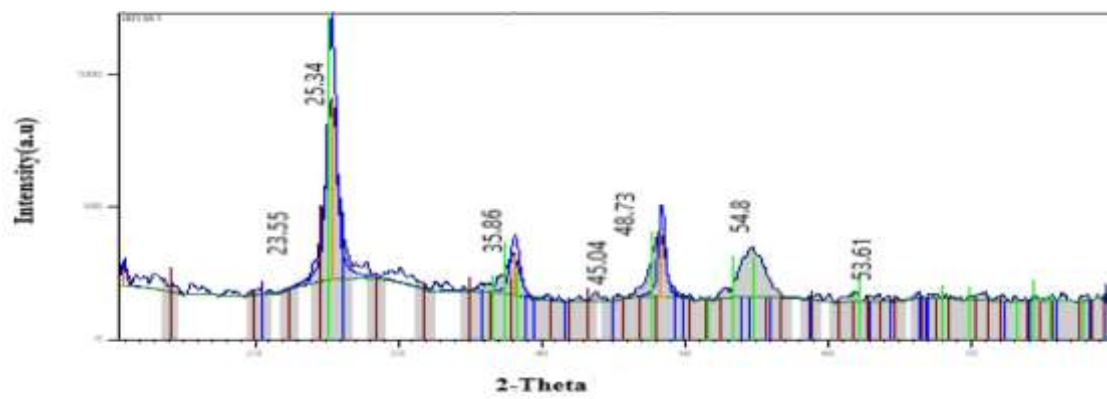
a

b

c

Figure 1- X-ray beam diffraction pattern (a) FTIR spectrum (b) SEM image (c) magnetic nanoparticle

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The results of FT-IR analysis

FT-IR device was used to investigate functional groups on the surface of N-TiO2@SiO2@Fe3O4 nanoparticles in the range of 450-14000 cm. According to Figure 1-b, the 602.32 band corresponds to the Fe – O vibration. The band 823.95 corresponds to the vibration of Ti –O– Ti and the band 1049.44 corresponds to Ti –O– Si, which indicates that the silica coating has been successfully placed on the Fe3O4 nanoparticle. Also, the band 1401.07 corresponds to N–Ti–O. The graph shows that the band at cm-11619.42 corresponds to the O-H bond. In this way, it can be stated that titanium and silica compounds are well placed on Fe3O4.

SEM and EDX analysis results

In Figure 1-c, the morphology of the synthesized N-TiO2@SiO2@Fe3O4 nanoparticles is shown with high precision by the SEM device at 12.5 kv. According to this figure, the elements in the N-TiO2@SiO2@Fe3O4 nanoparticle have a spherical structure and are uniformly placed on the surface. Also, the elements in the nanoparticles were analyzed by EDX device. The highest percentage is related to oxygen. The presence of ninogen indicates that the amine functional groups are placed on the surface of the nanoparticle.

The results of BET analysis

The most common method for measuring the specific surface area of nanoparticles is BET, which works based on measuring the volume of nitrogen gas absorbed and desorbed by the substance at a constant temperature of liquid nitrogen. According to the results of BET analysis of N-TiO2@SiO2@Fe3O4 nanocomposite, the specific area of the synthesized nanocomposite was equal to $51.288[\mathrm{m^2\,g^{-1}}]$.

Determination of pHzpc

In order to check the type and amount of surface charge of the studied nanoparticle at different pH and also to determine the pH of zero charge, the pHZPC determination test was conducted on the adsorbent. The results of the desired test are shown in Figure (2). As shown in the figure, the pH of zero charge point for nanoparticles is equal to 5.9.
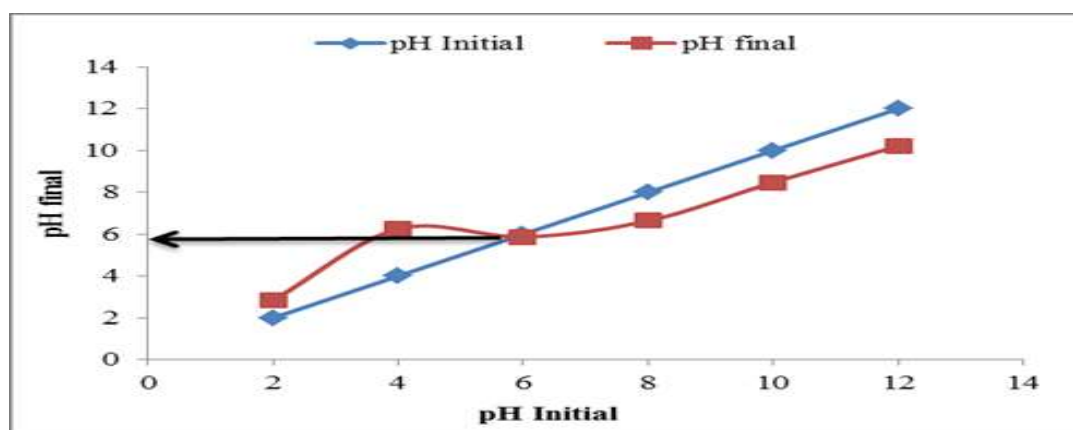
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Figure (2) isoelectric point (pHZPC) of synthesized magnetic nanoparticle

Results related to pollutant decomposition

Studying the process of pH changes on the decomposition process of 2-4 dichlorophenoxyacetic acid in the presence of ultrasonication:

Considering that the pH parameter affects the production of hydroxyl radicals, it is one of the main influencing factors in the efficiency of the advanced oxidation process in removing non-degradable substances. In order to investigate the process of pH changes on the efficiency of N-TiO2@SiO2@Fe3O4 nanocomposite process in the presence of ultrasonic in removing the herbicide 2- 4 dichlorophenoxyacetic, the target solution at initial pH (3-6-9), initial concentration mg/L5 of the pollutant, speed The stirrer was prepared at 300 rpm and the catalyst dose was 0.3 g/L. According to Figure (3-a), the highest removal efficiency of 2- 4 dichlorophenoxyacetic herbicide was obtained at pH=6 with a removal efficiency of 88.59%.

The study of changes in the initial concentration of the pollutant on the decomposition process of 2- 4 dichlorophenoxyacetic in the presence of ultrasonication:

The trend of changes in the initial concentration (5, 10, 15, 20, 25 mg/L) of the pollutant on the efficiency of the removal process (pH = 6, stirrer speed 300 rpm and catalyst dosage 0.3 g/L) in the presence of ultrasonication is shown in Figure (3-b) has been The results show that with the increase in the initial concentration of the pollutant, the removal efficiency decreased and the highest removal efficiency of 2-4 dichlorophenoxyacetic acid herbicide in the initial concentration of 5 mg/L in 90 minutes was obtained as 88.58%.

Studying the process of changes in stirrer speed on the decomposition process of 2-4 dichlorophenoxyacetic acid in the presence of ultrasonication:

Examining the process of changes in stirrer speed in the removal efficiency of 4-2-dichlorophenoxyacetic acid herbicide is shown in Figure (3-c). To optimize the stirrer speed (200, 250 and 300 rpm), poison solution with pH=6, optimal concentration of 5 mg/L and catalyst dose of 0.3 g/L were used in the presence of ultrasound. According to figure number (3-c), by increasing

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the speed of the stirrer and contact time, the removal efficiency of 2 and 4 dichlorophenoxyacetic acid herbicides increased and the removal percentage was 88.06.

Studying the process of changes in catalyst dosage on the decomposition process of 2,4 dichlorophenoxyacetic acid in the presence of ultrasonication:

In order to determine the optimal dose and investigate the process of catalyst dose changes on the removal efficiency of 4-2-dichlorophenoxyacetic acid herbicide, N-TiO2@SiO2@Fe3O4 nanocomposite in doses of 0.1, 0.2 and 0.3 g/L, in optimal conditions (pH 6 =, concentration 5 mg/L and stirrer speed 300 rpm) and was examined in the presence of ultrasonic. The results of the changes in the catalyst dosage on the photocatalyst process are shown in Figure (3-d). The results show that the removal efficiency in the presence of ultrasonication and catalyst dose of 0.3 g/liter is equal to 87.7%.
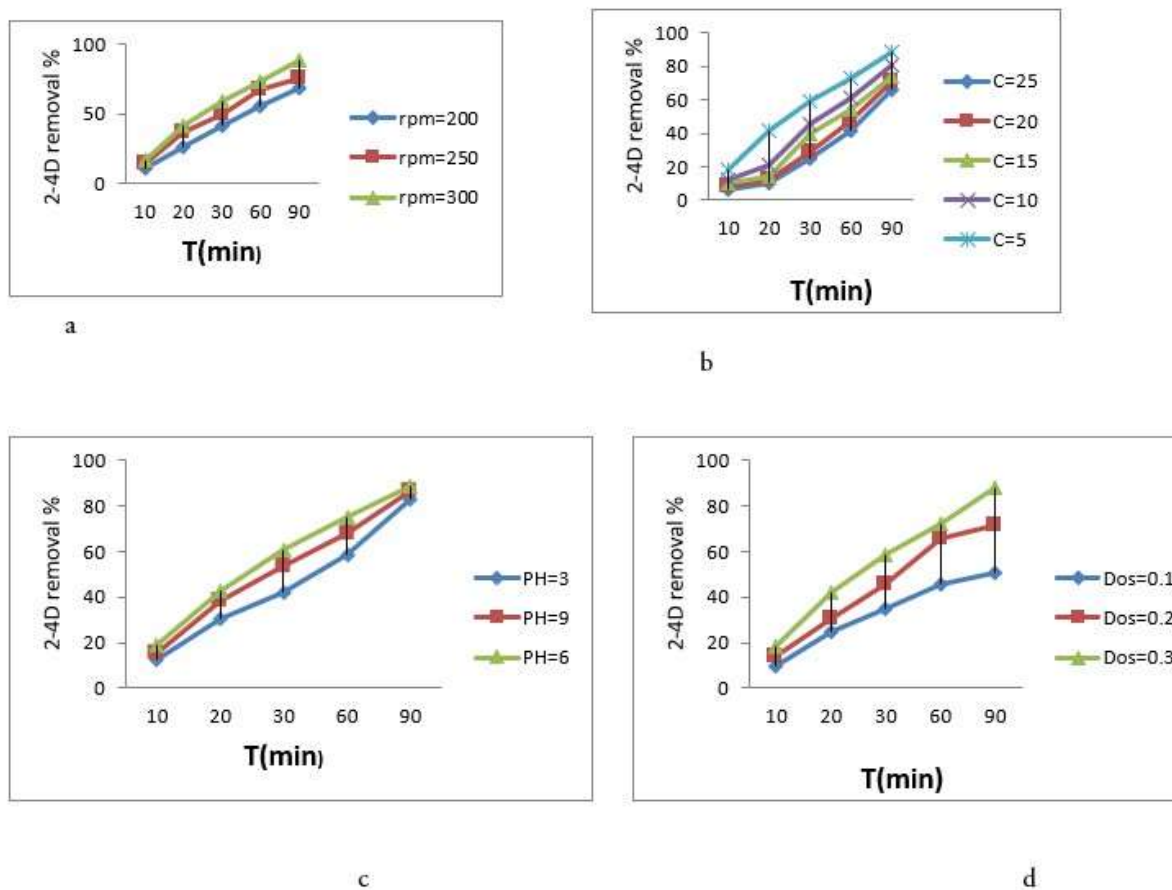

Figure (3) pH change process (a), 2,4 dichlorophenoxyacetic acid concentration change process (b), stirrer speed change process (c), catalyst dose change process (d) in N-TiO2@SiO2@Fe3O4 nanocomposite process and ultrasonic

Studying the process of changes in contact time on the decomposition process of 2-4 dichlorophenoxyacetic acid in the presence of ultrasonication:

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In order to influence the reaction time, which is considered as an important parameter in the removal of pollutants, optimal conditions (pH = 6, optimal concentration 5 mg/L, stirring speed 300 rpm and catalyst dosage 0.3 g/L in the presence of ultrasound on the efficiency of the photocatalytic removal process The selected time period was between 0 and 90 minutes (0, 10, 20, 30, 60, 90) minutes, the results of which are shown in figure number (4-a). According to the results, with increasing contact time, the herbicide removal efficiency 2-4 dichlorophenoxyacetic acid also increased and the removal percentage was 88.49% in 90 minutes.

Investigating the degree of mineralization of 2-4 dichlorophenoxyacetic acid solution in the presence of ultrasound:

The degree of mineralization by measuring TOC (total organic carbon) under environmental conditions of humidity 29%, temperature 25 degrees Celsius, under the standard and test method of ASTMD 2579, the samples were collected in a period of 90 minutes and then read by the multi N/C3100 TOC meter. According to figure 4-b, results showed that in the presence of ultrasonic, the highest removal efficiency of 66.81% was obtained in 90 minutes.
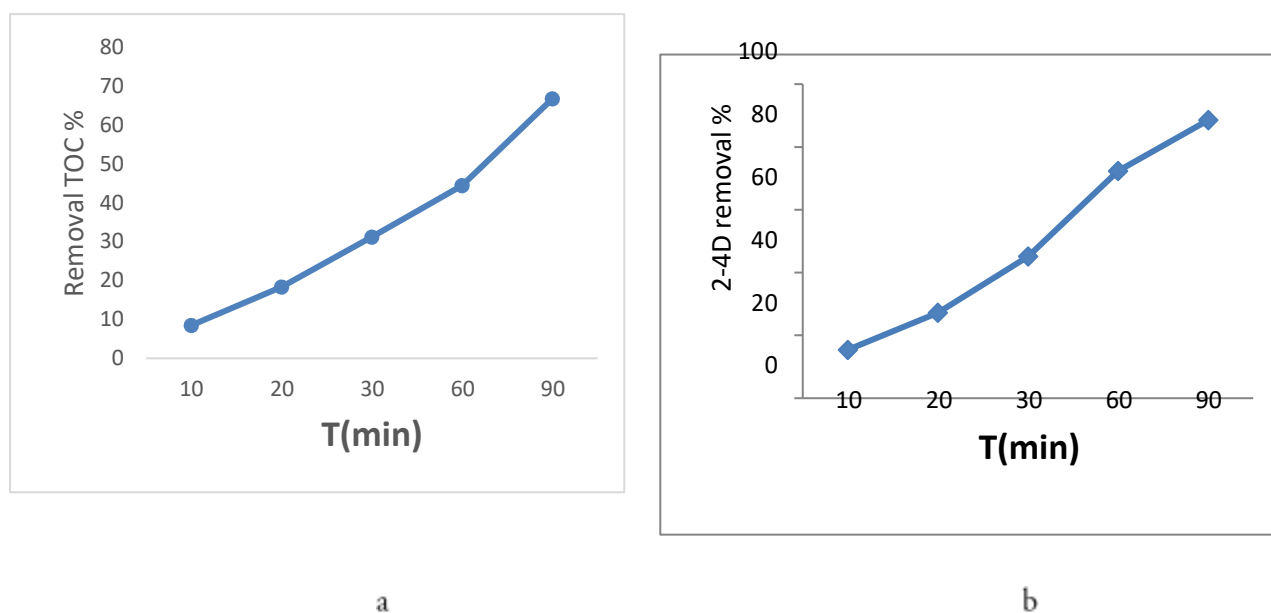

a   b

Figure (4): Contact time change process (a), mineralization change process in N-TiO2@SiO2@Fe3O4 nanocomposite and ultrasonic

Investigating the kinetics of the 2-4 dichlorophenoxyacetic acid decomposition process:
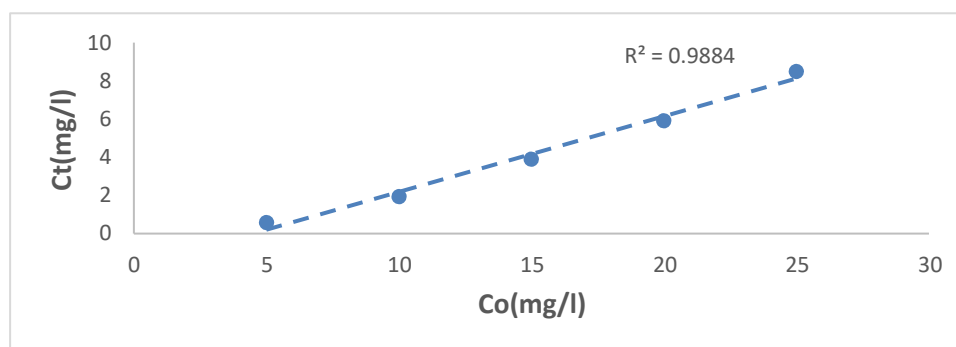
Figure (5) zero-degree kinetics of synthesized magnetic nanoparticles

Discussion

Characteristics of the synthesized catalyst

Catalyst activity is greatly affected by its crystal structure and particle size. When the size of the particles is reduced to nanometers, the catalytic activity increases due to the widening of the optical vacancy due to the quantum properties and increased surface area (8). Figure 1-a shows the XRD spectrum and shows that the amorphous TiO2 in the NTSF structure has transformed into a crystal and transferred to the anatase phase, and it is well suited for the synthesis of the core/shell crystal structure through the sol-gel method. The appearance of the peak at 25.34 angle limits confirms the structure of anatase TiO2. The presence of scattering at angles of 25 and 48 degrees indicates the anatase phase of TiO2. The peaks created at 23.55, 35.86, 45.04 and 53.61 angles indicate the presence of Fe3O4. By matching the peaks of these plates and their corresponding diffraction angles with JCPDScard 19-0629 and JCPDScard standard, 21, it is consistent and similar to the studies done(6,9,10,11).

According to Figure 1-b of FT-IR analysis, the bands related to nanoparticle appeared at wavelengths longer than 602.23, 823.95, 1049.404, 1401.07, 1619.42. The 602.32 band corresponds to the Fe – O vibration. The 823.95 band corresponds to the Ti–O–Ti stretching vibration and confirms the coating of titanium on the nanoparticle. The band 1049.40 corresponds to Ti –O– Si, which shows that the silica coating has been successfully placed on the Fe3O4 nanoparticle. The graph shows that the 1401.07 cm-1 bands are related to the Ti–O–N bond because the N doping on the TiO2 lattice was created by substituting N instead of Ti+4 on the

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TiO2 lattice (10). The bands above 1619.42 cm-1 are assigned to the O-H bond. In this way, it can be stated that titanium and silica compounds are well placed on Fe3O4. According to the FTIR results of the present study, it is similar to other studies by other researchers(10,12,14,15). It also leads to the increase of free radicals (11). The 12040.34 cm band is due to the bending vibration of the O-H bond, which is assigned to the absorbed water molecules, and the cm-13419.45 band is the stretching state of the O-H bond and is related to free water or the physical absorption of the hydroxyl group on the surface or the water in the pores(16,17,18). The size of TiO2 particles is larger than TiO2–SiO2 and N–TiO2–SiO2. Therefore, by adding nitrogen and silica to titanium dioxide, the particle size decreases(11,15,16). The presence of the elements in the magnetic nanocomposite synthesized by the EDX device indicates the presence of O, Fe, Ti and Si elements in the composition of the nanocomposite. As it is known, the dominant element in the nanoparticle structure is oxygen.

According to similar studies(6,9), the calcination of nanocomposite at 500°C, the organic materials on the surface of the nanocomposite are completely removed and the number of micro-holes on the catalyst increases. At this calcination temperature, BET is increased and at higher temperatures from 550 0C to 900 0C, the specific surface area decreases. The specific surface area of the synthesized nanocomposite was 51.28($m^3.g^{-1}$).

PH effect:

pH plays an important role in the decomposition of organic compounds in water environments. Hydroxyl radicals, which are the main factor in advanced oxidation processes, are produced more in an acidic environment. Changes in pH affect the rate of oxidation of organic substances through the production of various radicals, and the type and number of radicals produced in these processes are the most important causes of the decomposition of organic compounds in oxidation processes (16,17).The surface charge of pH The composition of TiO2@SiO2 is equal to 5. Also, the toxin 2- 4 dichlorophenoxyacetic acid is easily charged on a negative surface.

In the study of Rezajazinizadeh et al., in the removal of 2- 4 dichlorophenoxyacetic acid from aqueous environments using modified magnetic nanoparticles, the pH range was between 3 and 11. The optimum pH for removal was found to be 6. (19). In the study of Najmeh Arooji et al., in the removal of 2- 4 dichlorophenoxyacetic acid from aqueous environments using modified magnetic nanocomposite on granulated activated carbon, the pH ranged from 3 to 11. The optimal pH of removal was obtained 5 (20). In the study of Jokar et al., in the removal of 2- 4 dichlorophenoxyacetic acid using titanium dioxide and activated carbon, the pH value was considered to be 4,7,10. The optimal removal pH=4 was found to (1). In the study of Ali Esrafili et al., in the removal of 2 and 2- 4 dichlorophenoxyacetic acid from aqueous solutions using modified magnetic nanoparticles, the pH value was adjusted between 3 and 11. The optimal pH of removal was obtained 6 (2). According to the results of Figure (3-a), the highest removal efficiency of 2- 4 dichlorophenoxyacetic acid herbicide was obtained by N-TiO2@SiO2@Fe3O4

nanocomposite in the presence of ultrasonic at pH 6 with 88.59%. After that, pH 9 and 3 had the highest removal efficiency with 86.77% and 82.68% respectively. The high efficiency at pH equal to 6 can be due to the establishment of electrostatic force between the negatively charged molecules of 2- 4 dichlorophenoxyacetic acid and the positively charged absorbent surface (2).

The effect of initial concentration changes:

According to the available results, the removal efficiency of 2- 4 dichlorophenoxyacetic acid in the ultrasonic and nanocomposite process decreases with increasing the initial concentration of the pollutant. As shown in Figure (3- b), the removal efficiency for the initial concentration of 5 mg/L in the presence of ultrasonic is 87.5%, and in concentrations of 10, 15, 20 and 25, respectively, the removal efficiency of 2,4 dichlorophenoxyacetic acid herbicide. 80.6%, 74.06%, 70.5%, and 66.05% were obtained by N-TiO2@SiO2@Fe3O4 nanocomposite in the presence of ultrasonic. In the study of Reza Jezinizadeh et al., in the removal of 2,4 dichlorophenoxyacetic acid using N-TiO2@SiO2@Fe3O4 nanoparticles for concentrations of 5, 10, and 50%, the removal was obtained as 98.7%, 95%, and 67.66%, respectively. . Also, the results show that the removal efficiency decreases with the increase in pollutant concentration (2,19). With the increase in pollutant concentration, pollutant molecules are more absorbed on the catalyst surface, as a result, the production of interfering products increases in the interlayer space, which reduces the reaction of free radicals with pollutant molecules, and as a result, the degradation efficiency decreases (12,21).

Effect of mixer speed changes:

Figure 3- c shows that the removal efficiency of 2 and 4 dichlorophenoxyacetic acid increases by increasing the speed of the stirrer in 90 minutes. The highest removal efficiency of this toxin by N-TiO2@SiO2@Fe3O4 nanocomposite in the presence of ultrasonic at the stirring speed of 300 rpm was 88.06%, after which the speeds of 250 and 200 rpm had 75.07% and 68.6% removal efficiency, respectively. By increasing the speed of the stirrer, the rate of diffusion of adsorbed ions from the liquid bulk to the boundary layer around the catalyst increases due to the decrease in the thickness of the boundary layer (22). At low speeds, the mixing is not done well and the nanoparticle is not evenly distributed in the solution, and therefore it does not come into contact with the pollutant properly, and as a result, the removal efficiency is reduced (23).

The viscosity of the liquid around the herbicide 2- 4 dichlorophenoxyacetic acid decreased with the increase in the stirrer speed as a result of the contact between the pollutant and the catalyst increased, which increases the removal efficiency of this herbicide. The study by Reza Jezinizadeh et al. at a speed of 400 rpm shows that at higher speeds, the percentage of pollutants removal is higher (19).

Effect of changes in catalyst dosage:

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In the optimal conditions of optimal pH = 6, the optimal pollutant concentration is 5 mg/L, the stirring speed is 300 rpm, in the presence of ultrasonic doscatalyst (0.3 g/L) 87% and the doses of 0.1 and 0.2 were 71.2% and 50.4%, respectively. According to Figure (3 -d), by activating the catalyst sites, ultrasonic creates more electron holes and more OH$^\varepsilon$ radicals are produced. The increase of free radicals leads to more destruction and as a result increases the efficiency. The increase in the absorption percentage is due to the increase in the concentration of the adsorbent due to the active sites and more area on the adsorbent, which leads to an increase in the absorption of 2,4 dichlorophenoxyacetic acid on the surface (2,19).

Effect of contact time changes:

Reaction time is one of the important parameters for the design and management of a purification process. The reaction time is the time required to reach the optimal removal or absorption efficiency in a purification process. Also, the toxicity of the effluent is reduced, because the contact between the free radicals and the pollutant is increased, and as a result, the decomposition is more complete and the final efficiency increases. With the increase of time, the process of oxidation-reduction reactions and the production of hydroxyl free radicals continued, and the generated free radicals are spent on the decomposition of the pollutant and the by-products obtained (2,19,20,24,25). At contact times of 10, 15, 30, 60 and 90 minutes, the removal percentage was 15.4%, 27.2%, 45.1%, 72.3% and 88.49%, respectively. Therefore, with increasing contact time, the removal efficiency of 2- 4 dichlorophenoxyacetic acid also increases. 45% removal was done in the first 30 minutes. 72% removal was achieved within 60 minutes. By increasing the contact time, it is given the opportunity to produce more OH$^\varepsilon$ radicals (2,19,20,25,29).

Conclusion

This research showed that modified N-TiO2@SiO2@Fe3O4 nanoparticle in the presence of ultrasound is effective in removing 2- 4 dichlorophenoxyacetic acid from aqueous environments. On the laboratory scale, pH = 6, catalyst dose 0.3 g/L, contact time 90 minutes, stirrer speed 300 rpm and initial concentration 5 mg/L were the best conditions for rmmoval 2- 4 dichlorophenoxyacetic acid toxin.

References

1. Solaimany Nazar AR, Jokar Baloochi S, Farhadian M, Goshadrou A. 2, 4-dichlorophenoxyacetic acid adsorption from contaminated water through activated carbon reclaimed with zero-valent iron and titanium dioxide. Scientia Iranica. 2018;25(3):1395-411.
2. Esrafily A, Farzadkia M, Jonidi Jafari A, Izanloo M. Removal of 2, 4-Dichlorophenoxyacetic acid herbicide from aqueous solutions by Functionalization nanoparticles magnetic: Equilibrium, kinetic and thermodynamic studies. Journal of North Khorasan University of Medical Sciences. 2018;9(4):1-8.

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3. Haghighi Asl A, Ahmadpour A, Fallah N. Synthesis of Nano N-TiO2 for modeling of petrochemical industries spent caustic wastewater photocatalitic treatment in visible light using DOE method. Applied Chemistry. 201:253-86:(42)12;7

4. Nasseh N, Barikbin B, Taghavi L, Nasseri MA. Degradation of metronidazole antibiotic using a novel synthesized magnetic nanocomposite in heterogeneous Fenton-like catalytic process. Journal of Water and Wastewater/Ab va Fazilab. 2019.(4).

5. Haddadi S, Naseri S, Vaezi F, Mahvi AH, Nabizadeh R. Determining the effects of various factors on the effectiveness of ultrasonic treatment of secondary effluent. Journal of Water and Wastewater; Ab va Fazilab (in persian). 2007;18(3):31-8.

6. Kumar A, Khan M, Fang L, Lo IM. Visible-light-driven N-TiO2@ SiO2@ Fe3O4 magnetic nanophotocatalysts: synthesis, characterization, and photocatalytic degradation of PPCPs. Journal of hazardous materials. 2019;370:108-16.

7. Sarrafioun F, Jamehbozorgi S, Ramezani M. Synthesis of Tetrazoles Catalyzed by Novel Cobalt Magnetic Nanoparticles. Russian Journal of Organic Chemistry. 2019;55(11):1777-84.

8. Wei-Lin G, Xi-Kui W. Formation of the rutile TiO 2 under ultrasonic irradiation. Journal of materials Science.3265-6:(9)39;2004

9. Lu H, Wang J, Stoller M, Wang T, Bao Y, Hao H. An overview of nanomaterials for water and wastewater treatment. Advances in Materials Science and Engineering. 2016;2016.

10. Mungondori HH, Tichagwa L, editors. Photo-catalytic activity of carbon/nitrogen doped TiO2-SiO2 under UV and visible light irradiation. Materials Science Forum; 2013: Trans Tech Publ.

11. Hamzezadeh-Nakhjavani S, Tavakoli O, Akhlaghi SP, Salehi Z, Esmailnejad-Ahranjani P, Arpanaei A. Efficient photocatalytic degradation of organic pollutants by magnetically recoverable nitrogen-doped TiO2 nanocomposite photocatalysts under visible light irradiation. Environmental Science and Pollution Research. 2015;22(23):18859-73.

12. Zahedi F, Behpour M, Ghoreishi SM, Khalilian H. Photocatalytic degradation of paraquat herbicide in the presence TiO2 nanostructure thin films under visible and sun light irradiation using continuous flow photoreactor. Solar Energy. 2015;120:287-95.

13. Ju J, Chen X, Shi Y, Miao J, Wu D. Hydrothermal preparation and photocatalytic performance of N, S-doped nanometer TiO2 under sunshine irradiation. Powder technology. 2013;237:616-22.

14. Habila MA, ALOthman ZA, El-Toni AM, Labis JP, Soylak M. Synthesis and application of Fe3O4@ SiO2@ TiO2 for photocatalytic decomposition of organic matrix simultaneously with magnetic solid phase extraction of heavy metals prior to ICP-MS analysis. Talanta. 2016;154:539-47.

15. Yu J, Yu JC, Cheng B, Zhao X. Photocatalytic activity and characterization of the sol-gel derived Pb-doped TiO2 thin films. Journal of sol-gel science and technology. 2002;24(1):39-48.

Sead Mojtaba Hosseini et. Al
Investigating the effectiveness of 2-4 dichlorophenoxyacetic acid toxin removal using the combined
method of ultrasonic and N-TiO2@SiO2@Fe3O4 magnetic nanocatalyst from aqueous environments

16. Nguyen V-C, Nguyen T-V. Photocatalytic decomposition of phenol over N–TiO2–SiO2 catalyst under natural sunlight. Journal of Experimental Nanoscience. 20.233-42:(3)4;09

17. Nguyen T-V, Lee H-C, Yang O-B. The effect of pre-thermal treatment of TiO2 nano-particles on the performances of dye-sensitized solar cells. Solar Energy Materials and Solar Cells. 2006;90(7-8):967-81.

18. Seidmohammadi A, Amiri R, Faradmal J, Lili M, Asgari G. UVA-LED assisted persulfate/nZVI and hydrogen peroxide/nZVI for degrading 4-chlorophenol in aqueous solutions. Korean Journal of Chemical Engineering. 2018;35(3):694-701.

19. Zadeh RJ, Sayadi MH, Rezaei MR, editors. Removal of 2,4-dichlorophenoxyacetic acid from aqueous solutions by modified magnetic nanoparticles with amino functional groups2020.

20. Orooji N, Takdastan A, Jalilzadeh R, Jorfi S, Davami A. Photocatalytic degradation of 2,4-dichlorophenoxyacetic acid using Fe3O4@TiO2/Cu2O magnetic nanocomposite stabilized on granular activated carbon from aqueous solution. Research on Chemical Intermediates. 2020;46.

21. Ben W, Qiang Z, Pan X, Chen M. Removal of veterinary antibiotics from sequencing batch reactor (SBR) pretreated swine wastewater by Fenton's reagent. Water research. 2009;43(17):4392-402.

22. Kuśmierek K, Świątkowski A. The influence of different agitation techniques on the adsorption kinetics of 4-chlorophenol on granular activated carbon. Reaction Kinetics, Mechanisms and Catalysis. 2015;116(1):261-71.

23. KHODABAKHSHI A, AMIN MM, MOZAFFARI M, BINA B. REMOVAL OF CR (VI) FROM SIMULATED ELECTROPLATING WASTEWATER BY MAGHEMITE NANOPARTICLES. 2010.

24. Kermani M, Bahrami Asl F, Farzadkia M, Esrafili A, Salahshur Arian S, Arfaeinia H, et al. Degradation efficiency and kinetic study of metronidazole by catalytic ozonation process in presence of mgo nanoparticles. Studies in Medical Sciences. 2013;24(10):839-50.

25. Safa S, Mirzaei M. Photodegradation of the Herbicide,2-4 Dichlorophenoxyacetic Acid in the Presence of TiO2 and P25/βCD Nano Photocatalysts in the Photoreactor. 2018.

26. Murray CA, Goslan EH, Parsons SA. TiO2/UV: single stage drinking water treatment for NOM removal? Journal of Environmental Engineering and Science. 2007;6(3):311-7.