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Removal of Dexamethasone from Aqueous Solutions using Sono-Nanocatalysis Process

¹Hasan Rahmani, ²Kouros Rahmani, ³Ayat Rahmani and ⁴Mohammad-Reza Zare

¹Department of Environmental Health Engineering, School of Public Health, Ahvaz Jundishapur University of Medical Sciences, Ahvaz, Iran

²Department of Environmental Health Engineering, School of Public Health, Ardabil University of Medical Sciences, Iran

³Department of Environmental Health Engineering, School of Health, Shahid Beheshti University of Medical Sciences, Tehran, Iran

⁴Department of Environmental Health Engineering, School of Public Health, Isfahan University of Medical Sciences, Isfahan, Iran

Corresponding Author: Kouros Rahmani, Department of Environmental Health Engineering, School of Public Health, Ardabil University of Medical Sciences Tel: +98 45 33510052 Fax: +98 45 33512004

ABSTRACT

Degradation of dexamethasone (DEX) was investigated using nano-scaled Zero-Valent Iron (nZVI) in the presence of hydrogen peroxide and ultrasound (US). The experiments were performed in different variables such as pH, nZVI dose, H₂O₂ concentration, DEX concentration and ultrasonic frequency. Maximum removal (92%) was obtained at pH: 4, nZVI: 0.3 g L⁻¹, H₂O₂: 1.5 mmol, DEX: 15 mg L⁻¹ and US: 140 kHz. The pH was one of the most important factor influencing the process, also, determining the optimal dose of hydrogen peroxide had to be considered. In this study, degradation reaction kinetics of DEX and efficiency of the removal of COD were investigated in synthetic and actual wastewater.

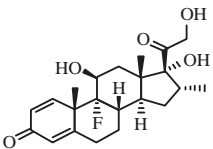
Key words: Dexamethasone, zero-valent iron, nanoparticle, hydrogen peroxide, sonolysis

INTRODUCTION

Dexamethasone (DEX) is a type of steroid medication with anti-inflammatory and immunosuppressant effects (Reid, 2000). It is used for the treatment of many conditions including; rheumatologic problems, a number of skin diseases, such as erythema multiform, severe allergies, asthma, chronic obstructive lung disease, croup and cerebral edema, in addition to other medications in tuberculosis and a number of other infectious diseases (Dimatteo *et al.*, 2002). It has contaminated surface and underground waters in various sites around the world and observed in sewage effluent (Herrero *et al.*, 2012). Table 1 shows, the properties and chemical structure of the DEX.

Several processes have been studied for the treatment of pharmaceutical wastewater. The Advanced Oxidation Processes (AOP_s) are one of the novel technologies for treating polluted sources of drinking water and industrial wastewater containing non-biodegradable organic pollutants, such as antibiotics (Farzadkia *et al.*, 2014; Rahmani *et al.*, 2014). The AOP_s can be applied to fully or partially oxidize pollutants, usually using a combination of oxidants. Ability and efficiency of various AOP_s depend on the generation rate of free radicals (especially, hydroxyl radical) and provide the necessary contact between the radicals and organic compound

Table 1: Properties and chemical structure of the DEX

Properties	Parameters
Formula	C ₂₂ H ₂₉ FO ₅
Mol. mass	392.461 g mol ⁻¹
λ _{max}	254 nm
Solubility	Ethanol: Soluble 1 mg mL ⁻¹
pK _{a1}	1.8
Chemical structure	

(Gogate and Pandit, 2004). Nano-scaled Zero-Valent Iron (nZVI) has been successfully used in the AOP system for the generation of $\bullet\text{OH}$ (Xu and Wang, 2011). In ultrasonic/ $\text{Fe}^0/\text{H}_2\text{O}_2$ systems, Fe^0 is a source of Fe^{+3} and Fe^{+2} species for contaminant adsorption (adsorptive size-exclusion) and sequestration. Using nano-scaled zero-valent iron, instead of iron oxides as a reagent source, can be exploited in the context of contaminant oxidation by Fenton's reaction that has high oxidation potential. The application of iron oxides in the Fenton systems has been limited with very low variable stoichiometric efficiency of oxidant production, especially at neutral pH values (Choi and Lee, 2012). This issue is related to free radical generation in the areas on the oxide surface that is inaccessible to the contaminants. These free radicals attack organic compound and depending on the type and structure of pollutants, completely mineralize them into CO_2 and water (Farzadkia *et al.*, 2014). Ultra sonication has been proved as an efficient method for the improved dissolution of iron particles in moderate acidic media as well as field applications (permeable reactive barriers) (Molina *et al.*, 2006). The concomitant use of zero-valent iron nanoparticles together with ultrasonic irradiation result in enhanced mass transport of reactants, where sonolysis process increases the defects and number of active sites while continuously cleaning it (Eren and Ince, 2010; Zhou *et al.*, 2008). Under low frequency ultrasonic irradiation, enhanced iron oxidative dissolution generates Fe^{+2} ions in the solution by keeping the iron surface particles devoid of the oxide scale for further Fe^0 dissolution. Contrary to high US frequencies (e.g., 400-800 kHz), 40 kHz ultrasonic irradiation is not able to promote the cavitation phenomena using the concomitant H_2O hemolysis and OH radical generation. The generated Fe^{2+} ions react with H_2O_2 additive and yield hydroxyl radicals ($\bullet\text{OH}$) are able to oxidize organic compounds. However, this process has a limiting step related to the low kinetic rate of Fe^{2+} regeneration mediated by the formation of $\text{Fe}(\text{OOH})^{2+}$ and $\text{Fe}(\text{OH})^{2+}$ complexes. Ultrasonic irradiation device, contrary to the silent system, is found to be efficient in rapidly releasing ferrous iron at the same time as the formation of hydroperoxy radical $\bullet\text{OOH}$ and $\bullet\text{OH}$ (Molina *et al.*, 2006). They are active species that can participate in redox reactions.

Few studies have been performed to remove DEX from wastewater (Sulaiman *et al.*, 2014; Arsand *et al.*, 2013). In this study, the degradation of the DEX from aqueous solutions was investigated by ultrasonic/ $\text{Fe}^0/\text{H}_2\text{O}_2$ systems. Efficiencies of the degradation of the DEX in different conditions were also compared.

MATERIALS AND METHODS

Chemicals and reagents: The ultrapure water was obtained from Milli-Q® equipment (Millipore). The oxidant hydrogen peroxide (35%, w/w, solution), sodium hydroxide, potassium iodide, sodium thiosulfate and sulfuric acid (H_2SO_4) used for pH adjustments were all purchased from Merck. DEX powder, acetonitrile and sodium formate were supplied by Sigma-Aldrich Company (Germany).

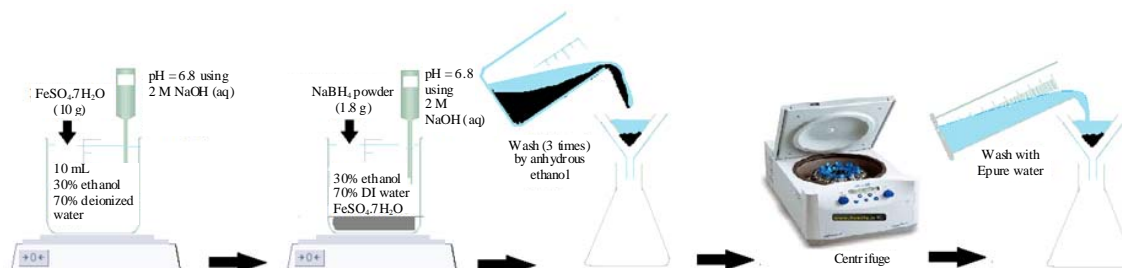


Fig. 1: Zero-iron nanoparticles synthesis steps

Preparing nano-sized zero-valent iron particles: The nZVI used in this study was made according to the method described by Ponder *et al.* (2000). As shown in Fig. 1, in this process, reduction of sodium borohydride (NaBH_4) was accrued in the presence of aqueous iron salt ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$). The iron solids were repeatedly washed (for 3 times) by anhydrous ethanol to remove the by-product salts and then slurry was gathered through centrifuging for 10 min at 5000 rpm, decanting and refilling with Epure water. The Fe^0 was stored at 4°C and solicated before use Ponder *et al.* (2000). The nanoparticle was characterized by Bruker AXS X-ray diffraction (XRD, X'Pert Pro MPD) and PHILIPS EM 208 Transmission Electron Microscope (TEM). The FESEM (field emission scanning electron microscope) image (Hitachi S4160, Japan) had excellent high-resolution quality that was particularly valuable when studying particles in the 1-200 μm size range. Images of nano-sized zero-valent iron particles were prepared in College of Engineering, University of Tehran (Fig. 2). The average particle size of the suspended iron particles was expected to be 50 nm.

Procedures: In this study, specific doses of zero-valent iron nanoparticles ($0.1, 0.2$ and 0.3 g L^{-1}) and certain concentration of hydrogen peroxide were added to the reactor. Different reaction times for each concentration of the pollutant and zero-valent iron nanoparticles were considered.

The reaction times from eight time intervals of 15, 30, 45, 60, 75, 90, 120 and 150 min were found during the investigation. The pH was considered in the range of 2, 4, 7 and 10. The samples containing nano-scaled iron particles after reaction time were transferred to the centrifuge set, centrifuged for 10 min at 5000 rpm to separate the Fe^0 solids from the aqueous solution and then passed through a $0.2 \mu\text{m}$ filter. In order to generate ultrasonic waves, an ultrasonic bath that could generate waves with the frequency of 37, 130 and 180 kHz and power of 500 W was applied. Then, the output values were measured by HPLC set. The DEX removal efficiency was also calculated by the following equation:

$$\text{Removal efficiency (\%)} = \frac{C_i - C_t}{C_i} \times 100$$

Where:

C_i : Initial concentration of the DEX before contact

C_t : Concentration of the DEX after the contact

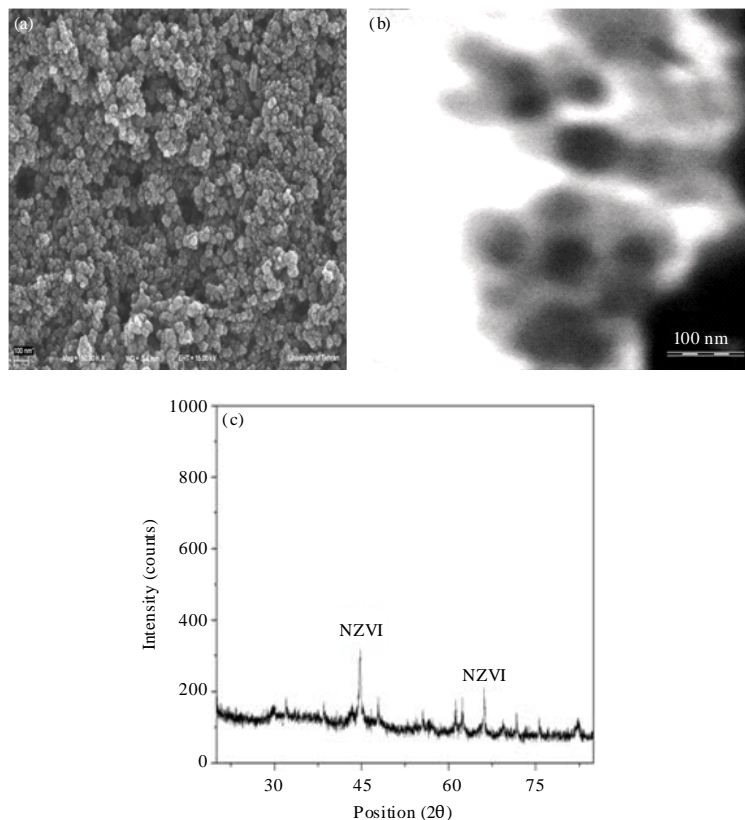


Fig. 2(a-c): Characterization of NZVI particles, (a) SEM, (b) TEM and (c) XRD

Sample analysis: After taking the input and output samples, the samples were filtered by a 0.2 μm PVDF membrane and a few drops of 1 M NaOH were added immediately to stop the reaction. In the following work, the prepared samples were injected into the HPLC set. The DEX concentration was measured by HPLC (HPLC, Shimadzu, LC10A HPLC; Detector Equipped with UV (SPD-10AV) in which the liquid chromatography column was a C_{18} reversed phase column (5 μm , 4.6 mm i.d. \times 250 mm long) and the measurement wavelength for detection was set at 254 nm. The used mobile phase was acetonitrile: formate buffer [30:70] (0.02 mol L^{-1} sodium formate, pH 3.5) and the flow rate was set to 0.5 mL min^{-1} . The retention time of DEX was 5.5 min under these conditions. The concentration of H_2O_2 was determined by the peroxidase-DPD method (Wang *et al.*, 2014). The amount of consumed hydrogen peroxide was obtained by the test error. All the experiments were performed twice and the mean values were reported.

RESULTS AND DISCUSSION

Effect of nano-sized zero-valent iron particles: In order to attain maximum removal, the optimal dose of nZVI on the removal of DEX with constant concentration of pollutant, hydrogen peroxide dosage and frequency of the ultrasonic bath was determined. Evidence showed (Fig. 3) that, in the fixed conditions (pH = 7, H_2O_2 = 1.5 mmol, DEX = 15 mg L^{-1} and US = 37 kHz) and after the initial Fe^0 loading was increased from 0.1-0.3 g L^{-1} , degradation rate was increased (40%).

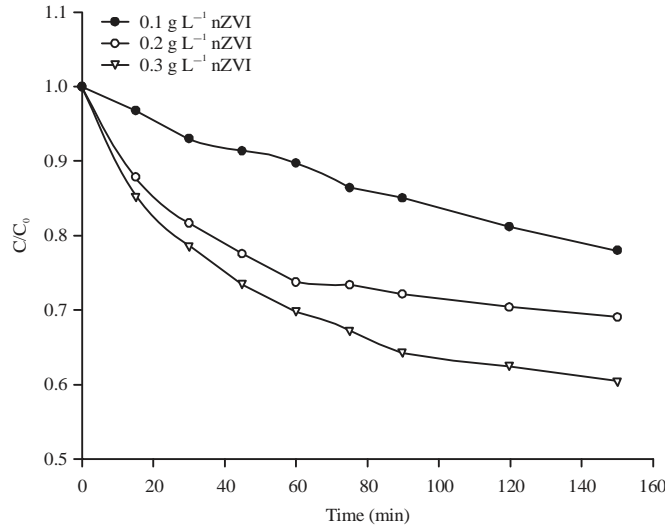


Fig. 3: Effect of nZVI concentration on DEX degradation (pH = 7, H₂O₂ = 1.5 mmol L⁻¹, DEX = 15 mg L⁻¹ and US = 37 kHz)

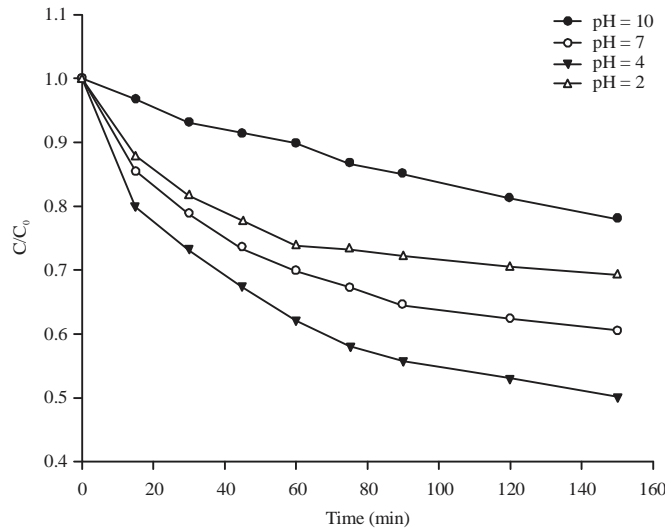


Fig. 4: Effect of pH on DEX degradation (nZVI: 0.3 g L⁻¹, H₂O₂ = 1.5 mmol L⁻¹, DEX = 15 mg L⁻¹ and US = 37 kHz)

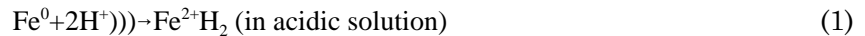
The Fe⁰ and its salt dosage had a great effect on the degradation rate. Nano-sized zero-valent iron particles were used individually; however, the results showed that the combination of oxidant agents, such as hydrogen peroxide would increase efficiency (Bergendahl and Thies, 2004). Based on the existing literature, enhancement of Fenton reaction can also occur under high ferrous concentration.

Effect of initial pH: Fenton oxidation is known as a highly pH-dependent process, since pH plays an important role in the mechanism of •OH production in the Fenton's reaction (Li *et al.*, 2015). In this study, the effect of pH 2, 4, 7 and 10 on the sono nanocatalyst was investigated. As can be seen in Fig. 4, the process showed the best performance at pH 4. At high pH (pH>4), the generation of

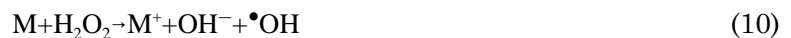
•OH became slower because of the formation of the ferric hydroxo complexes; the complexes would further form $[\text{Fe}(\text{OH})_4]$ when the pH value will be higher than 9.0 (Zhou *et al.*, 2015). On the other hand, at very low pH values (<2.0), the reaction was slowed down due to the formation of complex species $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$, which reacted more slowly with peroxide compared to that of $[\text{Fe}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$.

Effect of H_2O_2 concentration: The amount of hydrogen peroxide is another important parameter that influences a Fenton-like process. It is very important to observe the ratio between hydrogen peroxide and iron.

Due to the scavenging effect at elevated H_2O_2 loads, it is necessary to choose the optimum concentration of H_2O_2 according to the type and concentration of the pollutants (Ghauch *et al.*, 2011). At higher concentrations, other types of radicals ($\text{HO}^{\bullet 2}$ and $\text{O}_2^{\bullet -}$) are generated that are much less reactive than hydroxyl radicals (Babuponnusami and Muthukumar, 2012). Also, it is important to note that, at low H_2O_2 concentrations, degradation rate is very slow because of the production of insufficient hydroxyl radicals. On the other hand, using the hydrogen peroxide in the absence of iron powder due to the production of hydroxyl radicals energetic leads to the destruction of DEX bond. The production mechanism of hydroxyl radical in Fenton system in the presence of ultrasonic waves is given below (Ghauch *et al.*, 2011):



On the other hand, hydrogen peroxide can be decomposed at metal surface to produce hydroxyl radicals:



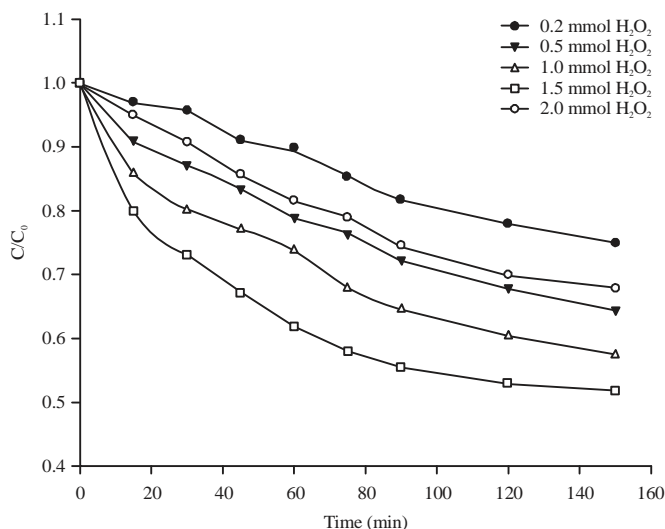


Fig. 5: Effect of H₂O₂ concentration on DEX degradation (pH = 7, nZVI: 0.3 g L⁻¹, DEX = 15 mg L⁻¹ and US = 37 kHz)



In this study, the highest DEX removal efficiency was obtained at the initial hydrogen peroxide concentration of 1.5 mmol. The obtained results for the effect of H₂O₂ concentration on DEX degradation are displayed in Fig. 5.

Ultrasonic input frequency: Although, the ultrasonic wave system is silent, it rapidly increases the efficiency of nZVI and iron salts with the increase of ultrasonic input frequency from 37-180 kHz. It is obvious that improvement of US input frequency has a positive effect on the degradation rate of DEX. Ultrasonic waves in water yield hydroxyl radicals and hydrogen atoms. Despite the fact that the hydroxyl radical produced in this pathway can break the pollutants down, the production values are very low. The primary role of ultrasonic waves in the present process is the dissolution improvement of zero-valent iron nanoparticles in the aqueous solution containing the hydrogen peroxide in moderate acidic media (Molina *et al.*, 2006) and inducing a set of complex redox reactions that will produce high levels of hydroxyl radicals (Ghauch *et al.*, 2011). The results show that sonolysis plays major roles in catalyzing the reactions (between hydrogen peroxide and zero-valent iron nanoparticles in this study), which could enhance efficiency and reduce reaction time (Rahmani *et al.*, 2014). Figure 6 shows that, for 0.3 g L⁻¹ Fe⁰ and 1.5 mM H₂O₂, DEX degradation can reach almost 92% after 150 min of sonication (180 kHz) at pH 4.

Effect of initial concentration of DEX: Since, the input concentration of pollutants is an important parameter, in this section, the effect of initial DEX concentration on ultrasonic/H₂O₂/Fe⁰ processes is investigated. The effect of concentration on process performance is illustrated in Fig. 7.

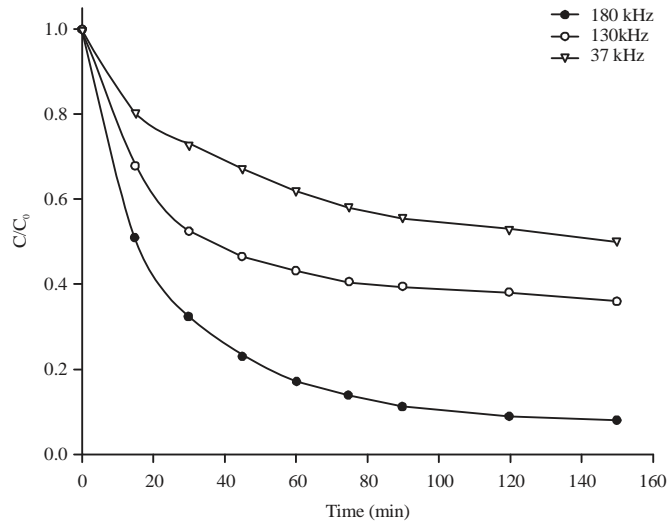


Fig. 6: Effect of ultrasonic input frequency on DEX degradation (pH = 7, nZVI: 0.3 g L⁻¹, H₂O₂ = 1.5 mmol L⁻¹ and DEX = 15 mg L⁻¹)

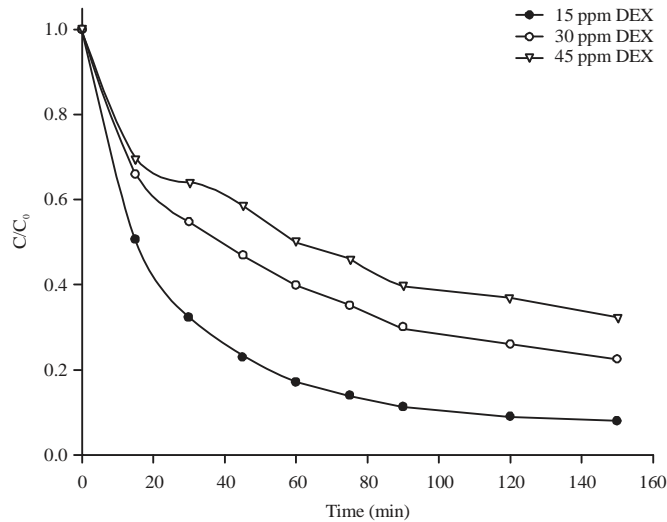


Fig. 7: Effect of initial concentration of DEX (pH = 7, nZVI: 0.3 g L⁻¹, H₂O₂ = 1.5 mmol L⁻¹ and US = 37 kHz)

It is evident that, with increasing initial DEX concentration from 15-45 mg L⁻¹, the percentage mineralization and decomposition is decreased from 92-66.7% for ultrasonic/Fe⁰/H₂O₂ process at 150 min. This issue can be attributed to the constant values for the amount of generated •OH (Rahmani *et al.*, 2014). Despite the increase in drug concentrations, the amounts of produced •OH are constant and so the percentage degradation decreases.

Degradation reaction kinetics of DEX: The degradation reaction kinetics of DEX can be described using the following equation:

$$\alpha_t/[C_0(1-\alpha_t)] = k_2t$$

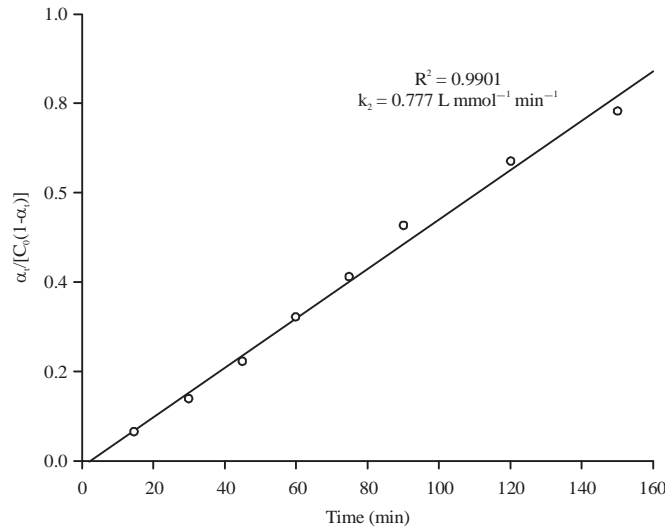


Fig. 8: Linear correlation between $\alpha_t/[C_0(1-\alpha_t)]$ and reaction time for the second-order degradation kinetics of DEX in US/nZVI/H₂O₂ system: (DEX concentration: 15 mg L⁻¹, nZVI: 0.3 g L⁻¹, H₂O₂: 1.5 mmol L⁻¹, pH:4.0 and ultrasound frequency = 180 kHz)

Table 2: Second order rate constants for the degradation reaction of DEX in US/nZVI/H₂O₂ system at 25°C

DEX (mg L ⁻¹)	pH	US (kHz)	nZVI dose (g L ⁻¹)	H ₂ O ₂ concentration (mmol L ⁻¹)	k ₂ (L mmol ⁻¹ min ⁻¹)	R ²
15	7	37	0.1	1.5	0.0188	0.9742
15	7	37	0.2	1.5	0.0297	0.9244
15	7	37	0.3	1.5	0.0436	0.9845
15	2	37	0.3	1.5	0.0297	0.9244
15	4	37	0.3	1.5	0.0663	0.9943
15	10	37	0.3	1.5	0.0188	0.9742
15	4	37	0.3	0.2	0.0222	0.9817
15	4	37	0.3	0.5	0.0366	0.9878
15	4	37	0.3	1.0	0.0493	0.9897
15	4	37	0.3	2.0	0.0313	0.9945
15	4	130	0.3	1.5	0.1186	0.9209
15	4	180	0.3	1.5	0.7772	0.9922
30	4	180	0.3	1.5	0.1144	0.9842
45	4	180	0.3	1.5	0.0466	0.9809

where, α_t is the degradation degree of DEX at reaction time t that can be obtained by $\alpha_t = (C_0 - C_t)/C_0$, C_0 is the initial concentration of the DEX, C_t is the DEX concentration at reaction time t and k_2 is the apparent rate constant for the degradation of DEX. The linear relationship between $\alpha_t/[C_0(1-\alpha_t)]$ and reaction time (with the correlation coefficient of 0.9901) of the initial concentrations of 0.3 g L⁻¹ of nZVI and 1.5 mmol L⁻¹ of H₂O₂ is shown in Fig. 8.

The obtained k_2 value of DEX by a linear least-square analysis that can be determined from the slope of the linear plot of $\alpha_t/[C_0(1-\alpha_t)]$ against t is included in Table 2.

The data of apparent rate constants can be used to study the effect of different parameters and variables such as nZVI and H₂O₂ on the degradation reaction rate of DEX in US/nZVI/H₂O₂ system. As shown in Table 2, in optimal conditions, when the initial concentration of pollutants was reduced, the k_2 values were increased from 0.0466-0.7772 L mmol⁻¹ min⁻¹ at the initial H₂O₂ concentration of 1.5 mmol L⁻¹ and the initial nZVI dosage of 0.3 g L⁻¹. Also, when nZVI dosage was increased from 0.1-0.3 g L⁻¹, the k_2 values were only increased from 0.0188-0.0436 L mmol⁻¹ min⁻¹ at the initial H₂O₂ concentration of 1.5 mmol L⁻¹. Generally, by reducing the concentration of DEX,

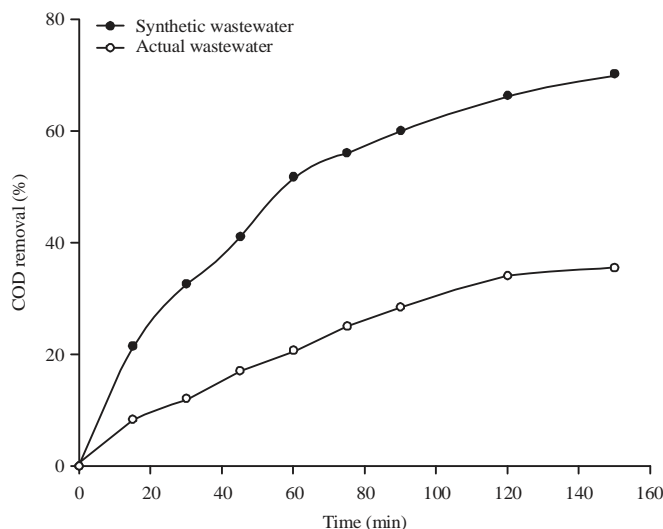


Fig. 9: Removal efficiency of DEX and COD by the ultrasonic/FeO/H₂O₂ process

pH and vice versa, by increasing the concentration of hydrogen peroxide, nZVI dosage and transmission frequency of the ultrasonic device, the k_2 values were increased. However, the initial concentration of H₂O₂ and nZVI dosage was found to have a significant influence. The linear correlation coefficients (R) achieved from linear regression analysis and the values of apparent rate constant k_2 are also listed in Table 2.

Elimination of COD: Chemical Oxygen Demand (COD) test measures the amount of oxygen required for the conversion of organic compounds into water and carbon dioxide (Priya *et al.*, 2009). The experiments in this section are carried out according to the standard methods (APHA, AWWA and WPCF., 2005). Figure 9 shows the removal efficiency of DEX and COD, as the ultrasonic/Fe⁰/H₂O₂ process was prolonged for 150 min.

The results showed that, with increasing contact time, COD removal rates were increased with less steep than the removal of the drug. In the ultrasonic/Fe⁰/H₂O₂ systems, maximum Chemical Oxygen Demand (COD) removal efficiency of 70 and 35.5% was reached while treating synthetic wastewater and actual sewage at 150 min, respectively.

CONCLUSION

The main objective of this study was to assess the performance of nano-sized zero-valent iron in the presence of hydrogen peroxide and ultrasonic waves for the destruction of dexamethasone in the aquatic environment. The effects of reaction time, initial pH, DEX concentration, H₂O₂ dose and nZVI concentration were examined for the degradation of DEX. Optimum condition for 92% removal of DEX was obtained at pH: 4, time: 150 min, nZVI: 0.3 g L⁻¹, US: 180 kHz and H₂O₂: 1.5 mmol L⁻¹. The results showed that, with increasing contact time, removal efficiency was increased in both cases. However, COD removal efficiency was less than that of DEX. The best removal efficiency of ultrasonic/Fe⁰/H₂O₂ process for DEX and COD was 92 and 70%, respectively. The COD removal efficiency was 35.5% for actual sewage. Finally, the study highlighted the promise of nano-sized zero-valent iron as excellent systems in water and wastewater remediation processes using sonolysis. The results of this study indicated that the use of ultrasonic waves had a significant effect on the promotion and increase of the system performance.

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