



A novel modified fenton-like process for efficient remediation of anthracene-contaminated soils before analysis by ultraviolet–visible spectroscopy

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ABSTRACT

Due to the persistence of polycyclic aromatic hydrocarbons (PAHs) in soil and sediments, and their toxic, mutagenic, and carcinogenic effects, the remediation of PAH-contaminated sites is an important role for environment pollution. In this study, the chemical oxidative remediation of anthracene-contaminated soils was investigated by magnetite nanoparticles (Fe_3O_4) catalyzed Fenton-like oxidation in the presence of hydrogen peroxide 30% (H_2O_2) and urea-hydrogen peroxide (UHP) at neutral pH. Urea-hydrogen peroxide (UHP), as a safer oxidizing agent, is used for the first time in the Fenton process. The magnetite nanoparticles improved the production of hydroxyl radicals, and the removal of polycyclic aromatic hydrocarbons (anthracene as a model compound) from the soil samples. The structure of Fe_3O_4 nanoparticles was characterized by Fourier-transform infrared spectroscopy (FT-IR), X-ray powder diffraction (XRD), scanning electron microscopy (SEM), and vibrating sample magnetometer (VSM). The removal efficiency of anthracene at an initial concentration $2500 \text{ (mg kg}^{-1}\text{)}$ was 95% for 2.5 mmol by using hydrogen peroxide and 93% for 0.1 mmol of UHP at the optimum oxidation condition. The anthracene reaction was analyzed by ultraviolet-visible spectroscopy (UV-Vis). The UHP safety and efficiency, neutral pH condition, the limited iron leaching and its easy magnetic separation makes magnetite nanoparticles-UHP a promising catalytic system in remediation of polycyclic aromatic hydrocarbons in contaminated soils.

1. Introduction

The sixteen polycyclic aromatic hydrocarbons (PAHs) in the United States environmental protection agency and European community (US, EPA) are considered as priority pollutants [1, 2] The PAHs are toxic organic contaminants with great environmental and health concern, which consist of

two or more fused aromatic rings. PAHs containing up to two fused benzene rings such as anthracene and phenanthrene are known as light PAHs and those containing more than four benzene rings such as ovalene and corannulene are called heavy PAHs[3]. The main source of PAHs contamination is incomplete combustion and pyrolysis of wood or fossil fuels, the motor oil and petroleum spill which are disposed of improperly each year into soil[4]. Owing to the persistence of PAHs in soil

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and sediments, and their toxic, mutagenic, and carcinogenic effects, the remediation of PAH-contaminated sites is an important environmental issue. Various remediation techniques including incineration, thermal conduction, solvent extraction/soil washing, chemical oxidation, bio-augmentation, bio-stimulation, phytoremediation, composting/bio-piles and bioreactors have been explored and studied for the removal of persistent PAHs from complex matrices like soil or sediments. Integrating physico-chemical and biological technologies is also widely practiced for better clean-up of PAH contaminated soils. Electrokinetic remediation, vermiremediation and biocatalyst assisted remediation are at the development stage[5] In situ chemical oxidation (ISCO) has emerged as a cost-effective and viable remediation technology for the treatment of several pollutants in ground waters, soils and sediments[6–8]. Remediation by chemical oxidation involves the injection of strong oxidants such as hydrogen peroxide[9], ozone gas[10], potassium permanganate[11], etc. In last two decades a lot of researches have been addressed to this aim and pointed out the prominent role of a special class of oxidation techniques defined as advanced oxidation processes (AOPs), which usually operated at or near ambient temperature and pressure[12, 13]. Advanced oxidation processes (AOPs) are attracting significant attention because of their effective and rapid degradation performance, including photocatalysis [4, 14, 15], ozonisation[16], electrochemical reactions[17] and Fenton method[18, 19]. Among chemical oxidation processes, special attention has been paid to the use of Fenton's reagent, which release the hydroxyl radicals with high oxidation potential ($E^\circ=2.73$ V), from the catalytic decomposition of H_2O_2 in the presence of Fe (II) or Fe (III) ions. The Fenton method has the ability to oxidize a wide range of organic pollutants and convert them to CO_2 , H_2O and inorganic compounds or, at least, transform them into harmless or biodegradable products[20–23]. This conventional Fenton's process is limited by the optimum pH (~3), such as at low pH results in negative impacts on soil

properties and is incompatible with subsequent biodegradation. In the novel process as known as Fenton-like oxidation, the iron minerals or organic chelating agents can be applied to extend its range of applicability at circumneutral soil pH. The degradation of PAHs has been reported by Fenton-like reaction catalyzed by various Fe (III) oxides like ferrihydrite, hematite or goethite[24–26]. Recently, Fe(II) bearing minerals such as magnetite (Fe_3O_4) were found to be the most effective nanocatalyst as compared to the only Fe(III) oxides for heterogeneous catalytic oxidation of organic pollutants[26-29]. The researchers must be very careful when dispensing oxidizers from storage containers, avoid spilling material and contaminating their skin or clothing which can cause serious accidents. Urea-hydrogen peroxide (UHP) contains solid and water-free hydrogen peroxide, which offers a higher stability and better controllability than liquid hydrogen peroxide when used as an oxidizing agent. Urea-hydrogen peroxide adducts (UHP) is stable, inexpensive and an easily handled reagent. So, the UHP is used as a solid state agent for efficient oxidation of different organic molecules.

In this study, the anthracene as a model polycyclic aromatic hydrocarbon was removed from contaminated soil by a modified Fenton's reaction, using hydrogen peroxide and urea-hydrogen peroxide separately in the presence of bare magnetite nanoparticles (Fe_3O_4) as a nanocatalyst at circumneutral soil pH.

2. Experimental

2.1. Materials and apparatus

Anthracene 96% (CAS 120-12-7) and H_2O_2 30% (CAS 7722-84-1) were used as a contaminant and oxidant respectively. Ethanol 99.7% (CAS 64-17-5), Iron (II) chloride tetra hydrate 99% (CAS 13478-10-9) and Iron (III) chloride hexahydrate 98% (CAS 10025-77-1) were purchased from Merck Company. All reagents were used without further purification. The FT-IR spectra were recorded on Bruker Alpha spectrophotometer in the region $400-4000$ cm^{-1} using pressed KBr discs. The

field emission-scanning electron microscopy (FE-SEM) was carried out by a MIRA III TESCAN-XMU. The hysteresis loop was measured at room temperature using a vibrating sample magnetometer (Model 7300 VSM system, Lake Shore Cryotronic, Inc., Westerville, OH, USA). The UV-Vis spectrophotometer (Agilent 8453) was used to determine the oxidation process.

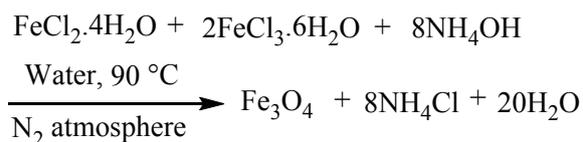
2.2. Soil Samples

Crushing and preparing of the samples was performed at geology department of Kharazmi University (Iran, Tehran) and powdering was done at the Iranian mineral processing research center (IMPRC). The analysis of whole-rock major and trace elements was conducted at ETH, Zurich. The major elements are summarized in Table 1.

2.3. Preparation of Fe₃O₄ nanoparticles

Magnetite nanoparticles (MNPs) was synthesized by co-precipitation method [31]. Aqueous solutions of FeCl₃.6H₂O (56 mmol) and FeCl₂.4H₂O (28

mmol) were prepared in de-ionized water (25 mL) and NaOH (3 M) solution was added to it slowly and stirred continuously using a magnetic stirrer to reach the pH=12. This solution was heated under N₂ atmosphere at 90 °C for 4 hours. The mixture was filtered and washed 3 times with deionized water DW/ ethanol before dried at 60 °C (Equation 1).



(Eq. 1)

2.4. Calibration curve

Figure 1 shows the UV-Vis absorption spectra and calibration curve of anthracene for different concentration. The absorption coefficient (ϵ) obtained by using the Lambert-Beer's law (Equation 2) [32].

$$A = \epsilon cd \quad (\text{Eq. 2})$$

Table 1. Total elemental analyses of soil sample.

Compound	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅
Wt.%	56.84	0.69	16.84	0.90	5.98	0.11	2.15	6.20	4.38	1.93	0.19

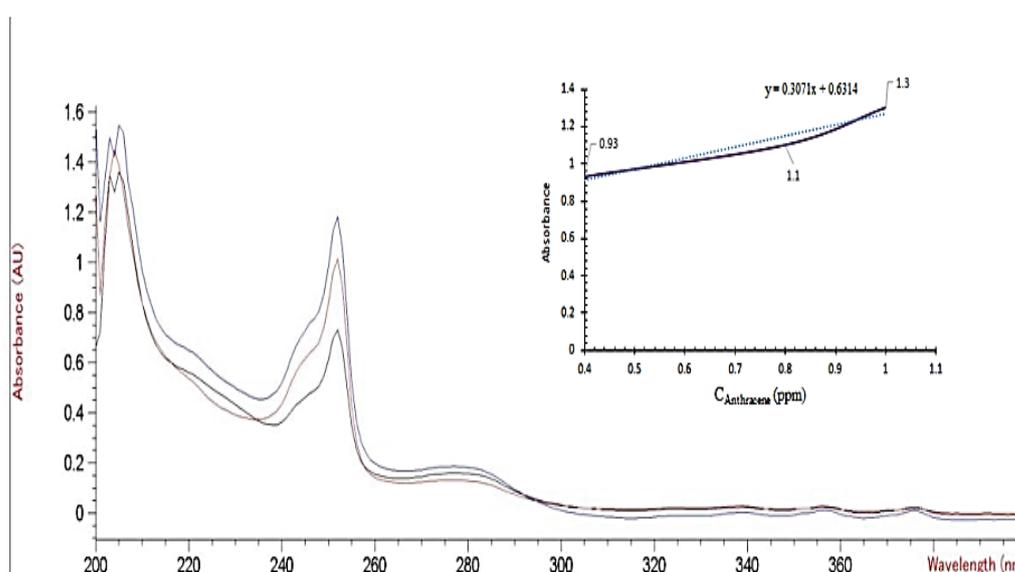


Fig. 1. UV-Vis absorption spectra and calibration curve of anthracene in the wavelength range 200-400 nm

2.5. Preparation of anthracene-contaminated soil

Soil samples was prepared as detailed in the literature,[33] where an ethanol solution with approximately 500 mg of anthracene was distributed and mixed manually onto 20 g of clean soil with a spatula which was homogenized.

2.6. Procedure od anthracene extraction

All experiments were carried out without pH adjustment and the experiments were done on a laboratory scale. All experimental runs were performed at room temperature. For all experiments, 1 gr (dry mass) of contaminated soil sample was placed in the tube, 2 mL of deionized water (DW) was added, followed by the required quantities of oxidants (H_2O_2 and urea- H_2O_2) and magnetite as a nanocatalyst (Table 2). The samples were shacked for 30 minutes. The residual anthracene in the soil sample was extracted in 8 mL of ethanol during 10 minutes and controlled the tube centrifugation for 15 min at 3000 rpm. The presence of anthracene in the solutions was analyzed by UV-Vis spectrophotometer ($\lambda_{\text{max}}=250$ nm). Figure 2 illustrates the oxidation process of anthracene in modified Fenton's reaction. The quantify decomposition of anthracene in soil was

shown in Equation 3 as follows,

$$X_{\text{Anthracene}} = \frac{C_0^{\text{Anthracene}} - C_t^{\text{Anthracene}}}{C_0^{\text{Anthracene}}} \times 100 \quad (\text{Eq. 3})$$

Where $X_{\text{Anthracene}}$ is the percentage of anthracene decomposed in soil, C_0 and C_t are the initial and final concentration of anthracene at a given time.

3. Result and discussions

3.1. Characterizations

The Fe_3O_4 nanoparticles were carefully prepared[34] and characterized by Furrier-transform infrared spectroscopy (FT-IR), X-ray powder diffraction (XRD), scanning electron microscopy (SEM), and vibrating sample magnetometer (VSM). The X-ray diffraction analysis (XRD) of Fe_3O_4 nanoparticles shows several diffraction peaks at $2\theta = 30.54, 35.89, 43.9, 54.28, 57.55, 63.3$ and 74.33 that attributed to the miller planes 220, 311, 400, 422, 511, 440 and 533 respectively (Fig. 3a). These results are in accordance with the standard patterns (JCPDS CardNo. 85-1436)[34] The FT-IR spectra of Fe_3O_4 MNPs is shown in Figure 3b. The appeared vibrational frequencies in the $584\text{-}631$ cm^{-1} region are attributed to the Fe-O bonds.

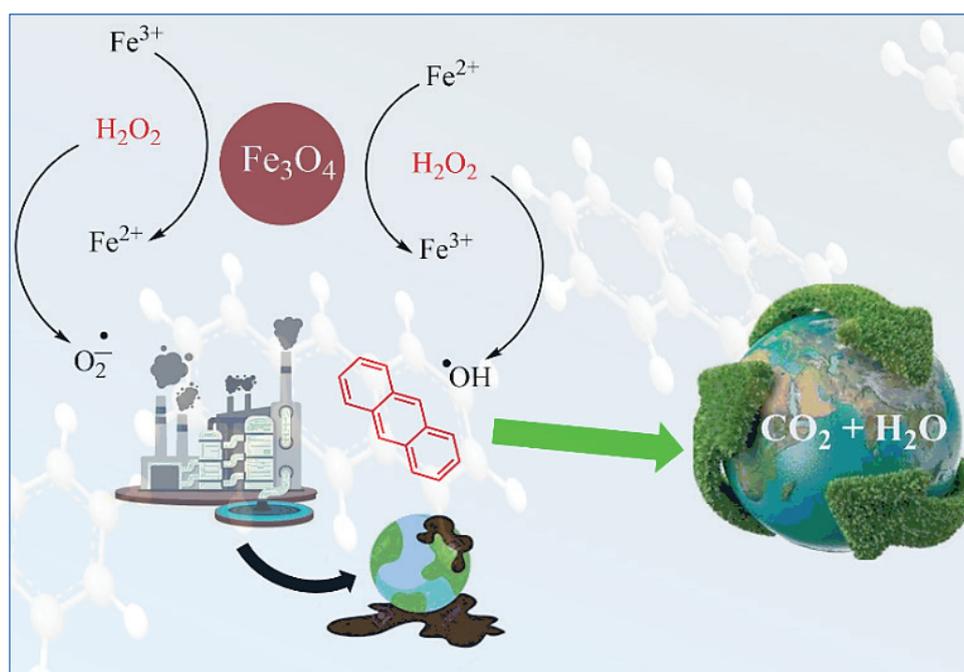


Fig. 2. The oxidation process of anthracene in modified Fenton's reaction

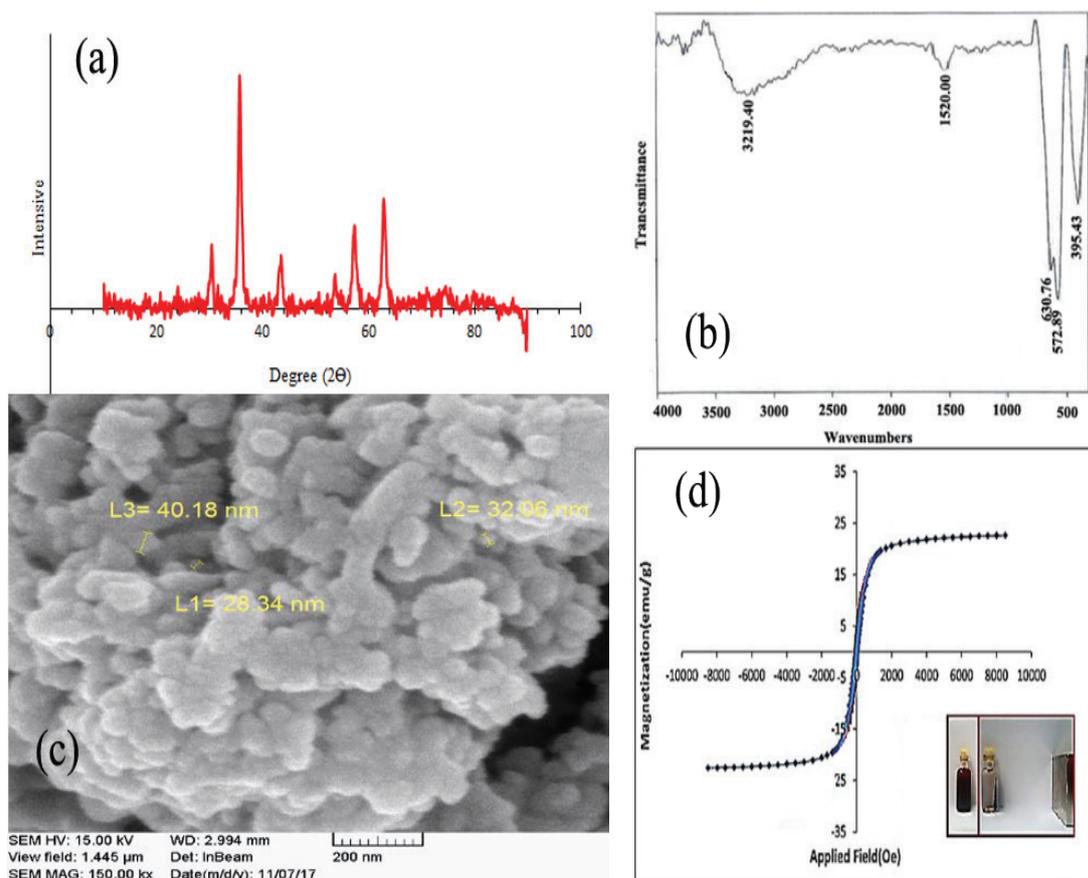


Fig. 3. The XRD spectra (a), The FT-IR spectra (b), The FE-SEM image (c) and The VSM (d) of Fe₃O₄ nanoparticles

The stretching frequencies of hydroxyl groups, on the surface of the nanoparticles, appeared at 3420 cm⁻¹ and the peak in the 1625 cm⁻¹ are related to the bending vibrations of OH groups. The morphology and particle size distribution of Fe₃O₄ nanoparticles was performed by FE-SEM technique. The average size of nanoparticle is 32 nm and confirm the spherical and regular shape of nanoparticles (Fig. 3c). The magnetic properties of the synthesized nanoparticles were determined by VSM at room temperature, which contains the magnetization curve (M) in terms of the applied magnetic field (H) (hysteresis curve) of Fe₃O₄ MNPs particles which shows the great paramagnetic properties (Fig. 3d).

3.2. The optimization of H₂O₂, urea-hydrogen peroxide and magnetite values

A different combination of magnetite and hydrogen peroxide was selected for optimization (Table 2).

First, the effect of varying H₂O₂ and urea-hydrogen peroxide concentrations on anthracene removal efficiency was investigated while the amount of magnetite was kept constant (Fig. 4). As H₂O₂ and UHP concentration rises, the removal of anthracene is increased and finally leveled off. The maximum removal efficiency of 95% at 0.2 mL H₂O₂ concentration and 93% at 6 mg UHP content was observed, respectively. Therefore, the H₂O₂ and UHP concentrations was optimized for further experiments. In the next stage, the effect of various amounts of magnetite on the Fenton oxidation of anthracene was investigated at optimum H₂O₂ concentration of 0.2 mL (2.5 mmol) and 6 mg UHP. The removal efficiency was increased with an increase in magnetite dosage up to 8 mg, and then was remained constant at higher concentrations (Fig. 5). The anthracene removal reached 93% at the optimum concentration levels of H₂O₂, UHP, and magnetite.

Table 2. Optimization of combination of magnetite and hydrogen peroxide

Entry	Samples	Magnetite (mg)	H ₂ O ₂ (ml)	Samples	Magnetite (mg)	Urea-H ₂ O ₂ (mg)
1	M ₁₀ ^a -H _{0.1} ^b	10	0.1	M ₁₀ -UHP ₃ ^c	10	3
2	M ₈ -H _{0.1}	8	0.1	M ₈ -UHP ₃	8	3
3	M ₆ -H _{0.1}	6	0.1	M ₆ -UHP ₃	6	3
4	M ₁₀ -H _{0.2}	10	0.2	M ₁₀ -UHP ₆	10	6
5	M ₈ -H _{0.2}	8	0.2	M ₈ -UHP ₆	8	6
6	M ₆ -H _{0.2}	6	0.2	M ₆ -UHP ₆	6	6
7	M ₁₀ -H _{0.3}	10	0.3	M ₁₀ -UHP ₁₀	10	10
8	M ₈ -H _{0.3}	8	0.3	M ₈ -UHP ₁₀	8	10
9	M ₆ -H _{0.3}	6	0.3	M ₆ -UHP ₁₀	6	10
10	M ₁₀ -H _{0.4}	10	0.4	M ₁₀ -UHP ₁₅	10	15
11	M ₈ -H _{0.4}	8	0.4	M ₈ -UHP ₁₅	8	15
12	M ₆ -H _{0.4}	6	0.4	M ₆ -UHP ₁₅	6	15
13	-	-	-	M ₁₀ -UHP ₂₀	10	20
14	-	-	-	M ₈ -UHP ₂₀	8	20
15	-	-	-	M ₆ -UHP ₂₀	6	20

^aMagnetite, ^bH₂O₂ 30%, ^cUrea-H₂O₂ (UHP)

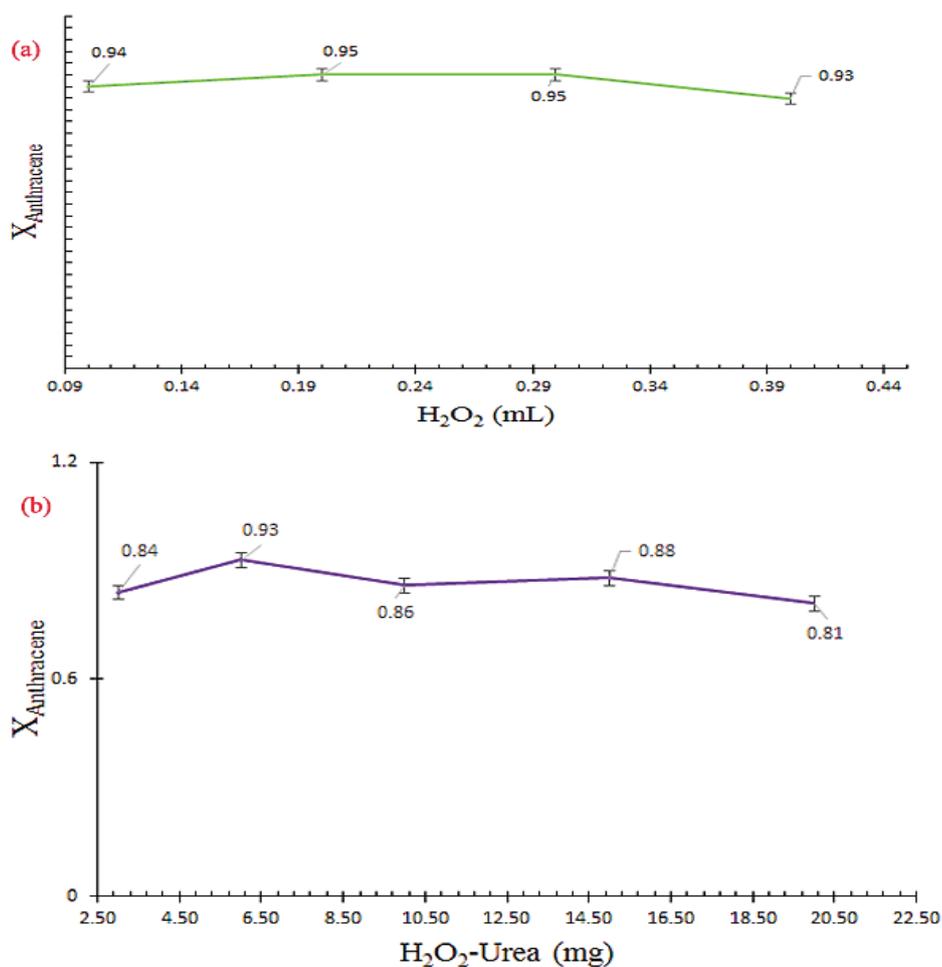


Fig. 4. The anthracene removal efficiency in varying (a) H₂O₂ concentrations of 0.1-0.4 mL (b) UHP 0.1-0.4 mg (reaction time of 30 min, pH=7 and magnetite concentration of 8 mg)

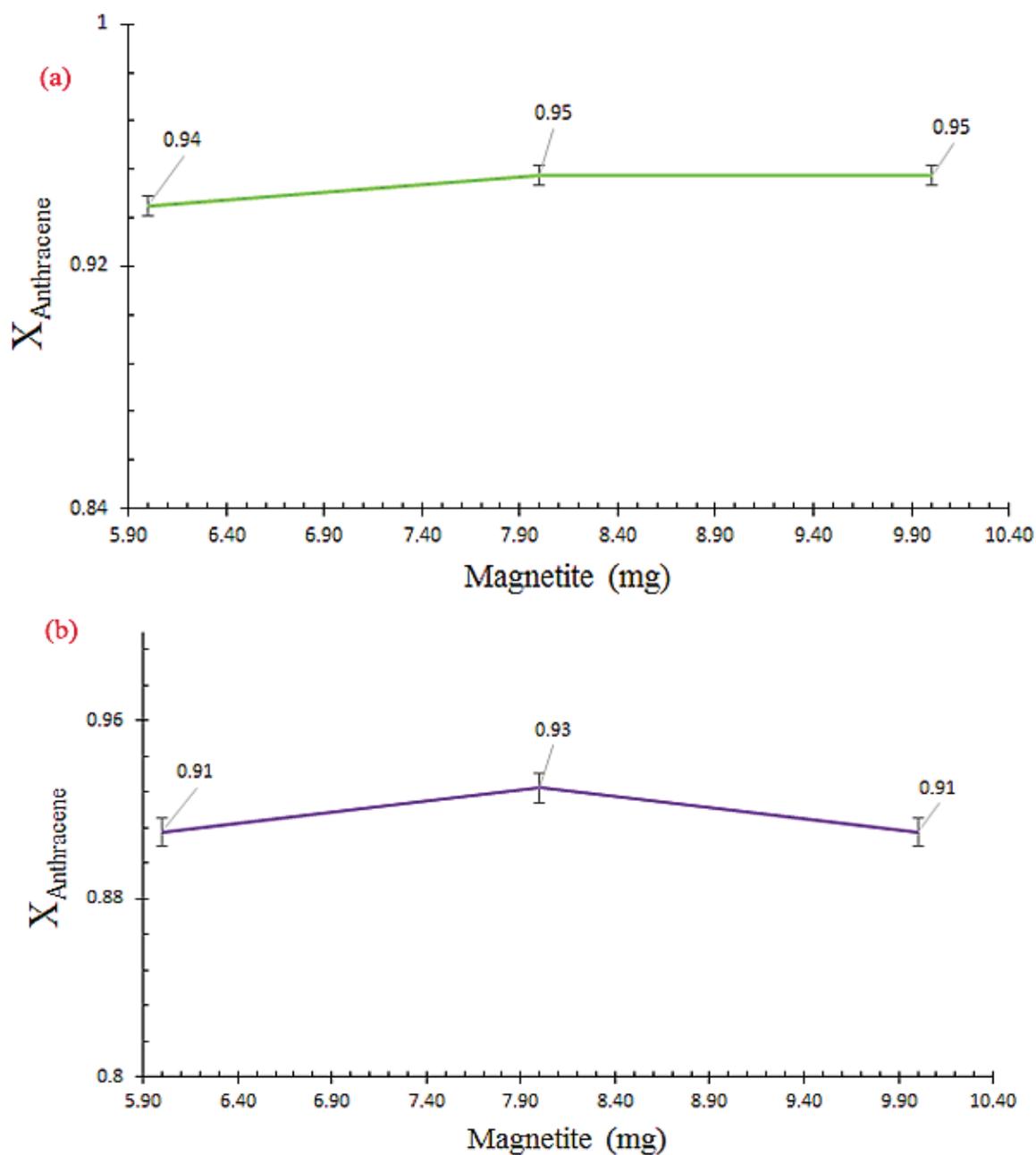


Fig. 5. The anthracene removal efficiency varying Fe₃O₄ content in optimized (a) H₂O₂ and (b) UHP concentration (reaction time of 30 min and pH=7)

3.3. The effect of contact time on anthracene removal

The effect of reaction time on anthracene removal at optimum H₂O₂ or UHP and magnetite concentration was investigated (Fig. 6).

The reaction time positively affected the removal efficiency and the anthracene removal of 98% was achieved after 30 min of contact time. After 24 h, about 99% conversion was achieved for all contaminants.

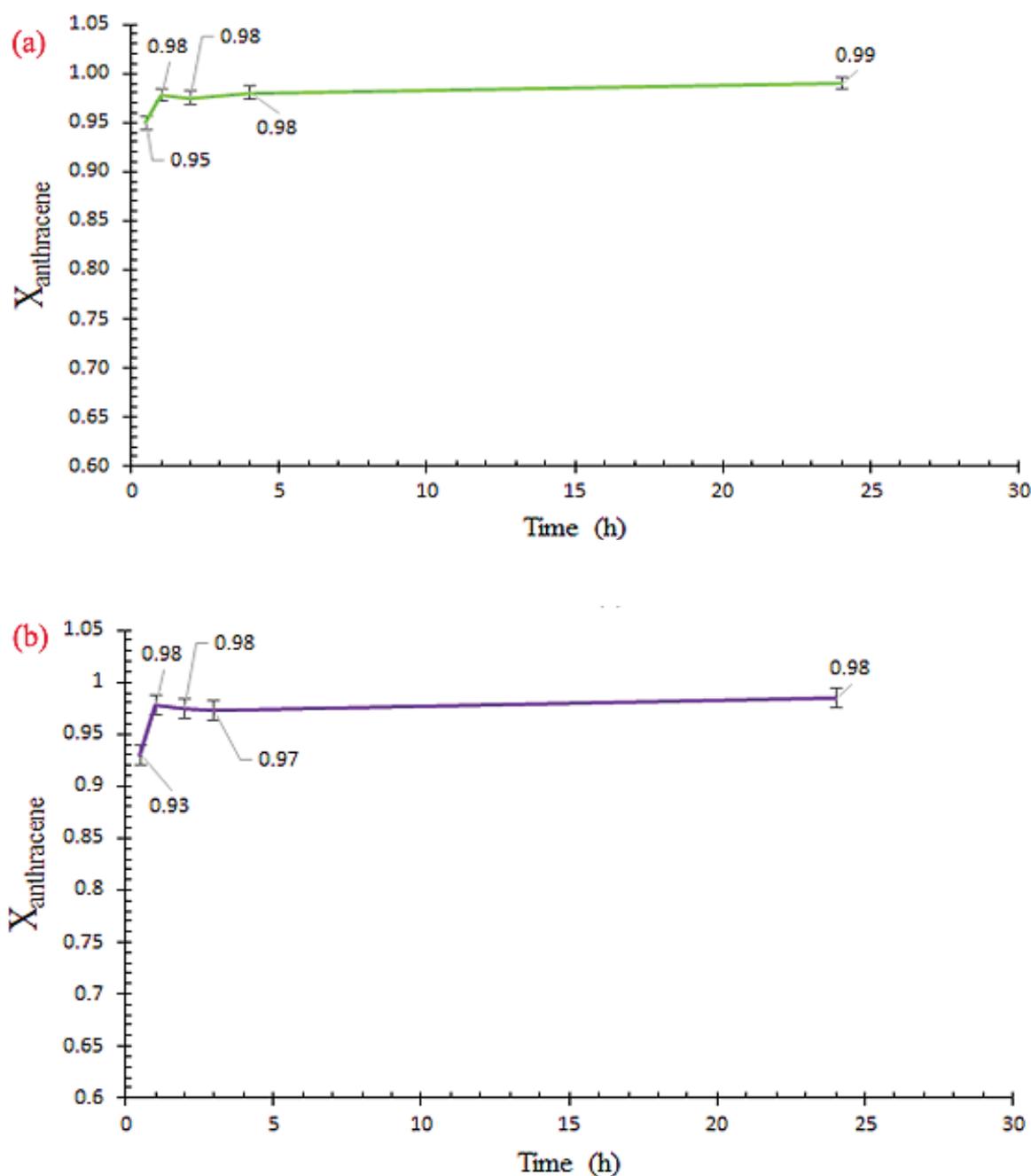


Fig. 6. The effect of contact time on anthracene removal in optimum H_2O_2 , UHP and magnetite concentrations at pH=7

3.4. The blank experiments

After the remediation experiments, two blank tests were performed. In a sample experiment, 2 ml of deionized water was used without adding the magnetite and hydrogen peroxide (blank 1) to contaminated soil. In other sample, only 0.2 mL H_2O_2 without magnetite was added (blank 2) to

contaminated soil. The evolution of the conversion of anthracene in blank 1 and blank 2 is shown in Figure 7. In the blank 1, the degradation is attributed to the natural attenuation during the reaction period (45 days). It is shown the low anthracene content (20%) in the soil was remediated during 45 days, which is attributed to biodegradation of anthracene.

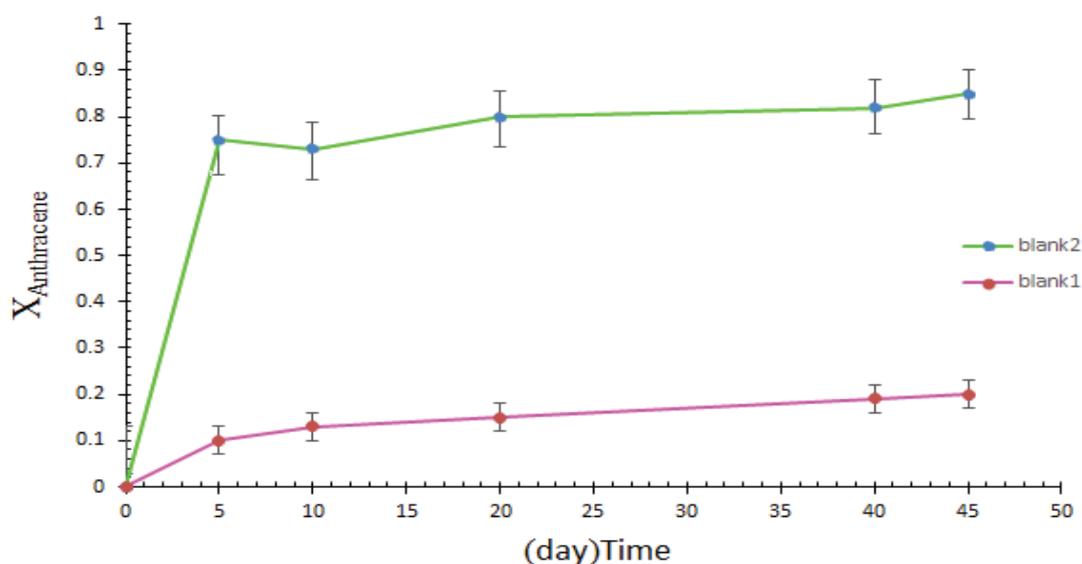


Fig. 7. The blank experiments in optimum oxidation condition

The comparative study confirmed the Fenton-like oxidative capability of the magnetic nanoparticles for efficient degradation of anthracene using 8 mg of the nanocatalyst, 0.2 mL H₂O₂ 30 % (2.5 mmol) and 6 mg urea-H₂O₂ (0.1 mmol) at neutral pH as optimum operational

parameters under mild reaction conditions. The solid urea-H₂O₂ is safer than liquid H₂O₂ (Fig. 8a). The magnetite (Fe₃O₄) is an efficient nanocatalyst for the degradation of anthracene and the urea-H₂O₂ with lower content has a better oxidizing effect than H₂O₂ (Fig. 8b).

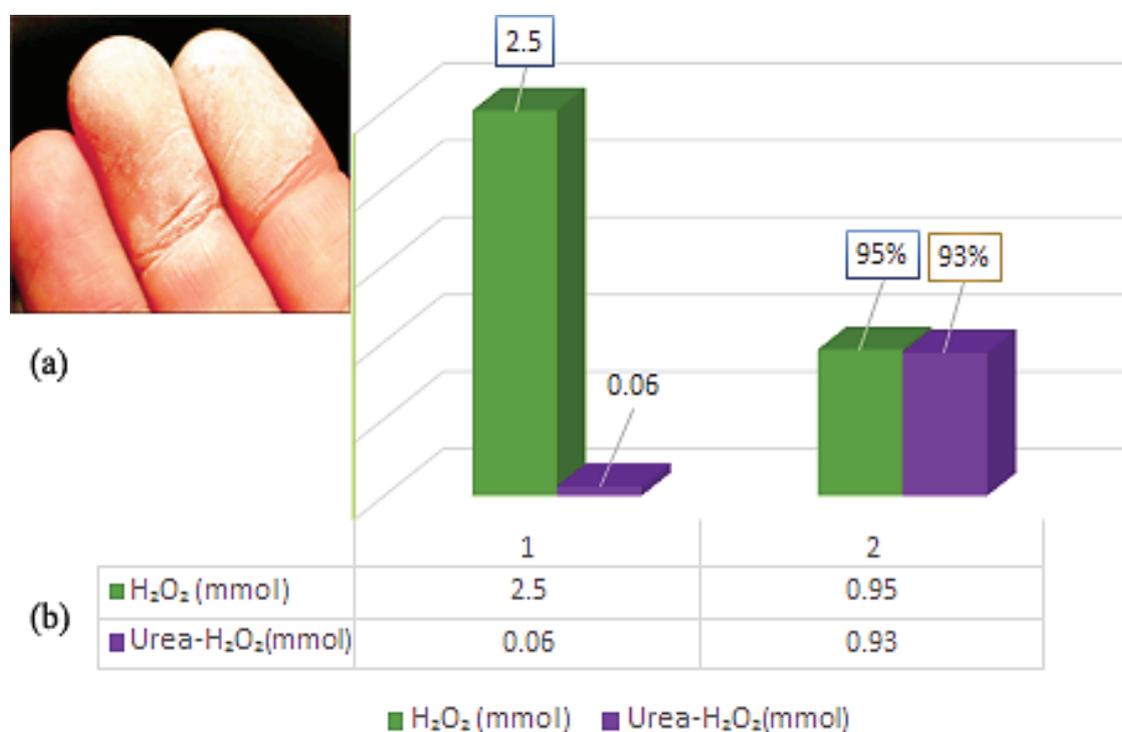


Fig. 8. (a) The sign of acute exposure of skin to hydrogen peroxide (H₂O₂ 30%)
(b) The comparison of H₂O₂ and urea-H₂O₂ as oxidants in Fenton's method

4. Conclusions

In the present study, the Fenton-like oxidation capability of the magnetite nanoparticles for the efficient degradation of anthracene at neutral pH under mild reaction conditions, was confirmed. The urea-H₂O₂ with lower content has a better oxidizing effect than H₂O₂. Furthermore, the solid urea-H₂O₂ is safer than liquid H₂O₂. The natural concentration attenuation during the treatment time (45 days) was less than 20% of the anthracene in soil. It was stated that the magnetite nanocatalyst could activate molecular oxygen via single-electron reduction pathway to produce reactive oxygen species, including hydroxyl radical (^oOH), which are capable of oxidizing contaminants. The generated hydroxyl radicals oxidized the polycyclic aromatic hydrocarbon contaminants by breaking them down into non-toxic products. Therefore, the magnetite/UHP system is a promising and environmentally benign catalytic process for the remediation of PAH-contaminated soils.

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