

## COMPARISON BETWEEN $Fe_3O_4$ AND $Fe_2O_3$ NANOPARTICLES FOR REMOVAL OF AMOXICILLIN FROM WASTEWATER USING PHOTO-FENTON PROCESS

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### Abstract

Water-related problems are likely to increase dramatically due to climatic changes and the increase in population growth. Therefore, the need to application performance, ecofriendly methods are to treat and remove pollutants with chemical composition and complex structure that are difficult to decompose in water, such as antibiotics. In this study, amoxicillin (AMX) was removed from wastewater using nanoparticles (NPs) made of UV/ $H_2O_2$ / $Fe_3O_4$  and  $Fe_2O_3$ . In batch studies, several operating conditions were utilized, including different doses of  $H_2O_2$  (25, 50, 75, 100, and 125 mg/l), pH (3, 5, 7, 9),  $Fe_3O_4$  (NPs), and  $Fe_2O_3$  (g/l), correspondingly. Three Ultra violet (UV) lamps were used and the detention time was kept constant (120 min). The best efficiency obtained under these conditions when using 10 mg/l of AMX, 5 mg/l of  $Fe_3O_4$  nanoparticles, pH=3, and  $H_2O_2$ = 25 mg/l was 99.5%; while, the best efficiency obtained for  $Fe_2O_3$  nanoparticles at AMX =10 mg/l, pH=3,  $H_2O_2$ = 50 mg/l, and 10 mg/l of  $Fe_2O_3$  was 97.3%. After Comparing the two NPs, it was found that  $Fe_3O_4$  was the best in the removal of AMX concentration (10 mg/l) with 99.5% efficiency within two hours by using  $Fe_3O_4$ = 5 mg/l, pH=3, and  $H_2O_2$ = 25 mg/l. While,  $Fe_2O_3$  nanoparticles were the best in removing AMX concentration (25 mg/l) with 97.7% efficiency by adding 50 mg/l of  $H_2O_2$  and 10 mg/l of  $Fe_2O_3$  in neutral condition within two hours.

**Keywords:** Advanced oxidation process, Photo-Fenton process,  $Fe_3O_4$  and  $Fe_2O_3$  (NPs), Iraq

### Introduction

Pharmaceutical substances have recently been deemed a hot area for study by conservationists due to population expansion and an increase in prescription pharmaceuticals (Aksu et al., 2005; Ardashiri et al., 2018). There is a lack of knowledge regarding their effects, potential hazards to the environment, and ultimate fate (Cokgor et al., 2004). Through a variety of sources, including the pharmaceutical industry and hospital wastewaters, a sizable number of drug compounds are introduced into effluent (Arfaeinia et al., 2016).

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This approach can degrade organic contaminants in effluents over the designated toxicity thresholds in a more efficient manner than would be possible with more conventional treatment methods (Babuponnusami et al., 2014). Dynamic stage (homogeneous and heterogeneous) or hydroxyl radical production mechanisms are used to classify AOPs (chemical, electro-chemical, sono-chemical and photochemical). Traditional AOPs are categorized according to the source of the hydroxyl radicals (Klavarioti et al., 2009). AMX was extracted using the Photo Fenton method and the Fenton treatment. This process is based on the production of  $\text{OH}\cdot$  via  $\text{H}_2\text{O}_2/\text{UV}$  photolysis, which involves the interaction of catalysts like metal ions like iron ions and oxidants like hydrogen peroxide with ultraviolet light.

The photo-Fenton process is the most promising approach for successfully treating pollutants like phenol, olive mill wastewater, and tetracycline, according to studies on AOPs (Guo et al., 2019; Lai et al., 2019). It has also been investigated how this mechanism breaks down organic pollutants, particularly antibiotics. In addition to UV radiation, this technique also uses iron salts and hydrogen peroxide. In contrast to the conventional Fenton procedure, UV radiation is known to speed Fenton reactions because it produces hydroxyl radicals, which reduces the need for  $\text{H}_2\text{O}_2$ . However, an acidic pH is required for increased treatment efficacy. For cleaning wastewater that contains organic contaminants such as antibiotics, the photo-Fenton system is crucial.

The comfort of use of efficient oxidation of contaminants is the main benefits of the photo-Fenton technique. Additionally, all components involved in this process, such as  $\text{Fe}^{2+}$ ,  $\text{H}_2\text{O}_2$ , and light sources, are accessible, simple to use, and environmentally benign (Ginn et al., 2014). Nanomaterials are attracting increasing amounts of attention in the age of nanotechnology. From biological and clinical diagnosis to their employment in the fields of chemical catalysis and environmental engineering, nanomaterials are emerging as an intriguing substitute for bulk chemicals in a variety of applications. For the treatment of industrial wastewaters, AOPs based on the usage of NPs have demonstrated considerable promise.

The advancement of nanotechnology is accelerated by technologies based on iron oxide nanoparticles (IONP). Among IONPs,  $\text{Fe}_3\text{O}_4$  and  $\gamma\text{-Fe}_2\text{O}_3$  are primarily investigated in depth (Noqta et al., 2019). Usually, there are numerous phases to iron oxides. The phrase "quantum size effect" has been used to describe this phenomenon (Tringides et al., 2007; Iriarte Mesa et al., 2020). The quantum effect, which influences the matter in the universe magnetic, electric, and optical properties, dominates IONP behavior in the nanoscale range.

At the nanoscale, distinct atoms or molecules have an effect, but in the bulk, behavior is determined by the average of all the quantum forces acting on all the atoms. For instance, super-paramagnetic and magnetic  $\text{Fe}_3\text{O}_4$  nanoparticles can be found at sizes smaller than 20 nm (Li et al., 2017). As the size of the nanoparticles diminishes, this characteristic evolves approaching diamagnetic or hyper paramagnetic magnetization. Therefore, improved super paramagnetic behavior will result from smaller nanoparticles (Sun et al., 2011). This study's goal is to learn more about the Photo Fenton method of eliminating AMX from wastewater, which was done using three UV lamps. Different operating parameters in batch systems, including hydrogen peroxide concentration, nanoparticles ( $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_3\text{O}_3$ ) concentration and pH, were investigated in order to achieve the

greatest removal efficiency and to compare the removal efficiencies of AMX between  $Fe_3O_4$  and  $Fe_2O_3$ .

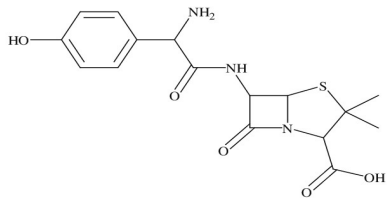
### Materials

Table (1) represents materials used in experimental work and table (2) represents the main characteristics of Amoxicillin.

**Table (1): The materials that were used in the experiments**

Material	Chemical formula	Vender
Hydrogen peroxide	$H_2O_2$	Thomas baker chemicals India 30% w/v
Magnetic iron oxide nanoparticles	$Fe_3O_4$	Purity 98%,(20-30) nm
Non- magnetic alpha iron oxide	$Fe_2O_3$	Hongwu international group (100-200)nm
Sodium hydroxide	NaOH	India ,98% purity
Sulfuric acid	$H_2SO_4$	Riedel-Dehean 99% purity

**Table (2): The main characteristics of Amoxicillin**

Molecular formula	$C_{16}H_{19}N_3O_5S$
Chemical structure	
Molecular weight	365.4 g/mole
Solubility (mg/l)	3430
Color	Yellowish white

### Experimental Work

The stock solution was prepared by adding 1g of (AMX purity: 97.5%, obtained from Pharmaceutical Manufacturing Company / Samarra, Iraq) to 1L of distilled water and then the solution was diluted to 10 mg in a 3 liter of distilled water. A batch system was used to conduct the current investigation. The processing method and the system's schematic diagram are shown in Figures 1 and 2, respectively. A 3 L Pyrex reactor with three low-pressure Hg lamps (sp6-tv/5 12w India) generating "UV light at 365 nm" and wrapped in a "quartz tube" make up the experimental setup. The "quartz tube" installed vertically at the top of the reactor is submerged in the (AMX) solution to guarantee the greatest amount of light irradiation, the UV lamp and reactor wall were separated by 5 cm (Mohammed et al. 2020). As indicated in figure (1), the dark pyrexreactor were stirred at 250 rpm with a magnetic bar at 25°C for 30 min then adjust pH by adding drops of  $H_2SO_4$ (2N) then adding amount of  $Fe_3O_4$  nanoparticles then adding  $H_2O_2$ The

experiment lasted for two hours, and the sample was taken every 15 minutes. The same steps were repeated with  $\text{Fe}_2\text{O}_3$  nanoparticles.

The removal efficiency (%) was intended using equation (1):

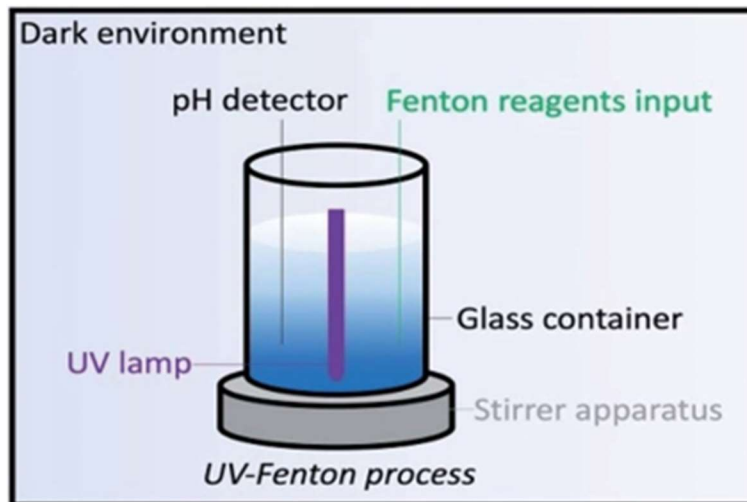
$$(\%) = \frac{C_o - C_t}{C_o} * 100 \dots \dots \dots (1)$$

Where  $c_o$ : initial concentration of Amoxicillin (mg/l); and  $c_t$ : concentration at any time (mg/l).

**Figure (1): Picture of Photo-Fenton process**



**Figure (2): Schematic of Photo-Fenton process**



### Analytical methods

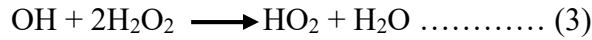
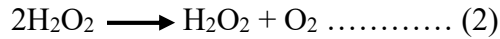
The samples subjected to several stages including placing these samples on a centrifuge (800 electric centrifuge) at 2800 rpm for 15 minutes then analyzed in UV Spectrophotometer (Shimadzu UV-1800 Refurnished Spectrophotometer, Japan) to compare of samples to a reference or control sample in order to determine how much discrete UV or visible light is collected by or reflected through the sample. Statistical analysis was carried out using of ANOVA in the Excel Microsoft Office (Gharban and Al-Shaeli, 2021).

### Results and discussion

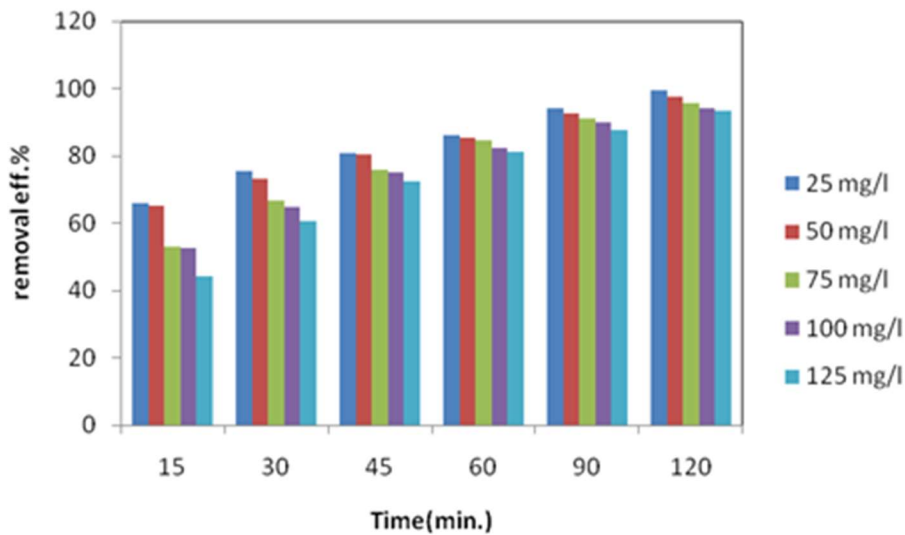
#### *Effect of $\text{H}_2\text{O}_2$ Concentration*

Figures (3 and 4) represent the consequence of "hydrogen peroxide" concentration on elimination efficiencies of AMX with time for  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_2\text{O}_3$  NPs respectively. It can be observed from the figures that the best concentration of  $\text{H}_2\text{O}_2$  is 25 mg/l for UV/  $\text{H}_2\text{O}_2$ /  $\text{Fe}_3\text{O}_4$  system to get 99.5 % removal efficiency. While, 50 mg/l of  $\text{H}_2\text{O}_2$  for UV/  $\text{H}_2\text{O}_2$ /  $\text{Fe}_2\text{O}_3$  system and 97.7% removal efficiency. When increasing the concentration of  $\text{H}_2\text{O}_2$  to more than 25 mg/l with  $\text{Fe}_3\text{O}_4$  and more than 50 mg/l with  $\text{Fe}_2\text{O}_3$ , the removal efficiencies will decrease. This is a result of the extra OH-radicals that were generated. The reaction rate plateaus at high hydrogen peroxide concentrations, and is occasionally adversely impacted by the hydrogen peroxide's steady rise. According to

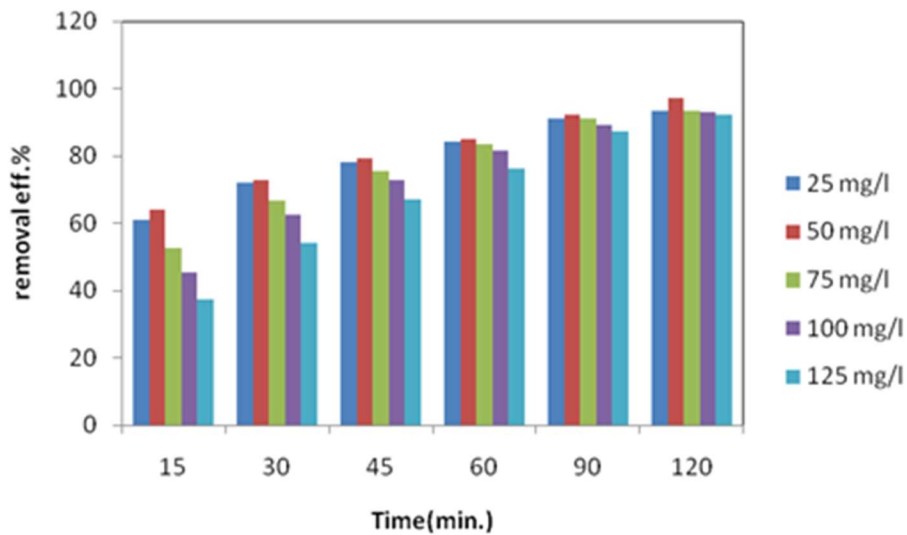
equations 2 and 3, this might happen as a result of the identity of  $H_2O_2$  into water and oxygen and the reunion of  $OH^-$  radical as:



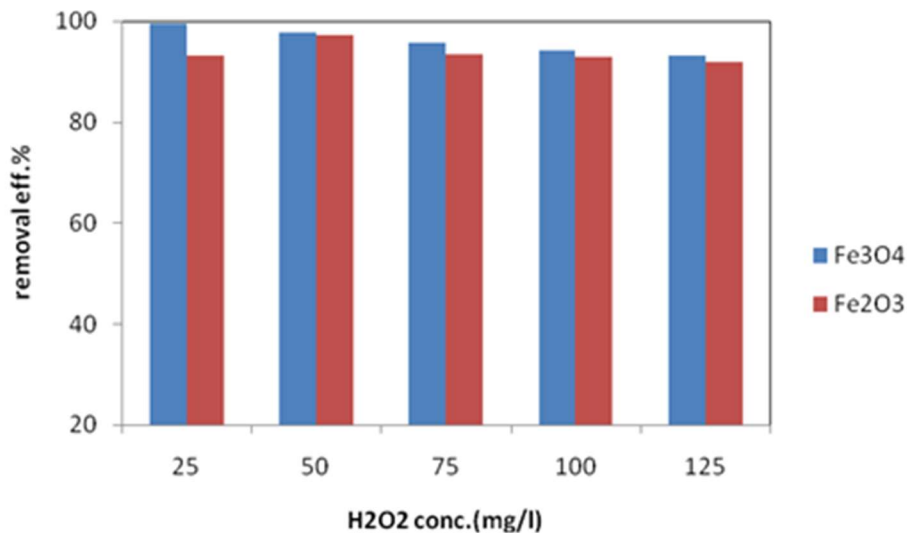
Even though  $H_2O_2$  alone helps to scavenge  $OH$  radicals, the additional  $H_2O_2$  is considered to be efficient in decreasing treatment efficiency. However, because auto-scavenging processes are more likely to take place at sophisticated  $H_2O_2$  concentrations, a large dose of  $H_2O_2$  causes a complex cohort of hydroxyl extremists. Hydrogen peroxide should be injected at the proper concentration for the best poverty (Ebrahiem et al. 2017). These results are in contract with those of (Mustafa et al. 2013). Figure (5) represents a comparison between the removal efficiencies at different  $H_2O_2$  concentrations for "UV/  $H_2O_2$ /  $Fe_3O_4$ " NPs and "UV/  $H_2O_2$ "/ $Fe_2O_3$  NPs systems. The removal efficiencies of UV/  $H_2O_2$ /  $Fe_3O_4$  NPs system > UV/  $H_2O_2$  / $Fe_2O_3$  NPs system.



**Figure (3): Effect of  $H_2O_2$  concentration on removal efficiency of AMX with time in UV/  $H_2O_2$ /  $Fe_3O_4$  (NPs) process as single system: 3 UV lamp conc. Of AMX = 10 mg/l,  $Fe_3O_4$  dose =5 mg/l pH=3, reaction time = 120 min, at 25°C**



**Figure (4):** Effect of H<sub>2</sub>O<sub>2</sub> concentration on removal efficiency of AMX with time in UV/ H<sub>2</sub>O<sub>2</sub> / Fe<sub>2</sub>O<sub>3</sub> (NPs) process as single system: 3 UV lamp conc. Of AMX = 10 mg/l, Fe<sub>2</sub>O<sub>3</sub> dose= 5 mg/l pH=3, reaction time = 120 min, at 25°C

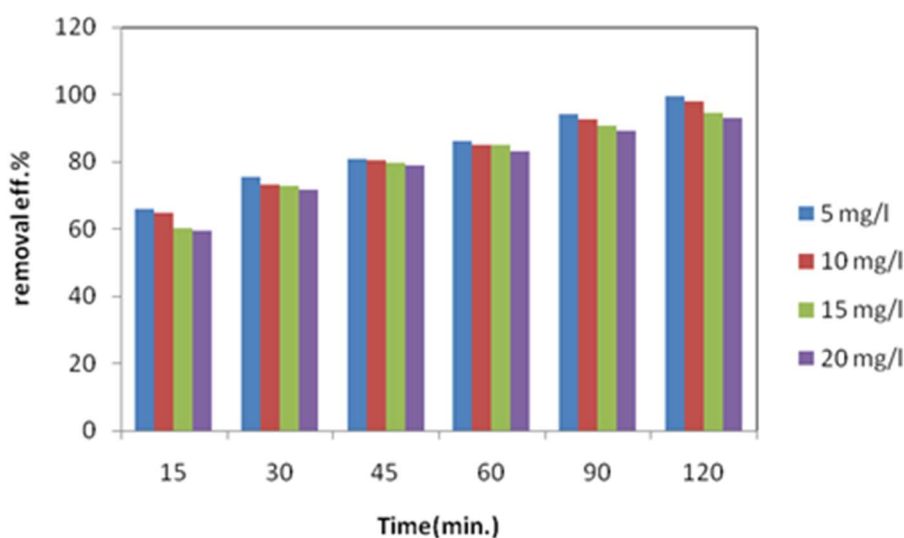


**Figure (5):** Comparison between the removal efficiencies of AMX for UV/ H<sub>2</sub>O<sub>2</sub> / Fe<sub>3</sub>O<sub>4</sub> and UV, H<sub>2</sub>O<sub>2</sub> / Fe<sub>2</sub>O<sub>3</sub> (NPs) systems at different H<sub>2</sub>O<sub>2</sub> concentrations

#### *Effect of Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>2</sub>O<sub>3</sub> NPs*

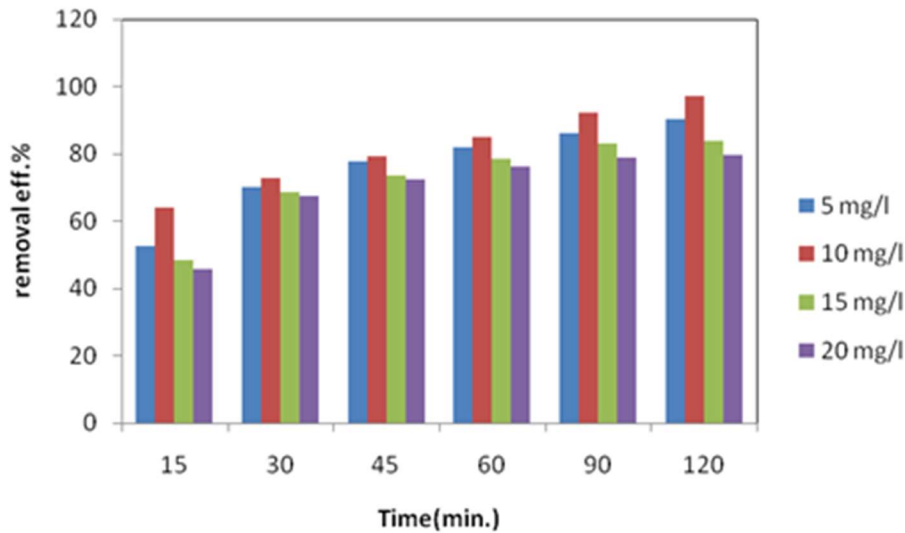
The relationship between the concentration of Fe<sub>3</sub>O<sub>4</sub> NPs and the rate at which AMX is removed over time is shown in figure (6). The other factors remained consistent. The Fe<sub>3</sub>O<sub>4</sub> compound formed at (Fe<sub>3</sub>O<sub>4</sub>= 5 mg/l, pH=3, conc. of AMX =10 mg/l, H<sub>2</sub>O<sub>2</sub> = 25 mg/l, Temp = 25°C throughout 120 min.) had the best removal efficiency of 99.5%. The influence of

$\text{Fe}_2\text{O}_3$  concentration on AMX removal efficiencies over time is exposed in Figure (7). The conditions of ( $\text{Fe}_2\text{O}_3=10$  mg/l, pH=3, conc. of AMX=10 mg/l,  $\text{H}_2\text{O}_2=25$  mg/l, Temp =25°C for 120 min) produced the greatest removal efficiency of 95%. When iron salt concentrations increased, organic pollutants decomposed more quickly until they reached a boundary rate of either iron either Fe (II) or Fe (III), which is why removal efficiencies fell when  $\text{Fe}_3\text{O}_4$  concentration was more than 5 mg/l and  $\text{Fe}_2\text{O}_3$  was more than 10 mg/l (III). Brown turbidity from increased iron salt addition inhibited "UV light" obligatory for photolysis from being absorbed and OH- radicals were recombined as a result. In this instance,  $\text{Fe}^{2+}$  worked as a scavenger by reacting with OH- radicals (Pouran et al., 2015) Figure 8 contrasts the removal efficiencies for UV/ $\text{H}_2\text{O}_2$ / $\text{Fe}_3\text{O}_4$  and UV/ $\text{H}_2\text{O}_2$ / $\text{Fe}_2\text{O}_3$  systems at various  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_2\text{O}_3$  concentrations.

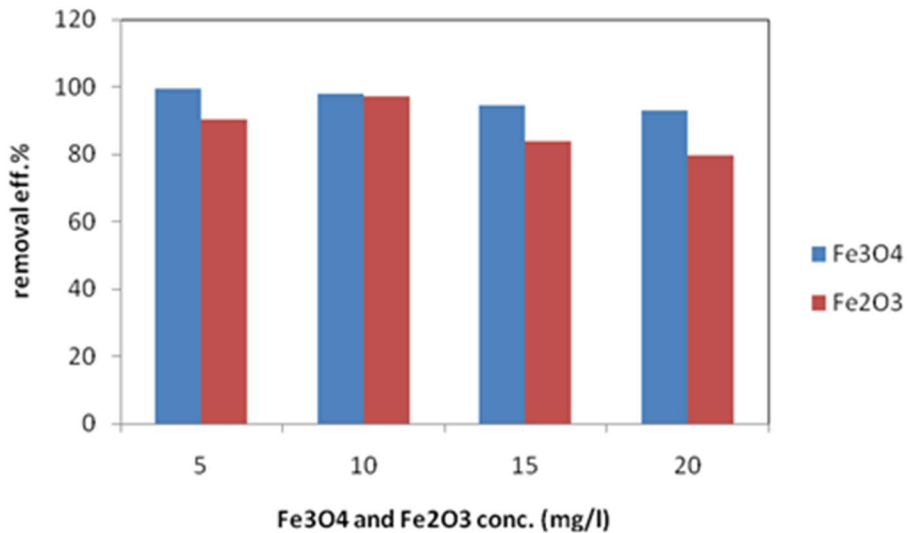


**Figure (6):** Effect of  $\text{Fe}_3\text{O}_4$  concentration on removal efficiency of AMX with time in UV/ $\text{H}_2\text{O}_2$ / $\text{Fe}_3\text{O}_4$  (NPs) process as single system: 3 UV lamp conc. Of AMX =10 mg/l,  $\text{Fe}_3\text{O}_4$  dose =5 mg/l,  $\text{H}_2\text{O}_2=25$  mg/l, reaction time = 120 min, at 25°C





**Figure (7):** Effect of Fe<sub>2</sub>O<sub>3</sub> concentration on removal efficiency of AMX with time in UV/ H<sub>2</sub>O<sub>2</sub> / Fe<sub>2</sub>O<sub>3</sub> (NPs) process as single system: 3 UV lamp conc. Of AMX = 10 mg/l, pH=3, H<sub>2</sub>O<sub>2</sub>=50 mg/l, reaction time = 120 min, at 25°C



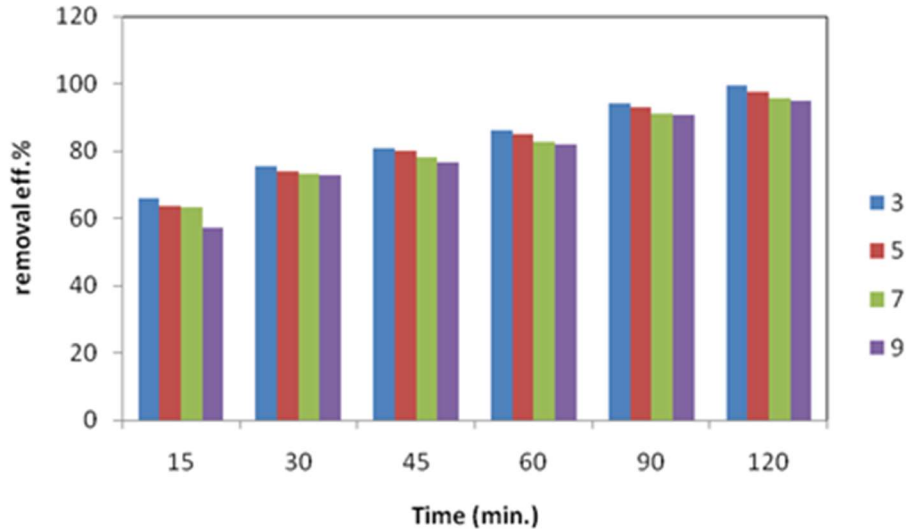
**Figure (8):** Comparison between the removal efficiencies of AMX for UV/ H<sub>2</sub>O<sub>2</sub> / Fe<sub>3</sub>O<sub>4</sub> and UV/ H<sub>2</sub>O<sub>2</sub> / Fe<sub>2</sub>O<sub>3</sub> (NPs) systems at different (Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>2</sub>O<sub>3</sub>) NPs concentrations

### *The Effect of pH*

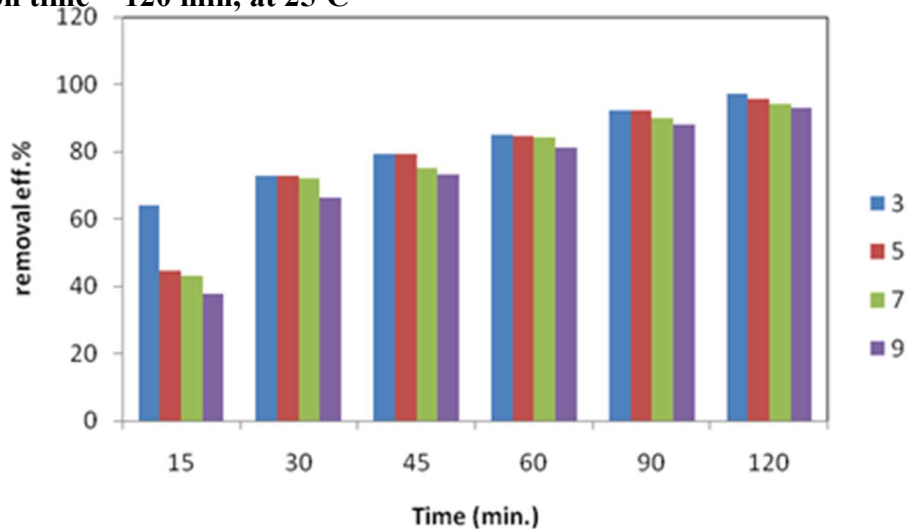
Figures (9 and 10) represent the effect of pH on removal efficiencies of AMX with time in different values of pH and keeping other parameters constant, the best removal efficiencies was 99.5% for Fe<sub>3</sub>O<sub>4</sub> at this condition (3UV, AMX=10 mg/l, H<sub>2</sub>O<sub>2</sub>= 25 mg/l, Fe<sub>3</sub>O<sub>4</sub>= 5 mg/l, Temp= 25°C), while the best removal efficiencies was 97.7% and keeping other parameters constant (3UV, AMX=10 mg/l, H<sub>2</sub>O<sub>2</sub>=50 mg/l, Fe<sub>2</sub>O<sub>3</sub> = 10 mg/l, Temp = 25°C) for Fe<sub>2</sub>O<sub>3</sub>. It is clear that a pH decrease increases the rate of AMX decomposition. This demonstrates that 3 for "Fe<sub>3</sub>O<sub>4</sub>" and Fe<sub>2</sub>O<sub>3</sub>" is the ideal pH for the Photo Fenton treatment of the selected substrates. The reduction in efficiency improvement at pH levels over 3 may be attributed to the inhibition of Hydrogen peroxide decomposition for the production of hydroxyl radicals caused by insufficient ion [H]<sup>+</sup>



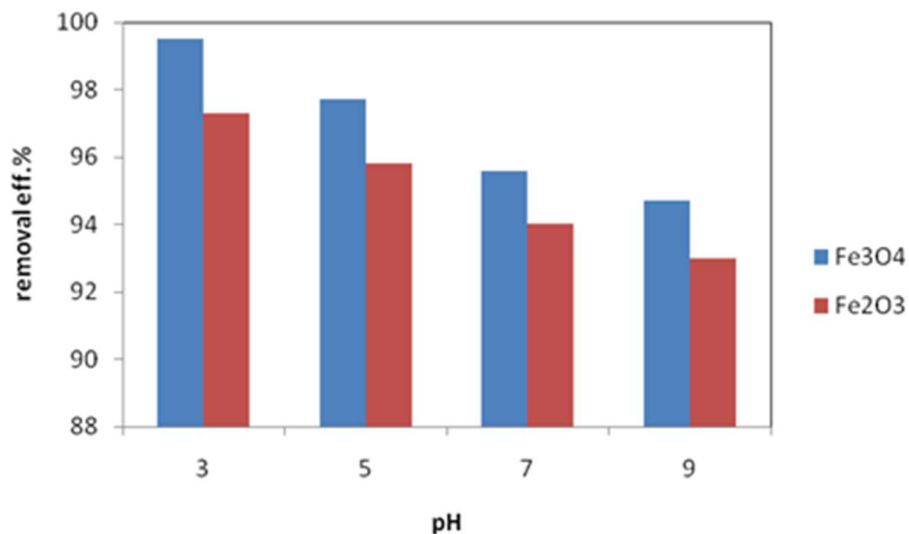
and rapid  $H_2O_2$  decomposition to water and oxygen (Rostamia et al., 2020). Figure (11), from Mustafa et al. (2014) compares the elimination effectiveness of UV/ $H_2O_2$ / $Fe_3O_4$  and UV/ $H_2O_2$ / $Fe_2O_3$  systems at different pH levels.



**Figure (9):** Effect of pH on removal efficiency of AMX with time in UV/  $H_2O_2$  /  $Fe_3O_4$  (NPs) process as single system: 3 UV lamp conc. Of AMX =10 mg/l,  $Fe_3O_4$  dose =5 mg/l,  $H_2O_2$ =25 mg/l, reaction time = 120 min, at 25°C



**Figure (10):** Effect of pH on removal efficiency of AMX with time in UV/  $H_2O_2$ /Fe<sub>2</sub>O<sub>3</sub> (NPs) process as single system: 3 UV lamp conc. Of AMX= 10 mg/l,  $Fe_2O_3$  dose =10 mg/l,  $H_2O_2$ =50 mg/l, reaction time = 120 min, at 25°C



**Figure (11): Comparison between the removal efficiencies of AMX for UV/ H<sub>2</sub>O<sub>2</sub>/ Fe<sub>3</sub>O<sub>4</sub> and UV/ H<sub>2</sub>O<sub>2</sub>/ Fe<sub>2</sub>O<sub>3</sub> (NPs) systems at different pH**

### ***Effect of AMX Concentration***

Figure (12) displays the consequence of AMX concentration with time when using Fe<sub>3</sub>O<sub>4</sub> and constant operating conditions (3UV, pH =3, H<sub>2</sub>O<sub>2</sub>= 25 mg/l, Fe<sub>3</sub>O<sub>4</sub>=5 mg/l, T= 25°C during 120 min). While, figure (13) represent the effect of AMX concentration with time when using Fe<sub>2</sub>O<sub>3</sub> and the operation conditions are (3UV, pH=3, H<sub>2</sub>O<sub>2</sub> = 50 mg/l, Fe<sub>2</sub>O<sub>3</sub>=10 mg/l, T=25°C during 120 min). It is obvious that the removal efficacy reduced when AMX concentration was increased as the poorer degradation effectiveness was related to an increase in "UV light" trapping and an inability to effectively interact with hydrogen peroxide molecules and ferric ions to generate OH<sup>-</sup>. A certain amount of OH<sup>-</sup> is created when all factors, particularly pH, low latency, hydrogen peroxide strength, and chelating iron content, are held constant. The generational ability of this radical allows for the breakdown and elimination of small quantities of organic compounds. The amount of OH<sup>-</sup> in the environment is therefore insufficient to eliminate the extra molecules of organic compounds if the baseline content of organic compounds rises (Malakootian et al., 2017).

Figure (14) likens the extraction efficiency for UV/H<sub>2</sub>O<sub>2</sub>/Fe<sub>3</sub>O<sub>4</sub> NPs and UV/H<sub>2</sub>O<sub>2</sub>/Fe<sub>2</sub>O<sub>3</sub> NPs systems at numerous AMX concentrations and illustrates how the photo-Fenton efficiency is reduced. This is in accordance with what was reported by (Elmolla et al., 2009). Research revealed that by cumulative the original concentration of the antibiotics amoxicillin, and cloxacill compared to the UV/ H<sub>2</sub>O<sub>2</sub>/ Fe<sub>2</sub>O<sub>3</sub>NPs system, the UV/ H<sub>2</sub>O<sub>2</sub>/ Fe<sub>3</sub>O<sub>4</sub>NPs system has better removal efficiency.

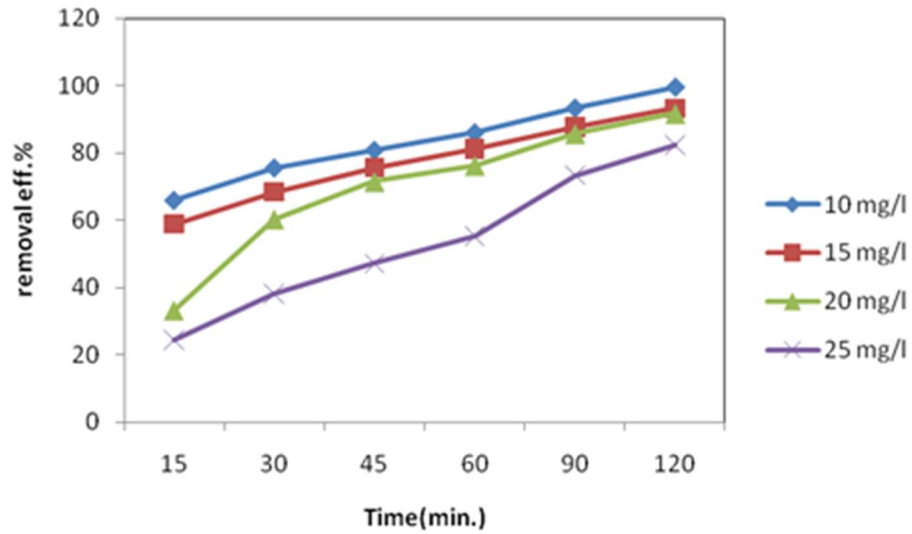


Figure (12): Effect of AMX concentration on removal efficiency of AMX with time in UV/ H<sub>2</sub>O<sub>2</sub> / Fe<sub>3</sub>O<sub>4</sub> (NPs) process as single system: 3 UV lamp, Fe<sub>3</sub>O<sub>4</sub> dose =5 mg/l, H<sub>2</sub>O<sub>2</sub>= 25 mg/l, pH=3, reaction time = 120 min, at 25°C

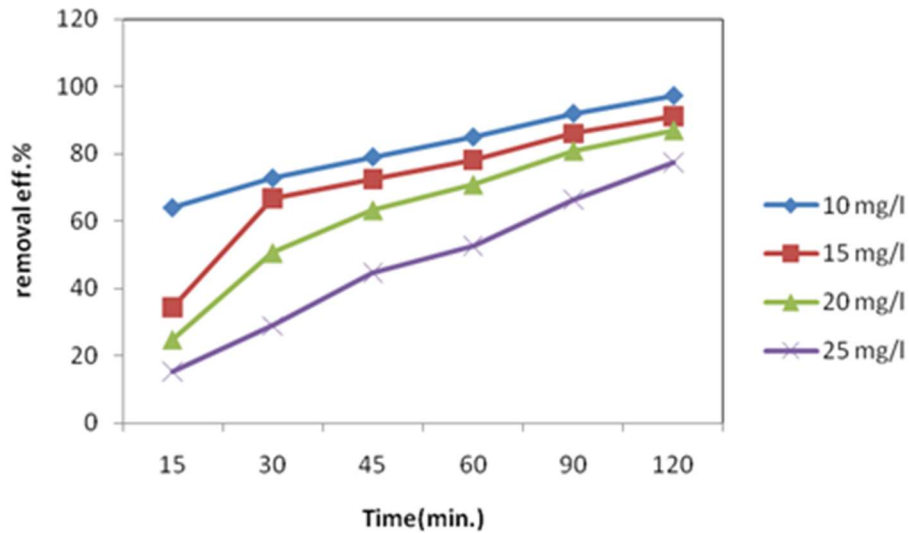
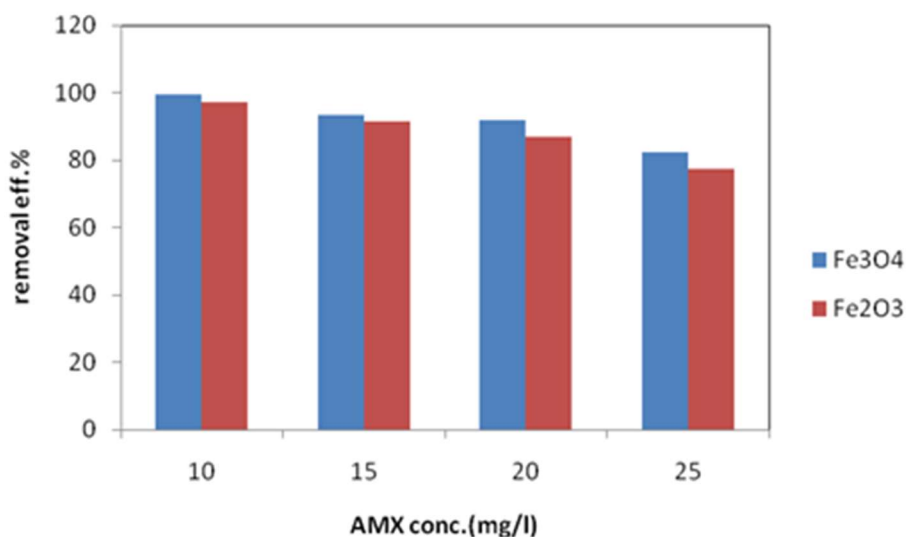


Figure (13): Effect of AMX concentration on removal efficiency of AMX with time in UV/ H<sub>2</sub>O<sub>2</sub> / Fe<sub>2</sub>O<sub>3</sub> (NPs) process as single system: 3 UV lamp, Fe<sub>2</sub>O<sub>3</sub> dose =5 mg/l, H<sub>2</sub>O<sub>2</sub>= 50 mg/l, pH=7, reaction time = 120 min, at 25°C



**Figure (14): Comparison between the removal efficiencies of AMX for UV/ H<sub>2</sub>O<sub>2</sub>/ Fe<sub>3</sub>O<sub>4</sub> and UV/ H<sub>2</sub>O<sub>2</sub>/ Fe<sub>2</sub>O<sub>3</sub> (NPs) systems at different AMX concentration**

### Conclusion

In this research, the photo Fenton process is utilized for the deterioration of AMX in wastewater. The reaction was influenced by this parameter (H<sub>2</sub>O<sub>2</sub> concentration, Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> NPs dose and pH). Two types of iron oxides NPs (Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub>) were used as catalyst and a comparison done between them. For UV/H<sub>2</sub>O<sub>2</sub>/Fe<sub>3</sub>O<sub>4</sub> the best operating conditions were (3UV, concentration of AMX=10 mg/l, pH= 3, Fe<sub>3</sub>O<sub>4</sub>= 5 mg/l, H<sub>2</sub>O<sub>2</sub>=25 mg/l, T=25°C) the removal efficiency was 99.5% during 120 min. For UV/H<sub>2</sub>O<sub>2</sub>/Fe<sub>2</sub>O<sub>3</sub> NPs the best operating conditions were (3UV, AMX =10 mg/l, PH=3, Fe<sub>2</sub>O<sub>3</sub>=10 mg/l, H<sub>2</sub>O<sub>2</sub>= 50 mg/l, and T= 25°C) and the removal efficiency was 97.7% during 120 min. The removal efficiencies of UV/ H<sub>2</sub>O<sub>2</sub>/ Fe<sub>3</sub>O<sub>4</sub> NPs system > UV/ H<sub>2</sub>O<sub>2</sub>/Fe<sub>2</sub>O<sub>3</sub> NPs system.

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