

Optimal conditions for treatment of contaminated waters with anthracene by Fenton processes in close system reactor

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Abstract

Advanced Oxidation Processes such as Fenton, Photo-Fenton and Electro-Fenton have been applied effectively to remove the organic pollutants from the water and soil previously. Fenton reaction principle is based on the addition of hydrogen peroxide to the contaminated water or waste water in the presence ferrous salts as a catalyst to generate hydroxyl radicals. In this study, the effect of different parameters on the degradation by Fenton processes have been reported such as concentration of Anthracene, amount of FeSO₄, pH value, temperature and hydrogen peroxide amount. The results indicate that the perfect conditions for degradation of Anthracene by Fenton process were: Anthracene concentration 16 mg l⁻¹, mass of FeSO₄ = 120mg, pH of solution =4, temperature of solution 50 °C and Concentration of hydrogen peroxide = 150 mg l⁻¹.

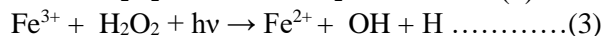
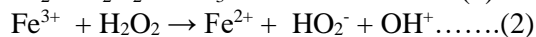
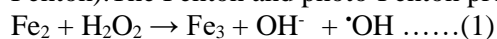
KEYWORD: Fenton, pollution with PAHs, degradation of Anthracene, water treatment.

1. INTRODUCTION

Polycyclic Aromatic Hydrocarbons (PAHs) are ubiquitous environmental contaminants that mainly originate by incomplete combustion of organic matter. Some of these have mutagenic and carcinogenic potentials (Paula 2009). Sixteen PAHs are classified as priority pollutants by United States Environmental Protection Agency (US-EPA). PAHs compounds are chemicals made up of two fused aromatic rings or more in a linear or clustered arrangement. These compounds are toxic, hydrophobic, high stability characterized by high resistance to natural degradation and are frequently encountered at manufactured wood treatment sites and gas plants (Garcia-Falcon 2006; Al-Gazally 2016).

Today, it exists several oxidation processes are suitable for waste water treatment, such as wet air oxidation, incineration, supercritical water oxidation and advanced oxidation processes (AOPs). One of the more important advantage of AOPs is can be used for the treatment of relatively low levels of pollutants in aqueous media. In Advanced oxide processes (AOP) method firstly generate of strong oxidizing agents such as hydroxyl radicals ([•]OH), this reactive radical capable of mineralizing organic pollutants (Saleh 1974; Alkhateeb 2005; Hussein 2007; Hussein 2010; Matloob 2011; Mohamed F. F. 2011; Al-Gazally 2015; Al-Gazally 2016; Al-gubury 2016)

The oxidation process of organic substrates by ferrous iron ions and hydrogen peroxide is called the "Fenton chemistry". H. J.H. Fenton who was the first observed the oxidation of tartaric acid by Hydrogen peroxide in the presence of ferrous iron ions (Paula 2009). Frequently, the name of "Fenton reagent" or "Fenton reaction" is often used. Fenton reagent was known for more than one century ago but its application as an oxidizing reagent for removing hazardous organic pollutants was not applied until the late 1960s (Dunford 2002). After this time the investigations showed that the Fenton reagent is very effective for treating different industrial waste water pollutants such as aromatic amines, a large variety of dyes, pesticides, and explosives. In general, Fenton reactions can be heterogeneously catalyzed (Fenton-like) or homogeneously catalyzed (conventional Fenton and modified Fenton). The Fenton and photo-Fenton processes mechanism, it can be summarized by the following reactions.



Electro kinetics also has been applied to remove organic pollutants such as (PAHs, pesticides, herbicides and chlorinated organic compounds) from the soil. Kyoungphile *et al.* (Kyoungphile 2001) were used biodegradation combined with a modified Fenton reaction to enhance the degradation of polycyclic aromatic hydrocarbons. Karam *et al.* (Karam 10.1155/2014/503825) studied degradation of anthracene by photocatalytic using titanium dioxide as catalyst. To this end, our aim in the present paper is to study the effect of parameters to enhanced degradation rate for Anthracene by Fenton reagent under different experimental conditions.

2. MATERIALS AND METHODS

The experiments were conducted in a 150mL dual wall reactor which connected with temperature controller (chiller unit) to maintain the required temperature. The outside of the reactor was covered with aluminum foil to protect from light. Homogeneous mixing was provided using a magnetic stirring bar. In each experiment, 100mL of anthracene solution at the desired initial concentration were inserted in the reactor. An aliquot was withdrawn for

further analysis. After that, the pH was adjusted with a sulphuric acid solution and another aliquot was collected. Then, the required amount of iron (II) salt was added. When the salt was totally dissolved a certain quantity of H_2O_2 solution was introduced, in order to start the reaction. Aliquots were taken from the reactor at selected time intervals and immediately analyzed. The arrest of Fenton's reaction was achieved with the addition of some drops of concentrated sulphuric acid in order to decrease the pH to less than 1.0. GC analysis was made on an instrument from the Shimadzu Model 2010 equipped with a flame ionization detector and an HP-5 column. More details on the analytical conditions are illustrated in Table 1.

Table.1. Chromatographic conditions used for determination Anthracene by GC:

Parameters	Details
Column	Type: Hp5(30m x Internal Diameter 0.28mm x Film thickness 0.25 μ m), temp.=130°C
Injection volume	1 μ L
Injector mode	Split less, temp. =275°C
Carrier gas	Nitrogen
Detector	Type: FID

3. RESULTS AND DISCUSSION

Effect of anthracene concentration: Thinking about the possibility to apply this method for treatment the contaminated water sample, it's very important to study the initial concentration of anthracene as the first step in this method. Therefore, it is essential to determine the suitable amount of anthracene to would be degraded with a fixed reagent concentration. In these experiments two concentrations for anthracene in the range (4 and 16 mg l^{-1}) were used. These results are shown in Figure 1 within the experimental condition solution pH equal to 4, temperature equal to 323.15K and $FeSO_4$ 120 (mg/100ml). It is found that the rate constant of reaction increased with increasing of initial anthracene concentration. As seen in Figure 1, the reaction occurs quickly in the first 45 minute with 16 mg l^{-1} of anthracene, the gradually increase the degradation rate with increasing time of reaction. Previous study proved that the removal of pollutants occurs after 90 minutes with percentage removal ranging 70% to 100%.

Effect of $FeSO_4$: Experiments were conducted in order to investigate the influence of ferrous ion concentration as (catalytic agent) on the process. These experiments were carried out by using different concentrations of $FeSO_4$ with anthracene. The results are shown in Figure 2. Other factors were kept constant for all these experiments (initial anthracene concentration 16 mg l^{-1} , pH solution 4 and temperature 323.15K). From these experiments, it was found that 120 mg of $FeSO_4$ /100ml of anthracene give the optimum activity. Reaction rate constants expressed in min^{-1} are calculated from the slopes of such linear reaction plots. Figure 2 show that a $FeSO_4$ mass of 120 mg is sufficient to achieve the maximum reaction rate. Figure 2, shows the relationship between the degradation rate and the amount of ferrous ion. Comparing the results, it was proved that is increasing degradation with the ferrous ion concentration. At all concentrations of ferrous were the degradation occurs quickly in the first 15 minute except at 90mg it need to 30 min. significant differences were found between 30mg and 120mg. The amount that used in these experiments considers huge comparing with previous work (Beltran 1998), was studied the effect of ferrous ion on the rate of reaction. They were used the initial ferrous ion concentration which ranged between 0.9 to 11 mg l^{-1} with removal percentage ranged "between" 40% to 100%.

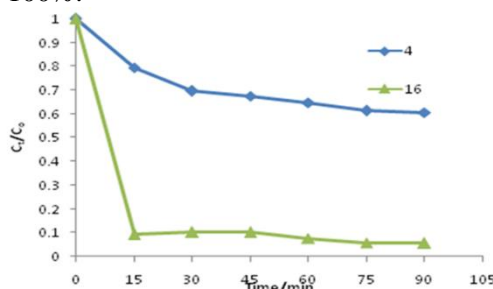


Figure.1. Effect of anthracene concentration on degradation efficiency by $FeSO_4$.

Effect of pH: The Fenton's reaction is depending on the pH value, because this value affects the hydroxyl radical's generation and consequently, the efficiency of degradation. pH plays an important role in the production of hydroxyl radicals. In these experiments used $FeSO_4$ to degrade of anthracene in the aqueous suspensions under the determined experimental condition, temperature equal to 323.15K, $FeSO_4$ concentration 120 (mg/100ml) and initial anthracene concentration of 16 mg l^{-1} . Using the pH range (2 – 5) as shown in Figure 3. The results in Figure 3 show the rate constant of reaction increases with increase of the solution pH up to the maximum level at pH 4 and then decreases. The degradation rate of anthracene increases with increase of pH. For this oxidation process, the optimal pH ranged mentioned in previous studies is 3 to 6. It can be observed that the removal efficiency was significant changed with pH increase from 2 to 5. At all pH values were the degradation occurs quickly in the first 15 minute. Comparing the

results of degradation at different pH values exhibit that the reaction at pH=4 faster than others about five times. The most rapid elimination of anthracene from the reaction mixture occurred at pH=4 as shown in Figure 3.

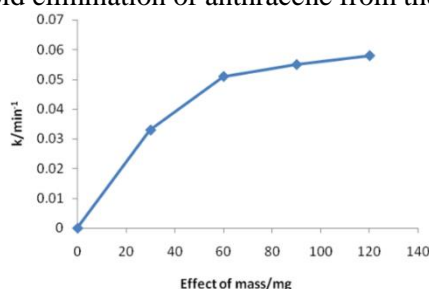


Figure.2.Effect of masses of FeSO₄ on rate constant

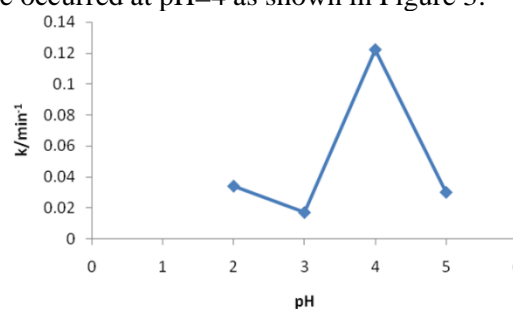


Figure.3.Effect of initial pH of solution on rate constant by FeSO₄

Effect of temperature: Experiments were conducted under the same conditions such as (amount of initial concentration of anthracene, amount of ferrous ion, pH value, Hydrogen peroxide concentration) at four different temperatures between (293.15 to 323.15) K to investigate the effect of these temperatures on the degradation rate of the aqueous solution of anthracene. An enhancement in the rate and even in the extent of degradation efficiency was observed with temperature increase. As known, at higher temperatures the thermal decomposition of PAHs increase and the hydrogen peroxide decomposition also accelerate results a decrease of the concentration of hydroxyl radicals, despite of this fact, the degradation reaction increased with temperature. The results in figure 4 shows that the higher temperature will have faster degradation rate of anthracene under experimental conditions, initial anthracene concentration of 16 mg l⁻¹, solution pH equal to 4 and FeSO₄ concentration 120 (mg/100ml). In these experiments used different temperature for FeSO₄ in the range 293.15-323.15 K. It is found that the degradation rate of anthracene increases with increase of temperature. In previous studies reported that the temperature lower than 281.3K results in slower initial kinetics, thus affects the reaction rate and removal efficiency while if the temperature is higher than 323.15 °C may negatively impact for removal performance(Samet 2011).

Results show high differences between results at temperature 323.15 K with others, the degradation being more than two times at fifteen minute comparing with other temperatures. Generally at all temperatures observed that the degradation increase quickly within the first fifteen minute of reaction.

Effect of H₂O₂: Hydrogen peroxide (H₂O₂) plays an important role in the production of hydroxyl radicals. In these experiments FeSO₄ was used to degrade of anthracene in the aqueous suspensions under the determined experimental condition, solution pH equal to 4, temperature equal to 323.15K, FeSO₄ concentration 120 (mg/100ml) and initial anthracene concentration of 16 mg l⁻¹. The effect of using different concentration of hydrogen peroxide (H₂O₂) in the range between (0 – 200) mMol l⁻¹ are shown in Figure 5. The results in Figure 8 show that the rate constant of reaction increases with increase of the hydrogen peroxide concentration. The experiments were carried out with initial concentration of Anthracene of 16 mg l⁻¹. Experiments were performed to determine the influence of hydrogen peroxide concentration on the process, the additions of 200 mg l⁻¹ and 150 mg l⁻¹ it was observed that the degradation increase quickly within the first fifteen minute of reaction, while in 100 mg l⁻¹ and 50 mg l⁻¹ addition the degradation need 30 min to increase. On the other hand, from Figure 5 it can also be seen that the increase of H₂O₂ concentration from 50 to 200 mg l⁻¹ yields raising removal efficiencies by increasing the rate of reaction. These results in agreement with previous work(Sun 2008) were they reported that increasing the dosage of hydrogen peroxide from (0-500)mM increases the efficiency of removal of pyrene in soil slurry.

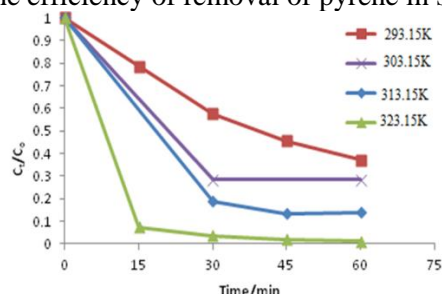


Figure.4.Effect of temperature on degradation of anthracene by using FeSO₄

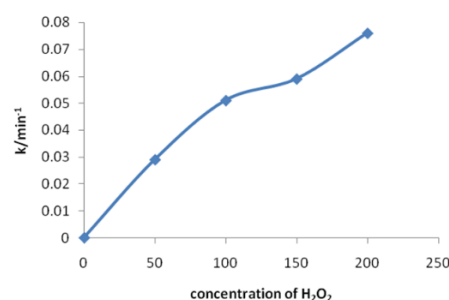


Figure.5.Effect of addition of [H₂O₂] on rate constant by FeSO₄

4. CONCLUSIONS

The treatment of Anthracene using Fenton reagent has achieved. The observations of these investigations demonstrate the importance of selecting the optimum parameters for degradation to obtain a high degradation rate, which is considered essential for any application of degradation by Fenton processes. The rate of degradation in

present of Fenton reagent has found to be maximum in acidic medium with optimum concentration of 16 mg l^{-1} of Anthracene. The optimum addition of FeSO_4 was 120 mg at $\text{pH } 4$ with media temperature at 323.15 K . The degradation of Anthracene increases with the increase of hydrogen peroxide in the range $(0-200) \text{ mMol l}^{-1}$.

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