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COD REMOVAL FROM SYNTHETIC WASTEWATER CONTAINING AZITHROMYCIN USING COMBINED COAGULATION AND A FENTON-LIKE PROCESS

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Abstract

In this study, the COD removal of Azithromycin from synthetic wastewater (produced to have a composition similar to industrial wastewater) using a Fenton-like (Fe°/H_2O_2) system in combination with coagulation has been investigated. Chemical oxygen demand (COD) was selected as the main parameter to assess treatment efficacy in the current study ($COD_{\circ}$ = 390mg/Lequivalent to 200mg/LAzithromycin). First, the coagulation process was carried out on the synthetic wastewater and the optimum conditions were determined and calculated. According to the results of this experiment, Poly Aluminum Chloride (PAX-18) was selected as the most appropriate coagulant. The results of the coagulation process indicated that COD removal efficacy under the optimum conditions of PAX-18 100mg/Land pH 7.0 was 82.14%. Then, a Fenton-like oxidation process was performed on the effluent of the coagulation process. The optimum conditions were determined and calculated for the Fenton-like process: $[Fe^{\circ}]$ = 0.36 mM/l, $[H_2O_2]$= 0.38 mM/l, and [pH]=7.0. Finally, in combined treatment (coagulation and the Fenton-like process together), the COD removal rose to 96.89% under optimum conditions. The findings of this study demonstrate that the combined processes of coagulation and Fenton-like oxidation under optimum conditions can play an important role in the COD removal of Azithromycin from industrial wastewater.

Key words: antibiotic, Azithromycin, coagulation, Fenton-like process, wastewater

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1. Introduction

Pharmaceutical waste products are among the most complex and toxic industrial wastes. The pharmaceutical industry often generates moderately-to-highly toxic wastewater with seasonal and operational factors affecting the quality and quantity of the effluent. Bulk pharmaceuticals are manufactured using a variety of processes including chemical synthesis, fermentation, extraction and other complex methods (Elmolla et al., 2012). Generally, only a fraction of the amount of antibiotics is transformed in the body and the rest are excreted in their native form or as metabolites (Elmolla and Chaudhuri, 2011). A variety of pharmaceuticals have been reported to be present in the effluent of sewage treatment plants (STPs), indicating their poor biodegradability in municipal sewage and STPs (Kulik et al., 2008). They may enter aquatic environments (surface water and groundwater) or soil and can lead to the development of resistance of microbial pathogens to antibiotics.

Hence, biological treatment of wastewater is insufficient in the case of antibiotics; therefore, a

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pretreatment process is often required prior to discharge into the sewage treatment system (Elmolla and Chaudhuri, 2010). Azithromycin is a member of the macrolide antibiotics. Azithromycin is a white powder which is very similar to erythromycin but is more effective in destroying Gram-negative bacteria, especially *Haemophilus influenzae* (Chisholm et al., 2009). Since Azithromycin demonstrates very low solubility in water, it can be removed using some common physical treatment processes, including coagulation and flocculation. However, these processes are largely ineffective for removing dissolved organic contaminants (Ternes et al., 2003; Westerhoff et al., 2005). Because drugs are toxic to microbes in biological treatment and are difficult to be degraded using biological processes, the use of new technologies to reduce pharmaceuticals in wastewater is essential.

Advanced oxidation processes (AOPs) are applied frequently for the oxidation of industrial sewage containing organic and toxic materials. These processes are based on the production of hydroxyl radicals which demonstrate great efficacy in breaking down organic material (Arsene et al., 2011).The efficacy of the various AOPs depends both on the rate of the generation of the hydroxyl radical ($^{\bullet}OH$) and the amount of contact between the hydroxyl radical and the organic compound (Zaharia et al., 2009). The radical $^{\bullet}OH$ is responsible for the destruction of organic pollutants and is capable of mineralizing them ultimately to CO_2 and H_2O. Among Advanced Oxidation Processes (AOPs), the Fenton process can be used as a chemical alternative to treat non-biodegradable wastewater. Fenton system consists of ferrous salts combined with hydrogen peroxide, whereas Fenton-like system uses iron powder (Fe°) in reaction with H_2O_2, at optimum pH, to produce $^{\bullet}OH$ for the destruction of the organic pollutants (Abdullah et al., 2014; Ma and Xia, 2013). The Fenton-like treatment process not only leads to oxidation, but also to coagulation by the formation of $Fe(OH)_3$. In a Fenton-like process, chemical coagulation acts as a refining step after Fenton-like oxidation (Ayyasmi et al., 2007; Gernjak et al., 2006). In this study, a chemical coagulation process was applied in combination with a Fenton-like process. The idea of using combined processes originated from the following considerations:

- because of the high costs of AOPs, the presence of a pre-treatment process before the use of AOPs can make the treatment process more cost-effective;
- because of the low solubility of Azithromycin, using coagulation as a pre-treatment for the Fenton-like process can reduce the high levels of COD and as a result can decrease the amount of organic load that enters the AOPs, which are expensive processes and respond to specific ranges of COD;
- since one of the important objectives of the treatment processes is the reduction of the organic load present in the sewage, using the combined processes of coagulation and advanced oxidation together can help reduce the COD in the wastewater to a great extent (Goget and Pandit, 2004).

During the coagulation process, the optimum value for each parameter (the optimum dosage of the coagulant and the optimum pH) was determined and calculated. Additionally, the effects of important variables such as H_2O_2 dosage, Fe° dosage, pH and reaction time in the Fenton-like process on COD removal were examined. The objectives of this study were as follows:

- to investigate the efficacy of COD removal by a chemical coagulation process;
- to investigate the efficacy of COD removal by a coagulation process in combination with a Fenton-like (Fe°/H_2O_2) process;
- to compare the efficacy of the coagulation process and the combined process (coagulation and Fenton-like (Fe°/H_2O_2) together) in the removal of COD.

2. Materials and methods

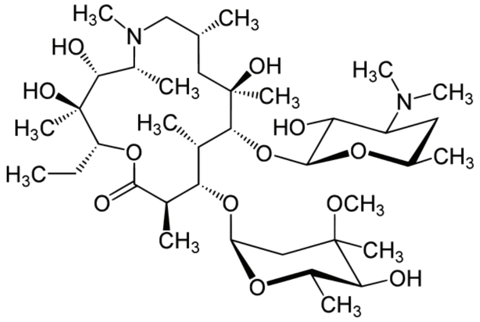
2.1. Materials

For all experiments, reported in this study, the synthetic wastewater was produced by dissolving 0.2 g Azithromycin in 1000 ml distilled water. The Azithromycin antibiotic (formula: $C_{38}H_{69}NO_{13}$ [synonyms: 9-deoxy-9a- aza-9a- methyl- 9a homoerythromycin A], Molecular weight = 748.984gmol^{-1}, Brand names: Zithromax, Sumamed, Zitrocin) was purchased from the Farabi pharmaceutical company (Farabi, 2012). The chemical and physical properties of Azithromycin are summarized in Table 1. Based on our analysis (the measurement of COD in this study), 200 mg/L of Azithromycin is equivalent to 390 mg/L COD (1mg/L of Azithromycin is equivalent to 1.95 mg/L COD). The coagulants, $Al_2(SO_4)_3.18H_2O$, $FeCl_3$, $Fe_2(SO_4)_3$ and PAX-18 used in bench-scale tests were analytical grade. The iron powder (95% Merk) was applied at a particle size of 70-100 μm. Iron powder and all the coagulants were purchased from the Merk Company. Other materials used in this study included Sulfuric acid (96%) and NaOH (98%) for pH adjustment, and hydrogen peroxide with the technical grade (30% w/w and density of 1.13 kgL^{-1}). All the solutions were prepared with distilled water.

2.2. Analytical methods

This study was designed to determine the optimum conditions for obtaining maximum COD removal (the dosage of the coagulant and the pH for the coagulation process) and (the Fe° and H_2O_2 dosages, the pH for the Fenton-like process). COD measurements were performed based on the Standard Method (by the closed reflux titrimetric method) (APHA, AWWA, WPCF, 2005). The COD samples were measured after filtration through a Millipore membrane filter with a pore size of 0.45 μm.

Table 1. Physical and chemical properties of Azithromycin (Farabi, 2012)

Molecular Weight (g mol^{-1})	747.96
Classification	Antibacterial, Antibiotic, Anti-infective Agent, Gastrointestinal Agent, Macrolide
Purity	99%
Solubility in Water	Insoluble (0.342 mg/L)
Physical State	White to off-white crystalline powder
Vapor Pressure	8.60E-27 (mmHg at 25 C)
Melting Point	220^{0}C
Molecular Structure	
Stability	Stable under ordinary conditions
Toxicity	Rat LD_{50} (Ora): 1270mg/kg

Initial and residual H_2O_2 amounts were determined by the spectrophotometry method. Presence of H_2O_2 leads to overestimating COD) (Lee et al., 2011). The pH measurement was performed using a pH meter (Model Jenway 3305). The optimum amounts of pH and the dosage of the coagulants were determined by the Jar test. Additionally, the concentration of iron in the solution was determined by the phenanthroline method based on the Standard Method (APHA, AWWA, WPCF, 2005). Each experiment was conducted three times.

2.3. Experimental set-up

2.3.1. Chemical coagulation

Initially, the chemical coagulation process was performed on the wastewater. In this study, we performed chemical coagulation experiments using four chemicals as coagulants. The selected coagulants were $Al_2(SO_4)_3.18H_2O$, $FeCl_3$, $Fe_2(SO_4)_3$ and PAX-18. In recent years, because of its great advantages (low sensitivity to temperature, reduction in sludge quantities, effectiveness in a wide pH range and a reduced need for lime to adjust the pH value of treated water with high turbidity) PAX-18 has been used extensively as a coagulant (Wang et al., 2004). In all cases, the experiments were carried out in the Jar test device, in five 500 mL glass beakers (100 ml of the solution was poured in each glass beaker). The important operating parameters included pH and the dosage of the coagulants. First, the optimum pH for each of the coagulants was determined.

To determine the optimum pH, the coagulant dosage was maintained at a fixed level (50 mg/L) and pH was altered within a range of 2-10 for each coagulant and the optimum pH for each coagulant was determined. During the second stage of the coagulation process, the optimum amount for each coagulant was determined. During this stage, the pH was set to the optimum level as determined above (8 for $FeCl_3$, 6 for $Al_2(SO_4)_3$, 9 for $FeSO_4$ and 7 for PAX-18) and the coagulant dosage was altered from 25 to 150 mg/L for each coagulant and the optimum dosage for each coagulant was obtained. Finally, the coagulant that had the highest yield under the optimum conditions for the COD removal was selected as the best coagulant. The mean velocity gradient G in rapid mixing and slow mixing process was calculated $700s^{-1}$ and $60s^{-1}$ respectively. During the coagulation process, the following operating stages were enacted: rapid mixing stage: 200 rpm for 1 min; slow mixing stage: 40 rpm for 30 min; the settling time: 30 min.

2.3.2. Fenton-like process

Fenton-like oxidation was performed on the effluent of the coagulation process. The Fenton-like oxidation experiments were performed in a cylindrical glass reactor with a magnetic stirrer using a constant speed of 200 rpm. In the Fenton-like oxidation experiments, the effects of pH, and Fe° and H_2O_2 concentrations on the removal efficiency of COD were examined and the optimum value for each parameter was determined.

The experiments were performed in three stages. In the first stage, the initial concentrations of Fe° (0.3mM/L) and H_2O_2 (0.3mM/l) were kept the same from run to run to determine the optimum pH for the solution for COD removal. While maintaining the optimum pH determined during the first stage (pH=7) and the same iron powder concentration (0.3mM/L), the optimum level for H_2O_2 was measured and determined during the second stage. Finally, while maintaining the optimum pH from the first stage (pH=7) and the H_2O_2 optimum concentration from the second stage (0.3mM/L), the optimum concentration for the iron powder was measured and determined in the third stage. All experiments were performed at $20^{\circ}C$.

2.4. Statistical analysis

In order to statistically evaluate any significant differences among mean values, one-way analysis of variance (ANOVA) test was used (SPSS for Windows, Version 11.0, SPSS, 2001). In all experiments, 5% significant difference between the critical values was achieved.

3. Results and discussion

3.1. Coagulation step optimization

3.1.1. Determination of the optimal pH

In the chemical coagulation process, the pH has a significant role in COD removal since the coagulation occurs within a specific range of pH for each coagulant. The effects of pH on COD removal for the four coagulants used in this study are shown in Fig. 1. While the coagulant dosage was maintained at a fixed level (50 mg/L), pH was altered within a range of 2-10 for each coagulant. The maximum COD removal rates achieved were 65% of COD at pH 6 for $Al_2 (SO_4)_3$, 57% of COD at pH 8.0 for $Fecl_3$, 52% of COD at pH 9 for $FeSO_4$ and 70% of COD at pH 7.0 for PAX-18 respectively ($P<0.05$).This variation may have occurred because the dominant mechanism in the coagulation process used in this study involves bridging between particles. The study conducted by Aguilar provides evidence for this conclusion since according to his study in pH levels above 8 for ferrous hydroxide and pH levels above 6 for aluminum hydroxide the mechanism of coagulation involves bridging between particles. (Aguilar et al., 2005)

It is necessary to mention that the coagulant PAX-18 demonstrated higher efficacy in comparison with the other coagulants. This may be due to the fact that the polynuclearity species are already present in this coagulant and the polymeric chains are partially hydrolyzed (Hyun et al., 2004). The important point is that PAX-18 acts in a wide range of pH levels compared with the other coagulants.

The wide range of optimum pH values indicates that in case of variations in the properties of the wastewater, no disruption in the system results and, consequently, the need for making adjustments and changes in pH values arises less frequently. Aguilar used Poly Aluminum Chloride in a coagulation process in a study designed to remove COD from wastewater. The optimum pH for this coagulant was determined to be 6 and the removal efficacy at this pH was 78% (Aguilar et al., 2005). In another study, Ciner and Akal Solmaz (2007) used chemical coagulation in the removal of radioactive paint from wastewater. In this study, the PAX-18 coagulant used at a pH of 5.5 demonstrated a removal efficacy of 98.5%.

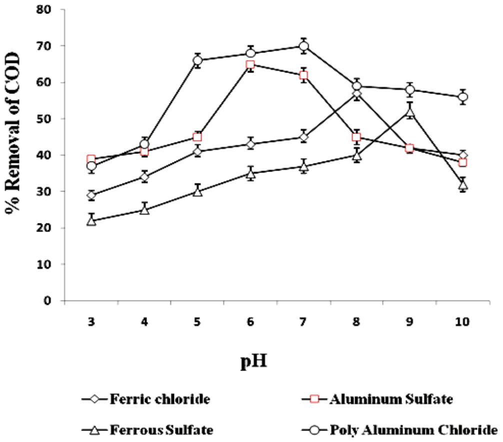


Fig. 1. The effect of pH on the removal rates of COD in the coagulation process (dosage of the coagulant = 50mg/L)

3.1.2. Determination of the optimal dosage for the coagulant

The pH selected for the determination of the optimum coagulant dosage was 8 for $FeCl_3$, 6 for $Al_2 (SO_4)_3$, 9 for $FeSO_4$ and 7 for PAX-18. Once the optimal pH for each coagulant had been determined, the coagulation process was carried out to determine the optimum dosage of each coagulant, using varying coagulant dosages of between 25 to 150 mg/L. Fig. 2 shows the relationship between the efficacy of COD removal and coagulant dosage. For all the coagulants, increasing the coagulant dosage up to the optimum amount increased the removal efficacy, but increasing the dosage higher than this amount had no effect on the efficiency of the process.

The optimal doses for $FeCl_3$, $Al_2 (SO_4)_3$, $FeSO_4$ and PAX-18 were 120, 100, 120 and 100 respectively. At optimum values for each coagulant, the highest COD removal rates could be obtained. This means that, at low dosages of coagulants, the performance is lower and it increases to maximum values with an increase in the dosage of the coagulant to the optimum dose.

Nevertheless, increasing the amount of the coagulant above the optimum dosage has no significant impact on the removal rates and there are no significant differences between the optimum dose and higher doses of the coagulants in terms of COD removal. The interactions of pH, coagulant dosage and COD removal are shown in Table 2. It indicates that, in order to achieve high COD removal rates (63% for $FeCl_3$, 69% for $Al_2 (SO_4)_3$, 59% for $FeSO_4$ and 82.14% for PAX-18($P<0.05$)), the pH and coagulant dosage should optimally be 8,120mg/L for $FeCl_3$, 6,100mg/Lfor $Al_2 (SO_4)_3$, 9, 120mg/L for $FeSO_4$ and 7, 100mg/Lfor PAX-18. A reduction in the concentration of dissolved $Al^{3+}$and Fe^{3+}ions in ($Fe(OH)_3$ and $Al(OH)_3$) solutions led to an increase in COD removal (Gregory and Dupon, 2001). From the results, presented in Table 2, it can be seen that with the maintenance of optimum conditions, the PAX-18 coagulant had a much more significant and positive effect on the removal of COD than the other coagulants.

The experimental results indicated that 82.14% of COD was removed under the optimum conditions of a dosage of 100 mg/Lof PAX-18 and a pH of 7.0. According to the findings of other studies, this effect may be due to the advantages of PAX-18 over the other coagulants including:

Polymeric metal salts like PAX-18 can contribute to the improvement and progression of the destabilization process in two ways, i.e., by bridging particles and by compressing the diffuse double layer) (Wang et al., 2004):

- flocs are formed very quickly and need less time to precipitate;
- when the water turbidity is high, this coagulant shows high efficiency rates and adjusting the pH requires less lime.

Choi et al. (2007) utilized a combination of coagulation and granular activated carbon to remove tetracycline antibiotics from raw water. The coagulant they used was Poly Aluminum Chloride. This coagulant showed the highest efficiency rates (40% for doxycycline-hyclate, 43% for chlortetracycline, 85% for tetracycline, and 94% for democlocycline) at the optimum dosage of 40 milligrams per liter. Xingjian and Huilong (2013) used coagulation combined with Fenton process for the treatment water-based printing ink wastewater, results showed that coagulation using polyaluminium chloride (PACl) as coagulant and ferrous sulfate ($FeSO_4$) as coagulant aid was an efficient pretreatment process, around 96.5% of color and 91.1% of chemical oxygen demand (COD) was removed at the condition of 750 mg L^{-1} PACl, 500 mg L^{-1} $FeSO_4$.

In another study, Carballa et al. (2005) used the processes of coagulation and flocculation in combination with floating to remove Galaxolide and Tonalide from the wastewater. The optimum range for the initial Poly Aluminum Chloride was 700 to 950 mg/L. The removal efficiency of Poly Aluminum Chloride was 63% for Galaxolide and 71% for Tonalide which shows a high level of efficacy for this coagulant.

The results of the coagulation process indicated that wastewater with low COD levels enters the Fenton-like process. This can be useful for two reasons:

- economically (because the AOP processes are more expensive);
- higher COD removal efficiency.

Thus, 82.4% COD removal was achieved by the coagulation process and COD was reduced from 390 mg/L($COD_{\circ}$) to 68.64 mg/L(COD_e). COD_e is the COD of coagulation effluent. The effluent of coagulation with COD= 68.64mg/Lenters the Fenton-like process.

3.2. Fenton-like oxidation step optimization

3.2.1. The effect of solution pH

To determine the optimum pH for the Fenton-like process, pH was varied from 3 to 11. Fig. 3 shows that COD removal by the Fenton-like process is affected by pH. As presented in Fig. 3, maximum COD removal was achieved at pH 7.0, 0.3mM/l H_2O_2 and 0.3mM/l Fe°. This higher COD removal at pH 7.0 can be compared to pH >7 and pH <7, ($P<0.05$). After a 30-min reaction, 97.2% of COD had been completely mineralized at a pH of 7.0 as compared to less than 95.2% at a pH of 3 and 92.6% at a pH of 11. At pH <7 a substantial decrease in the efficiency of COD removal was observed. These phenomena could be explained by: 1- $Fe(OH)^{2+}$ is formed, which reacts more slowly with H_2O_2 and, therefore, the degradation of H_2O_2 is slow, the scavenging effect of $^{\bullet}OH$ by H^+ becomes significant at very low ranges of pH according to reaction 1 (the ions of H^+ may have inhibited the generation of hydroxyl and perhydroxyl radicals that were necessary to achieve the Fenton-like oxidation) (Hong et al., 2008).

$$HO^{\bullet} + H^{+} + e^{-} \rightarrow H_2O \qquad (1)$$

At pH values higher than 7.0, a rapid decrease in COD removal was also observed. This occurs because in this pH range (alkaline solutions), Fe^{3+} ions begin to form flocs ($Fe(OH)_3$) or goethite FeOOH and precipitate and H_2O_2 is also unstable and decomposes to give O_2 and H_2O and consequently loses its oxidizing properties (Wang, 2008). At optimal pH, the Fenton-like process is most effective and COD removal increases significantly. In a study similar to the present one, Xing et al. (2010) used a combination of coagulation and advanced oxidation processes to remove the COD related to antibiotic fermentation wastewater. The pH of the wastewater entering the Fenton-like process was set to 4 and the COD removal efficiency after the combined process was measured as 93.5%. Increased removal efficiency at optimum pH might be because of two possible reasons (Wang, 2008):

- at this pH, the ratio of the dissolved Fe^{2+} increases;
- the oxidation potential of $^{\bullet}OH$ increases.

3.2.2. The effect of the solution H_2O_2

The cost of H_2O_2 accounts for most of the cost of AOP processes, so the determination of optimum H_2O_2 amount is quite important in the AOP processes. The results of COD removal for the determination of optimum H_2O_2 concentration are presented in Fig. 4. To determine optimum H_2O_2 concentration, experiments were conducted by varying the amount of H_2O_2 from 0.1 to 1.6 mM/L (pH was fixed at 7 and the Fe° dosage was 0.3 mM/L). Fig. 4 shows that the efficiency of COD removal for Azithromycin was highest at 0.38 mM/L of H_2O_2. It was observed that COD removal efficiency increased from 94.2% to 97.3% as H_2O_2 concentration went up from 0.1 to 0.38 mM/L ($P<0.05$). An increase in the concentration of H_2O_2 up to 0.38 mM/L did not significantly affect the removal of COD and there was no significant difference between the dosages of 0.38 and 1.6mM/L. Because at excessive amounts, H_2O_2 acts as a scavenger of the $^{\bullet}OH$ to produce the perhydroxyl radical ($HO_2^{\bullet}$) according to reaction 2 ($HO_2^{\bullet}$ has much lower oxidation capacities than $^{\bullet}OH$) (Zhihui et al., 2005).

$$H_2O_2 + HO^{\bullet} \rightarrow H_2O + HO_2^{\bullet} \qquad (2)$$

Reduction of H_2O_2 concentration from 0.38 to 0.1 mM/L resulted in a decrease in COD removal efficiency from 97.3 to 94.2 (because of partial oxidation of Fe^{2+} in H_2O_2 concentrations lower than optimum values).

In the optimum concentration of H_2O_2, ferrous ions completely oxidized; consequently, the generation of hydroxyl radicals increased (Elmolla and Chaudhuri, 2011). Therefore, an H_2O_2 dosage of 0.38 mM/L with a COD removal efficiency of 97.3% was chosen as the optimum dosage. The excess H_2O_2 interferes with the measurement of COD, because the residual amounts of H_2O_2 consume $K_2Cr_2O_7$, according to reaction 3, leading to an increase in COD levels (Lee et al., 2011).

$$Cr_2O_7^{2-} + 3H_2O_2 + 8H^+ = 2Cr^+ + 3O_2 + 7H_2O \qquad (3)$$

Masschelein et al. (1977) study group used a diluted enzyme catalyst solution made from Micrococcus Lysodeikticus to destroy unreacted H_2O_2 and the amount of residual H_2O_2 was determined via the molybdate-catalyzed iodometric spectrophotometry method. Arslan-Alatonand (2004) used Fenton-like advanced oxidation for the COD removal of penicillin from the wastewater. They determined the optimum H_2O_2 amount for the COD removal of penicillin was 1.5 mM. The large amount of H_2O_2 needed can be explained by the fact that they did not use any pretreatment processes before the Fenton-like process.

Table 2. The relationship between pH, coagulation dosage and COD removal efficiency in the coagulation process

Coagulant	*Dosage of coagulant (mg/L)*	*pH*							
		3	*4*	*5*	*6*	*7*	*8*	*9*	*10*
		% Removal of COD							
$FeCl_3$	25	25	31	35	38	39	40	38	35
	50	29	34	41	43	45	57	42	40
	100	35	39	49	51	53	59	49	45
	120	39	43	51	55	59	63	52	50
	150	38	39	46	52	57	61	50	47
$Al_2(SO_4)_3$	25	33	37	40	45	44	42	38	35
	50	39	41	45	65	62	45	42	38
	100	45	49	50	69	64	50	49	45
	120	43	47	49	68	61	49	48	42
	150	37	44	47	67	66	45	44	40
$FeSO_4$	25	19	23	25	27	31	33	35	30
	50	22	25	30	35	37	40	52	32
	100	28	35	38	40	43	45	54	36
	120	36	39	42	44	49	52	58	41
	150	32	35	40	42	45	51	57	39
PAX-18	25	35	40	55	55	57	56	55	50
	50	37	43	66	68	70	59	58	56
	100	39	47	78	79	82	65	63	59
	120	37	45	77	78	80	64	60	57
	150	35	43	75	75	78	62	58	56

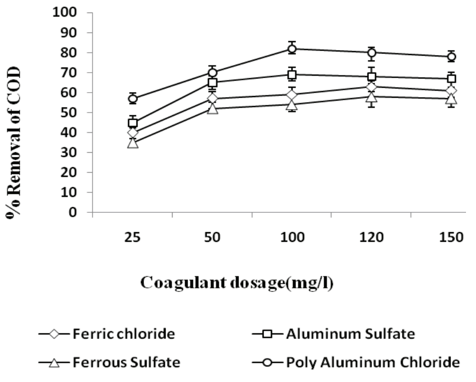


Fig. 2. The effect of coagulant dosage on the removal efficiency of the coagulation process at optimum pH for each coagulant

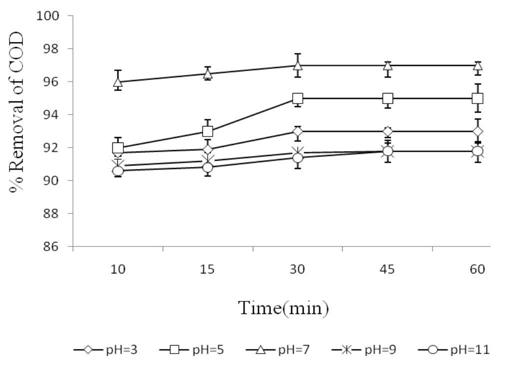


Fig. 3. The effect of pH on the removal of COD at different times by Fenton-like oxidation (Fe^0=0.3mM/l, H_2O_2=0.3 mM/L)

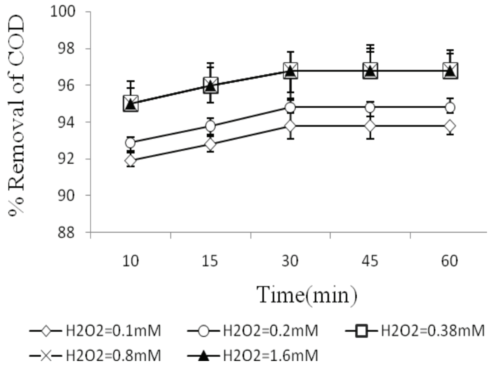


Fig. 4. The effect of H_2O_2 on the removal of COD at different times by Fenton-like oxidation (Fe^0=0.3mM/L, pH=7.0)

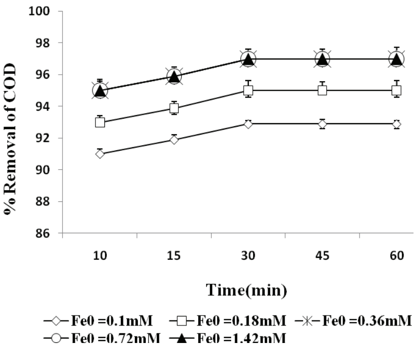


Fig. 5. The effect of $Fe^{\bullet}$ on the removal of COD at different times by Fenton-like oxidation (Fe^0=0.3mM/L, pH=7.0)

3.2.3. The effect of Fe° solution

Fig. 5 presents the effect of Fe° concentration on COD removal efficiency for Azithromycin. During this stage, the concentration of Fe° was changed from 0.1mM/L to 1.42mM/L at a constant H_2O_2 dosage of 0.38mM/L and pH of 7.0. At the Fe° dosage of 0.1mM/L and 0.36mM/L, the COD removal efficiency was 94.2% and 97.4%, $P<0.05$ respectively.

It is obvious that increasing Fe° from 0.1 to 0.38mM/L has a great effect on the efficiency of the Fenton-like reaction. Increasing the Fe° concentration from 0.38 to 1.6 mg/L resulted in no further increases in COD removal, and a slight increase from 97.4 to 97.5% was observed. This demonstrates that there is an optimum concentration for iron in the Fenton-like reaction designed to remove COD. This can be explained by the scavenging effect of overdoses of Fe^{2+} on OH radicals.

Because in higher dosages of Fe°, OH radicals may be scavenged by participating in reactions with Fe^{2+} as in reaction 4 (the formation of orange-brown iron precipitate ($Fe(OH)_3$ flocs), consequently, the COD removal could decrease (Elmolla and Chaudhuri, 2011).

$$Fe^{2+} + HO^{\bullet} \rightarrow HO^{-} + Fe^{3+} \tag{4}$$

Of course, it must be noted that the formed Fe^{3+} again enters a reaction with hydrogen peroxide and produces Fe^{2+} in the solution and this leads to an increase in the removal efficiency. Therefore, as the optimum COD removal (97.4%) occurs at $Fe^{\circ} = 0.36$ mM/L and given that no increase in COD removal was obtained by increasing the iron concentration more than the optimum amount.

Considering the above-mentioned results, a Fe° concentration of 0.36mM/L was selected as the optimum concentration for the removal of Azithromycin COD. Fana study group used a Fenton-like process in the removal of sulfasalazine in which the amount of the iron used was 0.35 mM and a COD removal efficiency of 84.2% was achieved (Fana, 2011).

4. Conclusion

Based on the results obtained, PAX-18 was selected as the best coagulant. The Azithromycin COD removal efficiency that was achieved using PAX-18 was 82.14% at optimal conditions (dosage of 100mg/Land pH of 7.0).

It was observed that the pretreatment of the wastewater containing the antibiotic (by the coagulation process) before entering the Fenton process led to a significant decrease in organic load. This can reduce the problems associated with advanced oxidation processes (including high costs and applicability to a limited range of COD). Then, a Fenton-like oxidation process was performed on the effluent of the coagulation process.

The optimal conditions for the Fenton-like process were determined to be $[Fe^{\circ}] = 0.36$ mM/L, $[H_2O_2]= 0.38$ mM/L, $H_2O_2/Fe^{\circ} \approx 1$ and pH=7.0. The coagulation process showed 96.89% COD removal under the selected conditions. Finally, given the ultimate obtained results from this research, it became clear that the combined processes of coagulation and Fenton-like demonstrate a high efficiency in COD removal.

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