Combination of coagulation and oxidation processes for treatment of real fish canning wastewater

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A two-stage, coagulation-Fenton and coagulation-Fenton’s-like processes were used for the treatment of fish canning wastewater (FCW). Each process was analyzed both individually and in combination with the other one. The coagulation–flocculation–decantation (CFD) process was performed by the application of aluminum sulfate (Al\textsubscript{2}(SO\textsubscript{4})\textsubscript{3}), poly-aluminum chloride, and ferric chloride (FeCl\textsubscript{3}). To evaluate the efficiency of organic material removal, advanced oxidation processes such as Fenton and Fenton-like were applied. The CFD processes (pH = 7.2, [Al\textsubscript{2}(SO\textsubscript{4})\textsubscript{3}] = 400 mg/L, rapid speed 120 rpm/1 min, slow speed 30 rpm/20 min, sedimentation time 10 min, temperature 298 K), and Fenton and Fenton-like processes (pH 3.0, [Fe\textsuperscript{2+}] = [Fe\textsuperscript{3+}] = 400 mg/L, [H\textsubscript{2}O\textsubscript{2}] = 400 mg/L, agitation 150 rpm, temperature 298 K, and reaction time 60 min) led to 58%, 68%, and 60% chemical oxygen demand (COD) removals, respectively. The application of a combined two-stage CFD-Fenton and CFD-Fenton-like process led to COD removals of 93% and 84%, respectively. The BMG model provided the best correlation of the data with an $R^2$ of 0.995 and 0.999 for the Fenton and Fenton-like processes, respectively. Therefore, it could be concluded that it is more advantageous to combine coagulation and Fenton processes for the treatment of FCW.

Keywords: Fish canning wastewater; CFD process; Aluminum sulfate; Fenton process; COD; BMG kinetic model.

1. Introduction

Fisheries and their associated facilities are a wide source of food and a large part of the world’s industry as well. The fish canning industry uses plenty of water in operational processes such as cleaning, washing, cooling the melt, and the like [1]. In general, fish canning wastewater (FCW) contains high levels of the nutrient, suspended solid compounds, and are high saline [2]. These components contain nitrogen, phosphate, protein, oil and grease (O&G), and salinity factors, such as Cl\textsuperscript{-}, Na\textsuperscript{+}, and SO\textsubscript{4}\textsuperscript{2-}, which are added through the used chemical materials in the process and seawater [3]. As a result, the manufacturing sector has a tremendous amount of waste, and due to the waste’s high levels of salt, fat and greases, and also due to the difficulty of removing these compounds, a suitable treatment method should be used. It is very important to determine the appropriate treatment method by taking an economic and environmentally friendly perspective [4].

A wide range of processes is used in FCW wastewater treatment, with the majority of them generally involving
initial screening and primary sedimentation of the raw wastewater followed by biological treatment. Many treatment processes such as solid–liquid separation [1], chemical–physical [5], and aerobic biological treatment methods [4,6,7] are used for fish canning wastewater treatment that the most important of which are chemical methods [4,8], membrane processes [9], electrochemical methods [10,11], and different types of biological treatment [4,6,12].

The initial stage of FCW treatment involves mechanical or physical treatment processes, which remove some 20%–30% of solids in the wastewater [13]. This chemical process involves destabilizing wastewater particles so that they aggregate during chemical flocculation. This method of stable oil emulsions is based on canceling the energy barrier that exists between the oil droplets. This is done by the addition of chemical compounds and the neutralization of the electric charge responsible for inducing the repulsion of the droplets. After larger particle groups are formed by creating bridges between them to bind the particles, sedimentation can be used to remove the particles from the mixture [4,14]. The three chemical groups commonly used for colloidal particle destabilization are acids compounds [15], metal salts [16], and polyelectrolytes [17]. The best choice for a particular application depends on the system.

The coagulation–flocculation–decantation (CFD) process is based on destabilization by creating an emulsion and breaking the energy barrier of oily substances and organic compounds; flotation or filtration is done by forming a neutral mass and then merging and compressed flocculation is conducted using coagulants and polyelectrolyte, and finally the separation of residual sludge using the centrifuge method [18]. The advantages of the CFD method are: (1) process simplicity, (2) high-quality separation of particles and water, (3) prevention of unpleasant odors, (4) commercial availability of a wide range of chemicals, (5) significant reduction in the chemical oxygen demand (COD) and biochemical oxygen demand (BOD), (6) being fast, efficient and easy to use, (7) ability to operate effectively over a wide range of pH and wastewater temperatures, (8) production of fewer chemical residues, (9) lower chloride or sulfate production, resulting in lower final TDS water, (10) lower operational costs, (11) bacterial inactivation capability, and (12) being highly efficient for SS and colloidal particles removal [18,19]. This method also has disadvantages such as physicochemical monitoring of the effluent (pH), increased sludge volume generation (management, treatment, and cost), and low removal of arsenic [18]. Three groups of chemicals can be used in the coagulation process, including metal salts [20], acids [21], and synthetic polyelectrolyte [17].

In this regard, membrane technology becomes an emerging technique for the separation of FCW due to its high separation efficiency compared to conventional methods. Also, electrochemical processes were assayed efficiently in the destabilization of such oily emulsions. These chemical-free processes outperform other treatment technologies with higher efficiency while producing minimal waste and using less energy and with more environmentally friendly remediation as well [22]. But the costs of operating these purification systems are high [23].

The amount of BOD and COD is an important parameter in determining the microbial activity and choosing the treatment method [24–26]. Biological processes are the most common method for treating the wastewater containing organic material [27]; in these processes, the organic matter is converted into a simple combination in an economical and environmentally friendly way [28]. However, some resistant compounds remain after the biological treatment and, thus, a secondary treatment method is needed [29]. Recently, coagulation/advanced oxidation processes have been considered, and used in the treatment of many effluents, due to their high treatment efficiency [30–34].

Fenton's process (Fe(III)/H₂O₂) is one of the methods of advanced oxidation process (AOPs) and is the most effective method for resistant organic compounds oxidation [35], as summarized in Eqs. (1)–(11). The process efficiency depends on parameters such as Fe(II), hydrogen peroxide (H₂O₂), pH, and time [36,37].

\[
\begin{align*}
\text{Fe}^{2+} + \text{H}_2\text{O}_2 &\rightarrow \text{Fe}^{3+} + \text{HO}^- + \text{OH}^- \quad (1) \\
\text{HO}^- + \text{H}_2\text{O}_2 &\rightarrow \text{H}_2\text{O} + \text{HO}_2^- \quad (2) \\
\text{H}_2\text{O}_2 + \text{HO}_2^- &\rightarrow \text{H}_2\text{O} + \text{HO}^+ + \text{O}_2 \quad (3) \\
\text{Fe}^{2+} + \text{HO}^+ &\rightarrow \text{Fe}^{3+} + \text{OH}^- \quad (4) \\
\text{HO}^- + \text{H}_2\text{O}_2 &\rightarrow \text{H}_2\text{O} + \text{HO}^- + \text{O}_2 \quad (5) \\
\text{Fe}^{2+} + \text{O}_2^- &\rightarrow \text{Fe}^{3+} + \text{O}_2 \quad (6) \\
\text{Fe}^{2+} + \text{H}_2\text{O}_2 &\rightarrow \text{Fe}^{3+} + \text{HO}^+ + \text{H}^+ \quad (7) \\
\text{H}_2\text{O}_2 + \text{HO}^- &\rightarrow \text{H}_2\text{O} + \text{O}_2 + \text{HO}^+ \quad (8) \\
\text{Fe}^{2+} + \text{HO}^- + \text{H}^+ &\rightarrow \text{Fe}^{3+} + \text{H}_2\text{O} \quad (9) \\
\text{HO}^- + \text{H}_2\text{O}_2 &\rightarrow \text{H}_2\text{O} + \text{O}_2 \quad (10) \\
\text{HO}^- + \text{HO}_2^- &\rightarrow \text{H}_2\text{O}_2 \quad (11)
\end{align*}
\]

By changing the catalyst from Fe(II) to Fe(III), a Fenton-like reaction can be used. Also, effective parameters such as the concentration of Fe(III), hydrogen peroxide (H₂O₂), pH, and reaction time should be investigated [38]. The general mechanism of the Fenton and Fenton-like processes begins with the formation of hydroxyl radicals. These reactions occur in an acid environment (pH 2.8–3). During the Fenton-like process, Fe(II) is regenerated to Fe(III) [36] (Eq. (12)).

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{HO}^- + \text{H}^+ \quad (12)
\]

According to Eqs. (1)–(12), the evidence can indirectly confirm that the association process of Fe(III) and H₂O₂ is obtained by the transfer of inner electrons. Moreover, Fe(II) can further associate with H₂O₂ through the transfer of its inner electrons to generate a compound with ring configuration or single-ended linear [39]. Using Fe(II) salt can reduce the cost of treatment. Also, the produced Fe(III) can react with H₂O₂ and hydroperoxyl radicals in the Fenton-like reaction, which leads to regenerating Fe(II) [40–42].
After a careful investigation, it was observed that there was a lack of information on the application of CFD processes in the treatment of FCW. Also, a lack of information regarding the application of Fenton and Fenton-like oxidation processes in the removal of organic matter from FCW was noticed. Therefore, in this study, CFD, Fenton, and Fenton-like methods were studied separately and in combination.

In order to answer these relevant questions, several objectives were defined: (1) optimization of CFD and oxidation processes for FCW treatment, (2) comparison of Fenton and Fenton-like processes, and (3) evaluation of the effect of combined CFD-oxidation process.

2. Experiment

2.1. Characteristics of FCW

As a case study, the output wastewater of the fish canning factory (in Bandar Anzali) was used. The plant produces 15 m³ of wastewater daily. After sampling and transporting the samples to the laboratory, at a temperature of 4°C the wastewater was studied and the initial analysis was conducted. The results are presented in Table 1.

<table>
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<tr>
<th>Parameter</th>
<th>Value</th>
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<tr>
<td>COD, mg O₅/L</td>
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<td>Oil &amp; grease, mg/L</td>
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<td>PO₄³⁻, mg/L</td>
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</tr>
<tr>
<td>NO₃⁻, mg/L</td>
<td>3.8</td>
</tr>
</tbody>
</table>

2.2. Reagents and analytical techniques

Ferric chloride (FeCl₃), aluminum sulfate (Al₂(SO₄)₃), polyaluminum chloride (PAC), anion polyelectrolyte (polyacrylamide), sodium hydroxide (NaOH), sulfuric acid (H₂SO₄), hydrochloric acid, (HCl), hydrogen peroxide solution 30% (H₂O₂), potassium dichromate (K₂Cr₂O₇), silver sulfate (Ag₂SO₄) and mercury(II) sulfate (HgSO₄) were purchased from Merck Co., (Darmstadt, Germany) and distilled water was used in all experiments.

Aqualytic multi-parameters device (model AL125) was used for pH and EC analysis. Aqualytic multi-parameters device (model AL125) was used for pH and EC analysis. A pH meter with a combined double junction glass electrode, calibrated against two standard buffer solutions at pH 4.0 and 7.0, was used for pH measurement. The pH of the solutions was adjusted using either 0.10 M H₂SO₄ (Fenton reaction) and HCl (Fenton-like reaction) or NaOH solutions. Standard methods for the examination of water and wastewater [43] were adopted for the measurement of total suspended solids (TSS), suspended solids (SS), COD, BOD₅, O&G, phosphate (PO₄³⁻), nitrate–nitrate (N nitrate), and ammoniacal nitrogen (N ammoniacal) [44]. SS and TSS were measured using an Imhoff funnel and spectrophotometry according to standard method 2540D using a Jenway spectrophotometer, respectively. The concentration of phosphate and nitrate was determined through spectrophotometry using the stannous chloride method (4500-P D) and UV spectrophotometric screening method (4500-NO₃ B), respectively. The ammonia nitrogen concentration and O&G concentration were measured through the Nessler method and partition-gravimetric method (5520 B) using the Jenway spectrophotometer. The efficiency of the method was investigated through the open and closed reflux method of COD analysis (aqualytic model AL250). Also, the total organic carbon (TOC) was measured after acidification of the samples with phosphoric acid to a final pH value of about 2 using TOC analyzer (Hach QuickD1200, United States, Loveland, Colorado). To determine of O&G, the spectrophotometric method was used.

2.3. CFD batch treatment experiments

In order to understand the effect of CFD process on FCW treatment, three different coagulants, Al₂(SO₄)₃, FeCl₃, and PAC, were tested in a jar-test device (Zagchemie, Iran), using 500 mL of wastewater in 1,000 mL beakers. After sedimentation, the supernatant was decanted, followed by filtration using Whatman paper. Several trials were performed in order to optimize CFD process: (1) 100–500 mg/L of coagulant was added to 500 mL wastewater, under these operational conditions: pH: 7.2, rapid speed: 120 rpm/1 min, slow speed: 30 rpm/20 min, sedimentation time: 10 min, and temperature: 298 K; (2) the pH of the 500 mL wastewater was varied from 3.0–12, under these operational conditions: [coagulant] = 400 mg/L, rapid speed: 120 rpm/1 min, slow speed: 30 rpm/ 20 min, sedimentation time: 10 min, and temperature: 298 K.

2.4. Oxidation batch treatment experiments

The Fenton and Fenton-like processes were performed in a stirred glass reactor, in which 500 mL of FCW was treated. After the oxidation process, the pH of the sample solution was increased to 8.5 to increase the formation of ferric hydroxide flocks, and then, the samples were filtered prior to analysis. The Fenton and Fenton-like processes were performed in the following way: (1) Variation of the H₂O₂ concentration (4–800 mg/L), under the operational conditions: pH: 3.0, [Fe²⁺] = [Fe³⁺] = 400 mg/L, agitation: 150 rpm, temperature: 298 K, and reaction time: 60 min; (2) Variation of the reaction time (10–120 min), under the operational conditions: pH 3.0, [Fe²⁺] = [Fe³⁺] = 400 mg/L, [H₂O₂] = 400 mg/L, agitation: 150 rpm, and temperature: 298 K.

2.5. Kinetic models

To investigate the mechanism of the treatment process and potential rate-controlling steps such as mass transfer.
and chemical reaction of Fenton and Fenton-like process, the experimental kinetic data for treatment of FCW were modeled by the first-order, and the second-order equations, and the Behnajady–Modirshahla–Chanbery (BMG) kinetic models [17] (Eqs. (13)–(15), respectively):

$$\ln \frac{C_0}{C_t} = K_1 \cdot t$$  \hspace{1cm} (13)

$$\frac{1}{C_t} - \frac{1}{C_0} = K_2 \cdot t$$  \hspace{1cm} (14)

$$\frac{t}{1 - \left( \frac{C_t}{C_0} \right)} = m + b \cdot t$$  \hspace{1cm} (15)

Eqs. (5)–(7), $C_0$ and $C_t$ show the COD concentration (mg/L) of FCW at initial ($t = 0$) and time $t$ (min), respectively; $K_1$ is the first-order kinetic parameter (1/min); $K_2$ is the second-order kinetic parameter (L/mg/min); $m$ (min) and $b$ are two characteristic constants of the BMG kinetic model, representing the relation between oxidation capacity and the reaction kinetics.

Also, in the filtration of supernatant, the solution was analyzed to determine the COD reduction percentage according to the following equation:

$$\text{Removal}(\%) = \frac{\text{COD}_{i} - \text{COD}_{f}}{\text{COD}_{i}} \times 100$$  \hspace{1cm} (16)

3. Results and discussion

3.1. Treatment by CFD process

3.1.1. Effect of coagulant concentration

To study the treatment efficiency of coagulation in FCW, three coagulants (Al$_2$(SO$_4$)$_3$, PAC, and FeCl$_3$) were tested. In these experiments, the COD of the FCW was approximately 2,500 mg O$_2$/L. Different concentrations of each coagulant (100–500 mg/L) were studied while the raw wastewater pH was about 7. Other parameters such as fast speed, slow speed, and ambient temperature were kept constant at 120 rpm/1 min, 30 rpm/20 min, and 298 K. Then, the settling process took place for 10 min and the supernatant was filtered. The results are shown in Fig. 1.

When the coagulant concentration was 100 mg/L, the COD removals were about 25%, 29%, and 35% for Al$_2$(SO$_4$)$_3$, FeCl$_3$, and PAC, respectively. With an increase to 400 mg/L, the COD removals were approximately 40%, 43%, and 57%, and when the coagulant concentration was 500 mg/L, the obtained COD removals were 44%, 46%, and 58% for Al$_2$(SO$_4$)$_3$, FeCl$_3$, and PAC, respectively. According to these results, an addition higher than 400 mg/L was not viable because the COD removal had a very small increase. When coagulants are added to the solution, a sequence of hydrolysis species is formed. The low change in COD removal efficiency could be due to the stabilization of colloidal particles when the coagulants were applied at dosages above the optimum value [45]. At high concentrations of coagulant, the formed precipitates can physically sweep away the colloidal particles from the solution, which is referred to as “sweep coagulation” [46,47].

3.1.2. Effect of pH

Fig. 2 shows the COD removal efficiency obtained as a function of the initial pH of wastewater. In the CFD process, pH has a very important role, because the process occurs in a specific range of pH for each coagulant [47]. For this purpose, a concentration of 400 mg/L of each coagulant was evaluated in the pH range of 3–12. It is necessary to mention, that after 1 min of rapid rotation at 120 rpm for coagulation, the mixture was slowly stirred at 30 rpm for a certain time (20 min) and then, the treated wastewater precipitated for 10 min.

In accordance with Fig. 2, it was observed that with increasing pH from 3.0 to 12, the efficiency of CFD process increased. This was observed by the increase in COD removal. As shown in Fig. 2, it was observed that with increasing pH from 3.0 to 12, the efficiency of CFD process increased. This was observed as a consequence of the increase in COD removal. These hydrolysis species have a positive or negative charge, depending on the pH of the solution, which can be different; hydrolysis species are positive at a pH of less than 6 and negative at higher pH. The positively charged hydrolysis species can be adsorbed on the surface of the colloidal particles and cause the particles to become unstable. In the process of CFD, this mechanism is called “charge neutralization.” Therefore, by decreasing pH (12–3) the COD removal efficiency decreased from 60% to 27% for Al$_2$(SO$_4$)$_3$, 46% to 25% for FeCl$_3$, and 43% to 32% for PAC. This is because, in acidic conditions, the existing H$^+$ in the environment prevents the formation of aluminum hydroxide [4]; but by increasing the pH > 7.0, little COD removal was observed for all coagulants [48]. The predominant charges during coagulation tend to be positive at lower pH and negative at higher pH. The organic compounds in FCW wastewater seem to be better removed in a pH range between 6 and 8 because this area is Fe(OH)$_3$, formation zone. Due to the presence of several hydrolyzed Fe(OH)$_3$, iron species and Fe(OH)$_3$ (soluble and insoluble) at the range of pHs, the reactions involved are probably numerous. At an acidic pH (5 and 6), the cationic species of iron are dominant. The possible reactions would be the formation of complexes, soluble or insoluble, based on the structure of the compound and the nature of the organic functions present in the wastewater [49]. Metal salts derived from Al$^3+$ tend to be present in the form of positively charged Al species in the effluent with pH values less than 6, which is favorable for charge neutralization to take place apart from adsorption [21]. Indeed, when pH was lower than 5.0, the primary hydrolyzates of PAC and Al$_2$(SO$_4$)$_3$, were some positive hydrolyzates, like Al(OH)$_3$, Al$_2$(OH)$_6$$_3^+$, Al(OH)$_3^2-$, and Al$_2$(OH)$_6$$_5^6-$ [50]. These positive hydrolyzates could easily neutralize the external negative charges of wastewater pollutants and additionally destabilize the colloids. They are also of advantage to the physical or chemical adsorption of the destabilized pollutants colloids, which lead to floe growth. When the initial pH range was between 6.0 and 8.0, there were some high polymeric
positive hydrolyzates and Al(OH)₃ formed in the solution [51]. The colloids were easily adsorbed and co-precipitated by the hydrolyzates, which had low solubility and a large surface area. Also, when pH was higher than 8.0, the suspension process was difficult to be destabilized because the hydrolyzates were transformed to Al(OH)₃ [50,51]. Teh et al. [21] has put emphasis on a higher rate of coagulation using Al₃(SO₄)₃ at a pH of 6 to 7. Also, PAC coagulant is less sensitive to pH [21]; so, the pH of the raw sample (pH 7.2) was considered as the optimum pH for the coagulation process.

By comparing the three coagulants, it can be concluded that Al₃(SO₄)₃ has higher COD removal efficiency (about 58%) compared to PAC and FeCl₃ (about 40% and 43%), with the concentration of all coagulants equal to 400 mg/L and pH = 7.2, a rapid speed of 120 rpm/1 min, a slow speed of 30 rpm/20 min, a sedimentation time of 10 min, and a temperature of 298 K. As a result, Al₃(SO₄)₃ was chosen as an optimal coagulant.

3.2. Treatment of FCW using AOPs

In Fenton and Fenton-like processes, the reaction takes place at an acidic pH. Because at pH > 4, there is a significant deduction of Fe(III) precipitates as Fe(OH)₃ [52,53], which prevents the reaction between Fe³⁺ and H₂O₂, and so Fe²⁺ is regenerated [52]. At the end of the Fenton and Fenton-like process, the contaminants are deposited in the form of sludge along with iron hydroxide, with the formed sludge making up about 0.05% of the effluent volume. Also, H₂O₂ declines quickly into H₂O and O₂ at a high pH [54]. The predominant soluble ferric iron species in the pH between 3–4 is the hydrated ferric iron complex ([Fe(OH)](H₂O)₅)³⁺. So, at pH < 3, the HO• efficiency of the process will be low due to the formation of [Fe(III)(H₂O)]⁶⁺ complex, which reacts more slowly with H₂O₂ than [Fe(OH)(H₂O)]³⁺ and, therefore, it produces lower hydroxyl radicals. So, at pH < 3, HO radicals can be consumed by the scavenging effects of H⁺ according to Eq. (17) [35,55].

\[
\text{OH}^• + \text{H}^+ + \text{e}^- \rightarrow \text{H}_2\text{O} 
\]  

Therefore, all studies were performed at pH 3.0.

3.2.1. Effect of H₂O₂ concentration

Oxidation treatment of FCW was performed by Fenton and Fenton-like processes. The concentration of H₂O₂ (oxidant agent) was varied (40–800 mg/L) while keeping constant the catalyst concentration (400 mg/L) under the operational conditions: pH 3.0, [Fe³⁺] = [Fe²⁺] = 400 mg/L, agitation: 150 rpm, and temperature: 298 K, and reaction time: 60 min. At the end of the reaction, in order to form ferric hydroxide flocks and remove contaminants from the solution, the pH of the wastewater samples was increased to 8.5 by 0.1 M NaOH. Then the sample was filtered and the COD was measured. Also, in order to select the best ratio of Fe²⁺ or Fe³⁺ with H₂O₂ for oxidizing organic pollutants, four H₂O₂/Fe ratios, 1:10, 1:4, 1:2, 1:1, and 2:1, were investigated by changing the concentration of H₂O₂. The obtained results are shown in Fig. 3.

According to the results shown in Fig. 3, it can be concluded that an increase in the oxidant/catalyst ratio from 1:10 to 1:1 leads to improved treatment efficiency and COD removal. The increase in the removal rate as a result of an increase in H₂O₂ is due to the increment in the HO• radicals. By increasing the H₂O₂ concentration, the H₂O₂ decomposition rises until an optimal H₂O₂ concentration is achieved [56]. When the H₂O₂/Fe ratio was 1:2, the COD removals were 54% and 55% for Fenton and Fenton-like processes, respectively. Two reactions may have occurred: (1) the oxidant concentration was low and there was insufficient production of HO• radicals; (2) also, due to a higher Fe concentration, there could be a scavenging effect by the iron [35,56]:

\[
\text{HO}^• + \text{Fe}^{\text{ii}} \rightarrow \text{HO}^- + \text{Fe}^{\text{ii}} \quad (18)
\]

When the H₂O₂/Fe ratio was 1:1, an ideal ratio was reached, in which there was a higher HO• radical and decreased scavenging reactions. COD removals of 68% and 60% were observed for Fenton and Fenton-like processes, respectively.

When the H₂O₂/Fe ratio was 2:1, there was an excess of H₂O₂ in solution. COD removals of 41% and 60% were obtained for Fenton and Fenton-like processes, respectively. The excess of H₂O₂ will compete with the organic matter for the HO• radicals and the COD removal will decrease, according to Eqs. (2), (10), and (11) [57].

3.2.2. Effect of reaction time

The reaction time is an important parameter in the advanced oxidation process. Increasing contact time causes a complete reaction between iron ions and hydrogen peroxide, produces more hydroxyl radicals, and thus increases the efficiency of COD removal. To study this effect, the effect of longer reaction time (time = 120 min) was tested under the operational conditions: pH 3.0, [Fe³⁺] = [Fe²⁺] = 400 mg/L, [H₂O₂] = 400 mg/L, agitation: 150 rpm, and temperature: 298 K. The results are shown in Fig. 4.

The results of this study showed that COD removals in the first 60 min were 68% and 60% for Fenton and Fenton-like process, respectively, and with increasing time to 90 and 120 min, COD removals of 68% and 70% for Fenton process, and 62% and 63% for Fenton-like process were observed. In fact, the oxidation of organic compounds in FCW using Fenton and Fenton-like processes can be separated into two phases.

The first phase was devoting to the rapid reaction, which occurs in the first 60 min and represents the fast generation of HO• from the H₂O₂ and iron ions, directly degrading organic. The second phase, occurred between 60 and 120 min, and it was slower, indicating a lower rate of HO• radical production. This could be due to the formation of intermediate compounds following long reaction times, which in turn reacted with the hydroxyl radicals as competitors to the primary compounds and acted as HO• snatchers. In previous studies on the degradation of organic compounds in wastewater by Fenton and Fenton-like processes, a similar behavior was also observed [35,38,42,58]. By increasing the reaction time, the hydrolysis of H₂O₂ increased, and a higher HO•
radical production was observed. However, the results indicated that when \( t > 60 \) min, the COD removal did not show a considerable increase and, therefore, 60 min was considered an ideal time for Fenton and Fenton-like processes [57].

### 3.2.3. Kinetic modeling

During the Fenton and Fenton-like reaction, the degradation of organic matter in FCW could be described quantitatively by reaction kinetics. In this study, the pseudo-first-order, pseudo-second-order, and BMG kinetic models were designed by the application of Eqs. (13)–(15). Some researchers have reported that the BMG model has effectively predicted the degradation of the Fenton and Fenton-like processes [59–62]. The results are shown in Fig. 5 and Table 2.

The experimental data in Table 2 and Fig. 5 show a very fast reaction followed by a slower one, and as a result the degradation of organics by Fenton and Fenton-like oxidations are not suitable to be modeled by first-order or second-order kinetics because the fitting of experimental data with those models would not be good and no high regression coefficients are observed for these two models \((R^2 < 0.860)\). Thus, the BMG kinetic model is proposed by some authors because it is the best model to describe the Fenton and Fenton-like oxidation processes in different reaction conditions [59,63,64]. Table 2 shows the values of \(1/m\), and the constants that indicate the reaction rate from the BMG model are higher than the rate constants for both first-order \((K_1)\) and second-order \((K_2)\) kinetics. So, the BMG model gives a better correlation related to a
faster reaction rate as compared with first and second-order kinetics ($R^2 > 0.990$ vs. $R^2 < 0.860$ for the two reactions).

In the Fenton and Fenton-like processes, high amounts of HO• radicals oxidized organic matter. As a result, the COD significantly decreased in the first 60 min of the reaction. Furthermore, the fitting of experimental data to the first-order and second-order kinetic models were not good enough since the values of $R^2$, which showed the correlation coefficient for both models, were slightly low. Meanwhile, the experimental data of COD degradation fitted well to the BMG kinetic model since the $R^2 = 0.995$ and 0.997 for Fenton and Fenton-like processes, respectively. Accordingly to these results, it could be concluded that the COD degradation of FCW by Fenton and Fenton-like processes were best explained by the BMG kinetic model.

### 3.3. Combination of CFD-oxidation processes

#### 3.3.1. Determination of best conditions in the CFD, Fenton, and Fenton-like processes

In the previous chapter, it was observed that the performance of CFD by the application of $\text{Al}_2(\text{SO}_4)_3$ had the highest COD removal in comparison with $\text{FeCl}_3$ and PAC under the operational conditions: pH = 7.2, $[\text{Al}_2(\text{SO}_4)_3] = 400$ mg/L, rapid speed: 120 rpm/1 min, slow speed: 30 rpm/20 min, sedimentation time: 10 min, and temperature: 298 K. The treatment of FCW by Fenton and Fenton-like processes were observed to be very effective. A high COD removal rate was observed under the operational conditions: pH 3.0, $[\text{Fe}^{2+}] = [\text{Fe}^{3+}] = 400$ mg/L, $[\text{H}_2\text{O}_2] = 400$ mg/L,

<table>
<thead>
<tr>
<th>Kinetic model</th>
<th>Fenton process</th>
<th>Fenton-like process</th>
</tr>
</thead>
<tbody>
<tr>
<td>First-order-kinetic</td>
<td></td>
<td></td>
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<tr>
<td>$K_1$ (min$^{-1}$)</td>
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<td>0.0054</td>
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<tr>
<td>$R^2$</td>
<td>0.8332</td>
<td>0.8177</td>
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<tr>
<td>Second-order-kinetic</td>
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<tr>
<td>$K_2$ (L/mg min)</td>
<td>$7 \times 10^{-6}$</td>
<td>$4 \times 10^{-6}$</td>
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<tr>
<td>$R^2$</td>
<td>0.8689</td>
<td>0.8476</td>
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<tr>
<td>BMG kinetic model</td>
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<tr>
<td>$1/m$ (min$^{-1}$)</td>
<td>0.089</td>
<td>0.059</td>
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<tr>
<td>$1/b$</td>
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</tr>
<tr>
<td>$R^2$</td>
<td>0.9949</td>
<td>0.9986</td>
</tr>
</tbody>
</table>

![Fig. 5. Kinetic models for COD degradation for Fenton and Fenton-like processes: (a) first-order, (b) second-order equations, and (c) BMG kinetic model.](image)
agitation: 150 rpm, temperature: 298 K, and reaction time: 60 min. In this chapter combined CFD-Fenton and CFD-Fenton-like processes were performed in order to achieve a higher COD removal. The results are shown in Fig. 6.

In Fig. 6, the COD removals obtained by a combination of CFD process/Fenton and CFD process/Fenton-like were 93% and 84%, respectively. Based on a separate study of CFD process, the COD of FCW decreased about 58% were 93% and 84%, respectively. Based on a separate study, the COD removals obtained by a combination of CFD process/Fenton and CFD process/Fenton-like were 93% and 84%, respectively. According to some other published works, Fenton-like could be as reactive as the Fenton process. However, in this study, it is concluded that in the operational conditions of CFD process with AOPs, the Fenton process is more reactive than the Fenton-like process. Also, it can be concluded from a comparison of the two processes (Fenton and Fenton-like) that combined CFD-Fenton treatment is more effective in COD reduction.

4. Conclusion

The aim of this study was to examine the treatment of fish canning wastewater. Attempt was made to optimize CFD, Fenton, and Fenton-like processes. The combined CFD-Fenton and CFD-Fenton-like treatment were also examined in order to achieve higher COD removals. According to the results, it is concluded that: (1) the application of Al(SO₄)₃ in CFD process achieves higher COD removal (58%) compared with the application of FeCl₃ (44%) and PAC (40%), (2) the performance of Fenton oxidation process achieves higher COD removal (68%) compared with Fenton-like process (60%), (3) the BMG kinetic model provides the best correlation for the experimental data obtained through the Fenton and Fenton-like processes, and (4) the combined CFD-Fenton process achieves higher COD removal (93%) in comparison with the combined CFD-Fenton-like process (84%).

References


