



## Removal of cyanide from synthetic wastewater by combined coagulation and advanced oxidation process

Mohammad Reza Heidari<sup>a</sup>, Mohammad Malakootian<sup>b,c,\*</sup>

<sup>a</sup>*Environmental Health Engineering, Department of Environmental Health, School of Public Health, Bam University of Medical Sciences, Bam, Iran, email: moheidari86@gmail.com*

<sup>b</sup>*Environmental Health Engineering Research Center, Kerman University of Medical Sciences, Kerman, Iran, Tel. +98 343 132 5128; Fax: +98 343 132 5105; email: m.malakootian@yahoo.com*

<sup>c</sup>*Department of Environmental Health, School of Public Health, Kerman University of Medical Sciences, Kerman, Iran*

Received 16 October 2017; Accepted 18 August 2018

### ABSTRACT

Cyanide is a toxic contaminant which exists in some industrial wastewaters. This substance is considered a serious threat, causing adverse effects on the environment and human health. The current study investigated the efficiency of the combined coagulation/advanced oxidation process (C/AOP) in the removal of cyanide from wastewater. The effect of this process was examined through the investigation of changes in pH, contact time, initial cyanide concentration, poly-aluminum-silicate-chloride (PASIC) dose, current intensity, and  $H_2O_2$  concentration, and the optimal conditions were obtained. Data analysis was performed with SPSS 17. Through usage of the combination of PASIC as coagulant and the sono electro fenton process, 94% of cyanide was removed. The maximum removal percentage of cyanide in the coagulation process with PASIC was observed at the dose of  $1.2 \text{ mg L}^{-1}$ , retention time of 60 min, and  $\text{pH} = 6.5$ . In the combined C/AOP, the maximum removal percentage was obtained at the concentration of  $H_2O_2 = 2,500 \text{ mg L}^{-1}$ , contact time of 60 min,  $\text{pH} = 3.5$ , and current intensity of  $10 \text{ mA cm}^{-2}$ . Cyanide removal by the combined process of coagulation and advanced oxidation can be considered efficient in the treatment of water and wastewater.

*Keywords:* Advanced oxidation process; Coagulation; Cyanide; Synthetic wastewater

### 1. Introduction

Cyanide is a toxic chemical which exists in some industrial wastewaters [1]. It enters water through different industrial processes, including plating, electroplating, metal processing, vehicle pieces, steel, photography, pharmacy, coal, plastic, the production of some chemicals such as pesticides, the extraction of gold and silver, many mining processes such as leaching, and different industrial wastewaters [2]. It then is ingested into the human body through drinking, respiration, and food [2]. Among the adverse effects of cyanide on humans are shortness of breath, tremors, nerve effects and damage, weight loss, and death [3].

German and Swiss regulations have a set limit of  $0.5 \text{ mg L}^{-1}$  of cyanide in sewage; the disposal limit for cyanide in Mexico has been set at  $0.2 \text{ mg L}^{-1}$ ; and the Central Pollution Control Board (CPCB) in India has set the minimal national standard (MINAS) limit for cyanide in effluent at  $0.2 \text{ mg L}^{-1}$  [2].

The coagulation and flocculation process is performed in the treatment of water and wastewater to remove colloidal particles [5,6]. Typical iron and aluminum salts as well as a new group of inorganic polymer flocculants (IPFs) are used for this purpose [7]. The superiority of IPFs in comparison with typical metal salts is related to their very high efficiency and lower cost. With the successful commercial production of IPFs, using a bonding agent to simplify the composition of subflocculants in water treatment operations has become a logical approach. Accordingly, the decomposition of subflocculants of major metal salts is a new approach along with the development of

\* Corresponding author.

this type of agent. Polyaluminum chloride (PACL) coagulant is an inorganic polymer coagulant used for different treatment conditions [8]. A wide pH range, lower sensitivity to heat, less residual in comparison with other metal flocculants, less produced sludge, and facilitated sludge drainage are among the advantages of PACL, causing its widespread application in water treatment [6–8]. Polyaluminum chloride has high power and speed in separating and extracting water impurities [9]. Its weight and molecular weight is less than those of typical metal salts. It also has less accumulability, and its stability against hydrolysis is also lower [10]. To improve the effect of flocculation, PACL and active silica are combined by polymerizing trivalent aluminum under special conditions, producing a new coagulant compound called *poly*-aluminum-silicate-chloride (PASIC). PASIC is a new generation of inorganic coagulants [5,10,11]. Niu et al. [7] investigated the performance of PASIC in the treatment of water. Gao et al. [12] compared the performances of PASIC and PACL in the removal of sludge, turbidity, oil, chemical oxygen demand, and total phosphate (TP) under experimental conditions. Tzoupanos et al. [10] examined the properties and behavior of PASIC. Mahvi et al. [13] researched the removal of natural organic compounds by PASIC.

Advanced oxidation processes (AOPs), including photocatalyst oxidation, ozonation, ultrasonic (US), Fenton oxidation, and photo-Fenton oxidation, have been used in treating hazardous materials in wastewater since 1990. In recent years, these processes have been used to treat wastewaters containing nonbiodegradable or toxic substances [14]. Meanwhile, Fenton agent ( $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ ) is considered one of the most effective processes for the removal of organic compounds from aqueous solutions because of its numerous advantages (simple usage, short reaction time, reaction at environmental and typical temperatures and pressure, high oxidation power, the inexpensiveness of its compounds (iron and hydrogen peroxide), low energy consumption due to the catalytic properties of iron, simple control and operation, and being economical) [15,16]. Fenton-type reactions have been identified as effective methods which produce hydroxyl radicals through the reaction between iron ions and hydrogen peroxide, which is employed at acidic pH. The basis of the Fenton process is the degradation of OH in acidic environments by bivalent iron ions (as catalyst) and the production of hydroxyl radicals [17]. One of the Fenton methods is the use of electrochemical processes called the electro-Fenton process [18]. The advantages of this method are the in situ production of hydrogen peroxide, no need to add iron, and the production of less sludge. Tian [18] studied the combined process of fiber carbon and advanced oxidation through Fenton for the removal of cyanide. Another research was conducted on the efficiency of the combined process of electro-Fenton on and absorption in the removal of acetamiprid [19]. Malakootian and Moridi [20] and Sohrabi et al. [21] investigated the efficiency of the Fenton oxidation process in dye removal. In recent years, US irradiation has received much attention, especially for the degradation of resistant pollutants. The application of US waves with the electro-Fenton process increases the degradation rate of contaminants through the physical US degradation and chemical degradation of electro-Fenton called sono electro fenton (SEF) (1) [22]. SEF causes an elevated mass

transfer rate between two electrodes, the clearance of the surface of electrodes, enhanced removal efficiency, and less energy consumption [23]. The combination of ultrasound irradiation with an enhanced Fenton-type system not only increases the rate and number of generated reactive radicals, but also reduces mass transfer resistance [22]. Successful results have been reported in the literature concerning the combination of ultrasound and Fenton-like systems in the removal of various compounds, such as phenol [22,23], bisphenol [24], sodium alginate [25], phenazopyridine [26], dyes [27–29], ibuprofen [30], and diazinon [31].

The study investigated the efficiency of the combined process of flocculation by PASIC and SEF advanced oxidation on the removal of cyanide from aqueous solutions so as to determine the effects of different parameters (pH, optimal PASIC concentration, optimal  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  concentrations, current intensity, contact time, and initial concentration of cyanide).

## 2. Material and methods

### 2.1. Material

The titrimetric method by spectrophotometer (Shimadzu, Japan) UV/VIS with quartz cell 1 and a length of 575 nm was used to measure the residual cyanide concentration. The pH test was performed using a pH meter (Eutech, USA). The cyanide concentration (4500-CN-E) was measured calorimetrically according to standard methods [32]. Across all of the experiments,  $\text{HNO}_3$  0.1 M and NaOH 0.1 M were used to measure the effect of pH on the removal efficiency of cyanide [18]. All of the employed chemicals were purchased from Merck, Germany.

### 2.2. Preparation of PASIC coagulant

First, 10.75 mL of water glass concentrated solution was slowly poured into HCl solution under stirring conditions in order to achieve a solution called poly silicate (PSI) with  $\text{SiO}_2$  1.5 M and pH = 2–2.5. In the next stage,  $\text{AlCl}_3$  solution was added to the fresh PSI solution, and then concentrated  $\text{Na}_2\text{CO}_3$  solution was gradually added under stirring conditions to obtain the OH/Al = 2 ratio. The above-described solution had a density of 1.5,  $p = 1.5$ –3.5, Al/Si = 10, and OH/Al = 2 [13].

### 2.3. Sono-electro-Fenton process (1)

The utilized reactor was made of Plexiglas. The cathode and anode used in this study were made of iron and had equal dimensions (5 cm × 5 cm × 0.5 cm). Dissolved iron ions in the aqueous solution were measured using 1,10-phenanthroline as a complexing agent [33]. To develop frequency, the US device (DUMAN-120) was used. Across all stages of the SEF process, the samples were stirred with a magnetic stirrer at 1,000 rpm and a constant frequency of 40 kHz [22]. Hydrogen peroxide was added and the power supply was turned on to initiate the reaction.

### 2.4. Analytical methods

First, the stock solution of 1,000 mg  $\text{L}^{-1}$  of cyanide potassium salt was prepared and covered with aluminum foil [4]. PASIC (0–2.1 g  $\text{L}^{-1}$ ) was added to the synthetic solution at

pH = 2–10, PASIC concentrations of 10–200 mg L<sup>-1</sup>, and cyanide initial concentrations of 5–20 mg L<sup>-1</sup> in a jar set device. The mixture was stirred at 380 rpm, followed by slow mixing at 30 rpm for 1 min, and sedimentation was performed for 20 min [13]. Thereafter, the wastewater resulting from the previous stage was fed into a 1-L reactor. The SEF process was carried out under the conditions of pH = 2–10, H<sub>2</sub>O<sub>2</sub> and Fe<sup>2+</sup> concentrations 0–3,000 and 0.5–20 mg L<sup>-1</sup>, respectively, contact times of 10–100 min, constant current densities of 5–20 mA cm<sup>-2</sup>, and initial cyanide concentrations of 50–200 mg L<sup>-1</sup> [29]. The efficiency of the combined process of coagulation and advanced oxidation in removing cyanide ions was considered significant using SPSS 17 with  $p \leq 0.05$ . The relevant diagrams were plotted using Excel software.

The removal efficiency was calculated as follows:

$$R = \frac{[\text{input}] - [\text{output}]}{[\text{input}]} \times 100 \quad (1)$$

### 3. Results and discussion

#### 3.1. Application of poly-aluminum-silicate-chloride coagulant

##### 3.1.1. Effect of PASIC dose

The dose of the consumed coagulant causes the formation of weak floc due to either under-concentration or over-concentration, and thus the level of the coagulant consumed in the removal process has an important effect [12]. The determined optimal values of the PASIC coagulant for cyanide removal are shown in Fig. 1.

With elevated levels of PASIC, the cyanide removal level also increased; 37% of cyanide was removed at the PASIC concentration of 1.2 mg L<sup>-1</sup>. However, increasing the coagulant above 2.5 mg L<sup>-1</sup> caused cyanide removal to decrease. Elevation of the coagulant had no considerable change. The best removal percentage was observed at the initial concentration of 1.2 mg L<sup>-1</sup>. With elevations in the initial cyanide

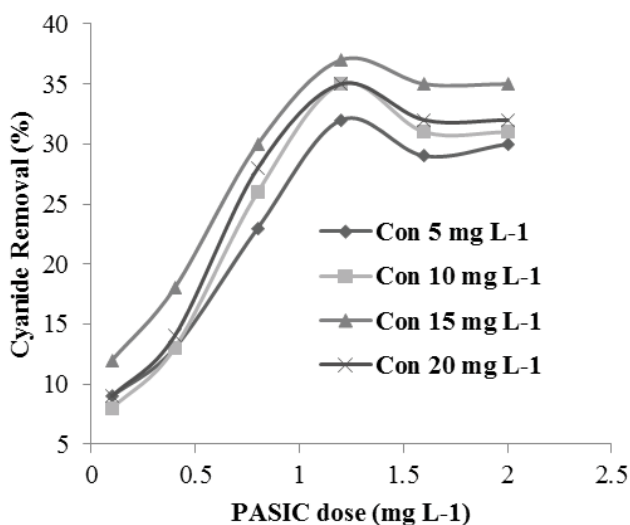


Fig. 1. The optimal dose of PASIC in removal of cyanide (pH = 6.5, initial cyanide concentration 5–20 mg L<sup>-1</sup>).

concentration, removal efficiency decreased because of the low solubility of aluminum (trivalent) in elevated cyanide concentrations, and, thus, its lower miscibility [7]. The appropriate amount of sludge production can reduce the sludge disposal problem, because the lower optimal PASIC dose caused less sludge to be produced compared with other coagulants [13]. There is a significant difference in the mean concentration in the extent of cyanide removal from wastewater before and after the process ( $p \leq 0.05$ ).

##### 3.1.2. Effect of pH on coagulation performance

The solution pH is one of the most important parameters affecting the coagulation process and removal of contaminant from aqueous solutions; the coagulant is able to remove the pollutant only within a desired pH range [5]. According to pK<sub>a</sub> amount of HCN (9.31), the predominant form of CN ion is HCN in pH < 9.31. Therefore, in acidic conditions, the solvation of CN is reduced and unstable ion cyanide, due to its hydrolysis to volatile HCN, is formed. Thereafter, the gas is released from the solution through stirring. Finally, its concentration in the aqueous environment is slightly diminished [25].

Fig. 2 presents the results associated with the effect of pH on coagulation efficiency for the coagulant.

The removal efficiency increased in pH values under 6.5 and then decreased with elevations of pH above 6.5. The maximum removal efficiency for cyanide (37.2%) was related to pH = 6 at an initial cyanide concentration of 15 mg L<sup>-1</sup>. A significant difference in the mean concentration of cyanide removed from wastewater before and after the process was observed ( $p \leq 0.05$ ). Cyanide removal by PASIC reached 37% at pH = 6.5. After being hydrolyzed in water, PASIC generated more positive charge in comparison with other coagulants due to the silicate. For the formation of Al(OH)<sub>3</sub>, Al<sup>3+</sup> cation should be liberated, the rate of which increases because of the presence of silicate at pH = 6.5. At lower pH, due to presence of H<sup>+</sup> ions, the neutralization of negatively

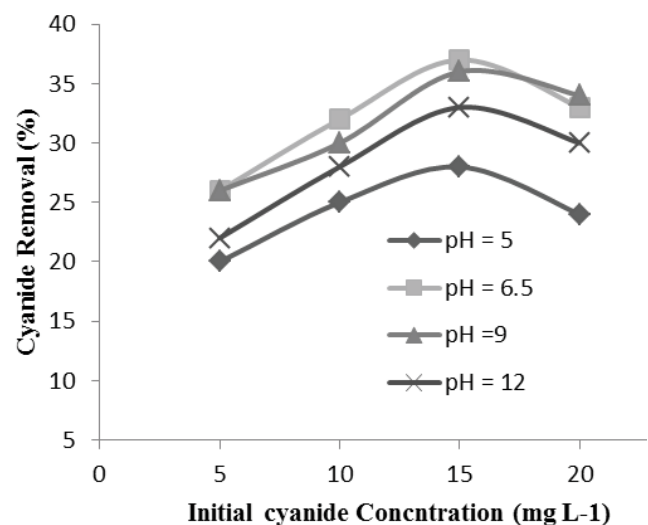


Fig. 2. The optimal pH in removal of cyanide by PASIC coagulant (initial concentration of cyanide 5–20 mg L<sup>-1</sup>, PASIC = 1.2 mg L<sup>-1</sup>).

charged materials stops [10]. Therefore, it is expected that silicate is influential in neutralizing the negative charge of cyanide in water. Furthermore, with the optimal pH, less coagulant materials are consumed and, in turn, less sludge is produced, which is economical [13]. These results are in agreement with those of Golbaz et al. [4] regarding the removal of cyanide by coagulation/sedimentation, those of a research by Yang et al. [34] on the removal of humic acid, and those of Mahvi et al. [13] who studied the effect of pH on the increased performance of coagulation by PASIC.

### 3.1.3. Effects of time on efficiency removal

The time required for the coagulation process affects the performance of other factors. Fig. 3 presents the optimal contact time for the removal of cyanide by PASIC.

Increases in retention time up to 40 min significantly increased removal efficiency. From 40 to 60 min, cyanide removal efficiency increased 10%. The maximum removal efficiency of cyanide was 37% within 60 min and at pH = 6.5. The results of the statistical test indicated that the mean concentrations of cyanide removed from the synthetic sample before and after the coagulation process were significantly different ( $p \leq 0.05$ ). Increasing the contact time of PASIC up to 60 min increased cyanide removal efficiency; mixing during reaction is very important for very fast reactions, especially in hydrogen systems such as cyanide reaction. A suitable contact time can enhance the reaction rate and develop suitable conditions for mixing positive aluminum and negative cyanide. Therefore, as shown by the results, the transfer of cyanide ions from the solution to the aluminum surface is a limiting step, prolonging the suitable contact time for the reaction rate. Also, increasing the initial cyanide concentration to more than the desired level decreases the reaction rate [6]. These results are in line with the studies by Gao et al. [12] regarding wastewater treatment by PASIC and Mahvi et al. [13] on the removal of organic compounds by PASIC.

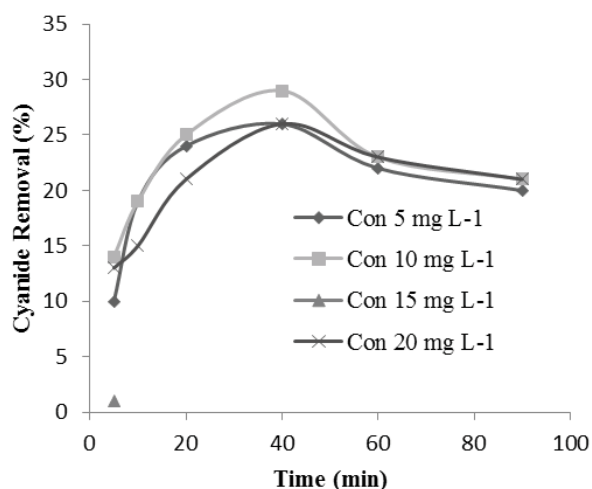


Fig. 3. The optimal contact time in removal of cyanide by PASIC (cyanide initial concentration 5–20 mg L<sup>-1</sup>, pH = 6.5, PASIC = 1.2 mg L<sup>-1</sup>).

## 3.2. Coagulation and advanced oxidation (C/AOP) process

### 3.2.1. Effect of pH

The pH of the solution has a determinant effect on the performance of the homogeneous Fenton process. The pH value also affects the production of hydroxyl radicals [35]; however, when the solution pH was higher than 10, the generated H<sub>2</sub>O<sub>2</sub> decomposed to HO<sub>2</sub><sup>-</sup> [36]. HO<sub>2</sub><sup>-</sup> anions had good stability, but their oxidation potential was lower than that of H<sub>2</sub>O<sub>2</sub>. Therefore, generating H<sub>2</sub>O<sub>2</sub> is limited in cyanide oxidation [30].

The results obtained regarding the effect of pH on the efficiency of the C/AOP process are shown in Fig. 4.

The amounts of cyanide removed at acidic and neutral pHs are larger than those at alkaline pHs. The maximum removal of 94% was obtained at pH = 3.5, but with the elevation of pH, removal efficiency decreased linearly. The SEF reaction follows first-order kinetics; thus, with greater amounts of chemical, the effectiveness of the process is enhanced. At pH = 3.5, the efficiency of C/AOP in cyanide removal was 94%. According to Eqs. (2) and (3), H<sub>2</sub>O<sub>2</sub> is degraded rapidly and eliminated from the environment at alkaline pHs [37].



Moreover, hydrogen peroxide changes into a stable form at high concentrations of hydrogen ions, forming electrophilic peroxide ions, and thereby decreasing the reaction with iron [30]. As observed, pH had a significant role in cyanide removal, and a sharp decline in removal efficiency was seen when pH was increased [23].

### 3.2.2. Effect of current density

Previous studies have shown that electric current is an important factor in the C/AOP process, as it affects efficiency,

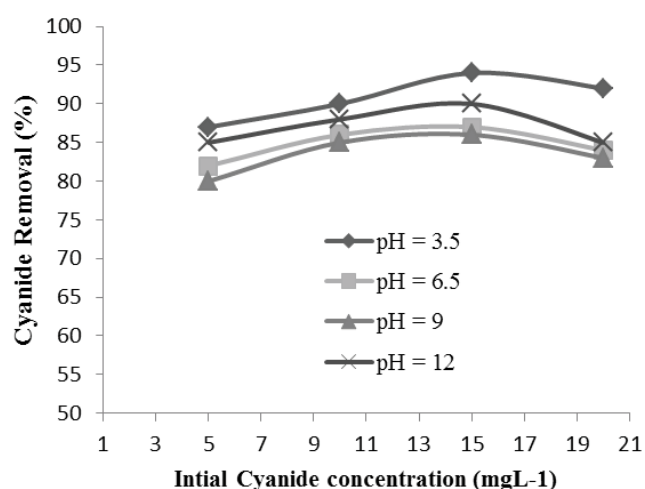


Fig. 4. The optimal pH for removal of cyanide by C/AOP process (current intensity = 10 mA cm<sup>-2</sup>, H<sub>2</sub>O<sub>2</sub> = 2,200 mg L<sup>-1</sup>, contact time = 60 min).

controls the dissolution of iron ions, and influences financial costs [30]. Fig. 5 presents the results of changes in current intensity on cyanide removal across different initial concentrations of cyanide.

Increasing the current intensity to under  $10 \text{ mA cm}^{-2}$ , cyanide removal efficiency increased 94.3%. However, with further increases in current intensity, removal efficiency declined with a low slope. The maximum removal level occurred at an initial concentration of  $1.2 \text{ mg L}^{-1}$ . Electric current intensity up to  $20 \text{ mA cm}^{-2}$  has a direct relationship with removal efficiency; with increased current intensity, the reaction between iron ions and hydrogen peroxide increased, eventually causing the formation of hydroxyl radicals [11]. Removal efficiency declined with elevations in electric intensity because of the interfering reactions which developed, including the degradation of hydroxyl radicals, according to Eq. (4) [5].



The efficiency of the SEF process increased with  $\text{Fe}^{2+}$  concentration, because the concentration of hydroxyl radicals, the main oxidizing agent in the Fenton process, increased with increases in  $\text{Fe}^{2+}$  concentration [24]. The appropriate ferrous ion concentration is an important factor in the electro-Fenton process. It is also important to estimate the value of electrically dissolved iron [23].

For the Fenton process, the dissolution of iron anode and cathode was calculated according to Eq. 5 (Faradays law) as follows:

$$W = \frac{I \times t \times M_w}{Z \times F} \quad (5)$$

where  $W(\text{g})$  is the dissolved iron concentration,  $I(\text{A})$  is current intensity,  $M_w$  is molecular weight of Fe ( $M = 55.85 \text{ g mol}^{-1}$ ),  $Z$  is number of electrons involved in the redox reactions ( $Z = 2$ ), and  $F$  is Faraday's constant ( $96,500 \text{ C mol}^{-1}$ ) [38].

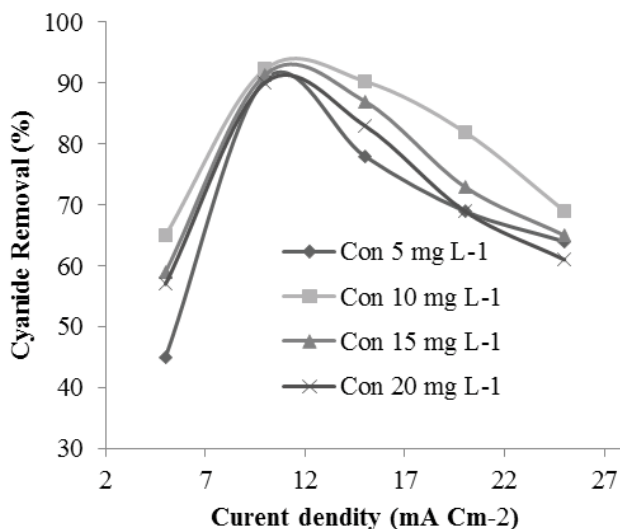


Fig. 5. The optimal current intensity for removal of cyanide by C/AOP process ( $\text{pH} = 3.5$ ,  $\text{H}_2\text{O}_2 = 2,200 \text{ mg L}^{-1}$ , contact time = 60 min).

### 3.2.3. Effect of $\text{H}_2\text{O}_2$ and $\text{Fe}^{2+}$ concentration

Hydrogen peroxide and iron ions have important roles in oxidation; they are the main source of hydroxyl radicals, yet their overuse not only diminishes removal efficiency, but also increases costs [39]. Figs. 6 and 7 show the effects of  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  concentrations on cyanide removal efficiency at  $\text{pH} = 3.5$ , current intensity =  $10 \text{ mA cm}^{-2}$ , initial cyanide concentration of  $5\text{--}20 \text{ mg L}^{-1}$ , and reaction time of 60 min.

As seen in Fig. 6, an increase in  $\text{H}_2\text{O}_2$  level significantly increases cyanide removal efficiency. Increasing  $\text{H}_2\text{O}_2$  from  $1,000$  to  $2,200 \text{ mg L}^{-1}$  resulted in cyanide removal efficiency increasing from 70% to 94%, suggesting the impressive effect of the level of  $\text{H}_2\text{O}_2$  present in the solution. The optimal level of hydrogen peroxide in the C/AOP process is  $2,500 \text{ mg L}^{-1}$ . Increasing the hydrogen peroxide concentration caused an increase in hydroxyl radicals, thereby enhancing removal efficiency [39]. With hydrogen peroxide levels higher than the optimal level, destructive radicals were produced, and

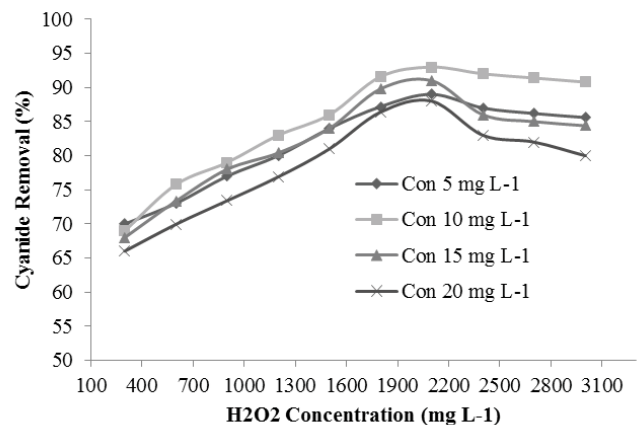


Fig. 6. Optimal  $\text{H}_2\text{O}_2$  for cyanide removal by C/AOP process ( $\text{pH} = 3.5$ , current intensity =  $10 \text{ mA cm}^{-2}$ , contact time = 60 min).

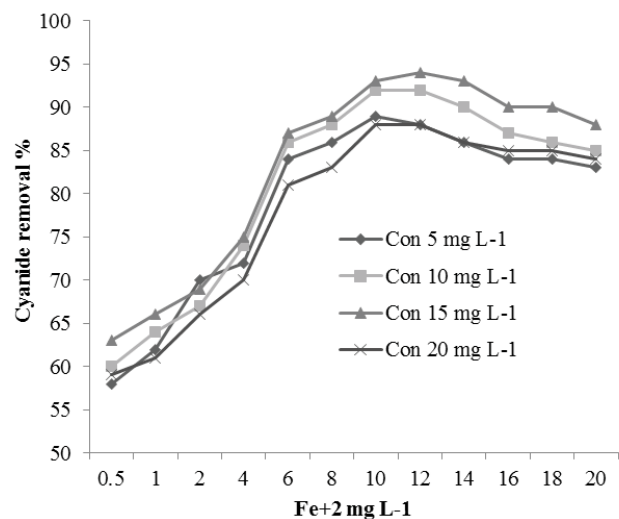
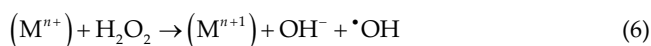


Fig. 7. Optimal  $\text{Fe}^{2+}$  for cyanide removal by C/AOP process ( $\text{pH} = 3.5$ , current intensity =  $10 \text{ mA cm}^{-2}$ ,  $\text{H}_2\text{O}_2 = 2,200 \text{ mg L}^{-1}$ , contact time = 60 min).



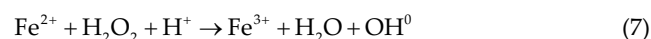
removal efficiency was decreased. The extra hydrogen peroxide consumed the hydroxyl radicals in the solution, which decreased the reaction rate [40]. Eq. (6) shows the reaction of hydrogen peroxide and the relevant ion.



The results of this study are in line with those of Malakootian and Moridi [20] and Sohrabi et al. [21] on dye removal by electro-Fenton and Fenton processes. Without iron, hydrogen peroxide cannot form hydroxyl radicals [41]. Excessive growth is ineffective on removal efficiency. In addition, further increases in iron content, exceeding the optimal level, causes the formation of complex iron sludge. Moreover, this overgrowth causes turbidity in water [17].

As expected, increases in cyanide removal were observed with an increase in  $Fe^{2+}$  concentration. This is due to the enhanced production of hydroxyl radicals by ultrasound, and such radicals are responsible for the oxidation of cyanide. In the SEF process, after 60 min of reaction time, cyanide removal rates were 63.1%, 77.98%, and 94%, for 0.5, 6, and 12 mg L<sup>-1</sup>  $Fe^{2+}$ , respectively. Further increases in  $Fe^{2+}$  concentration had a nonsignificant effect on cyanide removal and the removal observed for the  $Fe^{2+}$  dosage of 12 and 20 mg L<sup>-1</sup>.

Eq. (7) represents the reaction of iron with hydrogen peroxide:



These results are in line with the results obtained by Wang [43] on the removal of polyvinyl chloride by Fenton. Trivalent iron precipitates as  $Fe(OH)_3$  and large amount of Fe is also separated from the solution. Therefore, with the elevation of pH, the efficiency of the C/AOP process diminishes. At acidic pH, the aggressive effect of  $H^+$  on  $OH^0$  is far greater than  $OH^-$  on  $OH^0$  [43]. The catalytic behavior of iron is highly influenced by pH, according to Eq. (8). At acidic pHs,  $CO_2$  also leaves the water environment as a gas, while in an alkaline environment, the formation of agents such as carbonates causes the degradation of hydroxyl radicals [44]. These results are in accordance with the study by Rott et al. [45] on the removal of phosphate by Fenton and those of the study by Xu et al. [46] on the mechanism of the Fenton process.



The regeneration of  $Fe^{2+}$  from the intermediate complex ( $Fe-O_2H^2$ ) formed due to the reaction of  $Fe^{2+}$  with  $H_2O_2$  can be accelerated by US irradiation [22] as given in Eq. (9).



At this stage of the test, a large amount of hydroxyl radicals is formed [22] as given in Eqs. (10) and (11).

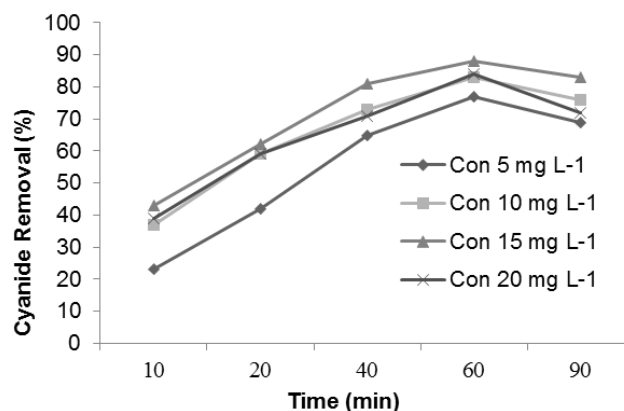


Fig. 8. The optimal contact time for cyanide removal by the C/AOP process (pH = 3.5, current intensity = 10 mA cm<sup>-2</sup>,  $H_2O_2 = 2,200$  mg L<sup>-1</sup>).

#### 3.2.4. Effect of oxidation time

Oxidation time is another parameter affecting the process efficiency. To determine the best time and its impact on the Fenton process, experiments were performed at 10–100 min. Fig. 8 demonstrates the extent of cyanide removal under the optimal conditions of pH = 3.5 and initial cyanide concentration = 5–20 mg L<sup>-1</sup> over time (in terms of minutes).

Over time, the extent of cyanide removal increases, such that at an oxidation time of 60 min, maximum removal was obtained, and in the course of the C/AOP reaction, the extent of removal remained constant. Increasing contact time up to 60 min increased removal efficiency due to the production of more active hydroxyl radicals and the sufficient opportunity for reaction with cyanide. At the optimal contact time, pH environment was alkaline because  $CO_2$  is removed so carbonate and bicarbonate are produced in the solution, reducing the effect of the hydroxyl radicals. Furthermore, with elevations in the initial cyanide concentration, due to consumption of hydroxyl radicals, removal efficiency decreased [47]. These results are in accordance with a study by Malakootian and Moridi [20] on dye removal by electro-Fenton.

## 4. Conclusions

The study investigated the efficiency of the combined process of flocculation by PASIC and SEF advanced oxidation on the removal of cyanide from aqueous solutions so as to determine the effects of different parameters (pH, optimal PASIC concentration, optimal  $H_2O_2$  and  $Fe^{2+}$  concentrations, current intensity, contact time, and initial concentration of cyanide). Based on the current results it can be concluded that, when using the combined process of PASIC with SEF for the removal of cyanide, the elevation in cyanide removal efficiency using PASIC coagulant is directly related with elevations in the amount of coagulant up to 1.2 mg L<sup>-1</sup>, elevations in pH by up to pH = 6.5, and low cyanide concentrations. Furthermore, considering the elevation in pH, the difference in electric intensity, and the initial cyanide concentration, the Fenton process has a direct effect on cyanide removal efficiency. Investigation of the effect of these two processes under optimal conditions resulting from the

current research showed that cyanide removal using C/AOP is 94%. The application of this process is more economical than similar methods, and it is simpler in terms of operation due to the synergistic effects of coagulation and advanced oxidation on each other and the elevated efficiency.

### Acknowledgments

This study was carried out in the Environmental Health Engineering Research Center of Kerman University of Medical Sciences and was sponsored by the Vice-Chancellor for Research and Technology of Kerman University of Medical Sciences. The authors take this opportunity to express their gratitude for the support and assistance extended by the facilitators during the conduct of the research.

### References

- [1] H. Uppal, S.S. Tripathy, S. Chawla, B. Sharma, M. Dalai, S. Singh, Study of cyanide removal from contaminated water using zinc peroxide nanomaterial, *Environ. Sci.*, 55 (2017) 76–85.
- [2] R. Dasha, A. Gaur, C. Balomajumder, Cyanide in industrial wastewaters and its removal: a review on biotreatment, *J. Hazard. Mater.*, 163 (2009) 1–11.
- [3] G. Asgari, A.M. Seid Mohammadi, A. Ahmadian, Removal of cyanide from aqueous solution by adsorption onto bone charcoal, *Fresenius Environ. Bull.*, 23 (2014) 720–727.
- [4] S. Golbaz, A.J. Jafari, M. Rafiee, R.R. Kalantary, Separate and simultaneous removal of phenol, chromium, and cyanide from aqueous solution by coagulation/precipitation: mechanisms and theory, *Chem. Eng. J.*, 253 (2014) 251–257.
- [5] Z. Yang, B. Liu, B. Gao, Y. Wang, Q. Yue, Effect of Al species in polyaluminum silicate chloride (PASiC) on its coagulation performance in humic acid-kaolin synthetic water, *Sep. Purif. Technol.*, 111 (2013) 119–124.
- [6] Y. Zhao, W. Liang, L. Liu, F. Li, Q. Fan, X. Sun, Harvesting *Chlorella vulgaris* by magnetic flocculation using Fe<sub>3</sub>O<sub>4</sub> coating with polyaluminum chloride and polyacrylamide, *Bioresour. Technol.*, 198 (2015) 789–796.
- [7] X. Niu, X. Li, J. Zhao, Y. Ren, Y. Yang, Preparation and coagulation efficiency of polyaluminum ferric silicate chloride composite coagulant from wastewater of high-purity graphite production, *J. Environ. Sci.*, 23 (2011) 1122–1128.
- [8] A. Matilainen, M. Vepsäläinen, M. Sillanpää, Natural organic matter removal by coagulation during drinking water treatment: a review, *Adv. Colloid Interface Sci.*, 159 (2010) 189–197.
- [9] Y. Zhao, S. Phuntsho, B. Gao, Y. Yang, J. Kim, H. Shon, Comparison of a novel polytitanium chloride coagulant with polyaluminum chloride: coagulation performance and floc characteristics, *J. Environ. Manage.*, 147 (2015) 194–202.
- [10] N. Tzoupanos, A. Zouboulis, C. Tzoleridis, A systematic study for the characterization of a novel coagulant (polyaluminum silicate chloride), *Colloids Surf., A*, 342 (2009) 30–39.
- [11] B. Yang, J. Zuo, X. Tang, F. Liu, X. Yu, X. Tang, Effective ultrasound electrochemical degradation of methylene blue wastewater using a nanocoated electrode, *Ultrason. Sonochem.*, 21 (2014) 1310–1317.
- [12] B. Gao, Q. Yue, Y. Wang, Coagulation performance of polyaluminum silicate chloride (PASiC) for water and wastewater treatment, *Sep. Purif. Technol.*, 56 (2007) 225–230.
- [13] A. Mahvi, M. Malakootian, M. Heidari, Comparison of polyaluminum silicate chloride and electrocoagulation process, in natural organic matter removal from surface water in Ghochan, Iran, *J. Water Chem. Technol.*, 33 (2011) 377–385.
- [14] S. Yuan, N. Gou, A. Alshawabkeh, A. Gu, Efficient degradation of contaminants of emerging concerns by a new electro-Fenton process with Ti/MMO cathode, *Chemosphere*, 93 (2013) 2796–2804.
- [15] G.E. Esra, Y. Seval, K.A. Savaş, G.Ö. Nezihi, Combined energy and removal efficiency of electrochemical wastewater treatment for leather industry, *J. Water Process Eng.*, 82 (2017) 1422–1430.
- [16] M. Ahmadian, S. Reshadat, N. Yousefi, S.H. Mirhossieni, M.R. Zare, S.R. Ghasemi, N.R. Gilan, R. Khamutian, A. Fatehizadeh, Municipal leachate treatment by Fenton process: effect of some variable and kinetics, *J. Environ. Public Health*, (2013), 1–6.
- [17] S.P. Moussavi, M.H. Ehrampoush, A.H. Mahvi, S. Rahimi, M. Ahmadian, Efficiency of multi-walled carbon nanotubes in adsorbing humic acid from aqueous solutions, *Asian J. Chem.*, 26 (2014) 821–826.
- [18] S. Tian, Y. Li, X. Zhao, Cyanide removal with a copper/active carbon fiber Cathode via a combined oxidation of a Fenton-like reaction and in situ generated copper oxides at anode, *Electrochim. Acta.* 180 (2015) 746–755
- [19] J. Mejjide, S. Rodríguez, M. Sanromán, M. Pazos, Comprehensive solution for acetamidiprid degradation: combined electro-Fenton and adsorption process, *J. Electroanal. Chem.*, 808 (2018) 446–454.
- [20] M. Malakootian, A. Moridi, Efficiency of electro-Fenton process in removing Acid Red 18 dye from aqueous solutions, *Process Saf. Environ.*, 111 (2017) 138–147.
- [21] M. Sohrabi, A. Khavaran, S. Shariati, S. Shariati, Removal of Carmoisine edible dye by Fenton and photo Fenton processes using Taguchi orthogonal array design, *Arabian J. Chem.*, 10 (2017) 3523–3531.
- [22] A. Babuponnusami, K. Muthukumar, Advanced oxidation of phenol: a comparison between Fenton, electro-Fenton, sono-electro-Fenton and photo-electro-Fenton processes, *Chem. Eng. J.*, 183 (2012) 1–9.
- [23] Y. Segur, F. Martínez, J. Melero, R. Molina, R. Chand, D. Bremner, Enhancement of the advanced Fenton process (FeO/H<sub>2</sub>O<sub>2</sub>) by ultrasound for the mineralization of phenol, *Appl. Catal., B*, 113 (2012) 100–106.
- [24] M. Dükkanc, Sono-photo-Fenton oxidation of bisphenol-A over a LaFeO<sub>3</sub> perovskite catalyst, *Ultrason. Sonochem.*, 40 (2018) 110–116.
- [25] Q. Zhou, Y. Liu, G. Yu, F. He, K. Chen, D. Xiao, X. Zhao, Y. Feng, J. Li, Degradation kinetics of sodium alginate via sono-Fenton, photo-Fenton and sonophoto-Fenton methods in the presence of TiO<sub>2</sub> nanoparticles, *Polym. Degrad. Stab.*, 135 (2017) 111–120.
- [26] A. Khataee, S. Rad, B. Vahid, S. Khorram, Preparation of zeolite nanorods by corona discharge plasma for degradation of phenazopyridine by heterogeneous sono-Fenton-like process, *Ultrason. Sonochem.*, 33 (2016) 37–46.
- [27] A. Hassani, C. Karac, S. Karac, A. Khataee, O. Açışlı, B. Yılmaz, Enhanced removal of basic violet 10 by heterogeneous sono-Fenton process using magnetite nanoparticles, *Ultrason. Sonochem.*, 40 (2018) 841–852.
- [28] P. Margan, M. Haghghi, Sono-coprecipitation synthesis and physicochemical characterization of CdO-ZnO nanophotocatalyst for removal of acid orange 7 from wastewater, *Ultrason. Sonochem.*, 40 (2018) 323–332.
- [29] X. Zhong, S. Royer, H. Zhang, Q. Huang, L. Xiang, S. Valange, J. Barrault, Mesoporous silica iron-doped as stable and efficient heterogeneous catalyst for the degradation of C.I. Acid Orange 7 using sono-photo-Fenton process, *Sep. Purif. Technol.*, 80 (2011) 163–171.
- [30] S. Adityosulindro, L. Barthe, K. Labrada, J. Haza, H. Delmasa, C. Julcour, Sonolysis and sono-Fenton oxidation for removal of ibuprofen in (waste) water, *Ultrason. Sonochem.*, 39 (2017) 889–896.
- [31] C. Wang, Y. Shih, Degradation and detoxification of diazinon by sono-Fenton and sono-Fenton-like processes, *Sep. Purif. Technol.*, 140 (2015) 6–12.
- [32] S. Clesceri, A. Greenberg, A. Eaton, Standard Methods for the Examination of Water and Wastewater, American Public Health Association, 2005, pp. 607–614.
- [33] S. Cho, T. Luong, D. Lee, Y. OH, T. Lee, Reuse of effluent water from a municipal wastewater treatment plant in microalgae cultivation for biofuel production, *Bioresour. Technol.*, 102 (2011) 8639–8645.
- [34] Z. Yang, B. Gao, W. Xu, B. Cao, Q. Yue, Effect of OH<sup>-</sup>/Al<sup>3+</sup> and Si/Al molar ratios on the coagulation performance and residual Al speciation during surface water treatment with poly-aluminum-silicate-chloride (PASiC), *J. Hazard. Mater.*, 189 (2011) 203–210.

- [35] J. Wu, F. Liu, H. Zhang, J. Zhang, L. Li, Decolorization of CI Reactive Black 8 by electrochemical process with/without ultrasonic irradiation, *Desal. Wat. Treat.*, 44 (2012) 36–43.
- [36] B. Thokchom, A. Pandit, P. Qiu, B. Park, J. Choi, J. Kim, A review on sonoelectrochemical technology as an upcoming alternative for pollutant degradation, *Ultrason. Sonochem.*, 27 (2015) 210–234.
- [37] P. Nidheesh, R. Gandhimathi, S. Ramesh, Degradation of dyes from aqueous solution by Fenton processes: a review, *Environ. Sci. Pollut. Res. Int.*, 20 (2013) 2099–2132.
- [38] D. Gümüş, F. Akbal, Comparison of Fenton and electro-Fenton processes for oxidation of phenol, *Process Saf. Environ. Prot.*, 103 (2016) 252–258.
- [39] Y. Ren, Z. Wu, M. Franke, P. Braeutigam, B. Ondruschka, D. Comeskey, Sonoelectrochemical degradation of phenol in aqueous solutions, *Ultrason. Sonochem.*, 20 (2013) 715–721.
- [40] N. Wang, T. Zheng, G. Zhang, P. Wang, A review on Fenton-like processes for organic wastewater treatment, *J. Environ. Chem. Eng.*, 4 (2016) 762–787.
- [41] D. He, X. Guan, J. Ma, X. Yang, C. Cui, Influence of humic acids of different origins on oxidation of phenol and chlorophenols by permanganate, *J. Hazard. Mater.*, 182 (2010) 681–688.
- [42] M. Bagal, P. Gogate, Wastewater treatment using hybrid treatment schemes based on cavitation and Fenton chemistry: a review, *Ultrason. Sonochem.*, 21 (2014) 1–14.
- [43] J. Wang, H. Wang, Fenton treatment for flotation separation of polyvinyl chloride from plastic mixtures, *Sep. Purif. Technol.*, 187 (2017) 415–425.
- [44] A. Ribeiro, O. Nunes, M. Pereira, A. Silva, An overview on the advanced oxidation processes applied for the treatment of water pollutants defined in the recently launched Directive 2013/39/EU, *Environ. Int.*, 75 (2015) 33–51.
- [45] E. Rott, R. Minke, U. Bali, H. Steinmetz, Removal of phosphonates from industrial wastewater with UV/Fe II, Fenton and UV/Fenton treatment, *Water Res.*, 122 (2017) 345–354.
- [46] T. Xu, R. Zhu, G. Zhu, J. Zhu, X. Liang, Y. Zhu, Mechanisms for the enhanced photo-Fenton activity of ferrihydrite modified with BiVO<sub>4</sub> at neutral pH, *Appl. Catal., B*, 212 (2017) 50–58.
- [47] V. Sáez, M. Esclapez, I. Tudela, P. Bonete, O. Louisnard, J. García, 20kHz sonoelectrochemical degradation of perchloroethylene in sodium sulfate aqueous media: influence of the operational variables in batch mode, *J. Hazard. Mater.*, 183 (2010) 648–654.