Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2017.21530

95 (2017) 96–108
November

Treatment of pulp and paper wastewater by lab-scale coagulation/SR-AOPs/ultrafiltration process: optimization by Taguchi

Moeen Gholami[a], Behrooz Abbasi Souraki[a], Alireza Pendashteh[b,*],
Saeed Pourkarim Mozhdehi[c], Mohammad Bagherian Marzouni[d]

[a]*Department of Chemical Engineering, Faculty of Engineering, University of Guilan, Rasht, Iran, Tel. +989372974846; email: gholami.moeen@gmail.com (M. Gholami), Tel. +989177126335; email: b.abbasi@guilan.ac.ir (B.A. Souraki)*
[b]*Department of Water Engineering and Environment, The Caspian Sea Basin Research Center, University of Guilan, Rasht, Iran, Tel. +989111329011; email: arpendashteh@guilan.ac.ir*
[c]*Department of Environmental Health Engineering, Faculty of Health, Guilan University of Medical Sciences, Rasht, Iran, Tel. +981334569165; email: saeedpoorkareem@yahoo.com*
[d]*Department of Civil and Environmental Engineering, Faculty of Water Sciences, University of Shahid Chamran, Ahvaz, Iran, Tel. +989115854710; email: marzooni@gmail.com*

Received 15 April 2017; Accepted 4 October 2017

ABSTRACT

In this study, the treatment of pulp and paper wastewater using combined approach of coagulation/sulfate radical-advanced oxidation process (SR-AOPs)/ultrafiltration (UF) was studied in the lab scale. In the beginning of this system, the performance of three coagulants such as polyaluminum chloride (PACl), ferric chloride ($FeCl_3$) and alum was evaluated to achieve high recycled fiber. According to the results yielded, the $FeCl_3$, with high fiber recycling (98%) and removal efficiency, was more efficacious. In the next step, the potassium persulfate (PPS)-Fe(II) and PPS-Fe(III) efficiency in the removal of the chemical oxygen demand (COD), aromatic compounds (UV_{254}) and the value of sludge volume index were evaluated using Taguchi design of the experiment. The results showed that the removal efficiency of COD and UV_{254} in the process of PPS-Fe(II) was 92.6% and 95.8% which had the better performance than the process of PPS-Fe(III). The results showed that electrical conductivity (EC) in coagulation/SR-AOPs had increased to 30.64%. Moreover, there was a significant amount of sulfate in the effluent; whereas, UF was applied. Accordingly, using UF after pretreatment by coagulation/PPS-Fe(II), the removal efficiency of sulfate, EC, COD and UV_{254} increased to 99.44%, 62.05%, 97.35% and 98.75%, respectively.

Keywords: Advanced oxidation processes; Sulfate radicals; Coagulation; Ultrafiltration; Taguchi

1. Introduction

The wastewater from paper industry has a significant role on polluting the surrounding environment as well as threatening the aquatic life and human health [1]. Due to raw materials usage as well as the additive chemical compounds that are employed during production processes, this kind of wastewater contains more than 200 recalcitrant organic compounds which may lead to considerable chemical oxygen demand (COD), total suspended solids (TSS), absorbable organic halogens (AOX), color and phenolic compounds [2]. Various physical, chemical and biological methods were used for the treatment and reducing the pollution load of pulp and paper industry. The biological processes have the high efficiency only for degradation of the wastewater containing organic materials, whereas the pulp and paper mill wastewater has a considerable amount of non-biodegradable matters [3]; therefore, the advanced chemical and physical methods in the treatment of this type of wastewater can be effective.

---

* Corresponding author.

The coagulation–flocculation process is widely used in the treatment systems because of its simplicity and cost-effective benefits [4]. Moreover, using this treatment method, the valuable fibers in the pulp and paper wastewater will be recyclable. On the other hand, some of the components are hardly removed using coagulation–flocculation process and still remain in the effluent. Therefore, to further removal of such components, the advanced treatment methods are needed. The advanced oxidation processes (AOPs) are considered more as the new methods for water and wastewater treatment and they have been widely used to remove the degradation-resistant pollutant [5,6]. Generally, the AOPs oxidize the pollutants and convert them to the harmless materials [7,8].

Recently, the sulfate radicals with the oxidation–reduction potential of 2.6 V (redox = 2.6 V) that is almost similar to the hydroxyl radicals oxidation–reduction potential, is significantly considered in AOPs [9]. The sulfate radicals are produced during activation of persulfate ions ($S_2O_8^{2-}$), while this oxidizing agent has characteristics of high resistance, high solubility and high redox potential [10]. Persulfate can be activated during exposure to the temperature and light (Eq. (1)) [11] or by chemical reaction with metal ions (Eq. (2)) and produce sulfate radicals [12].

$$S_2O_8^{2-} + \text{photon or heat} \rightarrow 2SO_4^{\bullet -} \tag{1}$$

$$S_2O_8^{2-} + Me^{n+} \rightarrow SO_4^{\bullet -} + Me^{(n+1)^+} + SO_4^{2-} \tag{2}$$

The most important limitation of the AOPs process is the high consumption of the chemical compounds for setting the pH, the iron sludge accumulation and the cost to collect the settled iron sludge [13]. Therefore, pretreatment of this type of wastewater employing coagulation and flocculation approach leads to a considerable reduction in the amount of oxidants and catalysts used in the AOPs. But, on the other hand, adding chemical agent in the AOPs, however, reduces the pollution in wastewater, and may increase the dissolved matters more than environmental standards. As a result, the post-treatment like filtration is needed for the abatement of this problem and also for the increment of the ultimate efficiency removal. The ultrafiltration (UF) is known as the effective method for dissolved matters such as sulfates and polyvalent salts. Using the coupled processes for the treatment of the industrial wastewater has been considered more and more in recent years. But employing coagulation/sulfate radical-advanced oxidation process (SR-AOPs)/UF for the treatment of the wastewater has not been reported yet. Also, few studies were conducted on real wastewater applying sulfate radical [14,15]. In our previous research, the UF as pretreatment process was used for SR-AOPs and AOPs; moreover, in addition to controlling membrane fouling, the removal efficiency of COD, UV_{254} and lignin (UV_{280}) reached more than 90% [14]. In the other research, Jaafarzadeh et al. [15] employed the electrocoagulation and UV-based sulfate radical oxidation for the treatment of the pulp and paper mill wastewater and reached the removal efficiency of 61% for COD.

The main purposes of this study are: (1) The performance evaluation of some coagulants such as PACl, $FeCl_3$ and alum in the removal of the COD, UV_{254} and TSS. (2) The optimization and review of the affecting factor in the processes of SR-AOPs and coagulation/SR-AOPs (PPS-Fe(II) and PPS-Fe(III)), employing Taguchi method. (3) Evaluation of the amount of remained sulfate and electrical conductivity (EC) at the end of the each process. (4) The performance evaluation of the removal efficiencies in hybrid processes of coagulation/SR-AOPs/UF.

2. Materials and methods

2.1. Experimental setup

The experimental study was conducted on a laboratory scale (Fig. 1). A laboratory system was formed by feed tank (V = 10 L), coagulation tank (5 L), SR-AOPs tank (5 L), membrane tank (5 L) and vacuum trap (4 L). The 4 L of wastewater was entered into the coagulation tank by a pump and in this point; the coagulant was added in the natural pH of wastewater. The coagulation process was started with the speed of 120 rpm and continued for 1 min. Then, the flocculation process was started with the speed of 30 rpm for 20 min. Subsequently, the flocs were settled down during 15 min.

In the following, by adding catalyst and oxidant, the SR-AOPs were started and after 15 min the process quenched. Different methods have been reported for the quenching of the SR-AOPs process. In some studies, sodium azide [16], $NaNO_2$ [17] or $Na_2S_2O_3$ [18] have been reported as a quenching substance. In addition, in some other papers, SR-AOPs process was completed by adding alkaline material to terminate this process [12,19]. In this study, by adding alkaline material, OH^- ions enter the solution, lead to the increase of pH, the sediment of catalyst (Fe) and the completion of the SR-AOPs process [14]. Also, based on previous studies, according to the SR-AOPs reaction rate, the initial reaction time was determined as the optimal time for the SR-AOPs process (between 5 and 30 min) [18,20]. So, in order to reduce the number of experiments and to investigate other effective parameters more precisely such as pH, catalyst and oxidant concentration; the reaction time was considered at 15 min. In the following, the pretreated wastewater was entered to the filtration tank in which the membrane was embedded in it. The UF membrane was fixed in the filtration tank vertically and with the vacuum trap made by a vacuum pump (Value 225 N) at the pressure of –1 atmosphere, the filtration process was carried out for 8–10 min. To control the pressure, a manometer was used and permeate flux of flow meter was measured. To control the pH in all steps, the multi-meter instrument of Aqualytic AL15 was employed.

2.2. Wastewater characteristics

This study was done on the types of wastewater which was taken from Iran Pulp and Paper Industry (Chuka). This factory with the wastewater flow rate of 25,000 m^3/d plays an important role in polluting the environment. The wastewater characteristics were mentioned in Table 1. No pretreatment was done on the samples, and the taken samples were kept safe at 4°C. According to the wastewater characterization,

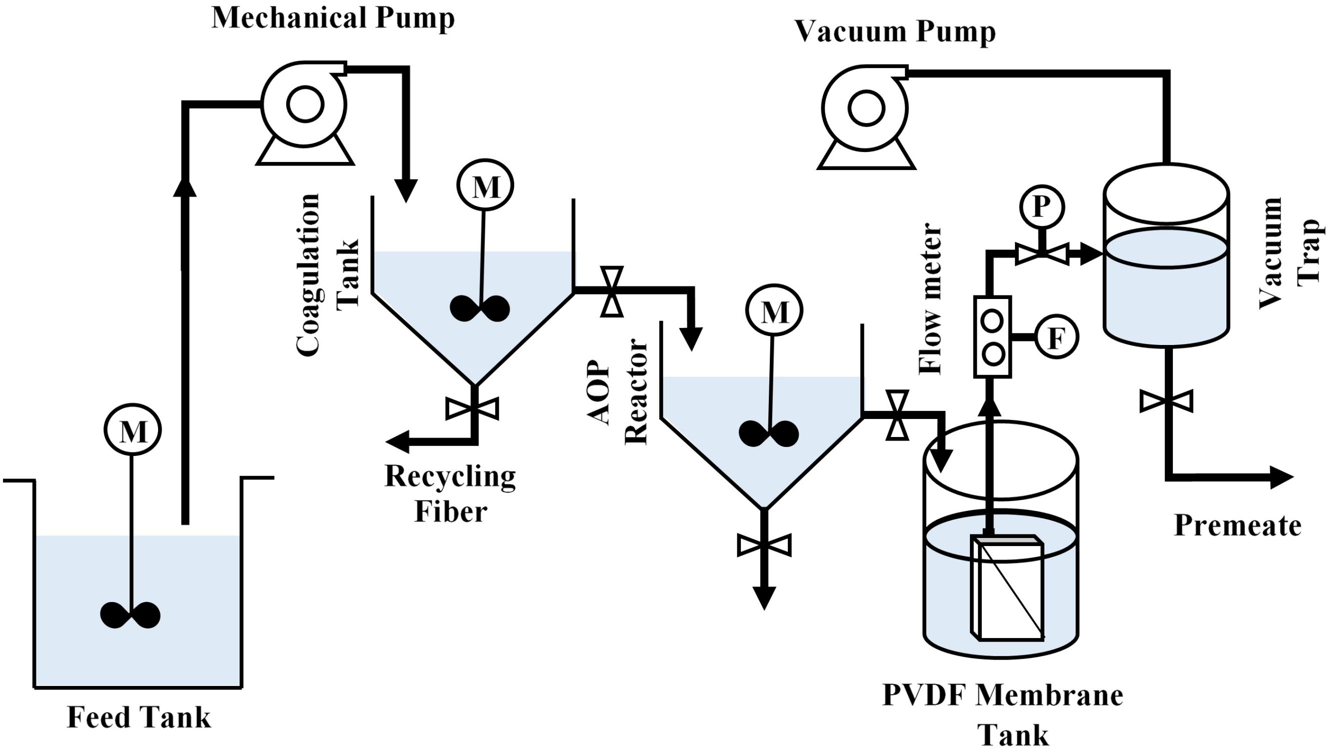


Fig. 1. Schematic diagram of the processes and their sequences.

Table 1
Wastewater characteristics

Parameters	Values
COD, mg/L	2,343 ± 50
BOD_5, mg/L	476 ± 30
BOD_5/COD	0.2
TSS, mg/L	2,772 ± 50
Sulfate, mg/L	965 ± 5
UV_{254}, 1/m	2.403 ± 0.1
Color	Dark brown
Turbidity, NTU	3,655 ± 50
EC, mS/cm	0.72 ± 0.01
pH	7.0 ± 0.05

the BOD_5/COD ratio of the wastewater was 0.2, which indicates the low degradability of this wastewater.

2.3. Chemical agents

The $FeSO_4.7H_2O$ and $FeCl_3$ as the source of Fe (II) and Fe (III) for the reaction with the $K_2S_2O_8$ were used for SR-AOPs, respectively. For this purpose, the stoke solutions of ferrous sulfate, ferric chloride, potassium persulfate and alum with the certain concentration in accordance with the standard methods were prepared [21]. To set the pH, the solutions of NaOH and H_2SO_4 were used. All chemicals used in this study were purchased from Merck, Germany. In the process of filtration, a plate and frame module of hydrophobic polyvinylidene fluoride UF membrane (Shanghai Sinap Membrane, China) with the effective area of 1,400 cm^2, pore diameter of 0.1 μm and molecular weight cut-off of 140 kDa was applied.

2.4. Analytical methods

The sample analysis for measuring the COD, TSS, sludge volume index (SVI), and sulfate was conducted in accordance with the standard methods [21]. The COD values were measured using AL125 – AQUALYTIC thermo-reactor and AL125 – AQUALYTIC COD meter. The value of UV_{254} was also identified using Jenway 7310. The SVI value was also determined after 30 min. The device of Aqualytic AL15 was employed for measuring the EC. Eq. (3) was applied for calculation of the removal efficiency. In the following equation, A_0 and A_f are the initial and final values of COD, UV_{254}, EC, sulfate and TSS, respectively.

$$R(\%) = \left(1 - \frac{A_f}{A_0}\right) \times 100 \tag{3}$$

2.5. Design of experiments

The Taguchi method was used for the design of SR-AOPs experiments in this study. According to the previous researches, the efficiency of the AOPs is heavily related to the variables such as pH, the oxidant concentration and the catalyst concentration [22]. The effects of parameters affecting the SR-AOPs were studied at four levels. The levels of the process parameters for SR-AOPs were presented in Table 2.

In normal mode, according to full factorial design, the $4^3 = 64$ number of experiments with different combinations of the independent parameters are needed for optimization and surveying the efficiency of the SR-AOPs, but using the Taguchi experimental design method according to its specific algorithm, the number of experiments decreased to 16. Minitab 17.1.0 Statistical Software was used to design the experiments. Using the Taguchi section of this software, the design of the experiments and their layout was presented in Table 3. The Taguchi method converts the responses to the signal-to-noise (S/N) ratio to analyze the data and determination of the optimum condition [23]. According to the type of optimization, the ratios of S/N are divided into three categories called "nominal-the-better", "larger-the-better" and "smaller-the-better" [24]. Whereas in this study the aim is to maximize the removal efficiency of COD and UV_{254} and minimize SVI, the S/N ratios were calculated for the removal efficiency of COD and UV_{254} based on the larger-the-better (Eq. (4)) and for SVI based on the smaller-the-better (Eq. (5)):

$$\text{S/N}\left(\text{dB}\right) = -10\log\left(\frac{1}{n}\sum_{i=1}^{n}\frac{1}{Y_i^2}\right) \quad \text{(larger-the-better)} \tag{4}$$

$$\text{S/N}\left(\text{dB}\right) = -10\log\left(\frac{1}{n}\sum_{i=1}^{n}Y_i^2\right) \quad \text{(smaller-the-better)} \tag{5}$$

In the above equations, Y_i is the measured response for each test in each experiment and n is the experiments replication.

Table 2
The levels of the process parameters

Parameters	Levels			
	1	2	3	4
pH	3	4	5	6
H_2O_2 (mM)	10	20	30	40
Fe(II) and Fe(III) (mM)	5	10	15	20

3. Results and discussion

3.1. Coagulation process

A significant amount of the cellulose fibers from the pulping process is entered into the wastewater, and in order to save the costs, it should be returned to the production line. According to the analysis, more than 90% TSS consisted of recycled fibers. For this purpose, the coagulation process was used to sediment all suspended solids and recover them. Therefore, the removal efficiency of TSS was considered as the index of fiber recycling in this study. In this step, the performance of three coagulants such as PACl, $FeCl_3$ and alum in the removal of COD, UV_{254} and fiber recycling was compared. For this purpose, the concentration of each coagulant in the initial pH of wastewater (pH = 7.0) was surveyed and the results were compared (Table 4). According to the results obtained, $FeCl_3$ in the

Table 3
L_{16} (4^3) randomized experimental plan

Exp No.	SR-AOPs			Coagulation/SR-AOPs		
	pH	PPS (mM)	Fe(II) (mM)	pH	PPS (mM)	Fe(II) and Fe(III) (mM)
1	3	10	5	3	4	2
2	3	20	10	3	6	4
3	3	30	15	3	8	6
4	3	40	20	3	10	8
5	4	10	10	4	4	4
6	4	20	5	4	6	2
7	4	30	20	4	8	8
8	4	40	15	4	10	6
9	5	10	15	5	4	6
10	5	20	20	5	6	8
11	5	30	5	5	8	2
12	5	40	10	5	10	4
13	6	10	20	6	4	8
14	6	20	15	6	6	6
15	6	30	10	6	8	4
16	6	40	5	6	10	2

Table 4
Effect of coagulants concentrations on the removal efficiency

Coagulants	Parameters	Concentration (mM)					
		0.5	1.0	1.5	2.0	2.5	3.0
Alum	COD removal (%)	16.3	21.0	24.5	33.6	35.8	28.6
	UV_{254} removal (%)	10.4	16.3	22.1	30.1	31.8	33.9
	Fiber recycling (%)	32	44	59	77	82	96
$FeCl_3$	COD removal (%)	12.1	30.2	39.5	41.2	43.3	40.2
	UV_{254} removal (%)	14.6	25.6	37.7	44.3	42.2	31.5
	Fiber recycling (%)	36	61	79	98	89	80
PACl	COD removal (%)	16.5	20.7	26.3	30.0	35	32.2
	UV_{254} removal (%)	9.3	16.5	21.5	25.9	29.6	30.0
	Fiber recycling (%)	24	46	66	73	95	88

concentration of 2 mM with the maximum removal efficiency and a high percentage of fiber recycling was known as the best coagulant. When ferric chloride is added to the solution, a sequence of hydrolysis species is formed. These hydrolysis species have positive or negative charge, depending on the pH of the solution that can be different, which hydrolysis species are positive at a pH less than 6 and negative at high pH. The positively charged hydrolysis species can be adsorbed on the colloidal particles surface and lead to the particles to become unstable. In the process of coagulation, this mechanism is called "charge neutralization". 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" [25]. In this study, since coagulation process was done in the natural pH of wastewater (pH = 7.0), mechanism of coagulation demonstrated properties of sweep coagulation. As a result, according to the mechanism of sweep coagulation, the fiber recycling, the removal efficiency of COD and aromatics compounds reached 98%, 41.2% and 44.3%, respectively. It will be good to mention that the pH of the effluent from the coagulation process reached about 6. Actually, by adding ferric salt to the solution, it works by reacting with wastewater's alkalinity [26,27]. The 0.92 mg/L of alkalinity is consumed by each mg/L of ferric chloride [28]. Therefore, it led to the reduction of pH to about 6.

3.2. The process of SR-AOPs (PPS-Fe(II))

According to the Taguchi method, the results of PPS-Fe(II) with the ratio of S/N are presented in Table 5. In this study, the removal efficiency of COD, UV_{254} and SVI was considered as the response functions for the evaluation of the PPS-Fe(II) process. By using Eqs. (4) and (5) the obtained results are converted to the response function of S/N.

The effect of each parameter on the removal efficiencies was identified at all levels by using the ratio of S/N. Fig. 2 shows the S/N ratios of each factor related to various levels for each response of the corresponding process. Forasmuch as the aim of the experiments was to survey the increment of removal efficiencies and the reduction in sludge production. Therefore, the maximum value of S/N ratio among the various levels of each parameter for removal efficiencies of COD, UV_{254} and the values of SVI show the optimal condition of the related factors.

The value of pH has the significant role in controlling catalytic activity of the iron and the stability of the oxidation [29]. In this study, the effect of pH at acidic pH range (3, 4, 5 and 6) was considered. In the acidic pH range, the hydrogen peroxide is produced by hydrolysis of persulfate which leads to the reaction with iron ions and the hydroxyl radicals are produced that beside the sulfate radicals cause further destruction of the pollutants [30]. Also, the sulfate radicals can hydrolysis the H_2O and produce more hydroxyl radicals; moreover, the superoxide radical ($O_2^{\bullet-}$) can also be another important factor in the removal of the pollutants [18]. It should be noted, at very low pH, iron complexes such as $[Fe(H_2O)_6]^{2+}$ are formed. These complexes react slowly with the oxidizing agent and lessen the amount of radical production [31]. According to Figs. 2(A) and (B), the maximum ratio of S/N occurred in the pH = 3 and this level had the maximum removal efficiency of COD and UV_{254}. According to Eq. (6), the complex species of $Fe(OH)^+$ is formed in pH = 3 which compared with non-complex species of Fe^{2+} has a higher activity in the advanced oxidation [32].

$$Fe^{2+} + H_2O \rightarrow Fe(OH)^+ + H^+ \tag{6}$$

Table 5
Experimental results of the PPS-Fe(II) process

PPS-Fe(II)						
Exp. No.				S/N (dB)		
	COD removal (%)	UV_{254} removal (%)	SVI (mL/L)	COD removal	UV_{254} removal	SVI (mL/L)
1	10.00	13.01	40.5	20.00	22.29	–32.15
2	33.45	48.34	46.5	30.49	33.69	–33.35
3	67.14	65.37	52.5	36.54	36.31	–34.40
4	66.00	56.24	71.0	36.39	35.00	–37.03
5	21.40	16.05	42.0	26.61	24.11	–32.46
6	13.16	11.35	50.0	22.39	21.10	–33.98
7	41.63	38.17	86.0	32.39	31.63	–38.69
8	69.23	70.09	73.5	36.81	36.91	–37.33
9	17.15	20.16	48.0	24.69	26.09	–33.62
10	18.85	22.65	77.0	25.51	27.10	–37.73
11	24.50	10.17	58.5	27.78	20.15	–35.34
12	56.84	48.53	73.0	35.09	33.72	–37.27
13	3.50	10.63	78.0	10.88	20.53	–37.84
14	30.10	40.24	70.5	29.57	32.09	–36.96
15	39.14	32.19	78.0	31.85	30.15	–37.84
16	16.10	7.53	64.0	24.14	17.54	–36.12

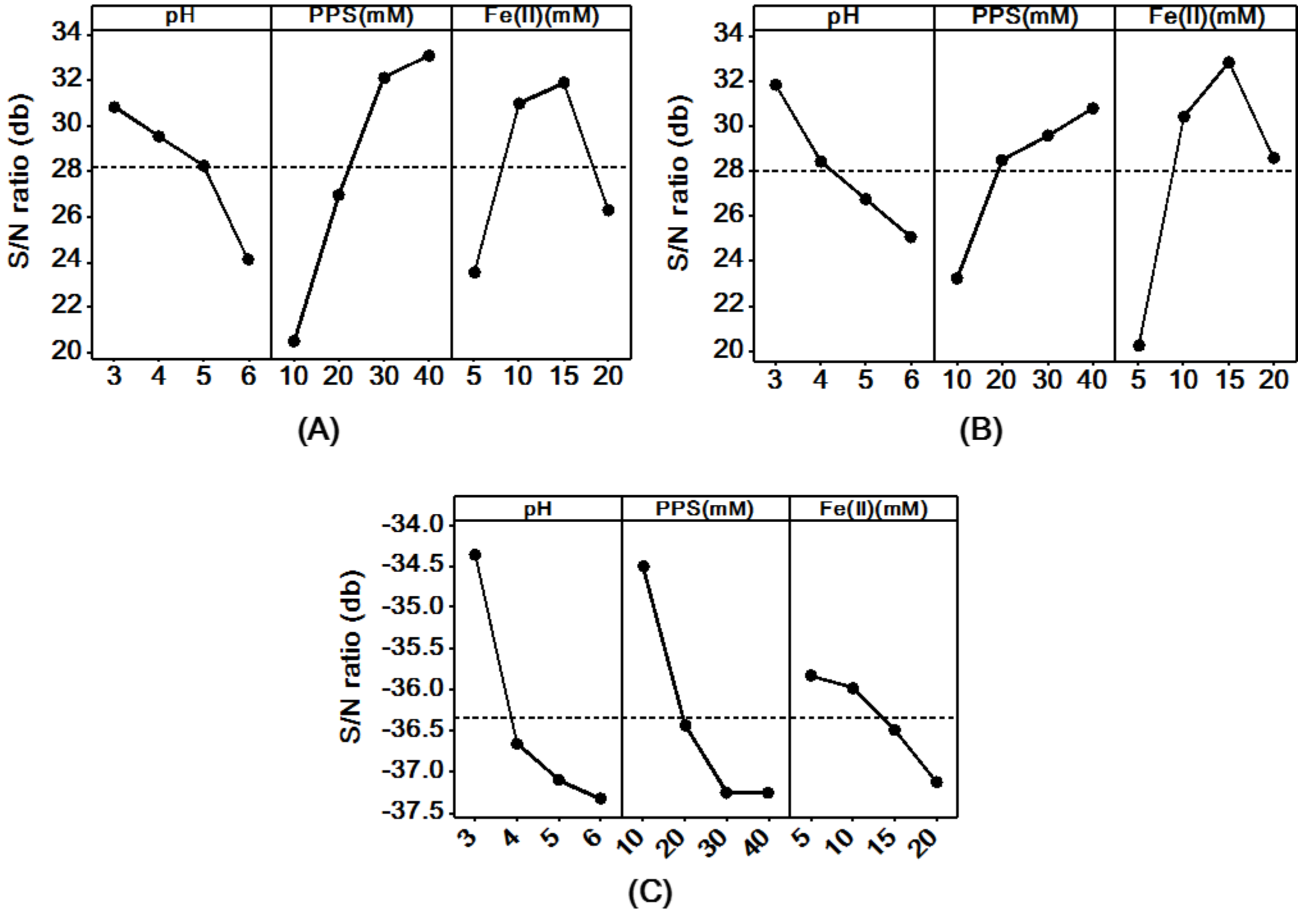


Fig. 2. The effect of experimental parameters on the S/N ratio for PPS-Fe(II). (A) COD removal, (B) UV_{254} removal and (C) SVI (mL/L).

On the other hand, in the pH higher than 3, the values of S/N for the removal efficiency of COD and UV_{254} rapidly decreased. This is due to the reduction of the amount of free catalyst in the solution which is a result of replacing the hydroxy complexes such as $Fe(OH)_3$ with the low activity in comparison with iron ions [5]. Also, the amount of soluble Fe^{2+} is reduced due to the formation of Fe(III) oxyhydroxides complexes such as $Fe_2(OH)_2^{4+}$, $Fe(OH)^{2+}$, $Fe(OH)_3^0$ and $Fe(OH)^{4+}$ have low efficiency for persulfate activation to produce sulfate radicals [33]. According to the results of the previous researches, pH = 3 was introduced as the optimum pH for the SR-AOPs [33,34].

According to the Taguchi results in the pH = 3, the maximum ratio of S/N was seen for SVI and in this pH value, the volume of the produced sludge reduced. This reduction in the volume of the produced sludge could be attributed to the reduction of the osmosis pressure and the effect of hydration in the acidic pH range [35].

As seen in Fig. 2, the effects of PPS and Fe(II) on the removal efficiency of COD and UV_{254} were shown. By increasing the concentration of the PPS up to 40 mM, the removal efficiency increased because of the increment in the production of the sulfate radicals (Eq. (7)) [18].

$$S_2O_8^{2-} + Fe(II) \rightarrow SO_4^{\bullet -} + SO_4^{2-} + Fe(III) \tag{7}$$

According to the Taguchi analysis, in the concentration of 15 mM for Fe(II), the maximum ratios of S/N were for the removal efficiency of COD and UV_{254}. By increasing the concentration of the catalyst, the rate of radical generation increases (Eq. (7)) but by increasing more than the optimum value, iron ions are increased which leads to the increment of the suspended solids in the solution. Moreover, this further increase leads to the reaction of the sulfate radicals with the remaining iron ions and finally the accessible free radicals and the oxidation efficiency reduced [36]. The similar studies also confirmed the effects of the iron ions and persulfate on the removal of the organic compounds [10,33,37,38].

$$SO_4^{-\bullet} + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{2-} \tag{8}$$

Fig. 2(C) shows the changes of produced sludge with regard to the concentrations of PPS and Fe. According to Fig. 2(C) by increasing the concentration of PPS and iron, the SVI also increased. Therefore, according to Fig. 2 the optimal levels of COD and UV_{254} removal efficiency were at pH = 3, [Fe(II)] = 15 mM and [PPS] = 40 mM, while the optimal conditions for SVI were at pH = 3, [Fe(II)] = 5 mM and [PPS] = 10 mM. In contrast to the optimal conditions for SVI which were in experiment 1 in Table 3, the optimal levels which were determined by the highest S/N ratio for the removal efficiency of COD and UV_{254} were not found in any of the experiments in Table 3. Therefore, re-experiments were carried out in the optimal conditions and then the removal efficiency of COD, UV_{254} and SVI value was 70.93%, 74.13% and 75.50 mL/L, respectively, that under these conditions, more efficiency was obtained than the optimum SVI conditions. Hence, the optimal conditions at pH = 3, [Fe(II)] = 15 mM and [PPS] = 40 mM were considered as the optimal conditions for the PPS-Fe(II) process.

3.3. Coagulation/SR-AOPs (PPS-Fe(II) and PPS-Fe(III))

In the previous section, the removal efficiency of SR-AOPs for raw wastewater was investigated. In this section, using the pretreated wastewater by the coagulation–flocculation process, the removal efficiencies, the SVI values and the impact of effective parameters were studied. The results of the two processes of PPS-Fe(II) and PPS-Fe(III) at their optimal points after pretreatment are presented in Tables 6 and 7, respectively.

As shown in Fig. 3, the maximum ratio of S/N of COD removal efficiency for the process of PPS-Fe(III) and PPS-Fe(II) occurred at pH = 5 and pH = 6, respectively. The results obtained from Taguchi statistical analysis showed that the ratio of S/N of the COD removal efficiency was increased by increasing the pH to 5 in the process of PPS-Fe(III) and PPS-Fe(III), and after that, the changes altered with negligible slope until the value of pH reached to 6. Similarly, the results obtained from the survey on the removal efficiency of UV_{254} showed that the values of S/N did not have a considerable difference in pH = 5 and pH = 6 in both processes. By rising the value of pH to 5, the amount of OH^- ions are increased, which react with sulfate radicals, and according to Eq. (9), it leads to produce more radicals than the acidic condition; therefore, produced sulfate and hydroxyl radicals can quickly destroy organic matters [14]. On the other hand, by increasing the pH to 6, iron ions are deposited in hydroxyl complexes such as $Fe(OH)_3$, hence the concentration of the required solvent catalyst for the oxidation reaction is significantly reduced, as a result sulfate radicals are greatly lessened [5,39]. Thus, the removal efficiency slightly decreased at pH 6. To compare the removal efficiency at pH 5 and 6, a slight difference was observed, therefore, with regard to reducing the amount of acid as well as the acidification problems, the pH = 6 equaling the pH of the effluent from the coagulation–flocculation process could be considered as the optimum pH in the removal efficiency of COD and aromatic compounds. Therefore, there was no need for application of the chemicals to reduce the pH. In the coagulation/AOP, the coagulation process, by eliminating a high percentage of suspended solids, likely acts as a barrier and allows the iron catalysts to continuously react with an oxidizing agent (persulfate) and prevents the involvement of iron catalysts with suspended colloidal particles [40,41]. Therefore, this led to the increase of optimal pH for coagulation/SR-AOPs in comparison with SR-AOPs. Zhang et al. [37] reported the neutral pH as the optimum pH for the removal of the aniline by the process of Fe^{2+}-activated persulfate oxidation. They showed that the sulfate radicals react with H_2O and OH^- (Eqs. (9) and (10)) and produce more radicals.

$$\text{Alkaline pH}: SO_4^{-\bullet} + OH^- \rightarrow SO_4^{2-} + {}^\bullet OH + H^+ \tag{9}$$

$$\text{All pH values}: SO_4^{-\bullet} + H_2O \rightarrow SO_4^{2-} + {}^\bullet OH + H^+ \tag{10}$$

When $FeCl_3$ was used as a coagulant, its optimum concentration was obtained. Based on the results, the concentration of Fe(III) in the treated effluent with the coagulation–flocculation process was less than 0.1 mM, which was

Table 6
Experimental results of the coagulation/PPS-Fe(II) processes

Coagulation/PPS-Fe(II)						
Exp. No.				S/N (dB)		
	COD removal (%)	UV_{254} removal (%)	SVI (mL/L)	COD removal	UV_{254} removal	SVI (mL/L)
1	58.17	62.62	16.5	35.29	35.93	–24.34
2	69.75	76.74	19.0	36.87	37.70	–25.57
3	70.89	72.60	26.5	37.01	37.21	–28.46
4	61.97	68.22	36.0	35.84	36.67	–31.12
5	67.71	74.19	22.0	36.61	37.40	–26.84
6	70.39	81.80	19.5	36.95	38.25	–25.80
7	64.34	72.07	41.0	36.16	37.15	–32.25
8	82.97	83.43	52.5	38.37	38.42	–34.40
9	64.13	70.57	33.0	36.14	36.97	–30.37
10	61.16	72.44	35.5	35.72	37.19	–31.01
11	87.12	83.66	26.0	38.80	38.45	–28.30
12	89.82	90.46	38.0	39.06	39.12	–31.60
13	58.89	60.85	32.5	35.40	35.68	–30.23
14	70.22	81.26	36.5	36.92	38.19	–31.24
15	92.63	95.81	25.0	39.33	39.62	–27.95
16	82.31	79.02	38.0	38.30	37.95	–31.59

Table 7
Experimental results of the coagulation/PPS-Fe(III) processes

Coagulation/PPS-Fe(III)						
Exp. No.				S/N (dB)		
	COD removal (%)	UV_{254} removal (%)	SVI (mL/L)	COD removal	UV_{254} removal	SVI (mL/L)
1	48.30	52.34	8.50	33.67	34.37	–18.58
2	65.15	65.36	18.00	36.27	36.30	–25.10
3	68.30	76.14	21.50	36.68	37.63	–26.64
4	66.34	68.84	32.00	36.43	36.75	–30.10
5	62.45	68.66	17.50	35.91	36.73	–24.86
6	60.43	60.34	15.50	35.62	35.61	–23.80
7	71.00	77.45	32.50	37.02	37.78	–30.23
8	82.60	85.63	37.00	38.33	38.65	–31.36
9	72.45	66.54	23.50	37.20	36.46	–27.42
10	70.00	78.65	28.00	36.90	37.91	–28.94
11	70.30	65.44	18.00	36.93	36.31	–25.10
12	77.60	85.50	24.50	37.79	38.63	–27.78
13	65.30	61.87	26.50	36.29	35.82	–28.46
14	76.41	79.36	30.00	37.66	37.99	–29.54
15	85.36	86.60	21.00	38.62	38.75	–26.44
16	64.30	65.34	23.50	36.16	36.30	–27.42

negligible compared with the concentration of added iron in the SR-AOPs process. Therefore, the effect of Fe(III) on the SR-AOPs process can be ignored. According to the Taguchi analysis, in the concentration of 4 and 6 mM for Fe(II) and Fe(III), the maximum ratios of S/N were for the removal efficiency of COD and UV_{254}, respectively. Also, the concentration changes of the PPS in the process of PPS-Fe(II) up to 10 mM and in the process of PPS-Fe(III) up to 8 mM was the maximum for the removal efficiency of COD. The changes of S/N ratio for the removal efficiency of UV_{254} (Figs. 3(B_1) and (B_2)) with the changes in the PPS concentrations showed that the concentration of 8 mM of PPS had the maximum ratio of S/N for the processes of PPS-Fe(III) and PPS-Fe(II). After that by increasing the concentration of PPS more than the optimal concentration, the $S_2O_8^{2-}$ acts as the radical scavenger (Eq. (11)), reacts with the sulfate radicals and leads to the formation of sulfate anions and $S_2O_8^{--}$ radicals, while these produced radicals have the lesser oxidation potential than sulfate radicals [42].

$$SO_4^{\bullet -} + S_2O_8^{2-} \rightarrow SO_4^{2-} + S_2O_8^{\bullet -} \quad (11)$$

By evaluating the changes of pH, PPS and Fe(II) in the amount of produced sludge in the process of coagulation/SR-AOPs, one can find out that these changes were the same as changes in the process of SR-AOPs. As a result, as mentioned, by increasing the concentration of catalyst and oxidant, the SVI was also increased.

3.3.1. Contribution ratios

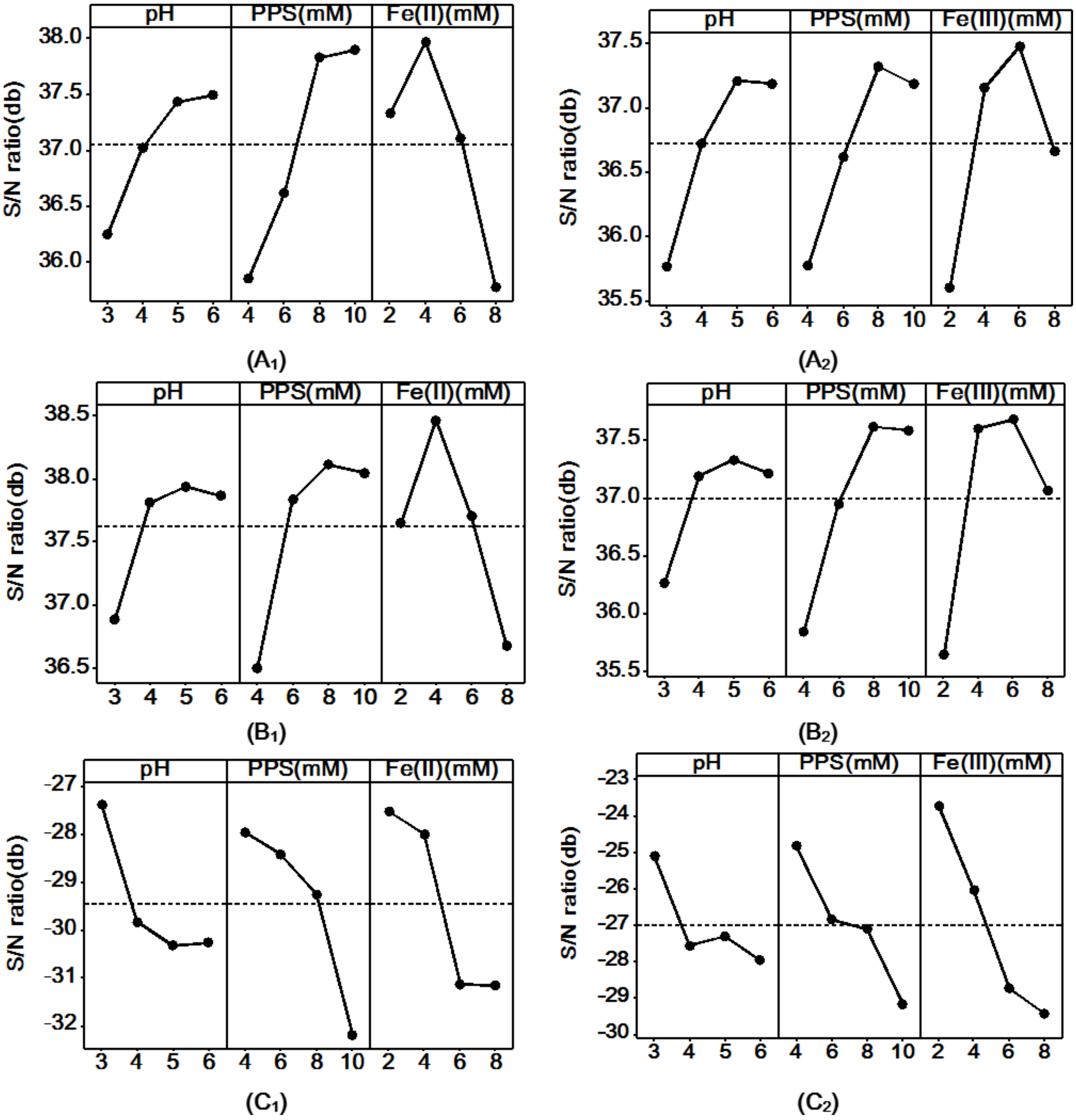
After the S/N analysis, the analysis of variance (ANOVA) for the determination of the relative importance of the various parameters and estimation of the error variance was done [43]. In the ANOVA, the sum of squares (SS), degrees of freedom (DF), mean square (MS) and *F* value are calculated [44]. The results of the statistical analysis on the removal efficiency for the ratio of S/N are presented in Table 8. The percentage contributions of each factor on response function are listed in Fig. 4 which were calculated by Eq. (12) [45].

$$P(\%) = \frac{SS_A - (DF \times MS_e)}{SS_T} \times 100 \quad (12)$$

According to Fig. 4, it can be seen that in the process of PPS-Fe(II), the concentration of the PPS and Fe(II) with the contributions of 42.52% and 36.64% for COD removal efficiency and the contributions of 38.73% and 35.9% for UV_{254} removal efficiency had the significant effect on the response (i.e., COD removal) with the $\alpha = 0.05$. This represented the high effect of oxidant and catalyst concentrations on the amount of free radical generation for the removal of the pollutants. The results of the similar studies also confirmed the considerable effects of oxidant and catalyst in the process of AOPs [32]. Also, the concentrations of the Fe(III) and PPS in the PPS-Fe(III) process had the more impacts on the removal efficiency. By evaluating the effectiveness of SVI affecting factors, it was observed that the concentration of Fe had more impact on the sludge of the produced iron, especially this effect was more in the process of PPS-Fe(III).

3.3.2. Verifying the results

After identifying the optimum condition and the analysis which was done for each response, the confirmation experiments were done to verify the results.



(A₁) (A₂)

(B₁) (B₂)

(C₁) (C₂)

Fig. 3. The effect of experimental parameters on the S/N ratio for coagulation/advanced oxidation processes (PPS-Fe(II) and PPS-Fe(III)). (A) COD removal, (B) UV_{254} removal and (C) SVI (mL/L).

In Table 9, the obtained results are compared with the predicted results obtained in the optimum conditions using statistical analysis. As seen in Table 9, the error percentage in all responses is in the acceptable range. Also, the 95% confidence interval for all the parameters was calculated and is presented in Table 9. The verification experiments illustrated that experimentally obtained results were in confidence interval.

According to the given results, in the process of PPS-Fe(II) and in the optimum condition of COD removal, the removal efficiencies of COD and UV_{254} were 93.83% and 86.21%, respectively, and SVI was equal to 31 mL/L. For the optimum condition of UV_{254} removal, the removal efficiencies of the COD and UV_{254} were 92.63% and 95.81%, respectively, and SVI was 25 mL/L. Also, in the minimum SVI, the removal efficiencies of COD and UV_{254} were 58.17% and 62.62%, respectively, and the SVI was 16.5 mL/L. By evaluating the obtained efficiencies under the various optimal conditions, it can be seen that under optimum condition of PPS-Fe(II) process, the removal efficiencies of COD and UV_{254} were appropriate; therefore, the condition of pH = 6, PPS = 8 mM and Fe(II) = 4 mM could be considered as the

Table 8
Statistical results based on S/N ratio

Coagulation/PPS-Fe(II)					Coagulation/PPS-Fe(III)				
Factors	DF	SS	Variance	*F* Ratio	Factors	DF	SS	Variance	*F* Ratio
COD removal (%)					COD removal (%)				
pH	3	3.91	1.30	9.62	pH	3	5.44	1.81	9.33
PPS	3	11.70	3.90	28.78	PPS	3	5.94	1.98	10.18
Fe(II)	3	10.14	3.38	24.94	Fe(III)	3	8.03	2.68	13.77
Error	6	0.81	0.14		Error	6	1.17	0.19	
Total	15	26.56			Total	15	20.57		
UV_{254} removal (%)					UV_{254} removal (%)				
pH	3	2.96	0.99	8.66	pH	3	2.93	0.98	3.75
PPS	3	6.91	2.30	20.19	PPS	3	8.21	2.74	10.52
Fe(II)	3	6.43	2.14	18.79	Fe(III)	3	10.64	3.55	13.62
Error	6	0.68	0.11		Error	6	1.56	0.26	
Total	15	16.99			Total	15	23.34		
SVI (mL/L)					SVI (mL/L)				
pH	3	23.35	7.79	11.21	pH	3	19.70	6.57	6.63
PPS	3	43.32	14.44	20.79	PPS	3	37.71	12.57	12.69
Fe(II)	3	46.31	15.44	22.22	Fe(III)	3	82.31	27.44	27.71
Error	6	4.17	0.69		Error	6	5.94	0.99	
Total	15	117.16			Total	15	145.6		

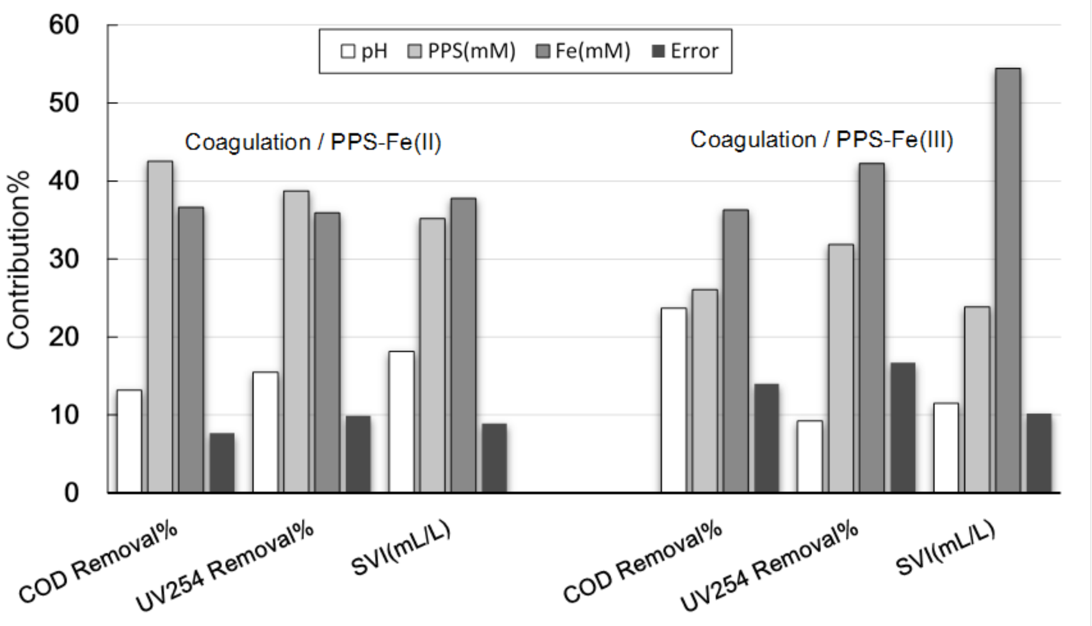


Fig. 4. The contribution ratios of each factor of coagulation/PPS-Fe(II) and coagulation/PPS-Fe(III).

overall optimal condition of PPS-Fe(II) process. Similarly, the process of PPS-Fe(III) also under optimal condition of COD or UV_{254} removal in pH = 6, PPS = 8 mM and Fe(III) = 6 mM altogether had the better removal efficiencies of COD and UV_{254} as well as the better SVI value compared with the optimal condition of SVI. By comparison between the performance of the two PPS-Fe(II) and PPS-Fe(III) processes, it can be observed that the PPS-Fe(II) process with the COD and UV_{254} removal efficiency of 92.63% and 95.81%, and the SVI value of 25 mL/L had the better performance than the PPS-Fe(III) process with the COD and UV_{254} removal efficiency of 88.73% and 90.39% and the SVI value of 28 mL/L. According to the results obtained by Rastogi et al. [34] the decomposition rate of 2-CB using

Table 9
Verifying the results

Responses	Operating parameters			Removal efficiency			Predicted removal efficiency			Confidence interval			Error (%)		
	pH	$K_2S_2O_8$ (mM)	Iron (mM)	COD (%)	UV_{254} (%)	SVI	COD (%)	UV_{254} (%)	SVI	COD (%)	UV_{254} (%)	SVI	COD	UV_{254}	SVI
Coagulation/PPS-Fe(II)															
COD	6	10	4	93.83	86.21	40.5	91.20	90.60	37.93	86.32–100	81.09–91.05	32.35–49.98	2.80	5.09	6.34
UV_{254}	6	8	4	92.63	95.81	25	90.67	91.35	26.43	91.09–95.91	86.50–100	19.50–33.84	2.11	4.65	5.72
SVI	3	4	2	58.17	62.62	16.5	57.85	60.66	13.31	35.60–67.05	56.92–67.69	13.80–22.53	0.55	3.12	19.33
Coagulation/PPS-Fe(III)															
COD	6	8	6	88.73	90.39	28	83.23	83.61	29.31	81.39–94.50	85.38–95.34	21.42–33.92	6.19	7.5	4.67
UV_{254}	6	8	6	88.73	90.39	28	83.23	83.61	29.31	81.39–94.50	85.38–95.34	21.42–33.92	6.19	7.5	4.67
SVI	3	4	2	48.30	52.34	8.5	46.69	45.88	8.18	41.45–54.08	47.86–55.66	5.80–14.53	3.33	12.34	3.76

Fe(II)–peroxymonosulfate (PMS) is more than the decomposition rate obtained by the Fe(III)–PMS process. During the redox, the electron transfer is done by the "bridged" and "outer sphere" mechanisms which Fe(II)–PMS followed by the outer sphere mechanism and because of more electron transfer rate in the outer sphere mechanism it is better than the bridged mechanism. The outer sphere mechanism does not require any transient bond formation, unlike the bridged mechanisms which makes it better to transfer electron [34].

By comparing the results of coagulation/SR-AOPs and SR-AOPs, it can be observed that the process of coagulation/SR-AOPs had the more removal efficiency compared with the process of SR-AOPs. Moreover, more than 80% of the oxidant and 50% catalyst could be saved employing coagulation as the pretreatment process. Additionally, the removal efficiencies of COD and UV_{254} in the pH close to the neutral range were appropriate and there was no need for acidification in the SR-AOPs. Therefore, the chemicals could be saved. Moreover, the amount of produced sludge in the process of SR-AOPs was much high. This is while using coagulation as the pretreatment, the amount of produced sludge in the process of SR-AOPs reduced down to 66%.

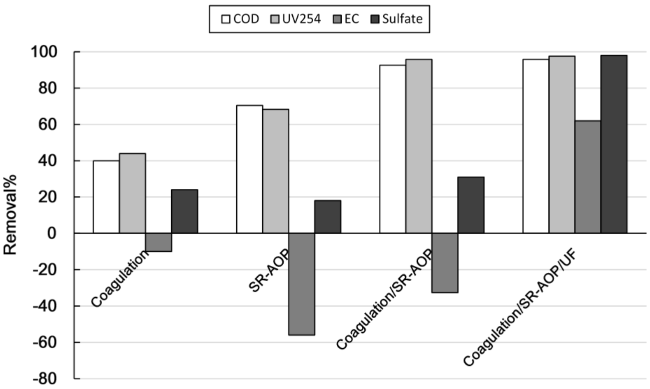


Fig. 5. The removal efficiency of coagulation, SR-AOP (PPS-Fe(II)), coagulation/SR-AOP (PPS-Fe(II)) and coagulation/SR-AOP (PPS-Fe(II))/ultrafiltration.

3.4. Combined treatment (coagulation/SR-AOPs (PPS-Fe(II))/ultrafiltration)

According to the results, although the removal efficiency of the coagulation/SR-AOPs process dramatically increased, but the effluent from the chemical unit had a considerable amount of sulfate and EC. So, to reduce the amount of remained sulfate and EC and generally the increase in the removal efficiency, the UF was employed. In Fig. 5, the removal efficiencies of COD, UV_{254}, EC and sulfate for the process of coagulation, SR-AOPs, coagulation/SR-AOPs (PPS-Fe(II)) and coagulation/SR-AOPs (PPS-Fe(II))/UF are presented. As shown in Fig. 5, in the coagulation, the amount of EC and sulfate removal efficiency increased up to 10.71% and 24.1%, respectively. By applying the pretreatment process, the removal efficiency of sulfate and EC compared with the process of SR-AOPs changed from 56.5% to 30.64% and 18.43% to 31%, respectively. According to the results obtained, using UF process after pretreatment by coagulation/PPS-Fe(II), the amount of sulfate, EC, COD and UV_{254} decreased to 99.44%, 62.05%, 97.35% and 98.75%, respectively. Beril Gönder et al. [46] also using UF and controlling the fouling condition reached high removal efficiency of sulfate and COD. The results showed that the hybrid system coagulation/SR-AOPs (PPS-Fe(II))/UF in addition to achieving high removal efficiency; the membrane fouling significantly reduced.

4. Conclusion

In this study, we showed that the pulp and paper wastewater can successfully be treated by combined approaches of coagulation/SR-AOPs (PPS-Fe(II))/UF. The following results can be concluded from the present work:

- The results of this study illustrated that using the $FeCl_3$ as the pretreatment process for SR-AOPs caused recovering a high percentage of fibers (98%).
- The sludge production and the amount of chemicals reduced up to 66% and 70%, respectively.
- The coagulation/PPS-Fe(II) process showed better performance with more than 90% removal efficiency in comparison with coagulation/PPS-Fe(III).
- The effects of pH, oxidant and catalyst concentration were evaluated for each of the processes, which the results represented the high effect of oxidant and catalyst concentration on the removal efficiency.
- The results of the confirmation experiments were in the confidence interval and the error percentage in all responses were in the acceptable range.
- The investigation indicated that the amount of sulfate and EC in the effluent of coagulation/SR-AOPs was still higher than environmental standards. In the final stage by using UF membrane, more than 95% of removal efficiency for sulfate, COD, aromatic compounds and 62% of removal efficiency for EC was observed.
- As the notable results of this study, we operated the SR-AOPs process after pretreatment without any change in the pH value and it significantly reduced the operating costs.
- At the end, we offer this method because of its simplicity and cost-effectiveness for the treatment of the pulp and paper wastewater.

Acknowledgment

The authors would like to thank Environmental Research Institute and Iran Pulp and Paper Industry (Chuka) for their support.

References

[1] L. Dsikowitzky, O. Botalova, S. Illgut, S. Bosowski, J. Schwarzbauer, Identification of characteristic organic contaminants in wastewaters from modern paper production sites and subsequent tracing in a river, J. Hazard. Mater., 300 (2015) 254–262.

[2] M. Kamali, Z. Khodaparast, Review on recent developments on pulp and paper mill wastewater treatment, Ecotoxicol. Environ. Saf., 114 (2015) 326–342.

[3] M. Ali, T.R. Sreekrishnan, Aquatic toxicity from pulp and paper mill effluents: a review, Adv. Environ. Res., 5 (2001) 175–196.

[4] F.J. Rivas, F. Beltrán, F. Carvalho, B. Acedo, O. Gimeno, Stabilized leachates: sequential coagulation–flocculation+chemical oxidation process, J. Hazard. Mater., 116 (2004) 95–102.

[5] C. Bouasla, M.E.-H. Samar, F. Ismail, Degradation of methyl violet 6B dye by the Fenton process, Desalination, 254 (2010) 35–41.

[6] K. Taghavi, A. Pendashteh, S.P. Mozhdehi, Combined Fenton-like oxidation and aerobic MBBR biological processes for treatment of the wastewater of detergent industries, Desal. Wat. Treat., 77 (2017) 206–214.

[7] E. Neyens, J. Baeyens, A review of classic Fenton's peroxidation as an advanced oxidation technique, J. Hazard. Mater., 98 (2003) 33–50.

[8] J. Bergendahl, S. Hubbard, D. Grasso, Pilot-scale Fenton's oxidation of organic contaminants in groundwater using autochthonous iron, J. Hazard. Mater., 99 (2003) 43–56.

[9] Y. Deng, C.M. Ezyske, Sulfate radical-advanced oxidation process (SR-AOP) for simultaneous removal of refractory organic contaminants and ammonia in landfill leachate, Water Res., 45 (2011) 6189–6194.

[10] S. Rodriguez, L. Vasquez, D. Costa, A. Romero, A. Santos, Oxidation of Orange G by persulfate activated by Fe(II), Fe(III) and zero valent iron (ZVI), Chemosphere, 101 (2014) 86–92.

[11] D. Salari, A. Niaei, S. Aber, M.H. Rasoulifard, The photooxidative destruction of CI Basic Yellow 2 using $UV/S_2O_8^{2-}$ process in a rectangular continuous photoreactor, J. Hazard. Mater., 166 (2009) 61–66.

[12] G.P. Anipsitakis, D.D. Dionysiou, Radical generation by the interaction of transition metals with common oxidants, Environ. Sci. Technol., 38 (2004) 3705–3712.

[13] E.E. Mitsika, C. Christophoridis, K. Fytianos, Fenton and Fenton-like oxidation of pesticide acetamiprid in water samples: kinetic study of the degradation and optimization using response surface methodology, Chemosphere, 93 (2013) 1818–1825.

[14] M. Gholami, B. Abbasi Souraki, A. Pendashteh, M. Bagherian Marzouni, Efficiency evaluation of the membrane/AOPs for paper mill wastewater treatment, Environ. Technol., 38 (2017) 1127–1138.

[15] N. Jaafarzadeh, M. Omidinasab, F. Ghanbari, Combined electrocoagulation and UV-based sulfate radical oxidation processes for treatment of pulp and paper wastewater, Process Saf. Environ. Prot., 102 (2016) 462–472.

[16] T.K. Lau, W. Chu, N.J. Graham, The aqueous degradation of butylated hydroxyanisole by $UV/S_2O_8^{2-}$: study of reaction mechanisms via dimerization and mineralization, Environ. Sci. Technol., 41 (2007) 613–619.

[17] J. Deng, Y. Shao, N. Gao, Y. Deng, C. Tan, S. Zhou, Zero-valent iron/persulfate (Fe^0/PS) oxidation acetaminophen in water, Int. J. Environ. Sci. Technol., 11 (2014) 881–890.

[18] L. Zhou, W. Zheng, Y. Ji, J. Zhang, C. Zeng, Y. Zhang, Q. Wang, X. Yang, Ferrous-activated persulfate oxidation of arsenic(III) and diuron in aquatic system, J. Hazard. Mater., 263 (2013) 422–430.

[19] P. Shukla, H. Sun, S. Wang, H.M. Ang, M.O. Tadé, Co-SBA-15 for heterogeneous oxidation of phenol with sulfate radical for wastewater treatment, Catal. Today, 175 (2011) 380–385.

[20] J. Kronholm, M.-L. Riekkola, Potassium persulfate as oxidant in pressurized hot water, Environ. Sci. Technol., 33 (1999) 2095–2099.

[21] A. Eaton, L.S. Clesceri, E.W. Rice, A.E. Greenberg, M. Franson, APHA: Standard Methods for the Examination of Water and Wastewater, Centennial Edition, APHA, AWWA, WEF, Washington, D.C., USA, 2005.

[22] M. Dehghani, E. Shahsavani, M. Farzadkia, M.R. Samaei, Optimizing photo-Fenton like process for the removal of diesel fuel from the aqueous phase, J. Environ. Health Sci. Eng., 12 (2014) 87.

[23] S. Aber, D. Salari, M. Parsa, Employing the Taguchi method to obtain the optimum conditions of coagulation–flocculation process in tannery wastewater treatment, Chem. Eng. J., 162 (2010) 127–134.

[24] N. Daneshvar, A. Khataee, M. Rasoulifard, M. Pourhassan, Biodegradation of dye solution containing Malachite Green: optimization of effective parameters using Taguchi method, J. Hazard. Mater., 143 (2007) 214–219.

[25] A. Ayguna, T. Yilmazb, Improvement of coagulation-flocculation process for treatment of detergent wastewaters using coagulant aids, Chemosphere, 1 (2010) 97–101.

[26] J.M. Ebeling, P.L. Sibrell, S.R. Ogden, S.T. Summerfelt, Evaluation of chemical coagulation–flocculation aids for the removal of suspended solids and phosphorus from intensive recirculating aquaculture effluent discharge, Aquacult. Eng., 29 (2003) 23–42.

[27] N.G. Pizzi, Water Treatment Operator Handbook, American Water Works Association, Loveland, 2011.

[28] T.L. Engelhardt, Coagulation, Flocculation and Clarification of Drinking Water, Drinking Water Sector, Hach Company, Loveland, 2010.

[29] M.I. Badawy, F.E. Gohary, M.Y. Ghaly, M.E.M. Ali, Enhancement of olive mill wastewater biodegradation by homogeneous and heterogeneous photocatalytic oxidation, J. Hazard. Mater., 169 (2009) 673–679.

[30] C. Liang, C.J. Bruell, M.C. Marley, K.L. Sperry, Persulfate oxidation for in situ remediation of TCE. I. Activated by ferrous ion with and without a persulfate–thiosulfate redox couple, Chemosphere, 55 (2004) 1213–1223.

[31] F. Benitez, J. Acero, F. Real, F. Rubio, A. Leal, The role of hydroxyl radicals for the decomposition of p-hydroxy phenylacetic acid in aqueous solutions, Water Res., 35 (2001) 1338–1343.

[32] G. Ginni, S. Adishkumar, J. Rajesh Banu, N. Yogalakshmi, Treatment of pulp and paper mill wastewater by solar photo-Fenton process, Desal. Wat. Treat., 52 (2014) 2457–2464.

[33] X.-R. Xu, X.-Z. Li, Degradation of azo dye Orange G in aqueous solutions by persulfate with ferrous ion, Sep. Purif. Technol., 72 (2010) 105–111.

[34] A. Rastogi, S.R. Al-Abed, D.D. Dionysiou, Sulfate radical-based ferrous–peroxymonosulfate oxidative system for PCBs degradation in aqueous and sediment systems, Appl. Catal., B, 85 (2009) 171–179.

[35] J.-P. Wang, Y.-Z. Chen, X.-W. Ge, H.-Q. Yu, Optimization of coagulation–flocculation process for a paper-recycling wastewater treatment using response surface methodology, Colloids Surf., A, 302 (2007) 204–210.

[36] C. Liang, I.-L. Lee, I.-Y. Hsu, C.-P. Liang, Y.-L. Lin, Persulfate oxidation of trichloroethylene with and without iron activation in porous media, Chemosphere, 70 (2008) 426–435.

[37] Y.-q. Zhang, X.-f. Xie, W.-l. Huang, S.-b. Huang, Degradation of aniline by Fe^{2+}-activated persulfate oxidation at ambient temperature, J. Cent. South Univ., 20 (2013) 1010–1014.

[38] H. Kusic, I. Peternel, N. Koprivanac, A. Loncaric Bozic, Iron-activated persulfate oxidation of an azo dye in model wastewater: influence of iron activator type on process optimization, J. Environ. Eng., 137 (2010) 454–463.

[39] X.-J. Ma, H.-L. Xia, Treatment of water-based printing ink wastewater by Fenton process combined with coagulation, J. Hazard. Mater., 162 (2009) 386–390.

[40] J. Naumczyk, J. Bogacki, P. Marcinowski, P. Kowalik, Cosmetic wastewater treatment by coagulation and advanced oxidation processes, Environ. Technol., 35 (2014) 541–548.

[41] W.K. Lafi, M. Al-Anber, Z.A. Al-Anber, M. Al-Shannag, A. Khalil, Coagulation and advanced oxidation processes in the treatment of olive mill wastewater (OMW), Desal. Wat. Treat., 24 (2010) 251–256.

[42] Y.-C. Lee, S.-L. Lo, P.-T. Chiueh, D.-G. Chang, Efficient decomposition of perfluorocarboxylic acids in aqueous solution using microwave-induced persulfate, Water Res., 43 (2009) 2811–2816.

[43] J.-M. Wang, H.-J. Yan, J.-M. Zhou, S.-X. Li, G.-C. Gui, Optimization of parameters for an aluminum melting furnace using the Taguchi approach, Appl. Therm. Eng., 33 (2012) 33–43.

[44] Z.B. Gönder, Y. Kaya, I. Vergili, H. Barlas, Optimization of filtration conditions for CIP wastewater treatment by nanofiltration process using Taguchi approach, Sep. Purif. Technol., 70 (2010) 265–273.

[45] Y.Ş. Yildiz, Optimization of Bomaplex Red CR-L dye removal from aqueous solution by electrocoagulation using aluminum electrodes, J. Hazard. Mater., 153 (2008) 194–200.

[46] Z. Beril Gönder, S. Arayici, H. Barlas, Treatment of pulp and paper mill wastewater using ultrafiltration process: optimization of the fouling and rejections, Ind. Eng. Chem. Res., 51 (2012) 6184–6195.