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Ozonation of an effluent of oil refineries for COD and sulfide removal

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ABSTRACT

Wastewater treatment for water reuse is one of the main concerns in oil refineries since it can lead to high economic and environmental benefits. This paper deals with treatment of an effluents of Shiraz oil refinery called Slops reservoirs effluent by means of ozone as an advanced oxidation agent. For this purpose, ozone is well dispersed at a dose of 5 g/h and effective transferred concentration of 2335 mg/L using a gas distributor into a semi-batch reactor containing 1 L of the wastewater. In order to determine the efficiency of the treatment, the removal percentage of COD and sulfide was selected as studying parameters. The effects of initial sulfide and COD concentrations, presence of UV light, initial pH, and temperature were investigated on the studying parameters. According to the obtained results, the highest removal rate occurred during the first 30 min reaction time. Also it has been observed that, for the initial sulfide concentration of 350 mg/L and the initial COD concentration of 975 mg/L, the ozonation process after 45 min resulted in 100% sulfide removal under optimum initial pH of 9.4 and optimum temperature of 15˚C and presence of UV light. While at the same conditions, 92% of COD removal has been achieved for 60 min ozonation. Also, water turbidity level significantly reduced during the treatment.

Keywords: Reuse; Effluents of Shiraz oil refinery; Slops; Ozonation; COD and sulfide removal

1. Introduction

Wastewater streams from oil refineries can contain a number of chemicals which originate from crude oil. Typical contaminants are petroleum hydrocarbons, heavy metals, phenolic compounds, sulfides, and ammonia. The concentrations of the toxic components in petroleum hydrocarbon are high and the problem is more intensive compared to other sources of pollution [1].

Shiraz oil refining company engages in crude oil refining and offers petroleum products, such as liquid petroleum gas, motor gasoline, kerosene, gas oil, fuel oil, sulfur, brimstone, jet fuel, and bitumen. The company was founded in 1973 and locates in the southwest of Iran. Knocked out drum and API unit

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(the unit in which a device designed to separate gross amounts of oil from the wastewater effluents of oil refineries), effluents of this refinery contain large amounts of hydrogen sulfide and petroleum hydrocarbons dissolved in water.

Petroleum hydrocarbons may contain aromatic compounds, such as benzene, toluene, ethyl benzene, and xylene (BTEX). These aromatic fractions are toxic and cause serious harmful effects on environment and human health [2]. Hydrogen sulfide (H_2S) is slightly soluble in water and gives water a characteristic "rotten egg" taste. It is very poisonous, corrosive, flammable and explosive, and can cause odor problems at concentration as low as 0.05 mg/L.

Based on the nature of the wastes, treatment techniques can be categorized into physical, chemical, and biological methods. A complete treatment system may consists of a combination of these methods. Selection of the best treatment option for remediation of industrial wastewaters depends on the quality standards to be met and the cost of the treatment.

The AOPs have been derived from high energy oxidants, such as ozone and H_2O_2 and/or photons that are able to produce highly reactive intermediates hydroxyl radicals (oxidation potential: 2.8 V) [3]. The hydroxyl radical ($^{\cdot}OH$) is a strong, non-selective chemical oxidant which acts very quickly with most organic and inorganic compounds. Hydroxyl radical first oxidizes organic contaminants and finally mineralizes them to CO_2 and H_2O (Reaction (1)) [4,5].

$$\text{Organic contaminants} + {}^{\cdot}\text{OH} \rightarrow \text{Intermediates} \rightarrow CO_2 + H_2O \quad (1)$$

AOPs are considered as a highly effective means of water treatment contributing to the effective removal of those organic pollutants not treatable by conventional techniques owing to their low biodegradability or high stability [6].

It has been extensively proved that AOPs can improve the biological treatability of wastewaters, thus enhancing the removal of both organic matter and recalcitrant compound and in order to reduce operating costs, AOPs can be used as pre- and/or post-treatment of biological systems [5,6]. There are several photochemical and non-photochemical methods for generation hydroxyl radicals. Some of them are as follows: ozonation at elevated pH, ozone + hydrogen peroxide (O_3/H_2O_2), ozone + catalyst (O_3/CAT), O_3/UV, H_2O_2/UV, O_3/H_2O_2/UV, and photocatalytic oxidation (UV/TiO_2). The main advantages of these methods are high rates of pollutant oxidation, flexibility concerning water quality variations, and small dimension of the equipment [6,7].

Ozone is typically produced by an electric discharge in gas-phase oxygen. It has been known as an environmental disinfector and safe oxidizer in water treatment area. Ozone can oxidize organic and inorganic matter present in wastewater, such as phenols, detergents, sulfides, and nitrates [8,9]. The ozonation is a promising treatment process due to its unique features, such as no sludge generation and the high potential for color removal. Also, it has been reported in the open literature that the taste, odor, and clarity of ozonated water are also improved [10,11]. Ozone is unstable in aqueous mediums; therefore, the degradation of species may occur due to a combination of reactions with $^{\cdot}OH$ radicals and with molecular ozone. The rate of the attack by $^{\cdot}OH$ radicals is typically 10^6–10^9 times faster than the corresponding reaction rate for molecular ozone [12].

UV oxidation will efficiently treat a wide range of industrial and process wastewaters without any pretreatment [13]. UV photons are able to activate O_3 and H_2O_2 molecules [14]. In this way, the formation of hydroxyl radicals is promoted. The capital and operating costs for the UV/O_3 and UV/H_2O_2 systems vary widely depending on the wastewater flow rate, types, and concentrations of contaminants present, and the required removal degree [15,16].

Data from water treatment plants showed that the ozonation process was more effective than prechlorination in reduction of effluent turbidities [17]. Coagulation-ozonation also can effectively reduce the coagulant dosage by improving particle destabilization and aggregation, decrease trihalomethanes, and also improve filtered and water turbidity [18–21].

Inorganic species are generally eliminated using preoxidation. In that way, metallic ions can be removed, as they form insoluble species upon oxidation [22]. Ozone is a strong oxidizer and effective in controlling sulfide and organic-related odors in wastewater collection and treatment systems [23]. Ozone is widely used alone or as a simple combined oxidant to treat various types of specific contaminants, such as haloacetic acid [24], dibutyl sulfide [25], antibiotics [26], colored and bio-refractory compounds [27], and cyanide [28].

Although some research has been conducted on the organic compounds removal from oil refineries wastewaters using AOPs [29–31], less attention has been given to the simultaneous removal of organic and inorganic compounds from industrial effluents.

Therefore, in this study, applying ozone for degradation of the Shiraz oil refinery effluent which contains large amounts of hydrogen sulfide and

Table 1
The characteristics of the raw wastewater and diluted wastewater

Parameter	Characteristics of raw wastewater	Characteristics of 50 times diluted wastewater
pH	9.5–10.5	9.4
COD (mg/L)	48,000–50,000	975
Sulfide (mg/L)	17,000–18,000	350
Turbidity (NTU)	17–20	14.1

petroleum hydrocarbons in a semi-batch system was investigated with the aim of generating water for reuse. The efficiency of the system is obtained by determining the percentage of sulfide and COD removal. The influence of different operating parameters, such as initial COD and sulfide concentrations, UV light, initial pH, and temperature have been studied. Finally, in the last section, the ability of the system to reduce water turbidity has also been checked.

2. Materials and methods

2.1. Wastewater characteristics

Raw wastewater was obtained from slops reservoirs of Shiraz oil refinery situated in southwest of Shiraz, Iran. Samples were collected from the point that the wastewater is just leaving the slops reservoirs. Currently, this waste was diluted about 200 times and sent to the biological treatment unit and after that, used for agricultural purposes afterwards.

Due to the pungent smell of wastewater and high concentrations of contaminants that would disrupt the measurement of the samples, raw wastewater was diluted 50 times with distilled water. This dilution was maintained through the entire experimental part. Sample bottles contain a stabilizing chemical were used to prevent the hydrogen sulfide from escaping when the bottle was opened at the lab and maintained at 4˚C to prevent volatile organic compounds to be vent out. Table 1 represents the characteristics of the raw wastewater and diluted wastewater which is used for the entire experiments.

2.2. Chemicals and apparatuses

$K_2Cr_2O_7$, H_2SO_4, $HgSO_4$,and Ag_2SO_4, all of analytical reagent grades, were purchased from Merck company in

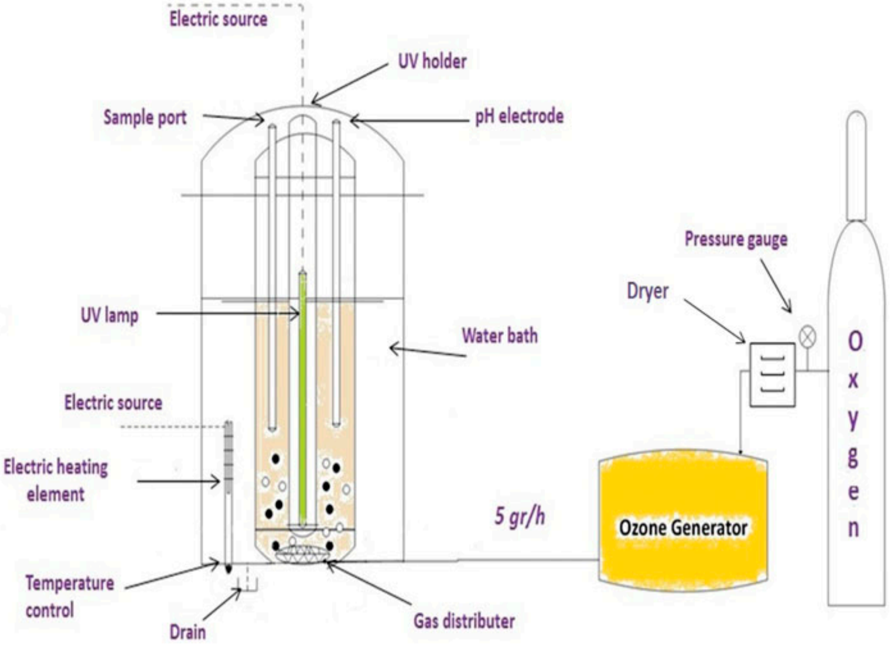

Fig. 1. Schematic diagram of used semi-batch AOP reactor.

order to prepare two synthetic solutions for COD tests. The COD was determined using the closed reflux colorimetric method, according to the standard methods [32]. Hach Lange, DR 2800 spectrophotometer was used to analyze and read COD and sulfide values. The turbidity was determined using 2100p Hach Lange Turbidimeter.

2.3. Procedure and analysis

A schematic diagram of the used semi-batch reactor system is shown in Fig. 1. Ozone was produced by an ozone generator using oxygen after passing through a set of column dryers. The dryers were equipped with molecular sieves of 5 A and 10 A. Ozone generator machine named MOG-5 was from French company of the ARDA Green Technology. The oxygen delivery machine was from BNP Ozone Technology Co. Ltd. When oxygen inlet rate was 1 L/min, this machine produced 5 g/h pure ozone. The effective transferred ozone under this condition was equal to 2,335 mg/L. The ozonated oxygen was well dispersed using gas distributor through a semi-batch reactor containing 1 L of the wastewater. An ultraviolet lamp (6 W, maximum intensity at a wavelength of 254 nm) was attached into the Pyrex glass tube in the center of the reactor for UV/O_3 experiments. Reactor temperature was adjusted with an electric heating element, which is located in a water bath around the reactor. The pH was measured using a HACH portable pH/mVmeter and the temperature was measured using a thermometer. Temporal samples were taken from the sampling port for COD and sulfide tests. The COD was determined using closed reflux colorimetric method. (Procedure is equivalent to Standard Method 5220-D). The spectrophotometer was used to analyze and read COD values under 600 nm wavelengths. The concentration of sulfide was determined using US.EPA Methylene Blue Method. (Procedure is equivalent to Standard Method 4500-S^{2-} D) [32]. Sample dilution was performed while required.

3. Results and discussion

Various tests were performed in order to determine the efficiency of the system in degradation of sulfide and COD. The percentage of sulfide and COD removal was determined as follows:

$$\%\ \text{Sulfide Removal} = \frac{[S^{2-}]_0 - [S^{2-}]_t}{[S^{2-}]_0} \times 100 \qquad (2)$$

$$\%\ \text{COD Removal} = \frac{[\text{COD}]_0 - [\text{COD}]_t}{[\text{COD}]_0} \times 100 \qquad (3)$$

3.1. Effects of initial concentration

Initial concentration is one of the main factors that influences on the removal efficiency of the substances. In order to analyze the effect of initial concentration of the pollutants, other than experiments with 50 times dilution, experiments using 25 times and 100 times dilution were also performed. Fig. 2(a) and (b) present the effect of the initial value of COD and sulfide at constant ozone addition rate. It can be observed that, both COD and sulfide removal increased with ozonation time. The initial COD and sulfide concentrations of 567 and 170 mg/L were obtained after 100 times dilution, respectively. Similarly, 1,771 and 680 mg/L

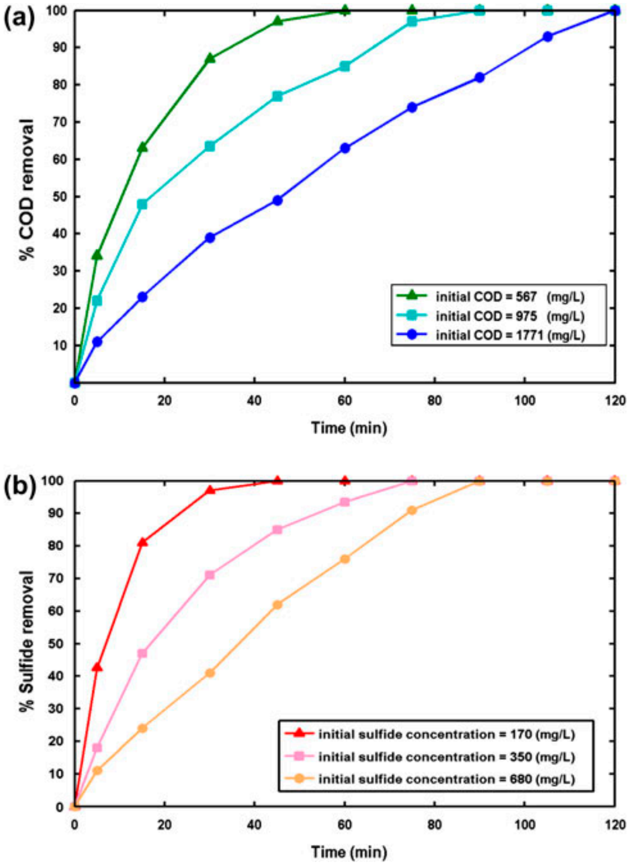

Fig. 2. Variation of (a) COD removal % and (b) Sulfide removal % with ozonation time at different initial concentration (Ozone flow rate: 5 g/h, Temperature: 25°C, Initial pH: 9.4).

were the initial COD and sulfide concentrations after 25 times dilution, respectively.

H_2S is in equilibrium with bisulfide ion (HS^-) and sulfide (S^{2-}); H_2S is prevailing up to pH 7, between pH 7, and 11 more than 50% is HS^- and above pH 11, S^{2-} predominates. At pH 9.4, most of the dissolved H_2S is in the form of HS^- and S^{2-} [33]. In an aqueous solution, ozone reacts with hydrogen sulfide in two competing simultaneous reactions, one to produce elemental sulfur (Reaction (4)), and one to produce sulfuric acid (Reaction (5)).

$$H_2S + O_3 \rightarrow S + O_2 + H_2O \tag{4}$$

$$3H_2S + 4O_3 \rightarrow 3H_2SO_4 \tag{5}$$

According to Fig. 2(a), the COD removal percentage has reduced from 87 to 39%, while the initial COD value increased from 567 to 1,771 mg/L for 30 min of ozonation. Also, as presented in Fig. 2(b), the percentage of sulfide removal has reduced from 97 to 41%, while the initial sulfide value increased from 170 to 680 mg/L for 30 min of zonation. These can be attributed due to the increased ozone consumption with an increase in the initial COD and sulfide concentration. As the ozone availability is fixed for a constant ozone mass flow rate (5 g/h), resulting in reduction of the percentage COD and sulfide removal, it should be noted that, for all initial COD and sulfide concentrations, all of the parameters are kept constant.

3.2. Effects of UV light

For an efficient ozone photolysis, UV lamps must have a maximum radiation output at 254 nm. Many organic contaminants absorb UV energy in the range of 200–300 nm and decompose due to direct photolysis or become excited and more reactive with chemical oxidants like hydrogen peroxide and ozone. Ozone readily absorbs UV radiation at 254 nm wavelength producing H_2O_2 as an intermediate, which then decomposes to $^{\cdot}OH$ (Reactions (6) and (7)) [2,17].

$$O_3 + h\nu \rightarrow O_2 + O(^1D) \tag{6}$$

$$O(^1D) + H_2O \rightarrow H_2O_2 \rightarrow 2^{\cdot}OH \tag{7}$$

During this process, ultraviolet radiation is used to cleave the O–O bond and increase the generation of the hydroxyl radicals.

For studying the effect of UV light, ozone injection was followed by a UV lamp (6 W, at a wavelength of 254 nm). The UV lamp was positioned inside a Pyrex tube and totally immersed in the reactor; therefore, the maximum light utilization was achieved. The intensity of ultraviolet light around the lamp at this wavelength was about 520 mW/cm^2.

Fig. 3(a) and (b) represent the variation of COD and sulfide removal percentage in the presence and absence of UV light, at a constant ozone addition rate. All other parameters were constant. The suspended solids will indeed form a surface upon which hydrophobic compounds will adsorb, and therefore slow their treatment rates. Therefore, the presence of UV light in conjunction with ozone only increased the removal efficiency about five percent.

It should be noted that, although addition of the UV light shows slight increase in removal efficiency, interactions with other parameters should be considered. As an example, pH plays an important role in stabilizing the organic compounds. Several studies have shown that the operating pH and the temperature indirectly affect the intensity of the UV radiation [34–36]. Therefore, all the subsequent experiments were conducted in the presence of UV light.

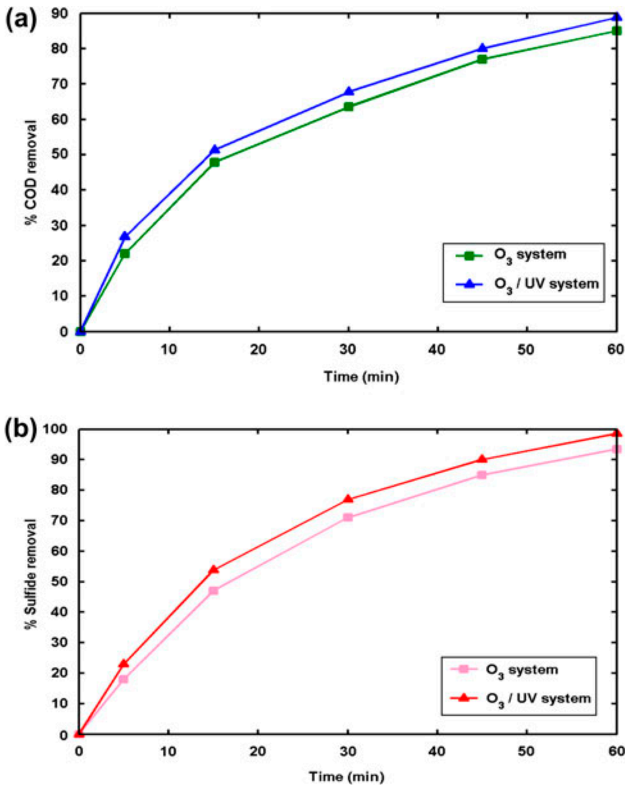

Fig. 3. Variation of (a) COD removal % and (b) Sulfide removal % with ozonation time at presence and absence of UV light (Initial COD: 975 mg/L, Initial Sulfide: 350 mg/L, Ozone flow rate: 5 g/h, Temperature: 25°C, Initial pH: 9.4).

3.3. Effect of pH

To evaluate the effect of the initial solution pH, removal of COD and sulfide were conducted covering acid, neutral, and basic conditions. The pH value is a key factor for ozone stability in aqueous solutions and also determines the manner in which the ozonation process occurs. Fig. 4(a) and (b) indicate the effect of the initial pH, on the COD and sulfide removal percentage. It can be ascertained from the Fig. 4(a) and (b) that for a 60-min ozonation time, while the solution pH increased from 3.5 to 9.4, the COD and sulfide removal percentages are increased from 48 to 89% and from 65 to 99%, respectively. Indeed, at acidic pH levels (less than 7), ozone reacts primarily as the O_3 molecule by relatively slow reactions; while at elevated pH (above 8), it decomposes rapidly into hydroxyl radicals.

At alkaline pH, hydroxyl anions react as initiators to accelerate the ozone decomposition, yielding $^{\cdot}OH$ radicals more rapidly. The hydroxyl radicals have a higher oxidizing potential than molecular ozone leading to an increased mineralization. At higher pH, ozone is decomposed according to Reactions (8) and (9). Previous studies have shown that the pH range of 8–10 is the most suitable range for organic molecules oxidation [12,37].

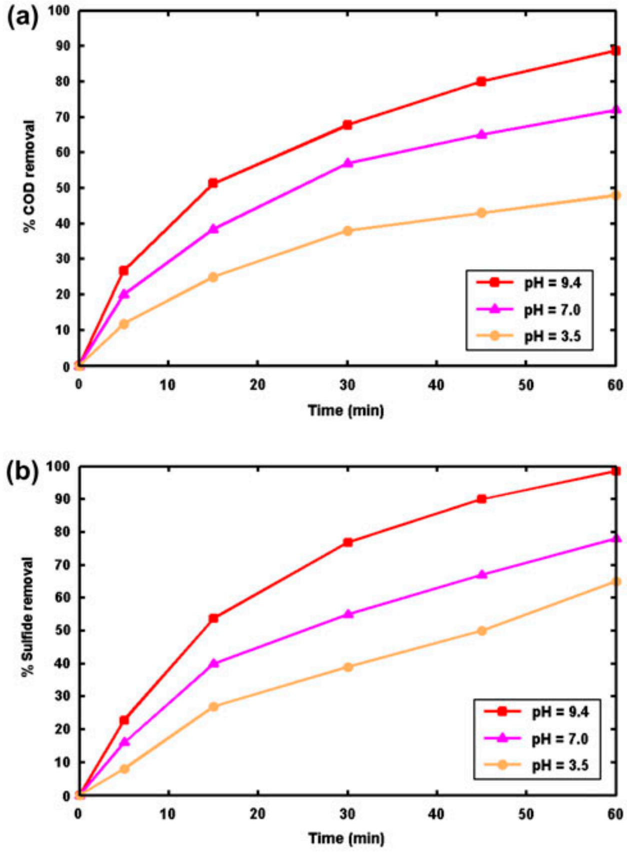

Fig. 4. Variation of (a) COD removal % and (b) Sulfide removal % with ozonation time at different pH (Ozone flow rate: 5 g/h, Initial COD: 975 mg/L, Initial Sulfide: 350 mg/L, Temperature: 25˚C).

$$O_3 + OH^{-1} \rightarrow HO_2^- + O_2 \tag{8}$$

$$O_3 + HO_2^- \rightarrow {}^{\cdot}OH + {}^{\cdot}O_2^- + O_2 \tag{9}$$

3.4. Effects of temperature

When ozone is used to treat water or wastewater, it must be transferred from gas phase, in which it is generated, to liquid phase. The single most important variable that affects ozone mass transfer is the concentration of dissolved ozone. Ozone generator received pure oxygen at the rate of 1 L/min and produced 5 g/h pure ozone. The effective transferred ozone under this condition was equal to 2,335 mg/L.

Solubility of a substance depends on the physical and chemical properties of the solute and solvent. Generally, gases become less soluble in water at higher temperature; therefore, increasing the temperature would decrease the production rate of hydroxyl radicals, and consequently the extent of COD and sulfide removal.

Fig. 5(a) and (b) represent the effect of the temperature on percentage of COD and sulfide. As Fig. 5(a) shows, COD removal gradually decreased with an increase in temperature. Actually, it was observed 25% less COD removal percent at 50˚C compared to that of 25˚C for a 60 min ozonation and given operating conditions. Although increase in temperature increases the rate constant of the reaction [38], the negative effect of temperature on COD removal percent mainly owes to the sharp reduction in ozone dissolution at high temperature.

On the other hand, as shown in Fig. 5(b), similar result was not observed in the case of sulfide reduction, and sulfide removal percent practiced has a considerable increase in temperature. Indeed, although rising the temperature reduces the solubility of ozone in water and consequently reduces the amount of ozone available for the reaction, it increases the rate of sulfide evaporation. The reason is, although at pH of 9.4, most of the dissolved sulfides are in the form of HS^- and S^{2-}, according to Le Chatelier's principle, increasing the temperature shifts the equilibrium toward molecular hydrogen sulfide (H_2S). Also, the solubility of hydrogen sulfide at atmospheric pressure and in temperature of 25˚C is 0.34 g/(100 g of water), while this value reduced to 0.19 g/(100 g of water) when temperature is increased to 50˚C [39,40].

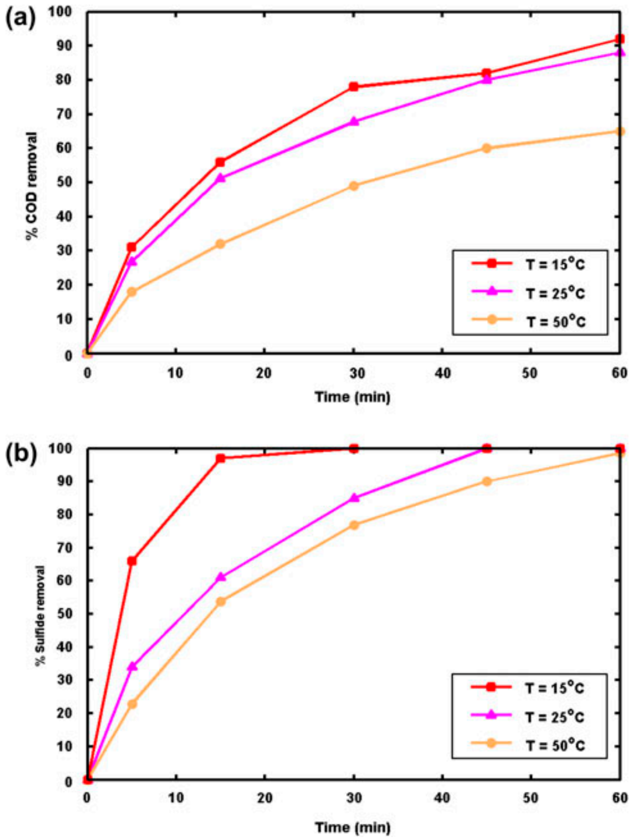

Fig. 5. Variation of (a) COD removal % and (b) Sulfide removal % with ozonation time at different temperature (Ozone flow rate: 5 g/h, Initial COD: 975 mg/L, Initial Sulfide: 350 mg/L, Initial pH: 9.4).

Therefore, at temperature ranges of more than 25℃, sulfide removal percent increases with temperature mainly due to evaporation, and at temperature less than 25℃, sulfide removal percent increases with a decrease in temperature mainly due to high ozone availability to oxidize sulfide [41].

3.5. Effect of the system on turbidity reduction

Fluids may contain suspended solid matter consisting of particles of different sizes. While some suspended materials are large and heavy enough to settle rapidly to the bottom of the container, some other small particles will settle only very slowly or not at all if the sample is regularly agitated. These small solid particles cause the liquid to appear turbid. Direct molecular reaction path of ozone promotes favorable effects of coagulation, while the organic matter becomes more polar [42]. Coagulating effects preceded by an ozonation process have often been termed as micro-flocculation or ozone-induced particle destabilization [43].

Mechanisms by which the ozonation process can influence the coagulation process and consequently improved the water turbidity are as follows [44]:

(1) Abatement in the molecular size and assists in particles destabilization of the absorbed organics.
(2) Formation of stable larger particles by an oxidative polymerization process, which may result in better settling of particles.
(3) Rupture of organometallic bonds permitting metals like, Fe(III) and Mn(IV), to act as coagulants to react with remaining organics, and thus ensure enhanced precipitation.
(4) Release of different biopolymers through lyses of algae cells which may act as coagulants, thereby enhancing the agglomeration process.
(5) Based on the obtained results, the zonation process under the optimum operating condition (temperature of 15℃ and pH of 9.4 and presence of UV light) reduced turbidity level from 14.1 in to 3.4 NTU after 60 min of reaction.

4. Conclusions

The AOPs were successfully employed to treat the wastewater including both organic and inorganic contaminants. In this paper, the performance of O_3 system on the degradation of sulfide and COD of one of the Shiraz oil refinery effluents was studied.

According to the obtained result, at the optimal temperature of 15℃ and initial of pH 9.4, the maximum COD removal of 92% was achieved after 60 min of ozonation in presence of UV light, while at the same condition, sulfide was completely removed after 45 min at the same condition. At this optimal condition, the treated wastewater found the required characteristic to be reused in cooling towers, boilers, and other process units.

Based on the results observed, the following conclusions can be made:

- The COD removal percentage is significantly influenced by the initial effluent concentration.
- Although rising in temperature causes an increase in the evaporation rate of the sulfide, temperature showed an adverse effect on the COD and sulfide removal efficiency due to the reduction of ozone solubility in the solution.
- The efficiency of the ozonation process is increased with pH enhancement.
- Water turbidity levels are significantly reduced under optimum condition.

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