

Chelate-modified fenton treatment of sulfidic spent caustic

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Abstract—Spent caustic can be treated by several treatment methods. Among the advanced techniques, Fenton reagent has many advantages. But since spent caustic contains excessive amounts of sulfide compounds, utilizing this technique in treatment of such wastewaters is not economical. The acid neutralization step, which was applied as the pretreatment process, showed an 84% COD abatement at temperature equal to 80 °C and a pH equal to 4.0. The acid neutralized wastewater was then introduced to the chelate-modified Fenton system and oxidized. Using a ratio of tartrate/Fe²⁺=1.1, reaction time=50 min, temperature=95 °C, Fe²⁺=110 mg/l and a ratio of H₂O₂/COD=1.2 in the chelate-modified Fenton system at an optimum pH value equal to 1.9, total COD abatement of the wastewater reached over 99.4%. Having tartrate added to the Fenton system, a series of photochemical reactions enhanced Fe²⁺ and hydroxyl radicals' generation. This method has proved to be the recommended technique for the contamination abatement of spent caustic.

Keywords: Chelate-modified Fenton Reagent, Fractional Factorial Design, Peroxidation, Tartrate, Spent Caustic

INTRODUCTION

Spent caustic is a waste byproduct of industrial processes like gas scrubbing, petroleum sweetening, and hydrocarbons washing in refineries and petrochemical plants [1]. The US Resource Conservation and Recovery Act classifies this compound as hazardous waste because of its noxious odor, hazardous characteristics and toxicity (Table 1) [2].

Different research groups have attempted to develop a more efficient alternative for spent caustic treatment. Wet air oxidation (WAO) was suggested to lower chemical oxygen demand (COD) in spent caustic [3]. In one study [4], 78% of COD was removed through wet air oxidation. Electrocoagulation was reported to achieve up to 80% of COD removal [5]. A biological treatment under halo-alkaline conditions was successfully developed to elim-

inate 93% of COD in spent caustic [6]. However, wet air oxidation is costly and a safety concern as it requires severe conditions including high temperature and pressure [7]. Furthermore, because of high concentrations of non-biodegradable compounds, the typical biological treatment of spent caustic has been unsuccessful and limited [8,9].

Hydrogen peroxide (H₂O₂) with standard electrode potentials of 1.80 and 0.87 V (at pH 0 and 14, respectively) is a strong oxidant [10] which can be utilized in the treatment of different inorganic and organic compounds and has been used for removal of cyanides, sulfites, and some other compounds [11].

Due to low rates of reaction at reasonable hydrogen peroxide concentrations, solo oxidation by hydrogen peroxide is not capable for treatment of recalcitrant wastewater chemicals such as cyanides and chlorinated aromatics. Hydrogen peroxide has to be

Table 1. Characteristics of typical refinery caustic streams [4]

	Naphthenic		Cresylic		Sulfidic
	Jet fuel/Kerosene	Diesel	Strong caustic operation	Dilute caustic operation	
NaOH, wt%	1-4	1-4	10-15	1-4	2-10
Sulfide as S ²⁻ , wt%	0-0.1	Trace	0-1	0-0.2	0.5-4
Mercaptide as S ⁻ , wt%	0-0.5	0-0.5	0-4	0-0.5	0.1-4
Naphthenic acids, wt%	2-10	2-15			
Carbonates as CO ₃ , wt%			0-0.5	0-0.1	
Cresylic, wt%	1-3	0-1	10-25	2-5	0-4
Ammonia					Trace
pH	12-14	12-14	12-14	12-14	13-14

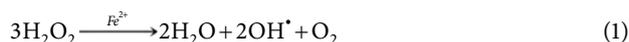
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activated to form hydroxyl radicals; thus its full oxidation potential may be exploited. This activation can be achieved by applying ultraviolet irradiation, ozone or a number of transition metal salts [12].

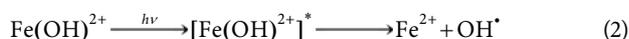
Advanced oxidation processes are categorized by those in which highly active radical intermediates are generated [13]. If hydrogen peroxide is activated by iron salts, the oxidation reaction obtained by this process is referred to as Fenton peroxidation or Fenton reaction. The intermediation of Fe^{2+} provides a path to the generation of hydroxyl radicals (OH^{\bullet}) that are more effective as an oxidizer than the nascent oxygen molecules (Eq. (1)).



Note that a fraction of ferrous ions oxidizes in this reaction to ferric salts leading to high consumption of iron besides generation of troublesome precipitates.

Although the chemistry of Fenton was introduced about 100 years ago, its application for organic pollutant degradation was not known until the late 1960s [14]. Among advanced oxidation processes, the Fenton reaction [15] has been used successfully for wastewater treatment. Since the Fenton reaction is fast, it is used as a highly efficient oxidation process in treatment of wastewaters with particularly high chemical oxygen demand [16].

One problem with the Fenton reaction is the weak absorption of free Fe^{3+} in the wavelength region between 290 and 400 nm, but there is enough evidence to verify that the hydrated or solvated complex iron pairs have different absorption spectra shifted towards the longer wavelengths. This phenomenon can make such species photo-chemically active in the presence of visible light [17]. Since its charge transfer band powerfully overlaps the solar ultraviolet-visible spectrum, it can be easily photo-dissociated under sunlight [18,19]. As a result of electron transfer from the ligand to ferric in the excited state, it is believed that the photolysis process can produce hydroxyl radicals (Eq. (2)) [20]:



If Fe^{3+} and carboxylate moieties are exposed to one another, hydroxyl radicals can be produced through another photochemical mechanism. Fe^{3+} can form persistent complexes with multidentate carboxylate ligands like citrate and tartrate. Therefore, in acidic conditions the photo-activity of Fe^{3+} species undergoes preferable changes in the presence of such complexes [20]. Complexing carboxylate ligands can be induced (through visible light radiation) to transfer electrons to Fe^{3+} in the excited complexes. In such conditions, the Fe^{3+} complexes have electron deficiency and can reduce O_2 to $\text{O}_2^{\bullet-}$ which eventually reacts to generate the OH radicals [21-23].

The fact that the photo-dissociation of ferric oxalate complexes can generate H_2O_2 and OH radicals was first demonstrated by Zuo and Hoigné [21]. Degradation and decolorization promotion of dyes in wastewaters by using Fe^{3+} -carboxylate complexes under ultraviolet and visible light irradiation was reported by Deng and Wu [24-26]. The yield of photo-dissociation can be improved by applying carboxylic acids.

Due to high chemical oxygen demand of spent caustic, this oxidation technique consumes a large amount of oxidant. In addition,

high S^{2-} concentration increases ferric ions consumption, which consequently decreases iron catalyst activity leading to the conclusion that Fenton reaction is a non-economical method for spent caustic treatment. The so-believed high photochemical activity of ferric tartrate complexes can promote the generation of some active species like hydroxyl radicals, which could have a significant cost reducing role in the treatment of wastewaters.

In this study, the potentially influential factors and their effects on chelate-modified Fenton peroxidation in spent caustic treatment were investigated through some experiments. In addition, by utilizing the tartrate ion as the chelating agent to modify the Fenton system, which is the first of its kind, the aforementioned problems are addressed. In fact, we tried to decrease the consumption of the oxidant and Fe catalyst and, at the same time, exploit the potential advantages of utilizing the chelating agent in the Fenton system to increase the efficiency of the mentioned treatment system.

EXPERIMENTAL PROCEDURE

1. Wastewater

Wastewater sample was obtained from an olefin plant manufacturing ethylene. Characteristics of the wastewater are presented in Table 2.

2. Fenton Peroxidation

This study shows that the treatment efficiency of sulfidic spent caustic by Fenton peroxidation depends mostly on reaction time, temperature, ferrous ion concentration, chelating agent/ferrous ion concentration ratio, hydrogen peroxide concentration/COD ratio, type and pH of the utilized acid.

3. Peroxidation System

The peroxidation system was conducted in two series of experiments, and tartrate ions were used as a chelating agent. The pH of a 100 ml wastewater sample was adjusted to the experiment conditions. The temperature was raised to 80 °C for neutralization pretreatment. It was brought back to ambient after pretreatment and then the mixture was transferred to a 600 ml glass Fenton reactor where hydrogen peroxide, ferrous sulfate and chelating agent (which was sodium tartrate in this study) were each added by a pre-calculated amount. The mixture of reactants was continuously mixed by a magnetic stirrer. The peroxidation conditions are presented in Table 3.

3-1. Effect of Reaction Time on COD Removal

Two different sets of experiment, one with and the other without chelating agent, were conducted to investigate the effect of

Table 2. Characteristics of the olefin plant spent caustic

Item	Value
S^{2-} (mg/l)	4130
NaOH (wt%)	6.7
COD (mg/l)	8900
Temperature (°C)	30
pH	13.8
BOD (mg/l)	93
TSS (g/l)	1.14

Table 3. Peroxidation conditions

Parameters	First series of experiments	Second series of experiments
Reaction time (min)	20-40	50-70
Temperature (°C)	50-70	75-95
[Fe ²⁺] (mg/l)	35-65	80-110
[Tartrate]/[Fe ²⁺] (mg//mg/l)	0.0-0.9	1.1-1.5
[H ₂ O ₂]/[COD] (mg//mg/l)	0.9-1.1	1.2-1.5
pH	0.5-1.5	1.9-2.5
Acid type	Sulfuric, hydrochloric, nitric	Sulfuric, hydrochloric, phosphoric

Table 4. Neutralization test results (pH=4.0, temperature=80 °C, time=30 min)

Test no.	Acid type	pH	COD concentration (mg/l)		COD removal eff. (%)
			Before neutralization	After neutralization	
1	98 wt% H ₂ SO ₄	4.0	8900	1380	84.49
2	85 wt% H ₃ PO ₄	4.0	8900	1520	82.92
3	37 wt% HCl	4.0	8900	1340	84.94
4	65 wt% HNO ₃	4.0	8900	1310	85.28

reaction time on COD removal. Samples were withdrawn at 2, 5, 10, 15, 30, 50, 70 and 90 minutes and then immediately analyzed. Each experiment set was conducted at pH values (0.5, 1.0, 1.5, 1.9, 2.2, 2.5, 4.0, 5.0 and 6.0), adjusted by sulfuric acid. In addition, to prevent the interference of hydrogen peroxide on COD analysis, the samples taken from Fenton reactor were pretreated [27]. To prohibit further propagation in Fenton peroxidation reaction, 1N sodium bicarbonate solution was added to the withdrawn samples as buffer. The excess hydrogen peroxide was eliminated by adding catalase enzyme. The generated iron hydroxides were removed through filtration and then the COD of withdrawn samples was measured. Peroxide test strips (Merck Co., Germany) were used to verify the absence of the excess hydrogen peroxide.

3-2. Chemicals and Analytical Methods

Total suspended solids (TSS), sulfide, sulfite and sulfate concentrations, chemical oxygen demand and biological oxygen demand analytical tests were conducted according to APHA standard methods [28]. All the tests, with exception of BOD, were conducted in triplicate (n=3).

Standard solutions, NaOH, H₃PO₄, HCl and H₂SO₄ all in 1 N concentration, 98 wt% sulfuric acid, 85 wt% phosphoric acid, 37 wt% hydrochloric acid, 65 wt% nitric acid, 35 wt% H₂O₂, sodium tartrate, ferrous sulfate heptahydrate, catalase (crystal suspension in water), silver nitrate and potassium dichromate were obtained from Merck Co. (Germany). The pH of the solution was measured with a HACH H260G pH meter.

RESULTS AND DISCUSSION

1. Original Characteristics of Wastewater

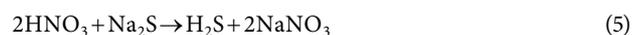
The wastewater was obtained from an olefin plant which produces ethylene. Initial characteristics of the spent caustic are presented in Table 2. The result of a BOD/COD=0.1 indicates that the wastewater must be considered as not biodegradable. On the other hand, the spent caustic contained a large amount of S²⁻ (4,130

mg/l), which mostly can be removed by acid neutralization. Note that almost all COD in original wastewater is of soluble type. The suspended solids do not exert appreciable amounts of COD. The analytical test results have indicated that the solids are metal oxide/hydroxide resulting from water hardness or corrosion products of pipelines and fittings. They might also have entered the effluent system by local wind and particulates with silt and sand origin.

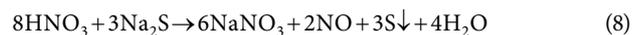
2. Acid Neutralization

The experimental results of acid neutralization by four different types of acid showed the average total COD removal reaching to about 84% (Table 4).

The neutralization reactions between the sulfides in wastewater and acids are as follows:



Note that the neutralization reactions are double-replacement reactions which occur in pH ranges higher than 2.0, but if the pH is lower than 2.0, sulfuric and nitric acids will act as oxidizing agents (Eqs. (7) and (8)):

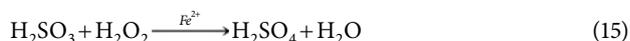
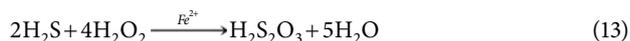


Since the neutralization reactions occur exposed to oxygen (of the air), the produced H₂S undergoes a series of autoxidation reactions as follows [29]:





The remaining H_2S is then oxidized into H_2SO_4 through Fenton reactions, according to Eqs. (13), (14) and (15) as follows [7]:



3. COD Removal

After neutralization, the wastewater samples with a COD concentration $\approx 1,340$ mg/l were exposed to peroxidation conditions in the Fenton reactor. The COD analyses demonstrated that the first series of experiments was successful to eliminate an average of 97.42% of the COD remained from neutralization step, where the second series of experiments showed a promising 99.4% average COD removal efficiency.

A fraction of sulfide that was not oxidized by acid neutralization into elemental sulfur, remains in the solution at different oxidation levels. SO_3^{2-} and SO_4^{2-} were predominant species detected among them (Table 5). The reported results exclude the samples which were exposed to sulfuric acid at any step in the neutralization and/or peroxidation experiments. The nature of the remaining chemical species in the treated samples was congruent to the species of the neutralized effluent, which are also provided in Table 5.

4. Effect of the Influential Operational Parameters on the COD Removal

4-1. Effect of Temperature on COD Removal

Very few studies have so far illustrated the effect of temperature

Table 5. Concentration of sulfur species in the raw and acid neutralized samples

Species	Raw sample (mg/L)	Treated sample (mg/L)
S^{2-}	4130.00	Nil
SO_3^{2-}	47.52	4.07
SO_4^{2-}	13.41	1093.11

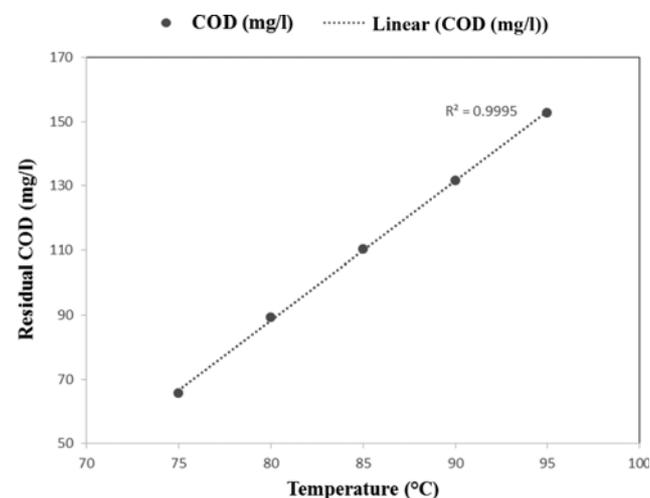


Fig. 1. Effect of temperature on COD removal.

on the efficiency of the Fenton system, and the few that exist are not in good agreement with one another [15,30]. Since the Fenton reaction is exothermic, if the temperature exceeds 75°C , cooling is strongly suggested [31]. As can be seen in Fig. 1, by increasing the temperature, the residual COD of spent caustic (initial COD $\approx 1,340$ mg/l) significantly increases.

It is believed that such behavior has two reasons. First, as the temperature rises, a larger fraction of hydrogen peroxide is used in water-oxygen production reactions, leaving a smaller amount for generation of OH radicals (Eq. (16)). Second, by increasing the temperature, the production rate of thiosulfuric acid is increased (Eq. (13)) [14].



Thiosulfate is more persistent towards oxidation in comparison to other sulfur compounds. It is suggested to employ temperatures below 75°C .

4-2. Effect of Reaction Time on COD Removal

Fig. 2 shows the COD removal, determined for pH values (0.5, 1.0, 1.5, 1.9, 2.2, 2.5, 4.0, 5.0 and 6.0). pH was adjusted by sulfuric acid.

The conditions under which Fig. 2 was obtained appear in Table 6. The same experiment was performed using chelating agent tartrate. The conditions under which Fig. 3 was obtained appear in Table 7. The pH was adjusted by sulfuric acid. Fig. 3 shows the effect.

It is noticeable that COD removal is slower in the first 10 min

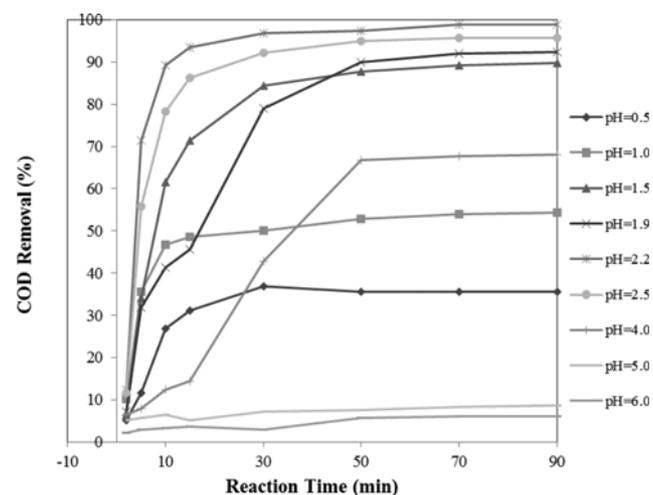


Fig. 2. Effect of reaction time on COD removal without using a chelating agent.

Table 6. Experiment conditions for COD removal without using a chelating agent

Variable	Value
Initial COD of the influent (mg/l)	1340
Total time of experiment (min)	90
Fe^{2+} concentration (mg/l)	110
$\text{H}_2\text{O}_2/\text{COD}$ (mg/mg)	1.35
Temperature	Ambient

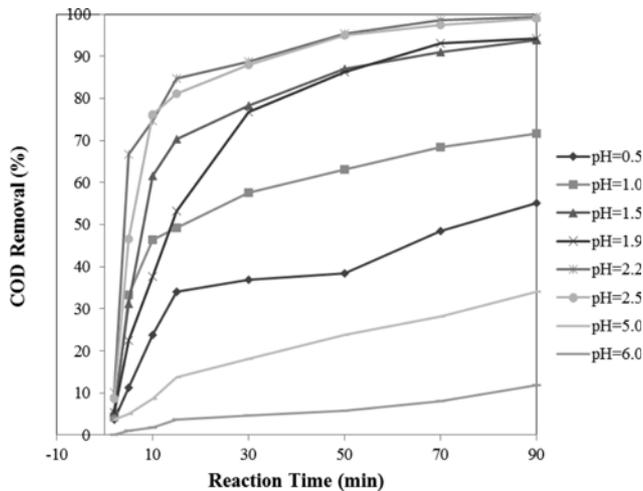


Fig. 3. Effect of reaction time on COD removal by using a chelating agent.

Table 7. Experiment conditions for COD removal with using a chelating agent

Variable	Value
Initial COD of the influent (mg/l)	1340
Total time of experiment (min)	90
chelating agent/Fe ²⁺ (mg/mg)	1.3
Fe ²⁺ concentration (mg/l)	110
H ₂ O ₂ /COD (mg/mg)	1.35
Temperature	Ambient

of peroxidation than that in Fig. 3. However, it finally ends up to a similar removal efficiency, which means the life-time of catalyst is longer than that in the first experiment. After 50 minutes of reaction, the reaction time has meager effect on COD removal. In fact, it can be observed that after the first 15-20 minutes of Fenton reaction, the rate of reaction will significantly decrease. This is due to OH radical consumption in the Fenton system. Since the overall life span of the Fenton catalyst is longer than hydrogen peroxide (due to simultaneous redox reactions) and also since the hydrogen peroxide is a raw material for the Fenton system and is exposed to consumption without any generation, after the first 15-20 minutes, the amount of hydrogen peroxide significantly decreases, therefore, eventually the amount of OH radicals decreases and thus, the reaction practically stops. At industrial scales, the suggested reaction time for this Fenton system is lower than 25 minutes. Such result is of paramount importance for the full scale application of the Fenton reagent, considering that it allows a noteworthy COD abatement in a brief period of time.

4-3. Effect of Catalyst Concentration on COD Removal

The negative impact of catalyst concentration on COD removal is well observed in Fig. 4. According to the Haber-Weiss cycle in the Fenton system (Fig. 5), Fe³⁺ is reduced to Fe²⁺. For this reaction to occur, two simultaneous events are needed: (a) Fe³⁺ must reduce to Fe²⁺ in presence of hydroperoxide and (b) Fe²⁺ must be able to transfer an electron to hydrogen peroxide. This is possible only if the standard electrode potential of Fe²⁺ is in the range of -324

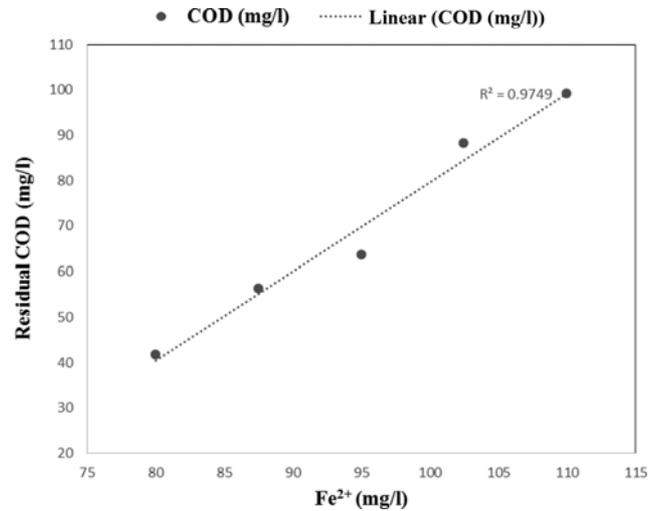


Fig. 4. Effect of catalyst concentration on COD removal.

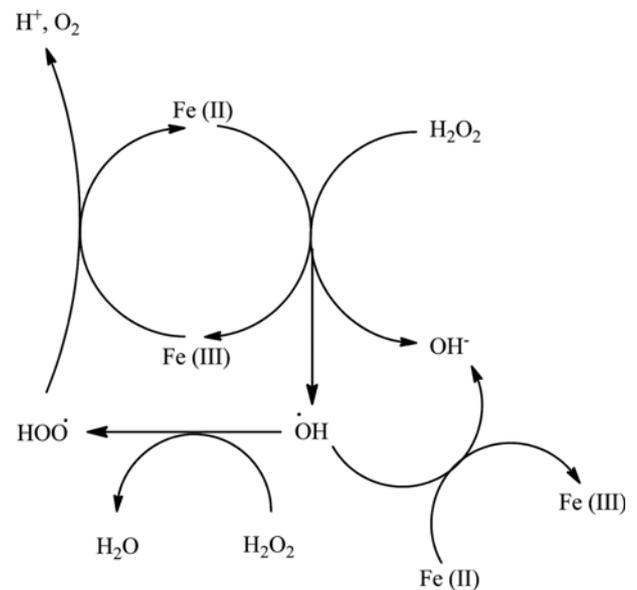


Fig. 5. Haber-Weiss cycle.

and +460 mV [31]. In addition, utilizing extended amounts of the Fe catalyst will cause an increase in the quantities of the unmarked Fe salts. This will lead to the increase of the undesired total dissolved solids of the treated effluent [15].

As the catalyst concentration increases, Fe³⁺ generation rate overtakes the hydroperoxide production rate; therefore, there would be trivial amounts of the Fe²⁺ present in the system. All these would point to a certain condition in which the Fenton system efficiency is poor and thus the COD of the under-treatment system increases. The reason for the slower hydroperoxide production rate than the Fe³⁺ generation is that the hydroperoxide production is a function of (a) the rate in which Fe²⁺ is oxidized to Fe³⁺ and (b) the rate in which hydroperoxide is generated from hydroxyl radicals and since the rate in which Fe²⁺ is oxidized to Fe³⁺ is under the influence of the amount of the hydrogen peroxide present in the Fenton system, catalyst concentration increment to the amounts in which could

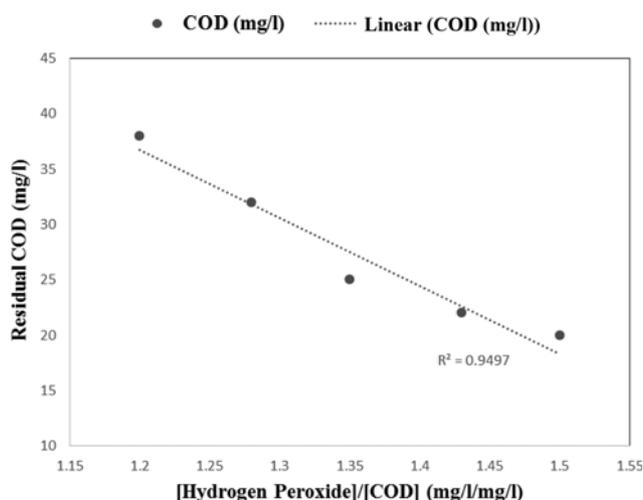


Fig. 6. Effect of the hydrogen peroxide concentration as $[H_2O_2]/[COD]$ on COD removal.

not satisfy this rate, would have a negative impact on Fenton system efficiency. In full scale applications, the lowest catalyst concentration (as long as such concentration is in the ideal range) is suggested.

4-4. Effect of Hydrogen Peroxide Concentration on COD Removal

Based on Fig. 6, increasing the hydrogen peroxide concentration is of a great benefit for the Fenton system. An increase in hydroxyl radical generation is followed by an increase in hydrogen peroxide concentration. In fact, the centrality of the Fenton system is based on the hydroxyl radicals' production rate. The more OH radicals present in the system, the more would be the efficiency of the system for COD removal. For safety measures it is suggested to employ the ratio $[H_2O_2]/[COD]$ below 1.5. Besides that, the unutilized H_2O_2 will have negative impact on COD analysis [15,32,33]. Note that if a biological treatment system is to be followed as a secondary or post-treatment system after a Fenton system, the excess amount of H_2O_2 from the Fenton system is lethal to almost all of the organisms. For a number of reasons it is advisable to avoid employment of excessive amounts of hydrogen peroxide in the Fenton system [34].

5. Effect of Other Operational Parameters on COD Removal

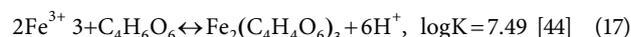
During this study we noticed that the acid type has the least influence among all influential variables.

The Fenton system is highly sensitive to pH. This is believed to be due to its effect on hydrogen peroxide and Fe species [30,33,35,36]. At higher pH ranges, oxohydroxides, which are relatively inactive species, are strongly present. These species are ultimately the cause of the formation of insoluble ferric hydroxides [36]. The precipitation of these species will lead to a situation in which less OH radicals are produced. It also has been reported that by increase of the pH, OH radicals will have lower oxidation potential. A decrease of 0.95 V versus normal hydrogen electrode is reported [37]. It also has been observed that at higher pH ranges, the acceleration of H_2O_2 auto-decomposition is significantly increased [38].

On the other hand, at lower pH ranges, the formation of some Fe-complexes, which are relatively inactive compared to other species, increases [39]. In addition, in the highly acidic solutions at a

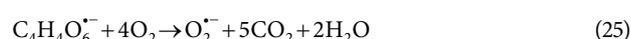
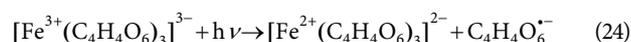
pH range of 0.5 to 1.0, H_3O^+ ions form. Hydrogen peroxide is more stable in presence of these ions and consequently has lower reactivity with ferrous ions [39-41], which can be well observed in Figs. 2 and 3. This explains the reduced activity of Fenton reagent in that range [42]. Therefore, to achieve a more efficient Fenton system, pH monitoring and control is of the utmost importance. The present study suggests an optimum pH between 1.9 and 2.5 for this chelate-modified system.

Tartrate ions react with Fenton reagents to form tartrate radicals, $C_4H_4O_6^{\cdot-}$, along with radicals generated through Fenton reaction (Eqs. (17)-(27)). These radicals take part in reactions leading to oxidation of organic compounds, thus promoting enhancement of these reactions [43]. Tartrate as a ligand also reacts with ferric ions to form a highly stable chelate



This reaction inhibits the formation of undesired Fe^{3+} precipitate.

The ferric carboxylate complexes behave as photochemically-active compounds in the visible range and undergo a series of photochemical ligand-to-metal charge transfer reactions through a reaction yielding Fe^{2+} ion and OH radical with a high quantum yield. It is believed that tartrate ion reacts with Fenton system as described below [43]:



By comparing Fig. 2 and Fig. 3, it can be noted that the overall mean COD removal in the case with tartrate (Fig. 3) is higher than the one without tartrate (61.07% in Fig. 2 versus 71.23% in Fig. 3). Hydroxyl radicals have higher quantum yield when the tartrate ions are present [45]. Fe^{3+} reduction also improves through chemical pathways that tartrate provides to the Fenton system [46]. The latter, in turn, increases the generation of hydroxyl radicals [47]. It is also believed that the solubility of hydrophobic pollutants in the Fenton system can be promoted in the presence of tartrate ions [48]. Furthermore, compared to typical Fenton system, photochemical reduction of Fe^{3+} to Fe^{2+} at near neutral pH can be enhanced through tartrate-modified Fenton system [45,47,49,50]. The overall effect of tartrate and its amplitude on Fenton system is presented in Fig. 7.

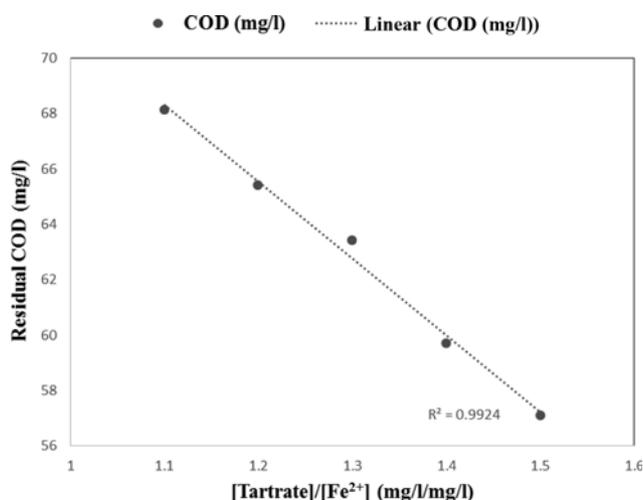


Fig. 7. Effect of the chelating agent concentration as $[\text{tartrate}]/[\text{Fe}^{2+}]$ on COD removal.

CONCLUSION

A major achievement in this study was to realize that about 84% of the sulfidic sulfur in a highly sulfide-concentrated effluent could be removed by a simple and cost effective acid neutralization step. Most of the remaining sulfide was oxidized to thiosulfate or sulfate by a chelate modified Fenton oxidation process. Operational parameters influencing the tartrate-modified Fenton peroxidation in spent caustic treatment have been studied. Seven factors were considered out of which four were later found to be not critically influential. The results show that temperatures higher than 75 °C have negative effect on COD removal. Such deduction is also true for when Fe^{2+} concentration is more than 80 mg/l. Although the higher ratio of $[\text{H}_2\text{O}_2]/[\text{COD}]$ results in higher efficiencies of the chelate-modified Fenton system, one should be careful to use ratios lower than 1.5 for the safety measures. During this study we observed that tartrate can enhance the Fenton system by providing photochemically favorable reaction pathways to promote the reduction of Fe^{3+} and improving the rate of quantum yield of active radicals' generation. In fact, an overall promotion about 10% in the COD removal yield was observed by employing the tartrate chelating agent. This elevation was observed to be around 20-25% when the pH most deviated from optimum, i.e., in the cases of highly acidic and near neutral conditions. In addition, this study showed that the ideal pH for the chelate-modified Fenton system is between 1.9 and 2.5, and the type of the utilized acid has almost no effect on the COD removal efficiency. The findings of this study showed the proposed method as an effective treatment system for this type of wastewaters.

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