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# Sulfide removal in petroleum refinery wastewater by chemical precipitation

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## Abstract

Sulfide removal by chemical precipitation from petroleum refinery wastewater was investigated. The wastewater samples were taken from the flocculation pond influent of TÜPRAŞ Kırıkkale Middle Anatolia Petroleum Refinery Wastewater Treatment Plant (WWTP) and physicochemical treatments using conventional coagulants which were partial precipitant [$FeCl_3 \cdot 6H_2O$ and $FeSO_4 \cdot 7H_2O$] and coagulant-aids [$Ca(OH)_2$ and $CaCO_3$] were applied to both raw and sulfide added wastewater. Sulfide and chemical oxygen demand (COD) removal efficiencies of $Fe^{3+}$ ions alone for sulfide added wastewaters having different pH values varied between 62–95 and 45–75%, respectively. In addition, removal efficiencies of sulfide (96–99%) and COD (50–80%) were obtained by using $Fe^{2+}$ ions together with $Ca(OH)_2$ as precipitant-aid under the same conditions. In experiments performed with raw wastewater which had different pH values, COD removal efficiencies of $Fe^{3+}$ and $Fe^{2+}$ ions together with $Ca(OH)_2$, were 50–80 and 32–50%, respectively.
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## 1. Introduction

Crude oil, as a mixture of hydrocarbons, is (theoretically) a biodegradable material. However, in very general terms (and as observed from elemental analyses), petroleum is a mixture of: (a) hydrocarbons; (b) nitrogen compounds; (c) oxygen compounds; (d) sulfur compounds; (e) metallic constituents [1]. Sulfur content is so important for refineries that crude oils are usually classified, in part, based upon the sulfur content. Thus, a sweet crude oil is one with low sulfur content, and a sour crude oil is one with high sulfur content [1,2]. Sulfur present in crude oil should be removed because of causing to spread unpleasant odor, spoiling properties of products, corrosion, inactivating the catalysts. Wastewater, generated by the catalytic hydrocracking and refining of various crude-oil fractions, contains, in addition to hydrocarbons, large amounts of nitrogen and sulfur, in the form of ammonia and hydrogen sulfide ($H_2S$), respectively [3]. Several problems are related to sulfide buildup, these include

corrosion of concrete sewer pipes, release of obnoxious odors to the urban atmosphere, safety hazards to sewer workers due to the toxicity of sulfide gas and negative impacts on the subsequent wastewater treatment [4,5]. Typical refinery wastewaters may contain 1 or 2 mg L$^{-1}$ sulfide, but certain units, such as sour water strippers, may produce sulfide concentrations as high as 150 mg L$^{-1}$ [2].

$H_2S$ is a highly toxic compound that can form in any aqueous system which contains both organic matter and sulfate. Such conditions are found in natural systems (e.g. the Black Sea) and can arise as a result of anthropogenic activities, including aquacultural practices and the production of anaerobic sewage and industrial wastewaters [6]. Hydrogen sulfide, as a highly undesirable contaminant, is produced in association with some industrial processes, such as gas streams from wastewater treatment, food processing, petroleum refining, tanneries, paper and pulp manufacturing and solid waste processing plants [3,7–10]. $H_2S$, which is the most important form of sulfur, exists in equilibrium with bisulfide ($HS^-$) and sulfide ($S^{2-}$) in aqueous solution and can volatilize to $H_2S$ gas [11]. As the most reduced form of sulfur, sulfide has a high oxygen demand of 2 mol $O_2$/1 mol $S^{2-}$ resulting in depletion of oxygen where sour wastewater is

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discharged [12]. $H_2S$ is a highly toxic compound to aquatic animal life in very low concentrations and has been the cause of mass fish mortality in aquaculture systems. The threshold limit value for fresh or salt water fish is 0.5 ppm [6,12].

Methods for sulfide removal in common use today are physicochemical processes which involve direct air stripping, oxidation or chemical precipitation [13,14]. However, biological methods for $H_2S$ removal have drawn attention since they are more efficient and more economical than physicochemical methods if proper operational conditions are maintained [15].

Sulfide removal may occur by precipitation with metals present in wastewater, such as iron, chromium, copper, zinc, nickel or cadmium. Sulfide precipitation is especially important in industrial wastewater and in anaerobic sludge digesters where metals have been concentrated in the sludge. The kinetics of the fast precipitation reaction between aqueous iron(II) and dissolved sulfide at 25 °C can be interpreted in terms of two competing reactions. These reactions may be represented by [16]:

$$Fe^{2+} + H_2S \rightarrow FeS_{(s)} + 2H^+ \qquad (1)$$

$$Fe^{2+} + 2HS^- \rightarrow Fe(HS)_{2(S)} \qquad (2)$$
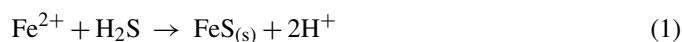
Only iron has been used as a chemical additive to intentionally remove sulfide; ferrous ions will precipitate sulfide as ferrous sulfide. Because the solubility product of ferrous sulfide is $3.7 \times 10^{-19}$ at 18 °C, the reaction is very effective in precipitating sulfides. Ferric ions will also precipitate sulfide through reduction of the iron to the ferrous ion and the sulfide is oxidized to sulfur. The ferrous ion is then available for direct precipitation with other sulfides, as shown by the following reaction:

$$2Fe^{3+} + S^{2-} \rightarrow 2Fe^{2+} + S^0 \qquad (3)$$

Several other iron sulfides may also form, including pyrrhotite, ferric sulfide ($Fe_2S_3$), smythite ($Fe_3S_4$) and $FeS_2$. Improved sulfide removal can be achieved through the addition of both ferric and ferrous salts. Experience in the field has shown that dissolved sulfide can be reduced to $0.2\,mg\,L^{-1}$ in this manner. The theoretical reaction to precipitate sulfide with ferrous and ferric ions is assumed to take the form shown by the following reaction [2]:

$$Fe^{2+} + 2Fe^{3+} + 4HS^- \rightarrow Fe_3S_4 + 4H^+ \qquad (4)$$
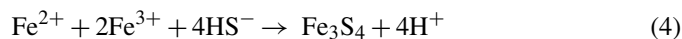
In this study, we precipitated sulfide in the petroleum refinery wastewater with conventional coagulants such as ferric chloride and ferrous sulfate. The objectives of this study were: (1) to determine optimum precipitant and its dosage for sulfide removal in both raw wastewater and sulfide added wastewater containing possible sulfide levels in order to prevent the damages of sulfide to activated sludge and other processes following the flocculation pond; (2) to contribute to treatment plant running with determined optimum dosages.

## 2. Materials and methods

### 2.1. Analysis

The total sulfide concentration, COD and alkalinity were determined using the iodometric method and open-reflux method described in standard methods [17] and titration method presented in water and wastewater technology [18], respectively. Conductivity and pH values were measured with conductimeter and pH electrode (Crison conductimeter 522 and Crison micro-pH 2000).

### 2.2. Solutions

The stock sulfide, iron(III) and iron(II) solutions were prepared by dissolving $Na_2S\cdot9H_2O$, $FeCl_3\cdot6H_2O$ and $FeSO_4\cdot7H_2O$ in deionized and distilled water, respectively. The concentrations of all stock solutions were $1000\,mg\,L^{-1}$. $Ca(OH)_2$ and $CaCO_3$ were added in solid form to the beakers at the beginning of mixing. All chemicals were analytical grade and were obtained from Merck GmbH.

### 2.3. Wastewater samples

The conventional treatment of the wastewater effluents in the Kırıkkale TÜPRAŞ refinery is based on the mechanical and physicochemical methods such as oil–water separation and coagulation and further biological treatment within the integrated activated sludge treatment plant. The refinery is refining crude oil both paraffinic and naphthenic base, an industry that is a discharger after purification into the Kızılırmak river, one of the most important rivers of Black Sea Basin. Wastewater samples for treatment were taken from flocculation pond influent of the WWTP. The flow scheme of the WWTP and sampling point are illustrated in Fig. 1.

### 2.4. Experimental procedures for chemical precipitation

In experimental studies, Jar test equipment (Welp Scientifica F.6/s) was used. Coagulants assumed to be partial chemical precipitants were added to 500 mL beakers and then stirred at 200 rpm (5 min) and 10 rpm (15 min). Beakers were left to settle for 30 min after stirring proceedings. In order to determine the effects of precipitant dosage on sulfide removal and other experimental parameters, samples were taken from 5 cm depth of supernatant surface after precipitation period.

Two conventional coagulants in part chemical precipitants were used in order to assess the effects to sulfide removal from petroleum wastewater. After physicochemical treatments (rapid and slow stirring, precipitation), samples which had supernatant with colorless, clear and no suspended solids were taken into account for determination of optimum precipitant dosage. In addition to physical characteristics mentioned, chemical results such as sulfide and COD removal efficiencies and economical respect of precipitants were evaluated in order to determine optimum dosages of them.
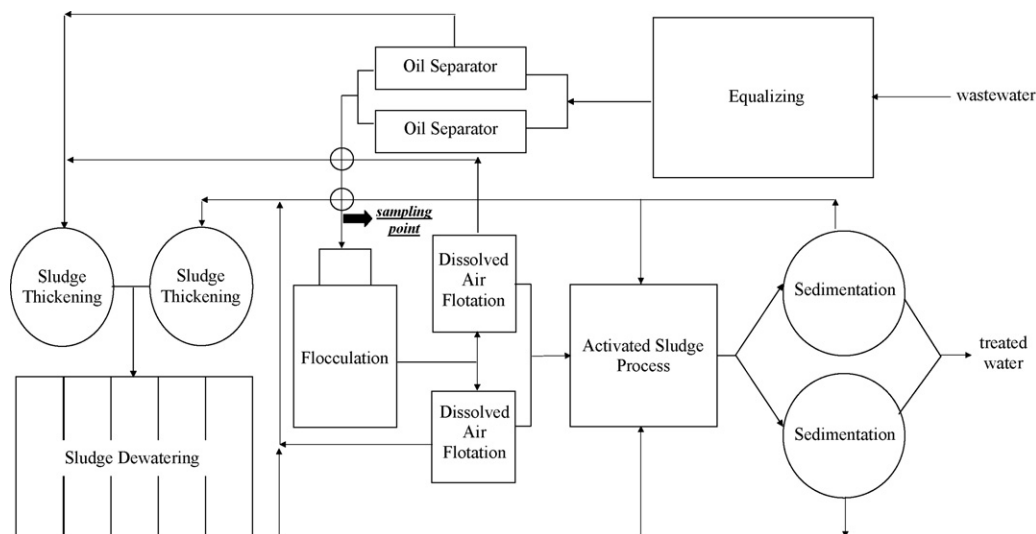
Fig. 1. The flow scheme of TÜPRAŞ Petroleum Refinery Wastewater Treatment Plant and sampling point.

## 3. Results and discussion

### 3.1. Precipitation experiments using $Fe^{3+}$ ion

#### 3.1.1. Raw wastewater

The characteristics of two raw wastewaters which one of them has high pH, and their changes after chemical precipitation using different $Fe^{3+}$ dosages between 10 and 60 mg L$^{-1}$ are presented in Table 1. Outcomes relating to raw wastewater with high pH (WW$_1$-B) are also given in Table 1. pH and total alkalinity values decreased, conductivity values increased with increasing $Fe^{3+}$ dosages. Buffering capacity of water had not remained and pH values had decreased below 5 for dosages above 40 mg Fe$^{3+}$ L$^{-1}$ for raw wastewater which had initial pH of 7.19 (WW$_1$-A). These conditions may involve risk to other treatment processes such as activated sludge in the plant. COD removal efficiencies between 50 and 70% were obtained at all chemical dosages.

Optimum precipitant dosage for WW$_1$-A may be selected as 30 mg Fe$^{3+}$ L$^{-1}$ considering characteristics of water after physicochemical treatments and other processes following flocculation unit in the treatment plant. As sulfide levels of raw wastewater were about 1 mg L$^{-1}$, COD parameter was considered to assess chemical dosages.

#### 3.1.2. Sulfide added wastewater

Sulfide levels around 20 mg L$^{-1}$ were considered because these concentrations inhibit the activated sludge process and around 40 mg L$^{-1}$ were taken into consideration as the highest level of sulfide existing in the wastewater. Sulfide added samples were subjected to chemical precipitation with Fe$^{3+}$ ion.

Fe$^{3+}$ dosages between 10 and 130 mg L$^{-1}$ with an increment of 10 mg L$^{-1}$ were applied to wastewater samples which contained about 20 mg S$^{2-}$ L$^{-1}$ (WW$_2$-A) and changes in parameters were observed. Furthermore, the chemical precipitation experiment was also carried out with no chemical addition in order to determine the mixing effect. At dosages between 10 and 30 mg L$^{-1}$, a black supernatant color and excess turbidity was observed and up to dosages of 60 mg L$^{-1}$, orange color of supernatants remained, so that, no precipitation was realized and the parameters were not examined for these dosages. The characteristics of wastewater and the results obtained from chemical precipitation using 0–120 mg Fe$^{3+}$ L$^{-1}$ dosages for

Table 1
The effect of Fe$^{3+}$ ion dosages used for sulfide removal by chemical precipitation on parameters of two raw wastewaters, WW$_1$, having different characteristics

| Parameters | WW$_1$ | | Precipitant dosage (mg Fe$^{3+}$ L$^{-1}$) | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | A | B | 0 | | 10 | | 20 | | 30 | | 40 | | 50 | | 60 | | 70 | |
| Sulfide (mg L$^{-1}$) | 2.2 | 1.6 | × | 1.4 | 2 | 0.8 | 1.2 | 0.6 | 1 | 0.6 | 0.7 | 0.4 | 0.8 | 0.4 | 1 | 0.6 | × | 0.4 |
| pH | 7.19 | 9.22 | × | 10 | 7.16 | 9.17 | 6.64 | 8.71 | 6.13 | 7.97 | 4.95 | 7.34 | 3.68 | 6.88 | 3.38 | 6.54 | × | 5.96 |
| T.Alk. (mg CaCO$_3$ L$^{-1}$) | 46 | 116 | × | 112 | 44 | 96 | 42 | 78 | 26 | 62 | 10 | 50 | 0 | 36 | 0 | 20 | × | 8 |
| COD (mg L$^{-1}$) | 220 | 192 | × | 172 | 100 | 96 | 84 | 80 | 72 | 68 | 44 | 64 | 72 | 68 | 68 | 64 | × | 16 |
| Conductivity (µS cm$^{-1}$) | 1473 | 1429 | × | 1389 | 1480 | 1427 | 1487 | 1460 | 1492 | 1502 | 1505 | 1509 | 1604 | 1517 | 1710 | 1519 | × | 1523 |
| Visual turbidity | + | + | × | − | − | − | − | − | − | − | − | − | − | − | + | − | × | − |
| Visual color | − | − | × | − | − | − | − | − | − | − | − | − | − | − | Orange | − | × | − |
| Sludge color | − | − | × | − | Orange–light brown | | | | | | | | | | | | | |

+: yes; −: no; ×: not done; A and B: separate wastewater samples taken from the flocculation pond influent of petroleum refinery WWTP at different dates.

Table 2

The effect of $Fe^{3+}$ ion dosages used for sulfide removal by chemical precipitation on parameters of two sulfide added ($\approx 20$ mg $S^{2-}$ $L^{-1}$) raw wastewaters, $WW_2$, having different characteristics

| Parameters | $WW_2$ A | B | Precipitant dosage (mg $Fe^{3+}$ $L^{-1}$) 0 | | 60 | | 70 | | 80 | | 90 | | 100 | | 110 | | 120 | | 130 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sulfide (mg $L^{-1}$) | 22 | 20.8 | 5.2 | 9.2 | × | 0.8 | × | 0.6 | 0.8 | 0.4 | 0.4 | 0.4 | 0.2 | 0.2 | 0.4 | 0.6 | 0.6 | 0.4 | × | 0.4 |
| pH | 8.44 | 9.28 | 8.37 | 10.1 | × | 7.08 | × | 6.79 | 6.57 | 6.52 | 6.2 | 6.27 | 4.1 | 6.17 | 3.47 | 5.88 | 3.21 | 5.5 | × | 4.95 |
| T.Alk. (mg $CaCO_3$ $L^{-1}$) | 86 | 136 | 84 | 132 | × | 44 | × | 38 | 20 | 30 | 14 | 28 | 0 | 24 | 0 | 14 | 0 | 10 | × | 4 |
| COD (mg $L^{-1}$) | 216 | 216 | 156 | 156 | × | 120 | × | 28 | 64 | 128 | 56 | 56 | 60 | 60 | 56 | 132 | 64 | 56 | × | 108 |
| Conductivity (µS $cm^{-1}$) | 1531 | 1455 | 1612 | 1421 | × | 1596 | × | 1607 | 1724 | 1587 | 1738 | 1602 | 1787 | 1624 | 1886 | 1664 | 1998 | 1673 | × | 1697 |
| Visual turbidity | + | + | + | − | × | − | × | − | − | − | − | − | − | − | − | − | − | − | × | − |
| Visual color | − | − | − | − | × | − | × | − | − | − | − | − | − | − | − | − | − | − | × | − |
| Sludge color | − | − | − | − | Orange–light brown | | | | | | | | | | | | | | | |

+: yes; −: no; ×: not done; A and B: separate wastewater samples taken from the flocculation pond influent of petroleum refinery WWTP at different dates.

$WW_2$-A and visual observations are summarized in Table 2. Optimum precipitant dosage may be selected 80 mg $Fe^{3+}$ $L^{-1}$ for this wastewater. At that dosage, sulfide level was reduced to 0.8 mg $L^{-1}$ and the removal efficiencies of COD and sulfide were 70.4 and 96.4%, respectively. The results obtained from sulfide added wastewater having high pH ($WW_2$-B) after treatments are also given in Table 2 in order to compare and evaluate of them.

In other experiments carried out with sulfide added wastewater, $Fe^{3+}$ dosages between 90 and 170 mg $L^{-1}$ with an increment of 10 mg $L^{-1}$ were applied to wastewater samples which contained approximately 40 mg $S^{2-}$ $L^{-1}$. As excess turbidity and orange color of supernatant remained after chemical precipitation, the experimental parameters were not examined for dosages between 90 and 110 mg $Fe^{3+}$ $L^{-1}$. The characteristics of wastewater and the results obtained from chemical precipitation using 120–170 mg $Fe^{3+}$ $L^{-1}$ dosages for wastewater containing about 40 mg $S^{2-}$ $L^{-1}$ ($WW_3$-A) and visual observations are summarized in Table 3. The results obtained from sulfide added wastewater with high pH ($WW_3$-B) after treatments are also tabulated in Table 3. Removal efficiencies of COD and sulfide versus $Fe^{3+}$ dosages applied to wastewaters containing different sulfide levels are illustrated in Fig. 2.

It was found that removal efficiencies for COD and sulfide at all dosages used changed between 60–80 and 90–97%, respectively. Optimum precipitant dosage may be selected as

120 mg $Fe^{3+}$ $L^{-1}$ for $WW_3$-A. At this dosage, sulfide level was reduced to 0.6 mg $L^{-1}$ and the removal efficiencies of COD and sulfide were 65.3 and 98.5%, respectively.

### 3.1.3. Raw wastewater having high pH level

Similar experimental studies were carried out with $WW_1$-B taken from the WWTP of the petroleum refinery at another date. The characteristics of that wastewater and the changes after chemical precipitation using different $Fe^{3+}$ dosages between 0 and 70 mg $L^{-1}$ are presented in Table 1.

It was observed that $WW_1$-B exhibited better flocculation characteristics than $WW_1$-A. Optimum precipitant dosage for $WW_1$-B may be selected as 20 mg $Fe^{3+}$ $L^{-1}$. It may be noted that increasing pH of wastewater decreases the required precipitant dosage for physicochemical treatment in the light of experimental studies.

### 3.1.4. Sulfide added wastewater having high pH level

$Fe^{3+}$ dosages between 60–130 and 120–170 mg $L^{-1}$ with an increment of 10 mg $L^{-1}$ were applied to $WW_2$-B and $WW_3$-B, respectively. Furthermore, chemical precipitation experiments were also carried out without chemical addition. The characteristics of $WW_2$-B and $WW_3$-B, and the results obtained from chemical precipitation are summarized in Tables 2 and 3, respectively. Removal efficiencies of COD and sulfide versus $Fe^{3+}$

Table 3

The effect of $Fe^{3+}$ ion dosages used for sulfide removal by chemical precipitation on parameters of two sulfide added ($\approx 40$ mg $S^{2-}$ $L^{-1}$) raw wastewaters, $WW_3$, having different characteristics

| Parameters | $WW_3$ A | B | Precipitant dosage (mg $Fe^{3+}$ $L^{-1}$) 0 | | 120 | | 130 | | 140 | | 150 | | 160 | | 170 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sulfide (mg $L^{-1}$) | 40 | 39.8 | × | 24.2 | 0.6 | 0.8 | 0.4 | 0.4 | 0.6 | 0.6 | 0.4 | 0.4 | 0.8 | 0.6 | 0.8 | 0.4 |
| pH | 9.2 | 10.2 | × | 10.1 | 6.06 | 6.51 | 5.41 | 6.44 | 3.7 | 6.22 | 3.28 | 6.03 | 3.15 | 5.76 | 3.03 | 4.87 |
| T.Alk. (mg $CaCO_3$ $L^{-1}$) | 114 | 160 | × | 174 | 24 | 26 | 8 | 24 | 0 | 22 | 0 | 14 | 0 | 10 | 0 | 4 |
| COD (mg $L^{-1}$) | 242 | 252 | × | 216 | 84 | 128 | 68 | 124 | 64 | 136 | 60 | 100 | 80 | 140 | 68 | 68 |
| Conductivity (µS $cm^{-1}$) | 1566 | 1460 | × | 1451 | 1858 | 1828 | 1877 | 1846 | 1969 | 1888 | 2150 | 1884 | 2230 | 1910 | 2310 | 1930 |
| Visual turbidity | + | + | × | − | − | − | − | − | − | − | − | − | − | − | + | − |
| Visual color | − | − | × | − | − | − | − | − | − | − | − | − | − | − | Orange | − |
| Sludge color | − | − | × | − | Orange–light brown | | | | | | | | | | | |

+: yes; −: no; ×: not done; A and B: separate wastewater samples taken from the flocculation pond influent of petroleum refinery WWTP at different dates.
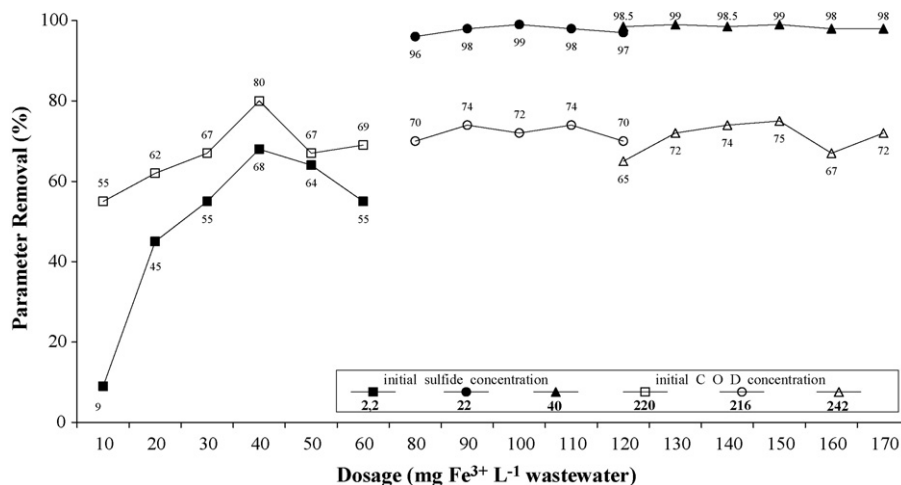
Fig. 2. The changes of COD and sulfide removal efficiencies depend upon $Fe^{3+}$ dosages and initial sulfide concentrations of wastewater.

dosages applied to both raw and sulfide added wastewaters with high pH are shown in Fig. 3.

Optimum precipitant dosage appears to be 60 and 120 mg $Fe^{3+}$ $L^{-1}$ for $WW_2$-B and $WW_3$-B, respectively. At 60 mg $Fe^{3+}$ $L^{-1}$ dosage, sulfide level was reduced to 0.8 mg $L^{-1}$ and the removal efficiencies of COD and sulfide were 44.4 and

96.1%, respectively. At 120 mg $Fe^{3+}$ $L^{-1}$ dosage for $WW_3$-B, sulfide level was reduced to 0.8 mg $L^{-1}$ and the removal efficiencies of COD and sulfide were 49.2 and 98%, respectively.

In the sight of experimental studies made for sulfide removal by manner of precipitation with ferric ion; it was found the following empirical statements between optimum $Fe^{3+}$ dosage
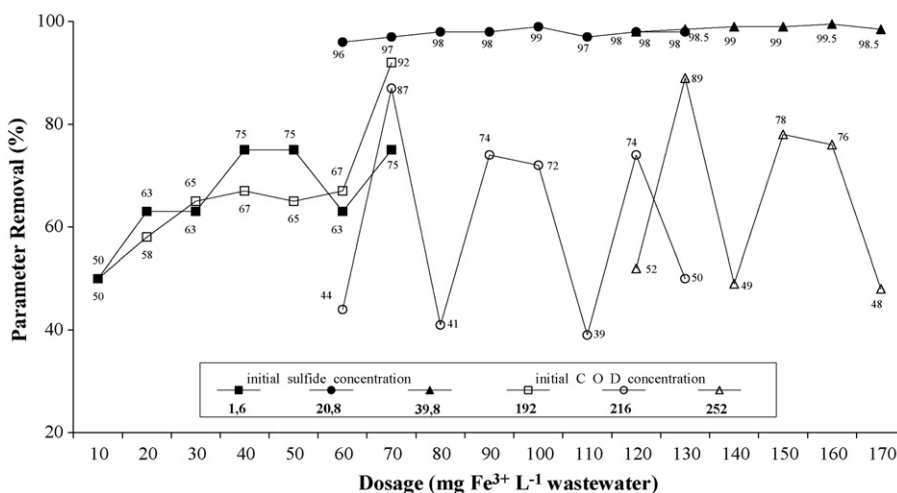


Fig. 3. The changes of COD and sulfide removal efficiencies depend upon $Fe^{3+}$ dosages and initial sulfide concentrations of wastewater having high pH.

Table 4
The effect of $Fe^{2+}$ ion and 200 mg $Ca(OH)_2$ $L^{-1}$ of precipitant-aid dosages used for sulfide removal by chemical precipitation on parameters of raw wastewater

| Parameters | Wastewater | Precipitant dosage (mg $Fe^{2+}$ $L^{-1}$) | | | | | |
|---|---|---|---|---|---|---|---|
| | | 2 | 4 | 6 | 8 | 10 | 12 |
| Sulfide (mg $L^{-1}$) | 0.8 | 0.4 | 0.4 | 0.4 | 0.4 | 0.4 | 0.4 |
| pH | 7.34 | 9.56 | 9.53 | 9.61 | 9.56 | 9.53 | 9.55 |
| T.Alk. (mg $CaCO_3$ $L^{-1}$) | 116 | 116 | 110 | 130 | 134 | 128 | 134 |
| COD (mg $L^{-1}$) | 248 | 168 | 120 | – | 112 | 224 | – |
| Conductivity (µS $cm^{-1}$) | 1855 | 1800 | 1810 | 1812 | 1824 | 1820 | 1830 |
| Visual turbidity | + | + | + | + | – | – | – |
| Visual color | – | Orange | Orange | Orange | – | – | – |
| Sludge color | – | Brown–dark grey | | | | | |

+: yes; −: no; ×: not done.

selected and initial $S^{2-}$ concentration according to the pH value of the wastewater:

$$7 < pH < 8.5 \quad y\,(mg\,Fe^{3+}\,L^{-1})$$
$$= 25.66 + 2.38x\,(mg\,S^{2-}\,L^{-1}) \quad [r^2 = 0.9987] \tag{5}$$

$$9 < pH < 10.5 \quad y\,(mg\,Fe^{3+}\,L^{-1})$$
$$= 12.41 + 2.62x\,(mg\,S^{2-}\,L^{-1}) \quad [r^2 = 0.9861] \tag{6}$$

### 3.2. Precipitation experiments using $Fe^{2+}$ ion

$Fe^{2+}$ ion as precipitant was added to raw wastewater samples in the order of 2, 4, 6, 8, 10, 12, 30, 40, 50, 60 and $100\,mg\,L^{-1}$. At the end of physicochemical treatments, desirable physical conditions for supernatant were not obtained. Consequently, pre-examinations were conducted for determination of precipitant-aid [$Ca(OH)_2$, $CaCO_3$]. As a result of pre-examination, $Ca(OH)_2$ was selected as precipitant-aid. After that, dosage determination examinations with both $Fe^{2+}$ and $Ca(OH)_2$ were carried out with raw and sulfide added petroleum refinery wastewater. Precipitant-aids were added in solid form to wastewater samples.

#### 3.2.1. Raw wastewater

It was found that sulfide concentrations of raw wastewaters which were taken from the WWTP at different dates were at safe levels for other units following physicochemical treatment, so in order to determine precipitant dosage, COD removal efficiency and physical properties of supernatant were taken into account. The characteristics of wastewaters and their changes after chemical precipitation using different $Fe^{2+}$ dosages between 2 and $12\,mg\,L^{-1}$ with a constant precipitant-aid dosage of $200\,mg\,Ca(OH)_2\,L^{-1}$ are presented in Table 4.

It was seen that the levels of experimental parameters such as pH, alkalinity and conductivity changed a little. pH value of wastewater should be decreased below 9.5 before entering an activated sludge process; otherwise, that process may be inhibited. Optimum precipitant dosage with constant $200\,mg\,Ca(OH)_2\,L^{-1}$ appears to be $8\,mg\,Fe^{2+}\,L^{-1}$ considering experimental data obtained. At this dosage, sulfide level was reduced to $0.4\,mg\,L^{-1}$ and the efficiencies of COD and sulfide removal were 54.8 and 50%, respectively.

#### 3.2.2. Sulfide added wastewater

Prepared samples which about $20\,mg\,S^{2-}\,L^{-1}$ were subjected to chemical precipitation with $Fe^{2+}$ ions and $Ca(OH)_2$ used at $20\,mg\,L^{-1}$ (WW$_A$), $100\,mg\,L^{-1}$ (WW$_B$) and $120\,mg\,L^{-1}$ (WW$_C$) dosages. $Fe^{2+}$ dosages between 20 and $90\,mg\,L^{-1}$ with an increment of $10\,mg\,L^{-1}$ were applied to the same wastewater samples and the changes of parameters were observed. The characteristics of wastewater and the gathered results obtained from chemical precipitation and visual observations with precipitant-aid of WW$_A$, WW$_B$ and WW$_C$ are summarized in Table 5.

Table 5
The effect of $Fe^{2+}$ ion and various precipitant-aid dosages [$Ca(OH)_2\,L^{-1}$] used for sulfide removal by chemical precipitation on parameters of three sulfide added ($\approx 20\,mg\,S^{2-}\,L^{-1}$) raw wastewaters

| Parameters | Wastewater | | | Precipitant dosage (mg $Fe^{2+}$ $L^{-1}$) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | WW$_A$ (20a) | WW$_B$ (100a) | WW$_C$ (120a) | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 80 | 80 |
| Sulfide (mg L$^{-1}$) | 16.4 | 18.4 | 20 | × | × | 0.6 | 0.4 | 0.6 | 0.4 | 0.2 | 0.6 | 0.6 |
| pH | 8.38 | 8.24 | 8.29 | × | 8.9 | 8.7 | 8.6 | 8.4 | 8.3 | 8.2 | 6.4 | 6.2 |
| T.Alk. (mg CaCO$_3$ L$^{-1}$) | 144 | 150 | 136 | × | 134 | 112 | 108 | 110 | 118 | 118 | 42 | 38 |
| COD (mg L$^{-1}$) | 144 | 80 | 96 | × | 32 | 30 | 20 | 22 | 20 | 20 | 60 | 48 |
| Conductivity (μS cm$^{-1}$) | 1975 | 1992 | 1982 | 1925 | 1929 | 1931 | 1951 | 1945 | 1962 | 1972 | 1893 | 1876 |
| Visual turbidity | + | + | + | × | + | − | − | − | − | − | − | − |
| Visual color | − | − | − | × | y^b | y | y | y | y | y | y | y |
| Sludge color | − | − | − | Dark blue | | | | | | | | |

+: yes; −: no; ×: not done.
a Constant precitant-aid dosage [mg $Ca(OH)_2$ L$^{-1}$].
b Yellow.

Table 6
The effect of $Fe^{2+}$ ion and $100\,mg\,Ca(OH)_2\,L^{-1}$ of precipitant-aid dosages used for sulfide removal by chemical precipitation on parameters of sulfide added ($\approx 30\,mg\,S^{2-}\,L^{-1}$) raw wastewater

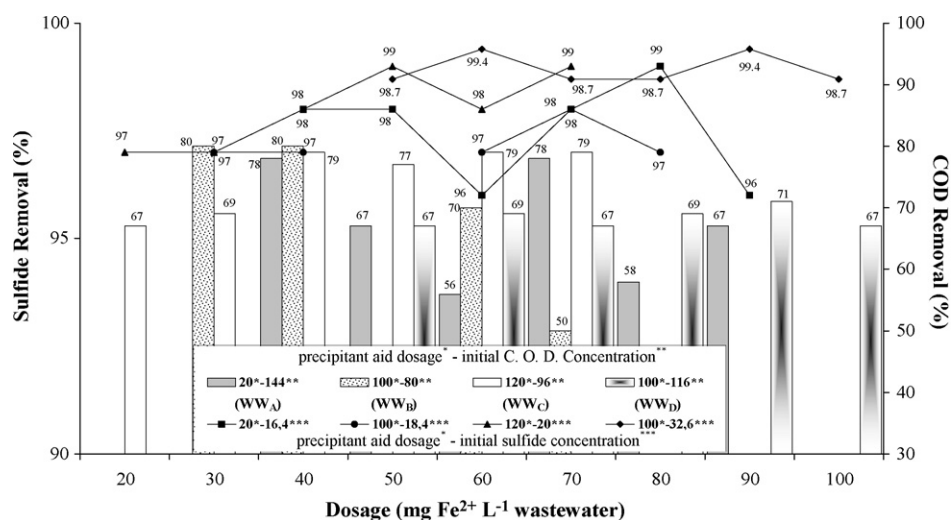| Parameters | Wastewater ($WW_D$) | Precipitant dosage ($mg\,Fe^{2+}\,L^{-1}$) | | | | | |
|---|---|---|---|---|---|---|---|
| | | 50 | 60 | 70 | 80 | 90 | 100 |
| Sulfide ($mg\,L^{-1}$) | 32.6 | 0.4 | 0.2 | 0.4 | 0.4 | 0.2 | 0.4 |
| pH | 8.8 | 8.63 | 8.49 | 8.39 | 8.26 | 7.97 | 7.63 |
| T.Alk. ($mg\,CaCO_3\,L^{-1}$) | 154 | 128 | 110 | 110 | 108 | 102 | 94 |
| COD ($mg\,L^{-1}$) | 116 | 38 | 36 | 38 | 36 | 34 | 38 |
| Conductivity ($\mu S\,cm^{-1}$) | 1952 | 1912 | 1923 | 1925 | 1948 | 1953 | 1966 |
| Visual turbidity | + | − | − | − | − | − | − |
| Visual color | − | − | − | − | − | − | Yellow |
| Sludge color | − | Dark blue | | | | | |

+: yes; −: no; ×: not done.



Fig. 4. The changes of COD and sulfide removal efficiencies depend upon $Fe^{2+}$ and precipitant-aid [$Ca(OH)_2$] dosages with initial sulfide concentrations of wastewater.

In other experiments carried out with sulfide added wastewater, $Fe^{2+}$ dosages between 40 and $100\,mg\,L^{-1}$ with an increment of $10\,mg\,L^{-1}$ were applied to wastewater samples which contained approximately $30\,mg\,S^{2-}\,L^{-1}$ ($WW_D$). Precipitant-aid dosage was determined as $100\,mg\,Ca(OH)_2\,L^{-1}$ as a result of pre-experiments. The characteristics of wastewater and the results obtained from chemical precipitation by using between 50 and $100\,mg\,Fe^{2+}\,L^{-1}$ and $100\,mg\,Ca(OH)_2\,L^{-1}$ dosages for sulfide added wastewater and visual observations are summarized in Table 6. Removal efficiencies of COD and sulfide at all dosages used were between 66–70 and 97–99%, respectively. Optimum $Fe^{2+}$ dosage appears to be $60\,mg\,L^{-1}$ for wastewater containing about $30\,mg\,S^{2-}\,L^{-1}$. At that dosage, sulfide level was reduced to 0.2 from $32.6\,mg\,L^{-1}$. The removal efficiency of COD was also obtained as 69%. In addition, sulfide levels of wastewater were decreased below $1\,mg\,L^{-1}$ at all chemical dosages. Removal efficiencies of COD and sulfide versus all dosages of $Fe^{2+}$ and precipitant-aid applied to wastewaters having different sulfide levels are shown in Fig. 4.

It was found the following empirical statement between optimum $Fe^{2+}$ dosages selected and initial $S^{2-}$ levels according to pH value of the wastewater with constant $Ca(OH)_2$ dosage of $100\,mg\,L^{-1}$:

$$7 < pH < 8.5 \quad y\,(mg\,Fe^{2+}\,L^{-1})$$
$$= 6.85 + 1.64x\,(mg\,S^{2-}\,L^{-1}) \quad [r^2 = 0.9998] \tag{7}$$

## 4. Conclusions

The wastewater reaching the treatment plant is contaminated with a light fraction of aliphatic and aromatic petroleum hydrocarbons, organochlorines originating from the cooling liquids and large amounts of nitrogen and sulfur, in the form of ammonia and $H_2S$, respectively. Removal of sulfide from the refinery wastewater was studied by physicochemical technique with conventional coagulant containing iron, and interactions between iron and sulfide in the wastewater were investigated.

In summary, we have found that sulfide in the studied wastewater may be effectively removed by $Fe^{2+}$ and $Fe^{3+}$ ions. Sulfide and COD removal efficiencies of $Fe^{3+}$ ions alone for sulfide added wastewaters having different pH values varies between 62–95 and 45–75%, respectively. In addition, removal efficiencies of sulfide (96–99%) and COD (50–80%) were obtained

by using $Fe^{2+}$ ions together with $Ca(OH)_2$ as precipitant-aid under the same conditions. In experiments performed with raw wastewater which had different pH values, COD removal efficiencies of $Fe^{3+}$, and $Fe^{2+}$ ions together with $Ca(OH)_2$, were 50–80 and 32–50%, respectively. In addition, increasing pH value of wastewater improved properties of flocculation and precipitation.

$Fe^{2+}$ ion is more economical than other precipitant for sulfide removal from the petroleum refinery wastewater having high pH as it is enough to be use alone. However, $Fe^{3+}$ ion is superior for this refinery wastewater with a pH value of near 7 and exhibited high sulfide removal alone in the point of operating view.

In practice, the attention should be paid to the use of chemicals, which contain $Fe^{2+}$ and $Fe^{3+}$; as $Fe^{2+}$ may be easily oxidized by oxygen in air, while $Fe^{3+}$ easily forms hydroxide in water which is neutral and weakly alkaline pH.

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