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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.

Keywords: Sulfide; Chemical precipitation; Petroleum refinery wastewater; Coagulants

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]:

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

$$Fe^{2+} + 2HS^- \rightarrow Fe(HS)_{2(S)} \tag{2}$$

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 3.7×10^{-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:

$$2Fe^{3+} + S^{2-} \rightarrow 2Fe^{2+} + S^0 \tag{3}$$

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]:

$$Fe^{2+} + 2Fe^{3+} + 4HS^- \rightarrow Fe_3S_4 + 4H^+ \tag{4}$$

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 $Na_2S \cdot 9H_2O$, $FeCl_3 \cdot 6H_2O$ and $FeSO_4 \cdot 7H_2O$ 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.