

Research Article

Complex Alumina-Ferrous Coagulant for Effective Wastewater Purification from Hydrogen Sulfide

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Received 10 February 2021; Revised 11 April 2021; Accepted 28 April 2021; Published 15 May 2021

Academic Editor: Gianfranco Carotenuto

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The article provides an overview of studies on the causes of the formation of hydrogen sulfide in anaerobic conditions of urban sewage systems and methods for neutralizing toxic reagent sulfur-containing compounds. It is noted that the presence of sulfur compounds and organic components in sewage flow leads to the formation and release of hydrogen sulfide into the atmosphere of settlements. Three main categories of methods for purifying sewage wastewater from hydrogen sulfide are presented. In this work, a complex alumina-ferrous coagulant has been developed from Kazakh raw materials. Based on natural ferruginous diatomite and middlings of sintered alumina, a complex alumina-ferrous coagulant has been synthesized, which is effective in purifying wastewater from hydrogen sulfide, accelerating the processes of sedimentation and clarification of sewage slurries. Experimental results also show that with the supply of increased amounts of coagulant, oil and oil films disappear from the surface of the cylinder, an almost complete purification of effluents from hydrogen sulfide compounds occurs, and the color of the liquid part is greatly reduced. In addition, the advantage of the developed reagent is that it is presented in the form of fine powder and can be easily dosed and added to a canalization pump station to interact with diluted hydrogen sulfide and be transported to sewage fields. Compared to other proposed methods in previous works, the reagent is suitable to be used directly in sewage systems such as sewage waters treatment plants and collectors to prevent hydrogen sulfide emission into the air atmosphere of populated areas, as well as at city sewage water treatment stations after air tanks and before secondary clarifiers to obtain better purified water suitable for watering agricultural plants.

1. Introduction

Hydrogen sulfide is a toxic, flammable, and corrosive gas that belongs to class II of compressed gas safety level (CGSL) hazard classification. In some of the main Kazakhstani cities such as Aktobe and Atyrau, high content of hydrogen sulfide gas can be observed in the atmosphere. Hydrogen sulfide concentration in these areas exceeds the permissible exposure limit of 0.008 mg/m³ in populated areas according to Sanitary Regulations and Standards No. 168 from 28.02.2015

[1]. According to the national hydrometeorological service of the Republic of Kazakhstan “Kazgidromet,” 59 cases of permissible exposure limit transcendence of hydrogen sulfide in the atmosphere were recorded in only a week time span, namely, between 9th to 15th June 2020.

Hydrogen sulfide is formed in sewage waters by sulfate-reducing bacteria that can occur naturally in water [2–4]. As a rule, sulfate concentration in sewage waters corresponds to its content in tap water. Nowadays, sulfate concentration tends to increase both in open waters and underground

waters that are used as water supply of towns and cities. Technogenic sulfur emission then leads to the substance precipitation on the surface of dry land, which has increased about 20 times within the last 100 years. For example, in water samples taken from both open and underground water sources used as water supply in Zhezkazgan region in Kazakhstan, the measured sulfate content ranges from 300 to 600 mg/l, depending on the season.

Formation of hydrogen sulfide in sewage waters can be stimulated by various conditions, which includes high contents of organic contaminants (high index of biological oxygen demand (BOD)), low concentration of diluted oxygen, presence of easily degrading organic substances, prolonged stay period of sewage waters in canalization systems, high temperature of sewage waters, and low pH of sewage waters. Furthermore, hydrogen sulfide formation also depends on speed of water flow and pipes diameter and length. In addition, there are also auspicious areas for hydrogen sulfide formation in sewage systems. They are mainly sewage pump stations (SPS) situated in residential districts, borders between under-pressure and gravity-flowing systems, parts of sewage systems next to SPS, and wastewater treatment plants (WWTP).

In the presence of reduced sulfur compounds, well-balanced process in biological purification facilities for sewage waters is violated by actively developed microorganisms that consume oxygen. Nitrification process slows down and deteriorates the quality of wastewater treatment. This problem, along with deterioration of biodegradation of main organic contaminants, can lead to hydrogen sulfide emission into the air at intermediate collectors and sewage pump stations situated all over the territory of populated areas, causing danger of being poisoned to the nearby population.

Broad review of methods to prevent hydrogen sulfide formation in sewage systems have been presented in articles [5, 6], which includes mechanical removal of biofilm from the inner surface of the pipes, oxygen or air injection to suppress anaerobic bacteria activity and sulfate reduction, and introducing different chemical substances to increase the reductive-oxidative potential of suppressing the process of sulfate reduction, as well as to increase the pH level of sewage waters in order to slacken the hydrogen sulfide formation. On the other hand, previous works have abundantly proposed various physical, chemical, and biological methods to diminish negative consequences of hydrogen sulfide in sewage water purification systems (reference). However, these methods are mainly to be implemented at industrial areas of sewage WWTP, which are situated beyond the borders of populated areas and equipped with all necessary premises and devices. As a result, the proposed methods still cannot solve the issue of hydrogen sulfide emission into the air of populated areas, due to the fact that hydrogen sulfide can still be formed along the pipes throughout the sewage systems. Hence, it is crucial and more practical to develop an efficient reagent that is capable of neutralizing and suppressing hydrogen sulfide formation directly inside the sewage systems, where the gas emission into the atmosphere of populated areas occurs.

2. Hydrogen Sulfide Neutralization Methods

Diluted hydrogen sulfide neutralization methods inside sewage systems can be divided into three categories, namely, air oxidation, chemical interaction with ferric and ferrous iron, and application of other oxidizing agents such as ozone, chlorine, hydrogen peroxide, and potassium permanganate [7]. The most widely used method of neutralizing hydrogen sulfide is air oxidation methods using prolonged aeration of sewage waters in air tanks. In this method, the waters' pH value is to be kept over 6.5 and as soon as the pH value falls below 5, wastewater purification from hydrogen sulfide stops [8]. However, air oxidation practice is only applicable at sewage waters treatment plants since there is a risk of polluting the air with hydrogen sulfide at the area where the plant is located.

Due to this disadvantage, the air oxidation method is gradually replaced with usage of chemical reagents for hydrogen sulfide neutralizing. One of the most efficient and affordable means for this purpose is using active forms of iron compounds. To expedite the reaction of ferrous and ferric iron salts with different forms of sulfides (S^{2-} , HS^- , and H_2S), the liquid medium is regulated at a pH value of between 7 and 8. In [9], a new agent has been synthesized, where nanoparticle-size, zero-valency iron is modified with ethylene glycol and alumina. This combination of components increases the efficiency of water-diluted sulfides removal. Application of this complex coagulant removes sulfides from the solution with the help of surface complexes, iron mercapto oxide (FeOSH), and precipitates of iron sulfide (FeS , FeS_2 , and FeS_n). Maximum adsorption capacity of this agent is 175 mg/g. In [10], hydrogen sulfide solution was oxidized to elemental sulfur with stabilized iron hydroxide (III), precipitated onto zeolite pellets. However, the obtained results showed that zeolite covered with iron hydroxide guarantees efficient removal of hydrogen sulfide only for relatively small water systems and can hardly be applied to purify wastewater sewage systems.

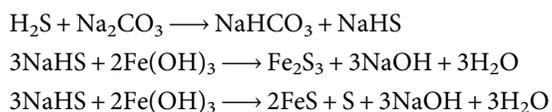
Sun et al. [11] proposed a following approach of diluted hydrogen sulfide removal using regeneration and recycle of used granulated iron hydroxide. After oxidizing diluted hydrogen sulfide to elemental sulfur with simultaneous reduction of solid Fe (III) to Fe (II), the reagent used is recovered to ferrous hydroxides (III) by mixing with water-containing dissolved oxygen. Several other previous works support this finding by concluding that the reagent prepared from mixture of grained ferrous hydroxide, grained iron oxide, and depleted matte scrap can remove hydrogen sulfide from residuals and water in sewage systems and can then be regenerated when brought in contact with diluted oxygen [12].

Transformation in oxidation-reduction process scheme of sulfur-containing compounds can be presented as follows [13]:

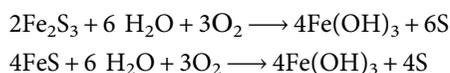
Organic sulfur (in oil and oil products, human ejections, proteins, amino acids, and other organic wastes) $\longrightarrow H_2S$ (hydrogen sulfide) $\longrightarrow HS^-$ (hydrosulphide ion) $\longrightarrow RS^-$ (mercaptans) $\longrightarrow S^0$ (elemental sulfur) $\longrightarrow S_2O_3^{2-}$ (thio-sulphate ion) $\longrightarrow S_4O_6^{2-}$ (tetrathionate ion) $\longrightarrow HSO_3^-$

(hydrosulfite ion) \longrightarrow SO_3^{2-} (sulfite ion) \longrightarrow H_2SO_4 (sulphuric acid) \longrightarrow SO_4^{2-} (sulfate ion).

Sulfur in reduced forms, e.g., S^{2-} , HS^- , and H_2S , are regarded as difficult to be used to remove pollutants. Sulfides can be sedated from sewage waters by using ferric and ferrous salts. However, for the completeness of the reaction of hydrogen sulfide with iron compounds, it is necessary to regulate the aqueous medium to neutral pH values of between 7 and 8. Some technological decisions introduce alkalizing of sewage waters with caustic ash, where interaction with iron hydroxides results in the following reactions:



The iron hydroxide-containing agent used in the purification process can be regenerated with air oxygen based on the following reactions:



As a conclusion, iron compounds are the most efficient and cheapest reagents for hydrogen sulfide neutralization. Speed and completeness of neutralizing diluted hydrogen sulfide with iron compounds are to a great extent defined by the form in which iron hydroxides are present in water solutions. The most efficient forms are colloid compounds that appear during hydrolysis of different iron-containing compounds such as sulphates, nitrates, and chlorides.

3. Methodology

In this work, a complex alumina-ferrous coagulant is developed based on natural ferrous diatomite and middlings of alumina production. Diatomite raw materials and middlings of alumina production can be used to obtain a number of industrial products [14–20]. X-ray analysis has been performed using DF8 Advance Diffractometer of BRUKER (emission α -Cu) for both ferriferous diatomite samples from Zhalpak deposit in Kazakhstan and sintered material from JSC Pavlodar Aluminum Plant. Iron in ferriferous diatomite is mainly presented by jarosite, as shown in Table 1.

As the second component of the complex coagulant, a sinter, which is a middling product of alumina production formed in the sintering process, is used. The phase composition of the cake is presented in Table 2.

The estimated amount of diatomite in Kazakhstan is over 200 million tons and is mainly found in Mugolzhhar district of Aktobe region. A part of them is in ferriferous form containing up to 30% of active $\text{Fe}(\text{OH})_3$ with microdispersed size and large area of interaction. Diatomites produce prospective raw materials for application in different branches of industry such as producing pigments, dry construction mixes, cements, foamed glass, mineral fertilizer carriers, sorbents, and binding materials by extraction of high strength chromium, manganese, iron, and nickel [18–20].

Alumina-ferrous coagulant is a middling of alumina production obtained during thermal processing of alu-

ferriferous silicate with caustic ash and limestone at 1200°C with addition of ferriferous diatomite from Zhalpak deposit. Interaction of this complex alu-ferrous coagulant with hydrogen sulfide in sewage waters can intercalyze the components, where high chemical activity is displayed.

First, ferruginous diatomite from Mugolzhhar deposit and alumina production middlings from JSC Pavlodar Aluminum Plant are finely gritted and mixed in necessary proportions defined experimentally depending on sulfide concentration and pH value of sewage waters. Then, the fine powder of this mixture is used to purify sewage waters from hydrogen sulfide.

4. Results and Discussion

Experiment on model sewage waters showed that with 100 mg of alumina-ferrous coagulant for 1.0 dm³ of sewage water, an intensive flocculation starts within 100 seconds and followed by quick sedimentation of slick and clarification. Initial chemical demand of oxygen of the tested sewage water was 152 mg/dm³ and reduced exponentially to 0.05 mg/dm³ with tested coagulant of 100 mg/dm³. The dependency of chemical demand for oxygen for sewage waters in the duration of interaction with coagulant is detailed in Figure 1.

According to the accepted experimental technique, 1 dm³ of wastewater was poured into two measuring cylinders with a capacity of 1 dm³. One of the cylinders acts as the control sample without supplying the reagent. The other cylinder was supplied with a coagulant suspension containing 50 mg of solid. Both cylinders were rapidly mixed three times with stirrers simultaneously. The start time of the experiment was recorded and the process of precipitation, coagulation of the precipitate, and purification of the aqueous phase began. The cleaning process has an induction period of about 5 seconds, where no visible changes occur. Then, in the cylinder fed with the reagent, a period of intense reaction and flocculation began, accompanied by rapid sedimentation and clarification of the pulp. When thickening process occurs in the control cylinder with the formation of a gel-like precipitate (averaged at 90 seconds), the upper liquid part in the cylinder with reagent was clarified to an almost colorless transparent solution and a rather dense solid precipitate was formed at the bottom of the cylinder. The experiment was then repeated with coagulant suspension containing 75 and 100 mg of solid.

The sample with 50 mg of dry coagulant had a weak hydrogen sulfide odor. When 75 and 100 mg of the reagent were fed, the odor disappeared completely. The initial chemical oxygen demand (COD) of the sewage effluent was 152.5 mg/dm³ and was reduced exponentially to 2.5 mg/dm³, 0.54 mg/dm³, and 0.05 mg/dm³ with coagulant consumption of 50 mg, 75 mg, and 100 mg, respectively, as shown in Figure 2. With the supply of increased amounts of coagulant, oil and oil films disappear from the surface of the cylinder, an almost complete purification of effluents from hydrogen sulfide compounds occurs, and the color of the liquid part is greatly reduced. Figure 2 shows the results of the experiment on removing hydrogen sulfide from sewage water with and without complex coagulant.

TABLE 1: Phase composition of ferruginous diatomite of the Zhalpak deposit.

Compound name	Formula	S-Q (%)
Quartz	SiO ₂	56 (1)
Jarosite	(K,H ₃ O)Fe ₃ (SO ₄) ₂ (OH) ₆	13 (7)
Albite	Na(AlSi ₃ O ₈)	12 (2)
Microcline	KAlSi ₃ O ₈	9 (8)
Muscovite	KAl ₂ Si ₃ AlO ₁₀ (OH) ₂	8 (2)

TABLE 2: Phase composition of the cake of JSC Pavlodar Aluminum Plant.

Compound name	Formula	S-Q (%)
Iron oxide	Fe ₃ O ₄	25 (41)
Magnetite	Fe ₃ O ₄	25 (9)
Calcium silicon aluminum sulfur oxide	Ca ₂ ((Si _{0.89} Al _{0.04} S _{0.07})O ₄)	18 (8)
Sodium aluminum silicate	Na ₄ Al ₂ Si ₂ O ₉	12 (31)
Perovskite, syn	CaTiO ₃	11 (46)
Srebrodolskite, syn	Fe ₂ Ca ₂ O ₅	5 (12)
Cristobalite beta	SiO ₂	2 (53)

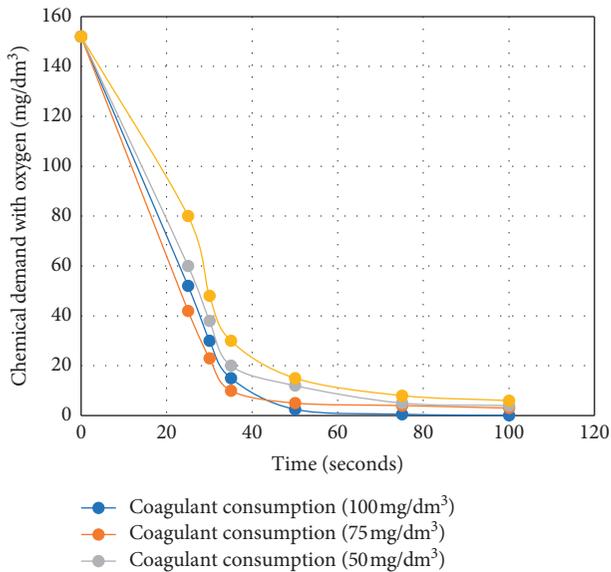


FIGURE 1: Dependence of chemical demand for oxygen for sewage waters in the duration of interaction with coagulant.

The mechanism of action of the coagulant is described as follows. At interaction of the coagulant powder with sewage water with slight stirring, sodium aluminate and ferrites dissolve, get hydrolyzed, and simultaneously interact with diluted hydrogen sulfide. Alkali from the coagulant interacts with acidic anions of the sewage water, which leads to formation of activated cations of ferrous iron that interact with diluted hydrogen sulfide to make insoluble iron sulfides. Another component of the coagulant, sodium aluminate, also gets hydrolyzed to form alumina which quickly stimulates sedated flakes. Ferruginous diatomite, apart from active iron hydroxide, contains amorphous silica, a perfect adsorbent for diluted impurities. The proposed alumina-ferrous coagulant simultaneously neutralizes and blocks



FIGURE 2: Results of the experiment on removing hydrogen sulfide from sewage water and residual sedimentation using a complex coagulant (left test tube) and without the use of a complex coagulant (right test tube).

formation of hydrogen sulfide, as it influences the pH value of sewage waters by decomposing and dissociating sodium and aluminum ferrites as well as speeds up sedimentation and clarification processes in condensed sewage waters.

The choice of complex coagulant composition, which consists of ferriferous diatomites and middlings of alumina production, can be explained by the following facts: comparatively high content of iron oxides and hydroxides (25–50% weight) in the mixture components; particle sizes of iron compounds and other mixture components included into the coagulant. For example, for natural Kazakhstani diatomite, the following main parameters are given in the article [16]: specific surface area, 29.41 m²/g; general pore space at gas filling, 68.52 ml/g; genuine pore space (calculated as liquid phase), 0.1068 ml/g.

At hydrolyzing cake component of the complex coagulant, sodium ferrite creates highly active forms of iron

hydroxides interacting with diluted hydrogen sulfide; sodium aluminate is destroyed creating aluminum hydroxides which help speedy sedimentation of iron sulfides; at hydrolyzing complex coagulant compounds, the alkali is produced which neutralizes acidity of sewage water up to pH 7–8.5, providing perfect conditions for appearing of practically nonwater-soluble forms of iron sulfides that help removing hydrogen sulfide from water.

Important factor of using the complex coagulant is the fact that it is easy to produce (as it is made from natural ferrous diatomite and alumina production middlings), inexpensive, and affordable. The coagulant can be used directly in sewage systems, for example, at water treatment plants and collectors to prevent hydrogen sulfide emissions into the air in residential areas or at city water treatment plants after air tanks and before secondary purification in order to obtain better purified water suitable for watering agricultural plants. The reagent is in the form of fine powder, thus it is easy to dose and to add into sewage pulp to interact with diluted hydrogen sulfide and to be transported to the purification fields.

5. Conclusions

In this work, on the basis of natural ferruginous diatomite and intermediate products of alumina production, a complex alumina-ferruginous coagulant was synthesized, which is effective for purification of wastewater from hydrogen sulfide, speeding up sewage pulps sedimentation and clarification processes.

Data Availability

The Microsoft Excel data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

Acknowledgments

The work was performed with financial support from the Science Committee of the Ministry of Education and Science of the Republic of Kazakhstan (Grant no. AP08855852).

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