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REMOVAL OF SULFIDE FROM WATER USING ALUMINA

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Abstract: Sulfides can cause the corrosion of pipes and the appearance of unpleasant odors. In drinking water sulfides affect organoleptic properties. Investigation of the adsorption onto various materials is increasing because this process gives the possibility for the use of low–cost adsorbents and it is a relatively simple technique for water treatment. Materials considered as adsorbents should primarily meet conditions such as particle size, porosity, and specific surface area. Due to their characteristics, alumina nanoparticles (Al_2O_3) have wide application in the ceramics industry, as abrasive material, in heterogeneous catalysis, and as sorbents. As an adsorbent, alumina nanoparticles have extensive application in the removal of undesirable compounds and contaminants from drinking water and wastewater. Alumina with a high content of aluminum oxide was used as an adsorbent to remove sulfides from aqueous solutions. This paper aims to examine the possibility of adsorption of sulfide ions onto alumina with a very high content of aluminum oxide (Al_2O_3). The results of the paper can serve as a starting point for further investigation of the adsorption characteristics of alumina, as well as the behavior of sulfides during adsorption on various adsorbents. Experiments in a column packed with alumina were conducted at room temperature. The effect of different initial concentrations and contact time on the sulfide removal efficiency was investigated. The best efficiency is achieved at low initial concentration and short contact time.
Keywords: sulfides, hydrogen sulfide, alumina, adsorption

INTRODUCTION

The presence of sulfides in the environment can be the result of natural processes and anthropogenic activities. Naturally, they are found in minerals, ores, and fossil fuels (oil and coal). Hydrogen sulfide (H_2S) in normal conditions is in the gaseous phase, present in ores and minerals, and as a product of volcanic activities (Clarisse et al, 2011; Ma et al., 2019). Gaseous hydrogen sulfide is toxic, flammable, colorless, with a recognizable odor of rotten eggs, so it is easy for detection in the air (Wu et al., 2018).

Hydrogen sulfide and sulfides of alkali and alkaline earth metals are soluble in water (Li and Lancaster, 2013). In groundwater, sulfides are naturally present due to the dissolution of mineral deposits in the aquifer. Hydrogen sulfide, which is a product of bacterial reduction of sulfate under anaerobic conditions, is very common in groundwater (Miao et al., 2012).

Conditions for sulfate reduction to sulfide are the following: the presence of sulfate source, the presence of reducing bacterias and their energy source, and the anaerobic environment (Fanning et al., 2002). Sulfides are present in both municipal and industrial wastewater. Dominant industrial sources are tanneries, paper mills, the petrochemical industry, and the textile industry (Vaiopoulou et al., 2005; Dutta et al., 2010; Pikaar et al., 2011).

Sulfides affect organoleptic properties of the drinking water. The odor and taste threshold for hydrogen sulfide in water is estimated to be between 0.05 and 0.1 mg/L. The health effects of hydrogen sulfide have not been proven yet, and therefore the maximum limit value of H_2S in water has not been officially defined (WHO, 2011). However, researches show that sulfides are very toxic for aquatic life, and they have a direct negative impact on the human central nervous system and respiratory system (Abdollahi & Hosseini, 2014; Huang et al., 2020). In addition, excessive intake of hydrogen sulfide through potable water can cause headaches, dizziness, fatigue, blurred vision, and other symptoms (Verma and Ratan, 2020).

Dissolved hydrogen sulfide and sulfide ions are undesirable primarily because they can lead to corrosion of the pipes, and the occurrence of unpleasant odors in the close environment (Dutta et al., 2010; Vaiopoulou et al., 2005). The most commonly used methods for removing sulfides from water are chemical and biological oxidation (Nielsen, & Vollertsen, 2021; Wilson et al., 2020). In addition to the above, other investigated techniques are adsorption, anaerobic digestion, precipitation, ion exchange, and electrochemical removal (Lito et al., 2012).

Investigation of the adsorption onto various materials is increasing because this process gives the possibility for the use of low–cost adsorbents and it is a relatively simple technique for water treatment. Materials considered as adsorbents should primarily meet conditions such as particle size, porosity, and specific surface area. Due to their characteristics, alumina nanoparticles (Al_2O_3) have wide application in the ceramics industry, as abrasive material, in heterogeneous catalysis, and as sorbents (Farahmandjou and Golabiyan, 2016). As an adsorbent, alumina nanoparticles have extensive application in the removal of undesirable compounds and contaminants from drinking water and wastewater. It is possible to use alumina for the removal of heavy metals, fluoride and nitrate adsorption, biological remediation, color degradation, desalination, etc. (Ghorai and Pant, 2004; Tripathy et al., 2006; Ravindhranath and Ramamoorty, 2017; Younssi et al., 2018).

This paper aims to examine the possibility of adsorption of sulfide ions onto alumina with a very high content of aluminum oxide (Al_2O_3). The results of the paper can serve as a starting point for further investigation of the adsorption characteristics of alumina, as well as the behavior of sulfides during adsorption on various adsorbents.

MATERIALS AND METHODS

The study of the potential of S^{2-} ions adsorption from aqueous solutions was performed in the laboratory of the Faculty of Technology Zvornik. Synthetic aqueous solutions of defined composition, similar to the composition of oligomineral natural waters, were used for the experimentation. Granular sodium sulfide (Na_2S) of analytical grade was used for the sulfide solution of known concentration. For each experiment, a new solution of sodium sulfide with double–distilled water was made. Solutions were prepared with initial sulfide concentrations ranging from 2.4802 mg/dm^3 to 40.9931 mg/dm^3, which were determined by the iodometric method (Clesceri et al., 1999).

Alumina, from the factory "Alumina" Ltd Zvornik, was used as an adsorbent for the adsorption of the sulfide ions. Determination of the chemical composition of the alumina sample was performed in the Alumina Research Laboratory using the ICP – OES SPECTRO GENESIS device, according to the standard method (BS EN ISO 11885, 2016). The loss on ignition was also determined according to the ISO standard method. (ISO 6606: 1986). Preparation of alumina for the adsorption included thermal treatment, where the sample was dried at a temperature of 300°C for 3 hours.

The adsorption was performed in an adsorption column with a diameter of 5cm and a length of 34cm. The filter paper was placed at the bottom of the column to prevent small granules from passing into the leaked solution. The experiment was conducted at room temperature. During the experiment, the variable parameters were the initial concentration of sulfide ions, and the contact time of the sulfide solution and the adsorbent.

The contact time between the sulfide solution and the alumina was 10, 20, and 30 minutes, with the volume of the leaked sulfide solution of 50 cm^3. The concentration of sulfide ions remaining in the solution, which was passed through the adsorbent, was monitored by spectrophotometric method (ISO 10530: 1992), using *UV–VIS 1800 Shimadzu* spectrophotometer, and measuring the absorbance at a wavelength $\lambda = 665$ nm. A 1 cm cuvette was used for analysis.

RESULTS AND DISCUSSION

— Chemical composition of the alumina sample

Alumina is anhydrous aluminum (III) oxide, which is confirmed with the low value obtained by loss on ignition (0.82%). Based on the results of the chemical analysis of alumina presented in Table 1, it can be seen that Al_2O_3 constitutes 98.80 wt.% of alumina, which is in accordance with the data presented in the studies (Hart & Lense, 1990; Morris et al., 2008).

Table 1. Chemical composition of the alumina sample

Chemical component	Weight percentage (wt. %)
Al_2O_3	98.80
Na_2O_{total}	0.33
CaO	0.02
Fe_2O_3	0.011
ZnO	0.01
SiO_2	0.006
Loss on ignition (1000 °C)	0.82

RESULTS OF SULFIDE ION ADSORPTION ON ALUMINA

As can be seen from the data shown in Tables 2 – 4 and Figure 1, the initial concentration of sulfide in the solution affects the adsorption efficiency. Regardless of the contact time of the alumina and the sulfide solution, at initial sulfide concentrations up to 20 mg/dm^3, a significant adsorption efficiency, over 80%, was achieved. An important decrease in the adsorption efficiency of sulfide ions is observed at initial sulfide concentrations higher than 30 mg/dm^3, at all examined contact times.

Increasing the initial concentration of sulfide, with approximately the same amount of adsorbent, leads to a decrease in the adsorption efficiency. The reason for this is the fact that the alumina surface is saturated faster with sulfide ions at a higher initial sulfide concentration.

Table 2. Sulfide adsorption on alumina at a contact time of 10 minutes

Initial sulfide concentration, c_0 [mg/dm^3]	Sulfide concentration after adsorption, c_1 [mg/dm^3]	Adsorbent dosage, m [g]	Adsorption efficiency [%]
2.4802	0.0223	108.70	99.10
10.0791	0.6350	109.01	93.70
20.4558	2.6572	107.98	87.01
31.1298	9.8962	109.00	68.21
40.9931	15.5815	107.70	61.99

Table 3. Sulfide adsorption on alumina at a contact time of 20 minutes

Initial sulfide concentration, c_0 [mg/dm^3]	Sulfide concentration after adsorption, c_1 [mg/dm^3]	Adsorbent dosage, m [g]	Adsorption efficiency [%]
2.4802	0.0295	108.70	98.81
10.0791	0.9374	109.01	90.69
20.4558	3.0663	107.43	85.01
31.1298	10.8301	109.03	65.21
40.9931	19.6808	107.98	51.99

Table 4. Sulfide adsorption on alumina at a contact time of 30 minutes

Initial sulfide concentration, c_0 [mg/dm^3]	Sulfide concentration after adsorption, c_1 [mg/dm^3]	Adsorbent dosage, m [g]	Adsorption efficiency [%]
2.4802	0.0374	108.95	98.49
10.0791	1.0458	108.81	89.62
20.4558	3.3149	107.98	83.79
31.1298	11.1149	109.02	64.29
40.9931	19.9875	109.01	51.24

Figure 1 shows that the contact time of the sulfide solution and alumina slightly affects the adsorption efficiency, at initial sulfide concentrations less than 30 mg/dm^3.

At initial sulfide concentrations higher than 30 mg/dm^3, the adsorption efficiency achieved at a contact time of 10 minutes (61.99%) is about 10% higher than the adsorption efficiency at a contact time of 20 minutes (51.99%) and 30 minutes (51.24 %).

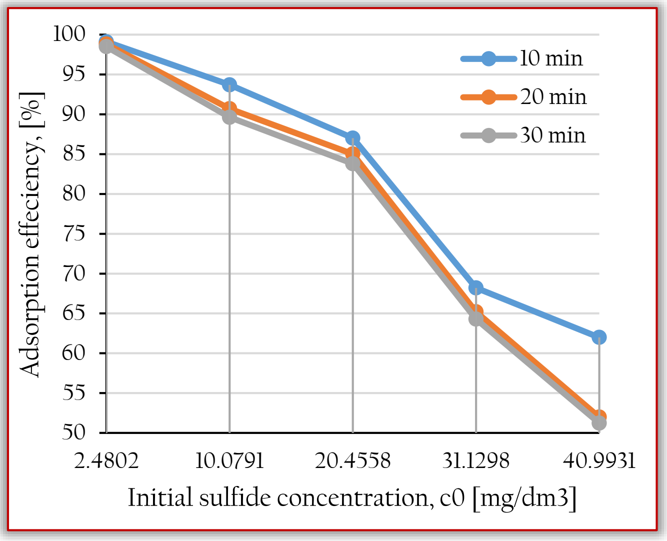

Figure 1. Adsorption efficiency at different initial sulfide concentrations and different contact times

CONCLUSION

Alumina with a very high content of aluminum oxide (Al_2O_3) was examined as an adsorbent for the removal of sulfide ions from aqueous solutions.

The experiment was conducted in a column (5x34cm), loaded with sufficient amounts of the adsorbent. The impact of contact time and the initial sulfide concentration was monitored. When initial concentrations are less than 30 mg/dm^3, the influence of the contact time is minor. Increasing the initial concentration negatively affects the adsorbent efficiency.

From above it can be concluded that alumina can be used as an efficient adsorbent for the removal of sulfide from water, in the conditions of low initial concentration and short contact time.

Further research should be focused on examining the influence of pH, temperature, and other relevant parameters.

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