The influence of reaction time on hydrogen sulphide removal from air by means of Fe(III)-EDTA/Fiban catalysts

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Abstract. The paper deals with a new method of hydrogen sulphide removal from air by its filtration and selective catalytic oxidation with the use of fibrous carriers of Fe(III)-EDTA complex. The basis of these filtering materials includes fibrous ion exchangers with the complex immobilized on their functional groups. It has been established that the degree of catalytic hydrogen sulphide decomposition depends on the reaction time. Thus, the required degree of hydrogen sulphide removal from air could be easily controlled by applying appropriate thickness of the filtering layer under a given filtering velocity. It allows applying very thin filtering layers of the Fe(III)-EDTA/Fiban AK-22 or Fiban A-6 catalysts. The obtained results of the research confirm the applicability of these materials for deep air purification from hydrogen sulphide.

1. Introduction

Hydrogen sulphide is a highly toxic compound. It has a very typical smell and can be perceived at concentrations as low as 0.5 ppb. At low concentration the gas has an unpleasant odour, whereas at higher it could be life-threatening. Breathing hydrogen sulphide at a concentration higher than 500 ppm can be fatal after few breaths, due to its broad spectrum toxicity [1].

The means of removing hydrogen sulphide depend on its concentration. Various well-established techniques are available for the removal of hydrogen sulphide from sour gases. On the industrial scale, removal is performed by a widely used Claus reaction, whereas at lower concentrations, adsorption or oxidation to sulphur oxides is preferred [2]. The electrochemical (anode oxidation) method was recently introduced as an alternative way for sulphide control in geothermal brines, sewage, and caustic solutions. Sulphide species are electrochemically active and the oxidation decreases the sulphide species concentration by forming a wide spectrum of intermediates and final products [3].

Adsorbents, especially activated carbons, play an important role in limiting the emission of sulphur compounds (in particular H2S) to the atmosphere. Thanks to their unique physicochemical properties, they can not only be effective adsorbents, but also catalysts or their carriers. Hence, the removal of gases containing sulphur can take place by physical or chemical adsorption or by catalytic oxidation on the carbon surface. The effectiveness of H2S removal by activated carbons can be improved by their impregnation with caustic materials such as NaOH or KOH, copper(II) ions and by incorporation of nitrogen, sulphur and oxygen functional groups into the carbon structure [4]. KMnO4 is dispersed on a porous support in order to remove hydrogen sulphide from ambient air. Adsorbents of this type have been prepared from silica or alumina. Manganese dioxide (MnO2) is also active in the removal of H2S. MnO2-impregnated sawdust has been successfully applied for the purification of ambient air [5]. A separate problem involves the removal of H2S present in the air in trace amounts (10-100 µg m-3) for clean rooms of fine mechanics, electronics, pharmaceutical productions as well as the purification
of air from hydrogen sulphide in the concentrations exceeding 10 mg m$^{-3}$ (maximum permissible concentration for working zones and surroundings of many productions) [6]. It is widely known that chelate complexes of trivalent iron convert hydrogen sulphide to elemental sulphur [7]. Bivalent iron formed in the reaction is oxidized by the atmospheric oxygen, so complex of trivalent iron is continuously regenerated and the overall process can be accounted as pseudo-catalytic [8]. Ferric chelates are widely used in purification of air from hydrogen sulphide i [9]. The catalyst is active only in strong alkali environment which causes serious corrosion problems [10]. In order to avoid these problems, fibrous ion exchangers were used as carriers of the catalyst. It was shown that the filtering layers with anion exchange package are much more active in the catalytic processes of hydrogen sulphide removal than cation exchanger and inert materials [11]. The latter worked only at RH (relative humidity) 80-90 % and higher. A higher catalytic activity of anion exchangers than that of cation exchanger and inert fibres proves that the Fe complex fixed on the cationic group of the fibre has a higher catalytic activity than that of the free complex. In the addition to the nature of the fibre (carrier of the catalyst), relative air humidity is a critical factor determining the efficiency of the material in purification of air from H$_2$S [12]. It was proven that the role of fibrous package involves improving the mass-transfer between the gas and liquid, buffering the pH of absorbing solution and catalysing the reactions of oxidation of sulphur and iron ions. The main parameters affecting the process of catalytic oxidation are: concentration of hydrogen sulphide in the air, relative humidity of the purified air, the process time and the content of Fe(III)-EDTA complex in the fibre [13]. It seems understandable that for a given set of conditions affecting kinetics of the process, the residence time in the mass-exchange unit controls the quality of the purified air. As that time simply depends on filtering layer thickness, conducting the presented research seemed reasonable.

2. Experimental

Fibrous ion exchangers Fiban used in the experiments were synthesized at the experimental production plant of the Institute of Physical Organic Chemistry National Academy of Sciences of Belarus (Minsk, Rep. of Belarus). The ion exchangers have been prepared by chemical modification of industrial polyacrylonitrile (PAN) fibre Nitron, produced in Polotsk petrochemical plant (Rep. of Belarus). The modification was performed with the staple fibres characterized by the fibre length 65 mm and effective diameter 20-22 µm. Chemically modified staple was processed to non-woven needle punctured canvas with surface density 500 g m$^{-2}$ and 5 mm thickness [14]. Fiban A-6 is a product of aminolysis of polyacrylonitrile fiber by dimethylaminopropylamine, followed by quaternization of the tertiary amino group with epichlorohydrine. The ion exchanger contains strong and weak basic groups with the capacities 1.80 mmol g$^{-1}$ and 0.65 mmol g$^{-1}$, respectively [6].

Fiban AK-22 is a polyampholyte containing primary and secondary amino groups and carboxylic acid groups. It is obtained by chemical modification of (PAN) polyacrylonitrile fibre. The predominant functional groups are R-COOH and R-CO-NH$_2$-CH$_2$CH$_2$NH-CH$_2$CH$_2$NH$_2$. The cationic exchange capacity is 1.5 mmol g$^{-1}$, the anionic exchange capacity is 4.0 mmol g$^{-1}$ [15].

Preparation of the H$_2$S fibrous sorbent-catalysts was performed by soaking the canvasses or by casting the impregnation solution onto the surface of the canvas. The impregnation solution was prepared by mixing 0.3 mol L$^{-1}$ solution of sodium salt of EDTA (ethylenediaminetetraacetic acid) and FeCl$_3$ $\cdot$ 6H$_2$O in molar ratio 1:2. Analytical grade reagents were purchased from POCH (Gliwice, Poland).

Removal of hydrogen sulphide from air was studied on the continuous flow experimental laboratory set presented in Figure 1. Hydrogen sulphide (1000 ppm H$_2$S + N$_2$, pure, Linde AG, Germany) was supplied from a gas cylinder (1) and it was diluted to the required concentrations by means of the air from a compressor (2). The air, before mixing with hydrogen sulphide, was humidified to obtain the relative humidity of the prepared mixture reaching approximately 90%. The relative humidity was measured by means of a hygrometer (AZ8721, Merazet, Poland). The concentrations of hydrogen sulphide in the air stream before and after purification were measured by GFM101 (Gas Data Ltd., U.K.) gas analyser (11). The filter used in all experiments was of a frame type. This filter contains layers of the ion exchange non-woven material (impregnated with Fe(III)-EDTA complex) fixed on rigid frames arranged, as shown in Figure 2 (view from the top). The surface area of the filter was 0.04
m² (4 layers, 10 cm x 10 cm each). The feed air passes through the filter medium where hydrogen sulphide is oxidized to elemental sulphur. The ion exchange fibre was rinsed within 5 minutes with the impregnation solution of Fe(III)-EDTA each half an hour of the filtration process. The samples of the purified air were taken to analysis 10 minutes after rinsing three times, each in 5 minute intervals. The hydrogen sulphide concentration was calculated as an average value from three measurements.

**Figure 1.** Scheme of experimental laboratory set-up (1 – source of hydrogen sulphide, 2 – air compressor, 3 – valve, 4 – flow meter, 5 – humidifier, 6 – mixing chamber, 7 – T-valve, 8 – filter with catalytic system Fe(III)-EDTA/Fiban, 9 – hygrometer, 10 – H₂S analyser).

**Figure 2.** Scheme of the air flow through the frame type filter (1 – inlet of the air, 2 – fibrous ion exchanger layer impregnated with Fe(III)-EDTA, 3 – outlet of the purified air).

In the conducted laboratory research, the influence of filtering layer thickness on removal of hydrogen sulphide from the air was investigated for Fiban A-6 and Fiban AK-22 fibrous carriers of the catalyst for different filtration velocities and initial concentrations of hydrogen sulphide in the purified air.

**3. Results and discussion**
The obtained results of laboratory experiments are shown in Tables 1 - 2.
Table 1. Removal efficiency of H$_2$S from air by means of catalyst Fe(III)-EDTA/Fiban AK-22 depending on filtration velocity and filtering layer thickness for different initial concentrations of hydrogen sulphide in the purified air.

| Initial H$_2$S concentration (ppm) | Flow velocity (m s$^{-1}$) | Filtering layer thickness (mm) | Removal efficiency (%) |
|-----------------------------------|----------------------------|-------------------------------|------------------------|
| 30                                | 0.005                      | 2                             | 94.45                  |
|                                   |                            | 6                             | 96.25                  |
|                                   |                            | 10                            | 97.40                  |
|                                   | 0.010                      | 2                             | 93.40                  |
|                                   |                            | 6                             | 95.65                  |
|                                   |                            | 10                            | 96.35                  |
|                                   | 0.020                      | 2                             | 91.15                  |
|                                   |                            | 6                             | 94.50                  |
|                                   |                            | 10                            | 95.30                  |
| 60                                | 0.005                      | 2                             | 92.46                  |
|                                   |                            | 6                             | 95.71                  |
|                                   |                            | 10                            | 96.96                  |
|                                   | 0.010                      | 2                             | 91.29                  |
|                                   |                            | 6                             | 93.63                  |
|                                   |                            | 10                            | 95.54                  |
|                                   | 0.020                      | 2                             | 87.98                  |
|                                   |                            | 6                             | 91.46                  |
|                                   |                            | 10                            | 93.75                  |

Table 2. Removal efficiency of H$_2$S from air by means of catalyst Fe(III)-EDTA/Fiban A-6 depending on filtration velocity and filtering layer thickness for different initial concentrations of hydrogen sulphide in the purified air.

| Initial H$_2$S concentration (ppm) | Flow velocity (m s$^{-1}$) | Filtering layer thickness (mm) | Removal efficiency (%) |
|-----------------------------------|----------------------------|-------------------------------|------------------------|
| 30                                | 0.005                      | 2                             | 98.97                  |
|                                   |                            | 6                             | 99.42                  |
|                                   |                            | 10                            | 99.58                  |
|                                   | 0.010                      | 2                             | 98.55                  |
|                                   |                            | 6                             | 99.00                  |
|                                   |                            | 10                            | 99.25                  |
|                                   | 0.020                      | 2                             | 97.83                  |
|                                   |                            | 6                             | 98.53                  |
|                                   |                            | 10                            | 98.95                  |
| 60                                | 0.005                      | 2                             | 98.67                  |
|                                   |                            | 6                             | 99.25                  |
|                                   |                            | 10                            | 99.46                  |
|                                   | 0.010                      | 2                             | 98.23                  |
|                                   |                            | 6                             | 98.88                  |
|                                   |                            | 10                            | 99.08                  |
|                                   | 0.020                      | 2                             | 97.37                  |
|                                   |                            | 6                             | 98.48                  |
|                                   |                            | 10                            | 98.83                  |

Table 1 presents the influence of filtering layer thickness of Fe-EDTA/Fiban AK-22 catalyst on the concentration of hydrogen sulphide in the purified air under three different filtration velocity settings.
and for two different initial concentrations of hydrogen sulphide. In the case of Fe-EDTA/Fiban A-6 material, the results of the same experiments were summarized in Table 2.

From the data presented one could see that the concentration of hydrogen sulfide in the purified air decreases with increasing filtering layer thickness for both tested catalytic systems. If relative humidity of the purified air is not lower than 90%, then 2 mm filtering layer of Fe-EDTA/Fiban A-6 material allows removing more than 97% of H₂S. In the case of Fe-EDTA/Fiban AK-22 material, assuming the same process parameters, it is possible to obtain the degrees of hydrogen sulphide removal exceeding 90% and the filtering layer thickness of at least 80 mm. While analyzing the results, it could be seen that residence time of the purified air in the filtering layer plays a decisive role in the process. This time, it is a simple function of filtering layer thickness (s) and flow velocity (v):

\[ t = \frac{s}{v} \]  

(1)

The dependence of the degree of hydrogen sulphide removal by Fe(III)-EDTA/Fiban catalysts on the residence time of the purified air in the mass-exchange unit for Fiban A-6 fibrous carrier is presented in Figure 3 and for Fiban AK-22 fibre – in Figure 4.

![Figure 3. The influence of reaction time on residual hydrogen sulphide in the air purified by means of Fe(III)-EDTA/Fiban A-6 catalyst.](image)

As could be seen from the results depicted in Figure 3, the degree of conversion of hydrogen sulphide to sulphur was higher than 99% if the residence time of the purified air in the mass-exchange unit was not under one second. Even for very short times of reaction, reaching 0.2 s, the residual hydrogen sulphide in the purified air was less than 2% of its initial amount. Very similar results, applying catalytic system Fe(III)-EDTA/Fiban A-6, were observed for both studied initial concentrations of hydrogen sulphide. For Fiban AK-22 fibrous carrier, the efficiency of the catalytic system in hydrogen sulphide removal is lower. Additionally, in this case the observed influence of the initial impurity concentration is stronger (see Figure 4). The obtained purifying results were noticeably worse in the presence of higher amounts of hydrogen sulphide, especially for short reaction time. Nevertheless, it was possible to remove more than 95% of the impurities with the reaction time of about 0.5 s for the lower studied concentration (30 ppm) and 1 s for the higher concentration (960 ppm).
Figure 4. The influence of reaction time on residual hydrogen sulphide in the air purified by means of Fe(III)-EDTA/Fiban AK-22 catalyst.

In order to improve the performance of the catalytic system under a given set of external conditions, it is enough to increase the residence time of the purified air in the filtering material. Thus, the required degree of hydrogen sulphide removal from the purified air could be easily controlled by applying appropriate filtration velocity and thickness of the filtering layer materials, paying attention to a satisfactory level of relative humidity characterizing the purified stream.

4. Conclusions
There are many parameters affecting the removal of hydrogen sulphide from air by its catalytic conversion to elemental sulphur by means of the filter with fibrous carrier of Fe(III)-EDTA catalyst. The conducted research proved that the reaction time is one of the most important factors. The degree of hydrogen sulphide removal from air is higher than 99% if the residence time of the purified air in the mass-exchange unit is not under one second. Even for higher filtration rates, when the reaction time is very short, reaching 0.2 s, the residual hydrogen sulphide in the purified air is less than 2% of its initial amount. It has been established that the application of the Fe(III)-EDTA/Fiban catalytic system, under appropriate conditions, led to a nearly complete decomposition of H₂S. The required degree of hydrogen sulphide removal from the purified air could be easily controlled by applying appropriate filtration velocity and satisfactory thickness of the filtering layer material. For a given set of the process conditions, the layer thickness and filtration velocity could be estimated on the basis of the enclosed figures.

5. References
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