Fibrous Ion Exchanger as a Carrier of the Fe-EDTA Catalyst for H_2S Emission Control

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The paper deals with a method of hydrogen sulphide removal from the air by its selective catalytic oxidation with the use of Fe-EDTA complex. The techniques based on this catalytic system are briefly described and discussed in many scientific papers. Except of many advantages the system has one very important drawback. The catalyst is active in strong alkaline environment which causes serious corrosivity problems. It was shown that the problem could be solved with the help of Fiban fibrous ion exchangers as carriers of the catalyst. The base of these materials is fibrous ion exchanger with Fe(III)-EDTA complex immobilized on their functional groups. The role of fibrous package is improving the mass-transfer between the gas and liquid, buffering the pH of absorbing solution and, probably, catalyzing the reactions of oxidation of sulphur and iron ions. The data presented show 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. The main parameters affecting the process of catalytic oxidation are: concentration of hydrogen sulphide in the air, relative humidity of the purified air and the process time. It was shown that application of the Fe(III)-EDTA/Fiban S system, under appropriate conditions, leaded to nearly complete conversion of H_2S to elemental sulphur.

1. Introduction

Hydrogen sulphide is a part of well-known environmental odour problem and is emitted into the environment as dissolved sulphide in wastewaters and as H_2S in waste gases. It has a very typical and irritating smell of rotten eggs and can be smelled at concentrations as low as 0.5 ppb (odour threshold 0.00047 ppm). Emission control of hydrogen sulphide is required for reasons of health, odour problems, safety and corrosivity problems. The means of removing hydrogen sulphide mainly depend on its concentration and kind of medium to be purified. For the removal of hydrogen sulphide from sour gases various well-established techniques are available. On the industrial scale, removal is affected by the Claus reaction or by the modification of the same process (Li and Cheng, 1996). At lower concentrations, adsorption or oxidation to sulphur oxides is preferred (Meeyoo et al., 1998). Since the conventional physicochemical methods for removing hydrogen sulphide from wastewaters and sour gases require large investment and operational costs (e.g. high pressures, high temperatures or special chemicals) the continuing search for more economical and more efficient methods has led to investigation into new technologies for purifying hydrogen sulphide containing gases (Busca and Pistarino, 2003). Nevertheless the air purification from hydrogen sulphide in concentrations exceeding the MPC (maximum permissible concentration) is real for working zones (MPC 10 mg/m^3) and surroundings of many productions. A separate problem is removal of H_2S present in the air in trace amounts 10-100 µg/m^3 for clean rooms of precise mechanics, electronics, pharmaceutical productions

(Soldatov and Kosandrovich, 2011). It is known that complex Fe (III) – ethylenediaminetetraacetate (EDTA) is an efficient and selective catalyst of hydrogen sulphide oxidation (Piche and Larachi, 2006). The complex of trivalent iron converts hydrogen sulphide to elemental sulphur. 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. Advantages of the system include the ability to treat both aerobic and non-aerobic gas streams, high H_2S removal efficiencies, great flexibility, essentially 100 % turndown on H_2S concentration in feedstock (Karimi et al., 2010). The main disadvantage of these processes is the fact that the catalyst is active in strong alkali environment which causes serious corrosivity problems (Piche et al., 2005). On the base of described research and presented results it seems that the problem can be solved with the help of fibrous ion exchangers as carriers of the catalyst.

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 (Wasag et al., 2008). Chemically modified staple was processed to non-woven needle punctured canvas with surface density 350 g/m^2 and thickness of 3 mm.

Fiban K-5 fibre was obtained by reaction of cross-linking of polyacrylonitrile fibre with hydrazine and following hydrolysis in strong alkali at 90 °C. Hydrolyzation causes formation of different nitrogen containing groups, most probable -NH=NH$_2$ and –NH$_2$=N and predominant carboxylic functional groups formed in the second step of hydrolyzation. The cationic and anionic exchange capacities of the sample were 4.20 and 1.22 meq/g respectively (Soldatov et al., 2004).

Fiban A-6 is a product of aminolysis of polyacrylonitrile fibre 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 and 0.65 meq/g respectively (Soldatov et al., 1996).

FIBAN AK-22 is a polyampholyte containing primary and secondary amino groups and carboxylic acid groups (Shunkevich et al., 2004). It is obtained by chemical modification of 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 meq/g, the anionic exchange capacity is 4.0 meq/g.
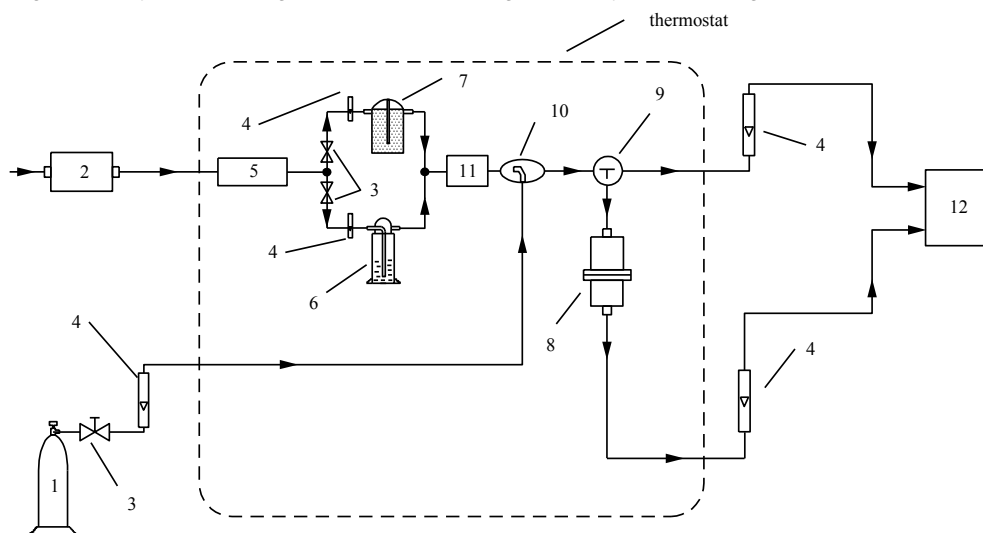

Figure 1: Scheme of experimental laboratory set-up (1 - source of hydrogen sulphide, 2 - air compressor, 3 - valve, 4 - flow meter, 5 - heat exchanger, 6 - humidifier, 7 - dryer, 8 - reaction chamber, 9 - T-valve, 10 - mixer, 11 - thermo hygrometer, 12 - H_2S analyser).

Preparation of the H$_2$S fibrous sorbent-catalysts was performed by soaking of the canvasses or by casting of the impregnation solution onto the surface of the canvas. The impregnation solution was prepared by mixing 0.3 M solution of EDTA and FeCl$_3$ 6H$_2$O in molar ratio 1:2.

Removal of hydrogen sulphide from air was studied on the continuous flow experimental laboratory set presented in Figure 1.

Hydrogen sulphide was supplied from a gas cylinder and it was diluted to required concentrations by means of air from a compressor. The air before mixing with hydrogen sulphide was dried or humidified depending on required relative humidity of the purified mixture. The relative humidity and the air temperature were measured by means of thermo hygrometer. Concentrations of hydrogen sulphide in the gas stream before and after the sorption process were measured electrochemically by GFM101 gas analyser (Gas Data Ltd.). The reaction chamber was a cylindrical shape with internal diameter of 20 mm. All experiments were carried out at the constant temperature of 25 °C. In the conducted laboratory experiments the influence of the following parameters on removal of hydrogen sulphide from air was investigated: kind of fibrous carrier of the catalyst, relative humidity of the purified air, concentration of hydrogen sulphide and the process time. The obtained results of laboratory experiments are presented in Table 1 and are illustrated at Figures 2 - 4.

3. Results and discussion

The data presented show that the filtering layers with anion exchange package are much more active in the catalytic processes of H$_2$S removal than cation exchanger and inert materials (see Table 1).

Table 1: Removal of hydrogen sulphide on the 3 mm filtering layer of different fibrous materials after one hour of work (initial concentration of H$_2$S - 60 mg/m^3, filtration rate 0.03 m/s).

RH (relative humidity) (%)	H$_2$S removal degree (%) for different carriers of Fe-EDTA catalyst					
	Cotton	PAN	Active carbon Carbapon	Fiban K-5 (Na$^+$ form)	Fiban AK-22 (OH$^-$ form)	Fiban A-6 (OH$^-$ form)
60	8 ± 1.00	10 ± 2.65	16 ± 3.46	31 ± 1.00	41 ± 1.73	74 ± 2.65
70	13 ± 1.73	19 ± 2.00	21 ± 1.00	45 ± 1.73	70 ± 3.00	89 ± 2.65
80	25 ± 1.73	33 ± 3.61	34 ± 1.73	53 ± 2.65	81 ± 1.73	94 ± 1.73
90	57 ± 2.65	62 ± 4.51	66 ± 2.00	68 ± 1.00	92 ± 1.73	98 ± 1.00

± the standard deviation

The latter worked satisfactory only at RH 80 - 90 % and higher. A higher catalytic activity of anion exchanges 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 efficiency of the material in the air purification from H$_2$S. The effect of RH on the percent of H$_2$S removal depends on the nature of ion exchanger. From the data Fiban A-6 appeared to be the only with high efficiency for purified air with relative humidity ranging from 80 to 90 %. It could be used even for the RH values ranging 60 % with very high degree of hydrogen sulphide conversion exceeding 70 %. Meanwhile Fiban AK-22 exhibited similar results for RH values between 70 – 80 %. Cation exchanger Fiban K-5 requires higher humidity for removal. However its efficiency in removal of H$_2$S is rather lower than 85 % even though the RH values higher than 90 %. This is due to characteristic of the examined carriers based on fibrous ion exchangers that could be explained with the help of water sorption isotherms.

As it was shown efficiency of the ion exchanger as a gas absorber is controlled (alongside with the other factors) by the amount of "free" water, not bound in strong hydrates and thus able to dissolve the gaseous component (Soldatov and Kosandrovich, 2011). If ion exchanger contains i types of hydrates containing q molecules of water per one functional group the total amount of moles of water in the ion exchanger is defined by the following Equation 1:

$$W = \sum_i q_i \cdot n_{h,i} + n_w \qquad (1)$$

where $n_{h,i}$ and n_w are numbers of moles of the hydrate and free water respectively. The hydrate formation is described by the constant of equilibrium (Equation 2 and 3):

$$RH + q_i H_2O \leftrightarrow RH \cdot q_i H_2O \qquad (2)$$

$$K_i = \frac{n_{h,i}}{n_{r,i} \cdot \alpha^{q_i}} \qquad (3)$$

For the system containing one mole of functional groups $n_{r,i} + n_{h,i} = 1$ and the total amount of water in the hydrates is (Equation 4) :

$$n_h = \sum_i q_i \cdot n_{h,i} = \sum_i \frac{q_i \cdot K_i \cdot \alpha^{q_i}}{1 + K_i \cdot \alpha^{q_i}} \qquad (4)$$

Assuming that the ion exchanger is an ideal mixture of the hydrates and free water molecules the amount of free water in the ion exchanger according to Soldatov and Kosandrovich (2011) is equal to (Equation 5):

$$n_w = \frac{\alpha \cdot (W_0 - \sum_i q_i \cdot n_{h,i}) \cdot f_w}{1 + W_0 - \sum_i q_i \cdot n_{h,i} - \alpha \cdot (W_0 - \sum_i q_i \cdot n_{h,i})} \qquad (5)$$
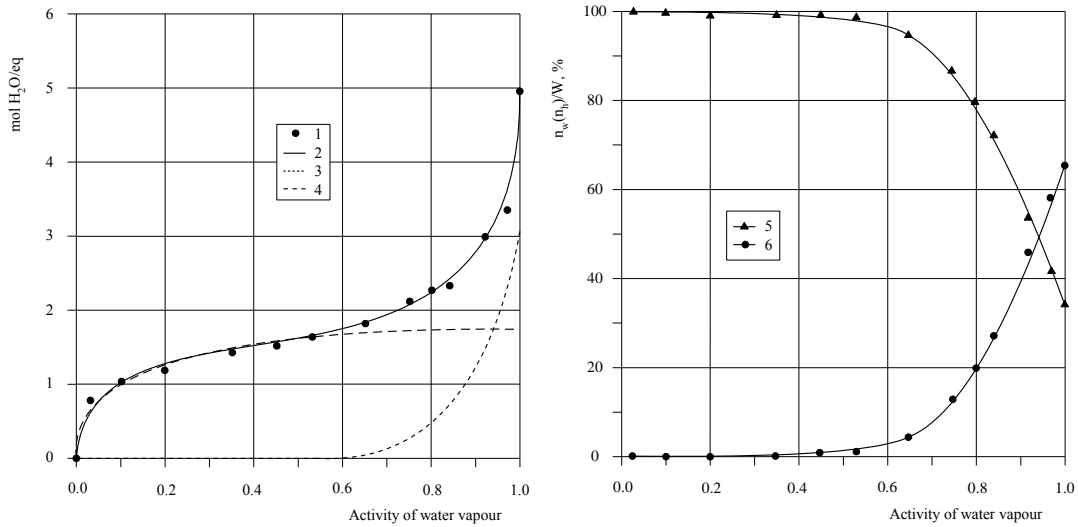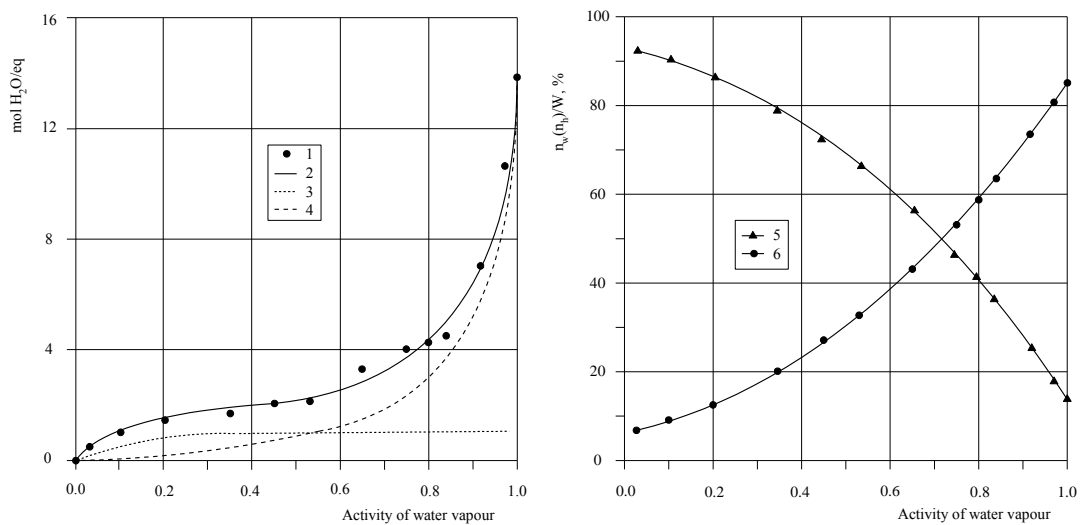

Figure 2: Water sorption isotherms by fibrous ion exchangers Fiban AK-22: 1 – experimental points; 2 – total amount of water; 3 – amount of the hydrate water; 4 – amount of the free water; 5 – percentage of the hydrate water; 6 – percentage of the free water; 2, 3, 4 – theoretical curves computed from Equations 1, 4 and 6 with the following parameters: $q_1 = 1$, $K_1 = 30$, $q_2 = 1$, $K_2 = 3$, $\lambda = 6$.

If water content in ion exchanger is too small to consider the system as an ideal mixture of the hydrates and "free" water then the activity coefficient could be approximated by empirical Equation 6:

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$$f_w = \alpha^\lambda$$

(6)

where λ is an empirical constant.

Application of this concept to the water sorption isotherms presented in Figures 2 – 3 shows that the reason for the higher efficiency of Fiban A-6 lies in the higher amount of available water in this fibre (curves 3, 4). The catalyst activity decreases with increasing the process time and increasing concentration of H_2S in the purified air (see Figure 4). It could be assumed that the reason for deactivation of fibrous catalyst in the hydrogen sulphide conversion process is blockage of the catalyst surface with accumulating colloidal particles of elemental sulphur.

Figure 3: Water sorption isotherms by fibrous ion exchangers Fiban A-6: 1 – experimental points; 2 – total amount of water; 3 – amount of the hydrate water; 4 – amount of the free water; 5 – percentage of the hydrate water; 6 – percentage of the free water; 2, 3, 4 – theoretical curves computed from Equations 1, 4 and 6 with the following parameters: q = 2, K=100, λ=0.
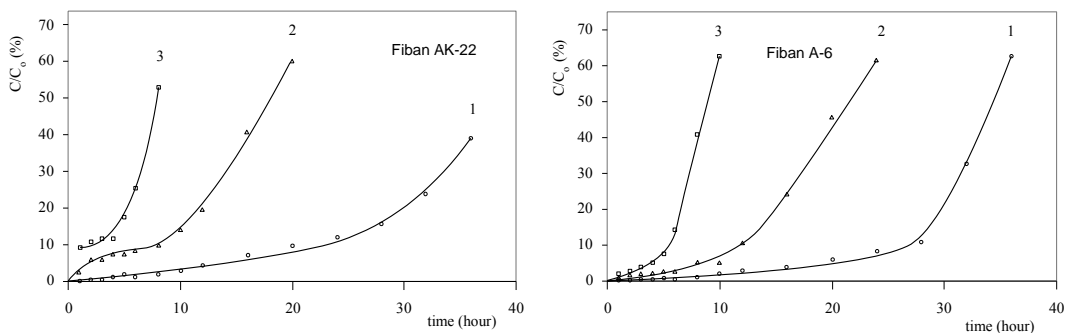

Figure 4: Effect of H_2S concentration in the air on its removal by Fe-EDTA/Fiban catalytic system (filtering layer thickness 3 mm, RH = 85-90 %, t = 25 °C, air flow 0.03 m/s, H_2S concentrations: 1 - 10; 2 - 30; 3 - 60 mg/m^3).

4. Conclusions

The data presented proved the possibility of obtaining fibrous filtering materials able to remove small concentrations of H_2S from the air. 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. Fibrous package was found to be improving the mass-transfer between the gas and liquid, buffering the pH of absorbing solution and, probably, catalyzing the reactions of oxidation of sulphur and iron ions. The process of H_2S removal from the air includes several stages including its dissolution in the solution of Fe(III)-EDTA complex, oxidation of the S^{2-} to S^0 and oxidation of Fe(II) to Fe(III) by the atmospheric oxygen. All of them can proceed in the solution. The catalyst activity decreases with increasing the process time and increasing concentration of hydrogen sulphide in the air. The observed deactivation of fibrous catalyst is probably caused by blockage of its surface with accumulating colloidal particles of elemental sulphur.

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