

Removal of Hydrogen Sulphide from Air by Means of Fibrous Ion Exchangers

H. Wasag

Abstract—The removal 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. The paper deals with a method of hydrogen sulphide removal from the air by its catalytic oxidation to elemental sulphur with the use of Fe-EDTA complex. The possibility of obtaining fibrous filtering materials able to remove small concentrations of H_2S from the air were described. The base of these materials is fibrous ion exchanger with Fe(III)-EDTA complex immobilized on their functional groups. 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. In the present paper properties of several fibrous catalysts based on ion exchangers with different chemical nature (weak acid, weak base and strong base) were described. It was shown that 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-EDTA complex in the fibres. 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. In the addition to the nature of the fibres relative air humidity is a critical factor determining efficiency of the material in the air purification from H_2S . It was proved that the most promising carrier of the Fe-EDTA catalyst for hydrogen sulphide oxidation are Fiban A-6 and Fiban AK-22 fibres.

Keywords—hydrogen sulphide, catalytic oxidation, odour control, ion exchange, fibrous ion exchangers, air deodorization

I. INTRODUCTION

HYDROGEN sulphide is a colourless compound which can be found in natural gases as well as in volcanic gases and hot springs. It is also produced in human and animal wastes and by different human industrial activities, such as rayon textiles manufacture, pulp and paper mills, oil refinery and natural gases treatment, meat rendering plant, etc. [1]. Hydrogen sulphide may be present in waste gas streams at concentrations between 2 and 1000 ppm [2]. It has a very typical and irritating smell of rotten eggs and can be smelled at concentrations as low as 0.5 ppb. However at 100 ppm, it can no longer be smelled. Breathing hydrogen sulphide at a concentration higher than 500 ppm can be fatal after a few breaths, due to its broad spectrum toxicity.

The US Occupational Safety and Health Administration (OSHA) established an acceptable ceiling concentration of 20 ppm at the workplace with a maximum concentration of 50 ppm for no more than 10 min. The US National Institute of Occupational Safety and Health (NIOSH) has set a maximum recommended exposure limit ceiling value (10 min) of 10 ppm [1].

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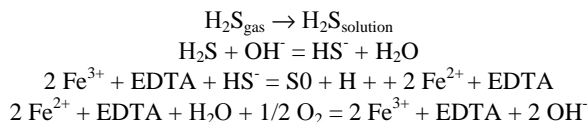
The removal of hydrogen sulphide is required for reasons of health, odour problems, safety and corrosivity problems [3]. The means of removing hydrogen sulphide mainly depend on the concentration and kind of medium to be purified [4]. In order to remove hydrogen sulphide from wastewater streams, a number of physicochemical processes are in common use today. Many of the methods are based on direct air stripping, chemical precipitation and oxidation. Oxidation processes used for sulphide removal are aeration (catalysed and uncatalysed), chlorination, ozonation, potassium permanganate treatment and hydrogen peroxide treatment. In all these processes, apart from elemental sulphur, thiosulphate and sulphate may also be formed as end products [5]. For the removal of hydrogen sulphide from sour gases various well-established techniques are available. On the industrial scale, removal is effected by the Claus reaction or by the modification of the same process [2]. At lower concentrations, adsorption or oxidation to sulphur oxides is preferred. In the latter case, allowable emission levels are higher and adsorption, particularly of sulphur trioxide, is more effective. Molecular sieves, silica gel and activated carbons have been used to adsorb hydrogen sulphide from waste gas streams [6]. Molecular sieves have the highest capacity for adsorption from dry gas streams [7]. Activated carbons are more efficient from wet gas streams, such as are generated by sewage [8]. In some cases, especially for large gas streams, the volume of the gas to be treated is reduced by concentrating the hydrogen sulphide. Concentration occurs by a chemical reaction or physical absorption under high pressure in an amine or glycol solution. The hydrogen sulphide rich gas (40 – 90 vol.%) is then treated in a Claus plant [9].

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 [10]. Nevertheless the air purification from hydrogen sulphide in concentrations exceeding the MPC is actual for working zones (10 mg/m^3 for working zones) and surroundings of many productions. A separate problem is removal of H_2S present in the air in trace amounts $10\text{-}100 \text{ }\mu\text{g/m}^3$ for clean rooms of precise mechanics, electronics, pharmaceutical productions [11].

It is understandable that OH^- forms of anion exchangers may absorb hydrogen sulphide as a result of ion exchange process. But the possibility of using this process for removal of H_2S from gaseous media it may not be used for practical air purification because of unfavourable competition with carbon dioxide, whose concentration in ambient air is about 300 mg/m^3 and greatly exceeds the MPC level of H_2S whose concentration in the contaminated air is usually below 100 mg/m^3 . In the addition, H_2S has the dissociation constant on the first dissociation step by 3 power of magnitude lower than

carbonic acid. Probably only ion exchange resins Amberlist XN-1007 and Amberlist A-27 can be used for this purpose because they selectively absorb H_2S in the presence of CO_2 . Also, cation exchangers in forms of ions, forming non-soluble sulphides (like Cu^{2+} , Ni^{2+} , Zn^{2+}) can be used for selective H_2S sorption [11]. However, the data reported does not allow concluding of their practical applicability to the air purification.

It is known that complex Fe (III) – ethylenediaminetetraacetate (EDTA) is an efficient and selective catalyst of hydrogen sulphide oxidation [12]. The scheme of this process can be formulated as follows:



The above liquid phase oxidation process using iron chelate catalytic solution (LOCAT) has been employed for treatment of acid gas stream [13]. The two most common processing schemes encountered in these systems are named ‘conventional’ and ‘auto circulation’. The first one is employed for processing gas streams, which are either combustible or cannot be contaminated with air. Here, absorption and regeneration reaction occur in separate reactors. The second one is used for processing acid gas streams in which absorption and regeneration reactions are carried out in a single vessel [14]. Advantages of these systems include the ability to treat both aerobic and non-aerobic gas streams, high H_2S removal efficiencies, great flexibility, effectively 100% turndown on H_2S concentration in feedstock. The main disadvantage of these processes is the fact that the catalyst is active in strong alkali environment which causes serious corrosivity problems [15]. It seems that the problem can be solved with the help of fibrous ion exchangers as carriers of the catalyst.

II. EXPERIMENTAL

Fibrous ion exchangers used in the conducted research 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 polyacrylonitrile (PAN) fibre [16]. The fibres had an effective diameter 20-22 μm . The chemical modification was performed with the staple fibres of 65 mm length. Chemically modified

staple was processed to non-woven needle punctured canvas with surface density 350 g/m^2 at the layer thickness of 3 mm. The canvasses were made on standard industrial textile equipment.

Fiban K-5 fibre was obtained by reaction of cross-linking of polyacrylonitrile fibres with hydrazine and following hydrolysis in strong alkali at 90°C. Hydrolyzation causes formation of different nitrogen containing groups, most probable $-\text{NH}=\text{NH}_2$ and $-\text{NH}_2=\text{N}$ 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 [17].

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 meq/g and 0.65 meq/g respectively [18].

FIBAN AK-22 is a polyampholyte containing primary and secondary amino groups and carboxylic acid groups [19]. It is obtained by chemical modification of polyacrylonitrile (PAN) fibre. The predominant functional groups are $\text{R}-\text{COOH}$ and $\text{R}-\text{CO}-\text{NH}_2-\text{CH}_2\text{CH}_2\text{NH}-\text{CH}_2\text{CH}_2\text{NH}_2$. The cationic exchange capacity is 1.5 meq/g, the anionic exchange capacity is 4.0 meq/g.

Preparation of the H_2S 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 sodium salt of ethylenediaminetetraacetic acid (EDTA) and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in molar ratio 1:2.

Removal of H_2S from the air was studied on the continuous flow experimental laboratory set presented at the Fig. 1.

Hydrogen sulphide was supplied from a gas cylinder and it was diluted at different 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 by GFM101 gas analyser (Gas Data Ltd.). All experiments were carried out at the constant temperature of 25°C.

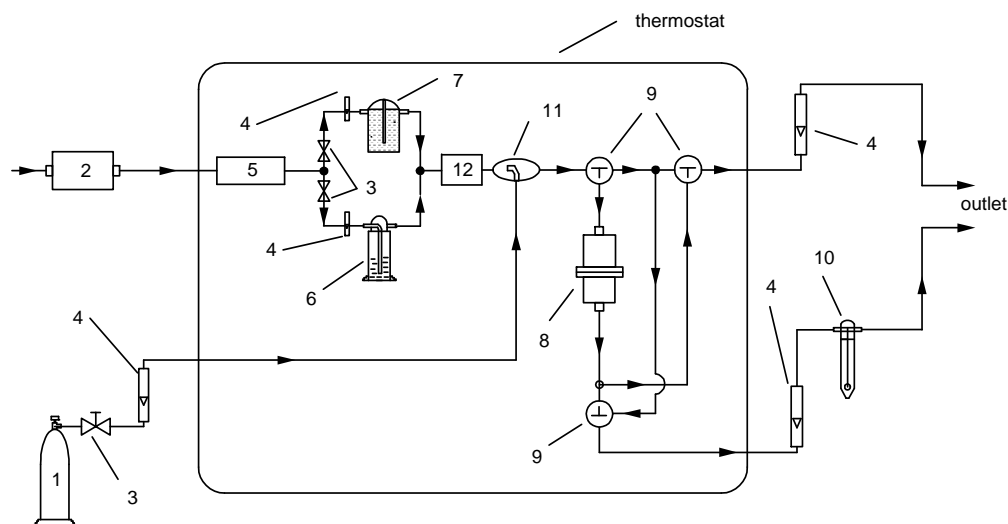


Fig. 1 Scheme of experimental laboratory set-up (1 - source of hydrogen sulphide, 2 - air compressor, 3 - valve, 4 - flow meter, 5 - heat exchanger, 6 - humidifier, 7 - dryer, 8 - conversion chamber, 9 - T-valve, 10 - aspirator, 11 - mixer, 12 - thermo hygrometer)

In the conducted laboratory experiments the influence of the following parameters on removal of hydrogen sulphide from the air was investigated: kind of fibrous carrier of the catalyst, relative humidity of the purified air, concentration of hydrogen sulphide, time of the process, concentration of Fe in the impregnated fibrous material and thickness of the filtering layer.

The obtained results of laboratory experiments are presented in Tables I -II and are shown in Figs. 2 – 5.

III. 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_2S removal than cation exchanger and inert materials (see Table I).

TABLE I

REMOVAL OF HYDROGEN SULPHIDE ON THE 5 MM FILTERING LAYER OF DIFFERENT FIBROUS MATERIALS AFTER ONE HOUR OF WORK (INITIAL CONCENTRATION OF H_2S - 60 MG/M^3 , FILTRATION RATE 0.03 M/S)

Carrier of Fe-EDTA (kind of fibrous material)	RH (%)	H_2S removal degree (%)
Cotton	90	60
PAN	90	65
Active carbon	90	70
Fiban K-5 (Na^+ form)	75- 80	70
Fiban AK-22 (OH^- form)	75- 80	95
Fiban A-6 (OH^- form)	75- 80	>99

The latter worked only at RH 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_2S .

The effect of RH on the percent of H_2S removal is dependent on the nature of ion exchanger as illustrated by Fig. 2.

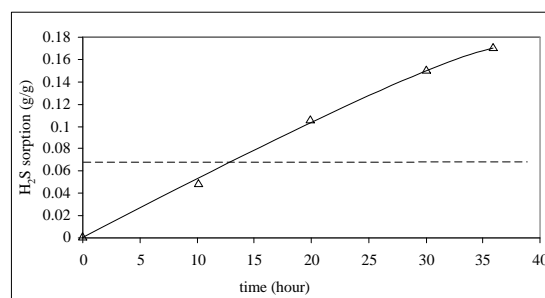
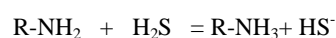


Fig. 2 The RH effect on the efficiency of hydrogen sulphide removal from the air; 1 - Fiban A-6; 2 - Fiban AK-22, 3 - Fiban K-5, (initial concentration of H_2S - 60 MG/M^3 , filtration rate 0.03 M/S)

From the data presented one could see that ion exchanger Fiban A-6 is only the one carrier efficient at relative humidity of the purified air below 70 - 80%. It could be used even for the RH values ranging 60% with very high degree of hydrogen sulphide conversion exceeding 90%. In case of fibrous ion exchanger Fiban AK-22 similar results were obtained for the RH values about 80%. Cation exchanger Fiban K-5 requires higher humidity but even at the RH values higher than 90% removal degree of H_2S is below 85%. From the dependence of the H_2S amount removed from the air per gram of fibre Fe-EDTA/ Fiban AK-22 as a function of the process time it is seen that the removal of H_2S from the air proceeds mainly because of its catalytic conversion into elemental sulphur (see Fig. 3). The dotted line on the figure relates to the maximal possible absorption of H_2S by anionic groups of the fibre by ion exchange reaction:



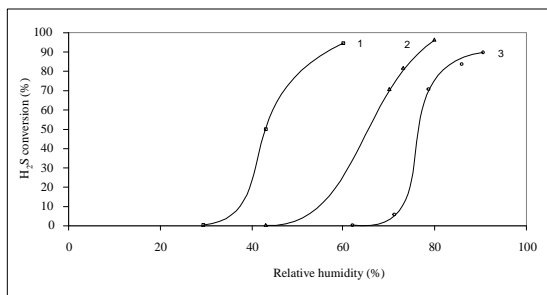


Fig. 3 Dependence of the H₂S amount removed from the air per gram of fibre Fe-EDTA/ Fiban AK-22 as a function of the process time (initial concentration of H₂S - 60 mg/m³, relative humidity 80%, filtration rate 0.03 m/s)

As could be seen from Fig. 4 performance of the catalytic system Fe-EDTA/ Fiban AK-22 depends on the Fe(III) concentration in the fibre.

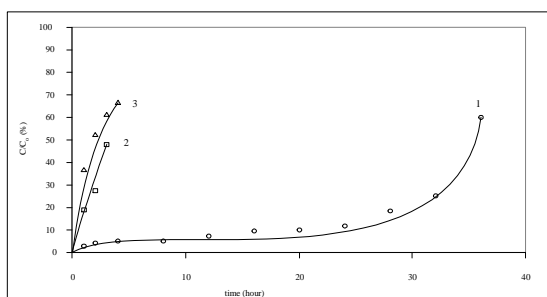


Fig. 4 Influence of Fe(III) content in the fibre on the air purification by the catalytic system on the base of Fiban AK-22 (RH = 80%, filtration rate 0.03 m/s, content of Fe(III): 1 - 0.62; 2 - 0.35; 3 - 0.26; 4 - 0.18 mmol/g)

Increase in iron concentration improves the catalyst performance at its low values and reaches nearly constant efficiency at its contents 0.35 mmol/g. The efficiency of air purification simply depends on the thickness of filtering layer and increases with the increase of the residence time of air in the filtering layer which is a function of layer thickness and flow velocity (Table 2).

TABLE II

INFLUENCE OF THE THICKNESS OF FILTERING LAYER ON THE EFFICIENCY OF H₂S REMOVAL FROM THE AIR BY Fe-EDTA/ FIBAN AK-22 MATERIAL (RH = 70%, FILTRATION TIME 1 HOUR, AIR FLOW VELOCITY 0.14 M/S, INITIAL H₂S CONCENTRATION 10 MG/M³).

Thickness of the filtering layer (mm)	Retention time of the air in the filtering layer (s)	C/C ₀
2	0.014	0.60
4	0.029	0.34
6	0.043	0.20
8	0.057	0.05

The catalyst activity decreases with increasing the process time and increasing concentration of H₂S in the purified air (see Fig. 5).

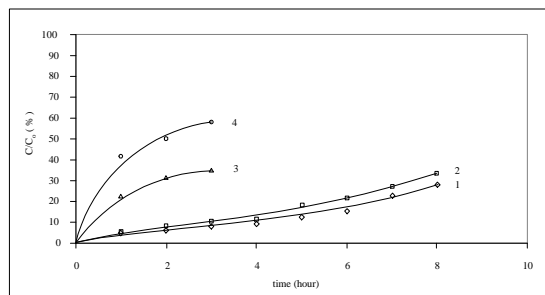


Fig. 5 Effect of H₂S concentration in the air on its removal by Fe-EDTA/Fiban AK-22 catalytic system (filtering layer thickness 3.5 mm, RH= 75-80%, t= 25°C, air flow 0.03 m/s, Fe(III) content 0.5 mmol/g, H₂S concentrations: 1 - 10; 2 - 60; 3 - 130 mg/m³)

It could be assumed that the reason for deactivation of fibrous catalyst in the conversion process $2\text{H}_2\text{S} + \text{O}_2 \rightarrow 2\text{H}_2\text{O} + 2\text{S}^0$ is blockage of the catalyst surface with accumulating colloidal particles of elemental sulphur.

IV. CONCLUSION

The data presented proved the possibility of obtaining fibrous filtering materials able to remove small concentrations of H₂S 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. 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 process of H₂S removal from the air includes several stages including its dissolution in the solution of Fe(III)-EDTA complex, oxidation of the S²⁻ to S⁰ and oxidation of Fe(II) to Fe(III) by the atmospheric oxygen. All of them can proceed in the solution. Accumulation of elemental sulphur in the solution is observed and it can be assumed that the reason for deactivation of fibrous catalyst in the conversion process is blockage of the catalyst surface with accumulating colloidal particles of elemental sulphur. Because of that the catalyst activity decreases with increasing the process time and increasing concentration of hydrogen sulphide in the air.

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REFERENCES

- [1] G. Busca, C. Pitarino, "Technologies for the abatement of sulphide compounds from gaseous streams: a comparative overview", *Journal of Loss Prevention in the Process Industry*, vol. 16, pp. 363 – 371, 2003.

- [2] V. Meeyoo, J. H. Lee, D. L. Trimm, N. W. Cant, "Hydrogen sulphide emission control by combined adsorption and catalytic combustion", *Catalysis Today*, vol. 44, pp. 67 – 72, 1998.
- [3] M. Schlegelmilch, J. Streese, R. Stegmann, "Odour management and treatment technologies: An overview", *Waste Management*, vol. 25, pp. 928-939, 2005.
- [4] N. Rakmak, W. Wiyaratn, C. Bunyakan, J. Chungsiriporn, "Synthesis of Fe/MgO nano-crystal catalyst by sol-gel method for hydrogen sulfide removal", *Chemical Engineering Journal*, vol. 162, pp. 84-90, 2010.
- [5] L. Deng, H. Chen, Z. Chen, X. Liu, X. Pu, L. Song, "Process of simultaneous hydrogen sulfide removal from biogas and nitrogen removal from swine wastewater", *Bioresource Technology*, vol. 100, pp. 5600-5608, 2010.
- [6] D. Panza, V. Belgiorno, "Hydrogen sulphide removal from landfill gas", *Process Safety and Environmental Protection*, vol. 88, pp. 420-424, 2010.
- [7] M.D. Soriano, J. Jimenez-Jimenez, P. Concepcion, A. Jimenez-Lopez, E. Rodriguez-Castellon, J.M. Lopez Nieto, "Selective oxidation of H₂S to sulphur over vanadium supported on mesoporous zirconium phosphate heterostructure", *Applied Catalysis B: Environmental*, vol. 92, pp. 271-279, 2009.
- [8] X. Wu, A.K. Kerchief, V. Schwartz, H.S. Overbuy, R. T. Armstrong, "Activated carbons for selective catalytic oxidation of hydrogen sulfide to sulfur", *Carbon* vol. 43, pp. 1084-1114, 2005.
- [9] A. J. H. Janssen, G. Lettinga, A. Keizer, "Removal of hydrogen sulphide from wastewater and waste gases by biological conversion to elemental sulphur: Colloidal and interfacial aspects of biologically produced sulphur particles", *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 151, pp. 389-397, 1999.
- [10] J. E. Burgess, S. A. Parsons, R. M. Stuetz, "Developments in odour control and waste gas treatment biotechnology: a review", *Biotechnology Advances*, vol. 19, pp. 35-63, 2001.
- [11] V. S. Soldatov, E. G. Kosandrovich, "Ion exchangers for air purification", in *Ion Exchange and Solvent Extraction, A Series of Advances*, vol. 20, K Arup, M. Sengupta Eds. New York, CRC Press, 2011, pp. 45-117.
- [12] S. Piche, F. Larachi, Dynamics of pH on the oxidation of HS⁻ with iron(III) chelates in anoxic conditions, *Chemical Engineering Science* vol. 61, pp. 7673-7683, 2006.
- [13] S. Piche, N. Ribeiro, A. Bacaoui, F. Larachi, "Assessment of a redox alkaline/iron-chelate absorption process for the removal of dilute hydrogen sulfide in air emissions", *Chemical Engineering Science*, vol. 60, pp. 6452-6461, 2005.
- [14] A. Karimi, A. Tavassoli, B. Nassernejad, "Kinetic studies and reactor modeling of single step H₂S removal using chelated iron solution", *Chemical Engineering Research and Design*, vol. 88, pp. 748-756, 2010.
- [15] J. F. Demmink, A. Mehra, A. A. C. M. Beenackers, "Absorption of hydrogen sulfide into aqueous solutions of ferric nitrilotriacetic acid: local auto-catalytic effects", *Chemical Engineering Science*, vol. 57, pp. 1723-1734, 2002.
- [16] H. Wasag, V. Soldatov, E. Kosandrovich, H. Sobczuk, "Odour control by fibrous ion exchangers", *Chemical Engineering Transactions*, vol. 15, pp. 387-394, 2008.
- [17] V.S. Soldatov, L. Pawlowski, H. Wasag, A. Schunkevich, "New materials and technologies for environmental engineering. Part I – Synthesis and structure of ion exchange fibres, Lublin, Poland, (Published Conference Proceedings style)," in. *Monographs of the Polish Academy of Sciences*, Lublin, 2004, vol. 21, pp. 1-127.
- [18] V. S. Soldatov, L. Pawlowski, H. Wasag, I. Elinson, A. Shunkievich, "Air pollution control with fibrous ion exchangers", in. *Chemistry for the Protection of the Environment*, 2, Plenum Press, New York, 1996, pp. 55-66.
- [19] A.A. Shunkevich, G.V. Med'jak, R.V. Martsinkevich, V.I. Grachek, V.S. Soldatov, "Fibrous chelating carboxylic acid ion exchangers", *Sorption & Chromatography Processes*, vol. 1, pp. 741-748, 2001.