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REMOVAL OF AMMONIA FROM AIR
BY FIBROUS ION EXCHANGERS

The paper presents the results of laboratory studies of ammonia sorption from air by fibrous ion-exchange materials containing acidic groups in concentration of 3–5 mmoles per gram as a function of the ammonia concentration (3–30 ppm), relative air humidity, air flow rate and the thickness of filtering layer. It follows from our experiments that non-woven fabrics with the thickness of above 2 mm and surface density of ~0.3 kg m^{-2} can efficiently reduce ammonia concentration in air to <1 ppm at flow rates of <0.2 m s^{-1}. The sorbent can be regenerated with acid solution to obtain salts that can be used as mineral fertilizers.

1. INTRODUCTION

Protecting the environment from emissions of ammonia can be considered from several aspects. The global control of ammonia release is possible only if legislative and technical measures are applied at the point of its emission. A good example is the Integrated Pollution Control Licensing (IPC) measure for pig and poultry production practised in Ireland. The relative guidance note, i.e. BATNEEC (Best Available Technology Not Entailing Excessive Cost), was issued in 1996 (EPA, 1996). As noted by HAYES et al. [7] EU Member States have now to prepare and implement a BAT note as required by related EU directive (96/61/EC).

The local control of indoor ammonia concentration in living quarters, public places, cattle farms and some industrial environments has to be implemented in the areas where the problem exists and may not be solved on a global level.

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Finally, individual means for protecting human microenvironment, such as escape masks, respirators or protective clothing, are needed for accidental exposures. This is a real problem since conventional protective means based on active carbon are not effective in the case of ammonia.

In the present paper, we describe new materials allowing removal of ammonia and other alkaline contaminants from the air. They are fibrous cation exchangers in hydrogen form. Due to their high chemical activity and suitable physical form such exchangers can be used in technological equipment as an absorbing fixed bed or active packing in acid scrubbers. Fibrous ion exchangers are similar in their function to granular ion-exchange resins. Their properties are described in many original reports and have been recently summarized in a monograph by SOLDATOV et al. [17]. The exchanger filaments have identical effective radii in the range of 5–20 μm and the length of 5–7 cm. The technologies for the production of fibrous ion exchangers containing different functional groups have been developed and some of these materials are produced on industrial scale under the trademark of FIBAN$^{®}$ (website http://ifoch.bas-net.by). They are strong acid and strong base ion exchangers based on polypropylene fibers and different carboxylic acid cation exchangers and polyampholytes obtained by chemical modification of polyacrylonitrile fibers. Cation-exchange fibers interact with ammonia in aqueous or gaseous media forming polymeric ammonium salts according to the reactions:

$$R-SO_3H + NH_3 \xleftrightarrow{\;H_2O\;} R-SO_3NH_4 \,,$$

$$R-COOH + NH_3 \xleftrightarrow{\;H_2O\;} R-COONH_4 \,.$$
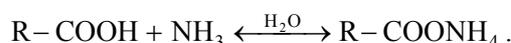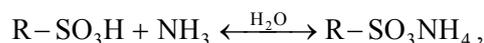
After sorption the ion-exchange fibers can be regenerated by treatment with acids. Attempts at practical applications of conventional ion-exchange resins have shown (GOSTOMCZYK [5], HASHIDA and NISHIMURA [6], VULIKH et al. [21]) that for removing acid or base impurities from air the sorption process is too slow if the resin beads are about 1 mm in diameter.

In contrast to granular ion exchangers, fibrous ion exchangers have all the advantages of resin technology but are free of the aforementioned drawbacks. The rate of sorption on ion-exchange fibers is 2–3 orders of magnitude faster than that of granules due to the small diameter of their filaments. The process rate is controlled by the diffusion of the absorbing molecule into the depth of the sorbent matrix and is inversely proportional to squared radius of granular or cylindrical particle (KOKOTOV et al. [8], YOSHIOKA and SHIMAMURA [24]). This allows the use of ion-exchange fibrous material in thin layers (few millimeters) and arrangement of the filtering device so that a large filtering area can be installed in a relatively small filtering chamber. Ion-exchange fibers are osmotically stable and are not destroyed in drying/wetting cycles (SOLDATOV et al. [19]) thereby making the use of the simple regeneration schemes, described in the following section, possible.

The purpose of the present paper was to investigate the effect of the main process parameters of ammonia sorption on its efficiency. This includes the nature of the ac-

tive group of the ion exchanger, relative air humidity, concentration of ammonia in the air as well as the contact time of the air and the fiber.

2. MATERIALS AND METHODS

2.1. FIBROUS ION EXCHANGERS

All fibrous ion exchangers described in the paper were standard materials produced at the experimental plant of the Institute of Physical Organic Chemistry, National Academy of Sciences of Belarus (Minsk, Republic of Belarus).

FIBAN K-1 is the product of sulfonation of the graft copolymer of styrene (ST, 98% mass) and divinylbenzene (DVB, 2% mass) which gives industrial polypropylene (PP) fiber (SOLDATOV et al. [19]). The graft copolymer was obtained by radiochemical grafting of ST-DVB mixture into PP fiber induced by ^{60}Co γ rays. It contained 1 g of ST-PP per gram of PP. The fibers had a diameter of 40±2 μm. FIBAN K-1 is a monofunctional strong acid ion exchanger containing only sulfonic groups. Its exchange capacity is 3 meq g^{-1}, the water uptake in H^+ form is 1 g H_2O g^{-1}.

FIBAN K-4 is monofunctional carboxylic acid ion exchanger obtained by post-irradiation grafting of polyacrylic acid (PAA) into the polypropylene staple fiber (ELINSON et al. [4], PRIGOZHAEVA et al. [14]). The filament diameter is 22±2 μm, exchange capacity, 4.5 meq g^{-1}; water uptake, 0.7 g H_2O g^{-1} of H^+ form.

FIBAN AK-22 is a polyampholyte containing primary and secondary amino groups and carboxylic acid groups. It is obtained by chemical modification of polyacrylonitrile (PAN) fiber Nitron produced by the Novopolotsk Petrochemical plant (Republic of Belarus) (SOLDATOV et al. [18]). The filament effective diameter is 12±2 μm, the predominant functional groups are R-COOH and R–CO–NH_2–CH_2CH_2NH–$CH_2CH_2NH_2$. The cationic exchange capacity is 1.5 meq g^{-1}, and the anionic exchange capacity is 4.0 meq g^{-1}. The water uptake in the free amine form is 1 g H_2O g^{-1}.

In all cases the ion exchangers were used in the form of non-woven material with a thickness of 3 mm and a surface density of 340 g m^{-2}. FIBAN AK-22 (H_2SO_4) and FIBAN AK-22 (H_3PO_4) materials were obtained by impregnating the parent FIBAN AK-22 with sulfuric and phosphoric acids, respectively. They contain different amounts (depending on the concentration of the impregnating acid) of the absorbed acids able to interact with ammonia. There was no free acid on the surface of the samples.

2.2. MEASUREMENT OF AMMONIA SORPTION

The samples were converted into hydrogen form by treating them with 1 M HCl, rinsed with water to pH 5.5 and dried in air. They were kept in an hermetically closed container.

The percentage of water in the air-dried samples was determined by drying them to a constant weight at 105 °C. One or several layers of the ion exchange non-woven material as disks of the filtering material with the 50-mm diameter of working area, in H form and with known mass were fixed in the measuring cell perpendicular to the air flow. A standard air sample with a known concentration of ammonia and water vapour was passed through the testing material and analyzed for ammonia in the outlet. All elements of the measuring set-up were placed in a thermostated chamber at a temperature of 25±0.1 °C.

3. RESULTS AND DISCUSSION

The performance of different ion exchangers in ammonia sorption from air flows is presented and discussed below.

3.1. FIBAN K-1

The experimental data on the sorption of ammonia from the air flow at different air relative humidities P/P_0 is presented in figure 1, which shows that a thin layer of FIBAN K-1 material (3 mm) provides complete purification of air from ammonia (residual concentration of NH_3 < 10 ppb) at a high flow rate, corresponding to ~300 $m^3 h^{-1} m^{-2}$ independently of the relative air humidity in a wide P/P_0 range. The time before the NH_3 breakthrough was ~1.5 hour. At this point the fiber absorbed 1.5 mmol $NH_3 g^{-1}$ (25.5 mg $NH_3 g^{-1}$), i.e. about 50% of its total capacity.
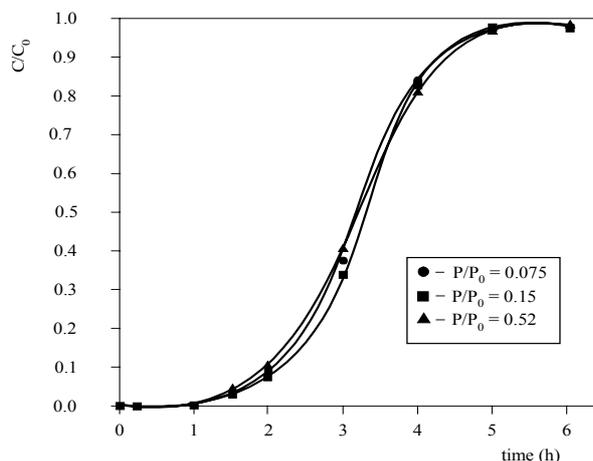

Fig. 1. Breakthrough curves of NH_3 on ion exchanger FIBAN K-1 at different air relative humidity.
Conditions of experiment: thickness of filtering layer, 3 mm; air flow rate, 0.081 m s^{-1};
concentration C_0 of NH_3 at inlet, 18 mg m^{-3}

It is seen from figure 2 that at the breakthrough points (3.5 and 39 hours, respectively) the working capacity of the filtering layer is the same and equal to 2.4 mmol NH_3 g^{-1}, which corresponds to 80% of the total capacity. The higher efficiency of filtration compared with the previous experiment is due to the thicker filtering layer.

We can conclude that the working sorption capacity of strong acid fibrous ion exchanger FIBAN K-1 is practically independent of the concentration of ammonia and its relative humidity in a wide range of these parameters.
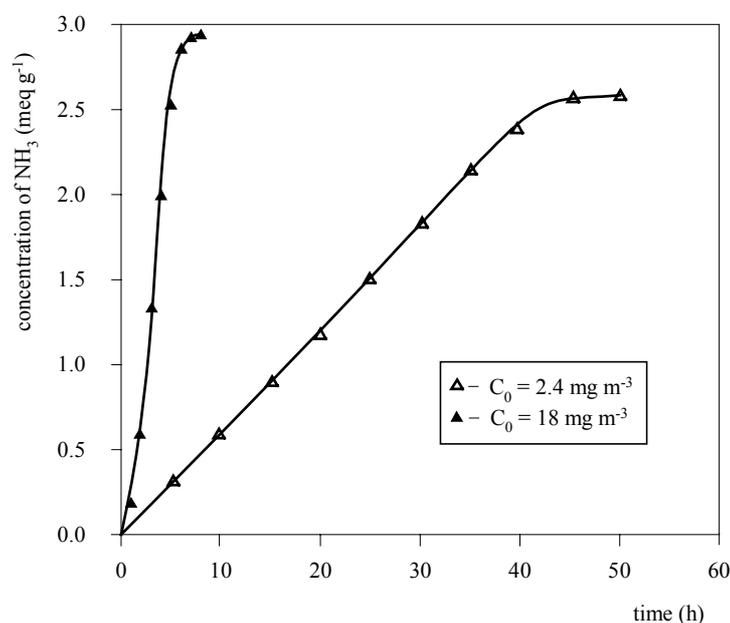

Fig. 2. Sorption of NH_3 from air flow by FIBAN K-1 at different NH_3 concentrations. Conditions of experiment: $P/P_0 = 0.49$, thickness of filtering layer, 6 mm

3.2. FIBAN K-4

Quite different results were observed for the carboxylic acid cation exchanger FIBAN K-4. As can be seen from figure 3, the sorption activity of FIBAN K-4 greatly depends on the relative humidity of the air flow. Both the working capacity at the breakthrough point and the equilibrium capacity sharply decrease with decreasing air humidity. This is caused by incomplete dissociation of the carboxylic acid groups of the fiber decreasing with decreasing air humidity. The lowest P/P_0 at which the fiber reveals complete retention of ammonia lies between 0.35 and 0.52.
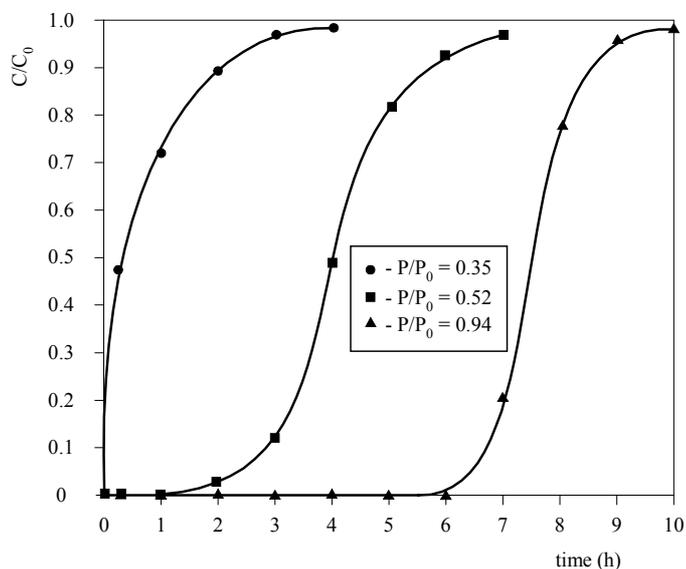
Fig. 3. Breakthrough curves of NH$_3$ on ion exchanger FIBAN K-4 at different air relative humidity.
Conditions of experiment: thickness of the filtering layer, 6 mm; air flow rate, 0.081 m s^{-1};
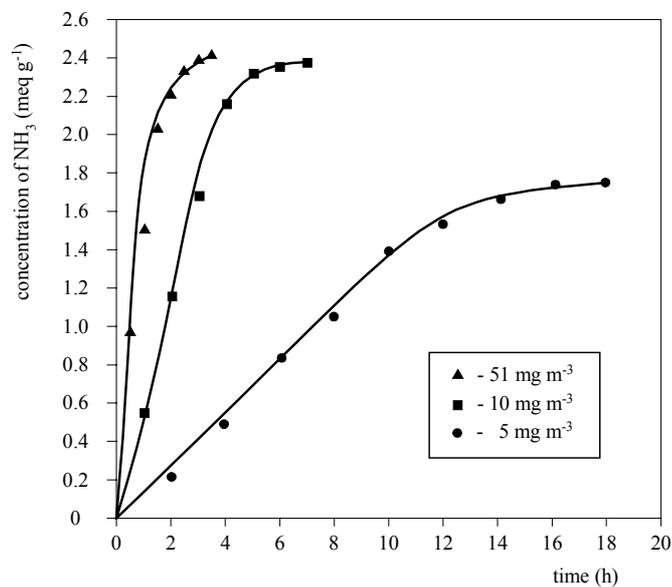concentration of NH$_3$ at inlet, C_0 = 18 mg m^{-3}

Fig. 4. Sorption of NH$_3$ from air flow by FIBAN K-4 at different NH$_3$ concentrations.
Conditions of experiment: P/P_0 = 0.56; thickness of filtering layer, 6 mm; air flow rate, 0.081 m s^{-1}

The sorption activity appeared to be dependent on the concentration of ammonia in the air. It follows from figure 4 that both the breakthrough and equilibrium capacities are independent of ammonia concentration if it is sufficiently high (18 and 51 mg m^{-3}), but drop sharply at NH$_3$ concentrations <5 mg m.$^{-3}$. This is due to a shift to the left of the sorption equilibrium, R–COOH + NH$_3$ ↔ R–COONH$_4$.

3.3. FIBAN AK-22

Aminocarboxylic polyampholyte FIBAN AK-22 reveals rather poor sorptive capacity for ammonia because its carboxylic acid groups are bound to amino groups forming an intra-polymer salt. These intra-polymer chains are destroyed by interaction with the strong acid H$^+$A$^-$ and the fixed carboxylate anion is protonized and substituted by the anion of strong acid. These processes can be depicted as follows:

$$RCOOH + H_2NR \leftrightarrow RCOO^-H_3N^+R + H^+A^- \leftrightarrow RCOOH + A^- H_3N^+R.$$

It has been found (POLKHOVSKI et al. [12], POLKHOVSKI and SOLDATOV [13]) that anion exchangers, especially polyampholytes, absorb much more additional acid than can be attributed to their electroneutrality (BOLTO and PAWLOWSKI [1]). This super-equivalent sorption is due to the formation of associates:

$$A^- H_3N^+R + H^+A^- \leftrightarrow HA_2^- H_3N^+R + H^+A^- \leftrightarrow H_2A_3^- H_3N^+R + H^+A^- \leftrightarrow ...$$
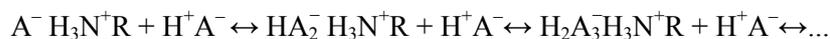
We have found that the amount of super-equivalently absorbed sulfuric and phosphoric acids is comparable to the capacity of ion-exchange resins (up to 4 meq g^{-1}). The super-equivalently sorbed acid can interact with ammonia, forming relative ammonium salts whose micro-crystals appear to be encapsulated inside of the ion-exchange fibers. In this case, the ion-exchange fiber plays the role of a carrier of the strong acid. The sorbed acid can be washed out with water. However, if the amount of acid solution is lower than the equilibrium value, the fiber with absorbed acid does not contain liquid on the surface and is suitable for the preparation of filtering materials.

We prepared such materials with ion exchanger FIBAN AK-22 impregnated with sulfuric and phosphoric acids and studied the sorption of NH$_3$ on the non-woven filtering layers. The experimental data obtained are illustrated by figures 5–7.

The impregnated materials appear to be efficient NH$_3$ sorbents. Their working and equilibrium capacities are comparable to those of the strong acid fiber FIBAN K-1 if the concentration of equilibrium acid is sufficiently high (see figure 5).
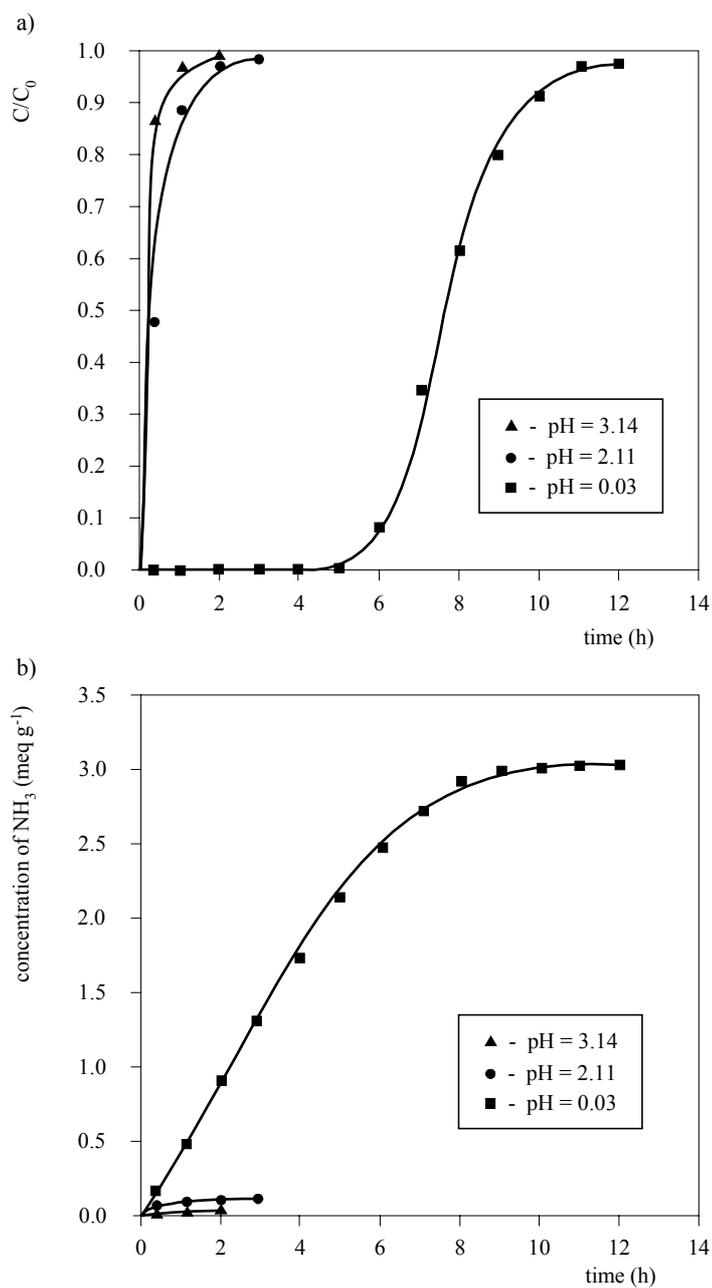
a)

b)

Fig. 5. Breakthrough curves (a); sorption curves of filtering layers of FIBAN AK-22 (H_2SO_4) (b). Conditions of the experiment: $P/P_0 = 0.5$; $C_{0\,NH_3} = 13$ mg m^{-3}; thickness of filtering layer, 6 mm; air flow rate, 0.081 m s^{-1}. Values of pH in figure relate to the solution of sulfuric acid equilibrium with parent FIBAN AK-22 fiber
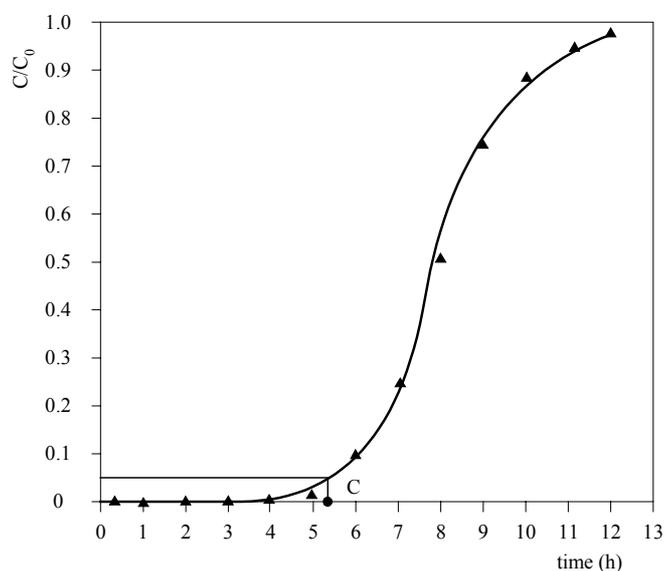
Fig. 6. NH_3 breakthrough curve through layer of AK-22 (H_3PO_4) non-woven fabric.
Fiber contains 0.54 g g^{-1} of super-equivalently sorbed phosphoric acid.
Conditions of experiment: $P/P_0 = 0.49$; $C_{0\,NH_3} = 18$ mg m^{-3}; thickness of filtering layer, 4 mm;
air flow rate, 0.081 m s^{-1}. Point *C* corresponds to breakthrough time
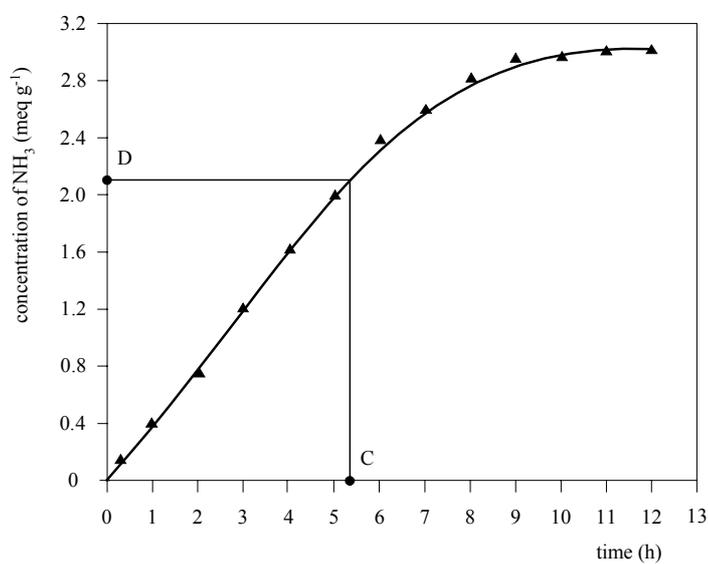

Fig. 7. Sorption curve of filtering layers of FIBAN AK-22 (H_3PO_4). Conditions of experiment:
see captions to figure 6. Point *D* corresponds to working capacity at breakthrough point

4. CONCLUSIONS

The data presented in the paper show that all three types of ion exchange filtering materials have a high capacity to sorb ammonia from air and can be used for the removal of ammonia from air. Nevertheless, each has advantages and drawbacks, predetermining possible areas of potential application. It is also worth noting that these sorbents remove other impurities of basic nature from air such as amines and indole derivatives that are important components of bad smells. This was observed in the course of exploitation of Neutraman horizontal scrubbers in which sulfuric acid was used as liquor sprayed onto the screens used as the air filters (MILLS [10]).

FIBAN K-1 appears to be a perfect material for deep air purification. It has a high sorption capacity and a high rate of sorption independent of the NH_3 concentration and air humidity within a wide range of these parameters. It can be used in the form of thin layers because the thickness of the mass-exchange unit is only 1.7 mm. This parameter was determined for the same experimental conditions as those discussed in this paper (KOSANDROVICH [9]). This value is an order of magnitude lower than that for sulfonic granular ion exchangers (VULIKH et al. [22]). FIBAN K-1 in the form of non-woven fabric can be used in indoor filtering devices and air conditioners. It has been successfully used in air-cleaning systems for the removal of the alkaline component of tobacco smoke ("smoking rooms") (Clear Air Ltd Smoking Room technical bulletin, 2001, Oy Cl;ea Air AB PL55, 07900 Loviisa, Finland). Non-woven fabrics of FIBAN K-1 perfectly satisfy the severe requirements for filtering materials for chemical respirators used in industry. The most valuable property of this material in such applications is its insensitivity to air relative humidity in combination with a high sorption rate.

Large-scale application of FIBAN K-1 material is difficult because the technology of its production is complicated. Furthermore, regeneration of the material saturated with ammonia is extremely difficult due to the affinity of ammonia for sulfonic groups. This results in the use of excessive amounts of acid solution. Therefore, application of FIBAN K-1 would only make sense if it is used as a disposable material or a centralized regeneration facility is available. At present it is used in the semiconductor industry for deep purification of air in clean rooms (info@mw-zander.com).

FIBAN K-4 can only be used in air purifying systems at relative humidity above $P/P_0 > 0.56$. At P/P_0 approaching 0.8 and ammonia concentrations of 10 ppm and higher, its sorption capacity is as high as that for FIBAN K-1. This means that FIBAN K-4 can be used in systems with high air humidity or in systems with additional air humidification. Filtering layers of FIBAN K-4 non-woven fabrics are longer than the mass transfer unit. KOSANDROVICH [9] estimates their length as 3.6 mm which means that the minimum thickness of the filtering layer in this case should be at least 5 mm. After saturation with ammonia, FIBAN K-4 is easily regenerated with almost an equivalent amount of diluted strong or weak acid solution.

FIBAN AK-22 fabrics impregnated with sulfuric or phosphoric acid are highly efficient in removing NH_3 from air and used as an active element of disposable filtering units in the semiconductor industry. The filtering element is a frame holding pleated fabric with thickness of 4–6 mm and mass of the filtering material of 3.6 kg. Such an element removes about 70 g of ammonia from air before breakthrough.

In conclusion, we note that all three types of fibrous ion exchangers can probably find a respective niche within environmental protection technologies.

ACKNOWLEDGEMENTS

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