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IMPREGNATED ACTIVATED CARBON MATERIALS FOR RESPIRATORY PURPOSE. CHEMISORPTION OF SULFUR DIOXIDE.

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The review is devoted to the use of impregnated activated carbon materials as chemisorbents of sulfur (IV) oxide. General methods for obtaining ordinary activated carbon, preparation of raw materials, their chemical activation with alkalis and acids followed by heat treatment (carbonization) in an inert environment or in the presence of a gaseous oxidizer, the role of acid-base and redox catalysts in this process are considered. The influence of the chemical composition of the activated carbon surface, the presence of functional groups, and their acid-base properties, as well as the products of surface reactions on the peculiarities of sulfur (IV) oxide adsorption is analyzed from the point of view of SO_2 removal efficiency and the possibility of SO_2 regeneration. An important role in these processes is played by the pore size, the possibility of co-adsorption of water, and the presence of an oxidant. The nature of adsorbent-adsorbate interactions on the surface of activated carbon, their energy, in particular, the contribution of so-called "physical" adsorption, van der Waals forces, hydrogen bonding, and the influence of surface functional groups are discussed. The activation of carbon raw materials with nitrogen-containing compounds leads to the N-doping of the surface, which increases the efficiency of SO_2 adsorption, facilitating not only van der Waals and electrostatic interactions, but also S←N binding. The influence of oxygen and oxygen-containing functional groups on SO_2 adsorption is also discussed.

To obtain impregnated activated carbon for SO_2 absorption, the original activated carbon of the required quality is impregnated with solutions of inorganic and organic compounds that remain on the inner surface of the activated carbon after drying. Impregnation blocks partly the porosity of activated carbon, but makes it more capable of chemical adsorption. Chemisorption, in which certain chemical bonds are formed between the surface of the activated carbon and the compound being adsorbed, is more selective than physical adsorption, where the size of molecules is critical for an effective capture process. It can be noted that unlike inorganic alkalis, which spoil the porous structure of activated carbon, treatment with a solution of ammonia or organic N-containing bases promotes SO_2 absorption. A special place in gas purification is occupied by activated carbon impregnated with ionic liquids, non-aqueous solvents being used for impregnation. A separate issue of the chemisorption of sulfur (IV) oxide by samples of impregnated activated carbon based on d-metals will be discussed in detail below.

Key words: impregnated activated carbon materials, sulfur dioxide, physical adsorption, chemisorption.

INTRODUCTION. The increase in the level of environmental danger in the conditions of war is associated with the destruction or damage, as a result of hostilities, of enterprises that are the largest (real or potential) polluters of the environment in peacetime [1]. Sulfur (IV) oxide, ammonia and aromatic hydrocarbons are among the main emergency emissions into the atmosphere by coke and by-product production enterprises [2–4]. One of the tasks of occupational health and safety departments at the enterprises of by-product coke industry is to provide workers and engineering and technical personnel with means of personal respiratory protection (MPRP) equipped with gas filter cartridges (GFCs), which are capable of absorbing toxic acid (in particular, SO_2) or/and basic (in particular, NH_3) gases, as well as vapors of organic compounds (in particular, C_6H_6 and C_6H_{12}), etc. [3].

In addition, to ensure the protection of the respiratory organs of workers and engineering and technical personnel of enterprises, civilians and military personnel in emergency situations, when the nature of the toxicant present in the air is unknown, it is desirable to have a gas filter of wide range of action.

The high porosity, large inner surface area, non-polarity, cheapness, chemical stability compared to other porous materials (zeolite, silica, alumina, etc.) of activated carbon (AC) make it suitable for removing toxic and irritating gases and vapors from the air [1–4]. The impregnation of a porous medium (in particular, AC) with carefully selected chemical compounds can significantly increase its absorption capacity for certain gases/vapors, as well as provide absorption capacity for gases/vapors that cannot be captured (detoxified) by non-impregnated AC [5–12]. This method has been used for many years in the production of gas filters and respiratory cartridges [13]. AC is widely used for the production of impregnated activated carbon materials (IACMs) – chemisorbents of chemically hazardous substances of inhalation action and acidic (SO_2, HCl, HF, Cl_2, F2, H_2S, CO_2, HCN, etc.), basic (NH_3, organic amines, etc.) and neutral (Hg, etc.) nature, as well as for the decontamination of volatile warfare agents from the air flow in the case of radioactive, biological and chemical contamination [5–9, 11, 14].

Methods of carbon activation.

To obtain ACs, which are used as adsorbents and catalyst carriers, methods of physical or chemical activation are usually used [5, 15–22]. Obtaining AC using physical activation includes the following stages: preparation of raw materials (separation, crushing, drying, etc.); pyrolysis (heat treatment in absence of oxidant at a temperature of 550–1000 °C; activation (heat treatment in the presence of an oxidant, CO_2 or water vapor at 700–1000 °C). The production of AC by the method of thermochemical activation is based on the introduction of chemical additives into the starting material followed by carbonization in an inert environment or in the presence of a gaseous oxidant. The transformation of raw materials into AC is carried out under the action of acid-base or redox catalysts ($ZnCl_2$, $FeCl_3$, Al_2O_3; HNO_3, H_2SO_4, H_3PO_4, $(NH_4)_2HPO_4$; carbonates, acetates or hydroxides of alkali metals, etc.) [5, 15–22]. Catalysts activate the transformation of aliphatic fragments, practically without touching aryl C-C bonds, remove oxygen, hydrogen and other heteroatoms with simultaneous carbonization and activation at temperatures generally below 700 °C. As a result, ACs with a developed porous structure are obtained.

According to the results of the physicochemical study of the products of alkaline activation of various raw materials, the specific surface area, the pore volume and size, the size distribution of pores depend on the nature of the raw material itself and the alkali used (LiOH, NaOH and KOH), as well as its content in the original mixture; the activating ability of hydroxides decreases in the order KOH > NaOH > LiOH [18]. Phosphoric acid leads to the expansion of micro- and mesopores in activated carbon [19, 20, 21, 23].

As a rule, acid treatment leads to an increase in the number of acid groups, removes mineral elements and improves the hydrophilicity of the surface, which will have greater access to the aqueous phase [24, 25].

Adsorption of SO_2 on the surface of activated carbon.

When studying SO_2 adsorption by AC, the researchers took into account such parameters as porosity, chemical composition of the surface, acid-base properties and ash content; the products of surface reactions were analyzed from the point of view of removal efficiency and the possibility of regeneration [26–31].

There is an optimal pore size (approximately 7 A) at which the adsorption of SO_2 [32] and its oxidation to SO_3 [33] are favorable. Although in such pores, the absorption potential is not maximal (σSO_2 = 4.29 E [34]), a high capacity is achieved due to the adsorption of SO_2 and SO_3 with the subsequent formation of H_2SO_4 [31]. In such pores, SO_2 together with H_2O can statistically cover the walls of pores, forming a monolayer. This makes oxidation and reaction with co-adsorbed water molecules possible. It should be noted that H_2SO_4 at 25 °C has a higher density (ρH_2SO_4 = 1.83 g/cm^3) than liquid SO_2 (ρSO_2 = 1.27 g/cm^3), but a lower density than that of SO_3 (ρSO_3 = 1, 93 g/cm^3). In addition, its boiling point is about 330 °C, which is much higher than that of SO_2 (-10 °C) and SO_3 (45 °C) [35]. Given the above, the amount of H_2SO_4 physically adsorbed from the vapor phase should be greater than the amount of SO_2 and/or SO_3 under the same conditions (pressure and temperature). It follows that the order of decreasing physical adsorption "capacity" should be as follows: $H_2SO_4 > SO_3 > SO_2$. If the pore size is too small, water molecules cannot be co-adsorbed near SO_2, preventing the formation of sulfuric acid. Apparently, as in the case of hydrogen sulfide adsorption [36], the uniform distribution of micropores affects the dispersion of active sites, where SO_2 can be oxidized to SO_3, which is then converted to H_2SO_4, which is adsorbed until all pores are filled. Increasing the pore size decreases the degree of $SO_2 \rightarrow SO_3$ conversion and thus the total amount of SO_2 retained by the AC sample. According to [37], the adsorption capacity of AC fibers for SO_2 is inversely proportional to the size and volume of pores.

Adsorbent-adsorbate interactions on the AC surface are very complex, as they include a wide range of physical and chemical properties of the adsorbent, and sometimes there are significant uncertainties regarding individual adsorption mechanisms [38]. Sulfur (IV) oxide is absorbed by AC with two adsorption energies: ~50 kJ/mol, ~80 kJ/mol; according to [27, 33, 39–43], the first is associated with the interaction of SO_2 and free sites on the surface due to "van der Waals forces" and corresponds to weak "physical" adsorption, and the second corresponds to chemisorption, which is enhanced in the presence of oxygen. However, the energy of formation of van der Waals

complexes is 20–40 kJ/mol [44]. The first energy can also correspond to the energy of formation of an "average" hydrogen bond (ΔH = 17–63 kJ/mol [45, 46]); directionality, not energy, is the defining feature of a hydrogen bond, which is one type of chemical interaction [47]. In addition to porosity, the acid-base properties of the surface are also an important factor that increases SO_2 adsorption [26–28, 30, 39, 40]. Surface functional groups play the role of active centers and predominate in SO_2 chemisorption [26, 27, 43]. Functional groups have a great influence on SO_2 adsorption and oxidation [40, 48, 49]. Currently, the experimental study of this effect was carried out by impregnating AC or raw materials for its production with aqueous solutions of HNO_3 [27, 29, 50–53], H_3PO_4 [53, 54], KOH [29, 33, 54–57], NaOH [39, 51, 58]); modification or activation by high-temperature gas or steam: CO_2 [33, 54], H_2O [33], etc.

Effect of chemical activator on AC properties.

Surface groups of pyrone and pyrone-like nature or centers having Lewis basicity are responsible for the adsorption of sulfur (IV) oxide with an energy of ~50 kJ/mol [39, 48]. Increasing the basic nature of carbon through the inclusion of basic forms of nitrogen turned out to be a positive factor affecting the absorption of SO_2 and its oxidation to sulfuric acid [31, 59–64]. Obviously, the above-mentioned first adsorption energy (~50 kJ/mol) in this case is determined not only by van der Waals interactions (dipole-dipole interactions and dispersion forces), but also by π-dative S←N or S←O bonding ($\Delta HS{\leftarrow}N$ = 20–90kJ/mol; $\Delta HS{\leftarrow}O$ = 10–55 kJ/mol [65]) with the formation of charge transfer complexes with Lewis bases and H-bonding, similarly to [65].

In the process of obtaining AC, the authors of [62, 66] carried out N-doping of various carbon raw materials (sub-bituminous coal, lignite; AC fabric based on viscose) by activation with steam enriched with ammonia or its derivatives ($(NH_4)_2CO_3$, H_2NNH_2, NH_2OH, $H_2NC(O)NH_2$; this leads to the formation of various N-containing groups (amides, imides, lactams, nitriles, pyrroles, pyridines, etc.) – Lewis basic centers, which favors S←O and S←N bonding, similarly to [65]. AC with a high N content was obtained [31] by the carbonization of macroporous vinyl pyridine polymers, which are themselves chemisorbents of acid gases, in particular SO_2 [67].

The authors of [43] indicate an increase in SO_2 adsorption efficiency as a result of the N-doping of the carbon surface due to increased physical adsorption. For a pristine carbon surface after N-doping, SO_2 physical adsorption mainly occurs on the basal plane through van der Waals (similarly to [68, 69]) or π-dative interactions (similarly to [65, 70]). N-doping redistributes electrons on carbon surfaces, thereby changing not only the intensity but also the types of interactions involved; quaternary N atoms contribute to SO_2 adsorption, mainly due to the enhancement of "van der Waals" interactions between the basal plane and SO_2 [43]. The improvement of SO_2 adsorption by pyridine and pyrrole compounds corresponds to enhanced electrostatic interactions in the edge regions. These results show that N-doping can increase SO_2 adsorption efficiency by facilitating not only van der Waals and electrostatic interactions [43], but also mainly S←N bonding.

The oxygen-containing functional groups on the AC surface include carboxyl, phenolic, quinone, lactone, carboxyanhydride groups,

cyclic peroxide, etc. [71]. According to the data of X-ray photoelectron spectroscopy [72], when sulfur (IV) oxide is absorbed, the relative content of the carbonyl (C=O) group, which exists mainly in the form of quinone and chromene on the AC surface [73], decreases, and that of the C–O (hydroxyl and ether [74]) group increases. The effect of ketone C=O groups on desulfurization activity was confirmed by passivation with phenylhydrazide [75]; they are the internal active centers of the desulfurization reaction on carbon materials. The centers of "physical" sorption can also be carboxyl or hydroxyl groups [31]. A small part of SO_2 can also react with OH groups to form hydrosulfite anions (as a chemisorption form) [42]; when SO_2 interacts with the C=C bond, 1,3,2-dioxathiolane and/or 1,2-oxathiethene-2-oxide are formed, which decompose with the formation of CO_2 and an intermediate episulfide [76]. There are data [30, 39] that oxygen present in the system can negatively affect the amount of adsorbed SO_2. This is due to its ability to react with the carbon matrix, its oxidation and, as a result, the reduction of the surface area [37, 77]. On the other hand, during SO_2 adsorption in the absence of water, oxygen functional groups significantly improve adsorption characteristics, which, according to [37], is due to surface reactions of quinones with SO_2 and water with the formation of diol and sulfuric acid. According to [33], removing oxygen from the surface forms new high-energy SO_2 adsorption/oxidation centers. Surface acid groups are a catalyst for SO_2 oxidation [27]; the adsorption capacity of AC for SO_2 is inversely proportional to the amount of O_2 adsorbed on its surface [29].

The reactivity of AC depends on the balance between the content and type of oxygen functional groups and the surface area [78]. The authors of [31, 33] found that pyridine functional groups, which are located at the edges of graphene layers, significantly increase the amount of SO_2 adsorbed and converted into sulfuric acid, especially when the groups are located in pores with a size of 7–8 E. The only negative point of this mechanism is a strong adsorption of H_2SO_4 and, as a result, difficulties in the regeneration of adsorbents [27].

The chemical nature of the activated carbon surface can be changed by oxidation treatment. After treatment with nitric acid, the total concentration of surface oxygen increases, the concentration of basic surface groups decreases significantly, and the content of acid groups significantly increases, which improves both the extraction of the formed sulfuric acid and the adsorption capacity for SO_2 and its oxidation [27].

The oxidation of SO_2 to H_2SO_4 (sulfates) on catalysts takes place via the Eli-Riedil (ER) [79–81], Langmuir-Hinshelwood (LH) [81, 82] or Mars-van Krevelen (MvK) [81] mechanisms: the LH and ER mechanisms account for the oxidation of SO_2 (adsorbed or from the gas phase) through surface-activated molecular oxygen, while the MvK mechanism is closely related to surface O lattices that generate atomic oxygen vacancies during the formation of SO_3 and H_2SO_4. Since the co-adsorption of SO_2 and O_2 on carbon catalysts has a large adsorption energy (-1.03 eV) compared to the individual adsorption of SO_2 (-0.45 eV) or O_2, then, according to [75], the oxidation of SO_2 on carbon materials is more likely to occur by the LH mechanism, compared to the ER mechanism. According to the data given in the review [83], when SO_2 is absorbed from a gas mixture (SO_2 : O_2 = 2 : 1), the catalytic ac-

tivity of adsorbents decreases in the following order:

$$АВ > V_2O_5 > графіт > Cr_2O_3 > Fe_2O_3.$$

The acidic and alkaline modifications of AC (by impregnating it with 1 M solutions of HNO_3 and KOH, respectively, at 70 °C) affect the concentration of functional groups on the surface of AC: they reduce the relative content of C–H, but increase the share of the functional groups C–O, C= O and O=C–O; and the former modification has a stronger effect than the latter one [84]. The BET specific surface area and the total pore volume of acid-modified AC were decreased, and those of alkali-modified AC were increased.

In the presence of air moisture, sulfur (IV) oxide on the AC surface forms a hydrate (reaction 1), which subsequently dissociates (reaction 2), which contributes to an increase in the acidity of the AC surface:

$$SO_2 + H_2O \rightleftarrows SO_2 \cdot H_2O, \quad (1)$$

$$SO_2 \cdot H_2O + H_2O \rightleftarrows HSO_3^- + H_3O^+ \quad (2)$$

Methods of obtaining IACM.

For the preparation of IACM, activated carbon of the required quality for a specific application is impregnated with solutions of inorganic and organic compounds (acids, bases, salts, etc.; see the table), which after drying or other stages of further treatment remain on the inner surface of activated carbon [3, 85, 86]. AC impregnation is carried out by soaking [14, 87–90], spraying [6], sublimation using a fluidized bed adsorption column [13, 14]. Impregnation is carried out:

– with some volume of the impregnating solution, which occupies a certain portion of the total volume of AC pores ($V_{р\text{-}ну}/V_{пор}$) [91, 92];

– by the initial moisture content method (capillary impregnation, dry impregnation) – limiting the volume of the solution only to fill the volume of pores (it is determined at what volume of the solution for the impregnation of a water-soluble compound, AC particles begin to adhere to each other or to the walls of the vessel for impregnation even after several minutes of mixing after adding the solution) [12–14, 87, 93–98];

– by the method of ultrasonic impregnation [36, 55, 99, 100];

– by the method of mechanical mixing [87, 100];

– by the spraying method [5] (AC is sprayed in a rotating chamber or in a fluidized bed under certain conditions);

– by the high- pressure impregnation method [100];

– by the hydrothermal sol-gel method [34].

In some cases, impregnated reagents are present in the form of hydroxides, carbonates, chromates or nitrates, which are subjected to heat treatment at higher temperatures (150–400 °C) to decompose the above anions. An even impregnation distribution on the inner surface of AC is important. Blocking of micro- and mesopores (responsible for physical adsorption) should be avoided in order that the impregnating chemical reagent remains accessible for adsorbates [5, 6].

AC impregnation partially blocks the porosity, but in turn makes AC more capable of chemisorption, which is necessary to capture some low-molecular-weight volatile pollutants [3]. Chemisorption is more selective than physical adsorption, where the size of molecules is critical for an efficient capture process. During chemisorption, certain chemical bonds are formed between the surface of activated

carbon and the adsorbed compound, so the choice of impregnating reagents depends on the field of application. The main technological requirement to the obtained fibrous IACMs for respiratory purposes is that after drying they remain elastic for the construction of filter elements [101].

Adsorption of SO_2 on the surface of impregnated activated carbon.

According to the data given in the table, chemisorbents of SO_2 can be AC impregnated with alkaline reagents (NaOH, KOH, K_2CO_3, ammonia, organic amines, etc.); oxidants ($KMnO_4$, $KClO_3$); ionic liquids (ILs); salts, oxides and hydroxides of transition metals (V, Cr, Mn, Cu, Zn, Ag, Mo, etc.). The protective properties against SO_2, such as dynamic activity (DA, mg of SO_2/g), of IACM samples are affected by the physicochemical characteristics of the carrier (AC), the nature of the applied reagents, impregnation and experimental conditions.

Microporous AC obtained by mixing anthracite with KOH or NaOH was distinguished by a large surface area, which makes it a promising sorbent for SO_2 capture [55]. In addition, the products of desulfurization are alkali metal sulfates (K_2SO_4, Na_2SO_4, etc.) applied to AC, which can be used as soil conditioners or prolonged fertilizers, eliminating the need for sorbent regeneration [32].

However, the impregnation of AC based on coal dust with aqueous NaOH solutions destroys the strength of the porous structure and causes its collapse during the adsorption process, thereby reducing the number of micromesopores and the specific surface area of the carrier and does not contribute to the adsorption of SO_2 by AC-NaOH samples [49]. According to X-ray photoelectron spectroscopy [40], pyridine and pyrrole fragments are present on the surface of AC-NH_3 samples obtained by impregnating AC fibers with aqueous solutions of NH_3 (for 40 hours) followed by drying at 100 °C, which causes its increased alkalinity and enhances catalytic sulfoxidation. The authors of [102, 103] obtained chemisorbents of SO_2 with prolonged action by impregnating AC with aqueous solutions of potassium iodide. According to the results of experimental studies by the authors of this review, the formation of molecular iodine (reaction 3) was observed on the surface of AC-KI based on the activated carbon fibers of the "Karbopon- β-Aktiv" material, in contrast to lavsan fibers [104, 105], which is obviously due to the presence of acid groups on the surface of the former:

$$4I^- + 4H_3O^+ + O_2 \rightarrow 2I_2 + 6H_2O. \qquad (3)$$

Thus, iodine formed on a carbon base has a promoting effect due to hydrolytic oxidation (reaction 4), improving protective characteristics, similarly to [105].

$$I_2 + HSO_3^- + 4H_2O \rightarrow 2I^- + SO_4^{2-} + 3H_3O^+ \quad (4)$$

According to [102], increasing the potassium iodide content of AC-KI to 16% improves its protective properties against SO_2 (τ_{pa} (SO_2)) according to equation (5); then when ωKI increases to 22%, this characteristic approaches an almost horizontal asymptote, after which it sharply decreases. This indicates that at high contents, KI (like K_2CO_3 [5], 1,8-diazobicyclooctane (DABCO) [106], triethanolammonium citrate (1:3) [107]) aggregates and/or blocks AC pores, which limits the accessibility of I_2 for SO_2. Along with this, increasing the KI content lowers the sorption capacity of KI with respect to C_6H_6 according to equation (6):

Characteristics of IACMs – chemisorbents of SO_2.

Raw material	Impregnation conditions: Modifier, Chemical formula, In the solution	Impregnation conditions: Modifier, Chemical formula, On the surface	Impregnation conditions: Modifier, Content, wt %, In the solution	Impregnation conditions: Modifier, Content, wt %, On the surface	Experimental conditions: T, K	Experimental conditions: SO_2 concentration in the gas-air mixture	Experimental conditions: T, K	DA, mg of SO_2/g	References
1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*
ACP	NaOH	NaOH			473	3000 ppm	298	151	[39]
ACP	NaOH	NaOH	0,1 M		323	600 ppm	343		[49]
GAC	KOH	KOH		14,29	368	1007 ppm	403	47,6	[93]
GAC	KOH					5 ppm	298	18,4	[96]
GAC	KOH	KOH		10		5 ppm	298	12	[123]
GAC	K_2CO_3	K_2CO_3	1,7–22,0			15000 ppm 1000 ppm			[87]
ACFs	$KMnO_4$	$KMnO_4$	6	43,3		50 ppm	293	76	[124]
ACFs	$KClO_3$	$KClO_3$		22		50 ppm	293	39	[124]
ACFs	$NH_3 \cdot H_2O$		13		373	300-1500 ppm	343	77	[125]
ACFs	$NH_3 \cdot H_2O$					2000 ppm	303	28,3	[126]
ABC	MDEA		10				393	156,2	[118]
ACG	DABCO		9–12			50 ppm	443	220	[106]
ACG	DABCO			6,49	368	57 ppm	298	374	[114]
ACG	[C2mim][Ac]		20			5 ppm	298	12,6	[96]
ACG	[C2mim][Ac]		50			5 ppm	298	~19	[96]

1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*
ACG	[C2mim][Ac]		70			5 ppm	298	~28	[96]
ACG	[C2mim][Ac]		86	36		5 ppm	298	54,8	[96]
ACG	[C2mim][Ac]			30		5 ppm	298	26	[123]
AC	$[TEAH]_3[Cit]$			20	293		298	0,256	[107]
AC	[TEAH][Lact]			20	293		298	0,230	[107]
ACP		$V(OH)_5$			373	200 ppm	298	0,803	[127]
		$Mn(OH)_2$			373	200 ppm	298	0,339	[127]
		$Cu(OH)_2$			373	200 ppm	298	0,436	[127]
GAC	CrO_3 $CuCO_3$ NH_4HCO_3 $AgNO_3$ DABCO			14,33 35,82 14,33 5,73 1,15		50 ppm	443	229	[106]
GAC	$Cu(NO_3)_2$ $AgNO_3$ $Zn(NO_3)_2$ Na_2MoO_4 DABCO	CuO Ag ZnO MoO DABCO		9,09	363	50 ppm		448	[14]

*ACP – activated carbon powder; ACFs – activated carbon fibers; ABC – activated biochar; GAC – granulated activated carbon.

$$\tau_{pa}(SO_2) = -11{,}787 + 17{,}739 \cdot \omega_{KI}, \quad R^2 = 0{,}9876;\ n = 12, \qquad (5)$$

$$\tau_{pa}(C_6H_6) = 380{,}36 - 87{,}78 \cdot \omega_{KI}, \quad R^2 = 0{,}9617;\ n = 12. \qquad (6)$$

where $\tau_{pa}(SO_2)$ is the time of the protective action against SO_2 (min) at CSO_2= 150 mg/m^3, a relative humidity of the GAM of 90-95%, a flow rate of the GAM of 2.0 cm/s; $\tau_{pa}(C_6H_6)$ is the time of protective action against C_6H_6 (min) at C_6H_6 = 500 mg/m^3, a relative humidity of the GAM of 90–95%, a flow rate of the GAM of 2.0 cm/s); ωKI is the mass fraction of KI, %.

The addition of a water-repellent additive (polytetrafluoroethylene) to AC-KI leads to the fact that the formed H_2SO_4 is continuously released from the surface of AC-KI [102]. However, AC-KI has disadvantages due to the carrying away of molecular I_2 from the surface with the air flow.

To remove acidic gaseous pollutants, IAC materials based on impregnating solutions of N-containing organic bases are used: monoethanolamine (MEA) [108-111], diethanolamine (DEA) [109, 110, 112], triethanolamine (TEA) [113], DABCO [14, 106, 112, 114–116], N-methyldiethanolamine (MDEA) [118], piperazine [111], etc., similarly to [119, 120]. IACs based on N-containing organic bases are also widely used for the sanitary removal of formaldehyde from the air [121]. As is known [122], ethanolamines and aminoguanidine are inhibitors of S(IV) → S(IV) sulfoxidation. However, no information was found in the literature about the effect of AC impregnation with the listed compounds on the course of the above reaction on the AC surface.

During the chemisorption of sulfur (IV) oxi de by carbamide-impregnated AC in the presence of oxygen and water vapor, the following reduction reactions are possible:

$$1{,}5SO_2 + (NH_2)_2CO \rightarrow 1{,}5S + N_2 + CO_2 + 2\,H_2O; \qquad (7)$$

$$H_2SO_4 + (NH_2)_2CO \rightarrow CO_2 + N_2 + S + 3H_2O; \qquad (8)$$

$$SO_3 + (NH_2)_2CO \rightarrow CO_2 + N_2 + S + 2H_2O. \qquad (9)$$

A special place in gas purification is occupied by IACs based on ionic liquids; in this case, impregnating solutions are prepared using nonaqueous solvents (methanol, ethanol) [96, 107, 123].

Based on data from thermogravimetric, IR and 1H NMR spectroscopic studies, it was established [96] that IAC based on 1-ethyl-3-methylimidazolium acetate ([C_2mim][Ac]; EMA) absorbs SO_2 through physical and chemical sorption. AC-EMA has a breakthrough absorption capacity for SO_2 that is 26 times and more greater than that of AC samples impregnated with other salts: 1-ethyl-3-methylimidazolium (lactate, methyl sulfate and hydrosulfate), 1-butyl-3-methylimidazolium (hydrosulfate and tetrafluoroborate), 1-hexyl-3-methylimidazolium (bis(trifluoromethylsulfonyl)imide and tris(pentafluoroethyl)-trifluorophosphate) and 1-allyl-3-methylimidazolium (chloride).

The chemisorption of SO_2 by the ionic liquid [C2mim][Ac] on the AC surface occurs as a result of displacement of acetate anions by sulfate and sulfite anions [123]. Since hydrosulfate (pK_b = 17.0 [128]) and hydrosulfite (pK_b = 12.9 [128]) are weaker bases than the acetate ion (pK_b = 9.24 [128]), in the presence of two acids (H_2SO_4 and $SO_2 \cdot H_2O$), CH_3COO- is protonated and replaced by

HSO_4– and H_SO_3– anions, which leads to the formation of CH_3COOH, [C2mim][HSO_4] and [C2mim][HSO_3]. Chemisorbed forms of SO_2 in the AC-[C2mim][Ac] sorbent can be AC-[C2mim][HSO_4], AC-[C2mim][HSO_3], H_2SO_4 and $SO_2 \cdot H_2O$.

It should be noted that most researchers, in contrast to [96, 105, 122, 129], do not pay due attention to the influence of water on the processes of SO_2 capture by both AC and IAC. The authors of [96] found that increasing the moisture content (from 50 to 80%) of purified air increases the protective characteristics of AC-EMA samples against SO_2, which indicates the predominance of chemical sorption over physical sorption in this case. Impregnation of the AC surface with IL: with ammonium citrate and triethanolamine lactate (3TEA·H3Cit and TEA·HLact, respectively) leads to an increase in their SO2 absorption capacity from 3.34 and 1.29 mol SO2/mol IL (for [$TEAH]_3$[Cit] and [TEAH][Lact]) to 6.60 and 1.95 mol SO_2/mol IL (for samples of AC-[$TEAH]_3$[Cit] and AC-[TEAH][Lact]) [107]. When impregnating with IL, thin films are formed on the AC surface, and the functional centers of AC are thereby exposed, which increases their reactivity towards SO_2. The issue of the chemisorption of sulfur (IV) oxide with IAC samples based on d-metals has been discussed in detail in research papers [6, 114, 130] and reviews [131, 132], which deserves special attention.

CONCLUSIONS. ACs are used as adsorbents and catalyst carriers to remove toxic and irritating gases and vapors from the air. In order to increase the chemisorption capacity of **AC for** chemically hazardous substances of inhalation action and acidic and basic nature, their impregnation with various reagents should be carried out. Chemisorbents of SO_2 can be **ACs** impregnated with alkaline reagents, oxidants, ILs, as well as salts, oxides and hydroxides of transition metals. The protective properties of **IACM** samples against SO_2 are influenced by the physical and chemical characteristics of the carrier **(AC),** the chemical nature of the applied reagents, the impregnation and experimental conditions. In this regard, **IACMs** based on impregnating solutions of N-containing organic bases are promising, however, due attention to this issue has not been given by researchers. No data on SO_2 sulfoxidation on the surface of the above chemisorbents were found in the literature. In our opinion, the influence of moisture on the chemisorption of SO_2 by **IACM** samples has been little investigated.

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ІМПРЕГНОВАНІ АКТИВОВАНІ ВУГІЛЬНІ МАТЕРІАЛИ РЕСПІРАТОРНОГО ПРИЗНАЧЕННЯ І ХЕМОСОРБЦІЯ ДІОКСИДУ СІРКИ

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Огляд присвячено використанню імпрегнованих активованих вугільних матеріалів як хемосорбентів оксиду сірки (IV). Розглянуто загальні способи отримання звичайного активованого вугілля, підготовки сировини, її хімічної активації лугами та кислотами з наступним термообробленням (карбонізацією) в інертному середовищі або за присутності газоподібного окислювача, роль у цьому процесі кислотно-основних та окисно-відновних каталізаторів.

Вплив на особливості адсорбції оксиду сірки (IV) хімічного складу поверхні активованого вугілля, присутності функціональних груп, їхніх кислотно-основних властивостей, а також продуктів поверхневих реакцій проаналізовано з точки зору ефективності видалення та можливості регенерації SO_2. Важливу роль у цих процесах відіграють розмір пор, можливість співадсорбції води, присутність окислювача. Обговорено природу взаємодій адсорбент – адсорбат на поверхні активованого вугілля, їхню енергію, зокрема внесок так званої «фізичної» адсорбції, ван-дер-ваальсових сил, воднево зв'язку, вплив поверхневих функціональних груп. Активація вугільної сировини азотовмісними сполуками призводить до N-легування поверхні, що підвищує ефективність адсорбції SO_2, полегшуючи не лише ван-дер-ваальсові та електростатичні взаємодії, а й S←N зв'язування. Обговорено також вплив на адсорбцію SO_2 кисню та кисеньвмісних функціональних груп.

Для отримання імпрегнованого активованого вугілля для поглинання SO_2 вихідне активоване вугілля потрібної якості просочують розчинами неорганічних та органічних сполук, які після сушіння залишаються на внутрішній поверхні активованого вугілля. Імпрегнування блокує частину пористості активованого вугілля, але робить його більш здатним до хімічної адсорбції. Хемосорбція, за якої утворюються певні хімічні зв'язки між поверхнею активованого вугілля і сполукою, що адсорбується, є більш селективною, ніж фізична адсорбція, де розмір молекул має вирішальне значення для ефективного процесу вловлювання. Можна відмітити, що на відміну від неорганічних лугів, які псують пористу структуру активованого вугілля, оброблення розчином аміаку або органічних N-вмісних основ сприяє поглинанню SO_2. Особливе місце у газоочищенні займає активоване вугілля, імпрегноване іонними рідинами, при просочуванні якими використовують неводні розчинники. Окреме питання хемосорбції оксиду сірки (IV) зразками імпрегнованого активованого вугілля на основі d-металів буде детально розглянуто далі.

Ключові слова: імпрегновані активовані вугільні матеріали, діоксид сірки, фізична адсорбція, хемосорбція.

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