KINETICS OF SULFUR DIOXIDE ADSORPTION ON MODIFIED ACTIVATED COAL PRODUCED FROM PEACH SHELLS

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ABSTRACT

The kinetics of sulfur dioxide adsorption on modified coal produced from the peach shell was investigated. It was determined the optimal conditions to produce modified activated coals for the processes of effective purification of gases from sulfur dioxide, confirmed by industrial tests. The most rapid adsorption of sulfur dioxide occurs on the shell treated by ZnCl2 (impregnation coefficient 0.4), followed by activation in the CO2 stream at a temperature of 773 K, the pore size of which is easily accessible to sulfur dioxide molecules regardless of their molecular weight and structure. The values of the dynamic characteristics show that with the increase of particle size, the «value of the dead layer» – disabled – increases, therefore, with the increase of particle size, the dynamic activity of the adsorbent decreases. With the increase of the gas flow speed, the time of the protective action is significantly reduced, the process proceeds intensively.

Keywords: Adsorption, Sulfur Dioxide, Adsorbent, Gas Purification, Modified Activated Coal, Peach Shell.

INTRODUCTION

One of the toxic components released in huge quantities by industrial enterprises into the atmosphere as sulfur dioxide. The main sources of sulfur dioxide pollution are thermal power plants, ferrous and non-ferrous metallurgy, chemical and oil refining industries. Sulfur-containing in fuels and ores turns into the aggressive gas during their combustion or processing. Preliminary desulfurization of fuel and ores cannot fully solve the problem of decreasing sulfur dioxide emissions into the atmosphere. In the chemical industry, the main source of atmospheric sulfur dioxide pollution is sulfuric acid production. The issue of sulfurous anhydride utilization from technological gases and its use for the production of

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valuable products (sulfuric acid, elemental sulfur, liquid sulfurous anhydride), as well as the issue of reduction of the air basin pollution, should be given the great attention.\textsuperscript{7,8} Adsorbents are an effective tool for recuperation and neutralization of sulfur dioxide, and their capabilities in this direction have not been determined yet. Carbon porous materials are mainly used for recuperation of sulfur dioxide.\textsuperscript{9,10} Adsorption methods for separation and purification of substances in the liquid and gas phases require the selection of effective and cost-effective adsorbents.\textsuperscript{11-15} In recent years, numerous studies have focused on the use of carbon materials produced from fruit shells and rice husk.\textsuperscript{16,17} Often the used carbon materials do not correspond to the requirements of the technological process, in some cases, their use is economically unjustified, because of the high cost and insignificant raw material base. Therefore, the production of new efficient and cheap natural carbon materials from available industrial raw materials is one of the urgent tasks for scientists and technologists. A new promising raw material for the production of carbon-containing materials is vegetable raw materials, in particular the shells of fruit trees.\textsuperscript{18,19} Vegetable cellulose of the peach shell is low-carbon, and its high density determines the possibility of obtaining on its basis of firm adsorbents with a high specific surface area. The production of cheap sorbents from food wastes can create the conditions for the introduction of new technologies and the decrease of harmful emissions into the environment.\textsuperscript{20-22} Also, the production of a wide range of powdered and granular sorbents from industrial wastes will allow us to obtain additional profits, as the necessity for such products at various enterprises is great.

EXPERIMENTAL

Tribochemical Activation of Peach Shell in the Presence of Surfactant

Production of activated coal was carried out by tribochemical activation of peach shell in a two-chamber shock-motion grinding mill in the presence of surfactant-alkylaryl sulfonate RArSO\textsubscript{2}OM. Tribochemical activation results in multiple expansion of porosity and the formation of a fresh surface.\textsuperscript{23} After activation in the first chamber of the mill in the air the pore volume of the shells reaches $0.5 \times 10^{-4}$ m$^3$/kg and in the second chamber of the mill in alkylaryl sulfonate the pores, volume reaches $1.8 \times 10^{-4}$ m$^3$/kg. For the determination of the separate elements of peach shells, the elemental analysis was carried out, which showed that the shell consists of carbon (76%), hydrogen (23.586%), and nitrogen (0.372%).\textsuperscript{24,25}

Thermal Activation of Peach Shells

Thermal activation of peach shells was carried out in a furnace for activation in the atmosphere of carbon dioxide\textsuperscript{26}. The temperature of the furnace was measured by a platinum-rhodium-platinum thermocouple, regulated by a thermoregulator. Activation was conducted at temperatures 573-1273 K with heating during 1-4 hours. Heat-treated samples of peach shells before measuring their adsorption properties were preserved in hermetic conditions.

Chemical Activation of Peach Shells

For the chemical activation of peach shells, equipment consisting of flask, electric heater, reverse refrigerator and thermometer was used\textsuperscript{27,28}. Before chemical treatment, the mechanoactivated shell was sifted through a sieve of 0.1 mm. Further, the chemical activation of the shell was carried out by sulfuric, hydrochloric, phosphoric acids and zinc chloride. After the samples were washed with hot distilled water, then dried at 378 K for 2 hours, then the shell was cooled in a desiccator.

Studies of Sulfur Dioxide Adsorption

For research of the adsorption extraction of sulfurous anhydride as the adsorbent, we used the peach shells activated by zinc chloride with the impregnation coefficient from 0.2 to 0.6, followed by heat treatment at temperatures from 573 K to 873 K in the CO$_2$ stream. To study the mass transfer issues during the adsorption of sulfurous anhydride, we used the experimental device, the main part of which is a glass tube with an internal diameter of 25 mm and a total height of 200 mm. The chosen diameter of the
dynamic tube was dictated by the necessity to achieve the uniformity of the flow distribution over the
tube cross-section and to ensure the thermostat of the layer during the experiment.

RESULTS AND DISCUSSION

The results of studies of sulfur dioxide adsorption are shown in Table-1 and Fig.-1, at the initial mass
concentration equal to 12% (vol). The best adsorption capacity on sulfur dioxide has the shells activated
at a temperature of CO₂ - 773 K and subsequently activated by ZnCl₂ with the impregnation coefficient
(0.4; 0.5; 0.3) and, as well as the shells activated at a temperature of CO₂ – 873 K and subsequently
activated by ZnCl₂ with the impregnation coefficient -0.4. These adsorbents almost completely remove
sulfur dioxide from the initial gas stream.

Table-1: Characteristics of the Adsorption Values of Sulfur dioxide From the Gas Medium by Activated Peach
Shells

| Impregnation Coefficient of ZnCl₂ | Temperature of Activation of CO₂, K | Pressure (millimeter of mercury) | Adsorption value \( \alpha \), % (weight) |
|----------------------------------|------------------------------------|---------------------------------|----------------------------------|
| 0.2                              | 773                                | 4                              | 4.2                              |
|                                  |                                    | 8                              | 7.7                              |
|                                  |                                    | 12                             | 9.6                              |
|                                  |                                    | 16                             | 9.8                              |
| 0.3                              | 773                                | 4                              | 5.1                              |
|                                  |                                    | 8                              | 9.3                              |
|                                  |                                    | 12                             | 11.8                             |
|                                  |                                    | 16                             | 12.3                             |
| 0.4                              | 573                                | 4                              | 3.6                              |
|                                  |                                    | 8                              | 6.7                              |
|                                  |                                    | 12                             | 8.0                              |
|                                  |                                    | 16                             | 8.5                              |
| 0.4                              | 673                                | 4                              | 2.5                              |
|                                  |                                    | 8                              | 5.2                              |
|                                  |                                    | 12                             | 7.2                              |
|                                  |                                    | 16                             | 7.6                              |
| 0.4                              | 773                                | 4                              | 8.5                              |
|                                  |                                    | 8                              | 12.1                             |
|                                  |                                    | 12                             | 13.9                             |
|                                  |                                    | 16                             | 14.8                             |
| 0.4                              | 873                                | 4                              | 7.0                              |
|                                  |                                    | 8                              | 11.1                             |
|                                  |                                    | 12                             | 13.2                             |
|                                  |                                    | 16                             | 14.2                             |
| 0.5                              | 773                                | 4                              | 6.2                              |
|                                  |                                    | 8                              | 10.5                             |
|                                  |                                    | 12                             | 13.0                             |
|                                  |                                    | 16                             | 14.0                             |
| 0.6                              | 773                                | 4                              | 3.1                              |
|                                  |                                    | 8                              | 5.6                              |
|                                  |                                    | 12                             | 7.4                              |
|                                  |                                    | 16                             | 8.0                              |

As it is seen from the data of Fig.-2, the most rapid adsorption of sulfur dioxide occurs on the peach shell,
activated by ZnCl₂ with the impregnation coefficient of ZnCl₂ equal to 0.4 and subsequently activated by
heat at a temperature of carbon dioxide equal to 773 K. The pore sizes, in this case, are easily accessible
to sulfur dioxide molecules, regardless of their molecular weight and structure. This is also due to the
previously identified features of the crystal-chemical structure of the adsorbent. Maximum adsorption of
sulfurous anhydride on activated shells occurs in 1.5-2 hours, but already at one-hour gas-phase contact of
the adsorbent with the gas mixture, we observe the sorption values (85-90) % from the maximum
achievable, which is due to the structure of sulfurous anhydride and the presence of selectively adsorbed functional groups in it. Adsorption extraction of sulfurous anhydride under dynamic conditions was carried out at several heights of activated carbon layers: 0.01 m; 0.03 m; 0.06 m; 0.09 m; 0.12 m. As the activated coal the fruit shell treated by zinc chloride with the impregnation coefficient equal to 0.4 and subsequently treated by heat with the temperature of CO₂ equal to 773 K was used.

The values of dynamic characteristics obtained as a result of mathematical processing by the Shilov N.A. equation are presented in Table-2. The protective effect time of the adsorbent layer was calculated:

\[ \tau_p = KL - \tau_0 \]

Where, \( \tau_p \) is the protective effect time of the adsorbent layer, h; \( \tau_0 \) is the time loss of protective effect, h; K is the protective effect coefficient; L is the adsorbent layer length, m.

The results show that with the increase of particle size, the value of the «dead layer» – non-working layer increases, therefore, with the increase of particle size, the dynamic activity of the adsorbent decreases. With the increase of the gas flow rate (Table-3), the protective action time is significantly reduced, i.e. the process proceeds intensively. The dependence of the protective effect time on the adsorbent layer height

![Graph showing isotherms of sulfur dioxide adsorption on activated peach shells.](image-url)

Fig.-1: Isotherms of Sulfur dioxide Adsorption on Activated Peach Shells: 1 - Impregnation Coefficient of ZnCl₂ - 0.4; CO₂ Temperature –773 K; 2 - Impregnation Coefficient of ZnCl₂ - 0.4; CO₂ Temperature –873 K; 3 - Impregnation Coefficient of ZnCl₂ - 0.5; CO₂ Temperature –773 K; 4 – Industrial Adsorbent BAU; 5 - Impregnation Coefficient of ZnCl₂ - 0.3; CO₂ Temperature – 773 K; 6 - Impregnation Coefficient of ZnCl₂ - 0.2; CO₂ Temperature – 773 K; 7 - Impregnation Coefficient of ZnCl₂ - 0.4; CO₂ Temperature – 573 K; 8 - Impregnation Coefficient of ZnCl₂ - 0.6; CO₂ Temperature –773 K; 9 - Impregnation Coefficient of ZnCl₂ - 0.4; CO₂ Temperature – 673 K.
is presented in Table-4. It is seen that the dependence of the protective effect time of the layer on its height is conditioned by two stages. The increase in the height of the working layer with the increase in the total height indicates that the initial layers, considered exhausted, in fact, during the adsorption process, continue to absorb sulfur dioxide and, due to the saturation of the initial layers, the static activity of the spent layers increases.

Table-2: The Value of the Dynamic Characteristics

| The Particle Size of the Adsorbent $l \cdot 10^{-3}$, m | The Working Layer Height $\lambda \cdot 10^{-3}$, m | The Height of «dead layer» $h \cdot 10^{-3}$, m | Protective Effect Time $\tau_3$, hour | The Time Loss of Protective Effect $\tau_0$, hour | Dynamic Activity $a$, g/100g |
|--------------------------------------------------------|--------------------------------------------|-----------------------------------|-----------------|------------------|------------------|
| Powdery 0.1                                             | 61                                         | 38                                | 2.5             | 0.9              | 15.9             |
| Granulated 1-3                                          | 73                                         | 43                                | 2.3             | 0.7              | 14.2             |

Table-3: The Dependence of Protective Effect Time From the Gas Flow Rate

| Particle Size of the Adsorbent $l \cdot 10^{-3}$, m | Protective Effect Time $\tau_3$, Hour |
|--------------------------------------------------------|----------------------------------------|
| Powdery 0.1                                             | 3.7                                    |
| Granulated 1-3                                          | 3.3                                    |

Table -4: The Dependence of Protective Effect Time From the Adsorbent Layer Height

| Particle Size of the Adsorbent $l \cdot 10^{-3}$, m | Protective Effect Time $\tau_p$ in Hours, for Adsorbent Layer Height $H$ in m |
|--------------------------------------------------------|----------------------------------|
| Powdery 0.1                                             | 1.9 | 2.5 | 3.3 | 3.9 | 4.3 |
| Granulated 1-3                                          | 1.6 | 2.3 | 2.9 | 3.6 | 4.1 |

To test the possibility of using the results to real gas emissions, containing sulfurous anhydride, a series of experiments was carried out in the section of dry electro filters at the metallurgical industry. Gas emissions on the main indicators were characterized by the following data: dust-100 mg/m$^3$, sulfur dioxide - (9% ± 0.5).

Previous studies have shown that the best adsorbent for the purification of model gas flows among activated coals was peach shell treated by zinc chloride with the impregnation coefficient equal to 0.4 and subsequently treated by heat with the temperature of CO$_2$ equal to 773 K. To test the efficiency of purification of real gas emissions of metallurgical and chemical industries, the same adsorbents were used. The dependence of the purification effect from the contact time of the adsorbent with the gas flow was studied under the same conditions as in experiments with model gas flows.

The presented kinetic curves of the dependence of adsorption from the contact time (Fig.-3 and 4) indicate that the process of adsorption of sulfur dioxide proceeds in the same regularity as in the case of purification of model gas flows. There is also a high rate of adsorption process in the initial time interval (1.5 – 2 hours). With the increase of the contact time to more than (2.5-3) hours, the rate of adsorption by adsorbents decreases sharply. Adsorption equilibrium in the system is achieved after 3 hours of contact of the adsorbent with sulfur dioxide. However, after 2.5 hours of contact with the activated shell with the gas flow, most of the sulfurous anhydride is extracted from the medium. By this time, the efficiency of purification is (97-98)%.

Thus, experiments, carried out with real gas flow, generally confirmed the results obtained in laboratory experiments with model gas flows. Experimental results of industrial tests at the enterprise of the metallurgical industry carried out with the experimental respirator designed and made by us serve as confirmation of the efficiency of use of the activated shell. The respirator is the front part and a cartridge with a filter installed in it. The filter is made in the form of a replaceable cassette, and the filter element is activated coal obtained from the peach shell.

The tests were carried out in comparison with the respirator RPG-67 (with two boxes of the brand «B»). Test results and characteristics of filter cartridges of respirators are given in Table-5. The proposed design
of the respirator provides a longer service life, the increase of protective effect time, in case of longer exploitation, the possibility of changing the used filter without stopping the respiratory protection. The use of the proposed highly porous activated coal from the fruit shells in the filter of the respirator allows increasing the operational properties by increasing the absorbing capacity of the filter element.

Fig.- 2: Kinetics of Sulfur dioxide Adsorption by Activated Peach Shell: 1 - Impregnation Coefficient of ZnCl₂ - 0.4; CO₂ Temperature – 773 K; 2 - Impregnation Coefficient of ZnCl₂ - 0.4; CO₂ Temperature – 873 K; 3 - Impregnation Coefficient of ZnCl₂ - 0.5; CO₂ Temperature – 773 K; 4 – Industrial Adsorbent BAU; 5 - Impregnation Coefficient of ZnCl₂ - 0.3; CO₂ Temperature – 773 K; 6 - Impregnation Coefficient of ZnCl₂ - 0.2; CO₂ Temperature – 773 K; 7 – Impregnation Coefficient of ZnCl₂ - 0.4; CO₂ Temperature – 573 K; 8 - Impregnation Coefficient of ZnCl₂ - 0.6; CO₂ Temperature – 773 K; 9 - Impregnation Coefficient of ZnCl₂ - 0.4; the Temperature of CO₂ – 673 K.

Fig.-3: The Influence Contact Time on the Efficiency of Sulfur dioxide Extraction by Activated Peach Shell
Table - 5: The Results of the Tests and Characteristics of Filter Elements of Respirators

| Protective equipment (respirators) | MAC, mg/m³ | Name of harmful impurities | Maximum permissible concentration for application, mg/m³ | Time of protective action (h) at different concentrations of gases and vaporous harmful impurities | Resistance to inhalation, not more, Pa |
|-----------------------------------|------------|---------------------------|-------------------------------------------------|-------------------------------------------------|--------------------------------------|
| RPG– 67                           | 10         | sulphur dioxide           | 150                                             | 50 mg/m³                                         | 30                                   | 15                                   | 58.8                                      |
| RU – 60M                          |            |                           |                                                 | Maximum permissible concentration for application, mg/m³ | 12                                   | 6                                    | 78.4                                      |
| Pilot Sample                      |            |                           |                                                 |                                                  | 20                                   | 10                                   | 72.7                                      |

CONCLUSION

Thus, the established regularities of changes in the adsorption properties of shells during their thermal and chemical activation allowed us to determine the optimal conditions for obtaining modified coals for the processes of effective purification of gases from sulfur dioxide, confirmed by industrial tests. The most rapid adsorption of sulfur dioxide occurs on the shell treated by ZnCl₂ (impregnation coefficient 0.4), followed by activation in the CO₂ stream at a temperature of 773 K, the pore size of which is easily accessible to sulfur dioxide molecules regardless of their molecular weight and structure. Maximum adsorption of sulfurous anhydride for activated bone shells occurs in 1.5-2 hours, but already with one-hour gas-phase contact of the adsorbent with sulfurous anhydride, we observe adsorption values of the order of 85-90% of the maximum achievable. The values of the dynamic characteristics show that with increasing particle size, the value of the «dead layer» – disabled – increases, therefore, with increasing particle size, the dynamic activity of the adsorbent decreases. With the increase of gas flow rate, the protective effect time is significantly reduced, i.e. the process proceeds intensively.

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