An adsorption technique applied by plants and factories for purifying gas emissions using modified wastes available at power plants

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Abstract: The paper proposes an adsorption-based method of how to remove sulfur dioxide from the gas emissions produced by industrial companies. A power plant waste – chemical water treatment sludge from Kazan CHPP-1 – was used as an adsorption material. The authors refer here to the chemical composition of the sludge and describe the method of its modification. A new sorption material based on power plant waste was tested for removal sulfur dioxide from the gases. This was resulted in kinetic dependence and adsorption isotherm. The mechanism of how the sulfur dioxide can be adsorbed by a new sorption material at different temperatures was studied. The tests revealed Gibbs free energy, differential heat, and adsorption activation energy. The economic and environmental effect of upgrading the process of removal of sulfur dioxide from gas emissions was calculated for the sodium bisulfite production line of L. Ya. Karpov Chemical Plant JSC

Introduction
Currently, new methods for reducing and limiting emissions release into the atmosphere generated by chemical, petrochemical, as well as fuel and energy industries are being actively developed. One of the toxic components of emissions are sulfur oxides and nitrogen oxides [1]. There are many methods for purification of gas emissions, one of the most effective methods is one that based on microporous sorbents adsorption. The performance indicators of adsorption treatment of gas emissions largely depend on the properties of adsorbents, the choice of which is determined by the energy and material costs spent for purification. Adsorbents must have a high sorption capacity, sufficient mechanical strength, be low-cost and made from affordable materials. Many materials of natural and artificial origin are known to be used as sorbents for purifying gas emissions: activated carbons, alumogels, silicates, silica gels, etc. [2]. Currently, the development of new sorption materials based on production waste is actively underway. The production of new cheap sorbents for purifying gas emissions is a challenge.

Results and discussion
Plants and factories are in the process of developing methods to reduce emissions release through the use of production waste. This production waste is the carbonate sludge of Water Treatment Plant (WTP) of Kazan CHPP-1. WTP sludge is a natural raw and stable mixture of a certain chemical composition, which depends on the chemical composition of raw water. The chemical composition of the WTP sludge produced by Kazan
CHPP-1 is as follows: calcite CaCO$_3$ – 72 %, brusite Mg(OH)$_2$ – 9 %, portlandite Ca(OH)$_2$ – 1 %, quartz SiO$_2$ – 0.5 %, other compounds – 17.5 %. The WTP sludge produced by Kazan CHPP-1 has the following characteristics: bulk density – 560 kg/m$^3$; total pore volume – 0.375 cm$^3$/g; radius of effective size fraction ranged 0.05-1.40 mm; slime moisture – 3 %, ash content – 89 % [5]; organic carbon content – 11 %, humic compounds – 12 %. The number of the latter is determined from the total mass of the sample, which was detected by gas chromatography-mass spectroscopy [3, 4]. It is the significant specific surface of the sludge, the presence of a large number of active sites on it that determines its sorption properties.

The technologies for purifying gas emissions of plants and factories use pelletized adsorbents. Therefore, adsorbents granular in shape are used to reduce the resistance to flow in the bed through which gas emissions are passed. The paper proposes to modify the power plant waste – sludge – into pellets. To produce pellets, fine-dispersed sludge 0.01 to 0.09 mm in size is mixed with liquid sodium glass at a mass and volume ratio of 2:1, respectively. This ratio was determined experimentally [6, 7]. With a lower ratio, the sludge is partially impregnated with liquid sodium glass, the adsorption capacity drops and the pellets are shedded during subsequent firing. With a larger ratio, the adsorption capacity does not increase significantly and the binder is overspent. Then the mixture is brought to a homogeneous mass by rolling. The resulting pellets are kept in a muffle furnace for 3 hours [8, 9]. The processing temperature varies from 100 to 450 °C in increments of 50 °C. Then the pellets are cooled down to room temperature in the desiccator. The new sorption material was named pelletized sorption material and abbreviated as PSM. Pellets are 1-3.5 mm in size, have an abrasion strength of 78 % and average hydrophilicity.

**Description of the pilot installation**

A dummy installation with a fixed PSM bed made at the Department of Water and Fuel Technology of the Kazan State Power Engineering University was used for studying the sorption properties of PSM in a gas atmosphere that is close in composition to the outgoing gases (Figure 1).

**Figure 1.** Pelletized sorption material (PSM) fixed bed reaction column.

1 – housing; 2 – adsorbent discharge pipe; 3 – purified gas discharge pipe; 4 – thermocouple; 5 – hatch for loading adsorbent; 6 – electric heater; 7 – hatch for unloading adsorbent; 8 – PSM bed; 9 – steel mesh with holes no more than 1 mm in diameter; 10 – sprayer; 11 – steam supply pipe; 12 – condensate discharge pipe; 13 – gas mixture supply pipe.
The reaction column is made of stainless steel, which ensures its resistance to corrosive
environments. The gas mixture was supplied and discharged through pipes 3 and 13. The pipe 13 is	hreaded to the sprayer 10. This ensures a uniform distribution of gases over the PSM bed 8 on the steel
mesh 9. The steel mesh 9 above the PSM bed prevents particles from carrying over. A thermostat with
an electric heater 6 was used to heat up the column. The gas temperature was 50 °C, which was
controlled by a chromel-drop type thermocouple.

The gas composition throughout the trial was as follows: O₂ – 4 to 5.7 %; N₂ – 75 to 78 %; H₂O to 3
%. The remaining volume of the gas mixture was CO₂. In the process of sorption, the concentration of
sulfur dioxide varied in the range of 0–5,500 mg/m³. The gas flow rate reduced to normal conditions
was 4×10⁻⁴ m³/s [10]. Sulfur dioxide was produced in the laboratory by reaction:

\[ \text{Na}_2\text{SO}_3 + 2\text{HCl} \rightarrow 2\text{NaCl} + \text{H}_2\text{O} + \text{SO}_2 \uparrow \]

The results of the studying the PSM sorption properties in terms of sulfur dioxide show that the
adsorption capacity of PSM happen during the first minutes of contact and after 16 minutes reaches 140
mg/g for sulfur dioxide. The adsorption capacity is 14 wt%. Figure 2 illustrates how the sorption capacity
of PSM kinetically changes with time.

![Figure 2. The PSM sulfur dioxide adsorption kinetic curve.](image)

The optimal parameters of industrial treatment plants can be obtained using the sorption isotherm –
the sorption capacity A vs. the change in the SO₂ concentration, as is shown in Figure 3a. The adsorption
isotherm corresponds to the L-type Langmuir isotherm. The convex shape of the isotherm confirms
effective physical adsorption. The adsorption isotherm is best described by the Freundlich equation
A=2.11C^{0.54}(R²>0.99) (Figure 3b).
Figure 3. Isotherm of SO$_2$ adsorption by pelletized sorption material (a) and its type in logarithmic coordinates (b).

For studying the mechanism of how the SO$_2$ is adsorbed by PSM, the process was studied under static conditions at different temperatures (293K, 313K, 323K, 333K). The resulting isotherm and isoster of adsorption on sulfur dioxide is shown in Figure 4 (during sorption of sulfur dioxide, the concentration varied in the range of 0–5500 mg/m$^3$).

Figure 4. Isotherms (a) and isosters (b) of SO$_2$ adsorption of PSM at different temperatures.

Isosters show the relationship between equilibrium temperatures and concentrations at a constant capacity of the sorbent.

An increase in temperature leads to a decrease in the SO$_2$ adsorption capacity, which is characteristic of the exothermic process and indicates the physical nature of the forces. The differential heat of adsorption was determined by the Clausius–Clapeyron relation (1):

$$\frac{\Delta T \ln C}{\Delta (1/T)} = -Q/R,$$

where $C$ is the equilibrium concentration of sulfur dioxide in the gas, mol/m$^3$; $T$ is the temperature, K; $Q$ is the differential heat of the adsorption isoster, J/mol; $R$ is the molar gas constant 8.341 J/mol·K.
The differential heat of the adsorption isoster is determined by the equation:

\[ Q = -R \frac{\Delta \ln C}{\Delta (1/T)} \]  

(2)

according to equation (2), the differential heat of adsorption of sulfur dioxide by PSM pellets was calculated according to the isoster angles of inclination. The calculation results are shown in Table1.

**Table 1.** Differential heat of adsorption of dissolved sulfur dioxide by PSM.

| Adsorption capacity, \( A \cdot 10^4 \), mol/g | Differential heat of adsorption \( Q \), kJ/mol |
|---------------------------------------------|---------------------------------------------|
| 17.19                                       | 9.31                                        |
| 21.88                                       | 12.17                                       |
| 22.97                                       | 13.64                                       |
| 23.44                                       | 14.22                                       |

Analysis of Table 1 shows that with the increase in adsorption of sulfur dioxide, the value of the differential heat of adsorption decreases.

The Gibbs energy of the adsorption process is determined by the equation (3):

\[ \Delta G = -RT \ln K_a. \]  

(3)

where \( \Delta G \) is the Gibbs energy, J/mol; \( T \) is the temperature, K; \( K_a \) is the adsorption equilibrium constant.

The resulting Gibbs free energy values change slightly with increasing temperature and confirm spontaneous \( \text{SO}_2 \) adsorption by PSM.

The kinetics of the \( \text{SO}_2 \) adsorption by PSM was studied. Kinetic dependences were obtained at different temperatures (Figure 5). Kinetic equations were used to determine the adsorption rate constants. It is shown that with the increase in temperature, the adsorption rate constants decrease, which is typical of non-activated adsorption (Table 2).

**Table 2.** Influence of the temperature on the adsorption rate constant of sulfur dioxide by PSM.

| Value                      | Temperature, K |
|----------------------------|----------------|
| \( K \cdot 10^3 \), s\(^{-1}\) | 293 313 323 333 |
| 9.54                      | 8.93 8.17 5.74 |

During adsorption, not all \( \text{SO}_2 \) molecules can penetrate the pores and be adsorbed, but only those that have an excess of energy – activation energy, so the rate of adsorption increases at high temperatures. The adsorption activation energy is calculated using the Arrhenius equation. The calculation results are shown in Figure 6. The value of the apparent activation energy (14.7 kJ/mol) indicates the course of physical adsorption.
The studies resulted in the following characteristics of the modified power plant waste – pelletized sorption material: the SO$_2$ adsorption capacity is 140 mg/g, the total pore volume is 0.450 cm$^3$/g, the specific surface area is 720 m$^2$/kg, and the abrasion strength is 78 %. The efficiency of PSM-based SO$_2$ removal was 99.9 %.

The pelletized sorption material has a high porosity, which is especially important when using its adsorption properties for gas passage. The low cost of sludge-based PSM, its availability, and the possibility of recovery, allow it to be used for purification of gas emissions produced by plants and factories with minimal costs and the greatest efficiency.

The obtained study results made it possible to propose upgrading the existing process of gas emissions purification for the sodium bisulfite production line at L. Ya. Karpov Chemical Plant JSC in the city of Mendeleyevsk. The main sources of sulfur dioxide emissions at the L. Ya. Karpov Chemical Plant are: Hyposulfite Salts Production Department, sulfite salts production, production of catalyst for the light paraffin hydrocarbon dehydrogenation, and production of extruded polystyrene plates [11]. According to [12], this chemical plant is classified as a hazard category III company.

The sodium bisulfite (NaHSO$_3$) production process has an adverse impact on the environment, since its production releases about 325 tons of SO$_2$ into the atmosphere annually. The output of sodium bisulfite at the L. Ya. Karpov Chemical Plant is about 1,750 t/y.

The sodium bisulfite process includes the following stages: production of sulfur dioxide, cooling of sulfur dioxide and its conveying, dissolution of soda ash, absorption of sulfur dioxide, preparation of sodium sulfate solutions and packaging. Figure 7 shows the current process of the sodium bisulfite production including the removal of sulfur dioxide from gas emissions.
Figure 7. Sodium bisulfite production flow diagram.
1 – sulfur smelter; 2 – settling tank; 3 – soda solution head tank; 4 – sulfur dioxide head tank; 5 – cyclone furnace; 6 – cooling tower; 7 – stage 1 absorber; 8 – stage 2 absorber; 9 – stage 3 absorber; 10 – circulation tank; 11 – bisulfite circulation tank; 12 – sanitary tank; 13 – spray trap; 14 – finished product tank; 15, 16, 17 – centrifugal pump.

For reduction of the sulfur dioxide content in the gas emissions in the process of sodium bisulfite production, it is proposed to convert the spray trap into an adsorber charged with PSM.

The optimal characteristics of the adsorber are calculated according to the isotherm of sulfur dioxide. The following initial parameters are accepted: pressure – 4.5 kPa; inlet gas flow rate – 300 m$^3$/h; sulfur dioxide content in the inlet gas – 1%. The duration of the adsorption and the amount of PSM per charge were calculated. The adsorber data are listed in Table 3.

Table 3. Adsorber data.

| Parameter                        | Value  |
|----------------------------------|--------|
| Diameter, m                      | 0.85   |
| Height, m                        | 1.7    |
| Specific surface area of PSM, m$^2$/kg | 720.0  |
| Amount of PSM for a single loading, kg | 47.3   |
| Height of PSM bed, m             | 0.91   |
| Duration of adsorption, h        | 46.2   |

The continuity of purification is secured by two adsorbers, one of which is used for gas adsorption cleaning, the other for sequential recovery of PSM, while the adsorption is combined with drying and cooling of the absorber.

The modification to the waste gas treatment will allow to remove up to 99.9 % of SO$_2$ from the gas emissions by using the carbonate sludge.

The modified gas emissions purification train with the sulfur dioxide removal bed was calculated for environmental and economic effect. The amount of prevented environmental damage from soil and land degradation for Kazan CHPP-1 was 2.90 kilo rubles per year. The cost of PSM is 13 kilo rubles per ton. The cost of removal of sulfur dioxide from gas emissions when using PSM is 6.76 rubles/m$^3$. 
Conclusion

1. A new sorption material based on power plant waste was tested for removal sulfur dioxide from the gases.
2. The process of adsorption of a dummy gas mixture containing SO$_2$ by a pelleted sorption material of water treatment was studied. The adsorption kinetics were analyzed. The adsorption isotherm corresponds to the L-type Langmuir isotherm. The convex shape of the isotherm confirms effective physical adsorption. The mechanism of how the sulfur dioxide can be adsorbed by the modified sorption material at different temperatures was studied. The tests revealed Gibbs free energy, differential heat, and adsorption activation energy.
3. The optimal data of a batch-operated adsorber with a fixed PSM bed are calculated: the diameter of the adsorber, the amount of PSM per charge, the height of the PSM bed, and the duration of adsorption.
4. Based on the study results, the gas emission purification train with the sulfur dioxide removal bed was modified at the L. Ya. Karpov Chemical Plant using the method of adsorption by pelleted sorption material.
5. The modified gas emissions purification train with the sulfur dioxide removal bed using the carbonate sludge-based PSM was calculated for environmental and economic effect. The prevented environmental damage will amount to 2.90 kilo rubles per year. The efficiency of removal of SO$_2$ from the gas emissions using PSM was 99.9 %.

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