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# Improving the technology of preparation of the adsorbent Uz-AD-1 based on the spent adsorbent SGCC, including the stage of modifying commercial carriers

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## Introduction

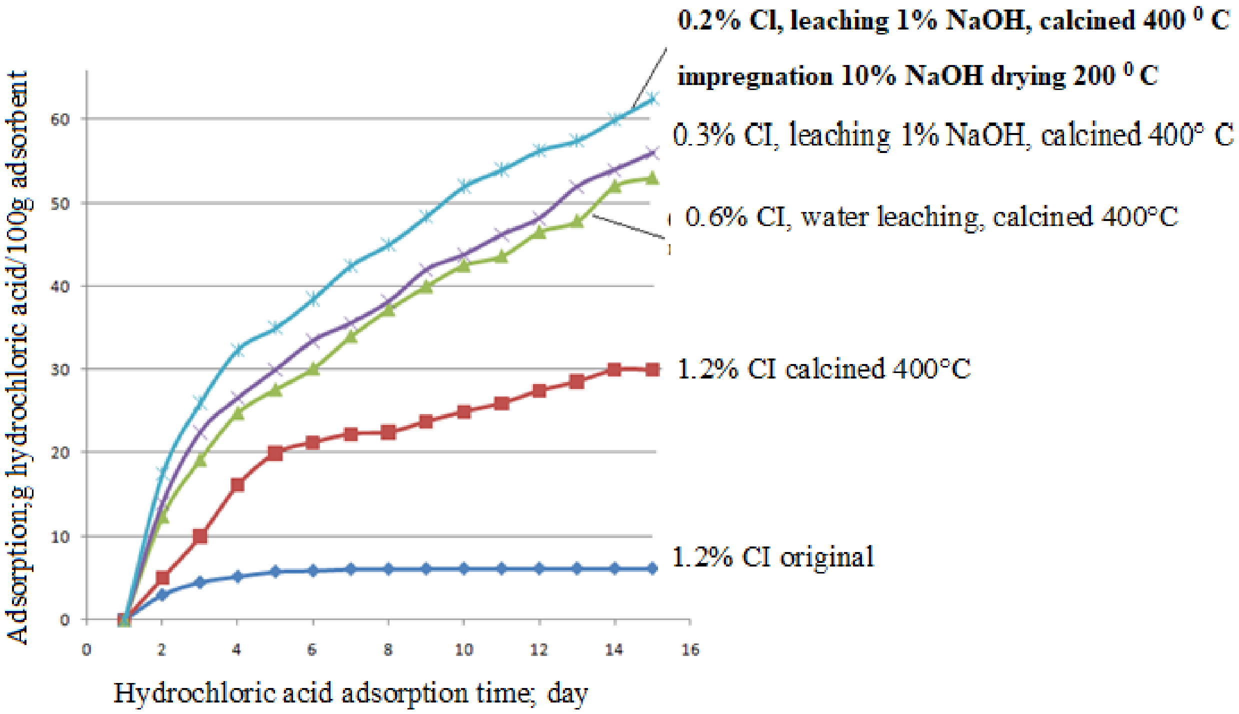
Due to the combination of thermal stability, the ability to control the pore structure, resistance to dripping moisture, commercial availability and the availability of raw materials for the production of aluminum oxide from natural minerals (bauxite, nepheline, alunite), etc. active alumina is one of the most common adsorbents. Aluminum oxide, both in pure form and after modification, is widely used for drying various gases and removing many types of other polar impurities [1, 2]. Its important consumer property is also resistance to multiple cycles of "adsorption-thermal desorption".The set of requirements for activated alumina is determined by the specific features of the processes in which it is used, however, among the many modifications of alumina, it is most often used as an adsorbent. $\gamma$-$Al_2O_3$.

## Main body of work

In this work, we have revealed the fundamental possibility of obtaining a new adsorbent, Uz-AD-1, based on the used adsorbent SHGCC, intended for gas purification from HCl and other polar compounds [3, 4]. The basic adsorption characteristics for chemisorption of model compounds included in the hydrogen-containing gas of heavy naphtha reforming and off-gases of CR 401 catalyst regeneration using tetrachlorethylene vapors are determined. It is shown that the cheaper domestic adsorbent based on the waste of the Shurtan GCC LLC is only 2-3% inferior in terms of the total capacity of HCl and $H_2O$ to the currently functioning imported AxTrap 860. According to the results of testing a new adsorbent - Uz-AD-1 in industrial conditions on the bypass line of the regenerative gas flow, with a maximum content of harmful halogen compounds, it was decided to conduct an experimental run on the scale of the full load of one of the operating adsorbers.

In the process of producing an experimental batch (100 kg) of the Uz-AD-1 adsorbent by processing the spent adsorbent SGCC according to the technological scheme, which includes the stage of leaching of unwanted impurities, insufficiently effective removal of deposits from its surface was found [4].



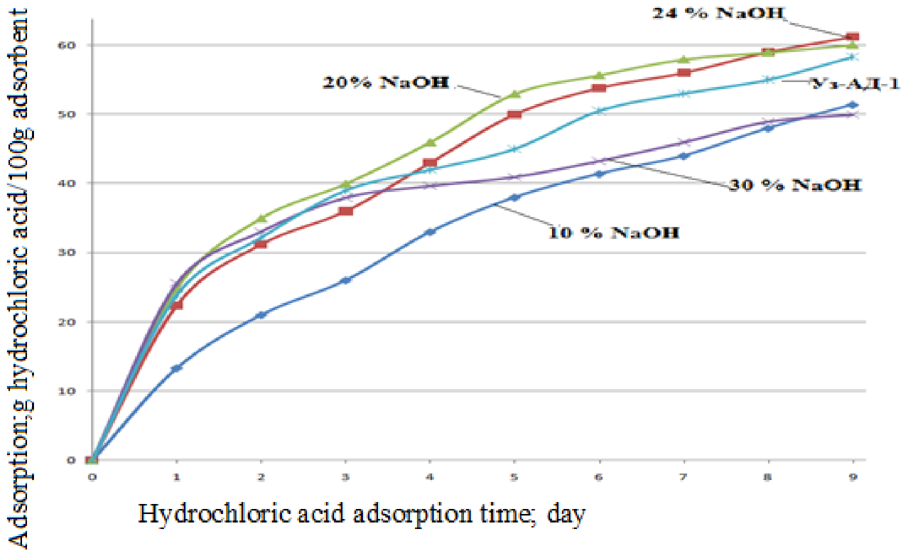

**Rice. 1. Influence of the composition of the solution for leaching of undesirable impurities from the spent adsorbent of the SGCC on the degree of leaching of chlorine compounds and the adsorption capacity of the adsorbents obtained after calcination at 400 $^{0}$C. Leaching time 20 hours, similar to the regulations for the preparation of Uz-AD-1**

At the same time, the results of determining the adsorption capacity quite convincingly showed an insignificant dependence of the total adsorption capacity for hydrogen chloride on the amount of residual chlorine in the composition of the spent SGCC adsorbent, both after the leaching procedure and subsequent modification with sodium hydroxide (Fig. 1).

Therefore, we carried out experimental work at the OEP UzKFITI aimed at improving the performance properties of the hydrogen chloride adsorbent and at the same time reducing labor and energy costs. As follows from Figure 1, the calcination of the initial spent adsorbent of the SGCC for the first 5 days was accompanied by an increase in the sorption capacity from 6 to 20 g of hydrochloric acid per 100 g of the adsorbent, that is, by 230%, compared with the uncalcined sample.

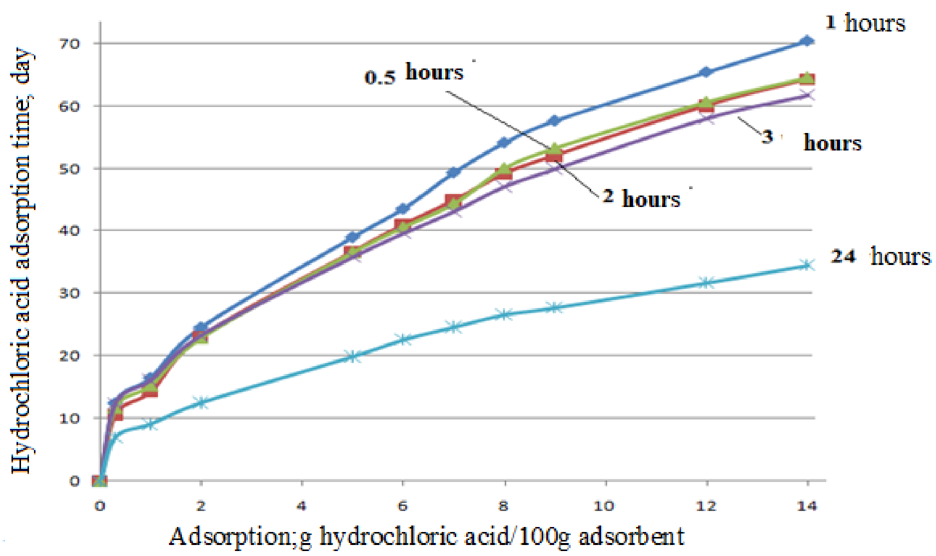
Preliminary leaching of sediments with water led to a decrease in the chlorine content by an average of 50%, as well as an increase in sorption capacity by 35%, compared with the sample calcined without preliminary leaching. Whereas, when leaching with 1% NaOH solution, the sorption capacity of the sample containing 0.3% chlorine increased by 50% compared to the sample calcined without preliminary leaching. Processing of the spent adsorbent from SGCC according to the technology similar to the preparation of Uz-AD-1 increased the sorption capacity by 72%.

Experiments have shown that an increase in the concentration of an alkaline solution was accompanied by an increase in the sorption capacity. Figure 2 shows the extreme dependence of the adsorption value of hydrochloric acid on the concentration of sodium hydroxide solution, without preliminary leaching of the spent SGCC adsorbent, at a fixed exposure time in the modifier solution of 20 hours. The optimal concentration of an alkaline solution (24% NaOH) was chosen based on the results of assessing the sorption capacity of test batches of the adsorbent obtained by a single impregnation with an alkaline solution, together with the strength characteristics of the finished product. But with prolonged exposure, negative phenomena increased: a decrease in mechanical strength and the yield of the finished adsorbent, due to the removal of aluminum along with the remnants of the impregnating solution. The optimal exposure time of the spent SHCC adsorbent granules in the modifying solution is 1 hour, taking into account that the unloading of 500 kg of the impregnated semi-finished product takes an average of 2.5-3 hours (Fig. 3). Similar experiments carried out during the modification of the fresh AN adsorbent, when obtaining the adsorbent of the supporting protective layer, showed that it is optimal to use the spent sodium hydroxide solution - the residue from the impregnation of the spent SGCC adsorbent when it is enriched with sodium hydroxide to a concentration of about 4% NaOH. The optimal exposure time for AN granules in solution is 10-15 minutes.




**Rice. 2. Influence of NaOH solution concentration on the value of hydrochloric acid adsorption by the prepared adsorbent. The time of exposure of the granules of the spent adsorbent SGCC in the modifying solution is**

**3 hours**

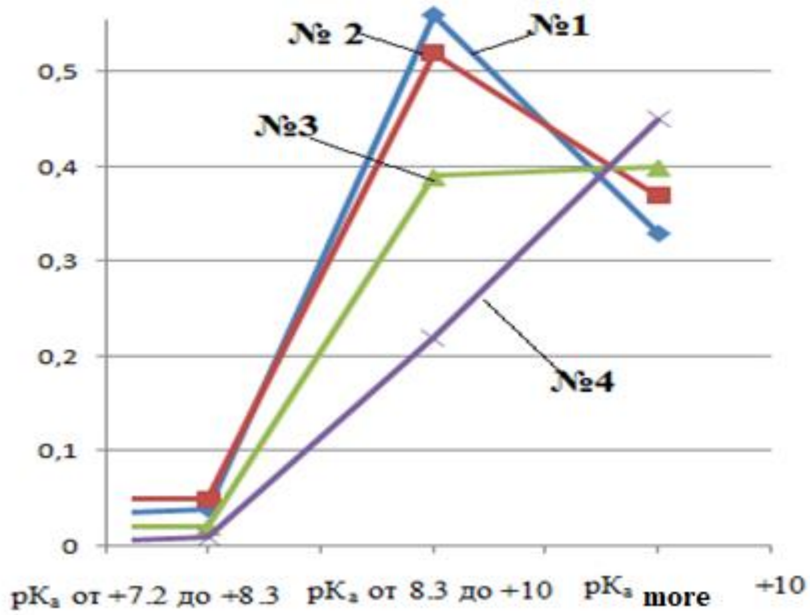



**Rice. Fig. 3. Effect of exposure time in 24% NaOH solution on the adsorption of hydrochloric acid by the finished adsorbent based on AN**

As noted [5], the main component of the adsorbent composition used in the form of powders, beads, or extrudates is aluminum oxide, aluminum hydroxide, or a mixture thereof, and the main alloying component is a compound of alkali, alkaline earth, and rare earth elements.

We [6] studied the formation of sodium aluminates - centers of actively chemisorbing HCl, in the composition of powder compositions prepared on the spent adsorbent SGCC, industrial pseudoboehmite with an admixture of gibbsite and bayerite. It is shown that under the same modification conditions, organometallic deposits on fine particles of spent SGCC slow down the interaction with sodium hydroxide and the formation of polyaluminates. $NaAl_{11}O_{17}$, $NaAl_7O_{11}$ и $NaAl_5O_8$. The unreacted sodium hydroxide settled in the pore space of aluminum oxide in the composition of the spent SGCC adsorbent and caused the appearance of strong basic centers with $pK_a \geq +10$ after calcination at a temperature of 590-600°C. In the case of industrial pseudoboehmite, when almost all of the modifying agent was included in the composition of the aluminates mentioned above, only surface centers with $pK_a \leq +9.3$ were detected. When applying 4 -6% wt. sodium (as part of the finished adsorbent) to aluminum hydroxides - products of deep processing Axsorb, Axstrap-860, and GOAbp, similar processes proceeded with the formation of weakly basic aluminates. Ratio matching Na: Al: $CO_3^{2-}$, found in the analysis of leaching products with distilled water, the approximate composition of the resulting mixture of water-soluble sodium aluminates and sodium carbonate was calculated. The method of X-ray phase analysis in this case was not informative.

due to the X-ray amorphous state of sodium aluminates in the temperature range under study. Indeed, in the composition of dried samples obtained by modifying fresh or industrial aluminum hydroxides, the composition of the mixture of sodium aluminates corresponded to the conditional formula $NaAl_{9.1-8.1}O_x$, and after calcination at 600 °C, the amount of aluminum in the composition of aluminates sharply decreased - $NaAl_{0.87-0.83}O_x$.




**Rice. 4. Influence of conditions for modifying granular adsorbents: No. 1-Uz-AD-1 and No. 3Uz-AD-1', dried at 100 °C;**

**No. 2-Uz-AD-1 and No. 4 Uz-AD-1 'after calcination 400 °C, on the distribution of the main centers by strength and concentration**

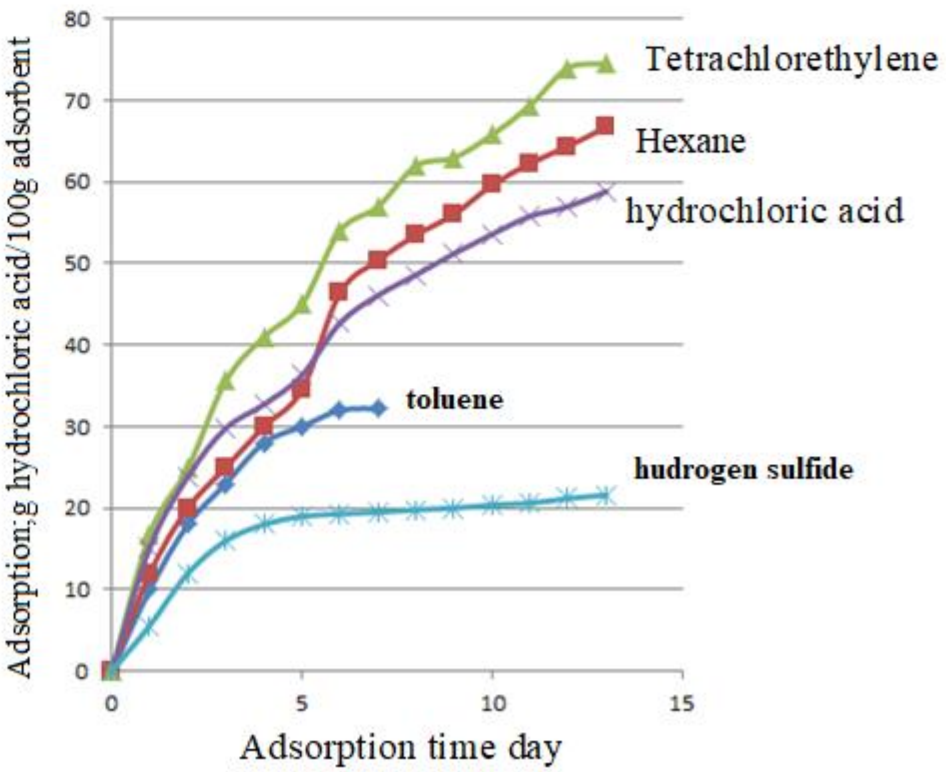
After drying the impregnated granules of the spent SGCC adsorbent, the composition of water-soluble sodium aluminates corresponded to the formula $NaAl_{5.05-4.04}O_x$, ready Уз-АД-1 – $NaAl_{0.69-0.64}O_x$, and in the finished Уз-АД-1' $NaAl_{0.62-0.55}O_x$. These calculations are in complete agreement with the revealed changes in the concentration of the main centers (Fig. 4) and the results of determining the adsorption properties of adsorbents (Table 2).

**Table 2.**

**Adsorption of Polar Substances by Synthesized Adsorbents in Dynamic Mode**

| | The amount of adsorption; g adsorbate per 100 g adsorbent | | | |
|---|---|---|---|---|
| | $H_2O$ | HCl | $C_2Cl_4$ | $H_2S$ |
| Уз-АД-4 | 18.2 | 13.3 | 23.8 | 3.8 |
| Уз-АД-1’ | 17.6 | 19.4 | 26.7 | 4.2 |
| Уз-АД-1” | 17.9 | 20.2 | 38.4 | 3.9 |
| ЗС-1 | 15.2 | 9.6 | 18.2 | 5.1 |
| Regenerated GO-70 (AKM) | 10.3 | 4.7 | 13.4 | 4.8 |
| Regenerated AKA-15 | 6.8 | 3.2 | 9.8 | 0.8 |




**Rice. 5. Adsorption of saturated vapors of various substances by the adsorbent Uz-AD-1' in static mode (temperature during the time of the experiment varied within 17-30 °C)**

As follows from Figure 5, the adsorption of acidic impurities of hydrogen sulfide and hydrochloric acid depended to a lesser extent on temperature fluctuations in the room during the experiment, compared to hydrocarbons. In a separate experiment, it was found that hexane, toluene, and, to a lesser extent, tetrachlorethylene are retained by the adsorbent mainly due to van der Waals adsorption and are easily desorbed in clean air. Acid impurities, on the contrary, are strongly retained by adsorbents at moderate temperatures due to the chemisorption mechanism. To partially remove them, for example, in the form of aluminum hexachloride, it is necessary to raise the temperature above 200 °C. According to the results of the analysis, even an increase in temperature to 500 °C does not lead to the complete removal of chlorine and sulfur compounds.

**Conclusions**

Thus, the optimal conditions for the dissolution of spent adsorbents of various origins were identified. A number of technological methods for obtaining active alumina, an adsorbent for preliminary drying of gases with high humidity before they enter deep drying with zeolite adsorbents, are considered. The technology of preparation of protective layer adsorbents for oxidative conversion of hydrogen sulfide (ZS-1) was mastered and the technology of preparation of Uz-AD-1 adsorbent for purification of hydrogen-containing gas of the Bukhara Oil Refinery was improved. Obtaining experimental data on the protective function of the synthesized samples, in particular, for the preliminary removal of droplet moisture from highly humidified gases before they enter deep drying with zeolite adsorbents, which should have a positive effect on increasing the service life of imported zeolites.

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