

ADSORPTIVE DESULFURIZATION OF INDUSTRIAL WASTEWATER

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Abstract. An alternative method of purification of aqueous sulfide-alkaline effluents from sulfide and hydrosulfide ions by their adsorption with mixed sorbents based on activated charcoal and kieselguhr has been investigated. High adsorption efficiency of mixed sorbents for purification of model sulfide- and hydrosulfide-containing solutions has been established. The dependence of the extraction degree of sulfide and hydrosulfide ions from aqueous solutions on their concentration, adsorption time and sorbent mass used has been investigated. The surface of mixed sorbents after purification of sulfide-alkaline model solutions was investigated by X-ray analysis, and the presence of various modifications of sodium sulfide on the surface was shown. The scheme of adsorption treatment of industrial sewage with the use of mixed sorbents has been offered.

Key words: adsorption, sulfides, hydrosulfides, sewage treatment.

1. Introduction

Substantial increase in the production of sulfur-containing oil and gas condensate over the last decade, as well as the increasing demands to environmental security of their extraction, transportation, storage, and processing, are pushing the development and introduction of new modern technologies for the desulfurization of these major energy resources. The main corrosive and biologically active sulfur-containing compounds are hydrogen sulfide and lower C₁-C₄ alkyl mercaptans, the physical and chemical characteristics of which are given in Table 1.

The data shown in Table 1 indicate that sulfur-containing compounds are potent toxic substances and are subject to compulsory extraction (desulfurization), both from gas or petroleum raw materials and their processing products [1].

Modern technologies of the desulfurization of light oil and gas condensate are based on the extraction of sulfur-containing compounds with 10–12% sodium hydroxide solution [2] or their catalytic air oxidation [3]. In the first case, sulfide (mercaptide)-alkaline solutions are formed, and in the second case, there are aqueous solutions of alkyl disulfides, sodium salts of sulfite, thiosulfate, and alkyl sulfonic acids [3, 4], which need to be further purified. The oxidation method is now considered as the most perspective process for the desulfurization of oil, oil fractions, and gas condensate in the world, which led to the development of the:

- process of desulfurization of the ASP series, Uni Pure (USA);
- process of desulfurization of ODS petroleum distillates using a hydroperoxide oxidizer, Lyondell Chemical Co;
- processes of desulfurization of DMS-1, DMS-1M, DMS-4, Tengizchevroil (Kazakhstan).

Besides the above methods, it is necessary to note the combined method of deep desulfurization of straight-run gas oil (Fig. 1) based on adsorption of sulfur-containing compounds by activated charcoal (AC) and their subsequent hydrotreating, which allows us to obtain final products with total sulfur content <10 ppm [5, 6].

However, all existing methods of desulfurization have significant drawbacks, above all, in terms of ecology.

Table 1

Physico-chemical properties of some sulfur-containing compounds

№	Compound	Boiling point, °C	LD ₅₀	Odor Threshold, mg/m ³	MPC _{one-time max} , mg/m ³	MPC _{w.z.} , mg/m ³	CAS №
1	hydrogen sulfide	-60	600 ppm; human, 0,5 hrs	$1,2 \cdot 10^{-2}$	$8 \cdot 10^{-3}$	10,0	7783-06-4
2	methyl mercaptan	+6	675 mg/m ³ , rat, 4 hrs	$2 \cdot 10^{-5}$	$9 \cdot 10^{-6}$	0,8	74-93-1
3	ethyl mercaptan	+35	1034 mg/m ³ , rat	$2 \cdot 10^{-6}$	$3 \cdot 10^{-5}$	1,0	75-08-1
4	isopropyl mercaptan	+60	–	$2 \cdot 10^{-4}$	$1 \cdot 10^{-4}$	1,5	75-33-2
5	n-butyl mercaptan	+98	–	$6 \cdot 10^{-5}$	$5 \cdot 10^{-5}$	1,5	109-79-5

Note: LD₅₀ is the dose of the product, that causes the death of 50 % of the experimental animals; MPC_{one-time max}, is one-time maximum permissible concentration in the air of the locality; MPC_{w.z.} is maximum permissible concentration in the working zone; CAS № is the international registration number of the chemical compound.

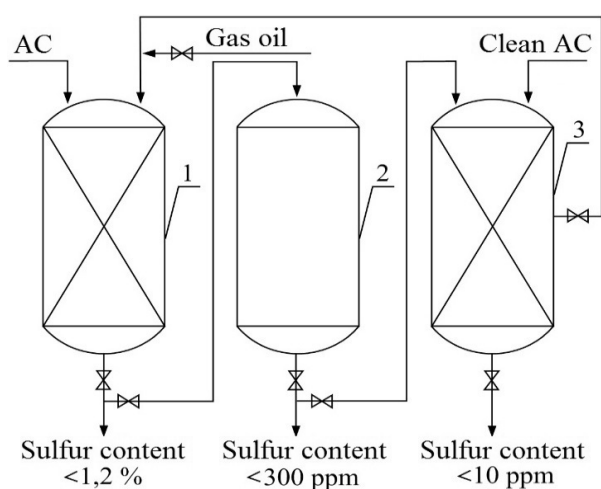


Fig. 1. Scheme of adsorption desulfurization of hydrotreated straight-run gas oil: 1, 3 – adsorbers with AC; 2 – catalytic hydrotreating reactor.

In view of the above, the purpose of the study was to investigate an alternative method of purification of aqueous sulfide-alkaline solutions (effluents) from sulfide and hydrosulfide ions by their adsorption with mixed sorbents comprising activated charcoal and diatomaceous earth (AC + K).

2. Experimental part

Desulfurization of model sulfide-alkaline solutions was carried out using a pre-regenerated sorbent mixture of Panda Production Company (Vinnytsia) [7, 8] comprising activated charcoal (AC) of the Decolar A brand and kieselguhr (K) of brands Becogur 200 and Becogur 3500 in 4:6 mass ratio, staggered on an INDURA filter press carton.

The study of the sorption of sulfide and hydrosulfide ions of industrial wastewater was performed on model solutions of sodium sulfide and hydrosulfide, which were close in concentration to the wastewater of the Kremenchug Refinery (PJSC “Ukratnafta”). The model

solutions contained sulfide and hydrosulfide ions with concentrations of 1.01 and 0.18 mol/l (9 % $S_{general}$) and 1.40 and 0.21 mol/l (12 % $S_{general}$), respectively.

Purification of water from sulfur-containing compounds was carried out on a laboratory unit, which consisted of a conical flask, a Liebig refrigerator, and a high-speed magnetic stirrer VELP AREC (VELP Scientifica, Italy), which provided intensive mixing of the regenerated mixed sorbent (AC + K). After stirring, the mixture was filtered under vacuum. The residual concentration of sodium sulfide and hydrosulfide was determined by iodometric titration in the filtrate, and the extraction degree (E , %) of sulfide and hydrosulfide ions was calculated by reducing their concentration in solution [9]:

$$E = \frac{[Sg]_0 - [Sg]_R}{[Sg]_0} \cdot 100,$$

where $[Sg]_0$ is the initial concentration of sulfide and hydrosulfide ions in solution, mol/l;

$[Sg]_R$ is the residual concentration of sulfide and hydrosulfide ions in solution, mol/l.

General method of desulfurization of aqueous solutions from sulfide and hydrosulfide ions.

100 ml of a model solution of sulfide and hydrosulfide ions was added to 0.5–40 g of regenerated mixed sorbent (AC + K). The resulting mixture was vigorously stirred on a magnetic stirrer (200–350 rpm) for 45–60 minutes at 20–25 °C and left for 24 hours to complete the process at the same temperature. The mixture was filtered, and the residual concentration of sulfide and hydrosulfide ions was determined according to the above procedure.

Surface studies of sorbents (AC + K) after purification of model aqueous solutions of sulfide and hydrosulfide ions were performed using a Dron-2 diffractometer in monochromatized Co- K_{α} radiation ($\lambda = 1.7902 \text{ \AA}$). The data of the X-ray phase analysis were identified by comparing the interplanar distances (d , \AA) and the relative intensities ($I_{\text{om}} - I/I_0$) of the experimental curve with the data of the PCPDFWIN electronic file system [10].

3. Discussion of the results

Despite the great variety of the investigated sorption materials of natural origin – zeolites, bentonite clays, alumina, silica; various modifications of activated charcoal – AG-3, BAU-A, OU-A, DU, polymeric organic absorbers or their various mixtures, the problem of industrial wastewater treatment from sulfur-containing compounds is currently relevant and depends on the chemical structure of the sorbent surface as well as on the objects of purification, the pH of the media, and some other factors [11].

In view of the above, we have carried out studies of purification of sulfide-alkaline solutions under the conditions given in the general method of desulfurization. The results obtained from the desulfurization of aqueous solutions are shown in Fig. 2, 3. We determined the dependence of the extraction degree (E , %) of sulfur-containing compounds from model solutions with different concentrations (9 and 12 % wt. $S_{general}$) on the time of adsorption at a fixed mass of the mixed sorbent (Fig. 2).

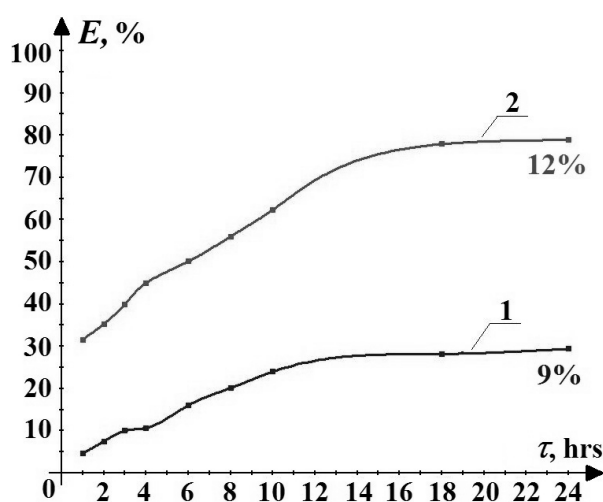


Fig. 2. Dependence of the extraction degree of sulfide and hydrosulfide ions on the time of adsorption at their initial concentration $S_{general}$, % wt: 1 – 9; 2 – 12. Conditions of the process: sorbent mass – 10 g; temperature – 25 °C.

The graphical dependence shown in Fig. 2 has the same character but different effectiveness for solutions of different concentrations of sulfur-containing compounds.

Thus, for the first solution (9 % wt.), the change in the extraction degree of sulfide and hydrosulfide ions (up to 25 %) mainly occurs in the first 11.5 hrs, whereas in the next 12.5 hrs it is only 4.4 %. That is, in graph 1 (Fig. 2) the slope of the curve of the first adsorption section is much larger than that of the second

inclined section. Obviously, such a change in the extraction degree over time can be explained by the adsorption/desorption phenomena of sulfide and hydrosulfide ions, which take place only on the surface of the mixed sorbents (AC + K).

For the second solution (12 wt. %), a major change in the extraction degree of sulfide and hydrosulfide ions was also observed in the first 14.0 hrs of the adsorption process. Over the next 10.0 hrs, the removal rate increased by only 4.9 %. However, despite the similar nature of changes in the extraction degree of sulfide and hydrosulfide ions for 9 % and 12 % wt. solutions, the numerical difference between them is almost 50 %. In our opinion, in the case of a more concentrated solution, besides adsorption on the surface of mixed sorbents (AC + K), there is adsorption associated with intra-diffusion processes.

Fig. 3 shows the graphical dependence of the extraction degree of sulfide and hydrosulfide ions from aqueous model solutions on the mass of the mixed sorbent (AC + K). However, with the amount of sorbent up to 20 g/100 ml solution, curve 1 (concentration 9 %) and curve 2 (concentration 12 %) differ slightly, and then gradually reach the maximum values of the extraction degree of sulfide and hydrosulfide ions.

The results of the desulfurization of the studied model solutions show the perspective and adaptability of the use of the regenerated mixed sorbents (AC + K), which was ensured by the high turbulence of the stirring mode of the reaction mass (200–350 rpm) at a temperature of 20–25 °C.

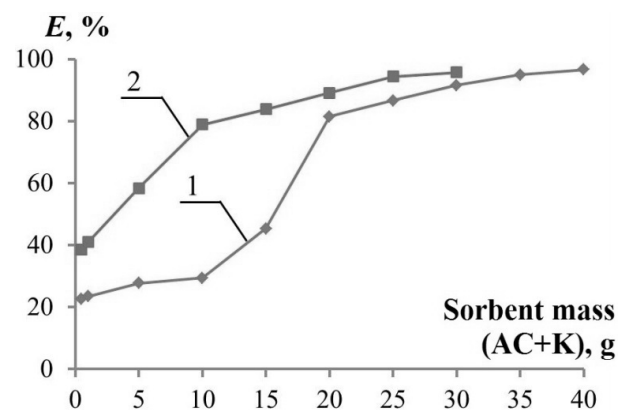


Fig. 3. Dependence of the extraction degree of sulfide and hydrosulfide ions on the sorbent mass (AC + K) at their initial concentration $S_{general}$, % wt: 1 – 9; 2 – 12. Conditions of the process: adsorption time – 24 hrs; temperature 25 °C.

It should be noted that the dependence of the extraction degree of sulfide and hydrosulfide ions on their concentration in the model solutions, on the mass of the sorbent, and the time of adsorption was also accompanied by the study of the surface of the mixed sorbents (AC + K, Fig. 4).

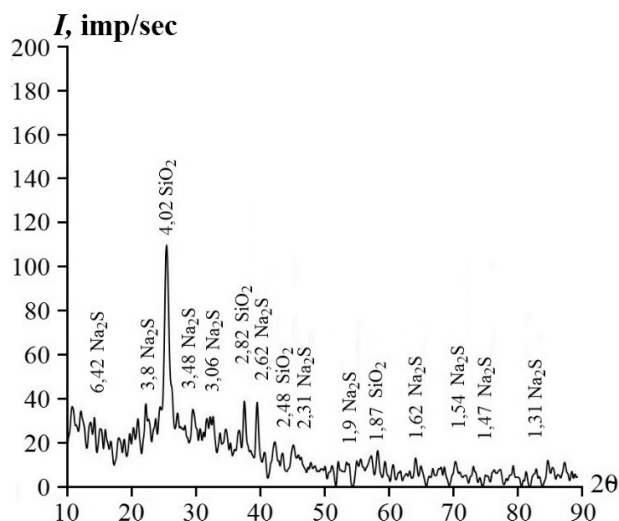


Fig. 4. X-ray diffraction pattern of Na_2S compound on the surface of mixed sorbents (AC + K)

The data shown in Fig. 4 confirm the amorphous composition of the activated charcoal and the presence of main SiO_2 crystallite, 4.02 in the left side of the diffraction pattern [8], as well as a number of peaks inherent in various modifications of Na_2S .

The high efficiency of adsorption extraction of sulfide and hydrosulfide ions from aqueous solutions using mixed sorbents (AC + K), as well as the dependence of their extraction degree on the concentration, time of adsorption and sorbent mass allow us to consider the general scheme of production of adsorption desulfurization.

Fig. 5 shows a schematic diagram of a three-stage adsorption purification of wastewater from sulfur-containing compounds. At stage I (reactor A-1), the recovery rate was 78.9 %; at stage II (reactor A-2), it was 86.4 %; at stage III (reactor A-3) – 92.6 %.

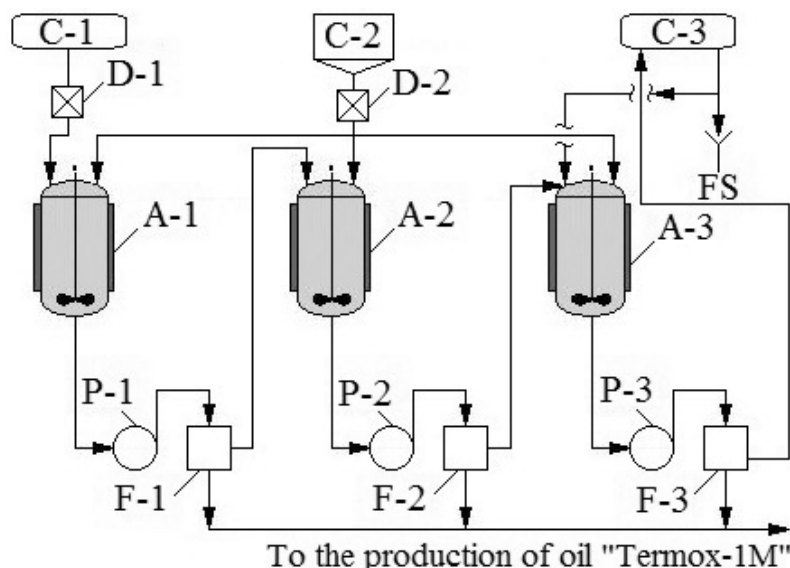


Fig. 5. Scheme of three-stage adsorption desulfurization of sulfur-containing industrial wastewater: A-1, A-2, A-3 – adsorbers; P-1, P-2, P-3 – pumps; F-1, F-2, F-3 – filter presses; C-1, C-3 – containers for liquid mixtures; C-2 – capacity for the regenerated mixture of sorbents (AC + K); D-1 – dispenser for liquid mixtures; D-2 – dispenser for sorbent; FS – factory sewer

Conclusions

High adsorption efficiency of mixed sorbents (AC + K) for purification of model sulfide and hydrosulfide containing model solutions has been established.

The dependence of the extraction degree of sulfide and hydrosulfide ions from aqueous solutions, depending on their concentration, adsorption time, and the sorbent mass (AC + K), has been investigated

A three-stage scheme of adsorption purification of industrial wastewater using mixed sorbents (AC + K) has been proposed.

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