

TECHNOLOGY OF COMPLEX SORPTION TREATMENT OF INDUSTRIAL WASTEWATER FROM SULPHIDE AND COPPER(II)-IONES

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Complex processing of industrial waste of individual industries, including wastewater treatment, containing sulfur anions and cations of heavy metals, in order to obtain both purified water and finished industrial products is an urgent task for today. The possibility of efficient use of regenerated mixed sorbent (AC+K), containing activated carbon (AC) and diatomaceous earth (K), for wastewater treatment of certain technological processes of chemical (petrochemical) industry and galvanic industries has been shown. The sorbent with the removed contaminants was offered to be utilized as a part of plastic lubricants of special purpose. The technological process of complex sorption treatment of industrial wastewater from sulfide and copper (II) ions includes the following main stages: sorbent regeneration; purification of sulfide-alkaline solutions; purification of washing waters of galvanic productions; obtaining plastic oils. The basic technological scheme of the site of regeneration of the spent mixed sorbent (AC+K) and purification of water-sugar solutions from organic impurities was developed. The material balance of regeneration of the spent mixed sorbent was calculated. The basic technological scheme of the site of combined treatment of industrial wastewater from sulfide and copper (II) ions, regeneration of spent industrial oils with regenerated sorbent (AC+K) and production of plastic oils has been developed. It was shown that the technology of complex sorption wastewater treatment is based on the most common technological processes - heating, cooling, adsorption and filtration and does not require complex schemes of automatic process control, and chemical equipment is typical for chemical enterprises in Ukraine. The economic effect of production of special purpose plastic oils was calculated.

Keywords: *basic technological scheme, industrial wastewater, technology of complex treatment, sorption methods, utilization*

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1. Introduction

The industrial wastewater of many chemical plants contains a significant amount of substances which are harmful to natural water bodies and human health, which contain sulfur anions and cations of a number of heavy metals. Therefore, toxic solutions containing such cations and anions are sometimes diluted with water to reduce the concentration below the MPC. However, this

procedure cannot always be performed, so there is a problem of mandatory water treatment. To implement such water treatment, various physicochemical methods are used, among which the most popular method of adsorption using a variety of both natural and synthetic adsorbents. To increase the sorption capacity, it is popular to modify the sorption matrix using harmless and available reagents. Analysis of recent research

and publications [9-12, 13] has shown that the joint processing and disposal of waste from different industries allows you to remove valuable chemical compounds and significantly improve the ecological condition of the environment in their storage. The complex utilization of industrial waste studied today concerns, first of all, reagent extraction of metal cations from sewage of galvanic productions and other chemical wastes by their interaction and formation of water-insoluble chemical compounds. The latter, as a rule, act as raw materials in their subsequent heat treatment. However, all existing methods of joint processing and utilization of waste from different industries have significant shortcomings, especially in the environmental plan.

Therefore, the aim of the work is to develop the technology of effective complex purification of industrial waters of copper processes from Cu^{2+} and sulfide-alkaline solutions of chemical and petrochemical productions from S^{2-} and HS^- in order to obtain both purified water and final industrial products.

2. Materials and methods

The subject of the study were complex adsorption technologies for wastewater treatment of individual industries, namely:

- sulfide-alkaline solutions, which in terms of concentrations of sulfide and hydrosulfide ions are close to the wastewater of the intermediate pond, which was located on the territory of the industrial zone of Kremenchug refinery (PJSC "Ukratnafta");
- wash water of the process of electrochemical copper plating, which was carried out using acid electrolytes;
- water-sugar solutions, which were subject to purification after regeneration of a mixed sorbent (AC+K), consisting of activated

carbon (AC) brand Decolar A and kieselguhr (K) brands Bekogur 200 and Bekogur 3500 in a mass ratio of 4: 6.

In addition, spent industrial oils I-40A and Arian MGE-46 B were subject to adsorption purification. Regenerated industrial oils were subsequently used as a component of special purpose plastic oils.

All studies are united by the fact that they were performed by using a single sorbent - regenerated mixed sorbent (AC + K).

Regeneration of the spent mixed sorbent (AC+K) after the stage of purification of sugar syrup production of soft drinks was carried out according to the method described in works [6, 7]. Methods of purification of water-sugar solutions are described in work [7], sulfide-alkaline solutions - in work [8–11], washing waters of the electrochemical copper plating process - in work [12]. Regeneration of waste industrial oils was carried out according to the method presented in work [13]. Plastic lubricants, which contained regenerated oils and spent sorbent after wastewater treatment from S^{2-} and Cu^{2+} ions, were prepared according to the method [10].

3. Results and discussion

An integrated approach to the adsorption method of wastewater treatment of individual industries and disposal of waste sorbents includes:

- regeneration of spent mixed sorbent (AC+K)_s after the stage of purification of sugar syrup for the production of soft drinks and purification of water-sugar solutions after regeneration of the sorbent using regenerated sorbent (AC+K);
- purification of sulfide-alkaline solutions of chemical (petrochemical)

productions from S^{2-} , HS^- ions with the use of regenerated sorbent (AC+K);

- purification of washing waters of galvanic productions from Cu^{2+} ions with the use of the modified sulfide ions of sorbent (AC+K+ Na_2S);

- regeneration of waste industrial oils using regenerated sorbent (AC+K);

- production of new carbon-sulfur-containing plastics using regenerated oils and spent sorbent (AC+K+CuS+S).

The developed technological scheme of complex sorption treatment of industrial wastewater from sulfide and copper (II) ions consists of:

- areas of regeneration of the mixed sorbent (AC+K) and purification of water-sugar solutions after regeneration of the sorbent;

- areas of combined treatment of industrial wastewater from Cu^{2+} , S^{2-} , HS^- ions, regeneration of spent industrial oils with regenerated sorbent (AC+K) and production of plastic lubricants.

3.1. Sorbent regeneration technology and its use for industrial water purification

Based on the results of research obtained in works [6, 7], we have developed a basic technological scheme of the regeneration of the spent mixed sorbent (AC + K) and purification of water-sugar solutions after regeneration of the sorbent, which is shown in Fig. 1. The operation of the first chain of collector-mixers concerns the regeneration of the spent sorbent (AC+K)_s after the stage of purification of the sugar syrup solution in the following sequence: R-1→R-2→R-3→R-4. In each of these collectors-displacers R-1÷R-4 using the source capacities C-1÷C-4 and the corresponding dispensers D-1 ÷ D-4 loaded

the calculated amount of spent source sorbent (AC+K)_s (collector- mixer R-1) and partially regenerated mixture of sorbents (AC+K)I ÷ (AC+K)III: (AC+K)I → in R-2; (AC+K)II → in R-3; (AC+K)III → in R-4. In the first collector-mixer R-1 was added water for primary washing of the spent sorbent (AC+K)_s from water-soluble organic compounds (sugar, glucose, etc.); in the second R-2 - 1% NaOH solution; in the third R-3 - 4% HCl solution; in the fourth R-4 (control) - water for final purification of the regenerated sorbent (AC+K)IV from mineral salts. Sequential movement of each subsequent cleaner fraction of sorbents (AC+K) was performed using pumps P-1 ÷ P-4 and the corresponding filters F-I ÷ F-4. The use of three-stage technology of regeneration of spent sorbents allows to 100% restore the sorption capacity of the regenerated mixture (AC+K)IV. It should be noted that the alkaline filtrate from the collector-mixer R-2 is neutralized by acid filtrate from the collector R-3 to pH=7 and fed into the technical water system of the enterprise.

The operation of the second chain of collectors-mixers of industrial water purification from organic impurities could be presented in the following sequence: R-5→R-6→R-7. In this case, from the storage tank of contaminated water to be purified C-5, through the dispenser D-5 in the collector-mixer R-5 contaminated water is supplied, which is subject to three-stage sorption purification in successive passage of the collector-mixers, which was mentioned earlier. The working sorbent is regenerated, according to the previously mentioned first chain of technological transformations, sorbent (AC+K)IV. Sequential movement of each subsequent cleaner volume of technical water F-1→F-2→F-3 was performed using

pumps P-5÷P-7 and the corresponding filters F-5÷F-7. The use of this three-stage technology of industrial water purification for one technological cycle allowed to reduce 2.9 times the amount of sugar in the water to be purified. It should be noted that the

technological operations of the first and second chains are interrelated. Thus, the sorbent (AC+K), which does not meet the technical requirements, is moved from the second technological chain to the first for its subsequent regeneration.

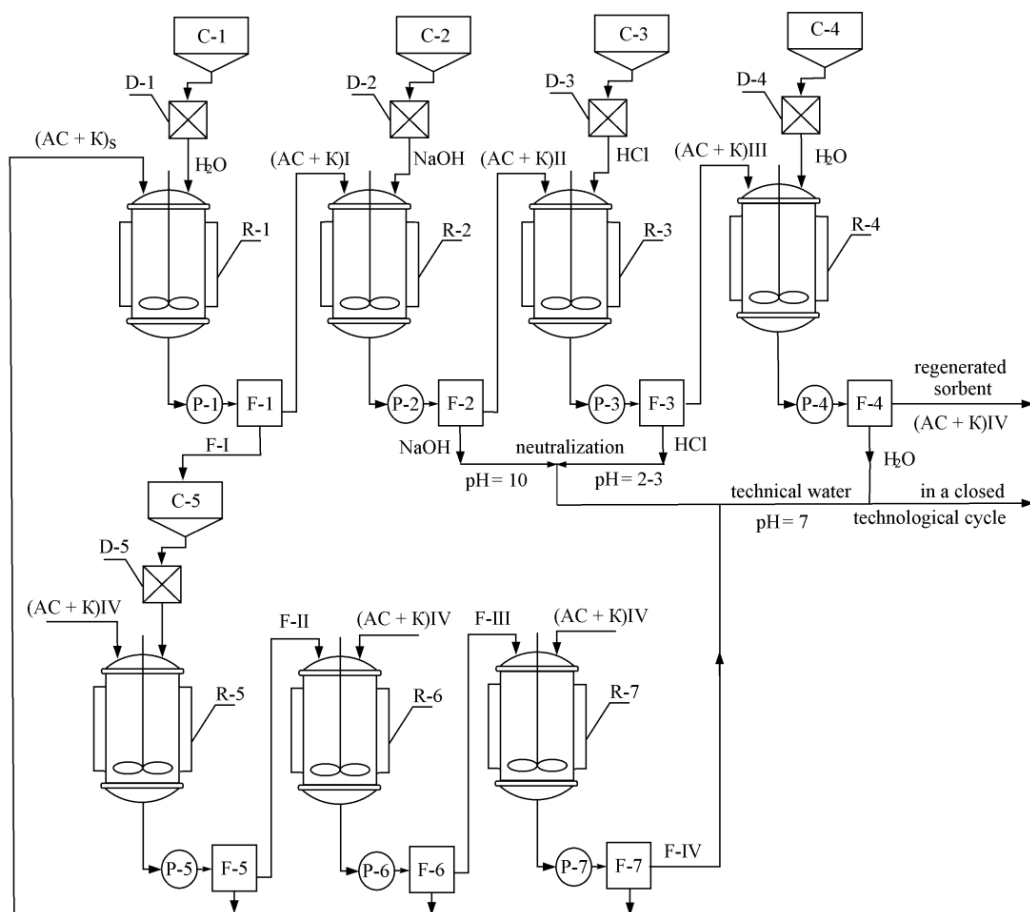


Fig. 1. Basic technological scheme of the area of regeneration of the spent mixed sorbent (AC+K) and purification of industrial water from organic impurities: R-1... R-7 - collectors-mixers; P-1... P-7 - pumps; F-1... F-7 - filters; D-1... D-5 - dispensers; C-1... C-5 - capacities; (AC+K)_S - spent mixed sorbent; (AC+K)I... (AC+K)III - mixed sorbent after I... III degree of purification; (AC+K)IV - regenerated mixed sorbent; F-I - solution after washing with water of the spent mixed sorbent; F-II, F-III - solutions after collectors-mixers R-5, R-6; F-IV - purified water

In order to determine the material costs for the regeneration of spent sorbent, we calculated the material balance of regeneration of 100 kg of spent mixed sorbent (AC+K) (Table 1). From the Table 1 data of the material balance of regeneration of the

spent mixed sorbent, the following conclusions can be drawn:

- the proposed technology of regeneration of spent sorbent (AC+K) allows to restore 100% of its sorption capacity with a yield of 98 %;

- a significant amount of technical water 995 dm³ (~ 83 %), which is used, is supplied for repeated sorption purification with the formation of a closed technological cycle;
- process water contains a small amount of non-toxic organic and inorganic pollutants;
- technology of regeneration of a mixture of sorbents (AC+K) (Fig. 1) includes typical chemical equipment and the simplest chemical operations - dissolution, adsorption, mixing and filtration.

Table 1. Material balance of regeneration of 100 kg of spent mixed sorbent

Downloaded			Received		
Name	Weight, kg	The mass fraction, %	Name	Weight, kg	The mass fraction, %
1. Spent mixed sorbent	100.0	9.09	1. Regenerated mixed sorbent	98.0	8.91
2. H ₂ O	800.0	72.73	2. Water contaminated with organic and inorganic substances:	997.0	90.64
3. NaOH, 1% of the mass. solution, of which	100.0	9.09	– sugar and other organic substances	0.5	0.04
– NaOH	1.0	0.09	– NaCl	1.46	0.13
– H ₂ O	99.0	9.00	3. Losses	5.0	0.45
4. HCl, 4% of the mass. solution, of which	100.0	9.09			
– HCl	4.0	0.36			
– H ₂ O	96.0	8.73			
Total	1100.0	100.0	Total	1100.0	100.0

3.2. Complex technology of sorption purification of industrial waters from Cu²⁺, S²⁻, HS⁻-ions and technical and economic substantiation of production of plastic lubricants with use of extracted components

Work of the basic technological scheme of the site of industrial water purification from Cu²⁺, S²⁻, HS⁻-ions, regeneration of the fulfilled industrial oil

I-40A and the production of plastic oils (Fig. 2) is based on the results of research presented in [1-5, 8].

The operation of the third line of collector-mixers in the sequence R-1→R-2→R-3 concerned the sorption purification of sulfide-alkaline solutions from S²⁻, HS⁻-ions, and the operation of the collector-mixer R-4 concerned the production of a modified mixture of sorbents

(AC+K+CuS+S). In each of these collectors-mixers R-1÷R-3 using the tank C-2 for the regenerated sorbent (AC+K)IV, as well as the tank C-1 for the original sulfide-alkaline solution and the corresponding dispensers D-1, D-2 downloaded the calculated amount of sorbent. The reaction mixture was stirred by using the pumps P-1÷P-3 and the corresponding filters F-1÷F-3 fed a modified mixture (AC+K+Na₂S) through the tank C-4

and the dispenser D-3 in the collector-mixer R-4. By adding from the tank C-5 through the dispenser D-4 galvanic copper washing water and the calculated amount of modified sorbent (AC+K+Na₂S), stirring the reaction mass in the collector-mixer R-4 was obtained a modified mixture of sorbents (AC+K+CuS+S). The degree of extraction of total sulfur (S_g) from sulfide-alkaline solutions is 97 %, and Cu²⁺ ions from wash water – 83 %.

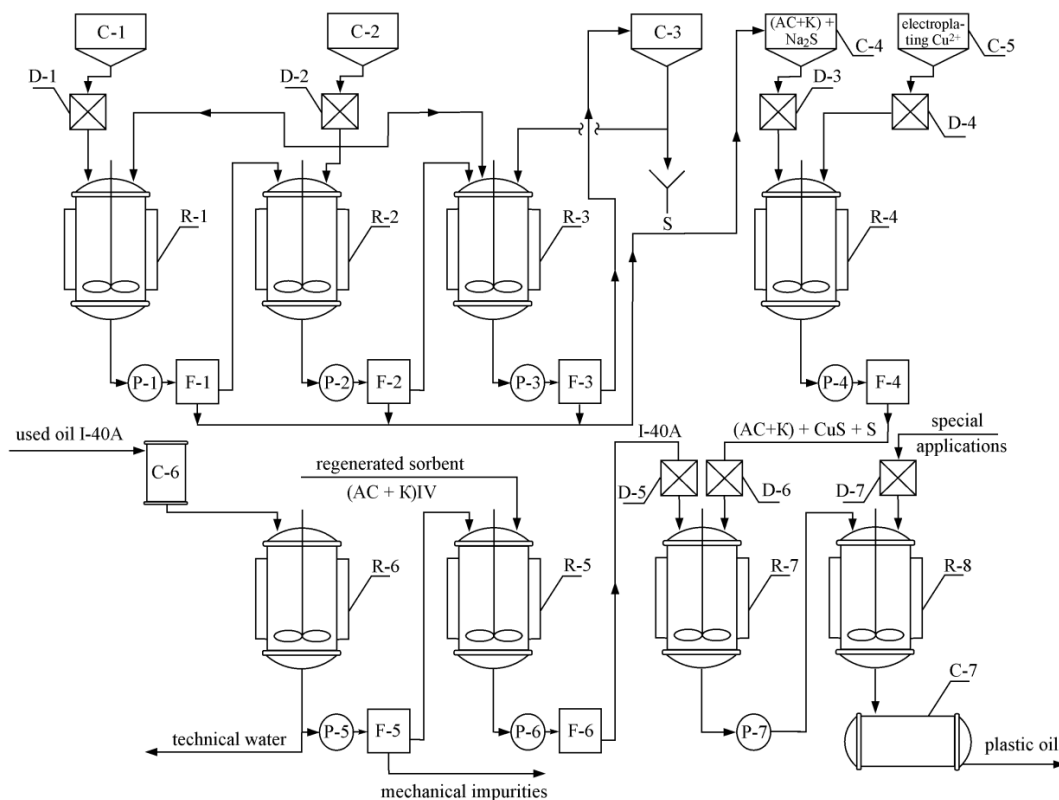


Fig. 2. Complex technological scheme of industrial water purification area from Cu²⁺, S²⁻, HS⁻ ions, regeneration of spent industrial oils and production of plastic oils: R-1... R-5 - collectors-mixers; R-7, R-8 - dispersants for plastic lubricants; C-1... C-6 - containers for working solutions and starting compounds; C-7 - capacity for finished products of PM; D-1... D-7 - dispensers for liquid and bulk products; P-1... P-7 - pumps; F-1... F-6 - filters; S - sewage system (sewerage)

The work of the fourth line of collectors-mixers R-6, R-5 concerned the sorption regeneration of industrial oil I-40A and obtaining in dispersants-mixers R-7, R-8 plastic oil of the PM series. To do this, the spent oil I-40 A from the tank C-6 was fed into the disperser-mixer R-6, mixed, if

necessary, heated to 50-60 °C, defended and separated from water and mechanical impurities. In the collector-mixer R-5 fed purified from water and mechanical impurities oil I-40A, as well as the calculated amount of sorbent (AC+K)IV from the first line of purification (regeneration) of the spent

mixture of sorbents (AC+K)_s (Fig. 1). Purified from oxidation products and clarified industrial oil I-40A through the dispenser D-5 and a modified mixture of sorbents (AC+K+CuS+S) through the dispenser D-6 was provided into the dispenser-mixer R-7. The homogenized mixture of composite lubricants from the dispenser R-7 was pumped P-7 into the dispenser-mixer R-8, through the dispenser D-7 added other special additives of plastic lubricants series PM and carried out the final homogenization to form a stable plastic mass. Ready-to-use plastic oils were collected in the C-7 tank.

Feasibility study for the production of plastic oils of the PM series was carried out by comparing the cost of 1 ton of plastic oils of the PM series with the cost of commercial oil Konstantin-1 (GOST 1957-73) as of 01.09.2019. It was calculated that the economic effect in the production of 1 ton of plastic oil series PM is 41584 UAH.

4. Conclusions

1. The basic technological scheme of the area of regeneration of the spent mixed sorbent (AC+K) with restoration of sorption capacity (AC+K) to 96,7–100% and purification of industrial water of production of soft drinks from organic impurity which can be successfully used in practice for regeneration mixed sorbent (AC+K) and reuse of purified water in closed technological cycles has been developed. It was shown that in one cycle the sugar content, as the main pollutant of industrial water, decreases by 2.9 times, which indicates the effectiveness of the developed technology.

2. The basic technological scheme of the site of industrial water purification from Cu²⁺, S²⁻, HS⁻-ions, regeneration of spent industrial oils and production of plastic oils is

developed, which can be successfully used in practice both for purification of industrial water from toxic pollutants and for production competitive technical products in the form of special purpose lubricants. The degree of extraction of total sulfur (Sg) from solutions is 97%, and Cu²⁺ ions –83%.

3. Feasibility study of expediency of production of plastic lubricants for special purposes with the use of modified mixed sorbent (AC+K+CuS+S) is carried out. It was calculated that the economic effect in the production of 1 ton of plastic oil series PM is 41584 UAH.

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ТЕХНОЛОГІЯ КОМПЛЕКСНОГО СОРБЦІЙНОГО ОЧИЩЕННЯ ПРОМИСЛОВИХ СТІЧНИХ ВОД ВІД СУЛЬФІД- ТА КУПРУМ(II)-ІОНІВ

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Комплексне перероблення промислових відходів окремих виробництв, зокрема і очищення стічних вод, що містять аніони сульфуру та катіони важких металів, з метою отримання як очищеної води, так і кінцевої промислової продукції є актуальним завданням сьогодення. Показано можливість ефективного використання регенованого сумішевого сорбенту (АВ + К), що містить активоване вугілля (АВ) та кізельгур (К), для очищення стічних вод окремих технологічних процесів хімічної (нафтохімічної) промисловості та гальванічних виробництв. Сорбент з вилученими забруднювачами запропоновано утилізувати у складі пластичних мастил спеціального призначення. Технологічний процес комплексного сорбційного очищення промислових стічних вод від сульфід- та купрум(II)-іонів включає такі основні стадії: регенерація сорбенту; очищення сульфідно-лужних розчинів; очищення промивних вод гальванічних виробництв; отримання пластичних мастил. Розроблено принципову технологічну схему ділянки регенерації відпрацьованого сумішевого сорбенту (АВ + К) та очищення водно-цукрових розчинів від органічних домішок. Розраховано матеріальний баланс регенерації відпрацьованого сумішевого сорбенту. Розроблено принципову технологічну схему ділянки комбінованого очищення промислових стічних вод від сульфід- та купрум(II)-іонів, регенерації відпрацьованих індустріальних олив регенованим сорбентом (АВ + К) та отримання пластичних мастил. Показано, що технологія комплексного сорбційного очищення стічних вод ґрунтується на найбільш поширених технологічних процесах – нагріванні, охолодженні, адсорбції та фільтруванні та не потребує складних схем автоматичного управління процесом, а хімічне обладнання є типовим для хімічних підприємств України. Розраховано економічний ефект виробництва пластичних мастил спеціального призначення.

Ключові слова: промислові стічні води, технологія комплексного очищення, сорбційні методи, принципова технологічна схема, утилізація