### Personality and Environmental Issues, 2022. Vol. 1(2).

## DOI: 10.31652/2786-6033-2022-1(2)-33-35

A.P. Ranskiy

Vinnytsia National Technical University, Doctor of Chemical Sciences, Professor(Ukraine); email: ranskiy@gmail.com; ORCID:0000-0002-9671-3018

T.S. Titov

Vinnytsia National Technical University, Candidate of Chemical Sciences, Associate professor (Ukraine);

email: tarastitov88@gmail.com; ORCID:0000-0003-3006-1966

O.M. Sandul

Vinnytsia National Technical University (Ukraine); email: sandulola11@gmail.com; ORCID:0000-0002-1775-0743

# COMBINED CHEMICAL REGENERATION OF INDUSTRIAL WASTE OF VARIOUS INDUSTRIES

In this paper has been shown the results of the studies on complex sorption purification of industrial waste of various industries with an obtaining new C,S,N-containing plastic lubricants which provide high performance. The conditions for obtaining diethylammonium salt from the obsolete pesticide Banvel D and its sorption on a mixed sorbent, which consist of activated carbon (AC) and kieselguhr (K), have been established. The conditions for obtaining potassium diethyldithiocarbamateon its surface and then, during subsequent treatment with copper(II) sulfate, bis-(diethyldithiocarbamato)copper(II) sorbed on a solid surface, have been examined. Obtainedsorbed substances of general composition [sorbent (AC+K)]·[( $C_2H_5$ )<sub>2</sub>NS(=S)S]<sub>2</sub>Cu have been studied as active components of plastic lubricants, which provide their high performance.

Keywords: industrial waste, sorption, regeneration, bis-(diethyldithiocarbamato)copper(II), C,S,N-containing plastic lubricants.

#### Introduction

Pollution of the environment by a huge amount of industrial and domestic waste from human activity can be considered as artificial man-made formations, which are valuable secondary raw materials and subject to purposed use. We have previously studied the regeneration of mixed sorbents (AC + K) from the production of soft drinks [1]; removal of active substances – 2-methoxy-3,6-dichlorobenzoic acid and dialkylammonium salts from obsolete pesticide Banvel D [2]; copper(II)ions from industrial washing waters of the copper-plating process [3]; high-toxic carbon disulfide from the head fraction of the crude benzene (HFCB) of coke productions [4] and regeneration of used industrial oil I-40 A [5], which formed the basis for obtaining new C, S, N-containing plastic lubricants as the purposed products of the above-mentioned industrial processes [6].Previously carried studies allow us to consider the regeneration of industrial waste from various industries as a closed technological cycle of obtaining new C,S,N-containing plastic lubricants.

The aim of this work is to study the complex sorption purification of industrial waste of various industries with an obtaining new C, S, N-containing plastic lubricants, which provide high load-bearing and heat-resistant properties.

#### **Results and discussion**

The peculiarity of this research is that all chemical components, except copper(II) sulfate, were obtained by sorption purification of industrial waste, including mixed sorbent (AC + K). Figure shows the logistic scheme of carried complex studies of purification different industrial wastewith an obtaining of special-purpose plastic lubricants required in various industries (mechanical engineering, metallurgy, mining and chemical industries).

Personality and Environmental Issues, 2022. Vol. 1(2).



Figure. Logistic scheme of purification different industrial wastewith an obtaining purposed C, S, N-containing plastic lubricants

Herewith the integrated approach to the treatment of various industrial waste using regenerated mixed sorbent (AC + K) from the soft drinks production includes the following technological operations:

 reagent processing of obsolete pesticide preparate (OPP)Banvel D with using the regenerated sorbent (AC + K) at the final stage according to the general scheme (cycle I):

$$Cl \xrightarrow{\text{COOH} \cdot \text{HN}(C_2H_5)_2} \xrightarrow{+ \text{HNO}_3} \xrightarrow{\text{COOH}} (Cl \xrightarrow{+ \text{ISorbent}} (AC + K)] \cdot [(C_2H_5)_2NH_2]$$

$$(Cl \xrightarrow{+ \text{OCH}_3} (Cl \xrightarrow{+ \text{OCH}_3} (Cl \xrightarrow{+ \text{ISOR}_3} (Cl \xrightarrow{+ \text{ISOR}_3$$

Reaction (1) leads to the formation of weak 2-methoxy-3,6-dichlorobenzoic acid $\underline{1}$  and diethylammonium salt  $\underline{2}$ sorbed on a solid surface;

 purification of HFCBof coke productions, which contains carbon disulfide, with the formation on the sorbent (AC + K) surface primarily potassium diethyldithiocarbamate followed by bis-(diethyldithiocarbamato)copper(II) formation according to the scheme (cycle II):

$$[\text{sorbent } (\text{AC} + \text{K})] \cdot [(\text{C}_2\text{H}_5)_2\text{NH}_2]\text{NO}_3 + \text{KOH} \xrightarrow{+\text{CS}_2} \text{[sorbent } (\text{AC} + \text{K})] \cdot [(\text{C}_2\text{H}_5)_2\text{NC}(=\text{S})]$$

$$\underline{2} \qquad 2)$$

Reaction (2) proceeds on cooling due to the volatility of diethylamine formed during chemical transformations. The final product of the interaction of compound <u>3</u>sorbed on the surface (AC + K) is bis-(diethyldithiocarbamato)copper(II)<u>4</u>, which is formed according to the scheme:

$$[\text{sorbent } (\text{AC} + \text{K})] \cdot [(\text{C}_2\text{H}_5)_2\text{NC}(=\text{S})\text{SK}] \xrightarrow{+\text{CuSO}_4 \cdot 5\text{H}_2\text{O}} [\text{sorbent } (\text{AC} + \text{K})] \cdot \{[(\text{C}_2\text{H}_5)_2\text{NC}(=\text{S})\text{S}] \xrightarrow{2} 0 - 25 \text{ °C} \xrightarrow{4} [\text{sorbent } (\text{AC} + \text{K})] \cdot \{[(\text{C}_2\text{H}_5)_2\text{NC}(=\text{S})\text{S}] \xrightarrow{3} 0 - 25 \text{ °C} \xrightarrow{4} [\text{sorbent } (\text{AC} + \text{K})] \cdot \{[(\text{C}_2\text{H}_5)_2\text{NC}(=\text{S})\text{S}] \xrightarrow{3} 0 - 25 \text{ °C} \xrightarrow{4} [\text{sorbent } (\text{AC} + \text{K})] \cdot \{[(\text{C}_2\text{H}_5)_2\text{NC}(=\text{S})\text{S}] \xrightarrow{3} 0 - 25 \text{ °C} \xrightarrow{4} [\text{sorbent } (\text{AC} + \text{K})] \cdot \{[(\text{C}_2\text{H}_5)_2\text{NC}(=\text{S})\text{S}] \xrightarrow{3} 0 - 25 \text{ °C} \xrightarrow{4} [\text{sorbent } (\text{AC} + \text{K})] \cdot \{[(\text{C}_2\text{H}_5)_2\text{NC}(=\text{S})\text{S}] \xrightarrow{3} 0 - 25 \text{ °C} \xrightarrow{4} [\text{sorbent } (\text{AC} + \text{K})] \cdot \{[(\text{C}_2\text{H}_5)_2\text{NC}(=\text{S})\text{S}] \xrightarrow{3} 0 - 25 \text{ °C} \xrightarrow{4} [\text{sorbent } (\text{AC} + \text{K})] \cdot \{[(\text{C}_2\text{H}_5)_2\text{NC}(=\text{S})\text{S}] \xrightarrow{3} 0 - 25 \text{ °C} \xrightarrow{4} [\text{sorbent } (\text{AC} + \text{K})] \cdot \{[(\text{C}_2\text{H}_5)_2\text{NC}(=\text{S})\text{S}] \xrightarrow{3} 0 - 25 \text{ °C} \xrightarrow{4} [\text{sorbent } (\text{AC} + \text{K})] \cdot \{[(\text{C}_2\text{H}_5)_2\text{NC}(=\text{S})\text{S}] \xrightarrow{3} 0 - 25 \text{ °C} \xrightarrow{4} [\text{sorbent } (\text{AC} + \text{K})] \cdot \{[(\text{C}_2\text{H}_5)_2\text{NC}(=\text{S})\text{S}] \xrightarrow{3} 0 - 25 \text{ °C} \xrightarrow{4} [\text{sorbent } (\text{AC} + \text{K})] \cdot \{[(\text{C}_2\text{H}_5)_2\text{NC}(=\text{S})\text{S}] \xrightarrow{3} 0 - 25 \text{ °C} \xrightarrow{4} [\text{sorbent } (\text{AC} + \text{K})] \cdot \{[(\text{C}_2\text{H}_5)_2\text{NC}(=\text{S})\text{S}] \xrightarrow{3} 0 - 25 \text{ °C} \xrightarrow{4} [\text{sorbent } (\text{AC} + \text{K})] \cdot \{[(\text{C}_2\text{H}_5)_2\text{NC}(=\text{S})\text{S}] \xrightarrow{3} 0 - 25 \text{ °C} \xrightarrow{4} [\text{sorbent } (\text{AC} + \text{K})] \cdot (\text{sorbent } (\text{AC} + \text{K})] \cdot (\text{sorbent } (\text{sorbent } (\text{AC} + \text{K})] \cdot (\text{sorbent } (\text{sorben } (\text{sorbent } (\text{sorbent } (\text{sorbent } (\text{sorbent$$

Reaction (3), which is part of cycle (II), also involves the binding of copper(II) cations in the metal chelate  $\underline{4}$ , which is sorbed on a solid surface. It should be noted that instead of model aqueous solutions CuSO<sub>4</sub>·5H<sub>2</sub>O, the galvanic wash water of copper plating can be successfully used;

 obtaining of new C, S, N-containing plastic lubricants, which include regenerated industrial oil I-40A SN 300 according to the previously described method (combined cycle III).

The presence of compounds  $\underline{2}$  and  $\underline{4}$  on the surface of the sorbent (AC + K) was confirmed by diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy using FTIR spectrometerNicolet iN 10FX (Thermo Fisher Scientific, USA)within a range 4000-525 cm<sup>-1</sup>. Decoding of the received spectra was performed using the IR spectra library from theOmnicPicta 1.5.126 software. Thus, the structural fragment [sorbent (AC + K)]·[(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NH<sub>2</sub>]NO<sub>3</sub> has, first of all, stretching and deformation vibrations of the N–H bond at 3355 and 1470 cm<sup>-1</sup>, respectively.Stretchingvibrations of the N–CH<sub>3</sub> bond at 2845 cm<sup>-1</sup> and vibrations of the quaternary diethylammonium salt [H<sub>2</sub>N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>] fragment at 2700 cm<sup>-1</sup>, as well as vibrations of nitrate anion at 1365 cm<sup>-1</sup>. Compound<u>4</u>, which is sorbed on solid surface (AC + K), has characteristic stretching and deformation vibrations of v (C–H) groupat 2930 cm<sup>-1</sup> and  $\delta$ (CH<sub>3</sub>) at 1375, 1355 cm<sup>-1</sup>; stretching vibrations v<sub>1</sub> (C–N) at 1520 cm<sup>-1</sup> and v<sub>2</sub> (C–N) at 1150 cm<sup>-1</sup>; stretching vibrations v (C–S) at 1275 cm<sup>-1</sup> and v (C=S) at 1070 cm<sup>-1</sup>. The obtained IR spectra for compounds <u>1</u>, <u>2</u>, <u>4</u> correspond to those given in [7].

# Personality and Environmental Issues, 2022. Vol. 1(2).

The table shows the compositions of new C,S,N-containing plastic lubricants that were obtained and studied by us in this work.Such special lubricants are used in high-temperature and high-loaded friction units, so they are important [8].

Composition, wt.%		Lubricant				
	PM-1	PM-2	PM-3	PM-4	PM-5	
1. Konstalin 1-13	100	25	25	30	30	
2. Industrial oil I-40A SN 300	-	10	10	10	10	
3. Modified sorbent [sorbent (AC + K)] $[(C_2H_5)_2NS(=S)S]_2Cu$	-	20	25	30	40	
4. Organic boron additive	-	15	15	10	10	
5. Oleic acid	-	10	10	10	10	
6. Graphite	-	20	15	10	-	

Table. Compositions of lubricants of the PM series

Thefinaltask of carried comprehensive research was an obtaining multifunctional lubricants (Table) that provided the following operational properties:

- uniformity and homogeneity (components 2 and 5: oil I 40A and oleic acid);
- wear and heat resistance (components 3, 6: modified structural fragments of the sorbent (AC + K), bis-(diethyldithiocarbamato)copper(II) and graphite;
- special functions (component 4: organic boron compound).

Laboratory tests of the developed lubricants (PM-2 – PM-5, see Table) were carried at the Department of Mechanical Engineering (Vinnytsia National Technical University) using the friction pair "St-40H – AL 9", and the industrial tests were carried out at PE "Exim" (Kherson). The operational researchshowed that when using the developed lubricants (see Table), the temperature in the friction units did not exceed the standard values and the surface of the roller bearings remained clean, smooth, without rolling and cracking during 12 months of preventive observations.

#### **Conclusions**

1. On the example of obtaining new C, S, N-containing plastic lubricants for special purposes, a complex technology for processing industrial waste from various industries is proposed. It is based on the use of regenerated mixed sorbent (AC + K), consisting of activated carbon (AC) and kieselguhr (K).

2. A number of topochemical reactions occurring on the sorbent surface (AC + K) during stepwise sorption purification of industrial waste from  $(C_2H_5)_2NH$ ,  $CS_2$  and  $Cu^{2+}$  cations have been proposed and studied by IR spectroscopy.

3. The prospects of industrial use of the developed new C, S, N-containing plastic lubricants in high-temperature and high-loaded friction units are shown.

#### References

1. A. Ranskiy, O. Khudoyarova, O. Gordienko, T. Titov, R. Kryklyvyi, Regeneration of Sorbents Mixture after the Purification of Recycled Water in Production of Soft Drinks, J. Water Chem. Technol., 41 (2019) 318–321.

2. A. Ranskiy, O. Gordienko, M. Evseeva, T. Avdienko, Disposal of chlorine-containing pesticides, VoprosyKhimii I KhimicheskoiTekhnologii, 5 (2010) 121–124.

3. O. Khudoyavora, O. Gordienko, T. Sydoruk, T. Titov, A. Ranskiy, Surface modification of mixed sorbents in sulfide ions for purification of galvanic industrial waters of the copper plating process, Bulletin of the National Technical University of Ukraine "Kyiv Polytechnic Institute namedafter Igor Sikorsky". Series "Chemical Engineering, Ecology and Resource Conservation", 2 (2020) 36–46.

4. A. Ranskiy, T. Titov, O. Gordienko, A, Balalaev, Technological aspects of reagent processing of carbon disulfide of the crude benzene head fraction of coke factories, Ecological Bulletin of Russia, 4 (2013) 48–51.

5. O. Khudoyarova, O. Gordienko, T. Titov, A. Ranskiy, A. Dykha, Adsorptive regeneration of waste industrial oils, Problems of Tribology, 25 (2020) 19–24.

6. O. Khudoyarova, O. Gordienko, A. Blazhko, T. Sydoruk, A. Ranskiy, Desulfurization of Industrial Water-Alkaline Solutions and Receiving New Plastic Oils, J. Ecol. Eng., 21 (2020) 61–66.

7. T. Titov, "Increase of environmental safety of coke production by chemical removal of carbon disulfide from benzene fraction," PhD Thesis, 2016.

8. Yu. Ishchuk, The Composition, Structure and Properties of Greases, NaukovaDumka, Kyiv, 1996.

Review received 22.12.2022