Effect of ultrasonic treatment on the sorption properties of the pyrolysis product of sludge

I A Nasyrov¹, G V Mavrin¹, I G Shaikhiev² и V V Terentyeva¹
¹Kazan Federal University, 423812, Russia, Naberezhne Chelny, Mira pr. 68/19
²Kazan National Research Tehnological University, 420015, Russia, Kazan, Karl Marx str., 68
chem_aleb@mail.ru

Annotation. In the article, the object of the study is a sorption material obtained by low-temperature pyrolysis from a sludge of a biological sewage treatment, and processed by ultrasound. Ultrasonic treatment is one of the methods for improving sorption characteristics by increasing the specific surface area. The adsorption capacity of pyrolysis products by methylene blue on a UNICO 2800 spectrophotometer and iodine by the titrimetric method was studied. An increase in sorption activity after ultrasonic treatment on the sorption material was found: by 2.3 times for methylene blue, 2.5 times for iodine. Sorption properties with respect to iron, copper, nickel, and zinc ions under static conditions using the atomic-emission spectrometry method with inductively coupled plasma on the Agilent 720-OES spectrometer were studied. The degree of extraction of heavy metal ions using the pyrolysis product of sludge after ultrasonic treatment reaches: for Fe – 98.7%, Ni – 84.4%, Cu – 90.5%, and Zn – 95.2%. Ultrasonic treatment with a frequency of 35 kHz for 30 minutes allows to increase the sorption capacity of the product of pyrolysis of mud sediments by Ni ions by 2.4 times, Cu - 1.2 times, Zn - 1.7 times.

Introduction
One of the effective methods of wastewater treatment from heavy metal ions is sorption purification. Such purification allows to carry out post-treatment to low concentrations of pollutant and re-use purified water in closed water circulation systems. The effectiveness of purification, depending on the sorbent used, can be 80-95%. As sorbents use activated carbon, carbon fibers, silica gels, synthetic sorbents [1]. At present, accessible and relatively cheap sorbents obtained from their wastes are increasingly being used for purification from heavy metal ions. The use of sludge after treatment with low-temperature pyrolysis as a sorption material allows to get rid of sludge accumulators and to improve the quality of wastewater treatment [2]. Sorption properties of the pyrolysis product are associated with the presence of carbon in its composition [3]. In addition, the properties of the pyrolysis product of the sludge can be changed by chemical or physical activation. One of the methods for improving the sorption characteristics of the pyrolysis product by increasing the specific surface area is ultrasonic treatment [4].

Materials and methods
The particle size distribution of the solid pyrolysis product of the sludge by size was determined by sieve analysis and using a laser particle size analyzer of the brand Microsizer 201C.
The adsorption activity by iodine of the pyrolysis product before and after ultrasonic treatment was determined in accordance with GOST 6217-74 "Active charcoal".

The adsorption activity of the pyrolysis product of sludge before and after ultrasonic treatment by the indicator methylene blue was determined in accordance with GOST 4453-74 "Coal active clarifying wood powdery".

The mineralization and specific conductivity were measured by means of the ANION-7020 conductometer.

Determination of the content of heavy metal ions and sorption properties with respect to heavy metal ions was carried out by atomic emission spectrometry using the Agilent 720-OES spectrometer.

The content of anions and cations in aqueous extract was determined by ion chromatography using a liquid chromatograph Stayer.

In order to study the sorption properties of the solid pyrolysis product, 1 g of ground sorbent and 50 ml of a model solution of the corresponding heavy metal ion with a concentration of 4-6 mg / dm³ were placed in a series of conical flasks before and after treatment, covered with a lid and stirred on a shaker for 30 min in the conditions of temperature control (20 ± 0.1 °C). Next, the filtrate was separated from the sorbent and the initial and final concentration of the heavy metal ion was determined by atomic emission spectrometry [2].

**Results and discussion**

The solid pyrolysis product of sludge was used as a sorption material. It is a powder of black color with a grayish shade without foreign inclusions.

The particle size distribution of the sludge, determined by the sieve analysis method and using a laser particle size analyzer of the brand "Microsizer 201C", is shown in Table 1 [5].

**Table 1. Particle size distribution (%)**

| Particle size, mm | Content, % |
|-------------------|------------|
| >5                | 22.3       |
| 3-5               | 20.9       |
| 1-3               | 29.3       |
| 0.5-1             | 9.9        |
| 0.1-0.5           | 12.3       |
| 0.05-0.1          | 1.7        |
| 0.01-0.05         | 1.8        |
| 0.001-0.01        | 1.6        |
| 0.0006-0.001      | 0.1        |
| <0.0006           | 0.1        |

The granulometric analysis showed that the solid pyrolysis product of sludge contains predominantly particles with sizes from 0.1 to more than 5 mm (82.4%). The presence in the sample of large particles with dimensions of more than 1 mm is due to the content of the particles of sludge that are not decomposed during pyrolysis.

The results of the microstructure investigation by the scanning electron microscope of the brand "Jeol JSM-6390 LA" indicate that the pyrolysis product has a porous structure (Fig. 1). The porous structure allows to predict sorption properties.
Figure 1. A microphotograph of a solid pyrolysis product of sludge

For processing as ultrasound have chosen fraction of 1-2 mm in a type of more high efficiency in dynamic conditions and rather high efficiency. The experiment was made for fractions less than 0.5 mm, 0.5-1 mm, 1-2 mm, 2-3 mm, 3 and more than mm.

The sample had the following characteristics: bulk density of the fraction (1-2 mm) - 642.8 kg/m³, humidity 0.9%, ash content 47%, specific surface area 261.7 m²/g, pore volume 0.156 cm³/g (Fig. 1).

It is known that the use of ultrasonic treatment increases the capacity of solid sorbents [6, 7, 8]. When acoustically acting on the sorbent, not only the surface layer of grains changes, but also the capillary structure of the sorbent [9].

Ultrasonic treatment of the investigated material with a particle size of 1-2 mm with a predetermined volume of water was carried out in an ultrasonic bath at a frequency of 35 kHz for 30 minutes. The mass ratio of the pyrolysis-water product was 1:10, respectively, 10 g of the sample in 100 ml of water.

During the ultrasonic treatment for different times, the exposure time was determined, which ensures the maximum extraction of heavy metal ions from model solutions.

Initially, the specific electrical conductivity (SEC) and the mineralization of the aqueous solution of the processed sample after ultrasonic treatment were determined (Table 2). For comparison, Table 2 shows the mineralization and SEC data for the aqueous drawing of the pyrolysis product after a half-hour mixing of 10 g sample in 100 ml water on a shaker.

Table 2. Indices of aqueous extract and solution after treatment

| sample                              | mineralization, mg/dm³  | SEC, µS/cm |
|-------------------------------------|-------------------------|------------|
| aqueous extract of pyrolysis product | 335                     | 693        |
| aqueous solution after ultrasonic treatment | 641                     | 1305       |

Ultrasonic treatment of the material leads to an increase in SEC and mineralization by a factor of 1.9. Probably, as a result of ultrasonic treatment, ions are washed from the pores by water-activated molecules of water, and the sample is demineralized.

In this case, we can observe a change in the emission of heavy metals and macro-ions into the aqueous extract from the pyrolysis product of the sludge without treatment and obtained after ultrasound treatment (Tables 3, 4 and 5).

The ultrasonic effect on the product of pyrolysis of the sludge results in isolation of heavy metals and macro-ions into the aqueous part of the working solution, including from the pores of the material. The ions that pass into the solution increase the value of the specific electric conductivity and
mineralization of the aqueous phase. As a result of this process, the ion emission in the aqueous extract of the treated material decreases.

**Table 3.** The content of heavy metals in the aqueous extract of the pyrolysis product

| sample                                           | Fe   | Ni   | Cu   | Zn   |
|--------------------------------------------------|------|------|------|------|
| without treatment (1:50)                         | 0.39 | 0.08 | 0.02 | 0.17 |
| without treatment (1:10)                         | 3.14 | 0.13 | 0.09 | 2.01 |
| after ultrasonic treatment (1:50)                | 0.12 | <0.01| <0.01| 0.09 |
| after ultrasonic treatment (1:10)                | 0.17 | 0.07 | 0.02 | 0.11 |

**Table 4.** Anion content in the aqueous extract of the pyrolysis product

| sample                                           | F^-  | Cl^- | NO_3^- | PO_4^{3-} | SO_4^{2-} |
|--------------------------------------------------|------|------|--------|-----------|-----------|
| without treatment (1:50)                         | 0.535| 7.13 | 0.03   | 5.41      | 66.5      |
| after ultrasonic treatment (1:50)                | 0.301| 2.32 | <0.02  | 3.19      | 15.1      |

**Table 5.** Cations content in the aqueous extract of the pyrolysis product

| sample                                           | NH_4^+ | Na^+ | K^+ | Mg^{2+} | Ca^{2+} |
|--------------------------------------------------|--------|------|-----|---------|---------|
| without treatment (1:50)                         | 12.4   | 7.27 | 10.4| 5.43    | 51.5    |
| after ultrasonic treatment (1:50)                | 4.02   | 2.87 | 2.95| 1.97    | 17.7    |

Assessment of adsorption was carried out on the basis of the results received by means of a technique of definition of adsorption on iodine and methylene blue.

**Table 6.** Sorption activity on methylene blue and to iodine

| index | pyrolysis product of sludge | without treatment | after ultrasonic treatment |
|-------|-----------------------------|-------------------|----------------------------|
| methylene blue, mg/g     | 16.7                        | 38.3              |                            |
| iodine,%                   | 15.4                        | 38.1              |                            |

The results obtained (Table 6) indicate an increase in sorption activity after the ultrasonic effect on the sorption material. By methylene blue sorption activity increased by 2.3 times, iodine by 2.5 times. This can be explained by an increase in the free pore volume and surface area as a result of the elution of ions from the pores.

Investigation of the sorption of heavy metal ions after ultrasonic treatment was carried out under static conditions (the ratio of the model solution and sorbent 1: 50, initial concentrations of iron, copper, nickel and zinc ions 4-6 mg/dm^3). Comparing the concentration of ions in the initial solution with the residual (equilibrium) concentration after contact of the sorbent with the model solution, it can be concluded that adsorption capacity [9].

The results of the determination of sorption properties with respect to heavy metal ions are presented in Table 7.
The results obtained indicate an increase in the adsorption capacity with respect to nickel, copper and zinc ions after ultrasonic treatment on the pyrolysis product of sludge.

The degree of purification from heavy metal ions using the pyrolysis product of sludge after treatment is: for Fe 98.7%, Ni 84.4%, Cu 90.5%, and Zn 95.2%. This treatment allows to increase the sorption capacity of the product of pyrolysis of sludge by Ni ions 2.4 times, Cu - 1.2 times, Zn - 1.7 times.

Table 7. Efficiency of purification the model solution from heavy metal ions

| heavy metal ions | initial concentration, mg/dm³ | concentration after sorption, mg/dm³ | efficiency, % |
|------------------|-----------------------------|----------------------------------|--------------|
|                  | without treatment           | after ultrasonic treatment       |              |
| Fe               | 4.44                        | 0.03                             | 99.3         | 98.7         |
| Ni               | 5.51                        | 3.59                             | 34.8         | 84.4         |
| Cu               | 6.08                        | 1.65                             | 72.9         | 90.5         |
| Zn               | 6.02                        | 2.56                             | 57.5         | 95.2         |

Thus, sonication is effective for wastewater treatment from iron, copper, zinc and nickel ions by the product of pyrolysis of sludge. The degree of sorption is almost inferior in terms of sorption to the commodity sorbent BAU [5].

Conclusions
1. As a result of ultrasonic treatment on the pyrolysis product of the sludge, heavy metals and macro-ions are released into the aqueous part of the working solution, which lead to an increase in SEC and mineralization by a factor of 1.9.
2. An increase in sorption activity after ultrasonic treatment on the sorption material was found: by 2.3 times for methylene blue, 2.5 times for iodine. This can be explained by an increase in the free volume of the pores and the surface area as a result of the washing out of the ions from the pores by the ultrasound-activated water molecules.
3. The ultrasonic effect at a frequency of 35 kHz for 30 minutes on the product of pyrolysis of sludge gives a positive result: in comparison with the untreated material, the residual concentration of iron, nickel, copper and zinc impurities decreased several times (for iron (III) - 74 times, copper II) - 10.5 times, nickel (II) - 6.4 times, zinc (II) - 20.8 times).
4. Ultrasonic treatment allows to increase the sorption capacity of the pyrolysis product of sludge by Ni ions 2.4 times, Cu - 1.2 times, Zn - 1.7 times.
5. The degree of extraction of heavy metal ions using the pyrolysis product of sludge after ultrasonic treatment reaches: for Fe 98.7%, Ni 84.4%, Cu 90.5%, and Zn 95.2%. This allows us to recommend the use of ultrasonic treatment to improve the sorption characteristics of the sorption material obtained by low-temperature pyrolysis of sludge and subsequent post-treatment of waste water from heavy metal ions.

Thus, in order to expand the name of sorption materials from carbon containing waste, an ultrasonic treatment of the solid pyrolysis product of the sludge was carried out. An increase in the sorption activity of processed products in relation to the standards of iodine and methylene blue solution and model solutions of heavy metal ions has been found.

References
[1] Lozinskaya E F, Kosolapova N I, Smorodko A V and Mitrakova T N 2015 Chemistry of plant raw materials 2 p 209.
[2] Nasyrov I A, Dvoryak S V and Shaikhiev I G 2016 Acta Technica 61 (4B/2016) p 307.
[3] Nasyrov I A et al 2017 *The Turkish Online Journal of Design, Art and Communication* *TOJDAC* **7 SE** p 1713 DOI: 10.7456/1070DSE/150.

[4] M. Xing et al 2010 *Bioresources* **5 (3)** p 1353.

[5] Nasyrov I A et al 2017 *Journal of Fundamental and Applied Sciences* **9 (1S)** p 1615

[6] Milushkin V M and Il'in A P 2009 *Sorption and chromatographic processes* *Volume 9 Issue 2* p 308.

[7] Leykin Yu A and others 2007 *Chemical Physics* *Volume 26 (10)* p 18.

[8] Jiménez de Haro M C et al 2005 *Applied Clay Science* *Vol. 30* p 11.

[9] Sharapova A V 2013 *Bulletin of the Nizhny Novgorod University. N.I. Lobachevsky* **1** p 109.