Investigation of the influence of ultrasonic treatment on the sorption properties of the pyrolysis product of wood waste

I A Nasyrov¹, G V Mavrin¹, D D Fazullin¹ and I G Shaikhiev²

¹ Naberezhnye Chelny Branch of the Kazan Federal University, 68/19 Mira pr., 423812, Naberezhnye Chelny, Russia
² Kazan National Research Technological University, 68 Karl Marx st., 420015, Kazan, Russia

E-mail: chem_aleb@mail.ru

Annotation. In the article, the object of study is the sorption material obtained by low-temperature pyrolysis from wood waste and treated with ultrasound. Ultrasonic treatment is one of the methods of improving the sorption characteristics of the pyrolysis product by increasing the specific surface area. The adsorption capacity of pyrolysis products was studied by titrimetric method using methylene blue on the UNICO 2800 spectrophotometer and iodine. An increase in sorption activity was found after ultrasonic action on the sorption material: 1.3 times for methylene blue, 3 times for iodine. Sorption properties of the product of wood waste pyrolysis were investigated after ultrasonic treatment in relation to ions of iron, copper, chromium, nickel and zinc under static conditions using atomic emission spectrometry with inductively coupled plasma on the Agilent 720-OES spectrometer. The sorption degree is calculated. The degree of purification from HMI with the use of wood waste pyrolysis product after ultrasonic treatment is: for Fe – 98%, Cu – 93.6%, Cr – 72.2%, Ni – 60.6%, and Zn – 77.9%. The paper shows that the product of pyrolysis of wood waste after ultrasonic treatment is almost equal to the degree the sorption of commercial sorbent BAU with respect to ions of iron, copper and chromium. Ultrasonic treatment to a frequency of 35 kHz for 30 minutes allows to increase the sorption capacity of the product of pyrolysis of wood waste by Fe ions by 8.8 times, Cu – 2.6 times, Cr – 1.1 times.

1. Introduction
Sorption treatment is an effective method of wastewater treatment from heavy metal ions (HMI). The efficiency of such cleaning, depending on the sorbent used, can be 80-95%. Activated carbon, carbon fibers, silica gels, synthetic sorbents are used as sorbents [1]. Currently, available and relatively cheap sorbents derived from waste are increasingly used for cleaning from HMI.

Wood waste, such as sawdust, has not yet found a wide and complete application as lump waste, although they have promising areas of use. Currently, no more than 30% sawdust is used of the total volume. A significant part is disposed of in landfills or incinerated uncontrollably. The problem of sawdust disposal in the Russian wood processing industry, as well as all wood waste, is at the initial stage of solution due to a number of reasons, the main ones are: low investment opportunities of domestic enterprises, worn-out equipment, outdated technologies [2].

Pyrolysis is an alternative method of wood waste disposal, in particular sawdust. As a result of processing by low-temperature pyrolysis it is possible to obtain a number of useful products: gaseous
pyrolysis fuel, liquid pyrolysis fuel and solid residue (solid pyrolysis product) containing a certain amount of carbon and therefore being a potential sorbent [3].

The sorption properties of wood waste pyrolysis product can be improved by physical activation. One of these methods is ultrasonic treatment. Improvement of the sorption characteristics of the pyrolysis product after ultrasonic exposure occurs due to an increase in the specific surface [4].

2. Materials and methods
The particle size distribution of the solid product of wood waste pyrolysis was determined by the sieve analysis method and using a laser analyzer “Microsizer 201C” [5]. The adsorption capacity of the product of pyrolysis of wood waste before and after ultrasonic treatment was studied on methylene blue using a spectrophotometer UNICO 2800 in the spectral range of 393 nm, iodine–titrimetric method. Mineralizing and the specific conductivity were measured using conductivity meter ANION-7020.

In order to study the sorption properties of the solid pyrolysis product before and after treatment 1 g of the crushed sample and 50 ml of the model solution of the corresponding HMI with a concentration of 4-21 mg/dm³ were placed in a series of conical flasks, flasks were closed with a lid and stirred on a filter shock for 30 minutes under thermostatic conditions (20±0.1°C). Then filtrate was separated from the sorbent and the initial and final concentrations of HMI were determined by atomic emission spectrometry [6,7].

3. Results and discussion
In this paper, the sorption material based on the product of low-temperature pyrolysis of wood waste (sawdust) is investigated, it is a black powder without foreign inclusions. The distribution particles of solid pyrolysis product of wood waste is presented in Table 1 it was determined by the sieve analysis method and by the laser particle size analyzer “Microsizer 201C” [3].

| Particle size, mm | Content, % |
|-------------------|------------|
| >5                | 1.1        |
| 3-5               | 2.5        |
| 1-3               | 28.8       |
| 0.5-1             | 10.9       |
| 0.1-0.5           | 46.9       |
| 0.05-0.1          | 5.6        |
| 0.01-0.05         | 3.5        |
| 0.001-0.001       | 0.3        |
| 0.0006-0.001      | 0.1        |
| <0.0006           | 0.3        |

The resulting solid pyrolysis product contains mainly particles with sizes from 0.1 to 3 mm (86.6%) according to the granulometric analysis.

The results of the study of the microstructure using scanning electron microscope Jeol JSM-6390 LA indicate that the pyrolysis product has a porous structure (figure 1). The porous structure allows to predict sorption properties [8].

A fraction of 1-2 mm was chosen for ultrasonic treatment due to higher performance under dynamic conditions (7.14 ml/min) and relatively high efficiency (96.4% for copper (II) ions). The experiment was conducted for fractions less than 0.5 mm, 0.5-1 mm, 1-2 mm, 2-3 mm, 3 and more mm. The sample had the following characteristics: bulk density of fraction (1-2 mm) — 295 kg/m³, humidity — 2.7%, ash content — 40%, specific surface area — 310.5 m²/g, pore volume 0.229 cm³/g.
Figure 1. Structure of pyrolysis product of wood waste.

It is known that the use of ultrasonic treatment increases the capacity of solid sorbents [9-11]. The ultrasonic action on the sorbent changes not only the surface layer of grains, but also the capillary structure of the sorbent [12]. Ultrasonic treatment of wood waste pyrolysis product with a particle size of 1-2 mm was carried out with a given volume of water in an ultrasonic bath at a frequency of 35 kHz for 30 min. The mass ratio of the pyrolysis product-water was 1:10, respectively — 10 g of the sample in 100 ml of distilled water. During the ultrasonic treatment for various times, the duration of exposure was determined, providing the maximum degree of extraction of HMI from the model solutions.

Initially, the specific electrical conduction (SEC) and mineralization of the aqueous solution of the treated sample after ultrasonic treatment has been determined (Table 2). For comparison, Table 2 presents data on mineralization and SEC for aqueous extraction of the pyrolysis product after a half-hour stirring on a filter shock 10 g of the sample in 100 ml of distilled water.

| Sample                        | Mineralization, mg/dm$^3$ | SEC, μS/cm |
|-------------------------------|---------------------------|------------|
| without processing            | 109                       | 223        |
| after ultrasonic treatment    | 394                       | 807        |

As a result of ultrasonic influence on the product of pyrolysis of wood waste, heavy metals and macroions are released into the aqueous part of the working solution, including water molecules that activated by ultrasound from the pores of the material. The value of SEC and mineralization of the aqueous phase increases due to the transition of ions into the solution. Ultrasonic treatment of the material leads to an increase in SEC and mineralization by 3.6 times.

The evaluation of adsorption were carried out on the basis of the results obtained with using the method of determining the adsorption on iodine and methylene blue (Table 3). The obtained results indicate an increase in sorption activity after ultrasonic exposure on the sorption material. On methylene blue sorption activity increased 1.3 times, iodine — 3 times. This can be explained that the increase in the free pore volume and surface area as a result of the leaching of ions from the pores.

The study of the process of sorption of heavy metal ions after ultrasound exposure was carried out under static conditions (the ratio of the sorbent and the model solution S:MS = 1:50, the initial concentrations of iron, copper, nickel and zinc ions 4-21 mg/dm$^3$).

| Index                        | Pyrolysis product of wood waste |
|------------------------------|---------------------------------|
|                              | Without processing | After ultrasonic treatment  |
| methyleneblue, mg/g          | 15.8               | 20.8                         |
| iodine, %                    | 16.5               | 50.8                         |
It can be concluded about the adsorption capacity if compared the concentration of ions in the initial solution with the residual (equilibrium) concentration after contact of the sorbent with the model solution [12].

Table 4 presents the results of determination of sorption properties in relation to HMI.

**Table 4. Mass content of heavy metal ions**

| Sample                                             | Concentration, mg/dm³ |
|----------------------------------------------------|-----------------------|
| stock solution                                     | 4.44 6.08 20.5 5.51 6.02 |
| filtrate from pyrolysis product of wood waste after ultrasonic treatment | 0.09 0.39 5.7 2.17 1.33 |

The sorption degree $R$ was calculated by the formula

$$R = \frac{C_0 - C_1}{C_0} \times 100\%,$$

where $C_0$ — initial concentration of HMI; $C_1$ — concentration of HMI after sorption. The results of the calculation of the sorption degree are presented in Table 5.

For comparison, Table 6 presents studies of the sorption degree for the initial solid products of pyrolysis (without ultrasonic treatment) and coal grade BAU [6] which is a common sorption material.

**Table 5. Degree of sorption**

| Sample                                             | $R$, % |
|----------------------------------------------------|--------|
| pyrolysis product of wood waste after ultrasonic treatment | 98 93.6 72.2 60.6 77.9 |

**Table 6. Degree of sorption**

| Sample       | $R$, % |
|--------------|--------|
| pyrolysis product of wood waste | 11.1 36.4 64 |
| activated carbon | 99.8 99.9 83.9 |

The results indicate an increase in sorption capacity in relation to ions of iron, copper and chromium after treatment of wood waste pyrolysis products by ultrasound. The degree of purification from HMI with the use of wood waste pyrolysis product after ultrasonic treatment is: for Fe — 98%, Cu — 93.6%, Cr — 72.2%, Ni — 60.6%, and Zn — 77.9%. Thus, the product of pyrolysis of wood waste after ultrasonic treatment is almost as good as the commercial sorbent BAU in the degree of sorption in relation to the ions of iron, copper and chromium. This treatment allows to increase the sorption capacity of the product of pyrolysis of wood waste in relation to Fe ions by 8.8 times, Cu — 2.6 times, Cr — 1.1 times.

4. Conclusions

Heavy metals and macroions are released into the aqueous part of the working solution as a result of ultrasonic action on the pyrolysis of wood waste, this leads to an increase in SEC and mineralization in 3.6 times.

An increase in sorption activity after ultrasonic action on the sorption material was found: 1.3 times for methylene blue, 3 times for iodine. This can be explained by the increase in the free pore volume and surface area as a result of the leaching of ions from the pores by ultrasound-activated water molecules.
The degree of purification from the HMI with the use of the product of pyrolysis of wood waste after processing by the ultrasound reaches: Fe — 98%, Cu — 93.6%, Cr — 72.2%, Ni — 60.6%, and Zn is 77.9%, which allows to recommend the use of ultrasonic treatment to improve the sorption properties of the material, and subsequent purification of sewage from HMI.

Ultrasonic treatment allows to increase the sorption capacity of wood waste pyrolysis product in relation to Fe ions by 8.8 times, Cu — 2.6 times, Cr — 1.1 times.

Thus, in this paper it is shown that the method of wood waste utilization by low-temperature pyrolysis allows to obtain a complex sorption material, sorption qualities of which can be improved by a special procedure — ultrasonic treatment. Studies of sorption properties have shown the possibility of using a solid pyrolysis product of wood waste that were treated of ultrasound as a sorption material intended for the removal of heavy metal ions from aqueous media.

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