Influence of wheat husk modification on sorption properties of heavy metal ions

N. Politaeva1, Y. Smyatskaya1, E. Safonova1, N. Barsukova1

1Higher School of Biotechnology and Food Technology, Peter the Great St. Petersburg Polytechnic University, 194021, Russia, St.Petersburg, Novorossiyskaya, 48-50

politaevana1971@gmail.com

Abstract. This article focuses on sorption properties of sorbents based on modified wheat husk. It presents kinetic characteristics and isotherms of sorbents sorption. We studied the influence of pH environment on the efficiency of wastewater treatment from heavy metal ions.

Introduction

Nowadays the problem of waste management is of urgent interest, and one of the main directions is wastewater purification [1–12]. Choosing a method of wastewater treatment is crucial not only for cleaning efficiency, but also for the cost of sorption material [13–24]. Thus production of sorbents based on waste has several advantages. Two problems are solved simultaneously: water purification and waste disposal. Availability and low cost of sorbents on the basis of agro-industrial complex waste attract attention of many Russian and foreign scientists. However, such sorbents often do not have high sorption characteristics, so the work associated with their modification and increase in physical, chemical, mechanical and adsorption properties is highly demanded.

Authors [25] studied the possibility of using waste of linen processing industry (short flax fiber) as a sorbent of zinc ions. It was shown that plasma modification of short linen fiber leads to an increase in its limiting sorption capacity in relation to zinc ions by 3 - 3.5 times. Modified husk of ripened sunflower seeds was used as sorbent for ions of iron and cadmium in [26].

To increase sorption properties of rice and buckwheat husks, scientists of Kazan State Technological University [27] suggest using special plasma plant for waste treatment. Sorbent is heated in the high-frequency plasma torch in an inert gas environment. The degree of purification of sewage from petroleum products with the help of such modified sorbents reaches 99% compared to no more than 70% without such treatment.

The waste of agricultural production - buckwheat husk is used in combination with polyurethane foam [28]. The composite material is used to collect oil, oil products and oils from the water surface.

Other authors propose the use of pine nuts shells as a raw material for the production of sorbent [29]. Researchers of Malaysian Institute of Chemical and Bioengineering Technology suggest using cheap sorbents for wastewater treatment such as tea leaves and coffee leaves that can simultaneously extract heavy metals (nickel, cadmium, chromium, zinc and lead) from polluted waters, and are also suitable for the elimination of turbidity [30].

Pakistani scientists suggest using leaves of the ficus as a sorbent for treating sewage from a number of organic and inorganic compounds [31]. Due to the composition of wood (cellulose, hemicellulose, pectin, lignin) and leaves (chlorophyll, carotene, anthocyanin, tannin), that contain functional
carboxyl, carbonyl, amino and nitro groups, high sorption characteristics for heavy metals are achieved.

The purpose of this work was to study the effect of modifying the waste of agricultural processing - wheat husks on their sorption properties with respect to heavy metal ions (HMI).

**Experimental part**

In this work we used wheat husk and its modified analogues as sorbents, namely:

- Sorbent P-1 - wheat husk without modification. The sorbent consisted of oily yellowish husk particles with a size of about 4-5 mm in length and 1.5-2.5 mm in width.
- Sorbent P-2 - wheat husk after heat treatment at a temperature of 300 °C for 20 minutes in a special form with limited air access. These heat treatment conditions make it possible to obtain a sorbent with higher sorption properties [32]. The sorbent was a coarse black powder.
- Sorbent P-3 - wheat husk activated in a 0.2 N solution of hydrochloric acid. To do this, 25 g of wheat was boiled for 10 minutes in 500 ml of acid, then washed with distilled water until negative reaction to chloride ions (qualitative reaction with a 10% solution of silver nitrate). To wash 2.5 g of sorbent, 200 ml of water was required. The sorbent was then dried at 110° C for 1 hour. The sorbent became white without visible traces of vegetable fats.
- Sorbent P-4 - wheat husks heat-treated in the same way as P-2 sorbent, and then activated by hydrochloric acid as P-3 sorbent. The sorbent was a fine powder of black color.

To study the efficiency of wastewater treatment from HMI, each sorbent in an amount of 10 g was placed in 100 ml of a model solution and held for 24 hours. A solution containing a mixture of cadmium, zinc and lead ions with concentrations of 10·10⁻³ gl⁻¹ was used as a model solution. The residual concentration was determined by the voltammetric method using the AKV-07 MK device manufactured by Aquilon. For final (Cfin) and initial (Cini) concentrations, the efficiency (E) of model wastewater treatment was calculated according to the formula:

\[
E = \frac{C_{ini} - C_{fin}}{C_{ini}} \times 100\%
\]

The analysis of the obtained data indicates that the highest purification efficiency with respect to the HMI was shown by P-4 sorbent. Sorbents P-2 and P-3 had similar values. The effectiveness of sorbents depends on their sorption properties, which, as our studies have shown, increase with modification.

The sorption capacity of the sorbent depends largely on the amount and size of the pores. The number of micropores is characterized by iodine absorption [33]. From the degree of filling of the pores of the sorbent with iodine molecules, it is possible to determine the number of pores with a size of about 1.0 nm. Sorbents from P-1 to P-4 were investigated according to the method described in [33]. The sorption capacity for iodine (Table 2) was determined by the formula:

| HMI | P-1 | P-2 | P-3 | P-4 |
|-----|-----|-----|-----|-----|
|     | Cfin mg/l | E,% | Cfin mg/l | E,% | Cfin mg/l | E,% | Cfin mg/l | E,% |
| Pb²⁺ | 0.68 | 93.2 | 0.538 | 94.6 | 0.415 | 95.8 | 0.101 | 98.9 |
| Cd²⁺ | 0.57 | 94.3 | 0.324 | 96.8 | 0.268 | 97.3 | 0.130 | 98.6 |
| Zn²⁺ | 0.19 | 98.1 | 0.051 | 99.5 | 0.068 | 99.3 | 0.020 | 99.8 |

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\[ E = \frac{(V_1 - V_2) \times 12.7}{M}, \text{ (mg/dm}^3) \]

Here \( V_1 \) is volume of sodium thiosulfate, used for filtration of the "zero" sample; \( V_2 \) is volume of sodium thiosulfate, used for filtration of the sample after treatment with a sorbent; 12.7 is volume of iodine solution taken to clarify the sample; \( M \) is the mass of the sorbent (0.25 g).

Table 2 Sorption capacity (E) of sorbents for iodine

| sorbent | P-1 | P-2 | P-3 | P-4 |
|---------|-----|-----|-----|-----|
| E \times 10^{-3} | 63.5 | 15.2 | 58.4 | 45.6 |

Sorption agents P-1 and P-3 (correspondingly 65.3-10^{-3} g l^{-1} and 58.4-10^{-3} g l^{-1}) possess the largest value of sorption capacity for iodine. Apparently, these sorbents have a larger number of pores with dimensions of about 1 nm. During the heat treatment of wheat husks the process of coking of particles is likely to occur. This process produces pores with large dimensions, which, accordingly, leads to a decrease in the sorption capacity of the material by iodine (\( E = 15.2-10^{-3} \text{ g l}^{-1} \)). According to the procedure [33], it is also possible to determine the sorption capacity of methylene blue, which characterizes the presence of mesopores (~ 1.5 - 1.7 nm). None of the sorbents investigated by us discolored the solution of methylene blue. Consequently, the number of pores with such a size in the structure of materials is minimal and our sorbents are basically microporous (pore size \( \leq 1 \text{ nm} \)).

Basic information about sorption properties of the material and the nature of sorption makes it possible to obtain the shape of the curve of the sorption isotherm. The sorption isotherm for liquid media characterizes the dependence of the sorption capacity on the concentration at a constant temperature. According to the shape of the isotherm, one can also judge the presence and number of macro- and micropores. For the construction of sorption isotherms, it is necessary to establish the time to achieve sorption equilibrium.

To determine the time of sorption equilibrium and the value of sorption capacity, the process of sorption of HMI under static conditions from aqueous solutions of lead sulphate was studied with stirring and thermostating of the solution (\( T = 293 \text{ K} \)). To obtain the kinetic curves of sorption, a sample of \( m = 0.1 \text{ g} \) of P-1 - P-4 sorbents and 10 ml \( (V) \) of an aqueous solution of lead sulphate with an initial concentration of \( C_0 = 10-10^{-3} \text{ g l}^{-1} \) was placed in a series of tubes and aged from 5 minutes and up to 48 hours. After certain time intervals, the solution was separated from the sorbent by filtration and the current concentration of lead ions \( C_t \) was determined by voltammetric method using the AKV-07 MK instrument. The sorption capacity \( A_i \) of the sorbent at each given period of time was calculated by the formula [33]:

\[ A_i = \frac{C_0 - C_t}{m} \times V \]

Based on the results of calculations, kinetic curves of sorption were constructed (Fig. 1)

Under steady-state equilibrium conditions, the equilibrium concentration of metal ions in the solution \( C_p \) was determined in the system, and the equilibrium sorption capacity \( A_p \) was calculated by the formula:

\[ A_p = \frac{C_0 - C_p}{m} \times V \]
Important characteristics of sorbents are the amount of sorption capacity and the time to achieve sorption equilibrium. Kinetic studies have shown that in the sorption of Pb\textsuperscript{2+} sorbents on the basis of wheat husks, the equilibrium in the system is established first for P-1 and P-4 sorbents (in 20 min), and the equilibrium sorption capacity increases for sorbents in the series:

\[ P\text{-}1(\text{A}_p=12.9) < P\text{-}2 (\text{A}_p=15.0) < P\text{-}3 (\text{A}_p=17.1) < P\text{-}4 (\text{A}_p=20.7) \]

For the construction of sorption isotherms, weighed samples of P-1, P-3 sorbents were placed in a series of tubes and 10 ml of a lead sulfate solution with initial concentrations of 5, 10, 20, 30, 50, 100 mg / dm\textsuperscript{3} was poured into them until equilibrium was reached. The solution was then separated from the sorbent by filtration and the final concentration of the HMI was determined therein (Fig. 2).

According to the BET theory [33] (Braunauer, Emmett and Teller), the shape of isotherms 1, 3, 4 in Fig. 2 indicates the presence of micropores in the sorbents. Steepness of the isotherm 4 and 3 characterizes the presence of ultramicropores. The curved shape of isotherm 2 is typical for sorbents with mixed micro- and macroporosity, which confirms our explanation of the minimum value for iodine absorption by P-2 sorbent (EP\textsuperscript{-}2 = 15.2 mg\textsuperscript{1}\textsuperscript{-1}). The presence of porosity in sorbents indicates the possibility of physical sorption of HMI from solutions.

From the literature data it is known that the sorption value determined by the HMI depends on the pH of the environment, which significantly affects the sorption processes of the HMI present in solutions in the form of various complex particles.

The stability of metal complexes decreases in the case of deviation of the pH of the environment from neutral reaction: at low pH, because proton competes with the metal ion for the binding sites in the molecules, and at high values, because of competition between the hydroxyl group and the ligand.
To determine optimal conditions for sorption by pH, model solutions containing copper, lead, zinc and cadmium ions with an initial concentration of $10 \cdot 10^{-3}$ g l$^{-1}$ were prepared, the pH of which was adjusted to pH = 2.0; 6.0; 8.0; 10.0. The necessary pH was adjusted with solutions (0.1 N) of sodium hydroxide or sulfuric acid. P-2 sorbent was used at the rate of 10 g of sorbent per 100 ml of the model solution. Solutions with the sorbent were held for 12 hours with stirring and thermostating ($T = 293$ K).

It can be seen from the Fig.3 that the most effective is the purification from zinc and cadmium ions in the range 6.0-10.0, from lead ions at pH=6-8, from copper ions at pH=6.0. In solutions with higher pH values (8, 10) copper precipitates as copper hydroxide.

The mechanism of sorption process by proposed sorbents on the basis of modified wheat husk can be explained as follows. The main composition of wheat husks is fiber and cellulose. Cellulose is a natural polymer, the elementary links of which -C$_6$H$_{10}$O$_5$ - are combined into long linear macromolecules with the help of a glucose bond or an oxygen bridge -O-. A characteristic feature of cellulose is the presence in each elementary unit of three hydroxyl groups -OH-. The functional hydroxyl group is able to interact with the HMI, keeping them in the pores and on the surface of the sorbent. Consequently, the mechanism of cleaning HMI with these sorbents occurs not only due to physical sorption but also chemisorption. Polymer macromolecules interact with each other using van der Waals forces and hydrogen bonds, due to the presence of hydroxyl groups [34]. After thermal treatment, the polymer is oxidized and carbonized, which increases the physical adsorption of HMI with P-2 sorbent in comparison to P-1 sorbent.

Wheat husk also contains hydrophobic components: lipids (ether extract), lignin and waxy substances that determine the hydrophobic properties of P-1 sorbent (unprocessed husk of wheat), which makes it difficult to adsorb HMI from aqueous solutions, because of poor wettability, slowing down penetration of the solution into the interior of the sorbent. After acid treatment (sorbent P-3), in addition to polymer oxidation, hydrophobic substances are removed, which leads to an increase in the porosity and hydrophilicity of the sorbent. This increases the availability of functional groups, which increases chemisorption and the ability to bind HMI. Therefore after complex thermal and acid modification (sorbent P-4) its adsorption and chemisorption properties improve.

Thus, obtained data show that modifying the husk of wheat leads not only to physical properties change (porosity, dispersity, bulk density), but also causes changes in the chemical composition of the material. We carried out physico-chemical studies using infrared spectroscopy (IRS) (Fourier spectrometer InfraLum FT-801 in tablets with KBr) of P-1 and P-2 sorbents. Samples analysis showed that P-1 sorbent contained cellulose, ester, protein and silicon compounds. After heat treatment at 300 °C, the absorption ester and protein groups disappeared from the P-2 composition and the absorption bands of the silicon compounds increased. At the same time, bands were found that indicate the appearance of carbon in the P-2 sorbent formed during coking due to the conversion of organic constituents.

Carried out research allowed us to establish kinetic dependences of sorption processes by HMI sorbents on the basis of the initial and modified husk of wheat. Modification by heat treatment and
hydrochloric acid promotes an increase in the porosity and hydrophilicity of the material and, as a result, increases the sorption capacity.

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