Research of pH influence on sorption properties of sorbents on a basis of residual biomass of microalgae *Chlorella sorokiniana* and duckweed *Lemna minor*

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Abstract. This scientific research is determined to a study of sorption process of heavy metal ions removal from aqueous solution at water purification with a help of sorption materials on a basis of residual biomass of microalgae and duckweed. It is known that *Chlorella sorokiniana* and duckweed *Lemna minor* have in their composition different valuable substances such as lipids, proteins, pigments, pectic substances. After their extraction residual biomass is formed. And in present study it is proposed for using as biosorbent for water purification. At different pH values the removal of ions of heavy metals (Zn(II), Cd(II), Pb(II), Cu(II)) occurs with varied efficiency; it is an important and informative parameter. Equilibrium and initial concentration of the solution with heavy metal ions were measured by voltammetric method of analysis with a use of special equipment. Chitosan was used as a component for making composite sorption materials with residual biomass of microalgae and duckweed. It is biopolymer which widely used in water purification. Due to this, prepared granules have good sorption properties. Nowadays in the era of technology and wide industrial production it is important and actual to develop new ecological technology and useful materials for water treatment and other fields for environment protection in general.

1 Introduction

Resources saving and environment protection in whole gain a prime value due to a load on natural systems. A sorption purification of water is one of the effective methods which allow reaching a high rate of the extraction of the different harmful substances, and ions of heavy metals also belong to this group. Therefore, research aimed to the search of new resources for sorption materials obtaining on their basis are current and perspective. Much attention is paid to the materials of the natural origin, for example to microalgae, to the higher water plants, because they are non-toxic initially and have a biosorption activity to the various kinds of the contamination [1–5].

Microalgae *Chlorella sorokiniana* and duckweed *Lemna minor* are the source of such useful substances as lipids, proteins, pigments, pectic substances and so on. After the extraction they can be used in different fields of industry: pharmaceuticals, cosmetology, medicine, food industry and many others [6–8]. On the final stage of valuable components extraction, a residual biomass is formed. It contains cellulose, lignin, hemicelluloses, which determine its sorption properties, therefore residual biomass can be used as a sorbent for water purification from heavy metal ions [1]. Applying of residual biomass is the one of stages of a complex use of microalgae and duckweed which consists of cultivation,

extraction of useful substances, obtaining of sorbents for water purification, their regeneration after sorption process, and then biogas production by fermentation the residual biomass and fulfilled sorption materials. Thus, a cyclic process with the use of renewable resources and minimization of formed waste is carried out.

Sorption is a kind of physical, chemical and biological processes which take place on boundaries between two phases which can be such systems: liquid-gas, liquid-liquid, solid-liquid and solid-gas. When molecules of the substance in an aqueous solution concentrate on surface or porous space of a solid material (sorbent), adsorption occurs [9]. Adsorption depends on many factors: nature and structure of a sorbent, its physico-chemical properties, sorbents quantity, pH, concentration and temperature of the purified solution [2]. And it is important to study an influence of each of these parameters. pH factor may affect the solubility and degree of ionization of the adsorbate (extracted contaminant) during the sorption process. And pH influences solution chemistry of the adsorbate, activity of the functional groups in the biosorbent and competition of sorbate substances [2].

Now a lot of various sorption materials are studied. It can be falling leaves [2, 10], nut shells, rice straw and husk [2, 11], chitosan, zeolite, waste of food production, agricultural by-products with or non-modification as well as waste materials from wood processing, eggshell,

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fruit peels, sugarcane bagasse, and even coconut tree sawdust [12] and other cellulosic materials which often are considered as waste. And all of them due to their structure have a sorption activity to ions of heavy metals (Zn(II), Cd(II), Pb(II), Cu(II), Ni(II), Cr(III), Cr(VI)).

Chitin is a natural biopolymer which is produced from shells of crab and shrimp, after deacetylation of chitin chitosan is formed [13]. Chitin has a structure like a cellulose, because of that it widely used in water treatment for removing ions of heavy metals. In general, using of plant materials is environment friendly, has practical and economical value, and also lead to minimization of waste and ions of heavy metals contamination.

2 Materials and methods

As an object of the research the residual biomass of microalgae *Chlorella sorokiniana* and duckweed *Lemna minor* were used, and sorption materials on the basis of this biomass were prepared included a chitosan as a binder substance to make a shape of granules. As it was mentioned before, chitosan also has sorption properties according to ions of heavy metals.

Granules with chitosan were obtained in following ratio of the components. First, 40 g of chitosan was dissolved in 960 g of 3% solution of acetic acid, during this process the mixture was stirring. It takes about 4–5 hours for total dissolution of chitosan after this it looks like a gel.

Then residual biomass of microalgae or duckweed, which was formed after extraction of value components (lipids, pigments, pectic substances), was added to obtained jelly-like mixture. On the next step this compound is dropwise added with the help of syringe into a NaOH solution (5%). For completing the process and final forming a shape of granules they were kept into alkali solution NaOH during 24 hours and after that these sorption materials were rinsed in distilled water to get pH ratio 7.0–7.5. The wet granules were dried at room temperature [1, 14].

Produced compositions of the sorption materials are:

1 – granules made with 100 ml of chitosan and 5 g residual biomass of microalgae (Figure 1a);

2 – granules made with 100 ml of chitosan and 5 g residual biomass of duckweed (Figure 1b).

Fig. 1. Sorption materials on a basis of residual biomass: a – chitosan + residual biomass of microalgae; b – chitosan + residual biomass of duckweed.

The study of pH influence on a sorption process has one of the main roles because it leads to different rate of molecule sorption interactions with surface of sorption material. Due to this, parameters of pH were studied on the first step of the sorption research. The equilibrium concentration of heavy metal ions after a sorption process was measured using inversion voltammetric method of analysis (using standard Russian method PND F 14.1.2:4.222-06) with the help of TA-Lab device (Russia, OOO «NPP«TOMANALIT») with inaccuracy of measuring technique 25 %. In general, voltammetric techniques are widely used in various fields of practice (ecology, pharmacy, medicine, inorganic, physical, analytical chemistry and many others). It is multipurpose method which allows determining quality and quantity of a substance in a solution. Due to this, it is possible to detect even trace of heavy metals with very small concentrations which depend only on instrument resolution and range of analysis method. The voltammetric technique is based on electrochemical accumulation of substance on a surface of working amalgamic electrode and then measurement of its concentration [15].

The efficiency of heavy metal ions removal from aqueous solution was calculated using following equation:

$$R = \frac{(C_{in} - C_{eq})}{C_{in}} \cdot 100 \%,$$

where R – removal efficiency of heavy metal ions from aqueous solution; C_{in} – initial concentration of heavy metal ions; C_{eq} – equilibrium concentration of heavy metal ions.

TA-Lab device uses three electrochemical cells and it allows obtaining accurate average result. The sorption process was conducted during 24 hours; the solution containing heavy metal ions (Zn(II), Cd(II), Pb(II), Cu(II)) with initial concentration 20 mg/l was intermixed for first 2 hours using the laboratory shaker Biosan OS-20 (Latvia) with the rate $v = 250$ rpm, then during remaining time (22 hours) the mixture was static. The weight of the biomass and the sorption materials with chitosan added to 100 ml solution was 2 g. Temperature conditions of the solution were $20 \pm 2^\circ\text{C}$. The required pH value was achieved with the use of solutions HNO_3 (7%) and NaOH (7%) and it was controlled using laboratory ion meter I-160MI (Russia, OOO «Izmeritelnaya tehnica»). After the sorption the biomass of microalgae and also duckweed was separated by filtration and the solution with granules was decanted.

3 Results and discussion

Optimal pH parameter was determined using three points: 2.0 ± 0.2 ; 4.0 ± 0.2 and 6.0 ± 0.2 pH units. Results of the research showed that at $\text{pH} = 2.0 \pm 0.2$ the efficiency of the purification is low and for some heavy metal ions does not exceed 60–70%. Increasing of pH leads to the rise of efficiency and in general these

conditions are conducive for the sorption process of all studied ions of heavy metals. Further, when pH reaches of 6.0 ± 0.2 units the extraction of ions achieves 72–99%. It was determined that $\text{pH} = 6.0 \pm 0.2$ is an conducive condition for heavy metals (Zn(II), Cd(II), Pb(II), Cu(II)) removing, and it is important to notice that at this values of pH ions exist into the solution in a soluble form and they still do not form salts. Heavy metal ions take a such chemical form like $\text{Zn}(\text{OH})^+$, $\text{Cd}(\text{OH})^+$, $\text{Pb}(\text{OH})^+$, $\text{Cu}(\text{OH})^+$ and they have lower hydration degree, smaller ion charge and large radius, and it causes their electrostatic interaction with the surface of sorbents and ion exchange reaction also occurs [16].

At first, ions of lead interact with a surface of residual biomass and obtained sorbents, because it has a large ion radius comparing with other metals in the solution $\text{Pb} > \text{Cd} > \text{Cu} > \text{Zn}$.

Residual biomass of microalgae and duckweed, and granulated sorbents with chitosan on their basis are biomaterials which contain lignin, cellulose, hemicellulose, sugar compounds which active groups determine sorption opportunity [17]. Also, with increasing pH value more than 6.0–7.0 units the degree of biosorption significantly reduced [2], it again indicates that obtained data of $\text{pH} = 6.0$ is conducive. Results of the research are shown at Figures 2–5.

Fig. 2. Residual biomass of *Chlorella sorokiniana*.

Fig. 3. Residual biomass of duckweed *Lemna minor*.

Fig. 4. Residual biomass of *Chlorella sorokiniana* + chitosan.

Fig. 5. Residual biomass of duckweed *Lemna minor* + chitosan.

4 Conclusions

1. Results of the research of sorption properties of residual biomass of microalgae *Chlorella sorokiniana* and duckweed *Lemna minor* were conducted at different pH values and the conducive pH for effective removing of heavy metal ions was chosen.
2. The sorption materials on a basis of residual biomass and chitosan were prepared and their sorption properties were studied also at different pH values.
3. It was established that $\text{pH} = 6.0 \pm 0.2$ is conducive for sorption process of heavy metal ions (Zn(II), Cd(II), Pb(II), Cu(II)). The efficiency of heavy metal ions removal achieves 77.0–99.0 %.

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