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Spent Biosorbents as Additives in Cement Production

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ABSTRACT

The research is related to solving the problem of rational use of materials and to the creation of resource-saving technologies for the protection of the environment from pollution. Sorption technologies are quite effective in wastewater treatment, but most sorbents are quite expensive, and their regeneration raises the question of recycling of spent solutions. The cheapness and availability of raw material base of biosorbents makes these technologies attractive for wastewater treatment. The research is aimed at investigation of the ways to effectively utilize the spent sorbents, which are obtained after water purification, in the production of building materials. The obtained results allow creating a complex low-waste technology of water demineralization and purification from heavy metal ions.

Keywords: spent biosorbent, utilization, building materials, low-waste technology

INTRODUCTION

Nowadays, surface and groundwater salinization, which are sources of water supply, have become quite acute. Ukraine is characterized by both quantitative and qualitative depletion of water resources due to their pollution resulting from the discharge of huge volumes of incompletely treated mineralized water. Heavy metals can infiltrate into the natural sources with wastewaters of different production of chemical and heavy industries; they can interact with other compounds of water and exhibit toxic effects towards living organisms (Duruibe et al. 2007, Buzylo et al. 2018).

High pollution of water bodies with mineralized water and toxic substances requires the development of effective methods to reduce this impact (Campos 2009). One of the priority tasks in the sphere of environmental protection is to find effective and safe wastewater treatment technologies (Trus et al. 2019). Today, sorption (Malovanyy et al. 2019), reagent (Radovenchik et al. 2001, Mazurak et al. 2019), membrane (Gomelya et al. 2014, Ambiado et al. 2017), electrochemical (Gomelya et al. 2018, Ghosh et al. 2008), ion exchange (Gomelya et al. 2017, Dizge et al. 2009), and biological (Wu et al. 2010) methods can be used for wastewater treatment from different pollutants.

At present, there are urgent problems of utilization of waste from agro-industrial complex, rational use of nature and transition to the use of environment-friendly and energy-efficient technologies (Skiba et al. 2018). One of the promising areas is the application of the principles of so-called "green chemistry", namely the development of technological processes using renewable raw materials. The recent publications show that expensive traditional sorbents can be replaced by the materials derived from natural raw materials based on cellulose and lignin, which can be easily modified. The natural biopolymers of plant origin have a number of valuable properties. That is why such materials can be used in chemical, food, pharmaceutical and many other branches of industry. The possibility of applying renewable raw materials in the production of materials and products for the improvement of the ecology and for the solution of the problems related to the technogenic pollution of water objects by various toxicants, including heavy metal ions, radioactive elements, petroleum products and others, is of particular interest. It is also important that when using "green" technology both in Ukraine and abroad, each region is able to choose its own raw material base depending on the specificity of the agro-industrial complex.

In order to ensure the sustainable development of the agro-industrial sector, the utilization of agricultural and food industry wastes should involve their secondary use as raw materials for the production of a wide range of materials, such as animal feed, fertilizers, fuels, medical and food products. Ukraine is one of the largest exporters of agricultural products to Europe and a large amount of plant wastes is generated each year. Burning constitutes one of the methods of their utilization. The efficiency of this method is very low because of the low heat capacity, and the huge impact on environment occurs. From the economic point of view, it is promising to use agro-industrial complex wastes as biosorbents (Galysh et al. 2017). Chemical activation and modification of a natural sorbent promoted the improvement in the indices of water purification (Kartel and Galysh 2017). Dynamic exchange capacity is the main indicator characterizing the quality of water purification (Pohrebennyk et al 2018). One of the possible ways of utilizing spent biosorbents can be their application in the composition of building materials (Trus et al. 2017).

The purpose of the work is to develop the efficient utilization of waste biosorbents as additives in the production of building materials, which will contribute to the creation of low-waste technologies and ensure the sustainable development.

MATERIALS AND METHODS

Lignocellulosic and cellulosic sorbents were obtained from walnut shells by organosolv and oxidative-organosolv pre-treatment as described in our previous paper (Halysh et al. 2018). Initial material and biosorbents were used as additives in combination with cement. In order to study the physical and mechanical properties of building composites, the cement of I/500 type was used. For this purpose, cements preparation was performed by mixing components in the ball mill for 20 min. The mixes were tested for normal density, coefficient of water removal, hardening time and compressive strength (Fleysher et al. 2015).

RESULTS AND DISCUSSION

The structure and sorption properties of materials based on biopolymers depend on the content of cellulose, hemicelluloses, lignin, extractives and mineral components, which affect the ability of complex formation and cation exchange ability. The pre-treatment of plant residues with a mixture of acetic acid and hydrogen peroxide, under specified conditions, results in the formation of biosorbents with different composition. One can modify the parameters of pre-treatment depending on the intended use of the final product. The chemical composition of initial walnut shells and obtained biosorbents of cellulosic and lignocellulosic types is shown in Figure 1. As can be seen, the treatment of the initial material with acetic acid at the temperature of 90°C during 2 h leads to the partial destruction of low-molecular polysaccharides, enrichment of the biosorbent with lignin and the formation of lignocellulosic biosorbent takes place. The acidic pre-treatment also promotes the removal of mineral components.

The application of a mixture of hydrogen peroxide and acetic acid for the pre-treatment of walnut shells promotes the removal of a larger portion of lignin, resulting in the formation of a cellulosic biosorbent due to the formation of peracetic acid at high temperatures, which is a strong delignification reagent (Halysh et al. 2019).

Due to the high availability and low cost of raw materials, such biosorbents can be easily disposed of without regeneration. An effective method of disposal of such spent materials has not been developed yet. The content of cellulose, hemicelluloses, lignin, extractives and mineral

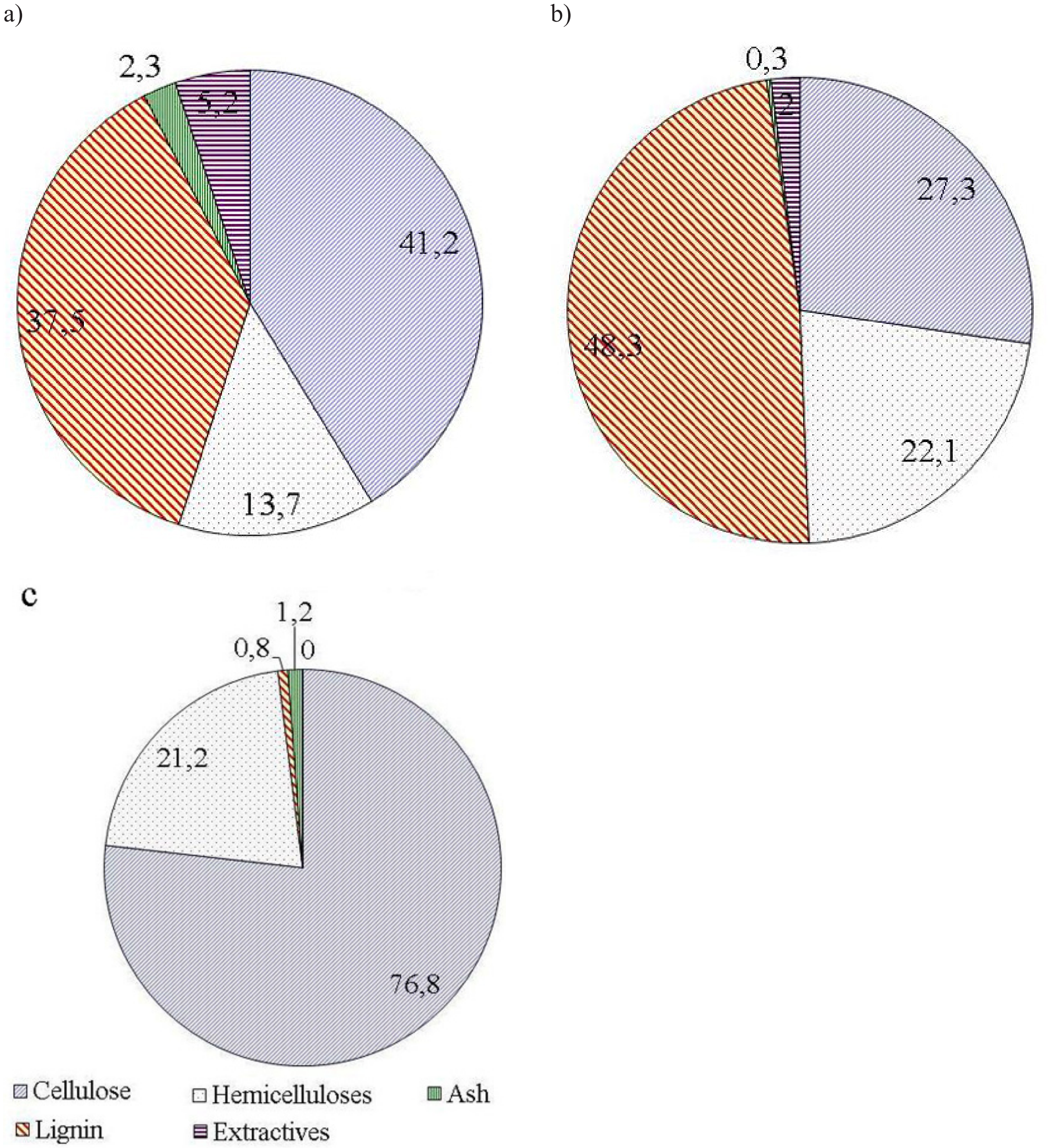

Fig. 1. Chemical composition of initial walnut shells (a), lignocellulosic (b) and cellulosic (c) biosorbents prepared from walnut shells

components in biosorbents affects the ability to swell in water. This feature is very important, so it must be taken into account when developing utilization method.

According to State standard of Ukraine it is allowed to enter up to 5 wt. % of additives. Therefore, unmodified walnut shells were introduced into the cement of type I-500-D0, which contains no additives, in order to evaluate the effect of the shells on the properties of cement. The shells in a form of fine powder with a particle size of 1–2 mm were used for this purpose. The influence of the modified walnut shells on the normal density of cement samples is shown in Figure 2.

The results of the study indicate that unmodified walnut shells act as a fine additive; the normal density is increased with the increase of the plant material content in the bulk of cement. The addition of 1% of shells leads to an insignificant change in normal density. Further increase in agricultural residue content up to 5% results in 1.2-fold increase of the parameter. The increase in the normal density takes place due to the fact that more water is

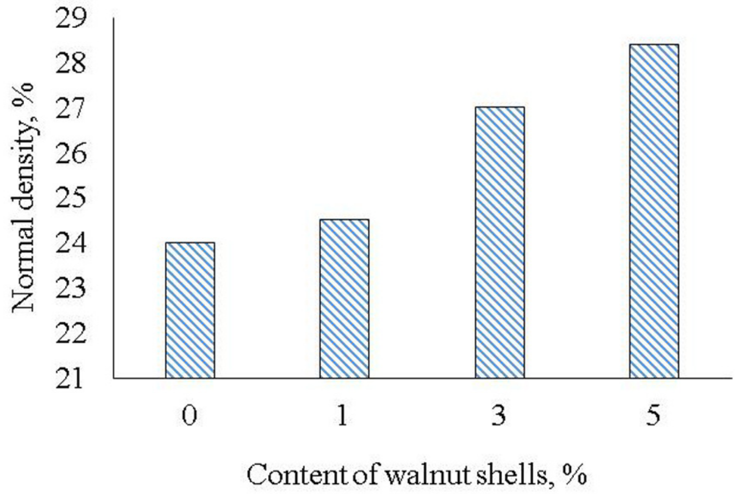

Fig. 2. Effect of walnut shells content on cement normal density

required to form adsorption water coats around fine particles of the shells. The higher the shells content, the more water is consumed to obtain the cement dough of normal density.

According to Figure 3, the hardening time is accelerated by 2.5 times if the content of walnut shells increased up to 5% The acceleration of hardening is taking place due to the fact that the fine additive acts as a thickener (similar to clay).

The walnut shells addition has a negative effect on the compressive strength of cement as can be seen from Figure 4; the strength of the samples with the addition of shells after 2 days is lower by 6–38%, while after 28 days – by 8–25%. Such results can be explained by the increased normal density of the cement dough. As the walnut shells do not react to hydration and hydrolysis and are unable to harden, the excess water that goes into the formation of adsorption coats around the shells particles is not expended on the hydration of the clinker minerals and remains in the free state (early hardening period) or evaporates, resulting in the formation of pores in the cement stone (late hardening period).

The value of coefficient of water removal insignificantly increases up to 6% with the increasing of walnut shells content form 1 to 3% in cement samples, a further increase in the shell content has no effect on this parameter (Fig. 5).

Therefore, unmodified walnut shells have a slightly negative effect on the strength and water removal from cement, so it can be recommended for the use as an additive in the composition of cement in an amount of no more than 1%.

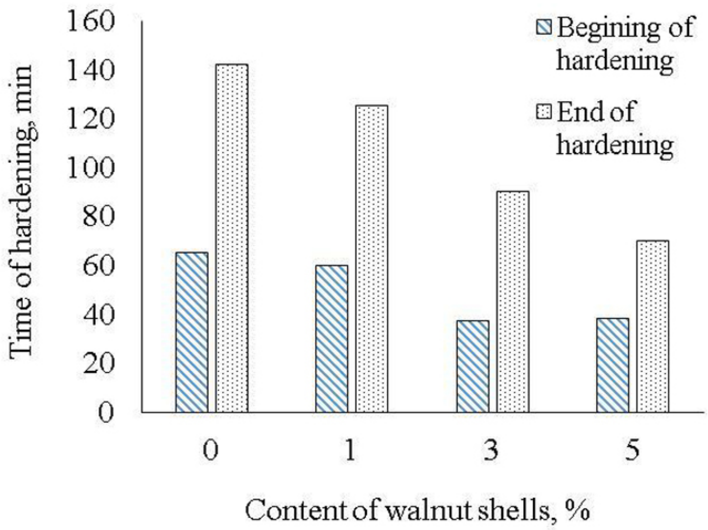

Fig. 3. Effect of walnut shells content on cement hardening time

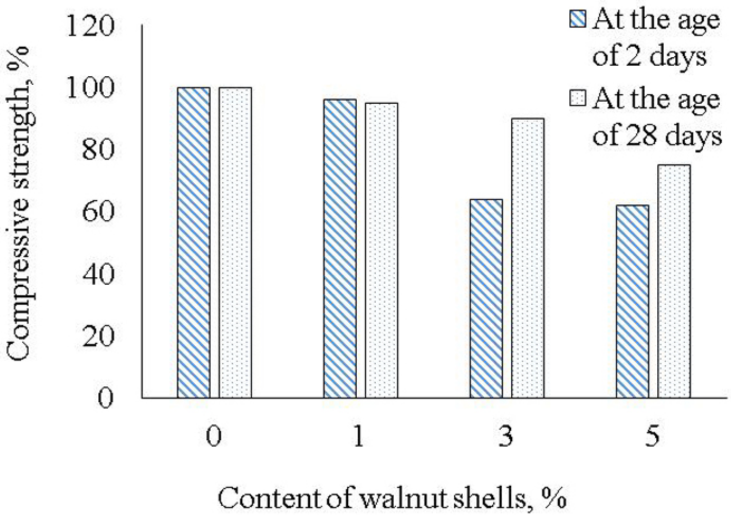

Fig. 4. Effect of walnut shells content on compressive strength of the cement

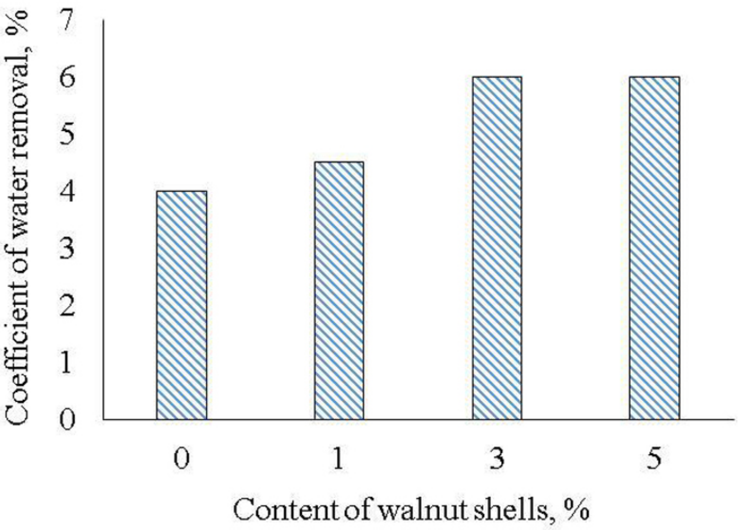

Fig. 5. Effect of walnut shells content on coefficient of water removal

The influence of the lignocellulosic and cellulosic biosorbents on the properties of cement was studied as well. The addition of 1% modified shells to cement also leads to an increase in the normal density of the samples, as shown in Figure 6. Cellulosic material has a greater impact on cement properties due to the fibrous structure and due to the presence of oxygen-containing groups on its surface, which can form additional hydrogen bonds with water molecules.

Both biosorbents accelerate the time of hardening (Fig. 7), and these values are affected by the nature of the material. The higher lignin content, the faster the hardening due to the presence of methoxy groups on its surface, which exhibit hydrophobicity. A cellulose sample has the longest period of hardening due to the ability to swell.

The results of the investigation on the compressive strength of cement with the plant materials in its composition are given in Figure 8. Cellulose in the composition of the modified shell slows hardening down, which is reflected in the strength of the cement samples at the age of 2 and 28 days. The addition of lignin-enriched biosorbent to the cement composition does not lead to a significant deterioration of the mechanical properties of the test sample. Modified plant materials in the composition of the cement have different effects on the water removal coefficient (Fig. 9). Cellulosic biosorbent reduces the dehydration ability of cement.

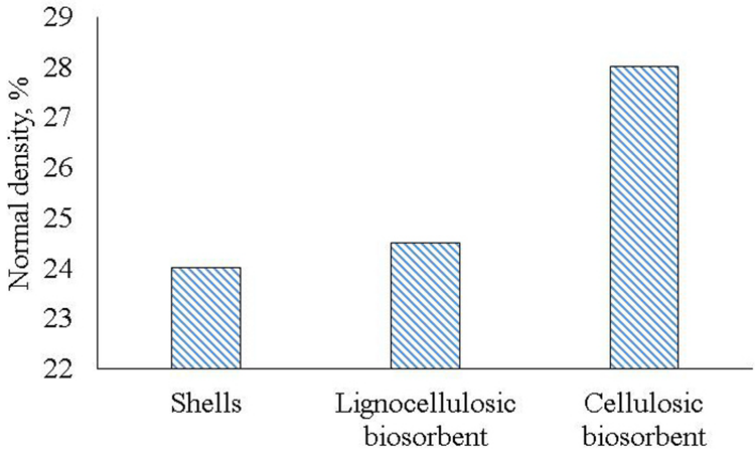

Fig. 6. Effect of lignocellulosic and cellulosic biosorbents on cement normal density

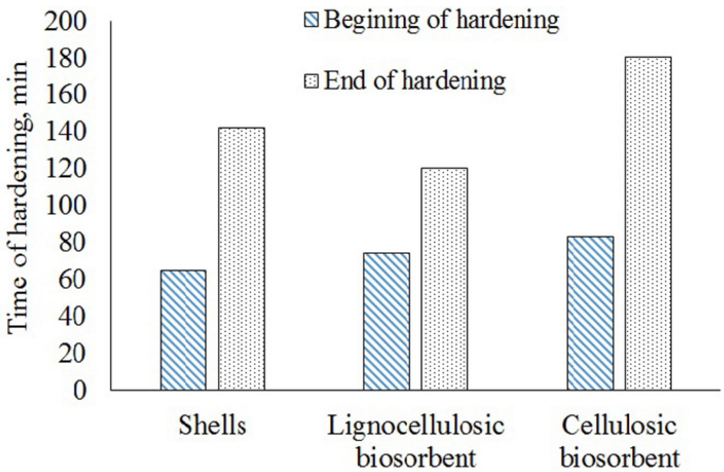

Fig. 7. Effect of lignocellulosic and cellulosic biosorbents on cement hardening time

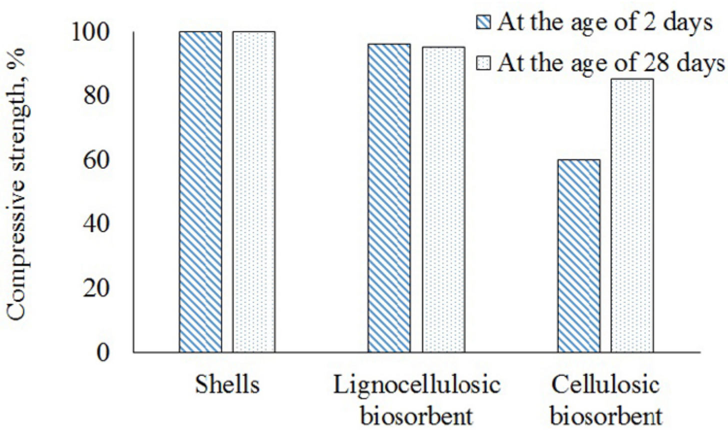

Fig. 8. Effect of lignocellulosic and cellulosic biosorbents on cement compressive strength

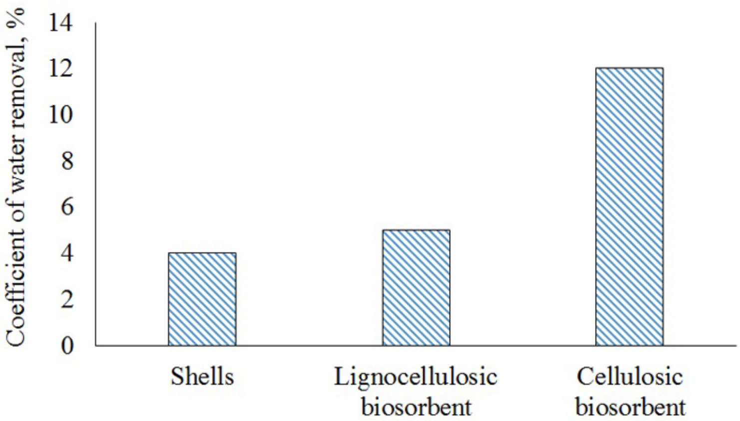

Fig. 9. Effect of lignocellulosic and cellulosic biosorbents on coefficient of water removal from the cement

Thus, a lignocellulosic biosorbent, similarly to the unmodified walnut shells, cannot be recommended for use as a cement additive in an amount greater than 1%. However, it is worth noting that a cellulosic biosorbent has a negative effect on all cement properties.

CONCLUSIONS

1. The possibility of utilizing biosorbents in the composition of building materials was studied. The obtained results show limited applicability of initial and modified walnut shells in the composition of cement.
2. Unmodified walnut shell acts as a fine additive, which increase the normal density and accelerates the hardening. The compression strength of the specimens is slightly reduced.
3. Studies showed that the lignocellulosic biosorbent enriched with lignin has a little effect on the physical and mechanical properties of the cement.
4. The utilization of cellulosic biosorbents by the application as additives in the production of cement cannot be recommended as the physical and mechanical properties are significantly reduced.

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