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Characterization of raw and treated sugar beet shreds for copper ions adsorption

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ABSTRACT

Lignocellulosic materials have a great potential to be converted into different high value products including biofuels, value-added chemicals, and cheap energy sources for microbial fermentation and enzyme production. Their multifunctionality and ability to reuse contribute to their great importance in terms of environmental protection and sustainable development. Such materials are sugar beet shreds (SBS) which are usually used as animal feed but since they are produced in large amount in sugar industry, they can also be used as an adsorbent or for bioethanol production. Bioethanol production from SBS includes pretreatment processes in order to remove pectic substances and lignin, followed by enzymatic hydrolysis of cellulose in order to obtain the solution of fermented sugars. A novelty in this work is the investigation if solid residues from the pretreatment process of SBS for bioethanol production can be used as adsorbents, the same as raw SBS. Textural characteristics and capacities for copper ions adsorption of raw SBS, depectinated SBS, and SBS residues after enzymatic hydrolysis were investigated. The Brunauer–Emmett–Teller (BET) surface areas of investigated materials are 0.8, 0.6, and 0.9 m^2/g, and copper adsorption capacities are 5.6, 4.0, and 4.7 mg/g, respectively. From the results of textural analysis performed by low-temperature nitrogen adsorption and mercury intrusion porosimetry methods, it can be concluded that studied samples are mainly macroporous materials without significant mutual differences. Although both treated SBS, which are generated as waste in bioethanol production process, have slightly lower efficiency of copper adsorption in comparison with raw SBS, they still can be successfully used as adsorbents.

Keywords: Adsorption; Sugar beet shreds; Copper

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1. Introduction

Recently lignocellulosic materials have gained increasing research interests because of their renewable nature. They are generated as industry or agricultural waste in large amounts but sadly they are often burned. These materials have a great potential to be converted into different high value products including biofuels, value-added chemicals, and cheap energy sources for microbial fermentation and enzyme production [1]. Additionally, solid residues left after some of these conversion processes can be further utilized for other purposes. Their multifunctionality and ability to reuse contribute to their great importance in

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terms of environmental protection and sustainable development.

Water contamination by toxic substances, such as heavy metals, became a significant environmental problem. Many industries discharge wastewaters that contain mercury, cadmium, copper, arsenic, chromium, zinc, etc. Some of these metal ions are toxic at even low concentrations, some are potent neurotoxic metals and all of them have major impact on the environment [2]. They are persistent, i.e. non-biodegradable, non-thermodegradable, and they readily accumulate to toxic levels. Therefore, it is very difficult to eliminate them from aqueous systems. Heavy metal removal methods from wastewater have progressed significantly and now can be applied for the protection of the environment and human health [3]. Due to the complexity of the problems associated with metal removal and recovery from wastewaters, numerous techniques are available for water purification, metal removal, and their recovery from wastewaters: chemical oxidation and reduction, ion exchange, filtration, electrochemical treatment, reverse osmosis, evaporative recovery and solvent extraction, chemical precipitation and adsorption [4,5]. To date, there is no efficient technology for the elimination of heavy metals from wastewaters that achieves a level low enough for their safe release into the environment [5]. One of the most commonly used methods is adsorption by different materials [6], but most of them are not economically suitable for wastewater treatment. Growing interest in searching for new low-cost adsorbents led to investigation of agricultural waste and industrial by-products of organic nature, which showed certain capacity for heavy metal sorption. Such materials are known as biosorbents [7]. Biosorption is an alternative technology for removal of different pollutants which has several advantages over conventional processes—it is effective, cheap, and applicable at low concentrations, metal can be recovered and adsorbent regenerated. For a large-scale use, suitable adsorbents should be abundant in nature as by-products or industry waste which does not require pre-processing [3]. Lignocellulosic waste materials fulfill most of the requirements and many have been reported as efficient adsorbents [8–10]. The main constituents of these materials are cellulose, lignin, and hemicellulose, but they also contain extractives, proteins, lipids, simple sugars, water-soluble hydrocarbons, and starch, with variety of functional groups which can bind metal ions [8].

Recently, sugar beet pulp, as abundant lignocellulosic waste from sugar industry, has been studied for heavy metal removal [11,12]. One-third of the world sugar production is based on sugar beet. After processing one tone of sugar beet, about 50 kg of by-product (on a dry weight basis) remains, i.e. sugar beet pulp or shreds [12]. They are used as animal feed but since they are produced in large amount they can also be used as an adsorbent or in bioethanol production [13,14]. Except of the cellulose and hemicelluloses, the third most important constituent of this material is pectin. It has been reported that sugar beet pulp and pectin strongly bind metal cations in aqueous solutions [11,12]. Bioethanol production from sugar beet shreds (SBS) includes pretreatment processes in order to remove pectic substances and lignin because commonly used fermentative microorganism is not capable to ferment these polymers. Raw material is usually treated by acid extraction to remove pectin substances, followed by alkali delignification. Next comes one of the most important steps of bioethanol production—degrading lignocellulosic biomass to fermentative sugars by hydrolysis. After releasing reducing sugars during enzymatic hydrolysis of cellulose in SBS, solid waste remains [15].

The objective of this study was to investigate whether the solid residues from the process of SBS treatment for the production of bioethanol could be used as adsorbents. Textural characteristics and the copper adsorption abilities of raw SBS and abovementioned residues were determined and compared.

2. Materials and methods

2.1. Materials

Dry SBS obtained from sugar refinery were used as adsorbent. Adsorbent was milled on a laboratory mill (Miag Braunschweig DOXY 71b/4) and sieved (BŰHLER MLU—300) in order to obtain particle diameter in ranges 224–400, 400–750, and 750–1,000 μm.

In adsorption experiments, an aqueous solution of initial copper ions concentration of about 50 mg/dm^3 was used. It was prepared by diluting 0.25 mol/dm^3 stock solution of $CuSO_4$ with demineralized water just before experiments. The pH adjustments were made using HNO_3 solution. All chemicals used were of analytical reagent grade.

2.2. Pretreatment of SBS and enzymatic hydrolysis

Raw SBS, with particle diameter in range 224–400 μm, were subjected to acidic pretreatment in order to remove pectic substances and then enzymatic hydrolysis was conducted according to Ivetić et al. [14]. The solid residues (depectinated and hydrolyzed SBS) obtained in these two processes were investigated in this paper.

Acidic pretreatment: Raw SBS were suspended in HCl solution at pH 1.5 and 85˚C for 4 h and then filtered through Macherey-Nagel MN 651/120 filter paper and washed with distilled water in order to remove the extra HCl. One part of the obtained filter cake was used as an adsorbent and other part as a substrate for enzymatic hydrolysis.

Enzymatic hydrolysis was conducted using commercial cellulase, Celluclast 1.5 L, (Novozyme) at enzyme concentration of 5 FPU/g expressed per gram of dry weight of substrate. Enzymatic reaction was conducted in 50 mM acetate buffer at pH 4.8 and 40˚C during 18 h. Then the reaction mixture was filtered through filter paper (Macherey-Nagel MN 651/120) and the filter cake was washed with distilled water until neutral pH of filtrate was reached. Obtained solid residue was used as an adsorbent.

After both processes, residues of SBS were dried at 40–50˚C to a constant weight.

2.3. Textural analysis

The analysis of surface area and pore size distribution (PSD) of the samples in mesoporous region was performed by low-temperature nitrogen adsorption at −196˚C (Micromeritics ASAP 2010 device). The surface area was determined by Brunauer–Emmet–Teller (BET) method. The PSD was calculated from the desorption isotherm using the Barret–Joyner–Halenda (BJH) equation. Mercury intrusion porosimetry (Hg Porosimeter Carlo Erba 2000 WS) was also used to analyze the PSD and the cumulative volume of pores in diameter range from 0.02 to 200 μm.

Scanning electron microscope (SEM) images of investigated adsorbents were obtained on a JEOL JSM 6460LV SEM.

2.4. Batch adsorption experiments

The batch adsorption experiments were performed on a shaker MLW THYS-2 using 300 cm^3 screw cap conical flasks at room temperature. 1 g of investigated adsorbent was added in 200 cm^3 of about 50 mg/dm^3 aqueous solution of Cu(II) at pH 4. Experimental pH value was chosen to be under the pH value that induces copper hydroxide precipitation [16]. Suspensions were shaken for 90 min and then adsorbent was separated from water solution by filtration through a filter paper (Macherey-Nagel 651/120). The initial (c_0) and equilibrium concentrations (c) of copper ions in aqueous solutions were determined by complexometric titration [17]. Experiments were duplicated and results were averaged.

The amount of heavy metal ions adsorbed per specified amount of adsorbent (q) was calculated as follows:

$$q = \frac{(c_0 - c)}{m} \tag{1}$$

where m is the mass of adsorbent per liter of solution.

Regarding pore size effect on adsorption capacity, Weber–Morris diffusion model [18] was applied in order to investigate the mechanism of biosorption process:

$$q = k \cdot t^{\frac{1}{2}} + C \tag{2}$$

where k ($mg/g\ min^{0.5}$) is the intraparticle diffusion rate constant and C is an arbitrary constant (mg/g).

Adsorption experiments were conducted under the same conditions but for different time intervals: 2, 5, 10, 20, 30, 60, 90, 120, and 180 min.

3. Results and discussion

3.1. Textural analysis of adsorbents

Common adsorbents have developed surface area, due to their high degree of microporosity and mesoporosity. The appropriate and most commonly used method for the measurement of the textural properties of microporous and mesoporous materials is low-temperature nitrogen adsorption. The results of the textural analysis of raw SBS, depectinated SBS, and SBS left after enzymatic hydrolysis (hydrolyzed SBS), with particle diameter in range 224–400 μm, measured by low-temperature nitrogen adsorption (surface area and BJH desorption cumulative pore volume) are given in Table 1. The surface areas of all the studied adsorbents are very low (lower than 1 m^2/g) and the value of the measured surface area has to be taken with caution since such values are within the range of the instrument measurement error. However, the comparison among the studied series is possible, since all the samples were analyzed under the same conditions.

The PSD of the investigated SBS and residues from bioethanol production measured by low-temperature nitrogen adsorption is presented in Fig. 1. Surface areas of all the studied samples are small compared to other adsorbents (e.g. activated carbon) and the differences among them can be neglected. The PSD shows one major fraction of broad range larger mesopores with average pore diameters from 30 to 70 nm and a smaller fraction of smaller mesopores with average pore diameters of about 11 nm. There is also an

Table 1
The results of the textural analysis of raw SBS and treated SBS (depectinated SBS and hydrolyzed SBS) performed by low-temperature nitrogen adsorption and mercury porosimetry

	Low-temperature nitrogen adsorption			Mercury porosimetry	
Sample	BET surface area (m^2/g)	PSD[a] and average diameter of pores (nm)	BJH desorption cumulative pore volume (cm^3/g)	PSD and diameter range of pores (μm)	Cumulative pore volume (cm^3/g)
Raw SBS	0.8	Multimodal, 3–6, 11, 70	0.0025	Bimodal, 2–4 and 4–16	0.2881
Depectinated SBS	0.6	Multimodal, 3.5–6, 11, 35	0.0019	Monomodal, 1–2	0.0617
Hydrolyzed SBS	0.9	Multimodal, 4–6.5, 11, 30	0.0066	Monomodal, 2–4	0.1307

[a] PSD—pore size distribution.

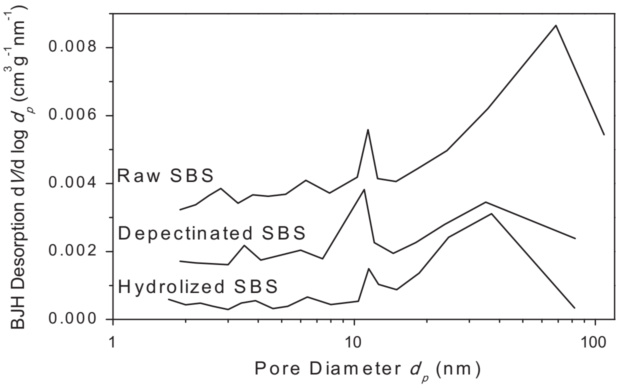

Fig. 1. Pore size distribution of raw SBS and treated SBS (depectinated SBS and hydrolyzed SBS) measured by low-temperature nitrogen adsorption.

indication of the formation of very small amount of small mesopores with an average pore diameters ranging from 3 to 6 nm in all studied samples. Since all of the studied adsorbents have small surface area, it can be concluded that they are not mesoporous and that the low-temperature nitrogen adsorption textural analysis is not the best method to study their porosity. In order to better characterize the materials mercury porosimetry analysis, a complementary textural analysis method appropriate for macroporous materials, was also performed. The textural analysis performed by low-temperature nitrogen adsorption confirmed that the samples are not mesoporous, which could not be established using only mercury porosimetry as textural analysis method.

The results of the mercury porosimetry analysis are given in Table 1 and in Fig. 2.

The much higher cumulative pore volume measured by mercury porosimetry than the cumulative pore volume measured by nitrogen adsorption indicates macroporous texture of the studied adsorbents.

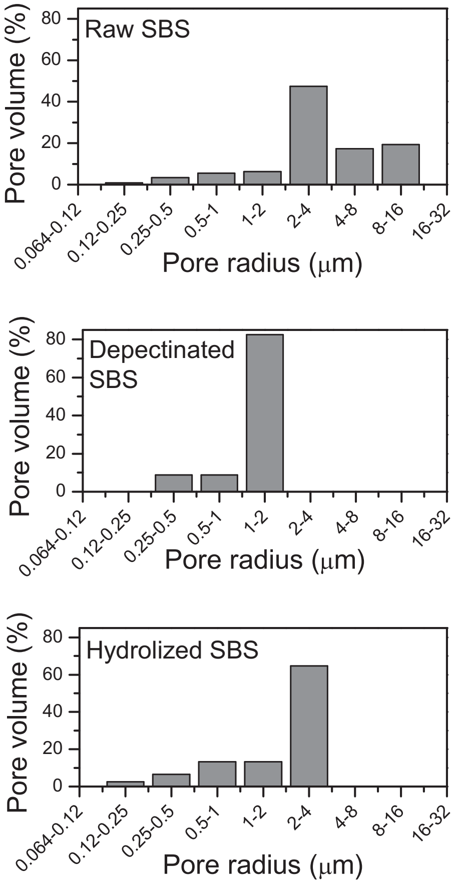

Fig. 2. Pore size distribution of raw SBS and treated SBS (depectinated SBS and hydrolyzed SBS) measured by Hg porosimetry.

The PSD varies among the studied samples. Raw SBS and SBS left after enzymatic hydrolysis (hydrolyzed SBS) have a dominant fraction of pores with diameters in range between 2 and 4 μm, whereas depectinated SBS has a dominant fraction of pores with somewhat smaller diameters in range between 1 and 2 μm. From the results of both textural analysis methods, it can be concluded that the studied adsorbents are mainly macroporous materials without significant mutual differences. These conclusions are confirmed by the SEM images of the investigated samples (Fig. 3).

3.2. Diffusion study

According to Eq. (2), a plot of q vs. $t^{1/2}$ should be a straight line from the origin if the intraparticle diffusion is the rate-controlling step of the process. If the plot does not pass through the origin then the pore diffusion is not the only rate-controlling step. The intercept, C, provides information about the thickness of the boundary layer [18].

Weber–Morris diffusion model was applied to three different particle sizes of raw SBS: 224–400, 400–750, and 750–1,000 μm. Adsorbents of larger particle sizes are taken into consideration since the diffusion resistance is more intensive and adsorption takes place mainly at the surface of particles. Results are shown in Figs. 4–6. The values of k, C, and R^2 obtained for the plots are given in the Table 2.

The data exhibit multi-linear plots, which mean that some other mechanism(s) along with the inraparticle diffusion is also involved [19,20]. None of the plots for all particle sizes does pass through the origin and, according to Weber and Morris [18], the intraparticle diffusion is not the only rate-limiting step. This may imply that boundary layer has some degree of control over adsorption rate. The value of the intercept indicates the thickness of the boundary layer. The larger the intercept the greater is the effect of boundary layer. The failure of the straight line to pass through the origin may be caused by the difference in the rate of mass transfer in the initial and final stages of adsorption process [21,22].

It has been proposed that these regions represent pore diffusion in pores of progressively smaller sizes [23]. Based on this and previous discussions, it can be assumed that diffusion into pores happens only in the smallest adsorbent particles. Only two regions on plots, fast saturation and the assumption that internally pores of larger particles are hardly accessible, it can be concluded that adsorption takes place only at the surface of the adsorbent and macropores.

Another cause of the limitation of pore diffusion rate may be the size of the adsorbate. Ionic radius of copper ions is 69 pm [24] which is small enough for diffusion into pores of raw and modified SBS but in aqueous solution they are hydrated. Because of their high enthalpy of hydration, Cu(II) ions are the most stable valence state of copper in aqueous solutions and exist as tetracopper cationic complex, $[Cu(H_2O)_4]^{2+}$, at pH ≤ 6 [25,26]. Therefore, Cu(II) ions in this form can also be found at pH 4, i.e. experimental conditions applied in this investigation.

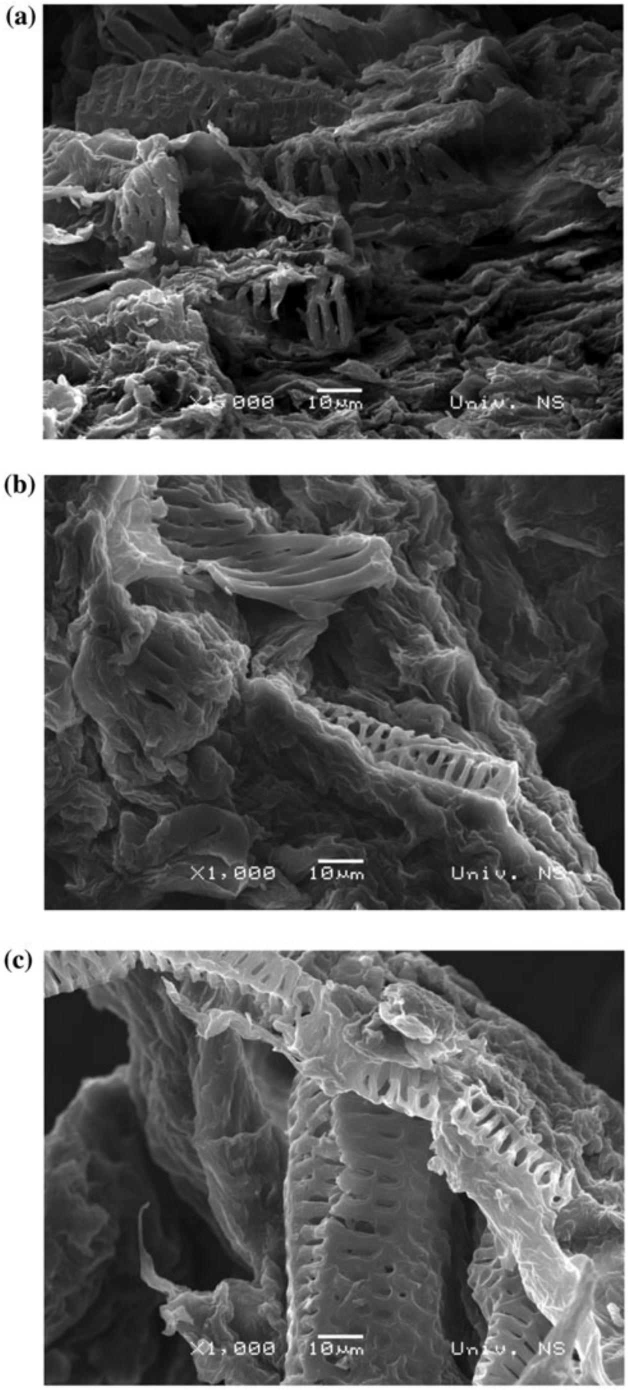

Fig. 3. SEM images of raw SBS (a), depectinated SBS (b), and SBS left after enzymatic hydrolysis (c).

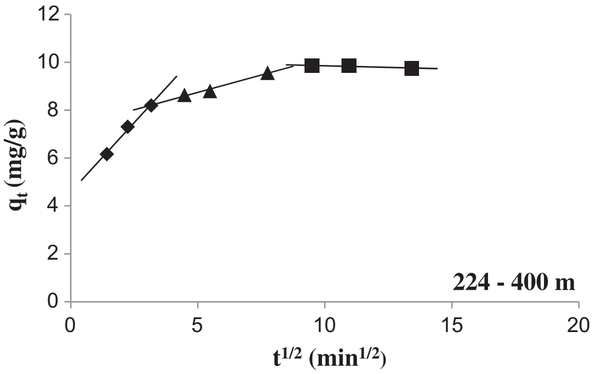

Fig. 4. Weber–Morris diffusion model for 224–400 µm raw SBS.

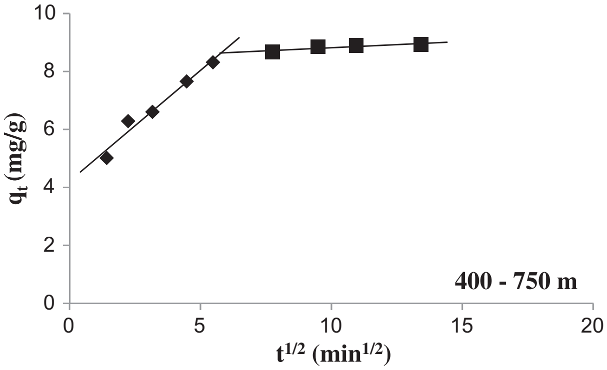

Fig. 5. Weber–Morris diffusion model for 400–750 µm raw SBS.

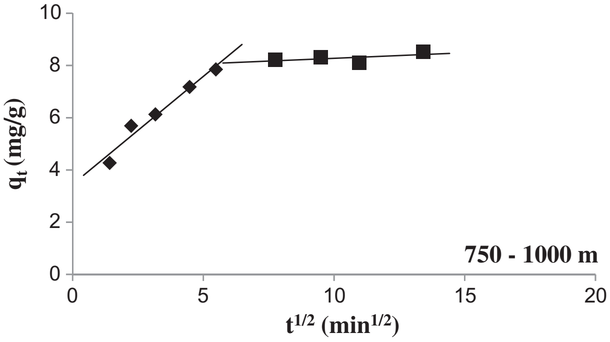

Fig. 6. Weber–Morris diffusion model for 750–1,000 µm raw SBS.

Lakshmi et al. [27] applied the same intraparticle model to the kinetics of Indigo Carmine dye onto rice husk ash as adsorbent. The adsorbent was characterized as mainly mesoporous material. For the initial concentration of 50 mg/l of adsorbate, they obtained one linear region on the plot of q vs. $t^{1/2}$ which they attributed to the mesopore diffusion as rate-limiting step.

3.3. Adsorption investigation

Adsorption experiments were conducted in order to investigate efficiency of heavy metal ions removal by raw and treated SBS, with particle diameter in range 224–400 µm. It has been reported that sugar beet pulp has certain capacity for heavy metal ions removal [11,12]. By acidic pretreatment and enzymatic hydrolysis, the structure of SBS is changed a little so the aim was to investigate how these treatments affected their adsorption capacities. In literature, very few information about adsorption by depactinated SBS can be found. Özer et al. [28] reported removal percentage of Cr(III) by depectinated sugar beet pulp of 86 for initial concentration of 10 mg/dm^3 at 20˚C and high dose of adsorbent (20 g/dm^3). Published data about adsorption characteristics of SBS left after enzymatic hydrolysis could not be found.

The results of adsorption experiments covered by this paper are shown at Fig. 4.

Raw SBS showed the high efficiency (about 77%). Similar results were published by Pehlivan et al. [29], whose investigation on copper adsorption by native SBS washed in acid showed efficiency of about 65%. Depectinated SBS have significantly lower removal efficiency probably due to the slightly lower surface area as well as obviously less number of active sites. Pectin substances account for more than 40% of the dry matter of SBS and they are complex heteropolysaccharides that contain galacturonic acid. Carboxyl functions of this acid are known to strongly bind cations in aqueous solutions [30]. Additionally, sugar-beet pectin gels have been reported as suitable for metal remediation technologies [31]. Also, during the acid treatment, the extraction of protein, phenol, and some fat is possible [15]. This might be an explanation for lower adsorption capacity of depectinated SBS. During enzymatic hydrolysis of cellulose in depectinated SBS, sugars are released and the structure of cell wall is destroyed which is followed by a slight increase in porosity. These changes can cause formation of additional surface for adsorption and occurrence of new active sites. All this can result in higher efficiency of copper removal compared to depectinated SBS (Fig. 7).

Pretreatment of SBS for bioethanol production affects adsorption capacity. It decreases due to changes in structure of material, but the size of particles also has certain effect. Smaller particles have relatively large exposed surface area and there is pore diffusion which results in higher adsorption capacity.

Table 2
Weber–Morris model parameters and correlation coefficients for different particle sizes of raw SBS

Particle sizes (μm)	k_1	C_1	R_1^2	k_2	C_2	R_2^2	k_3	C_3	R_3^2
224–400	1.159	4.590	0.989	0.290	7.290	0.980	−0.026	10.113	0.863
400–750	0.763	4.222	0.967	0.043	8.396	0.768	–	–	–
750–1,000	0.826	3.455	0.961	0.042	7.859	0.321	–	–	–

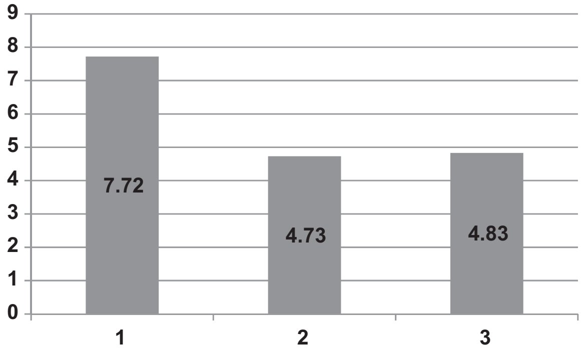

Fig. 7. Adsorption capacity (q) of copper ions by raw SBS (1), depectinated SBS (2), and SBS left after enzymatic hydrolysis (3).

Although both treated SBS, which are generated as waste in bioethanol production process, have lower efficiency of copper adsorption in comparison with raw SBS, they still can be successfully used as adsorbents. Compared to conventional adsorbents or other similar biosorbents [9,10], their capacities are not negligible especially since they are generated as waste after multiple uses and still can be applied for heavy metal removal.

4. Conclusion

Textural characteristics and adsorption experiments were conducted in order to compare efficiency of heavy metal ions removal by raw SBS, depectinated, and SBS left after enzymatic hydrolysis in the process of bioethanol production. By acidic pretreatment and enzymatic hydrolysis in bioethanol production, the structure of material is changed and it is expected that these materials have different adsorption characteristics. The results showed that raw material has the highest efficiency while depectinated shreds had significantly lower efficiency. Acidic pretreatment of SBS has negative effect on adsorption capacity probably due to removal of pectin substances which are known to bind heavy metal ions. Releasing reducing sugars during the enzymatic hydrolysis changes the structure of the cell wall. That can cause the formation of additional surface for adsorption and occurrence of new active sites and result in higher efficiency of copper removal compared to depectinated SBS. The surface areas of all samples are very low but similar. They also have similar PSD with one major fraction of broad range larger mesopores and a smaller fraction of smaller mesopores. From the results of both textural analysis methods conducted, it can be concluded that studied samples are mainly macroporous materials. All results indicate that raw SBS can be used as efficient adsorbent, what has already been reported. Investigated sugar beet shred residues from bioethanol production showed slightly lower adsorption efficiency of copper ions than raw shreds, but they still can be used as adsorbents. Their great advantage is that they are generated as a waste after multiple uses.

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