JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Article

pubs.acs.org/JAFC

Enrichment of Soybean Meal with Microelements during the Process of Biosorption in a Fixed-Bed Column

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Supporting Information

ABSTRACT: The aim of the present investigation was to enrich the mineral content of soybean meal with essential chromium and copper metal ions by a biosorption technique in a fixed-bed column. The values of column parameters were determined at various process conditions: pH, temperature, flow rate, and concentration of the feed solution; mass and size of the particles of the bed to determine the breakthrough curves. Biosorption efficiency at optimal conditions (pH 5.0, temperature = 20 °C, Cr^{3+} concentration = 200 mg/L, flow rate = 10 mL/min, and sorbent mass = 40 g) was 71.4%. Maximum uptake for Cr(III) and Cu(II) obtained in column was around 15.3 and 12.3 mg/g, respectively. The model constants obtained in this study can be used for design pilot plant systems. Soybean enriched with microelements by biosorption can be considered as biological carrier of microelements and therefore used as the component of livestock feed.

KEYWORDS: *biosorption, enrichment, feed additives, soybean meal, fixed-bed column, microelements*

INTRODUCTION

Generally, natural fodder is an insufficient source of microelements and cannot fulfill the nutritional needs of animals. The microelemental status of an organism has an impact on the growth of livestock and high productivity. The microelement content in the fodder is regulated by relevant diet norms. Due to the low content of chromium and copper in some fodders compared with the requirements and standards, supplementation of copper and chromium is necessary in livestock diets. For instance, copper and chromium requirements of pigs are 120−165 and 10 mg/kg, respectively,[1] whereas the recommendation for laying hens are 5−6 and 10 mg/kg, respectively.[2] However, values for goats and sheep remain within a rather small range of 10−20 mg copper/kg. Cu(II) and Cr(III) deficit and excess in livestock diet can have serious consequences for the animal health and growth.

The copper content of the feed depends on the amounts in the soil (so-called native copper) ,and it is particularly low in acidic soils.[3] According to Kujawiak,[4] fodders rich in micronutrients are brewer's yeast, extraction meal, and malt sprouts. The average copper and chromium ion contents are in forages and fish meal. However, the worst sources of copper are cereals and sugar beets. Natural feed provides only 20% of the daily nutritional elements laying hens require.[5]

Because natural fodder does not satisfy the requirements, fodder nutritional supplements are applied in rearing practice.[6] Nowadays, mostly inorganic salts and oxides are used as dietary supplements for animals. However, their drawback is that they are not easily absorbed by the animal body, which in turn results in their high levels in droppings and can adversely affect the environment and can cause environmental pollution. Due to their high price, chelates (metal ligand complexes) are used less frequently. Among the products currently available on the market, chelates are characterized by the highest bioavailability. Their ligands are amino acids or polysaccharides. The advantages of these compounds are stability and good solubility in water. However, the preparations based on mineral salts and chelates are highly concentrated, which makes it difficult to evenly mix them with the fodder, and this in turn is responsible for uneven distribution, that is, presence or lack, of the microelement.

Recently, a biosorption method for removal of metal ions using biomaterials has been widely investigated.[7,8] In other studies, this technique has been used as an alternative and ground-breaking method of enriching fodder with microelements.[9,10] The biosorption mechanism is complex and involves also the chelating and complexing of metals, and therefore biomass enriched by this method can be a great source of microelements in the form that is easily absorbed by laying hens.[11]

The use of biosorption as a process for producing fodder supplements requires a biological material with satisfactory sorption capacity and nutritional value. In the search of biomaterials for feed supplement, we found that soybean meal has the largest share in the production of fodder from oilseed plants. High-protein soybean meal, due to a low content of raw fiber, independent of animal species that are fed, has the highest level of metabolic and digestive energy and the highest nutrition value among all kinds of vegetable protein fodder. Soybean meal is a widespread protein supplement in countries where livestock farming is highly developed. Additionally, this fodder material is tasty and applicable to all animal species. It is predominantly used as fowl fodder but also as pig fodder and fodder for young ruminants.

Received: January 14, 2013
Revised: June 11, 2013
Accepted: July 1, 2013
Published: July 1, 2013

Soybean meal is produced mainly in Argentina and is used either as part of a phosphorus-based fertilizer or as an addition to biodiesel.[12] At present, the use of soybean meal as a biosorbent for retrieval of metal cations is undergoing laboratory testing.[13] However, from the practical viewpoint a large-scale biosorption process ought to be carried out in a dynamic system, for example, in bed columns. Fixed-bed column results give more useful information about the biosorption performance. Many studies showed that both batch and column studies exhibit different biosorption behaviors; thus, equilibrium conditions may vary in both systems.[14−16] Various ways of carrying out the process of biosorption were proposed and tested, including processes performed in vessel reactors with a mixer, in the bottom and top feeding columns, in fluid bed or trickle bed reactors, and in reactors with a hydraulic lift.[17] Among the continuous systems, the top-feeding bed reactor should theoretically be the most economical due to the use of the force of gravitation for the concentration of the solution flowing through the bed, but it is difficult to control the retention time in this type of device. This explains why the most popular is a bottom-feeding column, where it is easy to determine the length of time that the solution remains in the reactor; it can be characterized by a high operational efficiency and is easily applied in industry.[17]

Despite many advantages of the continuous operating process, a batch loading process, due to its simplicity and low cost compared to fixed-bed operation, seems to be more suitable for relatively small amounts of soybean meal requiring treatment and, therefore, can be performed on site.

This study presents a method of enrichment of soybean meal with micronutrients, which may be used as a supplement of the diet fed for livestock (mainly to hen) in their stage of growth. The novelty of this study is to use the biosorption process in fixed-bed column to enrich a soybean meal with Cu(II) and Cr(III), to obtain good quality fodder that has high productivity and nutritive value. Application of fixed-bed columns instead of batch biosorption improves the efficiency of the process and allows the system to scale-up. The influences of process conditions such as the pH, the concentration of the feed solution, the amount of the biosorbent, the size of the grains, the flow rate of the feed solution, and the effect of the temperature on the performance of the copper and chromium cations biosorption were investigated.

■ MATERIALS AND METHODS

Characteristics of the Biosorbent. The study on the biosorption of metal cations was conducted on soybean meal obtained from Vetos, Zebowice, Poland. The meal is commonly used as fodder material for livestock, mainly for hens. Soybean meal was sieved. For further experiments fractions with grain sizes 2−3, 3−4, and >4 mm were chosen.

The surface structure of biomass and elemental analysis were examined by scanning electron microscopy (SEM) coupled with energy dispersive X-ray analysis (SEM/Hitachi S-3400N/2007).

To measure the value of pH_{zpc}, 0.1 M KNO_3 aqueous solutions with a volume of 50 mL and pH ranging between 2 and 12 were prepared. Afterward, 0.5 g of soybean meal was added to each solution. The pH was determined by the application of 1 M solution of NaOH and HNO_3. The solutions were then agitated, and the pH was marked after 1, 2 and 24 h.

Column Biosorption Experiments. The experiments were carried out simultaneously in two glass columns with a fixed-bed biosorbent. The input solution was provided from an input tank through a peristaltic pump at the bottom of the adsorption column. The output solution was collected in output tanks as it left the column. Samples of the solutions were taken directly from the column at 15 min intervals from the beginning of the process, that is, from the moment when the biosorbent was wholly submerged in the column. When the samples were taken, the pH was measured at the input and output of the columns. During the research on the influence of temperature on the process of biosorption, an additional thermostat was used to heat the input solution.

Copper(II) sulfate and chromium(III) nitrate were weighed to a specific amount and then dissolved in distilled water in a volumetric flask or a control tank. To determine the proper pH of the feed solution, a 1 M aqueous solution of NaOH or HCl was prepared. After the experiment had been carried out (about 180 min), the pump was turned off and the process was stopped. The fixed bed was taken out of the column, rinsed three times with distilled water, put on a Petri dish, and placed in a dryer for 24 h at a temperature of 50 °C for the determination of the ion content in the biomass.

The concentration of chromium, copper, calcium, magnesium, and potassium ions was measured using inductively coupled plasma−optical emission spectrometry (ICP-OES; Varian Vista MPX, Australia, ata laboratory certified by the Polish Centre for Accreditation and ICAC-MRA according to method PN-EN ISO 17025).

This study has examined the effect of different process conditions (concentrations of Cu(II) and Cr(III) ions, 50−300 mg/L; pH 3−6' temperature, 20−40 °C; flow rate of the solution, 10−23 mL/min; bed mass, 10−40 g; size of the biomass particles, 2−4 mm) on the performance of biosorption in the fixed-bed column. The desorption of Cr^{3+} ions from the soybean meal in the column was carried out with 0.1 M HCl at the flow rate of 10 mL/min.

Mathematical Description of the Process of Biosorption. The driving force of the biosorption process is the difference between the current concentration of the solution around the grain of the sorbent and the equilibrium concentration that corresponds to the amount of the currently adsorbed substance on the grain.

The actual sorption capacity (q_0) of the biosorbent may be calculated from the experimental points of the curve as presented by eq 1

$$q_0 = \frac{C_0 \times Q}{1000 \times m_s} \int_0^t \left(1 - \frac{C_{out}}{C_0}\right) dt \quad (1)$$

where Q is volumetric flow rate, m_s is sorbent mass, t is time, and C_{out} and C_0 are solution concentration in the effluent and influent, respectively.

There are many models that are used to describe fixed-bed columns (Table 1). They allow the experimental data to be approximated by means of a relevant breakthrough curve.

Table 1. Models for Fixed-Bed Column Description

model	equation	ref
Bohart and Adams	$\frac{C}{C_0} = \frac{e^{k_{AB} \times C_0 \times t}}{e^{(k_{AB} \times N_0 \times Z/v)} - 1 + e^{k_{AB} \times C_0 \times t}}$	40
bed-depth service-time (BDST)	$t = \left(\frac{q_{max} \times Z}{C_0 \times v}\right) - \frac{1}{C_0 \times k_{BDST}} \times \ln\left(\frac{C_0}{C} - 1\right)$	41
Thomas	$\frac{C}{C_0} = \frac{1}{1 + \exp\left(\left(\frac{k_{Th}}{Q}\right) \times (q_{max} \times m_s - C_0 \times V_{ef})\right)}$	42
Yoon and Nelson	$\frac{C}{C_0} = \frac{e^{k_{YN} \times (t - \tau)}}{1 + e^{k_{YN} \times (t - \tau)}}$	30
Yan	$\frac{C}{C_0} = 1 - \frac{1}{1 + \left(\frac{C_0 \times V_{ef}}{q_{max} \times m_s}\right)^{a_Y}}$	43
Clark	$\frac{C}{C_0} = \left(\frac{1}{1 + A_C \times e^{-r \times t}}\right)^{1/(n_F - 1)}$	44

dx.doi.org/10.1021/jf400127z | J. Agric. Food Chem. 2013, 61, 8436−8443

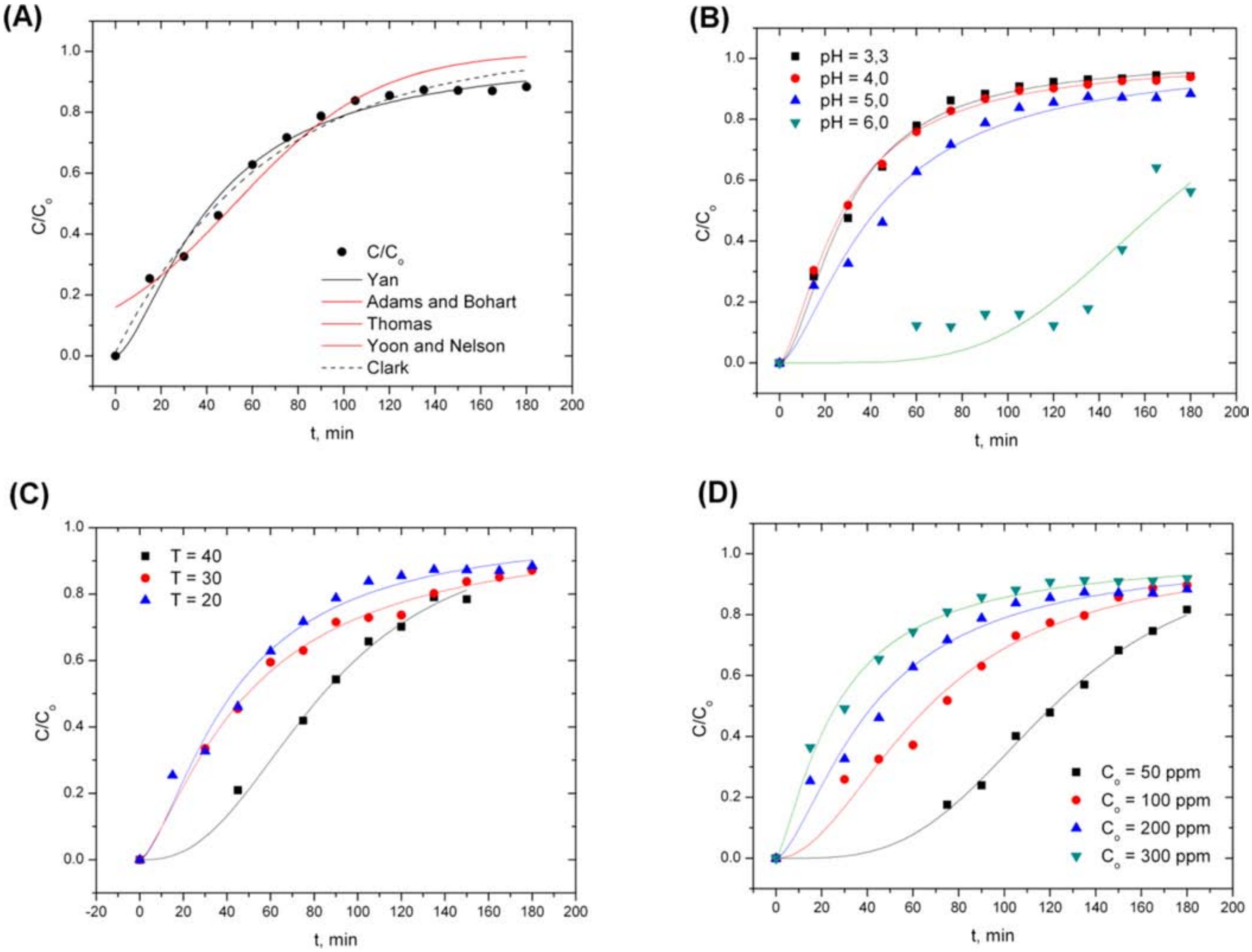

Figure 1. Breakthrough curves: (A) fitting of mathematical models (C_0 = 200 mg/L, pH 5.0, T = 20 °C, m_s = 10 g, Q = 10 mL/min); (B) different pH values (C_0 = 200 mg/L, T = 20 °C, m_s = 10 g, Q = 10 mL/min); (C) different temperatures (C_0 = 200 mg/L, pH 5.0, m_s = 10 g, Q = 10 mL/min); (D) different concentrations (pH 5.0, T = 20 °C, m_s = 10 g, Q = 10 mL/min) of feed solution.

All of the experiments were carried out in duplicate, and the average values were used in calculations. The maximum deviation was found to be +2%. All model parameters were evaluated by nonlinear regression using OriginPro8 software.

RESULTS AND DISCUSSION

Characteristics of the Biosorbent. The dry mass content of soybean meal ranged between 92 and 88% (humidity at 8–11%), with half of this mass being taken up by protein: 45–49%. The energetic value ranged between 18 and 23 MJ/kg.

Figure 1 of the Supporting Information presents the soybean meal grains before and after biosorption of Cr(III) and Cu(II). Enriched with microelement ions, grains have intense color, gray-green in the case of chromium ions and blue for copper ions. Figure 2 of the Supporting Information shows the structure of soybean meal grains that were observed under a scanning electron microscope (SEM). Grains that have been in contact with a solution of chromium ions are a little more rough. Cr(III) ion binding sites are visible on the biosorbent surface. More observation of soybean meal surface using SEM and EDX was presented in a previous paper.[13]

Each biosorbent is characterized by a different value of pH_{zpc} (pH at zero point of charge), at which the density of the electric charge on the surface of the biological material amounts to zero. At pH_{zpc} the net electric charge of the population of particles is zero; thus, the average number of functional groups that can bind positive charges is the same as the average number of negative charges. This means that the overall charge of the whole population is equal to zero.

This parameter allows for calculating the change of loading of the biosorbent surface with sorbed anions or cations. The measurements allow for making a graph $\Delta pH = f(pH_0)$ to calculate pH_{zpc}, as an intersection point of the curve with the x-axis (Figure 3 of the Supporting Information). It was measured that pH_{zpc} has a value of 6.1.

Adjustment of Mathematical Models. To approximate the experimental points as obtained during the laboratory research, five mathematical models were used: Yan, Bohart–-Adams, Thomas, Yoon and Nelson, and Clark. Figure 1A shows the fit of the discussed models.

As it turns out, the Yan model is the most accurate representation of the trace of the breakthrough curves as obtained experimentally. The experimental research confirmed that the Bohart–Adams, Thomas, and Yoon and Nelson models were equivalent mathematically: the breakthrough curves that describe the experimental points overlap.[18]

Table 2. Yan Model Parameters

metal ion	C_0 (mg/L)	pH	T (°C)	Q (mL/min)	m_s (g)	d_i (mm)	a_Y	b_Y (L)	q_{max} (mg/g)	R^2
Cr^{3+}	50	5.0	20	10	10	2−3	3.50	1.21	6.06	0.996
Cr^{3+}	100	5.0	20	10	10	2−3	1.98	0.67	6.69	0.979
Cr^{3+}	200	5.0	20	10	10	2−3	1.54	0.42	8.48	0.982
Cr^{3+}	300	5.0	20	10	10	2−3	1.41	0.28	8.31	0.996
Cr^{3+}	200	3.3	20	10	10	2−3	1.68	0.29	5.83	0.995
Cr^{3+}	200	4.0	20	10	10	2−3	1.50	0.28	5.53	0.998
Cr^{3+}	200	6.0	20	10	10	2−3	4.31	1.65	33.0	0.800
Cr^{3+}	200	5.0	30	10	10	2−3	1.39	0.49	9.88	0.995
Cr^{3+}	200	5.0	40	10	10	2−3	2.37	0.83	8.25	0.995
Cr^{3+}	200	5.0	20	23	10	2−3	1.09	0.25	4.90	0.970
Cr^{3+}	200	5.0	20	10	15	2−3	2.10	0.55	7.35	0.979
Cr^{3+}	200	5.0	20	10	20	2−3	2.07	0.66	6.57	0.978
Cr^{3+}	200	5.0	20	10	40	2−3	2.14	1.38	6.69	0.969
Cr^{3+}	200	5.0	20	10	10	3−4	1.07	0.38	7.52	0.928
Cr^{3+}	200	5.0	20	10	10	>4	1.18	0.26	5.14	0.980
Cu^{2+}	200	5.0	20	10	10	2−3	0.88	0.25	5.00	0.998

Moreover, Table1 shows the constants from the Yan model for the discussed experiments.

The higher the concentration of the feed solution, the greater the values of the constants of the Yan model. An opposite tendency was observed for the increase in the flow rate of the feed solution. The amount of the biosorbent bed does not significantly affect parameter a_Y; however, it causes a proportional increase in the value of the constant b_Y. In the remaining cases no significant tendency was observed. It is worth noting that a high coefficient of adjustment R^2 was found for all breakthrough curves under discussion. Only in the case of the biosorption of chromium(III) from the feed solution with pH 6.0 is $R^2 = 0.800$.

Influence of pH. The value of pH of the feed solution is an important parameter that influences the effectiveness of biosorption. The choice of a proper pH depends on the type of biosorbent and the sorbed metal. It is important to remember that the value of pH ought not to be too high because in an environment that is too acidic or alkaline, the structure of the biosorbent is being destroyed, which leads to the slowing of the process of biosorption.

In aqueous solutions metallic ions may form complexes with OH^- ions, which also adversely affects the rate of biosorption on the biological material.[19] The Cr(III) ion forms are mainly Cr^{3+} ions, which as a result of hydrolysis change into $Cr(OH)^{2+}$ and $Cr(OH)_2^+$ ions and then into amphoteric chromium hydroxide $Cr(OH)_3$. At higher pH also $Cr(OH)_4^-$ ions occur.[20,21]

A study was carried out to determine the influence of pH on the biosorption of chromium(III) ions in the fixed-bed column within the range of pH from 3.0 to 6.0 at a concentration of the feed solution of 200 mg/L, a temperature of 20 °C, a flow rate of 10 mL/min, and an amount of biosorbent of 10 g with a grain diameter of 2−3 mm. The results of the experiments are shown in Figure 1B. The breakthrough curves were calculated using the Yan model.

The equilibrium of the Cr(III)−H_2O system and the pH_{zpc} of the analyzed biomass are essential for determining the optimum value of pH. An increase in pH causes an increase in adsorption and equilibrium sorption capacity. This may be related to the degree of the ionization of the active groups of the analyzed biological material, which is connected with the determined value of pH_{zpc} 6.1. At low values of pH of the solution, sorbed metal cations compete with protons present in the solution, which slows the process of biosorption. An increase in solution pH results in an increase of biosorption performance, due to the predominance of hydroxyl ions over protons. As the pH increases, more functional groups such as carboxyl, phosphate, imidazole, and amino groups would be exposed and carried negative charges with subsequent attraction of metallic ions with positive charge and biosorption onto the cell surface.[22]

On the basis of the FT-IR analysis (data not shown) it was determined that it is the carboxyl groups that mainly take part in the process. Analysis of amino acid composition in soybean showed that it contains mostly acidic amino acids such as glutamic acid and aspartic acid, which in the alkaline pH (>3−4) are deprotonated and become negatively charged and therefore attract the positively charged metal cations, enhancing the biosorption process.[23−25] A significant increase in sorption capacity (q, defined as the ratio of the mass of sorbate to the unit mass of sorbent) and the degree of adsorption (S, the amount of ions adsorbed on biosorbent) at pH 6.0 is connected with the precipitation of the sediment on the surface of the fixed bed, and not with the increase in sorption of metal ions onto the biological material. This leads to the supposition that (according to the Cr(III)−H_2O diagram, Supplementary Figure 4 in the Supporting Information) when the pH is 5.0, then the precipitation of chromium(III) hydroxide occurs, which affects the process of biosorption. This means that the optimum value of pH at which the biosorption of chromium(III) ions on soybean meal ought to be carried is 5.0.

Influence of Temperature. A study was carried out to determine the influence of temperature on the biosorption of chromium(III) ions in the fixed-bed column within the range of 20−40 °C, at a concentration of the feed solution of 200 mg/L, pH 5.0, flow rate = 10 mL/min, and an amount of biosorbent 10 g with a grain diameter of 2−3 mm.

The higher the temperature, the greater the efficacy of the process, that is, the higher the degree of adsorption (Figure 1C). It can therefore be supposed that the process of biosorption proceeds according to the mechanism of chemical sorption (chelation and complexation), which is more effective at higher temperatures. Higher temperatures favor the effectiveness of the process of binding chromium(III) ions onto soybean meal. Consequently, the equilibrium sorption capacity of the investigated biomass increased. At a temperature

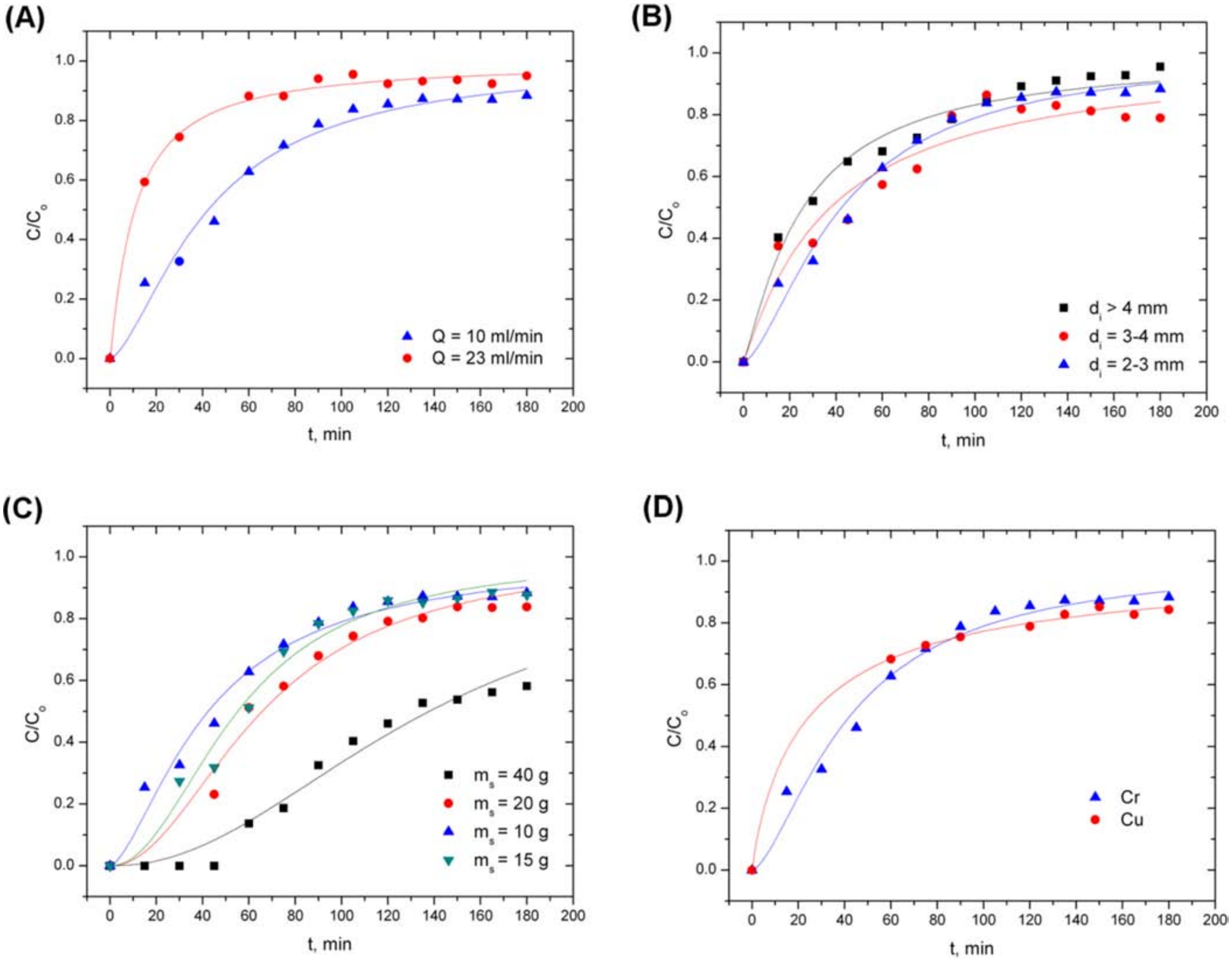

Figure 2. Breakthrough curves for different (A) flow rates of feed solution (C_0 = 200 mg/L, pH 5.0, T = 20 °C, m_s = 10 g); (B) sizes of grains (C_0 = 200 mg/L, pH 5.0, T = 22.5 °C, m_s = 10 g, Q = 10 mL/min), (C) masses of sorbent (C_0 = 200 mg/L, pH 5.0, T = 20 °C, Q = 10 mL/min), and (D) $Cr^{3+}$and Cu^{2+} ions (C_0 = 200 mg/L, pH 5.0, T = 20 °C, m_s = 10 g, Q = 10 mL/min).

of 40 °C (similarly as at pH 6.0), precipitation of sediment over the fixed bed of the biosorbent occurs, and it slows the process of the biosorption of Cr^{3+} ions onto the biological material.

Table 2 presents Yan model parameters assigned in different temperatures. One of them is maximum sorption capacity, which actually determines the concentration of cations absorbed on the column. The maximum sorption capacity increases with temperature to 30 °C and then decreases at 40 °C. This phenomenon can be explained by the fact that higher temperatures may cause the destruction of biological material, reducing its sorption capacity.

Concentration of the Feed Solution. A study was carried out to determine the influence of the concentration of the feed solution on the biosorption of chromium(III) ions in the fixed-bed column within the range of 50−300 mg/L, at pH 5.0, a temperature of about 20 °C, a flow rate of 10 mL/min, and an amount of biosorbent of 10 g with a grain diameter of 2−3 mm (Figure 1D).

The highest sorption capacity was achieved at the highest concentration of the feed solution. It appears that the greater the concentration, the higher the sorption equilibrium capacity, but the lower the degree of adsorption. The higher the concentration of the sorbed ions, the steeper are the breakthrough curves. In contact with a more concentrated solution of a metal cation, the bed becomes saturated earlier, which has to do with the gradient of concentration (ΔC) that becomes the driving force of the process. The higher the value of ΔC, the greater the rate of the process. At lower concentrations, the process develops more efficiently, because a higher degree of adsorption is obtained, which was shown by the experiments presented in this paper. Similar studies on the biosorption of metal cations were carried out on charred olive stones[26] and peels of citrus fruits.[27]

Influence of Flow Rate of the Feed. The flow rate of the feed solution is an important parameter that affects the process of biosorption, because it has an influence on the duration of the contact of the biosorbent with the solution. The greater the flow of the feed solution, the larger the amount of wastewater produced. Hence, two factors (effectiveness and profitability) are to be taken into consideration.

Observation of breakthrough curves could give information about the rate-limiting step of biosorption. If the external mass transfer is the rate-limiting step, higher flow rates cause decrease of the film boundary layer thickness and increase the biosorption efficiency. If the rate-limiting step is the intraparticle diffusion, a faster flow rate decreases the effectiveness of the process.[28]

A study was carried out to determine the influence of the flow rate of the feed solution on the biosorption of chromium(III) ions in the fixed-bed column for 10 and 23 mL/min, at a concentration of feed solution of 200 mg/L, pH 5.0, temperature of about 20 °C, and amount of biosorbent of 10 g with a grain diameter of 2−3 mm (Figure 2A).

The smaller the flow rate of the solution feeding the adsorption column, the higher the degree of adsorption. This was confirmed also by Calero et al.[29] and by Pereira et al.,[26] who conducted the biosorption of chromium(III) ions on olive stones and on charred olive stones, respectively. The smaller the flow rate through the fixed bed of the biosorbent, the longer the duration of the contact of the solution that contains chromium(III) ions with the biomass. However, a lower value of the equilibrium sorption capacity is also observable. Experimental data show that the possible rate-limiting step could be internal diffusion.

Influence of the Size of the Sorbent. Another series of experiments were carried out to determine the influence of the biosorbent grain size (grain size ranged over 2−3, 3−4, and >4 mm) on the process of the biosorption of chromium(III) ions (Figure 2B). It turned out that the average grain size of soybean meal does not have a significant impact on the degree of adsorption of chromium(III) ions, but considerably affects the equilibrium sorption capacity. In the mixture of particular fractions, the repeatability of the results is difficult to predict. That is why the biological material ought to have a homogeneous, predetermined grain size. This enables selection of these fractions for which the biosorption process is most efficient. Perez et al.[30] researched the influence of grain size (between 0.6 and 1.5 mm) of the biosorbent (orange peel) on the process of biosorption of chromium(III) ions in a cyclic system. The analyses of the experiments showed no significant difference in the degree of metal adsorption on biomass.

Influence of the Mass of the Biosorbent. The influence of biosorbent (bed mass = 10−40 g) on the process of biosorption was investigated. The smaller the amount of the fixed-bed biological material in the adsorption column, the greater the degree of adsorption, but the smaller the equilibrium sorption capacity (Figure 2C). This interrelationship was proved also for other biosorbents such as olive stones,[29] orange peels,[30] *Ulva reticulata* algae,[31] or *Artocarpu sheterophyllus* fruit.[32]

The tighter the packed bed in the column, the higher the phase contact surface and, thus, higher sorption capacity. However, too tightly packed biosorbent may impede the metal-bearing flow through the column.

Type of Sorbed Metal Ions. The study was carried out to determine the influence of the type of the sorbed metal cation on their individual biosorption capacity of efficiency in the fixed-bed column at a concentration of heavy metals of 200 mg/L, pH 5.0, temperature of about 20 °C, flow rate of the feed solution of 10 mL/min, and an amount of biosorbent of 10 g with a grain diameter of 2−3 mm. For this purpose one-component solutions containing either chromium(III) or copper(II) ions were used. Figure 2D presents the results of the experiments.

It appears that the degrees of adsorption of both copper and chromium ions on the analyzed biological material are comparable. However, the reference literature claims many cases where different sorption capacities were achieved for different metal cations on the same biological material during the process carried out in a cyclic and dynamic manner. The process of the biosorption of lead(II), copper(II), cadmium(II), and nickel(II) on anaerobic granulated biomass may serve as an example.[33] The highest sorption capacity was achieved for lead, whereas the lowest (>3 times as low) for nickel. Similar experiments were carried out for cadmium(II) and copper(II) biosorption on hay of *Triticum sativum*.[34] A higher sorption capacity was achieved for cadmium. Taking this into account, it can be said that some biosorbents are characterized by selectiveness toward respective metal cations.

Table 3 presents the values of sorption capacities of various biological materials that were studied in the fixed-bed column arrangement. The results of the biosorption on soybean meal are very much satisfactory as compared to other materials.

Table 3. Biosorption of Metal Cations in Fixed-Bed Columns: Comparison of Selected Biosorbents

metal ion	biosorbent	q_e (mg/g)	ref
Cr (III)	olive stones	0.8	29
	olive stones (carbon)	7.1	26
	rice wine processing waste sludge	32.3	36
	orange (*Citrus sinensis*) waste	12.53	30
	olive stones	5.19	37
	soybean meal	15.3	This work
Cu(II)	apple residues	6.6	23
	rice wine processing waste sludge	7.9	36
	wheat straw *Triticum sativum*	12.4	34
	Aspergillus niger	13.4	38
	marine algae *Gelidium*	13	39
	soybean meal	12.3	this work

Ion Exchange. The analysis of the composition of the solution at the moment of leaving the column was done to discover the presence of cations of alkali and alkaline metal ions that might participate in ion exchange (Figure 3). The solution contained ions of K^+, Ca^{2+}, and Mg^{2+}, which were released from biosorbent from the beginning of the experiment. The maximum concentration of ions was achieved in the 20th minute and then there was a decrease in the concentration to a few mg/L, and this level was maintained to the end of the process.

The results prove that the process of ion exchange occurred rapidly and was intensive and connected with the highest degree of Cr(III) and Cu(II) ions binding. Ion exchange was the predominant but not the only mechanism of biosorption. Due to the high pH_{zpc} of soybean meal, this material caused a local increase of pH at the surface of the sorbent. It is connected with the precipitation of insoluble Cr(III) and Cu(II) compounds and the hydrolysis of the Cr^{3+} and Cu^{2+} ions existing in water. Precipitation is considered as the other prevalent mechanism of biosorption of these microelements on the surface of soybean meal.

Effect of the Presence of Other Cations. The continuous column studies were carried out to detect metal uptake by soybean meal with a bed mass of 10 g at a flow rate of 10 mL/min from a binary metal ion system, containing two metal cations at pH 5.0 (Cr(III) and Cu(II) in concentration 50 mg/L each). It was found that the biomass of soybean meal in a multimetal system bound not as much of the metal ions as the

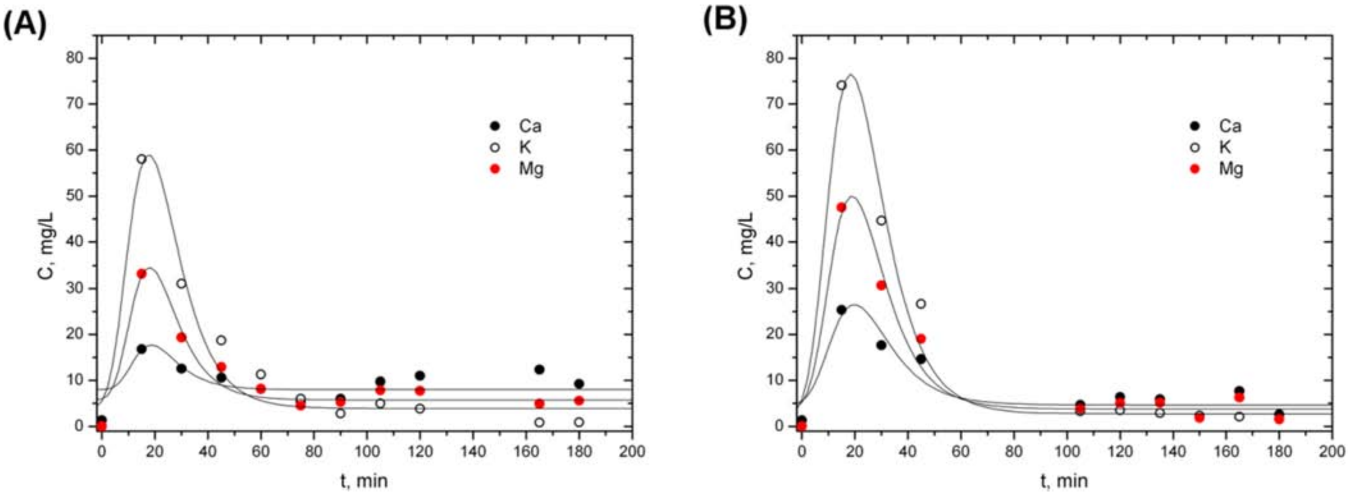

Figure 3. Concentration of cations (Ca, K, Mg) in the solution leaving packed-bed column: (A) Cr^{3+} biosorption; (B) Cu^{2+} biosorption.

single-metal system. The estimated uptake capacity for single Cr(III) solution was 6.06 mg/g. The presence of Cu(II) ions caused a decrease in Cr(III) uptake of around 42%; biosorption capacity was 3.49 mg/g. This could be elucidated by the competitive sorption taking place from the binary solution. Enrichment of soybean meal should be carried out for each metal separately, resulting in higher concentrations of micro-elements bound by the biomass. Using soybean meal from a single-metal system, it is possible to accurately regulate the composition of enriched in minerals feed according to the requirements for each animal species.[35]

Conclusions. This study has shown that soybean meal may be used as an inexpensive sorbent in the process of biosorption of the metal cations. Experimental data were well represented by the Yan model for variable conditions, such as different pH values and temperatures of feed solution, flow rates, metal ion feed concentrations, masses, and sizes of particles of the bed. The experiments carried out on soybean meal in column arrangement allowed for determining optimal conditions for the process of the biosorption of chromium(III) ions: pH 5.0, T = 20 °C, C_0 = 200 mg/L, Q = 10 mL/min, and m_s = 40 g, where the degree of adsorption equaled 71.4%. Maximum sorption capacities obtained in the column were around 15.3 and 12.3 for Cr(III) and Cu(III), respectively. The model constants obtained in this study can be used to design pilot plant systems. Pilot-scale experiments are currently performed in our laboratory to determine scale-up parameters.

■ ASSOCIATED CONTENT

Supporting Information

Additional figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Funding

The work was financed by a statutory activity subsidy from the Polish Ministry of Science and Higher Education for the Faculty of Chemistry of Wroclaw University of Technology; National Centre for Research and Development N R05 0014 10.

Notes

The authors declare no competing financial interest.

■ NOMENCLATURE

a_Y Yan model constant
A_C Clark model constant
b_Y Yan model constant, L
C_{out} solute concentration of the effluent of the column, mg/L
C_0 solute concentration in the influent to the column, mg/L
d_i particle diameter, mm
k_{AB} Bohart−Adams model rate constant, L/(mg·min)
k_{BDST} BDST model rate constant, L/(mg·min)
k_{YN} Yoon and Nelson model rate constant, 1/min
k_{Th} Thomas model rate constant, 1/min
m_s mass of sorbent, g
n_F Freundlich model constant
N_0 maximum sorption capacity, mg/L
q_0 initial sorption capacity, mg/g
q_e amount of adsorbate adsorbed at equilibrium, mg/g
q_{max} maximum sorption capacity, mg/g
Q volumetric flow rate, mL/min
r Clark model constant
S degree of adsorption
t time, min
T temperature, °C
τ time when $C = 0.5C_0$, min
v velocity, cm/min
V_{ef} volume of metal solution, L
Z biosorbent bed depth in the column, cm

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