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Metal ion sorption dynamics in a foamed chitosan structure

Paulina Rdzanek*, Joanna Marszałek

Faculty of Process and Environmental Engineering, Lodz University of Technology, Wolczanska 213, 90–924 Łódź, Poland, Tel. +48 42 631 36 76; email: rdzanek.paulina@wipos.p.lodz.pl (P. Rdzanek), Tel. +48 42 631 37 86; email: joanna.marszalek@p.lodz.pl (J. Marszałek)

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ABSTRACT

Industrial processes are responsible for heavy metal releases into the environment. Removal of excessive heavy metals has become a major concern, therefore, new economical and efficient methods of water treatment are now being explored. The experiments described in this paper relate to the removal of heavy metal cations from water. The adsorption process was carried out in a packed column containing foamed chitosan. Initially, a method of production of the foamed structure was developed. Subsequently, the foamed structure was properly prepared for testing. The adsorption process was continuous with constant ion concentration at the column inlet. Parameters such as sorption capacity of the chitosan bed, as well as influence of the initial ion concentration and feed flow rate were investigated. The Bohart–Adams model was used to describe the sorption dynamics.

Keywords: Sorption; Adsorption dynamics; Chitosan; Foamed chitosan structure

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1. Introduction

Exposure to heavy metals that are persistent in the environment causes serious health effects both in people and animals [1]. Development of industry is responsible for heavy metal releases into the environment. They can penetrate into the human body through the skin, they can be inhaled or ingested from animal and plant products. Migration of elements throughout the food chain and consequently into the human organism is restricted by biological barriers. However, when consumption of heavy metals increases the efficiency of biological barriers decreases, which brings negative impact on the environment and especially on human health. Therefore, removal of heavy metals from water has recently become a major concern. Many negative results of heavy metals are reported [2,3], hence new economical and efficient methods of water treatment are now being explored [4,5].

There are many techniques [6] of water purification such as sedimentation, filtration, ion exchange [7], and disinfection. Some of them require complex technical solutions or considerable investments [8] while others generate waste difficult to be managed. For this reason, researchers have been investigating new processes that would allow using cheap and available raw materials [9]. Adsorption methods seem highly attractive [10–12] as they effectively remove heavy metal ions from aqueous media. The advantage of these methods is that they use ecological sorbents and do not require advanced technological devices to be carried out.

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*Corresponding author.

Most adsorbents are classified with regard to their ability to remove contamination. Nowadays, more attention is focused on natural and biodegradable polymers. Biosorbents are attractive because of their abundance and availability in the market. Adsorbents containing natural polymers such as chitin and its deacetylated derivative named chitosan [13,14] are currently very popular among researchers [15].

Chitin (poly-β-1→4-N-acetyl-D-glucosamine) is a natural polysaccharide synthesized by living organisms. For commercial purposes chitin is isolated mainly from crab and shrimp shells. Chitin is insoluble and infusible due to its multiple hydrogen bonds. It is rather non-toxic and inert in the mammalian gastrointestinal tract, has antibacterial and gelling properties, and is biodegradable. In its natural form chitin is not very useful; however, its deacetylated derivative called chitosan can have many applications [16]. Chitosan and its derivatives have been reported to be suitable for purification of water and wastewater [17]. Chitosan has high adsorption capacity for metal ions because of its ability to form chelate compounds. Adsorption of metals can involve different mechanisms such as chelation or electrostatic attraction. The complexing properties toward metal ions are strictly related to the amine groups. The $-OH$ group is also involved in binding of metal ions but its effectiveness is lower than that of the $-NH_2$ group. Stability of the metal—chitosan complex is mainly influenced by the polymer properties such as deacetylation degree, length of polymer chain, its crystallinity, and physical form [18,19].

The main aim of this paper is to investigate a natural adsorbent, called chitosan, in removal of heavy metal ions from aqueous solutions. The adsorption process was performed in a continuous mode, i.e. a constant concentration solution was fed to the column without recycling. Then, the process was described by sorption dynamics equations.

2. Materials and methods

2.1. Materials

The foamed chitosan structure was obtained from the following reagents:

1. chitosan flakes—85% degree of deacetylation, molecular weight of 500, 800, 350, and 120 kD, purity grade A1 and A1.5, supplied by Heppe GmbH,
2. foaming agent—sodium bicarbonate, supplied by Chempur,
3. cross-linking agent—sodium tripolyphosphate (TPP) 90%, supplied by Fluka Guarante.

The studies were conducted using 99.5% acetic acid supplied by POCH SA. Heavy metal solutions were prepared using copper, nickel, zinc, cobalt, and cadmium sulfates supplied by Fluka Guarante.

2.2. Foam preparation

The experiments began with the selection of chitosan. Viscosity was the crucial parameter, because it influences properties of chitosan acetate. Five samples were prepared (3 wt% chitosan acetate solutions) with different deacetylation grades, molecular weights, and purity grades. To prepare the samples chitosan 85/350/A1 was selected as it had the highest viscosity.

Chitosan acetate solutions were initially prepared at chitosan concentrations of 3.0, 4.2, and 5.2 wt%, by taking appropriate amounts of chitosan and dissolving them in 2 wt% acetic acid. Then, the foamed chitosan structure was developed and its consistency was observed. At the highest concentration of chitosan it was difficult to mix foaming and cross-linking agents, while at the lowest concentration the foamed structure was nearly liquid. Finally, the studies were conducted using a 4.2 wt% solution which was stirred thoroughly and left to cool down (at 7°C) for 24 h.

Also, initial studies were conducted for different amounts of foaming and cross-linking agents. Use of cross-linking agents allows chitosan composites to work well under acidic conditions because chitosan can dissolve in acidic medium. After several trials, an optimal foamed structure was developed as follows: 15 g of sodium bicarbonate was added to 100 g of chitosan acetate and stirred vigorously, then 10 ml of 0.6 wt% TPP was added. The mixture was left for approx. 10 min to allow the structure to grow and stabilize.

2.3. Metal ions synthetic solutions

The heavy metal solutions were prepared by weighing metal sulfates. Their masses are given in Table 1. Then copper, nickel, zinc, cadmium, and

Table 1
Amounts of metal sulfates

Co (mg/dm^3)	Mass (g)				
	Cu	Ni	Zn	Co	Cd
5	0.4911	0.5981	0.5497	0.3577	0.2853
10	0.9823	1.1962	1.0993	1.1924	0.5706
20	1.9645	2.3925	2.1987	2.3849	1.1412

cobalt sulfates were mixed together and distilled water was added.

3. Column process

The foamed chitosan structure was placed in a column of 3.5 cm diameter and 60 cm height. Afterward, the bed height was measured. Experiments in the column were conducted at ambient temperature. Distilled water and the ion solution were pumped at the same volumetric flow rate. Within the first 24 h, distilled water was pumped to wash the bed and remove the cross-linking and foaming agents. During that time, height of the bed changed by approximately 30%.

Fig. 1 shows a schematic diagram of the experimental setup. Solutions of constant concentration of 5, 10, and 20 mg/dm^3 were fed from the tank (1) to the column (3) using the pump (2), without being recycled to the column. For 24 h, the heavy metal solution was passed through the column and samples (4) were taken at fixed time intervals. Then they were analyzed by ion chromatography (5) and the results were read from the screen (6). Sorption of copper, nickel, zinc, cobalt, and cadmium cations was observed. Before the experiments, blank samples were measured taken from the metal ion solutions.

Table 2 provides a list of all experiments. Analyses were performed for a heavy metal ions mixture (Cu^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, and Co^{2+} cations) to evaluate sorption capacity of the chitosan bed. The effects of initial ion concentration and feed flow rate on the adsorption process were analyzed.

The results were analyzed by ion chromatography (Dionex ICS-1000) using an external standard. Analyses were performed at the effluent flow rate of 1.2 ml/min and at the temperature of 30°C. The mixture was separated into ions in the Dionex IonPac CS5A column using the effluent consisting of 7.0 mM PDCA/66 mM potassium hydroxide/5.6 mM potassium sulfate/74 mM formic acid. Then the colored effluent transferred the cations onto the UV–vis spectrophotometer where the samples were analyzed.

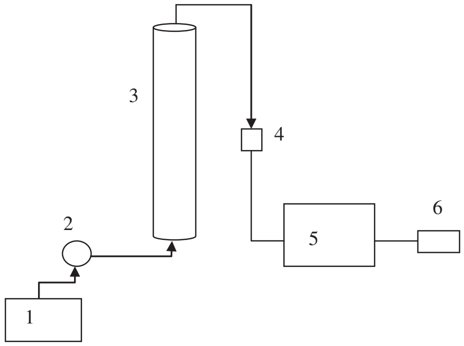

Fig. 1. Schematic diagram of heavy metal sorption in the chitosan packed column.
Notes: (1) Tank with a solution of metal ions, (2) Pump, (3) Column with chitosan bed, (4) Sampling, (5) Chromatographic analysis and (6) Analysis of results.

4. Results and discussion

4.1. Properties of the foam

Specific density, apparent density, porosity, and humidity were determined to identify the foamed chitosan structure. The results are summarized in Table 3.

The content of liquid in the wet material was 88% as shown by relative density, while specific density revealed a sevenfold increase in water weight when compared with the dried material. The foamed structure was highly porous.

Available technical papers show studies on lyophilized and hydrated foamed chitosan structures [20,21]. Properties of the lyophilized foamed chitosan structure (Fig. 2) differ significantly from those of the hydrated structure. The obvious differences lie in the specific humidity (0.25 $kg_{liquid}/kg_{d.w.}$) and specific density (1,420 kg/m^3) of the lyophilized material as well as its higher porosity (approximately 0.97). The photos below show the hydrated and lyophilized chitosan structures.

4.2. Analysis of the foamed structure

The foamed chitosan structure height and width changed during the first stage of the experiment when distilled water was passed through the column. It was related to shrinking of empty spaces of the foam structure on the surface of the bed. This change was mainly dependent on the flow rate. At 1 dm^3/h the height changed by approximately 32%, and at 1.5 dm^3/h by approximately 27%. Due to this shrinkage, flow rate of the solution through the column was not homogeneous, at the walls it was higher than in the remaining area of the column. Therefore, more often the metal ions came in contact with the surface of the packing material causing it to stiffen and thus hindering the penetration of further portions of the ions into the deeper layers of the foam structure. In addition, the surface layer of packing material, due to its shrinkage, contained a greater number of active chitosan groups adsorbing greater amounts of heavy metal ions. In the cross section of the material, ion-derived coloring was observed on about 20% of the surface. After being taken out from the column, the foamed chitosan structure was dried in a vacuum

Table 2
Summary of experiments

Analysis number	Flow rate (dm^3/h)	Initial metal ion concentration (mg/dm^3)
1	1	20
2		10
3		5
4	1.5	5
5		10

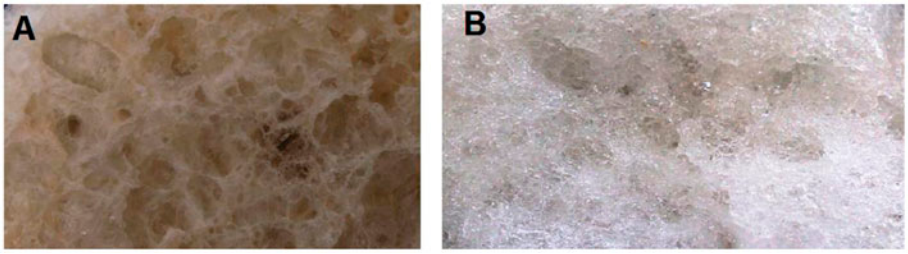

Fig. 2. Lyophilized (A) and hydrated (B) chitosan structures.

dryer at 80°C for 48 h. As a result of the drying, the material shrank more than twofold (Fig. 3).

This mechanism was confirmed by pictures of cross-fulfillment. The center of the chitosan foamed structure in the column adsorbed less metal than the surface.

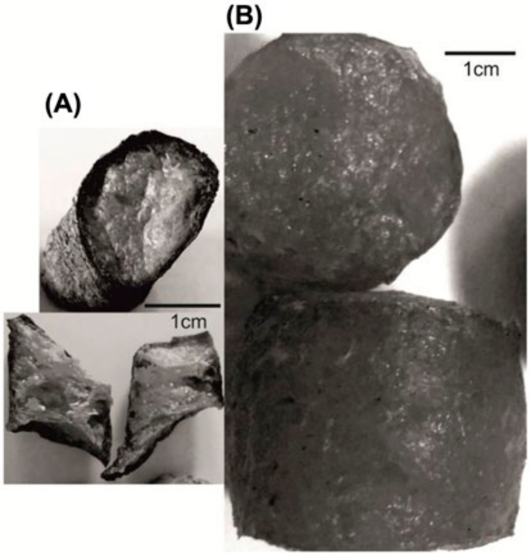

Fig. 3. Chitosan foamed structure after the column process, before (B) and after drying (A).

At the same time, flushing with distilled water caused the foaming and cross-linking agents to be washed out of the bed, which was reflected in the change of the feed solution pH. After 24 h it stabilized at 6.5.

4.3. Dynamics of sorption

The column sorption process is controlled by the chemical reaction kinetics. Chemical bonding between heavy metals and functional groups can occur as a result of ion exchange, adsorption, and chelation. Fig. 4 shows the most popular metal ion—chitosan bonds. Besides chemisorption on the sorbent surface, physical adsorption, microprecipitation, or redox reactions can take place. Sorption of heavy metals can also be a combination of the above mechanisms. Therefore, the mechanism of binding heavy metal ions to natural sorbents is not fully recognized [18,22].

In general, sorption of metal ions is possible thanks to $–NH_2$ groups. Creating coordinate bonds [24], amine groups become donors able to join metal ions by donating a lone pair of electrons. However, amine groups can easily be protonated in acidic solutions. Protonation of these groups may cause an electrostatic attraction of anionic compounds including metal anions [25].

The sorption of several metal ions, i.e. Cu^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, and Co^{2+}, onto the foamed chitosan bed

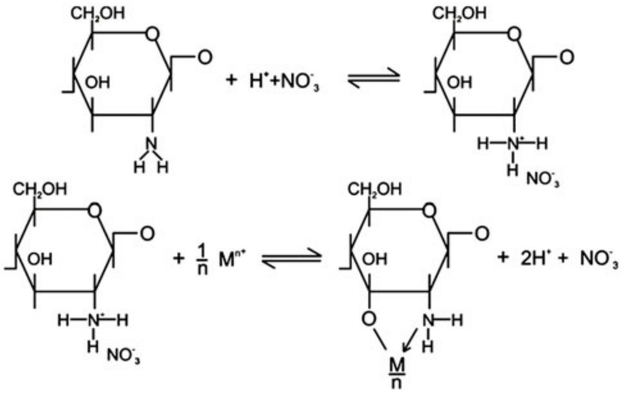

Fig. 4. Mechanism of metal ions binding [23].

was carried out at different flow rates and initial solution concentrations (Figs. 5 and 6). In the process, mutual influence of ions should not be neglected.

The curves obtained for ion solutions represented as a change of the ratio of effluent and influent concentrations (C_{out}/C_{in}) with time are shown in Figs. 5 and 6. Their shapes are similar for different initial concentrations of the solution. However, an increase in the initial concentrations of ions causes the curves to become steeper. For the initial concentration of 5 mg/dm^3 (Fig. 5) the equilibrium was not reached, even after 24 h, while for 10 mg/dm^3 the equilibrium was achieved by four ions after 5 h (Fig. 6). At the same time, the curve obtained for Cu(II) was still rising.

The results at constant bed depth and various flow rates show that when the flow rate increases the breakthrough time linearly decreases; therefore, the breakthrough can be observed. This leads to a shorter contact time between the ions and sorbent at higher flow rates.

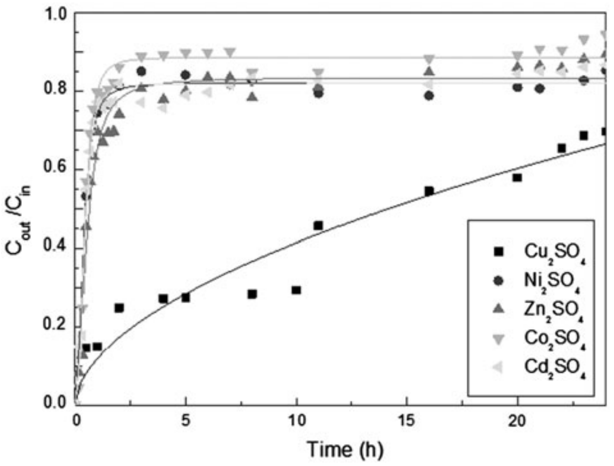

Fig. 6. Relation between C_{out}/C_{in} and time for the flow rate of $Q = 1$ dm^3/h and initial concentration of $C_{in} = 10$ mg/dm^3.

In order to make the results more readable, Figs. 7 and 8 show only the sorption of single cations onto the bed (not the mixture of ions as presented previously). As can be seen in these figures, the breakthrough point cannot be observed because of too high feed flow rates.

Analyses performed for cobalt sulfate and zinc sulfate show that the curves are similar regardless of the process parameters. The same is observed for other sorbed cations.

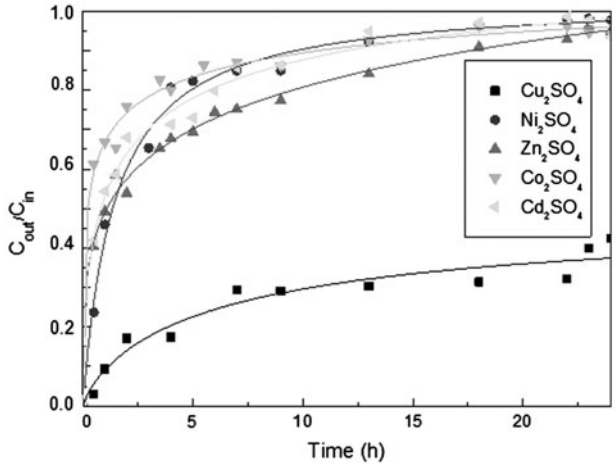

Fig. 5. Relation between C_{out}/C_{in} and time for the flow rate of $Q = 1$ dm^3/h and initial concentration of $C_{in} = 5$ mg/dm^3.

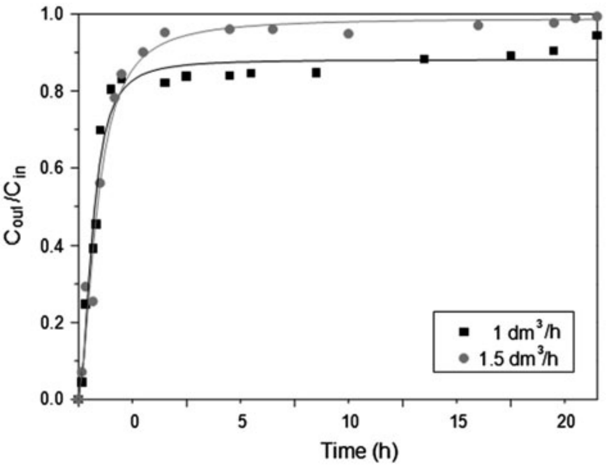

Fig. 7. Relation between C_{out}/C_{in} and time for Co(II) ion at different flow rates and initial concentration of $C_{in} = 10$ mg/dm^3.

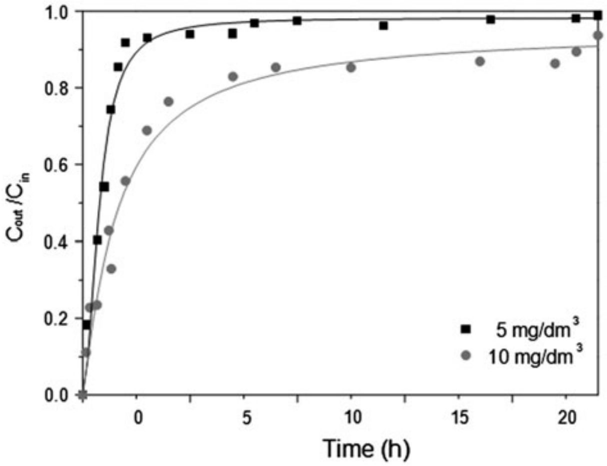

Fig. 8. Relation between C_{out}/C_{in} and time for Zn(II) ion at different initial concentrations and flow rate of $Q = 1.5$ dm^3/h.

Fig. 7 shows that at the flow rate of 1 dm^3/h the curve reaches an equilibrium much faster, which means that the process is stabilized and a lower amount of ions has been adsorbed. Thus, the flow rate of 1.5 dm^3/h is more efficient for sorption onto the bed. Fig. 8 shows that at the feed concentration of 10 mg/dm^3 the bed gets saturated faster than at the concentration of 5 mg/dm^3. It implies that within the same period of time the bed adsorbs more metal ions.

4.4. Sorption capacity

Many equations have been proposed for description of sorption kinetics [26–28]. Pseudo-first-order, pseudo-second-order equations as well as Langmuir and Freundlich isotherms are most widely applied. However, it is more difficult to find reports on sorption dynamics [29,30] concerning various adsorbents. Technical literature does not report so many studies on sorption dynamics as it does on sorption kinetics with regard to different sorbents. The available data are related to e.g. sorption of Cr(III) ions onto NaX zeolite or removal of hexavalent chromium by chitosan flakes [31].

In this work, the sorption capacity of N (mg/dm^3) was determined using the Bohart–Adams equation (BDST) [29].

Sigmoidal curve equation:

$$\frac{C_{out}}{C_{in}} = \frac{a}{1 + e^{b - c \cdot t}} \qquad (1)$$

where a is a maximum value of the C_{out}/C_{in} ratio, while b and c refer to the midpoint time:

$$C_{out} = 0.5 \cdot a \cdot C_{in} \quad \text{for} \quad t = \frac{b}{c} \qquad (2)$$

The factor a was introduced instead of unity considering the fact that the curves are not perfectly symmetrical for $C_{out} = 0.5 \cdot C_{in}$.

Figs. 5–8 show the plot of C_{out}/C_{in} with time, which represents the sorption dynamics. Based on the determined factors a, b, and c it was possible to determine the adsorption rate constant and adsorption capacity using the following formulas:

$$K = \frac{c}{a \cdot C_{in}} \left[\frac{\text{dm}^3}{\text{mg min}}\right] \qquad (3)$$

$$N = \frac{b \cdot v}{K \cdot D} \left[\frac{\text{mg}}{\text{dm}^3}\right] \qquad (4)$$

where K—adsorption rate constant [dm^3/mg min], N—adsorption capacity per bed volume [mg/dm^3], D—bed depth [cm], v—linear flow rate through the bed [cm/min], C_{in}—influent concentration of metal ions [mg/dm^3], and C_{out}—effluent concentration of metal ions [mg/dm^3].

Tables 4 and 5 contain values of the sorption capacity N [mg/dm^3] calculated using Eq. (6.4) derived from the Bohart–Adams equation.

Tables 4 and 5 show relations between the sorption capacities N for different feed flow rates. Apparently, Cu^{2+} is sorbed best. Process parameters influence the order in which other ions are sorbed. Furthermore, the table data indicate that adsorption capacity of the bed increases with the increase of initial concentration of any given ion.

The available studies suggest that the relation between sorption capacity and process parameters can be described with multiple mathematical models [31]. During sorption of dyes (methylene blue) in columns packed with common hazel shells, sorption capacities are 10 times lower than capacities achieved using the foamed chitosan structure [29]. In the case of multi-component mixture, total sorption needs to be considered in addition to that regarding individual components. Comparison of different chitosan forms and their adsorption abilities is troublesome because the published research is mainly related to the process kinetics [32,33]. There are several recommended methods of chitosan synthesis and chemical modification of its structure [34,35], which substantially complicates correlating the results of different studies.

Table 3
Physicochemical properties of the foamed chitosan structure

Specific density (kg/m^3)	Apparent density (kg/m^3)	Porosity (–)	Specific humidity ($kg_{liquid}/kg_{d.w.}$)	Relative humidity (%)
932.427	312.675	0.665	7.307	87.962

Table 4
List of sorption capacity values for individual cations at the flow rate of 1 dm^3/h

Initial metal ion concentration (mg/dm^3)	Sorption capacity for individual ions (mg/dm^3)				
	Cu^{2+}	Zn^{2+}	Cd^{2+}	Ni^{2+}	Co^{2+}
5	0.188	0.238	0.166	0.303	0.086
10	1.830	0.187	0.157	0.154	0.169
20	7.752	0.403	0.376	0.354	0.327

Table 5
List of sorption capacity values for individual cations at the flow rate of 1.5 dm^3/h

Initial metal ion concentration (mg/dm^3)	Sorption capacity for individual ions (mg/dm^3)				
	Cu^{2+}	Zn^{2+}	Co^{2+}	Ni^{2+}	Cd^{2+}
5	0.763	0.279	0.084	0.075	0.079
10	2.123	0.860	0.950	0.432	0.427

Tables 3 and 4 show significant differences in N values depending on the flow rates. The best sorption results were obtained for copper ions. The optimal process parameters are the initial concentration of 10 mg/dm^3 and flow rate of 1.5 dm^3/h for all ions. When the flow rate remains constant, the ion concentration becomes the decisive factor. With increasing inlet concentrations the flow rates also increase. In the experiments, the sorption capacity increases with increasing ion concentrations and the initial feed flow rate.

5. Conclusions

The study was conducted in order to evaluate the sorption of copper, nickel, zinc, cobalt, and cadmium ions. The experiments were carried out at ambient temperature in the column packed with chitosan foamed structure. To determine the sorption capacity five process analyses were performed and the influence of parameters such as initial ion concentration, feed flow rate, and change of bed height on adsorption process was estimated.

The results show that the amount of separated ions is proportional to their initial feed concentration and is also dependent on the feed flow rate. With regard to most ions, the sorption capacity is higher at the flow rate of 1.5 dm^3/h and increases with the initial concentration of a particular ion. The sorption capacity of chitosan is even 10 times greater compared with other natural sorbents. The flow rate may be considered a key parameter because it affects both the bed height and initial sorption process, and the end effect (for each concentration) is similar.

Based on the references and research presented in the paper, flow rate applied during experiments on sorption dynamics should be lower. Analysis of the hydrated chitosan structure demonstrated that due to its compact nature, ion sorption occurs only on its surface and not within the entire structure. It is possibly caused by decreasing its porosity while rinsing the bed with distilled water (at 1 dm^3/h the height changed by approximately 32%, and at 1.5 dm^3/h by approximately 27%). The material shrank more than twice after drying, which means that it was highly hydrated.

In the available technical articles, research on sorption dynamics referring to the chitosan foamed structure is rare, while sorption kinetics studies are much more popular. There are a variety of chitosan based adsorbents consequently, comparison between adsorbents is almost impossible since usually the parameters and adsorbate used are different. Therefore, experiments presented in this paper can bring opportunities for further sorption dynamics research using natural sorbents.

List of symbols

C_{out} — effluent concentration of metal ions (mg/dm^3)
C_{in} — initial metal ions concentration (mg/dm^3)
K — rate constant of adsorption (dm^3/mg min)
N — adsorption capacity per volume of bed (mg/dm^3)
a — maximum value of the ratio ($C_{\mathrm{out}}/C_{\mathrm{in}}$)
b — constant in Eq. (1)
c — constant in Eq. (1) (min^{-1})
Q — flow rate (dm^3/h)
K — rate constant of adsorption (dm^3/mg min)
N — adsorption capacity per volume of bed (mg/dm^3)
D — bed depth (cm)
v — linear flow rate through the bed (cm/min)

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