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SORPTION FROM MULTICOMPONENT SOLUTIONS ON FREEZE-DRIED CHITOSAN

SORPCJA Z ROZTWORÓW WIELOSKŁADNIKOWYCH NA CHITOZANIE SUSZONYM SUBLIMACYJNIE

Abstract: The process of adsorption in time-variable conditions in a column packed with lyophilized chitosan beads modified with polyvinyl alcohol (CH-PVA), ethylenediaminetetraacetic acid (CH-PVA-EDTA) or 3-chloropropionic acid (CH-PVA-3CPA) was analyzed. Experiments were carried out in a column filled with freeze-dried chitosan beads of diameter $\phi = 2.5$ mm and fed with water ternary solutions of Cu(II), Ni(II) and Zn(II). Sorption efficiency of single ions was analyzed. Additionally, the influence of initial concentration and flow rate was determined. A pseudo-second order equation was used in the description of ion sorption. Sorption equilibrium on freeze-dried chitosan beads with PVA at 25 ºC in static conditions was determined. Freundlich equation was recommended in this case.

Keywords: chitosan, lyophilization, sorption equilibrium, heavy metal ions

Chitosan is a natural polymer formed from easily available chitin. Its properties often surpass those of much more expensive synthetic polymers. Chitosan has many valuable features [1–3], including bioactivity (acting on living organisms through inhibition or activation of their life processes), biodegradability (an ability to decompose under the influence of natural environmental factors), biocompatibility and biocomplexing, as well as unique sorption and chelating properties for many heavy metal ions [4–6]. Heavy metals are a special hazard because even in small amounts they can accumulate in living organisms. Thus, from the technological and first of all ecological point of view it is important to remove heavy metals from aqueous solutions. Processes which enable a significant decrease of the concentration of heavy metal ions include chemical precipitation and filtration, coagulation, ion exchange, membrane processes and adsorption [7]. Due to its properties, chitosan often finds application in sorption processes. However, we still search for a chemical formula which would allow us to modify chitosan by adding other chemical compounds, eg polyvinyl alcohol (PVA), ethylenediaminotetraacetic acid (EDTA) or 3-chloropropionic acid (3CPA) that increase its

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sorption abilities and mechanical structure and enhance its durability. A mathematical description of the kinetics of heavy metal ion sorption is also searched for.

The process of adsorption in static conditions and in the column packed with a bed of freeze-dried chitosan beads is discussed in this study. The efficiency of sorption of heavy metal ions, ie copper(II), zinc(II) and nickel(II), from a multicomponent solution was investigated.

Scope of experiments

Formation of chitosan beads

Chitosan beads were made from 90/1000/A1,5 chitosan flakes produced by Heppe GmbH (Germany) with deacetylation degree 90 %. Other reagents were purchased at "Chempur" (Poland). The process of beads formation consisted of several stages. 10 g of chitosan flakes were dissolved in 500 cm^3 acetic acid (2 %). The vessel with chitosan and acetic acid was placed in a water bath at a temperature of 60 ^{o}C for 30 minutes stirring continuously and then it was left for 24 h. 15 g polyvinyl alcohol (PVA) was dissolved in 150 cm^3 distilled water. The solutions of chitosan and PVA were combined and mixed at a temperature of 60 ^{o}C, next a substance modifying chitosan sorption abilities was added (5 g EDTA or 3-chloropropionic acid in 50 cm^3 H_2O). The next stage was drop formation under pressure [7]. Chitosan beads with gel structure of diameter 2.8 to 3.4 mm and moisture content 95.4 % (20.74 kg H_2O/kg d.m.) were formed. Then, the beads were freeze-dried in an ALPHA 2–4 freeze dryer using freezing to –25 ^{o}C and working pressure 0.630 mbar. In this way, beads of diameter ca 2.5 mm, moisture content 5 % and density 175 kg/m^3 characterized by good mechanical properties were obtained. This method was selected because lyophilization has been known as a method for preservation of food, drugs, tissues, etc. which preserves their primary features by dehydration in frozen state (sublimation of ice crystals) under high vacuum.

Photo 1 illustrates appearance of the beads prior to and after drying in a freeze dryer. Photos 2 and 3 show a single chitosan bead and 100-time magnification of its surface which reveals high porosity of the bead after lyophilization.
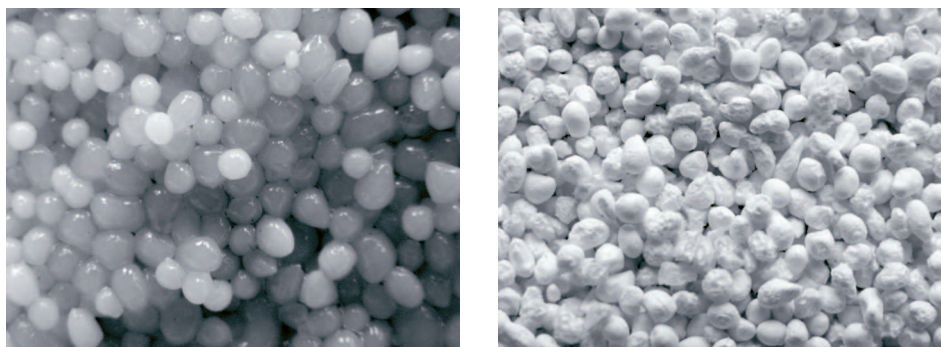

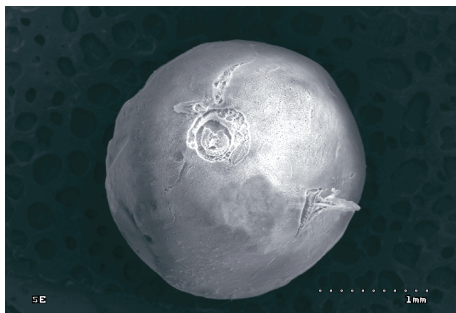Photo 1. Wet and freeze-dried chitosan beads with PVA
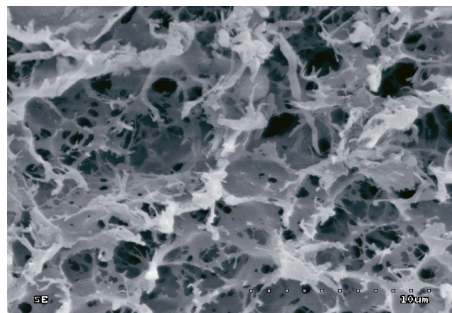
Photo 2. SEM photo of freeze-dried CH-PVA bead   Photo 3. SEM Photo of CH-PVA bead surface

Experimental set-up

Experiments were carried out at a temperature of 25 $^{\circ}$C in two systems: static and dynamic in a column. In the first case in conical flask about 4 g freeze-dried chitosan beads were placed and 200 cm^3 of the mixture of tested salts solutions in the concentration range from 10 to 50 mg/dm^3 were added. Next, they were put into a thermostat (Photo 4) and stirred continuously. A source of particular ions were water solutions of copper(II) (CuSO$_4$ · 5H$_2$O), nickel(II) (NiSO$_4$ · 6H$_2$O) and zinc(II) (ZnSO$_4$ · 7H$_2$O). The experiments were carried out at pH = 5 to 6. Samples for analysis were taken every 30 min until reaching the state of equilibrium.

Photo 4. The set-up for determination of heavy metals sorption equilibrium

In the second case the experiments were performed in the column 0.567 dm^3 in volume with feeding solution flow, packed with a sorbent, ie freeze-dried chitosan beads. The whole was placed in a transparent casing equipped with a threaded head and vent valve. The measuring set-up consisted of a metering pump for solution (BL 1.5 model with the maximum delivery 15 dm^3/h) and a vessel with salt solution. The pump took the salt solution from the vessel by means of an aspirator and pumped it to the
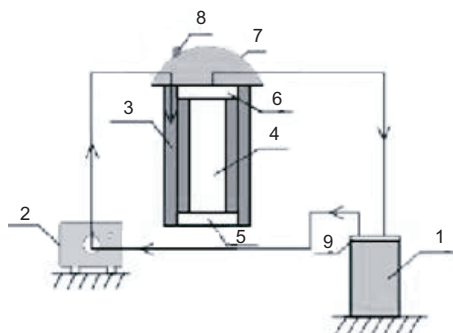
Fig. 1. Schematic diagram of the measuring set-up: 1 – thermostated supply vessel, 2 – metering pump, 3 – column casing, 4 – sorption column, 5 – base, 6 – upper cover, 7 – sealing head, 8 – vent valve, 9 – cover of the supply vessel

column through holes in its lower part from the bottom up to the bed top. After passing through the bed, the solution was fed back to the supply vessel.

Measurements were made for ternary water solutions of salts which contained Cu(II), Ni(II) and Zn(II) ions. The column packing was freeze-dried chitosan mixed with polyvinyl alcohol (CH-PVA) and ethylenediaminotetraacetic acid (EDTA) [9]. Experiments with 3-chloropropionic acid (3CPA) were also carried out. However, despite literature reports [10], they did not bring about expected results.

The measurements were made for initial salt concentrations ranging from 10 to 50 mg/dm^3 and for changeable volumetric flow rate from 1.1 to 5.8 dm^3/h. Each measurement took about 200 min. Determinations were made using a Dionex ICS-1000 ionic chromatograph.

A mathematical description of sorption kinetics

Prediction of sorption kinetics is one of the important topics concerning design of the equipment for carrying out this process. The final rate of adsorption in a packed column depends on constituent processes. The adsorption rate reaches the highest value in the moment when the fluid contacts the adsorbent for the first time. Next, the rate decreases with the process time. In this case, the process of adsorption in a column is controlled by the kinetics of a chemical reaction between chitosan and metal ions. In such a case, the pseudo-first and pseudo-second order, equations are proposed in the literature [11].

In this study the psudo-second order equation (2) is used because this equation is recommended for the metal – biosorbent system and gives good fitting [12, 13].

$$\frac{dq}{dt} = k(q_e - q)^2 \qquad (1)$$

Upon integration of equation (1) in the range (t = 0, q = 0) and (t, q), equation (2) is obtained

$$\frac{q}{q_e} = \frac{kq_e t}{1 + kq_e t} \tag{2}$$

After transformation of equation (2), its form suitable for calculation of coefficients k and q_e is obtained

$$\frac{t}{q} = \frac{1}{k \cdot q_e^2} + \frac{t}{q_e} \tag{3}$$

$$q = (C_0 - C_t) \cdot \frac{V}{m} \tag{4}$$

To determine constants K and q_e, a graph of the function in the system of coordinates (t/q, t) should be made basing on results of the measurements. The graph was described by the equation of a straight line using the least squares method.

Based on the results, it was found that equation (2) well described sorption kinetics in all analyzed cases. The correlation coefficients ranged from 0.998 to 1.

Results and discussion

Figures 2 and 3 show a description of sorption equilibrium with the use of Freundlich isotherm – equation (5). For each case constants K and n were determined from equation (6) and correlation coefficient R was calculated.

$$q = KC_e^n \tag{5}$$

After finding the logarithm

$$\log q = \log K + n \log C_e \tag{6}$$

It was observed that in the case of a ternary solution, sorption was the best for Cu(II) ions reaching the value of ca 5 mg/(g dry chitosan). Lower values, about 2.5 mg/g and 2 mg/g, were obtained for Ni(II) and Zn(II) ions, respectively.
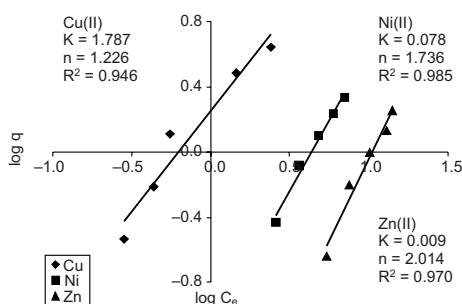

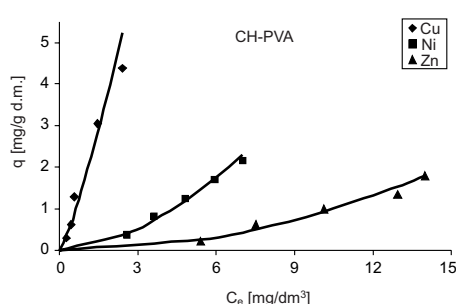Fig. 2. Examples of constants K and n determined from Freundlich equation

Fig. 3. Description of sorption equilibrium from ternary solution by Freundlich equation
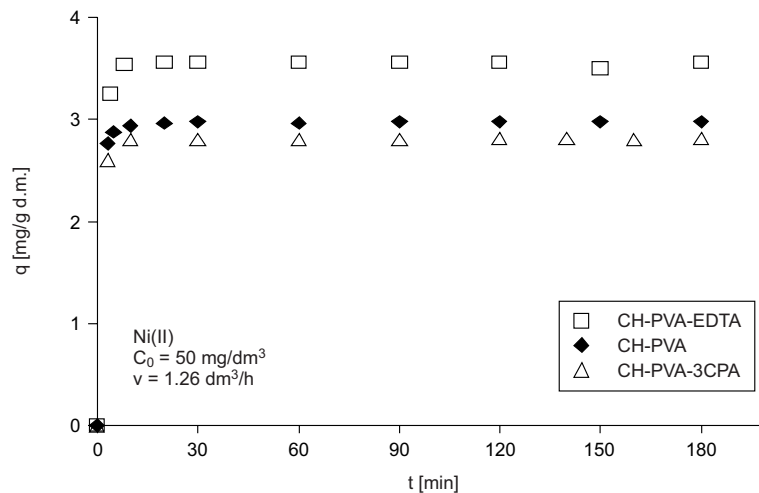
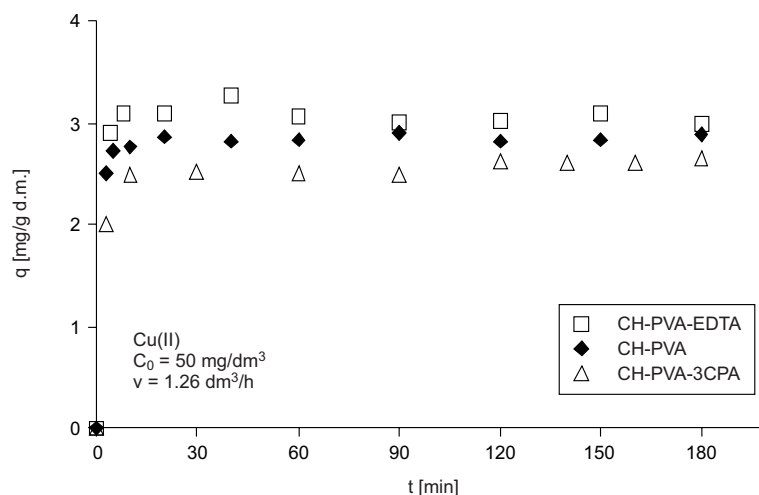Fig. 4. Effect of additions to chitosan on sorptivity of Cu(II)

Fig. 5. Effect of additions to chitosan on sorptivity of Ni(II)

Further in the study, metal ion sorption in the column was compared for three types of freeze-dried chitosan: CH-PVA, CH-PVA-EDTA and CH-PVA-3CPA. As follows from Figures 4 and 5, the addition of EDTA causes an increase of sorption abilities of chitosan, while 3-chloropropionic acid, despite of reports presented in the literature, decreases these sorption abilities. Therefore, further studies were carried out for chitosan with the addition of PVA and EDTA, in which the effect of the amount of held-up heavy metal ions depending on the initial concentration of a solution was determined. Figures 6 and 7 show relations which were also confirmed in the case
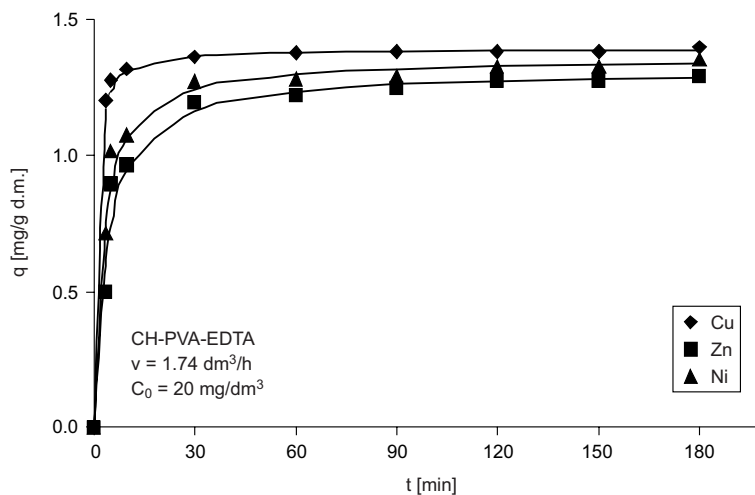
Fig. 6. Sorption isotherm of Cu(II), Ni(II), Zn(II) for $C_0 = 20$ mg/dm^3

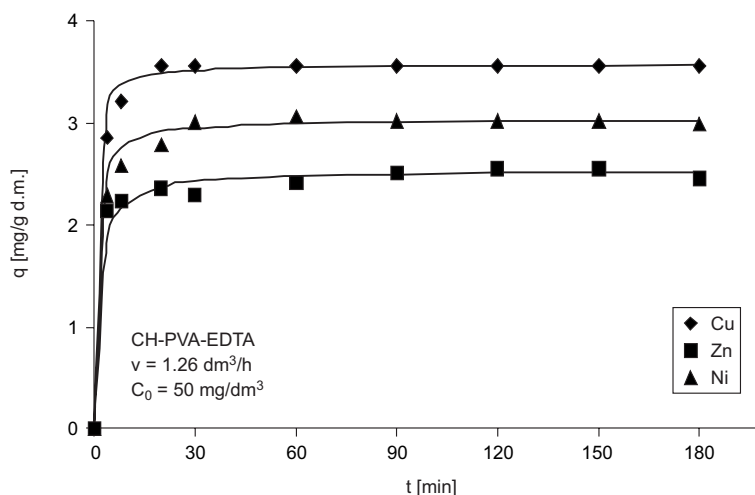Fig. 7. Sorption isotherm of Cu(II), Ni(II), Zn(II) for $C_0 = 50$ mg/dm^3

of other concentrations – for higher concentrations bigger values of equilibrium concentrations were obtained. The results confirm some selectivity of chitosan in relation to metal ions expressed by the sequence: Cu(II) > Ni(II) > Zn(II).

In the next part of this work, for example for nickel ions, the effect of volumetric flow rate on the amount of adsorbed ions is presented (Fig. 8). It was found that the rate of liquid stream flow through the bed had no significant influence on the process intensification.

Figure 9 illustrates the effect of the initial concentration of heavy metal complexes on the amount of adsorbed ions of one type, in this case copper. It was also observed for
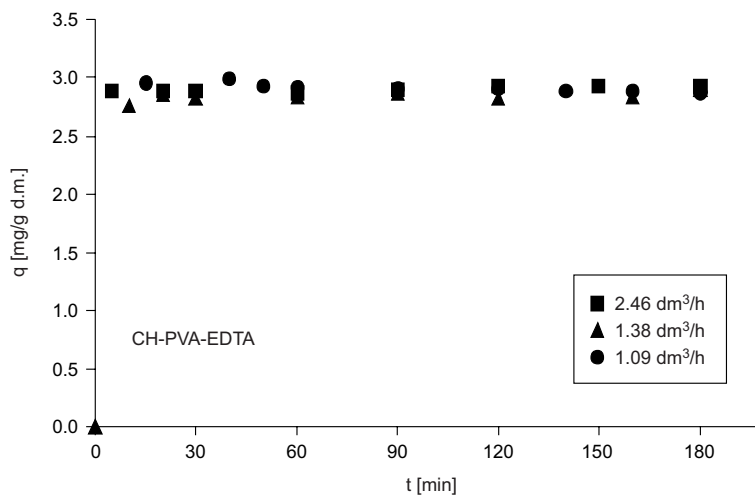
Fig. 8. Effect of volumetric flow rate on sorption properties of Ni(II) ions
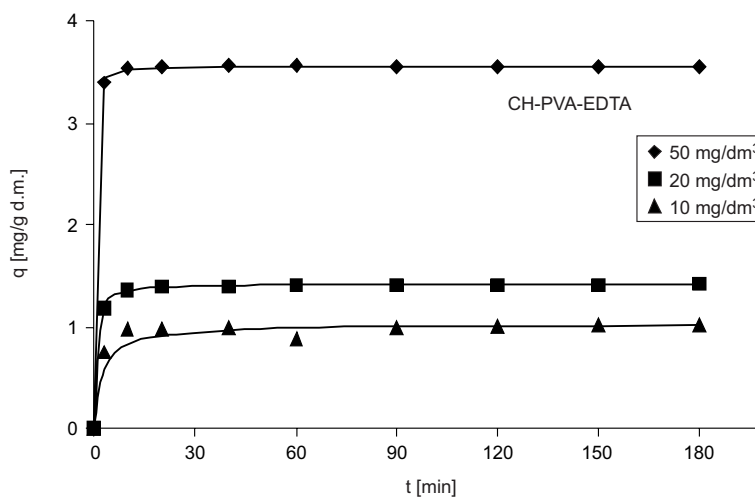

Fig. 9. Kinetics of Cu(II) ion sorption vs initial concentration

other ions that with an increase of the concentration, the load of ions trapped by the sorbent grew.

Conclusions

The following conclusions have been drawn from the experiments:

1. Freeze drying of chitosan leads to formation of stable structures with good mechanical properties and prolonged durability, which is important for storage and distribution of the obtained product. High porosity promotes sorption processes.

2. Freeze-dried chitosan in the form of beads, modified with polyvinyl alcohol and EDTA, is good packing of the column for Ni^{2+}, Zn^{2+} and Cu^{2+} ion sorption from water solutions. The process of sorption controlled by a chemical reaction reaches equilibrium already after about 60 minutes.

3. The best effects of sorption from a ternary mixture were obtained for copper ions, and next for nickel and zinc ions.

4. The degree of metal ion hold-up on a chitosan bed increases with an increase of initial concentration of the solution.

5. No effect of the volumetric flow rate in the column on ion sorption was observed.

6. The sorption kinetics is well described by the pseudo-second order equation, which is confirmed by the statistical estimation, while sorption equilibrium is well characterized by the Freundlich equation.

Symbols

C_e – sorption equilibrium of metal ions [mg/dm^3],
C_0 – initial concentration of the solution [mg/dm^3],
C_t – solution concentration at the column outlet after time t,
k – constant in the second order equation [g/(min · mg)],
K, n – Freundlich constants describing sorption equilibrium,
m – dry mass of chitosan [mg d.m.],
t – time [min],
q – the amount of adsorbed metal ions [mg/g d.m. chitosan],
q_e – equilibrium amount of adsorbed ions [mg/g d.m. chitosan],
V – solution volume [dm^3].

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**SORPCJA Z ROZTWORÓW WIELOSKŁADNIKOWYCH
NA CHITOZANIE SUSZONYM SUBLIMACYJNIE**

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Abstrakt: Badano proces adsorpcji prowadzony w warunkach zmiennych w czasie na złożu z lofilizowanych kulek chitozanowych modyfikowanych alkoholem poliwinylowym (PVA) z dodatkiem kwasu etyleno-diaaminotetraoctowego (EDTA) lub kwasu 3-chloropropionowego (3CPA). Proces ten prowadzono w kolumnie wypełnionej kulkami o średnicy ok. ϕ = 2,5 mm dla mieszaniny jonów w roztworach wodnych: miedzi(II) ($CuSO_4 \cdot 5H_2O$), niklu(II) ($NiSO_4 \cdot 6H_2O$) oraz cynku(II) ($ZnSO_4 \cdot 7H_2O$). Analizowano kinetykę sorpcji pojedynczych jonów występujących w roztworze trójskładnikowym. Dodatkowo określano wpływ stężenia początkowego i objętościowego natężenia przepływu. Do opisu badanego procesu zastosowano równanie pseudodrugiego rzędu. Określono równowagę sorpcyjną dla liofilizowanego chitozanu z PVA w 25 °C w warunkach statycznych. W tym przypadku zastosowano równanie Freundlicha.

Słowa kluczowe: chitozan, liofilizacja, równowaga sorpcyjna, jony metali ciężkich