

CHITOSAN MICROSPHERES PREPARED BY MEMBRANE EMULSIFICATION FOR CHROMIUM REMOVAL FROM AQUEOUS SOLUTIONS

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Abstract

Chitosan is naturally abundant biopolymer that could be used as chelating sorbent for removal of metal ions from aqueous solutions. In this study the uniform-sized chitosan microspheres and their modified derivatives were prepared by using the one stage membrane emulsification process. The obtained sorbents were used for removal of chromium VI ions. The sorption evaluation was carried out at different initial ion concentrations and allowed to fit the experimental data to Langmuir isotherm in the case of unmodified materials and to Freundlich isotherm in the case of modified microspheres. The highest sorption towards chromium has been shown by unmodified chitosan with medium molecular weight. The calculated maximum sorption capacity for this polymer was found to be 1.6 mmol/g.

Key words: *chitosan, microspheres, membrane emulsification, modification, biosorption, chromium VI*

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1. Introduction

Chitosan is a natural polysaccharide comprising copolymers of glucosamine N-acetylglucosamine [1] and can be derived by partial deacetylation of chitin. After cellulose, it is the most abundant natural polysaccharide on the earth and can be obtained from exoskeleton of marine crustaceans such as crabs, lobsters, shrimps and krill on the large scale. Chitosan is a copolymer of 2-amino-2-deoxy-D-glucose and 2-acetoamido-2-deoxy-D-glucose units linked with beta-(1→4)bonds [2]. Its properties depend largely on the degree of deacetylation and on its molecular weight. Due to the easy availability of free amino groups in chitosan, it carries a positive charge and thus it reacts with many negatively charged surfaces/polymers and undergoes chelation with metal ions [3] such as: copper, chromium, cadmium, nickel, cobalt, calcium [4, 5].

Metals are one of the most basic environmental pollutants discharged to various aquifers. Waste streams from metal cleaning and plating facilities, mining, corrosion and electronic device manufactures may contain considerable amount of toxic heavy metals [6]. Heavy metals persist in the environment and have tendency to accumulate in organisms, and in consequences, they contribute to various diseases. To the very dangerous heavy metals can be counted chromium (Cr), and nickel (Ni). These metals are category 1 of heavy metals according to the International Agency for Research on Cancer [7] report.

Chromium exists in two stable oxidation states Cr^{3+} and Cr^{6+} . This element is ubiquitous in the air, water and soil in the form of different compounds. Chromium is emitted from natural sources as rocks, soils and by volcanic activity [8]. It comes from various living organisms where is necessary for the proper their functioning [8]. As a result of industrial activities to the environment released detrimental form of chromium, hexavalent chromium. Chromium compounds are present in the industrial wastes mainly from leather tanning, textile industries, electroplating, metal finishing, auto industries and from aircraft industries [9, 10]. Hexavalent chromium, Cr(VI) , is a highly harmful ion that is suspected to cause cancer in mammals and is toxic to aquatic life at low concentrations. At the moment, the World Health Organization (WHO) Guidelines give a provisional value for total chromium of 0.05 mg/L [10]. The hexavalent form of chromium is 10–100 times more toxic than the trivalent form when both are introduced by oral ingestion [2]. In aqueous solution, Cr(VI) forms several species depending on both pH and total concentration. In basic environmental it is found as chromate ions: CrO_4^{2-} , while in acidic environmental appear dichromate ions $\text{Cr}_2\text{O}_7^{2-}$ or dimers of HCrO_4^- if the concentration of chromium exceed 1 g/L [9,10].

The most popular sorbent using for removal of heavy metals is activated carbon. This material has a very good sorption properties, because of its good porosity and large surface area. Activated carbon has a many disadvantages, as high cost of regeneration, or different efficiency depending on applied carbon. It is the reason why new materials capable for removal of heavy metals from waste water are still searched for. A good alternative seems to be natural materials, such as polysaccharides [11]. These materials are commonly used as sorbents in the form of beads, due to their larger surface area. In such structures, microspheres have gained the growing interest due to their unique features [12]. Microspheres can be obtained from various polymers by crystallization or by removal of solvent from emulsion or suspension. Sometimes, the precipitative polymerization is applied [13, 14]. One of the method for preparing the monodisperse microspheres is membrane emulsification process. The method in comparison to emulsion stirring method provides fairly uniform beads that size can be controlled mostly by pore size of membrane. Membrane emulsification is also characterized by consumption of lower portion energy than classical stirring method [14].

The goal of this paper was to establish a method for preparation of monodisperse chitosan beads and to check the process conditions that allowed crosslink the obtained spheres.

Additional goal was to form the solvent impregnated particles with the best extractant for hexavalent chromium – Aliquate 336 – and evaluate its sorption properties.

2. Materials and Methods

2.1. Materials

Chitosan with low (20 kDa) and medium (200 kDa) molecular weight with deacetylation degree of 75-85%, Aliquate 336, glutaraldehyde 50% solution in water, polyethyleneimine (PEI) (60 kDa), Span 80 and Span 20 was supplied by Sigma-Aldrich. NaCl, glacial acetic acid, potassium dichromate, ethanol and acetone were purchased from Avantor Performance Materials Poland S.A.

2.2. Preparation of chitosan solutions

The given type of chitosan was dissolved in 5 wt.% aqueous solution of acetic acid, which contain 0.4 wt.% of NaCl. The solution was additionally filtrated to remove impurity. That prepared solutions were subjected to a process of membrane emulsification. The content of chitosan in the solution was 0.7, 1.0, 1.5 and 2.0 wt.%.

2.3. Preparation of chitosan microspheres and modified chitosan microspheres

2.3.1. Preparation of water in oil emulsion

The membrane emulsification, ME, process was carried in a commercial unit delivered by Micropore Ltd. that layout is described in [15]. The system was equipped with metal membrane that had regularly arranged pores with size of 40 μm . The compositions of the chitosan and oil phases are shown in Table 1. The 50 mL of chitosan phase was forced to flow through the membrane to the 120 mL of oily phase. The flow rate was set up 1 mL/min. Rotation rate of the stirrer was set at 600 rpm. During this part of study the composition of oily phase was changed, viz. type of oily phase and concentration of surfactant, as well as properties of aqueous phase was varied, molecular mass of chitosan and its concentration.

Table 1. Compositions of oil and water phases

| Continuous phase | |
|--|----------------------|
| Paraffin oil: isooctane volume ratio: | 5:5 or 7:5 |
| Span 20: | 0-9 wt.% |
| Span 80: | 0-9 wt.% |
| Dispersed phase | |
| Chitosan with molecular mass: | low or middle |
| Concentration of chitosan in 5% solution of acetic acid: | 0.7-2.0 wt.% |

2.3.2. Crosslinking process of chitosan

The emulsion prepared in the ME system was placed into the flask equipped with a mechanical stirrer, and the crosslinking process was performed for 24 h at room temperature. The amount of glutaraldehyde in all cases, was kept twice more with respect to the content of chitosan in the emulsion. After completing the crosslinking process, the dispersion was filtrated then the microspheres were washed with isooctane and with ethanol and finally dried at 60°C.

2.3.3. Modification of chitosan microspheres

2 g of chitosan microspheres, were shaken for 1 hour with 2 g of Aliquate 336 dissolved in 8 mL of acetone. Then the acetone was evaporated for 1 day. To encapsulate Aliquate 336 into particles, microspheres were shaken for 1 day with 35 mL of 15 wt.% aqueous solution of PEI (60 kDa), washed with large amount of water, and crosslinking with 1 % aqueous

solution of glutaraldehyde for 1 day. Eventually, modified microspheres were washed with large amount of water, ethanol and dried at 60°C.

2.4. Evaluation of the Sorption Properties

2.4.1. Batch-mode sorption

Sorption of hexavalent chromium was studied in a batch mode with 0.5 mmol/L Cr(VI) solutions at $22 \pm 2^\circ\text{C}$. About 0.05 g of sorbent was shaken with 25 mL of solution for 48 hours. After that time the resins were filtrated and concentration of chromium was determinate spectrophotometrically. The distribution coefficient ($\log K_{Cr6+}$) was calculated as a ratio of amount of chromium VI adsorbed on 1 g of resin and the amount of Cr(VI) at equilibrium in 1 mL of solution.

2.4.2. Sorption isotherms

Synthesized sorbents were evaluated for the sorption isotherms. The sorbent samples of 0.05 g were gently shaken with 25 mL of solutions containing 0.10 – 1.0 mmol/L Cr(VI) at $22 \pm 2^\circ\text{C}$ for 48 h. After that time hexavalent chromium concentration was determined. The maximum chromium uptake (q_{max}) and the distribution of binding sites was calculated from Langmuir, Freundlich and Dubinin-Radushkevich isotherms.

2.4.3. Sorption kinetics

Sorption kinetics were determined for all samples. Typical procedure was as follows: a flask with a capacity of 1000 mL was filled with sorbent to give a suspension of 0.5 g dry polymer/L. Chromium VI solution (1.0 mmol/L, 500 mL) was added to the flask and mixed gently. The samples with 3 mL solution were taken out at different time to determine chromium concentration.

2.5. Analysis of microspheres

Average diameter of microspheres as well as SPAN number were detected by means of Mastersizer X (Melvern Instruments GmbH, Germany). $SPAN = (d_{90} - d_{10}) / d_{50}$ where d_{90} , d_{50} , d_{10} are diameters for 90, 50 and 10 percent of particle population.

The morphology of beads was investigated by SEM microscope Carl Zeiss EVO LS15, operated at 10.00 kV. Prior microscopy evaluation, the surface was sputter coated with gold.

Water regain (W_{H2O}) of the polymers was measured by the centrifugation method in which ca. 1 g of swollen spheres was centrifuged for 5 minutes at 3000 rpm, weighted, dried at 105°C for 24 h and weighted again. Water regain was calculated as follows:

$$W_{H2O} = (m_w - m_d) / m_d \quad (1)$$

where:

m_w is the weight of the swollen polymer after centrifugation,

m_d is the weight of dry polymer [16].

Nitrogen content (Z_N) in the polymer was measured by Kjeldahl method after mineralization of the sample (about 200 mg) in concentrated sulfuric acid containing copper sulfate and potassium sulfate [17].

3. Results and Discussion

3.1. Effect of membrane emulsification conditions

The study was focused on selection of such process parameters that offered preparation of narrow dispersed microspheres. The size of droplet and microspheres (d) can be related to the pore size of the membrane (d_m) by a linear relationship $d = x \cdot d_m$, where x can range typically from 2 to 10 [14]. In our study one membrane with nominal pore diameter of 40 μm was used. The first step of the research was to find the optimal process parameters for

membrane emulsification by alteration of composition of continuous and/or dispersed phase. As an oily phase two type mixture of paraffin oil and isooctane, with the volume ratio of 5:5 and 7:5, were tested. Effect of presence of non-ionic surfactants was checked also. The 1:1 mixtures of Span 80 - Span 20 were applied with concentration ranging from 3 wt.% to 9 wt.%. It was found that the best composition for preparing spherical chitosan droplets was the mixture of paraffin oil and isooctane set at volume ratio 7:5 with surfactants mixture amount of 2.5 wt.%. In the case of other compositions some irregular aggregates with large diameter were formed (See Fig.1).

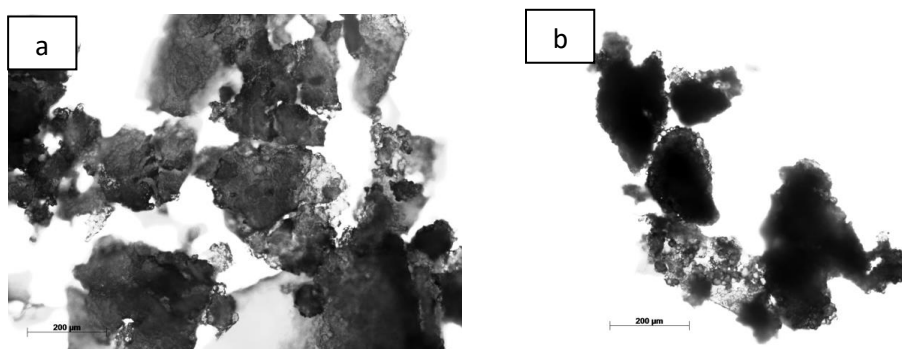


Figure 1. Pictures of the materials obtained for different compositions.

a: paraffin oil:isooctane 5:5, mixture of surfactants 2.5 wt.%, aqueous phase: 0.7 wt.% chitosan with low molecular weight; **b:** paraffin oil:isooctane 7:5, mixture of surfactants 5 wt.%, aqueous phase: 0.7 wt.% chitosan with low molecular weight.

The second stage of this part of study was to find the proper concentration of chitosan in aqueous phase. To increase the process efficiency, one can use larger concentration of polymer in the aqueous phase. However, in such case the increase of viscosity is observed and consequently higher transmembrane pressure is needed to form the emulsion. The increase of transmembrane pressure increases usually the diameter of the formed droplets and prepared spheres [14]. The concentration of chitosan varied between 0.7 – 2.0 wt.%. The higher content of polymer was not possible to obtain due to homogeneity of chitosan solution and troubles with pumping the viscous solution through the membrane. Figure 2 shows the relationship between the diameter of chitosan microspheres and concentration and type of used chitosan. It can be emphasized that this parameter has the critical effect on the microspheres structure; with increase of chitosan concentration an increase of spheres diameter and size their polydispersity was observed (Figures 2 and 3). The molecular weight of chitosan seems to had a significant effect on the properties of obtained polymeric particles. In the case of microspheres synthesized from chitosan with low molecular weight the uniformity of obtained polymer beads were smaller than for materials obtained from chitosan with high molecular weight (see Fig. 3). It seemed that the best concentration of chitosan was 1.5 wt.%. Using high molecular weight chitosan with 1.5 wt.% it was possible to prepare sorbent with relatively low value of SPAN parameter. Materials obtained in these conditions were subjected to the next stages of research.

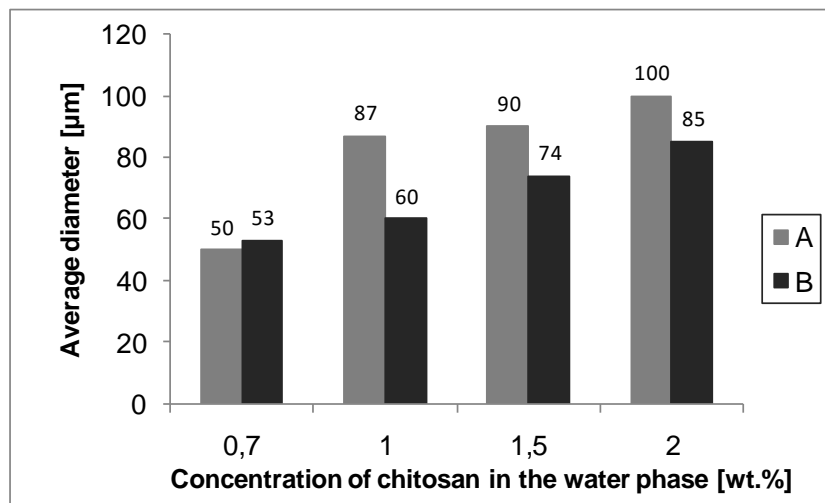


Figure 2. The effect of chitosan concentration and chitosan molecular weight on size of microspheres. Conditions of emulsification: membrane pore diameter = 40µm, RPM= 600, volume of oily phase 120 mL, volume of aqueous phase 50 mL).

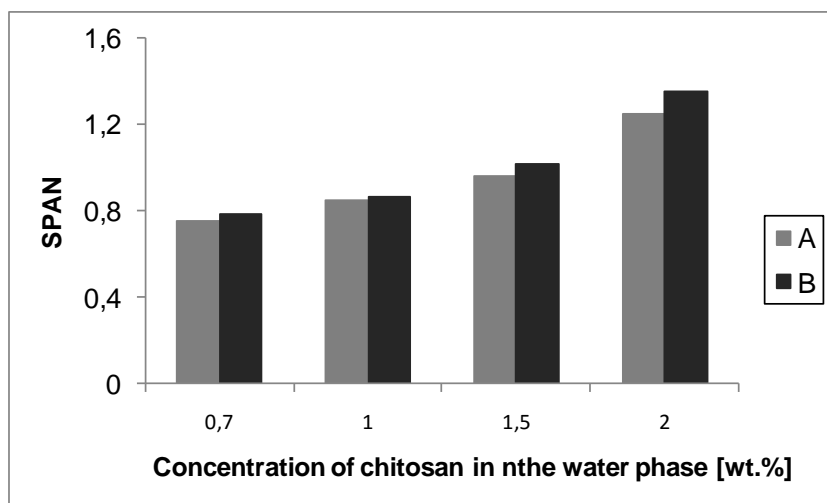


Figure 3. The effect of chitosan concentration and chitosan molecular weight on microspheres size polydispersity. Conditions of emulsification: membrane pore diameter 40µm, RPM= 600, volume of oily phase 120 mL, volume of aqueous phase 50 mL).

In the next step of search for efficient chitosan sorbent the best material, taking into account its shape, size and diameter polydispersity, was crosslinked to stabilize it and to keep its structural properties. The amount of glutaraldehyde was twice higher than the amount of chitosan in the aqueous phase. After this process the microspheres were washed, part of them was subjected to impregnation with Aliquate 336 followed with coating with PEI. Part was not modified and served as a reference.

The shape of obtained unmodified and modified chitosan microspheres was observed by SEM. The pictures of obtained particles are shown in Figure 4a-d.

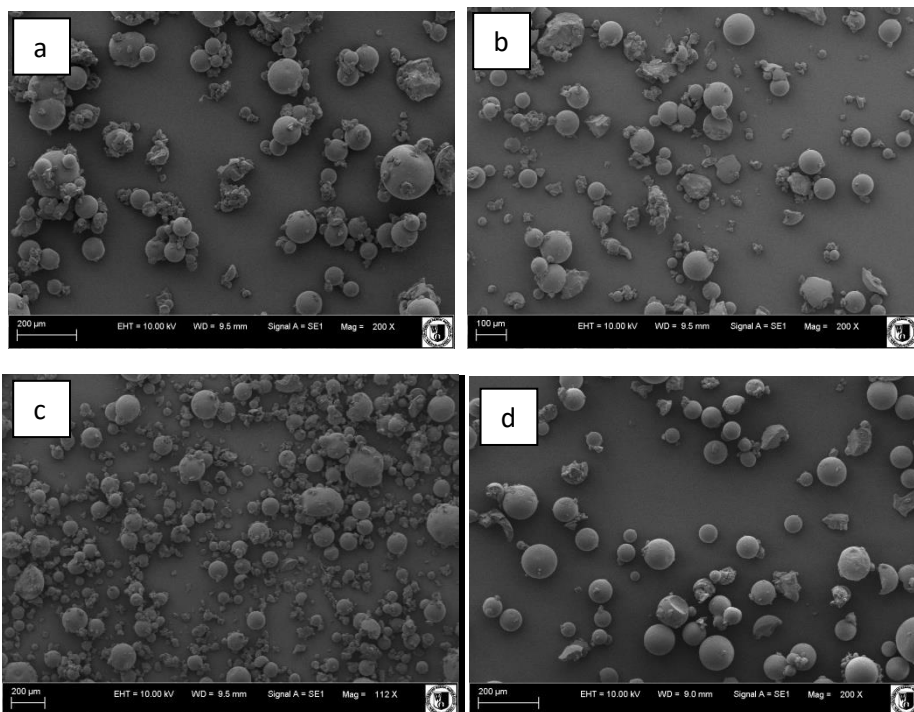


Figure 4. SEM picture of unmodified microspheres with low molecular weight (a) and medium molecular weight (b), and sample of modified microspheres for low molecular weight (c), medium molecular weight (d) chitosan particles.

It can be observed that some aggregates can be observed especially in the case of material from chitosan of low molecular weight. Even after modification the aggregates still exist. Modification of the chitosan particles with PEI does not affect the shape of microspheres. Sorbent obtained from the chitosan with medium molecular weight had lower amount of contaminants and its uniformity seemed to be the best.

The prepared sorbents were characterized by a set of physicochemical properties that are typical for sorbent description. They were the content of nitrogen and water regain (Table 2). It was shown that sorbents without additional modification had lower nitrogen content and water regain and when samples were modified the sorbents carried more nitrogen groups.

Table 2. Properties of chitosan microspheres with and without modification

| Sample | M_{chitosan} | modification | W_{H_2O} [g/g] | Z_N [mmol/g] | $\log K_{Cr^{6+}}$ |
|--------|-----------------------|--------------|------------------|----------------|--------------------|
| A | low | no | 1.1 | 2.8 | 3.7 |
| A-1 | low | yes | 2.4 | 3.2 | 3.6 |
| B | medium | no | 1.2 | 3.0 | 3.9 |
| B-1 | medium | yes | 2.5 | 4.0 | 3.2 |

M_{chitosan} - molecular weight of chitosan, W_{H_2O} - water regain, Z_N - content of nitrogen

3.2. Evaluation of sorption properties

At this stage of the sorbent evaluations the ability to adsorb hexavalent chromium ions were investigated for unmodified and modified chitosan particles. The distribution coefficients of Cr (VI) are shown in Table 2. The materials modified with PEI showed a little bit lower sorption capacity towards Cr⁶⁺ than unmodified sorbent. The largest distribution coefficient ($\log K_{Cr^{6+}}=3.9$) was detected for sorbents B prepared from the chitosan with the higher molecular weight. It was observed that samples impregnate with Aliquate 336 and coated with PEI had worse sorption capacity than unmodified materials.

3.3. Sorption isotherms

The preliminary studies prompted us to investigate the sorption properties of synthesized materials in details. The sorption isotherms were investigated for four samples subjected to the deeper analysis. The isotherms are shown in Figure 5. The sorption process was examined by fitting the experimental data to the Langmuir, Freundlich and Dubinin-Radushkevich models.

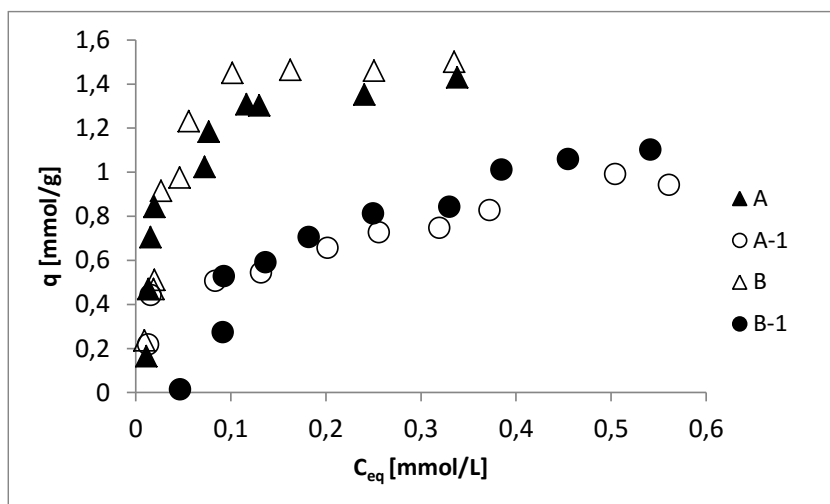


Figure 5. Sorption isotherms for all investigated materials

The Langmuir equation (eq.2) served to calculate the maximum uptake of chromium (q_{max}) [18,19]:

$$q = \frac{q_{max}bc}{1+bc} \quad (2)$$

where: q is the uptake at equilibrium concentration (mmol/g), q_{max} is the maximal uptake (mmol/g), c is the equilibrium concentration (mmol/L), b is a constant related to the free energy of adsorption (L/mmol).

Values of q_{max} and b were graphically determined from the linearized form of Langmuir model (eq. 3):

$$\frac{1}{q} = \frac{1}{q_{max}bc} + \frac{1}{q_{max}} \quad (3)$$

The calculated maximal uptake and free energy of adsorption for investigated samples are collected in Table 3.

As can be seen the data presented in Table 3 confirm the previous analysis. The highest capacity for chromium VI had sorbent prepared from chitosan with higher molecular mass. It can be seen that sorbent modification lowered the maximum capacity of about 20% in comparison to unmodified samples. In the case of sorbent prepared from low molecular weight chitosan the difference between maximal sorption for unmodified and modified samples reached even 30% value.

The Freundlich isotherm model assumes a power functional relationship between q and c , and the model is easily applicable when the experimental data are plotted in $\log q$ versus $\log c$ format (eq.4) [18,20].

$$\log q = m \log c + \log a \quad (4)$$

In this model there are two fitting parameters a and m that express a measure of physical binding. The m parameter is known as the heterogeneity index. For homogeneous materials, m should be equal to 1 and when surface gets heterogeneous character m parameter moves to zero [18, 20]. The results of fitting the sorption data to Freundlich isotherm are given in Table 3.

As can be seen the Freundlich model was not suitable to describe unmodified materials – the R^2 parameter was low. For modified materials the model was much better. What is more, according to the analysis the prepared materials were heterogenous, the m parameter was much more lower than 1 for all of them.

Table 3. Langmuir and Freundlich fitting parameters for samples

| Sample | Langmuir | | | Freundlich | |
|--------|---------------------|-------|--------------|------------|-------|
| | q_{\max} [mmol/g] | R^2 | b [L/mmol] | m | R^2 |
| A | 1.4 | 0.970 | 0.01 | 0.223 | 0.879 |
| A-1 | 1.0 | 0.907 | 0.10 | 0.362 | 0.970 |
| B | 1.6 | 0.963 | 0.10 | 0.531 | 0.827 |
| B-1 | 1.3 | 0.967 | 0.15 | 0.437 | 0.981 |

The Dubinin-Radushkevich isotherm approach helps to study interaction between adsorbate and sorbent [20]. The approach is used generally to distinguish the nature of sorption: if it is physical or chemical one. The isotherm is expressed by equation 5.

$$\ln q = \ln q_{\max} - K_{DR} \varepsilon^2 \quad (5)$$

where: q_{\max} is the maximum adsorption capacity of material [mmol/g], K_{DR} is the Dubinin-Radushkevich constant [kJ^2/mol^2], ε is the Polanyi potential (equation 6):

$$\varepsilon = RT \ln\left(1 + \frac{1}{c}\right) \quad (6)$$

K_{DR} is related with the free energy (E , [kJ/mol]) of adsorption per molecule of adsorbate when it is transferred to the surface of the solid from infinity. The adsorption behavior could be predicted from the sorption energy (equation 7 [20]).

$$E = (2K_{DR})^{-0.5} \quad (7)$$

When the E value is in the range of 1 – 8 kJ/mol the process is controlled by physical, and when is larger than 8 kJ/mol by chemical sorption. The parameters of Dubinin-Radushkevich isotherm are given in Table 4.

Table 4. The Dubinin-Radushkevich fitting parameters for samples

| Sample | q_{\max} [mmol/g] | R^2 | E [kJ/mol] |
|--------|---------------------|-------|------------|
| A | 1.5 | 0.955 | 6.2 |
| A-1 | 1.0 | 0.906 | 5.1 |
| B | 1.8 | 0.916 | 6.0 |
| B-1 | 1.2 | 0.951 | 4.5 |

For all investigated samples the value of E was located between 1 – 8 kJ/mol. It meant that in both cases physical adsorption dominated. The maximum sorption capacity was similar to value obtained for the Langmuir model.

Figure 6 shows kinetics of chromium VI uptake. It could be noted that maximum uptake of ions for sample A and B was reached after 7 hours. For modified samples A-1 and B-1 the maximum uptake of chromium was reached within 5 hours. For all samples chromium was quite quickly sorbed at the first minutes of the process (50% of maximum uptake was observed after 75 min for modified chitosan and after 90 min for unmodified samples). It should be noted that modification decreased the sorption capacity but accelerated the sorption process.

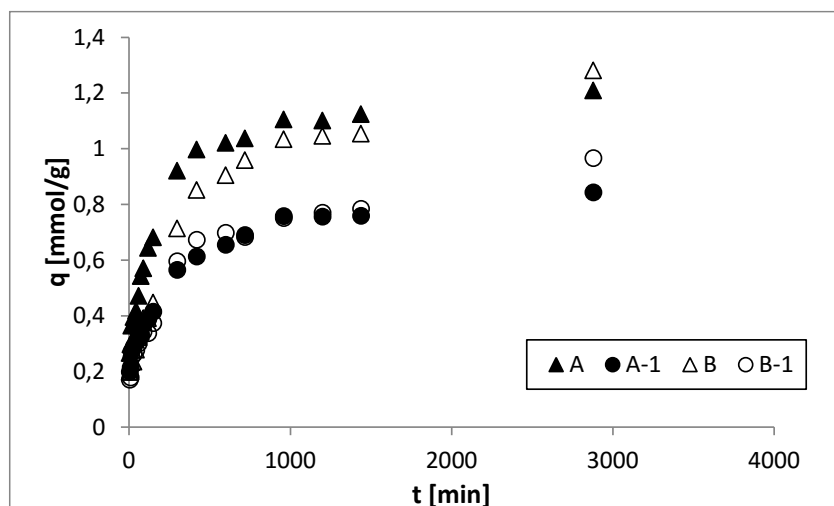


Figure 6. Kinetic sorption for investigated samples.

Sorption kinetics is the other major characteristics to define the efficiency of sorbents. In order to examine the rate controlling mechanism, the diffusion model and conventional kinetics modeling of sorption were applied.

The kinetic data were fitted to diffusion models derived the second Fick's law (equations 8 and 9) to find the rate determining steps [21, 22].

$$k_a t = -\ln\left(1 - \frac{q_t}{q_e}\right) \quad (8)$$

where : q_t and q_e represent the amount of adsorbed species (mmol/g) at any time t and at equilibrium time, respectively, k_a represents the sorption rate constant (min^{-1}).

Sorption rate constant k_a (min^{-1}) can be calculated from the plot of $-\ln(1 - \frac{q_t}{q_e})$ vs. time.

$$k_a t = -\ln(1 - (\frac{q_t}{q_e}))^2 \quad (9)$$

where: k_b is the sorption rate constant (min^{-1}), q_e and q_t are the amount of adsorbed species (mmol/g) at equilibrium and at time t .

Sorption rate constant k_b (min^{-1}) can be calculated from the plot of $-\ln(1 - (\frac{q_t}{q_e})^2)$ vs. time.

Table 5 gives the slope values, the linear correlation coefficients, and the calculated values of k_a and k_b . Analyze of k_a and k_b could show for which material the process of sorption was faster. For both pair of samples, the relationship between modified and unmodified sample changed in relation to molecular weight of chitosan. For pair obtained from small molecular mass, both parameters (k_a and k_b) had the same values and they were a little higher than for pair of sorbents of higher molecular weight chitosan. It meant that for both investigated pairs of samples the sorption equilibrium was reached faster for modified chitosan microspheres. The analyze of the correlation coefficients could show what kind of diffusion controlled the process mostly. However, for the investigated samples that comparison is not so simple as R^2 coefficients have almost the same value.

Table 5. Analysis of kinetic studies

| Sample | $k_a t = -\ln(1 - \frac{q_t}{q_e})$ | | $k_b t = -\ln(1 - (\frac{q_t}{q_e})^2)$ | |
|--------|-------------------------------------|-------|---|-------|
| | k_a | R^2 | k_b | R^2 |
| A | $2.8 \cdot 10^{-3}$ | 0.993 | $2.7 \cdot 10^{-3}$ | 0.996 |
| A-1 | $3.0 \cdot 10^{-3}$ | 0.988 | $2.9 \cdot 10^{-3}$ | 0.991 |
| B | $2.2 \cdot 10^{-3}$ | 0.976 | $1.8 \cdot 10^{-3}$ | 0.989 |
| B-1 | $2.3 \cdot 10^{-3}$ | 0.973 | $1.9 \cdot 10^{-3}$ | 0.983 |

In order to predict the mechanism involved to the sorption process, several different kinetic models are applied. They are as follows: Lagergren pseudo-first and pseudo-second-order, Elovich equation, and parabolic diffusion model. Among them, the sorption kinetics is usually described by two simple kinetic models: by pseudo-first or by pseudo-second-order model [21, 23].

The sorption kinetics following the pseudo-first order model is given by equation 10 [21]:

$$\frac{dq}{dt} = k_1 (q_e - q_t) \quad (10)$$

where: q_t and q_e represent the amount of adsorbed species (mmol/g) at any time t and at equilibrium time, respectively, and k_1 represents the sorption rate constant (min^{-1}).

Integrating Eq. (10) with respect to boundary conditions $q=0$ at $t=0$, and $q=q_t$ at $t=t$, one obtains

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1 t}{2.303} \quad (11)$$

Sorption rate constant k_1 (min^{-1}) can be calculated from the plot of $\log(q_e - q_t)$ versus time.

The kinetic data can be analyzed by means of pseudo-second-order kinetics also [21]:

$$\frac{dq}{qt} = k_2 (q_e - q_t)^2 \quad (12)$$

where: k_2 is the pseudo-second-order rate constant (g/mmol min), q_e and q_t are the amount of adsorbed species (mmol/g) at equilibrium and at time t .

Varying the variables in Eq. (12) one gets

$$\frac{dq}{(q_e - q_t)} = k_2 dt \quad (13)$$

and integrating Eq. (13) for the boundary conditions $q=0$ at $t=0$, and $q=q_t$ at $t=t$, one obtains the final form:

$$\frac{t}{q_e} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (14)$$

A plot t/q versus t gives the value of the constants k_2 (g/mmol h). It is also possible to calculate q_e (mmol/g).

The experimental data were fitted with equations 11 and 13 that served for calculation of k_1 and k_2 constants the correlation coefficients (R^2). The results of kinetic analysis are given in Table 6.

Table 6. Kinetic parameters of chromium sorption

| Sample | Pseudo-first | | Pseudo-second | | |
|--------|---------------------|-------|---------------------|-------|-------|
| | k_1 | R^2 | k_2 | R^2 | q_e |
| A | $3.7 \cdot 10^{-3}$ | 0.993 | $1.2 \cdot 10^{-2}$ | 0.998 | 1.3 |
| A-1 | $2.5 \cdot 10^{-3}$ | 0.985 | $2.6 \cdot 10^{-2}$ | 0.994 | 0.8 |
| B | $2.3 \cdot 10^{-3}$ | 0.993 | $6.3 \cdot 10^{-3}$ | 0.994 | 1.4 |
| B-1 | $2.3 \cdot 10^{-3}$ | 0.981 | $1.3 \cdot 10^{-2}$ | 0.991 | 0.9 |

It can be seen that sorption kinetics for both materials fits well to pseudo-second-order mechanism. It can be seen that modification of chitosan microspheres increase the speed rate of sorption, in both cases the k_2 parameter for modified samples is higher than for unmodified analogues. Maximum sorption capacity for all materials are very similar to value obtained during analysis of sorption isotherms. The higher efficiency for chromium removal have unmodified chitosan microspheres, but the differences are not so large between modified and unmodified pair.

4. Conclusions

The membrane emulsification allowed to obtain chitosan microspheres with relatively narrow particle size distribution. The condition of emulsification influenced the properties of

synthesized beads. The best composition of continuous phase was the mixture of paraffin oil and isoctane in volume ratio 7:5 which contains two surfactants Span 20 and Span 80 in the amount 2.5 wt.% each. The optimal chitosan concentration in the dispersed phase was 1.5 wt.%, that amount of polymer in aqueous phase allowed to obtain spheres with relatively small average diameter and with high product yield.

The modification with Aliquate 336 and PEI chitosan microspheres did not change the shape of the obtained material, but affected its physicochemical properties. Modified chitosan microspheres were characterized by higher values of water regain and nitrogen content that proved an introduction of additional material containing nitrogen. However, after sorbent modification its effectiveness of chromium sorption was smaller than for unmodified microspheres.

For unmodified polymers the process of sorption followed the Langmuir model, while modified samples were better described by Freundlich model. Analysis of kinetics showed that the sorption process followed the pseudo-second model.

5. Acknowledgements

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