P-09

THE EFFECT OF TEMPERATURE AND CHITOSAN FORM ON THE PROCESS OF METAL IONS SORPTION

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1. Introduction

Unique sorptive and chelating properties of chitosan enable to bind it with metal ions, cholesterol, fatty acids, proteins [1, 2]. The reactive amine group in the glucosamine mers is responsible for the bioactivity and sorption properties of chitosan. Sorption and chelating effectiveness depends not only on the properties of chitosan, such as: degree of deacetylation, degree of polymerization, but also on the form it is used. The process of metal sorption was specially investigated from the point of view of waste water treatment and water purification. Chitosan has good metal sorption properties with regard to solutions with low metal concentrations (mg/l) [3]. Chitosan was tested for the sorption of noble metals, especially platinum [4]. Unmodified (raw) chitosan is most effective in acidic medium, particularly in a form of solution, while in alkaline or neutral media its efficiency decreases [1, 5].

Microcrystalline chitosan (MCCh) deserves special attention as it has high ability to bind metal ions in neutral and alkaline environment. Independently of transformations in acidic medium, microcrystalline chitosan is an active chelating ligand in relation to cobalt (II), zinc (II), nickel (II) and manganese (II) ions (forms complexes with the participation of amine group nitrogen) at a pH corresponding to physiological conditions and a hydrolizing agent to copper (II) [6, 7].

Metal ions and their biological function in human organism have been interest to scientists for a long time. It is a well-known fact that they play important roles in biological systems and processes. However, the concentration of metal ions in an organism is an essential factor and it must be maintained with in the right limits. Both, the deficits and excessive amounts of elements the organism is supplied with lead to occurrence of metabolic disorders. Maintaining the balance between supplying and demand, use and excretion of bioelements from a human organism is particularly important [8]. Adjuvant preparations in the treatment of obesity, e.g. 'Chitosan' and 'Chitinin', lower cholesterol level in blood. However, due to the ability of chitosan to chelate meal ions, the diet should be supplemented with mineral salts of: iron, zinc, manganese, calcium, magnesium.

The present work is a part of the investigations focussed on sorption of metals, especially zinc, calcium and magnesium, on different form of chitosan. The carried out experiments point to the effect of temperature (20-60 °C) and the form of polymer on the process of sorption.

2. Materials

Samples of shrimp chitosan from Primex (Norway) and Chemopol (India) were obtained from the Institute of Chemical Fibres in Łódź. Shrim chitosan obtained from Tech Food Trading Sp. z o.o. (Warsaw) and krill chitosan from Sea Fisheries Institute (Gdynia) were also used in the study. Chitosan samples were in the form of flakes of various size, granulated powder, lyophilised and membrane. The membrane was obtained from microcrystalline chitosan gel.

The selected properties of the studied forms of chitosan are presented in Table 1.

Complexometric titration method was used to determine metal ions content in the solution after completion of the sorption process by selected chitosan samples [9].

3. Results and discussion

The influence of the polymer form (gel, flakes, powder) on the process of metal ions sorption was studied. As it is indicated by the results of the determinations of the swelling

Tabela 1. *The selected properties of the studied forms of chitosan; Mv – average molecular weight, DD – deacetylation degree, SD – swelling degree (SD was calculated from the formula: SD (%) =* $(m_1 - m_0)/m_0 \times 100\%$*; where* m_1 *– weight of wet membrane before drying (mg),* m_0 *– weight of membrane after drying (mg),.*

Sample	Form	Obtained from	Mv, kDa	DD, %	SD, %
Ch 1	large flakes	IWCh (Chemopol)	269	91.0	82.2
Ch 2	flakes	IWCh (Chemopol)	200	75.0	91.0
Ch 3	flakes	IWCh (Chemopol)	240	72.6	123.9
Ch 4	membrane	IWCh (Chemopol)	196	80.6	142.4
Ch 5	flakes	IWCh (Chemopol)	284	73.4	246.9
Ch 6	powder	Tech Food Trading	201	90.3	282.4
Ch 7	flakes	MIR	667	70.0	331.5
Ch 8	lyophilised	IWCh (Primex)	237	84.3	382.2
Ch 9	fine flakes	MIR	261	93.0	649.0
Ch 10	fine flakes	MIR	649	93.0	696.4
Ch 11	lyophilised	IWCh (Chemopol)	202	90.0	707.4
Ch 12	hydrogel (3.2%)	IWCh (Chemopol)	196	80.6	868.0

degree (SD) of the studied chitosans (Table 1), this parameter depends on their form, which in turn is apparent in the sorption ability of metal ions (Figure 1).

As it is indicated by the results from (Figure 1) the amount of adsorbed metal ion depends on the swelling ability of chitosan. This dependence is more visible for zinc ions, less for calcium ions and the least for magnesium ions.

The dependence of chitosan samples sorption ability on temperature was proved. The effectiveness of metal ion sorption (Zn^{++}, Mg^{++} and Ca^{++}) by the selected samples of chitosan at three temperatures (20 °C, 40 °C i 60 °C) is compared in Figure 2.

Chitosan in the form of fine flakes with high degree of swelling and deacetylation effectively binds zinc ions already at 20 °C (over 50%). The sorption ability of this chitosan with regard to zinc ions and also calcium ions increases along with the rise in temperature. At higher temperature, particularly at 60 °C, also the samples of chitosan of smaller degree of fragmentation and swelling show high effectiveness of sorption regarding these ions. The influence of temperature and swelling degree on sorption ability of the polymer with regard to magnesium ions was less noticeable. Chitosan in the form of fine flakes turned out to be a better sorbent for these ions.

The sorption of metal ions at various temperatures by two forms of microcrystalline chitosan (hydrogel and membrane obtained from it) is compared in Figure 3.

As it is show in Figure 3, the physical form of microcrystalline chitosan (MCCh) affects the adsorption ability of metal ions. Metal ions, particularly zinc and calcium ions, are more

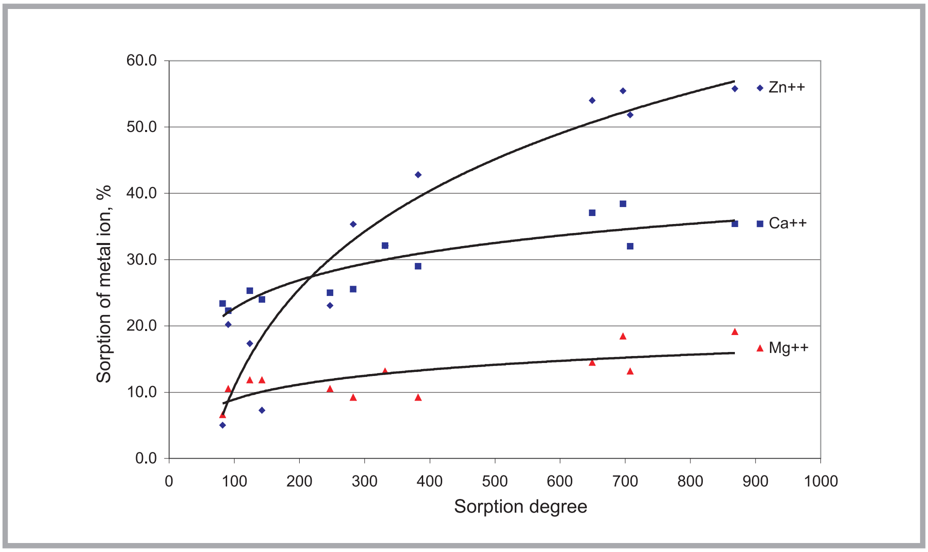

Figure 1. *The influence of the sweeling degree of the studied chitosans on ability of sorption metals ions.*

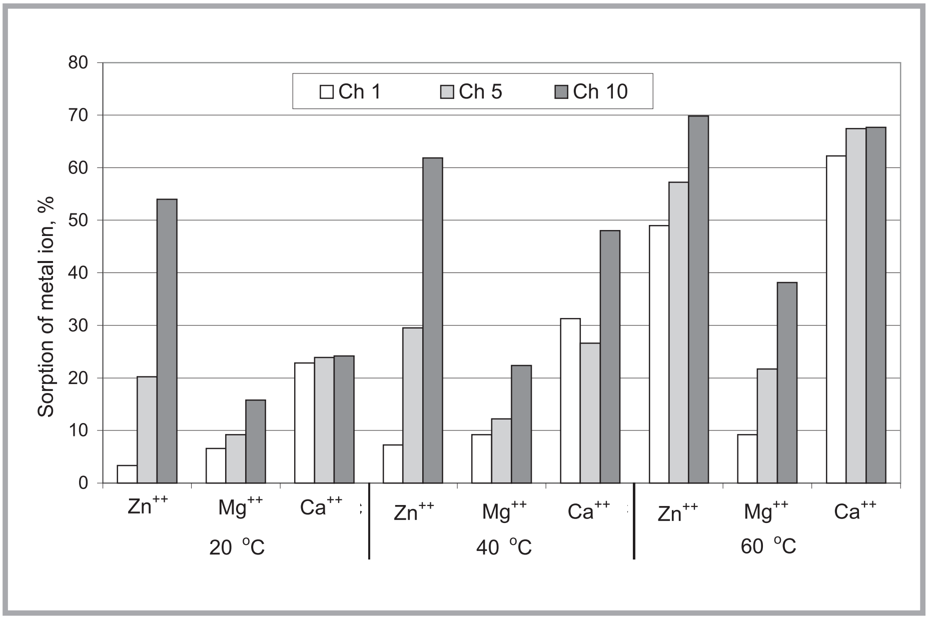

Figure 2. *The dependence of chitosan samples sorption ability on temperature.*

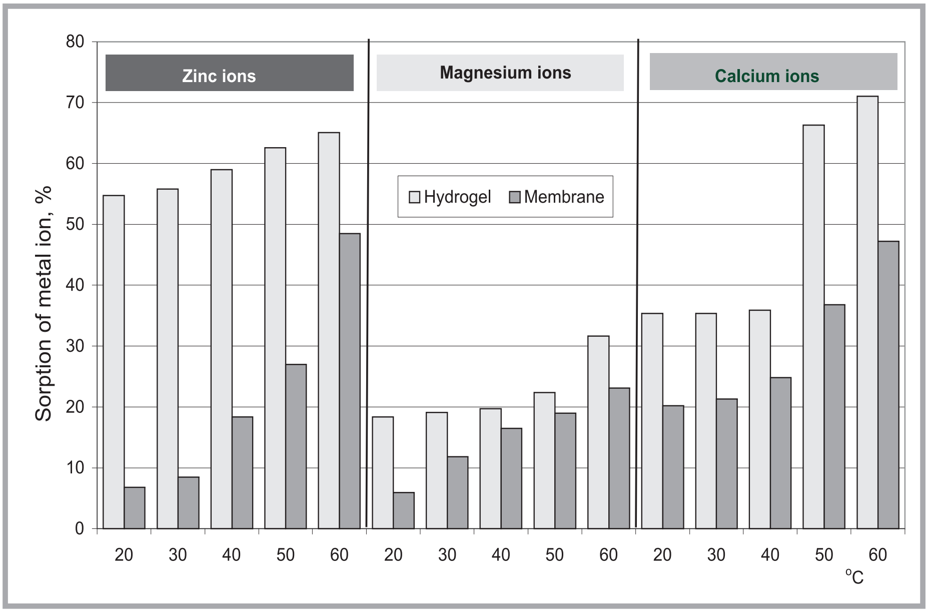

Figure 3. *The influence of temperature on sorption of metal ions by hydrogel and membrane of chitosan.*

effectively bound by the sample of MCCh in the form of hydrogel of the highest degree of water absorption. The developed inside surface of MCCh in the form of a hydrogel has an influence on a better availability for the solvent, metal ion and therapeutic substance. Over 50% of zinc ions from the solution were adsorbed by this form of chitosan already at room temperature. Adsorption with regard to calcium and magnesium ions remains at a lower level (from about 20% to about 30%). The sorption ability of hydrogel towards metal ions increases along with the rise in temperature (particularly for calcium ions). The membrane shows lower sorption ability with regard to all metal ions in comparison to hydrogel.

The process of Zn^{++}, Mg^{++} and Ca^{++} desorption from chitosan membrane at temp. 20 °C and 40 °C was investigated (Figure 4).

As it results from Figure 4 desorption of zinc ions from the membrane keeps at the level below 40%, irrespective of the temperature. Extending the desorption time to 2 hours did not improve the effectiveness of sorption. Irrespective of the temperature, the process of desorption of calcium and magnesium ions undergoes very quickly and already after 10 minutes over 85% of ions are released and it reaches 90% after one hour.

Preparations supplementing zinc e.g. Zincteral (zinc sulphate) are applied in the treatment or prevention of the deficit of this element in an organism. In an earlier study [10] the influence of MCCh was investigated on the rate of release of zinc sulphate, a substance easily soluble in water. The investigation of chitosan preparation revealed prolongation of the release of the therapeutic substance after combination with chitosan (Figure 5). It allows to state that

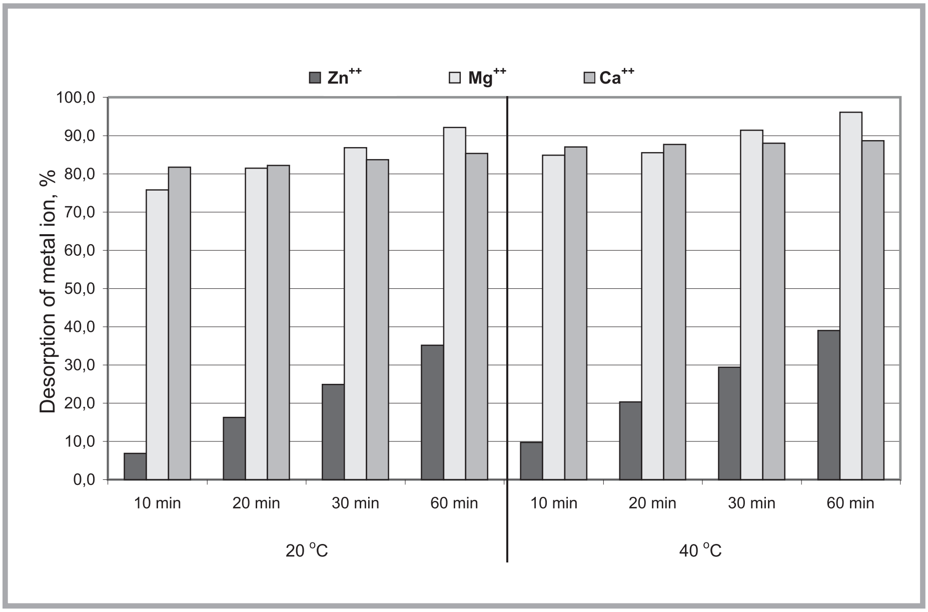

***Figure 4**. The process of metal ions desorption from chitosan membrane (Ch 4).*

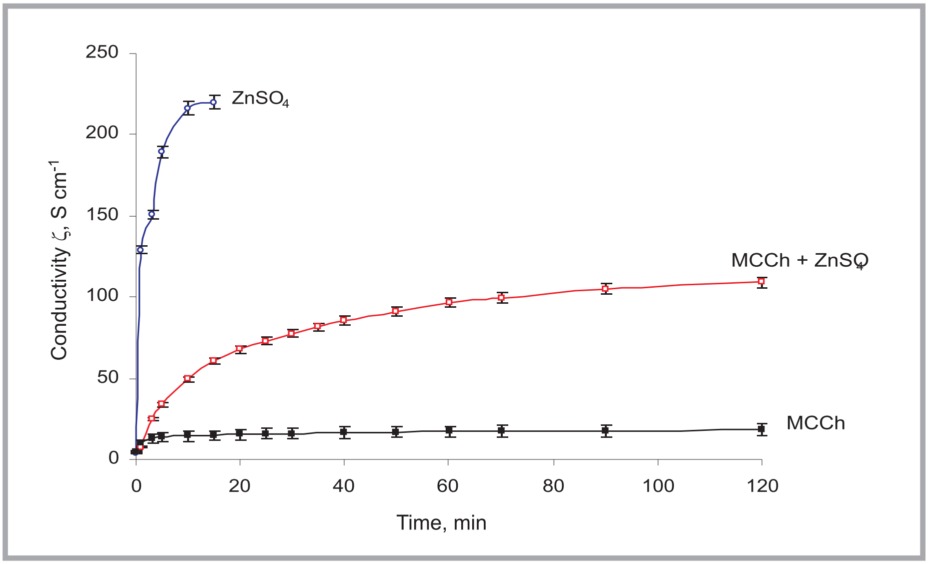

Figure 5. *Changes of conductivity values during dissolving and releasing zinc salts from chitosan preparation to water.*

microcrystalline chitosan can be used as a matrix in sorption and chelation of ions of metals playing important functions in biological processes.

4. Conclusions

The influence of the surface dimensions associated with the form of chitosan on the ability of sorption as regards metal ions was confirmed. Chitosan in the form of hydrogel had the highest effectiveness in contrary to chitosan in the large flakes which had the least effectiveness.

The dependence of chitosan samples sorption ability on temperature was proved. The increase of temperature to 60 °C distinctly affects the process of metal ions sorption (zinc, calcium and magnesium) on all forms of chitosan.

The process of Zn^{++} desorption from the membrane of chitosan was significantly slower as compared to calcium and magnesium ions, which points to prolonged release

It allows to state that microcrystalline chitosan can be used as a matrix in sorption and chelation of ions of metals playing important functions in biological processes.

5. References

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