



Sorption of copper by chitosan hydrogel: Kinetics and equilibrium



Zofia Modrzejewska^{a,*}, Grzegorz Rogacki^a, Witold Sujka^a, Roman Zarzycki^b

^a Lodz University of Technology Faculty of Process and Environmental Engineering, 90-924 Lodz, Wolczanska 213, Poland

^b Higher Vocational State School of President Stanislaw Wojciechowski in Kalisz, 62-800 Kalisz Nowy Swiat 4, Poland

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ABSTRACT

Experimental and theoretical investigation on sorption of copper ions (A) in very broad range of concentration of CuSO_4 , by chitosan hydrogel (ch) has been studied. Equilibria were described by Langmuir, Freundlich, Langmuir-Freundlich, Redlich-Peterson, Toth and Dubinin-Raduszkiewicz equations. To describe sorption kinetics a new model was proposed, which combine chemical reaction on sorbent surface and intraparticle diffusion. The process of sorption is described by two parameters: diffusion coefficient $D_{AB} = 0.623 \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1}$ and surface process rate constant $k_v = 16.9 \cdot 10^{-4} \text{ s}^{-1}$. Calculation base on the model properly correlates with experimental data.

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1. Introduction

Chitosan is a copolymer of (1,4- β -)-2-acetylamino-2-deoxy-D-glucopyranose and (1,4- β -)-2-amino-2-deoxy-D-glucopyranose with a chemical structure shown in Fig. 1. It is the main derivative of chitin formed as a result of its alkaline deacetylation.

It is a polymer which is characterized by good adsorption properties, mainly in relation to metal ions – it is able to form chelate compounds. Thus, it is possible to apply chitosan in binding metal ions, e.g. to remove heavy metal ions and radioisotopes from wastewater, recover valuable metal ions and also eliminate unnecessary metal ions from drinking water. In biomedical engineering it is used to adsorb fats, cholesterol and mycotoxins [1–3].

Primarily, amino and hydroxyl groups are involved in the process of binding metal ions by chitosan. Hence, the complex-forming properties and durability of a metal-chitosan complex depend on polymer parameters, i.e. deacetylation degree, the length of a polymer chain and crystallinity. Equally important is the physical form of an adsorbent and properties of an adsorptive, such as composition, pH and ionic strength [4–11].

The rate of adsorption depends among the others on the rate of inner diffusion, so it is determined by the geometric form of the adsorbent. Therefore, chitosan is modified physically by preparing different forms, such as powders (micro- and nanoparticles), gel beads, foam, membranes: fibers or capillary fibers [12–21].

Hydrogel beads are the basic adsorptive material. Their unique adsorptive properties result from the fact that they have a very well developed inner surface and contain water in their structure which increases the rate of metal ion transport into the bead.

Sorption kinetics is mainly controlled by various steps including diffusion and reaction processes. Four steps can be enumerated and applied to copper ion removal:

1. Bulk diffusion – ion transfer from the bulk solution to the boundary film bordering the sorbent surface.
2. Film diffusion – ion transport from the boundary film to the surface of the sorbent
3. Intraparticle diffusion – transfer of ion from the surface to the intraparticle active sites
4. Chemical reaction – uptake of the metal ion on the active sites, via chelating, ion-exchange or complexation.

To describe sorption kinetics of metal ions onto chitosan simplified models can be used. The pseudo-first order model, pseudo-second order model, and intraparticle diffusion model are most widely used [22–38].

In the present study, sorption properties of copper (kinetics and equilibrium) for spherical hydrogel structures formed by the phase inversion method are determined. For the analysis of adsorption the selected the copper ions due to the fact that the chemical mechanism of sorption of these ions are most often described in the literature, but the adsorption process (kinetics and equilibrium) is limited. Also the chitosan hydrogels may be used in the removal of these ions from aqueous solutions and the hydrogel sorbent may be used as antibacterial agent, eg. in the biomedical or

* Corresponding author.

E-mail address: zofia.modrzejewska@p.lodz.pl (Z. Modrzejewska).

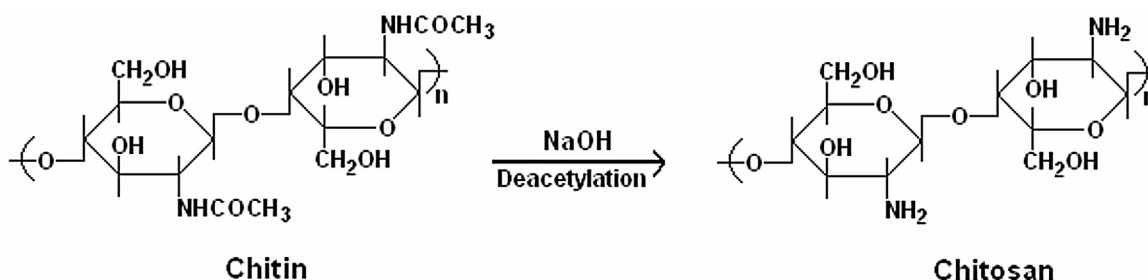


Fig. 1. Chemical structure of chitin and chitosan.

environmental engineering. The kinetics was described using models known from the literature. Our own model was also developed. The model assumes that during sorption of ions in hydrogel the process of diffusion in inside the granule structure (adsorbent pores) occurs at the same time as the irreversible chemical reaction on inner granule walls. Such a model has not been proposed in the literature so far. This is an important novelty of the present study.

2. Experimental

2.1. Structural characteristics of the adsorbent

Hydrogel beads were produced by the phase inversion method. To form the beads 4% chitosan solutions with molecular mass $M_w = 688$ kDa [$M_n = 131$ kDa] and 84% deacetylation degree were used. A solvent was 2% acetic acid. Prior to formation, the solutions were deaerated under the pressure of 5×10^3 Pa. Coagulation was carried out at 10% NaOH.

The chitosan solution was supplied from a tank by a peristaltic pump to capillary needle. The forming drops of chitosan were directed to a coagulation bath in which they stayed for 24 h. Next, chitosan beads were rinsed with distilled water until reaching neutral pH of water. The structure is shown in Fig. 2.

Fig. 2 shows hydrogel granules without magnification and their structure seen under the electron microscope in different places. It is characterized by wide pores with diameters ranging from 30 to 300 μm . On the external surface the pore diameter ranges from 300 to 350 μm . While passing to the center, the granule diameters

decrease to 30–50 μm . However, there are still broad channels as compared to the sorbed ion.

2.2. Experimental methods

In order to describe sorption kinetics of Cu^{2+} ions, the adsorbent was placed in the water solution of CuSO_4 at initial $\text{pH}_0 = 3.5$ and after specified time the concentration of Cu^{2+} ions in the liquid phase was measured. The adsorbent mass was 20 g of wet granules. An adsorptive were 250 ml samples of CuSO_4 solution with the following initial concentrations of Cu^{2+} ions: 0.157, 0.7, 1.57, 3.14, 4.72, 6.29, 7.87, 11.8 and 15.7 $\text{mmol Cu}^{2+}/\text{dm}^3$. The process carried out in batch conditions was combined with stirring in a shaker at the inclination amplitude of 8 mm, keeping temperature at a constant level of 20 °C. The stirring rate ensured elimination of the effect of external diffusion resistance on the process – the change of concentration in time at the inclination amplitudes 6 and 8 were analogous (the inclination was not bigger than $\pm 5\%$). Samples for analysis were taken every 15 min in the first hour, every 1 h in subsequent 6 h, and next once a day or every few days.

Equilibria were determined after 24 and 96 h of the process. Initial pH of the adsorptive was 5 and 3.5, respectively. Two variants were considered: i) pH was growing automatically in the process (marked by an arrow), and ii) pH was constant.

2.3. Analytical methods

The concentration of copper in the CuSO_4 solution was determined using a Perkin Elmer Plazma 400 atomic

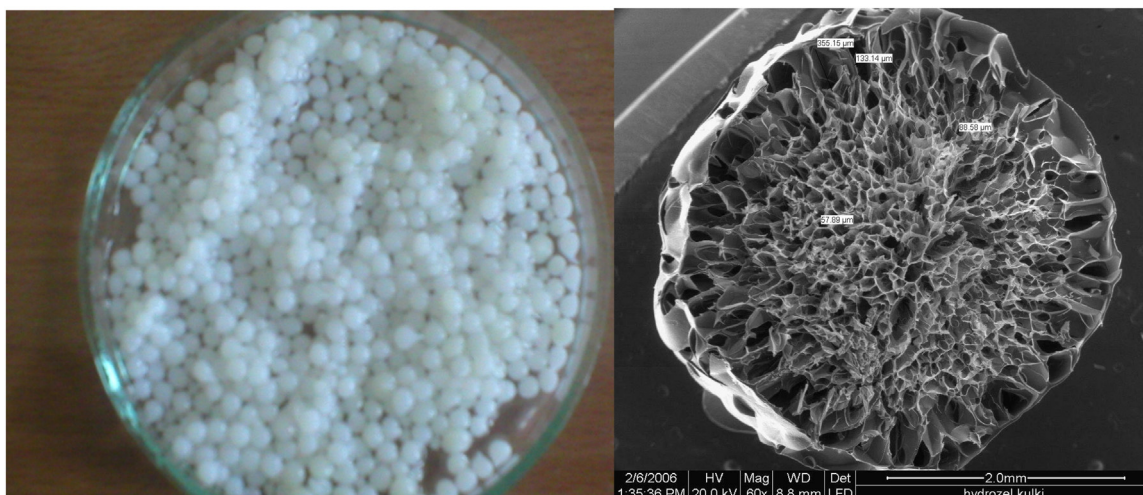


Fig. 2. Hydrogel beads formed by the phase inversion method.

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