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REMOVAL OF HEAVY METAL IONS: COPPER, ZINC AND CHROMIUM FROM WATER ON CHITOSAN BEADS

The paper deals with the application of chitosan in the form of beads to the removal of copper, zinc and chromium ions from water. The main element of the experimental equipment was a glass column, 5 cm in diameter and 30 cm high. The column was filled with chitosan beads. The research was carried out in one-, two- and three-component solutions, at the initial concentrations c_0 ranging from 50 to 70 mg/dm^3.

In the description of metal sorption kinetics, the second-order equation was used. It well describes experimental data (its correlation coefficient ranged from 0.94 to 0.99).

Keywords: *heavy metals, chitosan beads, adsorption*

1. INTRODUCTION

Industrial wastewaters often contain considerable amounts of toxic and polluting metals. It is well known that heavy metals are particularly hazardous for human health. Metals, such as mercury, lead, chromium, nickel, copper, cadmium and zinc usually demonstrate the tendency to accumulate in living organisms. In such a form they are highly toxic. There are many methods of removing heavy metal ions from water, i.e. ion exchange, reverse osmosis, adsorption, complexing or precipitation. Adsorption seems to be the most efficient and most popular technique [1], [2].

The sorption based on natural materials such as chitosan (a biopolymer produced from chitin by means of deacetylation of its acetoamide groups [3], [4]) is especially interesting for researchers. Chitin is a natural polymer found in crustacean shells, e.g. shrimps or crabs. Chitosan is characterized by many valuable fea-

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tures, e.g. bioactivity, biodegradability and unique sorption and chelating properties in relation to metal ions, including heavy metals.

The mechanism of binding metal ions to chitosan has not been fully understood yet. Various processes such as adsorption, ion exchange, and chelation are discussed as the mechanisms responsible for complex formation between chitosan and metal ions [5], [6], [7].

2. BEAD FORMATION

The subject of this paper was the use of chitosan beads applied as a packing in the column for removal of copper, chromium and zinc ions from water.

In the formation of beads from a natural polymer, the following stages can be distinguished: 1 – solving the polymer in an organic acid, 2 – formation of droplets, 3 – coagulation, 4 – washing of beads in distilled water. To improve the adsorption efficiency, chitosan was modified by addition of polyvinyl alcohol (PVA).

There are many methods of droplet formation. In this study, a pressure method was used. It is based on supplying compressed air at the overpressure below 1 kPa to a tank with chitosan solution. The chitosan solution is pressed through an orifice with a thin capillary needle (2.0 mm in diameter) mounted at the end. The pressed droplets fall freely into a cylinder filled with sodium hydroxide. The process of coagulation needs to be carried out at constant mixing.

For the purpose of this study chitosan of relatively high viscosity (50 Pa·s) was used (the beads made from chitosan of low viscosity (35 Pa·s) were less resistant to physical factors and had poorer sorption abilities, particularly at high concentrations of metal ions). The diameter of the beads ranged from 2.0 to 4.0 mm.

3. DESCRIPTION OF SORPTION KINETICS OF COPPER, CHROMIUM AND ZINC IONS

3.1. SCOPE OF THE STUDIES

The research was carried out at initial concentrations of copper, chromium and zinc ions ranging from 50 to 70 mg/dm^3, at different bed heights, i.e. 10 and 20 cm, and at variable volumetric flow rates of the solution tested, i.e. 50 and 100 cm^3/min. The efficiency of adsorption of dissolved single elements and their mixtures by chitosan beads was compared. To increase the adsorptivity of the beads, chitosan was modified by addition of polyvinyl alcohol (PVA).

3.2. RESULTS AND DISCUSSION

The sorption efficiency depends on the height of the bed – it rises with an increase in the bed height (figure 2). A similar correlation can be observed between the volumetric flow rate of the solution tested and the sorption efficiency (figure 3), i.e. the latter is significantly greater at the flow rate of 100 cm^3/min than at the flow rate of 50 cm^3/min.

The efficiencies of adsorption of copper, zinc and chromium ions from solvents containing single elements and their mixtures have been compared as well.

Whereas sorption of copper ions (figure 4) appears to be fastest when they occur with zinc ions, it is less effective when chromium and zinc ions occur simultaneously, and even slower when copper ions occur with chromium ions only. Copper ions are adsorbed least effectively when they do not occur with either of the two other elements.

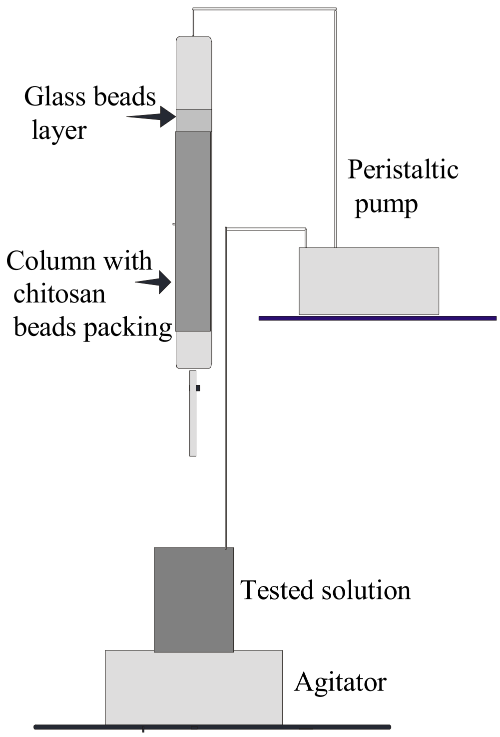

Fig. 1. Schematic diagram of the experimental set-up

In the case of chromium ions (figure 5), their sorption seems to be most effective in the presence of both copper and zinc ions at the same time. Less impressive results have been achieved with solvents containing additionally copper ions and still poorer in zinc ions. Again, the sorption has been slowest in the case of the solvent containing only the element tested.

Slightly different results have been achieved in the case of zinc ions, whose sorption turns out to be stimulated best by the presence of chromium ions, next – by copper ions, and still further – with no additives when carried out in the three-element solvent. The presence of both copper and chromium ions appears to have a negative impact on the effectiveness of zinc sorption.

In order to explore the possibilities of increasing the sorption capacity of chitosan beads, a certain amount of beads has been made from chitosan modified by polyvinyl alcohol (PVA) and tested in the solvent containing chromium ions. The sorption capacity of the PVA-modified chitosan has been greater than that of the pure chitosan, as shown in figure 7.

Figure 1 shows the experimental equipment. Its main element is a glass column, 5 cm in diameter and 30 cm long. The column is packed with chitosan beads. A layer of glass beads ensures that the solution is evenly distributed on the entire surface of the chitosan bead packing. The adsorption process was carried out in a flooded column.

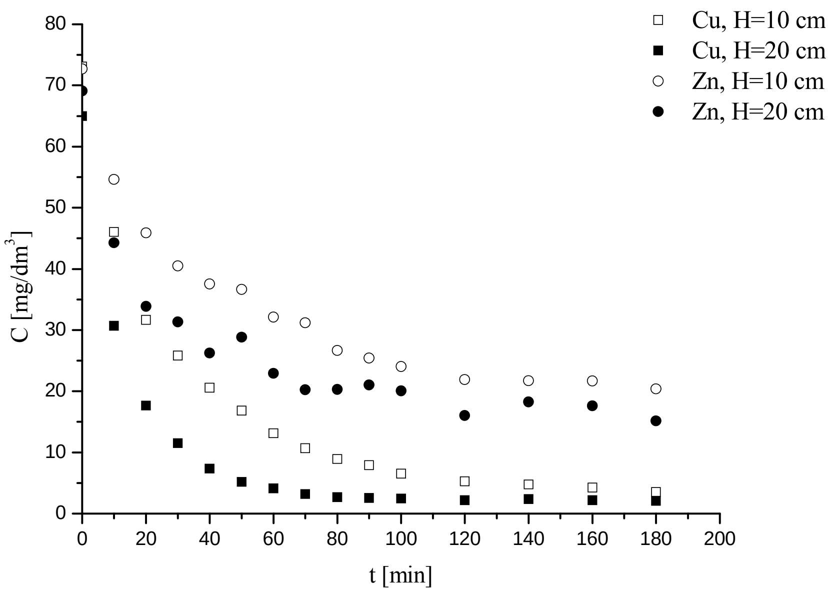

Fig. 2. Comparison of the adsorption efficiency of copper and zinc ions at two different heights of the bed: 10 and 20 cm

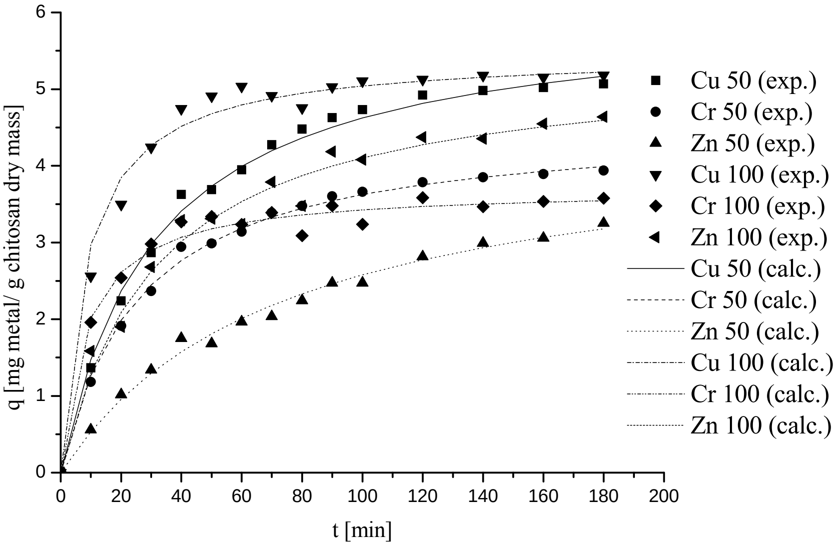

Fig. 3. Comparison of the adsorption efficiency of copper, chromium and zinc ions at two different flow rates of the solution tested (50 and 100 cm^3/min)

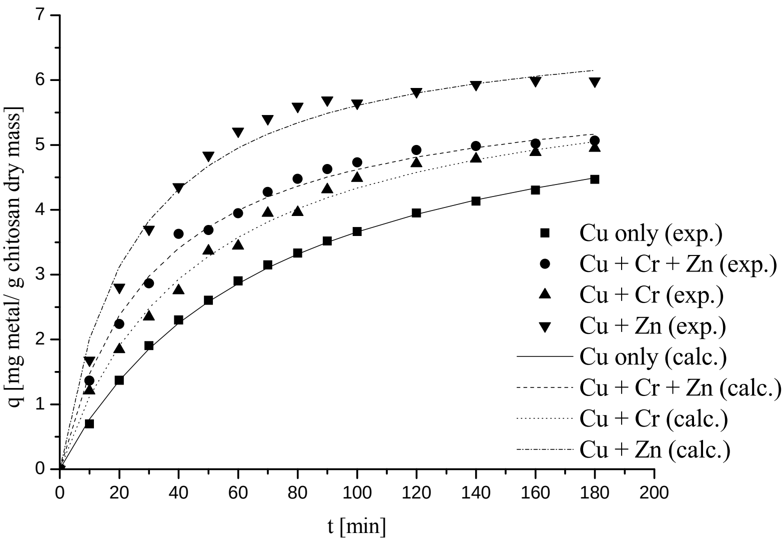

Fig. 4. Comparison of the adsorption efficiency of copper ions from the single-component solution and from the solution containing additionally chromium and zinc ions

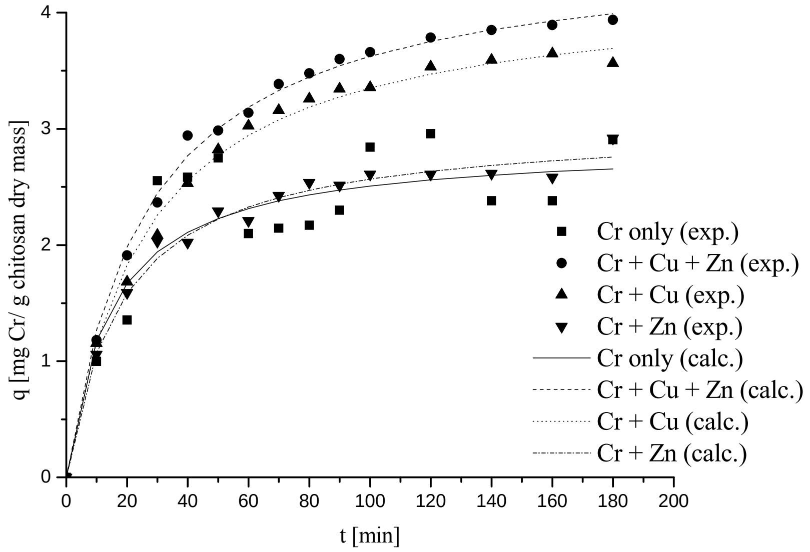

Fig. 5. Comparison of the efficiency of chromium ion adsorption from the single-component solution and from the solution containing additionally copper and zinc ions

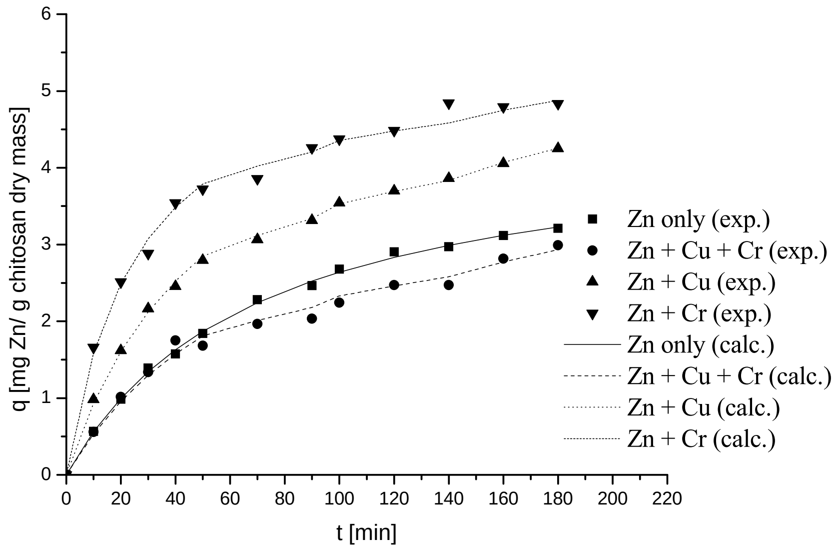

Fig. 6. Comparison of the efficiency of zinc ion adsorption from the single-component solution and from the solution containing additionally copper and chromium ions

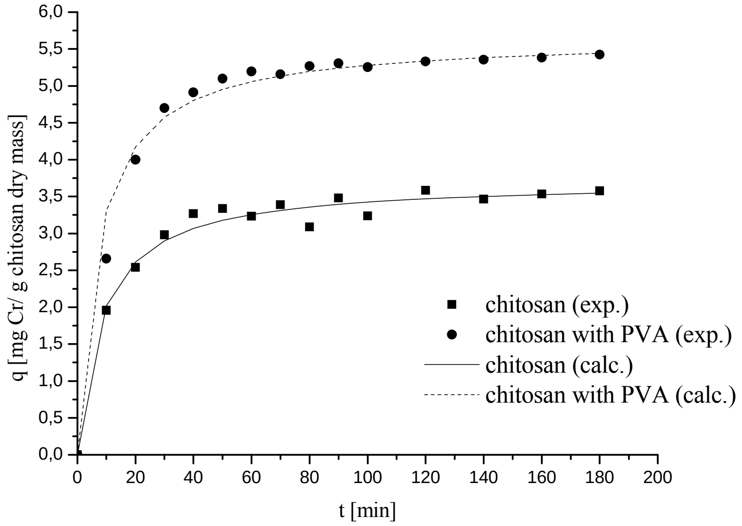

Fig. 7. Comparison of the efficiency of chromium ion adsorption by pure chitosan and PVA-modified chitosan beads

The following equation was used to describe the sorption kinetics [8]:

$$\frac{t}{q_t} = \frac{1}{K' \cdot q_e^2} + \frac{t}{q_e}, \tag{1}$$

where the adsorption capacity q_t is

$$q_t = (C_0 - C) \cdot \frac{V}{m}, \tag{2}$$

and the equilibrium adsorption capacity q_e is

$$q_e = (C_0 - C_e) \cdot \frac{V}{m}. \tag{3}$$

In the above equations:

C_0 – the initial ion concentration (mg/dm^3),
C – the ion concentration after the time t (mg/dm^3),
C_e – the equilibrium ion concentration (mg/dm^3),
V – the solution volume (dm^3),
m – the dry mass of the sorbent (g),
t – the time (min),
q – the adsorption capacity (mg/g),
K' – the constant of sorption kinetics (g/mg·g).

In order to determine the constants K' and q_e, the straight-line plots representing t/q_t against t were used (figures 7, 8, 9). Figure 10 shows a comparison of experimental and calculated values.

The adsorption kinetics of metal ions in the column is reliably described by equation (1). The correlation coefficient ranging from 0.94 to 0.99 confirms good agreement of calculated values with experimental data.

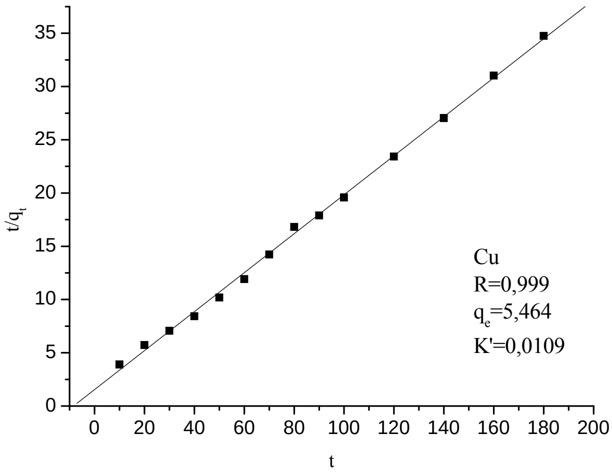

Fig. 8. Determination of constants K' and q_e of copper ion adsorption (height of the bed of chitosan beads H = 10 cm; volumetric flow rate Q = 100 cm^3/min)

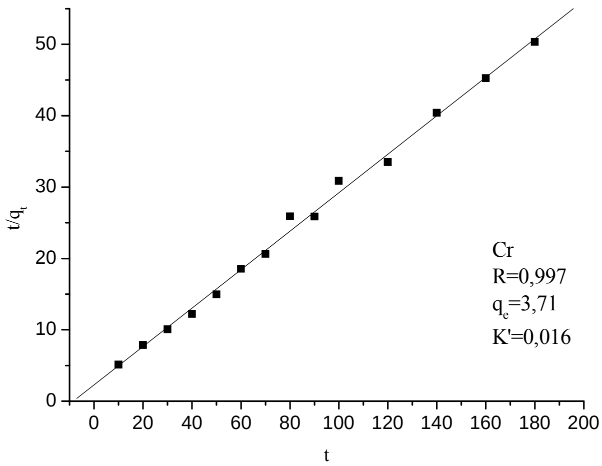

Fig. 9. Determination of constants K' and q_e of chromium ion adsorption (height of the bed of chitosan beads H = 10 cm; volumetric flow rate Q = 100 cm^3/min)

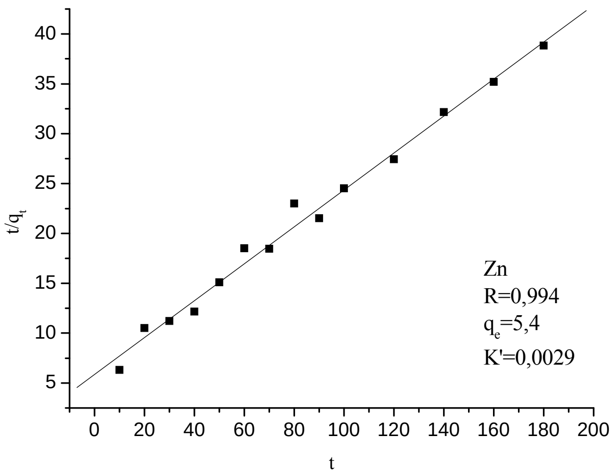

Fig. 10. Determination of constants K' and q_e of adsorption of zinc ions
(height of the bed of chitosan beads H = 10 cm; volumetric flow rate Q = 100 cm^3/min)

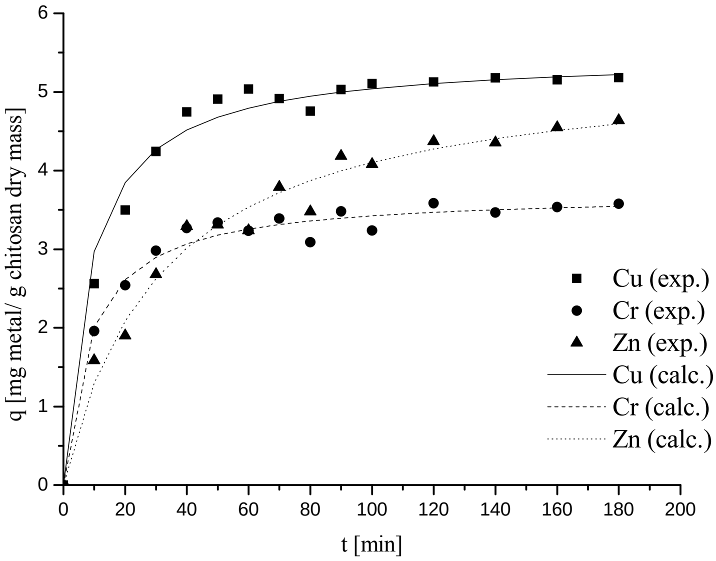

Fig. 11. Comparison of experimental data and values calculated from the formula
for adsorption of copper, chromium and zinc ions (height of the bed of chitosan beads
H = 10 cm, volumetric flow rate Q = 100 cm^3/min)

4. CONCLUSIONS

The subject of this paper was to analyse the process of adsorption of copper, chromium and zinc ions on the beads made of pure chitosan and PVA-modified chitosan. First of all, chitosan beads modified by polyvinyl alcohol more efficiently remove chromium ions from water than pure chitosan. Secondly, other metal ions in the solution have a significant influence on the adsorption of copper, chromium and zinc ions. According to experimental results an adsorption of metal ions is much more efficient in the solutions of mixtures than in the solutions of single ions.

As expected, the higher the bed and the greater the volumetric flow rate of the solution tested, the more efficient the process of metal ions' adsorption.

The experimental results obtained were used to describe the adsorption kinetics. The comparison of the calculated and experimental values reveals that equation (1) is in good agreement with the experimental data, which is confirmed by the correlation coefficient ranging from 0.94 to 0.99.

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