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# Adsorption of Cr(VI) on Cross-Linked Chitosan Beads

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**Abstract:** A possibility of Cr(VI) removal by the adsorption method is discussed in the paper. An adsorbent were hydrogel chitosan beads are produced by the phase inversion method (by changing pH). The possibility of removing Cr(VI) ions by both pure chitosan hydrogel and its chelate compounds (chitosan cross-linked with Cu(II) and Ag(I) ions) was investigated. The adsorption proceeded from the solutions of potassium dichromate and ammonium dichromate $(NH_4)_2Cr_2O_7$ and $K_2Cr_2O_7$. The process rates and adsorption isotherms were determined and described by relevant equations. The process rate was described by the pseudo- and second-order equations, and adsorption equilibria by the Langmuir equations. A slight advantageous change in adsorption properties of chitosan beads was revealed after cross-linking (for chromium concentration up to $10\,g/dm^3$). A maximum adsorption was $1.1\,g_{Cr}/g$ chitosan. Results of the studies show that chitosan hydrogel proves useful in the removal of Cr(VI) ions, additionally, cross-linking with Cu(II) and Ag(I) ions has an advantageous effect in the case of low-concentrated solutions.

**Keywords:** Chitosan, adsorption, Cr(VI) ions

## INTRODUCTION

Chromium groups belong to the metals that are important because of their practical applications. Chromium oxide(VI) $CrO_3$ which is a chromic acid

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anhydride is well soluble in water (166 g $CrO_3/100$ g $H_2O$), and its solution reveals a strongly oxidizing action. For this reason, the chromic acid anhydride is the basic component of all electrolytic baths used for deposition of metallic chromium and finds application as an oxidizing agent. A problem is, however, its high toxicity and even carcinogenic properties (a lethal dose for man is 3.0 g), hence it is necessary to reduce it to a safe concentration.

Adsorption is one of the frequently applied methods for the removal of pollutants from liquid and gas media. The efficiency of this method depends first of all on the selection of a proper adsorbent to remove a compound.

A polymer with interesting adsorption properties is chitosan, a chitin derivative. Chitin is a polymer of N-acetyl-D-glucosamine with $\beta$-1,4 glycosidic bonds. Chitosan is a product of its deacetylation.

Adsorption properties of chitosan and its ability to form chelate compounds were used mainly in the separation of metal ions of transient groups, and particularly in removing toxic ions of heavy metals. Many studies have been published on the adsorptivity of Cu(II), Ni(II), Zn(II), Cd(II), Pb(II), and Hg(II) (1–15).

Chitosan was also applied to remove Cr(VI) ions. The removal of these anions in an adsorption column packed with a chitosan bed was presented in literature (15). The authors removed Cr(VI) ions during membrane separation using hydrogel chitosan membranes and the same membranes cross-linked with Cu(II) ions (16, 17), and also during adsorption using hydrogel chitosan beads and cross-linked Ag(I) ions (18). Relatively high values of the maximum equilibrium adsorption reaching 1 g/g were obtained. For comparison, in the studies presented in literature, a maximum adsorption of Cr(VI) ions on other sorbents of natural origin was markedly lower and reached 57 for clay, 43.9 for peat and 0.65 (mg/g) for zeolite.

The aim of this study was to determine adsorption properties of hydrogel chitosan beads and their chelate compounds (with copper and silver) to remove Cr(VI).

## MATERIALS AND METHODS

### Characteristics of the Adsorption Bed

Adsorption of Cr(VI) was a static process. An adsorbent consisted of porous hydrogel chitosan beads $3.2 \times 10^{-3}$ m in diameter. They were produced by the phase inversion method from a 4% chitosan solution with mean molecular weight $2 \cdot 10^5$ D and deacetylation degree 68%—produced from Antarctic krill by the Sea Fisheries Institute in Gdynia—Poland. 4% acetic acid was used as a chitosan solvent. The beads were coagulated in 10% sodium hydroxide and left in it for 24 h; afterwards they were washed with distilled water until reaching a neutral pH of the water in which the beads were left.

A chelate chitosan beads was obtained by chitosan cross-linking with Cu(II) and Ag(I) ions. The cross-linking was obtained by placing chitosan beads in the solutions of cross-linking ions at different concentrations [$CuSO_4$: 0.2, 1.0, 40 $g_{Cu}/dm^3$; $Ag_2SO_4$: 0.2, 1.0, 5.4 $g_{Ag}/dm^3$]. After having reached equilibrium conditions, the beads were washed with water.

## Characteristics of the Tested Medium

Adsorption proceeded from the solutions of potassium dichromate $K_2Cr_2O_7$ and ammonium dichromate $(NH_4)_2Cr_2O_7$ at Cr(VI) concentrations from 0.1 to 44 $g/dm^3$.

## Analytical Methods

The concentration of Cr(VI) was determined by the ICP method using a Plasma 400 emission spectrometer (Perkin Elmer) and by the spectrophotometric method in a Lambda 11 spectrometer of the same make.

## Investigations

The studies covered:

- Description of the adsorption of Cr(VI) ions on hydrogel chitosan beads formed by the phase inversion method—(specification of adsorption isotherms and process rate).
- Determination of the effect of cross-linking of hydrogel beads with Cu(II) and Ag(I) ions on adsorption properties and selection of an optimum concentration of a cross-linking ion.

### Description of Adsorption of Cr(VI) Ions on the Bed of Chitosan Beads Formed by the Phase Inversion Method

The process was investigated in a static system, at the temperature 20°C, using samples of the volume 0.25 $dm^3$. Adsorption isotherms were prepared for Cr(VI) concentrations ranging from 0.1 $g/dm^3$ to 44 $g_{Cr}/dm^3$. The process rate was determined on the basis of changes in the mass of Cr(VI) adsorbed in 350 h. The mass of adsorbed Cr(VI) was determined in terms of a mass unit of dry adsorbent. The adsorbent consisted of hydrogel chitosan beads of mass 20 g (1 g pure chitosan).

The process rate, i.e. the change of mass of adsorbed Cr(VI) in time is illustrated in Fig. 1 and the adsorption isotherms are shown in Fig. 2.

From the curves that describe the process rate it follows that in the static system adsorption occurs mainly in the first hour. Equilibrium conditions are

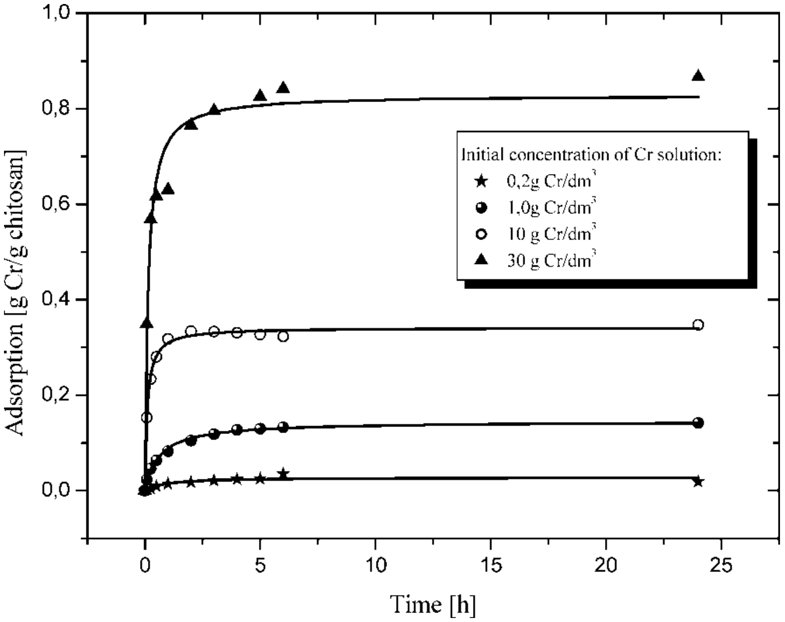

***Figure 1.*** Cr(VI) adsorption rate.

established after six hours. To describe the process of adsorption in time, a simple pseudo-first order model (Ho, McKay, Lagergren) frequently used in a solid–liquid system was applied:

$$\frac{dq_t}{dt} = k_1(q_e - q_t)$$

where:

$k_1$ – adsorption rate constant

$q_e$ – equilibrium adsorption is calculated from the Langmuir isotherm and kinetic pseudo-second order model used by Hamadi:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$$

where:

$k_2$ – rate constant for pseudo-second order adsorption.

The process can be described with a small error by pseudo, or better by second order equation, except for the concentrations being at the limit of solubility. In this case the process proceeds at two stages: up to 5 h the run is like that at lower concentrations, and then adsorption increases significantly which can be due to crystallisation. The correlation equations for subsequent concentrations are given in Table 1.

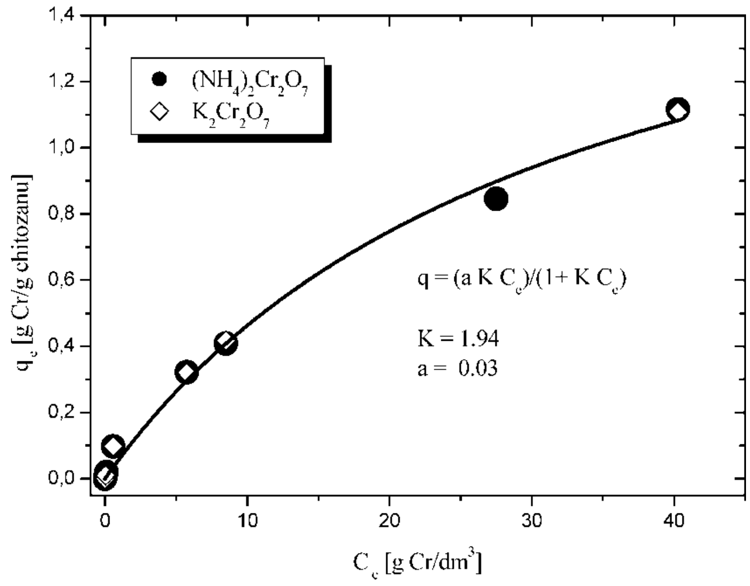

***Figure 2.*** Cr(VI) adsorption isotherm.

The isotherms of Cr(VI) ion adsorption from the solution of both ammonium and potassium dichromate, can be described by the Langmuir equation $q = aKC_e/1 + KC_e$. The values of coefficients K and a for subsequent isotherms are given in Table 3. Constants a and K in the equations describing the two isotherms differ only slightly.

***Table 1.*** Description of Cr(VI) adsorption process

| Initial concentration | $q_t = q_e(1 - e^{-k_1 t})$ $q_e\ [g_{Cr}/g_{chitosan}]$, $k_1\ [1/h]$ | $q_t = q_e(q_e k_2 t/1 + q_e k_2 t)$ $q_e[g_{Cr}/g_{chitosan}]$, $k_2\ [1/h]$ |
|---|---|---|
| $0.2\,g_{Cr}/dm^3$ | $R^2 = 0.87$<br>$q_e = 0.026 \pm 0.002$<br>$k_1 = 0.738 \pm 0.249$ | $R^2 = 0.84$<br>$q_e = 0.028 \pm 0.004$<br>$k_2 = 39.791 \pm 24.570$ |
| $1.0\,g_{Cr}/dm^3$ | $R^2 = 0.97$<br>$q_e = 0.129 \pm 0.004$<br>$k_1 = 1.163 \pm 0.166$ | $R^2 = 0.99$<br>$q_e = 0.145 \pm 0.003$<br>$k_2 = 10.718 \pm 1.085$ |
| $10\,g_{Cr}/dm^3$ | $R^2 = 0.98$<br>$q_e = 0.327 \pm 0.006$<br>$k_1 = 5.596 \pm 0.631$ | $R^2 = 0.99$<br>$q_e = 0.342 \pm 0.003$<br>$k_2 = 27.644 \pm 2.144$ |
| $30\,g_{Cr}/dm^3$ | $R^2 = 0.89$<br>$q_e = 0.724 \pm 0.012$<br>$k_1 = 6.469 \pm 1.771$ | $R^2 = 0.93$<br>$q_e = 0.766 \pm 0.029$<br>$k_2 = 11.920 \pm 3.693$ |

## The Effect of Cross-Linking with Cu(II) and Ag(I) Ions on Bed Adsorption Properties

To determine changes in chitosan hydrogel adsorptivity induced by previous cross-linking with Cu(II) and Ag(I) ions, the isotherms of Cr(VI) ion adsorption on these cross-linked hydrogel beads were determined in similar conditions.

Figures 3a and 3b shows sorption isotherms for chitosan hydrogel cross-linked with Cu(II) ions and Fig. 4 illustrates the isotherms for a hydrogel cross-linked with Ag(I) ions. An example of the adsorption process proceeding in time for the initial adsorptive concentration equal to 0.1 and 1 $g_{Cr}/dm^3$ on a hydrogel chitosan adsorbent and the one cross-linked is shown in Fig. 5 and 6.

The isotherms of Cr(VI) ion adsorption on the beads cross-linked with Cu(II) ions indicate the following:

- cross-linking of the beads with Cu(II) ions has a slight effect on changes in the adsorption properties of the chitosan hydrogel,

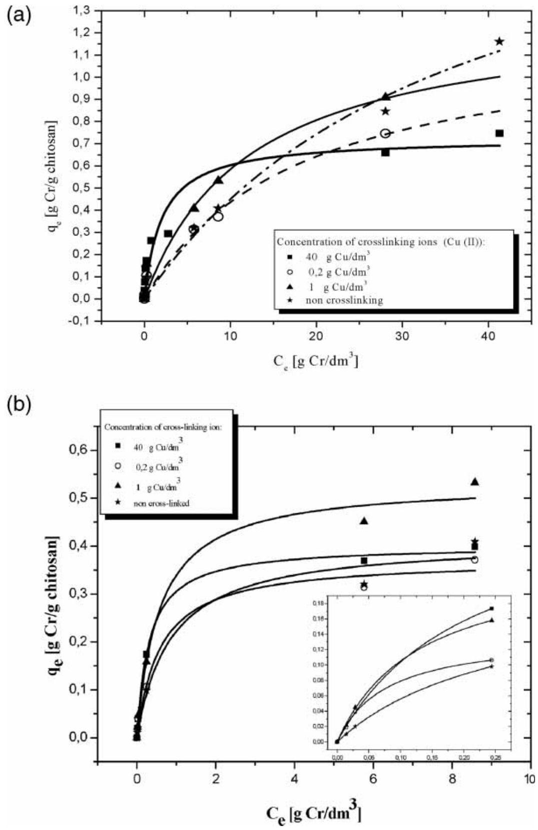

***Figure 3.*** (a, b) Isotherms of Cr(VI) adsorption on the beds cross-linked with Cu(II) ions.

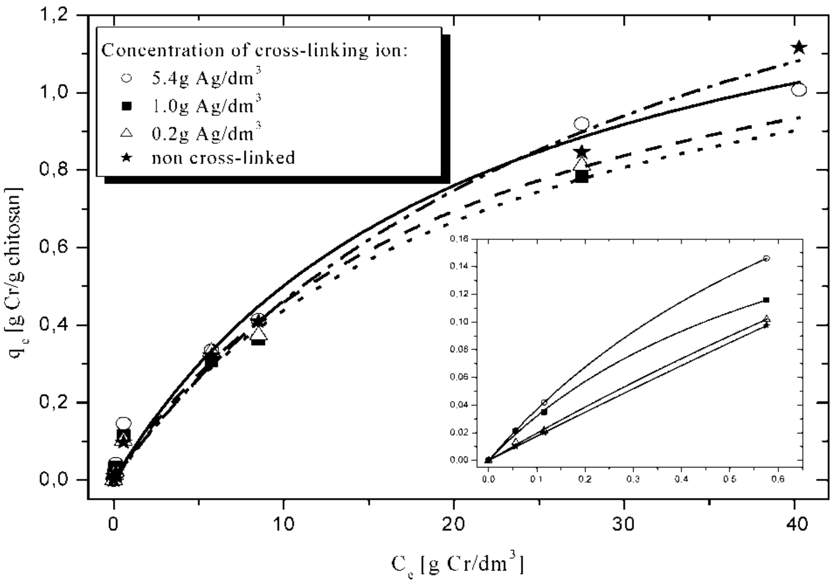

*Figure 4.* Isotherms of Cr(VI) adsorption on the beads cross-linked with Ag(I) ions.

- advantageous effect on the adsorption process is observed only at the concentration up to 10 $g_{Cr}/dm^3$,
- at higher concentrations the adsorption properties of the cross-linked beads decrease as compared to a not cross-linked adsorbent,
- an optimum value of the concentration of a cross-linking ion is about 1 $g_{Cu}/dm^3$.
- Analogous studies on the adsorption of Cr(VI) ions on a chitosan hydrogel cross-linked with Ag(I) ions also indicate that:
- cross-linking with Ag(I) ions has a slightly advantageous effect on the adsorption process, while a definitely favourable influence is observed in the range of chromium concentrations from 0.1 to 1.0 $g/dm^3$,
- the optimum concentration of the cross-linking ion is about 5.4 g $Ag/dm^3$.

Summing up, it follows from the investigation that

- there is an optimum concentration of the cross-linking ion both for Cu(II) and Ag(I) ions which causes an increase of the beads adsorption properties,
- in both cases, the cross-linking has an advantageous effect on the adsorption of Cr(VI) ions only for solutions at low concentrations.

The above statements are illustrated in Fig. 5 which presents the rate of Cr(VI) ion adsorption from a solution at the concentration 0.1 $g/dm^3$, on not cross-linked and cross-linked beads. The process runs in time can be described with good approximation by pseudo- and second-order equations.

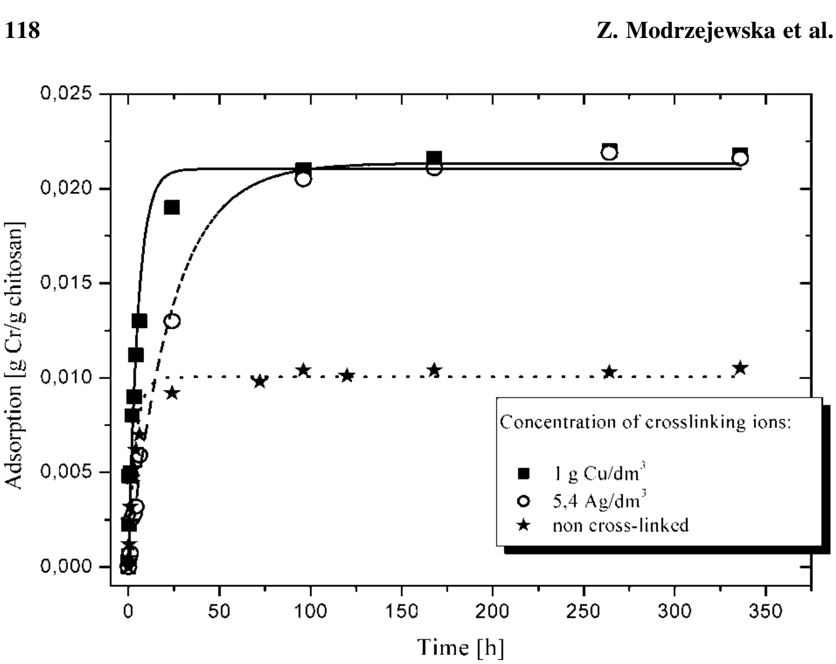

***Figure 5.*** Cr(VI) ion adsorption rate—adsorption from solution at the initial concentration 0.1 $g_{Cr}/dm^3$.

The correlation is presented in Table 2. For cross-linked beds the adsorption was doubled, additionally, for the beads cross-linked with Cu(II) ions the equilibrium is set-up faster.

The isotherms of Cr(VI) ion adsorption both in the chitosan hydrogel beads not cross-linked and cross-linked with Cu(II) and Ag(I) ions can be described by the Langmuir equations. The values of coefficients K and a for subsequent isotherms are given in Table 3.

Parameter a of the Langmuir isotherm is defined as the capacity of a monolayer, and corresponds to a maximum amount of particles combined with active centers on the adsorbent surface. This parameter for pure chitosan beads is the biggest. Cross-linking causes a decrease of the monolayer capacity, probably because part of the reactive groups in chitosan has been bounded already with cross-linking ions. Probably, there is also an ion exchange. For a beads cross-linked with Cu(II) ions at concentrations up to 1 $g/dm^3$ the capacity decreases by 30–37%, and in the case of cross-linking with Cu(II) ions at maximum concentrations, it decreases by 66%. For the beads cross-linked with Ag(I) ions the capacity decreases by 18–28%, the smallest decrease is observed at the cross-linking ion concentration equal to 5.4 $g_{Ag}/dm^3$.

The other parameter of the Langmuir isotherm shows the nature and size of adsorbent-adsorbate interactions. The stronger they are, the more convex is the equilibrium curve and the more it approaches a rectangular isotherm. Analysis

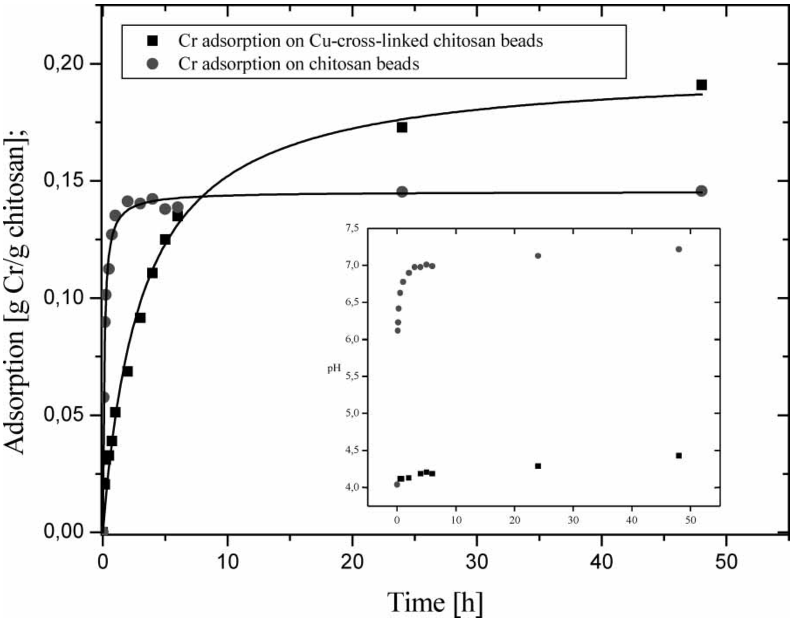

***Figure 6.*** Adsorption of Cr(VI) in time—adsorption from solution at the initial concentration 1 $g_{Cr}/dm^3$.

of this parameter for a chitosan beads shows that the strongest interactions appear between chromium ions and the chitosan beds that are maximally cross-linked with Cu(II) ions, while the lowest ones on pure chitosan. For the bed cross-linked with Cu(II) ions the interactions get stronger with an increase of the cross-linking ion concentration. For the beads cross-linked

***Table 2.*** Description of Cr(VI) adsorption process on the beads cross-linked with Cu(II) and Ag(I) ions

| | $q_t = q_e\,(1 - e^{-k_1 t})$<br>$q_e[g_{Cr}/g_{chitosan}]$, $k_1[1/h]$ | $q_t = q_e(q_e k_2 t/1 + q_e k_2 t)$<br>$q_e[g_{Cr}/g_{chitosan}]$, $k_2\,[1/h]$ |
|---|---|---|
| Beads cross-linked with Cu(II) ions: | $R^2 = 0.98$<br>$q_e = 0.021 \pm 0.001$<br>$k_1 = 0.196 \pm 0.020$ | $R^2 = 0.99$<br>$q_e = 0.022 \pm 0.000$<br>$k_2 = 12.330 \pm 1.086$ |
| Beads cross-linked with Ag(I) ions: | $R^2 = 0.99$<br>$q_e = 0.021 \pm 0.000$<br>$k_1 = 0.043 \pm 0.002$ | $R^2 = 0.99$<br>$q_e = 0.024 \pm 0.000$<br>$k_2 = 2.095 \pm 0.169$ |
| Not cross-linked beads | $R^2 = 0.98$<br>$q_e = 0.010 \pm 0.000$<br>$k_1 = 0.263 \pm 0.025$ | $R^2 = 0.99$<br>$q_e = 0.010 \pm 0.000$<br>$k_2 = 37.877 \pm 2.538$ |

***Table 3.*** Coefficients of the Langmuir equations

| Adsorbent type | a<br>$[g_{Cr}/g_{chitosan}]$ | K<br>$[dm^3/g_{Cr}]$ |
|---|---|---|
| Not cross-linked–Cr adsorption with $(NH_4)_2Cr_2O_7$ | 1.940 | 0.031 |
| Not cross-linked–Cr adsorption with $K_2Cr_2O_7$ | 1.907 | 0.034 |
| Cross-linked with Cu ions at concentration: 40 $g_{Cu}/dm^3$ | 0.646 | 0.303 |
| Cross-linked with Cu ions at concentration: 1 $g_{Cu}/dm^3$ | 1.297 | 0.082 |
| Cross-linked with Cu ions at concentration: 0.2 $g_{Cu}/dm^3$ | 1.212 | 0.056 |
| Cross-linked with Ag ions at concentration: 5.4 $g_{Ag}/dm^3$ | 1.568 | 0.047 |
| Cross-linked with Ag ions at concentration: 1 $g_{Ag}/dm^3$ | 1.389 | 0.046 |
| Cross-linked with Ag ions at concentration: 0.2 $g_{Ag}/dm^3$ | 1.421 | 0.048 |

with Ag(I) ions, the interaction with Cr(VI) ions is stronger as compared to the beads that is not cross-linked (by around 30%), however it is practically constant and does not depend on the cross-linking ion concentration.

To explain the mechanism of Cr(VI) adsorption in chitosan hydrogel, pH was determined during the process.

During adsorption in the non-cross-linked hydrogel, pH of the adsorptive changes abruptly in the first hour (growth from 4 to 6.6-7), which is shown in Fig. 6.

An increase of pH suggests protonisation of amino groups in the chitosan hydrogel:

$$RNH_2 + H + \Longleftrightarrow RNH_3^+$$

Character of the curve representing pH growth is the same as that of adsorption in time. This might indicate that protonated amino groups take part in the adsorption of Cr(VI) ions in the form of $Cr_2O_7^{2-}$ anion, and the adsorption is due to electrostatic interaction ($NH_3^+$ with $Cr_2O_7^{2-}$anion). In the case of cross-linking, the growth of pH is small–practically constant, nevertheless, adsorption proceeds in a higher degree than in the case of non-cross-linked hydrogel. Higher adsorption in the cross-linked hydrogel can take place because of stabilised lower pH of the adsorptive, or this may suggest chelate formation [chitosan – Cu(II) or Ag(I) – Cr(VI)]. Amino groups are chelated by Cu(II) or Ag(I) ions according to the reaction presented in literature:

$$Cu^{2+} + RNH_2 \Longleftrightarrow Cu(RNH_2)^{2+}$$

So, they should give an additional positive load to the hydrogel and assuming that adsorption takes place due to electrostatic interactions, higher adsorption of Cr(VI) ions on cross-linked hydrogel is justified by a higher positive load.

However, further studies, concerning mainly the electrostatic potential and NMR spectra, are required to explain the problem.

## CONCLUSIONS

The following conclusions have been drawn from the investigations carried out within this project

1. Hydrogel chitosan beads reveal an ability to adsorb Cr(VI) ions. A maximum equilibrium adsorption was about 1.1 $g_{Cr}/g$ chitosan.
2. Isotherms of Cr(VI) ion adsorption both from the $(NH_4)_2Cr_2O_7$ and $K_2Cr_2O_7$ solutions and on cross-linked beads can be described by the same Langmuir equation.
3. Adsorption properties of the chitosan cross-linked with Cu(II) and Ag(I) ions change depending on the concentration of the cross-linking ion and initial concentration of Cr ions in the solution.
   a. an optimum concentration of the cross-linking Cu ion is about $1\ g_{Cu}/dm^3$.
   b. an optimum concentration of the cross-linking Ag ion is about $5.4\ g_{Ag}/dm^3$.
4. The maximum process efficiency for the initial concentration of Cr(VI) solution – $0.1\ g_{Cr}/dm^3$ is as follows:
   - not cross-linked beads: ca. 44%
   - beads cross-linked with Cu ($1\ g_{Cu}/dm^3$): ca. 98%
   - beads cross-linked with Ag ($5.4\ g_{Ag}/dm^3$): ca. 97%
5. These results indicate that chitosan hydrogel can be useful for the removal of Cr(VI) ions, at low Cr(VI) concentrations it seems advantageous to cross-link the hydrogel with Cu(II) or Ag(I) ions.

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