

# The effect of pH on the sorption of copper ions by alginates

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The effect of pH on copper ions sorption by alginates has been investigated. The granules of the sorbent obtained from sodium alginate (type DMF, manufactured by KELCO) have been applied. By using a new method of gelation a biosorbent containing from 11.3 to 20.3% mas. of alginate has been produced. Investigations have been carried out at a constant temperature of 25°C and the pH values ranging from 3 to 5. The obtained experimental results have been described by the Langmuir equation. It has been found that with the increasing pH of the solution the maximum biosorbent sorption capacity increased.

**Keywords:** sorption, effect of pH, alginates, copper ions, biosorbent.

## INTRODUCTION

Alginates are the natural polysaccharides obtained from the sea algae. They are built of long straight chains made up of D-mannuronic and L-guluronic acids, bound by 1,4-glycoside bonds. Owing to a wide usage in a number of applications alginates are relatively cheap biopolymers. They can also be applied as heavy metal sorbents.

Sorption of metallic ions by alginates results from ionic exchange. The carboxylic groups that are present in the alginates structure and which take part in the ionic exchange are frequently called „active sites”. According to the literature data their availability depends on pH<sup>1-6</sup>. Sorption of the metallic ions by alginates increases with the increasing pH values.

Sorption of Cu(II) ions is also dependent on pH<sup>2,4,5,7-10</sup>. Together with the increasing pH of the solution sorption of the Cu(II) ions increases up to a maximum value, and then it begins to rapidly deteriorate<sup>7</sup>. At pH>5 copper begins to precipitate in the form of Cu(OH)<sub>2</sub><sup>6</sup>. Ibanez and Umetsu<sup>4,5</sup> established that at pH<3 sorption of Cu-ions was small or it did not exist at all. According to the literature the maximum sorption of Cu(II) has been obtained at pH equal to about 5<sup>1</sup>. All the literature data deal with the granules of small concentration of alginate (up to 6% dry mass).

The main disadvantage of granules containing small amounts of alginate lies in their low sorption capacity with respect to the granules volume. Therefore, the usage of such a sorbent on an industrial scale results in the necessity of constructing reactors of a large volume as well as preparation and operating with a large amount of biosorbent granules. Hence, using granules containing greater concentration of alginate would enable one to significantly reduce the reactor volume. However, producing such granules would be a problem. The methods so far known in which the solutions of sodium alginate are used, made it possible to get gels of concentrations up to 6.5% mas. However, high viscosity of the aqueous solutions of sodium alginate, applied in the sorbent preparation, is here an obstacle. A new method of granules preparation containing high concentration of biosorbent has been elaborated. It is based on using a suspension of sodium alginate particles.

The aim of the present work has been to study the effect of pH on the Cu(II) ions sorption by the concentrated alginate gels.

## EXPERIMENTAL PART

The pH-values from 3 to 5 have been examined since within this range the greatest changes in the sorption capacity had been observed. Moreover, a large number of the reference data for this range of pH can be treated as a good comparative material. All experiments have been carried out at a constant temperature 25°C. The granules obtained from the alginate manufactured by DMF KELCO containing from 11.3 to 20.3% mas. of the sorbent have been taken.

### Production of calcium alginate granules

The calcium alginate granules have been produced according to a newly elaborated procedure based on using a sodium alginate suspension. The alginate manufactured by DMF KELCO was the initial substance used during the granules production. This is a generally available and commonly applied material. The granules production started with the preparation of the alginate suspension. Ethyl alcohol of the 96% vol. concentration was used to prepare the suspension. At first, ethyl alcohol was mixed with distilled water at appropriate proportions. Then, the prescribed amount of sodium alginate was added to the previously prepared mixture. The obtained suspension, after careful stirring, was dripped into the crosslinking solution – 0.18M CaCl<sub>2</sub> solution. Mechanical extrusion was used by sucking off the suspension to a syringe and extruding it into the crosslinking solution by means of an infusion pump. The formed granules were maintained for 24 hours in the 0.18M CaCl<sub>2</sub> solution and then kept in a refrigerator in a 0.01M KCl solution. Before using the granules were rinsed with distilled water.

By making use of such a method 3 types of the alginate granules of different alginate content have been produced. The properties of the obtained granules are listed in Table 1.

### Determination of sorption equilibria

Based on the earlier experiments it has been established that the alginate – Cu(II) ions system reached an equilibrium after 24 hours, starting from the moment of the process initiation. After that time the alginate granules did not reveal any evident changes in sorption capability and the concentration of the metal ions in the solution practically did not change.

**Table 1.** The properties of alginate granules

Mass of alginate [g]	Mass of ethyl alcohol [g]	Mass of water [g]	Dry mass of the obtained granules [%]	Diameter of the granules [mm]
4	12	36	11.3	3.0
7	12	36	16.0	3.4
10	12.5	36	20.3	2.9

Sorption equilibria have been determined in a closed system. The determination was based on placing a specified number of the alginate granules (from 10 to 40) in the Erlenmeyer flasks containing 50 cm<sup>3</sup> of the Cu(II) solution. The concentration of Cu(II) ions in the solution was precisely predetermined and was equal from 20 to 500 mg/dm<sup>3</sup>. Then the flasks were shaken in a shaker („Elpin”, type 357, produced by „Elpin”, Poland), maintained at a constant temperature of 25°C. All experiments were carried out till reaching equilibrium in the system. Then, the samples of the solution were collected and the concentration of Cu(II) ions was determined using the method of atomic absorption spectroscopy. For this purpose the AAS 210 VGP spectroscope, manufactured by Buck Scientific, was applied.

The equilibrium sorption capacity,  $q_{\infty}$  was calculated from Eq. (1):

$$q_{\infty} = \frac{V_L \cdot (C_{L0} - C_{\infty})}{m_s} \quad (1)$$

where  $V_L$  is volume of the solution (dm<sup>3</sup>),  $C_{L0}$  – initial copper concentration in the solution (mg/dm<sup>3</sup>),  $C_{\infty}$  – equilibrium copper concentration in the solution (mg/dm<sup>3</sup>) and  $m_s$  is alginate content with respect to dry mass (mg).

The amount of biosorbent (with respect to dry mass),  $m_s$ , was determined based on the known mass of a single granule, the alginate content in the granules and the number of granules used in the experiment.

Since (as it has earlier been tested) the Langmuir curve describes the experimental data much better than the Freundlich one, therefore, the sorption Langmuir isotherms for the obtained data were plotted. From the Langmuir equation (2)

$$q_{\infty} = q_{\max} \cdot \frac{b \cdot C_{\infty}}{1 + b \cdot C_{\infty}} \quad (2)$$

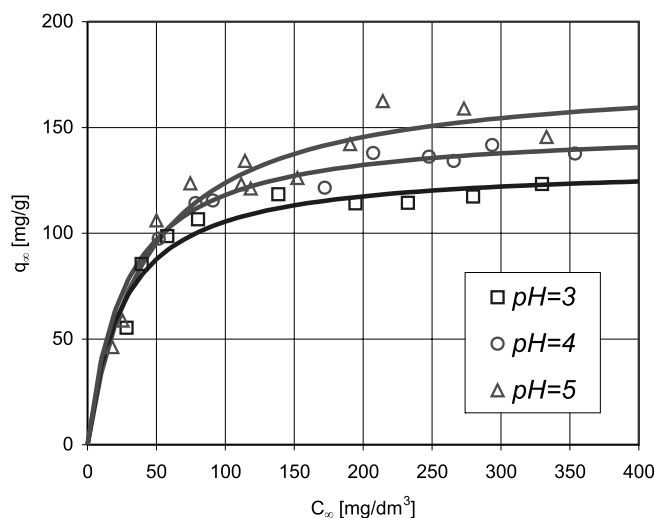
the coefficients  $b$  (expressing sorbent affinity to the sorbate, dm<sup>3</sup>/mg) and  $q_{\max}$  (a maximum sorption capacity, mg/g, under given experimental conditions) at each pH-value were estimated. The constants were directly determined from the Langmuir equation using a computational program SLIDE WRITE Plus, based on the Levenberg-Marquardt optimization procedure.

## RESULTS AND DISCUSSION

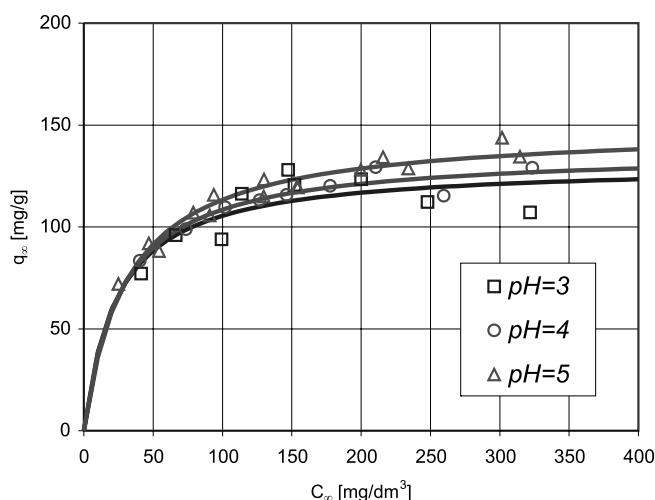
The effect of pH on the sorption of the Cu(II) ions by the granules containing 11.3%, 16.0%, 20.3% and of alginate has been presented in Figs. 1, 2 and 3, respectively.

The effect of pH on both the equilibrium as well as the maximum sorption capacity of the applied granules has been examined. An improper behaviour has been observed: independent of the alginate content in the granules, at very small equilibrium concentrations, the pH value of the solution had no significant influence on the equilibrium sorption capacity of the alginate granules. However, when  $C_{\infty}$  cross some limiting value (characteristic of the given granules), an increase in pH results in an increased value of  $q_{\infty}$ . The limiting value depended on the alginate content in the granules and this was a reciprocal proportionality dependence:

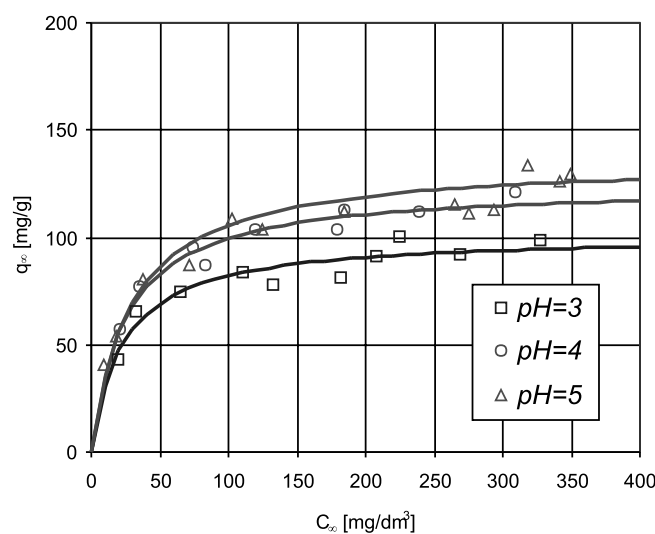
- for the alginate of 11.3% mas. the limiting values was  $C_{\infty} = 50 \text{ mg/dm}^3$ ,
- for the alginate of 16.0% mas. –  $C_{\infty} = 40 \text{ mg/dm}^3$ ,
- for the alginate of 20.3% mas. – as  $C_{\infty} = 30 \text{ mg/dm}^3$ .



**Figure 1.** Sorption isotherms illustrating the effect of pH on the sorption of Cu(II) ions by granules containing 11.3% mas. of alginate



**Figure 2.** Sorption isotherms illustrating the effect of pH on the sorption of Cu(II) ions by granules containing 16.0% mas. of alginate

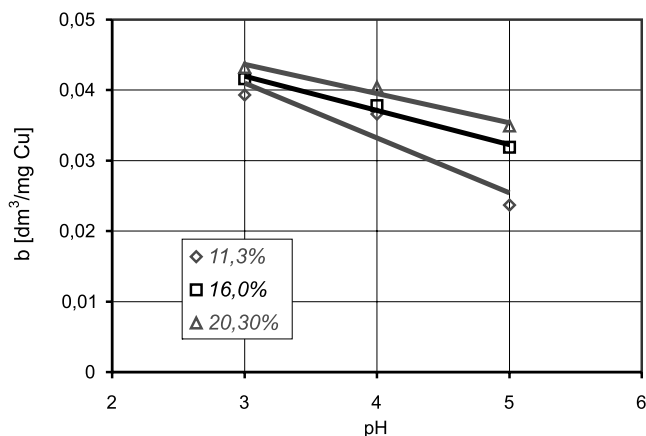


**Figure 3.** Sorption isotherms illustrating the effect of pH on the sorption of Cu(II) ions by granules containing 20.3% mas. of alginate

Independent of the alginate content in the granules the maximum sorption capacity of the biosorbent always increased with an increasing pH of the solution (within the studied range of this parameter), while the value of the coefficient  $b$  de-

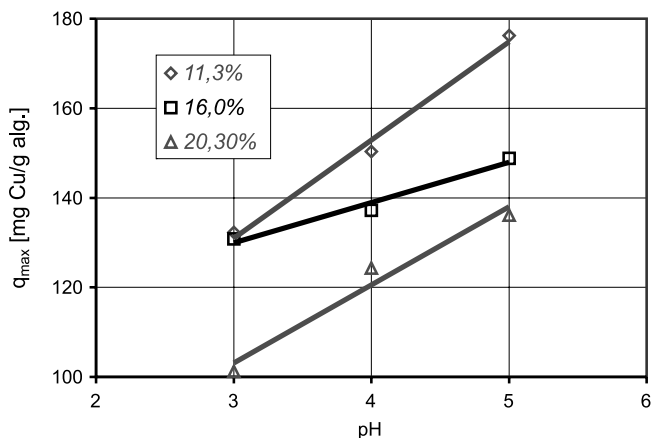
creased, which indicates increasing the affinity of the biosorbent with respect to the sorbate. This is in agreement with the available reference data<sup>2, 4, 5-7</sup>.

The effect of pH on the values of  $b$  for different alginate content in the granules is shown in Fig. 4. With an increasing pH the coefficient diminishes, hence the alginate affinity with respect to the sorption of Cu(II) ions increases. In addition, the smallest affinity (independent of pH) has been revealed for the granules containing 20.3% mas. of the alginate.



**Figure 4.** The effect of pH on the coefficient  $b$  for different alginate content in the granules

The effect of pH on  $q_{max}$  for different alginate content in the granules is presented in Fig. 5. With an increasing pH the maximum sorption capacity of the biosorbent granules increases. Moreover, the greater alginate content in the granules, the lower the value of  $q_{max}$  at each studied pH value is.



**Figure 5.** The effect of pH on  $q_{max}$  for different alginate content in the granules

According to the literature the availability of the sites where the copper ions are bound depends on  $pH^2$ . Therefore, the reason that sorption of the Cu(II) ions on calcium alginate increases with an increasing pH is most likely connected with the increased number of the active sites and with an increased value of the negative charge. At a higher pH the available number of sites that bind the copper ions (the active sites) is greater so that the removal effectiveness of these ions increases with an increasing pH. Furthermore, with an increasing pH the more negatively charged active sites become available for the Cu(II) ions.

Undoubtedly, the pH of the solution containing sorbate is an important factor that significantly affects the sorption of the Cu(II) ions by calcium alginate. From the present investiga-

tions, the greatest sorption of the Cu(II) ions by calcium alginate has been observed at pH equal to 5.

## CONCLUSIONS

- Independent of the alginate content in the granules the maximum sorption capacity of the biosorbent always increases with an increasing pH of the solution while the coefficient  $b$  decreases.

- Independent of the alginate content in the granules the coefficient  $b$  always decreases with an increasing pH of the solution.

- The greatest sorption capacity and the greatest biosorbent affinity to the sorbate has been obtained at  $pH = 5$ .

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