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# PRELIMINARY STUDIES ABOUT Co (II) METALLIC IONS RETENTION FROM AQUEOUS SOLUTIONS ONTO PVA-CELLULOSE COMPOSITE HYDROGELS

BY

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**Abstract.** A direction for the use of composite hydrogel based on PVA and cellulose is the preparation of efficient adsorbents in the adsorption/ sorption/biosorption processes of inorganic chemical species from aqueous systems, including wastewaters. Thus, the PVA-cellulose hydrogel (Ox25C) was studied as adsorbent in the removal of $Co^{2+}$ metallic ions from aqueous solutions. Batch experimental studies focused on the determination of the influence of some important physical operating parameters on the adsorption of metallic ions, such as: pH, adsorbent dose, phases contact time, temperature, and metal ion concentration were performed. The experimental results recommend the use of PVA-cellulose composite hydrogel (Ox25C) in the removal of heavy metal ions from aqueous systems, predominantly by adsorption process types.

**Keywords:** adsorption; aqueous medium; hydrogel adsorbent; inorganic chemical pollutants.

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## 1. Introduction

A new generation of innovative adsorbent materials, based on renewable resources has been developed in the last times. Hydrogels category is one type of these innovative adsorbent materials.

Hydrogels are three-dimensional, hydrophilic arrays, with polymeric networks capable of absorbing large quantities of water or biological fluids. Hydrogels may be chemically stable or may be degradable and eventually possible to be disintegrated and dissolved (Kurecic and Smole, 2012; Nica *et al*., 2018; Ullah *et al*., 2015). This kind of materials exhibit pore controlled sizes which renders them useful in retaining many chemical species with various molecular weights. In this association, cellulose-based composite hydrogels are intensively studied mainly for (i) retention of chemical pollutants, and (ii) valuable and efficient matrix for controlled release of various chemical species of biological interest (Hokkanen *et al*., 2016; Kalia *et al*., 2011; Kurecic and Smole, 2012; Olivera *et al*., 2016; Varaprasad *et al*., 2017).

Polyvinyl alcohol (PAV) is a biodegradable polymer, largely used in the last years for the production of biodegradable composite materials, as a substitute of traditional polyethylene or polypropylene polymers. However, PAV has the disadvantage of weak mechanical properties, and also requires cross-linking with certain compounds capable of improving these properties. To achieve this challenge, cellulose (C) has been proposed in our studies as an ecological and renewable alternative to the synthetic polymers, in order to prepare hybrid PAV-C hydrogels. Several composite hydrogels were synthesized, varying the amount of cellulose embedded in the polymer matrix. Previous studies have shown that the PAV-25C (25% cellulose) material is the one that exhibited the best adsorbing properties of the tested chemical species (Nica *et al*., 2018).

Moreover, adsorption is a cheap treatment method which requires relatively simple equipments with an affordable price. Also, it can be used a large wide variety of materials with adsorbent properties that ensure the desired purpose: medium purification and removal of undesirable chemical compounds. Adsorbents can be provided by chemical synthesis, or can be obtained from agricultural-industrial by-products or natural products (Zaharia and Șuteu, 2012).

In this paper, it will be considered the study and identification of the main operating parameters with significat influence on the adsorption of metallic ions, such $Co^{2+}$, from aqueous media onto the composite hydrogel based on PVA and cellulose (Ox25C) in order to perform an optimal adsorption efficiency and also high rate of removal for other studied chemical species in aqueous media.

## 2. Experimental Part

### 2.1. Materials

*Metalic ion.* $Co^{2+}$ ions were selected as polluting inorganic species, presented as solutions of $CoSO_4$ and tested in the concentration range of 36.62-207.52 mg of $Co^{2+}$/L. The stock solution concentration was and 599.064 mg $Co^{2+}$/L, respectively.

*PAV-25C hydrogels.* These hydrogels are characterized by the presence in their molecule of an amount of 25% cellulose functionalized by selective oxidation at C6, and a pore size of 45-65 mm (Fig. 1).

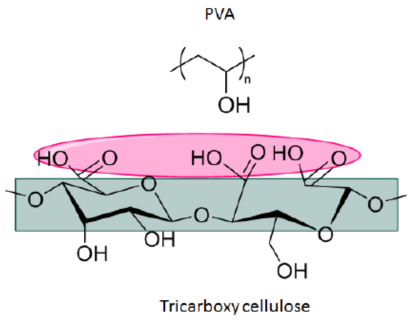


Fig. 1 – Structure of studied hydrogel molecular unit based on PVA and cellulose.

### 2.2. Adsorption Methodology

The influence of selected operating parameters (*i.e.* pH solution, amount of adsorbent, initial concentration of metallic ion, phase contact time, and temperature) will be studied in batch experiments in order to establish their best values in this studied adsorptive process. Thus, the working technique consists in contacting different amounts of adsorbent (composite hydrogel) with metallic ion ($Co^{2+}$) solutions with different concentrations. The keeping of temperature constant was ensured by using a Poleko SLW 53 thermostatic bath.

The adsorption systems have undergone to discontinuous stirring. After 24 h, it was considered that the equilibrium was reached, and the residual metallic ion concentrations in aqueous solution were determined using an UV-VIS Digital Spectrophotometer, model S 104D /WPA.

The determination of the metal ion concentration was based on the reading of the aqueous sample absorbance at the characteristic wavelength of the colored complex formed by the metal ion with 0.05% rubeanic acid in borate buffer medium (pH = 9) in the case of $Co^{2+}$. The readings were made on a UV-VIS spectrophotometer model S 104D / WPA in compliance with the Lambert-Beer law, based on the calibration curve (Fig. 2) (Fornea *et al.*, 2017).

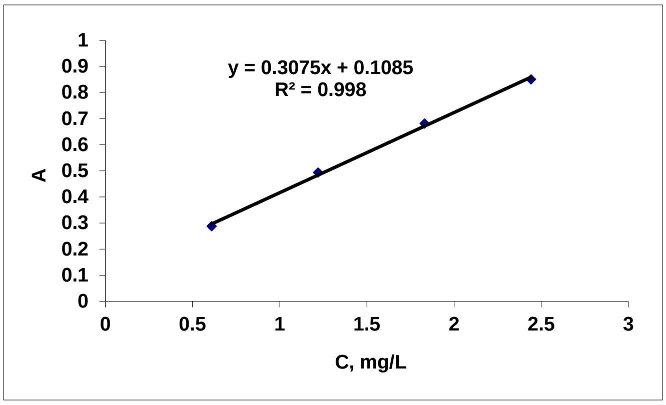


Fig. 2 – Calibration curves for spectrophotometric determination with rubeanic acid of $Co^{2+}$ calibration curve ($\lambda_{max}$ = 450 nm).

One of the more important quantitative adsorption characteristics was evaluated by means of the amount of adsorbed metallic ions and, consequently, adsorption capacities of the composite hydrogel (Eq. (1)):

$$q = \frac{C_0 - C}{G} \cdot V \quad (1)$$

where: $C_0$ and $C$ are the initial and at equilibrium concentration of metallic ion in aqueous medium (mg/L), $G$ is the amount of adsorbent (g) and $V$ is the volume of aqueous sample (L).

## 3. Results and Discussions

The adsorption process of the metallic ions can be influenced by some physical-chemical operating parameters that can influence the establishment of a certain ionic form of the functional groups in the structure of the adsorbent or on the ionic form of the metal, on the retention/adsorption capacity and the rate of the adsorption process. Thus, it was considered the study of the influence of a few physical-chemical parameters as (*i*) the *pH* of the metal ion solution, (*ii*) the *adsorbent amount* per each aqueous sample volume, (*iii*) the concentration of metallic ion species, (*iv*) the contact time between the two phases (solid/water) and (*v*) the temperature at which the adsorption process takes place.

### 3.1. The pH Influence on the Metallic Ions Adsorption

The pH of the solution is an important physical parameter in the adsorption process because it influences both the surface of the adsorbent by ionizing the functional groups and the metal ion, determining the existence of a certain ionic species in the system.

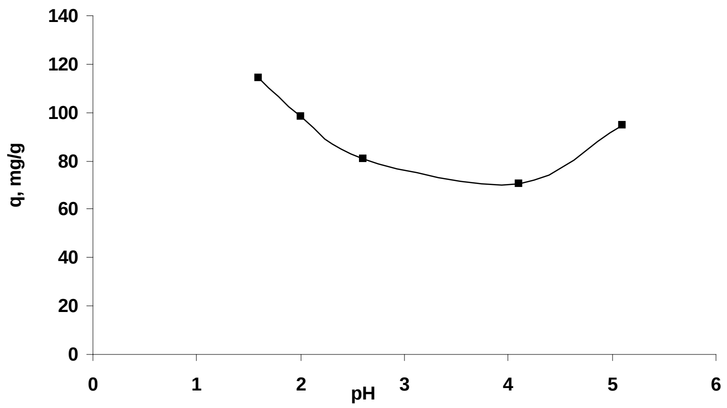


Fig. 3 – The pH influence on the metallic ion adsorption. Operating conditions: $C_0$ ($Co^{2+}$) = 122.07 mg/L; adsorption time (t) = 24 h, T = 20°C; adsorbent amount = 0.01g hydrogel per 25 mL of aqueous sample.

The study of Fig. 3 shows that metallic ions will be retained efficiently in acidic environment: 1.6 for $Cu^{2+}$ ions, pH provided by the addition of 0.1N $H_2SO_4$ and its measurement with a portable high precision KL-009(I) pH meter (Hanna Instruments).

### 3.2. Composite Hydrogel Amount Influence on Metal Ion Adsorption

A second significant operating parameter of the adsorption process is the adsorbent concentration (g/L) which can be also expressed in terms of adsorbent amount (g) per a known aqueous metallic ion sample volume or when it is working with the same aqueous sample volume with the adsorbent amount per each experiment. The composite hydrogel amount per each metal ion sample volume (25 mL) or each experiment is represented in Fig. 4, being studied in the variation range of 0.2-2.0 g/L.

From Fig. 4 it is observed for $Co^{2+}$ metal ions that the adsorbent concentration to obtain the highest adsorption capacity in the experimental variation field of adsorbent concentration is 0.4 g/L, respectively an adsorbent amount of 0.01g OxC25 hydrogel per 25 mL of aqueous metallic ion sample. Higher adsorbent amount was not required due to the fact that it seems that the best value of adsorption capacity in retaining of $Co^{2+}$ ions on the studied composite hydrogel is performed for the lowest value of adsorbent concentration (or amount per each experiment).

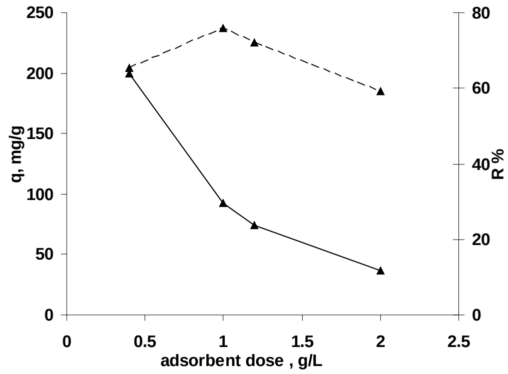


Fig. 4 – The influence of the hydrogel amount: $Co^{2+}$: $C_0$ = 101.725 mg/L; pH = 2.9; adsorption time = 24 h, T = 20°C.

### 3.3. Temperature and Initial Metal Ion Concentration Influence on its Adsorption

Significant influence can also have the temperature and initial metallic ion concentration in the aqueous sample on their adsorption efficiency. Thus, some adsorption experiments were performed for an initial metallic ion concentration in range of 0-220 mg/L and at relative low and common room temperature for no possible composite hydrogel decomposition/contamination or its structure alteration. Thus, the tested temperatures were closed to those for the room temperature, meaning 20°C and very low temperature of 2°C.

The adsorption capacity behaviour/variation of the studied composite hydrogel for the studied metallic ions ($Co^{2+}$) are presented in Fig. 5.

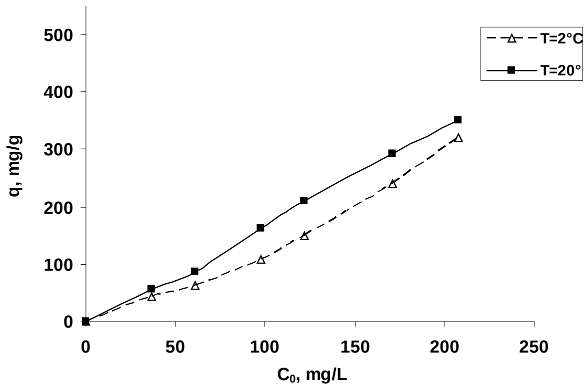


Fig. 5 – Influence of temperature and initial metal ion concentration in the aqueous solution on adsorption capacity: $pH_{Co}{}^{2+}$ = 2.9; adsorption time = 24 h; 0.01g hydrogel per 25 mL of aqueous sample; T=2°C or 20°C.

From Fig. 5 it is observed that an increase of the temperature at which the adsorption process of the studied metal ions is carried out leads to an increase of the adsorption capacity of the OxC25 composite hydrogel, explained by the intensification of the ions agitation and the diffusion process development. This behaviour suggests that the adsorption could be an exothermic process, which must be confirmed by complete studies of adsorption equilibrium and process thermodynamics.

### 3.4. The Initial Metal Ion Concentration and Time Influence on Adsorption Behaviour

The adsorption time or the contact time between the two phases involved (solid adsorbent and aqueous solution containing the studied metallic ions) can be very important in continuous adsorption processes or in combined treatment processes which must occur in relatively short operating times meaning, no more than 1-3 h or a shift (8 h).

The variation in time of the adsorption capacity for retaining metal ions onto the studied composite hydrogel at two initial metal concentrations (121.092 and 170.663 mg/L) is pointed in Fig. 6 for $Co^{2+}$ ions.

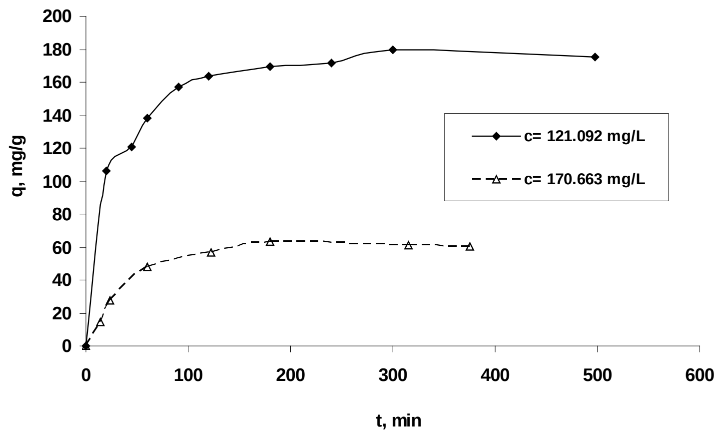


Fig. 6 – The contact time (S/W contact time) influence on the metal ions adsorption. Operating conditions: $C_0$ ($Co^{2+}$) = 101.725 mg/L; pH = 2.9; T = 20°C.

The analysis of graphs in Fig. 6 shows a slow increase of the adsorption capacity of the metal ions with the increasing of the contact time (S/W phases contact period of time) until the equilibrium value is reached at about 300 min, after which the value of the adsorption capacity remains at the constant sign that the saturation capacity has been reached of the adsorbent. The highest adsorption capacity in the case of $Co^{2+}$ ions is of around 180 mg/g.

## 4. Conclusions

1. Composite hydrogel based on PVA and cellulose (25%) namely Ox25C could be an efficient adsorbent for metallic ions species from different aqueous systems, such as waste waters or aqueous solutions of biological interest, if it is taken into account that the two metal ions belong to the category of microelements necessary for the harmonious development of the human body.

2. The retained amount of metallic ions (q, mg/g) depends on the solution pH registering a better performance in acid medium at T=20°C and for an adsorbent concentration of 0.4 g/L.

3. The amount of metal ions retained increases with the contact time increasing until a maximum amount is reached (after about 300 min), followed by a relative slow growth or even constancy.

4. Further studies will be continue with the study of the adsorption equilibrium, kinetics and thermodynamics of the adsorption process for $Co^{2+}$ metallic ions and other metallic ions, in a static and/or dynamic system.

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## STUDII PRELIMINARE PENTRU REȚINEREA IONILOR METALICI DE Co (II) DIN SOLUȚII APOASE PE HIDROGELURI COMPOZITE PE BAZĂ DE PAV-CELULOZĂ

(Rezumat)

O direcție pentru utilizarea hidrogelului compozit pe bază de PAV și celuloză este prepararea de adsorbanți eficienți în procesele de adsorbție/sorbție/biosorbție a unor specii chimice anorganice din sisteme apoase, inclusiv ape uzate. Astfel, hidrogelul PAV-celuloză (Ox25C) a fost studiat ca adsorbeant în reținerea ionilor metalici de $Co^{2+}$ din sisteme apoase. Studii experimentale statice axate pe analizarea influenței unor parametri operaționali fizico-chimici asupra adsorbției ionilor metalici, precum: pH, doză de adsorbant, timpul de contact, temperatură și concentrația inițială de ion metalic au fost efectuate. Rezultatele experimentale recomandă folosirea hidrogelului PAV-celuloză (Ox25C) în reținerea ionilor metalelor grele din medii apoase predominant prin tipuri de procese de adsorbție.