Hydrogel biocomposites as eco-friendly fertilizers for slow release of micronutrients

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Abstract:

The aim of this work is producing eco-friendly fertilizers via immobilization of the goldenrod in alginate/carboxymethyl cellulose matrix (ALG/CMC). Two types of biocomposites were produced with different biosorbent contents (2 wt% (B1) and 5 wt% (B2)). The physicochemical (pH_{ZPC}, swelling) and sorption properties of the hydrogel capsules were determined. Kinetic data was described using pseudo-first order reaction, pseudo-second order reaction and general rate law equations models. The pseudo-second model best fits the experimental data and the determined kinetics rate constants were $1.09\ 10^{-3}$ *and* $2.0\ 10^{-3}$ $dm^3\ mol^{-1}\ min^{-1}$ for B1 and B2, respectively. To determine the sorption capacity of biocomposites, the Langmuir, Freundlich and Sips models were used. Sips isotherm turned out to be the best fit and the sorption capacities are *6.95 and 7.54* $mg\ g^{-1}$ for a composite with a biosorbent content of 2% and 5%, respectively. To investigate the possible use of capsules as controlled release fertilizers, desorption of Cu^{2+} ions in various media was performed. Based on the results, hydrogels possess binding and controlled release of micronutrients properties, which is a potential use in the agricultural sector as micronutrient carriers.

Keywords: alginate, goldenrod, slow release, fertilizer, microelements

1. Introduction

The demographic rise and the associated necessity to create new buildings lead to a reduction of green areas. Dynamic urban development and lifestyle change deepen the problem of the declining number of farms. Intensified cultivation on small areas leads to a decrease in the amount of necessary minerals in the soil. During the harvest, large amount of mineral compounds is removed from the soil, which negatively affects its fertility. Contaminated and impoverished soil disturbs the plant vegetation.

Decomposition of organic material is a natural way to supply the soil with the necessary minerals. It often happens that the soil contains a lot of nutrients, but in forms which are not absorbed by plants. Therefore, the intensified yielding in small areas and the slowly occurring process of mineralization causes that the demand for micro and microelements significantly exceeds the natural possibilities of soil enrichment.

The use of biomass as a carrier of micronutrients does not solve the problem of leaching nutrients to deeper layers of soil. The solution to this problem is the use of fertilizers with controlled release of micronutrients. Currently, the slowed release is obtained by coating traditional mineral fertilizers with synthetic polymers. The polymer coating reduces the dissolution rate of fertilizers (Wu, 2008). A very important aspect, due to environmental protection, is the degradation of the polymer coating. Controlled release of micronutrients can be obtained by immobilizing post-extraction biomass in a polymer matrix. Closure of the fragmented biomass in the hydrogel structure positively affects the sorption capacity of the sorbent. The matrix may be composed of one or more polymers, which affects the physicochemical properties of the biocomposite (Šillerová et al., 2015).

One of the widely used polymers for immobilizing biomass is alginate. The alginate is composed of monomers of β-D-mannuronic acid and α-L-guluronic. The most common variant of alginate is the sodium salt of alginic acid, which is derived from brown algae. The biggest advantage of this biodegradable polymer is the ability to create 3D networks in the presence of divalent cations (most commonly Ca^{2+}). Calcium ions react with the blocks of guluronic units, creating ion bridges between adjacent chains to form hydrophilic 3D structures (Nair and Laurencin, 2007). The mechanism of cross-linking with calcium ions is shown in Fig. 1. In order to increase the mechanical properties of the composites, the alginate can be mixed or co-polymerized with other polymers (carboxymethyl cellulose, chitosan) (Wang et al., 2012). Carboxymethylcellulose is a polysaccharide obtained by chemical modification of cellulose. Carboxymethylcellulose is biodegradable and can form 3D structures in the presence of multivalent cations. The presence of this additive increases the mechanical strength of the hydrogels, but also increases their porosity, which positively affects the sorption processes. The pore size of the crosslinked composites increases with increasing carboxymethyl cellulose content (Ren et al., 2016).

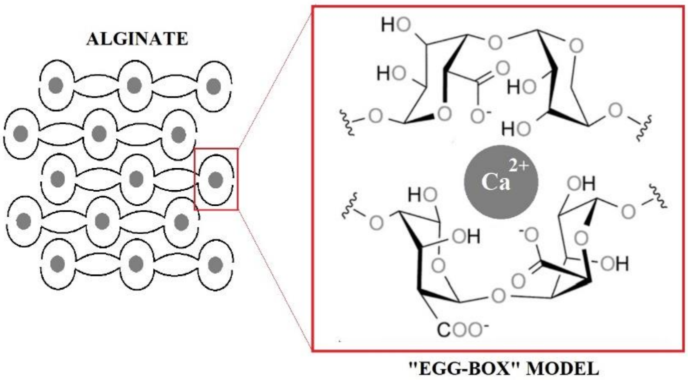

Fig 1. *The mechanism of cross-linking of alginate with calcium ions*

Hu et al. (2018) presented in their work the possibility of using a composite composed of sodium alginate and carboxymethylcellulose to remove Pb (II) ions. It has been demonstrated 86% efficiency of removal of ions from aqueous solution. It has also been confirmed that the presence of carboxymethyl cellulose has contributed to the increase in the sorptive capacity of the composite and the stability of the composite. Ting et al. (2013) presented in their work sorption of Cu(II) ions on free cells and cells immobilized in an alginate matrix. The immobilization of the material increased the efficiency of removing metal ions from the aqueous solution. Sorption time increased twice for immobilized cells. The reason for this phenomenon was the appearance of a hydrogel barrier that hinders the pathway of cations to active sites. Ding et al. (2019) showed that immobilization of biomass in a polymer matrix affects the multistage character of the sorption process. The binding process of ions with functional groups consists of the following stages: transport of cations to the surface of sorbent (1), diffusion into the interior of the capsule (2), binding to active sites in the matrix (3), adsorption on the surface of the biomass (4). Based on the research, it was concluded that the first two sorption stages are associated with a mechanism based on complexation and ion exchange. Diagram of ion binding on biocomposites is shown in Fig. 2. Adsorption at the biomass surface is associated with chelation. Researchers carried out desorption of related cations to study the stability and suitability of the produced structures. The release efficiency was around 80%. Based on the results, the immobilization of biomass in the alginate matrix can be used in industry.

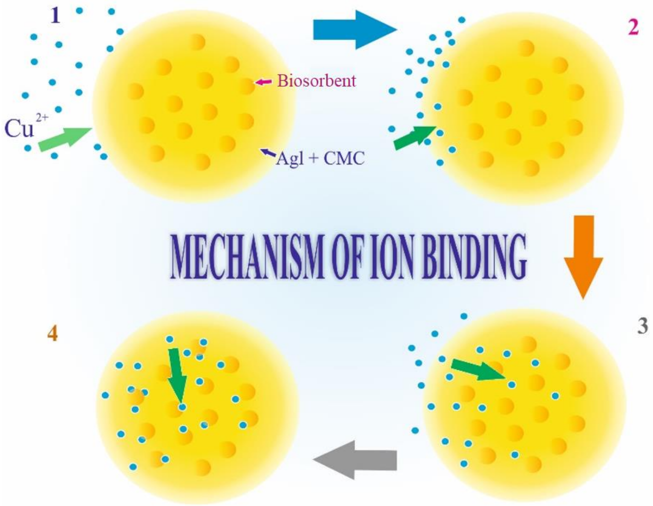

Fig. 2. *Diagram of microelements binding on biocomposites*

2. Materials and methods

2.1. Materials

Goldenrod as waste after the supercritical extraction was obtained from a local producer. Sodium alginate (ALG) and carboxymethylcellulose (CMC) were purchased from Sigma Aldrich. Copper(II) sulphate ($CuSO_4$) and calcium chloride ($CaCl_2$ as crosslinker) were purchased from POCH Poland.

2.2. Preparation of beads

2.5 wt.% ALG solution and 1 wt.% CMC solution were prepared by dissolving the appropriate amounts of these salts in distilled water at 60°C. After cooling, 2 wt.% ground goldenrod was added to the mixture (composite B1). To investigate the effect of the sorbent amount on the sorption capacity of the beads, an additional solution was prepared: 2.5 wt.% ALG, 1 wt.% CMC and 5 wt.% of goldenrod (composite B2). Both solutions was dropped into crosslinking solution (0.2M $CaCl_2$) and left for 24h. After this time, structures were washed several times and stored in distilled water for future experiments.

2.3. Analytical measurements

The structures of hydrogel biocomposites were observed under the optical microscope (DMi8, LEICA, Germany). The concentration of Cu^{2+} ions was measured with the ICP-OES. Mathematical modelling of experimental data was performed using the OriginLab (8 Technology, OriginLab Corporation, United States).

2.4. Physicochemical properties

2.4.1. Swelling properties

To investigate the degree of hydration structures in various media, 5 conical flasks containing 50 ml of aqueous solution at pH 3, 0.1M citric acid, 1 wt.% aqueous NaCl, 1 wt.% aqueous $NaNO_3$ and water were prepared. 1,5 g of composites was weighed and transferred into each of the media. Next, biocomposites were weighted after 24 h and 96 h. The percentage changes in mass are shown with reference to the zero sample.

2.4.2. pH_{ZPC}

To determine the point of zero charge of the composites, 8 conical flasks containing 1wt.% aqueous NaCl at the pH range from 2 to 9 were prepared. The samples were left on laboratory shaker for 24 h. After this time, the pH of the solutions was again measured. The pH_{ZPC} were determined by means of a graph $pH_{24} - pH_0 = f(pH_{fixed})$

2.4.3. Influence of pH

In order to select the most favorable conditions for sorption of Cu^{2+} ions on composites, the influence of the pH of solutions containing Cu^{2+} ions on the sorption capacity of the produced structures was examined. For this purpose, 4 conical flasks with 50 mL aqueous solution with a concentration of Cu^{2+} ions 200 mg L^{-1}, at the pH range from 3 to 6 were prepared. 1.5 g of composites was weighed and transferred into each of the solutions. The samples were placed on an orbital shaker and left for 24 h. After this time, the solution was analysed for the Cu^{2+} ions concentration.

2.5. Sorption of Cu(II) ions

2.5.1. Kinetics

200 ml aqueous solution with concentration of Cu^{2+} 200 mg L^{-1} with fixed pH=5.00 was prepared in Erlenmeyer flasks. 1.5 g of composite was weighed and transferred to a solution of Cu^{2+} ions. The flaks with the beads were agitated in an orbital shaker. The samples was taken at specific time intervals to determinate the content Cu^{2+} ions. Sorption was carried out until reaching equilibrium (26h). Parameters of kinetics were determined using the pseudo-first (Eq. 1) and pseudo-second order model (Eq. 2) as well as general rate law equation (Eq. 3) (Kumar et al., 2013):

$$Q_t = Q_e \cdot (1 - e^{-k_1 \cdot t}) \qquad (1)$$

$$Q_t = \frac{Q_e^2 \cdot k_2 \cdot t}{1 + Q_e \cdot k_2 \cdot t} \qquad (2)$$

$$Q_t = Q_e - (Q_e^{1-n} + (n-1) \cdot k_n \cdot t)^{\frac{1}{1-n}} \qquad (3)$$

where: Q_e – equilibrium sorption capacity (mg g^{-1}), k_1 – process rate constant (min^{-1}), k_2 –process rate constant (g mg^{-1} min^{-1}), k_n – process rate constant (g mg^{-1} min^{-1}), n – order rate of the reaction

2.5.2. Equilibrium

6 flasks containing 50 ml aqueous solution with a concentration of Cu^{2+} ions range from 50 to 500 mg L^{-1} with fixed pH=5.00 was prepared. 1.5 g of composite was weighed and transferred to a solution of Cu^{2+} ions. The flaks were agitated in an orbital shaker. After 24 h, the samples was analyzed for the Cu^{2+} ions concentration. To determine the equilibrium parameters, the Freundlich (Eq. 4), Langmuir (Eq. 5), and Sips (Eq. 6) isotherms were used (Ahmad et al., 2018; Freundlich, 1907; Sips, 1948)

$$Q_e = Q_{max} \cdot \frac{K_b \cdot C_e}{1 + K_b \cdot C_e} \qquad (4)$$

$$Q_e = K_F \cdot C_e^{\frac{1}{n_F}} \qquad (5)$$

$$Q_e = Q_{max} \cdot \frac{K_S \cdot C_e^{\frac{1}{n_S}}}{1 + K_S \cdot C_e^{\frac{1}{n_S}}} \qquad (6)$$

where C_e - the equilibrium concentration of metal ions in the solution (mg g^{-1}), Q_{max} - the maximum sorption capacity of sorbent (mg g^{-1}), K_b - the Langmuir constant related to sorption affinity (L mg^{-1}), K_F - the Freundlich constant related to uptake capacity (L mg^{-1}), n_F, n_S - the constant known as sorbent intensity (-), K_S - the Sips constant related to sorption affinity (L mg^{-1}).

3. Results and discussion

3.1. Swelling properties

Fig. 3 shows swelling degree of biocomposites as a function of time in different aqueous media. It was observed that samples in NaCl 1%, NaNO$_3$ and water solutions stopped swelling after 24 h in case of B1 processing issue. On the other hand B2 mass absorption ratio is scientifically larger after 96 h in comparison to the 24 h samples in corresponding solutions except NaCl 1%. pH 3 groups continues to swell after 2 4h in both cases. Desorption rate of biomass in citric acid is very promising due confirmation of microelements availability in those pseudo-soli test and valorization of biocomposites as fertilizers. B1 mass decrease stopped after 24 h and B2 continues mass drop at the end of that time. Increasing goldenrod mass content results in overall improvement of swelling/shrinking properties (from 15.9% in case NaCl 1% solutions to 133% in case of pH 3) and has the influence on the time of achieving maximal saturation period. Differences between 24h and 96h are more visible in B2 in comparison to the B1 experiments. Therefore, may be assumed that initial goldenrod absorption rate is limited due the diffusion resistance of biopolymer layer, which leads to extended preparation time of capsules. In lower pH swelling rate is lower than in neutral environment, which is similar to tendency reported for other polymers (Estrada Villegas et al., 2018)

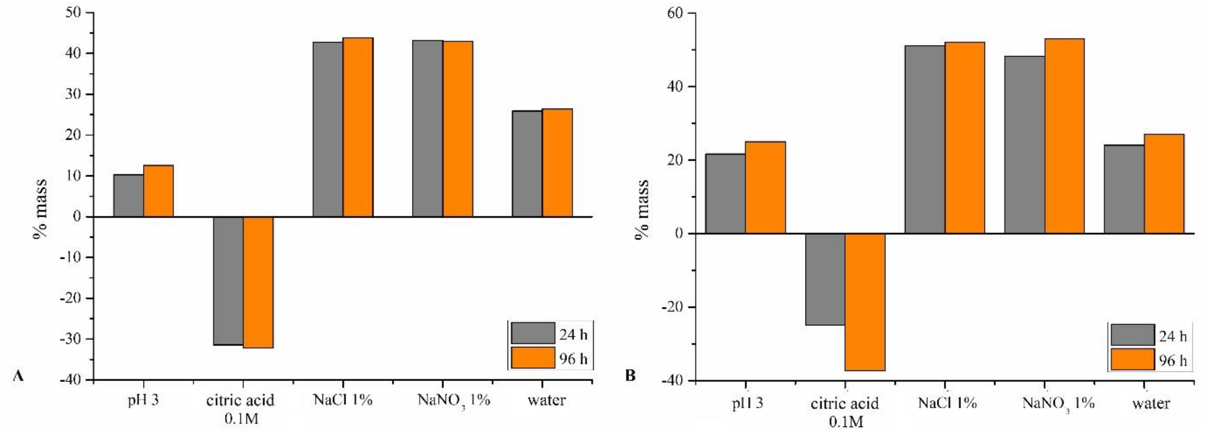

Fig. 3 *Swelling of biocomposites B1 (A) and B2 (B) in various media (T:20°C; sorbent dosage 30 g* L^{-1}*; contact time: 96 h; media: aqueous solution of pH 3, 0.1M citric acid, NaCl 1 wt.% , NaNO*$_3$ *1 wt.% and water)*

3.2. pH$_{PZC}$

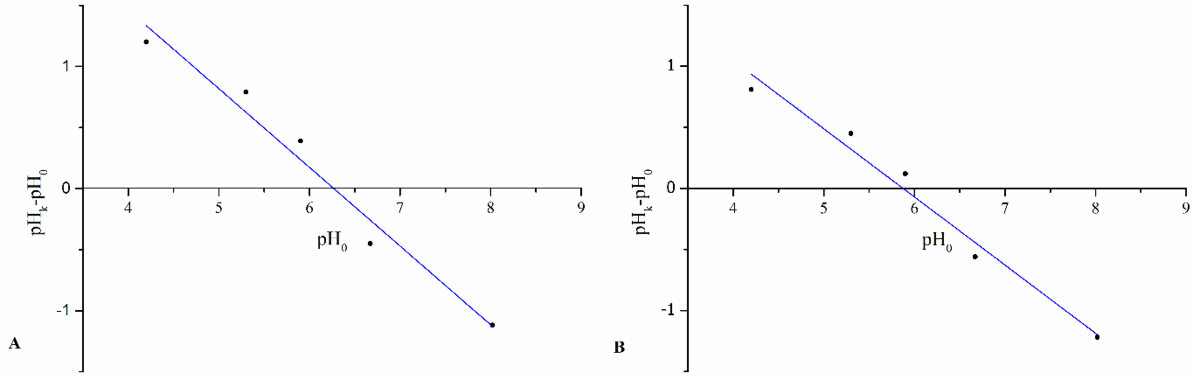

Fig. 4 *pH_{PZC} for biocomposites B1 (A) and B2 (B) (T:20°C; sorbent dosage 10 g* L^{-1}*; contact time: 24 h; pH: 5-9)*

Fig.4 presents values of pH_{PZC} for biocomposites with different goldenrod concertation. In both cases zero electrical charge density is achieved in acidic environment (6.31 for B1 and 5.94 for B2). Increasing biomass content results in shifting pH_{PZC} into lower values due to presence of functional groups on to plant surface. In comparison to the other alginate based beads researches values obtained in those experiments are higher than for example pH_{PZC} 5.2 for Ba/active carbon/alginate complex (Kumar et al., 2013). This may be explained by differences in activity and structure of biomass carriers inside polymer matrix.

3.3. Influence of pH

Batch sorption conditions such as pH and metal concentration, were adjusted to avoid precipitation of copper species. Figure 3 presents the variation in Cu^{2+} sorption percentage at various pH values for B1 and B2 biocomposites. Both sorbents follow the same behavior with increasing pH. The sorption was the highest in pH between 4-5. At acidic conditions (pH 3) functional groups on the sorbent surface are protonated and interact with copper ions more weakly than in higher pH. As pH increases, reactive sides become negatively charged and form bonds with positive copper ions. This phenomenon is observed for oH 4 and 5, while at pH 6 sorption percentage drops again, which may be due to changes in the polymer structure as a result of swelling behavior. A decrease of sorption with increasing pH is in contrary to what is expected on the basis of pH_{ZPC} of the biocomposites, which was around 6 for both sorbents.

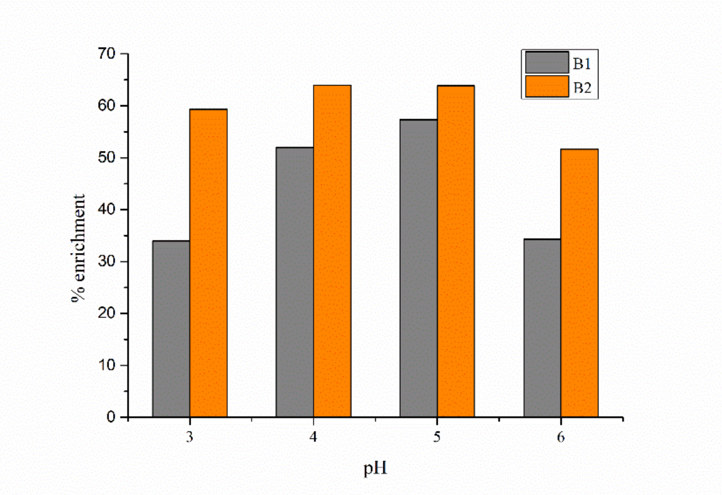

Fig. 5 *The influence of pH on the sorption process on B1 (A) and B2 (B) ((T:20°C; sorbent dosage 30 g L^{-1}; contact time: 24 h; pH:3-6; C0: 200 mg L^{-1})*

3.4. Kinetics

The experimental data of the Cu^{2+} binding kinetics was represented by the first-order (PFORE), second-order (PSORE) and general (GRLE) models. Figure 4 showing the plots of Qt versus time, obtained by nonlinear regression, indicates the applicability of the proposed models for modelling of the kinetics. Copper ion uptake by both biocomposites was rapid in the first 200 minutes; however over 1400 minutes of contact time was required to reach an equilibrium and to access to the core of the composites. Table 1 presents the estimated kinetic parameters and correlation coefficients (R^2) for the binding of copper ions by biocomposites. As expected a comparison of correlation coefficients indicates that binding kinetics for both investigated materials (B1 and B2) was better described by the GRLE model. However, a comparison of correlation coefficients of two-parameter models (PFOR and PSOR) revealed that the sorption process follows the pseudo first-order mechanism, which corresponds to physical adsorption rather than chemisorption (Daria Podstawczyk and Anna Witek-Krowiak, 2016). The similarity of kinetics parameters such as equilibrium time and sorption capacity between B1 and B2 biocomposites means that the sorption process is independent on the presence of goldenrod. On the other hand, the sorption rate was higher for B2 than for B1 due to the higher content of biomass as a better adsorbent than CMC and alginate.

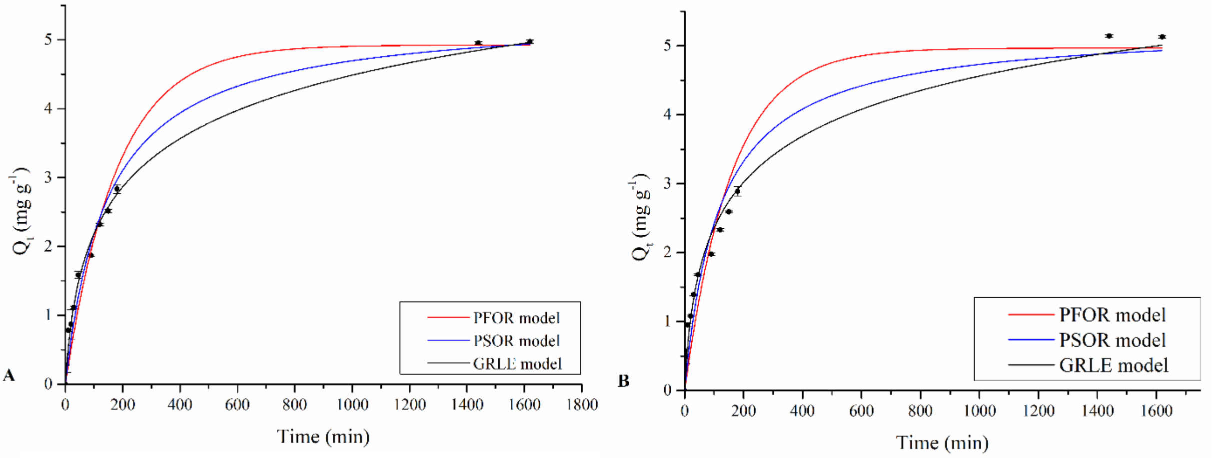

Fig. 6 *Kinetics of binding of* Cu^{2+} *for biocomposites B1 (A) and B2 (B): dashed line - PFORE, PSORE and GRLE (T:20°C; sorbent dosage 30 g* L^{-1}*; contact time: 26 h; pH:5;* C_0*: 200 mg* L^{-1}*)*

Tab. 1 *Analysis of PFOR, PSOR and GRLE adsorption kinetics parameters for biocomposites by non-linear regression method*

Biocomposite	**PFOR**			**PSOR**			**GRLE**			
	k_1	**Q_e**	**R^2**	**k_2**	**Q_e**	**R^2**	**k_n**	**n**	**Q_e**	**R^2**
	min^{-1}	*mg g^{-1}*		*$dm^3 mol^{-1} min^{-1}$*	*mg g^{-1}*				*mg g^{-1}*	
B1	5.59E-03±6.45E-05	4.92±0.021	9.85E-01	1.0E-03±2.1E-05	5.38±0.23	9.90E-01	1.92E-21±3.82E-25	19.78±0.151	23.50±0.303	9.95E-01
B2	6.31E-03±1.0E-04	4.967±0.0401	9.62E-01	2.0E-03±3.7E-03	5.29±0.036	9.79E-01	3.62e-21±4.40e-23	20.16±0.408	22.77±0.424	9.94E-01

3.5. Sorption isotherms

The sorption isotherm presents the relationship between the ions present in the solution and the sorbent. Langmuir, Freundlich and Sips models were used to describe experimental points. The Langmuir model assumes a single-layer sorption on a homogeneous surface, while the Freundlich model has multi-layer sorption on a heterogeneous surface. The Sips model combines the assumptions of both models (Ahmad et al., 2018). Fig. 7 shows the experimental data described by three non-linear models. The determined parameters are shown in Tab. 2. Both the Langmuir isotherm model and the Freundlich isotherm model well described equilibrium data for two types of composites ($R^2 > 0.99$). The experimental data were best described using the Sips model.. The Sips equation introduces an additional third parameter (*n)* that logically improves the quality of the mathematical fit. The sorption capacities obtained do not differ significantly from the parameters determined by the Langmuir isotherm. The determined parameter n decreases with increasing number of components. The n values closer to one correspond to the sorbent with relatively homogeneous bond locations, while the values close to zero are usually related to the heterogeneity of the surface (Benettayeb et al., 2017). The determined maximum sorption volumes were 6.9 mg g^{-1} and 7.5 mg g^{-1} for B1 and B2 respectively. Sorbents with higher biomass concentration showed higher sorption capacity, which is closely related to the greater number of active sites in the biocomposite.

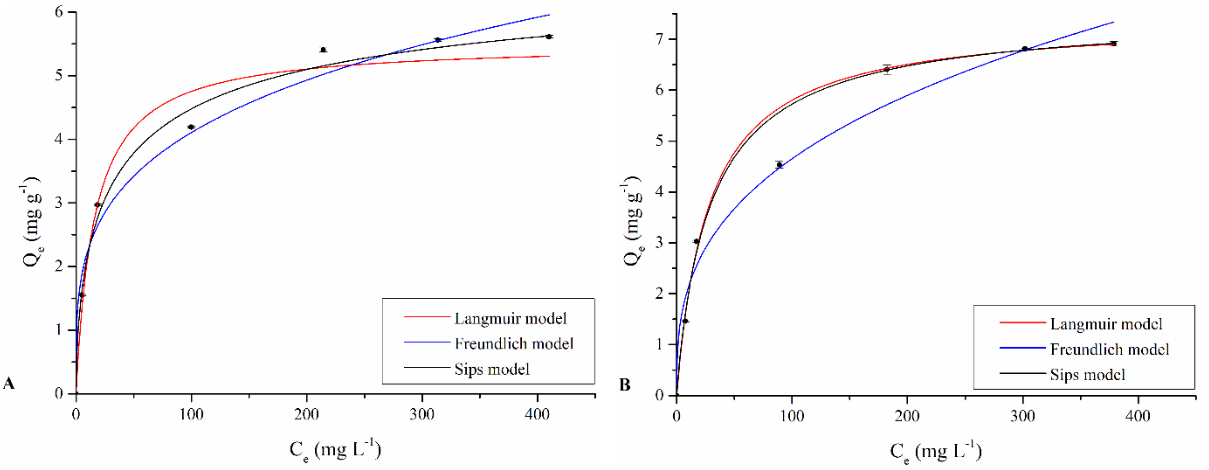

Fig. 7 *Equilibrium of binding of* Cu^{2+} *ions for biocomposites B1 (A) and B2 (B) (dashed line: Langmuir, Freundlich and Sips model; T:20°C; sorbent dosage: 30 g* L^{-1}*, contact time: 24 h; pH:5;* C_0*: 50 - 500 mg* L^{-1}*)*

Tab. 2 *Analysis of Langmuir, Freundlich and Sips sorption isotherm parameters for biocomposites by non-linear regression method*

Langmuir			**Freundlich**			**Sips**			
Q_{max}	**K_L**	**R^2**	**K_F**	**n_F**	**R^2**	**Q_{max}**	**K**	**n**	**R^2**
mg/g	*dm^3/mg*					*mg/g*			
5,11±0,26	0.0626±0.001	9.93E-01	1.22±0.151	3.79±0.037	9.92E-01	**6.95±0.113**	1.14E-01	2.10E-03	9.96E-01
7,403±0,162	0.036±0.0004	9.98E-01	0.09637±0.0171	2.9248±0.276	9.95E-01	**7.544±0.096**	0.04036±0.0026	0.946±0.0238	9.99E-01

3.6. Desorption

Considering the potential use of biocomposites as fertilizers, the key aspect was to investigate the desorption of Cu^{2+} ions from enriched structures in various solutions. The results of the experiment are shown in Fig. 8. The highest percentage of Cu^{2+} ions released was observed in an acid environment (about 95% and 91% for composite B1 and B2, respectively). As a result of hydrolysis at low pH, crosslinked alginate can transform into alginic acid causing weakening of the composite structure and even lead to its degradation. (Bajpai and Sharma, 2004). The ion exchange between H^+ and Ca^{2+} also contributes to the relaxation of the structure. The decrease in the concentration of Ca^{2+} ions in composite structures leads to the loosening of the structure and the rapid release of valuable micronutrients in the form of Cu^{2+} ions (An et al., 2013). The structures of the beads are also sensitive to the strong electrostatic interactions caused by the Na^+ ions present in the solution. The bead structures are also sensitive to the strong electrostatic interactions caused by the Na^+ ions present in the solution, which lead to the release of Cu^{2+} ions from the enriched structures (Bajpai and Sharma, 2004). Based on the results, it was observed that the more biosorbent in the composite, the Cu^{2+} ion desorbed slower.

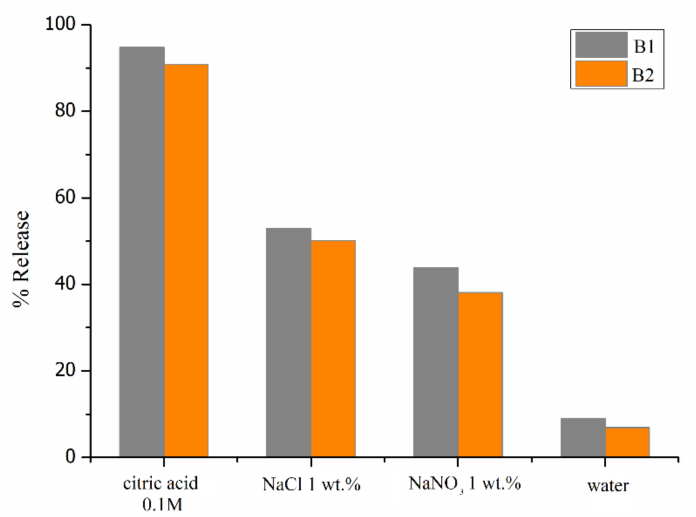

Fig.8 *Release of copper(II) ions in various media for biocomposites (aqueous solution of citric acid 0.1M, NaCl 1 wt.%,* $NaNO_3$ *1 wt.% and water)*

4. Conclusion

Goldenrod immobilized in a polymer matrix is a very good sorbent of Cu^{2+} ions. Sorption equilibrium was best described by the Sips model. The composites with a 5% biomass concentration showed greater sorption capacity (Q_{max} - 6.9 mg g^{-1} and 7.5 mg g^{-1} for B1 and B2 respectively). Biocomposites have demonstrated the properties of the slow release of ions in water and in the simulating soil solution. The results showed that biocomposites with immobilized goldenrod are a very good material for potential applications as a controlled release fertilizer.

Acknowledgements

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