



Research Article

Preparation of hydrogel composites using Ca^{2+} and Cu^{2+} ions as crosslinking agents

K. Mikula¹ · D. Skrzypczak¹ · B. Ligas¹ · A. Witek-Krowiak¹

© The Author(s) 2019 **OPEN**

Abstract

The aim of this work was to investigate the influence of the crosslinking agent on the production of biopolymer composites with immobilized eggshells. Capsules with various chemical composition were produced: pure alginate (ALG) and alginate with carboxymethylcellulose and different content of biosorbent (5 wt% and 10 wt%). Two crosslinking agents have been used for the production of composites, i.e. Cu^{2+} ions and Ca^{2+} ions. Physicochemical properties (drying kinetics, swelling) and sorption properties of the structures were examined. Composite functional groups responsible for binding Cu^{2+} cations using Fourier transform infrared spectroscopy were located. Desorption of Cu^{2+} ions was performed to investigate the effect of crosslinkers on the release of cations (composites crosslinked with Ca^{2+} ions slower desorb the Cu^{2+} ions). The results showed that the type of the crosslinking agent has a significant influence on the physicochemical properties of biocomposites, as well as the binding and release of Cu^{2+} ions. Based on the result, biocomposites with immobilized biomass crosslinked with Ca^{2+} ions could be used in the future as controlled release fertilizers.

Keywords Microelements · Copper · Fertilizers · Alginate · Carboxymethylcellulose · Biosorbent

List of symbols

C_0	Initial concentration of Cu^{2+} (mg L^{-1})
C_e	Equilibrium concentration of Cu^{2+} in the solution (mg L^{-1})
C_t	Concentration of Cu^{2+} after contact time (mg L^{-1})
k	Empirical coefficients in models (h^{-1})
k_1	Process rate constant (1 min^{-1})
k_2	Process rate constant ($\text{min mg}^{-1} \text{ s}^{-1}$)
k_p	Rate of intra-particle diffusion ($\text{mmol g}^{-1} \text{ min}^{-0.5}$)
K_b	Langmuir constant related to sorption affinity (L mg^{-1})
K_F	Freundlich constant related to uptake capacity (L mg^{-1})
K_S	Sips constant related to sorption affinity (L mg^{-1})
n	Empirical constant in models (–)
n_1	Order rate of the reaction (–)
n_F	Constant known as sorbent intensity (–)
n_s	Constant known as sorbent intensity (–)
pH_0	Initial pH of the solution (–)

pH_k	Final pH of the solution (–)
Q_e	Equilibrium sorption capacity (mg g^{-1})
Q_{max}	Maximum sorption capacity of sorbent (mg g^{-1})
Q_t	Sorption capacity over time (mg g^{-1})
t	Time (min)
V	Volume of the solution (L)

Abbreviations

ALG	Sodium alginate
CMC	Carboxymethyl cellulose
PFOR	Pseudo-first order reaction
PSOR	Pseudo-second order reaction
GRLE	General Rate Law Equation

1 Introduction

The main problem of traditional fertilizers is the release rate of mineral substances into the soil. The ingredients penetrate quickly enough that the plants are unable to take the

✉ K. Mikula, katarzyna.mikula@pwr.edu.pl | ¹Department of Chemical Engineering, Faculty of Chemistry, Wrocław University of Science and Technology, Norwida 4/6, 50-373 Wrocław, Poland.



total amount. Accumulation of unused components, their leakage to groundwater and introduction of subsequent doses of fertilizers pose a threat to the environment. Reduction of nutrient losses and increased fertilization efficiency can be provided by controlled-release fertilizers (CRF) [1]. The process of releasing nutrients from polymer coated granules takes place in a few stages. The water present in the soil solution migrates inside the granule and dissolves the nutrients. If the coating can withstand rising pressure, nutrients will gradually penetrate into the soil. Compared to traditional fertilizer, the diffusion of these substances is slower. The coating provides a barrier by which the release rate is more adapted to the nutritional requirements of plants. The material and thickness of the polymer coating plays an important role in the release process [2].

Controlled release fertilizers have gained a lot of interest, but the degradation of the polymer coating can act negatively on the environment [3]. The promising alternative may be biosorbents immobilized in a biopolymer matrix. The enrichment of biomass with valuable micronutrients and immobilization in the gel structure gives the opportunity to create composites that release substances gradually and are environmentally safe—a coating material is biodegradable, biocompatible and non-toxic. Such features have alginate and chitosan, which belong to the group of biopolymers. Composites based on biopolymers are used not only in agriculture but also as drug carriers in the pharmacy and medicine [4].

Alginate is a non-branched polysaccharide composed of monomers of β -D-mannuronic acid and α -L-guluronic acid [5]. It has the ability to form a three-dimensional gel structure. This phenomenon is described as egg—box model. Hydrogels can be obtained by adding sodium alginate to a crosslinking solution in which divalent ions are present. Divalent ions interact with guluronic monomers and form ionic bridges that lead to the formation of a hydrophilic 3D structure [6]. The stability of the structures produced is influenced by the type and concentration of the crosslinking agent. The size of the ions and their diffusion capacity is also crucial in the formation of alginate composites. Ions of larger sizes can fill larger space in the alginate structure and create a more compact system than smaller ions. The appropriate structural integrity of the hydrogel can reduce the permeability of solutes and gases, and also slow down the release of active ingredients [7].

Biocomposites can be easily modified. The introduction of a new component may change the properties of the hydrogel. Alginate with the addition of carboxymethylcellulose forms composites characterized by higher porosity and better mechanical strength. Similarly, carboxymethylcellulose is an eco-friendly biopolymer that can form 3D structures in the presence of multivalent cations [8, 9]. These two biodegradable compounds

combined with immobilized biomass give the opportunity to create porous structures with new properties that can be used as innovative controlled release fertilizers.

The aim of this work was to produce composites enriched with micronutrients using various crosslinking agents— Ca^{2+} and Cu^{2+} ions. Calcium chloride is a commonly used crosslinking agent for obtaining alginate beads. The CuSO_4 solution was also used as a crosslinking agent because Cu^{2+} ions belong to the group of essential micronutrients. Eggshells were used for research as easily available waste material (reduction of production costs). The effect of individual components of the hydrogel on its physicochemical properties and sorption capacity was also investigated. This study focuses on enriching composites with copper ions as an example of a micronutrient that is necessary for the initial stages of plant growth.

2 Materials and methods

2.1 Materials

Eggshells were obtained from a local producer as waste from the agri-food sector. The cleaned and dried biosorbent was ground and sieved. The size of the crushed particles was $0.43\ \mu\text{m}$. Sodium alginate and carboxymethylcellulose were purchased from Sigma Aldrich. Calcium chloride (CaCl_2) and copper (II) sulfate (CuSO_4) (POCH, Poland) were used as crosslinkers.

2.2 Preparation of beads

2.2.1 Crosslinking with Ca^{2+} ions

The 2.5 wt% solution of sodium alginate was prepared by dissolving sodium alginate in distilled water at $50\ ^\circ\text{C}$. After cooling, 1 wt% sodium carboxymethyl cellulose and 10 wt% ground eggshells were added to the alginate solution. In order to investigate the effect of individual components of the hydrogel on its physicochemical properties, an additional three solutions were prepared analogously with various contents of sodium alginate, carboxymethylcellulose and biosorbent. The chemical composition of the hydrogels is shown in Table 1. Each of the solutions was dropped into 0.2 M CaCl_2 solution and crosslinked for 24 h. After this time, the structures formed were washed several times with distilled water and stored for further experiments at $4\ ^\circ\text{C}$.

2.2.2 Crosslinking with Cu^{2+} ions

2.2.2.1 Kinetics of the crosslinking ions of copper (II) The composites crosslinked with Cu^{2+} ions were produced using the 0.05 M CuSO_4 , analogously to the point 2.2.1.

Table 1 Chemical composition of biocomposites

	Types of samples			
	ALG	CMC	B5	B10
Composition of the biocomposites				
Sodium alginate	2.5 wt%	2.5 wt%	2.5 wt%	2.5 wt%
Sodium carboxymethylcellulose	–	1 wt%	1 wt%	1 wt%
Eggshells	–	–	5 wt%	10 wt%

During the dropwise addition of an alginate solution with/without additives to a solution of Cu^{2+} , the crosslinker solution was sampled to examine the content of Cu^{2+} ions.

The sorption capacity of the produced structures was determined using the equation [10]:

$$Q_t = \frac{(C_0 - C_t) \cdot V}{m} \quad (1)$$

where Q_t —sorption capacity over time (mg g^{-1}), C_0 —initial concentration of Cu^{2+} (mg L^{-1}), C_t —concentration of Cu^{2+} after time t (mg L^{-1}), V —volume of the solution (L), m —mass of biocomposite (g).

Parameters of Cu^{2+} crosslinking kinetics were determined using the pseudo-first (Eq. 2) and pseudo-second order model (Eq. 3) as well as general rate law equation (Eq. 4) [11].

$$Q_t = Q_e \cdot (1 - e^{-k_1 \cdot t}) \quad (2)$$

$$Q_t = \frac{Q_e^2 \cdot k_2 \cdot t}{1 + Q_e \cdot k_2 \cdot t} \quad (3)$$

$$Q_t = Q_e - (Q_e^{1-n} + (n-1) \cdot k_n \cdot t)^{\frac{1}{1-n}} \quad (4)$$

where Q_e —equilibrium sorption capacity (mg g^{-1}), k_1 —process rate constant (min^{-1}), k_2 —process rate constant ($\text{g mg}^{-1} \text{min}^{-1}$), k_n —process rate constant ($\text{g mg}^{-1} \text{min}^{-1}$), n —order rate of the reaction.

2.3 Physicochemical properties of hydrogels

2.3.1 Drying kinetics

To determine the water content of the composites produced, 20 beads of each type were weighed at specific intervals of 24 h. The loss of mass allowed to determine the relative water content in composites described by the equation [12]:

$$\text{MR} = \frac{u_t}{u_0} \quad (5)$$

Two models were used to describe the kinetics of drying and determine the parameters of this process: the Newton model (Eq. 6) and the Page model (Eq. 7) [12].

$$\text{MR} = \exp(-k \cdot t) \quad (6)$$

$$\text{MR} = \exp(-k \cdot t^n) \quad (7)$$

where MR —relative water content ($\text{g}_{\text{H}_2\text{O}} \text{g}^{-1}$ dry mass), u_0 —initial water content ($\text{g}_{\text{H}_2\text{O}} \text{g}^{-1}$ dry mass), u_t —content above after time t ($\text{g}_{\text{H}_2\text{O}} \text{g}^{-1}$ dry mass), k —empirical coefficients in models (min^{-1}), t —time (min), n —empirical constant in the Page model (–).

2.3.2 FTIR

To identify functional groups, which are responsible for the binding of Cu^{2+} ions, Fourier transform infrared spectroscopy was used (FTIR). The study was conducted in the 4000–400 cm^{-1} wave range.

2.3.3 Swelling properties

To examine the degree of hydration of composites in various media, 7 conical flasks containing 50 ml of distilled water, 1 wt% aqueous NaCl, 1 wt% aqueous NaNO_3 , 0.1 M citric acid, aqueous solutions at pH 3, pH 7 and pH 10 were prepared. 1 g of composites was weighed into each of the media.

The samples were weighed again after 24 h and 96 h. The experiment was carried out for composites crosslinked with calcium ions as well as copper (II) ions.

Biocomposites weight change was determined by the equation [13]:

$$\%mas. = \frac{m_t - m_0}{m_0} \cdot 100 \quad (8)$$

where $\%mas.$ —change in weight of the composite (%), m_0 —the initial mass of the composite (g), m_t —mass of composite after time t (g)

2.4 Kinetics of biocomposites enrichment with Cu^{2+} ions

200 ml aqueous solution with concentration of Cu^{2+} 200 mg L^{-1} with fixed pH 5.00 was prepared in Erlenmeyer flasks. Appropriate mass of beads (15 g L^{-1}) was weighed and transferred to a solution of copper (II) ions. The flasks with the beads were agitated on an orbital shaker at room temperature. At specific intervals, the pH was measured and a sample was taken to determine the content of copper (II) ions by the ICP–OES. The test was conducted only for composites crosslinked with calcium ions. The experiment was carried out until reaching equilibrium (after 24 h

for ALG and CMC composites, after 48 h for B5 and B10 composites).

The sorption capacity was determined by the Eq. 5 given in Sect. 2.2.2.1.

Parameters of Cu²⁺ ion sorption kinetics were determined using the pseudo-first (Eq. 6) and pseudo-second order model (Eq. 7) as well as general rate law equation (Eq. 8) (Sect. 2.2.2.1).

The kinetics of the sorption process was also described using the internal particle diffusion model proposed by Weber–Morris (Eq. 9) [14]:

$$Q_t = k_p \cdot t^{\frac{1}{2}} + C \tag{9}$$

where k_p —rate of intra-particle diffusion ($\text{mg g}^{-1} \text{min}^{-0.5}$), C —constant (–)

2.5 Release of cations in various media

2.5.1 Beads crosslinked with calcium ions

The biocomposites (15 g L^{-1}) were added to 2 L of Cu(II) ions solution with the initial concentration of 200 mg L^{-1} (pH 5.0). After 48 h, beads were separated and rinsed with distilled water in order to remove the residual Cu²⁺ ions solution. Then, three aqueous solutions were prepared: pH 3, pH 7 and 1 wt% NaNO₃.

To examine the effect of various media on the desorption of Cu²⁺ ions, appropriate mass of beads was weighed (the initial content of copper (II) in all composites was the same) and transferred to 100 ml of prepared solutions. Desorption was carried out for 14 days. Samples were

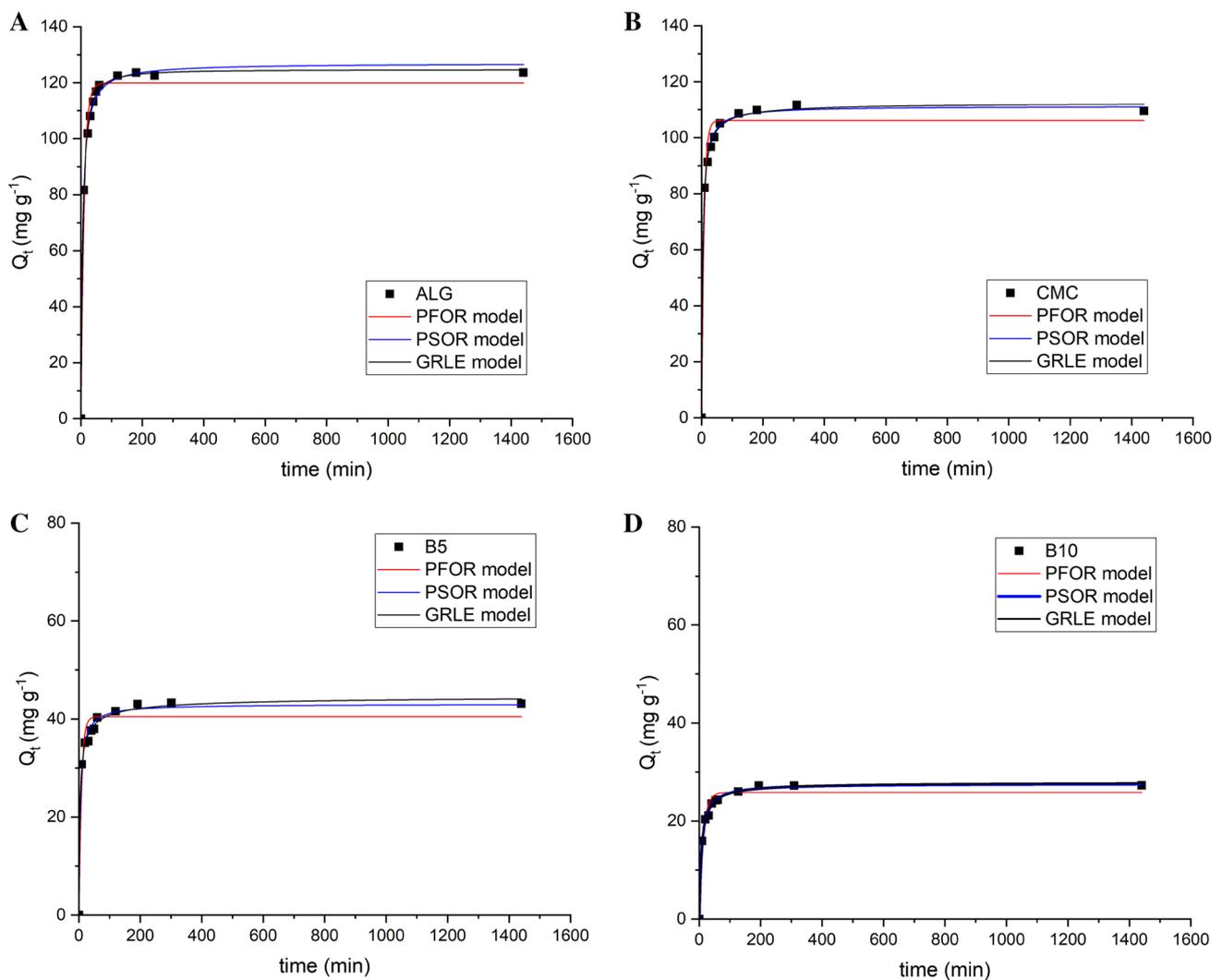


Fig. 1 Kinetics of crosslinking of Cu²⁺ ions for ALG (a), CMC (b), B5 (c) and B10 (d) biocomposites (dashed line: PFOR, PSOR and GRLE model; T: 20 °C; contact time: 24 h)

taken for analysis on the content of Cu²⁺ ions in solutions and the eluent was replaced at various time intervals.

2.5.2 Beads crosslinked with copper (II) ions

Three aqueous solutions were prepared: pH 3, pH 7 and 1 wt% NaNO₃. To examine the effect of various media on the desorption of Cu²⁺ ions, appropriate mass of beads was weighed (the initial content of copper (II) in all composites was the same) and transferred to 100 ml of prepared solutions. Desorption was carried out for 14 days. Samples were taken for analysis on the content of Cu²⁺ ions in solutions and the eluent was replaced at various time intervals.

3 Results and discussion

3.1 Kinetics of the crosslinking with copper (II) ions

In order to investigate the rate of formation of 3D structures during crosslinking with Cu²⁺ ions, kinetic profiles for composites of different composition were created (Fig. 1). The fastest cation binding was observed for a composite containing pure alginate (ALG) because the equilibrium was reached after 60 min. The addition of carboxymethylcellulose reduces the porosity of the composite, and thus the crosslinking process stabilizes longer (120 min for the CMC composite). The rate of structure formation depends on the diffusion of cations from the solution until the Cu²⁺ ions bind to the composite functional groups. The immobilization of the biosorbent in the polymer matrix additionally prolongs the crosslinking process, because the internal diffusion of Cu²⁺ ions proceeds slowest. As a result, the time required to reach equilibrium for composite B5 amounted to approx. 190 min. Increasing the amount of biosorbent in the biocomposite leads to the multiplication of active sites, which react with cations. A large number of different functional groups may cause binding of Cu²⁺ ions to be based on various physicochemical phenomena, i.e. chemisorption, ion exchange, complexation or physical adsorption [11]. Composite B10 was characterized by diversified chemical composition and the largest amount of biosorbent, therefore the mechanism of Cu²⁺ binding was the most complex. The achievement of equilibrium lasted the longest (300 min).

Modeling of experimental data allowed to determine the parameters of Cu²⁺ ions kinetics (Table 2). For all types of composites, the best-fitting model was the GRLE, as evidenced by R² values. The rate constants for the Cu²⁺ ion binding process of the ALC, CMC, B5 and B10 composites were determined, which are 5.30e-03 g mg⁻¹

Table 2 Analysis of PFOR, PSOR and GRLE crosslinking kinetics parameters for ALG, CMC, B5 and B10 biocomposites by non-linear regression method

Composite	PFOR		PSOR		GRLE	
	k ₁ (min ⁻¹)	Q _e (mg g ⁻¹)	R ²	k ₂ (min ⁻¹)	Q _e (mg g ⁻¹)	R ²
ALG	9.75e-02 ± 8.95e-03	119.90 ± 1.71	0.986	1.48e-03 ± 9.32e-05	126.98 ± 0.88	0.998
CMC	1.27e-01 ± 1.70e-02	106.15 ± 2.04	0.978	2.30e-03 ± 1.74e-04	111.26 ± 0.81	0.997
B5	1.20e-01 ± 1.97e-02	40.51 ± 1.01	0.961	4.97e-03 ± 6.70e-04	43.05 ± 0.54	0.992
B10	7.63e-2 ± 8.30e-02	25.83 ± 0.61	0.967	4.70e-03 ± 3.52e-04	27.67 ± 0.24	0.996
				k _n (min ⁻¹)	Q _e (mg g ⁻¹)	R ²
				5.30e-03 ± 1.88e-03	124.67 ± 0.86	0.999
				8.85e-04 ± 8.46e-04	112.61 ± 1.61	0.998
				4.80e-04 ± 6.94e-04	44.98 ± 1.31	0.996
				3.19e-04 ± 3.76e-03	27.95 ± 0.49	0.997

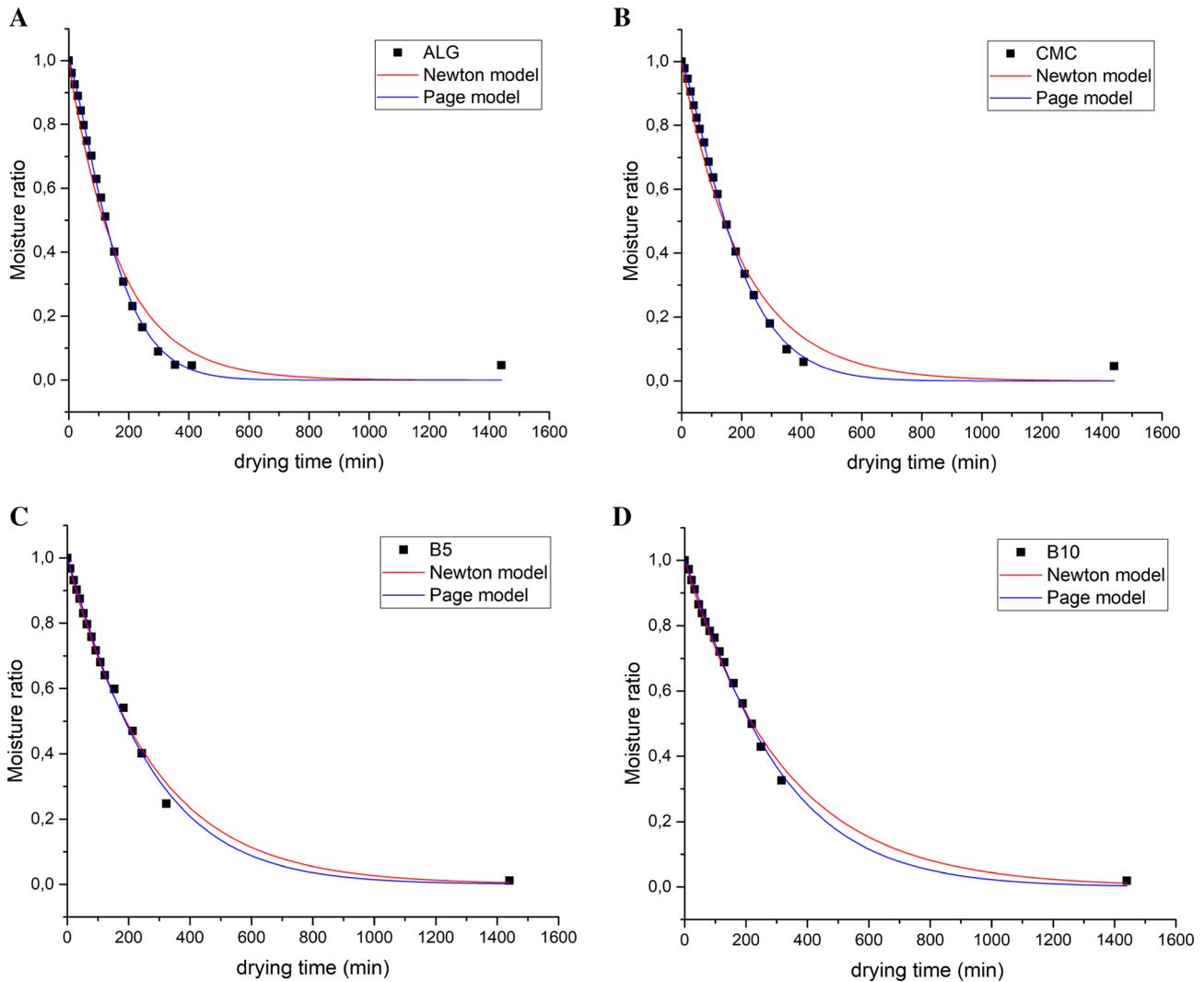


Fig. 2 Drying kinetics of ALG (a), CMC (b), B5 (c) and B10 (d) biocomposites crosslinked with Ca^{2+} ions (dashed line: Newton model, Page model; T: 20 °C; dosage: 20 capsules; time: 24 h)

Table 3 Analysis of Newton and Page drying kinetics parameters for ALG, CMC, B5 and B10 biocomposites crosslinked with Ca^{2+} ions by non-linear regression method

Composite	Newton model		Page model		
	k (min ⁻¹)	R ²	k (min ⁻¹)	n	R ²
ALG	5.95e-03 ± 2.63e-04	0.978	2.37e-03 ± 1.82e-04	1.32 ± 2.99e-02	0.998
CMC	4.92e-03 ± 1.95e-04	0.981	1.81e-03 ± 1.62e-04	1.28 ± 2.62e-02	0.998
B5	3.13e-03 ± 7.12e-05	0.994	1.23e-03 ± 3.81e-04	1.11 ± 3.14e-02	0.996
B10	3.02e-03 ± 6.00e-05	0.995	1.21e-03 ± 2.59e-04	1.08 ± 1.67e-04	0.997

min⁻¹, 8.85e-04 g mg⁻¹ min⁻¹, 4.80e-04 g mg⁻¹ min⁻¹ and 3.19e-04 g mg⁻¹ min⁻¹, respectively. Sorption capacities were found, which are 124.67 mg g⁻¹ for the ALG composite, 112.61 mg g⁻¹ for the CMC composite, 44.98 mg g⁻¹ for the B5 composite and 27.95 mg g⁻¹ for the B10 composite. The estimated sorption capacities differ from the values resulting from the experimental data. The equation

defining the sorption capacity describes this parameter as the ratio of the difference in concentrations of Cu^{2+} ions in the solution to the mass of the composite. It follows that the higher the mass of the composite, the smaller the sorption capacity. During the investigation of crosslinking kinetics, the largest loss of Cu^{2+} ions in the solution

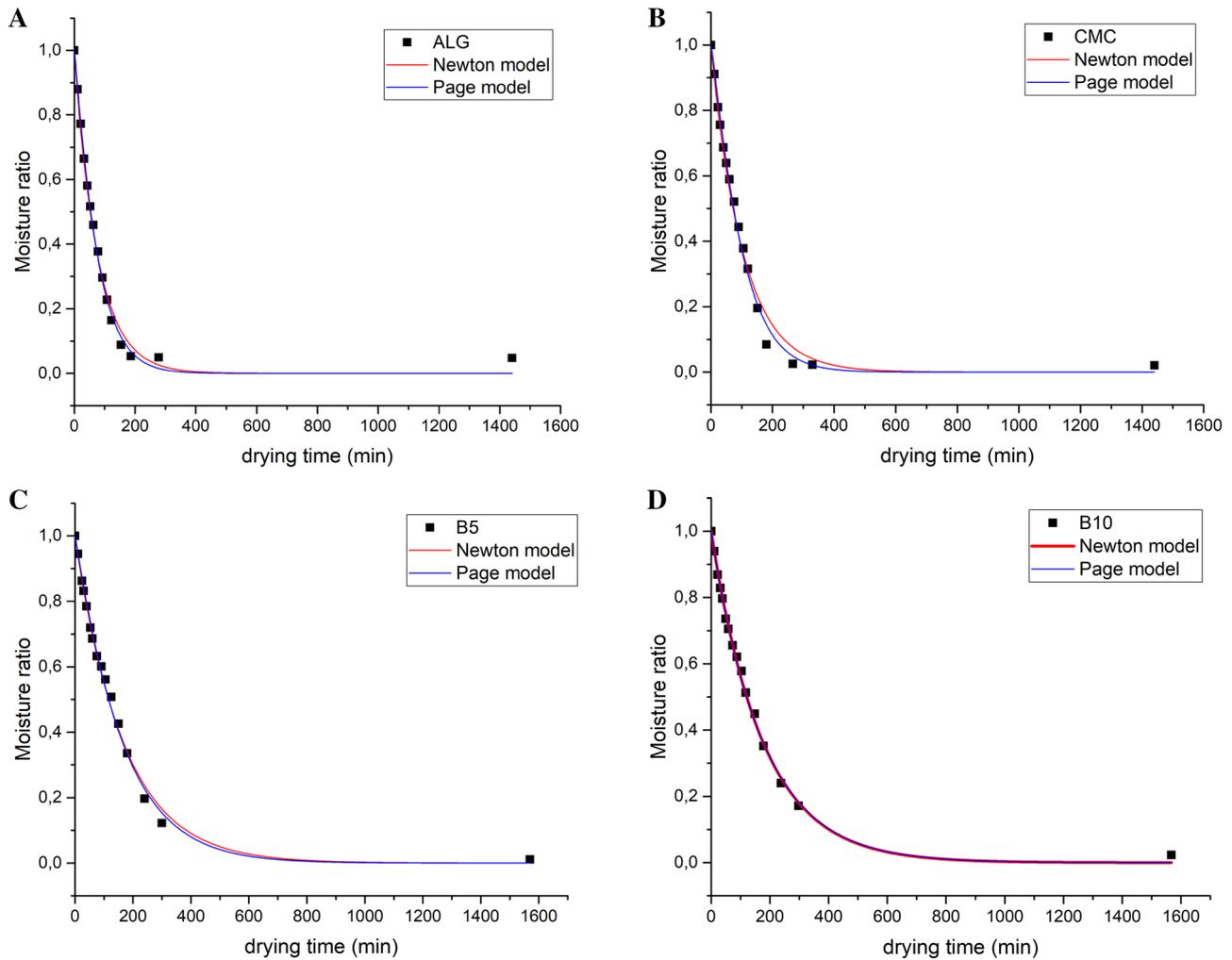


Fig. 3 Drying kinetics of ALG (a), CMC (b), B5 (c) and B10 (d) biocomposites crosslinked with Cu^{2+} ions (dashed line: Newton model, Page model; T: 20 °C; dosage: 20 capsules; time: 24 h)

Table 4 Analysis of Newton and Page drying kinetics parameters for ALG, CMC, B5 and B10 biocomposites crosslinked with Cu^{2+} ions by non-linear regression method

Composite	Newton model		Page model		
	k (min ⁻¹)	R ²	k (min ⁻¹)	n	R ²
ALG	1.314e-02 ± 3.19e-04	0.993	8.64 ± 1.49e-03	1.10 ± 3.99e-02	0.995
CMC	9.67e-03 ± 3.04e-04	0.989	5.93 ± 1.09e-03	1.14 ± 4.78e-02	0.994
B5	5.99e-03 ± 1.22e-04	0.994	5.07 ± 8.23e-04	1.04 ± 3.50e-02	0.993
B10	5.73e-03 ± 7.88e-05	0.997	4.86 ± 6.77e-04	0.993 ± 2.36e-02	0.997

containing B10 composites was recorded, which indicates that the largest sorption capacity is obtained.

3.2 Physicochemical properties of hydrogels

3.2.1 Drying kinetics

The water content decreases exponentially over time for composites crosslinked with Ca^{2+} ions, which is shown in

Fig. 2. To determine the parameters of the drying kinetics, a regression analysis of changes in the relative water content of the composites was carried out over time [15]. The coefficients k determining the rate of removal of water from composites are shown in Table 3 [16]. The values of this parameter vary for the Newton model and the Page model, but show the same relationship. The fastest water was removed from the composite containing pure alginate. The change in the porosity resulting from the

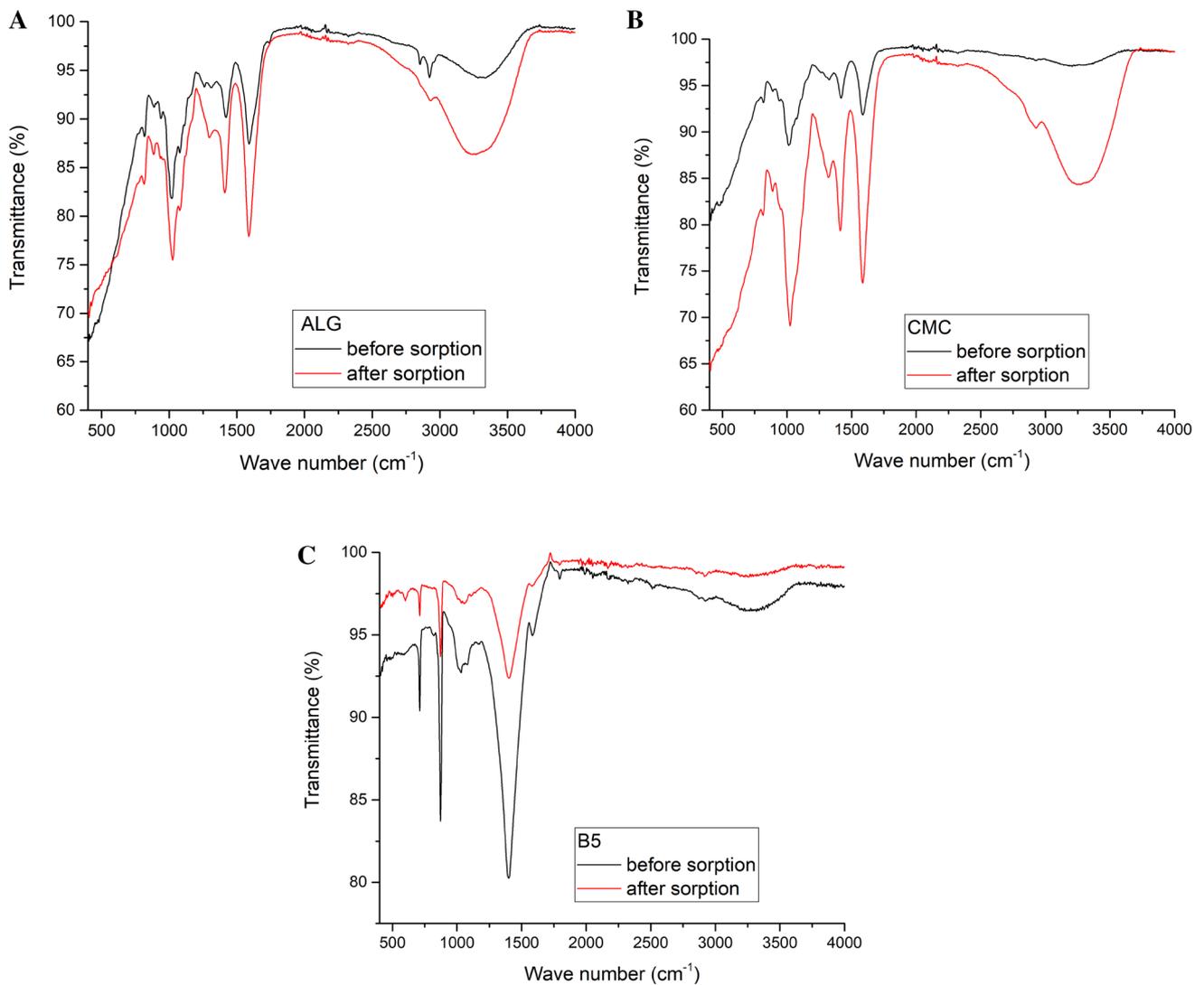


Fig. 4 FTIR spectra for ALG (a), CMC (b), B5 (c) biocomposites crosslinked with Ca^{2+} ions before and after sorption of Cu^{2+} ions

Table 5 Functional groups observed on the ALG biocomposite by FTIR spectroscopy

No.	Wave number (cm^{-1})	Before sorption	After sorption	Differences	Bond	Functional group
1	3355–3322/ 3297–3255	3333	3264	–69	O–H stretching	Alcohols
2	2950–2877/ 2958–2806	2923	2930	7	C–H stretching	Alkanes
3	1718–1488/ 1772–1488	1590	1589	–1	COO^- stretching	Carboxylic acids
4	1490–1348/ 1490–1336	1420	1411	–9	C–C bending	Alcohols
5	1072–954/ 1024–958	1020	1020	0	C–O–C stretching	Ethers
6	902–867/ 912–844	889	885	–4	–CH deformation	Alkanes

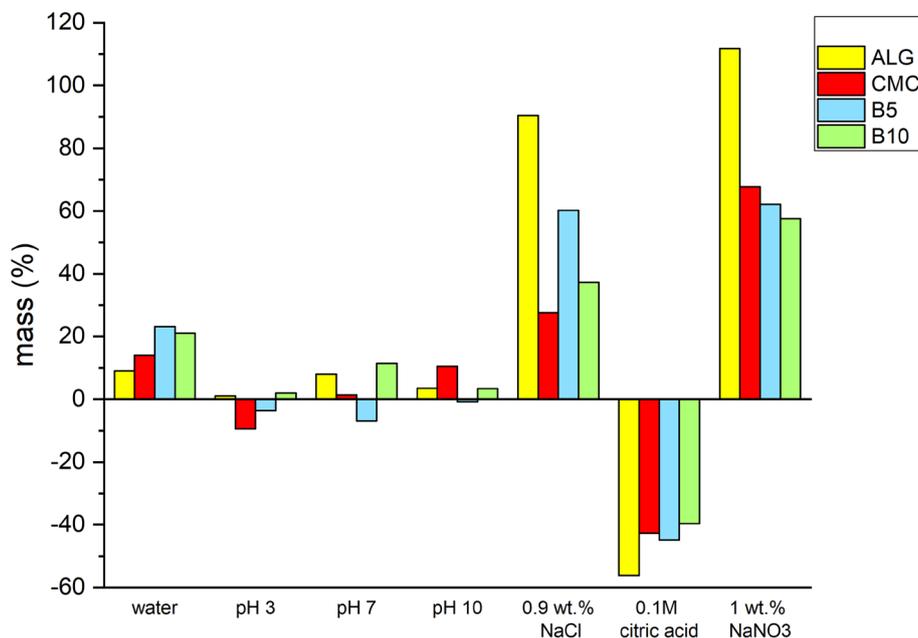
Table 6 Functional groups observed on the CMC biocomposite by FTIR spectroscopy

No.	Wave number (cm ⁻¹)	Before sorption	After sorption	Differences	Bond	Functional group
1	3222–3195/3259–3236	3207	3247	40	O–H stretching	Alcohols
2	2948–2925/2690–2765	2931	2928	–3	C–H stretching	Alkanes
3	1620–1508/1783–1488	1586	1586	0	COO ⁻ stretching	Carboxylic acids
4	1490–1357	1420	1413	–7	C–C bending	Alcohols
5	1363–1269/1359–1197	1327	1322	–5	C–H stretching	Alkanes
6	1199–1107/1197–956	1012	1025	13	C–O–C stretching	Ethers

Table 7 Functional groups observed on the B5 biocomposite by FTIR spectroscopy

No.	Wave number (cm ⁻¹)	Before sorption	After sorption	Differences	Bond	Functional group
1	3309–3325/3255–3269	3318	3260	–58	O–H stretching	Alcohols
2	2900–2937	2923	2916	–7	C–H stretching	Alkanes
3	1554–1726	1584	1581	–3	COO ⁻ stretching	Carboxylic acids
4	1189–1554/1223–1547	1401	1404	3	CO ₃ ²⁻	Carbonic acid
5	1016–1050	1032	1033	1	C–H stretching	Ethers
6	825–891/866–885	872	873	1	CO ₃ ²⁻	Carbonic acid
7	673–727	712	712	0	CO ₃ ²⁻	Carbonic acid

Fig. 5 Swelling of ALG, CMC, B5 and B10 biocomposites crosslinked with Ca²⁺ ions in various media (T: 20 °C; sorbent dosage 20 g L⁻¹; contact time: 96 h; media: water, aqueous solution at pH 3, 7 and 10, 0.1 M citric acid, 1 wt% NaCl, 1 wt% NaNO₃)



introduction of additional substances (carboxymethylcellulose, biosorbent) as well as the increase in the amount of biosorbent (B10) causes the drying process to occur more slowly. The equations describing the drying kinetics differ only by the parameter n , which ensured a better fit of the Page model to the experimental data ($R^2 > 0.996$). The drying rate constant was $2.37e-03 \text{ min}^{-1}$ for the ALG composite, $1.81e-03 \text{ min}^{-1}$ for the CMC composite,

$1.23e-03 \text{ min}^{-1}$ for the B5 composite and $1.21e-03 \text{ min}^{-1}$ for the B10 composite.

The drying kinetics study was also carried out for composites crosslinked with Cu²⁺ ions (Fig. 3). To determine the process parameters, the same logarithm models were used (the Newton model and the Page model). The drying rate constant was $8.64e-03 \text{ min}^{-1}$ for the ALG composite, $5.93e-03 \text{ min}^{-1}$ for the CMC composite, $5.07e-03 \text{ min}^{-1}$ for the B5 composite and $4.86e-03 \text{ min}^{-1}$ for the B10

composite (Table 4). Same as the composites crosslinked with Ca^{2+} ions, the dehydration process occurs fastest in the composite ALG and the slowest for the composite B10. Comparing the same types of composites, it was noticed that composites crosslinked with Cu^{2+} ions have higher values of k parameters than composites crosslinked with Ca^{2+} ions. This means that composites crosslinked with Cu^{2+} ions dry faster because they were more porous.

3.2.2 FTIR

To identify the functional groups present responsible for the binding of divalent cations, Fourier transform infrared spectroscopy (FTIR) was used. The analysis comprised dry ALG, CMC and B5 composites crosslinked with Ca^{2+} ions before and after enrichment with Cu^{2+} ions (Fig. 4). The composition of the B5 and B10 composites was the same, they differed only in the percentage content of the biosorbent, and thus the functional groups are identical.

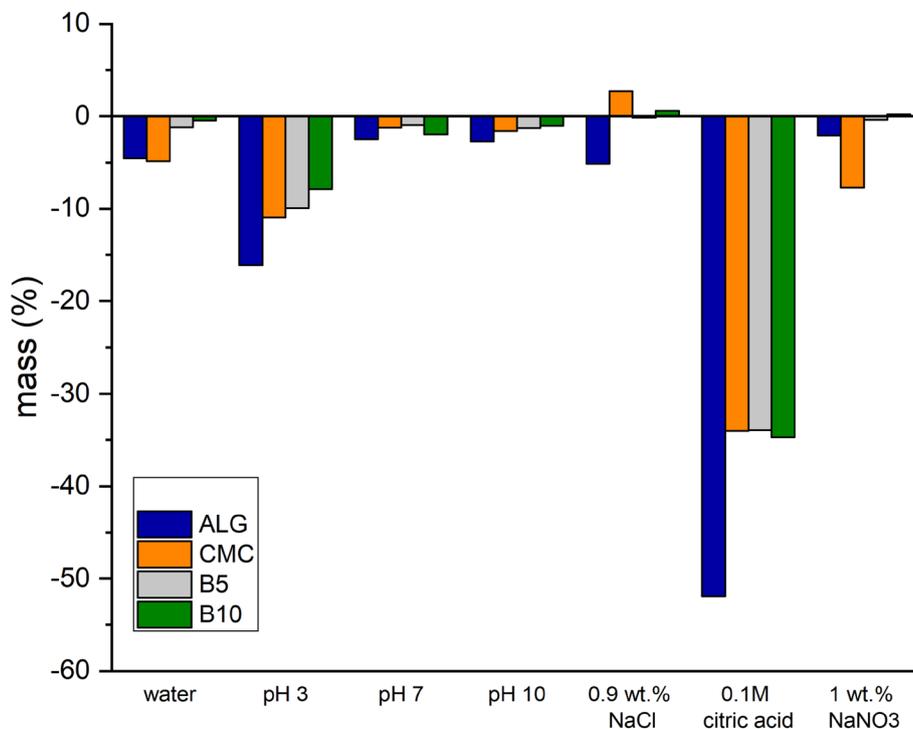
FTIR spectra for ALG composite before and after sorption of copper (II) ions are shown in Fig. 4a. Spectral analysis showed the presence of carboxyl groups. Their identification is related to the stretching vibrations $-\text{OH}$ at 3333 cm^{-1} and the stretching vibrations $-\text{CH}$ at 2923 cm^{-1} . What's more, the peak located at 1590 cm^{-1} also has a connection to the carboxyl group—it concerns the stretching of COO^- bonds [17]. Absorption bands in the region below 1500 cm^{-1} are the fingerprint region, which is characteristic of a given molecule. Bending vibration

$\text{C}-\text{C}$ at 1420 cm^{-1} and a band at 889 cm^{-1} corresponding to deformation $-\text{CH}$ of β -mannuronic acid residues belong to the “fingerprint” area of the alginate [18]. Changing the shape of the spectrum and its shift after the Cu^{2+} ion sorption process confirmed that localized functional groups in the ALG composite (Table 5) actively participate in the binding of Cu^{2+} ions.

The FTIR spectra for the CMC biocomposite are shown in Fig. 4b. Spectral analysis showed that both alginate and carboxymethylcellulose present in the composite possess Cu^{2+} ion-binding groups in the sorption process (Table 6). Stretching vibrations of the carboxyl groups with $-\text{OH}$ 3207 cm^{-1} are characteristic not only of the alginate, but also for the carboxymethylcellulose [19]. The absorption band in the region of 2931 cm^{-1} is related to the vibration stretching $-\text{CH}$ of hydrogen atoms derived from the carboxymethylcellulose methane ring. The “fingerprint” range of carboxymethylcellulose is located at 1012 cm^{-1} , because $\text{C}-\text{O}-\text{C}$ stretching vibrations in this area have a polysaccharide backbone [20].

FTIR spectra for composite B5 before and after Cu^{2+} ion biosorption process are presented in Fig. 4c. In addition to alginate and carboxymethylcellulose, the composite contained a biosorbent in the form of ground eggshells. The main component of the dry shell is calcium carbonate (85–95%), similarly to known sorbents, i.e. limestone or calcite. Therefore, the binding of copper (II) ions with the participation of B5 composite should take place mainly by ion exchange [21]. Spectral analysis revealed three

Fig. 6 Swelling of ALG, CMC, B5 and B10 biocomposites crosslinked with Cu^{2+} ions in various media (T: $20\text{ }^\circ\text{C}$; sorbent dosage 20 g L^{-1} ; contact time: 96 h; media: water, aqueous solution at pH 3, 7 and 10, 0.1 M citric acid, 1 wt% NaCl, 1 wt% NaNO_3)



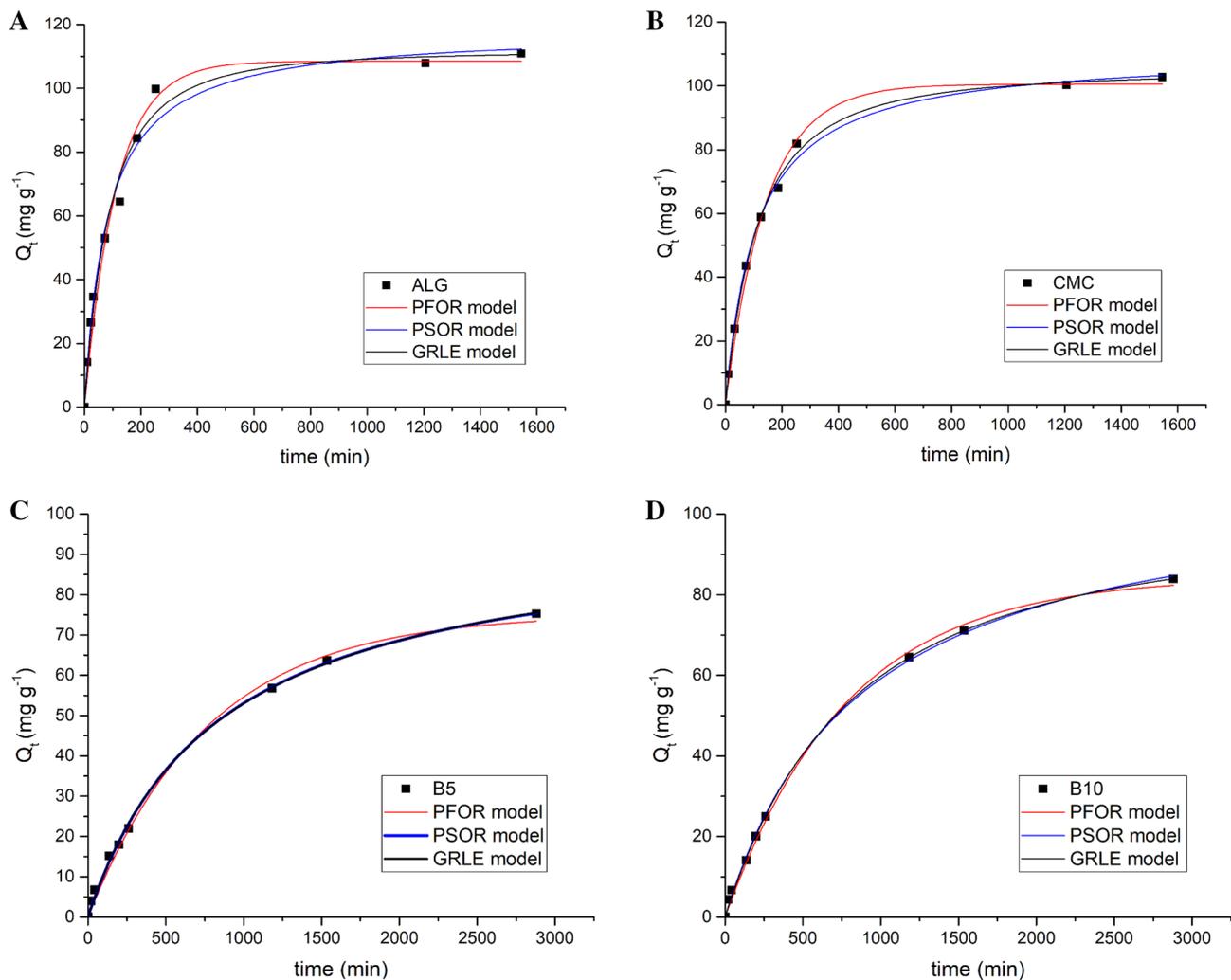


Fig. 7 Kinetics of binding of Cu^{2+} ions for ALG (a), CMC (b), B5 (c) and B10 (d) biocomposites crosslinked with Ca^{2+} ions (dashed line: PFOR, PSOR and GRLE model; T: 20 °C; sorbent dosage 15 g L⁻¹; contact time: 48 h; pH: 5; C₀: 200 mg L⁻¹)

characteristic peaks, which confirm the participation of carbonate minerals in the sorption of Cu^{2+} ions (1401 cm⁻¹, 872 cm⁻¹ and 712 cm⁻¹) [22, 23]. As a result of the presence of CO_3^{2-} , bands in the area of 872 cm⁻¹ and 712 cm⁻¹ exhibit, deformation beyond the plane and in the plane, respectively [24, 25]. Visible shift of the spectrum confirmed changes occurring in the biocomposite during the sorption process of Cu^{2+} ions. Functional groups of composite B5 responsible for binding Cu^{2+} cations are shown in Table 7.

3.2.3 Swelling properties

Changes in the degree of hydration of composites crosslinked with Ca^{2+} ions in various aqueous solutions are shown in Fig. 5. B5 and B10 composites are characterized by high porosity resulting from the presence of

biosorbent, therefore they have better water absorption capabilities than ALG and CMC structures. The highest weight gain for all types of composites was observed in 0.9 wt% NaCl solution and 1 wt% NaNO_3 solution. Sodium ions do not bind in any way to functional groups of composites, but they interact electrostatically with COO^- carboxyl groups present in polysaccharides chain. The resulting ionic strength causes strong enough interactions that may even destroy the structure of the hydrogels [26]. Degradation of all composites crosslinked with Ca^{2+} ions was observed in the 0.9 wt% solution NaCl after 24 h. In the case of salt solutions containing Na^+ cations, the salt anion also influences the degree of swelling of the structures. Chloride anions have a higher diffusion coefficient than the anions of NaNO_3 . This means that the sodium chloride solution penetrates into the composite faster than sodium nitrate solution [27]. Considering the

Table 8 Analysis of PFOR, PSOR and GRLE adsorption kinetics parameters for ALG (A), CMC (B), B5 (C) and B10 biocomposites crosslinked with Ca²⁺ ions by non-linear regression method

Composite	PFOR			PSOR			GRLE			
	k ₁ (min ⁻¹)	Q _e (mg g ⁻¹)	R ²	k ₂ (min ⁻¹)	Q _e (mg g ⁻¹)	R ²	k _n (min ⁻¹)	n	Q _e (mg g ⁻¹)	R ²
ALG	8.85e-03 ± 8.29e-04	108.49 ± 3.44	0.983	1.04e-04 ± 1.48e-05	118.21 ± 3.87	0.985	1.12e-03 ± 1.46e-04	1.48 ± 0.29	111.64 ± 4.69	0.987
CMC	6.91e-03 ± 4.03e-04	100.54 ± 2.09	0.993	8.25e-05 ± 5.91e-06	110.56 ± 1.86	0.997	6.15e-04 ± 4.80e-04	1.56 ± 0.17	104.63 ± 2.54	0.998
B5	1.30e-03 ± 1.13e-04	75.19 ± 2.34	0.994	1.24e-05 ± 1.23e-05	97.18 ± 2.69	0.997	7.38e-05 ± 1.96e-05	2.10 ± 0.51	99.79 ± 15.35	0.998
B10	1.28e-03 ± 7.86e-05	84.47 ± 1.85	0.997	1.06e-05 ± 8.23e-07	110.00 ± 2.44	0.998	1.00e-06 ± 1.12e-04	1.55 ± 0.22	97.35 ± 6.95	0.999

possibility of using biocomposites as controlled release fertilizers, the key aspect was to investigate the degree of hydration in the NaNO₃ solution because it imitates soil conditions. Slower diffusion of the “soil solution” is advantageous because it will not damage the structure of the hydrogels, and thus will not disturb the controlled release of micronutrients from the polymer matrices. Approximately 40% of the weight loss of the composites in the citric acid solution was also noted. Moreover, the structures of the B5 and B10 hydrogels were degraded (gas bubbles were observed that raised the beads to the surface of the solution). The main component of the biosorbent (calcium carbonate) decomposed due to H⁺ ions, which led to the formation of carbon dioxide.

The influence of the aqueous environment on swelling properties was also tested for composites crosslinked with Cu²⁺ ions. The results are shown in Fig. 6. In comparison to composites crosslinked with Ca²⁺ ions, all structures crosslinked with Cu²⁺ ions shrink in aqueous solutions. The largest loss in weight was also observed for the composites immersed in a solution of citric acid. Structures B5 and B10 were damaged by decomposition of calcium carbonate. In addition to floating spheres, a loss of the blue color of the composites was noted after 94 h. Discoloration of composites indicates the removal of Cu²⁺ ions from hydrogels. Based on the results, cations from the crosslinking agent have an effect on structural integrity. This may be due to the size of the cations. Ca²⁺ ions have a larger ionic radius (0.097 nm) than Cu²⁺ ions (0.072 nm). Therefore, Ca²⁺ ions form a more compact system, filling up more space in the alginate structure. The matrix of composites crosslinked with Cu²⁺ ions is characterized by a looser structure and the diffusion of the liquid occurs faster [7].

3.3 Kinetics of enrichment with Cu²⁺ ions of composites crosslinked with Ca²⁺ ions

The PFORE, PSORE and GRLE models were used to describe the process of enrichment with Cu²⁺ ions of composites crosslinked with Ca²⁺ ions, which relate to the rate of reaction occurring in the biosorption process [11]. Fitting these models to experimental data is shown in Fig. 7. The complexity and multistage character of the Cu²⁺ sorption process confirm the high values of the R² parameter of the GRLE model, which proved to be the best fit for the experimental data. The determined coefficients *k* describing the rate of binding of Cu²⁺ ions for ALG, CMC, B5 and B10 composites are respectively: 1.12e-03 min⁻¹, 6.15e-04 min⁻¹, 7.38e-05 min⁻¹ and 1.00e-06 min⁻¹ (Table 8). Based on the determined parameters of the kinetics as well as the graphs, it was noted that the sorption process is fastest for ALG composite and the slowest for B10 composite. It was observed that the equilibrium established only in the

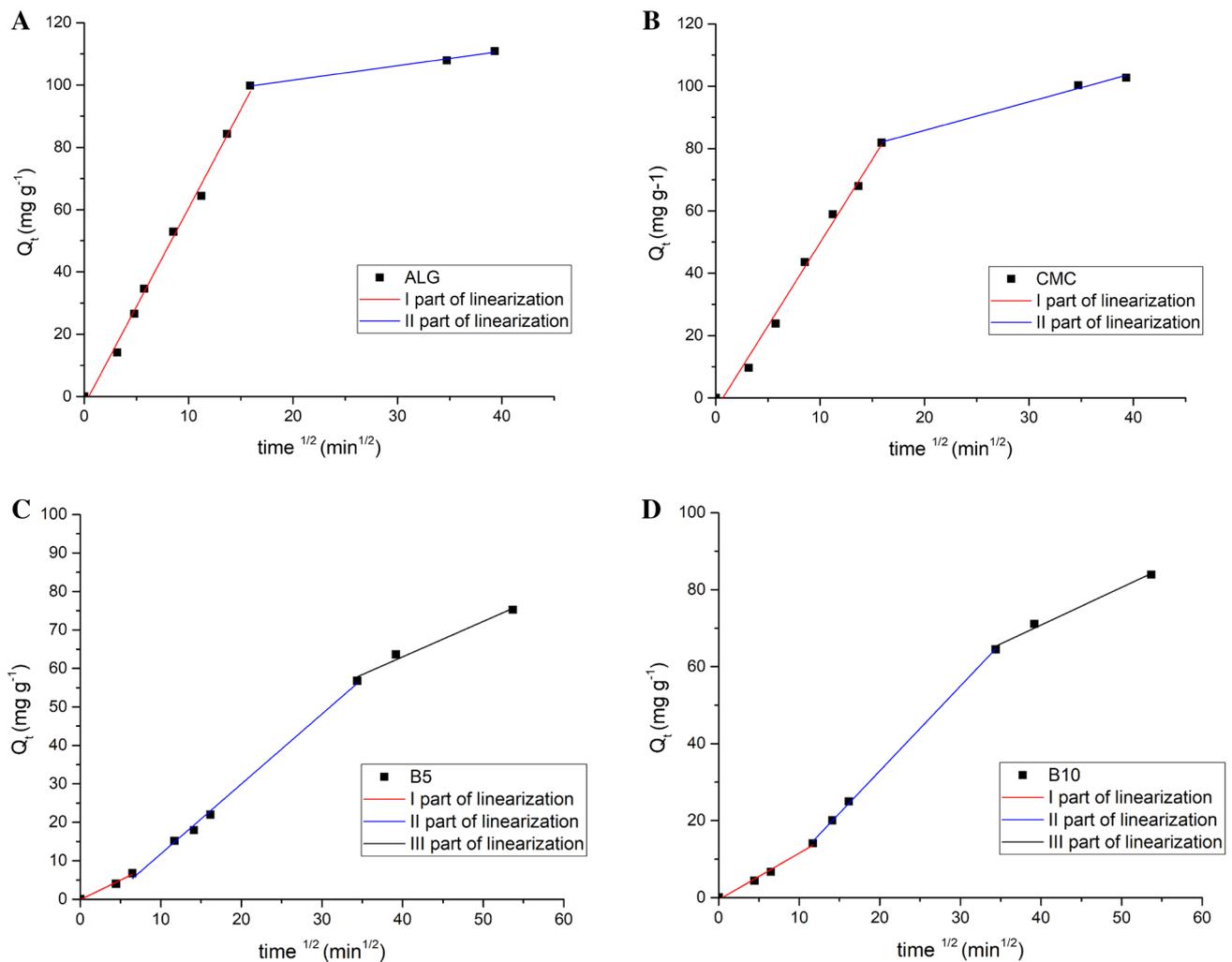


Fig. 8 Kinetics of binding of Cu²⁺ ions for ALG (a), CMC (b), B5 (c) and B10 (d) biocomposites crosslinked with Ca²⁺ ions (dashed line: Weber–Morris model; T: 20 °C; sorbent dosage 15 g L⁻¹; contact time: 48 h; pH: 5; C₀: 200 mg L⁻¹)

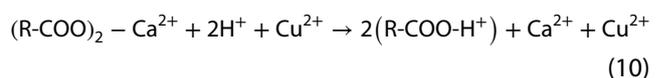
case of ALG and CMC composites (Fig. 7a, b). To determine the cause of this phenomenon, the mechanism of binding of Cu²⁺ ions to biocomposites was examined using the Weber–Morris diffusion model.

The biosorption process includes not only chemical reactions, but also diffusion, which can significantly reduce the rate of binding of Cu²⁺ ions. Straight lines that illustrate the biosorption stages for all types of composites crosslinked with Ca²⁺ ions are shown in Fig. 8. Parameters determined using the Weber–Morris model are collected in Table 9. Based on the results, ALG and CMC composites are characterized by a simplified, two-step mechanism of Cu²⁺ ion binding, which involves the transport of cation from the solution to the composite surface (first area of linearization) and internal cation diffusion into the interior of the composite (second linear section). In the case of B5 and B10 hydrogels, an additional step can be distinguished, which concerns the binding of Cu²⁺ ions to the

surface and interior of the biosorbent immobilized in the polymer matrix (third area of linearization).

3.4 Release of cations in various media

The percentage of Cu²⁺ ions released during desorption of crosslinked with Ca²⁺ composites is shown in Fig. 9. In an acidic environment, the biopolymer structure is loosened. More specifically, the bond between the hydrogen and the carboxylic acid group present in the alginate is relaxed. At low pH, there is also an ion competition between H⁺ and Cu²⁺, which can be described by the following equation [28]:



The ALG composite quickly releases Cu²⁺ ions from all types of hydrogels crosslinked with Ca²⁺ ions. Carboxymethylcellulose as an additional biopolymer component

Table 9 Analysis of Weber–Morris model parameters for wet and dry biocomposites for ALG (A), CMC (B), B5 (C) and B10 biocomposites crosslinked with Ca²⁺ ions method by linear regression

	Composite			
	ALG	CMC	B5	B10
I part of linearization				
t (min)	0–253	0–253	0–42	0–137
k _{WM} (mg g ⁻¹ min ^{0.5})	6.332 ± 0.180	5.345 ± 0.220	1.019 ± 0.108	1.212 ± 0.090
C _{WM}	-2.808 ± 1.697	-3.651 ± 2.18	0.126 ± 0.493	-0.535 ± 0.639
R ²	0.994	0.992	0.989	0.989
II part of linearization				
t (min)	253–1545	253–1545	42–1182	137–1182
k _{WM} (mg g ⁻¹ min ^{0.5})	0.462 ± 0.037	0.915 ± 0.072	1.819 ± 0.062	2.204 ± 0.030
C _{WM}	92.361 ± 1.169	67.538 ± 2.294	-6.408 ± 1.183	-11.145 ± 0.639
R ²	0.987	0.994	0.997	0.999
III part of linearization				
t (min)	-	-	1182–2880	1182–2880
k _{WM} (mg g ⁻¹ min ^{0.5})	-	-	0.921 ± 0.124	0.978 ± 0.097
C _{WM}	-	-	26.142 ± 5.373	31.685 ± 4.192
R ²	-	-	0.982	0.990

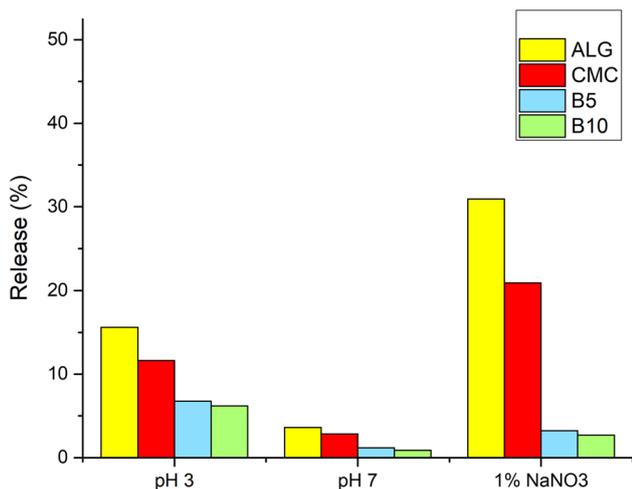


Fig. 9 % release of Cu²⁺ ions in various media for ALG, CMC, B5 and B10 biocomposites crosslinked with Ca²⁺ ions (T: 20 °C; contact time: 14 days; media: aqueous solution at pH 3 and 7, 1 wt% NaNO₃)

in CMC, B5 and B10 hydrogels strengthens the structure, thanks to which the desorption process takes place more slowly. Na⁺ ions present in the sodium nitrate solution due to strong electrostatic interactions with the carboxylic groups COO⁻ also contribute to the relaxation of the hydrogel structure, causing the release of Cu²⁺ ions.

Compared to composites crosslinked with Ca²⁺ ions, hydrogels crosslinked with Cu²⁺ ions are more sensitive to the relaxation of structures in the presence of an acidic environment or as a result of strong electrostatic effects of Na⁺ ions, because they release larger amounts of Cu²⁺ ions in the desorption process (Fig. 10). Once again, the

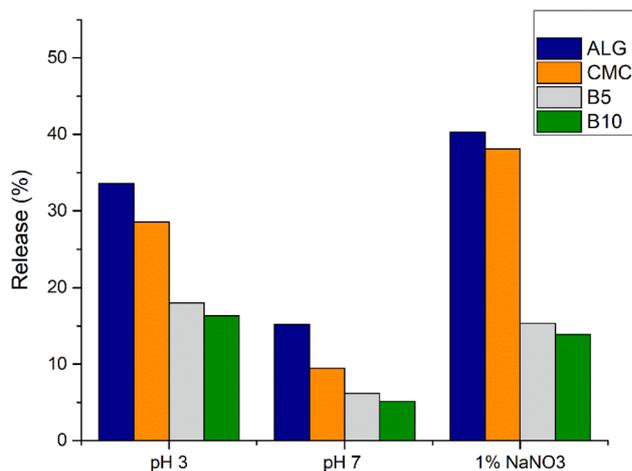


Fig. 10 % release of Cu²⁺ ions in various media for ALG, CMC, B5 and B10 biocomposites crosslinked with Cu²⁺ ions (T: 20 °C; contact time: 14 days; media: aqueous solution at pH 3 and 7, 1 wt% NaNO₃)

importance of the crosslinking agents for the durability and coherence of hydrogels was observed. Composites crosslinked with Ca²⁺ ions release the Cu²⁺ ions more slowly than those crosslinked with Cu²⁺ ions.

4 Conclusions

The type of crosslinking agent has a significant impact on the physicochemical properties of biocomposites as well as the sorption and release of Cu²⁺ ions. Composites crosslinked with Ca²⁺ ions have greater structural

integrity than those crosslinked with Cu^{2+} . The combination of alginate and carboxymethylcellulose gives the possibility of creating porous structures used for sorption processes. Immobilization of biomass inside a polymer matrix increases the sorption capacity of hydrogels, generating new properties that can be used in the creation of innovative fertilizers with controlled release of micro-nutrients. Considering the potential use of composites as controlled release fertilizers, calcium ions have been the better crosslinking agent.

Acknowledgements The work was financed by a statutory activity subsidy from the Polish Ministry of Science and Higher Education for the Faculty of Chemistry of Wrocław University of Science and Technology Number 0401/0124/18.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

Open Access This article is distributed under the terms of the Creative Commons Attribution 4.0 International License (<http://creativecommons.org/licenses/by/4.0/>), which permits unrestricted use, distribution, and reproduction in any medium, provided you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.

References

- Shaviv A (2001) Advances in controlled-release fertilizers. *Adv Agron* 2113:1–49
- Shavit U, Reiss M, Shaviv A (2003) Wetting mechanisms of gel-based controlled-release fertilizers. *J Control Release* 88(1):71–83
- Wu L, Liu M (2008) Preparation and properties of chitosan-coated NPK compound fertilizer with controlled-release and water-retention. *Carbohydr Polym* 72(2):240–247
- Liew CV, Chan LW, Ching AL, Heng PWS (2006) Evaluation of sodium alginate as drug release modifier in matrix tablets. *Int J Pharm* 309(1–2):25–37
- Nair LS, Laurencin CT (2007) Biodegradable polymers as biomaterials. *Prog Polym Sci* 32(8–9):762–798
- Kühbeck D, Mayr J, Häring M, Hofmann M, Quignard F, Díaz D (2015) Evaluation of the nitroaldol reaction in the presence of metal ion-crosslinked alginates. *New J Chem* 39(3):2306–2315
- Bierhalz ACK, da Silva MA, Braga MEM, Sousa HJC, Kieckbusch TG (2014) Effect of calcium and/or barium crosslinking on the physical and antimicrobial properties of natamycin-loaded alginate films. *LWT Food Sci Technol* 57(2):494–501
- Kim MS, Park SJ, Gu BK, Kim CH (2012) Ionically crosslinked alginate-carboxymethyl cellulose beads for the delivery of protein therapeutics. *Appl Surf Sci* 262:28–33
- Ren H, Gao Z, Wu D, Jiang J, Sun Y, Luo C (2016) Efficient Pb(II) removal using sodium alginate-carboxymethyl cellulose gel beads: preparation, characterization, and adsorption mechanism. *Carbohydr Polym* 137:402–409
- Šillerová H, Komárek M, Liu C, Poch J, Villaescusa I (2015) Biosorbent encapsulation in calcium alginate: effects of process variables on Cr(VI) removal from solutions. *Int J Biol Macromol* 80:260–270
- Michalak I, Chojnacka K, Witek-Krowiak A (2013) State of the art for the biosorption process—a review. *Appl Biochem Biotechnol* 170(6):1389–1416
- Toğrul IT, Pehlivan D (2003) Modelling of drying kinetics of single apricot. *J Food Eng* 58(1):23–32
- Belalia F, Djelali N (2016) Investigation of swelling/adsorption behavior of calcium alginate beads. *Rev Roum Chim* 61(10):747–754
- Weber WJ, Morris JC (1963) Kinetics of adsorption on carbon from solutions. *J Sanit Eng Div* 89:31–39
- Ertekin C, Yaldiz O (2004) Drying of eggplant and selection of a suitable thin layer drying model. *J Food Eng* 63(3):349–359
- Jakubczyk E (2009) Charakterystyka suszenia konwekcyjno-mikrofalowego spienionego przecieru jabłkowego. *ŻYWNOSĆ. Nauka. Technologia. Jakość* 1(62):109–118
- Kondaveeti S et al (2018) Microbicidal gentamicin-alginate hydrogels. *Carbohydr Polym* 186:159–167
- Lim G-P, Ahmad MS (2017) Development of Ca-alginate-chitosan microcapsules for encapsulation and controlled release of imidacloprid to control dengue outbreaks. *J Ind Eng Chem* 56:382–393
- Rozali MLH, Ahmad Z, Isa MIN (2015) Interaction between carboxy methylcellulose and salicylic acid solid biopolymer electrolytes. *Adv Mater Res* 1107(April):223–229
- Chai MN, Isa MIN (2013) The oleic acid composition effect on the carboxymethyl cellulose based biopolymer electrolyte. *J Cryst Process Technol* 03(01):1–4
- Chojnacka K (2005) Biosorption of Cr(III) ions by eggshells. *J Hazard Mater* 121(1–3):167–173
- Al Mijan M, Kim DH, Kwak HS (2014) Physicochemical properties of nanopowdered eggshell. *Int J Food Sci Technol* 49(7):1751–1757
- Carvalho J, Araujo J, Castro F (2011) Alternative low-cost adsorbent for water and wastewater decontamination derived from eggshell waste: an overview. *Waste Biomass Valoriz* 2(2):157–167
- Engin B, Demirtaş H, Eken M (2006) Temperature effects on egg shells investigated by XRD, IR and ESR techniques. *Radiat Phys Chem* 75(2):268–277
- Tsai WT, Yang JM, Lai CW, Cheng YH, Lin CC, Yeh CW (2006) Characterization and adsorption properties of eggshells and eggshell membrane. *Bioresour Technol* 97(3):488–493
- Matyash M, Despang F, Ikonomidou C, Gelinsky M (2014) Swelling and mechanical properties of alginate hydrogels with respect to promotion of neural growth. *Tissue Eng Part C Methods* 20(5):401–411
- Kwiatkowska-Marks S, Milek J (2017) Współczynnik spowolnienia dyfuzji soli metali ciężkich w granulach alginianowych. *Inż Ap Chem* 56(3):82–83
- An B, Son H, Chung J, Choi JW, Lee SH, Hong SW (2013) Calcium and hydrogen effects during sorption of copper onto an alginate-based ion exchanger: batch and fixed-bed column studies. *Chem Eng J* 232:51–58

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.