Artículo de Investigación. Revista Ciencia e Ingeniería. Vol. 47, No. 2 pp. 143-152, abril-julio, 2026.
ISSN 1316-7081. ISSN Elect. 2244-8780 Universidad de los Andes (ULA)

Synthesis and characterization of hydrogels of poly(acrylamide-*co*-itaconic acid) (AAm/IA) and poly(acrylamide-*co*-dimethoxyethyl itaconate) (AAm/DEI) semi interpenetrated with carboximethyl starch

Síntesis y caracterización de hidrogeles de poli(acrilamida-*co*-ácido itacónico) (AAm/IA) y poli(acrilamida-*co*-dimetoxietil itaconato) (AAm/DEI) semi interpenetrados con almidón carboximetilado

Luis José Rojas-Rojas, Amal El Halah, Gabriela Andarcia, Sandra Fajardo, María Solandreina Rondón and Francisco López-Carrasquero*
Grupo de Polímeros-ULA, Departamento de Química, Facultad de Ciencias, Universidad de Los Andes, Mérida, 5101-A, Venezuela
*flopezcarrasquero@gmail.com

Abstract

This study presents the synthesis and characterization of two series of semi-interpenetrating polymer network (semi-IPN) hydrogels based on acrylamide (AAm) combined with either itaconic acid (IA) or dimethoxyethyl itaconate (DEI) in a 70:30 molar ratio, incorporating carboxymethyl starch (CMS) in proportions of 0 to 20 wt%. Quantitative yields confirmed the total integration of CMS into the synthetic lattice. Swelling capacity was primarily governed by the nature of the comonomer: AAm/IA systems exhibited super-desiccant behavior, where swelling decreased upon CMS addition due to volume exclusion, whereas CMS enhanced the initial hydrophilicity of AAm/DEI systems. Kinetic analysis revealed anomalous (non-Fickian) transport in both series, with CMS acting as a modulator of diffusive flux. In 0.02 M $CuSO_4$ solutions, the AAm/IA series showed high adsorption efficiency, evidenced by a drastic network contraction and a shift toward a Fickian-controlled mechanism. Finally, 16-week compost biodegradation assays showed that AAm/DEI samples with 20% CMS lost a corresponding amount of mass, whereas control hydrogels remained intact. This demonstrates that CMS degrades selectively, leaving the polymer matrix intact; thus, CMS functions as a biodegradable 'jacket' or 'vest' for the hydrogel. Microorganisms selectively metabolize the polysaccharide component, enhancing the environmental vulnerability of the material while maintaining the structural integrity of the synthetic matrix during service.

Keywords: Semi-IPN Hydrogels, Carboxymethyl Starch (CMS), Swelling Kinetics, metal Ion Adsorption, Biodegradation.

Resumen

Este estudio presenta la síntesis y caracterización de dos series de hidrogeles de red polimérica semi-interpenetrada (semi-IPN) basados en acrilamida (AAm) combinada con ácido itacónico (IA) o itaconato de dimetoxietilo (DEI) en una relación molar 70:30, incorporando carboximetilalmidón (CMS) en proporciones del 0 al 20% en peso. Los rendimientos cuantitativos confirmaron la integración total del CMS en la red sintética. La capacidad de hinchamiento estuvo gobernada principalmente por la naturaleza del comonómero: los sistemas AAm/IA exhibieron un comportamiento superdesecante, donde el hinchamiento disminuyó al añadir CMS debido a la exclusión de volumen, mientras que el CMS mejoró la hidrofilicidad inicial de los sistemas AAm/DEI.El análisis cinético reveló un transporte anómalo (no Fickiano) en ambas series, con el CMS actuando como modulador del flujo difusivo. En soluciones de $CuSO_4$ 0,02 M, la serie AAm/IA mostró una alta eficiencia de adsorción, evidenciada por una contracción drástica de la red y un cambio hacia un mecanismo controlado por la difusión de Fick. Finalmente, los ensayos de biodegradación en compost durante 16 semanas mostraron que las muestras de AAm/DEI con un 20% de CMS perdieron una cantidad proporcional de su masa, mientras que los hidrogeles de control permanecieron intactos. Esto demuestra que el CMS se degrada selectivamente, dejando la matriz polimérica intacta; por lo tanto, el CMS funciona como una 'chaqueta' o 'chaleco' biodegradable para el hidrogel. Los microorganismos metabolizan selectivamente el componente de polisacárido, aumentando la vulnerabilidad ambiental del material mientras mantienen la integridad estructural de la matriz sintética durante su uso.

Palabras clave: Hidrogeles Semi-IPN, carboximetilalmidón (CMS), cinética de hinchamiento, adsorción de iones metálicos, biodegradación.

Introduction

In recent decades, hydrogels have emerged as state-of-the-art materials in polymer science due to their exceptional swelling capacity, biocompatibility (Zhang, et al, 2025), and stimuli-responsive behavior (El-Hamshary, 2007; González *et al.*, 2015; La Gatta *et al.*, 2021). These three-dimensional networks are pivotal in diverse fields, ranging from tissue engineering and controlled drug release (Suhail, et al, 2025) to environmental remediation via pollutant adsorption (Ahmadi *et al*., 2020; Zhou, *et al.,* 2026). Nevertheless, enhancing their mechanical integrity and functional tunability remains a significant challenge. A robust strategy to modulate these properties is the synthesis of semi-interpenetrating polymer networks (semi-IPN). In these systems, a crosslinked polymer network physically entangles a linear or branched polymer without covalent bonding between the phases (González *et al.*, 2013 and 2018). This architecture provides unique synergy, combining the structural stability of the crosslinked matrix with the specific functionalities of the guest polymer (An, *et al*. 2026). This study presents the development and characterization of semi-IPN hydrogels based on an acrylamide (AAm) and itaconic acid (IA) or dimethoxyethyl itaconate (DEI), (AAm/I) matrix integrated with carboxymethyl starch (CMS). The AAm/I combination yields a network with a high density of reactive functional groups; specifically, the carboxylic groups of itaconic acid confer pH-sensitivity and superior chelation capacity for metallic cations in aqueous solutions (El Halah, *et al,* 2015, 2019). The incorporation of CMS is a determining factor in the material design. As a cost-effective, biodegradable starch derivative, CMS enhances hydrophilicity through its carboxymethyl groups (Barrios, *et al,* 2012 y Balsamo, *et al,* 2011) and acts as a biodegradable phase that enmeshes with the synthetic matrix. Consequently, CMS would modulate physicochemical properties and facilitates material fragmentation post-service life, thereby reducing environmental persistence. The objective of this work is to synthesize and comprehensively characterize the morphology and swelling kinetics of AAm/IA and AAm/DEI semi-IPN hydrogels (70/30 molar ratio) with CMS loadings of 0, 5, 10, 15, and 20% w/w. Furthermore, AAm/IA/CMS Cu^{2+} adsorption capacity is evaluated as a preliminary study for effluent remediation, and AAm/DEI/CMS degradation susceptibility under composting conditions is analyzed to validate their eco-friendly nature.

Experimental

Materials

Itaconic acid (IA) (Aldrich), metoxiethanol (Aldrich) acrylamide (AAm) (Aldrich), ammonium persulfate (APS) Riel de Haën), and N,N´-methylene bis(acrylamide) (MBAm) (Ultrapure Bioreagent GT) were used without further purification. Double distilled water was used for the polymerization reactions and swelling studies. Other solvents were used as received. Cassava starch with an amylose content of about 17%, estimated according to the procedure of (McGrance, Cornell, and Rix, 1998), was kindly supplied by Agroindustriales Mandioca S.A., Venezuela. Other chemicals and solvents were of analytical grade and employed without further purification. Water used in the preparation of carboximethyl starch (CMS) was distilled and deionized before use.

The carboximethyl starch (CMS) were synthesized and characterized according to the procedures previous reported and all the details are described there (Barrios, *et al,* 2012 and Bálsamo, *et al,* 2011). In this work carboxymethyl starch was obtained with a degree of substitution of 0.11. Dimetoxyethyl itaconate (DEI) was prepared by the method previously described. (Rojas, *et al,* 2011, Katime, *et al,* 1989).

Synthesis of semi interpenetrated Hydrogels

The synthesis of semi-IPN hydrogels was carried out in aqueous solution using APS as the initiator and MBAM as the crosslinking agent, both at 1 mol% relative to the total moles of comonomers. The synthesis followed this procedure: a predetermined amount of comonomers, AAm with either IA or DEI in a 70:30 molar ratio, was dissolved in water in glass tube (A). In tube (B), the required amounts of initiator and crosslinking agent were dissolved in 2 mL of water. Both solutions were added to tube (C), which contained a previously stirred CMS aqueous solution thermostated at the reaction temperature to ensure complete dissolution.

The total water volume was 10 mL for the polymerization of DEI and 12 mL for IA. The reaction mixture was then placed in a thermostatic bath at 60 °C for 24 or 48 h. After polymerization, the hydrogels were recovered by breaking the glass tubes. The resulting fresh hydrogels, obtained in cylindrical shapes, were cut into fine pellets and washed several times with distilled water. Finally, the hydrogels were air-dried at room temperature for several days until reaching a constant weight. The chemical structure of the hydrogels was confirmed by FTIR spectroscopy.

In this study, several syntheses were performed to ensure sufficient quantities of hydrogel (HG) for swelling analyses. Tables 1 and 2 show the preparation conditions for one representative batch. Figure 1 schematically illustrates the synthesis procedure, and the idealized structure of the AAm/DEI/CMS semi-IPN HG, which may be consider representative for both series, is shown in **Scheme 1**.

Characterization

Infrared spectra (FTIR) of the HGs were recorded on a Perkin-Elmer 2000 instrument using KBr pellets prepared with xerogel samples. All spectra were acquired using 32 scans with a spectral resolution of ±4 cm^{-1}.

Swelling Measurements

The maximum swelling degree (%S) was measured using a conventional gravimetric procedure. Dry gel samples (xerogels) were immersed in double-distilled water and in a 0.02 M $CuSO_4$ solution at 25 °C until equilibrium was reached. Subsequently, the HGs were removed from the solution, gently wiped with filter paper to remove surface water, and weighed on an electronic balance. The swelling ratio (%S) and equilibrium water content (EWC) were calculated using Equations 1 and 2 (Karadağ, *et al*, 2002):

$$\%S = [(W_t - W_0)/W_0] \times 100 \qquad (1)$$

$$EWC = [(W_\infty - W_0)/W_\infty] \times 100 \qquad (2)$$

Where W_t is the weight of swollen hydrogel at time t, and W_0 is the weight of the dry gel at time 0 and W_∞ is the weight of the sample swollen at equilibrium. All swelling measurements were done by triplicate.

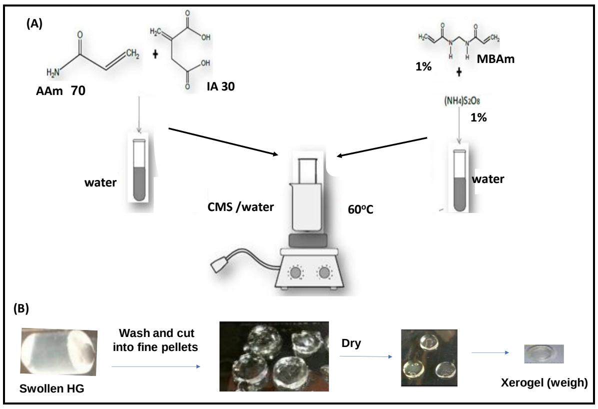
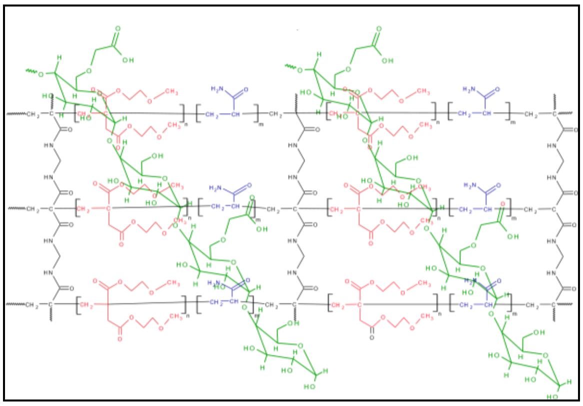


Fig. 1. (A) Synthesis protocol for semi-IPN hydrogels; (B) Post-synthesis processing to obtain dry xerogel pellets.



Scheme 1. Idealized structure of the semi-IPN of AAm/DEI/CMS.

Qualitative studies for Cu^{+2} ion absorption followed the same procedure as the swelling tests. Xerogel pellets (AAm/IA/CMS) of known mass were placed in beakers containing a 0.02 M copper sulfate pentahydrate solution.

Preliminary Biodegradation Studies

To study the degradation of the semi-IPN hydrogels, two systems were established using plastic boxes. One contained control gels (AAm/DEI without carboxymethyl starch) and the other contained AAm/DEI/CMS gels (with 20% CMS). Both boxes were filled with composted soil. Xerogel tablets of known mass were buried in rows of three at a depth of approximately 5 cm. Each sample location was identified with a wooden marker, as shown in Figure 2. The samples were kept moist by adding water weekly.

Fig.2. Experimental setup for preliminary biodegradation studies in composting soil.

Results and Discussion

Synthesis

Synthesis semi IPN hydrogels of AAm/IA, and AAm/DEI 70/30 (mol:mol) with CMS in weigh proportion of 0, 5, 10 15 and 20 % were prepared in water, with the aim to determine the effect of the CMS in their swelling properties. In all cases approximately 1 g of AAm was chosen for carry out all the reactions. For this amount of AAm, 10 mL of water for the synthesis used DEI and or 12 mL IA were adequate using all the proportions of CMS. When the amount of CMS was larger than 20%, CMS precipitated even when the volume of water was increased. At the end of the reactions, As can be seemed in Tables 1 and 2 In all cases, semi IPN hydrogels were obtained with quantitative conversions, for AAm/IDE yields were very close to 100% and for AAm/IA were above this value, this fact can be attributed to moisture retained in the network of all the AAm/IA/CMS, probably due to associate water. This behavior was also observed for AAm/IA HG which are more hydrophilic than AAm/DEI (El Halah, *et al*, 2015). AAm/DEI and AAm/IA free of CMS were colorless and transparent, but those with CMS were slightly opaque with light pink or amber colors.

Table 1. Synthesis parameters and feed composition for AAm/IA/CMS semi-IPN hydrogels and the obtained yield(a).

Sample	CMS (b) (%)	AAm (g)	IA (g)	CMS (g)	(APS) (g)	(MBAm) (g)	Yield(c) (%)
AAm/AI /0	0	0.9954	0.7807	-	0.0466	0.0309	115.7
AAm/AI /5	5	0.9962	0.7802	0.0893	0.0457	0.0311	113.1
AAm/AI /10	10	0.9965	0.7803	0.1775	0.0469	0.0310	109.9
AAm/AI /15	15	0.9964	0.7802	0.2671	0.0463	0.0308	111.5
AAm/AI /20	20	0.9952	0.7807	0.3552	0.0474	0.0313	111.5

(a)Carry out in 12 mL of water with 1% (mol:mol) of the initiator (APS) and crosslinker (MBAm) during 24h at 60 °C. (b) w:w referred to the mass of AAm and IA. (c) Based on the initial reactants mass.

Table 2. Synthesis parameters and feed composition for AAm/DEI/CMS semi-IPN hydrogels and the obtained yield [(a)].

Sample	CMS[(b)] (%)	AAm (g)	IDE (g)	CMS (g)	(APS) (g)	(MBAm) (g)	Yield[(c)] (%)
AAm/DEI /0	0	1.0001	0.6779	0.0000	0.0314	0.0214	99.84
AAm/DEI /5	5	1.0005	0.6770	0.0859	0.0315	0.0215	98.14
AAm/DEI /10	10	1.0002	0.6773	0.1708	0.0317	0.0215	98.47
AAm/DEI /15	15	1.0014	0.6772	0.2559	0.0319	0.0213	99.71
AAm/DEI /20	20	1.0006	0.6774	0.3417	0.0313	0.0218	98.51

[(a)]Carry out in 10 mL of water with 1% (mol:mol) of the initiator (APS) and crosslinker (NMBA) during 48h at 60 °C. [(b)] w:w referred to the mass of AAm and DEI. [(c)] Based on the initial reactants mass.

The structure of these materials was studied by FTIR spectroscopy. **Figure 3** displays the spectra of the series of AAm/DEI that could be consider representative of both series.

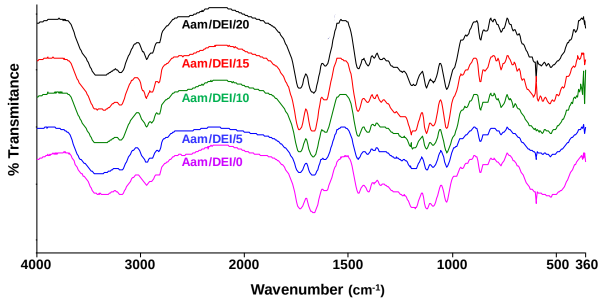


Fig. 3. FTIR spectra of the AAm/DEI/CMS semi-IPN HG with different proportions of CMS.

All de spectra are quite similar to the previous reported for the AAm/DEI hydrogels, showing all the signals of those (Halah, *et al* 2015]. There are noticeable the presence of the bands at 1672 cm^{-1} (Amide I,) and 1614 cm^{-1} (Amide II) characteristic of the AAm moiety and the stretching vibration of carbonyl group of DEI moiety at 1733 cm^{-1}. The characteristic CMS bands cannot be observed in the spectra because, in addition to being overlapping with those of the HG, the CMS is present in a smaller proportion. However, although CMS cannot be observed by IR spectroscopy, the quantitative yields and the formation of insoluble networks are sufficient evidence of the successful synthesis of semi-IPN hydrogels and the effective entrapment of CMS in the tridimensional lattice (**Scheme 1**).

These structural characteristics, along with the observed differences in water affinity between IA and DEI series, are expected to dictate the mass transport properties. Therefore, the following section examines the swelling kinetics to determine how CMS loading and chain relaxation govern the diffusion mechanisms in these matrices.

3.2. Swelling studies

After the HG were characterized, a swelling study in water was carried out and the results of this study indicated that the swelling ability of these hydrogel depends of the proportion of CMS in de semi-IPN HG. Hydrogels water absorption (%S) was followed as function of time until they reach equilibrium state and as may be seen in **Figures 4** and **5** all of them display typical swelling isotherms. In all cases the swelling behavior is reproducible after drying the samples and swell again. The equilibrium water content (EWC) was determined using the same methodology; although the corresponding kinetic plots are not shown, the results are summarized in **Table 3**.

The values of S_{eq} and EWC are given in the **Tables 3**. From there is clear that the swelling of semi-IPN AAm/I/CMS HG is influenced by the nature of the comonomer (IA or DEI), and the proportion of CMS used in the synthesis.

Regarding the AAm/IA/CMS semi-IPN hydrogel series, the swelling degree of all CMS-containing samples was lower than that of the pristine AAm/IA hydrogel. While CMS contents of 5, 10, and 15% resulted in a more or less similar reduction in swelling, the decrease became more pronounced at 20% (**Table 3** and **Figure 6**). This diminished absorption capacity upon CMS incorporation is attributed to the fact that, despite its hydrophilic nature, CMS is significantly less hydrophilic than the AAm/IA matrix. Consequently, water uptake is predominantly governed by the latter. Furthermore, CMS occupies a substantial portion of the network's free volume, imposing a physical constraint on water ingress. Thus, the volume exclusion effect of the starch overrides its inherent absorption capacity, leading to a reduction in swelling proportional to the CMS loading.

In contrast, the AAm/DEI/CMS hydrogels exhibit a distinct behavior. The base AAm/IDE hydrogel reaches a maximum swelling degree (%S) of only 4.124, as IDE is considerably less hydrophilic than IA. However, the incorporation of CMS initially enhances the swelling capacity, peaking at a 10 wt% starch content; beyond this threshold, swelling progressively declines (**Figure 6**). This phenomenon stems from the low hydrophilicity of IDE (El Halah, *et al*, 2015, 2019). Since the absorption capacity of CMS is comparable to or exceeds that of the AAm/IDE matrix, its initial addition improves the overall hydrophilicity of the system. Nevertheless, as CMS concentration surpasses 10%, the free volume occupied by the starch begins to physically restrict the network—a volume exclusion effect analogous to that observed in the previous series. Notably, even at 20% CMS, the swelling degree remains superior to that of the starch-free control.

Finally, using equation 2, the percentage of water by weight of the hydrogels was determined, and their classification according to their capacity to absorb water was established. These results are summarized in Table 3.

The diffusion of small molecules into a hydrogel depends on the network's physical properties and segment-molecule interactions. According to Fick's second law, the water transport mechanism can be determined using the power law equation (3):

$$F = W_t / W_\infty = Kt^n \qquad (3)$$

Where F is the fractional swelling W_t and W_∞ are the water uptake at time t and at equilibrium, respectively; K is a structural constant, and n is the swelling exponent that characterizes the transport mechanism.

The value of n depends on the relative rates of water diffusion and polymer chain relaxation (Franson and Peppas

1983):

$n \approx 0.50$ (Case I / Fickian): Diffusion is much slower than relaxation.

$0.50 < n < 1.00$ (Anomalous / Non-Fickian): Diffusion and relaxation occur at comparable rates.

$n = 1.00$ (Case II): Diffusion is much faster than relaxation.

$n < 0.50$ (Less Fickian): Water penetration is significantly slower than the relaxation rate.

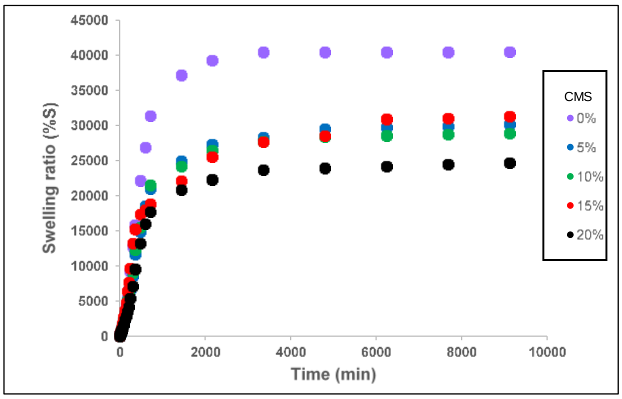


Fig. 4. Swelling isotherms of semi-IPN AAm/IA (70/30) hydrogels in distilled water at 25°C.

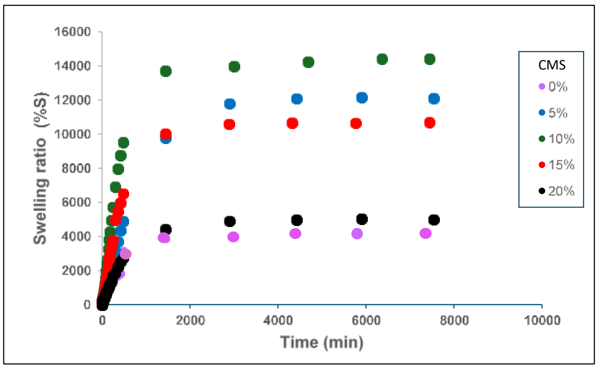


Fig. 5. Swelling isotherms of semi-IPN AAm/DEI (70/30) hydrogels in distilled water at 25°C.

Table 3. Values of swelling of semi-IPN HG of AAm/IA/CMS, and AAm/DEI/CMS(a).

	AAm/IA (70/30)(b)		**AAm/IDE (70/30) (c)**	
Sample	**S_{eq}(d) (%)**	**EWC(e) (%)**	**S_{eq}(d) (%)**	**EWC(e) (%)**
AAM/I/0	40,485	99.75	4,124	97.63
AAM/I/5	30,182	99.67	12,104	99.18
AAM/I/10	28,881	99.65	14,414	99.31
AAM/I/15	31,301	99.68	10,682	99.07
AAM/I/20	24,692	99.60	5,030	98.05

a)Synthesized at 60ºC for 24h for AAm/AI/CMS and 48h for AAm/DEI/CMS, using AMS as initiator (1% molar) and MBAm as crosslinking agent (1% molar) (b) All of them classify as Super-desiccant. (c) All of them classify as High swelling.

The parameters n and K were determined from the slope and intercept of the plot of $\ln W_t / W_\infty$ vs. $\ln t$ for the initial swelling stage ($F < 0.6$).

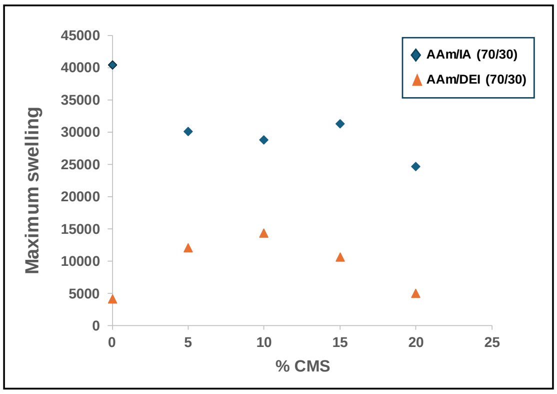


Fig. 6. Maximum swelling degree (%S) vs. CMS content for AAm/IA/CMS and (AAm/DEI/CMS series.

The curves of both series (not showed) also indicate that the swelling process follows a zero-order behavior and the parameters n and K obtained from them, are listed in **Table 4.**

Table 4. Diffusion exponents (n) and swelling rate constants k determined for the semi-IPN AAm/IA/CMS and AAm/DEI/CMS hydrogel series as a function of CMS content.

	AAm/IA/CMS		**AAm/DEI/CMS**	
Sample	**n**	**k*10^3 (min-1)**	**n**	**k*10^3 (min-1)**
AAm/I/0	0,95	0.76	0.62	8.39
AAm/I/5	0,93	0.89	0.76	2.71
AAm/I/10	0.91	1.17	0.89	2.38
AAm/I/15	0.89	1.53	0.81	3.26
AAm/I/20	0.92	1.03	0.69	6.31

Parameters n and k were calculated from the power law $F = kt^n$ using the initial swelling data ($F < 0.6$). Values represent the mean of three independent measurements (n=3). Correlation coefficients (R^2) for all samples ranged between 0.966 and 0.992.

Kinetic parameters in **Table 4** indicate that the transport mechanism for both hydrogel series follows anomalous (non-Fickian) behavior, arising from the simultaneous contribution of solvent diffusion and viscoelastic polymer chain relaxation (Kim *et al*, 2003, El-Hamshary, 2007). For the AAm/IA/CMS system, n values ranging from 0.90 to 0.95 suggest that diffusive flux predominates over matrix relaxation. This is attributed to the carboxylic groups of itaconic acid (IA), which enhance charge density and network hydrophilicity, thereby promoting osmotic water diffusion.

Notably, carboxymethyl starch (CMS) acts as a synergistic transport modulator; its incorporation into the AAm/DEI matrix increases n from 0.62 to values near or above 0.80. This shift demonstrates that the hydrophilic nature of CMS compensates for the hydrophobic character of DEI, driving a transition toward a predominantly diffusion-controlled regime.

Table 4 reveals higher kinetic constants (k) for the AAm/DEI series compared to AAm/IA. Although AAm/IA possesses superior absorption capacity, its swelling rate is restricted by the slow chain relaxation required to accommodate large solvent volumes (Case II transport). Conversely, the less hydrophilic AAm/DEI reaches equilibrium faster through a diffusion-dominated process with minimal structural reconfiguration. Essentially, "*AAm/IA behaves like a large balloon—offering high capacity but filling slowly as the material must stretch—whereas AAm/DEI acts like a small vessel, reaching its limited capacity almost instantly."*

Preliminary study of the adsorption of Cu^{+2} in aqueous solutions 0.02 M

Acrylamide-based (AAm) hydrogels are well-established materials for the removal of heavy metal ions from aqueous solutions (El Halah, *et al,* 2018). Previous comparative studies between AAm/IA and AAm/DEI matrices revealed that IA-containing systems exhibit significantly higher adsorption efficiencies than DEI and other reported hydrogels (El Halah, *et al,* 2019; García-Manzano and, Alvarez-Igarzabal, 2010; Orzay *et al,* 2009). This enhanced performance is linked to the high chelating potential of itaconic acid moieties. Building upon these findings, this study investigates semi-IPN AAm/IA/CMS hydrogels to evaluate the specific role of carboxymethyl starch (CMS) in Cu^{+2} adsorption.

Figure 7 illustrates swelling kinetics in Cu^{2+} solution exhibited an initial maximum followed by a contraction toward equilibrium. This profile suggests a competitive mechanism where rapid water diffusion initially expands the network, followed by displacement by Cu^{2+} ions. The formation of metal-carboxylate complexes increases the effective crosslinking density, leading to network collapse and stabilization at a lower equilibrium swelling capacity. As observed in **Table 5**, the equilibrium swelling ratio (%S) in the copper solution decreased drastically (from ~40,000 to < 250) compared to distilled water. This massive network contraction is attributed to the screening of electrostatic repulsions between carboxylate groups upon complexation with Cu^{2+}.

Experiments conducted by adding 20 mg of CMS to 30 mL of either pure water or $CuSO_4$ solution did not significantly alter the final pH or the xerogel mass increment. The lack of chromatic changes in isolated CMS–copper solutions suggests that the modified starch acts primarily as a structural matrix modifier rather than participating directly in the coordination of copper ions within this semi-IPN system.

Finally, upon reaching physicochemical equilibrium in 0.02 M $CuSO_4$, the hydrogels were removed and dried at room temperature to a constant weight. Gravimetric analysis revealed a uniform mass increase of approximately 6% AAm/IA semi-IPN xerogels, regardless of the CMS content indicating that Cu is incorporated in to the HG like a complex with de carboxylic groups of the itaconic acid moiety structure similar to de previous reported for Cooper complex with IA (El Halah *et al*, 2020). The formation of this complex is further supported by the HG's transition from colorless to blue, a property that persists upon dehydration (**Figure 8**).

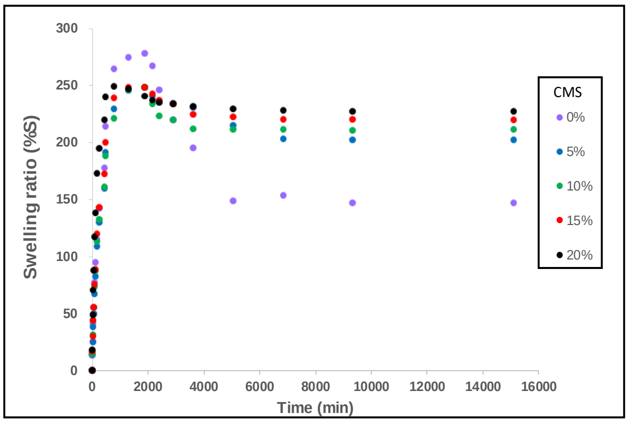


Fig. 7. Swelling kinetics of AAm/IA/CMS hydrogels in 0.02 M $CuSO_4$ solution.

Table 5. Maximum swelling indices (%S) and maximum weight water percentages (EWC) of semi-IPN AAm/IA hydrogels in $[CuSO_4]$ = 0.02 M, according to % of CMA; as well as their classification.

Sample	**Seq in Cu^{2+} (%)**	**EWC$^{(e)}$ (%)**	**Clasification**
AAm/IA/0	147.44	59.59	Medium swelling
AAm/IA/5	202.87	66.98	Medium swelling
AAm/IA/10	211.21	67.87	Medium swelling
AAm/IA/15	220.52	68.80	Medium swelling
AAm/IA/20	227.80	69.49	Medium swelling

Copper solution transport mechanisms in hydrogels

To analyze the initial swelling kinetic process in a 0.02M CuSO4 solution, the corresponding plots were constructed using the transport equations (Eq. 3). The results, obtained in quadruplicate to ensure repeatability, indicate that the swelling process follows zero-order kinetics.

As shown in Table 6, an increase in the CMA content within the semi-IPN hydrogels leads to a decrease in the diffusion coefficient, characterizing a non-Fickian transport mechanism. This behavior contrasts significantly with that observed in pure water, where n values near 0.9 reflect a process primarily controlled by polymer chain relaxation (Case II transport).

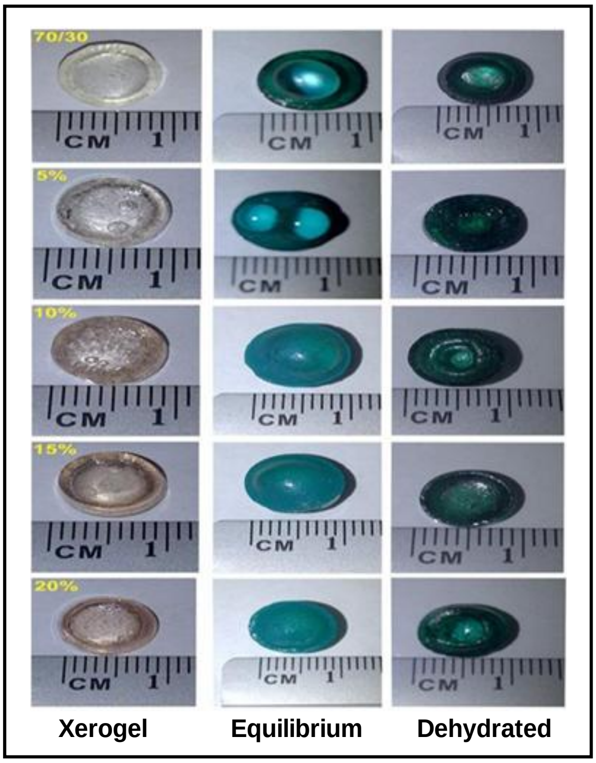


Fig. 8. Color change of HGs before, in the equilibrium and after be dried.

As shown in **Table 6**, an increase in the CMA content within the semi-IPN hydrogels leads to a decrease in the diffusion coefficient, characterizing a non-Fickian transport mechanism. This behavior contrasts significantly with that observed in pure water, where n values near 0.9 reflect a process primarily controlled by polymer chain relaxation (Case II transport).

In the metallic solution, the shift of n toward values approaching 0.5 suggests that Cu^{2+} ions establish coordination interactions with the functional groups of the polymer network, acting as ionic cross-linking points. This interaction restricts segmental mobility and hinders structural relaxation; consequently, the Fickian diffusion mechanism becomes predominant over chain relaxation in the overall swelling kinetics.

Preliminary biodegradation study of AAm/DEI/CMS

A preliminary biodegradation study was conducted under composting conditions to evaluate the role of carboxymethyl starch (CMS) in the environmental degradation of semi-IPN hydrogels. The process was monitored over 16 weeks via weight loss (gravimetry) and surface morphological analysis.

The hydrogels initially exhibited a smooth, white surface. Following compost exposure, samples developed surface irregularities and significant discoloration, shifting from white to brown, with black spots appearing specifically in CMS-containing samples (**Figure 9**). These changes are attributed to microbial colonization and the diffusion of minerals from the compost into the polymer matrix during the swelling phase.

Table 6. Diffusion exponents n and swelling rate constants (k) determined for AAm/AI/CMS semi-IPN hydrogels according to CMA content in a 0.02M Cu^{2+} ion solution.

Sample	n	$K*10^2$ (min-1)
AAm/I/0	0.61	2.10
AAm/I/5	0.57	1.85
AAm/I/10	0.53	2.29
AAm/I/15	0.54	2.25
AAm/I/20	0.51	3.48

Parameters n and k were calculated from the power law $F = kt^n$ using the initial swelling data ($F < 0.6$). Values represent the mean of three independent measurements (n=3). Correlation coefficients (R^2) for all samples ranged between 0.966 and 0.992.

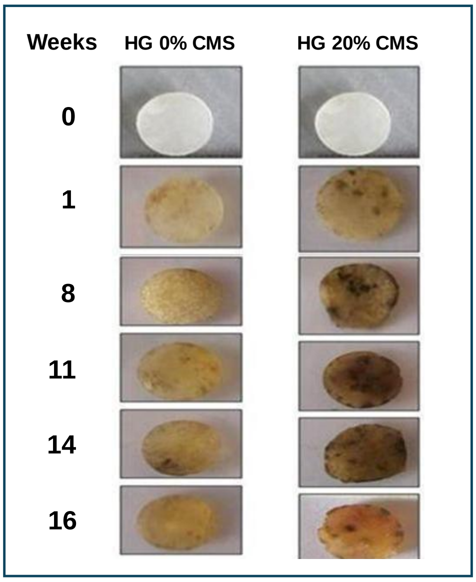


Fig. 9. Appearance of the samples taken from the compost at different treatment times.

As shown in **Figure 10**, weight retention results indicate that control hydrogels (0% CMS) underwent negligible degradation. Conversely, semi-IPN hydrogels with 20% CMS showed consistent weight loss starting from the first week.

Although data dispersion was observed due to compost heterogeneity and moisture gradients within the experimental setup, samples located in the high-moisture central zone exhibited weight losses between 15% and 20%. These values, which correlate closely with the initial CMS content, suggest a selective degradation mechanism. In this process, microorganisms specifically metabolize the starch component without inducing significant cleavage or fracture of the synthetic tridimensional network. Consequently, while the polysaccharide is bioassimilated, the primary hydrogel structure remains largely intact under the studied conditions.

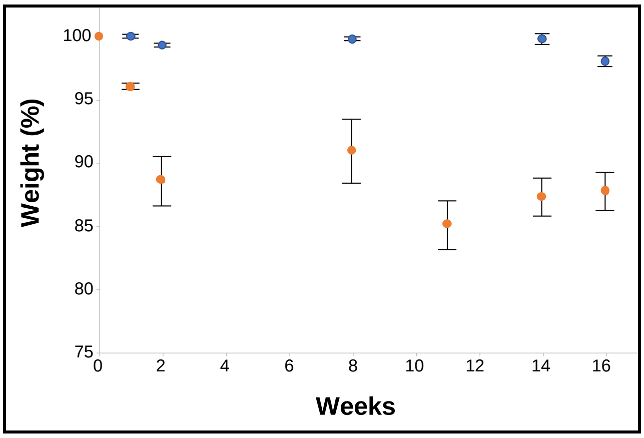


Fig.10. Mass loss percentage as a function of composting time for control (0% CMS) (Blue dots) and semi-IPN (20% CMS) (Yellow dots dots) hydrogels.

Conclusions

Semi-interpenetrating polymer network (semi-IPN) hydrogels based on AAm/IA and AAm/DEI were successfully synthesized with quantitative yields. The insolubility of the resulting networks confirms the effective physical entrapment of carboxymethyl starch (CMS) within the three-dimensional lattice, ensuring structural stability.

The water absorption capacity is primarily governed by the chemical nature of the itaconate comonomer. Due to its high hydrophilicity, the AAm/IA system functions as a super-desiccant material, whereas the AAm/DEI system exhibits a lower, yet significant, swelling capacity, categorizing it as a high-swelling hydrogel.

CMS acts as a critical transport modulator. In highly hydrophilic networks (AAm/IA), its incorporation reduces swelling through a volume exclusion effect. Conversely, in less hydrophilic systems (AAm/DEI), CMS enhances the initial absorption capacity by introducing additional carboxymethyl functional groups into the matrix.

Kinetic analysis revealed anomalous (non-Fickian) behavior for both series. In the AAm/IA system, the process is predominantly controlled by polymer chain relaxation (Case II transport), while in the AAm/DEI system, the incorporation of CMS shifts the mechanism toward a diffusion-controlled regime, compensating for the inherent rigidity of the synthetic matrix**.**

AAm/IA-based hydrogels exhibited high affinity for Cu^{2+} ions, undergoing a drastic network contraction upon the formation of coordination complexes. This ionic self-crosslinking phenomenon shifts the transport mechanism toward Fickian behavior, validating the potential of these materials for wastewater remediation.

Composting assays revealed that CMS undergoes preferential degradation without altering the structural integrity of the synthetic polymeric matrix. In this regard, the CMS acts as a biodegradable "jacket" or "vest" that envelops and protects the hydrogel during its service life; upon degradation, it facilitates the eventual fragmentation and mass loss of the material in the environment.

The incorporation of up to 20% CMS enables the development of materials with tunable functional properties and a reduced environmental footprint. The observed mass loss (up to 20% over 16 weeks) confirms that the inclusion of biopolymers is an effective strategy to increase the biological vulnerability of otherwise persistent acrylic polymers.

References

Ahmadi, S., Pourebrahimi, S., Malloum, A., Pirooz, M., Osagie, C., Ghosh, S., Zafar, M. y Dehghani, M. (2024). Hydrogel-based materials as antibacterial agents and super adsorbents for the remediation of emerging pollutants: A comprehensive review. *Emerging Contaminants*, 10 (3), 100336. https://doi.org/10.1016/j.emcon.2024.100336

An, S., Huang, S., Perumal, R. K., et al. (2026). Fabrication of starch-based hydrogels as drug controlled release carriers: Characterization, anti-bacterial, and cytotoxicity assessment. *International Journal of Biological Macromolecules*, 337 (Part 2), 149568. https://doi.org 10.1016/j.ijbiomac.2025.149568.

Araque, J., Martín, M. y Fygueroa, S. (2006). Estudio de la combustión en un motor de gasolina. *Ciencia e Ingeniería*, 27 (3), 119-127. http://erevistas.saber.ula.ve/index.php/cienciaeingenieria/article/view/308/327

Arredondo Peñaranda, A. y Londoño López, M. (2009). Hidrogeles. Potenciales biomateriales para la liberación controlada de medicamentos. Rev. ing. biomed., 3 (5), 21-30. ISSN 1909-9762

Balsamo, V., López-Carrasquero, F., Laredo, E., Contó, K., Contreras, J. y Feijoo, J. (2011). Preparation and Thermal Stability of Carboxymethyl Starch/Quaternary Ammonium Salts Complexes. *Carbohydrate Polymers*, 8 (4), 1680-1689. https://doi.org/10.1016/j.carbpol.2010.10.025

Barrios, S., Contreras, J., López-Carrasquero, F. y Müller, A. (2012). Chemical modification of cassava starch by carboxymethylation reactions using sodium monochloro acetate as modifying agent. *Revista de la Facultad de Ingeniería UCV*, 27 (2), 97-105. ISSN 0798-4065.

El Halah, A., Contreras, J., Rojas-Rojas, L., Rivas, M., Romero, M. y López-Carrasquero, F. (2015). New superabsorbent hydrogels synthesized by copolymerization of acrylamide and N-2-hydroxyethyl acrylamide with itaconic acid or itaconates containing ethylene oxide units in the side chain. *J Polym Res*, 22 (233), 1-13. https://doi.org/10.1007/s10965-015-0876-2

El Halah, A., López-Carrasquero, F. y Contreras, J. (2018). Applications of hydrogels in the adsorption of metallic ions. *Ciencia e Ingeniería*, 39 (1), 57-69. http://www.redalyc.org/articulo.oa?id=507555109006. ISSN: 2244-8780

El-Halah, A., Machado, D., González, N., Contreras, J. López-Carrasquero, F. (2019). Use of super absorbent hydrogels derivative from acrylamide with itaconic acid and itaconates to remove metal ions from aqueous solutions. *Journal of Applied Polymer Science*, 136 (4), 46999. https://doi.org/10.1002/app.46999

El-Halah, A., Boide-Trujillo, V., Erder-Concordia, M., Vizcaya, M., Delgado, G., Lopez-Carrasquero F. (2020) Synthesis and characterization of Cu(II), Zn(II) and Sm(III) metal complexes with itaconic acid. Avances en Química, 15(2), 49-56. https://doi.org 10.35207/avances.v15i2.314

El-Hamshary, H. (2007). Synthesis and water sorption studies of pH sensitive poly(acrylamide-co-itaconic acid) hydrogels. *European Polymer Journal*, 43, 4830-4838. https://doi.org/10.1016/j.eurpolymj.2007.08.018

Franson, N. and Peppas, N. (1983). Influence of copolymer composition on non-Fickian water transport through glassy copolymers. *Journal of Applied Polymer Science*, 28, 1299–1310. https://doi.org/10.1002/app.1983.070280404

García-Manzano MF, Alvarez-Igarzabal CI (2010) Síntesis de hidrogeles de N-[3-(dimetilamino) propil] metacrilamida para la retención de metales. Revista Iberoamericana de Polímeros 11(7):428-441. ISSN 1988- 4206.

González, N., Contreras, J., López Carrasquero, F., El Halah, A., Torres, C., Prin, J., Benítez, J. y Rojas de Gáscue, B. (2013). Estudio de la síntesis y caracterización de hidrogeles semi-ipn obtenidos a partir de poliacrilamida y el biopolímero poli(hidroxibutirato-co-hidroxivalerato). *Interciencia*, 38 (6), 430-436. ISSN: 0378-1844 http://www.redalyc.org/articulo.oa?id=33928571003

González, N., El-Halah, A., Contreras, J. y Rojas de Gascue, B. (2018). Estudio de la capacidad de absorción en hidrogeles semi-interpenetrados de poliacrilamida/poli(hidroxibutirato-co-hidroxivalirato). *Rev. Colomb. Quim.*, 47 (3), 19-27. https://doi.org/10.15446/rev.colomb.quim.v47n3.69280

Karadağ, E., Üzüm, Ö. y Saraydın, D. (2002). Swelling equilibria and dye adsorption studies of chemically-crosslinked superabsorbent acrylamide/maleic acid hydrogels. *Eur. Polym J.*, 38, 2133-2141. https://doi.org/10.1016/s0014-3057(02)00117-9

Katime, I., Palomares, F., Lesteros, L., Laborra, C. y Domínguez, E. (1989). Non-classical free-radical polymerization Part 2. The polymerization of mono-2-methoxyethyl and mono-2-ethoxyethyl itaconate. *Thermochim. Acta*, 142, 317-328. https://doi.org/10.1016/0040-6031(89)85028-2

Kim, B., La Flamme, K. y Peppas, N. (2003). Dynamic swelling behavior of pH sensitive anionic hydrogels used for protein delivery. *Journal of Applied Polymer Science*, 89, 1606–1613. https://doi.org/10.1002/app.12337

La Gatta, A., Schiraldi, C., Esposito, A., D'Agostino, A. y De Rosa, A. (2009). Novel poly(HEMA-co-METAC)/alginate semi-interpenetrating hydrogels for biomedical applications: Synthesis and characterization. *J of biomedical Materials Research*, 90A (1), 292-302. https://doi.org/10.1002/jbm.a.32094

Laya, J., Marfisi, S., López, G., Pastrana, J., de Sousa, M., Peña, G. y Rojas de Gascue, B. (2017). Hidrogeles semi-interpenetrados de poliacrilamida/poli (vinil alcohol): estudio de su estructura, capacidad de absorción y propiedades mecánicas. *Avances en Química*, 12 (2-3), 37-40. http://www.redalyc.org/articulo.oa?id=93357608003

Masaro, L. y Zhu, X. (1999). Physical models of diffusion of polymer solutions gel and solids. *Prog Polym Sci*, 24, 731-775. https://doi.org/10.1016/S0079-6700(99)00016-7

McGrance, S., Cornell, H. y Rix, C. (1998). A Simple and Rapid Colorimetric Method for the Determination of Amylose in Starch Products. *Starch/Stärke*, 50 (4), 158–163. https://doi.org/10.1002/%28SICI%291521-379X%28199804%2950%3A4%3C158%3A%3AAID-STAR158%3E3.0.CO%3B2-7

Ozay O, Ekici S, Baran Y, Aktas N, Sahiner, N (2009) Removal of toxic metal ions with magnetic hydrogels. Water Research 43:4403-4411. https://doi.org/10.1016/j.watres.2009.06.058

Rojas, L., El Halah, A., Contreras, J., Romero, M., Rangel, E. y López-Carrasquero, F. (2011). Estudio preliminar de la copolimerización de acrilamida con el itaconato de mono y dimetoxietilo. A*vances en Química*, 6 (2), 21-28. www.saber.ula.ve/avancesenquimica, https://doi.org/10.53766/AVANQUIM

Suhail, M., An S., Kiran, B., Huang, S., Abdul Wahab, A., Yang S., Kong, X., Iqbal, M. Z., Wu, P-C. (2025). Formulation, characterization, anti-bacterial, anti-inflammatory, anti-cancer, and cytotoxicity assessment of collagen/gelatin-based hydrogels as controlled drug release agents. International Journal of Biological Macromolecules,328, Part 2,147653. https://doi.org/10.1016/j.ijbiomac.2025.147653.

Zhang, B-G., Liu Q., Ma, T., Liu J-J., Zhang, Y., Liu, F., Wen, X -M., Wang, D-X., Jiang, Wei., An W-B. (2025). Mechanism and application of injectable hydrogel as carrier system in the treatment of osteoarthritis. Frontiers in Bioengineering and Biotechnology 13, 1-22 https://doi.org/10.3389/fbioe.2025.1636518

Zhao, J., Zhao, X., Guo, B. y Ma, P. (2014). Multifunctional Interpenetrating Polymer Network Hydrogels Based on Methacrylated Alginate for the Delivery of Small Molecule Drugs and Sustained Release of Protein. *Biomacromolecules*, 15 (9), 3246–3252. https://doi.org/10.1021/bm5006257

Zhou Z-X, Zheng, W-X., Tan,Y-Z., Wang,Y., Guo,Y-R., Pan Q-J. (2026). Fabrication of chitosan-magnesium hydroxide hydrogels for efficient removal of copper ions. International Journal of Biological Macromolecules, 340, Part 2, 150081. https://doi.org/10.1016/j.ijbiomac.2026.150081.

Received: *December 30, 2025*

Accepted: *March 24, 2026*

Luis J. Rojas Rojas Licenciado en Química ULA, MSc en Quimica aplicada. Profesor asociado Grupo de Polímeros-ULA, Departamento de Química, Facultad de Ciencias, Universidad de Los Andes, Mérida, 5101-A, Venezuela. ljrojas2021@gmail.com
https://orcid.org/ 0009-0009-1494-7098

Amal El Halah Licenciada en Química ULA, Dra. en Química aplicada Universidad de los Andes. Fue Profesora Asistente del Grupo de Polímeros-ULA, Departamento de Química, Facultad de Ciencias, Universidad de Los Andes, Mérida, 5101-A, Venezuela. aelhalah@gmail.com
https://orcid.org/ 0000-0002-75584-5221

Gabriela Andarcia Licenciada en Química ULA. Departamento de Química, Facultad de Ciencias, Universidad de Los Andes, Mérida, 5101-A, Venezuela.
https://orcid.org/0009-0008-6793-8155

Sandra Fajardo Licenciada en Química ULA. Departamento de Química, Facultad de Ciencias, Universidad de Los Andes, Mérida, 5101-A, Venezuela.

https://orcid.org/0009-0000-8675-8143

María Solandreina Rondón Licenciada en Química ULA, MSc en Química aplicada ULA. Profesora del Grupo de Polímeros-ULA, Departamento de Química, Facultad de Ciencias, Universidad de Los Andes, Mérida, 5101-A, Venezuela.
mariasrondons1@gmail.com
https://orcid.org/ 0009-0007-3839-8017

Francisco López-Carrasquero Licenciado en Química USB, Dr. en Ciencias Químicas Universidad Politécnica de Cataluña. Profesor Titular y Coordinador del Grupo de Polímeros-ULA, Departamento de Química, Facultad de Ciencias, Universidad de Los Andes, Mérida, 5101-A, Venezuela.
https://orcid.org/ 0000-0002-0012-2839