SEMI-INTERPENETRATING HYDROGELS BASED ON CHITOSAN, VINYL BENZYL TRIMETHYLAMMONIUM CHLORIDE, AND POLY (ETHYLENE GLYCOL) DIACRYLATE WITH ANTIBACTERIAL PROPERTIES FOR WASTEWATER TREATMENT

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The present study investigates the role of source-dependent chitosan in shaping the structural and functional properties of some semi-interpenetrating (semi-IPN) hydrogels for wastewater treatment. Novel hydrogels were synthesized via free-radical polymerization using vinyl benzyl trimethylammonium chloride as the functional monomer, poly (ethylene glycol) diacrylate as the crosslinker, and three chitosan types: commercial chitosan, chitosan from commercial chitin, and calcium carbonate-containing chitosan from shrimp shells. FTIR, TGA, SEM, XPS, and swelling analyses proved the hydrogels' structure and composition. Hydrogels composed of chitin-derived and mineral-enriched chitosan demonstrated superior stability and antimicrobial activity, offering promise for advanced wastewater treatment.

Keywords: semi-interpenetrating hydrogels, poly (ethylene glycol) diacrylate, wastewater treatment, chitosan, antibacterial activity

1. Introduction

Wastewater treatment has emerged as a crucial environmental and public health concern since ancient times. Over time, various advanced methods have been developed, ranging from physical and chemical treatments, such as membrane filtration [1], coagulation/flocculation [2], and adsorption [3], to biological and electrochemical processes. Each method offers unique advantages, but challenges such as high operational costs, energy demands, and secondary pollution have motivated research into low-cost, sustainable alternatives.

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Among these alternatives, adsorption-based treatment has attracted considerable attention due to its efficiency in removing organic and inorganic contaminants, as well as pathogenic microorganisms. Domestic sewage, in particular, contains high concentrations of disease-causing microbes, including Coliform bacteria, which are widely used as indicators of fecal contamination. Removing these pathogens is critical to preventing waterborne infections and ensuring the safety of drinking water. Traditional adsorbents, such as activated carbon [4], are highly effective but often expensive, prompting the exploration of polymer-based materials with abundant functional groups and adsorbent properties, such as hydrogels. Polymers derived from natural sources, including chitosan, chitin, alginate, and cellulose, are rich in functional groups such as hydroxyl, amino, carboxyl, sulfonic, and amide, which provide multiple sites for the binding of contaminants and microorganisms [5,6,7]. Chitosan is widely used alone in wastewater treatment due to its abundant amino groups, which provide strong positive charges for effective binding of negatively charged pollutants such as dyes [8] via electrostatic interactions and chelation.

Recent studies have demonstrated that these polymeric adsorbents not only efficiently remove heavy metals and organic pollutants but also reduce microbial loads in wastewater, offering a dual benefit of chemical and biological purification. In this context, semi-interpenetrating network (semi-IPN) hydrogels, which combine natural and synthetic polymers, have gained interest as effective adsorbent materials. The non-covalent association between the two phases maintains structural integrity and facilitates greater exposure of active adsorption sites [9].

Several studies have reported the use of vinyl benzyl trimethylammonium chloride (VBTAC) in new material formulations for water purification. For example, Palacio et al. described the use of poly(VBTAC-co-acrylic acid) and n-alkylated chitosan, both featuring ammonium salt groups, for antibiotics adsorption, reporting removal rates of 75% at pH 9 for polyVBTAC and 65% at pH 7 for alkylated chitosan [10]. Druvari et al. demonstrated the efficiency of multilayer antimicrobial coatings, where poly VBTAC showed antifouling properties under real immersion conditions [11]. Additionally, his group studied superabsorbent hydrogels based on quaternary ammonium chitosan-g-poly (acrylic acid-co-acrylamide), which exhibited significant antibacterial activity against *E. coli* and *S. aureus*. [12]

In a previous study [13], we described the synthesis and characterization of some semi-IPN hydrogels based on VBTAC and chitosan, with N, N′-methylenebisacrylamide (MBA) as the crosslinker, which showed good performance for water purification applications, but lacked structural stability. The present work aims at solving this deficiency by using poly (ethylene glycol) diacrylate with 700 g/mol molecular weight (PEGDA) as the crosslinker instead of MBA, in combination with both VBTAC and chitosan. By using a hydrophilic PEG macromonomer as the crosslinking agent, we expected to obtain hydrogels with a more relaxed and, therefore, more stable network, as compared to the MBA-crosslinked ones. Indeed, the novel hydrogels synthesized displayed both high water uptake and monomer conversion, as well as superior antibacterial properties, while maintaining their structural integrity.

2. Materials and Methods

Three types of chitosan were used for the synthesis of the semi-IPN hydrogels: commercial chitosan (CC, Sigma-Aldrich, ≥75% deacetylation degree, Mn=$2.056\cdot10^5$ g/mol), chitosan from commercial chitin (CCH, ≥78% deacetylation degree, Mn=$5.729\cdot10^5$ g/mol), and calcium carbonate-enriched chitosan from shrimp shells (SHC, ≥75%, deacetylation degree, Mn=$9.059\cdot10^3$ g/mol) which were obtained in the laboratory by a previously reported method [14]. Vinyl benzyl trimethylammonium chloride (VBTAC, Sigma-Aldrich, 99%), 2,2'-azobis(2-methylpropionamidine) dihydrochloride (AAPH, Sigma-Aldrich, 97%), and poly (ethylene glycol) diacrylate (PEGDA, Mn=700 g/mol, Sigma-Aldrich), employed as monomer, free-radical initiator, and crosslinking agent, respectively, were used without any purification. Acetic acid (Sigma-Aldrich, 99%) and demineralized water were also used to solubilize chitosan.

2.1. Preparation of semi-IPN hydrogels

The semi-IPN hydrogels were synthesized by free radical polymerization, according to a procedure described previously by our group [13], with slight modifications. For a better understanding of the influence of monomer concentration and crosslinker concentration, two sets of samples were prepared. Firstly, the polyVBTAC sample without chitosan was obtained by preparing 5 mL of aqueous solution containing 10 wt. % VBTAC and 1 mol% PEGDA (relative to VBTAC). After thorough homogenization of the monomer solution, 1 mol% of AAPH initiator (relative to VBTAC) was added. For the samples containing chitosan, to an aqueous solution (4 ml) containing various amounts of VBTAC and PEGDA (Table 1), 1 mL of a 1 wt.% chitosan solution (CC, CCH, SHC) and the AAPH initiator (1 mol% to VBTAC) were successively added. The polysaccharide solution was previously prepared by dissolving chitosan in a 9:1 wt./wt. mixture of water and acetic acid under continuous stirring for 24 hours. The reaction mixtures were then introduced into glass vials, sealed with rubber caps, thoroughly shaken, and placed into an oil bath at 50 °C for 24 hours. At the end of the reaction time, the hydrogels were recovered by breaking the glass vials and cut into 1 cm height pieces. For purification, the hydrogels were introduced into 100 mL of distilled water and left undisturbed at room temperature for a full week. The water was refreshed every 24 hours to eliminate residual monomers and initiator. After 7 days, the hydrogels were placed in an oven at 40°C and dried for 48 hours until a constant weight was achieved. The monomer conversion (C%) was determined gravimetrically according to Eq. 1, where m_{xsyn} is the mass of the xerogel immediately after synthesis, while m_{xpur} represents the mass of the xerogel after purification.

$$C\% = \frac{m_{xpur}}{m_{xsyn}} * 100 \quad (1)$$

Table 1

Sample composition - Variation of PEGDA and VBTAC content

Sample		VBTAC (g)	$PEGDA_{700}$ (mol % rel. to VBTAC)	AAPH (mol %, rel. to VBTAC)	Chitosan (CC/CCH/SHC) (g)
CC/CCH/SHC	P0.5	0.7	0.5	1	0.01
	P1	0.7	1	1	0.01
	P2/V0.7	0.7	2	1	0.01
	P4	0.7	4	1	0.01
	V0.3	0.3	2	1	0.01
	V0.5	0.5	2	1	0.01
polyVBTAC		0.5	2	1	-

Fig. 1. Swollen hydrogels obtained from three types of chitosan and various monomer-to-crosslinker ratios, as expressed in Table 1.

2.2. Characterization methods for the prepared samples

The Fourier Transform Infrared spectra (FTIR) of the finely ground xerogels were recorded on a Nicolet™ Summit PRO FTIR Spectrometer in the 400÷4000 cm^{-1} range with 16 scans and a resolution of 4 cm^{-1}, as KBr pellets.

The thermal behavior was analyzed using a Netzsch TG 209 F1 Libra equipment, in N_2 atmosphere with a 10°C/min constant heating rate, within the 25-700°C temperature range.

Scanning Electron Microscopy (SEM) images were recorded by using a Hitachi TM4000plus II, table-top scanning electron microscope at 15kV. The swelled hydrogels were manually fractured to expose fresh cross-sections, which were imaged without gold coating to allow direct observation of their internal structural features.

X-ray photoelectron spectroscopy (XPS) was performed using a K-Alpha (Thermo Scientific) instrument with an Al Kα (1486.6 eV) monochromatic source. The analyses were performed on xerogel samples at a pressure of 2×10^{-9} mbar and an energy of 200 eV, and for a better resolution, at 20 eV. The electric charges were compensated using an argon ion gun.

The swelling degree (SD) of the hydrogels was determined as previously reported by our group [13] by placing a weighed xerogel disk (m_x) in distilled water at room temperature. The swollen disks were removed from the medium from time to time, excess water was wiped with filter paper, the hydrogel mass (m_s) was weighed, and reintroduced into the liquid medium. Measurements were carried out until the swollen gels reached a constant weight, corresponding to equilibrium swelling. The degree of swelling at equilibrium (SD) was calculated by Eq.2.

$$SD = \frac{m_s - m_x}{m_x} \text{ (g water/ g dry polymer)} \quad (2)$$

2.3. Batch wastewater bacteriological testing

Industrial wastewater (WW) samples were taken directly from the homogenization basin of the sewage water (SW) source at multiple intervals, coordinated with the factory's production schedule. Each sample underwent vacuum filtration through 0.45 μm polyether sulfone (PES) membrane filters, and the filtrate was analyzed for bacteriological parameters. The results were compared against an unfiltered WW serving as the control. All experiments were performed under static, isothermal conditions, with every analysis performed in triplicate and the standard error of means calculated as previously described [13]. For standard measurements, about 0.5 g of xerogel was placed in a glass flask and covered with 150 mL of WW. The flask was sealed and kept in the dark at room temperature (24°C) for 24 hours. After this contact period, the supernatant was collected and refiltered using standard membrane techniques. Following the 24-hour contact, average counts of coliforms and *C. perfringens* were determined via membrane filtration and compared with control values. For the microbiological assays, the PES filters were carefully placed on agar plates to avoid trapping air bubbles, then incubated for 24 hours at 44 ± 0.5°C in a Hach incubator. After incubation, the filters were transferred to chromogenic/TSC agar, and bacterial colonies were counted with a Funke Gerber colony counter roughly 15 minutes after removal from the incubator.

3. Results and discussion

The synthesized hydrogels are displayed in their swollen form in Fig. 1. All samples were clear enough, indicating that no extensive phase separation occurred within the material, which leads to the conclusion that chitosan was fully compatible with the polyVBTAC-PEGDA network. Size differences between the hydrogel samples could also be noticed, suggesting different swelling degrees as a function of VBTAC and crosslinker concentrations, as will be discussed later.

To better understand their structure and properties, the hydrogels were characterized by several methods, such as monomer conversion and swelling degree determinations, FTIR spectroscopy and thermogravimetric analysis to confirm the chemical structure and composition of the samples, SEM imaging to provide an insight into the morphology of the hydrogels, XPS characterization of the surface elemental composition, and bacteriological testing to prove their potential application in wastewater treatment.

3.1. Monomer conversion and swelling degree

The semi-IPN hydrogels were characterized to determine the influence of each main component of the polymerization mixture, i.e., VBTAC, PEGDA, and chitosan, on monomer conversion (Table 2). The gravimetric method was used to provide a direct measure of the efficiency of polymerization and crosslinking, reflecting the fraction of monomers successfully incorporated into the stable hydrogel network. The results showed that a PEGDA/VBTAC mole ratio increase within the 0.5 - 4 mole% range did not notably influence the overall monomer conversion, at constant VBTAC concentration. This may be explained through a higher reactivity of VBTAC in a copolymerization process with acrylates, which led to its inclusion in the hydrogel network at the maximum level allowed by the experimental conditions (see below), irrespective of PEGDA concentration. The amount of unreacted PEGDA was probably different as a function of its concentration, but this had a small effect on the total monomer concentration, due to its low amount in the polymerization mixture. The experiments with variable VBTAC concentrations (at constant PEGDA/VBTAC mole ratio) revealed that lower VBTAC concentrations led to reduced total monomer conversions. This may be explained by the low mole concentrations of both monomers and initiator (1 mole % based on VBTAC), which led to lower polymerization rates.

The overall monomer conversion was influenced by the chitosan type as well. The results displayed in Table 2 revealed a lower total monomer conversion in the case of CCH-type chitosan, which may be attributed to the presence of impurities with retarding characteristics in the free radical polymerization, limiting the total monomer conversion to around 85%.

The semi-IPN hydrogels were also characterized by equilibrium swelling degree (SD) measurements, and the influence of PEGDA700 and VBTAC concentrations was assessed (Tables 3 and 4). The results showed that a gradual increase in both PEGDA (Table 3) and VBTAC (Table 4) concentrations led to lower swelling degrees. In the first case, the SD decreased due to the increasing crosslinking degree of the hydrogel as the crosslinker, i.e., PEGDA, concentration increased [15]. In the second case, the behavior was a consequence of the formation of a higher proportion of chain entanglements and of a network with fewer defects at higher monomer concentrations [15,16]. Notably, although different types of chitosan were used, the SD values were similar across all cases, indicating that the chitosan type does not significantly affect the swelling capacity of the hydrogels.

Table 2

Influence of VBTAC and PEGDA concentrations and chitosan type on the total monomer conversion

Sample	C%	Sample	C%
CC-P0.5	95	**CC-V0.3**	89
CC-P1	93	**CC-V0.5**	93
CC-P2/V0.7	96	**CC-P2/V0.7**	96
CC-P4	93		
CCH-P0.5	87	**CCH-V0.3**	79
CCH-P1	86	**CCH-V0.5**	86
CCH-P2/V0.7	86	**CCH-P2/V0.7**	86
CCH-P4	86		
SHC-P0.5	93	**SHC-V0.3**	77
SHC-P1	88	**SHC-V0.5**	96
SHC-P2/V0.7	96	**SHC-P2/V0.7**	96
SHC-P4	95		

Table 3

Influence of PEGDA concentration upon SD

Sample	CC-P0.5	CC-P1	CC-P2	CC-P4
SD (g/g)	169	115	49	26
Sample	**CCH-P0.5**	**CCH-P1**	**CCH-P2**	**CCH-P4**
SD (g/g)	294	113	50	23
Sample	**SHC-P0.5**	**SHC-P1**	**SHC-P2**	**SHC-P4**
SD (g/g)	205	110	49	25

Table 4

Influence of VBTAC concentration upon SD

Sample	**CC-V0.3**	**CC-V0.5**	**CC-V0.7**
SD (g/g)	466	112	51
Sample	**CCH-V0.3**	**CCH-V0.5**	**CCH-V0.7**
SD (g/g)	425	112	43
Sample	**SHC-V0.3**	**SHC-V0.5**	**SHC-V0.7**
SD (g/g)	464	95	48

3.2. Infrared spectroscopy of the semi-IPN hydrogels

Characteristic FTIR spectra of the semi-IPN hydrogels based on VBTAC, PEGDA, and chitosan (CC, CCH, SHC) are shown in Fig. 2. The FTIR spectra of the composite xerogels exhibited characteristic peaks corresponding to the VBTAC monomer, the PEGDA crosslinker, and the chitosan component. The presence of VBTAC was confirmed by peaks at 3024 cm^{-1} and 2924 cm^{-1} corresponding to -CH and -CH_2 stretching vibrations in the polyVBTAC backbone and the peak at 1488 cm^{-1}, specific to the vibration of the C–$N(CH_3)_3$ group [17]. The incorporation of PEGDA within the hydrogel matrix was evidenced by the characteristic vibrational bands of ether groups observed in the 1200–1250 cm^{-1} region. Since the hydrogels differ only in the type of chitosan used in the semi-IPN network, the spectra did not show major differences. The presence of chitosan in the semi-IPN networks was confirmed by the peak at 1586 cm^{-1}, ascribed to the stretching vibrations of primary and secondary amines in the chitosan structure.

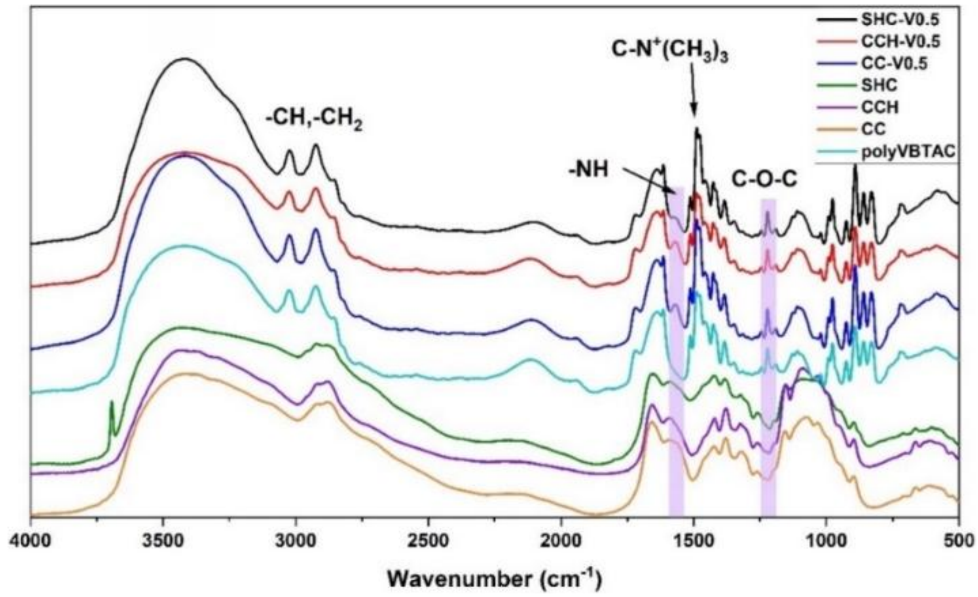

Fig. 2. FTIR spectra of the semi-IPN hydrogels and the corresponding type of chitosan

3.3. Thermogravimetric analysis TGA/DTG of the composite hydrogels

Thermogravimetric analysis was used to provide supplementary proof of the structural composition of the semi-IPN hydrogels. Fig. 3 (A, B, C) displays the TGA and DTG curves of the hydrogels based on CC, CCH, and SHC chitosan types alongside the reference polyVBTAC. All samples showed similar multi-step degradation profiles, indicating two main degradation steps as compared to the raw chitosan samples, which displayed a single-stage thermal decomposition. For the polyVBTAC sample, the first degradation step with a maximum at 264°C was attributed to the thermal decomposition of quaternary ammonium groups in the material's structure. The second degradation event, at ~400°C, corresponded primarily to the degradation of the polyVBTAC backbone, potentially overlapping with minor contributions from PEGDA crosslinker [18]. In the semi-IPN hydrogels, the first degradation stage occurs at lower temperatures for CC- and SHC-based samples (~240-250°C) compared to the polyVBTAC reference (Fig. 3A, C), indicating a contribution of chitosan decomposition overlapping with VBTAC. In the CCH-based hydrogel, the first degradation stage is shifted to slightly higher temperatures (~260-305°C), similar to VBTAC, likely due to the influence of the radical polymerization retarders mentioned above, which could also delay the thermal decomposition process. The second degradation stage in all hydrogels occurred at almost 400°C and was practically identical to that of polyVBTAC. PEGDA decomposition was not clearly shown due to its low content and likely overlapped with the polyVBTAC backbone degradation.

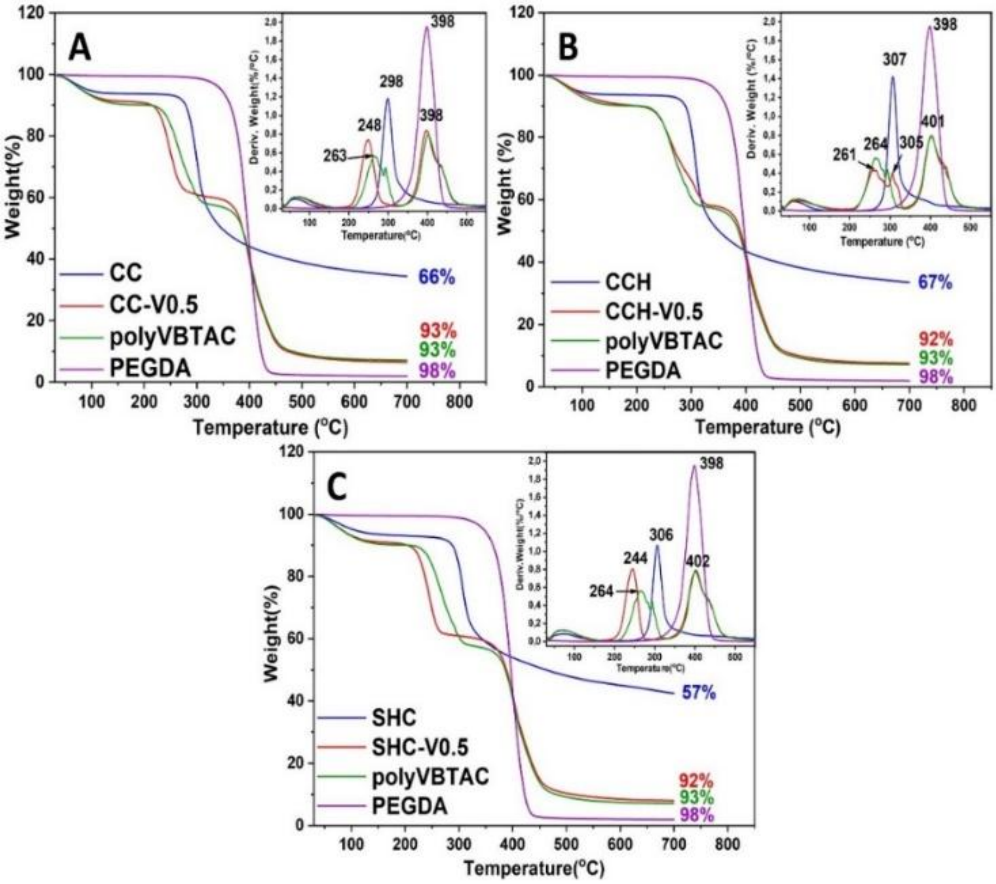

Fig. 3. TGA and DTG curves of polyVBTAC, PEGDA, and chitosan-based hydrogels. (A) CC-V0.5 and CC, (B) CCH-V0.5 and CCH, and (C) SHC-V0.5 and SHC

3.4. Scanning electron microscopy

Fig. 4 (A, B, C, D) shows the morphological characteristics of the semi-IPN hydrogels and the simple polyVBTAC hydrogel, recorded on fractured cross-sections of the swollen samples at magnifications of 300 and 100 µm. The SEM images highlight a relatively porous structure in the reference hydrogel (polyVBTAC), with large pores even on the sample surface. The hydrogels containing CC and CCH exhibit a smoother surface and a similar internal structure relative to their porosity. In Fig. 4D, displaying the sample containing SHC, the appearance of fine particles distributed in the structure of the swelled hydrogel can be observed, as a consequence of the minerals in the structure of the chitosan extracted from shrimp shells.

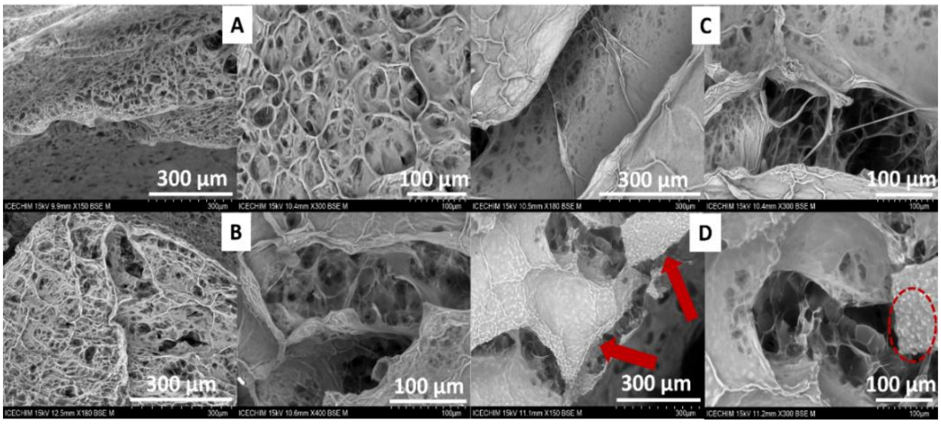

Fig. 4. SEM images of polyVBTAC (A), CC-V0.5 (B), CCH-V0.5 (C), and SHC-V0.5 (D) at sizes of 300 and 100 µm

3.5. X-ray photoelectron spectroscopy

The XPS analysis was performed to identify the main surface components of semi-IPN hydrogels and to confirm the incorporation of key components within the network. Distinct peaks for carbon (C), oxygen (O), nitrogen (N), and chlorine (Cl) were detected, supporting the presence of both monomers and chitosan constituents. Table 5 shows the relative atomic concentrations and binding energies of the mentioned elements found on the surface of the synthesized hydrogels.

Table 5

Relative atomic concentrations (%) of the surface elements detected in the studied samples

Sample	C1s	O1s	N1s	Cl2p	Ca2p	Si2p	Mg1s	P2p
CC	63,3	29,17	7,53	-	-	-	-	-
CC-V0.5	83,21	5,56	5,24	5,99	-	-	-	-
CCH	65,93	24,7	5,74	-	0,75	2,88	-	-
CCH-V0,5	80,64	8,98	3,68	4,11	-	2,59	-	-
SHC	32,05	41,76	3,47	-	11,86	1,54	1,96	7,36
SHC-V0,5	84,24	5,94	4,31	5,07	0,44	-	-	-
polyVBTAC	80,98	11,78	1,25	5,99	-	-	-	-

The presence of VBTAC in the semi-IPN materials was supported by the detection of chlorine in all hydrogel samples. Also, the presence of chitosan in all semi-IPN hydrogels was demonstrated by their nitrogen content being larger than that of the polyVBTAC sample, while the oxygen amount present in the polyVBTAC hydrogel can be ascribed to the PEGDA crosslinking agent. Some other elements identified within the materials originated from the process of obtaining chitosan. Thus, the silicone trace found in the samples likely came from the incomplete demineralization of the chitosan precursor, while the Ca amount detected in the SHC-based semi-IPN hydrogel originated from SHC, which contained higher concentrations of mineral elements (11.86 % Ca, 1.96% Mg, 7.36% P, and 1.54% Si) due to the absence of a demineralization step during the synthesis [19].

3.6. Batch bacteriological evaluation results

To evaluate the antimicrobial potential of the synthesized semi-IPN hydrogels for wastewater treatment applications, antibacterial activity tests were conducted against coliforms and *Clostridium perfringens* bacterial strains. As shown in Fig. 5 (A, B), all semi-IPN hydrogel formulations achieved substantial reductions in bacterial counts relative to the control sample, confirming their strong antimicrobial efficacy. The incorporation of chitosan into the VBTAC/PEGDA network enhanced the polyVBTAC hydrogel's antibacterial performance, owing to the combined action of chitosan's polycationic structure and the quaternary ammonium groups of VBTAC. For coliforms, the CCH-V0.5 sample achieved the greatest reduction, nearly 90% compared to approximately 47% for polyVBTAC alone, demonstrating a clear improvement due to chitosan addition. Similarly, CC-V0.5 reduced coliforms by 70% while the SHC-V0.5 sample showed only a 43% reduction, suggesting that the addition of SHC had little to no effect on overall coliform reduction. For *C. perfringens,* polyVBTAC alone showed a removal efficiency of about 21%, while the incorporation of chitosan had minimal additional effect in the case of the CC-V0.5 sample, with around 18% reduction, and CCH-V0.5 around 19%. Interestingly, the SHC-V0.5 sample indicated a strong reduction of 41% suggesting that native minerals within shrimp-shell chitosan do not compromise the bactericidal outcome.

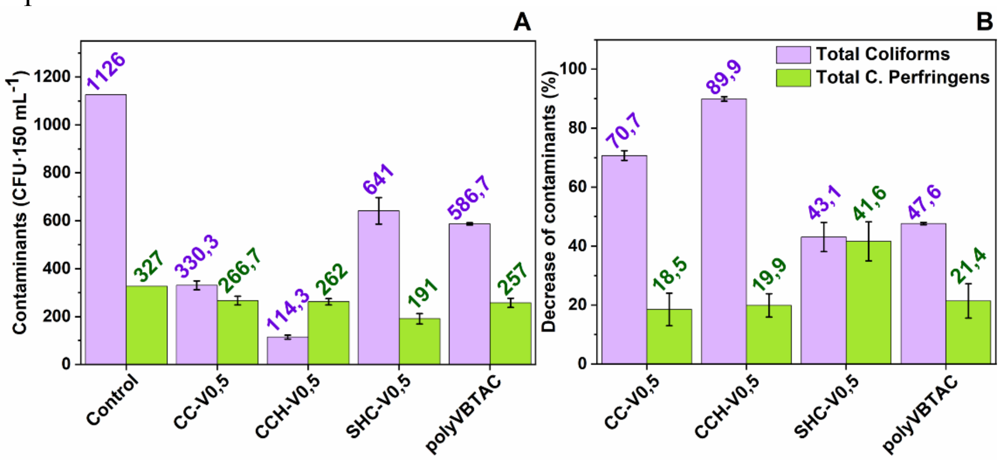

Fig. 5. Antibacterial activity of the synthesized hydrogels against coliforms and *C. Perfrigens* bacterial strains: (A) Concentration of contaminants before and after the contact of the WW with the hydrogels, (B) Percentage decrease of contaminant concentration after the contact of the WW with the hydrogels. *CFU=colony-forming unit

These results indicate that chitosan's polycationic nature can enhance coliforms inhibition, particularly when using CCH, likely due to its higher degree of deacetylation and stronger electrostatic interactions with bacterial cells. Overall, the data showed that chitosan incorporation can clearly improve antibacterial activity in some hydrogel formulations (e.g., CCH-V0.5 for coliforms), highlighting its complementary role in the semi-IPN network, while in others, the activity remains relatively the same.

4. Conclusions

The present study describes the successful synthesis and characterization of some novel semi-IPN hydrogels based on commercial chitosan and laboratory-obtained chitosan (from shrimp shells and commercial chitin), vinyl benzyl trimethylammonium chloride, and polyethylene glycol diacrylate.

The FTIR, SEM, TGA/DTG, and XPS analysis confirmed the expected composition and successful integration of VBTAC, PEGDA, and different types of chitosan within the semi-IPN structure. Monomer conversion was generally high for all hydrogels, with only CCH-containing formulations showing slightly lower values. Equilibrium swelling was within a 23 - 466 g/g range, being primarily influenced by VBTAC and PEGDA concentrations, while the chitosan type had minimal impact. The samples with higher VBTAC or PEGDA content showed lower swelling due to the formation of denser networks. All hydrogel formulations exhibited strong antimicrobial activity. Chitosan, particularly CCH, enhanced coliform inhibition, achieving reductions up to 90%, while effects on *Clostridium perfringens* were generally limited, with SHC formulation showing a notable exception. Together, these results confirm that the semi-IPN hydrogels successfully combine the properties of polyVBTAC, chitosan, and PEGDA, creating materials with antibacterial activity suitable for potential wastewater treatment applications.

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