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Novel Sulfonate Functionalized Sodium Carboxymethyl Cellulose-Based Polyelectrolyte Membranes for Drug Delivery, Toxic Metal Ion Removal, and Fuel Cell Applications

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ABSTRACT

Polyelectrolyte membranes (PEMs) have gained much attention in the last decade, mainly due to their potential industrial applications. This work aims to develop sulfonate functionalized sodium carboxymethyl cellulose (NaCMC)-based PEMs and evaluate their application in drug delivery, toxic metal ion removal, and fuel cells. In the first attempt of this work, graft copolymers are synthesized, that is, NaCMC-g-2-acrylamido-2-methyl-1-propanesulphonic acid (NaCMC-g-AMPS) and NaCMC-g-4-vinylbenzene sulfonate (NaCMC-g-SVBS). In the second attempt, prepared PEMs of sodium carboxymethyl cellulose (NaCMC)-based graft-copolymers (that are NaCMC-g-AMPS and NaCMC-g-SVBS) and poly(vinyl alcohol) (PVA) along with their composites with phosphomolybdic acid (PMA). Graft copolymers as well as PEMs are characterized by the Fourier-transform infrared spectroscopy, X-ray diffraction, differential scanning calorimetry, scanning electron microscopy, and energy-dispersive X-ray analysis. The fabricated PEMs were studied for their adeptness in drug delivery, heavy metal ion removal, and fuel cell applications. All the developed PEMs exhibited significant swelling at room temperature and a high ionic exchange capacity. PMA-doped PEMs were studied further in terms of methanol permeability, and proton conductivity. PMA undoped PEMs demonstrated controlled release characteristics for the anticancer drug 5-fluorouracil and as a sorbent for the removal of Cu²⁺ metal ions.

Key words: Graft copolymer, Carboxymethyl cellulose, Poly(vinyl alcohol), Drug delivery, Toxic metal ion removal and fuel cell.

1. INTRODUCTION

Advanced development in material science and technology has explored various carbohydrate-based polymeric systems for health care, energy, and environmental applications [1,2]. It is due to their potential characteristics, that is, biocompatibility, biodegradability, and physicomechanical property [3-7]. Various synthetic polymer (poly(vinyl alcohol) [PVA], poly(ethylene oxide), poly(N-vinyl pyrrolidone), poly(methyl methacrylate), etc.), and natural polymers (sodium alginate, pectin, guar gum, cellulose, etc.) can be used for preparation of polyelectrolyte membranes (PEMs).

Among natural polymers, sodium carboxymethyl cellulose (NaCMC) is one of the potential biopolymers due to the presence of two hydroxyl groups one carboxymethyl group on D-anhydroglucopyranose unit [8]. Hence, the free hydroxyl groups of NaCMC are readily available for further modification, that is, based on the required property or targeted martials [8]. After grafting the NaCMC with various vinyl monomers usually by a free radical polymerization process, the resultant grafted polymers have been used in various fields including drug delivery, toxic metal ion removal, organic dye removal, and flocculant properties [9,10]. In this connection, we have fabricated NaCMC-based graft copolymers with AMPS and SVBS with an aim to synthesize their blend membranes with PVA. The NaCMC graft copolymer-PVA-based membranes are studied further in drug delivery, toxic metal ion removal, and fuel cell applications.

In this work, we describe the fabrication, optimized grafting conditions, and the characterization of fabricated graft copolymers such as NaCMC-g-AMPS and NaCMC-g-SVBS using Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and differential scanning calorimetry studies.

2. EXPERIMENTAL

2.1. Materials

The following ingredients were purchased from Aldrich Chemicals in Missouri, USA: 2-Acrylamide-2-methyl-1-propanesulphonic acid (AMPS), sodium 4-vinylbenzene sulfonate (SVBS), PVA (MWt: 75000), phosphomolybdic acid (PMA), and 5-fluorouracil (5FU). Merck, Mumbai, India, supplied the following materials: sodium carboxymethyl cellulose (NaCMC, MWt: Medium), ammonium persulfate, potassium persulfate, glutaraldehyde (GA), hydrochloric

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Received: 15th March 2023; **Revised:** 08th April 2023; **Accepted:** 20th April 2023. acid, acetone, and methanol. According to our prior research, the NaCMC-g-AMPS and NaCMC-g-SVBS graft copolymers were synthesized. Cupric nitrate trihydrate that is extra pure obtained from FINAR chemicals, Ahmedabad, India. The water used for all experiments was double distilled.

2.2. Methods

All experimental procedure and methods were followed as per our earlier reports [11,12].

3. RESULTS AND DISCUSSION

All membranes are made from blends of sulfonated NaCMC (NaCMC-g-AMPS/NaCMC-g-SVBS) and PVA. Two grams of NaCMC-g-AMPS/NaCMC-g-SVBS were dissolved in 40 mL of distilled water in a separate beaker. Fixed concentrations of PVA (3 g) aqueous solution were made at 80°C, and the resulting solution was cooled to room temperature after full dissolution of PVA. The two polymer solutions were mixed and stirred for 12 h. The resulting blend solution was allowed in rest mode for 2 h to eliminate any bubbles formed; finally, this solution was then casted on a clean glass plate so that the solvent can evaporate. The dried membranes were cross-linked with an acetone: water (50:50) mixture bath comprising 2.5 mL glutaraldehyde (GA) as the cross-linker and 2.5 mL HCl as the catalyst. These membranes are known as pristine PEMs, namely, NaCMC-g-AMPS-PVA (CMCAM) and NaCMC-g-SVBS-PVA. (CMCSB). In addition, composite PEMs are made by adding 10% PMA to polymer mix solutions due to casting, and these membranes are named as NaCMC-g-AMPS-PVA-PMA (CMCAM-PMA) and NaCMC-g-SVBS-PVA-PMA (CMCSB-PMA). The representative schematic structures of PMA incorporated membrane are shown in Scheme 1.

3.1. FTIR Studies

Figure 1 is the FTIR spectra of PEMs (NaCMC-g-AMPS-PVA, NaCMC-g-AMPS-PVA-PMA, NaCMC-g-SVBS-PVA, and NaCMCg-SVBS-PVA-PMA). A strong absorption between 3100 and 3600 cm^{-1} along with the absorption at ~2900 cm^{-1} in all these spectra represents the O-H stretching and C-H bond stretching of carbohydrate backbone, PVA and AMPS/SVBS. The absorption at around 1095 cm⁻¹ in all the spectra represents carbohydrate C-O-C stretching. The absorption bands at ~1725 and ~1645 cm^{-1} are the representative of C=O stretching of carboxyl, carboxylate, and amide functions along with C=C stretching. The peaks at \sim 1440 and \sim 1380 cm⁻¹ indicate the CH₃/CH₂/CH bending and CH₃/CH₂/CH scissoring mode of vibrations. In addition, the PMA embedded membranes showed absorption at ~1060, ~960, and ~805 cm^{-1} representing the Mo-O-Mo (corner sh), Mo=O (terminal) and P-O bond stretching (Figure 1b and d). These analyses indicate the formation of PVA-blended membranes and their PMA composites.

FTIR analysis of 5-FU-loaded PEMs showed both the characteristics of PEMs and 5-FU (**Figure 1f** and **g**). The 5-FU showed representative peaks of =C-H and C-F groups at 3070 and 1244 cm⁻¹ [13-15] (**Figure 1e**). The 5-FU-loaded NaCMC-g-AMPS-PVA displayed absorption at 3074 and 1218 cm⁻¹ (**Figure 1f**) representing =C-H and C-F groups and 5-FU-loaded NaCMC-g-SVBS-PVA displayed the absorption related to these groups at 3080 and 1215 cm⁻¹ (**Figure 1g**). This analysis indicates the 5-FU encapsulation in to the membranes. The considerable shift of the absorption positions toward high wavelengths of C=O and -SO₃ functional groups in the FTIR spectra of Cu²⁺ ion-treated membranes (**Figure 1i** and **j**) indicated the adsorption of Cu²⁺ ions by the PEMs.



Scheme 1: (a and b) The plausible chemical structure of NaCMC-g-AMPS-PVA-PMA and NaCMC-g-SVBS-PVA-PMA membranes.

3.2. XRD Studies

XRD patterns of PMA (A) NaCMC-g-AMPS-PVA (B), NaCMC-g-SVBS-PVA (C), NaCMC-g-AMPS-PVA-PMA (D), and NaCMCg-SVBS-PVA-PMA (E) are shown in the Figure 2; XRD results are presented in the range of 10°–80° of 20 values. Pristine PEMs have exhibited semicrystalline peaks at 20 of 20° [16]. From Figure 2a, PMA exhibited characteristic crystalline peaks at 22, 27, 33, and 37 for (210), (221), (311), and (321), respectively [17,18]. However, PMA incorporated PEMs are not shown such crystalline peaks, which indicates that PMA is molecularly dispersed in PEMs.

3.3. Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray Analysis (EDAX) Studies

SEM images of pristine PEMs, PMA incorporated PEMs, 5-FU encapsulated PEMs, and Cu²⁺ sorbed PEMs are presented in **Figure 3**. NaCMC-g-AMPS-PVA and NaCMC-g-SVBS-PVA membranes displayed smooth surfaces with non-porous structure (**Figure 3a** and **b**). However, PMA incorporated NaCMC-g-AMPS-PVA and NaCMCg-SVBS-PVA membranes showed rough surfaces and homogeneous distribution (**Figure 3c** and **e**). In general, Cu²⁺ ions of aqueous solution are sorbed by PEMs due to the interactions between the functional groups (-SO₃⁻, -CONH, -OH, and -COO⁻) and sorbed Cu²⁺ ions. **Figure 3e** and **f** shows the images of 5-FU sorbed PEMs; the surface is very rough, and this may be due to the recrystallization of encapsulated 5-FU during the drying process of PEM. **Figure 3g** and **H** shows the images of Cu²⁺ ion sorbed PEMs, and many well-dispersed



Figure 1: Fourier-transform infrared spectroscopy spectra of NaCMC-g-AMPS-PVA (a), NaCMC-g-AMPS-PVA-PMA (b), NaCMC-g-SVBS-PVA (c), NaCMC-g-SVBS-PVA-PMA (d) and 5FU (e); ATR-FTIR spectra of NaCMC-g-AMPS-PVA-5FU (f), NaCMC-g-SVBS-PVA-5FU (g), Cu(NO3)2.3H2O (h) NaCMC-g-AMPS-PVA-Cu(II), (i) and NaCMC-g-SVBS-PVA-Cu(II) (j).

 ${\rm Cu}^{2+}$ ion salts formed on the surface of the PEM, which resulted in the rougher surface.

Figure 4 showing the EDAX spectra analysis of 5-FU encapsulated PEMs and Cu^{2+} ion adsorbed PEMs confirmed that 5-FU and Cu^{2+} ions are distributed inside as well as on the surface of the polymer network consisting of O, N, and S. EDAX results of NaCMC-g-AMPS-PVA-5FU and NaCMC-g-SVBS-PVA-5FU demonstrate that PEMs consisted the elements C, O, N, S, Na, and F; however, the weight percentages of fluorine were 5.49 and 4.16 based on the intensity of the fluorine peak. Moreover, EDAX results of NaCMC-g-AMPS-PVA-Cu²⁺ and NaCMC-g-SVBS-PVA-Cu²⁺ demonstrate that PEMs consisted of elements C, O, N, S, Na, and Cu; however, the weight percentages of copper 41.11 and 20.67 were based on the intensity of the copper peak.

Table 1, that is, 318 \pm 7.6, 260 \pm 3.9, 234 \pm 6.8, and 118 \pm 5.5 for NaCMC-g-AMPS-PVA, NaCMC-g-SVBS-PVA, NaCMC-g-AMPS-PVA-PMA, and NaCMC-g-SVBS-PVA-PMA, respectively. The results indicate that %S_e decreased with the incorporation of PMA. This may be due to the formation physicochemical interaction between the polymer and inorganic polyacid [19].

3.4. Equilibrium Swelling Studies

Swelling studies play crucial role in estimating the physicochemical characteristics of polymer membrane, which helps us understand the



Figure 2: X-ray diffraction patterns of phosphomolybdic acid (a) NaCMC-g-AMPS-PVA (b), NaCMC-g-SVBS-PVA (c), NaCMC-g-AMPS-PVA-PMA (d), and NaCMC-g-SVBS-PVA-PMA (e).

water holding capacity. It depends on the nature of functional groups and the type of dopant present in the matrix. Therefore, swelling studies were performed for both pristine PEMs and PMA incorporated membranes. The %Equilibrium swelling ratios (%S_e) are presented in Table 1.

3.5. 5-Fluorouracil Drug Delivery

The in vitro drug release studies of 5-FU-loaded NaCMC-g-AMPS-PVA and NaCMC-g-SVBS-PVA were evaluated at pH-1.2 and 7.4 at 37°C, the data are presented in Figure 5. The 5-FU-loaded PVA, NaCMC-g-AMPS-PVA, and NaCMC-g-SVBS-PVA membranes are released drug moderately in both pH environments, but in specific, release is higher in the alkaline region when compare to acidic region. The 5-FU-loaded PVA cumulative drug release found at 94.08 % in 60 min, 94.84 % in 120 min and, 180 min in 96.58 % was released, but release is not pH dependent. At pH-1.2, NaCMC-g-SVBS-PVA membrane, cumulative drug release is found 32.22 % in 60 min, 64.40 % in 120 min, 74.91 % in 180 min, and 96.0 % in 300 min; the NaCMC-g-AMPS-PVA cumulative drug release is found 43.59 % in 60 min, 71.17 % in 120 min, 81.57 % in 180 min, and 98.0 % in 300 min. However, the percentage of cumulative release is more in pH 7.4. Table 2 shows the various drug release models (zero order, first order, Higuchi, Hixson-Crowell, and Korsmeyer-Peppas) fitted with the 5-FU release kinetics data. The best R^2 observed for all the kinetic models, however, is maximum Hixson-Crowell and Korsmeyer-Peppas models at pH-1.2 with slope value (n) ranges from 0.309 to 0.94, that is, 0.309 < n < 0.94. These results demonstrate that drug

Table	1:	Composition,	%S _e ,	IEC,	proton	conductivity,	and	methanol	permeabil	ity of	various	PE	M	s.
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Membrane	PVA (g)	NaCMC-g-AMPS/ NaCMC-g-SVBS (g)	PMA (g)	% EE of 5-FU	$Q_e (mg.g^{-1})$	%S _e	IEC	Proton conductivity (mS/cm)	Methanol permeability (cm ² /s) (10 ⁻⁶)
NaCMC-g- AMPS-PVA	3	2	0.5	74±1.8	233.31±4.9	318±7.6	0.46±0.07	20.76±1.8	2.092±0.19
NaCMC-g- AMPS-PVA-PMA	3	2	0.5			234±6.8	0.67±0.13	49.40±1.5	0.861±0.12
NaCMC-g- SVBS-PVA	3	2	0.5	62±2.6	213.15±5.1	260±3.9	0.54±0.10	17.93±2.7	2.053±0.18
NaCMC-g- SVBS-PVA-PMA	3	2	0.5			118±5.5	0.91±0.16	61.90±3.4	0.974±0.32

PEMs: Polyelectrolyte membranes



Figure 3: Scanning electron microscope images of NaCMCg-AMPS-PVA (a), NaCMC-g-SVBS-PVA (b), NaCMC-g-AMPS-PVA-PMA (c), NaCMC-g-SVBS-PVA-PMA (d), NaCMC-g-AMPS-PVA-5FU (e), NaCMC-g-SVBS-PVA-5FU (f), NaCMC-g-AMPS-PVA-Cu2+ (g), and NaCMC-g-SVBS-PVA-Cu2+ (h).

release followed the non-Fickian drug transport mechanism, that is, the dissolution of water-soluble drug in PEM network [20-22]. Similar mechanisms are also observed in the case of pH-7.4.

3.6. Copper Ion Removal

Figure 6 shows the effect of Cu²⁺ ion concentration on NaCMC-g-AMPS-PVA and NaCMC-g-SVBS-PVA PEMs in pH-5.5 aqueous media at 30°C. The presence of functional groups, such as carboxyl group of NaCMC, amide and sulfone group of AMPS/SVBS, and hydroxyl group of PVA, is a key factor in either chemisorption or physisorption of metal ions. In the present study, the maximum adsorption capacities were observed in pH 5.5 at 30°C, and 233.31 ± 4.9 and 213.15 ± 5.1 mg.g⁻¹ were achieved for NaCMC-g-AMPS-PVA and NaCMC-g-SVBS-PVA, respectively.

Biopolymers are non-toxic, selective, efficient, and inexpensive, making them a viable alternative to ion-exchange resins and activated carbon [21-23]. Hence, cross-linked biopolymer-based materials (blends of chitosan and PVA) were used to remove Cu^{2+} ions from aqueous media [24,25], and orange peel xanthate was used to remove Cu²⁺ and Ni²⁺ ions [26]. Cavus et al. synthesized poly(2-acrylamido-2-methyl-1-propane sulfonic acid-co-itaconic acid) polymers for the removal of Pb^{2+} , Cu^{2+} , and Cd^{2+} from aqueous solutions [27]. To remove bivalent metal ions (Zn^{2+}), a set of hybrid biosorbents made from pectin and polysaccharide additives (arabic, tragacanth, guar, karaya, xanthan, gellan, carob gums, agar-agar) or lecithin (phospholipid) were investigated [28]. Due to the putative metalbinding mechanism of pectin, that is, developing an egg-box model, pectin and its composite materials have been employed to remove Cu^{2+} ions [29]. These findings show that pectin engages in electrostatic interactions, hydrogen bonding, and van der Waals forces with metal ions [30-32]. The present results compared with the literature [22,33-35] with respect to adsorbent to adsorbate (mg.g⁻¹) are shown in Table 3.

3.7. Ion Exchange Capacity, Oxidative Stability Proton Conductivity, and Methanol Permeability Studies

The necessary features for PEMFC or DMFC are (i) good mechanical and chemical stability in a highly oxidizing environment and (ii) high conductivity of protons that may be achieved by altering the membrane composition as well as thickness [3,36]. Several efforts have been made to synthesize cost-effective and thermally stable membranes using sulfonated monomers such as AMPS and SVBS-based polymers. Another advantage of AMPS and SVBSbased membranes is their reported high mechanical and chemical stability with high proton conductivity. Further, these polymers are characterized by their enriched hydrophilicity and high ionic character [37,38]. Due to their polyelectrolytic nature, AMPS and SVBS are freely soluble in water, making them easy to anchor the polymer chains

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Figure 4: Energy-dispersive X-ray analysis patterns of NaCMC-g-AMPS-PVA-5FU (a), NaCMC-g-SVBS-PVA-5FU (b), NaCMC-g-AMPS-PVA-Cu2+ (c), and NaCMC-g-SVBS-PVA-Cu2+ (d).

Table 2: In vitr	o drug release	kinetics	models.
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Sample code	Zero order		First order		Higuchi		Hixson–Crowell	Korsmeyer–Peppas						
						pH-	1.2		pH-7.4	ł	K	R	п	k
	R	K _θ	R	K_I	R	K _h	R	K _{hc}	R	n				
PVA	0.943	5.8	0.98	4.4	0.98	1.9	0.98	4.3	0.979	0.091	8.71	0.99	0.08	8.89
NaCMC-g-AMPS-PVA	0.969	1.49	0.95	2.9	0.955	1.28	0.969	2.4	0.995	0.236	0.05	0.99	0.83	11.3
NaCMC-g-AMPS-PVA	0.936	6.06	0.986	2.8	0.986	1.24	0.984	2.6	0.989	0.339	0.64	0.995	0.77	15.1

PVA: Poly (vinyl alcohol)

of PVA, pectin, and other functionalized polymers. The incorporation/ grafting of APMS and SVBS to PEMs improves physicochemical characteristics and mechanical strength [39-41]. Hetero polyacids such



Figure 5: FU release characteristics of PVA, NaCMC-g-SVBS-PVA, and NaCMC-g-AMPS-PVA in pH-1.2 and 7.4 at 37°C.



Figure 6: Cu²⁺ ion adsorption by NaCMC-g-SVBS-PVA and NaCMC-g-AMPS-PVA in pH-5.5 at 30°C.

as phosphotungstic acid and PMA act as both strong Brönsted acid and solid electrolyte [42,43]. Polyacids are generally water-soluble and may have strong interactions with polymer membranes, resulting in an increase in fuel cell performance. Li and Wang have fabricated PVAbased proton-conducting membranes embedded with a polyacid.

These membranes demonstrated that increasing the polyacid content increased the properties such as proton conductivity and methanol permeability [38]. In addition to drug delivery and sorption studies of metal ions, fabricated membranes with and without PMA are examined for the suitability to function as PEMs for fuel cells. In this context, %S_e, ion exchange capacity (IEC), proton conductivity study, and methanol permeability of the PEM were tested (**Table 1**). **Figure 7** shows the proton conductivity study and methanol permeability of NaCMC-g-AMPS-PVA, NaCMC-g-SVBS-PVA, NaCMC-g-AMPS-PVA-PMA, and NaCMC-g-SVBS-PVA-PMA at 30°C under atmospheric pressure. IEC and %S_e are the key factors influencing the proton conductivity study and methanol permeability.

Proton conductivity of PEMs is in the order of 10^{-3} S/cm; however, it significantly increased with incorporation of 10% PMA into the PEMs. This may be due to proton transfer (i.e., in the form of H_3O^+ , $H_5O_2^+$, and $H_9O_4^+$) across the membrane with the help of the functional groups -COO⁻, -CONH, and -SO₃H., where hydronium ion dissociates and forms hydrogen bonds (*Grotthus Mechanism*) [42]. This is also supported by high %S_e (over the 100%), that is, the more hydrophilic nature of PEMs enhances the ionic nature of PEMs [43]. On the



Figure 7: Proton conductivity and methanol permeability of the polyelectrolyte membranes.

Table 3: Comparison of maximum adsorption capacity of Cu(II) ion by NaCMC based materials.

S. No.	Name of the polymer	Qe (mg. g^{-1})	References
1.	Xanthate-modified cross-linked magnetic chitosan/poly (vinyl alcohol) particles	139.797	[30]
2.	Lignocellulose-based adsorbent	64.94	[31]
3.	2,3-Dialdehyde nanofibrillated celluloses	32.15-64.94	[32]
4.	Sodium alginate-gelatin	43.51	[22]
5.	Sodium alginate	140.55	[33]
6.	Calcium alginate-immobilized Chlorella Sorokiniana	179.90	[34]
7.	Pectin-based films		[35]
8.	Sodium alginate-g-SVBS-PVA membranes	181.22	[11]
9.	Sodium alginate-g-AMPS-PVA membranes	188.91	
10.	Pectin-g-SVBS-PVA membranes	190.1	[12]
11.	Pectin-g-AMPS-PVA membranes	206.7	
12.	NaCMC-g-SVBS-PVA	233.31	Present work
13.	NaCMC-g-AMPS-PVA	213.15	Present work

contrary, PMA incorporated PEMs $(49.40 \times 10^{-6} \text{ cm}^2/\text{s} \text{ and } 61.90 \times 10^{-6} \text{ cm}^2/\text{s})$ demonstrated lower methanol permeability when compared to pristine PEMs $(0.861 \times 10^{-6} \text{ cm}^2/\text{s} \text{ and } 0.974 \times 10^{-6} \text{ cm}^2/\text{s})$. This is due to its polyacid *pseudo liquid phase* nature [44,45].

4. CONCLUSION

This study describes the synthesis of sulfonate functionalized sodium carboxymethyl cellulose (NaCMC)-based PEMs and also PMA embedded PEMs. The chemical structure of PEMs was verified by the FTIR. Crystallinity of PEMs was analyzed by the XRD studies. The PEMs without PMA were studied for drug delivery and toxic metal ion removal capacities using 5-FU (a significant chemotherapeutic agent) and aqueous Cu²⁺ solutions. The drug release kinetics showed that the drug release follows the non-Fickian drug transport process. The PEMs-assisted adsorption studies displayed the adsorption capacities as 233.31 and 213.15 mg.g⁻¹ for NaCMC-g-AMPS-PVA and NaCMCg-SVBS-PVA, respectively. The surface morphology and elemental composition of the PEMs were recorded by scanning electron micrograph and energy-dispersive X-ray analysis, respectively. The results of present study demonstrate that, a simple and cost-effective approach to fabricate environment friendly PEMs from sulfonated CMC and PVA that may be potentially employed as anticancer drug delivery systems for various cancer types, as adsorbent for removal of bivalent heavy metal ions and as polyelectrolyte membrane for transport of ions.

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