



Article Chitosan Gel Hydroxypropyl Methylcellulose Membranes: A Novel Approach for the Remediation of Cadmium in Aqueous Solutions and Soils

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Abstract: Cadmium (Cd^{2+}) pollution in soil and water bodies is a significant environmental concern, necessitating effective remediation strategies. Traditional methods often fall short in efficiency, costeffectiveness, and environmental sustainability. This study develops and evaluates the effectiveness of chitosan-gelatin-hydroxypropyl methylcellulose (CS-GEL-HPMC) membranes for Cd²⁺ removal from polluted environments. CS-GEL-HPMC membranes were synthesized with varying HPMC concentrations. Their structural and morphological characteristics were analyzed using UV-visible absorption spectroscopy and FT-IR. The membranes' stability across different pH levels and their morphological traits were assessed. The adsorption efficiency for Cd^{2+} ions was evaluated in both aqueous solutions and soil environments under varying conditions of pH, initial ion concentration, and contact time. The CS-GEL-HPMC membranes demonstrated significant structural integrity and stability, especially at higher HPMC concentrations. UV-visible and FT-IR analyses confirmed the successful integration of HPMC into the CS-GEL matrix. In aqueous solutions, the membranes exhibited efficient Cd²⁺ adsorption, with the best performance observed for the CS30-GEL30-HPMC40 membrane. The adsorption capacity was influenced by contact time, initial Cd²⁺ concentration, and pH. In soil treatments, the membranes effectively reduced Cd^{2+} concentrations, with higher membrane dosages yielding better results. The incorporation of additives like (hydroxyapatite) HAP, fly ash (FA), and cement further enhanced the remediation efficiency. In summary, CS-GEL-HPMC membranes, particularly when combined with additives, emerge as a promising, sustainable solution for Cd²⁺ remediation in both soil and water bodies. This study highlights the potential of biopolymerbased composites in environmental clean-up efforts, offering a novel approach that is both effective and eco-friendly.

Keywords: chitosan; gel; HPMC; cadmium removal; wastewater; soil

1. Introduction

The scourge of heavy metal pollution, especially from cadmium (Cd), has emerged as a global environmental crisis (present mostly in soil or water [1]) and is observed and managed by all means worldwide because Cd is characterized by its persistence and bioaccumulation and poses severe risks to ecological systems and human health, causing several diseases [2–4]. With industrialization resulting in waste management and agriculture, heavy metal pollution has increasingly impacted human health in the last 50 years [5]. Recent techniques used for reducing Cd content from industrial waste are chemical precipitation, adsorption, ion exchange, electrolytic methods, and membrane filtration [6–13]. Recently, new materials such as HAP [14], CNTs [15], and CS [16] presented good remediation of Cd pollution without recovery when used either in aqueous or soils. Thus,



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Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). addressing this threat requires effective, sustainable, and economically viable remediation strategies to address Cd pollution in the environment, according to the increasingly strict requirements set forth by environmental protection and public health [17–19].

Chitosan (CS), a hydrophilic and natural cationic polymer formed by N-deacetylation of chitin, is present in fungi, insects, and crustaceans [20]. The presence of these amino groups increases the adsorption capacity of chitosan compared with that of chitin [21,22]. Thanks to its large number of reactive groups (-NH₂/-OH), CS can coordinate with various heavy metal ions to form metal chelates, along with biodegradability, compatibility, antibacterial properties, and lack of toxicity [1,23]. Thus, CS and its composites have been used for the removal of Cd from aqueous solutions and the remediation of Cd species in contaminated soils as well [24,25]. CS—GEL membranes show poor dimensional stability and poor durability because of the low mechanical properties of CS, which negatively limits the direct application of CS-GEL membranes in the environmental remediation fields [26]. Thus, CS-GEL polymer membranes are expected to provide an important mechanical enhancement. Fortunately, an enhancement in the performance of polymer films modified by hydroxypropyl methylcellulose (HPMC) was reported, along with its good mechanical properties [27]. The use of HPMC for improving the mechanical and rheological properties of foods has been demonstrated as well [28,29]. Importantly, the H-bonding interaction between the matrix and the enhancer (HPMC) is also stable in aqueous environments [30]. In addition, HPMC exhibits biocompatibility [31] and has good potential to form composites with various materials as it is water soluble because of its amphiphilic properties [32,33]. These materials have been rarely reported as environmental materials for the remediation of Cd from both aqueous and soil environments with subsequent recovery and reusability.

In this paper, we report a simple green chemical synthesis method for membrane polymers, chitosan (CS)–gelatin (GEL), enhanced by hydroxypropyl methylcellulose (HPMC). Then, the CS-GEL-HPMC membranes are used to remove a heavy metal, cadmium (Cd), from a soil and water environment. This study demonstrates that (1) the CS-GEL-HPMC membrane materials structure can be controlled by the content of hydroxypropyl methylcellulose (HPMC) in the polymer. (2) The mechanical strength of membranes relates to the dynamic stability and effectiveness of Cd removal. (3) Furthermore, the combinations of membranes and other additives such as hydroxyapatite (HAP), fly ash (FA), and cement are developed for optimization of soil Cd remediation. (4) This research holds significant potential, offering an environmentally sustainable, cost-effective, and highly efficient solution for Cd pollution. This study could lead to a significant advancement in sustainable environmental remediation in both aqueous (or wastewater) and soil environments, using biodegradable and eco-friendly materials, an environmentally benign synthesis method, effective and sustainable remediation strategies, and the reusability of the developed membranes.

2. Results and Discussion

2.1. Structure Analysis

XRD patterns of various CS-GEL-HPMC material compositions (Figure S1) present a main peak at 20 between 20 and 25°, corresponding to the amorphous carbon in the polymers, such as CS [34] and HPMC [35]. Notable changes correlating with increasing HPMC content are revealed in samples CS0.5-GEL0.5, CS0.35-GEL0.35-HPMC0.3, and CS0.25-GEL0.25-HPMC0.5. Specifically, the primary peak (20 between 20 and 25°), indicative of the carbon chain structure, exhibits a slight shift toward higher degrees, which is attributed to the higher crystallinity of HPMC compared with the CS and GEL polymer matrix [36]. Consequently, the incorporation of HPMC not only enhances the crystalline structure but also contributes to a more stable phase. This stability is particularly beneficial in the application of these membrane materials for the remediation of Cd²⁺-contaminated water and soil, suggesting a potential improvement in performance because of the structural integrity imparted by HPMC, especially the dynamic stability in aqueous environment (discussed in detail in Table 1). UV–visible absorption spectra and the coefficient vs. photo energy of a series of CS-GEL-HPMC samples with an increasing mass ratio of HPMC from 0 to 40 wt% are provided in Figure 1a and Figure 1b, respectively. The CS-GEL and CS-GEL-HPMC membranes do not have an absorption peak in the visible range (400–700 nm) as they have no UV or visible chromophores [37]. However, CS-GEL-HPMC_40 presents a lower bandgap (~5.1 eV) than that of the CS-GEL composite (bandgap ~5.5 eV). As a result, the change in the photo absorption proves that HPMC was successfully incorporated into the CS-GEL matrix. As expected, CS-GEL-HPMC exhibits a pronounced absorption band at ~280 nm, which becomes weaker and even fades away, proving that the HPMC content increases in the composite.



Figure 1. (a) UV–vis absorption spectra and (b) coefficient vs. photo energy of different CS-GEL-HPMC membranes (respectively, CS50-GEL50, CS45-GEL45-HPMC_10, CS40-GEL40-HPMC_20, CS35-GEL35-HPMC_30, CS30-GEL30-HPMC_40, and CS25-GEL25-HPMC_50). (c) FT-IR spectra of CS-GEL and CS30-GEL30-HPMC_40 (the inset illustration corresponds to the enlargement of the blue square area).

Composition	pH 2	pH 3	pH 4	pH 5	pH 6	pH 7	pH 8	pH 9
CGH-0	Unstable	Stable						
CGH-1	Unstable	Unstable	Unstable	Unstable	Stable	Stable	Stable	Stable
CGH-2	Unstable	Unstable	Stable	Stable	Stable	Stable	Stable	Stable
CGH-3	Unstable	Stable	Stable	Stable	Stable	Stable	Stable	Stable
CGH-4	Stable	Stable						
CGH-5	Unstable	Unstable	Stable	Stable	Stable	Stable	Stable	Stable

Table 1. Stability collection of membrane samples in solution with different pH values.

The FT-IR spectra of the base film (CS-GEL) and CS-GEL-HPMC samples, shown in Figure 1c, present the structure of the membrane samples. In the case of the samples with 40% HPMC content, they both show strongly bonded hydroxyl bands (wavenumber at 3200~3600 cm⁻¹) and the typical C-H alkyl stretching band (wavenumber at 2850~3000 cm⁻¹), according to the FT-IR spectrum of the pure HPMC membrane sample as a reference [38]. We can find the bending vibration of the single bond -NH peaking at $\sim 1640 \text{ cm}^{-1}$ on the spectrum of CS-GEL, suggesting the -NH₂ group in the chitosan polymeric matrix. An additional small sharp band at ~2925 cm⁻¹ is attributed to the stretching vibration of the single bond in -CH groups and the single bond in -CH₂ groups, and the presence of a single bond -CH peaked at ~1398 cm⁻¹. The region of 1120–1020 cm⁻¹ (C-O-C) presented coincident bands for both polymers. C-O stretching can be observed at 1030 cm⁻¹, confirming the amide groups in the chitosan matrices [39,40]. Gelatin also possesses the following similar functional groups: 3404 cm^{-1} (-OH and -NH), 2920 cm⁻¹ (-CH), 1374 cm⁻¹ (-CH), 1653 cm⁻¹ (-NH), and 1079 cm⁻¹ (C-O stretching vibration in the single bond -COH) [41,42]. Significantly, the possible reaction of the -NH₂ of CS cross-linking with -OH of HPMC is attributed to the shifting peak from ~1640 cm⁻¹ to ~1635 cm⁻¹ (single bond -NH) and peak ~1535 cm⁻¹ (-NH₂ group) shifting to ~1520 cm⁻¹ [26,43]. In addition, the single peak at ~873 cm⁻¹ corresponds to the 40 wt% of HPMC content introduced [44]. All the spectra characterizations together demonstrated the successful synthesis of the target product, CS-GEL-HPMC polymer materials.

2.2. Stability in the Solution

The stability of chitosan-based materials faces the challenge of exposure to a wide range of pH values, which is usually the main factor restricting their practical application. Thus, the solvability of a series of CS-GEL-HPMC membranes controlled by varying amounts of the HPMC enhancer was characterized to evaluate the stability of the membranes (in Table 1) and then the best one was selected for further research. A pH range from 2 to 9 was tested. Based on the result, CS-GEL is not stable and it is soluble in the solution with a pH value < 8. The other HPMC-modified membrane samples are stable in a solution with pH values from 6 to 9. Only CS30-GEL30-HPMC_40 (CGH-4, in Table 1) demonstrates good stability in the solution at pH = 2; thus, it was selected finally by virtue of having the widest applicability.

The stability of the membranes in an acid solution depends on the content ratio of HPMC. It can be elucidated that the cross-linking of the HPMC enhancer and the chitosangel base and the stability of membranes can be improved with the appropriate addition of HPMC content. Briefly, since the HPMC enhancer effectively hinders the molecular motion of the CS-GEL matrix and inhibits the swelling process, the CS-GEL-HPMC composites become increasingly stable with a ratio of HPMC from 0 to 40 wt%. However, excessive reinforcement destroys the integrity of the matrix, causing the membrane material to break apart under the action of molecular motion and external force. Thus, the stability of CS-GEL-HPMC composites decreased with the continually increasing HPMC content from 40 to 50 wt%.

2.3. Morphological Analysis

The morphological characteristics of the unmodified and HPMC-modified CS-GEL membranes were investigated by scanning electron microscopy (SEM, Figure 2a–c). A good softness of the CS-GEL-HPMC membranes represented by the CS-GEL matrix is shown in the digital image in Figure 2d. Further, the optical micrographs of (b) CS50-GEL40-HPMC_10 and (c) CS20-GEL20-HPMC_40 show a good distribution and reduced agglomeration in the membranes with an increasing amount of HPMC content from 10 wt% to 40 wt%.



Figure 2. (**a**–**c**) SEM images of (**a**) CS50-GEL50, (**b**) CS50-GEL40-HPMC_10, and (**c**) CS30-GEL30-HPMC_40 (scale bar, 1 μm); (**d**) digital picture of CS50-GEL50; and (**e**,**f**) polarizing microscope of (**e**) CS50-GEL40-HPMC_10 and (**f**) CS30-GEL30- HPMC_40 (scale bar, 100 μm).

Compared with the CS-GEL membranes (Figure 2a), the surfaces of the CS-GEL-HPMC membranes (Figure 2b,c) become increasingly rough. The larger surface area of the CS-GEL-HPMC membranes is related to the content of HPMC from 10 wt% to 40 wt%. The reason may be attributed to the HPMC enhancer stably existing in the CS-GEL matrix. Thanks to the rough surface because of the introduction of cellulosic content, as a result, CS-GEL-HPMC membranes obtain enhanced stability and form a larger surface area for better removal of heavy metal ions because the metal ions can be trapped and adsorbed on the membrane surface. Thus, there is no obvious stratification or degradation, as supported by the results of SEM (Figure 2b,c) and polarizing microscope images (Figure 2e,f), suggesting that the HPMC content is completely incorporated into the CS-GEL matrix. This indicates the success of the synthesis and the increase in the surface area resulting from the HPMC modification.

2.4. Application of Cd^{2+} Ion Sorption in Water Solution

Following the scheme of a modeling experiment using membrane materials for treating wastewater (Figure 3a) and the scheme of the mechanism of removal of Cd^{2+} (Figure 3b), the relationship between contact time and Cd^{2+} removal by the CS30-GEL30-HPMC_40 membrane was further studied. Figure 3c shows the real-time concentration and removal percentages of Cd^{2+} ions as a function of contact time. As contact time increases from 0 to 40 min, the Cd^{2+} concentration obviously decreases from 1 ppm to 0.55 ppm. Then, it slowly goes to 0.53 ppm with a slight fluctuation. On the other hand, the removal percentage of Cd^{2+} quickly increases from 0 to 40% during the first 30 min; it reaches 45% in 40 min

and then 47% in 60 min, but then, the concentration did not obviously change. However, at higher initial concentrations of Cd²⁺, such as 200 ppm, Figure 3d shows a completely different result. With increasing contact time from 0 to 5 min, the Cd^{2+} concentration obviously decreases from 200 ppm to ~130 ppm. Then, it slowly goes to ~100 ppm over another 5 min with a slight fluctuation. Later, the balance of the reaction led to a final concentration of ~100 ppm in this situation. This perhaps originates from the diffusion constraints of the Cd²⁺ sorption process. At low concentrations, the ratio of Cd²⁺ to the number of available adsorption sites or ion-exchange sites is comparably low, which leads to a driving force of mass transfer between the solution and solid phases with low uptake. Conversely, a higher initial concentration provided an important driving force to overcome the mass transfer resistances of the system, thus increasing the uptake [45]. Thus, to justify the mechanism, Figure 3e shows the effect of higher initial concentrations on the removal of Cd^2 ions onto 0.2 g of CS-GEL-HPMC membranes. The removal was carried out at different initial concentrations ranging from 100 to 500 ppm at pH 7 and at 25 °C with 60 min of contact time. The results show the adsorption capacity increasing from \sim 70 mg/g to \sim 130 mg/g as the initial concentrations increase from 100 to 500 ppm.

Figure 3f shows the effect of pH on the removal of Cd^{2+} ions onto the CS30-GEL30-HPMC_40 membrane. The removal percentage was found to increase with an increasing pH value from 3 to 11. The pH value significantly affects Cd^{2+} ion removal. This is partly because hydrogen ions compete with Cd^{2+} ions strongly. For example, the higher concentration and mobility of H⁺ ions indicate a high solubility and ionization of Cd^{2+} in an acid medium [46]. At this point, it seems that a false electrostatic attraction occurred between the CS-GEL-HPMC membrane and Cd^{2+} ions. With a higher pH value of the solution, the removal amount of Cd^{2+} is increased because the concentration of H⁺ ions is reduced and, therefore, Cd^{2+} is adsorbed [47]. The new HPMC-CS-GEL membrane can be used with such a good removal ability of Cd from the original environment.

Additionally, as presented in Figure S2, 5 mL of 0.1 M HNO₃ was sufficient for the whole elution of the Cd²⁺ ions with a recovery of ~95%. In five consecutive adsorption–desorption cycles, no significant changes (less than 15%) in the adsorption capacity were observed, suggesting excellent reusability of this membrane material. Their recovery and reusability together highlight the sustainability of the new CS-GEL-HPMC membrane material, which leads to a lower cost of services.



Figure 3. Cont.



Figure 3. (a) The scheme of the modeling experiment using CS30-GE30L-HPMC_40 membrane treatment of wastewater (original concentration of Cd^{2+} ions = 1 ppm or 200 ppm, T = 25 °C). (b) The scheme of the mechanism for using the CS30-GE30L-HPMC_40 membrane for the removal of Cd^{2+} ions in wastewater. (c,d). Effect of contact time on the removal of Cd^{2+} ions onto CS30-GE30L-HPMC_40 membrane surfaces (original concentration of Cd^{2+} ions = 1 ppm or 200 ppm, T = 25 °C). (e). Effect of the initial Cd ²⁺ ions concentration in the removal onto the CS-GEL-HPMC membrane surface (pH = 7; T = 25 °C). (f). Effect of the pH value of the solution on Cd²⁺ removal from the solution (T = 25 °C).

2.5. Application of Soil Remediation

Following the scheme of an indoor modeling experiment for the removal of Cd^{2+} in soil, using membrane materials (Figure 4a) and the mechanism of removal of Cd^{2+} in soil (Figure 4b), 1–5 wt% membrane materials were added into the soil at the beginning. Generally, the 3–5 wt% membrane materials can cause the Eh of soil to decrease more significantly than the 1 wt% membrane. In detail, soil Eh decreased from 540 to much less than 500 mV on the first day, to less than 460 mV on the fifth day in the early stage. Then, soil Eh slowly decreased to ~420 mV (1 wt% membrane), ~402 mV (3 wt% membrane), and ~400 mV (5 wt% membrane) until the 27th day, and then showed relative stability (27th~42nd day). The 1 wt% membrane treatment can cause the soil Eh of CK to range from ~540 to ~420 mV during 42 days, and this value can even finally decrease to ~350 mV following treatment by 3–5 wt% membrane materials (Figure 4c).

Soil pore water pH (Figure 4d) in the 1 wt% membrane treatment was the lowest (5.0–5.5), which was 0.5–1.0 units lower than in the 3–5 wt% membrane treatment (~6.0). During incubation, the pH values in the soil with the 1 wt% membrane treatment increased rapidly in the first 14 days and then reached ~5.3. Similarly, the pH values quickly increased to 5.8 in the 3–5 wt% treatments, but only slightly reached 6.0 from the 21st to the 42nd day.

The Cd²⁺ concentrations in soil pore water decreased with time (duration of 42 days) in the membrane treatments compared with the CK sample (Figure 4e). In addition, the Cd²⁺ concentrations in the treatment with the 1 wt% membrane decreased from ~250 μ g/kg (or μ g/L) to ~40 μ g/kg (or μ g/L). With a further increase in the membrane to 3–5 wt%, the Cd²⁺ concentration substantially decreased to 15~20 μ g/kg (or μ g/L). Thus, compared



with CK and the membrane treatments, Cd²⁺ concentrations in pore water decreased with time and increasing dosage of membrane treatment.

Figure 4. (a) The scheme of the modeling experiment using the CS30-GE30L-HPMC_40 membrane treatment of Cd-polluted soil (original concentration of Cd^{2+} ions = 250 ppm). (b) The scheme of the mechanism for using the CS30-GE30L-HPMC_40 membrane for the removal of Cd^{2+} ions from the soil. (**c**–**e**) Changes in soil redox potential (**c**), pore water pH (**d**), and Cd^{2+} concentrations (**e**) during flooding incubation of soil treated by the membrane materials with 1–5% weight percentages of soil.

2.6. Optimized Application via Compound Use with Other Additives

To further optimize the application of the membrane into soil treatment and its redox potential, 3 wt% of the membrane in compound use with other additives was studied. Figure 5 shows the changes in soil redox potential including the following: Eh, pore water pH, and Cd^{2+} concentrations during flooding incubation of soil treated by the 3 wt% membrane material compound combined with 1–5 wt% additives of (a–c) HAP, (d–f) FA (fly ash), and (g–i) cement.

Generally, the addition of HAP contributes to a reduction in the Eh value, while 1 wt% HAP used as an additive does not affect the Eh value obviously, compared with the 3 wt% membrane only. When increasing the HAP amount as much as 3–5 wt%, the Eh of the soil decreased quickly at the beginning and then reached ~350 mV slowly from the 32nd to the 42nd day. The pH values of the four samples exhibit a similar rising trend, rapidly increasing in the first 3 days and then slowly increasing to their maximum until the end of the 42nd day. The final pH values (ranging from 5.6 to 6.5) increased with the amount of the HAP additive (from 0–5 wt%). The Cd²⁺ concentration in soil pore water decreased from 250 µg/L with time. After the 42-day treatment, all the final concentrations of Cd²⁺ in soil pore water ranged between 10 and 30 µg/L, and the minimum concentration of ~10 µg/L was achieved by the 3 wt% HAP treatment. This means the compound with 3 wt% membrane and 3 wt% HAP can be selected for the treatments of the soil because of the decreased Cd²⁺ in the soil pore water.

Fly ash (FA), as another additive instead of HAP, can be a compound used to treat soil polluted with Cd^{2+} . The addition of FA generally contributes to a reduction in the Eh value. Using 1 wt% HAP as an additive significantly affects the Eh value, unlike the 3 wt% membrane. There was a rapid decrease in the Eh of the soil from the beginning to the end, followed by a gradual decline to ~350 mV. When the FA amount was increased

to 3–5 wt%, similar changes could be found in the other two curves. The pH of the soil samples exhibits a consistent upward trend, rapidly increasing in the first three days and then gradually rising to a peak by the forty-second day. The final pH values, ranging from 5.6 to 6.0, increase in correlation with the FA additive concentration, which varies from 0 to 5 wt%. Additionally, the concentration of Cd^{2+} in the soil pore water decreased over time, starting from 250 µg/L as well. After 42 days of treatment, the final concentration of Cd^{2+} in the soil pore water $\sim 20 \mu g/L$ did not show an obvious improvement due to the additive.



Figure 5. Changes in soil redox potential: (a,d,g) Eh, (b,e,h) pore water pH, and (c,f,i) Cd²⁺ concentrations during flooding incubation of soil treated by 3 wt% membrane materials composited with 1–5 wt% additives of (a-c) HAP, (d-f) FA (fly ash), and (g-i) cement.

Interestingly, the cement additives were able to improve the membrane effect on the soil potential obviously, compared with the previous two additives. The soil Eh value decreased with time and with the cement amount (Figure 5g). The soil treated with 3 wt% cement and membrane presented the lowest final Eh value of ~100 mV on the 42nd day. On the other hand, the soil pore water pH of the soil with 1 wt% cement additive and the 3 wt% membrane treatment (~6.5) was much higher compared with the one only treated by the 3 wt% membranes (~6.0). With further increases in the cement amount, the pH values in the soil increased faster than before and then finally reached 6.5 as well. In addition, the concentration of Cd²⁺ in the soil pore water decreased over time for all samples in the 42 days, and due to the additional amounts of cement added (more than 1 wt%), the final concentration (<5 µg/L) was much less than that with only the 3 wt% membrane treatment (~20 µg/L). Thus, the compound with 3 wt% membrane and 3 wt% cement effectively treated the soil and decreased Cd²⁺ in the soil.

In summary, according to the parameters of soil Eh, pore water pH, and the Cd^{2+} concentration in pore water, the compounds with the 3 wt% membrane and 3 wt% ad-

ditive effectively treated the soil potential and decreased Cd^{2+} in the soil. The order of effectiveness of the several additives was as follows: cement > HAP > FA.

2.7. Soil pH and CaCl₂-Extractable Cd Concentration

Soil pH increased across all treatments with the membrane with or without other additives, compared with CK, with at least a 1.0 unit increase. The highest pH (6.0) was observed in the soil treated by the 3 wt% membrane with the additive of 5 wt% cement, which was 1.5 units higher than with the membrane only (Figure 6a). Treatment with the 3 wt% membrane combined with 1–5 wt% HAP additives resulted in the pH value of the soil increasing by 0.25–0.5 units compared with the sample with only the 3 wt% membrane treatment, while treatment with the 3 wt% membrane and 3–5 wt% FA additives led to a ~0.25 unit increase in pH.



Figure 6. (a) Soil pH and (b) CaCl₂-extractable Cd concentration after flooding incubation.

The highest concentrations of CaCl₂-extractable Cd (~430 μ g/kg or μ g/L) were observed in CK (Figure 6b). CaCl₂-extractable Cd significantly decreased in the membraneonly treatments (225 μ g/kg). And the value decreased even more with further increasing dosages (1–5 wt%) of additives, for example, HAP (195–156 μ g/kg), FA (210–180 μ g/kg), and cement (120–60 μ g/kg). Thus, cement as an additive resulted in a positive effect on the treatment of soil Cd, no matter the pH or the Cd²⁺ concentration extracted by CaCl₂.

3. Materials and Methods

3.1. Materials

Hydroxypropyl methylcellulose (HPMC, 700–1500 mPa·s), glacial acetic acid, hydrated cadmium sulfate (CdSO₄· $8/3H_2O$), ammonia, and sodium hydroxide were obtained from Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). Chitosan (95% deacetylated,

100–200 mPa.s viscosity) and gelatin (type A, swine-based, 240–270 bloom) were sourced from Guide Chem. Co., Ltd. in Hangzhou, China. Potassium pyroantimonate (1 wt%) and other chemicals came from Sinopharm Chemical Reagent Co., Ltd., Beijing, China. All reagents, of analytical grade, were used as received without additional purification.

3.2. Preparation of Membranes

The membrane samples were synthesized by a modified sol-gel method in an aqueous system using potassium pyroantimonate as the ionic crosslinker solution [26]. Briefly, 0.03 g/mL chitosan (CS) in acetic acid and gelatin (GEL) solution were mixed in equal volumes to make 10 mL. To this, 1.5 mL of 0.05 g/mL potassium pyroantimonate (PA) crosslinker (1 wt%) and 0.04 g of HPMC were added, creating a uniform solution. This was stirred for 1 h, poured onto a 20 cm \times 20 cm PMMA plate, and dried at room temperature for 24 h. The resulting membranes were peeled off, washed with 0.1 mol/L ammonia to eliminate acetic acid residue, and finally dried under vacuum at 50 °C for 6 h to achieve a final thickness of about 50 µm [26]. The synthetic process is shown in Scheme 1.



Scheme 1. Structure of the synthesis of the CS-GEL-HPMC membranes and the further modeling application for the removal of Cd²⁺ ions from wastewater and soil using CS30-GE30L-HPMC_40 membrane materials.

The stability of membrane materials can be immediately measured in aqueous environments with varying pH values (from 2 to 9). Briefly, the cut membranes ($20 \text{ mm} \times 20 \text{ mm}$) were exposed to various pre-prepared solutions with continued stirring for 24 h. All the samples were then recovered. According to their morphology, an evaluation of the membranes' stability was completed as follows: the samples with a square shape could be noted as "stable", while the broken membranes could be evaluated as "unstable". The results are recorded in Table 1.

3.3. Structural Characterization

XRD was carried out using a PANalytical X'Pert Pro powder diffractometer (XPert PRO, 141 Malvern Panalytical Ltd., Malvern, UK) equipped with a Cu K α radiation source (λ = 1.5418 Å) operating at 40 kV and 30 mA. The obtained XRD pattern was analyzed with "HighScore Plus". FT-IR spectra were obtained using a Nicolet NEXUS-470 spectrometer (Thermo Fisher Scientific, Madison, WI, USA). UV-vis absorption spectra were recorded on a TU-1901 UV-vis spectrophotometer (Beijing Purkinje General Instrument Co., Ltd., Beijing, China).

3.4. Morphological Characterization

SEM was performed on a Hitachi SU8010 SEM (Hitachi High-Technologies Co., Tokyo, Japan, 15 kV).

3.5. Adsorption Studies

To evaluate the adsorption efficiency of the CS-GEL-HPMC membranes for Cd^{2+} removal, aqueous solutions of cadmium sulfate (CdSO₄·8/3H₂O) were prepared at various concentrations (1 ppm to 200 ppm). The following procedure was used to ensure consistent and accurate preparation of these solutions: A mother solution of 1000 ppm (mg/L) Cd²⁺ was prepared by dissolving 2.28 grams of hydrated cadmium sulfate (CdSO₄·8/3H₂O) in deionized water and diluting it to 1 liter in a volumetric flask. The stock solution was then diluted with deionized water to obtain working solutions with the desired concentrations of Cd²⁺ (1 ppm, 5 ppm, 10 ppm, 50 ppm, 100 ppm, and 200 ppm). For example, to prepare a 1 ppm solution, 1 mL of the mother solution was diluted to 1000 mL with deionized water. Similar dilutions were made to achieve other concentrations as per the requirements of the experiments. The prepared solutions were stored in polyethylene bottles at room temperature until use in adsorption experiments. The solutions were gently mixed before use to ensure homogeneity.

Batch adsorption experiments involved stirring 0.1 g of the membrane in 10 mL of a 1.0 ppm Cd²⁺ ion solution for 60 min on a horizontal bench shaker (Orbitek-Teqip-ACT/EQ/454) at 200 rpm. After shaking, the solution was filtered to measure the remaining Cd²⁺ ions in the filtrate using a UV-vis spectrophotometer with xylenol orange as the detection agent. The percentage of heavy metal ion removal was then calculated from the experimental data using a mass balance equation as follows:

$$R = (C_0 - C_e) / C_0 \times 100\%$$

where C_0 and C_e are, respectively, the initial and equilibrium final Cd^{2+} ions concentrations (ppm) of the solutions.

3.6. Desorption Studies

A desorption study was carried out as well after the sorption of the metal-loaded CS-GEL-HPMC membrane (initial concentration, 2.0 ppm; pH 7; room temperature). After attaining equilibrium, a centrifuge was employed to separate the materials from the solution. Metal ions were eluted using different concentrations of HNO₃ (aq). The desorption percentage (%) was calculated as follows:

$$D = C_{des} - C_0 \times 100\%$$
.

where C_{des} (ppm) is the Cd²⁺ concentration after desorption and C_0 (ppm) is the initial Cd²⁺ ion concentration.

3.7. Application in Soil Remediation

The flooding incubation experiments were conducted in PVC tanks (1 L, diameter: 10 cm and height: 15 cm). First, 500 g of soil was mixed with a quantity of CS-GEL-HPMC membrane materials and additives. To effectively immobilize Cd, CS-GEL-HPMC membranes were added to the soil at a dosage of 1–5 wt% [48]. Furthermore, 1–5 wt% additives were added to the soil to optimize the effect of soil remediation [48]. In each tank, a soil pore water sampler was placed 2 cm above the bottom, and the tanks were then incubated for 42 days at RT (18–28.5 °C). The soil was kept continuously flooded, with water levels maintained 2 cm above the soil surface [14]. Soil Eh was monitored 2 cm below the soil–water interface every 3 days. Soil pore water samples were collected for pH measurement on days 1, 3, 7, 14, 21, 28, and 42, while the levels of soluble phosphate and Cd were analyzed on days 14, 28, and 42. At the end of the experiment (day 42), soil pH and the concentration of CaCl₂-extractable Cd were also measured. Soil Eh was determined using a platinum electrode and a silver–silver chloride electrode. The pH values of soil and pore water were measured with a pH test strip. CaCl₂-extractable Cd was extracted from 4 g of soil using 20 mL of a 0.01 mol/L CaCl₂ solution [14].

3.8. Statistical Analysis

In this study, all values are shown as the mean carried out after 3 repetitions, with error bars indicating any significant difference between sample types. The figures were drawn using Origin 8.0 (OriginLab, Northampton, MA, USA).

4. Conclusions

This study successfully develops innovative chitosan–gelatin–hydroxypropyl methylcellulose (CS-GEL-HPMC) membranes, with a "green chemistry" approach, as a sustainable and efficacious approach to removing cadmium (Cd²⁺) pollution from soil and wastewater systems worldwide. Multiple structural and morphological analyses verified the integration of HPMC into the CS-GEL matrix, significantly enhancing membrane stability and heavy metal adsorption capacity. Batch investigations clearly demonstrated the membrane's reliable efficiency in capturing aqueous Cd²⁺ ions across varying conditions like pH levels, initial Cd concentrations, and contact times. Consecutive adsorption–desorption cycles further proved its reusable potential without compromising performance.

In soil treatments, amending contaminated systems with increased CS-GEL-HPMC membrane doses substantially reduced soluble and extractable Cd in situ, while concurrently increasing the pH and maintaining a reduced state. Additionally, compound modifications using (hydroxyapatite) HAP, fly ash (FA), and cement mixtures identified cement as the most potent additive, clearly synergizing the membrane's immobilization functionality. At optimized ratios, the combined application immobilized soil Cd down to $60 \mu g/kg$, presenting an economical, scalable, and eco-friendly technological innovation for managing Cd pollution.

This work puts forward an innovative green chemistry approach that could provide a foundation for engineering specialized biopolymer composites to address heavy metal contamination globally. Additional large-scale field testing and demonstrations may soon help transition this membrane-based passive pollution control from the laboratory to successful on-the-ground remediation. Ultimately, this impactful and interdisciplinary solution resonates powerfully with worldwide commitments to restore environmental quality and human health by tackling ubiquitous toxicity challenges.

In the future, special adsorption and selectivity in both aqueous and soil environments could be studied with modifications for CS-GEL-HPMC membranes, such as "ion imprinting", particularly in the presence of competing ions like Cu²⁺ or Pb²⁺. This would be valuable for completely understanding the broader applicability and limitations of the developed material in complex environments where multiple heavy metals are present.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/coatings14040421/s1, Figure S1: XRD patterns of the membranes. Figure S2. Aqueous environmental adsorption efficiency of membrane materials after recovery with desorption treatments.

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