



Preparation and characterization of chitosan/hyaluronic acid/itaconic acid hydrogel composite to remove manganese in aqueous solution

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ABSTRACT

In this work, new hydrogel composites composed of chitosan (CS)/hyaluronic acid (HA)/itaconic acid (IA) were synthesized by gamma radiation. Triple combination was prepared using gamma rays (25 kGy) at ambient temperature through simultaneous free radical polymerization and crosslinking. The swelling and diffusion properties of the hydrogels were investigated before submission to the adsorption experiment for removal of manganese (Mn) in aqueous solutions. The equilibrium mass percentage swelling of CS/HA hydrogels increased from 2,400 to 7,786 as the addition of IA in the CS/HA formulation. Fourier transform infrared and scanning electron microscopy were used for the surface characterization and chemical structure of the hydrogels. Mn uptake and release properties of the newly prepared composites improved with the including IA in the gel formulation of the CS/HA hydrogels. Adsorption capacity of Mn increased from 15.46 to 18.23 mg/g with the inclusion of IA in the formulation of CS/HA. It was found that adsorption capacities of Mn by both gels were competitive with some of the CS based composites used in Mn adsorption studies.

Keywords: Adsorption; Chitosan; Gamma radiation; Hyaluronic acid; Hydrogel; Itaconic acid; Manganese

1. Introduction

Environmental pollutants in water raised the demand for new polymeric composites for the removal of toxic heavy metal ions in industrial wastewater [1]. Chitosan (CS) has received much attention in different areas, particularly environmental biotechnology since it has a high adsorption capacity for heavy metal ions at reasonably low costs [1]. It has also shown that CS is an excellent polymer for the preparation of hydrogels with many monomers in the applications such as engineering, biomedical applications [2,3]. CS hydrogel was attempted for adsorption of heavy metals in industrial wastewater [4–6]. Kutlusoy et al. [7] found that hyaluronic acid (HA) as a biological product and Vasvani et al. [8] noticed that the addition of CS in the

structure of the gels caused a noticeable increase in the swelling rate. In the past few years, many papers reported on the poly(N-isopropylacrylamide-co-itaconic acid) hydrogels [9–13]. The authors showed that the use of IA in the gel formulation enhanced swelling properties of NIPAAm. Various treatment methods such as physico-chemical, flocculation, precipitation, membrane filtration, coagulation, ion exchange, and adsorption have been applied to remove metals from wastewater [14–21]. Of these wastewater treatment methods, the adsorption is one of promising processes and recently, biocomposites attracted much attention and proved to be highly efficient in this regard and a number of reports highlighted the use of biocomposite for the removal of diverse types of pollutants [22–27].

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Therefore, in this work, it is aimed to synthesize by radiation technique and characterization of new hydrogels containing CS and hyaluronic acid (HA) and in the presence of itaconic acid (IA). In our study, this triple combination is to be first time used for manganese adsorption. The synthesized hydrogels were analyzed by Fourier transform infrared (FTIR) spectral analysis, and scanning electronic microscopy (SEM) techniques. The experiments on swelling, diffusion of hydrogel composites were performed prior adsorption of manganese ion from an aqueous solution.

2. Materials and methods

2.1. Chemicals

Chitosan powder (CS) was supplied by Fluka chemical (Turkey), acetylation degree 14%. The viscosity average-molecular weight is 70,000 kDa. Itaconic acid (IA) was purchased from Fluka Chemical Company (Turkey). Hyaluronic acid was purchased from Sigma-Aldrich Chemical Company (Turkey). $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ was obtained from Merck, Turkey (CAS #1.05941). All the reagents were of analytical grade and used as received. All the solutions were prepared using distilled water.

2.2. Preparation of chitosan/hyaluronic acid/itaconic acid hydrogels

Hydrogel synthesis started by adding hyaluronic acid at 10% (w/v) aqueous solution on to the 10 mL of the CS (1% w/v) solution. Then, glutaraldehyde (0.4% wt.) solution was put to the prepared CS/HA solution. Later, in sample 1, the prepared solutions (CS/HA) were put in the glass tubes with 5 mm inner diameter. In sample 2, 20 mg of itaconic acid (IA) was added to the CS/HA solution and the mixed solutions were placed in the glass tubes with 5 mm inner diameter.

All the prepared solutions were irradiated with a total dose of 25 kGy using a ^{60}Co gamma source (Nordion-Canada model JS 9600 model gamma irradiator in Gamma-Pak Ind & Trade Inc., Turkey) under air at 25°C. The prepared hydrogels were kept in a double distilled water at room temperature and dried in a vacuum oven at 30°C.

2.3. Theory and calculation for hydrogels

Calculation of the mass swelling and equilibrium mass swelling percentages were proceeded according to Eqs. (1) and (2) given in the following:

$$\text{Mass Swelling (\%)} = \frac{(m_t - m_0)}{m_0} \times 100 \quad (1)$$

$$\text{Equilibrium Mass Swelling (S}_{\text{eq}} \text{ \%)} = \frac{(m_{\infty} - m_0)}{m_0} \times 100 \quad (2)$$

where m_0 is the dry gel mass, m_t and m_{∞} is the swollen gel mass at time t and at equilibrium, respectively [12].

For the characterization of hydrogels, the diffusion coefficient (D) was calculated the following equation in order to determine the nature of diffusion of Mn solution into hydrogels [28,29]:

$$F = \frac{M_t}{M_{\infty}} = kt^n \quad (3)$$

Here F is the fractional uptake, M_t/M_{∞} , where M_t is the amount of absorbed at time t , M_{∞} is the maximum amount absorbed, k is a constant, n is the diffusional exponent. For Fickian diffusion, $n \leq 0.50$, whereas n is 0.50–1.00 for non-Fickian diffusion [28].

The diffusion coefficient of hydrogel is calculated according to Eq. (4) [30]:

$$F = 4 \left(\frac{Dt}{\pi r^2} \right)^{1/2} - \pi \left(\frac{Dt}{\pi r^2} \right) - \frac{\pi}{3} \left(\frac{Dt}{\pi r^2} \right)^{3/2} \quad (4)$$

where D is the diffusion coefficient, r is the radius of the gel, and t is time.

2.4. Adsorption experiments

The adsorption time was determined as a result of the swelling experiments of the hydrogel, and since the hydrogel swelling continued for 23–24 h, 24 h was accepted for adsorption to obtain high removal efficiency. In addition, since hydrogel is a high-cost material, it has been concluded that it would be more appropriate to use low-dose hydrogel for long-term adsorption. Since the prepared hydrogels do not have temperature-sensitive properties, the effect of temperature on the adsorption property of the composites has not been investigated. To study the adsorption of Mn, hydrogels were placed in 100 mL of Mn solutions. The dry hydrogels (0.5 g/L) were transferred into the five different concentrations of Mn solutions (5–7.5–10–12.5–15 mg/L) and allowed to equilibrate for 24 h at room temperature.

In our previous adsorption studies on the hydrogels composed of IA, it was shown that the amount of adsorbed metal ions increased with the increase in pH of the solution because carboxyl groups of IA complexed with metal ions. At lower pH values (pH = 2–3), the functional groups (e.g., $-\text{COOH}$) are mostly protonated and cannot bind with the metal cation [12,13]. For this reason, the adsorption studies were performed at pH 7. The solution pH was adjusted to 7.0 adding H_2SO_4 and NaOH at the beginning of adsorption. Samples were taken after 24 h and determined the Mn concentration in the solutions. Calculation details of the maximum adsorption capacity (q_{max}) and Langmuir and Freundlich isotherm models were explained elsewhere [12,13].

For reusability of hydrogel, 0.5 g/L dry hydrogel was put into the 100 mL of Mn solutions between 5 and 15 mg/L, and pH was adjusted to 7. After 24 h adsorption, samples were taken and Mn concentrations were analyzed. Hydrogels were rinsed distilled water and dried at room temperature. Dry hydrogels were put into the 0.1 N HCl (100 mL) solutions for 24 h to determine the desorption ratio. After desorption during 24 h, the supernatant was taken to determine Mn concentration. Then hydrogels were rinsed in distilled water and dried at room temperature before the second adsorption experiments that were performed following the same procedure with first use as explained above.

2.5. Analytical methods

Manganese analysis was performed according to DIN 38406-2 method and measured on a UV-visible spectrophotometer (Shimadzu UV-2401, Turkey) using the Merck manganese test kit (1.14770.0001). FTIR spectroscopy (Bruker VERTEX 70 ATR, Turkey) was used for the chemical characterization of the CS/HA/IA hydrogel. The surface characteristics of the CS/HA/IA hydrogel were analyzed using an electron SEM-energy dispersive X-ray analyzer (EDX) (FEI-QUANTA FEG 250).

3. Results and discussion

3.1. FTIR and SEM analysis

FT-IR spectrum of CS/HA/IA hydrogel is shown in Fig. 1. For CS, the vibration of the NH_2 group is shown at about $1,542.53 \text{ cm}^{-1}$ and the carbonyl group is at about $1,648.78 \text{ cm}^{-1}$ [31]. The broad peak appears at $3,290.15 \text{ cm}^{-1}$ showing to hydroxyl groups (OH) and hydrogen bond formation took place within CS. The C=N imine peaks can be illustrated at $1,648.78 \text{ cm}^{-1}$ for the glutaraldehyde cross-linked CS gel. This band shows that the carbonyl (C=O) group of glutaraldehyde and the amine ($-\text{NH}_2$) group of the CS are reacted. For HA, characteristic ether peak at $1,030.65 \text{ cm}^{-1}$ coming from the primary alcohols (C–OH) was also illustrated. The peak at 874.76 cm^{-1} may prove that the reaction between CHO groups of HA and CS took place. The carbonyl (C=O) stretching band corresponding to IA acid is also illustrated at $1,720 \text{ cm}^{-1}$ [10].

SEM image of CS/HA/IA hydrogel is shown in Fig. 2. SEM analysis shows that prepared hydrogel has a smooth surface morphology.

3.2. Swelling properties of hydrogels

Fig. 3 illustrates the swelling properties of hydrogels at 25°C . According to the Fig. 3, mass swelling increases as time increases, and then the hydrogels reach the equilibrium. In the aqueous solution, CS/HA hydrogel swells and goes to equilibrium mass swelling of 2,470% during the equilibrium time of 24 h. The amount of IA included in the CS/HA gel has resulted in a remarkable increase in the swelling [7,10]. The equilibrium mass swelling of the CS/HA/IA was found at 7,786%.

3.3. Diffusion

n and k values were calculated from the slope and intercept of the lines shown in Figs. 4 and 5 by using Eq. (5) and these values are listed in Table 1. In this work, n was found to be over 0.50 (Table 1). So, the diffusion of water and Mn into CS/HA/IA shows a non-Fickian character [13,32]. The diffusion coefficients of CS/HA/IA in water and Mn solutions were also illustrated in Table 1. It was expected that as the equilibrium mass swelling increases, the diffusion coefficients also increase [10–12].

3.4. Adsorption of manganese using hydrogels

The proposed adsorption mechanism is shown in Fig. 6.

In adsorption experiments, higher Mn removal was obtained with the studies carried out with CS/HA/IA hydrogel than CS/HA hydrogel. Removal of Mn was achieved at 88.8%, 80.0%, 69.0%, 58.4%, and 51.3% using CS/HA hydrogel while a 93.6%, 83.6%, 73.5%, 66.2%, and

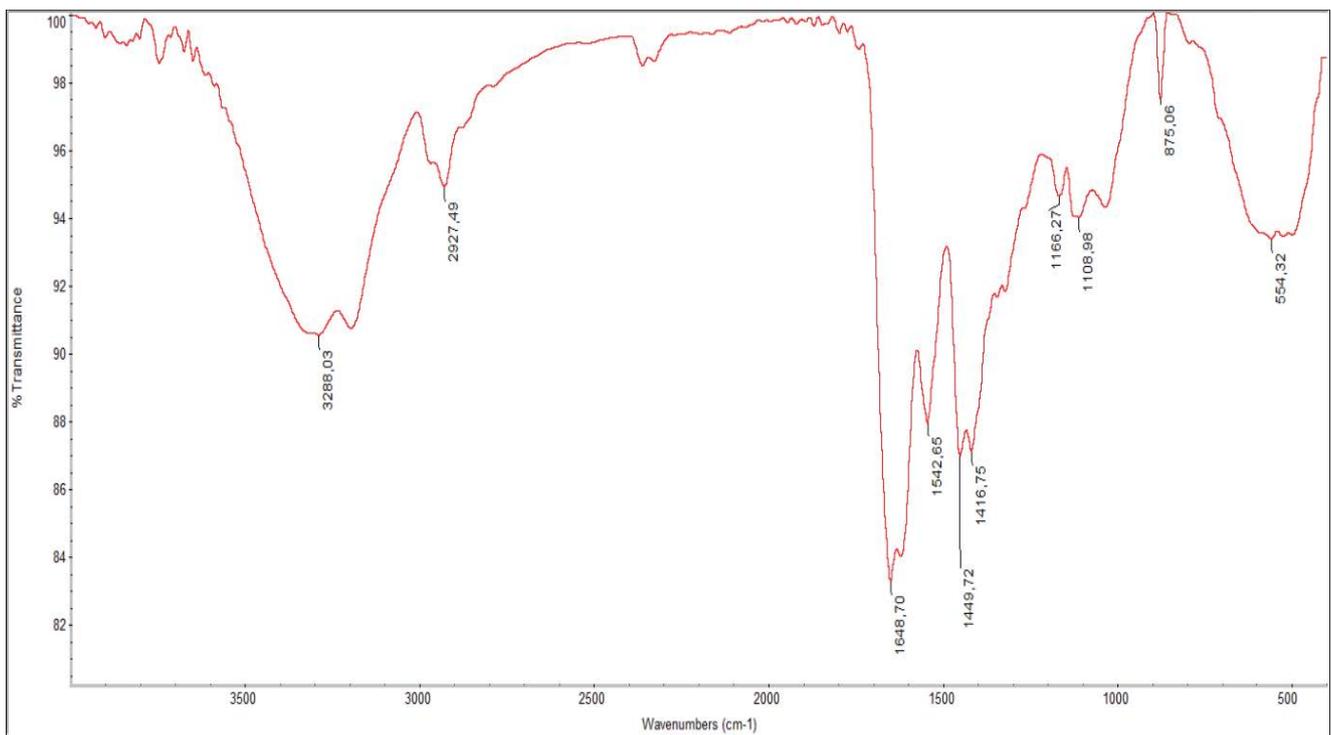


Fig. 1. FT-IR spectrum of CS/HA/IA hydrogel.

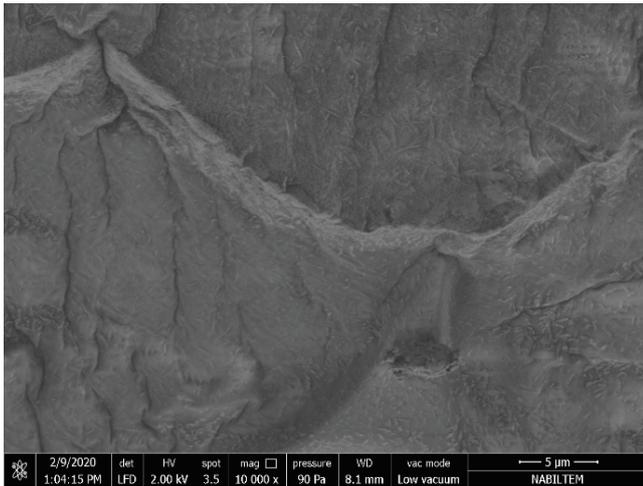


Fig. 2. SEM image of CS/HA/IA hydrogel.

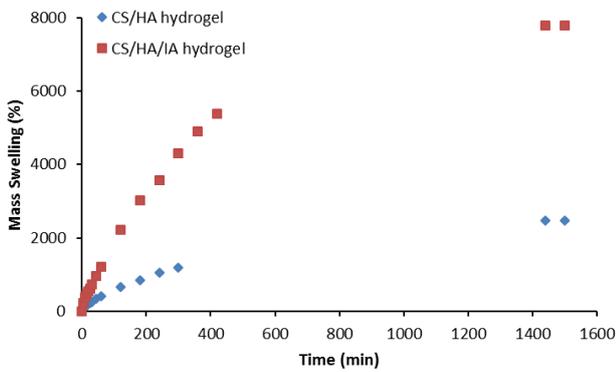


Fig. 3. Percentage mass swelling as a function of time for the CS/HA and CS/HA/IA hydrogels in distilled water.

59.2% of Mn removal was obtained at 5, 7.5, 10, 12.5, and 15 mg/L initial Mn concentrations using CS/HA/IA hydrogel (Fig. 7). These increases are in accordance with the improved swelling characteristics of CS/HA/IA hydrogel. This improvement due to the addition of IA was also observed in the previous adsorption studies with hydrogels [12,13,33]. Because the addition of IA to the CS/HA hydrogel could increase carboxyl groups which can increase interactions between cationic Mn.

Consequently, the calculations showed that Mn adsorption capacities of the hydrogels increased from 9.5 to 15.5 mg Mn/g dry hydrogel and from 11.1 to 18.2 mg Mn/g dry hydrogel for CS/HA hydrogel and CS/HA/IA hydrogel respectively when Mn concentration was increased from 5 to 15 mg/L.

Comparison of q_{max} values of hydrogels used for Mn adsorption is shown in Table 2. It is clearly seen that q_{max} value of CS/HA and CS/HA/IA hydrogels synthesized in this study were found to be higher than poly(vinylpyrrolidone/acrylic acid) copolymer (PVP/AAC) [34], acrylic acid/acrylamide (AAc/AAM) [35], and polyvinyl alcohol/chitosan binary dry blend hydrogel (PVA/CS) [36]. Although some of those polymer composites containing CS provided much higher adsorption capacities than

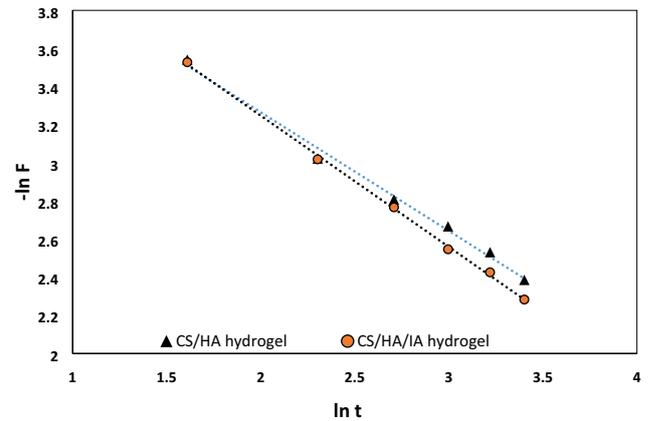


Fig. 4. Plot $\ln F$ vs. $\ln t$ for the CS/HA and CS/HA/IA hydrogels in water.

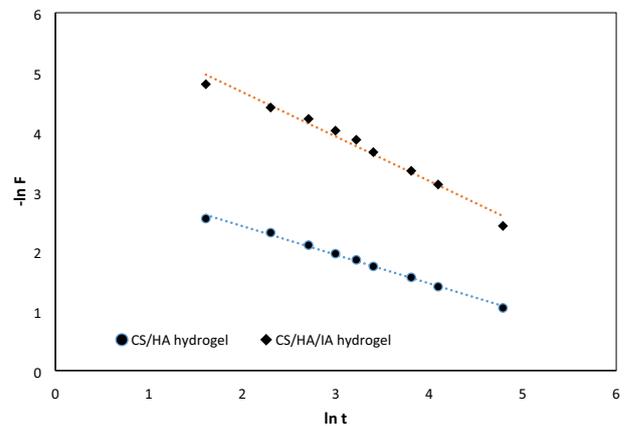


Fig. 5. Plot $\ln F$ vs. $\ln t$ for the CS/HA and CS/HA/IA hydrogels in Mn system.

CS/HA/IA hydrogel, the biological molecule aspect of this newly synthesized hydrogel is not able to use it in water and wastewater treatment.

3.5. Isotherms evaluation for Mn adsorption

When the adsorption isotherms were evaluated, it was seen that Mn adsorption data shown in Fig. 7, well-fitted Langmuir isotherm ($R^2 > 99.9\%$) better than Freundlich isotherms ($R^2 > 0.90$) as shown in Table 3. According to Langmuir isotherm, q_{max} improved from 15.46 to 18.23 mg/g when using CS/HA/IA hydrogel. In the Langmuir isotherm, the R_L value gives the tendency of the adsorption process and adsorption is favorable when the R_L is in the range of 0–1 [39]. In the range of 5–15 mg/L of initial Mn concentrations, R_L values were calculated to be between 0.03–0.084 and 0.018–0.051 for CS/HA and CS/HA/IA hydrogels respectively. These values indicate that both CS/HA and CS/HA/IA hydrogels are favorable for adsorption of Mn and accordingly the IA significantly contributed to increasing the adsorption capacity of CS/HA hydrogel.

3.6. Reuse of hydrogels

Reuse capacity of hydrogels after first and second use cycles for Mn adsorption is in Fig. 8. When the desorption process was applied to synthesized hydrogels, a range of

80.4%–82.7% and 80.7%–86.4% of the adsorbed Mn could be desorbed in CS/HA and CS/HA/IA hydrogel systems, respectively. Although Mn removal efficiency decreased by 12%–16% in the second use in the adsorption with CS/HA hydrogel, 76% of Mn removal was obtained at 5 mg/L initial Mn concentration.

In CS/HA/IA hydrogel system, the reduction of Mn removal for the second use of hydrogels was lower at lower initial Mn concentrations and contrarily, at higher initial Mn concentrations. 93.6% and 90.0% of Mn removals

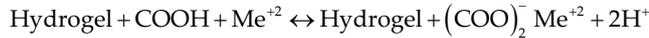


Fig. 6. Proposed adsorption mechanism of the hydrogel.

Table 1
Diffusion of water and Mn into the hydrogels

Hydrogels	$k \times 100$ (in water)	n (in water)	$k \times 100$ (in Mn)	n (in Mn)	$D \times 10^8$ (cm ² /s)	
					(in water)	(in Mn)
CS/HA	1.10	0.62	0.98	0.48	8.4	3.7
CS/HA/IA	0.98	0.69	0.13	0.75	19.3	5.9

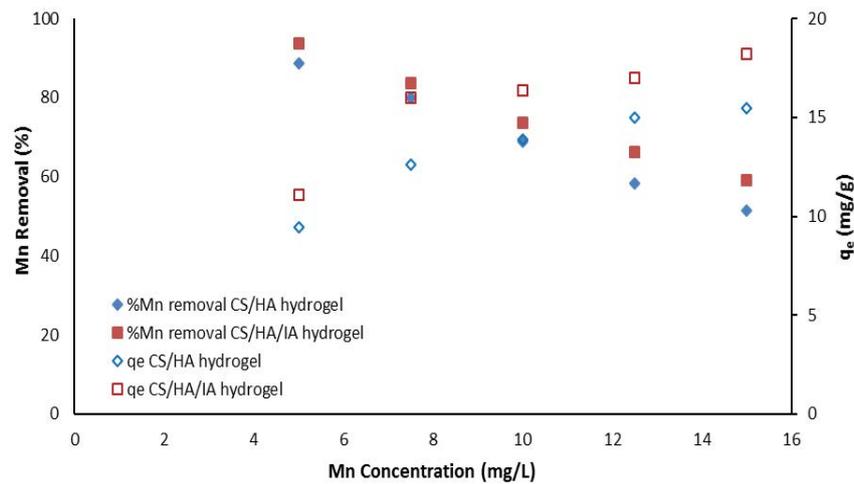


Fig. 7. Comparison of Mn removal and adsorption capacity of hydrogels at different initial Mn concentrations (hydrogel dose: 0.5 g/L, pH 7, and adsorption time: 24 h).

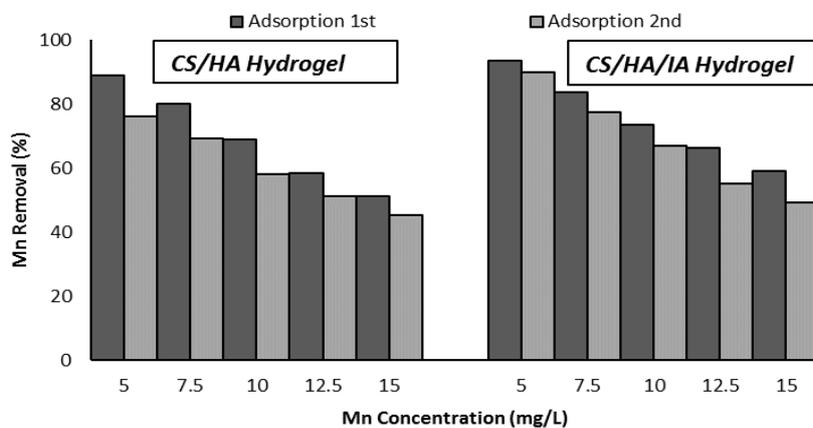


Fig. 8. Mn removal first and second use of hydrogels (pH 7, 0.5 g/L dry hydrogel, and adsorption time: 24 h).

Table 2
Comparison of Mn adsorption capacity of hydrogels

Hydrogels	Hydrogel composition	Adsorption Conditions	q_{max} (mg/g)	References
CS/HA hydrogel	-	Hydrogel: 0.5 g/L, Mn concentration: 5–15 mg/L, and time: 24 h	15.46	In this study
CS/HA/IA hydrogel	-		18.23	
PVP/AAc hydrogel	PVP/AAc mol ratio 50/50–80/20	Hydrogel: 10 g/L, Mn concentration: 500 mg/L, and time: 24 h	1–14	[34]
AAc/AAm hydrogel	AAc/AAm ratio: 1/1.7	Hydrogel: 10 g/L, Mn concentration: 0.1–8 mM, and time: 1 h	3.91	[35]
5.3% kaolinite AAc/AAm hydrogel	AAc/AAm ratio: 1/1.7		5.02	
PVA/CS hydrogel	PVA/CS ratio: 1/1	Hydrogel: 8 g/L, Mn concentration: 5–100 mg/L, and time: 2 h	10.515	[36]
GO/SA hydrogel beads	-	Hydrogel: 3 g/L, Mn concentration: 10–150 mg/L, and time: 120 min	28.49	[37]
CS	-	Hydrogel: 0.1 g/L, Mn concentration: 0–10 mg/L, and time: 1 h	14.619	[38]
CS-PMDA hydrogel	PMDA: 0.0228 mol		67.114	
CS-BTDA hydrogel	BTDA: 0.0154 mol		49.019	
CS-FDA hydrogel	FDA: 0.0112 mol		23.255	
CS-ODPA hydrogel	ODPA: 0.016 mol		31.948	

PVP/AAc: poly(vinylpyrrolidone/acrylic acid) copolymer, GO/SA: graphene oxide/sodium alginate, AAc/AAm: acrylic acid/acrylamide copolymer, PVA/CS: polyvinyl alcohol/chitosan binary dry blend hydrogel, CS: Chitosan; CS-PMDA: chitosan-pyromellitic dianhydride, CS-BTDA: chitosan-benzophenone-3,3',4,4'-tetracarboxylic dianhydride, CS-FDA: chitosan-4,4'-(hexafluoroisopropylidene) dipthalic anhydride, CS-ODPA: chitosan-4,4'-oxydiphthalic dianhydride

Table 3

Isotherm parameters of Mn adsorption on to CS/HA and CS/HA/IA hydrogels (pH: 7.0 and 0.5 g/L dry hydrogel, adsorption time: 24 h)

	CS/HA hydrogel	CS/HA/IA hydrogel
Langmuir isotherm		
$q_{max,exp}$	15.46	18.23
q_{max}	16.34	18.66
K_L	2.186	3.697
R_L^*	0.03–0.084	0.018–0.051
R^2	0.9996	0.9976
Freundlich isotherm		
n	5.30	6.33
K_F	11.00	13.99
R^2	0.9787	0.9043

* R_L was calculated between 5 and 15 mg/L initial Mn concentrations.

were obtained when CS/HA/IA hydrogel was reused for the first and second time at 5 mg/L initial Mn concentration. It is noted that Mn removal decreased about 6%–10% at 5–10 mg/L initial Mn concentrations and around 17% at 12.5–15 mg/L initial Mn concentrations when CS/HA/IA hydrogel was used for the first and second use for adsorption of Mn, respectively. Thus, it can be deduced that IA improved the desorption and reusability of newly synthesized CS/HA hydrogel for Mn adsorption as IA could improve carboxyl groups in the hydrogel to interact with Mn [12,40].

4. Conclusion

In this work, CS/HA hydrogel composite was synthesized in the presence of IA by radiation-induced polymerization. The swelling, diffusion and adsorption, and desorption of manganese behaviors of the hydrogel are investigated. The successful synthesis of the composite hydrogels was proved with the FTIR spectroscopy and SEM analysis. The swelling experiments show that the presence of IA improved the swelling behavior of the CS/HA hydrogel. The improvement in the Mn adsorption capability of CS/HA hydrogel with the inclusion of IA in the gel formulation that was noted the first attempt in the scientific literature was achieved. Manganese adsorption capacities of both CS/HA and CS/HA/IA hydrogels newly synthesized were found to be at competitive grade compared to some of the CS-based copolymers.

The adsorption and reuse studies for Mn as model pollutant were preliminary attempts for the synthesized hydrogels in this work. Further investigations are necessary to produce a prototype for metal recovery.

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