



Physical hydrogel based on alginate and poly(2-hydroxyethyl methacrylate) for water treatment

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ABSTRACT

Sodium alginate (Alg) chains were physically cross-linked by poly(2-hydroxyethyl methacrylate) (PHEMA) via hydrogen bonding. The interactions occurred between the carbonyl groups of carboxylate anions of alginate and the hydroxyl groups of PHEMA. The PHEMA content in the prepared hydrogels was varied from 18–32 wt.%. The H-bond interaction and morphology of the hydrogels were characterized using Fourier-transform infrared spectroscopy, X-ray diffraction, and scanning electron microscopy. Moreover, the thermal behavior of prepared hydrogels was studied by thermal gravimetric analysis technique. Alg/PHEMA Physical hydrogels showed an excellent ability for the removal of basic dyes and heavy metal ions.

Keywords: Sodium alginate; Hydrogels; Physical cross-linking; Dye uptake; Heavy metal ions

1. Introduction

Hydrogels are three-dimensional network insoluble materials formed through the cross-linking of hydrophilic polymers [1]. The networks are established through chemically or physically cross-linking [2]. Chemically cross-linked networks have covalent linkages, whereas, physical networks have transient interactions as hydrogen bonds, ionic or hydrophobic interactions [3]. The outstanding importance of hydrogels results from their biocompatibility, hydrophilicity, and from their high water uptake capacity without being soluble, which makes them ideal for applications in medicine and industrial fields [4,5].

Alginate is a water-soluble polysaccharide composed of β -D-mannuronic acid (M) and α -L-guluronic acid (G) [6]. Two monomeric units (G and M) are linked in blocks and the blocks are either identical (GGGG-MMMM) or in a regular sequence of G and M (as GMGMGM) [6]. Materials based on alginate have unique properties regarding low cost, non-toxicity and bio-degradability [7], which enable them to be

used in different fields like pharmaceuticals and biological sciences [8], and dentistry [9]. Alginate-based hydrogels are attractive in the water treatment field [10–12]. Alginate has efficiency in binding toxic ingredients of wastewater. Recently, there is a study on the adsorption capacity of rare-earth (III) using an efficient alginate/poly- γ -Glutamate hydrogel [13]. There are various hydrogels based on poly(2-hydroxyethyl methacrylate) (PHEMA) with Chitosan [14], and copolymerized with itaconic acid and acrylamide for drug delivery applications [15]. Alginate has been used as an adsorbent for the removal of heavy metals in different forms; for example, alginate cross-linked by tetraethylenepentamine to form beads has been used for adsorption of Cr(VI) from aqueous solution [16]. On the other hand, alginate has been developed as a hybrid hydrogel for water treatment in the presence of (SiO₂) microspheres [17].

PHEMA has also importance in water treatment and it has been used as nanobeads for removing diethyl phthalate from aqueous media [18] and as a gel for fluoride adsorption from water [19].

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The essential goal of this study is to synthesize physically cross-linked hydrogels based on alginate and PHEMA and estimate their efficiencies in water treatment through the removal of heavy metal ions and organic dyes from aqueous media.

2. Materials and methods

2.1. Materials

Sodium alginate (Viscosity 1,000–1,200 cPs) was purchased from Nice Chemicals Pvt. Ltd., (Kerala, India). 2-hydroxyethyl methacrylate (HEMA), chloride salts of calcium(II), cadmium(II) and chromium(VI) were obtained by Sigma-Aldrich Chemie GmbH Eschenstrasse 5 d-82024 Taufkirchen, Germany. Acidic (Congo Red) and basic (Maxilon Blue) dyes were supplied by G.T. Gurr, (London) (Fig. 1).

2.2. Preparation of sodium alginate/PHEMA physical hydrogel

2.2.1. Polymerization of 2-hydroxyethyl methacrylate

HEMA was polymerized via free radical polymerization technique. HEMA was dissolved in dimethylformamide at a concentration of 164 mmol L⁻¹. The polymerization was performed under a nitrogen atmosphere using azobis(isobutyronitrile) as the initiator (0.2 mmol L⁻¹) for 3 h at 60°C. PHEMA was precipitated from acetone and washed several times with ethanol till constant weight. Finally, PHEMA was dried and characterized by Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), thermogravimetric analysis (TGA) and its viscosity average molecular mass (\bar{M}_v) was determined according to the method described in [20] and it was found to be equal to 17,250 g mol⁻¹.

2.2.2. Sodium alginate/PHEMA hydrogels

Various hydrogels were obtained via H-bond interactions between alginate and PHEMA as illustrated in Fig. 2. Sodium alginate (0.06 mol.) was dissolved in distilled water (where the Mwt of sodium alginate-based on the molecular weight of repeating units; α -D-mannuronic acid (M) and β -L-guluronic acid (G) is equal to 216.121 g mol⁻¹), whereas PHEMA was dissolved in methanol. The two solutions were mixed and stirred for 24 h at room temperature. Finally, the prepared hydrogels were washed several times by water, followed by methanol to get rid of all unreacted sodium alginate and PHEMA. The prepared hydrogels were then dried in an air oven until constant weight. The gelation percent was calculated according to Eq. (1) to be 18%, 25%, and 31.5% in respect to molar ratios between mole_{annuronic acid}:mole_{PHEMA} [21,22].

$$\text{Gelation \%} = \frac{W}{W_0} \times 100 \quad (1)$$

where W is the weight of sodium alginate and W_0 is the weight of the purified hydrogel

2.3. Characterization of the prepared hydrogels

2.3.1. Fourier-transform infrared spectroscopy

PHEMA and the different hydrogels were characterized using FTIR (Tescan Shimadzu, (Japan) Infra-Red spectrophotometer, Model 8000), and the KBr pressed disk method was applied for samples preparation. The scanning range was 4,000–600 cm⁻¹.

2.3.2. X-Ray diffraction

XRD of the prepared hydrogels was determined using an X-ray diffractometer (PANalytical X'Pert Pro, Tube voltage and current are 45 kV and 40 mA, respectively).

2.3.3. Scanning electron microscopy

The morphology of Alg/PHEMA hydrogels was observed using scanning electron microscopy (SEM) (Quanta 250 FEG (Field emission gun) microanalyzer at 30 KV). The gold layer covered the dry samples with 100 μ m thickness by sputter coating unit (JEOL S150A, Japan) for 2 min.

2.3.4. Thermal analysis

The thermal behavior of sodium alginate, PHEMA, and the differently prepared hydrogels was tested by TGA (TGA-50H Shimadzu, Japan). TGA analyses of the tested samples were established from 0°C to 500°C under N₂ atmosphere (with heating rate 10°C min⁻¹)

2.3.5. Colorimetric spectrophotometry

The adsorption of dyes and metal ions was determined via Colorimetric spectrophotometry (Unico 1200 Spectrophotometer). The working wavelength for Congo Red, Maxilon Blue, and all investigated metal ions (Cr⁶⁺, Cu²⁺, Ni²⁺ or Cd²⁺) at λ_{max} 480, 580 and 780 nm, respectively.

Equilibrium adsorption amount of heavy metal ions (Q_e), (mM g⁻¹) was calculated according to Eq. (2) [12]:

$$Q_e = (C_0 - C_e) \frac{V}{M} \quad (2)$$

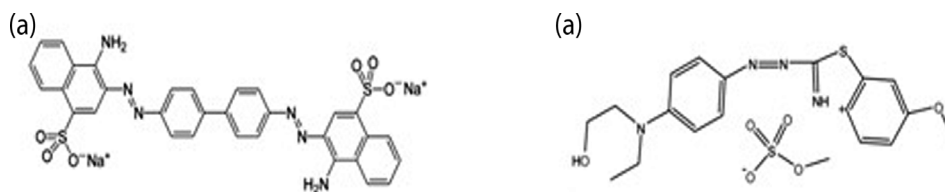


Fig. 1. Structures of (a) Congo Red acidic dye and (b) Maxilon Blue basic dye.

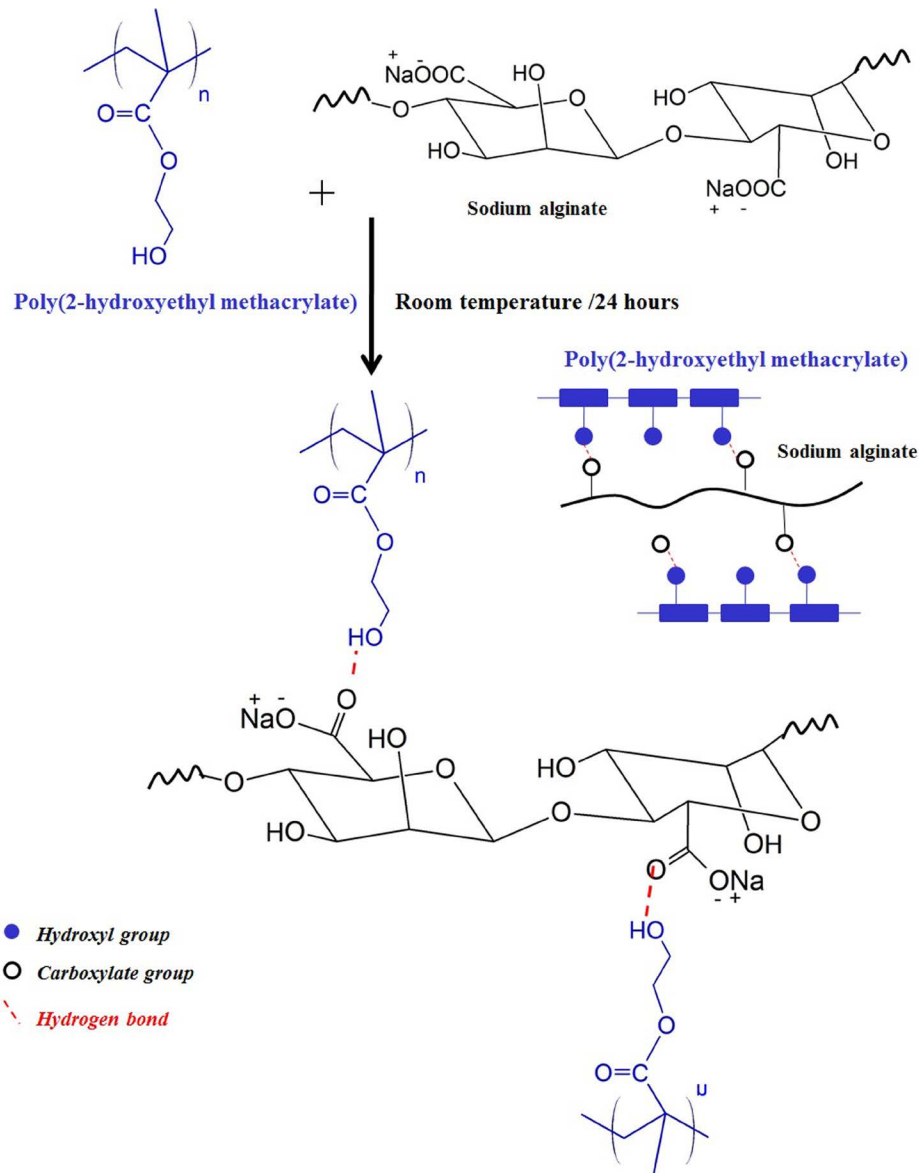


Fig. 2. Proposed mechanism for the prepared hydrogels via hydrogen bonding between alginate and poly(2-hydroxyethyl methacrylate).

where C_0 and C_e are the initial and the metal ions concentration at equilibrium, respectively, V (mL) is the volume of metal ions solution and M (g) is the weight of the hydrogel.

2.3.6. Swelling study

The degree of water uptake capacity by the different investigated hydrogels was tested in different buffer solutions (buffer solutions with pHs 4, 7 and 10) at room temperature under continuous stirring till reaching the equilibrium. The swelling degrees % (SD) of the hydrogels were calculated according to Eq. (3) [23]:

$$\text{SD \%} = \left(\frac{W_{\text{eq}} - W_d}{W_d} \right) \times 100 \quad (3)$$

where W_d is the dry weight of the hydrogel and W_{eq} is the swollen weight of the hydrogel at equilibrium.

3. Results and discussion

3.1. FTIR analysis

The FTIR spectrum of alginate had proven the presence of four absorption peaks at 1,155; 1,073; 1,030; and 895 cm^{-1} which are characteristic peaks of the polysaccharide structure as illustrated in Fig. 3a. The broad absorption peak at 3,600–3,200 cm^{-1} could be due to the stretching vibration of –OH groups of alginate and bending of –OH group at 1,030 cm^{-1} . The peaks at 1,420 and 1,620 cm^{-1} related to the symmetric and asymmetric stretching vibration of the carboxylate group. Fig. 3e, the broadband within 3,600–3,150 cm^{-1} is attributed to the stretching vibration of the hydroxyl groups (O–H) in

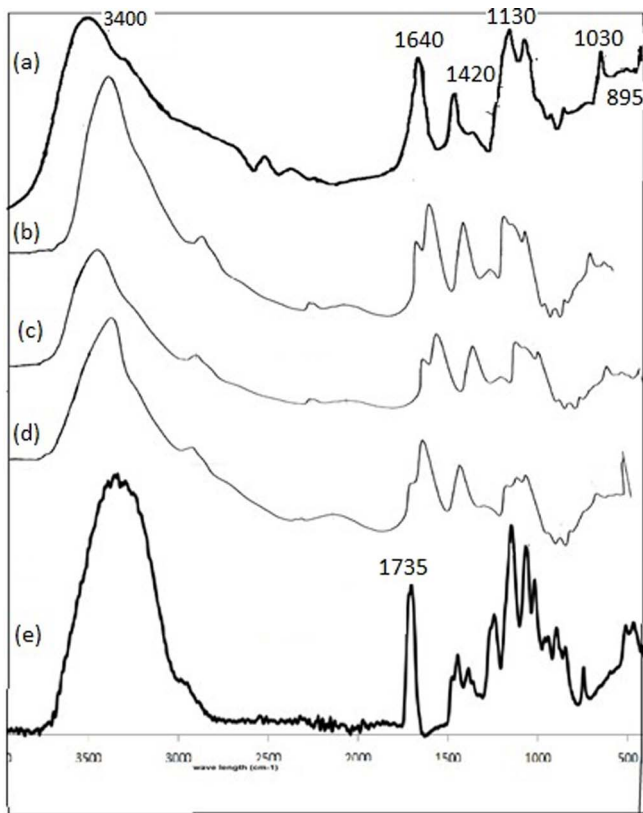


Fig. 3. FTIR spectra of (a) Sodium alginate, (b) hydrogel (Alg:PHEMA/1:1), (c) hydrogel (Alg:PHEMA/1:2), (d) hydrogel (Alg:PHEMA/1:3), and (e) PHEMA.

the PHEMA, a characteristic peak at 1735 cm^{-1} indicated the carbonyl of the ester groups present in PHEMA [24]. On the other hand, the FTIR spectra of the various investigated hydrogels showed all the characteristic peaks of sodium alginate and PHEMA, Figs. 3b–d together with a very broad-band within $3,000\text{--}3,600\text{ cm}^{-1}$ which is attributed to the overlapped stretching vibration of O–H groups of alginate and PHEMA and another two peaks within $1,640\text{--}1,750\text{ cm}^{-1}$ that are attributed to the ester and carboxylate groups of PHEMA and alginate, respectively.

3.2. XRD analysis

XRD pattern of sodium alginate showed sharp peaks at 31.7 , 33.8 and 45.4 \AA indicating the crystalline nature of alginate (Fig. 4a). While, XRD pattern of PHEMA showed a dominant broad diffraction peak that can be seen at 18.7 \AA and two very broad peaks at 32 and 43 \AA , due to the amorphous nature of the polymer as shown in Fig. 4b. The prepared hydrogels with different molar ratios between alginate and PHEMA (1:1 and 1:2/Alg:PHEMA) (Fig. 4c and d) showed approximately planar XRD pattern and that pointing to the amorphous nature of both hydrogels and that is in good agreement with the literature [25]. On the other hand, the XRD of hydrogel with the high molar ratio of PHEMA (1:3/Alg:PHEMA) showed a sharp peak at 28.8 \AA related to the high crystalline nature of the hydrogel resulting from

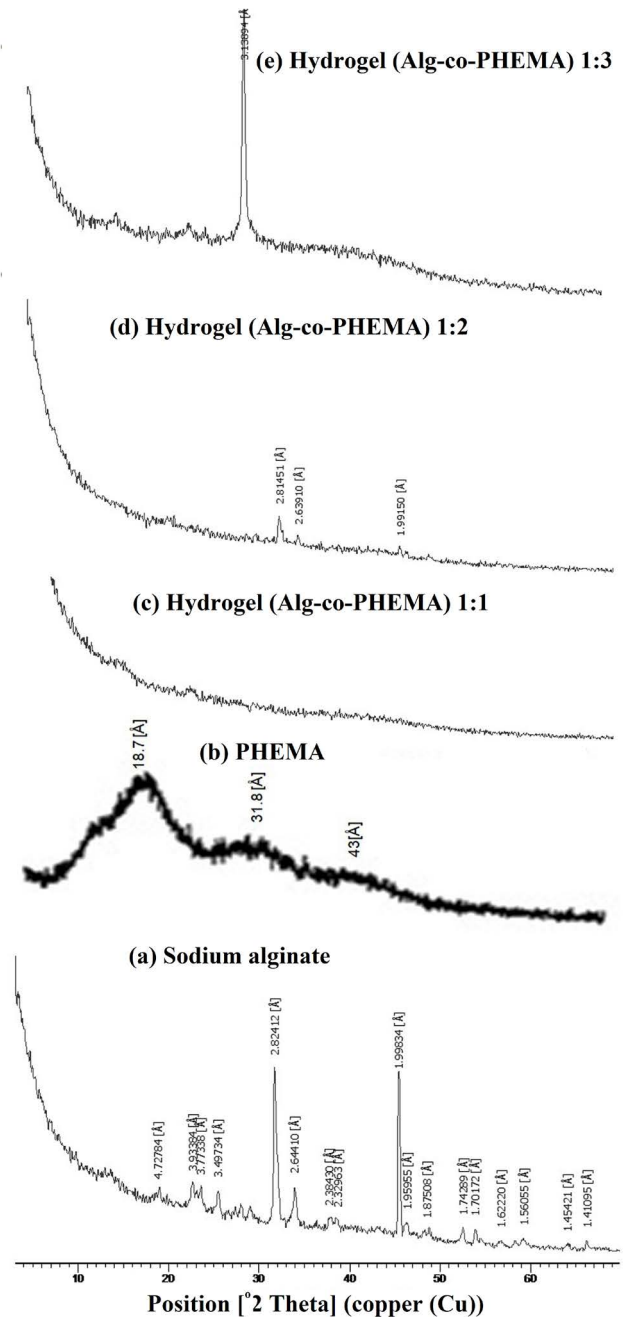


Fig. 4. XRD charts of (a) Sodium alginate, (b) PHEMA, (c) hydrogel (Alg:PHEMA/1:1), (d) hydrogel (Alg:PHEMA/1:2), and (e) hydrogel (Alg:PHEMA/1:3).

the interaction between functional groups on alginate and PHEMA via H-bonding (Fig. 4e).

3.3. SEM analysis

SEM analyses of sodium alginate, PHEMA and their hydrogels with different molar ratios (1:1; 1:2 and 1:3/Alg:PHEMA) with gelation percent 18%, 25%, 32%, respectively are illustrated in Fig. 5. Sodium alginate as represented in Fig. 5a shows an irregular aggregate. Figs. 5c–e clearly

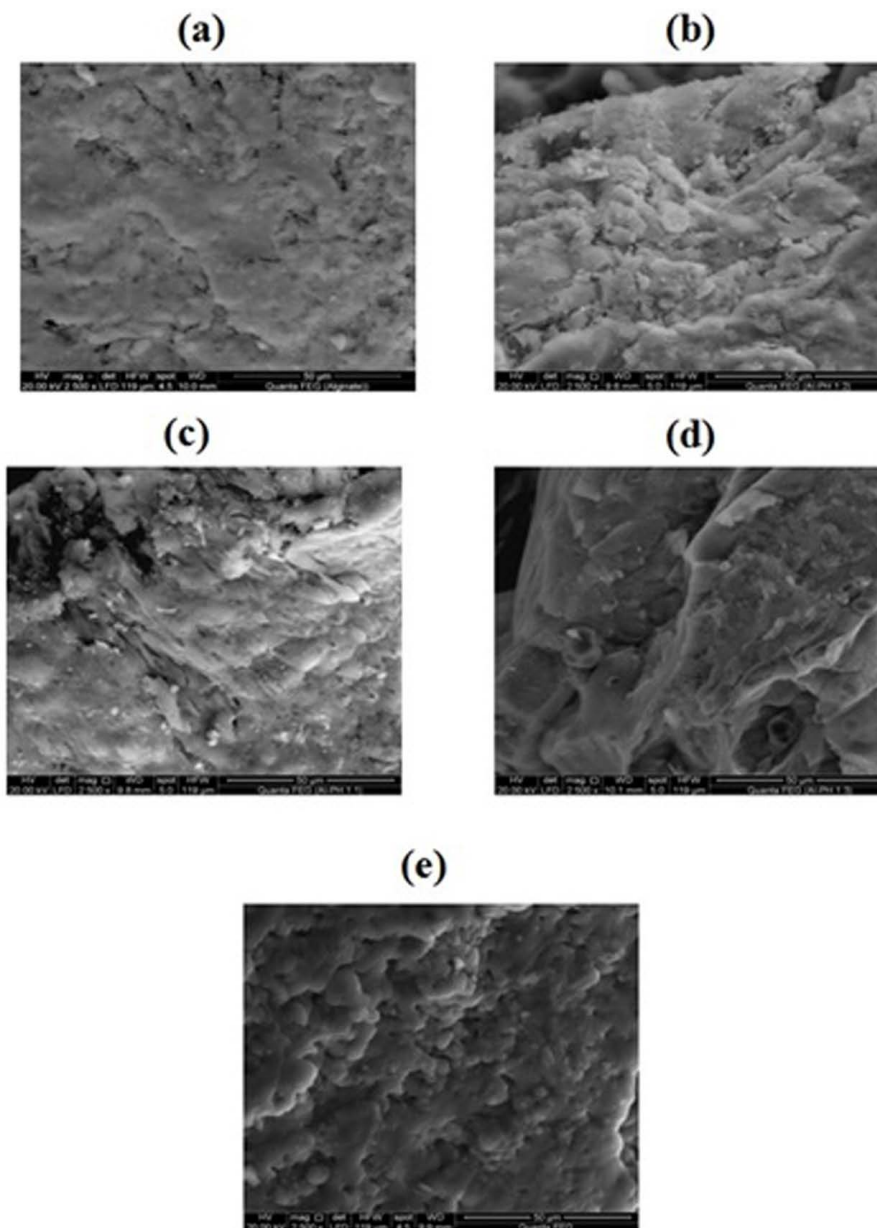


Fig. 5. SEM pictures of (a) Sodium alginate, (b) PHEMA, (c) hydrogel (Alg:PHEMA/1:1), (d) hydrogel (Alg:PHEMA/1:2), and (e) hydrogel (Alg:PHEMA/1:3).

illustrate the formation of ropes all over the surface of alginate, which was confirmed through the morphological structure of PHEMA (Fig. 5b). By increasing the concentration of PHEMA in the hydrogels, the PHEMA structure appeared more obvious on the surface of alginate.

3.4. TGA analysis

Table 1 and Fig. 6 illustrate the thermal behavior of sodium alginate and its hydrogels with PHEMA. TGA of sodium alginate showed two degradation processes, one process occurred over the range of temperature from 246°C to 275°C resulting from the decarboxylation and liberation of CO₂. The second degradation was observed from 625°C

to 700°C due to the depolymerization of the polymer which leads to the carbonaceous residue and Na₂CO₃ [26]. PHEMA had one weight loss region (210°C–400°C) due to the degradation of the PHEMA backbone. Therefore, the network structure conferred a slight thermal stabilization to the polymer [27]. In contrast, the hydrogels had three weight loss regions; one is in between 213°C and 294°C, due to the degradation of the H-bond and consequently carboxylic groups of alginate in the hydrogel structure and the second zone is in the region of 340°C–455°C, owing to the degradation of the PHEMA present in the hydrogel structure. The extra zone starting from 620°C resulted from the depolymerization of alginate. Consequently, there were no differences in the thermal stability of the different investigated hydrogels.

Table 1
Thermal behavior of alginate and its hydrogels with PHEMA

| Polymer/Hydrogel | Initial decomposition temperature (IDT) (°C) | Temperature weight loss 20% | Weight loss at 300°C |
|------------------|--|-----------------------------|----------------------|
| Sodium alginate | 225 | 253 | 25 |
| PHEMA | 240 | 280 | 30 |
| Hydrogel 18% | 205 | 210 | 47 |
| Hydrogel 25% | 210 | 218 | 43 |
| Hydrogel 32% | 205 | 220 | 44 |

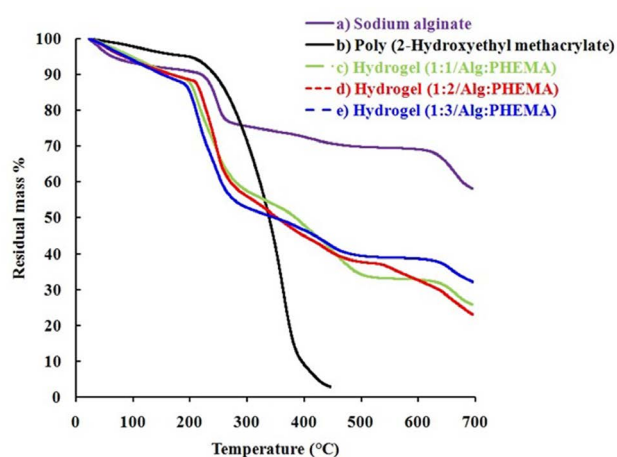


Fig. 6. Thermogravimetric analyses of (a) Sodium alginate, (b) PHEMA, (c) hydrogel (Alg:PHEMA/1:1), (d) hydrogel (Alg:PHEMA/1:2), and (e) hydrogel (Alg:PHEMA/1:3).

3.5. Water uptake

The swelling of hydrogels based on alginate and PHEMA with different gelation % 18%, 25%, and 32% were studied and compared to the swelling of calcium alginate hydrogel in solutions of different pHs (pH = 4, 7 and 10) (Fig. 7). In acidic pH = 4, the swell ability decreased with increasing the PHEMA content due to increasing the number of cross-links via hydrogen bond formation between $-COONa$ groups of Alginate and $-OH$ groups of PHEMA. In basic pH = 10, the swell ability highly decreased with increasing PHEMA content, while in neutral pH = 7, the swell ability of calcium alginate hydrogel showed the highest degree of swell ability. This experimental finding could be explained by the higher hydrophilic nature of alginate and the absence of acidic and basic groups in the hydrogel. Accordingly, the ordering of swell ability degree of hydrogels based on alginate and PHEMA to the change in the solution pH was as follows: $7 > 4 > 10$.

4. Performance of hydrogels for treating water

4.1. Removal of dyes

The adsorption capacity of calcium alginate hydrogel and the prepared hydrogels based on alginate and PHEMA was studied using Congo Red and Maxilon Blue

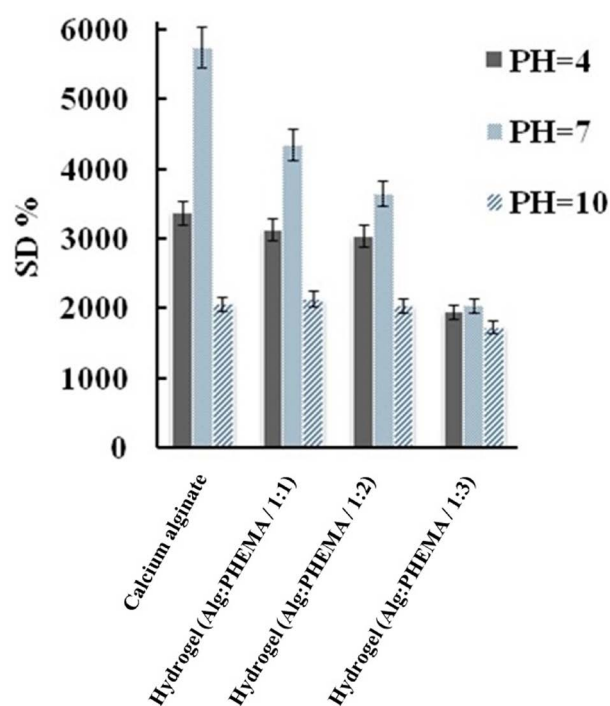


Fig. 7. Swelling degree (SD) of hydrogel s based on alginate/PHEMA as compared with calcium alginate at different pH solutions as (a) calcium alginate, (b) hydrogel (Alg:PHEMA/1:1), (c) hydrogel (Alg:PHEMA/1:2), and (d) hydrogel (Alg:PHEMA/1:3).

as examples of acidic and basic dyes, respectively. In the case of Congo Red, (Fig. 8a), the dye adsorption increased with increasing the PHEMA content as compared to calcium alginate hydrogel. This could be due to the interaction between the hydroxyl groups of PHEMA and the amino groups of the dye through H-bonding. So, by increasing the PHEMA content in the hydrogel, the number of hydroxyl groups increased and consequently increased the capacity of adsorption of Congo Red dye.

On the other hand, the adsorption of Maxilon Blue basic dye, (Fig. 8b) was found to be greatly higher than that of Congo red acidic dye irrespective of the molar ratios of Alg:PHEMA hydrogels and that of calcium alginate hydrogel. Moreover, the data revealed the higher adsorption capacity of calcium alginate hydrogel for Maxilon Blue basic dye as compared with PHEMA. The adsorption capacity

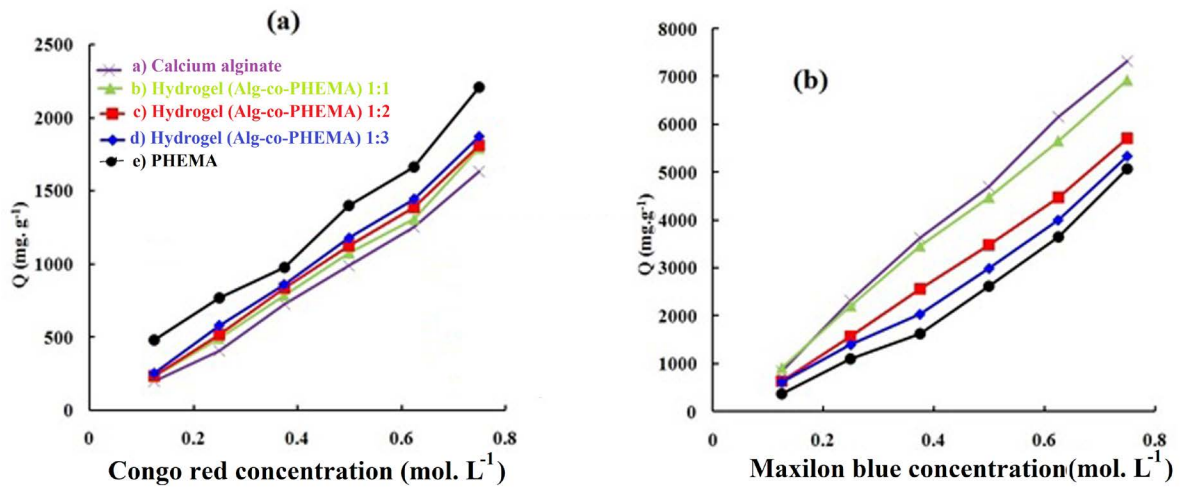


Fig. 8. Variation of the concentration of adsorbed dye by (a) calcium alginate, (b) hydrogel (Alg:PHEMA/1:1), (c) hydrogel (Alg:PHEMA/1:2), and (d) hydrogel (Alg:PHEMA/1:3).

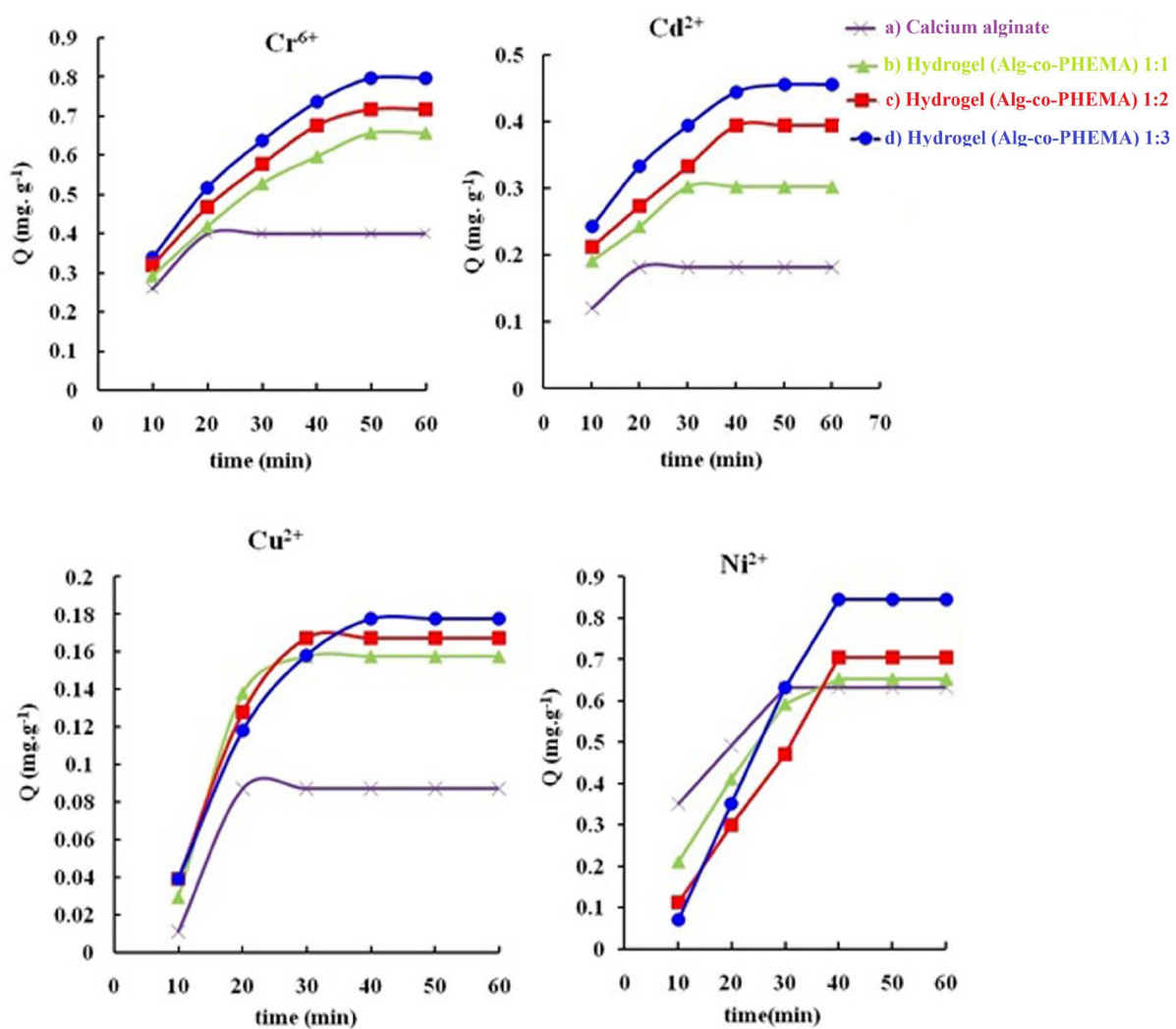


Fig. 9. Adsorption of Cr(III), Cd(II), Cu(II) and Ni(II) ions by the various investigated Alg:PHEMA hydrogels and with respect to calcium alginate hydrogel.

of the basic dye by the prepared copolymer hydrogels was found to be less than calcium alginate hydrogel, but higher than the PHEMA hydrogel. The adsorption of dye was found to decrease with the increase of PHEMA content in the order: Hydrogel (1:1/Alg:PHEMA) > Hydrogel (1:2/Alg:PHEMA) > Hydrogel (1:3/Alg:PHEMA), that could be explained based on the fact that by increasing the percentage of PHEMA, the number of free carboxylate groups on alginate decreased and consequently, the adsorption of basic dye also decreased.

4.2. Removal of heavy metal ions

Fig. 9 reveals that the hydrogels based on alginate and PHEMA showed higher adsorption of the investigated metal ions than calcium alginate. Moreover, the adsorption capacity for the same type of metal ions increased with increasing gelation %. The metal ions adsorptions on the investigated hydrogels were due to the formation of coordination complexes on the electron-donor oxygen of PHEMA and the ionic interaction with the carboxylate groups of sodium alginate [28]. As shown in Fig. 9, by comparing the adsorption of all the investigated metal ions by the hydrogel with the high content of PHEMA (1:3/Alg:PHEMA), the ordering of adsorption was found to be: $\text{Cr}^{6+} > \text{Cu}^{2+} > \text{Ni}^{2+} > \text{Cd}^{2+}$. The adsorption of the metal ions in the mentioned sequence could be explained by the difference in stability degrees of complexes formed between the investigated metal ions and the co-polymer hydrogel [29].

5. Conclusion

Physical hydrogels were synthesized from sodium alginate and PHEMA and were characterized using different tools including FTIR, XRD, SEM, thermal analysis and by measuring its swell ability in aqueous solutions of different pHs. Dye uptake of the hydrogels was studied using Congo Red and Maxilon Blue as examples of acidic and basic dyes, respectively. The dye uptake of the basic dye was higher than that of acidic dye. Heavy metal ions removal was also investigated using the chloride salts of different metal ions. The ordering of the investigated heavy metal ions adsorption with respect to the prepared alginate/PHEMA hydrogels was as follows: (hydrogel (1:3/Alg:PHEMA) > hydrogel (1:2/Alg:PHEMA) > hydrogel (1:1/Alg:PHEMA) and with respect to the type of heavy metal ions: $\text{Cr}^{6+} > \text{Cu}^{2+} > \text{Ni}^{2+} > \text{Cd}^{2+}$. From the obtained results, it is possible to recommend the prepared hydrogels (alginate/PHEMA) to be used in the field of water treatment.

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