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# Alginate-based hydrogel for water treatment

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## ABSTRACT

Hydrogels based on sodium alginate and poly(4-vinylpyridine) were successfully prepared via physical cross-linking by ionic interaction. Different hydrogels with different percentages of gelation were prepared by varying the molar ratio between sodium alginate and poly(4-vinylpyridine). The prepared hydrogels were characterized using different techniques as FT-IR spectroscopy, X-ray diffraction (XRD), thermal gravimetric analyses (TGA) and scanning electron microscope (SEM). Increasing of initial decomposition temperature of alginate due to interaction with poly(4-vinylpyridine) was observed. Industrial wastewater mainly contains toxic heavy metal ions and/or dyes (acidic and cationic). In the current study, the removal of heavy metal ions and dyes are studied. Moreover, the behaviors of prepared hydrogels in different buffer solutions were determined. The results show that degree of swelling (DS) is increasing with the increase in the content of poly(4-vinyl pyridine) in the hydrogels. This increasing in DS is much more pronounced in acidic pH than neutral and alkaline pH. The presence of poly(4-vinyl pyridine) in the hydrogels increases the metal ions adsorption as compared with calcium alginate based hydrogel in the ordering $Cr^{6+} > Cu^{2+} > Ni^{2+} > Cd^{2+}$ . Hydrogels based on poly(4-vinylpyridne) improves acidic dye uptake as compared to hydrogel based on calcium alginate.

*Keywords:* Poly(4-vinylpyridine); Thermal stability; Swelling degree; Dye uptake; Heavy metal ions

## 1. Introduction

Alginate is a linear polysaccharide composed of (1,4)-linked α-D-mannuronic acid (M) and its C-5 epimer, β-L-guluronic acid (G) residues and they covalently linked in different sequences or blocks [1]. It is extracted from brown algae, moreover it can be obtained via bacterial biosynthesis from *Azotobacter* and *Pseudomonas* [2]. It has importance in pharmaceutical and biomedical applications as drug delivery systems due to its biodegradability and biocompatibility [2,3]. Gels based on alginate have importance also in the field of water treatment [4–9]. Recently, there are many researches about the efficiency of alginate beads against toxic heavy metal ions uptake as studied the competitive sorption of divalent ions and the regenerated beads by inorganic acid [10]. Another study investigated the binding properties of alginate against toxic ingredients of tannery wastewater [11]. The authors observed high heavy metal ions uptake capacity and removal of organic constituents. Hydrogels can be synthesized via chemically or physically cross-linked [12]. Physically cross-linking occurred via ionic interaction, hydrophobized natural polymers or hydrogen bonds [12–14]. The advantage of physically cross-linking enables to avoid the toxicity of cross-linking agents commonly used [12]. Recently, different hydrogels based on alginate and polymers with suitable functional groups were prepared [15–19]. On another hand, poly(4-vinylpyridine) is a polycation hydrophobic polymer. It is one of the important pH-sensitive polymer which converts into hydrophilic polymer in lower pH due to protonation of pyridine group [20]. Hydrogel based on copolymer of poly(4-vinylpyridine) and acrylamide was prepared in presence of crosslinking agent N,N′-methylene-bisacrylamide [21]. The authors investigated its efficiency toward different heavy metals ions.

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To the best of knowledge, the system of hydrogel based on alginate and poly(4-vinylpyridine) has not yet been studied. For this, In the current study, hydrogels based on alginate and poly(4-vinylpyridine) are physically cross-linked via ionic interaction. Poly(4-vinylpyridine) was synthesized by free-radical polymerization of 4-vinyl pyridine, and the resulting polymer interacted ionically with sodium alginate in different proportions forming hydrogels via physical cross-linking.

## 2. Materials and methods

### 2.1. Materials

4-vinyl pyridine (95%) is purchased from Sigma-Aldrich, Germany. Sodium bisulfite purchased from Mallinckrodt, INC , USA. Potassium Persulfate (purchased from Hopkin&Wallimas, LTD, London. Sodium Alginate supplied from Nice Chemicals Pvt. Ltd., Kerala, India. $CuCl_2{\cdot}2H_2O$ (≥99), $CdCl_2$ (≥99), $CrCl_6$ (≥99), $NiCl_2$ (98%), $CaCl_2$ and DMF (≥99.8) were purchased by Sigma-Aldrich. Congo Red (Fig. 1a) and Maxilon Blue (Fig. 1b) dyes were supplied from G.T. Gurr, London.

### 2.2. Experimental studies

#### 2.2.1. Free radical polymerization of 4-vinylpyridine

2.5 $mol{\cdot}L^{-1}$ of 4-vinylpyridine (4-VP) was dissolved in 50 mL of distilled water. Solution of potassium persulfate and sodium bisulfite with concentration equal $4\times10^{-2}$ $mol{\cdot}L^{-1}$ in 5 mL of distilled water was added to the prepared solution of 4-VP at 60ºC. The polymerization was conducted under nitrogen atmosphere and was stopped after 3 h and the polymer was filtered and washed several times with distilled water till free from unreacted monomer [20,22]. Finally, poly(4-vinylpyridine) (P4VP) was dried at 40ºC till constant weight. Prepared P4VP was characterized using FT-IR spectroscopy.

#### 2.2.2. Synthesis of hydrogels

#### 2.2.2.1. Physically cross-linked between alginate and P4VP

Different hydrogels are based on alginate and P4VP were prepared via ionic interaction as shown in Scheme 1. 0.06 mol. of sodium alginate (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) was dissolved in 120 mL of distilled water. 0.06, 0.12 or 0.18 mol of P4VP was dissolved in 0.1 M HCl/DMF, and dimethylformaide is preferred than aqueous solution because solubility of P4VP in DMF/HCl is higher than its solubility in aqueous solution at lower acidic pH. To prepare different hydrogels with different percent of P4VP, the prepared solutions of P4VP were added to sodium alginate solution and leave stirring for 24 h at room temperature. Finally, the hydrogels were filtrated and washed several times with DMF then distilled water and dried at 40ºC. Hydrogels based on $\text{mole}_{annuronic\ acid}$:$\text{mole}_{4VP}$ as 1:1, 1:2 and 1:3 founded gelation percent 33, 43 and 58%, respectively, according to Eq. (1), Hydrogels (1:1; 1:2 and 1:3/Alg:P4VP). The solubility test was done in different organic solvents and showed the purified product insoluble in all solvents used such as DMF, Acetone, Methanol and Ethanol. Prepared hydrogels were characterized by FT-IR spectroscopy, TGA, DTG, XRD and SEM.

The calculation of gelation percent according to the following equation [23]

$$Gelation\ \% = \frac{W}{W_0} \times 100 \tag{1}$$

where $W$ and $W_0$ are the weight of sodium alginate and weight of purified hydrogel, respectively.

#### 2.2.2.2. Calcium alginate

Calcium alginate gel is formed using $CaCl_2$ solution via diffusion method [24,25]. 0.5 M of calcium chloride solution was dropping into solution (2%, wt./wt.) of sodium alginate. Gel of Ca-alginate was filtered and dried.

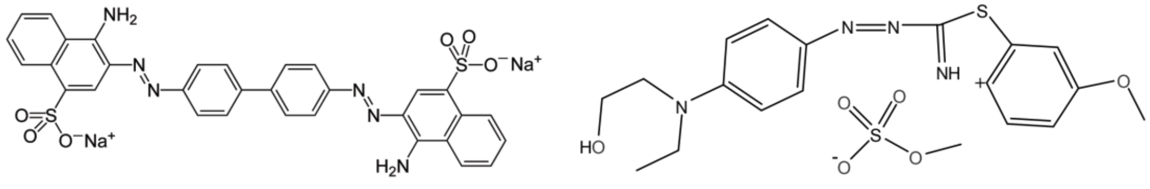
### 2.3. Instrumental

#### 2.3.1. Fourier transform infrared spectroscopy (FTIR)

FT-IR spectra were recorded on Testcan Shimadzu Infra Red-Spectrophotometer (model 8000), over range of wave number 400–4000 $cm^{-1}$ at 25ºC.

#### 2.3.2. Thermal analysis

Thermogravimetric Analyzer (TGA-50H Shimadzu) was used to evaluate thermal behavior of polymers and hydrogels. The heating rate was $10ºC{\cdot}min^{-1}$ under $N_2$ atmosphere and temperature range 0–700ºC.



(a)

(b)

Fig. 1. Structures of (a) Congo Red and (b) Maxilon blue.

### *2.3.3. Scanning electron microscopy (SEM)*

Scanning Electron Microscope used model Quanta 250 FEG (Field Emission Gun) linked to EDX Unit (Energy Dispersive X-ray Analyses), with accelerating voltage 30 kV, magnification14× and resolution for Gun.1n).

### *2.3.4. X-Ray diffraction*

XRD patterns were recorded using equipment model X'Pert PRO with secondary monochromator, Cu-radiation ($\lambda = 1.542$Å) at 50 Kv and scanning speed 0.02°/s were used.

### *2.3.5. Colorimetric spectrophotometer*

- Colorimetric spectrophotometry was determined on Unico 1200 Spectrophotometer at $\lambda_{max}$ 480 nm for Congo red dye and $\lambda_{max}$ 580 nm for Maxilon blue dye.
- Colorimetric spectrophotometry was determined on Unico 1200 Spectrophotometer at $\lambda_{max}$ 780 nm for $Cr^{6+}$, $Cu^{2+}$, $Ni^{2+}$ or $Cd^{2+}$.

Equilibrium adsorption amount of heavy metal ions ($Q_e$), ($mM \cdot g^{-1}$) is calculated according to the following equation [9]:

$$Q_e = \left(C_0 - C_e\right)\frac{V}{M} \tag{2}$$

where $C_o$ and $C_e$ are initial and equilibrium metal ions concentration, respectively, $V$ (mL) is volume of metal ions solution and $M$ (mM) is mass of hydrogel used.

### *2.3.6. Swelling in different pH buffers*

Swelling degree of the hydrogels was evaluated by immersing dried hydrogel with definite weight in different buffer solutions (buffer solutions with pH 4, 7 and10) at room temperature. The hydrogels were removed from the buffer solutions after equilibrium (at 24 h). They were weighed immediately. Swelling degree % (SD) of the hydrogel was calculated according to Eq. (3) [23,26]:

$$SD\% = \left(\frac{Weq - Wd}{Wd}\right)\times 100 \tag{3}$$

where *Weq* and *Wd* dried and swollen weight at equilibrium of hydrogel, respectively.

## 3. Results and discussion

### *3.1. Scanning electron microscopy (X 4000)*

SEM images of sodium alginate and its hydrogels with different content of P4VP (1:1; 1:2 and 1:3/Alg:P4VP) are shown in Fig. 2. SEM images showed the formation of white aggregates indicating the presence of P4VP as in Fig. 3b).

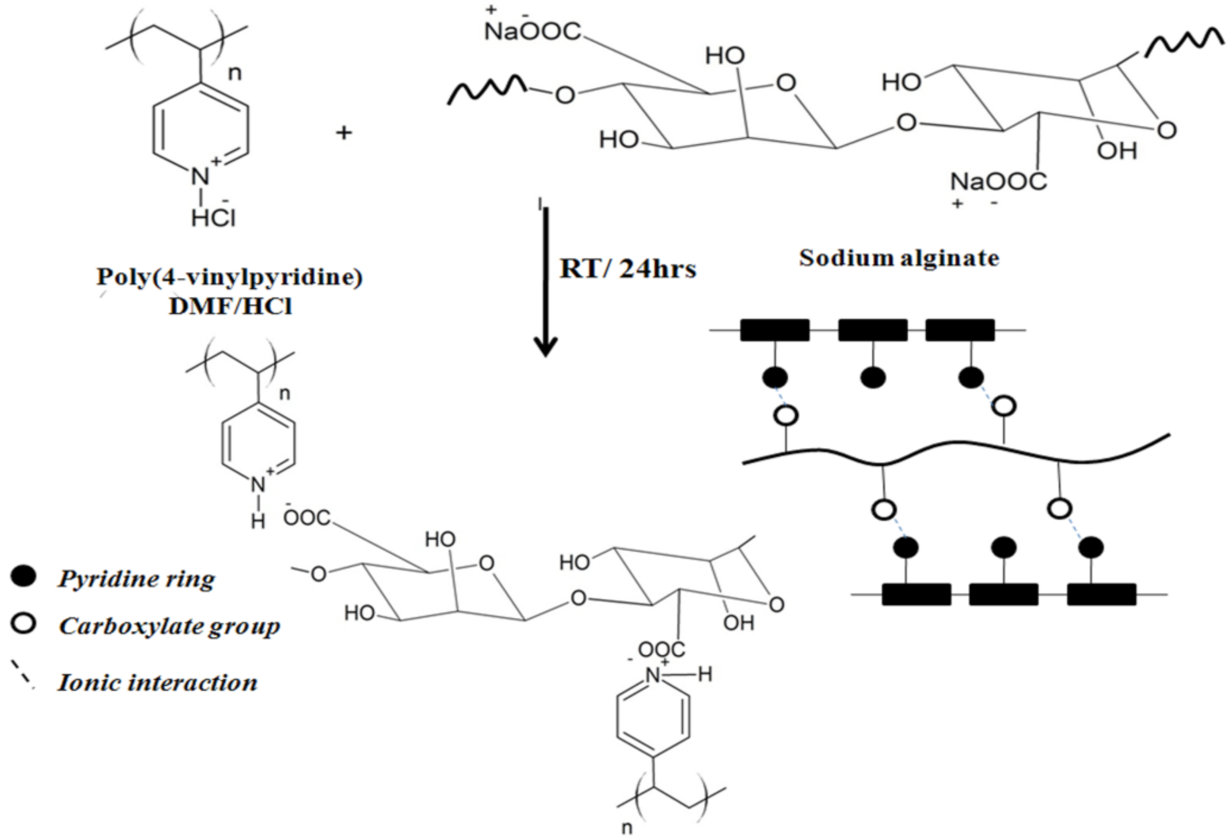


Fig. 2. Hydrogel based on alginate and poly(4-vinylpyridine) via ionic interaction.

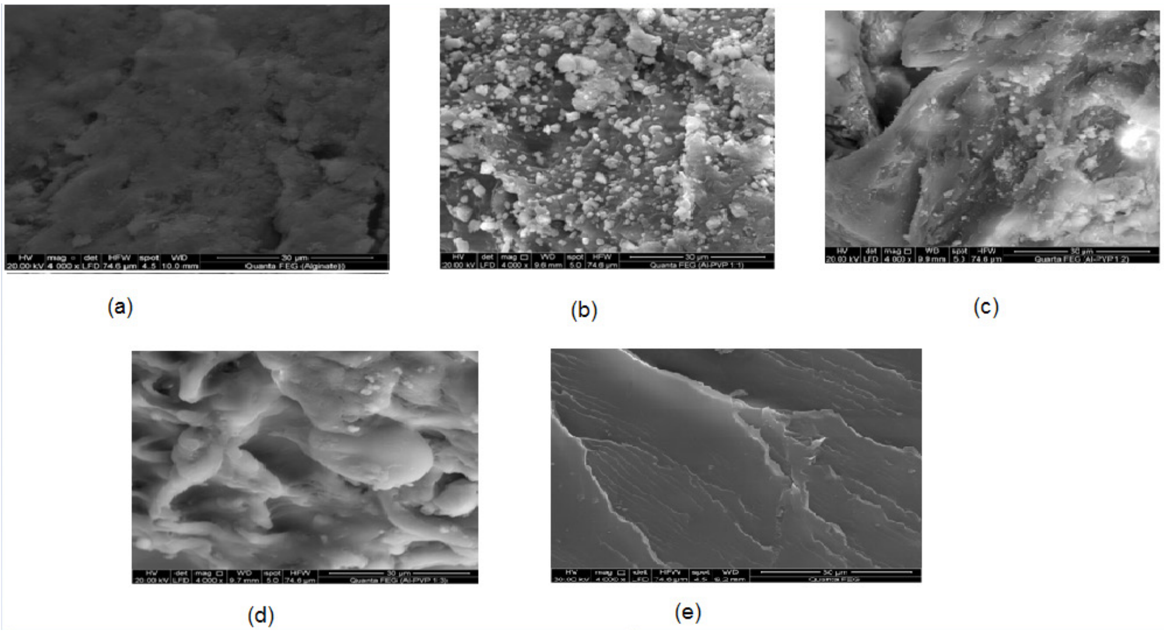


Fig. 3. SEM pictures of a) Sodium alginate b) Hydrogel (1:1/Alg:P4VP), c) Hydrogel (1:2/Alg:P4VP) and d) Hydrogel (1:3/Alg:P4VP) and e) Poly(4-vinylpyridine).

After increasing the concentration of P4VP above certain concentration, it is occurred swelling take place due to interaction between P4VP and alginate as in Figs. 3c,d so the white aggregates decreased that might be due to the P4VP inter inside the alginate.

### 3.2. X-Ray diffraction

X-ray diffraction pattern of sodium alginate shows three peaks at 31.7º, 33.8º and 45.4º indicating its crystalline nature (Fig. 3). While, XRD pattern of P4VP shows only one broad peak at 20° indicates on its amorphous nature. The hydrogels with gelation % (1:1 and 1:2/Alg:P4VP) Figs. 3b,c show characteristic peaks of alginate at 31.7º and 45.4º. In addition, characteristic peak at 20º related to amorphous nature of P4VP in good agreement with literature (Fig. 4) [22,27]. While XRD of hydrogels with gelation percent (1:3/Alg:P4VP) showed peak related to P4VP at 20º and only one peak related to alginate at 31.7º which is the presence of high P4VP content in the hydrogel.

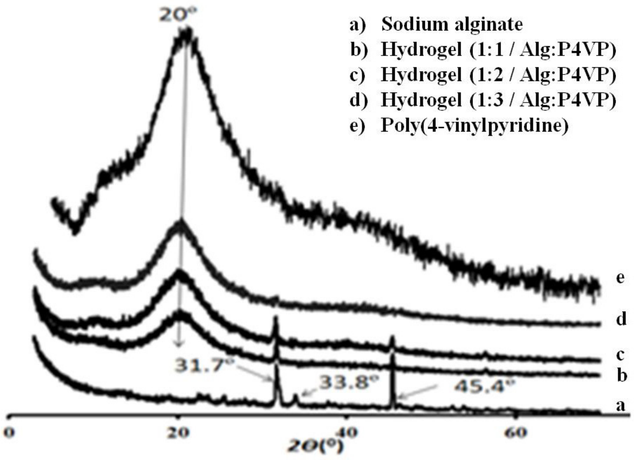


Fig. 4. XRD patterns of a) Sodium alginate, b) Hydrogel (1:1/Alg:P4VP), c) Hydrogel (1:2/Alg:P4VP), d) Hydrogel (1:3/Alg:P4VP) and e) Poly(4-vinylpyridine).

### 3.3. FT-IR

FTIR investigation of alginate had proven the presence of four strong absorption peaks at 1155, 1073, 1030, and 895 cm$^{-1}$, which are characteristic peaks of the polysaccharide structure as shown in Fig. 5a. The very strong broad absorption peak around 3600–3200 cm$^{-1}$ could be assigned to the stretching vibration of –OH groups of alginate with –OH group bending at 1030 cm$^{-1}$. Peaks around 1620 and 1420 cm$^{-1}$ related to carboxylate group –COO$^{-}$, these results are in good agreement with those repeated in the literature [22].

Moreover the peak around 3200–2800 cm$^{-1}$ was due to the stretching modes of –CH and –CH$_2$ groups, the peaks characteristic of –CH group bending of the aromatic ring of the 4-vinyl pyridine are shown at 1605 and 877 cm$^{-1}$. Figs. 5b,c and d show very strong broad absorption peak around 3600–3200 cm$^{-1}$ could be assigned to the stretching vibration of –OH groups of alginate and –NH groups which were formed by physical cross-linking and formed prydinium ion $^{+}$NH. The interaction between prydinium and carboxylate groups is proofed by the peak at 1620 cm$^{-1}$ which overlapped with peak indicating on carboxylate group. As shown in Figs. 5b,c and d, the intensity of this peak increased with increasing P4VP % in the hydrogel due to increasing number of bonds between prydinium and carboxylate groups.

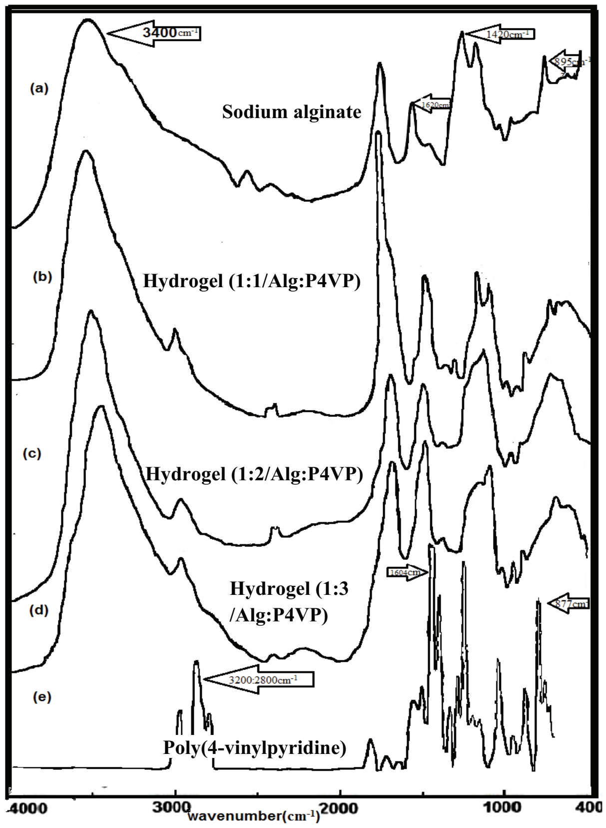


Fig. 5. FT-IR charts of hydrogels based on alginate and P4VP a) Sodium alginate b) Hydrogel (1:1/Alg:P4VP), c) Hydrogel (1:2/Alg:P4VP) and d) Hydrogel (1:3/Alg:P4VP) and e) Poly(4-vinylpyridine).

### 3.4. Thermal behavior

Thermal behavior of alginate and its hydrogels is investigated by combining the results of TGA and the differential thermogravimetric data (DTG) for sodium alginate, P4VP and Hydrogels (1:1; 1:2 and 1:3/Alg:P4VP). DTG results are the derivative of the weight loss percent against temperature or time –($d_m/d_t$). As shown in Fig. 6a, TGA of sodium alginate showed to two degradation processes, one process occurred over the range of temperature from 246 to 275°C (Fig. 6a). Degradation is coming from the decarboxylation and liberation of $CO_2$. Second degradation was observed in the range 625–700°C due to the degradation of the polymer which leads to carbonaceous residue and $Na_2CO_3$. The thermal degradation behavior of alginate is in good agreement with literature [28,29]. DTG showed two peaks indicating the two thermal degradation processes one at 246°C and the second at 663°C (Fig. 6b). On another hand, TGA curve of poly(4-vinylpyridine) shows one degradation stage over range 250–400°C and corresponding peak in DTG appears at 345°C. By using information of sodium alginate and poly(4-vinylpyridne) got from TGA and DTG, TGA curves of the hydrogels showed different stages one over a range between 200–270°C which is coming from alginate and the second stage between 320–425°C corresponding to the degradation of poly(4-vinylpydridine), but is shifted due to interaction with alginate. The two stages observed in TGA curves presence corresponding peaks in DTG one peak at 225°C and second peak at 385, 387 and 399°C for hydrogels 1:1; 1:2 and 1:3/Alg:P4VP, respectively (Fig. 6a). Moreover, initial decomposition temperatures (IDT) of sodium alginate, Poly(4-vinylpyridine) and their hydrogels 1:1; 1:2 and 1:3/Alg:P4VP are obtained equal to 225, 280, 345, 350 and 360°C, respectively (Table 1). As shown in the Fig. 6, TGA thermograms show increasing of initial decomposition temperature of hydrogel than alginate and Poly (4-vinylpyridine) and this is in a good agreement with literature [30]. TGA and DTG Figures show alginate degradation but with small degree because it is not coming from all carboxylate of alginate just from unreacted alginate. For comparison at high temperature equal 300°C, sodium alginate and Poly(4-vinylpyridine) show higher weight loss percentage than their hydrogels.

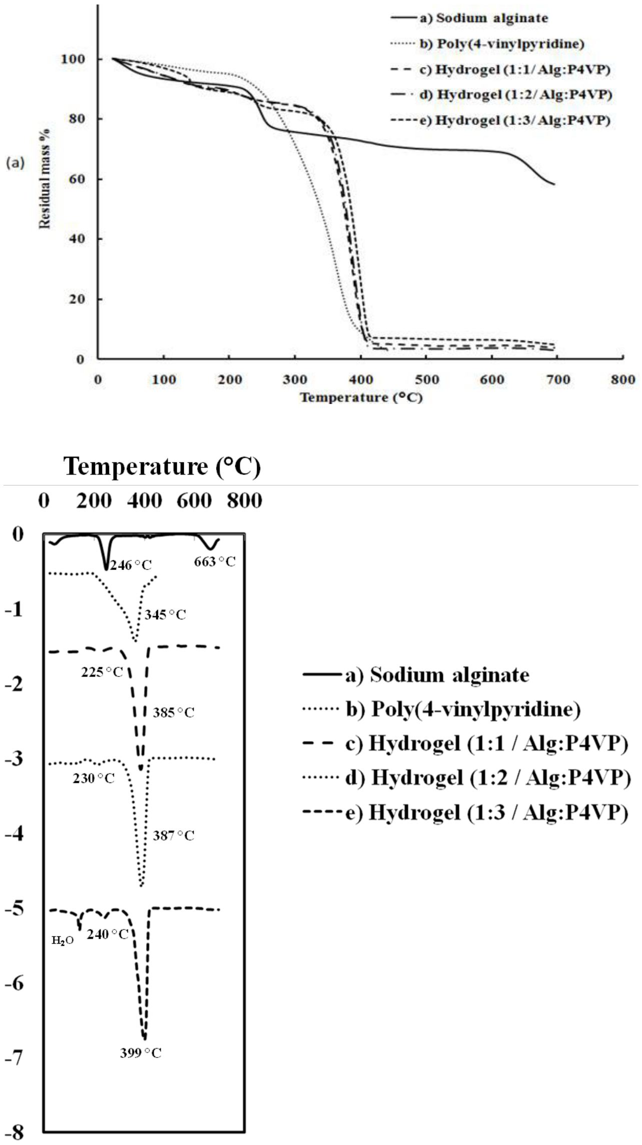


Fig. 6. (a) TGA and (b) DTG of a) Sodium alginate b) Poly(4-vinylpyridine) c) Hydrogel (1:1/Alg:P4VP), d) Hydrogel(1:2/Alg:P4VP) and e) Hydrogel (1:3/Alg:P4VP).

Table 1
TGA of sodium alginate and its hydrogels with P4VP

| Polymer/hydrogel | Initial decomposition temp. (IDT) (°C) | Temperature (°C) | | Weight loss (%) at 300°C |
|---|---|---|---|---|
| | 10 % wt. loss | 20% wt loss | | |
| Sodium alginate | 225 | 240 | 253 | 25 |
| Poly (4-vinylpyridine) | 280 | 243 | 279 | 29 |
| Hydrogel (1:1/Alg:P4VP) | 345 | 200 | 335 | 15 |
| Hydrogel (1:3/Alg:P4VP) | 350 | 200 | 338 | 15 |
| | 360 | 200 | 338 | 18 |

### 3.5. Swelling behavior of hydrogels in different pH

The swelling degrees of hydrogels 1:1; 1:2 and 1:3/ Alg:P4VP were studied and compared to hydrogel based on calcium alginate using different buffer solutions (Fig. 7). The swelling of hydrogel based on calcium alginate is higher than the hydrogels based on alginate and poly(4-vinylpyrdine) and that could be explained by the higher hydrophobic nature of P4VP. On the other hand, the ordering of swell ability degree of hydrogels based on alginate and P4VP increase with the increases in the gelation degree in different medium Hydrogel (1:3/ Alg:P4VP ) > Hydrogel (1:2/Alg:P4VP) > Hydrogel (1:1/Alg:P4VP) due to the increasing of number of the inter cross linked region with increasing the amount of P4VP consequently increasing the amount of absorbed water.

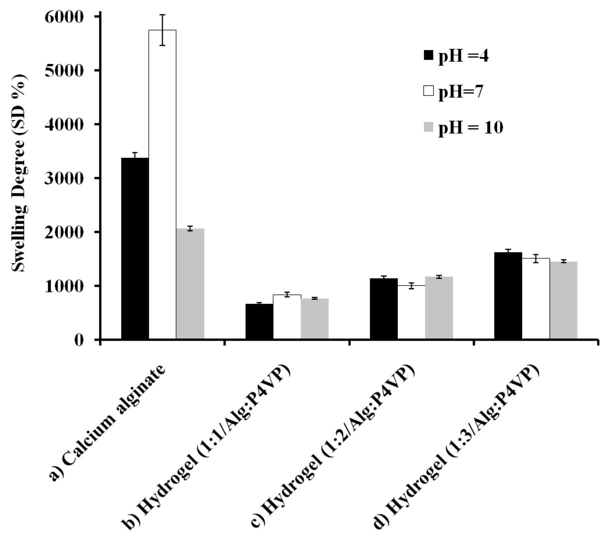


Fig. 7. Swelling degree of hydrogels based on alginate/poly(4-vinylpyridine) as compared with calcium alginate at different PHs.

## 4. Performance of hydrogels for treating water

### 4.1. Removal of dyes

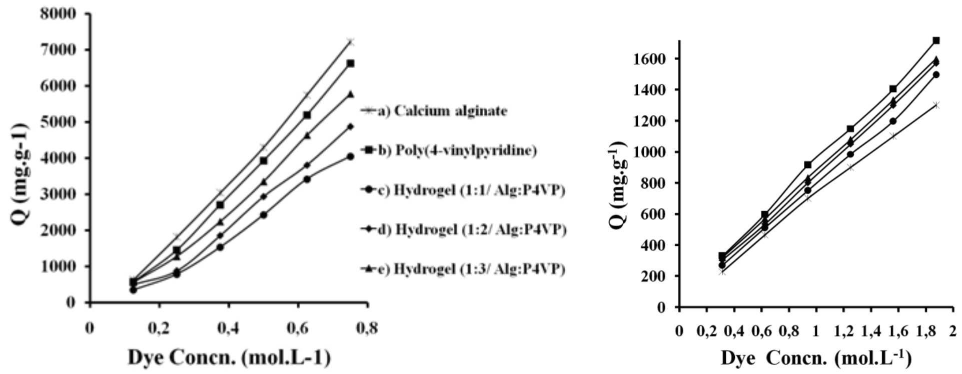
The adsorption of the investigated hydrogels for Congo red acidic dye and maxilon blue basic dye is represented in Fig. 8. The results indicated the increase in the adsorption of congo red dye with the P4VP content as compared to the hydrogel based on calcium alginate. This might be due to increase in the basic nature of the pyridine rings. On contrary, the adsorption of maxilon blue basic dye by calcium alginate was higher than its adsorption by the hydrogels based on alginate/P4VP. The result is reasonable due to the acidic nature of (anionic character) of carboxylate anion. Increasing the basic character of the hydrogels (i.e. increasing the P4VP content) will with no doubt lower the adsorption of basic dyes. As shown in Fig. 7, the adsorption of acidic dyes increases with increasing the poly(4-vinylpyridne) content that due to adsorption contributing of pyridine rings. High adsorption ability of poly(4-vinylpyridne) for congo red dye was observed (Fig. 7). The present results are in good agreement with literature [22].

### 4.2. Removal of heavy metal ions

Hydrogels based on alginate/poly(4-vinylpyridine) showed adsorption of metal ions higher than calcium alginate and adsorption in both cases coming from the free carboxylate groups of alginate. Moreover, the adsorption capacity increases with increasing gelation % with respect to the same metal ions. This experimental finding could be explained by the presence of the pyridine groups which are good chelating agent for metal ions. As shown in Fig. 9, different hydrogels have ability to adsorb Cu$^{2+}$ ions more than Ni$^{2+}$ ions and these results are in good agreement with the work done in literature on alginate hydrogel beads [10]. By comparing the uptake of all the metal ions adsorptions, the ordering of adsorption was observed as Cr$^{6+}$ > Cu$^{2+}$ > Ni$^{2+}$ > Cd$^{2+}$ and that ordering is in good agreement with work in literature study the adsorption performance for heavy metal ions using 4-vinylpyridine (4VP) resin [31]. The ordering may be explained by the difference of the stability constants of the systems. This conclusion based on the study is done for complex formation using barbituric acid with Ni$^{2+}$ and Cu$^{2+}$ salts [32]. The authors observed that the ordering of adsorption of Cu$^{2+}$ is higher than Ni$^{2+}$. They concluded that due to stability constants of the systems. This conclusion based on the study is done for complex formation using barbituric acid with Ni$^{2+}$ and Cu$^{2+}$ salts [32]. The authors observed that the adsorption of Cu$^{2+}$ was higher than Ni$^{2+}$ and that was explained by the stability constant of Cu$^{2+}$ was higher than Ni$^{2+}$.

## 5. Conclusions

Hydrogels based on alginate and different percentage of poly(4-vinylpyridine) were prepared. Thermal analyses showed the improvement of alginate thermal stability via physical cross-linking with poly(4-vinylpyridine). Hydrogels based on alginate and different percentages of P4VP showed adsorption of heavy metal ions Cd$^{2+}$, Cr$^{6+}$, Cu$^{2+}$ and Ni$^{2+}$ more than calcium alginate. In addition, the ability of adsorption increases with increasing P4VP percentage due to the chelating potency of pyridine groups. They showed



**Maxilon blue** **Congo red**

Fig. 8. Variation of the concentration of adsorbed Congo red and Maxilon blue by (a) Calcium alginate (b) Hydrogel$_{33}$, (c) Hydrogel$_{43}$ and (d) Hydrogel$_{58}$ (e) Poly(4-vinylpyridine).

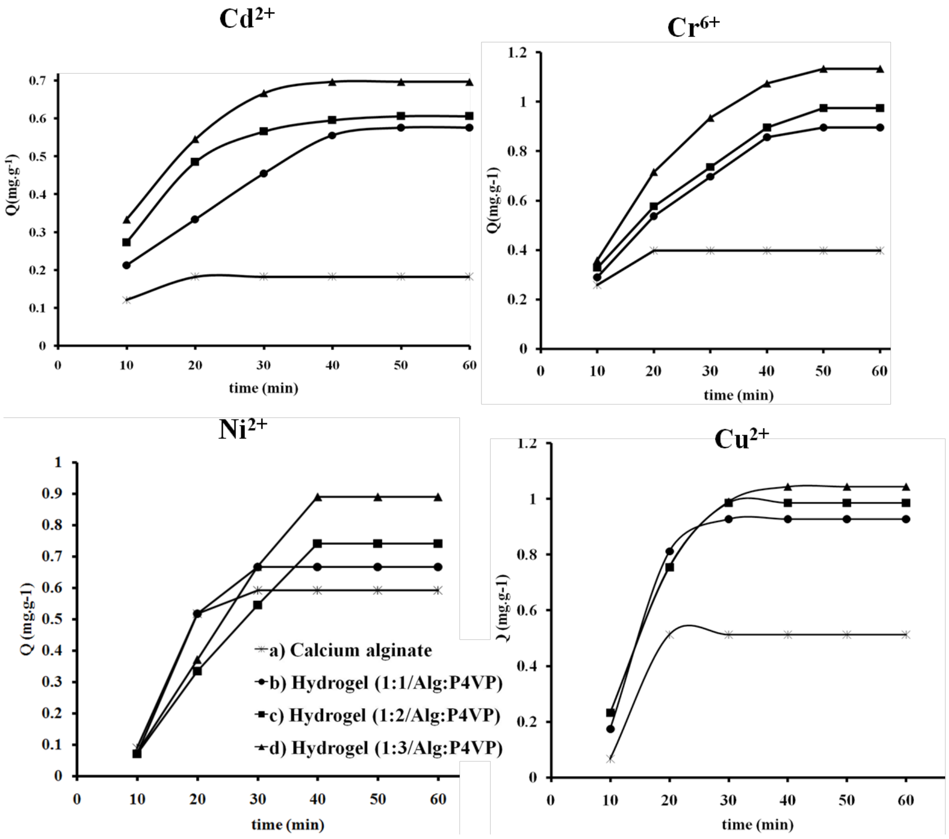


Fig. 9. Relations between metal ions uptake a) calcium alginate b) Hydrogel (1:1/Alg:P4VP), c) Hydrogel(1:2/Alg:P4VP) and d) Hydrogel (1:3/Alg:P4VP).

also higher capacity forwards acidic dye as compared to calcium alginate hydrogel. The prepared physically crosslinked hydrogels based on alginate/P4VP could be recommended for industrial wastewater treatment.

## References

[1] A.D. Augst, H.J. Kong, D.J. Mooney, Alginate hydrogels as biomaterials, Macromol. Biosci., 6 (2006) 623–633.

[2] K.Y. Lee, D.J. Mooney, Alginate: properties and biomedical applications, Prog. Polym. Sci., 37(1) (2012) 106–126.

[3] P. Li, Y-N. Dai, J-P. Zhang, A.-Q. Wang, Q. Wei, Chitosan–alginate nanoparticles as a novel drug delivery system for nifedipine, Int. J. Biomed. Sci., 4(3) (2008) 221–228.

[4] R. Lago, J.R. Rodrigues, Kinetic analysis of metal uptake by dry and gel alginate particles, Biochem. Eng. J., 46 (2009) 320–326.

[5] L.K. Jang, S.L. Lopez, S.L. Eastman, P. Pryfogle, Recovery of copper and cobalt by biopolymer gels, Biotechnol. Bioeng., 37 (1991) 266–273.

[6] A.K. Pandey, S.D. Pandey, V. Misra, Removal of toxic metals from leachates from hazardous solid wastes and reduction of toxicity to Microtox by the use of calcium alginate beads containing humic acid, Ecotoxicol. Environ. Saf., 52 (2002) 92–96.

[7] A.K. Pandey, S.D. Pandey, V. Misra, A.K. Srimal, Removal of chromium and reduction of toxicity to Microtox system from tannery effluent by the use of calcium alginate beads containing humic acid, Chemosphere, 51 (2003) 329–333.

[8] R.M.P. Silva, J.P.H. Manso, J.R.C. Rodrigues, R.J.L. Lagoa, A comparative study of alginate beads and an ion-exchange resin for the removal of heavy metals from a metal plating effluent, J. Environ. Sci. Health A, 43 (2008) 1311–1317.

[9.] T.J. SudhaVania, N. Sivagangi Reddy, P. Ramasubba Reddy, K.S.V. Krishna Rao, J. Ramkumar, A.V.R. Reddy, Synthesis, characterization, and metal uptake capacity of a new polyaniline and poly(acrylic acid) grafted sodium alginate/gelatin adsorbent, Desal. Water Treat., 52 (2014) 526–535.

[10] B. An, H. Lee, S. Lee, SH. Lee, J.W. Choi, Determining the selectivity of divalent metal cations for the carboxyl group of alginate hydrogel beads during competitive sorption, J. Hazard. Mater., 298 (2015) 11–18.

[11] M.M. EL-Tayieb, M.M. El- Shafei, M.S. Mahmoud, The role of alginate as polymeric material in treatment of tannery wastewater, IJAST, 2(2) (2013) 219–224.

[12] J. Maitr, V.K. Shukl, Cross-linking in hydrogels - a review, Amer. J. Polym. Sci., 4(2) (2014) 25–31.

[13] A.C. Jen, M.C. Wake, A.G. Mikos, Review: hydrogels for cell immobilization, Biotechnol. Bioeng., 50 (1996) 357–364.

[14] H. Zhang, F. Zhang, J. Wu, Physically crosslinked hydrogels from polysaccharides prepared by freeze–thaw technique, React. Funct. Polym., 73(7) (2013) 923–928.

[15] E.A. Kamoun, E.S. Kenawy, T.M. Tamer, M.A. El-Meligy, M.S. MohyEldin, Poly (vinyl alcohol)-alginate physically crosslinked hydrogel membranes for wound dressing applications: Characterization and bio-evaluation, Arabian J. Chem., 8(1) (2015) 38–47.

[16] Y-H. Lin, H-F. Liang, C-K. Chung, M-C. Chen, H-W. Sung, Physically crosslinked alginate/N,O-carboxymethyl chitosan hydrogels with calcium for oral delivery of protein drugs, Biomaterials, 26 (2005) 2105–2113.

[17] R. Popeski-Dimovski, S. Rendevski, N. Mahmudi, Change in gellation time of sodium alginate biopolymer hydrogels with change of dose of gamma irradiation, Physica Macedonica., 45 (2012) 67–72.

[18] A.K. Higham, C.A Bonino, R.S. Raghavan, S.A. Khan, Photo-activated ionic gelation of alginate hydrogel: real-time rheological monitoring of the two-step crosslinking mechanism, Soft Matter., 10 (2014) 4990–5002.

[19] J.O. Kim, J.K. Park, J.H. Kim, S.G. Jin, C.S. Yonga, D.X. Li, J.Y. Choi, J.S. Woo, B.K. Yoo, W.S. Lyoo, J-A. Kim, H.G. Choi, Development of polyvinyl alcohol–sodium alginate gel-matrix-based wound dressing system containing nitrofurazone, Int. J. Pharm., 359 (2008) 79–86.

[20] J.D. Roach, M.M. Bondaruk, A. Al-Abdulghani, Z. Shahrori, Counterion binding in aqueous solutions of poly(vinylpyridines) as assessed by potentiometric titration, Adv. Mater. Phys. Chem., 6 (2016) 249–261.

[21] H. El-Hamshary, M. El-Garawany, F.N. Assubaie, M. Al-Eed, Synthesis of poly(acrylamide-co-4-vinylpyridine) hydrogels and their application in heavy metal removal, J. Appl. Polym. Sci., 89 (2003) 2522–2526.

[22] M.W. Sabaa, N.A. Mohamed, R.R. Mohamed, S.M. Abd El Latif, Chemically induced graft copolymerization of 4-vinylpyridine onto carboxymethyl chitosan, Polym. Bull., 67 (2011) 693–707.

[23] H. BodugoÈz, N. Pekel, O. GuÈven, Preparation of poly(vinyl alcohol) hydrogels with radiation grafted citric and succinic acid groups, Radiat. Phys. Chem., 55 (1999) 667–671.

[24] G. Skjåk-Bræk, H. Grasdalen, O. Smidsrød, In homogeneous polysaccharide ionic gels, Carbohydr. Polym., 10 (1989) 31–54.

[25] T. Tripathy, R.P. Singh, Characterization of polyacrylamide-grafted sodium alginate: a novel polymeric flocculant, J. Appl. Polym. Sci., 81 (2001) 3296–3308.

[26] S.N. Pawar, K.J. Edgar, Alginate derivatization: A review of chemistry, properties and applications, Biomaterials, 33 (2012) 3279–3305.

[27] P. Ilgin, H. Durak, A. Gür, A novel pH-responsive p(AAm-co-METAC)/MMT composite hydrogel: synthesis, characterization and its absorption performance on heavy metal ions, Polym. Plast. Technol. Eng., 54 (2015) 603–615.

[28] J-Y. Sun, X. Zhao, W.R.K. Illeperuma, O. Chaudhuri, K.H. Oh, D.J. Mooney, J.J. Vlassak, Z. Suo, Highly stretchable and tough hydrogels, Nature, 489 (2012) 133–136. *Supplementary Information* (doi:10.1038/nature11409).

[29] C.X. Liang, K. Hirabayashi, Improvements of the physical-properties of fibroin membranes with sodium alginate, J. Appl. Polym. Sci., 45 (1992) 1937–1943.

[30] F.O. Abreu, C. Bianchini, T. BL Kist, M.M.C. Forte, Preparation and properties of core–shell alginate–carboxymethylchitosan hydrogels, Polym. Int., 58 (2009) 1267–1274.

[31] Y. Chen, W. Zhao, J. Zhang, Preparation of 4-vinylpyridine (4VP) resin and its adsorption performance for heavy metal ions, RSC Adv., 7 (2017) 4226–4236.

[32] N. Türkel, M.S. Aksoy, Complex formation of nickel(II) and copper(II) with barbituric acid, ISRN Anal. Chem., (Article ID 243175) 2014 (2014) 1–5.