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IONIC INTERACTIONS IN CROSS-LINKED POLY(VINYL ALCOHOL) HYDROGEL BLENDED WITH STARCH

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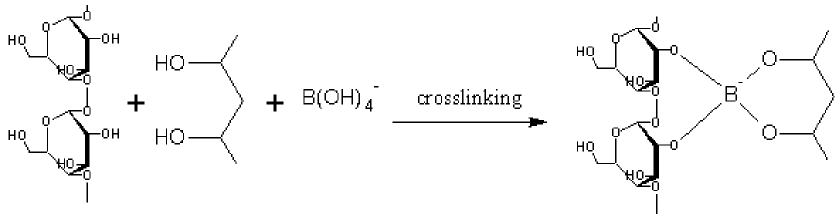

Polymeric hydrogels having ions captivating sites serve as a good conductive source and are widely utilized for many applications. Adsorption of alkali and alkaline metal ions was studied using poly(vinyl alcohol) hydrogels cross-linked with borax. Adsorption isotherms were used to investigate the mode of interaction and assimilation of ions through hydrogel system with and without the involvement of starch at 303 K. The applicability of isotherms was tested based on statistical evaluations using linear regression coefficient "R^2" values. Adsorption process is found to be physical in nature as it obeys Freundlich, Temkin and Dubinin-Radushkevich isotherms. The adsorption takes place in pores of hydrogel. Ionic interactions between metal ions and hydrogel units were also observed. FTIR analysis of hydrogels was carried out for confirmation of interaction between metal ions and hydrogel.

INTRODUCTION

Polymeric hydrogels are magnificent materials due to the water holding and releasing abilities~~,~~ upon variation in external stimuli. The modification in the composition of hydrogels by blending and cross-linking makes them suitable source for the transportation of ionic species. There are wide applications of hydrogels incorporating poly(vinyl alcohol) and starch, in the field of agricultural, electrical and medical sciences. Starch is a polysaccharide composed of numbers of glucose units joined via 1,4-glycosidic linkages. Starch is cheap, naturally available, non-toxic and biodegradable material, known due to its adhesiveness and gluing ability.[1] Indulging starch with poly(vinyl alcohol) (PVOH) brings the modification in mechanical ability, gelatin ability, and biodegradability of PVOH-Starch blend.[2,3] For specified applications, further enhancement in the properties of PVOH-Starch blend was needed, with the incorporation of plasticizers; 1,4- butandiol, 1,2,6-hexanetriol, pentaerythritol, xylitol, mannitol were found to enhanced thermal stability.[4] Maltitol, sorbitol~~,~~ and glycerol enhanced chain mobility and blend processability.[5] The involvement of cross-linkers~~;~~ like citric acid and formaldehyde showed non toxicity, epichlorohydrin enhanced flexibility and borate increased the mechanical ability.[6] The biodegradability found to decrease upon cross-linking.

For the polymers having hydroxyl moiety in the molecular structure, borax was used as crosslinker.[7] Borax has an ability to interact with hydroxyl group in the formation of cross-linked units between chains of polysaccharides.[8,9] PVOH-Starch borate hydrogel is formed due to interaction of borax with hydroxyl groups present in both

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PVOH and starch.[10,11] Similar interactions between the hydroxyl groups in cellulose and PVOH with borate ions were available in the literature.[12,13] Water holding ability of hydrogel and the presence of BO_4^- in cross-linked PVOH-Starch make it attractive for the maintenance and release of ionic substances, making it suitable for external drug delivery for wounds via bandages[14,15] and use as a controlled release system for agricultural needs.[16] The present study was designed by focusing the ion-capture ability of PVOH-Starch borate hydrogel system, which concerned with the analysis of adsorption isotherms for alkali and alkaline metal chlorides through hydrogel system.

RESULTS AND DISCUSSION

Adsorbed amount

Adsorption of lithium, sodium, potassium, magnesium and calcium chloride was carried out using PVOH-borate and PVOH-Starch borate hydrogel. The data obtained were used to study adsorption isotherms. The amount of alkali and alkaline metal chlorides adsorbed in PVOH hydrogel were determined using the relation (1).

$$q = \frac{V}{M}(C_i - C_e) \tag{1}$$

where: "q" is the amount of electrolyte adsorbed, "V" is the volume of electrolyte, "M" is mass of PVOH hydrogel, "C_i and C_e" are concentrations of electrolyte present initially and after adsorption. It was observed that the amount of adsorbed electrolyte increased on enhancing the initial concentration of metal ion solution. Indulgence of starch also favored the adsorption of metal ions in hydrogel moiety. The results were tabulated in Table 1.

Freundlich isotherm

The nature and involvement of ions interactions during sorption process was analyzed by the amount of adsorbed electrolyte and used to validate various isotherms on adsorption process.[17]

Freundlich isotherm represents both physicosorption and chemisorption phenomenon on the heterogeneous surface of the adsorbent. Freundlich adsorption isotherm is represented as (2),

$$\ln q_e = \ln k_f + \frac{1}{n}\ln C_e \tag{2}$$

where: "q_e" is the amount of ions adsorbed at equilibrium, "C_e" is the concentration of ions at equilibrium. "k_f" and "n" are Freundlich isotherm constants, representing the sorption capacity and the sorption intensity. R^2 values for Freundlich isotherm are approaching unity, therefore, adsorption of electrolytes in PVOH hydrogels obeys the Freundulich adsorption isotherm. Involvement of starch in PVOH hydrogel enhanced the adsorption capacity of ions. The adsorption capacity of monovalent electrolytes in PVOH-Starch borate hydrogel was found to be in order KCl > NaCl > LiCl and divalent electrolytes in order $CaCl_2$ > $MgCl_2$ which showed that the involvement of starch favored the adsorption of large cations in PVOH hydrogel which focused the availability of large pore sizes in comparison with PVOH-borate hydrogels. The increased value of adsorption intensity revealed that adsorption of electrolytes is more favorable in PVOH-Starch borate hydrogel. The adsorption capacity of monovalent cations in hydrogel was found to be greater than that of divalent cations. This is due to the fact that hydrogel has BO_4^- units which have different mode of interaction for various cations. Monovalent cations interacted directly with BO_4^- units in ratio of 1:1 as $BO_4^-\ldots M^+$ while, divalent cations associate two BO_4^- units in ratio 1:2 as $(BO_4^-)_2\ldots M^{2+}$ resulting in lesser adsorption capacity by bridging cross-linked units which shrink PVOH hydrogels causing reduction in volume and pore size of hydrogel. The adsorption capacity (k_f) and intensity (n) for each electrolyte adsorbed in PVOH hydrogels are shown in Table 2. The plot lnq vs lnC for Freundlich isotherm is given in Figure 1.

Langmuir isotherm

Langmuir isotherm relates to the chemisorption process on the homogenous surface of adsorbent represented by the relation (3),

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \tag{3}$$

where: "q_m" and "K_L" are the Langmuir adsorption constants representing the maximum adsorption capacity and the affinity of binding sites, respectively. The Langmuir's adsorption isotherm showed deviations in R^2 values from unity, for the adsorption of electrolytes in PVOH-Starch borate hydrogels.

Table 1

Amount of electrolyte adsorbed in PVOH hydrogels at 303 K

[Electrolyte] (g.L^{-1})	Amount adsorbed (mg.g^{-1})				
	LiCl	NaCl	KCl	$MgCl_2$	$CaCl_2$
PVOH-borate hydrogel					
20	97.65	84.87	73.95	40.43	36.78
30	145.3	131.2	110.9	68.44	58.90
40	169.3	157.7	135.8	88.39	79.89
50	198.4	183.8	175.4	114.4	102.6
60	252.1	235.1	221.8	143.7	132.6
70	296.4	256.4	238.7	177.4	158.4
80	339.4	292.4	262.9	200.4	180.6
PVOH-Starch borate hydrogel					
20	101.6	107.8	110.9	49.43	55.78
30	151.3	159.2	162.9	81.44	88.90
40	177.3	184.7	191.3	106.4	114.7
50	222.3	232.4	242.6	136.4	143.9
60	264.1	276.1	286.8	169.7	177.6
70	310.4	329.4	332.4	208.4	215.7
80	355.4	363.4	379.8	234.4	242.6

Table 2

Freundlich adsorption isotherm parameters

Electrolytes	K_f (mg.g^{-1})	n --	R^2 --
PVOH-borate hydrogel			
LiCl	6.995	1.141	0.987
NaCl	6.385	1.147	0.992
KCl	4.525	1.070	0.993
$MgCl_2$	1.314	0.871	0.997
$CaCl_2$	1.140	0.864	0.990
PVOH-Starch borate hydrogel			
LiCl	7.245	1.132	0.997
NaCl	7.760	1.371	0.996
KCl	7.988	1.141	0.995
$MgCl_2$	1.742	0.893	0.998
$CaCl_2$	2.378	0.947	0.998

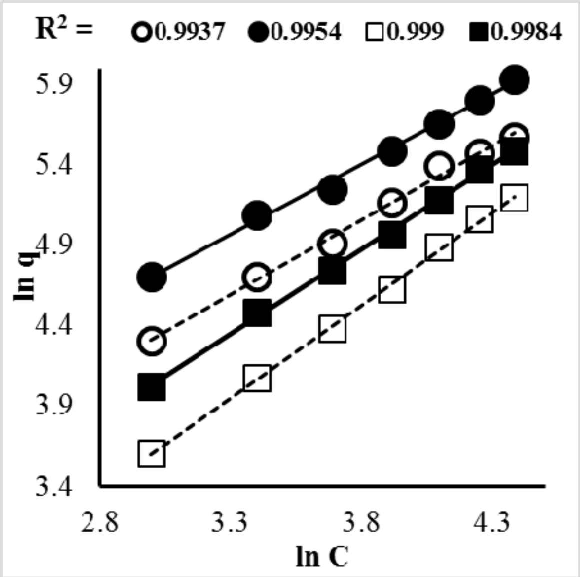


Fig. 1 – Representative plot for Freundlich adsorption isotherm for KCl in ○ PVOH-borate, ● PVOH-Starch borate and $CaCl_2$ in □ PVOH-borate, ■ PVOH-Starch borate hydrogel at 303 K.

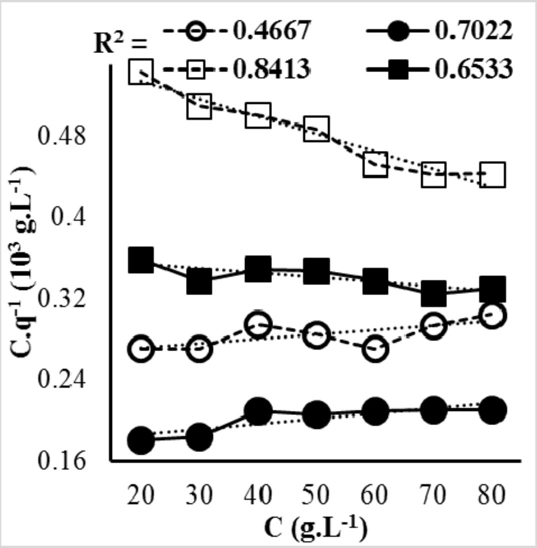


Fig. 2 – Representative plot for Langmuir adsorption isotherm for KCl in ○ PVOH-borate, ● PVOH-Starch borate hydrogel & $CaCl_2$ in □ PVOH-borate, ■ PVOH-Starch borate hydrogel at 303 K.

The representative plot for Langmuir isotherm is shown in Figure 2. The adsorption process does not obey the Langmuir isotherm and following Freundlich isotherm to a greater extent indicated that the adsorption of electrolytes in PVOH-Starch borate hydrogel is a physicosorption phenomenon.

Isotherms supporting physicosorption

Temkin and Dubinin–Radushkevich (D-R) isotherms supported the physical nature of adsorption and explained the mechanism involved in physicosorption. Obeying Temkin isotherms showed that physicosorption is due to an interaction between metal ions and PVOH hydrogels and D-R isotherms portray physicosorption with the pore-filling mechanism on the adsorbent surface. Temkin and D-R isotherms were presented in relations 4 and 5, respectively.

$$q_e = \frac{RT}{b}\ln K_T + \frac{RT}{b}\ln C_e \qquad (4)$$

$$\ln q_e = \ln q_d - \beta R^2 T^2 \ln[1 + \frac{1}{C_e}]^2 \qquad (5)$$

where: "q_e" is the amount of ions adsorbed at equilibrium, "R" is molar gas constant, "T" is temperature, "b" is Temkin isotherm constant, and "K_T" is Temkin isotherm constant representing equilibrium binding of adsorbate. "q_d" is D-R isotherm constant which portrays theoretical saturation capacity of sorbate and "β" is free energy constant. For evaluating Temkin isotherm, the graphs between q_e and $\ln C_e$ were plotted; constants "b" and "K_T" were calculated from the slope and intercept of plots. The heat of electrolyte adsorption per mole of hydrogel was calculated based on values of constant "b" using relation. It was found to be lesser than 20 $kJ\cdot mol^{-1}$, which confirmed that process is physicosorption.[18,19] The heat energy of electrolyte per mole of hydrogel was increased on the inclusion of starch in hydrogel. The presence of more water molecules in hydrogel moiety utilized more energy for substitution of water molecules with cations in pores of PVOH-Starch borate hydrogel. Temkin isotherm parameters are shown in Table 3.

Free energy is derived from D-R isotherm using relation and has value lesser than 8 $kJ.mol^{-1}$ confirming physical nature of adsorption.[18,19] Starch enhanced the saturation capacity of PVOH-borate hydrogel and found to be greater for potassium ions due to large cationic radius among other ions. D-R adsorption isotherm parameters are given in Table 4.

FTIR analysis of hydrogels

FTIR elucidation of the aqueous PVOH-Starch blend, PVOH-Starch borate hydrogel, and K^+, Ca^{2+} adsorbed PVOH-Starch borate hydrogel confirmed the crosslinking between polymers and BO_4^- units and association of K^+ and Ca^{2+} in PVOH-Starch borate hydrogel moiety. The attributions of different peaks in FTIR spectra are given in Table 5. FTIR spectra are shown in Figure 3. The peak obtained in region 1382-1384 cm^{-1} confirmed the association between hydroxyl groups of polymers and BO_4^- units in a tetrahedral fashion.[20] The disappearance of the peak in region 2079-2088 cm^{-1}

which was assigned to the liberation of free water molecules also confirmed the binding of polymers with cross-linker. The values of C-O stretching vibrations were found increased upon adsorption of cations. M-O-H stretching vibrations appeared in spectrum of electrolyte adsorbed hydrogel. The interaction of cations in hydrogel moiety was confirmed from the elucidations of stretching C-O and appearance of M-O-H peaks.[21]

Table 3

Temkin adsorption isotherm parameters

Electrolytes	K_T (L.g^{-1})	b –	B (J.mol^{-1})	R^2 –
PVOH-borate hydrogel				
LiCl	0.0782	14.941	168.60	0.930
NaCl	0.0812	17.182	146.61	0.962
KCl	0.0757	17.896	140.76	0.966
$MgCl_2$	0.0619	21.938	114.83	0.943
$CaCl_2$	0.0614	24.178	104.19	0.945
PVOH-Starch borate hydrogel				
LiCl	0.0780	14.144	178.10	0.949
NaCl	0.0782	13.460	187.15	0.952
KCl	0.0794	13.264	189.92	0.951
$MgCl_2$	0.0633	18.910	133.21	0.947
$CaCl_2$	0.0712	20.512	122.81	0.951

Table 4

Dubinin-Radushkevich adsorption isotherm parameters

Electrolytes	q_d (mg.g^{-1})	$\beta\times10^6$ (mol^{2}J^{-2})	E (J.mol^{-1})	R^2 –
PVOH-borate hydrogel				
LiCl	435.19	2.560	441.88	0.929
NaCl	393.46	2.584	439.83	0.961
KCl	374.61	2.766	425.10	0.960
$MgCl_2$	297.97	3.392	383.90	0.960
$CaCl_2$	269.18	3.411	382.85	0.957
PVOH-Starch borate hydrogel				
LiCl	464.98	2.599	438.55	0.945
NaCl	485.33	2.582	440.03	0.936
KCl	498.19	2.572	440.92	0.946
$MgCl_2$	345.84	3.309	388.69	0.961
$CaCl_2$	347.58	3.112	400.58	0.961

Table 5

Peak assignment of adsorption in PVOH-Starch borate hydrogels

Aqueous PVOH	Aqueous Starch	Hydrogel	K^+ adsorbed	Ca^{2+} adsorbed	Assignment of peaks
		Wave numbers in cm^{-1}			
---	---	---	3753	3730	M-O-H, stretching (M = K, Ca)
3367	3460	3460	3452	3450	O-H stretching
2950	---	2900	2926	2940	C-H stretching
---	---	---	2372	2368	B-M stretching (M = K, Ca)
2088	2079	---	---	---	H-O-H liberation for free water
1635	1635	1633	1649	1639	H-O-H bending of bound water
1433, 1315	1390	---	1467, 1429	---	C-H bending
---	---	1382	1384	1382	B-O-C stretching (tetrahedral)
1093	1018	980	1014	1014	C-O stretching
---	---	600	---	---	O-B-O stretching

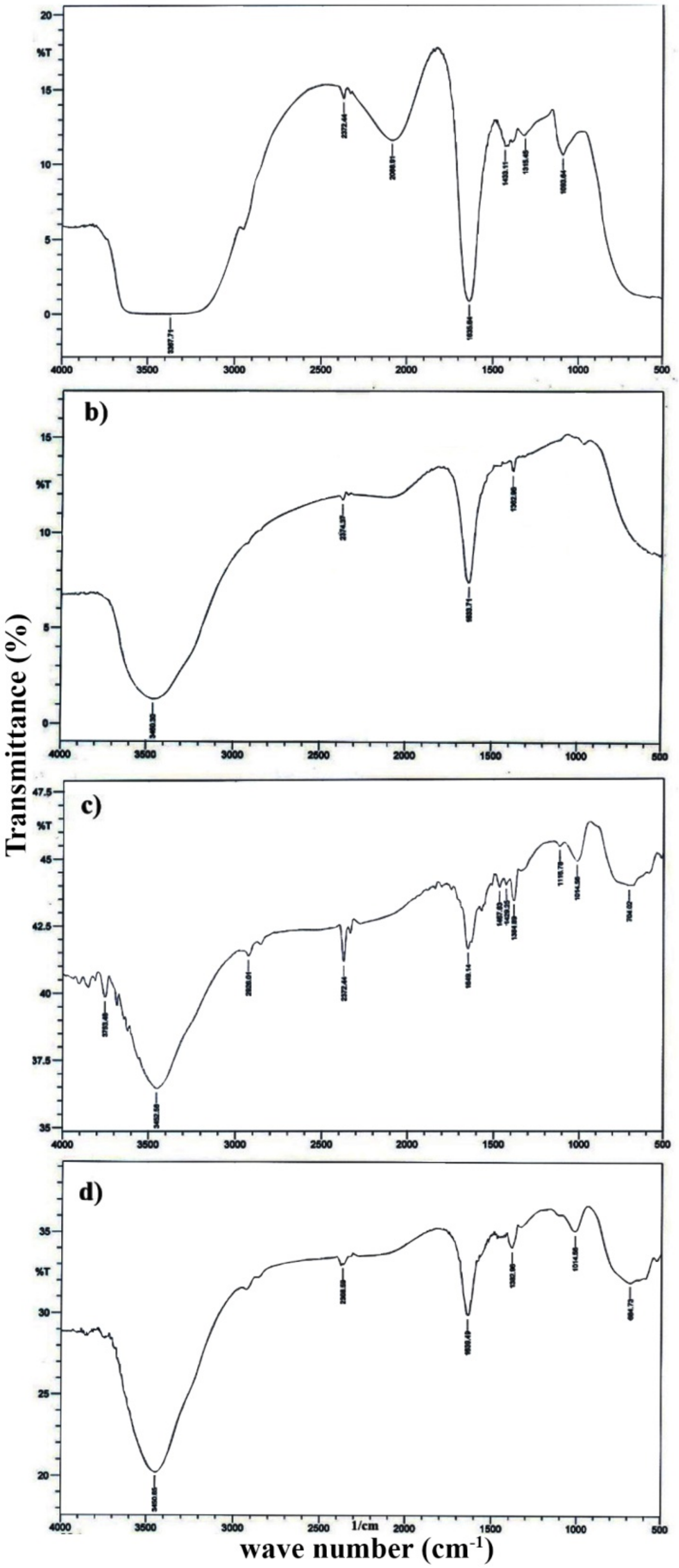
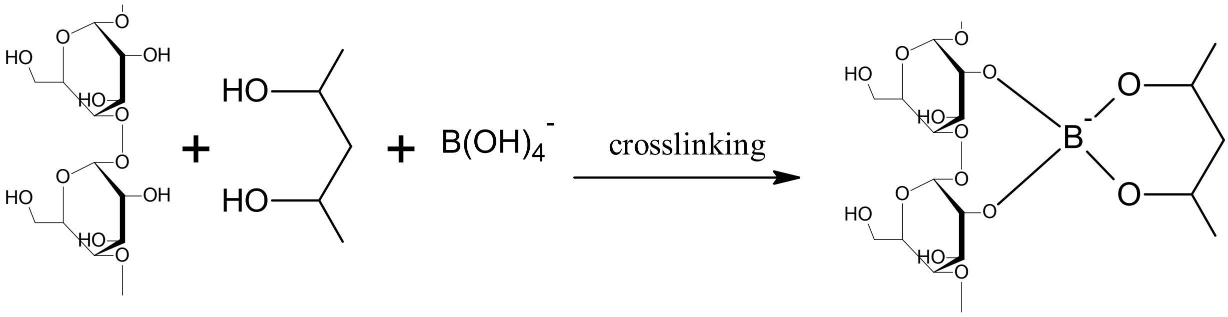


Fig. 3 – FTIR spectra (a) Aqueous PVOH, (b) PVOH-Starch borate hydrogel, (c) K^+ adsorbed PVOH-Starch borate hydrogel, (d) Ca^{2+} adsorbed PVOH-Starch borate hydrogel.

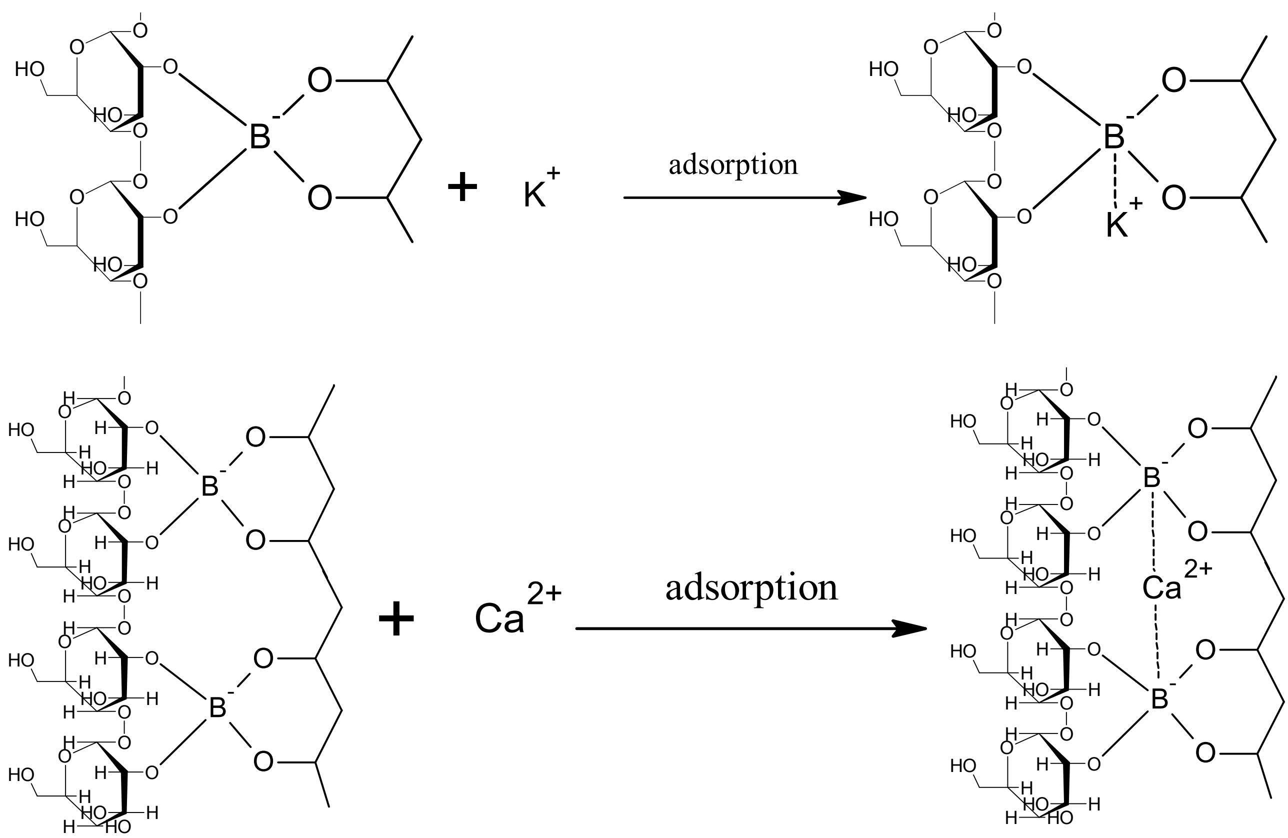
Mechanism of adsorption

The interaction of borate ions with the hydroxyl groups of polysaccharides,[8,9] PVOH-Starch[6, 10,11] and PVOH-cellulose[12] was reported. The interaction with borax, create cross-linked units utilizing hydroxyl groups of both PVOH and starch forming PVOH-starch borate hydrogel. The possible reaction between PVOH-Starch blend and borax was shown in Scheme 1.

The excess negative charge on BO_4^- units along with the presence of pores in the hydrogel made it suitable for the caging of ions. Thus, adsorption of M^+ proceeds with the interaction of M^+ with the BO_4^- units in PVOH-Starch borate hydrogel which later on continue with the filling of ions in pores present in hydrogel up to the saturation level of PVOH-Starch borate hydrogel replacing water molecules that persist in the pores of hydrogel.[22] Similarly M^{2+} associates two BO_4^- units of PVOH-Starch borate hydrogel. The interaction of K^+ and Ca^{2+} ions in PVOH-Starch borate hydrogel is shown in Scheme 2.



Scheme 1 – The possible reaction between PVOH-Starch blend and borax.



Scheme 2 – The interaction of K^+ and Ca^{2+} ions in PVOH-Starch borate hydrogel.

EXPERIMENTAL

Glasswares of Pyrex-A quality were used. Chemicals include polymers: poly(vinyl alcohol) $(CH_2\text{-}CH\text{-}OH)_n$ and starch $(C_6H_{10}O_5)_n$; crosslinking agent: borax $Na_2B_4O_7.10H_2O$ (99% pure, E. Merck); electrolyte: lithium chloride, sodium chloride, potassium chloride, magnesium chloride and calcium chloride (99.9% pure E. Merck). Deionized water with conductivity 0.06 $\mu S.cm^{-1}$, and reagents: silver nitrate, hydrochloric acid and sodium hydroxide (99% pure, E. Merck) were used. Adsorption studies were carried out at 303 K for which thermostatic bath (circulator, model YCW-0.1 Taiwan) was used to maintain temperature.

PVOH and starch are dissolved in deionized water at 80 ± 1^oC and 100 ± 1^oC, respectively, with continuous stirring to prepare (5 $g.dL^{-1}$) solution. PVOH-Starch borate hydrogel was prepared by mixing 1:1 PVOH:starch by weight and stirred until a homogeneous blend was obtained after which 0.05 $mol.L^{-1}$ borax solution was added to blend in the ratio 4:1 blend: borax by volume with vigorous stirring until a homogeneous hydrogel was obtained.

Electrolytes of different concentration were prepared by dissolving definite amount in deionized water to obtain solutions in the range of 20-80 $g.L^{-1}$.

Adsorption was carried out~~,~~ using (4.0±0.1 g) PVOH-Starch borate hydrogel in a sintered glass cell having (25.0±0.1 mL) electrolyte for two hours. After two hours remaining electrolyte was analyzed by ion-exchange chromatography and argentometry for detection of the amount of adsorbed cations and anions, respectively. The obtained data were used for isotherm study.

CONCLUSIONS

Isotherms for the adsorption of electrolytes in PVOH-borate hydrogels were studied. The indulgence of starch in polymeric hydrogel enhanced the adsorption capacity and favored adsorption of large cations. The applicability of isotherm was decided on the basis of linear regression coefficient R^2 values. Lower R^2 values of Langmuir isotherms deny the chemisorption nature of adsorption process. Adsorption followed Freundlich, Temkin and D-R isotherms which conveyed that adsorption of electrolyte in PVOH-Starch borate hydrogel is physicosorption in nature along with involvement of interaction of electrolyte with BO_4^- units and pores present in PVOH hydrogel. The peak around 1380 cm^{-1} confirmed the crosslinking of PVOH hydrogels and appearance of new peaks confirmed the association of metals ions in PVOH hydrogel.

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REFERENCES

1. J. BeMiller and R. Whistler, "Starch: Chemistry and Technology" Elsevier Inc, 2009.
2. N. Tudorachi, C.N. Cascaval, M. Rusu and M. Pruteanu, *Polym. Test.,* **2000,** *19*, 785–799.
3. N. A. Azahari, N. Othman and H. Ismail, *J. Phys. Sci.,* **2011,** *22*, 15–31.
4. A. A. Aydına and V. Ilberg, *Carbohydr Polym*., **2016,** *136*, 441–448.
5. M. A. L. Russo, R. Truss and P. J. Halley, *Carbohydr. Polym.,* **2009,** *77*, 442–448.
6. B. Sreedhar, M. Sairam, D. K. Chattopadhyay, P. A. S. Rathnam, and D. V. M. Rao, *J. Appl. Polym. Sci*., **2005,** *96*, 1313–1322.
7. B. Balakrishnan and A. Jayakrishnan, *Biomaterials,* **2005,** *26*, 3941-3951.
8. I. Ali, S. U. Rehman, S. H. Ali and A. Javaid, *J. Appl. Polym. Sci*., **2013,** *128*, 3672–3677.
9. S. Gao, J. Guo and K. Nishinari, *Carbohydr. Polym*., **2008,** *72*, 315–325.
10. S. Widiarto, *J. Sains. Tek*., **2005,** *11*, 51-57.
11. S. Maiti, D. Ray and D. Mitra, *J. Polym. Environ*., **2012,** *20*, 749–759.
12. J. Han, T. Lei and Q. Wu, *Cellulose*, **2013,** *20*, 2947-2958.
13. S. Spoljaric, A. Salminen, N. D. Luong and J. Seppala, *Eur. Polym. J*., **2014,** *56*, 105–117.
14. Y. Dou, B. Zhang, M. He, G. Yin, Y. Cui and I. N. Savina, *Polymers*, **2015,** *7*, 580-591.
15. E. R. Kenawy, E. A. Kamoun, M. S. M Eldin and M. A. E. Meligy, *Arab J. Chem*., **2014,** *7*, 372–380.
16. X. Han, S. Chen and X. Hu, *Desalination*, **2009,** *240*, 21-26.
17. K. Y. Foo and B. H. Hameed, *Chem. Eng. J*., **2010,** *156*, 2–10.
18. A. O. Dada, A. P. Olalekan, A. M. Olatunya and O. Dada, *IOSR J. Appl. Chem*., **2012,** *3*, 38-45.
19. A. U. Itodo and H. U. Itodo, *Life Sci. J*., **2010,** *7*, 31-39.
20. C. A. Cozzolino, G. Campanella, H. Tureb, R. T. Olsson and S. Farris, *Carbohydr. Polym*., **2016,** *143*, 179-187.
21. R. Saeed and Z. U. Abdeen, *Int. J. Sci. Technol*., **2013,** *3*, 132-142.
22. Z. Abdeen and R. Saeed, *Polym. Sci. Ser. A*., **2016,** *58*, 689-696.