CELLULOSE CHEMISTRY AND TECHNOLOGY

PREPARATION OF CARBOXYMETHYL CELLULOSE AND POLYVINYL ALCOHOL (CMC/PVA) HYDROGELS USING FREEZE–THAW PROCESSES FOR ADSORPTION OF Zn^{2+} AND Cu^{2+}

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The preparation of carboxymethyl cellulose and polyvinyl alcohol (CMC/PVA) composites is proposed in the present work. The CMC/PVA hydrogels were prepared using freeze–thaw processes. The effects of freezing time and of the number of freeze–thaw cycles on the swelling ratio and gel fraction of achieved hydrogels were evaluated using response surface methodology. The multiple regression analysis suggested second order polynomial equations as models for predicting changes of the studied hydrogel characteristics by selected process variables, with relatively high coefficients of determination (R2 > 0.82). The numerical optimization suggested that freezing the polymer solutions for 5 h and repeating the freeze–thaw process for 5 times would give the most desirable hydrogels with highest either swelling ratio or gel fraction. Remarkably, the ion adsorption studies showed that the adsorption of Cu^{2+} and Zn^{2+} ions by the hydrogels obeys zero order kinetics and the high capability of the produced optimum hydrogels to adsorb selected ions from synthetic waste was confirmed.

Keywords: hydrogels, polyvinyl alcohol, carboxymethyl cellulose, freeze–thaw, Cu^{2+} adsorption, Zn^{2+} adsorption

INTRODUCTION

Hydrogels are water-insoluble three-dimensional polymeric composites with great water sorption ability and, consequently, wide applications in various fields. Hydrogels can be manufactured through either chemical or physical techniques.[1] While, in chemical techniques, bond formation between polymers or using cross-linking agents or initiators is necessary, the hydrogels prepared by physical methods are purer, without any host linking molecules, which makes them expedient for pharmaceutical and therapeutic applications. However, most of the physical procedures require high energy sources, such as X or γ-rays, electron beam *etc*., which are expensive and complicated techniques.[2]

Crystallization is a convenient physical routine to prepare hydrogels that can be achieved via various cycles of freeze–thaw procedures. The phase separation in polymer solution would occur after repetitive freeze–thaw cycles, leading to the formation of hydrogels. Likewise, the crystallites of polymers form due to exposure of the polymer to lower temperatures, acting as intersection areas and making insoluble networks of polymers. The hydrogels obtained via freeze–thaw processes are desired due to their better elastic properties, as compared to those made by chemical methods. The physicochemical characteristics of these freeze–thawed hydrogels can be improved by adjusting the freezing time and temperature, the thawing time and temperature, the number of freeze–thaw cycles and the nature and concentrations of polymers. Moreover, the freeze–thaw cycles can give a porous structure to hydrogels due to the space created by melting ice crystals during thawing processes.[2,3]

Lately, hydrogels have been investigated as efficient adsorbents to eliminate heavy metal ions from wastewater. While the water diffuses into hydrogels, metal ions move towards the polymer networks and bind to the functional groups of the hydrogels, and thus, can be removed from aqueous solutions.[1,4,5] Various natural and synthetic polymers can be incorporated to make

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composite hydrogels, such as cellulose based polysaccharides and polyvinyl alcohol (PVA). Carboxyl methyl cellulose (CMC) is one of the main derivatives of cellulose, where carboxyl methyl groups substitute some of the hydrogen atoms of the -OH groups on the cellulose backbone. CMC is biocompatible, has good water solubility and biodegradability. CMC can be used in various fields, for example, as stabilizing and thickening agents in food and pharmaceutical emulsions. CMC can also adsorb metal ions via its -OH and –COOH groups.

PVA is a partially crystalline polymer manufactured through the hydrolysis of polyvinyl acetate. Good water-solubility, biocompatibility and biodegradability make its uses interesting in various applications in the food industry, pharmaceutics and textiles. The hydrogel networks between PVA chains can be formed by hydrogen bonding on the -OH groups of the repeating unit in PVA.[2,3,6]

Recently, Wang and Wang[3] prepared CMC/PVA hydrogels and used them as adsorbent to remove various heavy metal ions, such as Ag^+, from synthetic waste. They concluded that using CMC/PVA hydrogels containing one-third of CMC and two-thirds of PVA would give the most desired properties. Thus, this study has been conducted in line with their research, and CMC and PVA were used to prepare composite hydrogels, using the freeze–thaw process. The CMC to PVA weight ratio was set as 1:2, according to their optimum reported proportions. Also, in the present work, we relied on the FTIR and XRD data reported by the cited authors, which have already confirmed the formation of composite gels. However, we assumed that, in the freeze–thaw gelation technique, the freezing time period and the number of freeze–thaw cycles can significantly affect the characteristics of obtained composite hydrogels. Therefore, the present research aimed to evaluate the effects of the main freeze–thaw process parameters to optimize them in order to get the most desired CMC/PVA composite hydrogels. Moreover, the kinetics of Cu^{2+} and Zn^{2+} adsorption by the suggested optimum product was investigated, which had not been considered in the study conducted by Wang and Wang.[3]

EXPERIMENTAL

Materials

Polyvinyl alcohol (PVA), with a molecular weight of 88000 (M.W. = 88000), and carboxyl methyl cellulose (CMC), with a molecular weight of 250000 (M.W. 250000), zinc sulphate (ZnSO4) and copper sulphate (CuSO4) were provided from Merck Co. (Darmstadt, Germany). Deionized water and all analytical grade solvents were purchased from Dr Mojallali Co. (Iran, Tehran) and used without further purification.

Methods

Preparation of CMC/PVA composite hydrogels

CMC/PVA hydrogels were obtained using several freeze–thaw cycles. The CMC solution was obtained by dissolving 1 g of CMC in 100 mL of deionized water at 50 ± 5 °C. The PVA aqueous solution was prepared by dissolving 5 g of PVA in 100 mL of deionized water at 75 ± 5 °C. These two solutions were mixed together with the CMC to PVA ratio of 1:2 (CMC solution:PVA solution = 1:2). The mixture was frozen at −20 °C for various time periods, according to the experimental design in Table 1, and then thawed at room temperature (25 ± 5 °C). These freeze–thaw cycles were repeated various times according to Table 1.[3]

Gel fraction analysis

The gel fraction of the CMC/PVA hydrogels was assessed using the gravimetric technique. Samples with equal sizes were dried in an oven at 40 ± 5 °C. The weight of the dried hydrogels was denoted as W_0. The dried hydrogels were then soaked in deionized water for 24 h to eliminate their soluble parts and re-dried under previously mentioned conditions. The weights of the second time dried samples were denoted as W_1. The gel fractions were calculated using Equation (1):[3]

$$\text{Gel fraction } \% = (W_1/W_0) / W_0 \times 100\% \qquad (1)$$

Swelling ratio analysis

The swelling ratio was also evaluated by immersing equal quantities of dried hydrogels (W_0) in deionized water at room temperature overnight. Then, the weight of the wet hydrogels (W_e) was determined after wiping off surface water. The swelling ratio of the hydrogels was obtained by Equation (2).[3]

$$\text{Swelling ratio } \% = (W_0 - W_e) / W_0 \times 100\% \qquad (2)$$

Adsorption measurements of metal ions by hydrogels

The adsorption ability of the optimum CMC/PVA hydrogels toward Cu^{2+} and Zn^{2+} was estimated by immersing 1 cm^2 × 1 cm^2 of hydrogels in 100 mL of Cu^{2+} and Zn^{2+} solutions, with the concentration of 1000 mg/L (ppm), for 24 h at room temperature. Competitive adsorption was also evaluated by immersing the hydrogel into binary metal ion solutions. The ion content of the solution for various intervals of immersion time was obtained using ICP (inductively coupled plasma). ICP analyses were performed using a flame atomic absorption device (VARIAN FAAS model AA240).

The atomic absorption is based on the radiation and absorption of neutral atoms at a temperature less than the radiation spectrum (2000 °C). The solution containing the measuring ion is burned at 2000° in order to neutralize most of the ions in the solution. After this steaming step, the remaining ions are neutralized by a cathode lamp (a special lamp for each element). Thus, the radiation intensity of the primary radiation is decreased. The difference between the intensities corresponds to the concentration of the ions in the solution. Then, by calculating the radiation absorbed by the detector and the calibration curves, the ion concentration in the solution can be obtained.[7,8]

Table 1
Experimental data and response characteristics in preparation of PVA/CMC composite hydrogel

Sample No.	Freeze time (h)	Cycle	Swelling (% w/w)	Gel fraction (% w/w)
1	9	8	119	72
2	9	8	112	69
3	9	8	110	78
4	9	8	110	66
5	9	8	114	70
6	10	8	116	76
7	9	5	110	88
8	7	10	130	90
9	7	6	145	88
10	11	10	145	88
11	11	6	104	94
12	9	8	110	69
13	9	8	110	77
14	9	8	110	69
15	6	8	122	77
16	9	11	145	98

FE-SEM

The morphology of the hydrogels was observed using a FE-SEM scanning electron microscope (TESCAN MIRA3-FEG-SEM, USA). The final ion-adsorbed optimum hydrogels were dried and coated by a thin layer of gold.[7]

Experimental design and statistical analyses

To study the effect of selected process parameters, namely, the number of freeze–thaw cycles and the freezing time in each freeze–thaw cycle, on the swelling ratio and the gel fraction of the obtained CMC/PVA composite hydrogels, as well as to attain the best hydrogels with the highest gel fraction and swelling ratio, response surface analysis with a central composite design was used. The results were evaluated through ANOVA, the regression and optimization results of the applied statistical analysis, as well as the created contour and 3D plots of response changes by independent process factors. 16 hydrogels were prepared using various numbers of freeze–thaw cycles at various freezing time (Table 1), and Minitab 17 software was used to evaluate the linear, quadratic and interaction effects of the selected processing parameters on the characteristics of the obtained hydrogels. The number of freeze–thaw cycles and the freezing time differed at 5 levels, coded as -1, -α, 0, +α and +1. At the coded level of 0, samples preparation was repeated 8 times in order to estimate the associated variability and exclude it from the analysis. Moreover, the experiments were performed randomly to avoid systematic errors. Various polynomial second order equations were suggested by regression analysis in order to predict the changes of hydrogel characteristics caused by the studied process variables. The significance of either linear, quadratic or interaction terms of the suggested model was also evaluated by comparing their p-value and F-ratio, obtained by ANOVA analysis, in which the terms with p-value <0.05 were considered as significant terms in a 95% confidence interval. Furthermore, according to statistical rules, the terms with a lower p-value and a greater F-ratio influence more significantly the variation of each characteristic. Single and multiple optimizations were also performed in order to find the optimum number of freeze–thaw cycles and freezing time leading to the preparation of hydrogels with the highest swelling ratio and gel fraction, individually or in combination.[9,10]

To find the best kinetic model explaining the adsorption kinetics of Cu^{2+} and Zn^{2+} onto the PVA/CMC hydrogels prepared under optimum process conditions, regression analysis (nonlinear regression) was used.[11] The experimental design, statistical analysis and model presentation were carried out using Minitab 17 statistical software.

RESULTS AND DISCUSSION

General aspects

The CMC/PVA hydrogels were prepared through freeze−thaw cycles, in which during the freezing process, the frozen water in the CMC-PVA mixture led to phase separation into a water-rich phase and a polymer-rich phase. The polymer chains in the polymer-rich area created hydrogen bonds and crystallites. The thawing process promoted the interactions between the polymers and the crystalline regions. Thus, the hydrogel networks were created. The ice crystals also gave a porous structure to the hydrogels and acted as porogens during the melting process.[1,3]

The gel fraction and swelling ratio of the achieved products varied from 66 to 94% and from 104 to 145%, respectively. The second order polynomial equations could predict the variation of these characteristics as a function of freezing time and number of cycles, with acceptable precision ($R^2 > 82\%$). Thus, more than 82% of the data could be estimated by the presented models. While the number of freeze−thaw cycles had a higher effect on the gel fraction of the hydrogels, the swelling ratio was more significantly influenced by the freezing time.

Gel fraction

The regression analysis and ANOVA results with regard to the gel fraction of the samples were listed in Table 2. According to Table 2, the quadratic term of the number of cycles with the lowest p-value, at 95% confidence interval, was the most significant term for the gel fraction of the prepared hydrogels. Regarding the R^2 value of the suggested model for this response, 82% of the points followed the proposed model.

The gel fraction variation of the CMC/PVA hydrogels as a function of the studied independent variables is shown in Figure 1. As can be seen in Figure 1, the gel fraction of the hydrogels decreased by increasing the freezing time up to a certain time period (between 8 and 9 h), but a higher increase of the freezing time led to a significant rise of this response. A similar trend was also observed for the gel fraction as a function of the number of cycles. Thus, repeating the freeze−thaw process several times (approximately 8) would minimize the gel fraction of the samples, which is not desired. It can also be concluded that fewer freeze−thaw cycles at longer freezing time or shorter freezing time with more freeze−thaw cycles led to the production of hydrogels with the highest gel fraction.

The negative coefficient of the linear term of either freezing time or number of cycles, as well as the positive sign of their quadratic terms (Table 2) reconfirmed the mentioned trends.

Table 2
Model coefficients, p-value and F-ratio obtained from the analysis of variance of freezing time and number of cycles for swelling ratio and gel fraction in the preparation of PVA/CMC composite hydrogels

Model terms	Swelling ratio (%, w/w)			Gel fraction (%, w/w)		
a_0	p	F	Coefficients	p	F	Coefficients
a_1	0.000	2569	592.7	0.000	1712	303.2
a_2	0.043	5.55	-55.3	0.880	0.20	-23.1
$a_1 \times a_1$	0.089	3.64	-60.8	0.642	0.23	-33.9
$a_2 \times a_2$	0.090	3.60	1.433	0.023	7.49	1.585
$a_1 \times a_2$	0.019	8.19	2.122	0.002	18.03	2.417
R^2	83.89%			82.06%		

a_0 is constant, a_1 and a_2 are linear coefficients, $a_1 \times a_1$ and $a_2 \times a_2$ are quadratic terms and $a_1 \times a_2$ is interaction term, 1 represents freezing time and 2 represents number of cycles

In fact, when the gels prepared by the freeze−thaw process are placed in water, upon water penetration into the gel structure, two main processes occur in opposite directions, namely, melting of smaller crystalline areas and dissolution of a number of PVA chains in the resulted water.[3,6,12] In the first stage, due to the low polymer content, the amount of polymer chains participating in the formation of crystalline structures was lower. However, by increasing the number of freeze−thaw cycles, the amount of water absorbed by the hydrogels decreased, which revealed that by increasing the number of cycles, the gels exhibited a denser structure and the number of PVA chains in the formation of crystalline structures would be increased. If gels formed by the freeze–thaw process are immersed into water, over time, their weight will be lower than their initial weight, and as a result, the gel fraction of the hydrogels will decrease. This can be explained by extreme gel densities and the elimination of some of the water present in these gels, as well as by the reduction of the chains (PVA) in water.[1,3,13]

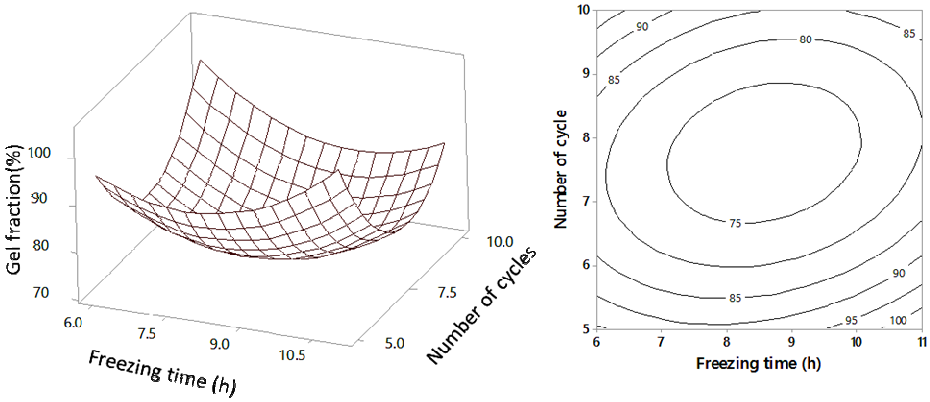

Figure 1: Effects of freezing time and number of cycles on gel fraction of hydrogels

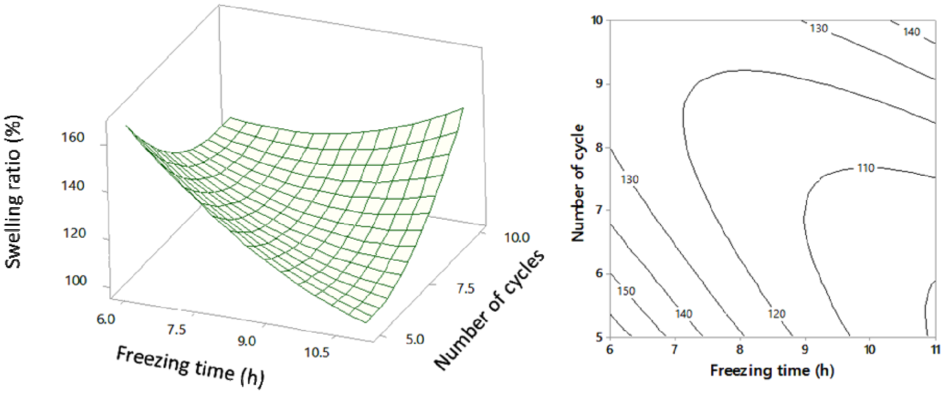

Figure 2: Effects of freezing time and number of cycles on swelling ratio of hydrogels

Swelling ratio

The regression coefficients of the suggested model, predicting the variation of the swelling ratio of the hydrogels by the number of freeze–thaw cycles and freezing time in each cycle, as well as the p-values and F-ratio of each term, are shown in Table 2. As can be observed, while the linear term of the number of cycles and the quadratic term of the freezing time were insignificant in relation to the swelling ratio of the hydrogels at a 95% confidence interval, all the linear, quadratic and interaction terms were significant with regard to this response at a 90% confidence interval (p-value <0.1). The interaction term had the greatest effect on the variation in the rate of inflation of the hydrogels. According to R^2 = 83.89%, more than 83% of the swelling ratio of the hydrogels can be predicted by the suggested model.

The negative coefficient of the linear terms of either the freezing time or the number of freeze–thaw cycles (Table 2), as well as the positive sign of their quadratic terms, indicated that, by increasing the freezing time and the number of freeze–thaw cycles up to a certain point, the inflation rate decreased. However, further increase of these parameters adversely affected the behaviour of the hydrogels, increasing their inflation. This trend can be seen in Figure 2, especially at low levels of freezing time, with the increase in the number of cycles, and at high levels of the number of cycles, with the increase in the freezing time. However, the decrease of the swelling ratio with increasing freezing time, and the increase of this response with increasing number of cycles were the prevailing trends observed at low levels of the number of cycles and high levels of freezing time, respectively. During the freezing stages, the water in the PVA and CMC mixed solution was frozen at low temperature, which caused the phase separation into a polymer-rich phase and a water-rich phase. The polymer chains in the polymer-rich phase caused the development of hydrogen bonding and crystallites. In addition, the thawing procedure facilitated the interactions and the crystalline regions between the remaining polymers, leading to the formation of hydrogel networks.[1-3,14] Also, when the polymer was subjected to low temperatures under freezing conditions, their structure became more compacted, forming a water-insoluble polymer network. By repeating the freeze−thaw cycles, the crystals of frozen water melted, thus creating free space and imparting a porous nature to the polymer. This porous nature of hydrogels with high surface area offers penetration sites for water absorption and metal ions adsorption as well.[3,6,15] As the freeze−thaw cycles increased, the weight of the swollen gel (W_t) decreased relative to the dry gel weight (W_d) and, consequently, this difference reduces the percentage of hydrogel inflation.

In general, the increase of freeze−thaw cycles or freezing time would increase the strength of the produced hydrogel network. The simultaneous increase of both parameters leads to the production of composites with a very rigid network. It seems that a greater amount of water can slowly penetrate into this rigid polymeric network. Thus, after immersion of the hydrogel into water for sufficient duration, the hydrogels can swell greatly and absorb large quantities of water.[1-3,14]

Optimization and validation

Single and multiple parameter optimizations were performed in order to find the best process conditions allowing to obtain hydrogels with the highest gel fraction and swelling ratio. The results of the optimization process indicated that using 5 freeze−thaw cycles and freezing time periods of 11 and 6 hours would give hydrogels with the highest gel fraction (≈100%) and swelling ratio, respectively. The multiple parameter optimization also suggested that freezing the hydrogels for the minimum time period (5 hours), thawing them at room temperature and the repetition these freeze−thaw cycles for 5 times would yield the best hydrogels, with the highest values of both: gel fraction and swelling ratio. Under these optimum process conditions, the achieved hydrogels exhibited 97% gel fraction and 166% swelling ratio.

The validation analysis was also performed by comparing the experimental data with the ones estimated by models, using the t-test. The obtained p-value (equal to 1) > 0.05 and F-ratio (equal to zero) confirmed the suitability of the model. Moreover, hydrogels were also prepared according to the optimum suggested process conditions (freezing time = 5 h, number of cycles = 5), with three replications, and were subjected to gel fraction and swelling ratio measurements. The obtained experimental data (gel fraction = 97±0.9% and swelling ratio = 171±6.1%) were also compared with the predicted ones using the Tukey test. No significant differences between the two sets of data have reconfirmed the accuracy of the model.[9]

Adsorption kinetics

The adsorption kinetics of Zn^{2+} and Cu^{2+} ions onto the optimum CMC/PVA hydrogels was also studied, fitting the various functions of ion concentrations *versus* time to common kinetic models and calculating their R^2 values. The results are listed in Table 3.

Regarding the R^2 of the fitted equations, it can be concluded that the linear equation between the log of ion concentrations *vs*. time with the highest R^2 is the most suitable for describing the adsorption of all ions onto the optimum prepared PVA/CMC hydrogel. Thus, the kinetics of adsorption follows 1st order kinetics.

Cu^{2+} ions showed a higher adsorption rate than Zn^{2+} ions. This finding is in agreement with those of previous research, which demonstrated that Cu^{2+} could be adsorbed faster and better by various adsorbents, compared to other heavy metal ions, such as Ni^{2+}, Co^{2+}, Zn^{2+} *etc*.[16,17] The 1st order kinetic model is constructed on the postulation that the adsorption procedure is physical and depends on the presented metal ions' concentrations in the aqueous solution and the accessible sites on the adsorbent hydrogel at any specific time period.[11,18]

Table 3
Kinetics of metal ion adsorption onto PVA/CMC composite hydrogel

Common kinetic models		Cu	Zn	Binary (Zn+Cu)
Rate = K	Equation	0.1723t + 988.13	C = 0.1987t + 986.53	C = 0.371t + 1974.7
Linear	R^2	0.8342	0.9650	0.9306
Rate = KC	Equation	LnC = 0.0002t+6.8958	LnC = 0.0002t + 6.8944	LnC = 0.0002t + 7.5882
1st order	R^2	0.9641	0.9901	0.9805
Rate = KC^2	Equation	1/C = -2E-07t+0.001	1/C = -2E-07t + 0.001	1/C = -9E-08t + 0.0005
2nd order	R^2	0.8340	0.9398	0.9304
Rate = $\frac{KC}{KC + Vm}$	Equation	1/C = 3E-06 (1/t) + 0.001	1/C = 4E-06 (1/t) + 0.001	1/C = 2E-06 (1/t) + 0.0005
Michaelis–Menten	R^2	0.5968	0.7617	0.7326
Rate = KC^n Logarithmic	Equation	Ln C = 0.001 (Ln t) + 6.8957	Ln C = 0.0013 (Ln t) + 6.8939	Ln C = 0/0011 (Ln t) + 7.588
	R^2	0.7052	0.9517	0.8564

Thus, it can be concluded that physical adsorption governed the adsorption process of the studied ions by the prepared hydrogels. In addition, the obtained R^2 values for either the 2^{nd} order or the logarithmic kinetic equations (>0.80) indicated that limited ion diffusion and chemical adsorption also occurred in this system.

Therefore, the diffusion was not the rate-limiting step and the ions could easily enter the hydrogel matrix, and due to the surface area of the hydrogel, they would physically bind to the functional groups of CMC and PVA in the hydrogel structure.[6,11]

Morphology

According to Figure 3 A and B, the optimum CMC/PVA hydrogels present cylindrical to spherical porous structure, with irregular distribution of pores. The micrographs of the prepared hydrogels reveal that the particle sizes are in the nano ranges. Thus, the resulting hydrogels are nanostructured and have a particle size range of 20-30 nm. The adsorption of ions onto the hydrogels increased the mean sizes of the pores due to the ion-gelation effect. These results are compatible with previous findings reported for polysaccharide-based hydrogels. Previous studies concluded that the swelling ability of hydrogels determines their pore sizes. Accordingly, the hydrogels with adsorbed ions have lower water uptake and, consequently, larger pore sizes, as compared to fresh hydrogels.[18,19]

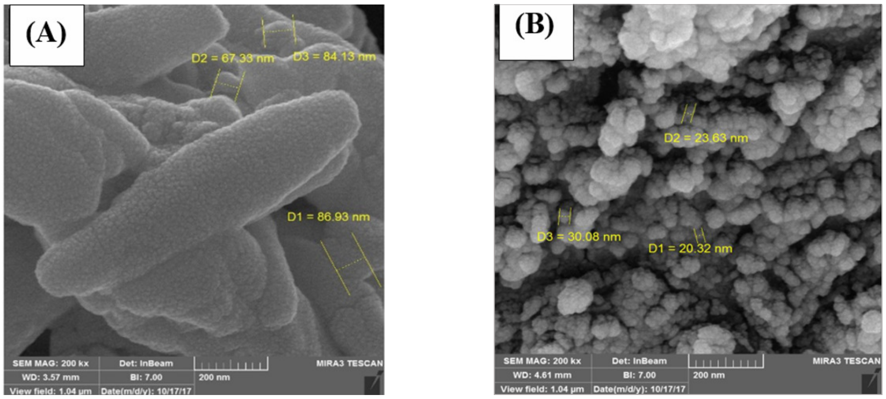

Figure 3: SEM images of (A) PVA/CMC hydrogels after adsorption and (B) before adsorption

CONCLUSION

PVA/CMC hydrogels were prepared using the freeze−thaw technique. Response surface methodology was successfully applied to study the effects of process conditions, namely, freezing time and number of freeze−thaw cycles on the gel fraction and swelling ratio of the hydrogels and to optimize them in order to achieve the most desirable hydrogels, with maximum gel fraction and swelling ratio. Second order polynomial equations were also suggested to predict the variation of the responses as a function of the selected parameters. The prepared optimum CMC/PVA hydrogels had nano-sized structure and could successfully adsorb Zn^{2+} and Cu^{2+} ions, the adsorption process following zero-order kinetics. In conclusion, the prepared PVA/CMC composite hydrogels showed excellent adsorption capacity for the adsorption of heavy metal ions. Therefore, the CMC/PVA hydrogel can be a prospective candidate for several applications, including elimination and recovery of heavy metal ions, as well as the synthesis of metal/PVA/CMC composites for various biomedical applications.

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