

Optimization of Synthesis Conditions of a Novel Carrageenan-Based Superabsorbent Hydrogel by Taguchi Method and Investigation of Its Metal Ions Adsorption

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ABSTRACT: The Taguchi method, a robust experimental design, was used for optimization of synthesis of a novel biopolymer-based superabsorbent hydrogel, kappa-carrageenan (κ -C)-*g*-acrylic acid (AA)-*co*-2-acrylamido-2-methylpropanesulfonic acid (AMPS). The Taguchi method was applied for the experimental and standard 18 orthogonal arrays (OA) with seven factors and three levels for each factor. In the synthesis of the superabsorbent, *N,N'*-methylene bisacrylamide (MBA) as crosslinker, ammonium persulfate (APS) as initiator, monomer ratio (AA/AMPS), κ -C concentration, Total Monomer, neutralization percent (NU), and reaction temperature were used as important factors. After analyzing with analysis of variance (ANOVA) results

showed that maximum water absorption capability for optimized final product was found to be 1195 g water per one gram of dry hydrogel powder. The proposed mechanism for the grafting and chemically crosslinking reactions was proved with FTIR, SEM, and TGA methods. Furthermore, the absorption capability of the hydrogels towards bivalent metal ions was evaluated. Therefore, the hydrogels may be based-considered as a candidate to develop an efficient bio-film absorbent in water treatment applications. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 2970–2976, 2008

Key words: superabsorbent; Carrageenan; acrylic acid; Taguchi method; metal absorption

INTRODUCTION

Because of their extensive application in various industries, materials with the high ability of water absorption have remained as an important topic in research and investigations. Some of these materials are polymers which can absorb water up to few hundred times of their own weight. These polymers are often called water superabsorbents or polymer hydrogels.^{1–9} A kind of superabsorbent polymers have been emerged in recent years possessing polysaccharide base. These polymers are synthesized by graft copolymerization of vinylic monomers such as acrylonitrile, acrylamide, and acrylic acid onto polysaccharides such as starch, chitosan, and cellulose.^{10–12}

According to World Health Organization, the metals of most immediate concern are chromium, nickel, copper, lead, mercury, and zinc. Usually, while using methods such as chemical precipitation and reverse osmosis for the removal of metal ions from their aqueous solutions, metal removal is incomplete. Moreover, these processes have high reagent and energy requirement and the toxic sludge produced requires careful disposal. The need for cost-effective and safe methods for removing toxins has resulted in the development

of polymeric and co-polymeric materials, which have the ability to remove metal ions through complexation and ion-exchange mechanism. Recently, considerable interest has been generated in the development of such polymeric materials, as a tool for removing metal ions in polluted surface waters. Most of the polymeric materials employed for this purpose are usually resins.^{13,14} In addition to ion-exchange resins, swellable hydrogels have also been used for the same purpose. A novel chelating hydrogel system, based on *N*-vinyl imidazole and acrylonitrile, has been developed for removing uranyl ions from sea water.¹⁵

The Taguchi method¹⁶ is a powerful design of experiments developed by G. Taguchi. It provides a simple, efficient, and systematic approach to optimize the designs for performance, quality, and cost. The parameter design is the key step in the Taguchi method to achieve high quality without increasing cost and the same is adopted in this paper. The evaluation of results has been standardized by this method, which can easily be applied by researchers. Among other advantages of Taguchi method, one can name the possibility of performing experiments in a parallel form.^{17–22}

In this work, optimization of synthetic conditions of a carrageenan-based hydrogel to achieve maximum water absorbency was performed by Taguchi method. Also its absorbency of heavy metal ions was studied.

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TABLE I
Experimental Layouts of an L₁₈ Orthogonal Array
According to Taguchi's Suggestion (the Numbers in Each
Column Indicate the Levels for the Specific Factors)

Trial number	Factor and their levels						G
	A	B	C	D	E	F	
1	1	1	1	1	1	1	1
2	1	2	2	2	2	2	2
3	1	3	3	3	3	3	3
4	2	1	1	3	2	3	3
5	2	2	2	2	3	1	1
6	2	3	3	1	1	2	2
7	3	1	2	1	3	2	3
8	3	2	3	2	1	3	1
9	3	3	1	3	2	1	2
10	1	1	3	3	2	2	1
11	1	2	1	1	3	3	2
12	1	3	2	2	1	1	3
13	2	1	2	3	1	3	2
14	2	2	3	1	2	1	3
15	2	3	1	2	3	2	1
16	3	1	3	2	3	1	2
17	3	2	1	3	1	2	3
18	3	3	2	1	2	3	1

EXPERIMENTAL

Materials

The polysaccharide, κ -C (Condinson Co., Denmark); MBA, AA, AMPS, Cobalt acetate tetra hydrates (99% purity), copper nitrate monohydrate (99% purity), copper acetate monohydrate (99% purity), nickel acetate tetra hydrate (99% purity), and zinc acetate dihydrate (99% purity) from Merck; APS from Fluka were of analytical grade and used without further purification.

Instrumental analysis

Samples were characterized as KBr pellets using an ABB Bomem MB-100 FTIR spectrophotometer. An atomic absorption spectrometer (Varian AA-5) was used for the measurements of the metal ion absorption. Samples morphology was evaluated by scanning electron microscopy, SEM (Leo, 1455 VP). A simultaneous thermal analyzer (STA-625, Reometric Scientific) was used for thermogravimetric analysis of κ -C, AA co AMPS and carrageenan-g-AA co AMPS hydrogel under nitrogen atmosphere. The heating rate was 20°C/min. The sample weight taken for TG was 10.0 mg.

Experimental design

Selection of factors and their levels

The reaction variables were reaction temperature (T), crosslinking agent (MBA), initiator (APS), monomer ratio (AA/AMPS), κ -C concentration, total monomer, and neutralization percent (NU), which are generally

factors in synthesis of superabsorbents. Three levels for each factor selected as shown in Table II.

Selection of orthogonal array and assignment of factors

Standard tables known as orthogonal arrays (OA) are used for the design of the experiments in the Taguchi method. An OA with a three level and seven factors are shown in Table I.

This OA is particularly designed with the symbol of L₁₈. Each row in the array represents a trial condition with the factor levels, which are indicated by the numbers in the row. The columns correspond to the factors specified in this study and each column contains three levels. Conditions (a total of 18 conditions) for the factors were assigned in Table I. Evaluation of results has been standardized by this method which can easily be applied by other researchers.

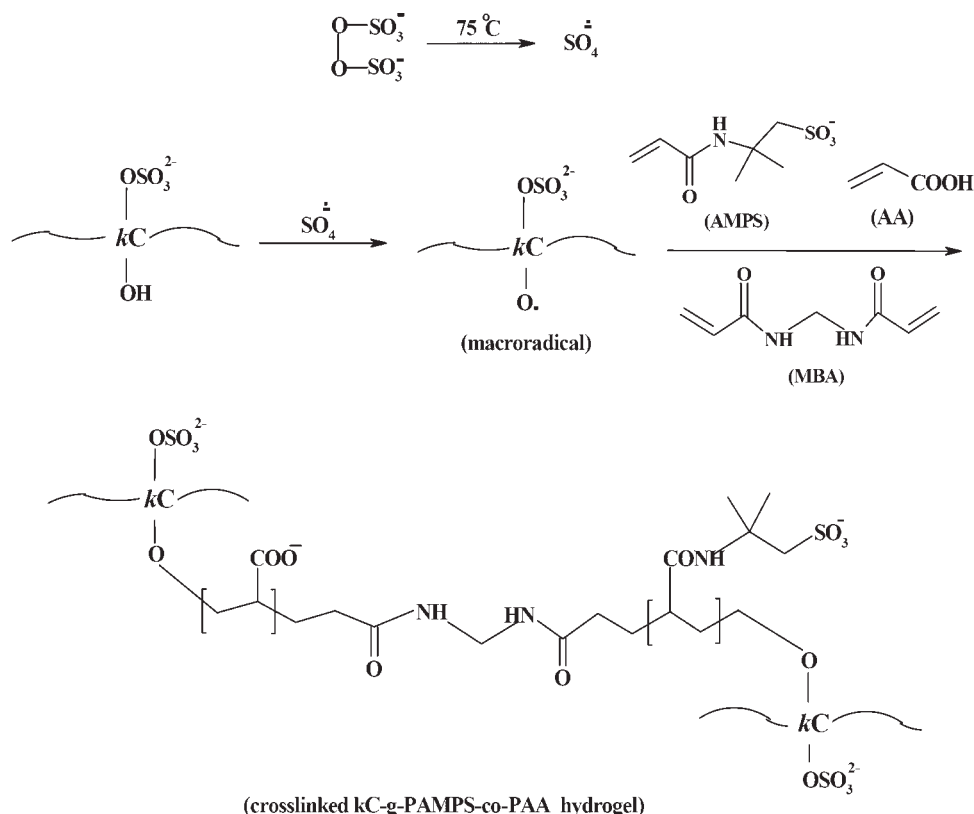
Software package Qualitek-4 version 6.3 was used for Selection of Orthogonal, optimum conditions, and contribution of each factor.²³

Graft copolymerization

Certain amounts of water (25 mL) and κ -C (0.25–0.75 g) were added to a three-necked reactor equipped with a mechanical stirrer (Heidolph RZR 2021). While stirring (200 rpm), the reactor was placed in a thermostat water bath preset at desired temperature (75–85°C) for 20 min. After dissolving κ -C and homogenizing the mixture, the monomers and crosslinker solutions, AA, AMPS, and MBA were simultaneously added and the reaction mixture was stirred for 15 min. Then the APS as initiator was added and gelation was observed after around 10–15 min (final volume of solution = 35 mL). Then the mixture was treated with 1 N sodium hydroxide solution for neutralization (30–50%). The reaction product was allowed to cool to ambient temperature. Ethanol (200 mL) was added to the gelled product while stirring. After complete dewatering for 24 h, the product was filtered, washed with fresh ethanol and dried at 50°C to constant weight. After grinding, the powdered superabsorbent hydrogel was stored away from moisture, heat, and light.

TABLE II
Experimental Control Factors and Their Levels

Control factor	Level 1	Level 2	Level 3
T (°C)	75	80	85
MBA (mol/L)	0.003	0.005	0.007
APS (mol/L)	0.003	0.007	0.011
AA/AMPS (g/g)	50/50	60/40	70/30
Carrageenan (g)	0.25	0.5	0.75
Total Monomer (g)	3.5	4	4.5
Nu %	30%	40%	50%



Scheme 1 A proposed mechanism for synthesis of κ -C-g-PAA-co-PAMPS superabsorbent hydrogel.

Swelling measurements using tea bag method

Tea bag (i.e. a 100 mesh nylon on screen) containing an accurately weight powdered sample (0.1 ± 0.0001 g) with average particle size between 40 and 60 mesh (250–420 μm) was immersed entirely in distilled water (250 mL) or desired salt solution (100 mL) and allowed to soak for 3 h at room temperature. The tea bag was hung up for 15 min in order to remove the excess fluid. The equilibrated swelling (ES) was calculated twice using the following equation:

$$\text{ES}(\text{g/g}) = (W_s - W_d)/W_d \quad (1)$$

Where W_s and W_d are the weights of the swollen gel and the dry sample, respectively. So absorbency was calculated as gram of water per gram of hydrogel (g/g). The accuracy of the measurements was $\pm 4\%$.

Metal ion sorption measurement

First, solutions with a concentration of 2000 ppm from copper acetate, cobalt acetate, nickel acetate, and zinc acetate were prepared in Erlenmeyer flasks. Exactly 0.500 g optimized final hydrogel (particle size of 250–420 μm) was added to each flask. The mixture was shaken for 24 h by a rotary shaker to complete the equilibrium. An exact amount of the

supernatant (5.0 mL) was pipetted for metal ion measurements. Metal ion absorbed was measured and by subtracting the final amount of ion from the initial one, absorbed amount calculated. Wavelengths applied for Copper acetate, Nickel acetate, Cobalt acetate, and Zinc acetate were 324, 232, 240.7, and 213.9 nm, respectively.

RESULTS AND DISCUSSION

Mechanism of hydrogel formation

Crosslinking graft copolymerization of AA and AMPS onto κ -C was carried out by using of APS as a free radical initiator and MBA as a hydrophilic crosslinker. The proposed mechanism for the grafting and chemically crosslinking reactions are outlined in Scheme 1. The persulfate initiator is decomposed under heating to generate sulfate anion-radical. The radical abstracts hydrogen from the hydroxyl group of the κ -C to form alkoxy radicals on the substrate. So this persulfate-saccharide redox system results in active centers on the substrate in order to radically initiate polymerization of AA-co-AMPS leading to a graft copolymer. Since a crosslinking agent, e.g. MBA, presents in the system, the copolymer comprises a crosslinked structure. A similar observation was recently reported by

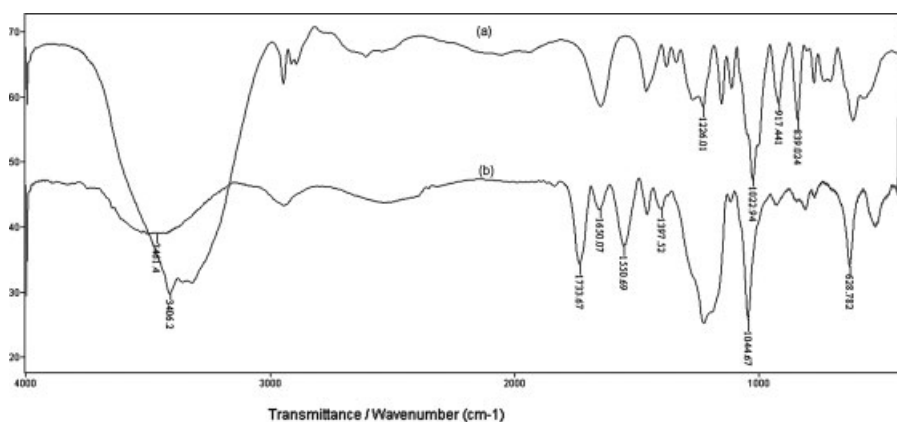


Figure 1 FTIR spectra of κ -C (a) and crosslinked κ -C-g-PAA-co-PAMPS (b).

Hsu et al. in the case of degradation of chitosan with potassium persulfate.²⁴

Spectral characterization

The grafting was confirmed by comparing the FTIR spectra of the polysaccharide substrate with the grafted products. Figure 1 shows the FTIR spectra of polysaccharide, κ -C (a), and κ -C-g-PAA-co-PAMPS (b). The bands at 839, 917, 1022, and 1226 cm^{-1} can be attributed to D-galactose-4-sulfate, 3,6-anhydro-D-galactose, glycosidic linkage and ester sulfate stretching of κ -C backbone, respectively [Fig. 1(a)]. The broad band at 3406 cm^{-1} is due to stretching of —OH groups of κ -C. The FTIR spectrum of the κ -C-g-PAA-co-PAMPS [Fig. 1(b)] shows seven new characteristic absorption bands at 1733 cm^{-1} (carbonyl stretching of the carboxylic acid group), 1550 cm^{-1} (symmetric stretching mode of carboxylate group), 1397 cm^{-1} (asymmetric stretching modes of carboxylate group), 1650 cm^{-1} (stretching mode of amide group), 1044 cm^{-1} (stretching mode of SO group), 1226 cm^{-1} (stretching mode of CO), 3461 cm^{-1} (stretching mode of OH group) verifying the formation of graft copolymer product.

Thermal characterization

The grafting was confirmed by comparing the DTGA profile polysaccharide with the grafted products. The grafted κ -C has shown improvement in thermal stability as clear from DTGA curves (Fig. 2). The maximum decomposition rate at 251, 376, and 416°C can be attributed to κ -C [Fig. 2(a)], κ -C-g-AA-co-AMPS [Fig. 2(b)] and, AA-co-AMPS [Fig. 2(c)], respectively. These observations have clearly indicated that grafting of poly (AA-co AMPS) has improved the thermal stability of κ -C.

Optimization of the grafting conditions

The relationship between the swelling ratio and network structure parameters given by Flory²⁵ is usually used as the following Equation:

$$q_m^{5/3} \cong \frac{(i/2v_u S^{*1/2})^2 + (1/2 - \chi_1)/v_1}{v_e/V_0} \quad (2)$$

where q_m is the swelling ratio; i/v_u is the concentration of the fixed charge of the no swollen networks; S^* is the ionic strength of the swollen solution; v_e/V_0 is the crosslinking density which refers to the number of effectively crosslinked chains in unit volume. The term $v(1/2 - \chi_1)/v_1$ stands for the network-medium affinity.

According to Eq. (2), different variables affect the ultimate swelling capacity (i.e. T, MBA, APS, AA/AMPS, κ -C concentration, Total Monomer, and NU). After identification of the effective parameters (factors) in the reaction, based on past experiences about synthesis of hydrogels, levels of factors were determined (Table II). After selection of factors and their levels, an orthogonal array appropriate for seven factors with each factor in three levels should be applied. Software Qualitek-4 proposes the L18 OA

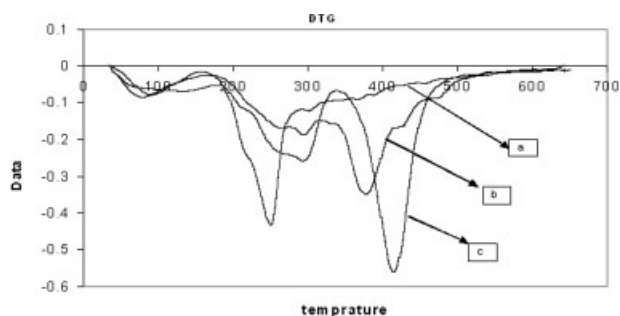


Figure 2 DTGA thermograms of κ -C (a), crosslinked κ -C-g-PAA-co-PAMPS (b) and AA-co-AMPS (c) superabsorbent. Heating rate 20°C/min, under N₂.

TABLE III
Methods of Performing Experiments According to Orthogonal Array (L18)

Trial number	T (°C)	MBA (mol/L)	APS (mol/L)	AA/AMPS (g/g)	Carrageenan (g)	Total monomer (g)	Nu %
1	75	0.003	0.030	1.75/1.75	0.25	3.5	30
2	75	0.005	0.007	2.4/1.6	0.5	4	40
3	75	0.007	0.011	3.15/1.35	0.75	4.5	50
4	80	0.003	0.003	2.7/1.8	0.5	4.5	50
5	80	0.005	0.007	2.45/1.05	0.75	3.5	30
6	80	0.007	0.011	2/2	0.25	4	40
7	85	0.003	0.007	2/2	0.75	4	50
8	85	0.005	0.011	2.7/1.8	0.25	4.5	30
9	85	0.007	0.003	2.45/1.05	0.5	3.5	40
10	75	0.003	0.011	2.8/1.2	0.5	4	30
11	75	0.005	0.003	2.25/2.25	0.75	4.5	40
12	75	0.007	0.007	2.1/1.4	0.25	3.5	50
13	80	0.003	0.007	3.15/1.35	0.25	4.5	40
14	80	0.005	0.011	1.75/1.75	0.5	3.5	50
15	80	0.007	0.003	2.4/1.6	0.75	4	30
16	85	0.003	0.011	2.1/1.4	0.75	3.5	40
17	85	0.005	0.003	2.8/1.2	0.25	4	50
18	85	0.007	0.007	2.25/2.25	0.5	4.5	30

(Table I). Methods of performing experiments were given in Table III. After synthesis of 18 hydrogels with conditions proposed by Taguchi statistical method, results for their water absorption are given in Table IV.

Finding the optimum conditions and contribution of each factor was performed by ANOVA analysis neglecting the interaction between factors. Optimum conditions proposed by software Qualitek-4, after analysis performed by this software, are shown in Table V. It refers to reaction with 1195 (g water/g dried gel) in which the optimum conditions are as follow: T, 75°C; MBA, 0.003 (mol/L); APS,

0.003 (mol/L); AA/AMPS, 2/2 (g/g); κ -C concentration, 0.25 (g); Total Monomer 4 (g); NU 30%.

Scanning electron microscopy

Hydrogel water absorbency and its retention rate depend on hydrogel porosity and mean pore size. Hence, one of the most important properties, which must be considered, is hydrogel microstructure morphologies. Figure 3(a,b) shows the SEM micrographs of κ -C and optimized final product. It is supposed that these surfaces are the regions of water permeation and interaction sites of external stimuli with the hydrophilic groups of the graft copolymers.

Studies on absorption of metal ions

The binding properties of a series of bivalent metal ions, i.e. copper, cobalt, nickel, and zinc with optimized final product were determined. The copper sorption capacity was the highest with 4.3 mmol g⁻¹. The sorption capacities of cobalt, nickel, and zinc were measured as 2.31, 3.13, and 2.18 mmol g⁻¹, respectively. Therefore, the adsorption capacities were

TABLE IV
Experimental Results for Swelling of Superabsorbents for 18 Trials

Trial number	ES (g water/g dried gel)
1	1170.7
2	697.1
3	252.5
4	807.6
5	618.4
6	465.1
7	829
8	517.9
9	543
10	973
11	747.6
12	360.2
13	631.9
14	549.2
15	464.4
16	1055.1
17	430.6
18	707.4

TABLE V
Optimum Conditions

Factor	Level description	Optimum condition
T (°C)	1	75
MBA (mol/L)	1	0.003
APS (mol/L)	1	0.003
AA/AMPS (g/g)	1	2/2
Carrageenan (g)	1	0.25
Total monomer (g)	2	4
Nu%	1	30

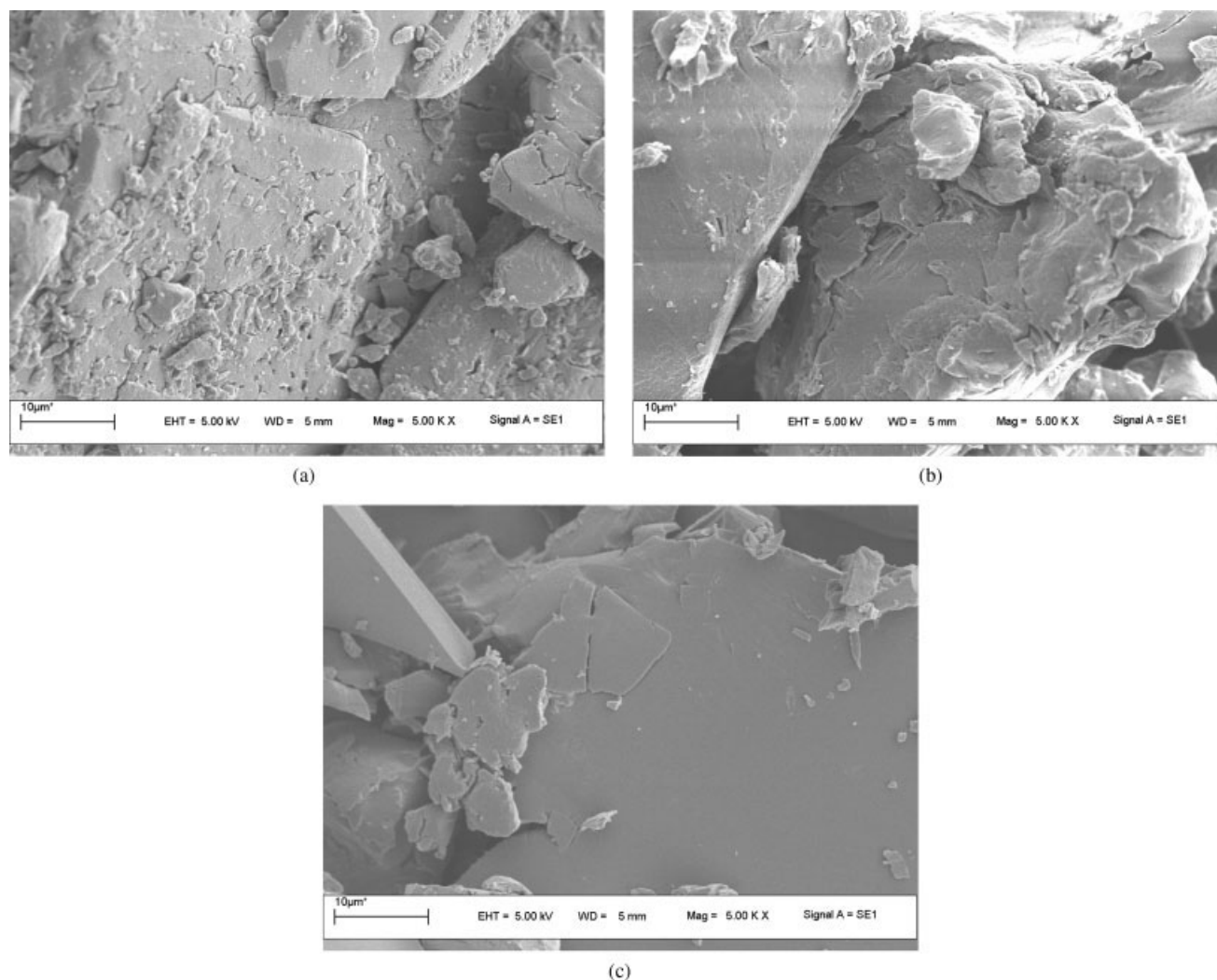


Figure 3 SEM photographs of κ -C (a), optimized final product before absorption (T, 75°C; MBA, 0.003 (mol/L); APS, 0.003 (mol/L); AA/AMPS, 2/2 (g/g); κ -C concentration, 0.25 (g); Total Monomer 4 (g); NU 30%) (b) And after absorption (c).

found to be in order $\text{Cu}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+} > \text{Zn}^{2+}$. A brief comparison of the metal ion sorption capacity of this hydrogel and that of some recently reported hydrogels is given in Table VI.^{26–30}

After the adsorption process, the resin with adsorbed Cu^{2+} was observed by SEM. The morphology with a magnification of 5000× of the loaded and unloaded resins is shown in Figure 3(b,c). The SEM

TABLE VI
A Comparison Between the Metal Ion Absorption (mmol/g) of the Hydrogel with Optimized Final Product (T, 75°C; MBA, 0.003 (mol/L); APS, 0.003 (mol/L); AA/AMPS, 2/2 (g/g); κ -C concentration, 0.25 (g); Total Monomer 4 (g); NU 30%) Repaired in the Present Work and Some Known Commercial/Reported Superabsorbent Hydrogels

Hydrogel	(mmol metal/ 1g dried gel)	Reference
Cellulose-based IPN	$\text{Cu}(\text{NO}_3)_2/7.8$	26
Phosphated cellulose	$\text{Cu}(\text{NO}_3)_2/0.014$	27
Carboxymethyl starch	$\text{Cu}(\text{NO}_3)_2/2.5$	28
Starch-g-poly(acrylamide)	$\text{Hg}(\text{NO}_3)_2/7.3$	29
Poly(sodium acrylate co- acrylamide)	$\text{Cu}(\text{NO}_3)_2/0.0016$	30
κ C-g-poly (AA-co-AMPS)	$\text{Cu}(\text{OAC})_2/4.3$	In this work
κ C-g-poly (AA-co-AMPS)	$\text{Co}(\text{OAC})_2/2.31$	In this work
κ C-g-poly (AA-co-AMPS)	$\text{Zn}(\text{OAC})_2/2.18$	In this work
κ C-g-poly (AA-co-AMPS)	$\text{Ni}(\text{OAC})_2/3.13$	In this work

images visually show the morphological differences of the surface of the resins.

CONCLUSION

Synthesis conditions of κ -C-g-AA-co-AMPS hydrogel were optimized using Taguchi method performing 18 experimental runs. A maximum value of 1195 (g water/g hydrogel) for water absorption was obtained. Main advantages of this method of optimization can be significant reduction in time of optimization and determination of the most suitable conditions resulting in maximum absorption of water. FTIR, SEM and TGA data show grafting and chemical crosslinking.

Also absorption of heavy metal ions such as copper (II), cobalt (II), nickel (II), and zinc (II) was studied. Compared with other Hydrogels given in Table VI an acceptable level of absorption of ions was observed.

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