Optimization of Synthetic Conditions of a Novel Collagen-Based Superabsorbent Hydrogel by Taguchi Method and Investigation of its Metal Ions Adsorption

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ABSTRACT: A novel biopolymer-based superabsorbent hydrogel was synthesized through chemical crosslinking by graft copolymerization of partially neutralized acrylic acid onto the hydrolyzed collagen, in the presence of a crosslinking agent and a free radical initiator. The Taguchi method, a robust experimental design, was employed for the optimization of the synthesis reaction based on the swelling capacity of the hydrogels. This method was applied for the experiments and standard L_{16} orthogonal array with three factors and four levels were chosen. The critical parameters that have been selected for this study are crosslinker (N,N'-methylene bisacrylamide), initiator (potassium persulfate), and monomer (acrylic acid) concentration. From the analysis of variance of the test results, the most effective factor to control equilibrium swelling capacity was obtained and maximum water absorbency of the optimized final product was found to be 500 g/g. The surface morphology of the gel was examined using scanning electron microscopy. Furthermore, the sorption capacity of the hydrogel toward bivalent metal ions was evaluated. Therefore, the hydrogel may be considered as a candidate to develop as an efficient biopolymer-based chelating hydrogel for water treatment. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 4878–4885, 2006

Key words: collagen; hydrogels; taguchi method; swelling; graft copolymers

INTRODUCTION

Superabsorbent polymers (SAPs) are hydrophilic three-dimensional networks that can hold huge amount of water or biological fluids while maintaining the physical dimension structure.[1] These materials have been found to have many applications in agricultural and pharmaceutical industries and other industries where an excellent water-holding property was of prime importance. Some of the most important application of these promising materials includes disposable pads, sheets, and towels for surgery, adult incontinence, and other products. Furthermore, they were introduced to agriculture about 30 years ago to improve the water-holding capacity of sandy soils to promote the germination of seeds and plant growth.[2–6]

Hydrogels made from synthetic polymers, such as polyacrylate possess excellent water-absorbing properties. Despite the advantages of these hydrogels, there are also severe limitations to this type of material which are worth noting. In fact their toxicity and nonbiodegradability might pose long-time environmental problems and limit their use in drug delivery systems and consumer products. Because of these shortcomings, natural-based SAPs have attracted much attention in recent years. Considerable interest has been focused on chemical modification of polysaccharides by grafting of synthetic polymers onto natural ones such as cellulose,[7,8] chitosan,[9,10] agar,[11] Na-alginate,[12,13] starch.[14,15]

Proteins are widely distributed in nature and are synthesized mainly in animals, i.e., collagen, keratin, gelatin, and etc., and in a few plants such as Soya. In general, proteins are high-molecular-weight polymers and their solubility in aqueous solutions is difficult. Two efficient methods for preparation of aqueous soluble proteins are alkaline and enzymatic hydrolysis. Only a few studies have been reported in the case of protein-based SAPs.[16,17]

To optimize the affecting variables on swelling capacity of SAPs, Taguchi method can be used.[18] The Taguchi method[19] is a powerful design of experiments tool developed by G. Taguchi. It provides a simple, efficient, and systematic approach to optimize 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 article. 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.[20–23]

TABLE I
Experimental Control Factors and Their Levels

	MBA (mol/L)	KPS (mol/L)	AA (mol/L)
Level-1	0.0076	0.0006	0.46
Level-2	0.011	0.0015	0.92
Level-3	0.014	0.003	1.39
Level-4	0.017	0.006	1.85

The removal of polluting metal ions from industrial effluents, water suppliers, and mine waters has received much attention in recent years. Various techniques such as filtration, chemical precipitation, neutralization, chelating ion-exchange and adsorption have been evaluated.[24–28] Toxic metal ion removal by using chelating polymers would be of great importance in environmental applications.[29–32] Comparing to industrial ion exchangers, mainly because of very low mechanical strength of the gel particles, SAPs cannot naturally exhibit desired specifications. However, these highly swollen hydrogels have been evaluated for probable applications in ion adsorbers in another way, e.g., in the form of sheets, films, or membranes usable in water treatment.

In continuation of our systematic work on SAPs,[33–38] we now use the Taguchi method for optimization of the crosslinking graft copolymerization of partially neutralized acrylic acid onto the hydrolyzed collagen as a natural polymeric backbone to achieve maximum water absorption. Adsorption of heavy metal ions was also studied.

EXPERIMENTAL

Materials

Hydrolyzed collagen (from Parvar Novin-E Tehran, Iran) was industrial grade containing nearly 25% insoluble phosphate salts. N, N'-Methylene bisacrylamide (MBA, from Merck, Darmstad, Germany), potassium persulfate (KPS, from Fluka, Switzerland), and acrylic acid (AA, from Merk), cobalt acetate tetra hydrates (99%, from Merck), copper acetate monohydrate (99%, from Merck), zinc acetate dihydrate (99%, from Merck), nickel acetate tetra hydrate (99%, from Merck) were of analytical grade and used without further purification. Double distilled water was used for the hydrogel preparation and swelling measurements.

Instrumental analysis

Samples were characterized as KBr pellets using a Mattson-1000 FTIR spectrophotometer. An atomic absorption spectrometer (Varian AA-5) was used for the measurements of the metal ion concentrations. Morphology of the dried gel structures was studied by scanning electron microscopy (SEM). Dried superabsorbent powder were coated with a thin layer of palladium–gold alloy and imaged in a SEM instrument (Leo, 1455 VP).

Experimental design

Selection of factors and their levels

According to the basic knowledge of SAP hydrogels,[1] the concentration of crosslinker (MBA), initiator (KPS), and monomer (AA) are the key synthetic factors affected on the final swelling properties of the hydrogels. These parameters were varied at four levels as shown in Table I. The applied ranges of the variables were based on the literature[1] and our preliminary experiments.

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 four level and three factors are shown in Table II.

This OA is particularly designed with the symbol of L_{16}. 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 four level 1, four level 2, four level 3, and four level 4 conditions (a total of 16 conditions) for the factors assigned to the column. Therefore, the evaluation of results has been standardized by this method, which can easily be applied by researchers.

In this article, the results were analyzed statistically by the analysis of variance (ANOVA) method using Qualitek-4 software.

TABLE II
Experimental Layout of an L_{16} Orthogonal Array According to Taguchi's Suggestion[a]

Trial number	Factors and their levels		
	F1	F2	F3
1	1	1	1
2	1	2	2
3	1	3	3
4	1	4	4
5	2	1	2
6	2	2	1
7	2	3	4
8	2	4	3
9	3	1	3
10	3	2	4
11	3	3	1
12	3	4	2
13	4	1	4
14	4	2	3
15	4	3	2
16	4	4	1

[a] The numbers in each column indicate the levels for the specific factors.

Graft copolymerization

Hydrolyzed collagen (1.33 g) was dissolved in 50 mL distilled water and filtered to remove its insoluble phosphate salts. Then the filtrate was added to a three-neck reactor equipped with a mechanical stirrer (Heidolph RZR 2021, three blade propeller type, 300 rpm). The reactor was immersed in a thermostated water bath preset at 80°C. Then the initiator solution (0.01–0.1 g KPS in 5 mL H₂O) were added to the mixture. After stirring for 10 min, certain amounts of AA (2–8 g) and MBA (0.07–0.16 g) in 5 mL H₂O were added to the reaction mixture. After the completion of the reaction, to neutralize 70% acrylic groups, appropriate amount of NaOH (aq) was added. The obtained gel was poured to excess nonsolvent ethanol (200 mL) and remained for 3 h to dewater. Then ethanol was decanted, and the product cut into small pieces (diameter ∼ 5 mm). Again, 100 mL fresh ethanol was added, and the hydrogel was kept for 24 h. The dried gel particles were filtered and placed in an oven at 45°C for 24 h. After grinding, the powdered superabsorbent hydrogel was stored away from moisture, heat, and light.

Swelling measurements

An accurately weighed sample (0.1 ± 0.0001 g) of the powdered superabsorbent with average particle sizes between 40 and 60 mesh (250–400 μm) was immersed in 200 mL distilled water for 2 h. The equilibrium swelling (ES) capacity was measured twice at room temperature by "tea bag" method and using the following formula:

$$ES \ (g/g) = \frac{W_2 - W_1}{W_1} \qquad (1)$$

where W_1 and W_2 are the weights of dry and swollen gel, respectively.

Swelling kinetics

For studying the rate of absorbency of the hydrogels, certain amount of samples (0.5 ± 0.001 g) were poured into numbers of weighed tea bags and immersed in 200 mL distilled water. At consecutive time intervals, the water absorbency of the hydrogel was measured according to the aforementioned method.

Metal ion sorption measurement

Dried samples (0.500 g each) of hydrogel 2 (particle size 250–400 μm) were equilibrated by stirring for 24 h in 200 mL of 2000 ppm Cu²⁺, Co²⁺, Ni²⁺, and Zn²⁺ solutions at 25°C. An exact amount of the supernatant (5.0 mL) was pipetted for metal ion measurement. The metal ion concentrations in the solutions were measured before and after the gel immersion by dilution to an appropriate concentration with distilled water and measured with atomic absorption spectrometer.
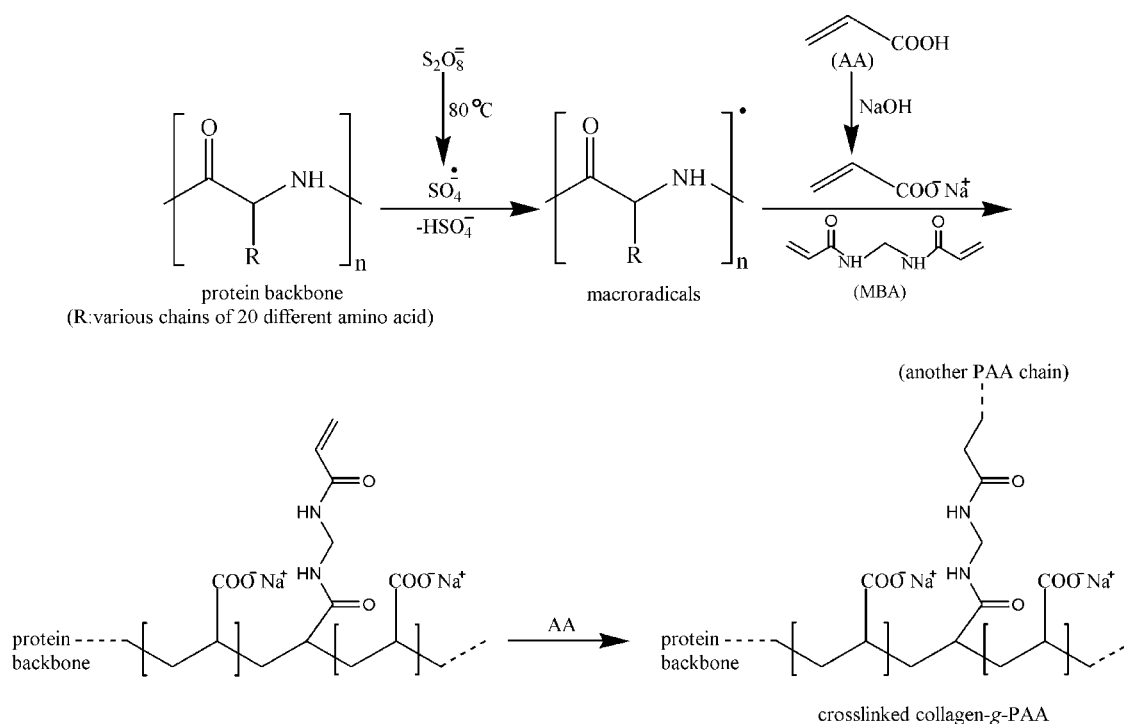
Scheme 1 Proposed mechanistic pathway for synthesis of the collagen-based hydrogel.
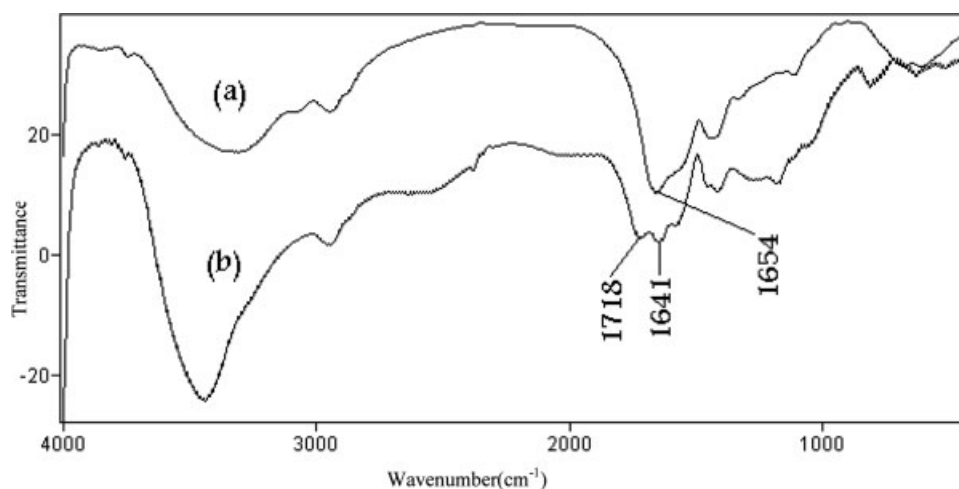
Figure 1 FTIR spectra of hydrolyzed collagen (a) and the collagen-based hydrogel (b).

RESULTS AND DISCUSSION

Synthesis and mechanism aspects

Grafting of AA onto hydrolyzed collagen was carried out by using of KPS 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. Then the anion-radical abstracts hydrogen from one of the existing functional groups in the protein backbone (i.e., COOH, SH, OH, and NH_2) to form corresponding macroinitiator. So, this system results in active centers on the substrate to radically initiate polymerization of AA led to a graft copolymer. Since a crosslinking agent, e.g. MBA, is presented in the system, the copolymer comprises a three-dimensional crosslinked structure.

To obtain additional evidence of grafting, a similar graft copolymerization reaction was conducted in absence of the crosslinker. After extracting the homopolymer (poly acrylic acid), appreciable amount of synthetic polymer percentage of the graft copolymer (80%) were concluded. The graft copolymer spectrum was very similar to Figure 1(b). Also, according to preliminary measurements, the sol (soluble) content of the hydrogel networks was as little as 1.0%. This fact practically proves that all AA is involved in the polymer network. So, the monomer percent in the network will be very similar to that of the initial feed of reaction.

Infrared spectroscopic analysis

The grafting was confirmed by comparing the FTIR spectra of the hydrolyzed collagen with that of the grafted products. Figure 1 shows the FTIR spectra of
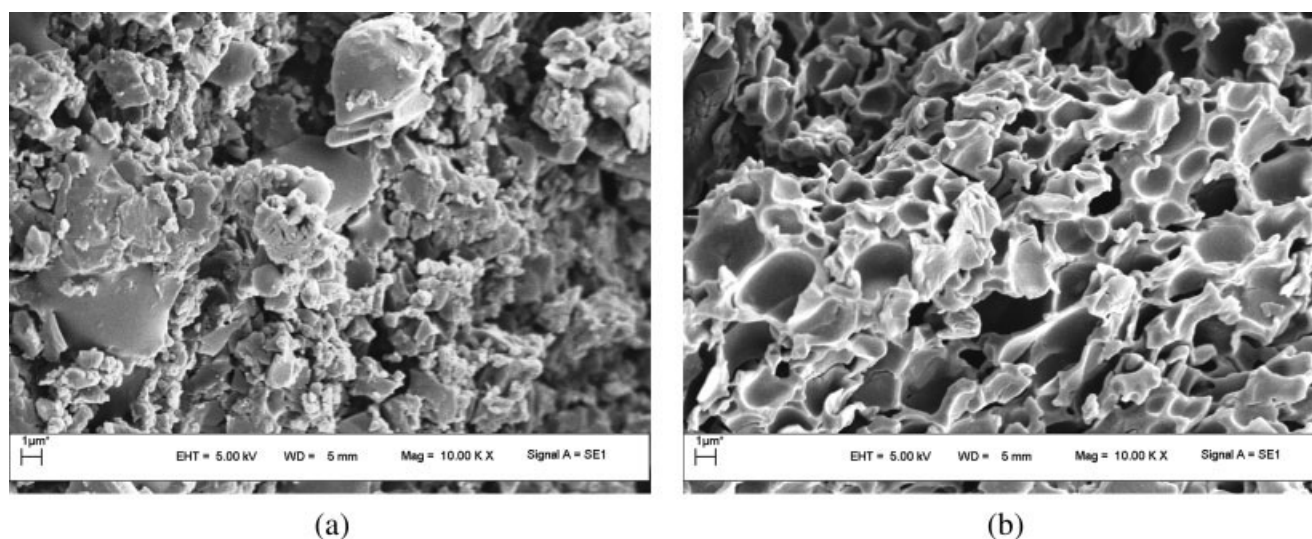

Figure 2 SEM photographs of hydrolyzed collagen (a) and sample 15 (b). Surfaces were taken at a magnification of ×10,000 and the scale bar is 1 μm.

TABLE III
Experimental Layout after Assigning the Values of the Parameters

Trial number	MBA (mol/L)	KPS (mol/L)	AA (mol/L)
1	0.0076	0.0006	0.46
2	0.0076	0.0015	0.92
3	0.0076	0.003	1.39
4	0.0076	0.006	1.85
5	0.011	0.0006	0.92
6	0.011	0.0015	0.46
7	0.011	0.003	1.85
8	0.011	0.006	1.39
9	0.014	0.0006	1.39
10	0.014	0.0015	1.85
11	0.014	0.003	0.46
12	0.014	0.006	0.92
13	0.017	0.0006	1.85
14	0.017	0.0015	1.39
15	0.017	0.003	0.92
16	0.017	0.006	0.46

hydrolyzed collagen and synthesized hydrogel. The band observed at 1654 cm^{-1} can be attributed to C=O stretching in carboxamide functional groups of substrate backbone [Fig. 1(a)]. The broad band at 3200–3600 cm^{-1} is due to stretching of —OH groups of the collagen. The hydrogel comprises a protein backbone with side chains that carry carboxylate functional groups, which are evidenced by two new characteristic absorption bands at 1641 and 1718 cm^{-1} [Fig. 1(b)]. These peaks attributed to symmetric and asymmetric stretching modes of carboxylate groups, respectively.[39]

Scanning electron microscopy

Figure 2 showed the SEM pictures of collagen and sample 15. These pictures verify that graft copoly-

TABLE IV
Experimental Results for Equilibrium Swelling (ES) Capacity

Trial number	ES (g water/g dried gel)
1	0
2	478.6
3	392.9
4	300.8
5	0
6	0
7	272.5
8	234.8
9	0
10	252.8
11	0
12	210.7
13	248.5
14	210.7
15	170.1
16	0

TABLE V
Reaction Composition for the Preparation of Optimized Collagen-_g_-poly(acrylic acid) Hydrogel

Factor	Level description	Optimum conditions
MBA (mol/L)	1	0.0076
KPS (mol/L)	2	0.0015
AA (mol/L)	4	1.85

mers have a porous structure. It is supposed that these pores are the regions of water permeation and interaction sites of external stimuli with the hydrophilic groups of the graft copolymers.

Optimization of the grafting conditions

The relationship between the swelling ratio and network structure parameters given by Flory[40] 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 swelling ratio; i/v_u, is the concentration of the fixed charge of the unswollen 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 sentence $(1/2 - \chi_1)/v_1$ stands for the network-medium affinity.

According to eq. (2), there are many variables affecting the ultimate swelling capacity. Some of these variables have been selected in this research. These parameters and the related levels are presented in Table I. After selecting the mentioned variables, an OA table was formed by Qualitek-4 software (Table II). The experimental layout after assigning the values of the parameters is shown in Table III. According to Table III, 16 experiments were carried out and the ES capacities measured. The test results are shown in Table IV. Having used the Qualitek-4 software, the optimized circumstances and the contribution of each factor are obtained by ANOVA analysis. It should be emphasized that the interaction between the variables were neglected. As it is obvious from Table V, the optimized values of the ES capacity, MBA, KPS, and AA concentration are 500 g/g, 0.0076 mol/L, 0.0015 mol/L, and 1.85 mol/L, respectively. After conducting the synthesis of hydrogel with above optimized

TABLE VI
The ANOVA Table

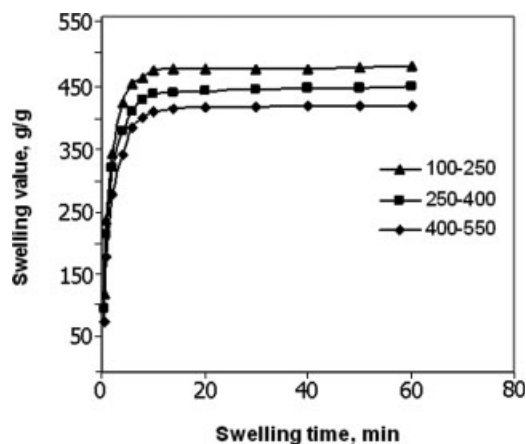| Factor	Degree of freedom	Sum of square	Contribution of factor %
MBA	3	79,685	25.008
KPS	3	70,534	22.137
AA	3	168,406	52.853

Figure 3 Representative swelling kinetics of the collagen-*g*-PAA hydrogel with various particle sizes.

reaction composition for three times and measuring the ES capacities, following data were obtained: 525, 500, 480 (g water/g dried gel). Observed slight errors can be attributed to applied materials and apparatus for the synthesis.

The ANOVA table derived for this study is as shown in Table VI. It can be seen from the ANOVA results, the most effective factor is AA concentration. The contribution of AA is 52.853%, and those of the KPS and MBA are 22.137% and 25.008%, respectively.

Swelling kinetics

In practical applications, not only a higher swelling capacity is required, but also a higher swelling rate is needed. Buchholz has suggested that the swelling kinetics for the superabsorbents is significantly influenced by factors such as swelling capacity, size distribution of powder particles, specific size area, and composition of polymer.[41] Figure 3 represents the dynamic swelling behavior of the superabsorbent samples with various particle sizes in water. Initially,

the rate of water uptake sharply increases and then begins to level off. The time required to reach the equilibrium swelling capacity was achieved after ∼ 20 min. A power law behavior is obvious from Figure 3. The data may be well fitted with a Voigt-based equation (eq. 3)[42]:

$$S_t = S_e(1 - e^{-t/\tau}) \tag{3}$$

where S_t (g/g) is swelling at time t (min), S_e is equilibrium swelling (power parameter, g/g); and τ (min) stand for the rate parameter. The rate parameters for superabsorbent are found to be 1.41, 1.54, and 1.75 min for superabsorbents with particle sizes of 100–250, 250–400, and 400–550 μm, respectively. It is well-known that the swelling kinetics for the SAPs is significantly influenced by particle size of the absorbents.[43] With a lower the particle size, a higher rate of water uptake is observed. An increase in the rate of absorption would be expected from the increase in surface area with decreasing particle size of hydrogel.

Studies on sorption of metal ions

The binding properties of a series of bivalent metal ions, i.e., copper, cobalt, nickel, and zinc with sample 2 were determined. The copper sorption capacity was the highest with 1.39 mmol/g. The sorption capacities of cobalt, nickel, and zinc was measured 0.93, 0.81, and 0.79 mmol/g, respectively. Therefore, the adsorption capacities were found to be in order $Cu^{2+} > Co^{2+} > Ni^{2+} > Zn^{2+}$. A brief comparison of the metal ion sorption capacity of this hydrogel and that of some recently reported hydrogels is given in Table VII.[31,44–48] According to this table, collagen-based hydrogel, like most other resins, adsorbs copper cations stronger than other metal ions.

SAPs swell (expand) in aqueous solutions in some extent. This surface expansion improves the adsorption of metal ions. Therefore, higher swelling rate

TABLE VII
Metal Ion Sorption Capacity (MSC, mmol/g) of the Collagen-Based Hydrogel Prepared in the Present Work in Comparison with that of Some Recently Reported Resins

| Hydrogel	Metal	Maximum MSC achieved	References
Cellulose-based IPN hydrogel	Cu(II)	7.8	Ref. 44
Phosphated cellulose	Cu(II)	0.014	Ref. 45
Carboxymethyl starch	Cu(II)	2.5	Ref. 46
Starch-*g*-poly (acrylamide)	Hg(II)	7.3	Ref. 47
Poly(acrylic acid-*co*-AAm) hydrogel	Cu(II)	0.0016	Ref. 31
κC-*g*-poly(sodium acrylate)	Cu(II)	14.8	Ref. 48
κC-*g*-poly(sodium acrylate)	Co(II)	14.7	Ref. 48
Collagen-*g*-poly(acrylic acid)	Cu(II)	1.39	This work
Collagen-*g*-poly(acrylic acid)	Co(II)	0.93	This work
Collagen-*g*-poly(acrylic acid)	Zn(II)	0.79	This work
Collagen-*g*-poly(acrylic acid)	Ni(II)	0.81	This work
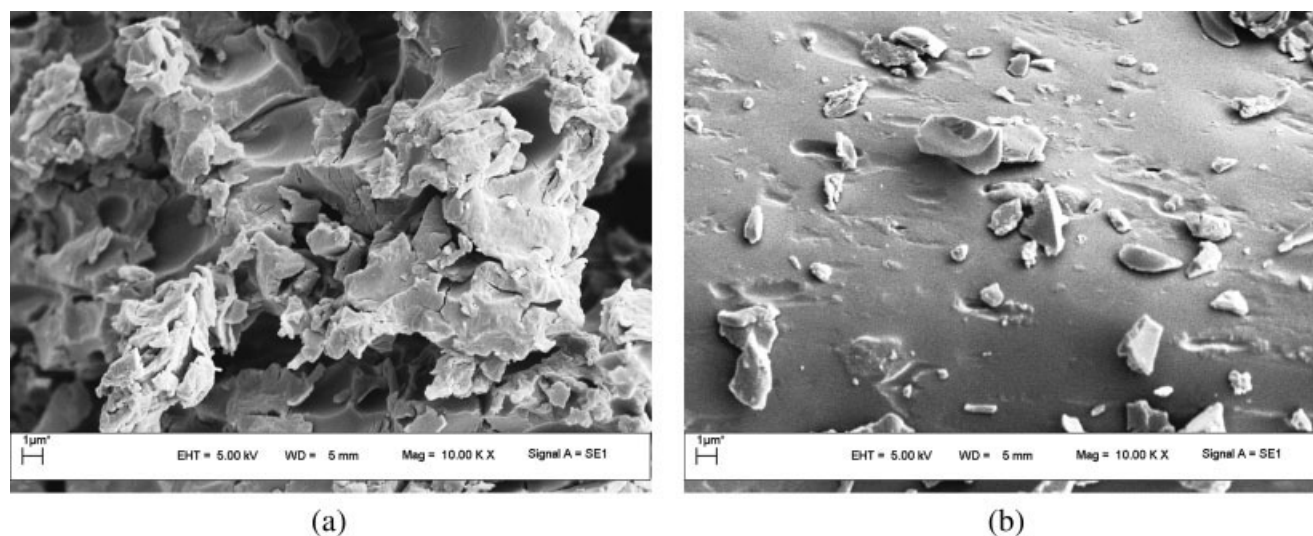
Figure 4 SEM photographs of sample 2 before and after adsorption process; (a) before adsorption; (b) after adsorption. Surfaces were taken at a magnification of ×10,000 and the scale bar is 1 μm.

will result in a faster adsorption of metal ions. After the adsorption process, the resin with adsorbed Cu^{2+} was observed by SEM. The morphology with a magnification of 10,000× of the loaded and unloaded resins is shown in Figure 4. The SEM images visually show the morphological differences of the surface of the hydrogels. The smooth morphology of the metal-adsorbed surface is logically related to filling the surface pores by atomic-scale metal particles. A proposed mechanism for metal ion chelating action of the hydrogel is shown in Scheme 2. The carboxylate anions have several ways in which they can behave as ligands, as distinct from ionic behavior, in say, sodium acetate. The type of structure shown is quite common.[49]

CONCLUSIONS

In this work, a novel superabsorbent hydrogel, collagen-*g*-poly(acrylic acid) was prepared, by graft copolymerization of AA onto protein backbones. The synthesis of superabsorbent hydrogel was optimized by Taguchi method. The maximum water absorbency (500 g/g) was achieved under the optimum conditions that found to be MBA 0.0076 mol/L, KPS 0.0015 mol/L, and AA 1.85 mol/L. Among the different variables, the AA concentration had the greatest effect on the results. The Taguchi method was found to be promising tool to obtain the optimum
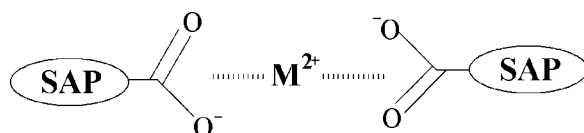
Scheme 2 A proposed mechanism for resin-metal ion chelating action.

conditions for such studies. The sorption capacity of the hydrogel toward bivalent metal ions (Cu^{2+}, Co^{2+}, Ni^{2+}, and Zn^{2+}) also was studied. The copper sorption capacity was the highest with 1.39 mmol/g. The sorption capacities of cobalt, nickel, and zinc were measured 0.93, 0.81, and 0.79 mmol/g, respectively. So, the hydrogel may be considered as a candidate to develop as an efficient biopolymer-based chelating hydrogel for water treatment.

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