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Synthesis and application of acrylamide/sodium vinylsulfonate/carboxymethylcellulose/zeolite hybrid hydrogels as highly swollen effective adsorbents for model cationic dye removal

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ABSTRACT

This report investigates the equilibrium swelling and dye sorption properties of a series of a novel hybrid/biohybrid composite hydrogel sorbent systems containing polysaccharide/zeolite polyelectrolyte based on acrylamide/sodium vinylsulfonate and carboxymethyl cellulose, and a mineral component such as zeolite. Novel hydrogels were synthesized with free radical solution polymerization by using ammonium persulfate/*N,N,N′,N′*-tetramethylethylenediamine as redox initiating pair in the presence of poly(ethylene glycol) diacrylate as a crosslinker. Swelling experiments were performed in water at 25°C, gravimetrically. The hydrogels, the semi-interpenetrating polymer networks, and the hybrid/biohybrid composite hydrogel systems that synthesized in this study have showed high swelling performance. The swelling and diffusion properties were calculated, and discussed for the hydrogels prepared under various formulations. The equilibrium swelling factor of the hydrogel systems ranges were 6.61–31.97. Fourier transform infrared spectroscopy analysis and scanning electron microscopy technique were applied for structural characterization. For sorption of water-soluble cationic dye such as “methyl violet” into the hydrogel systems was studied by batch sorption technique at 25°C. For equilibrium sorption studies, dye sorption percentage, dye uptake performance, and partition coefficient of the hydrogels have been investigated. The values of dye sorption percentage were changed among 53.12%–88.60%. Consequently, the hydrogel systems developed in this study could serve as a potential sorbent device for water and dye (and/or similar model molecules) sorption.

Keywords: Acrylamide/sodium vinylsulfonate; Biohybrid hydrogel; Swelling; Dye sorption; Methyl violet; Carboxymethyl cellulose; Zeolite

1. Introduction

In recent time, advanced functional materials such as hybrid/biohybrid composite polymers are novel materials which have produced properties asked by the development of specialized areas such as water treatment industry, biotechnology, and nanotechnology. Functional polymers have promising potentials for development and application in this area, because of a variety of physicochemical properties (form, size, size distribution, porosity, etc.) that can be tailored and possibility of their modification by inserting various functional groups. For the sensitivity of them to change of the external stimuli and general reversibility of adsorption process, they have been enabled by easy and complete regeneration without significant decrease in adsorption capacities [1–8]. The use of many synthetic and naturally derived materials as biopotential sorbent or carriers for the removal of the model molecules from aqueous solutions of them has been continued to attract considerable attention in recent years [9–18]. Hybrid polymeric hydrogels can be defined as water-swollen materials, which maintain a distinct three-dimensional structure simultaneously and they

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are composed of polymeric material and inorganic material or different polymeric materials. Polymer/clay or polymer/zeolite (ZEO) hybrid composite hydrogels have received great attention because of their relatively low production cost and high adsorption capacity for some dyes and metal. Swelling or water sorption property of hydrogels accounts for a great number of biomedical and technological applications [1,5,6,9,10,16,19–21].

Some hazardous materials such as wastewater mostly released from the industrial plants and big cities introduce many toxics and hazardous pollutants. The increasing content of toxic industrial waste has led to the development of various methods for its elimination and removal from wastewaters. Ion exchange or adsorption using different polymeric materials and synthetic resins is the method of choice in many wastewater treatment processes for removing dyes, or water treatment from chemical process industries in certain developed countries [9–18].

Natural polymers such as polysaccharides have been studied by many researchers [1,8–13,21–26]. Due to their specific properties, they have been used in many fields of biomedical and biotechnological applications. Carboxymethyl cellulose (CMC) is anionic carboxymethyl ether of cellulose with tasteless, non-toxic, and water-soluble characteristics. It has got some potential applications in industrial fields as stabilizing agent, thickening agent, and bonding agent [21,23–26]. CMC has got a lot of polar carboxyl groups, so CMC is chemically reactive and strongly hydrophilic. With this for properties, CMC can be easily modified through its grafting with hydrophilic vinyl monomers to synthesize new hydrogel systems [21,23–26].

ZEOs are a large group of crystalline, hydrated aluminosilicates, characterized by three-dimensional structure with pores which can accommodate water molecules, different cations, positively charged atomic groups, and even smaller organic molecules [5,11,12,14,27–30]. ZEO structure is composed of SiO_4 and AlO_4 tetrahedral, connected by oxygen atoms. Because of unique combination of properties: strong acidity, uniformity of pore size, selectivity, and stability, ZEOs are used in ion-exchange, separation, catalysis, and adsorption processes [27–30].

The present paper reports that swelling in water and sorption study of methyl violet (MV) by a novel type of polysaccharide/ZEO polyelectrolyte hydrogels based on the acrylamide/sodium vinylsulfonate (AAm/SVS) hydrogels and CMC and/or ZEO via free radical solution polymerization method. Here, it was of interest to increase the water and dye sorption capacity of AAm hydrogels by copolymerization with monomers containing highly hydrophilic functional groups. It was reported that some groups has been synthesized SVS-based crosslinked polymers and/or copolymers [31–34]. Here, AAm is a highly hydrophilic monomer, and SVS is anionic monomer, CMC is a natural polymer, and ZEO is a mineral structure composed of hydrated aluminosilicates, SiO_4 and AlO_4. In this respect, a series of copolymeric hydrogels were synthesized by changing the content of SVS, CMC, and ZEO. Then, some swelling, and some diffusional properties of AAm/SVS hydrogels, AAm/SVS/CMC semi-interpenetrating polymer networks (semi-IPNs), AAm/SVS/ZEO hybrid hydrogels, and AAm/SVS/CMC/ZEO biohybrid hydrogel were studied in water by dynamic swelling studies for swelling characterization. Water uptake and dye sorption properties of the hydrogels were investigated as a function of chemical composition of the hydrogels.

2. Experimental setup

2.1. Raw materials

AAm, the initiator ammonium persulfate (APS), the activator *N,N,N′,N′*-tetramethylethylenediamine (TEMED) and ZEO were supplied by Sigma, Steinheim, Germany. ZEO is a synthetic product of Sigma (Sigma product number is 96096 and particle size of it was <10 μm powder). The synonyms of ZEO are molecular sieves, Abscents 3000 or Agrolithe 15/25. Anionic co-monomer such as sodium vinylsulfonate (vinylsulfonic acid, sodium salt, tech., 25 wt. % solution in water) (SVS) and a multifunctional crosslinker such as poly(ethylene glycol) diacrylate (PEGDA, $M_n = 700$) as a crosslinker were supplied from Aldrich, Steinheim, Germany. Polysaccharide sodium CMC and cationic dye MV (basic violet 1) used in sorption studies were purchased from Fluka, Steinheim, Germany. All chemicals were used as received.

2.2. Sorbent synthesis

The hydrogels, the semi-interpenetrating polymer networks, and the hybrid/biohybrid composite hydrogel systems developed in this study were prepared by free radical crosslinking copolymerization of AAm monomer with addition of SVS and a multifunctional crosslinker such as PEGDA as a crosslinker.

For the synthesis of chemically crosslinked AAm hydrogel systems, AAm weighing 1.0 g/14.07 mmol was dissolved in 1.0 mL of water. Then, for AAm/SVS hydrogels containing 60 μL of SVS, 60 μL (0.544 mmol) of SVS was added to aqueous other AAm solution at room temperature (25°C). Then, 120 μL (1.088 mmol), 180 μL (1.633 mmol), 240 μL (2.176 mmol), and 300 μL (2.72 mmol) of SVS were added to other aqueous AAm solutions, respectively, for containing different amount of SVS in AAm/SVS hydrogel systems. After these additions, for the synthesis, 0.25 mL/0.004 mmol of 1% concentration of PEGDA and 0.2 mL/0.044 mmol aqueous solutions of APS (5.0 g APS/100 mL water) and 0.25 mL/0.017 mmol of 1% concentration of TEMED were added to these aqueous solutions [9,10,21] (Table 1).

In preparation, the solutions were placed in special cylindrical plastic molds (having 7.0 mm of diameter and 3.0 mm of height) (Fig. 1), then, they were waited for an hour for gelation. After gelation, the samples were washed with distilled water by several times. Then, they were dried in air and vacuum, and stored for swelling and sorption studies [9,10,21].

For the synthesis of AAm/SVS/CMC semi-IPNs, they were prepared by using the same preparation method. But, 0.5 mL of water and 0.5 mL of 2.0% aqueous CMC solution was used instead of 1.0 mL of distilled water in the related preparation method. To prepare AAm/SVS/CMC semi-IPNs (containing different contents of CMC), same method was used as mentioned above with addition of 0.25, 0.75, and 1.0 mL of aqueous solution of 2.0% of aqueous CMC to 0.75 0.25, and 0.0 mL of water containing 1.0 g AAm and 240 μL of SVS [9,10,21] (Table 1).

Table 1
Compositions of the hydrogel systems containing AAm, SVS, ZEO, and CMC

Abbreviation	SVS (μL)	Water (mL)	ZEO (mL) (2.0% ZEO/water suspension system)	CMC (mL) (2.0% aqueous CMC solution)
AAm/SVS	0–300	1.0	–	–
AAm/SVS/ZEO	0–300	0.50		0.50
AAm/SVS/CMC	0–300	0.50	0.50	–
AAm/SVS/ZEO/CMC	0–300	–	0.50	0.50
AAm/SVS/ZEO (for ZEO changing)	240	0.75–0.50–0.25–0.00	0.25–0.50–0.75–1.00	–
AAm/SVS/CMC (for CMC changing)	240	0.75–0.50–0.25–0.00	–	0.25–0.50–0.75–1.00

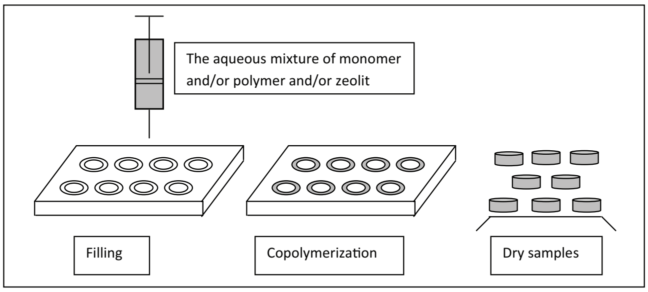


Fig. 1. Schematic representation of the preparation of the hydrogel systems.

Highly swollen AAm/SVS/ZEO hybrid hydrogel systems were prepared by using the same preparation method. 0.5 mL of distilled water and 0.5 mL of 2.0% of ZEO/water suspension system was used instead of 1.0 mL of distilled water in the related preparation method. For AAm/SVS/ZEO hybrid hydrogel (containing different contents of ZEO) systems, same method was used as mentioned above with addition of 0.25, 0.75, and 1.0 mL of 2.0% of ZEO/water suspension system to 0.75, 0.25, and 0.0 mL of water containing 1.0 g of AAm and 240 μL of SVS [9,10,21] (Table 1).

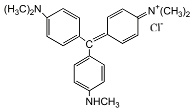
AAm/SVS/CMC/ZEO biohybrid hydrogel systems were prepared by using the same preparation method. But, only, 0.5 mL of 2.0% of aqueous CMC solutions and 0.5 mL of 2.0% of ZEO/water suspension system was used instead of 1.0 mL of distilled water in the related preparation method [9,10,21] (Table 1).

Schematic representation of preparation of AAm/SVS hydrogels, AAm/SVS/CMC semi-IPNs, AAm/SVS/ZEO hybrid hydrogels, and AAm/SVS/CMC/ZEO biohybrid hydrogel systems have been presented in Fig. 1.

2.3. Dye sorption performance

All sorption experiments, batch sorption studies were applied. Cationic dye MV (basic violet 1) was used in sorption studies. Some properties of MV were given in Table 2. Aqueous solutions of MV concentration range between 0.75×10^{-5} and 75.0×10^{-5} M in distilled water were prepared. AAm/SVS hydrogels, AAm/SVS/CMC semi-IPNs, AAm/SVS/ZEO hybrid hydrogels, and AAm/SVS/CMC/ZEO biohybrid hydrogel systems were used in a known volume of dye solution until equilibrium was reached. For SVS, CMC, and ZEO effects on the dye sorption, aqueous solutions of concentration of 2.5×10^{-5} M of MV were used. After sorption, dye solution was separated by decantation from the hydrogels. Spectrophotometric method was applied to dye solutions. Spectrophotometric measurements were carried out using a Shimadzu UV 1601 model UV–VIS spectrophotometer (Australia) at ambient temperature. The absorbances of these solutions were read at 584 nm for MV [35–37]. Distilled water was chosen as the reference. The equilibrium concentrations of the cationic dye solutions were determined by means of precalibrated scales.

Table 2
Some properties of methyl violet (MV)

Name	Chemical formula	Molar mass (g mol^{-1})	λ_{mak} (nm)	C.I. No.
Methyl violet (basic violet 1; MV)		393.5	584	42535

2.4. Sorbent characterization

For dynamic swelling characterization, the dried hydrogel systems were accurately weighted and transferred into water. Water uptake with respect to time was obtained by periodically removing the samples from water; quickly blot drying, and reweighing. The measurements were conducted at 25°C ± 0.1°C in a water bath.

For structural characterization, fourier transform infrared spectroscopy (FTIR)/attenuated total reflectance (ATR) analysis was made. The functional groups on the prepared AAm/SVS hydrogels, AAm/SVS/CMC semi-IPNs, AAm/SVS/ZEO hybrid hydrogels, and AAm/SVS/CMC/ZEO biohybrid hydrogel systems were analyzed with FTIR spectrophotometer-Thermo Scientific Nicolet is 10 smart FT-IR (USA) using ATR apparatus.

The surface morphology of AAm/SVS hydrogels, AAm/SVS/CMC semi-IPNs, AAm/SVS/ZEO hybrid hydrogels, and AAm/SVS/CMC/ZEO biohybrid hydrogel systems was visualized by a scanning electronic microscope Philips XL-30S FEG (Netherlands).

3. Results and discussion

Novel AAm/SVS hydrogels, AAm/SVS/CMC semi-IPNs, AAm/SVS/ZEO hybrid hydrogels, and AAm/SVS/CMC/ZEO biohybrid hydrogel systems were prepared by free radical solution polymerization [9,10,21]. In Fig. 2, chemical structures of monomers and the probable binding and crosslinking mechanism have been presented for AAm/SVS copolymer or hydrogel systems. The dried hydrogels are glassy and very hard, but swollen gels are soft. The hydrogel systems via radical chain polymerization are a well-established procedure. Upon swelling the hydrogels were strong enough to retain their shape. There have been presented the digital camera images of AAm/SVS hydrogels and AAm/SVS/CMC/ZEO biohybrid hydrogels in Fig. 3 as dry state or swollen state. The capacity of swelling of the hydrogels can be seen from Fig. 3.

3.1. FTIR analysis

The FTIR spectra of novel AAm/SVS hydrogels, AAm/SVS/CMC semi-IPNs, AAm/SVS/ZEO hybrid hydrogels, and AAm/SVS/CMC/ZEO biohybrid hydrogel systems show the characteristic absorptions of AAm, SVS, CMC, and a typical aluminosilicate such as ZEO. FTIR spectra of AAm/SVS/ZEO hybrid hydrogels are presented in Fig. 4 as representative. The peak at 1,600–1,700 cm^{-1} corresponds to the carbonyl group and the peak at 1,400–1,500 cm^{-1} corresponds to the C–N stretching of the AAm unit. On the other hand, the peaks at 2,800–2,900 cm^{-1} and 1,400 cm^{-1} show $-CH_2-$ groups on the polymeric chain. In the FTIR spectra of the hydrogels, the broad bands observed between 3,500 and 3,000 cm^{-1} corresponds to hydrogen bonded O–H and N–H stretching of the polymeric hydrogels [9,10,21,35,37]. The bands at 1,600–1,700 cm^{-1} could be attributed to a shift in stretching vibration associated with hydrogen that is bonded directly to an overtone of the strong carbonyl absorption. The peaks observed between 1,600 and 1,700 cm^{-1} corresponding to the C=O group of the acrylate unit of SVS. Fig. 4 shows a wider peak at 3,000–3,500 cm^{-1}. The reason of this wider peak can be due to OH groups in ZEO. The peak at 1,000–1,100 cm^{-1} corresponds to the Si–O stretching of the mineral component such as ZEO. The FTIR data indicate that the AAm/SVS-based hydrogels all had the expected characteristic groups.

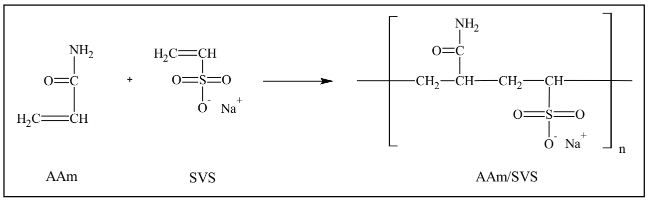


Fig. 2. Chemical structures of monomers and the probable binding mechanism of AAm/SVS copolymers.

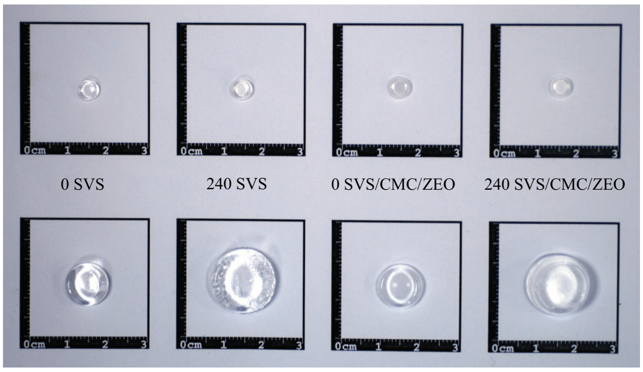


Fig. 3. The digital camera images of AAm/SVS hydrogels and AAm/SVS/CMC/ZEO biohybrid hydrogels (as dry state or swollen state).

3.2. SEM analysis

Scanning electron microscopy (SEM) analysis is the most used technique to investigate the shape, size, morphology, crosslink, and porosity of hydrogels, or other related materials. SEM images of AAm hydrogels, ZEO, AAm/SVS hydrogel (containing 240 μL SVS), and AAm/ZEO hybrid hydrogel are presented in Fig. 5 as representative. The microstructural differentiations and a large number of porous can be followed from Fig. 5 [9,21,38]. It is obvious that the structure of the AAm-based hydrogel systems is porous.

3.3. Swelling performance

The swelling factor (S) of the hydrogels in distilled water was calculated from the following relation:

$$S = \frac{m_t - m_o}{m_o} \tag{1}$$

Here, m_t is the mass of the swollen gel at time t and m_o is the mass of the dry gel at time 0.

The water intake of initially dry hydrogels was followed for novel AAm/SVS hydrogels, AAm/SVS/CMC semi-IPNs, AAm/SVS/ZEO hybrid hydrogels, and AAm/SVS/CMC/ZEO biohybrid hydrogel systems crosslinked by PEGDA in water, and swelling isotherms of AAm/SVS/ZEO hybrid hydrogels shown in Fig. 6 as representative.

Fig. 6 shows that swelling/water sorption increases with time up to certain level, then levels off. This value of S may be called as the "equilibrium swelling factory" (S_{eq}). S_{eq} values of the hydrogel systems are given in Table 3. Table 3 shows that S_{eq} of AAm hydrogels is 7.72, but S_{eq} of AAm/SVS hydrogels are 9.08–26.07 with the incorporation of SVS groups into chemically crosslinked AAm copolymers.

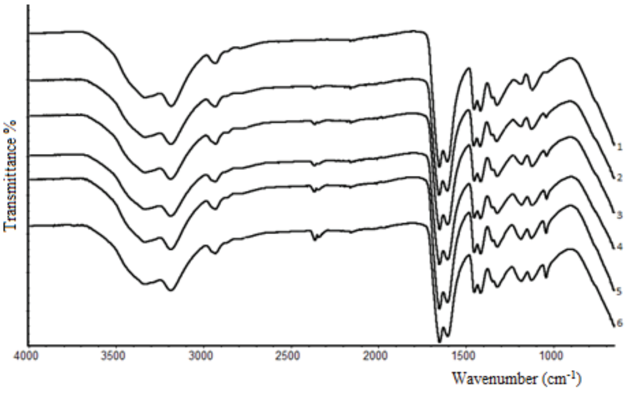
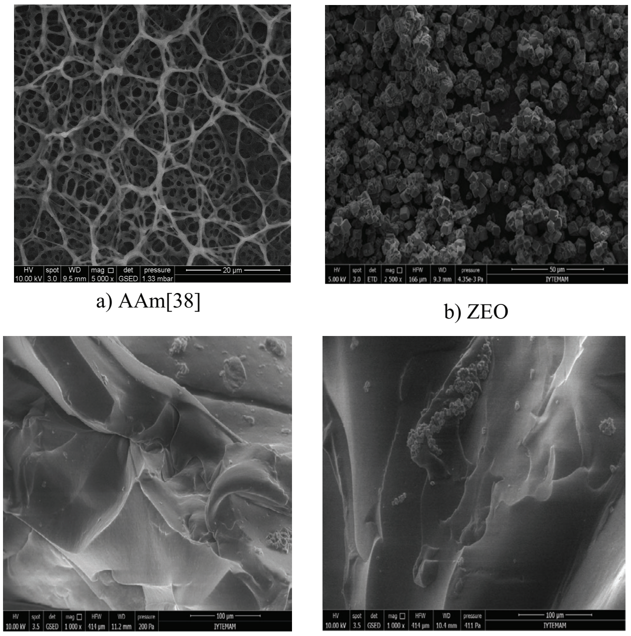


Fig. 4. FTIR spectra of AAm/SVS/ZEO hybrid hydrogels including various contents of SVS: (1) 0SVS/ZEO, (2) 60SVS/ZEO, (3) 120SVS/ZEO, (4) 180SVS/ZEO, (5) 240SVS/ZEO, and (6) 300SVS/ZEO.

S_{eq} of AAm/SVS/ZEO hybrid hydrogels containing 1.0% of ZEO are 7.97–24.99 with the incorporation of ZEO groups into AAm/SVS hydrogels, while S_{eq} of AAm/ZEO hybrid hydrogels is 6.61. On the other hand, the values of S_{eq} of AAm/SVS/CMC semi-IPNs containing 1.0% of CMC are 10.27–31.97 with the incorporation of CMC into AAm/SVS hydrogels, while S_{eq} of AAm/CMC semi-IPNs is 7.62.

S_{eq} of AAm/SVS/CMC/ZEO biohybrid hydrogels containing 1.0% of CMC and 1.0% of ZEO are 10.16–26.02 with the incorporation of CMC and ZEO into AAm/SVS hydrogels, while S_{eq} of AAm/ZEO/CMC biohybrid hydrogels is 6.71 (Table 3). In Table 3, the values of S_{eq} of the hydrogels increased with the SVS content in the crosslinked copolymers. S_{eq} of AAm/SVS hydrogels, AAm/SVS/CMC semi-IPNs, AAm/SVS/ZEO hybrid hydrogels, and AAm/SVS/CMC/ZEO biohybrid hydrogel systems are higher than S_{eq} of AAm hydrogels. Also, this hydrophilic effect has been shown in our previous studies using some hydrophilic comonomers such as zinc acrylate [9], sodium acrylate [10], 2-acrylamido-2-methyl-1-propanesulfonic acid [21], 4-styrenesulfonic acid sodium salt [35], and maleic acid [38]. In these studies, the swelling/water sorption increase is due to an increase in the anionic units [9,10,21,35,38]. It is well known that the swelling of a hydrogel is induced by electrostatic repulsion of the ionic charges of its network. The salt group is almost completely ionized, and a large number of hydrophilic groups occur. An anionic comonomer such as SVS contains ionizable groups, so more SVS groups on the copolymeric chain contain many ionizable groups. The hydrophilic group numbers of AAm/SVS hydrogels, AAm/SVS/CMC semi-IPNs, AAm/SVS/ZEO hybrid hydrogels, and AAm/SVS/CMC/ZEO biohybrid hydrogel systems are higher than those of AAm, and so the values of S_{eq} of AAm/SVS hydrogels, AAm/SVS/CMC semi-IPNs, AAm/SVS/ZEO hybrid hydrogels, and AAm/SVS/CMC/ZEO biohybrid hydrogel systems are greater than that of the values of S_{eq} of AAm [9,10,21,35,38].


a) AAm[38]

b) ZEO

c) AAm/SVS

d) AAm/ZEO

Fig. 5. SEM images of AAm hydrogels (a), ZEO (b), AAm/SVS hydrogel (containing 240 μL of SVS) (c), and AAm/ZEO hybrid hydrogel (d).

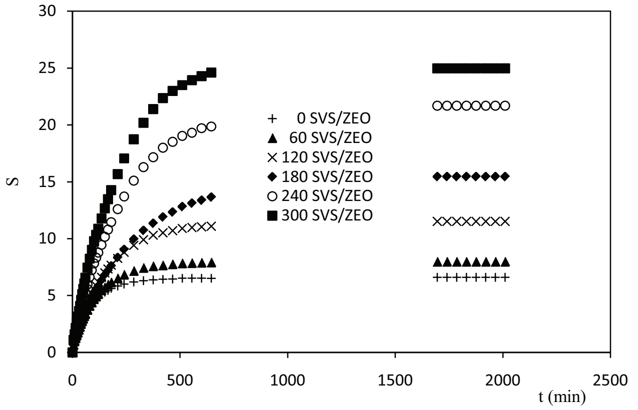


Fig. 6. Swelling isotherms of AAm/SVS/ZEO hybrid hydrogels.

It was shown that apartially decrease of the values of S_{eq} of AAm/SVS/CMC semi-IPNs, AAm/SVS/ZEO hybrid hydrogels, and AAm/SVS/CMC/ZEO biohybrid hydrogels when CMC and ZEO have been added to the hydrogel systems. Incorporation of CMC and ZEO into the copolymer network leads to lower degrees of swelling. The reason of this may be the polymeric structure of CMC and structure of ZEO. Here, it could be said that a lot of number of group of CMC and ZEO chains were placed in the crosslinked polymeric systems, instead of crosslinked AAm and SVS monomers. So, it was seen that decreasing of the value of S_{eq}, because of decreasing of partially hydrophilic character at crosslinked polymeric systems. But, on the other hand, it can be said that there is no good relation between the values of S_{eq} of the hydrogels, when CMC and ZEO have been added to the polymeric systems. For understanding the effect of SVS content on the swelling behavior, the values of S_{eq} of the hydrogels vs. the content of SVS is plotted in Fig. 7. In Fig. 7, the values of S_{eq} of the hydrogels gradually increased with increasing of SVS content in the hydrogels.

The water absorbed by AAm/SVS hydrogels, AAm/SVS/CMC semi-IPNs, AAm/SVS/ZEO hybrid hydrogels, and AAm/SVS/CMC/ZEO biohybrid hydrogels quantitatively represented by equilibrium water capacity (EWC) also, and they can be calculated by the following equation [9,38–41].

$$\mathrm{EWC} = \frac{m_{eq} - m_o}{m_{eq}} \tag{2}$$

Here, m_{eq} is the mass of the swollen gel at time t (equilibrium), and m_o is the mass of the dry gel at time 0. The values of EWC of the hydrogel systems were calculated. These values of EWC of the hydrogels are tabulated in Table 3. They are changed between 0.8636 and 0.9696. It is seen that an increasing of the values of EWC, if SVS has been added to the hydrogel systems. Here, the main effect is the hydrophilic character of SVS groups. But decreasing of the values of EWC is observed if CMC and ZEO have been added to the hydrogel systems.

Table 3
The values of the equilibrium swelling factory (S_{eq}) and equilibrium water capacity (EWC) of the hydrogel systems

SVS/µL	0	60	120	180	240	300
	Equilibrium swelling factor (S_{eq})					
AAm/SVS	7.72	9.08	13.09	16.77	24.61	26.07
AAm/SVS/ZEO	6.61	7.97	11.53	15.46	21.69	24.99
AAm/SVS/CMC	7.62	10.27	13.28	15.59	22.83	31.97
AAm/SVS/CMC/ZEO	6.71	10.16	11.15	13.19	17.68	26.02
	Equilibrium water capacity (EWC)					
AAm/SVS	0.8853	0.9008	0.9290	0.9437	0.9606	0.9630
AAm/SVS/ZEO	0.8686	0.8886	0.9202	0.9392	0.9559	0.9615
AAm/SVS/CMC	0.8841	0.9113	0.9300	0.9328	0.9580	0.9696
AAm/SVS/CMC/ZEO	0.8703	0.9104	0.9177	0.9295	0.9464	0.9629

3.4. Water sorption kinetics

In order to examine the controlling mechanism of the water sorption processes, several kinetic models are used to test experimental data. The large number and array of different chemical groups of AAm/SVS hydrogels, AAm/SVS/CMC semi-IPNs, AAm/SVS/ZEO hybrid hydrogels, and AAm/SVS/CMC/ZEO biohybrid hydrogels chains (e.g., amide, carbonyl) imply that there are many types of polymer–solvent interactions. It is probable that any kinetics is likely to be global. From a system design viewpoint, a lumped analysis of swelling rates is thus sufficient to the practical operation.

A simple kinetic analysis is a second-order equation in the form of:

$$\frac{dS}{dt} = k_{2,S}\left(S_{eq} - S\right)^2 \tag{3}$$

where $k_{2,S}$ is the rate constant of swelling and S_{eq} denotes the equilibrium swelling factory (S_{eq}) at equilibrium [41,42]. After definite integration by applying the initial conditions $S = 0$ at $t = 0$ and $S = S$ at $t = t$, Eq. (3) becomes:

$$\frac{t}{S} = A + Bt \tag{4}$$

Here, A is reciprocal of initial swelling rate, (r_o) or $1/k_{2,S}\,S_{eq}^{\,2}$ and B is inverse of the equilibrium swelling factory at equilibrium (S_{max}) [41,42].

To test the kinetics model, (t/S) vs. (t) graphs are plotted and representative graphs are illustrated in Fig. 8. The calculated kinetic parameters are tabulated in Table 4. As it can be seen from Table 4, kinetics model is agreement with the results of swelling experiments, since, as depicted in Table 3, S_{max} (theoretical) is increased with SVS content.

3.5. Water diffusion

The following equation is used to determine the nature of diffusion of water into hydrogels [9,35,38,41,43].

$$F = \frac{M_t}{M_\infty} = kt^n \tag{5}$$

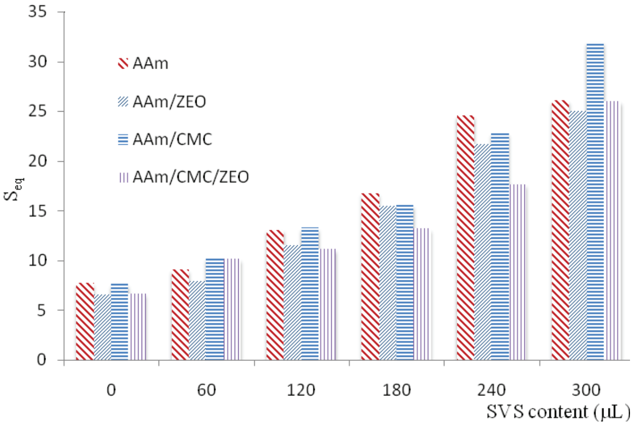


Fig. 7. Changing of S_{eq} values of the hydrogel systems by various contents of SVS.

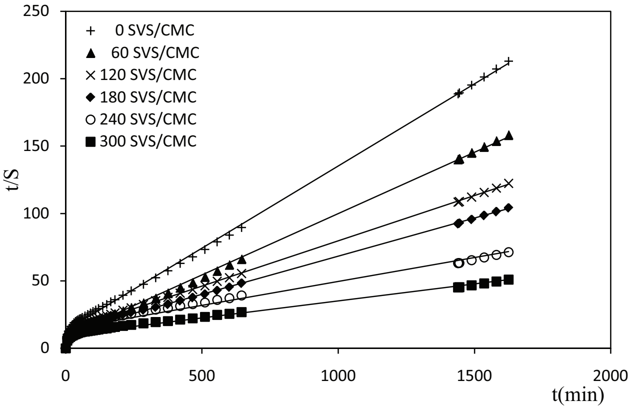


Fig. 8. Swelling kinetics curves of AAm/SVS/CMC semi-IPN hydrogels.

Here, F is the fractional uptake at time t. M_t and M_∞ are the mass uptake of the solvent at time t and the equilibrium, respectively. The values of diffusion exponent (n) and diffusion constant (k) were calculated from the slope and the intercept of the plot of ln$F$ against ln$t$, respectively. Eq. (5) is valid for the first 60% of the fractional uptake. Fickian diffusion

Table 4
Swelling kinetics parameters of the hydrogels

SVS/μL	0	60	120	180	240	300
	Initial swelling rate (r_0) $(\mathrm{d}S/\mathrm{d}t)_0$. g_w/g_{gel} min					
AAm/SVS	0.07	0.11	0.07	0.06	0.12	0.16
AAm/SVS/ZEO	0.15	0.12	0.11	0.08	0.13	0.17
AAm/SVS/CMC	0.07	0.11	0.08	0.08	0.07	0.10
AAm/SVS/CMC/ZEO	0.29	0.15	0.14	0.09	0.19	0.13
	Swelling rate constant ($k_s \times 10^6$) g_{gel}/g_w min					
AAm/SVS	1,035.9	1,247.5	369.1	175.2	158.5	187.6
AAm/SVS/ZEO	3,244.5	1,797.7	786.2	299.1	233.7	239.6
AAm/SVS/CMC	1,127.6	939.9	365.2	276.1	89.3	65.6
AAm/SVS/CMC/ZEO	6,214.6	1,378.1	994.3	427.9	552.1	145.8
	Theoretical equilibrium swelling factor ($S_{\max}$) g_w/g_{gel}					
AAm/SVS	8.33	9.61	14.66	19.57	28.33	29.41
AAm/SVS/ZEO	6.80	8.33	12.24	17.12	23.87	27.25
AAm/SVS/CMC	8.19	10.99	14.86	17.67	28.17	39.53
AAm/SVS/CMC/ZEO	6.85	10.71	11.88	14.64	18.98	29.94

and Case II transport are defined by n values of 0.5 and 1.0, respectively. Anomalous transport behavior (non-Fickian diffusion) is intermediate between Fickian and Case II. That is reflected by n between 0.5 and 1.0 [9,38,41,43,44].

For AAm/SVS hydrogels, AAm/SVS/CMC semi-IPNs, AAm/SVS/ZEO hybrid hydrogels, and AAm/SVS/CMC/ZEO biohybrid hydrogels, ln$F$ vs. ln$t$ graphs are plotted and representative results are shown in Fig. 9. Diffusional exponents (n) and diffusion constant (k) are calculated and listed in Table 5.

Table 5 shows that the values of the number determining the type of diffusion (n) are between 0.5785 and 0.7573. Hence, the diffusion of water into the hydrogel systems is generally found to have a non-Fickian character. When the diffusion type is anomalous behavior, the relaxation and diffusion time are of the same order of magnitude [9,38,41,43,44].

The study of diffusion phenomena of water in hydrogels is of value in that it clarifies polymer behavior. For hydrogel characterization, the diffusion coefficients can be calculated by various methods. The diffusion coefficient (D) of the water was calculated using the following equation [9,38,41,45,46].

$$D = \pi \mathrm{r}^2 \left(\frac{k}{4} \right)^{1/n} \tag{6}$$

Here, D is in cm^2 min^{-1}, r is the radius of a cylindrical polymer sample, n is the diffusional exponent and k is a constant incorporating characteristic of the macromolecular network system and the penetrant. The values of diffusion coefficient determined for AAm/SVS hydrogels, AAm/SVS/CMC semi-IPNs, AAm/SVS/ZEO hybrid hydrogels, and AAm/SVS/CMC/ZEO biohybrid hydrogels are listed in Table 5. Table 5 shows that the values of the diffusion coefficient of the hydrogel systems change from 16.36×10^{-5} cm^2 min^{-1} to 136.57×10^{-5} cm^2 min^{-1}. It can be said that there is no good adaptation between the values of the diffusion coefficient of AAm/SVS hydrogels, AAm/SVS/CMC semi-IPNs, AAm/SVS/ZEO hybrid hydrogels, and AAm/SVS/CMC/ZEO biohybrid hydrogels.

3.6. Water sorption rate

Other important diffusion parameter can be "water sorption rate constant" (K_{sr}). This parameter can be calculated by the water sorption equation [9,47]. This equation is as follows:

$$-\ln(1 - F) = K_{\mathrm{sr}} t + E \tag{7}$$

where t is sorption time, K_{sr} is water sorption rate constant. F was described before, and E is a constant. The plots of $[-\ln(1 - F)]$ vs. $[t]$ where F is equal to (M_t/M_s) are shown in Fig. 10 for AAm/SVS hydrogels as representative. The water sorption rate constants of AAm/SVS hydrogels, AAm/SVS/CMC semi-IPNs, AAm/SVS/ZEO hybrid hydrogels, and AAm/SVS/CMC/ZEO biohybrid hydrogels calculated from the slope of the plots, and they are tabulated in Table 5. They are changed among range vary from 2.05×10^{-3} min^{-1} to 20.00×10^{-3} min^{-1}. Table 5 shows that water sorption rate constants of AAm/SVS hydrogels, AAm/SVS/CMC semi-IPNs, AAm/SVS/ZEO hybrid hydrogels, and AAm/SVS/CMC/ZEO biohybrid hydrogels are lower than that of AAm hydrogels, AAm/CMC semi-IPNs, AAm/ZEO hybrid hydrogels, and AAm/CMC/ZEO biohybrid hydrogels. The reason of this may be the hydrophilic and ionic characteristics of SVS. Every SVS molecules have got an anionic group such as vinyl sulfonate group having negative charge. Because of the more charged structure, water sorption into the hydrogel systems may be irregular. On the other hand, it can be said that more irregular forms could be occurred in crosslinked structure by adding of CMC and ZEO.

3.7. CMC and ZEO effect on the swelling and diffusion

For investigation of the effect of mass/content of CMC and ZEO on the swelling and diffusional properties of AAm/SVS hydrogels, AAm/SVS/CMC semi-IPNs, AAm/SVS/ZEO hybrid hydrogels, and AAm/SVS/CMC/ZEO biohybrid hydrogels, the related swelling isotherms and related swelling kinetic curves of hydrogel systems were constructed and, plots of ln*F* vs. ln*t* for AAm/SVS/ZEO hybrid hydrogels containing 240 μL of SVS was shown in Fig. 11 as representative. Effect of CMC and ZEO on some swelling, kinetics, and diffusion parameters of AAm/SVS/CMC semi-IPNs and AAm/SVS/ZEO hybrid hydrogels having 240 μL of SVS with different volume (as mL) of 2.0% of ZEO–water suspension or 2.0% of aqueous CMC solutions were tabulated in Table 6.

Also for good description of content of SVS on swelling characterization, column plots of S_{eq} vs. various contents of SVS for AAm/SVS hydrogels, AAm/SVS/CMC semi-IPNs, AAm/SVS/ZEO hybrid hydrogels, and AAm/SVS/CMC/

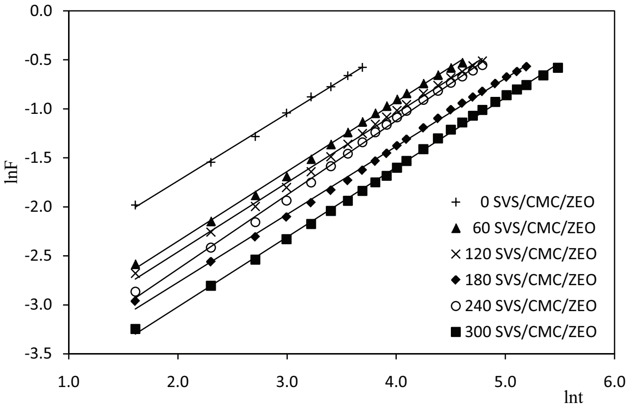


Fig. 9. Plots of ln*F* vs. ln*t* for AAm/SVS/CMC/ZEO biohybrid hydrogels.

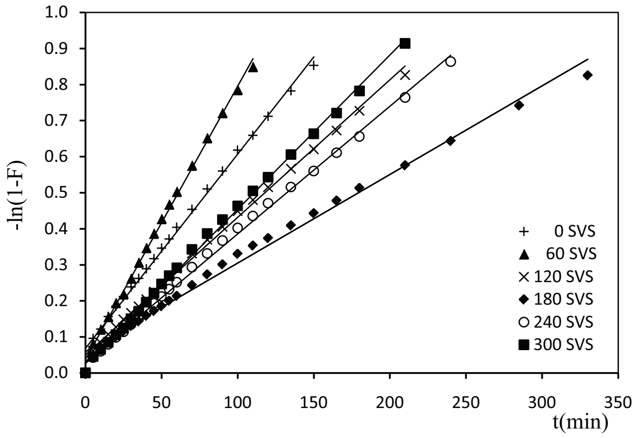


Fig. 10. Plots of [–ln(1 – *F*)] vs. time for AAm/SVS hydrogels.

Table 5
Some diffusion parameters of the hydrogels

SVS/μL	0	60	120	180	240	300
	Diffusion exponent (*n*)					
AAm/SVS	0.5785	0.6783	0.6401	0.6334	0.7270	0.7453
AAm/SVS/ZEO	0.6882	0.6752	0.7028	0.6760	0.7280	0.7552
AAm/SVS/CMC	0.6586	0.6820	0.6650	0.6772	0.6908	0.7282
AAm/SVS/CMC/ZEO	0.6862	0.7111	0.7077	0.6940	0.7573	0.7120
	Diffusion constant ($k \times 10^3$)					
AAm/SVS	30.99	23.94	18.33	14.66	14.68	11.61
AAm/SVS/ZEO	30.97	26.16	18.59	14.68	12.15	11.63
AAm/SVS/CMC	22.93	21.96	16.31	14.63	9.31	8.01
AAm/SVS/CMC/ZEO	44.77	22.98	20.75	15.62	15.78	11.74
	Diffusion coefficient ($D \times 10^5$)					
AAm/SVS	19.48	56.33	34.31	16.36	99.20	85.52
AAm/SVS/ZEO	112.40	88.83	82.53	52.04	83.86	123.30
AAm/SVS/CMC	45.84	67.50	45.55	54.20	40.95	65.71
AAm/SVS/CMC/ZEO	136.57	106.77	103.95	72.69	178.43	90.08
	Water sorption rate constant ($K_{sr} \times 10^3$)					
AAm/SVS	5.39	7.58	3.82	2.46	3.54	4.28
AAm/SVS/ZEO	11.80	8.58	6.20	3.56	4.06	4.62
AAm/SVS/CMC	6.09	6.76	3.83	3.58	2.05	2.25
AAm/SVS/CMC/ZEO	20.00	8.80	7.45	4.52	7.04	3.37

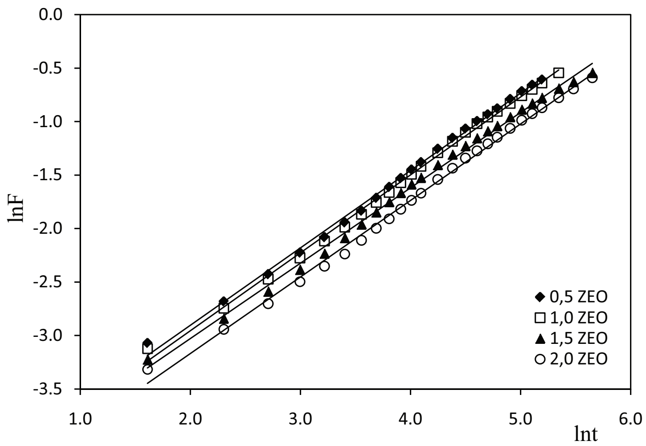


Fig. 11. Plots of ln*F* vs. ln*t* for AAm/SVS/ZEO hybrid hydrogels containing 240 μL of SVS.

ZEO biohybrid hydrogels including various contents of SVS could have been discussed here again (Fig. 7). It was seen that the values of S_{eq} of the hydrogels increased with the SVS content in the crosslinked copolymers, again.

It was shown that an increasing of the values of S_{eq} of AAm/SVS/CMC semi-IPNs and AAm/SVS/ZEO hybrid hydrogels having 240 μL of SVS with different CMC and different ZEO contents, when CMC and ZEO have been added to the hydrogel systems. Incorporation of CMC and ZEO into the copolymer network leads to higher values of S_{eq}. The reason of this increasing may be the polymeric structure and partially hydrophilic character of CMC and ZEO. So, it was seen that increasing of the value of the S_{eq}, because of increasing of hydrophilic character at crosslinked polymeric systems. On the other hand, again it can be seen that similar characteristic behavior on the some swelling, kinetics, and diffusion parameters, if Table 6 have been investigated.

Table 6
Some swelling kinetics and diffusion parameters of AAm/SVS/ZEO and AAm/SVS/CMC biohybride hydrogels having of 240 μL SVS with different ZEO and different CMC content

2.0% of ZEO–water suspension or 2.0% of aqueous CMC solution (mL)	0.25	0.50	0.75	1.00
	Equilibrium swelling factor (S_{eq})			
ZEO	20.82	22.83	25.62	31.27
CMC	18.06	21.69	22.93	25.13
	Equilibrium water capacity (EWC)			
ZEO	0.9475	0.9559	0.9582	0.9617
CMC	0.9541	0.9580	0.9624	0.9690
	Initial swelling rate r_0 $(dS/dt)_0$ g_w/g_{gel} min			
ZEO	0.11	0.12	0.10	0.10
CMC	0.16	0.06	0.16	0.10
	Swelling rate constant ($k_s \times 10^6$) g_{gel}/g_w min			
ZEO	278.08	214.85	151.37	114.83
CMC	309.60	83.42	196.90	72.93
	Theoretical equilibrium swelling factory (S_{max}) g_w/g_{gel}			
ZEO	20.28	24.57	26.17	29.67
CMC	22.93	28.65	28.90	38.31
	Diffusion exponent (*n*)			
ZEO	0.7229	0.7280	0.7042	0.7148
CMC	0.7472	0.6908	0.7678	0.7043
	Diffusion constant ($k \times 10^3$)			
ZEO	12.9184	12.1503	11.8396	10.0860
CMC	13.3612	9.3199	11.0503	9.6528
	Diffusion coefficient ($D \times 10^5$)			
ZEO	66.2376	83.8678	64.1160	70.1967
CMC	94.1897	40.9540	131.5800	58.3362
	Water sorption rate constant ($K_{sr} \times 10^3$)			
ZEO	4.30	4.06	3.08	2.80
CMC	5.29	2.05	4.72	2.44

3.8. Equilibrium sorption performance

To observe the sorption of MV onto of AAm/SVS hydrogels, AAm/SVS/CMC semi-IPNs, AAm/SVS/ZEO hybrid hydrogels, and AAm/SVS/CMC/ZEO biohybrid hydrogels, the hydrogel systems were placed in aqueous solutions of MV and allowed to equilibrate for 4 d at 25°C. At the end of this period AAm/SVS hydrogels, AAm/SVS/CMC semi-IPNs, AAm/SVS/ZEO hybrid hydrogels, and AAm/SVS/CMC/ZEO biohybrid hydrogels, in the MV solutions showed the dark coloration. But AAm hydrogel did not sorb any dye from solution. Here, the photographs of AAm/SVS/CMC/ZEO biohybrid hydrogels in different molar concentrations of aqueous MV solutions are shown in Fig. 12 as representative.

In the sorption system at equilibrium, the total solute (dye) concentration; C_o was evaluated by using the following equation:

$$C_0 = C_b + C \tag{8}$$

Here, C_b is the equilibrium concentration of the dye (MV) on the sorbent per liter solution (bound solute concentration) and C is the equilibrium concentration of the solute in the solution (concentration of free dye, MV). The value of the bound concentration may be obtained by using Eq. (8).

For equilibrium sorption studies, dye sorption percentage (DS%), dye up take performance (q) (mass amount as "mol" of sorption per unit mass (as gram) of the adsorbent, and partition coefficient (K_d) can be investigated. The value of DS% of the hydrogels was calculated by following equation:

$$\text{DS\%} = \frac{C_0 - C}{C_0} \times 100 \tag{9}$$

Here, C_o and C were defined earlier.

The dye uptake performance (q) of AAm/SVS hydrogels, AAm/SVS/CMC semi-IPNs, AAm/SVS/ZEO hybrid hydrogels, and AAm/SVS/CMC/ZEO biohybrid hydrogels were evaluated by using the following equation [9,10,35,37,38]:

$$q = \frac{(C_b)v}{m} \tag{10}$$

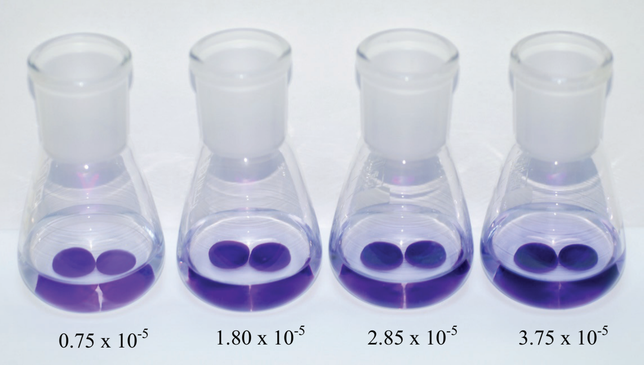


Fig. 12. The photographs of AAm/SVS/CMC/ZEO biohybrid hydrogels in different molar concentrations of aqueous MV solutions.

where q is the dye uptake performance of the hydrogel systems (mol g^{-1}), v is the volume of the aqueous phase (L), and m is the mass of dry hydrogels. C_b was defined earlier.

First, it was examined that effect of contents of SVS monomers for the uptake of the dye. The dye uptake performance, the amount of dyes sorbed onto unit dry mass of the gel was calculated for uptake of dye within the hydrogel in aqueous solutions of 2.5×10^{-5} M of MV, and presented in Table 7. Also, the values of DS% of the hydrogel systems have been calculated, and presented in Table 7, too.

Table 7 presents that the values of DS% of AAm/SVS hydrogels, AAm/SVS/CMC semi IPNs, AAm/SVS/ZEO hybrid hydrogels, and AAm/SVS/CMC/ZEO biohybrid hydrogels (53.12–88.60%) and the values of q of AAm/SVS hydrogels, AAm/SVS/CMC semi IPNs, AAm/SVS/ZEO hybrid hydrogels, and AAm/SVS/CMC/ZEO biohybrid hydrogels (5.91×10^{-6}–9.07×10^{-6} mol g^{-1}) are generally, increased with increasing content of SVS. If the values of DS% and the values of q of the hydrogel systems are examined, it was seen that it was not good relationship with addition of CMC and ZEO (Table 7).

Equilibrium sorption isotherms of AAm/SVS hydrogels, AAm/SVS/CMC semi-IPNs, AAm/SVS/ZEO hybrid hydrogels, and AAm/SVS/CMC/ZEO biohybrid hydrogels were plotted and equilibrium sorption isotherm of AAm/SVS/CMC semi-IPNs and AAm/SVS/CMC/ZEO biohybrid hydrogels have been presented in Figs. 13 and 14 as representative.

The value of q (mol amount of sorption MV per unit mass) of the hydrogel systems are increased with the increasing concentration of MV sorbed onto unit dry mass of the gel (Figs. 13 and 14). The reason of this is the hydrophilic effect and dye uptake performance of comonomer.

Partitioning of dissolved constituents between an aqueous phase and adsorbents in waters and sediments has commonly been described by an empirical partition coefficient that simply relates the total concentration of a dissolved species to the total concentration of the adsorbed species [9,10,35,37,38,48].

$$K_d = \frac{C_b}{C} \tag{11}$$

Here, K_d is empirical partition coefficient at equilibrium. C_b and C were defined earlier. Partition coefficients of MV between dye solution and AAm/SVS hydrogels, AAm/SVS/CMC semi-IPNs, AAm/SVS/ZEO hybrid hydrogels, and AAm/SVS/CMC/ZEO biohybrid hydrogels were calculated, and shown in Table 7. In Table 7, K_d values of the hydrogel systems are 1.13–7.78. Here, K_d values of the hydrogels are higher than 1.0. So, it can be said that synthesized AAm/SVS hydrogels, AAm/SVS/CMC semi-IPNs, AAm/SVS/ZEO hybrid hydrogels, and AAm/SVS/CMC/ZEO biohybrid hydrogels could be used as potential water and dye adsorbent [9,10,35,37,38,48].

There can be many reasons for non-covalent interactions in the binding of MV by AAm/SVS hydrogels, AAm/SVS/CMC semi-IPNs, AAm/SVS/ZEO hybrid hydrogels, and AAm/SVS/CMC/ZEO biohybrid hydrogels. Some interactions between the hydrogel and the cationic dye such as MV may be hydrophobic and hydrogen bonding. Specially, hydrogen bonding will be expected to occur between amine

Table 7
Some sorption parameters of the hydrogels in aqueous solutions of MV

SVS/μL	60	120	180	240	300
	Dye sorption percentage (DS%)				
AAm/SVS	53.12	77.18	81.87	84.24	84.17
AAm/SVS/ZEO	83.51	85.52	87.84	86.82	87.25
AAm/SVS/CMC	85.84	88.06	87.07	87.06	87.25
AAm/SVS/CMC/ZEO	80.54	86.22	88.01	88.60	87.52
	Dye uptake performance ($q \times 10^6$)				
AAm/SVS	6.84	6.59	8.33	6.87	9.07
AAm/SVS/ZEO	7.44	7.11	6.51	6.67	7.09
AAm/SVS/CMC	7.69	5.91	8.15	6.71	7.98
AAm/SVS/CMC/ZEO	7.96	7.77	7.81	7.13	7.99
	Partition coefficient (K_d)				
AAm/SVS	1.13	3.38	4.52	5.35	5.32
AAm/SVS/ZEO	5.07	5.91	7.23	6.59	6.84
AAm/SVS/CMC	6.07	7.38	6.74	6.73	6.85
AAm/SVS/CMC/ZEO	4.14	6.26	7.34	7.78	7.02

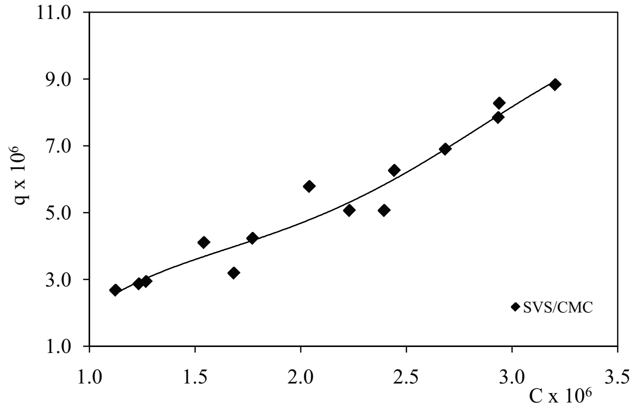


Fig. 13. Equilibrium sorption isotherms of AAm/SVS/CMC semi-IPN hydrogels in aqueous solutions of MV.

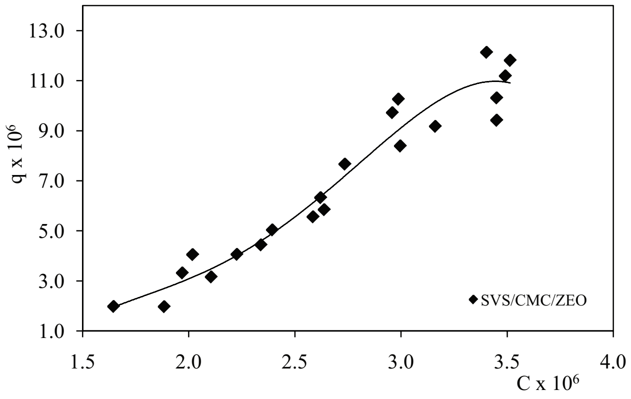


Fig. 14. Equilibrium sorption isotherms of AAm/SVS/CMC/ZEO biohybrid hydrogels in aqueous solutions of MV.

groups and nitrogen atoms on the dye molecules and the amine and carbonyl groups and sulfur atoms on the repeating units of crosslinked polymer (Fig. 2 and Table 2).

3.9. CMC and ZEO effects on the sorption of MV

For investigation of CMC and ZEO effects on MV sorption, some adsorption parameters such as DS%, dye uptake performance (q), and partition coefficient (K_d) of AAm/SVS/CMC semi-IPNs, and AAm/SVS/ZEO hybrid hydrogels having 240 μL of SVS with different CMC and ZEO contents in aqueous solutions of MV were calculated, and they are tabulated in Table 8.

It was shown that the values of q of AAm/SVS/CMC semi-IPNs, and AAm/SVS/ZEO hybrid hydrogels between 6.09×10^{-6} and 9.44×10^{-6} mol g^{-1}. Also, incorporation of CMC and ZEO into the copolymer network leads to generally higher values of DS% (85.06%–88.08%) and partition coefficient (5.70–7.40) of AAm/SVS/CMC semi-IPNs, and AAm/SVS/ZEO hybrid hydrogels. On the other hand,

Table 8
Some sorption parameters of and AAm/SVS/CMC semi-IPNs and AAm/SVS/ZEO hybrid hydrogels having 240 μL of SVS with different ZEO and CMC contents

2.0% of ZEO–water suspension or 2.0% of aqueous CMC solution (mL)	0.25	0.50	0.75	1.00
	Dye sorption percentage (DS%)			
ZEO	87.40	87.85	87.31	85.14
CMC	87.40	86.04	88.08	85.06
	Dye uptake performance ($q \times 10^6$)			
ZEO	8.54	6.09	9.44	7.93
CMC	8.27	7.21	7.09	8.49
	Partition coefficient (K_d)			
ZEO	6.94	7.24	6.89	5.73
CMC	6.94	6.17	7.40	5.70

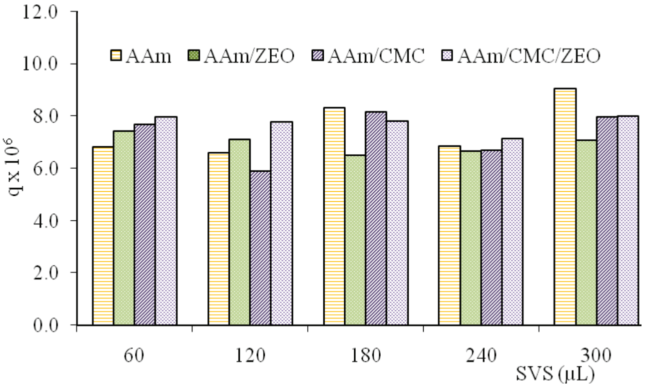


Fig. 15. The values of dye uptake performance of the hydrogel systems with various content of SVS.

here, K_d values of the hydrogels are very higher than 1.0. So, again, it can be said that synthesized AAm/SVS/CMC semi-IPNs, and AAm/SVS/ZEO hybrid hydrogels could be used as potential water adsorbent for removal of the dye molecules or other big molecular structures similar as dye molecules [9,10,35,37,38,48]. For good sorption characterization, the effect of SVS content on the dye sorption behavior, the values of q of the hydrogel systems vs. the content of SVS is plotted in Fig. 15. In Fig. 15, the values of q of the hydrogels gradually increased with increasing of SVS content in the hydrogels.

4. Conclusion

AAm/SVS hydrogels, AAm/SVS/CMC semi-IPNs, AAm/SVS/ZEO hybrid hydrogels, and AAm/SVS/CMC/ZEO biohybrid hydrogels have been synthesized successively by free radical solution polymerization method. The hydrogel systems showed high water absorbency. Some swelling and diffusion properties were discussed for the hybrid hydrogel systems prepared under various formulations. AAm/SVS hydrogels, AAm/SVS/CMC semi-IPNs, AAm/SVS/ZEO hybrid hydrogels, and AAm/SVS/CMC/ZEO biohybrid hydrogels have been sorbed cationic dye such as MV from aqueous MV solutions. To determine the sorption characteristics of MV into the hydrogel systems, some sorption parameters such as DS%, dye uptake performance, and partition coefficient of the hydrogel systems have been investigated. The values of the partition coefficient of the hydrogel systems are higher than 1.0. So, it can be said that the hydrogel systems could be used as potential water adsorbent for removal of the dye molecules or other big molecular structures similar as dye molecules. Consequently, AAm/SVS hydrogels, AAm/SVS/CMC semi-IPNs, AAm/SVS/ZEO hybrid hydrogels, and AAm/SVS/CMC/ZEO biohybrid hydrogels developed in this study may serve as a potential sorbent device for water and dye (and/or similar model molecules) sorption.

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References

[1] E.S. Dragan, A.I. Cocarta, M. Gierszewska, Designing novel macroporous composite hydrogels based on methacrylic acid copolymers and chitosan and in vitro assessment of lysozyme controlled delivery, Colloids Surf., B, 139 (2016) 33–41.
[2] M.H. Mousa, Y. Dong, I.J. Davies, Recent advances in bionanocomposites: preparation, properties, and applications, Int. J. Polym. Mater. Polym. Biomater., 65 (2016) 225–254.
[3] N. Sivagangi Reddy, K.S.V. Krishna Rao, Polymeric hydrogels: recent advances in toxic metal ion removal and anticancer drug delivery applications, Ind. J. Adv. Chem. Sci., 4 (2016) 214–234.
[4] H.Y. Atay, Polymer Composites; Properties, Performance and Applications, A. Méndez-Vilas, A. Solano-Martín, Eds., Polymer Science: Research Advances, Practical Applications and Educational Aspects, Formatex Research Center, Badajoz, Spain, 2016, pp. 420–428.
[5] E.S. Dragan, M.V. Dinu, G. Shankar, Recent developments in composite biosorbents and their applications for wastewater. A review, Res. J. Chem. Environ., 19 (2015) 42–58.
[6] E.S. Dragan, Design and applications of interpenetrating polymer network hydrogels. A review, Chem. Eng. J., 243 (2014) 572–590.
[7] G. Jing, L. Wang, H. Yu, W.A. Amer, L. Zhang, Recent progress on study of hybrid hydrogels for water treatment, Colloids Surf., A, 416 (2013) 86–94.
[8] G. Crini, Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment, Prog. Polym. Sci., 30 (2005) 38–70.
[9] E. Karadağ, H. Ödemiş, S. Kundakçi, Ö.B. Üzüm, Swelling characterization of acrylamide/zinc acrylate/xanthan gum/sepiolite hybrid hydrogels and its application in sorption of Janus Green B from aqueous solutions, Adv. Polym. Technol., 35 (2016) 248–259.
[10] E. Karadağ, S. Kundakçı, Application of highly swollen novel biosorbent hydrogels in uptake of uranyl ions from aqueous solutions, Fibers Polym., 16 (2015) 2165–2176.
[11] E.S. Dragan, M.V. Dinu, Progress in polysaccharide/zeolites and polysaccharide hydrogel composite sorbents and their applications in removal of heavy metal ions and dyes, Curr. Green Chem., 2 (2015) 342–353.
[12] X. Wang, A. Wang, Equilibrium isotherm and mechanism studies of Pb(II) and Cd(II) ions onto hydrogel composite based on vermiculite, Desal. Wat. Treat., 48 (2012) 38–49.
[13] M. Vakili, M. Rafatullah, B. Salamatini, A.Z. Abdullah, M.H. Ibrahim, K.B. Tan, Z. Gholami, P. Amouzgar, Application of chitosan and its derivatives as adsorbents for dye removal from water and wastewater: a review, Carbohydr. Polym., 113 (2014) 115–130.
[14] A.C. Lopes, P. Martins, S. Lanceros-Mendez, Aluminosilicate and aluminosilicate based polymer composites: present status, applications and future trends, Prog. Surf. Sci., 89 (2014) 239–277.
[15] H. Yang, W. Wang, J. Zhang, A. Wang, Preparation, characterization, and drug-release behaviors of a pH-sensitive composite hydrogel bead based on guar gum, attapulgite and sodium alginate, Int. J. Polym. Mater. Polym. Biomater., 62 (2013) 369–376.
[16] C.S. Patrickios, Polymer networks: recent developments, Macromol. Symp., 291–292 (2010) 1–11.
[17] N. Şahiner, W.T. Godbey, G.L. McPerson, V.T. John, Microgel, nanogel and hydrogel–hydrogel semi-IPN composites for biomedical applications: synthesis and characterization, Colloid. Polym. Sci., 284 (2006) 1121–1129.
[18] A. Krestou, A. Xenidis, D. Panias, Mechanism of aqueous uranium (VI) uptake by natural zeolitic tuff, Miner. Eng., 16 (2004) 1363–1370.

[19] W.A. Laftah, S. Hashim, A.N. Ibrahim, Polymer hydrogels: a review, Polym. Plast. Technol. Eng., 50 (2011) 1475–1486.

[20] R. Singhal, K. Gupta, A review: tailor-made hydrogel structures (classification and synthesis parameters), Polym. Plast. Technol. Eng., 55 (2016) 54–70.

[21] E. Karadağ, S. Kundakcı, A. Nalbantoğlu, Ö.B. Üzüm, Highly swollen polymer/clay composite sorbent-based AAm/AMPS hydrogels and semi-IPNs composed of carboxymethyl cellulose and montmorillonite and cross-linked by PEGDA, Polym. Plast. Technol. Eng., 53 (2014) 54–64.

[22] L. Zhu, L. Zhang, Y. Tang, X. Kou, Synthesis of sodium alginate graft poly (acrylic acid-co-2-acrylamido-2-methyl-1-propane sulfonic acid)/attapulgite hydrogel composite and the study of its adsorption, Polym. Plast. Technol. Eng., 53 (2014) 74–79.

[23] A. Salama, N. Shukry, M. El-Sakhawy, Carboxymethyl cellulose-*g*-poly(2-(dimethylamino)ethyl methacrylate) hydrogel as adsorbent for dye removal, Int. J. Biol. Macromol., 73 (2015) 72–75.

[24] H.M. Nizam El-Din, A.W.M. El-Naggar, F.I. Abu-El Fadle, Radiation synthesis of pH-sensitive hydrogels from carboxymethyl cellulose/(poly(ethylene oxide) blends as drug delivery systems, Int. J. Polym. Mater. Polym. Biomater., 62 (2013) 711–718.

[25] H.M. Nizam El-Din, S.G. Abd Alla, W.M. El-Naggar, Swelling and drug release properties of acrylamide/carboxymethyl cellulose networks formed by gamma irradiation, Radiat. Phys. Chem., 79 (2010) 725–730.

[26] A.K. Bajpai, A. Giri, Water sorption behavior of highly (carboxymethylcellulose-*g*-polyacrylamide) hydrogels and release of potassium nitrate as agrochemical, Carbohydr. Polym., 53 (2003) 271–279.

[27] M. Zendehdel, A. Zendehma, F. Hoseini, M. Azarkish, Investigation of removal of chemical oxygen demand (COD) wastewater and antibacterial activity of nanosilver incorporated in poly(acrylamide-co-acrylic acid)/NaY zeolite nanocomposite, Polym. Bull., 72 (2015) 1281–1300.

[28] V. Panic, S.J. Velickovic, Removal of model cationic dye by adsorption onto poly(methacrylic acid)/zeolite hydrogel composites: kinetics, equilibrium study and image analysis, Sep. Purif. Technol., 122 (2014) 384–394.

[29] W.S. Ngah, L.C. Teong, R.H. Toh, M.A.K.M. Hanafiah, Comparative study on adsorption and desorption of Cu(II) ions by three types of chitosan-zeolite composites, Chem. Eng. J., 223 (2013) 231–238.

[30] S. Khoonsap, S. Amnuaypanich, Mixed matrix membranes prepared from poly(vinyl alcohol) (PVA) incorporated with zeolite 4A-graft-poly(2-hydroxyethyl methacrylate) (zeolite-g-PHEMA) for the pervaporation dehydration of water–acetone mixtures, J. Membr. Sci., 367 (2011) 182–189.

[31] A. Pourjavadi, H. Ghasemzadeh, Carrageenan-g-poly (acrylamide)/poly(vinysulfonic acid sodium salt) as a novel semi-IPN hydrogel: synthesis, characterization and swelling behavior, Polym. Eng. Sci., 47 (2007) 1388–1395.

[32] T. Miyazaki, M. Imamura, E. Ishida, M. Ashizuka, C. Ohtsuki, Apatite formation abilities and mechanical properties of hydroxyethylmethacrylate-based organic-inorganic hybrids incorporated with sulfonic groups and calcium ions, J. Mater. Sci., 20 (2009) 157–161.

[33] R. Chanthateyanonth, S. Ruchirawat, C. Srisitthiratkul, Preparation of new water-soluble chitosan containing hyperbranched-vinylsulfonic acid sodium salt and their antimicrobial activities and chelation with metals, J. Appl. Polym. Sci., 166 (2009) 2074–2082.

[34] Y.M. Mohan, J.P. Dickson, K.E. Geckeler, Swelling and diffusion characteristics of novel semi-interpenetrating network hydrogels composed of poly[(acrylamide)-co-(sodium acrylate)] and poly[(vinylsulfonic acid), sodium salt], Polym. Int., 56 (2007) 175–185.

[35] S. Kundakcı, E. Karadağ, Preliminary swelling and dye sorption studies of acrylamide/4-styrenesulfonic acid sodium salt copolymers and semi-interpenetrating polymer networks composed of gelatin and/or PEG, Polym. Bull., 71 (2014) 351–370.

[36] Y. Wang, L. Zeng, X. Ren, H. Song, A. Wang, Removal of methyl violet from aqueous using poly(acrylic acid-co-acrylamide) attapulgite composite, J. Environ. Sci., 22 (2010) 7–14.

[37] E. Karadağ, S. Kundakcı, A novel polymeric adsorbent for water and dye uptake: acrylamide/sodium acrylate copolymers and semi-interpenetrating polymer networks composed of gelatin and/or PVA, Polym. Plast. Technol. Eng., 51 (2012) 1513–1523.

[38] E. Karadağ, F. Topaç, S. Kundakcı, Ö.B. Üzüm, Novel composite sorbent AAm/MA hydrogels containing starch and kaolin for water sorption and dye uptake, Bull. Mater. Sci., 37 (2014) 1637–1646.

[39] S.J. Lee, S.S. Kim, Y.M. Lee, Interpenetrating polymer network hydrogels based on poly (ethylene glycol) macromer and chitosan, Carbohydr. Polym., 41 (2000) 197–205.

[40] S.J. Kim, S.J. Park, S.I. Kim, Synthesis and characterization of interpenetrating polymer network hydrogels composed of poly(vinyl alcohol) and poly(*N*-isopropylacrylamide), React. Funct. Polym., 55 (2003) 61–67.

[41] D. Saraydin, E, Karadağ, Y. Işıkver, N. Şahiner, O. Güven, The influence of preparation methods on the swelling and network properties of acrylamide hydrogels with crosslinkers, J. Macromol. Sci., Pure Appl. Chem. A, 41 (2004) 421–433.

[42] S. Azizian, Kinetic models of sorption: a theoretical analysis, J. Colloid Interface Sci., 276 (2004) 47–52.

[43] N.A. Peppas, N.M. Franson, The swelling interface number as a criterion for prediction of diffusional solute release mechanisms in swellable polymers, J. Polym. Sci., 21 (1983) 983–997.

[44] M.T. Am Ende, N.A. Peppas, Transport of ionizable drugs and proteins in crosslinked poly(acrylic acid) and poly(acrylic acid-co-2-hydroxyethyl methacrylate) hydrogels. II. Diffusion and release studies, J. Controlled Release, 48 (1997) 47–56.

[45] R. Dengre, M. Bajpai, S.K. Bajpai, Release of vitamin B_{12} from poly(*N*-vinyl-2-pyrrolidione)-crosslinked polyacrylamide hydrogels, J. Appl. Polym. Sci., 76 (2000) 1706–1714.

[46] T. Çaykara, S. Kiper, G. Demirel, Thermosensitive poly(*N*-isopropylacrylamide-co-acrylamide) hydrogels: synthesis, swelling and interaction with ionic surfactants, Eur. Polym. J., 42 (2006) 348–355.

[47] A.E. Ali, H.A. Shawky, H.A. Abd El Rehim, H.A. Hegazy, Synthesis and characterization of PVP/AAc copolymer hydrogel and its applications in the removal of heavy metals from aqueous solution, Eur. Polym. J., 39 (2003) 2337–2344.

[48] L.M. Schwarte, N.A. Peppas, Novel poly(ethylene glycol)-grafted, cationic hydrogels: preparation, characterization and diffusive properties, Polymer, 39 (1998) 6057–6066.