

Environmentally Sensitive Vinylpyrrolidone/methacrylic Acid Inter-complex Amphoteric Hydrogel: Preparation, Characterization, and Use in the Binding of Copper Ions

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Research Article

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**Environmentally sensitive
vinylpyrrolidone/methacrylic acid inter-complex amphoteric hydrogel:
Preparation, characterization, and use in the binding of copper ions**

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Abstract

Environmentally sensitive hydrogels (ESH) with inter-complex and amphoteric properties were prepared by thermal free radical polymerization of vinylpyrrolidone (VP), methacrylic acid (MA), and N,N'-methylene bisacrylamide. Spectroscopic and thermal characterizations of ESHs were performed using FTIR and TGA. To determine the effects of ESHs on swelling properties, swelling and diffusion studies were performed at different pHs, temperatures, and salt solutions. While the inter-complex formation between VP and MA was monitored with UV, the amphoteric property and environmental sensitivity of VP/MA-H were determined by swelling studies. In the binding of Cu(II) ion binding onto VP/MA-H experiments, a Langmuir type (L) adsorption was observed concerning the Giles classification system. Binding parameters such as equilibrium constant (K_L), monolayer coverage (Q_m), and maximum fractional occupancy (FO%) were calculated as $0.16 \text{ L g}_{\text{ESH}}^{-1}$, $30 \text{ MgCu(II) g}_{\text{ESH}}^{-1}$, and 81%, respectively. In the light of these findings, it can be said that strong electrostatic interactions between the anionic groups in the VP/MA-H and Cu (II) cations are more effective in the interaction of the heavy metal ions with the hydrogel. The outputs of this study are important in the preparation of effective vinylpyrrolidone/methacrylic acid for hydrogel applications in electrostatic interactions, adsorption, and removal of organic toxic wastes.

Keywords: vinylpyrrolidone, methacrylic acid, inter-complex, amphoteric, environmentally sensitive hydrogel

Introduction

While hydrophilic cross-linked polymeric structures are defined as hydrogels [1, 2], hydrogels that respond with volume changes to external stimuli such as pH, temperature, ionic strength, solvent, electric field, light, magnetic field, physiological fluids, are environmentally sensitive is named [3].

Homo-polymeric and co-polymeric polymers and gels prepared from vinylpyrrolidone, a water-loving monomer, are widely used in the scientific and technological field [4-11]. The unique physical and chemical properties (such as biocompatibility, non-toxicity, chemical stability, good solubility in water and many organic solvents, the tendency to complex with both hydrophobic and hydrophilic substances) of VP polymers and hydrogels have made it suitable as a biomaterial in several important medical and non-medical applications (pharmaceutical industry and medicine, optics and electrical applications, membranes, adhesives, ceramics, paper, coatings and inks, household, industrial and institutional, lithography and photography, fibers and textiles, environmental applications) [4-11].

While the number of publications on VP polymers since 1970 is around 5400, 230 of these publications are VP hydrogels in SCI. These publication numbers show that the research and development of VP hydrogels are still in their infancy compared to the continued and significantly increased efforts to develop hydrogels [12]. However, although methacrylic acid is mentioned in about 30 of these publications (such as crosslinking with gamma rays [13-18], photopolymerization [19], polymerization by ATR method [9], grafting polymerization [20], and IPN formation [21]), there are no studies on the preparation of copolymeric hydrogels by free radical polymerization using azobisisobutyronitrile (AIBN) initiator.

We aimed to prepare, characterize and investigate the Cu(II) ion binding properties of methacrylic acid copolymeric hydrogels of vinylpyrrolidone by free radical polymerization using an AIBN initiator. To improve the swelling properties of vinylpyrrolidone/methacrylic acid gels and to impart pH sensitivity it has been copolymerized for a monoprotic methacrylic acid (MA). The resulting gel is responsive to both pH, temperature, and salt solutions changes. By copolymerization with a suitable monomer, the hydration degree and swelling kinetics of the final hydrogel are easily tuned.

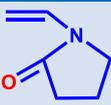
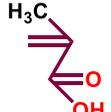
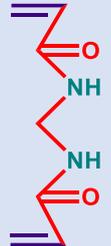
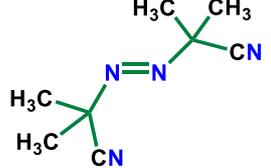
Experimental

Chemicals

The monomers such as vinylpyrrolidone (VP), methacrylic acid (MA), and a crosslinker such as N,N'-methylenebisacrylamide (N-Bis), and an initiator such as azobisisobutyronitrile (AIBN) were purchased from Aldrich, Milwaukee Company. The chemical names, synonyms,

abbreviations, and chemical structures of the monomers, crosslinker, and initiator are given in Table 1. The copper (II) sulfate used in the adsorption process was obtained from Merck KGaA, Darmstadt, Germany. The chemicals used were analytical purity (99%).

Table 1. The chemicals used in the preparation of the hydrogels

chemicals	abbreviation	structure
Vinylpyrrolidone (1-ethenylpyrrolidin-2-one, 1-vinyl-2-pyrrolidone)	VP	
methacrylic acid (propenoic acid 2-methyl, methyl acrylic acid)	MA	
N, N'-methylenebisacrylamide (N, N'-methylenediacrylamide, methylenebisacrylamide)	N-Bis	
Azobisisobutyronitril (2,2'-azobis(2-methylpropionitrile), α, α' -azobis(2-methylpropionitrile))	AIBN	

Preparation of hydrogels

Homo-polymeric hydrogels

The vinylpyrrolidone hydrogel was synthesized by free radical homopolymerization using 0.81 mL of VP in 0.81 mL of distilled water. The initiator was (AIBN) (2.0 wt.%) and the crosslinker was N-Bis (2, 4, 6, or 8 wt.%) for the total mass of the monomers. We used deionized double distilled water as a solvent.

The methacrylic acid hydrogel was made in the same way as the vinyl pyrrolidone hydrogel preparation and 0.81 mL of MA was used instead of VP. However, since AIBN is insoluble in water, the initiator was first dissolved in MA.

The homopolymeric hydrogel prepared from vinylpyrrolidone monomer was named VP-H, and that prepared from methacrylic acid was designated MA-H.

Copolymeric hydrogels

In the preparation of vinylpyrrolidone/ methacrylic acid hydrogel, 0.81 mL of VP, 0.81 mL of MA, and 1.62 mL of distilled water were used and made with the same technique as homo-polymers. The co-polymeric hydrogel prepared from the co-monomer of vinylpyrrolidone monomer and methacrylic acid was named VP/MA-H.

Both the homo-polymer and co-polymer mixtures were transferred to flexible PVC straws with a heat-sealed bottom and placed in the oven at 65°C for 5 hours. After synthesis, the gels were removed from the tubes and cut to be approximately equal to each other. The hydrogels, which were washed several times with distilled water, were first dried at room temperature for 24 hours and then dried in an oven at 50 °C for 24 hours. These dry gels were used in characterization, swelling, and adsorption tests.

Characterization and swelling

UV spectra of the aqueous mon solutions of VP, MA, and the mixture of VP and MA were taken at the Biochrom WPA Biowave II UV/Visible Spectrophotometer (Cambridge, UK) Biowave2 model UV-VIS spectrophotometer at wavelengths between 200 and 400 nm.

FTIR spectra were recorded with FTIR Perkin Elmer spectrophotometer (Waltham, Massachusetts, USA) in the 4000–400 cm⁻¹ range, on grinded hydrogel pilled with KBr, and 32 scans were taken at 4 cm⁻¹ resolutions.

TG thermal analyzer (Perkin Elmer Pyris 1 TGA, Shelton, USA)) was used for the thermogravimetric analysis of the hydrogels. ~10 mg of hydrogel (ESH) was heated from 10 °C to 600 °C at a heating rate of 10 °C min⁻¹ and a flow rate of 20 mL min⁻¹ nitrogen gas.

The swelling values of homo- or co-polymeric hydrogels ($S, g\ g_{ESH}^{-1}$) were determined from the following equation [26] by measuring the masses of hydrogels in different aqueous media (such as different temperature, pH, or ionic solutions).

$$S = \frac{m_t - m_i}{m_i} \quad (1)$$

where m_i and m_t are the initial mass and the mass of swollen hydrogel at any time, respectively.

Binding

The cupric ion binding capacities of the VP/MA hydrogel were determined using an aqueous Cu(II) solution. The procedure was started by adding VP/MA hydrogel (~ 0.1 g) to the stock solution (100 mL) in an Erlenmeyer.

The initial metal ion concentration was 125 ppm for kinetic studies, and increasing cupric ion concentrations were also taken to evaluate the binding isotherms.

mixture of monomer and co-monomer showed a small hypsochromic shift (blueshift) with hypochromic effect relative to VP and MA. Thus, a hydrogen bond is formed between the free electron pair in $-C=O$'s and the hydroxyl group proton. Here, the energy of the n orbital decreases by the energy of the hydrogen bond, and a blueshift occurs. With these evaluations, it can be said that an inter complex is formed between VP and MA with the help of H-bonds.

Possible interactions and complex formation between N-vinylpyrrolidone and methacrylic acid in VP/MA-H can be illustrated in Figure 2.

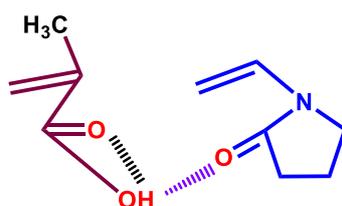


Figure 2. Intra- (||||) and inter-molecular (▶) interactions between VP and MA.

As shown in Figure 2, the intramolecular and intermolecular interactions are hydrogen bonds formed by the interaction between the carbonyl groups in vinylpyrrolidone and methacrylic acid and the hydroxyl group of methacrylic acid.

Synthesis of hydrogels

Poly(vinylpyrrolidone/methacrylic acid) copolymeric hydrogel (VP/MA-H) as a new adsorbent for heavy metal ion adsorption, thermal free radical in the presence of N,N'-methylenebisacrylamide (N-Bis) crosslinker in an aqueous solution of vinylpyrrolidone and methacrylic acid prepared by crosslinking and copolymerization. Azobisisobutyronitrile was used as an initiator. In addition, poly(vinylpyrrolidone) hydrogel (VP-H) and poly(methacrylic acid) hydrogel (MA-H) were prepared by a similar method for homopolymeric hydrogels. A plausible polymerization mechanism of VP/MA-H is shown in Figure 3. Vinylpyrrolidone, methacrylic acid homopolymers, or vinylpyrrolidone/methacrylic acid co-polymer can be polymerized and crosslinked using a chemical initiator such as azobisisobutyronitrile (AIBN). AIBN decomposes above 60 °C to form free radicals due to the possibility of radical formation (free radical formation) during the reaction. The first possible step for polymerization is the transfer of an unpaired electron to make the monomeric units reactive, and the reaction between the VP (or MA) molecules and the radical. The free radical then reacts with the vinylpyrrolidone monomer or methacrylic acid comonomer, breaking the double bond of the monomer or

comonomer and retaining an unpaired electron at the base of the formed chain, forming a new free radical (propagation step; homopolymerization or copolymerization). This species then interacts with the crosslinker (N-Bis), forming species with two radical sites that combine in the molecule and form a chain of crosslinked vinylpyrrolidone/methacrylic acid copolymers (propagation step; crosslinking). The reactivity ratios of monomer VP and co-monomer MA are given as r_1 (=44.66) and r_2 (=3.38) [13]. Due to the high r_1 and low r_2 values, the polymerization ability of VP with itself and other monomers is quite strong. For this reason, the mixing ratio of the feed was chosen as 1:1. Since $r_1 > 1$ and $r_2 > 1$, not every radical has a preference and the copolymer has a completely random sequence of VP and MA monomers [13]. However, VP is more reactive than MA. As a result, the copolymer will consist of a more substantial portion of the more reactive sample in the array of random repeat units. Thus, it can be said that VP/MA hydrogels are randomly copolymerized.

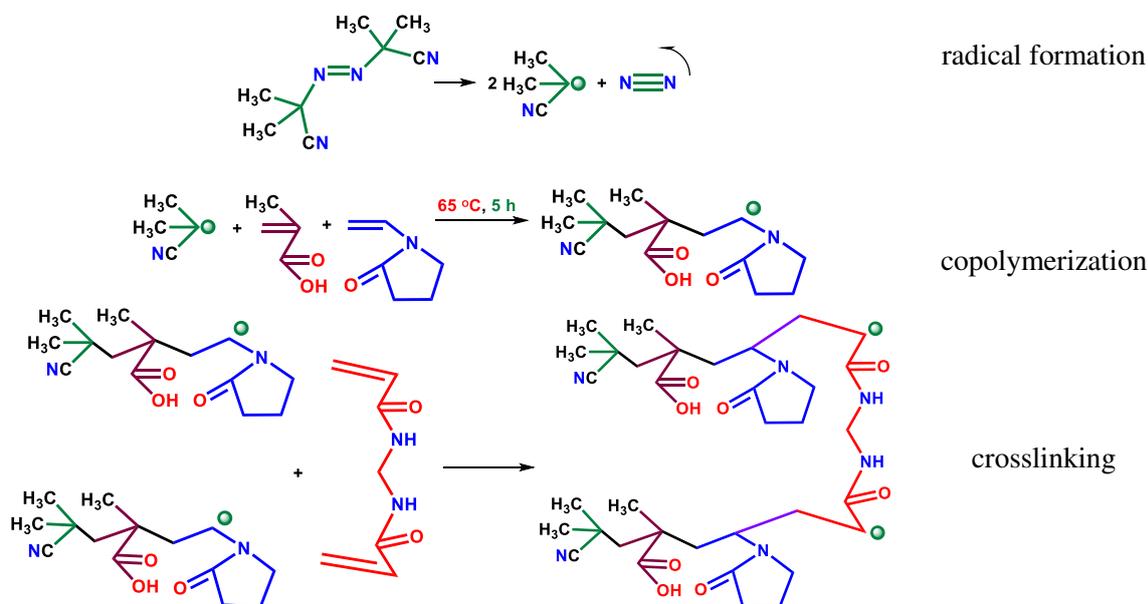


Figure 3. Plausible copolymerization and crosslinking mechanism of VP/MA hydrogel.

FT-IR analysis

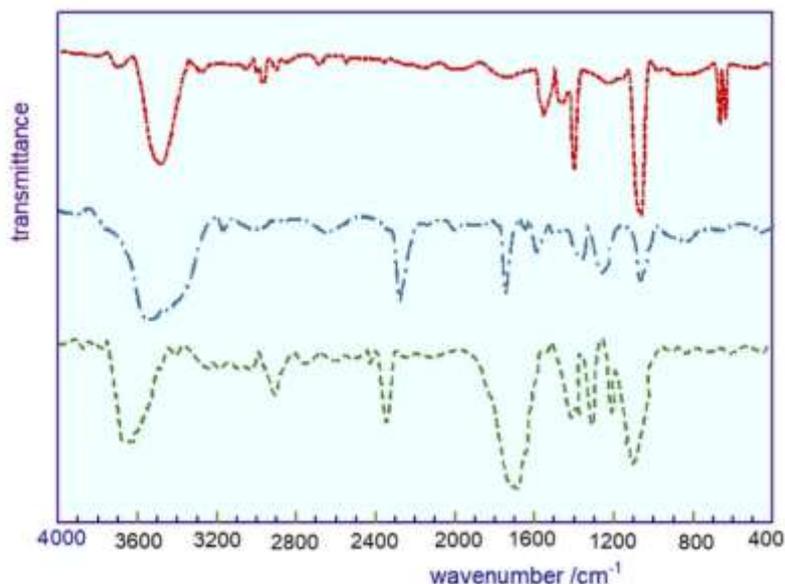


Figure 4. FTIR spectra of the hydrogel, ······; VP-H, ······; MA-H, - - - -; VP/MA-H.

The bands observed around 3700 -3500 cm^{-1} in the FT-IR spectra of the hydrogels shown in Figure 3 show O-H stretching. The band at 1750 cm^{-1} in the spectrum of MA and the bands at 1750 cm^{-1} in the other spectra depend on C=O stretching. In particular, the shift of the band at 1750 cm^{-1} in the spectrum of MA to 1700 cm^{-1} in that of the mixture can be interpreted as the formation of intermolecular H-bonds between the carbonyl group in VP and the carboxyl group in MA [15]. The inability to observe the N-C=O bending band at 568 cm^{-1} observed in VP in the mixture may also be due to the formation of intermolecular H-bonds. While C-H bending band at 1400 cm^{-1} and the CH₂ band at 1020 cm^{-1} were observed in all spectra, CH₂ wagging band was observed at 1300 cm^{-1} in the spectrum of the mixture. These bands may be an indication that the crosslinker has entered the structure. In the spectrum of the hydrogel obtained from a monomer, a comonomer, and a crosslinker at a 1:1 feed ratio, the observation of all functional groups in VP, MA, and crosslinker may be an indication of the formation of a crosslinked vinyl pyrrolidone/methacrylic acid hydrogel.

The thermogram for VP/MA-H is presented in Figure 5.

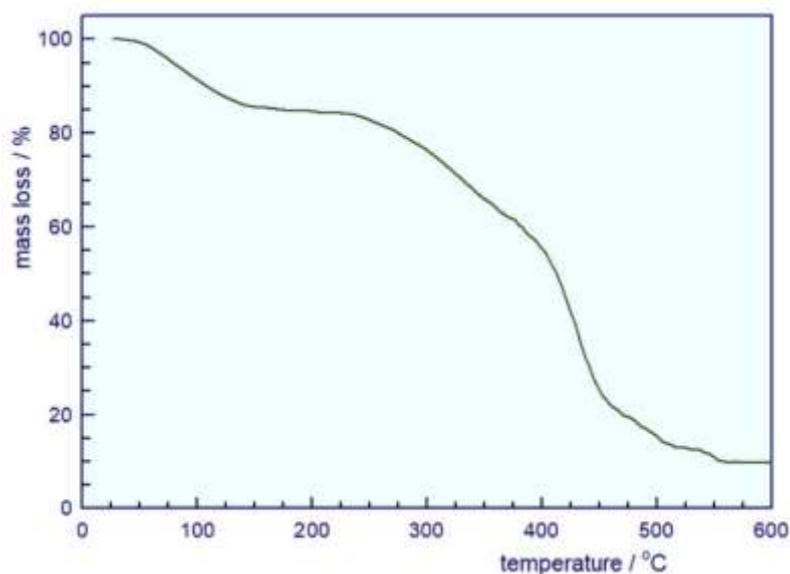


Figure 5. The thermogram of VP/MA-H.

In this thermogram in Figure 5, three decomposition regions of the hydrogel are seen. There is a mass loss of approximately 16.4% in the region up to 200 °C. Water-loving groups such as -OH, -NH, or -C=O in the hydrogel absorb a lot of moisture and bind water. Thus, mass loss in this region occurs by removing bound water and moisture from the hydrogel. There is a 25.5% mass loss in the second field between 200-350 °C. The mass loss here may correspond to the separation of the side groups from the main chain. Subsequent degradation begins at 350°C and continues up to 440°C. The degradation of about 50% of the hydrogel can be interpreted as main chain breakage. Final degradation starts at 470°C and continues up to 550-600°C; this can be thought of as disconnection of the remaining main chain, destruction of the entire hydrogel, and carbonization. Up to this stage, about 90% of the material has decomposed. At 600 °C, approximately 8% of residue remains at the end of VP/MA-H thermal decomposition. [6,15].

Swelling

The swelling of the VP-H, MA-H, and VP/MA-H occurs because of the osmotic pressure difference caused by the presence of the water-loving repeat units in the three-dimensional cross-linked network. Penetrant intake of initially dry VP-H, MA-H, and VP/MA-H was followed for a while, gravimetrically [24, 25]. All the hydrogels absorbed the fluids and swelled at a higher rate in the beginning. After a certain period, the fluid uptake became constant, and the VP-H, MA-H, and VP/MA-H hydrogels achieved their equilibrium swelling capacity (S_{eq}).

Influences of cross linker concentration on swelling

The equilibrium swelling values of hydrogels prepared with different concentrations of N-Bis between 2% and 8% were plotted against the crosslinker concentration and shown in Figure 6.

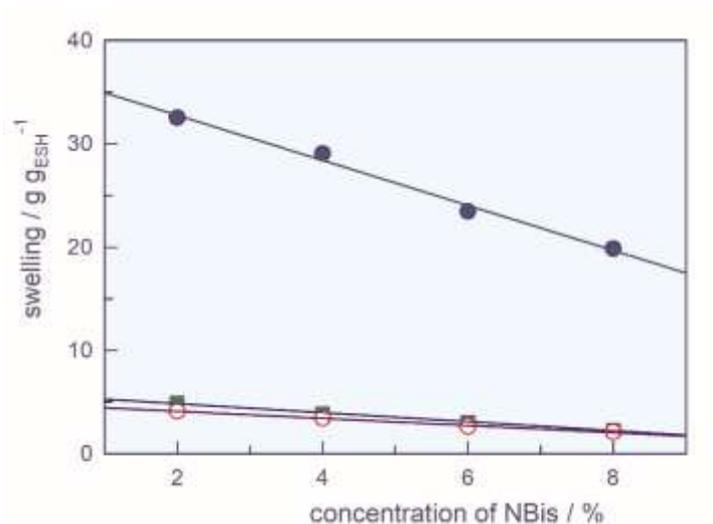


Figure 6. The effect of crosslinker concentration on the swelling of the hydrogels, ●; VP-H, ○; MA-H, ■; VP/MA-H.

As can be seen in Figure 6, the equilibrium swelling values of the hydrogels decreased as the crosslinker concentration increased. By increasing the crosslinker concentration up to a certain concentration, a more intense bonding between the main chains, an increase in cross-linking points, and consequently pore shrinkage occur. This makes it harder for the penetrant to penetrate the hydrogel and reduces swelling.

In this study, it was preferred to use the crosslinker concentration giving the highest swelling value.

Influence of hydrogels type on the hydrogels swelling

Swelling plots were constructed and represented in Figure 7 for the homo-polymers VP-H, MA-H, and co-polymer VP/MA-H hydrogels.

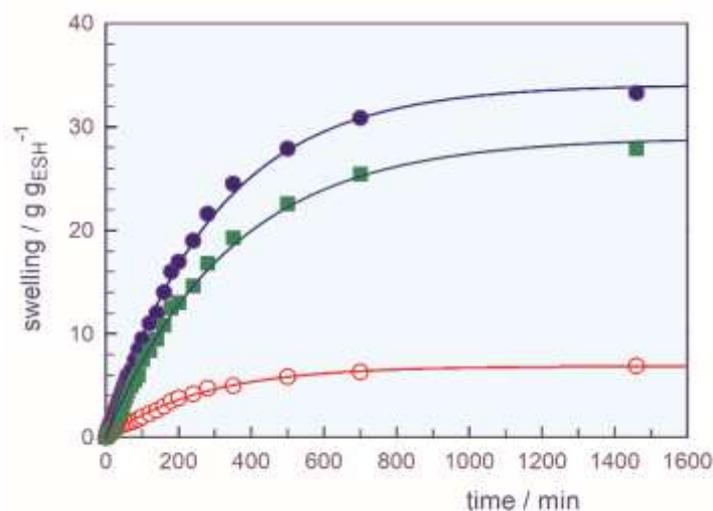


Figure 7. The effect of hydrogel type on the swelling of the hydrogels, ●; VP-H, ○; MA-H, ■; VP/MA-H; model fit.

Figure 7 shows the variation in the swelling capacity of the VP-H, MA-H, and VP/MA-H hydrogels with time at 25 °C. All the hydrogels absorbed the fluids and swelled at a higher rate in the beginning. After a certain period, the fluid uptake became constant, and the VP-H, MA-H, and VP/MA-H hydrogels achieved their equilibrium swelling capacity (S_{eq}).

The time ($t_{1/2}$, min) at which the swelling is one-half the equilibrium value ($S_{1/2}=S_{eq}/2$) was found in Figure 7. Considering that swelling shows a first-order kinetic behavior, swelling rate constants of the prepared hydrogels were found from the equation $k = 0.693 / t_{1/2}$. Experimental S_{eq} , $t_{1/2}$, and k_{exp} values of the hydrogels are given in Table 2.

Table 2. Experimentally found swelling parameters

Hydrogel	$S_{eq} / g \text{ gESH}^{-1}$	$t_{1/2} / \text{min}$	$k_{exp} \times 10^3 / \text{min}^{-1}$
VP-H	33.26	209	3.32
MA-H	6.89	172	4.03
VP/MA-H	27.89	220	3.15

Table 2 shows that the values of S_{eq} of the VP-H, MA-H, and VP/MA-H hydrogels are changed among 6.89–33.26 $g \text{ gESH}^{-1}$. The swelling of VP-H is about 4.8 times greater than the swelling of MA-H. this may be because VP contains more water-loving groups than MA and

the hydrophobic CH₃ group is present in MA. The swelling of VP/MA-H is 1.2 times less than VP-H and 4.1 times more than MA-H, as expected. The swelling of hydrogels was increased in the following order; VP-H > VP/MA-H >> MA-H. Moreover, swelling rate constants of all hydrogels around 10⁻³ min⁻¹ indicate that the prepared hydrogels swell at a slow rate.

In addition, in Figure 7, which represents the dynamic swelling behavior of hydrogels, it is seen that the rate of penetrant uptake increases rapidly in the early times and begins to flatten in the following times. In this case, the swelling behavior may be compatible with the exponential rise to the maximum equation. By adapting the exponential rise to maximum relation to determine swelling parameters of the hydrogels [24], the following equation can be written;

$$S = S_{\max}(1 - e^{-k_s t}) \quad (3)$$

where S (g g_{ESH}⁻¹) is swelling at time t, power parameter S_{max} is equilibrium swelling (g g_{ESH}⁻¹), t is time (min) for swelling, and k_s (min⁻¹) stand for the swelling rate constant. The value of the rate constant is a measure of the ease with which the fluid penetrates the hydrogel. The inverse of the rate constant value (1/k_s) gives the rate parameter (τ, min). A high value of the power parameter indicates that the swelling is very high, while a small rate parameter indicates that the swelling is fast. Also, the ratio of power parameter to the rate parameter gives the swelling rate (SR, g g_{ESH}⁻¹ min⁻¹) at time τ, and τ value is a measure of the SR (i.e. the lower the τ value, the higher the rate of swelling) [24].

Nonlinear regression was applied to equation (1) to calculate the parameters. The correlation coefficients (r²) of the graphs drawn according to equation (1) (in Figure 7) are 0.991 and above, indicating that 1 equation can be used to find the swelling parameters of the prepared hydrogels.

The S_{max} and k_s values found in equation (1), along with the standard error (SE) and correlation coefficients (r²), are given in Table 3. Calculated τ and SR values are also added to Table 3.

Table 3. Calculated swelling parameters

Hydrogel	$S_{\max} / \text{g g}_{\text{ESH}}^{-1}$	k_s / min^{-1}	r^2	τ / min	$\text{SR} / \text{g g}_{\text{ESH}}^{-1} \text{min}^{-1}$
VP-H	34.094 ± 0.356	$3.357 \times 10^{-3} \pm 6.69 \times 10^{-5}$	0.998	297.858	0.114
MA-H	6.893 ± 0.147	$3.772 \times 10^{-3} \pm 0.16 \times 10^{-5}$	0.991	265.083	0.026
VP/MA-H	28.971 ± 0.000	$2.919 \times 10^{-3} \pm 0.00 \times 10^{-5}$	1.000	342.581	0.084

The calculated power parameter values were quite close to the experimentally found values. The rate parameter values were calculated between 4.5 and 5.5 hours. (Table 3). It means that according to the model (Eq. 1), these samples absorb approximately 63% of their maximum absorption capacity [24] during 4.5-5.5 hours. While these values show that the prepared hydrogels swell quite slowly, the fact that the swelling rate and rate parameter are different values from hydrogel to hydrogel also shows that the hydrogel type affects swelling.

Diffusion

The following equation is used to determine the nature of diffusion of a penetrant into hydrogels.

$$F = k_D t^n \quad (4)$$

where F is the fractional uptake at time t , k_D is a constant incorporating characteristic of the network system and the penetrant, and n is the diffusion exponent, which is indicative of the transport mechanism. Equation 2 is valid for up to rate parameter of swelling of the polymer. For a cylindrical gel, $n = 0.45-0.50$ corresponds to Fickian-type diffusion process, while $0.50 < n < 1.0$ indicates non-Fickian or anomalous transport and $n = 1$ implies case II (relaxation controlled) transport [23]. For the prepared hydrogels, F versus t graphs are plotted and are shown in Figure 8.

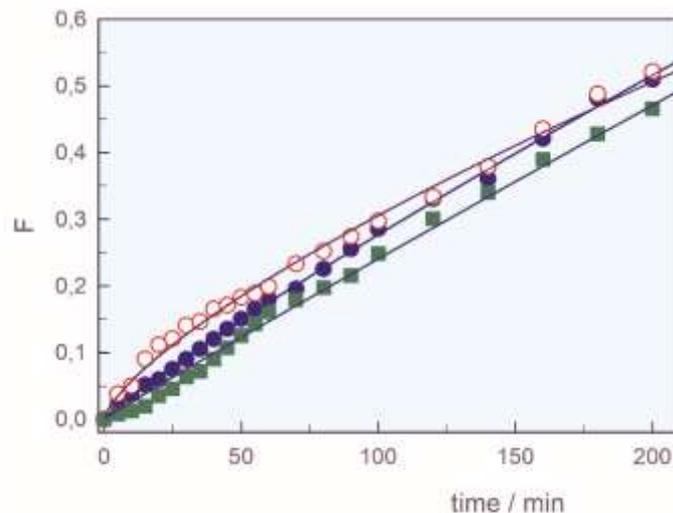


Figure 8. Diffusional behavior of the hydrogels, ●; VP-H, ○; MA-H, ■; VP/MA-H, —; model fit.

Diffusion exponents (n) and diffusion constants (k) were calculated from the nonlinear regression of the F and t plots from the experimental data shown in Figure 8 and are summarized in Table 4 along with the standard error (SE) and correlation coefficients (r^2).

Table 4. Diffusional parameters of the hydrogels

Hydrogel	k_D	n	r^2
VP-H	$4.433 \times 10^{-3} \pm 0.219 \times 10^{-3}$	0.898 ± 0.010	0.999
MA-H	$10.700 \times 10^{-3} \pm 0.717 \times 10^{-3}$	0.728 ± 0.014	0.996
VP/MA-H	$2.781 \times 10^{-3} \pm 0.285 \times 10^{-3}$	0.969 ± 0.020	0.995

Diffusion exponents (n) are calculated between 0.97 and 0.73, thus suggesting the anomalous or non-Fickian type diffusion. When the diffusion model shows anomalous behavior, the relaxation and diffusion time are of the same order of magnitude. Therefore, as the penetrant diffuses into the hydrogel, there is a delay in rearrangement (rupturing) within the polymer chains [23, 24].

Influence of pH on the swelling

The polymeric networks containing ionizable functional groups exhibit pH responsivity [25-29]. The responsibility of surrounding media pH on the swelling values of the prepared hydrogels at 25 °C between pH = 1–13 is shown in Figure 9.

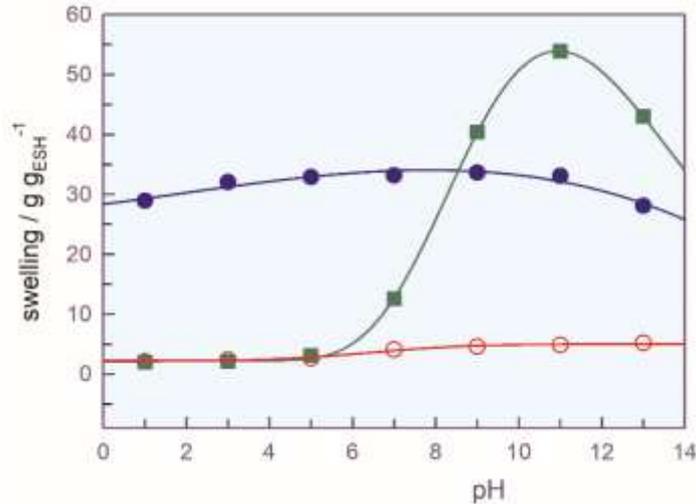


Figure 9. The effect of pH on the swelling, ●; VP-H, ○; MA-H, ■; VP/MA-H.

As seen in Figure 9, MA-H shows an inflection point at about pH=6.4, while VP shows a peak between pH=6-10. The highest point of this peak corresponds to approximately 7.3. VP/MA-H, on the other hand, shows a more interesting swelling behavior with the effect of pH. While swelling shows a linear value up to approximately pH=6, swelling increases rapidly after pH=6, reaches the highest swelling value at approximately pH=10.9, and then decreases.

Methacrylic acid, a weak carboxylic acid, has a pK_a of 4.86 [30]. The inflection point of MA-H was a pH shift of about 1.3 units towards larger pHs due to the polymeric structure. After this pH value, the ionization of MA begins, and swelling increases as a result of the interaction of water and carboxylic groups.

Vinylpyrrolidone is neutral up to approximate pH. As a result of keto-enol tautomerism around pH=7, a positive charge on the tertiary nitrogen atom on the pyrrolidone ring and a negative charge on the carbonyl group may occur [31-35]. Swelling of VP-H, which increases slightly with the interaction of water-loving groups with water up to pH 7, gives a small transition point around pH=7.8 due to keto-enol tautomerism. As a result of the interactions of these charges formed in the structure with the increasing OH^- ions in the environment, the swelling again decreases slightly until pH=11. After pH=11, the carboxylate group is formed with the opening of the pyrrolidone ring in the vinylpyrrolidone unit [26], and when this group interacts with the excess OH^- ions in the environment, swelling decreases as a result of electrostatic repulsions.

The swelling of the VP/MA-H with increasing pH continued by the pH-varying conformation of the monomer and co-monomer forming the hydrogel. VP/MA-H from low pHs to pH=6 showed the same swelling value with increasing pH since VP and MA had not yet

dissociated. The swelling of VP/MA-H increased rapidly from pH=6 to pH=11 due to the ionic charges formed as a result of the acidic decomposition of the MA unit and the keto-enol tautomerism of the VP unit. After pH=11, swelling of VP/MA-H decreased due to ring-opening in the VP unit. Conformational changes in VP/MA-H with increasing pH are illustrated and presented in Figure 10.

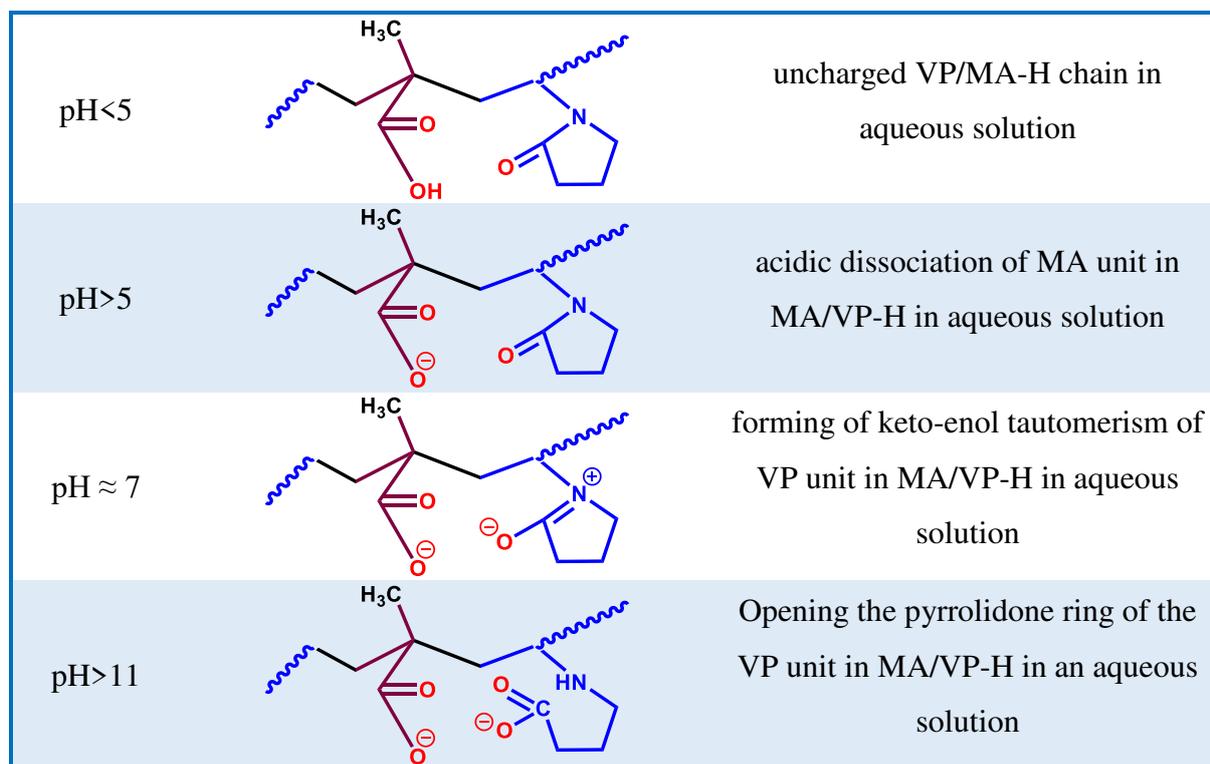


Figure 10. Changes in the conformation of VP/MA-H with increasing pH.

As a result, it can be said that the prepared VP-H, MA-H, and VP/MA-H are sensitive to pH, and these pH sensitivities can be calculated from the maximum and minimum swelling values difference as 5.68, 3.09, and 51.93 g_{ESH}⁻¹, respectively.

Influence of temperature on the swelling

To examine the effect of temperature on swelling [36-39], the hydrogels were inflated to equilibrium at 25 and 50 °C. The variation of swelling with temperature is shown in Figure 11 with a bar graph.

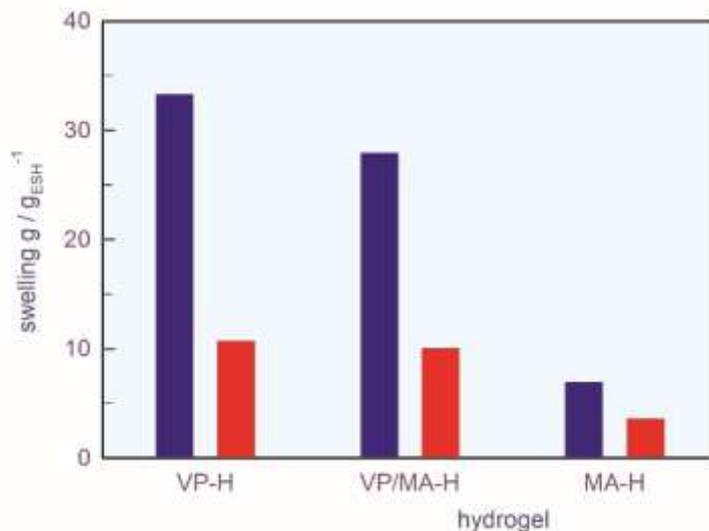


Figure 11. The effect of temperature on the swelling, ■; 25 °C, ■; 50 °C.

The swelling of the hydrogels decreased with increasing temperature. The reason why the swelling of the hydrogels decreases with increasing temperature may be that the hydrophobicity of the $-CH_3$ group on the MA unit and the pyrrolidone ring on the VP unit prevents hydrogen bond formation [40-42].

As a result, it can be said that the prepared VP-H, MA-H, and VP/MA-H are sensitive to temperature, and these temperature sensitivities can be calculated from the maximum and minimum swelling values difference as 22.58, 3.34, and 17.89 g g_{ESH}⁻¹, respectively.

Influence of ions on the swelling

The ions and counter ions play an important role in the swelling behavior of hydrogels [3, 43]. Ion-sensitive swelling behavior was investigated in aqueous solutions of NaCl, KCl, and Na₂CO₃ salts at 0.1 mol L⁻¹ concentrations at 25 °C, and ion-sensitive swelling of hydrogels is shown in Figure 12.

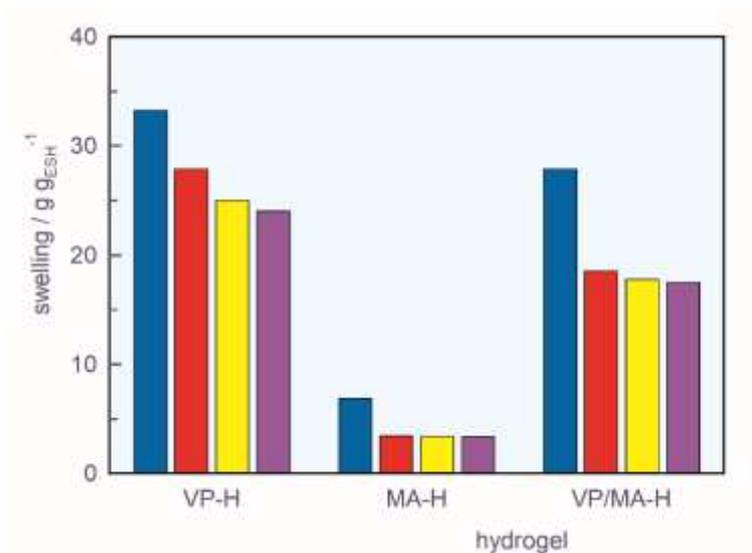


Figure 12. The effect of ions on the swelling, ■; water, ■; NaCl, ■; KCl, ■; Na₂CO₃.

Hydrogels swell less in salt solutions than in water. The swelling values decreased according to the following sequence water, NaCl, KCl, Na₂CO₃. As the hydrogels were swelled in saline solutions, the acid and pyrrolidone ring groups were neutralized by the cations in the external solution, and the swelling were decreased. When the fixed charges on polymeric side chains were fully neutralized, the hydrogel showed nonionic behavior. In various saline solutions, hydrogels showed the Donnan effect when the charges on the polymeric side chain were neutralized and then showed a salting-out effect with the gels going to a nonionic state [3].

These hydrogels, which are prepared by using the pH-, temperature- and ion- sensitivity of the vinylpyrrolidone monomer and the pH- and ion- sensitivity of the methacrylic acid comonomer, with are a durable, homogeneous appearance, can be defined as environmentally sensitive, stimuli-responsive, smart or intelligent hydrogels.

Cu(II) Binding

To observe uptake of heavy metal ions [44] by the VP/MA-H were placed in aqueous solutions of Cu(II), and allowed to equilibrate for 2 days. At the end of this time, VP/MA-H in Cu(II) solutions showed the dark blue coloration of the original solutions. These hydrogels have many carboxylate groups which can cause an increase of electrostatic (ionic) interaction between cationic Cu(II) ions and the carboxylate and enolate of pyrrolidone ring groups in the hydrogels [45, 46]. The possible electrostatic interactions between Cu(II) ions and VP/MA-H are shown in Figure 13.

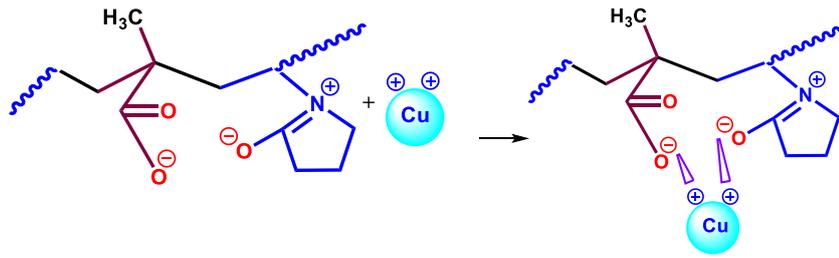


Figure 13. Binding of copper ions to MA/VP-H in aqueous solution.

Binding kinetics

The binding of solute molecules to the surface of an adsorbent is the adsorption process. Adsorption kinetics, on the other hand, is a curve (or line) that describes the rate at which a solute is retained or released from an aqueous medium to the solid-phase interface at a given adsorbent dose, temperature, and pH [47].

The differential and integral representations of the pseudo-first and second-order binding kinetics equations can be written as follows [47].

$$\text{First-order} \quad \frac{dQ}{dt} = k_1(Q_e - Q_t) \quad Q_t = Q_e(1 - e^{-k_1 t}) \quad (5)$$

$$\text{Second-order} \quad \frac{dQ}{dt} = k_2(Q_e - Q_t)^2 \quad Q_t = \frac{t}{A + Bt} \quad A = \frac{1}{k_2 Q_e^2} \quad B = \frac{1}{Q_e} \quad (6)$$

In these equations, Q_t (mg g^{-1}) and Q_e (mg g^{-1}) are the amounts of adsorption at time t (min) and equilibrium. k_1 (min^{-1}) and k_2 ($\text{mg}^{-1} \text{g min}^{-1}$) are pseudo-first and pseudo-second-order rate constants, respectively.

The binding kinetics of Cu(II) to the VP/MA-H was studied and is given in Figure 14. The curves of the integral equals of pseudo-order applied to these data are also shown on the same graph.

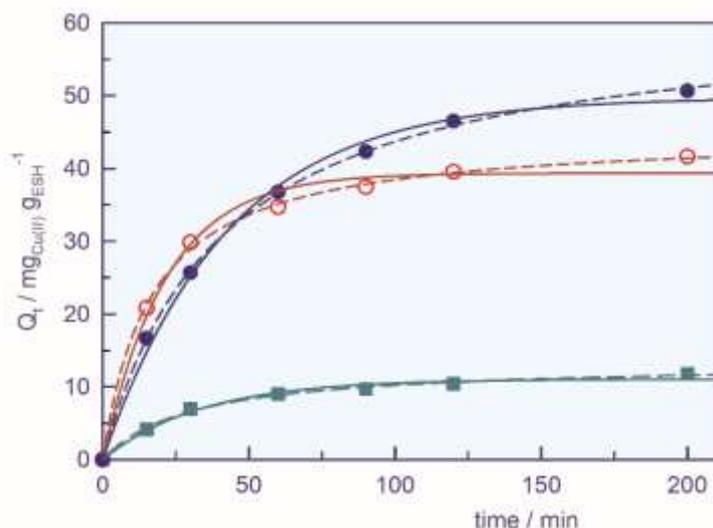


Figure 14. The binding kinetics of Cu(II) to the VP/MA-H, - - -; pseudo-first-order model fit and, —; pseudo-second-order model fit.

According to Figure 14, the binding of Cu(II) to the hydrogel at all pHs first increases over time and reaches equilibrium after a certain time. However, with the increase in pH, the amount of Cu(II) binding to the hydrogel also increases. While little adsorption is observed in an acidic medium when the solution medium is changed from acidic to neutral and alkaline, the binding rate changes and increases significantly. The reason for the copper binding to the hydrogel with the increase in pH may be the conformational changes in the VP/MA. At acidic pH, the side groups in the main chain do not dissociate, preventing the copper(II) from binding to the hydrogel. At alkaline pHs, the carboxylate group is formed by opening the pyrrolidone ring, and the bonding between Cu(II) and VP/MA hydrogel increases. These binding increases are 3.5 times at pH=7 and 4.2 times at pH=11 compared to pH=2, and 1.2 times at pH=11 compared to pH=7. These differences in the amount of binding indicate that the increase in binding is high in the transition from acidic to neutral pH, but less in the transition from neutral to basic pHs.

On the other hand, the parameters found as a result of the pseudo-first- and second-order non-linear kinetic models applied to the experimental data are presented in Table 5 together with the standard error and correlation coefficients.

Table 5a. Pseudo-first order Cu(II) binding kinetics parameters of the VP/MA-H

pH	Q_e	k_1	r^2	$t_{1/2}$
2	11.0602±0.3659	0.0299±0.0033	0.9875	23.2
7	39.3560±0.9417	0.0465±0.0046	0.9897	14.9
12	49.7579±1.1154	0.0235±0.0016	0.9958	29.5

Table 5b. Pseudo-second order Cu(II) binding kinetics parameters of the VP/MA-H

pH	A	B	r^2	Q_e	k_2	$t_{1/2}$
2	2.2752±0.1526	0.0750±0.0020	0.9958	13.3333	2.2472x10 ⁻³	30.3
7	0.3702±0.0166	0.0223±0.0003	0.9988	44.8431	1.3433x10 ⁻³	16.6
12	0.6622±0.0139	0.0163±0.0002	0.9996	61.3497	0.4012x10 ⁻³	40.6

The fact that the r^2 values of the first-order binding kinetic curve at all pHs are smaller than the r^2 values of the second-order curve and the second-order curve better overlaps with the experimental points, indicating that the binding of Cu(II) to VP/MA follows a second-order kinetic. In this model, the rate of binding of the solute is assumed to be proportional to the available sites on the hydrogel, and the reaction rate depends on the amount of solute on the surface of the adsorbent, that is, the driving force ($Q_e - Q_t$) is proportional to the number of active sites present in the hydrogel [48].

Binding isotherm

Binding isotherms indicate the distribution of adsorbate molecules between a liquid phase and a solid phase when the adsorption process reaches an equilibrium state [24]. To determine the binding of the Cu(II) onto VP/MA-H, a plot of the amount of adsorption (Q) against the free concentration (C) of ion solution is shown in Figure 15.

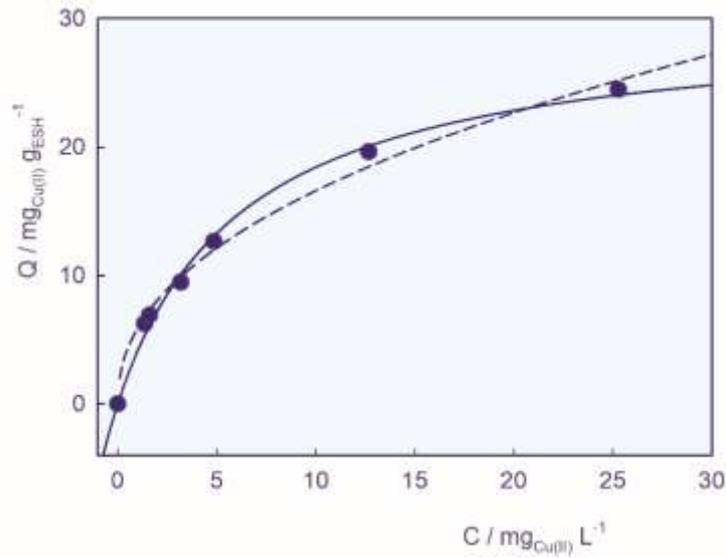


Figure 15. Binding isotherm of Cu(II) ions on VP/MA-H, - - -; Freundlich model fit and, —; Langmuir model fit.

The binding curve of Cu(II) ions on VP/MA-H in Figure 13 resembles a hyperbola. Although curves resembling hyperbola generally show L (Langmuirian) type in Giles adsorption classification, binding types such as S, C, L in this classification are determined by the exponential value (n_F) of the Freundlich equation. n_F is a measure of the deviation of isotherm from the linear form, i.e. heterogeneity factor. The Freundlich equation is given as:

$$Q = k_F C^{1/n_F} \quad (7)$$

where k_F is the Freundlich constant, equal to adsorption capacity at $C = 1$. The n_F values are related to the Giles classification, S, L, and C type isotherm. $n_F < 1$ correspond to S shape, $n_F = 1$ to C type, and $n_F > 1$ to L type [24]. On the other hand, higher values of k_F represent an easy uptake of adsorbate from the solution.

Freundlich parameters are calculated from the nonlinear regression of the plots in Figure 15. The correlation coefficient value was found to be $r^2=0.993$. The calculated Freundlich exponent n_F to take a value of 2.22 indicates that the binding of Cu(II) ions to the VP/MA hydrogel is the L-type isotherm.

L-type (Langmuir type) binding isotherms in the Giles classification system for adsorption of a solute from its solution [46]. In this type of bonding isotherm, the initial curvature indicates that as more sites in the substrate are filled, it becomes increasingly difficult for a bombarding solute molecule to find a suitable free space. This means that the solute molecule adsorbed is not in strong competition with the solvent.

The binding equation for Langmuirian isotherms is as follows;

$$Q = \frac{Q_m K_L C}{1 + K_L C} \quad (8)$$

Where K_L is the binding constant, i.e., the equilibrium constant for the attachment of a cupric ion onto a site by a specific combination of noncovalent forces. Here Q_m is the site density (the limiting value of Q for monolayer coverage) which is therefore of the density of the sites along the polymer chain.

Langmuir parameters of binding are calculated from the nonlinear regression of the plots in Figure 15 and are summarized in Table 7 along with the standard error (SE) and correlation coefficients (r^2).

Table 6. Langmuir parameters for Cu(II)-VP/MA-H binding system

$Q_m K_L$	K_L	r^2	Q_m	FO%
4.7661±0.3317	0.1587±0.0164	0.994	30.0321	80.8488

Also, using the experimentally found maximum Q value (Q_{exp}) and the calculated monolayer capacity values (Q_m), the fractional occupancy percentage (FO%) can be calculated from the given equation [46];

$$FO\% = \frac{Q_{exp}}{Q_m} \times 100 \quad 9$$

The notations in this equation are already defined. The calculated FO% value is added to the last column of Table 6.

The monolayer coating value of Cu(II) binding to the VP/MA-H was found to be approximately 30 $MgCu_{(II)} g_{ESH}^{-1}$ and it was observed that approximately 20% of the binding surface could still be filled with cupric ions.

Thermal degradation of Cu(II) loaded VP/MA hydrogel

TG thermogram of Cu(II) loaded VP/MA-H was taken and presented in Figure 16.

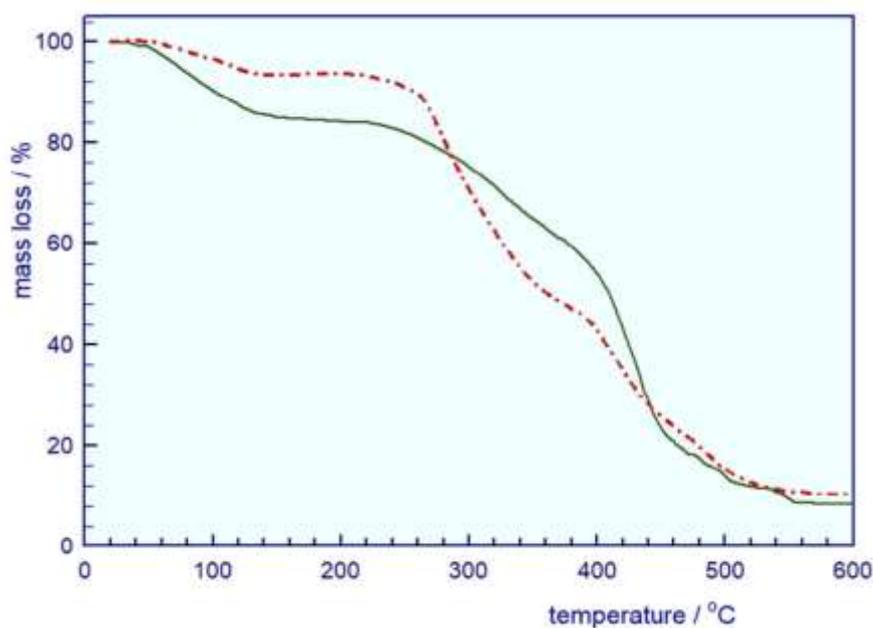


Figure 16. TG thermograms of Cu(II) unloaded (—) and loaded (- - -) VP/MA-H.

In the thermograms given in Figure 16, the mass loss (removal of water) in the Cu(II) unloaded hydrogel is higher than in the Cu(II) loaded hydrogel in the region up to 200 °C. In the region between 200-470 °C, the presence of Cu(II) accelerates the degradation of the hydrogel. In the final degradation, Cu(II) loaded VP/MA-H remained more residue than Cu(II) unloaded. This shows that the loaded copper(II) in the hydrogel affects the thermal degradation of VP/MA-H.

Conclusion

Prepared VP/MA-H, amphoteric property since the VP units in the hydrogel carry simultaneously positive and negative charges as a result of keto-enol tautomerism, inter-complex property due to interactions between VP units and MA units, environmentally sensitive property due to pH-, temperature- and ion-sensitive swelling behavior shows. In addition, VP/MA-H showed a high affinity to Cu(II) ions and bound to itself.

In conclusion, it can be said that the VP/MA hydrogel is a model hydrogel for removing heavy metal ions and cationic pollutants from the environment, as well as in environmentally sensitive swelling areas.

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Conflict of Interest:

Nothing to declare.

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