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

Sepehrianazar, Amir*+

Department of Chemistry, Ahar Branch, Islamic Azad University, Ahar, I.R. IRAN

ABSTRACT: *In this study for wastewater remediation, we aimed to prepare environmentally sensitive hydrogels (ESHs) with specific properties to remove copper (Cu^{2+}) from wastewater. ESHs were prepared with inter-complex and amphoteric properties by the free radical polymerization method. We prepared two monomers, vinylpyrrolidone (VP) and Methacrylic Acid (MA). N,N'-methylenebisacrylamide was a cross-linker agent to prepare ESHs for binding Cu2+ to remove from wastewater. To characterize the structural behavior of synthesized ESHs, we used FT-IR. Thermal properties were investigated by using TGA. We used Scanning Electron Microscopy (SEM) micrographs for morphologic studies. Swelling and diffusion studies were performed at different pH, temperatures, and salt solutions. The amphoteric property and inter-complex formation between VP and MA were monitored by UV spectroscopy. In the Cu^{2+} bindings onto ESH experiments, a Langmuir-type (L) adsorption was observed regarding 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 L 1/g_{ESH}, 30 MgCu^{2+}1/g_{ESH}, and 81%, respectively. We found a powerful electrostatic effect between the ionic part of ESH and cationic Cu^{2+}. These interactions denote the removal of cationic heavy metals and organic toxic wastes for water treatment.*

KEYWORDS: *TGA; Water remediation; Adsorption; FT-IR; Swelling properties; Inter-molecular complex.*

INTRODUCTION

Hydrogels are cross-linked 3-D polymers that cannot dissolve in water because of functional groups. They got swelled after water abrogation [1, 2]. Hydrogels show interesting behavior and respond to volume changes when encountering external stimuli. Some stimuli are variations in pH, temperature, ionic strength, solvent, electric field, light, magnetic field, and physiological fluids. Because of these specifications, their name is Environmentally Sensitive Hydrogels (ESHs) [3].

There are different kinds of solvents in the water solution of the oceans. The seawater's current nature causes oceans to be an equilibrated homogenous electrolytic solution. The total electrolytes concentration in seawater is about 0.6 M. Heavy metal ions are assigned

---

* *To whom correspondence should be addressed.*
\+ *E-mail: Amir.Sepehrianazar@iau.ac.ir*
1021-9986/2023/1/1-18 18/$/6.08

about 6-10 M of concentration. In industry, elements of about 65 mg/L in sweaters have been utilized [4].

Industry waste products cause environmental pollution of water. Therefore, there is an increasing need for novel polymeric materials to remove toxic heavy metal ions through different mechanisms such as complexation and ion exchange. The chelatogens are metal ion chelating polymers. They consist of one or more electron donor atoms such as N, S, O, and P, which can form coordinate bonds with most toxic heavy metal ions [5-7].

Heavy metals jeopardize the environment. In low concentrations, they are essential for some virtual functions, but when they exceed in amount, they display toxic effects [8]. Industrial activities such as electronics, automotive, mining, and metallurgical processes result in heavy metal accumulation in soil and water. Copper, Nickel, Cadmium, Mercury, Lead, and Chromium are considered heavy metals. Copper and Lead are common groundwater contaminants. The toxic level of Copper in water and the environment can cause nausea, diarrhea, anemia, high blood pressure, gastrointestinal upset, and vomiting of blue matter. Furthermore, high amounts of Copper and Lead can mix with soil and water and lead to severe complications in humans. Damages with a high amount of Copper and Lead to the nervous system, kidneys, and blood can be fatal. On the other hand, low exposure to these heavy metals disrupts many biochemical processes and physiological functions [5-8].

One of the current solutions and technology is limiting the number of heavy metal ions in effluent before incorporation in the environment by electro-deposition, ion oxidation-reduction, extraction by the liquid-liquid surface, and separation methods [9, 10]. Noteworthy, the adsorption method is the most efficient, cost-effective, and wildly used process for heavy toxic metal elimination from wastewater. For wastewater purification, cost-effective and highly efficient methods to eliminate pollutants are necessary. Nowadays, hydrogels have shown the perspective capability for adsorbing impurities from wastewater. Hydrogels are a type of super absorbent that can efficiently absorb water more than thousands of times their dry weight. Hydrogels are cross-linked polymeric chains via physical or covalent bonds that show a three-dimensional network [11, 12].

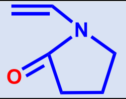
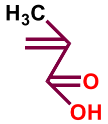
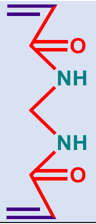
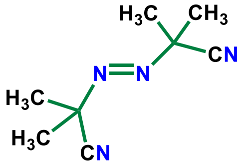
Homopolymers the copolymers of vinylpyrrolidone (VP) are hydrophilic materials. They have unique physical and chemical properties (such as biocompatibility, non-toxicity, chemical stability, good solubility in water and many other organic solvents, and a tendency to complex with both hydrophobic and hydrophilic substances). They work as a biomaterial in several medical and non-medical applications (as the pharmaceutical industry and medicine, optics and electrical applications, membranes, adhesives, ceramics, paper, coatings and inks, household, industrial, institutional, lithography and photography, fibers and textiles, and environmental applications) [13-20].

While the number of publications on VP polymers since 1970 is around 5400, 230 of these publications are about VP hydrogels. Therefore, the research and development of VP hydrogels are still in their infancy compared to continued and significantly increased efforts to develop hydrogels [21].

Jozaghkar et al. synthesize amphiphilic semi-interpenetrating network (semi-IPN) hydrogels based on acrylic acid and chitosan and characterize their swelling behavior. For this purpose, free radical polymerization was performed using AIBN as an initiator and N,N'-methylenebisacrylamide as a cross-linking agent. The effect of chitosan content, pH value, temperature, time, and media salinity on the prepared hydrogels' swelling properties were evaluated. Moreover, kinetics and diffusion studies were also carried out [22]. *Sepehrianazar et al.* studied the swelling behavior of the semi-IPN responsive hydrogels based on PAAc/PAlAm and PAAc/PAH and investigated the adsorption of nitrophenol by using these hydrogels. FT-IR confirmed the synthesis of the hydrogels by pH, temperature, and salt sensitivity. It was investigated by measuring equilibrium swelling ratios in different environmental solutions. [23] In another study, they synthesized amphiphilic hydrogels based on N,N'-dimethylacrylamide/acrylic acid using N,N′-methylenebisacrylamide as a cross-linking agent and azobisisobutyronitrile (AIBN) as an initiator. The kinetics and diffusion studies were performed. The chemical structure and thermal behavior of the synthesized hydrogel were assessed using FTIR and TGA, respectively [24a].

In this work, we synthesized MA with VP copolymer in a (1:1) mole ratio on feed composition by free radical polymerization method. This work is experimental research where the swelling properties are calculated in different pH, temperature, and ion effects also, the maximum swelling was obtained. In the recently published papers, the swelling of hydrogels was calculated mathematically by simulation method [24b,24c].

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	

We aimed to prepare, characterize and investigate the Cu^{2+} ion binding properties of Methacrylic Acid (MA) copolymeric hydrogels of vinylpyrrolidone by free radical polymerization using AIBN as an initiator. The swelling properties of ESHs were investigated in different pH, temperature, and salt solutions. The diffusion properties, hydration degree, swelling kinetics, and Cu^{2+} binding to ESH are carefully investigated.

EXPERIMENTAL SECTION

Chemicals

Vinylpyrrolidone (VP), methacrylic acid (MA), N,N'methylenebisacrylamide (N-Bis), and azobisisobutyronitrile (AIBN) were purchased from Aldrich, Milwaukee Company. The chemical names, synonyms, abbreviations, and chemical structures of the monomers, cross-linker, and initiator are given in Table 1. The $Cu^{2+}So_4$ used in adsorption was obtained from Merck KGaA, Darmstadt, Germany. The chemicals used were analytical purity (99%).

Preparation of hydrogels

Homopolymeric hydrogels

The vinylpyrrolidone hydrogel was prepared by the free radical polymerization method using 1.6 mL of VP in 2.4 mL of distilled water. The initiator was AIBN (2.0 wt. %). Cross-linker was N-Bis (2, 4, 6, or 8 wt.%) to the total mass of the monomers. Doubly distilled and deionized water was used as a solvent. In the same way, the Methacrylic Acid Hydrogel (MA-H) as the Vinylpyrrolidone Hydrogel (VP-H) preparation, 0.85 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 vinylpyrrolidone-hydrogel (VP-H), and that prepared from methacrylic acid was designated as methacrylic acid hydrogel (MA-H).

Copolymeric hydrogels

In preparing VP/ MA-H, 1.6 mL of VP, 0.85 mL of MA, and 2.4 mL of distilled water were used and made in the same technique as homo-polymers. Both homopolymer and copolymer mixtures were transferred to flexible polyvinylchloride (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. The hydrogels were washed with distilled water, dried at room temperature for 24 h, and then dried in an oven at 50 °C for 24 h. The dried gels were used in characterization, swelling, and adsorption tests.

Characterization and swelling

UV spectroscopy

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

FT-IR spectroscopy

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

TGA (Thermal Gravimetry Analysis)

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

Scanning Electron Microscopy (SEM) analysis

Two mg of the samples used in the analysis were covered with Au and a vacuum evaporator. Morphologies of the sample were determined by using a Jeol JSM-6060LV model SEM.

Determination of swelling percent

The swelling percent of homo-, co-polymeric hydrogels (S%) were determined by the following equation: [24-26]

$$S\% = \frac{m_t - m_i}{m_i} \times 100 \tag{1}$$

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

$$S = S_{max}\left(1 - e^{-k_s t}\right) \tag{2}$$

Where S (g_{ESH}/g) is swelling at time t, power parameter S_{max} is equilibrium swelling (g_{ESH}/g), t is time (min) for swelling, and k_s (1/min) stand for the swelling rate constant.

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

$$F = k_D t^n \tag{3}$$

Where F is the fractional uptake at time t, kD is constant incorporating characteristics of the network system and the penetrating characteristics, and n is the diffusion exponent, indicative of the transport mechanism.

Binding

The cupric ion binding capacities of the VP/MA hydrogel were determined using an aqueous Cu^{2+} 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.

The concentrations of Cu^{2+} ions were determined using UV spectrometry at 383 nm. The equilibrium binding capacity of the VP/MA hydrogels (Q, g_{ESH}/ $g_{Cu}{}^{2+}$) was estimated by the following equation;

$$Q = \frac{(C_o - C_e)}{m} \times V \tag{4}$$

C_o and C_e are the concentrations of the Cu^{2+} metal ion in the aqueous solution (g Cu^{2+}/L) before and after bindings, respectively. m is the hydrogel mass (g_{ESH}), and V is the total solution volume (Liter).

The swelling and binding experiments were carried out at pH=7 and 25°C.

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

First-order

$$\frac{dQ}{dt} = k_1(Q_e - Q_t) \quad , \quad Q_t = Q_e\left(1 - e^{-k_1 t}\right) \tag{5}$$

Second-order

$$\frac{dQ}{dt} = k_2(Q_e - Q_t)^2 \tag{6}$$

$$Q_t = \frac{t}{A + Bt} \qquad A = \frac{1}{k_2 Q_e^2} \qquad B = \frac{1}{Q_e}$$

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

n_F is a measure of the deviation of isotherm from the linear form, i.e., heterogeneity factor. The Freundlich equation is given as follows:

$$Q = k_F C^{1/n_F} \tag{7}$$

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.

RESULT AND DISCUSSION

In this study, we prepared hydrogels from VP and MA by the free radical polymerization method. We obtained a 1:1 mole ratio of feed composition hydrogel to absorb Cu^{2+} in wastewater. In the last three years, various studies used different monomers such as Pullulan graft poly(acrylic acid-co-acrylamide) [26a], Pectin with different esterification degrees [26b], Chitosan with polyvinyl alcohol [26c], and Vinyl imidazole-Acrylamide [26d]. One of the distinct points of our study from recent research is a characterization of the hydrogel swelling ratio in different pH, temperature, and ionic strength effects. These hydrogels can be known for excellent swelling properties. Also, the capability of hydrogel to absorb Cu^{2+} from wastewater differs from 10 to 130 mg, and we could establish 30 mg absorption of Cu^{2+} from wastewater by VP-MA hydrogel.

Intercomplex formation

The complex formation [25] between VP and MA was investigated by the UV spectra of the aqueous solutions of monomer and co-monomer and their 1:1 mixture (Fig. 1).

While the maximum wavelength ($\lambda_{max)}$ values for N-vinylpyrrolidone, MA, and the mixture were found to be 288 nm, 290 nm, and 286 nm, respectively. These solution absorbances (A) values were found to be 1.69, 2.06, and 1.45 in the same order. As seen in the UV spectra (Fig. 1), the mixture of monomer and co-monomer showed a slight hypochromic shift (blueshift) with a 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. As a result, we can say an inter-complex formed between VP and MA with the help of H-bonds. Possible interactions and complex formation between N-vinylpyrrolidone and MA in (vinylpyrrolidone/methacrylic acid-Hydrogel) VP/MA-H are illustrated in Fig. 2.

As shown in Fig. 2, the intra-molecular and inter-molecular interactions are hydrogen bonding effects formed by the interaction between the carbonyl groups in VP and MA in the hydroxyl group.

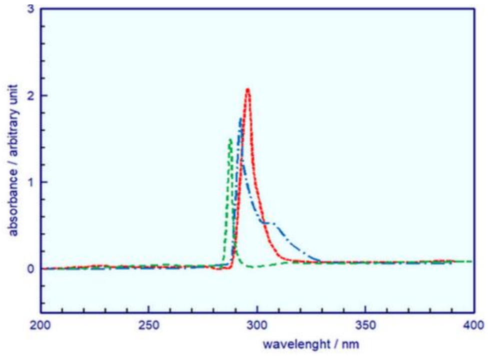


***Fig. 1:** UV spectra of monomers and their mixture, -·-·-·-·-; VP, ········; MA, ------; 1:1 monomer mixture.*

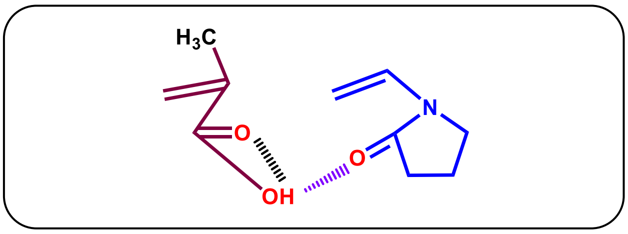


***Fig. 2:** Intra- (||||||) and inter-molecular (▶) interactions between VP and MA.*

Synthesis of hydrogels

A plausible polymerization mechanism of VP/MA-H is shown in Fig. 3. The first possible step for polymerization is the transfer of an unpaired electron to make the monomeric reactive units and the reaction between the VP or (MA) molecules and the radical. First, free radical reacts with the VP monomer or MA co-monomer, then breaks the double bond of monomer or co-monomer and retains an unpaired electron at the base of the formed chain. A new free radical is formed (propagation step; homopolymerization or copolymerization). This species then interacts with the cross-linker (N-bis), forming species with two radical sites that combine in the molecule and form a chain of cross-linked VP/MA copolymers (propagation step; cross-linking). The reactivity ratios of monomer VP and co-monomer MA are given as (r_1 =44.66) and (r_2 =3.38). [27] 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 an entirely random sequence of VP and MA monomers. [27] However, VP is more reactive than MA. As a result,

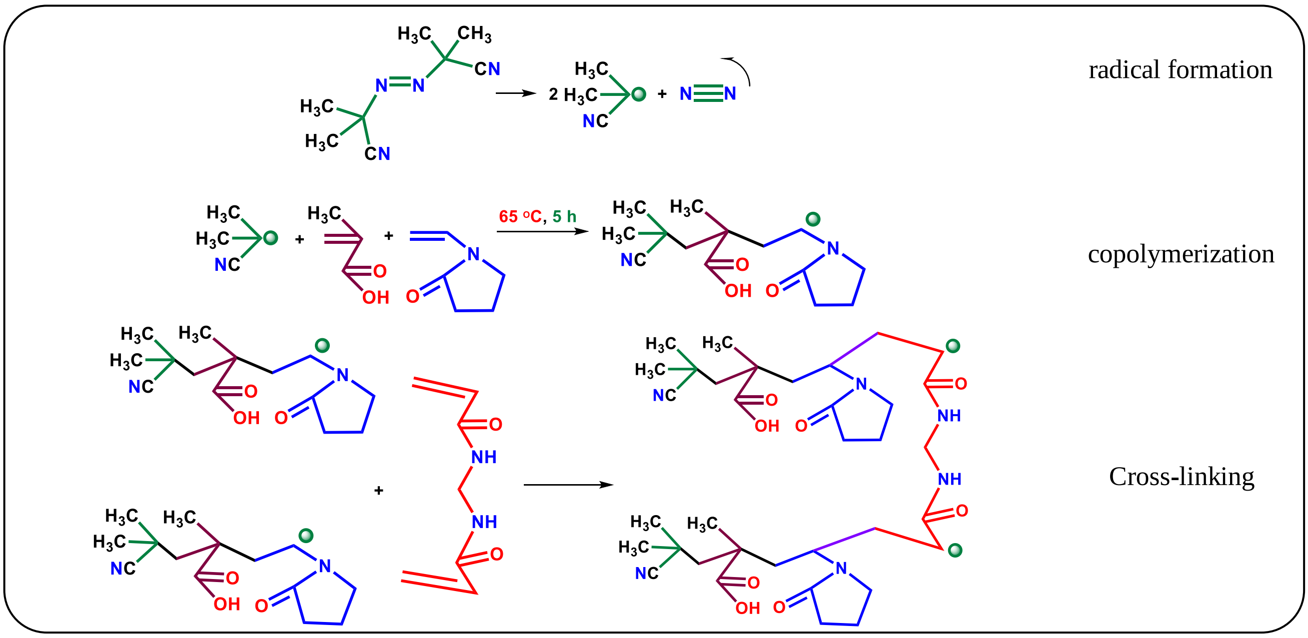


Fig. 3: Plausible copolymerization and cross-linking mechanism of VP/MA hydrogel.

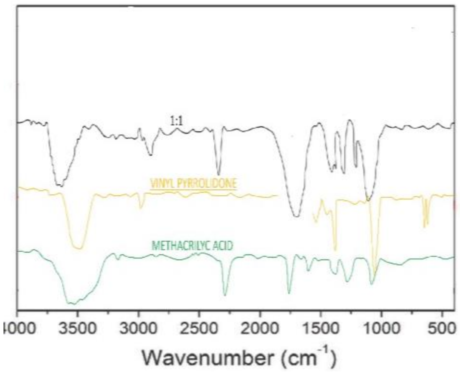


Fig. 4: FTIR spectra of the hydrogel, -·-·-·-·-; VP-H, ·········; MA-H, ------; VP/MA-H.

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.

FT-IR analysis

Fig. 4 shows FT-IR spectra of VP-H, MA-H, and the 1:1 mole ratio of feed composition VP/MA-H.

The bands observed around 3700-3500 1/cm show O-H stretching. The band at 1750 1/cm in the spectrum of MA and the bands at 1750 1/cm in the other spectra depend on the C=O stretching of VP. The band at 1750 1/cm in the MA spectrum and bands at 1750 1/cm in other spectra depend on C=O stretching of VP. Mainly, the band's shift from 1750 1/cm in the MA spectrum to 1700 1/cm in the mixture can interpret as inter-molecular H-bonds formation between the carbonyl group in VP and the carboxyl group in MA. [27] The inability to observe the N-C=O bending band at 568 1/cm observed in VP in the mixture may be due to the formation of intermolecular H-bonds. All spectra observed the C-H bending band at 1400 1/cm and the CH_2 band at 1020 1/cm. CH_2 wagging band was observed at 1300 1/cm in the mixture spectrum. These bands may be an indication that the cross-linker has entered the structure. In the spectrum of the hydrogel obtained from a monomer, a comonomer, and a cross-linker at a 1:1 feed ratio, the observation of all functional groups in VP, MA, and cross-linker may be an indication of the formation of a cross-linked VP/MA-H.

TG analysis

The thermogram of the 1:1 mole ratio of feed composition VP/MA-H is presented in Fig. 5.

In Fig. 5, three decomposition regions of the hydrogel are seen. There is nearly 16.4% mass loss in the region up to 200 ^{o}C. Hydrophilic groups such as -OH, -NH, or -C=O in the hydrogel absorb 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 ^{o}C. The mass loss may correspond to separating 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. [15,27]

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 hydrophilic repeat units in the three-dimensional cross-linked network. Penetrant intake of initially dry VP-H, MA-H, and VP/MA-H 1:1 mole ratio of feed composition was followed for a while gravimetrically. [24,28] All the hydrogels absorbed the fluids and swelled at a higher rate initially. After a certain period, fluid uptake became constant, and the VP-H, MA-H, and VP/MA-H 1:1 mole ratio of feed composition hydrogels achieved equilibrium swelling capacity (S_{eq}).

Influence of cross-linker concentration on the hydrogel swelling

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

As shown in Fig. 6, the equilibrium swelling values of the hydrogels decreased as the cross-linker concentration increased. By increasing the cross-linker concentration to a particular concentration, a more intense bonding between the leading chains, an increase in cross-linking points, and consequently pore shrinkage occurs. That makes brutal penetration of the influent to hydrogel and reduces swelling.

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

Influence of hydrogel type on the hydrogel swelling

Swelling plots were constructed and represented in Fig. 7 for the homo-polymers VP-H, MA-H, and copolymer VP/MA-H 1:1 mole ratio of feed composition hydrogels.

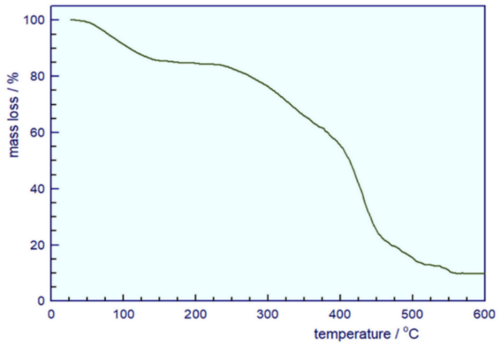


Fig. 5: The thermogram of 1:1 mole ratio of feed composition VP/MA-H.

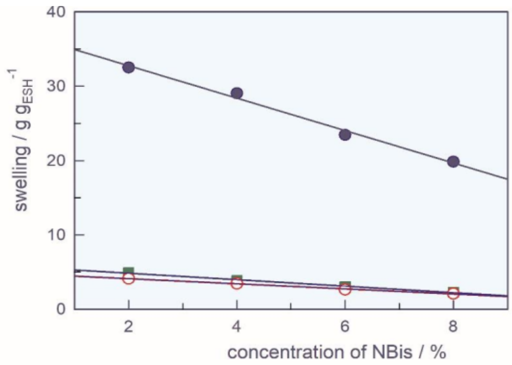


Fig. 6: The effect of cross-linker concentration on the swelling of the hydrogels, ●; VP-H, ○; MA-H, ■; VP/MA-H 1:1 mole ratio of feed composition*pH=7, T= 25 °C.

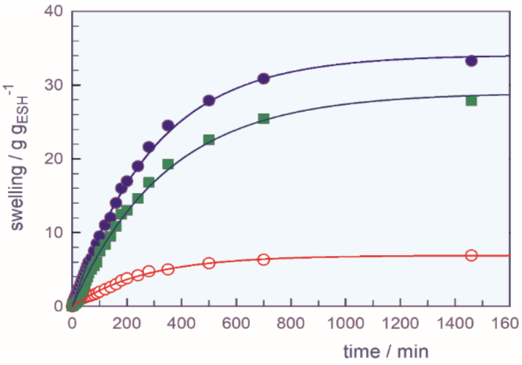


Fig. 7: The effect of hydrogel type on the swelling of the hydrogels, ●; VP-H, ○; MA-H, ■; VP/MA-H1:1 mole ratio of feed composition; model fit. *pH=7, T= 25 °C, Cross-linker amount = 2%.

Fig. 7 shows the variation in the swelling capacity of the VP-H, MA-H, and VP/MA-H 1:1 mole ratio of feed composition hydrogels with time at 25 °C. All the hydrogels

Table 2: Experimentally found swelling parameters.

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

Table 3: Calculated swelling parameters.

Hydrogel	S_{max} / g/g_{ESH}	k_s / 1/min	r^2	τ / min	SR/ g_{ESH} min/g
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

absorbed the fluids and swelled at a higher rate initially. After a certain period, the fluid uptake became constant, and the VP-H, MA-H, and VP/MA-H 1:1 mole ratio of feed composition hydrogels achieved 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 Fig. 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 shows that the values of S_{eq} of the VP-H, MA-H, and VP/MA-H 1:1 mole ratio of feed composition hydrogels are changed among 6.89–33.26 g_{ESH}/g. The swelling of VP-H is about 4.8 times greater than the swelling of MA-H. That is because VP contains more hydrophilic groups than MA and the hydrophobic CH_3 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. The swelling of hydrogels was increased in the following order; VP-H > VP/MA-H >> MA-H. Moreover, the swelling rate constants of all hydrogels around 10-3 1/min indicate that the prepared hydrogels swell slowly.

In addition, in Fig. 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 adopting the exponential rise to maximum relation to determine the swelling parameters of the hydrogels. [29]

The value of the constant rate 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 power parameter value indicates that the swelling is very high, while a small rate parameter indicates that the swelling is fast. Also, the ratio of the power parameter to the rate parameter gives the Swelling Rate (SR, g_{ESH} min/g) at time τ, and the τ value is a measure of the SR (i.e., the lower the τ value, the higher the rate of swelling) [29] .

Nonlinear regression was applied to Eq. (1) to calculate the parameters. The correlation coefficients (r^2) of the graphs drawn according to Eq. (1) (in Fig. 7) are 0.991 and above, indicating that Eq. (1) can be used to find the swelling parameters of the prepared hydrogels.

The S_{max} and k_s values found in eEquation (1), along with the Standard Error (SE) and correlation coefficients (r^2), are given in Table 3. Calculated τ and SR values are also added to Table 3.

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). According to the model (Eq. (1)), these samples absorb approximately 63% of their maximum absorption capacity [29] during 4.5-5.5 hours. While these values show that the prepared hydrogels swell pretty 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

Eq. (3) is valid for up to the rate parameter of

Table 4: Diffusional parameters of the hydrogels

Hydrogel	k_D	n	r^2
VP-H	$4.433x10^{-3}±0.219\ x10^{-3}$	0.898±0.010	0.999
MA-H	$10.700x10^{-3}±\ 0.717x10^{-3}$	0.728±0.014	0.996
VP/MA-H	$2.781x10^{-3}±\ 0.285x10^{-3}$	0.969±0.020	0.995

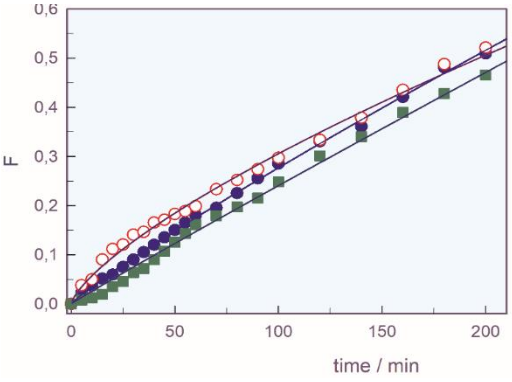


Fig. 8: Diffusional behavior of the hydrogels, ●; VP-H, ○; MA-H, ■; VP/MA-H 1:1 mole ratio of feed composition, —; model fit. *pH=7, T= 25 °C.

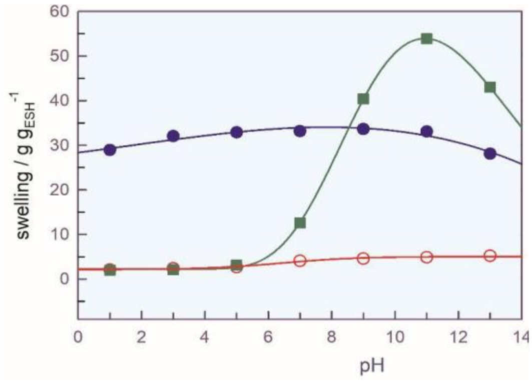


Fig. 9: The effect of pH on the swelling, ●; VP-H, ○; MA-H, ■; VP/MA-H1:1 mole ratio of feed composition *Different pH, T= 25 °C, Cross-linker amount = 2%.

swelling of the polymer. For a cylindrical gel, n = 0.45–0.50 corresponds to the 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. [22-24] *F* versus *t* graphs for the prepared hydrogels are plotted and shown in Fig. 8.

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 Fig. 8 and are summarized in Table 4 along with the standard error (SE) and correlation coefficients (r^2).

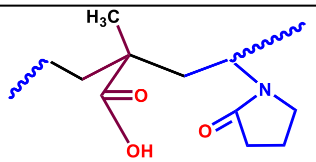
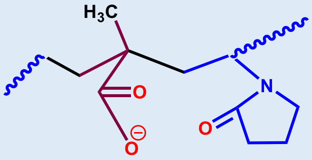
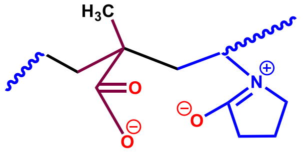
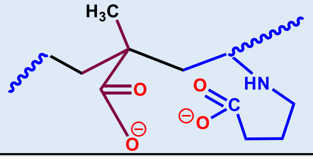
Diffusion exponents (n) are calculated between 0.97 and 0.73, thus suggesting anomalous or non-Fickian-type diffusion. When the diffusion model shows anomalous behavior, the relaxation and diffusion time are of the same order of magnitude. Therefore, as the penetrant diffuses into the hydrogel, there is a delay in rearrangement (rupturing) within the polymer chains. [22-24,29] We investigated the diffusion properties in pH=7 and T=25 °C for all hydrogels.

Influence of pH on the swelling

The polymeric networks containing ionizable functional groups exhibit pH responsivity. [20-36] The responsibility of surrounding media pH on the swelling values of the prepared hydrogels at 25 °C between pH = 1–13 is shown in Fig. 9.

Fig. 9 depicts that 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. On the other hand, the VP/MA-H 1:1 mole ratio of feed composition 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 value at approximately pH=10.9, and then decreases. MA, a weak carboxylic acid, has a pK_a of 4.86. [22-24] 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. VP is neutral up to approximate pH. The keto-enol tautomerism at pH around seven causes an augmented positive charge on the tertiary nitrogen atom on the pyrrolidone ring and an increment in the negative charge on the carbonyl group. [36-38] Swelling of VP-H, which increases slightly with the interaction of hydrophilic groups with water up to pH 7, gives a small transition point around pH=7.8 due to keto-enol tautomerism. Charge interactions formed in the structure along with increasing OH- ions in the environment decrease the swelling rate until pH reaches 11. In pH=11, the carboxylate group

Table 5: Changes in the conformation of VP/MA-H with increasing pH.

pH<5		uncharged VP/MA-H 1:1 mole ratio of feed composition chain in aqueous solution
pH>5		acidic dissociation of MA unit in MA/VP-H 1:1 mole ratio of feed composition in aqueous solution
pH ≈ 7		forming of keto-enol tautomerism of VP unit in MA/VP-H 1:1 mole ratio of feed composition in aqueous solution
pH>11		Opening the pyrrolidone ring of the VP unit in MA/VP-H 1:1 mole ratio of feed composition in an aqueous solution

forms by opening the pyrrolidone ring in the vinylpyrrolidone unit, and when this group interacts with the excess OH- ions in the environment, swelling decreases as a result of electrostatic repulsions. The swelling of feed composition's (vinylpyrrolidone/methacrylic acid-Hydrogel) VP/MA-H 1:1 mole ratio with increasing pH continued by the pH-varying conformation of the monomer and co-monomer forming the hydrogel. VP/MA-H 1:1 mole ratio of feed composition 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 the VP/MA-H 1:1 mole ratio of feed composition 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 1:1 mole ratio of feed composition decreased due to ring-opening in the VP unit. [22-24] Conformational changes in VP/MA-H 1:1 mole ratio of feed composition with increasing pH are illustrated and presented in Table 5.

We state that the prepared VP-H, MA-H, and VP/MA-H 1:1 mole ratio of feed composition are sensitive to pH. The pH sensitivities can be calculated from the maximum and minimum swelling values difference as 5.68, 3.09, and 51.93 g_{ESH}/g, respectively.

Influence of temperature on the swelling

The effect of temperature on the swelling rate [22-24] of hydrogels was inflated to equilibrium at 25, 50, and 70 °C. The variation of swelling with temperature is shown in Fig. 10.

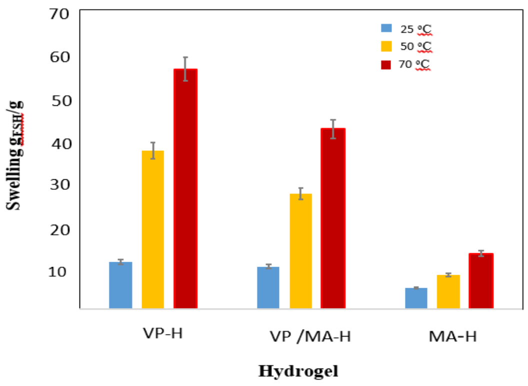


Fig. 10: The effect of temperature on the swelling, 🟦; 25 °C, 50 °C 🟥; 70 °C.

The swelling of the hydrogels increased with increasing temperature. With increasing the temperature inter- and intra-molecular forces, and hydrogel bonding were broken. In polymeric chains, the amount of free volume is increasing therefore, swelling is increasing. Also, the electrostatic forces are broken and swelling increases. As a result, free volume increases, and more water penetrates the copolymer network, so swelling increases. [39-41]

Influence of ions on the swelling

The ions and counter ions play an essential role in the swelling behavior of hydrogels. [3,41] Ion-sensitive swelling behavior was investigated in aqueous solutions of NaCl, KCl, and Na_2CO_3 salts at 0.1 mol/L concentrations at 25 °C, and ion-sensitive swelling of hydrogels is shown in Fig. 11.

Hydrogels swell less in salt solutions than in water. The swelling values decreased according to the following sequence water, NaCl, KCl, and Na_2CO_3. 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 was decreased. The hydrogel showed nonionic behavior when the fixed charges on polymeric side chains were fully neutralized. 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 VP monomer and the pH- and ion- sensitivity of the MA comonomer are a durable, homogeneous appearance, can be defined as environmentally sensitive, stimuli-responsive, smart or intelligent hydrogels.

Cu^{2+} Binding

To observe the uptake of heavy metal ions [42], VP/MA-H 1:1 mole ratio of feed composition was placed in aqueous solutions of Cu^{2+} and allowed to equilibrate for two days. At the end of time, the dark blue coloration of the original solutions appeared. These hydrogels have many carboxylate groups. They increase electrostatic (ionic) interaction between Cu^{2+} ions and ring groups (carboxylate and enolate of pyrrolidone) in hydrogels. [43] The possible electrostatic interactions between Cu^{2+} ions and VP/MA-H 1:1 mole ratio of feed composition are shown in Fig. 12.

Binding kinetics

The adsorption process is the binding of solute molecules to the surface of an adsorbent. 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 [44].

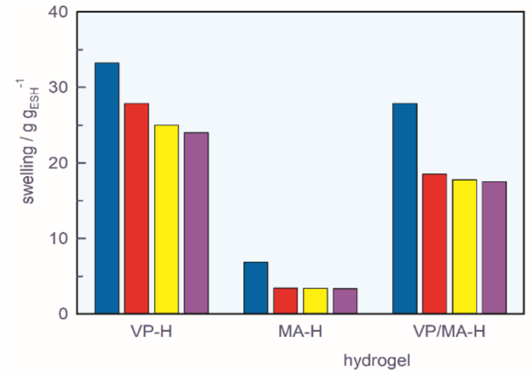


Fig. 11: The effect of ions on the swelling, 🟦; water, 🟥; NaCl, 🟨; KCl, 🟪; Na_2CO_3.

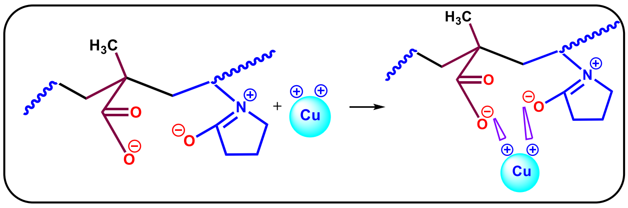


Fig. 12: Binding of copper ions to MA/VP-H in aqueous solution.

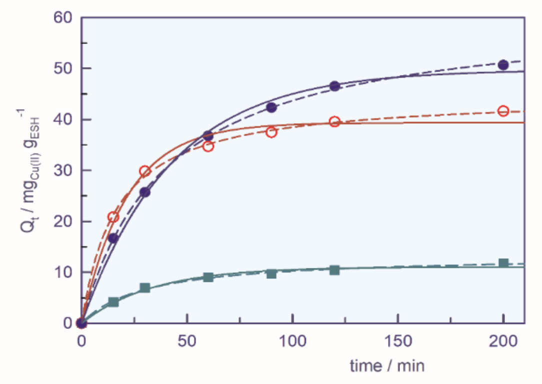


Fig. 13: The binding kinetics of Cu^{2+} to the VP/MA-H 1:1 mole ratio of feed composition, - - - -; pseudo-first-order model fit and, ——; pseudo-second-order model fit. Blue color pH=2, Red color pH=7, and Navy color pH=12.

The binding kinetics of Cu^{2+} to the VP/MA-H 1:1 mole ratio of feed composition are studied and given in Fig. 13. The curves of the integral equals of pseudo-order applied to these data are also shown on the same graph.

First, the Cu^{2+} binding to the hydrogel at all pHs increases (Fig. 13) and, over time, reaches equilibrium after a particular time. However, with the increase in pH, the amount of Cu^{2+} binding to the hydrogel also increases. At the same time, negligible adsorption is observed

Table 6a: Pseudo-first order Cu^{2+} binding kinetics parameters of the VP/MA-H 1:1 mole ratio of feed composition.

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 6b: Pseudo-second order Cu2+ binding kinetics parameters of the VP/MA-H 1:1 mole ratio of feed composition.

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	$2.2472 x 10^{-3}$	30.3
7	0.3702±0.0166	0.0223±0.0003	0.9988	44.8431	$1.3433 x 10^{-3}$	16.6
12	0.6622±0.0139	0.0163±0.0002	0.9996	61.3497	$0.4012 x 10^{-3}$	40.6

in an acidic medium; when the solution medium is changed from acidic to neutral and alkaline, the binding rate changes and increases significantly. The copper binding to the hydrogel with the increased pH may be due to the conformational changes in the VP/MA. At acidic pH, the side groups in the main chain do not dissociate, preventing the Cu^{2+} from binding to the hydrogel. The carboxylate group is formed by opening the pyrrolidone ring at alkaline pH. Also, bonding increases between Cu^{2+} and VP/MA-H 1:1 mole ratio of feed composition. 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 pH.

On the other hand, the parameters found due to the pseudo-first- and second-order non-linear kinetic models applied to the experimental data are presented in Table 6, together with the standard error and correlation coefficients.

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^{2+} to VP/MA follows a second-order kinetic. In this model, the solute's binding rate is assumed to be proportional to the available sites on the hydrogel. 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 [45].

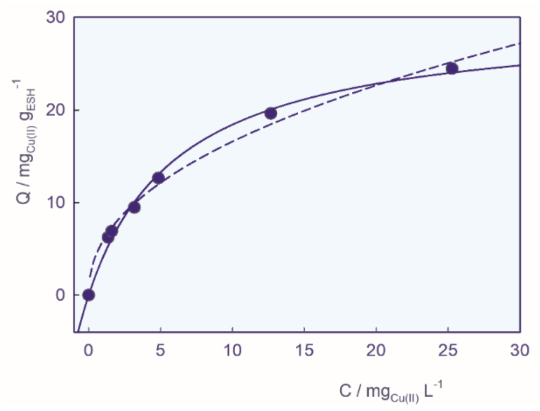


Fig. 14: Binding isotherm of Cu^{2+}ions on VP/MA-H 1:1 mole ratio of feed composition, - - - -; Freundlich model fit and, ——; Langmuir model fit.

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. [29] To determine the binding of the Cu^{2+} onto VP/MA-H 1:1 mole ratio of feed composition, a plot of the amount of adsorption (Q) against the free concentration (C) of ion solution is shown in Fig. 14.

The binding curve of Cu^{2+} ions on VP/MA-H 1:1 mole ratio of feed composition in Fig. 13 resembles a hyperbola. Although curves resembling hyperbola generally show L (Langmurian) type in Giles adsorption classification, binding types such as S, C, and L in this classification are determined by the exponential value (n_F) of the Freundlich equation. [29]

Table 7: Langmuir parameters for Cu^{2+} -VP/MA-H binding system.

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

On the other hand, higher values of k_F represent an easy uptake of adsorbate from the solution. Freundlich parameters are calculated from the non-linear regression of the plots in Fig. 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^{2+} ions to the VP/MA-H 1:1 mole ratio of feed composition is the L-type isotherm. *L*-type (Langmuir type) binding isotherms in the Giles classification system for adsorption of a solute from its solution. [43] 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. That means the solute molecule adsorbed is not competing strongly with the solvent.

Binding studies

The binding equation for Langmuirian isotherms is as follows;

$$Q = \frac{Q_m K_L C}{1 + K_L C} \tag{8}$$

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

Langmuir parameters of binding are calculated from the non-linear regression of the plots in Fig. 14 and are summarized in Table 6 along with the Standard Error (SE) and correlation coefficients (r^2).

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 [43];

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

The calculated FO% value is added to the last column of Table 7.

The monolayer coating value of Cu^{2+} binding to the VP/MA-H 1:1 mole ratio of feed composition was found to be approximately 30 $MgCu^{2+}$ $1/g_{ESH}$, and it was observed that approximately 20% of the binding surface could still be filled with cupric ions.

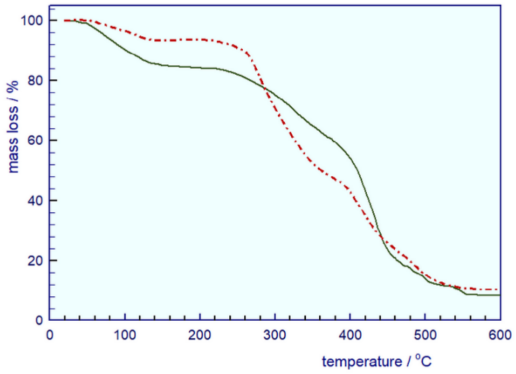


Fig. 15: TG thermograms of Cu^{2+} unloaded (—) and loaded (- - -) VP/MA-H.

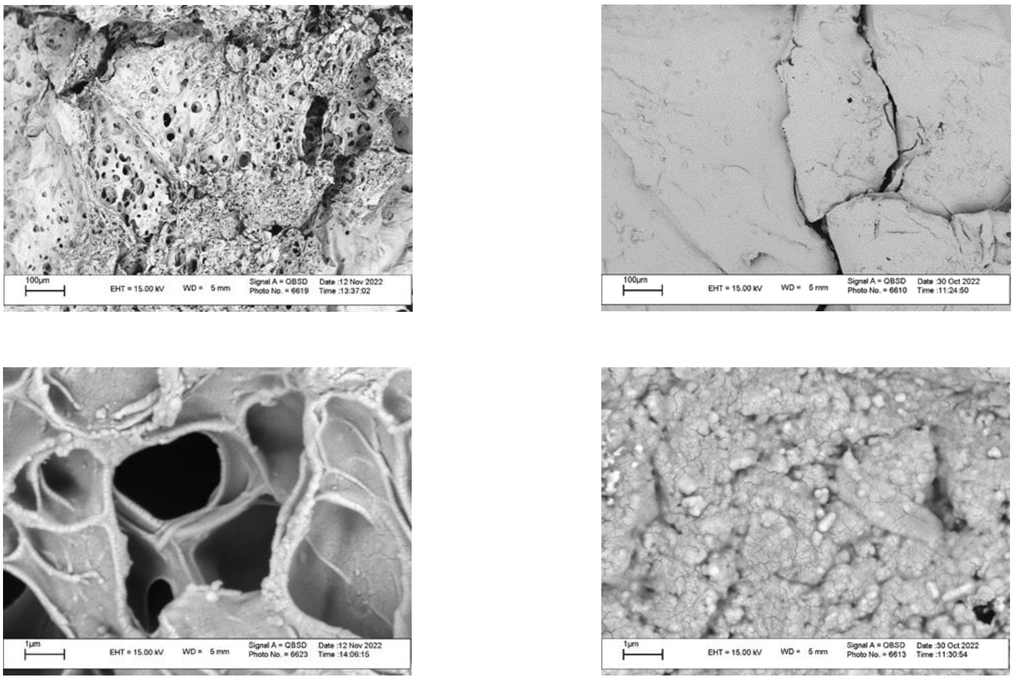
Thermal degradation of Cu^{2+} loaded VP/MA 1:1 mole ratio of feed composition hydrogel

TG thermogram of Cu^{2+} loaded VP/MA-H 1:1 mole ratio of feed composition was taken and presented in Fig. 15.

In the thermograms in Fig. 15, the mass loss (removal of water) in the Cu^{2+} unloaded hydrogel is higher than in the Cu^{2+} loaded hydrogel in the region up to 200 °C. In the region between 200-470 ºC, the presence of Cu^{2+} accelerates the degradation of the hydrogel. In the final degradation, Cu^{2+} loaded VP/MA-H 1:1 mole ratio of feed composition remained more residue than Cu^{2+} unloaded. It shows that the loaded Cu^{2+} in the hydrogel affects the thermal degradation of the feed composition's VP/MA-H 1:1 mole ratio.

Investigation of morphology of hydrogels

To obtain morphologic properties VP/MA (1:1) mole ratio of feed composition of hydrogels without Cu^{2+} loading and after Cu^{2+} absorption, we showed SEM micrographs. Considering Fig. 16, we claim that the VP/MA-H (1:1) mole ratio of feed composition can bond copper ions and remediate wastewater. It had many pores before Cu^{2+} absorption, but Cu^{2+} covered nearly all pores after absorption.



a) Before

b) After

Fig. 16: SEM micrographs of (1:1) mole ratio VP/MA-H before(a), and after(b) Cu^{2+} absorption.

CONCLUSIONS

VP-H and MA-H, 1:1 mole ratio of feed composition co-hydrogel were prepared by the free radical polymerization method and 65 °C for 5 hours. The VP units in the hydrogel simultaneously carry positive and negative charges due to keto-enol tautomerism and show amphoteric properties. Intercomplex formation between VP and MA was shown in aqua solution by UV spectrometry. A hydrogen bond is formed between the free electron pair in the carbonyl group and the hydroxyl group proton. The structural behavior of synthesized hydrogel was investigated by FT-IR spectroscopy. Characteristic peaks showed that the critical parameter is the formation of intermolecular hydrogen bonds between the carbonyl group in VP and the carboxyl group in MA. The inability to observe the N-C=O bending band at 568 1/cm observed in VP in the mixture might be due to the formation of the intermolecular hydrogen bond. TGA investigated the thermal properties of the 1:1 mole ratio of feed composition. SEM micrographs confirmed the Cu^{2+} absorption by VP/MA-H. The final degradation started at 470 °C and continued at 660 °C. It can be thought of as the disconnection of the remaining main chain, destruction of the entire hydrogel, and carbonization. The equilibrium swelling of hydrogels was prepared in different concentrations of N-bis. With the higher cross-linker agent, the swelling percentage is low. Swelling hydrogels were increased in the following order:

VP-H > VP/MA-H >> MA-H.

Diffusion exponents (n) are calculated between 0.97 and 0.73. It suggests the non-Fickian type diffusion. The swelling percent in different pH for the MA-H shows an inflection point pH=6.4 while VP-H shows a peak between 6 and 10. The highest point of the peak corresponds to approximately 7.3. After pH= 11, swelling of co-hydrogel decreased due to ring-opening in the VP unit.

When the temperature is high, the swelling percentage gets high. It can show for MA-H, VP-H, and co-hydrogel. A binding isotherm indicates the distribution of adsorbate molecules between the liquid and solid phases when the absorption process reaches an equilibrium state. Although curves resembling hyperbola generally show Langmurian type in Giles adsorption classification. Freundlich parameters are calculated from the non-linear regression. 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 bending of Cu^{2+} ions to the VP/MA hydrogel is the L-type isotherm. Langmuir parameters of bending are calculated from non-linear regression. It obtained $Q_m = 30.0321$ and FO% = 80.8488. Approximately 20% of the binding surface could still be filled with cupric ions.

Received : Jun. 9, 2022 ; Accepted : Dec. 5, 2022

REFERENCES

[1] Saraydın D., Karadağ E., Güven O, Relationship Between the Swelling Process and the Releases of Water-Soluble Agrochemicals from Radiation Crosslinked Acrylamide/Itaconic Acid Copolymers, *Polym. Bull.*, **45(3)**: 287–294, (2000). doi:10.1007/s002890070033

[2] Karadağ E., Üzüm Ö. B., Saraydın D., Güven O, Swelling Characterization of Gamma-Radiation Induced Crosslinked Acrylamide/Maleic Acid Hydrogels in Urea Solutions, *Mater. Des*, **27(7)**: 576–584 (2006). doi:10.1016/j.matdes.2004.11.019

[3] Işıkver Y., Saraydın D., Smart Hydrogels: Preparation, Characterization, and Determination of Transition Points of Crosslinked N-isopropyl Acrylamide/ Acrylamide/Carboxylic Acids Polymers, *GEL*, **7(3)**:113 (2021). doi:10.3390/gels7030113

[4] Çaykara T., İnam R., Determination of the Competitive Adsorption of Heavy Metal Ions on Poly(N-Vinyl-2-Pyrrolidone/Acrylic Acid) Hydrogels by Differential Pulse Polarography, *J. Appl. Polym. Sci.*, **89(8)**: 22 (2003). https://doi.org/10.1002/app.12328

[5] Yetimoğlu E.K., Kahraman M.V., Ercan Ö., Akdemir Z.S., Apohan N.K., N-Vinylpyrrolidone/Acrylic Acid/ 2-Acrylamido-2-Methylpropane Sulfonic acid Based Hydrogels: Synthesis, Characterization and their Application in the Removal of Heavy Metals, *React Funct Polym*, **67**: 451-460 (2007). https://doi.org/10.1016/j.reactfunctpolym.2007.02.007

[6] Ali A.E., Shawky H.A., Rehim H.A., Hegazy E., Synthesis and Characterization of PVP/Aac Copolymer Hydrogel and its Applications in the Removal of Heavy Metals from Aqueous Solution, *Eur. Polym. J*, **39**: 2337-2344 (2003). https://doi.org/10.1016/S0014-3057(03)00150-2

[7] Lee W.F., Yuan W.Y., Thermoreversible Hydrogels X: Synthesis and Swelling Behavior of the (N-Isopropylacrylamide-Co-Sodium 2-Acrylamido-2-Methylpropyl Sulfonate) Copolymeric Hydrogels, *J Appl Poly Sci*, **77(8)**: 1760-1768 (2000). DOI:10.1002/1097-4628(20000822)77:8<1760::AID-APP13>3.0.CO;2-J

[8] Maskawat Marjub M., Rahman N., Dafader N., Sultana Tuhen F., Sultana S., Tasneem Ahmed F., Acrylic Acid-Chitosan Blend Hydrogel: A Novel Polymer Adsorbent for Adsorption of Lead(Ii) and Copper(Ii) Ions from Wastewater, *J. Polym. Eng.*, **39(10)**: 883-891 (2019). https://doi.org/10.1515/polyeng-2019-0139

[9] Zhai S., Xiao H., Shu Y., Zhao Z., Countermeasures of Heavy Metal Pollution, *Chin. J. Geochem.*, **32(4)**: 446-450 (2013). https://doi.org/10.1007/s11631-013-0654-y

[10] Seko N., Tamada M., Yoshii F., Current Status of Adsorbent for Metal Ions with Radiation Grafting and Crosslinking Techniques, *Nucl Instrum Methods Phys Res B.*, **236(1-4)**: 21-29 (2005). https://doi.org/10.1016/j.nimb.2005.03.244

[11] Hu B., Jia X., Hu J., Xu D., Xia F., Li Y., Assessment of Heavy Metal Pollution and Health Risks in the Soil-Plant-Human System in the Yangtze River Delta, China, *Int. J. Environ. Res. Public Health 10*, **14(9)**: 1042 (2017). doi: 10.3390/ijerph14091042.

[12] Tong S., Schirnding Y.E.V., Prapamontol T., Environmental Lead Exposure: A Public Health Problem of Global Dimensions, *Bulletin of the World Health Organization*, **78(9)**: 1068-1077 (2000).

[13] Suberlyak O., Skorokhoda V., “Hydrogels Based on Polyvinylpyrrolidone Copolymers in Hydrogels”. Edited by Haider S. and Haider A. Intech Open, London, UK 23-44, (2017). doi:10.5772/intechopen.72082

[14] Teodorescu M., Bercea, M., Poly(vinylpyrrolidone) – A Versatile Polymer for Biomedical and Beyond Medical Applications, *Polymer-Plastics Technology and Engineering*, **54(9)**: 923–943 (2015). doi:10.1080/03602559.2014.979506

[15] Ofridam F., Tarhini M., Lebaz N., Gagnière É., Mangin D., Elaissari A., pH-Sensitive Polymers: Classification and Some Fine Potential Applications, *Polym Adv Technol*, **32(4)**: 1455–1484 (2021). doi:10.1002/pat.5230

[16] Knipe J.M., Chen F., Peppas N.A., Multiresponsive Polyanionic Microgels with Inverse pH-Responsive Behavior by Encapsulation of Polycationic Nanogels. *J. Appl. Polym. Sci.*, **131(7)** (2013). doi:10.1002/app.40098

[17] Franco P., De Marco I., The Use of Poly(N-vinylpyrrolidone) in the Delivery of Drugs: A Review, *Polym. J.*, **12(5)**: 1114 (2020). doi:10.3390/polym12051114

[18] Chen G., Liu J., Yang Y., Zhang L., Wu M., Ni H., Preparation of pH-Sensitive Nanoparticles of Poly (Methacrylic Acid) (PMAA)/Poly (Vinylpyrrolidone) (PVP) by ATRP-Template Miniemulsion Polymerization in the Aqueous Solution, *Colloid Polym. Sci*, **293(7)**: 2035–2044 (2015). doi:10.1007/s00396-015-3554-3

[19] Ponratnam S., Rao S.P., Joshi S.G., Kapur S.L., Copolymerization of Methacrylic Acid and N-vinylpyrrolidone in Aqueous Solution, *J. Macromol. Sci. A*, **10(6)**: 1055–1062 (1976). doi:10.1080/00222337608061236

[20] Devine D.M., Higginbotham C.L., Synthesis and Characterization of Chemically Crosslinked N-Vinyl Pyrrolidinone (NVP) Based Hydrogels, *Eur. Polym. J.*, **41(6)**: 1272–1279 (2005). doi:10.1016/j.eurpolymj.2004.12.022

[21] Husain M.S.B., Gupta A., Alashwal B.Y., Sharma S., Synthesis of PVA/PVP Based Hydrogel for Biomedical Applications: A Review, *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, **40(20)**: 2388-2393, (2018). doi:10.1080/15567036.2018.1495786

[22] Jozaghkar M.R., Sepehrian Azar A., Ziaee F., Preparation, Assessment and Swelling Study of Amphiphilic Acrylic Acid/Chitosan Based Semi-Interpenetrating Hydrogels Available online (2022). 10.12.2021 DOI: 10.3906/kim-2109-50

[23] Jozaghkar M.R., Sepehrian Azar A., Ziaee F., Synthesis and Characterization of Semi-Interpenetrating Polymer Network Hydrogel Based on Polyacrylic Acid/Polyallylamine and its Application in Wastewater Remediation. *Polym. Bull.* (2022). https://doi.org/10.1007/s00289-022-04162-w

[25] a) Jozaghkar M.R., Sepehrian Azar A., Ziaee F., Preparation, Characterization, and Swelling Study of N,N'-Dimethylacrylamide/Acrylic Acid Amphiphilic Hydrogels in Different Conditions, *Polymer Bulletin*, **79**: 5183–5195 (2021). https://doi.org/10.1007/s00289-021-03760-4
b) Jiang X., Li C., Han Q., Modulation of Swelling of PVA Hydrogel by Polymer and Crosslinking Agent Concentration, *Polym. Bull.*, **80**: 1303–1320 (2023). https://doi.org/10.1007/s00289-022-04116-2
c) Ji S., Li X., Wang S., Li H., Duan H., Yang X., Lv P., Physically Entangled Antiswelling Hydrogels with High Stiffness. *Macromol. Rapid Commun*, **43(19)**: 2200272 (2022) https://doi.org/10.1002/marc.202200272

[25] Gorshkov N.I., Murko A.Y., Gavrilova I.I., Bezrukova M.A., Kipper A.I., Krasikov V.D., Panarin E.F., Synthesis of Water-Soluble Copolymers of N-Vinylpyrrolidone with N-Vinyldithiocarbamate as Multidentate Polymeric Chelation Systems and Their Complexes with Indium and Gallium. *Molecules*, **25(20)**: 4681 (2020). doi:10.3390/molecules25204681

[26] a) Sonmez B., Celikkol A.N., Pullulan Based Hydrogels for the Removal of Various Metal Ions from Aqueous Solutions, *J. Environ. Chem. Eng.*, **9(5)**: 106188, (2021). https://doi.org/10.1016/j.jece.2021.106188
b) Shen B., Guo Z., Huang B., Zhang G., Fei P., Hu S., Preparation of Hydrogels Based on Pectin with Different Esterification Degrees and Evaluation of their Structure and Adsorption Properties, *Int. J. Biol. Macromol.*, **202**: 397-406 (2022). https://doi.org/10.1016/j.ijbiomac.2021.12.160
c) Jamnongkan T., Mongkholrattanasit R., Wattanakornsiri A., Wachirawongsakorn P., Takatsuka Y., Hara T., Green Adsorbents for Copper (II) Biosorption from Waste Aqueous Solution Based on Hydrogel-Beads of Biomaterials, *S. Afr. J. Chem. Eng.*, **35**: 14-22 (2021). https://doi.org/10.1016/j.sajce.2020.10.005

d) Tirtom V.N., Dinçer A., Effective Removal of Heavy Metals from an Aqueous Solution with Poly(N-Vinylimidazole-Acrylamide) Hydrogels, *Sep. Sci. Technol.*, **56(5)**: 912-924 (2021). https://doi.org/10.1080/01496395.2020.1735434

[27] Torun M., Şolpan D., The Removal of Cationic Dyes from Aqueous Solutions by Using Poly(N-Vinylpyrrolidone-Co-Methacrylic Acid) Hydrogel Adsorbents: Effects of pH and Composition on Adsorption. *Fibers Polym.*, **16(4)**: 735–743 (2015). doi:10.1007/s12221-015-0735-0

[28] Sharpe L.A., Vela Ramirez J.E., Haddadin O.M., Ross K.A., Narasimhan B., Nicholas A. Peppas, pH-Responsive Microencapsulation Systems for the Oral Delivery of Polyanhydride Nanoparticles, *Biomacromolecules*, **19(3)**: 793-802 (2018). https://doi.org/10.1021/acs.biomac.7b01590

[29] Saraydin D., Işıkver Y., Karadağ E., A Study on the Correlation Between Adsorption and Swelling for Poly(Hydroxamic Acid) Hydrogels-Triarylmethane Dyes Systems, *J Polym Environ*, **26(9)**: 3924–3936 (2018). doi:10.1007/s10924-018-1257-9

[30] Knipe J.M., Chen F., Peppas N.A., Multiresponsive Polyanionic Microgels with Inverse pH Responsive Behavior by Encapsulation of Polycationic Nanogels, *J. Appl. Polym. Sci.*, **131(7)**: 40098(1-8) (2013).

[31] Chongyang Zhu, Ning Tang, Jing Gan, Xiaojun Zhang, Yang Li, Xin Jia, Yongqiang Cheng, A pH-sensitive Semi-Interpenetrating Polymer Network Hydrogels Constructed by Konjac Glucomannan and Poly (Γ-Glutamic Acid): Synthesis, Characterization and Swelling Behavior, *Int. J. Biol. Macromol.*, **185**: 229-239 (2021). https://doi.org/10.1016/j.ijbiomac.2021.06.046.

[32] Nurkeeva Z.S., Mun G.A., Khutoryanskiy V.V., Bitekenova A.B., Dubolazov A.V., Esirkegenova S.Z., pH Effects in the Formation of Interpolymer Complexes Between Poly(N-Vinylpyrrolidone) and Poly(Acrylic Acid) in Aqueous Solutions, *EPJ E*, **10(1)**: 65–68 (2003). doi:10.1140/epje/e2003-00003-4

[33] Kozlovskaya V., Kharlampieva E., Mansfield M.L., Sukhishvili S.A., Poly(methacrylic acid) Hydrogel Films and Capsules: Response to pH and Ionic Strength, and Encapsulation of Macromolecules, *Chem. Mater.*, **18(2)**: 328–336 (2005). https://doi.org/10.1021/cm0517364

[34] Atta A.M., Arndt K.-F., Swelling Behavior of pH- and Temperature-Sensitive Copolymers Containing 2-Hydroxy-Ethyl Methacrylate and N-Vinyl-2-Pyrrolidone Crosslinked with New Crosslinkers, *Polym. Int.*, **53(11)**: 1870–1881 (2004). doi:10.1002/pi.1606

[35] Jin S., Liu M., Zhang F., Chen S., Niu A., Synthesis and Characterization of Ph-Sensitivity Semi-IPN Hydrogel Based on Hydrogen Bond Between Poly(N-Vinylpyrrolidone) and Poly(Acrylic Acid). *Polym. J.*, **47(5)**: 1526–1532 (2006). doi:10.1016/j.polymer.2006.01.009

[36] Behera M., Ram S., Inquiring The Mechanism of Formation, Encapsulation, and Stabilization of Gold Nanoparticles by Poly(Vinyl Pyrrolidone) Molecules in 1-Butanol, *Appl. Nanosci.*, **4(2)**: 247–254 (2013). doi:10.1007/s13204-013-0198-9

[37] Wang J., Tsuzuki T., Tang B., Cizek P., Sun L., Wang X., Synthesis of Silica-Coated Zno Nanocomposite: The Resonance Structure of Polyvinyl Pyrrolidone (PVP) as a Coupling Agent. *Colloid Polym. Sci.*, **288(18)**: 1705–1711 (2010). doi:10.1007/s00396-010-2313-8

[38] Das J.K., Das N., Bandyopadhyay S., Effect of PVP Intermediate Layer on the Properties of SAPO 34 Membrane, *Adv. Mater. Sci. Eng.*, 1–7 (2012). doi: 10.1155/2012/650217

[39] Zhunuspayev D.E., Mun G.A., Hole P., Khutoryanskiy V.V., Solvent Effects on the Formation of Nanoparticles and Multilayered Coatings Based on Hydrogen-Bonded Interpolymer Complexes of Poly(acrylic acid) with Homo- and Copolymers of N-Vinyl Pyrrolidone, *Langmuir*, **24(23)**:13742–13747 (2008). doi:10.1021/la802852h

[40] Kharlampieva E., Erel-Unal I., Sukhishvili S.A., Amphoteric Surface Hydrogels Derived from Hydrogen-Bonded Multilayers: Reversible Loading of Dyes and Macromolecules. *Langmuir*, **23(1)**: 175–181 (2006). doi:10.1021/la061652p

[41] Muta H., Miwa M., Satoh M., Ion-Specific Swelling of Hydrophilic Polymer Gels. *Polym. J.*, **42(14)**: 6313–6316 (2001). doi:10.1016/s0032-3861(01)00098-2

[42] Kemik Ö.F., Ngwabebhoh F.A., Yildiz U., A Response Surface Modelling Study for Sorption of Cu^{2+}, Ni^{2+}, Zn^{2+} and Cd^{2+} Using Chemically Modified Poly(Vinylpyrrolidone) and Poly(Vinylpyrrolidone-Co-Methylacrylate) Hydrogels, *Adsorp. Sci. Technol.*, **35(3-4)**: 263–283 (2016). doi:10.1177/0263617416674950

[43] Ekici S., Işıkver Y., Şahiner N., Saraydın D., Adsorption of Some Textile Dyes onto Crosslinked Poly(N-vinylpyrrolidone), *Adsorption Science and Technology*, **21(7)**: 651–659 (2003). doi:10.1260/026361703772776439

[44] William Kajjumba G., Emik S., Öngen A., Kurtulus Özcan H., Aydın S., Modeling of Adsorption Kinetic Processes—Errors, Theory, and Application, "Advanced Sorption Process Applications", Edited by Edebali, S., IntechOpen, London, UK (2018). doi:10.5772/intechopen.80495

[45] Tran H.N., You S.J., Hosseini Bandegharaei A., Chao H.P., Mistakes and Inconsistencies Regarding Adsorption of Contaminants from Aqueous Solutions: A Critical Review.*Water Res.*, **120**: 88-116 (2017). https://doi.org/10.1016/j.watres.2017.04.014