

## Synthesis of Poly(*N*-methylol Methacrylamide/Vinyl Sulphonic Acid) Hydrogels for Heavy Metal Ion Removal

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In this study, poly(*N*-methylol methacrylamide) (NMMAAm) and poly(*N*-methylol methacrylamide/vinyl sulphonic acid) (NMMAAm-VSA) hydrogels were synthesized by  $^{60}\text{Co}$ - $\gamma$  ray irradiation at an ambient temperature. The graphs belonging to the gelation percent- percent-dose and swelling curves were drawn by using data which were obtained from water and different pH solutions. Characterization of hydrogels was performed by FTIR and DSC-TGA analysis. Heavy metal ion ( $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ) removal capacities of hydrogels were investigated in aqueous solutions, which had different concentrations (100-1500 mg/L). In metal ion removal studies, pH value of aqueous medium was kept constant at 5.0. Maximum metal ion removal values were obtained for NMMAAm-VSA (1:3 mole ratio) hydrogels. Metal ion removal capacities of NMMAAm-VSA (1:3 mole ratio) hydrogels were found as 82 mg/g and 98 mg/g for  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  ions, respectively.

**Key Words :** Acrylamide type hydrogels, Vinyl sulphonic acid, Gamma irradiation, Adsorption

### Introduction

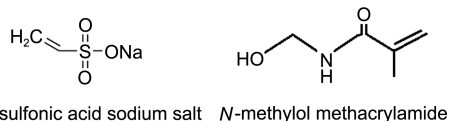
Heavy metals pose a threat to the environment and living things. Some heavy metals are essential for the fulfilment of vital functions, but while the amount is exceeded, they display toxic effects. Accumulation of heavy metals in water and soil is come out from the industrial activities such as electronics, automotive, mining and metallurgical processes, *etc.* Nickel and cobalt ions placed in 4<sup>th</sup> period of periodic table have toxic effects on human beings. Cobalt is essential to all animals, including humans but repeated or long term contact to cobalt compounds may cause skin sensitization and exposure to repeated or long term inhalation may cause asthma. Some cobalt compounds may have effects on the heart, thyroid and bone marrow. Cobalt is used in preparation of magnetic materials, petrochemical and plastic industry, ceramic industry, detergent production industry *etc.*<sup>1</sup> Nickel also has important roles in the biology of microorganisms and plants. The main ways of nickel intake for mammalian are ingestion, inhalation and absorption through the skin. Intake of overdose nickel may cause allergic reactions and kidney damage. Nickel particles as dust or fumes can be a carcinogen. Nickel is used in electroplating, transportation, chemical industry, electrical equipments *etc.*<sup>2</sup> For these reasons, removal of heavy metals from water and soil is an important issue. Physical, chemical and biological processes are implemented to remove heavy metal ions.<sup>3,4</sup> The removal of heavy metal ions from aqueous solutions by using polymers especially hydrogels has become a popular and widely studied research subject.<sup>5-9</sup> Hydrogels are hydrophilic polymer networks including several cross-links, crystalline regions or entanglements, so hydrogels are insoluble materials. They swell in water more than 10-100 times of their own masses due to the presence of hydrophilic functional groups such as

-OH, -COOH, -NH<sub>2</sub>, -CONH<sub>2</sub>, *etc.* along the polymer chains. Therefore, hydrogels are used as adsorbent materials to remove heavy metal ions from aqueous systems, as biomedical devices for controlled drug delivery, as artificial materials for treatment of some damaged organs, *etc.*<sup>3-10</sup> Compared to conventional methods (solution polymerization, suspension polymerization, *etc.*) for preparation of hydrogels, the usage of ionizing radiation in hydrogel preparation has some advantages and these advantages are as follows; it provides easy process control, enables to combine hydrogel formation and sterilization in one technological stage, there is no need to add any initiators, cross-linkers, *etc.*, which may be harmful and difficult to remove, there is no waste, and it provides relatively low running costs. All these advantages make irradiation the method of choice in the synthesis of hydrogels, especially for biomedical applications.<sup>11</sup>

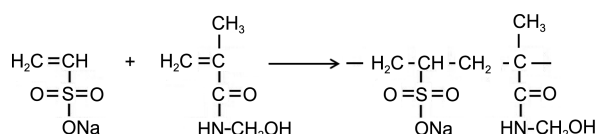
In this study, polymers having  $-\text{SO}_3^-$ ,  $-\text{NH}$  and  $-\text{OH}$  groups functional groups playing a significant role in the metal adsorption process were preferred. Hydrophilic copolymers were synthesized by irradiation of binary mixtures of *N*-methylol methacrylamide and vinyl sulphonic acid.  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  removal capacities of copolymeric hydrogels from aqueous solutions were investigated by using a batch adsorption experiments.

### Experimental

**Chemicals.** *N*-Methylol methacrylamide (NMMAAm) (60 wt % in H<sub>2</sub>O, 1.1 g/mL at 25 °C) was provided from Meryer Chemicals (China) and vinyl sulphonic acid (VSA) sodium salt (25 wt % in H<sub>2</sub>O, 1.176 g/mL at 25 °C) was provided from Aldrich (Milwaukee, WI), both reagents were used as they were purchased.



**Synthesis of Hydrogels.** 1:1, 1:2, and 1:3 NMMAAm:VSA mole ratios were used in the present study. NMMAAm was mixed with VSA at the ratios given above; placed into PVC straws; then exposed to irradiation at different doses by means of  $^{60}\text{Co}$ - $\gamma$  source having a dose rate of 64.6 Gy/h (Gammacell 220) in air at room temperature. The reaction between the monomers was given below.



**Determination of Gelation (%).** After irradiation, hydrogels obtained in long cylindrical shapes were cut into pieces of 1–2 mm length. After dried in vacuum oven at 40 °C, irradiated mixtures were immersed into water to remove the un-reacted monomers and uncross-linked soluble fractions. Then hydrogels were dried in vacuum oven again. Percentage of their gelations to insoluble network was gravimetrically determined by using Eq. (1).<sup>11</sup> The amount of sulfonic acid in monomer, polymer and/or copolymer form was determined by the titration of the solution containing residues which are un-reacted materials against NaOH (0.05 M) to phenolphthalein end point. The percentage of gelation was calculated by using the following equation:

$$\text{Gelation \%} = \frac{w}{w_0} \times 100\% \quad (1)$$

where,  $w_0$  is the initial weight of dry gel and  $w$  is the weight of dry gel after standing in water.

**Swelling Studies.** Dried hydrogels following water extraction were accurately weighed and transferred into water and phosphate buffer solutions at different pHs (2–13).<sup>11</sup> During all swelling experiments, ionic strength of buffer media was kept constant at  $I = 0.02$  M as obtained from preliminary experiences. The higher the ionic strength becomes, the more negatively charged sulphonyl groups can be masked and as a result of that the swelling reduces. Swollen gels were periodically removed from the swelling medium, lightly blotted to remove excess water from their surface, and then reweighed at room temperature. The following equation<sup>12</sup> was used to calculate the percentage of swelling:

$$\text{Swelling \%} = \frac{(w_t - w_0)}{w_0} \times 100 \quad (2)$$

where  $w_0$  is the weight of the dry gel before swelling and  $w_t$  is the weight of the dry gel after swelling at time  $t$ .

**Characterization of Hydrogels.** In order to investigate structural and thermal characteristics, hydrogels were ground into small particles and then were pressed into pellets with KBr. The infrared spectra of samples were recorded in a Spectrum One FT-IR spectrometer, which is one of the

Perkin Elmer Instruments. The thermal characterization was performed by using Shimadzu DTG-60H model thermal analyzer, in dynamic  $\text{N}_2$  atmosphere (100 mL/min) at a heating rate of 10 °C/min.

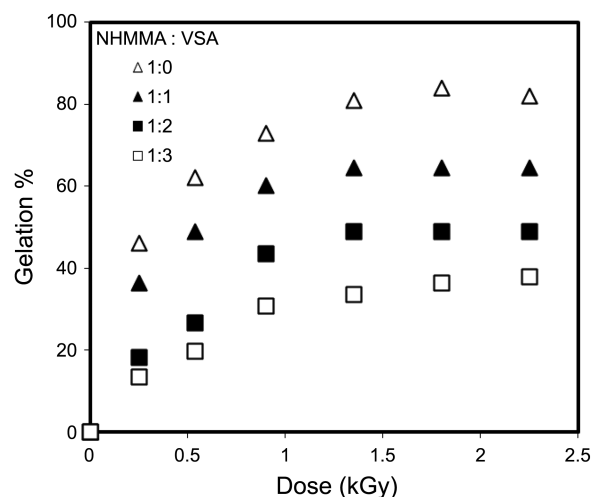
**Removal of Metal Ions.** The adsorption trials for  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  ( $\text{Me}^{2+}$ ) were carried out with pre-determined pH (5.0, adjusted with phosphate buffer) and different concentrations of solutions of  $\text{NiCl}_2$  and  $\text{CoCl}_2$  (obtained from BDH-Poole, UK) to display the metal ion uptake behaviour of hydrogels. Plain NMMAAm and NMMAAm-VSA hydrogels with a weight of 0.01 g were added into 10 mL of  $\text{Me}^{2+}$  solutions, and then they were stirred at  $25 \pm 1$  °C for a pre-determined period (2 days). Adsorption experiments were conducted for 2 days to ensure access to the functional groups that were placed in the inner part of hydrogels. Hydrogel particles were decanted by using centrifugation; clear solutions were analyzed for remaining metal ions by means of UV-Vis Spectrophotometer (Shimadzu 1601 model). The amount of metal ions adsorbed on hydrogels (mg metal ions/g dry hydrogel) was calculated by using Eq. (3).<sup>13</sup>

$$q_e = \frac{(C_0 - C_e) \times V}{m} \quad (3)$$

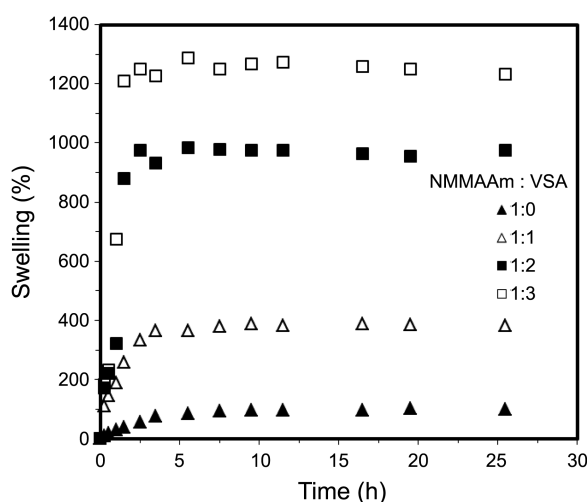
where  $q_e$  is the amount of adsorbed metal ions per unit weight of hydrogel (mg/g);  $C_0$  and  $C_e$  are initial and equilibrium concentration of the metal ions in the aqueous solution (mg/L), respectively;  $V$  is the volume of the aqueous solution (L) and  $m$  is the weight of the dry hydrogel (g).

## Results and Discussion

**Gelation (%).** Gelation (%) values were calculated by using Eq. (1). Figure 1 has shown the gelation % curves of NMMAAm, NMMAAm-VSA (1:1 mole ratio), NMMAAm-VSA (1:2 mole ratio) and NMMAAm-VSA (1:3 mole ratio) gel systems. Maximum gelation (about 80%) reached approximately at 2 kGy dose. 2 kGy dose-irradiated samples were used for further experiments.



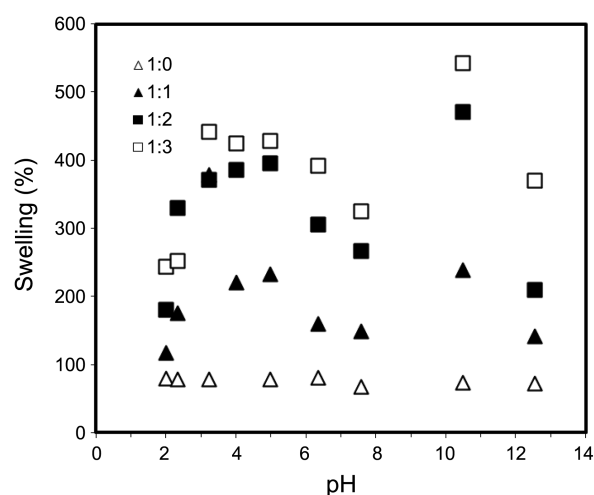
**Figure 1.** Gelation % - dose curves for NMMAAm and NMMAAm-VSA hydrogels.



**Figure 2.** Swelling curves for NMMAAm and NMMAAm-VSA hydrogels in deionized water.

As shown in Figure 1, the extent of gelation decreased with the increase of VSA content in the feed composition. This was probably caused by VSA, which acted as an effective chain transfer agent in the copolymerization of NMMAAm. As it is well-known,<sup>14</sup> chain transfer occurs when a radical species reacts with a nonradical species called as chain transfer agents. After that, the current chain finishes. A new chain may start or not, which depends on new radical reactivity. In this study, the increase in the amount of VSA led copolymerization to finish in the beginning of copolymer composition, which was followed by the formation of chain transfer reactions.

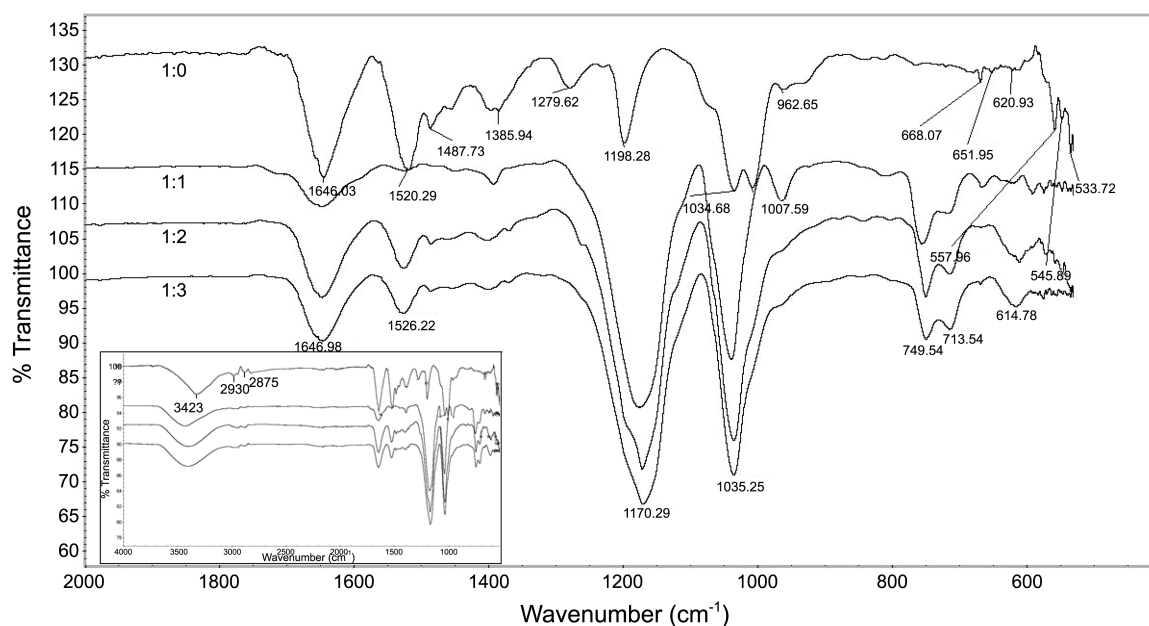
**Swelling (%) Properties of Hydrogels.** Figure 2 has shown the dependence of swelling on the composition of the hydrogel systems. The highest swelling degree was obtained for NMMAAm-VSA hydrogels of 1:3 mole ratio. There was a substantial increase in the swelling degree of NMMAAm hydrogel by the incorporation of VSA resulting from the hydrophilic  $-\text{SO}_3^-$  groups. Increase of the amount of VSA decreased the conversion into polymer but increased the average molecular weight between the crosslinks and decreased the crosslink density, which resulted in higher swelling ratios.<sup>12</sup> Swelling behaviour of hydrogels was investigated in solutions of different pH ranging from 2 to 13. The effect of pH on the degree of swelling of hydrogels was given in Figure 3. As it can be monitored from the figure, NMMAAm is a slightly ionic polymer which showed no considerable amount of swelling in the whole range of the investigated pH. However, VSA has a strong acidic character due to the presence of ionizable  $-\text{SO}_3\text{H}$  groups in its structure, which caused higher swelling values. Two maxima have been observed in all swelling-pH curves obtained for NMMAAm-VSA hydrogel systems. Reasonable assumptions can be made to explain these two maxima. The  $\text{p}K_a$  value of sulfonic acid is known from literature as  $-2$  (showing very strong acidity).<sup>15</sup> At pH 4, all  $-\text{SO}_3\text{Na}$  groups are in form of  $-\text{SO}_3^-$ . In the first maximum observed around pH 4.5, when the all  $-\text{SO}_3\text{Na}$  groups of VSA have released  $\text{Na}^+$



**Figure 3.** Effect of pH on the degree of swelling of hydrogels.

into the solution, the strong repulsion between  $-\text{SO}_3^-$  groups has led to increase in swelling. It is known that a high concentration of charged ionic groups in the hydrogel increases the swelling due to osmosis and charge repulsion.<sup>16</sup> In the region of pH 5–8,  $-\text{SO}_3^-$  groups have formed potential H-bonded bridge complexes with  $-\text{NH}$  and  $-\text{OH}$  groups of NMMAAm through the presence of water molecules, which caused decrease in swelling. In the second maximum observed around pH 10, there were a great number of  $\text{OH}^-$  groups in the solution. These  $\text{OH}^-$  groups blocked the interactions between  $-\text{SO}_3^-$  and  $-\text{NH}$  and  $-\text{OH}$  groups of NMMAAm, then large amounts of disentangling  $-\text{SO}_3^-$  groups repelled each other through strong anionic interactions, so the swelling reached to higher values. When the pH value exceeds 10, the swelling ratio decreases due to the shielding effect of other ions, which prevents efficient anion–anion repulsion. Similarly at a high value of pH, the  $\text{Na}^+$  belonging to  $-\text{SO}_3$  groups and other cations have come out from phosphate buffer chemicals; therefore, this interaction has caused hydrogels to be swollen in less proportion.<sup>17,18</sup>

**Characterization of Hydrogels.** Fourier Transform Infrared Spectroscopy was used to confirm the structure of both NMMAAm and NMMAAm-VSA hydrogels. Results have been presented in Figure 4. In order to observe the changes in detail, spectra were given in the range of  $2000\text{--}400\text{ cm}^{-1}$  and full range spectra were inserted into it. At a first glance, there are two important points to be remarked about these spectra: Firstly, there are no peaks appeared at  $900\text{--}1000\text{ cm}^{-1}$  of the evidence of monomeric double bonds, so both components were considered to be successfully polymerized. Secondly, single broad band at  $3330\text{ cm}^{-1}$  which was free  $-\text{NH}$  and  $-\text{OH}$  groups of NMMAAm shifted to  $3430\text{ cm}^{-1}$  due to the formation of H-bonds between OH and NH groups by the contribution of  $-\text{SO}_3^-$  groups of VSA. A very broad band was centred at  $3430\text{ cm}^{-1}$ , which represents the distribution of the hydrogen bonded OH groups. The wide signal for the hydrogen-bonded OH groups has shifted to higher frequency– to  $3423, 3459, 3466$  and  $3470\text{ cm}^{-1}$ . These changes have derived from transformations of strong intra-

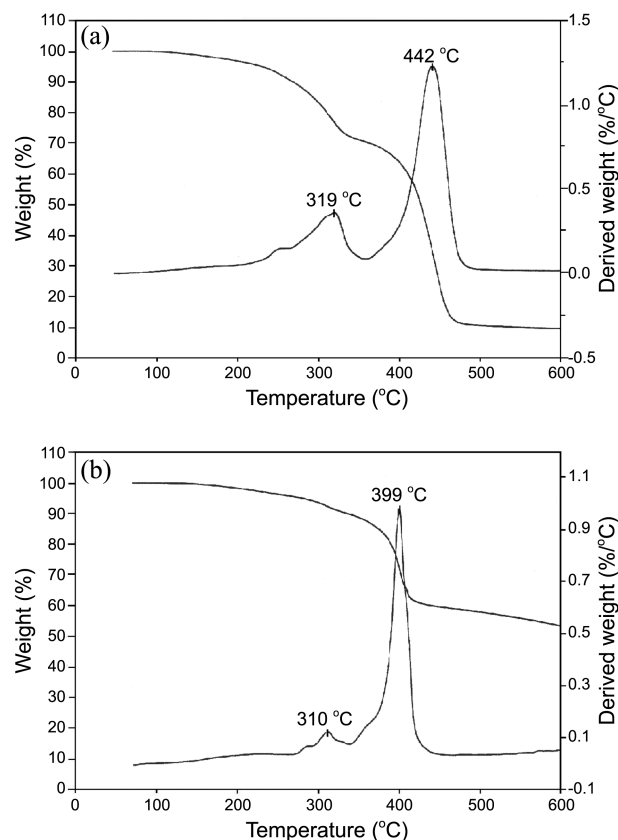


**Figure 4.** FT-IR spectra of homo- and co-polymeric hydrogels.

molecular  $\text{OH}\cdots\text{OH}$ , and  $\text{SO}_3\cdots\text{OH}$  into weak intermolecular  $\text{OH}\cdots\text{C}=\text{O}$  bonds.<sup>19,20</sup> The width of this band has increased with the increase of VSA content.<sup>18,19</sup> The band at  $2900\text{ cm}^{-1}$  has been responsible for main chain asymmetric  $-\text{CH}_2$  stretching vibrations. The  $\text{C}=\text{O}$  stretching vibration of NMMAAm was located at  $1650\text{ cm}^{-1}$ . From the copolymer spectra, the bands, which were located at  $1170\text{ cm}^{-1}$ ,  $1035\text{ cm}^{-1}$ ,  $750\text{ cm}^{-1}$ ,  $713\text{ cm}^{-1}$ , and minor shoulder at  $1270\text{ cm}^{-1}$  were attributed to symmetrical stretching mode of  $\text{SO}_2$ , stretching mode of  $\text{S}=\text{O}$ , antisymmetrical and symmetrical stretching modes of  $\text{C}-\text{S}$  and antisymmetrical stretching mode of  $\text{SO}_2$ , respectively.<sup>21</sup> Based on this information, it is possible to say that copolymers were formed so as to include both NMMAAm and VSA components.

Thermal stability studies provide useful information on the selection of materials with the best properties for specific applications.<sup>22</sup> In order to observe the thermal behaviour of the NMMAAm and NMMAAm-VSA hydrogels, they were ground into small pieces, and thermograms were taken in an  $\text{N}_2$  atmosphere. The thermal degradation behaviours of plain NMMAAm hydrogel and its copolymers with VSA were studied in the range of  $50\text{--}600\text{ }^\circ\text{C}$ . Figure 5(a) showed the two main stages of NMMAAm degradation with maximal decomposition rates at  $319\text{ }^\circ\text{C}$  and  $442\text{ }^\circ\text{C}$ . The first stage of decomposition occurred mainly due to the rupture of the side chain. The major decomposition came out because of the main chain decomposition. TGA data on NMMAAm-VSA copolymers (with a mole ratio of 1:3) displayed again a two-stage decomposition (Figure 5(b)). The first decomposition at maximum  $310\text{ }^\circ\text{C}$  may also be attributed to rupture of the side chain as NMMAAm. The second decomposition stage at maximum  $399\text{ }^\circ\text{C}$  occurred due to the decomposition of copolymers NMMAAm-VSA. The prominent matter of this figure is that the maximum decomposition temperatures shifted to lower temperatures depend on incorporation of

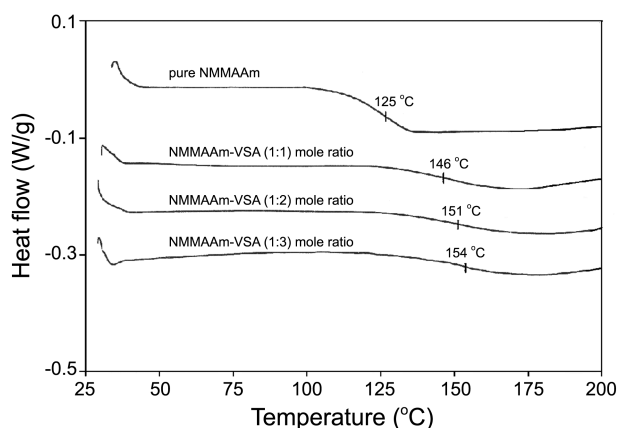
VSA, which has led to a more open pore structure of the copolymer. In addition, you could pay attention to a point where polymer stability increases further with the increase of VSA. This is because of the increase of hydrogen bond formation between the two components. The other important points about Figure 5(a) and (b) are the amounts of residues.



**Figure 5.** TG-DTG curves for NMMAAm hydrogel (a) NMMAAm-VSA (1/3 mole ratio) hydrogels (b).

**Table 1.** Weight loss and corresponding decomposition temperatures for NMMAAm and different mole ratio of NMMAAm-VSA hydrogel systems

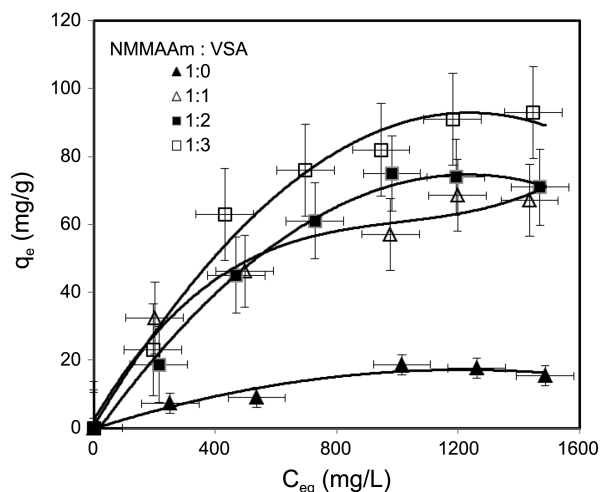
Hydrogel	Temperature (°C)		Weight loss at 600 °C (%)
	T <sub>max1</sub>	T <sub>max2</sub>	
NMMAAm	319	442	90
NMMAAm-VSA (1/1)	298	392	60
NMMAAm-VSA (1/2)	303	395	50
NMMAAm-VSA (1/3)	310	399	45

**Figure 6.** DSC thermograms of homo- and co-polymeric hydrogels.

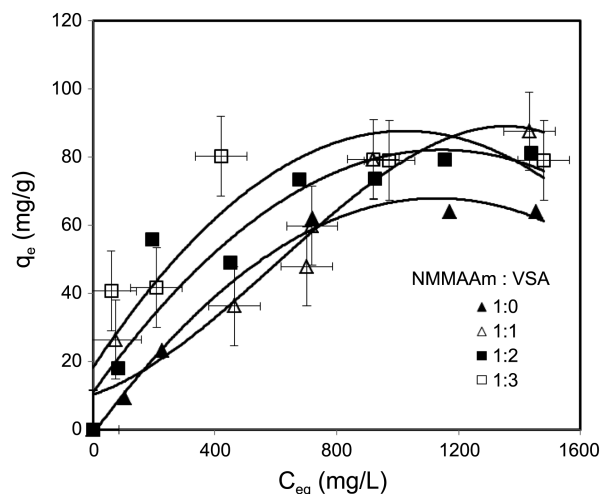
After heating up to 600 °C, maximum residual weights were observed on polymers containing VSA. At 600 °C, NMMAAm was completely carbonized. On the other hand, VSA containing polymers have been more stable than NMMAAm itself due to the presence of the  $-\text{SO}_3^-$  groups which made more stable structures *via* H-bond formation. Moreover, the heating process up to 600 °C has not been sufficient for the removal of S-O compounds from the structures completely. All these statements have been acceptable for other two copolymers (with mole ratios of 1:1 and 1:2) and results were tabulated in Table 1.

In order to improve interpretations made about thermal behaviour of both hydrogel systems, DSC thermograms were taken. As shown in the Figure 6,  $T_g$  values, at which the polymer starts to display a rubbery appearance, an increase came out with the increase of VSA content of co-polymeric hydrogel systems. As mentioned previously, this has been come out from H-bond formation between amide and sulphonyl groups of hydrogel. The  $T_g$  value of NMMAAm hydrogel was found at 125 °C. Incorporation of VSA to NMMAAm chains increased  $T_g$  into higher values. This could probably be caused by higher extent of H-bonding which depended on increasing amount of VSA in co-polymeric hydrogel.

**Co<sup>2+</sup> and Ni<sup>2+</sup> Adsorption Behavior of Hydrogels.** The adsorption of NMMAAm-VSA hydrogels was tested in the aqueous solutions containing cobalt and nickel ions. The heavy metal ions removal studies were carried out with pre-determined constant pH of 5.0. As it is known, the metal salt

**Figure 7.** Adsorption isotherms for Co<sup>2+</sup> ( $m = 0.01$  g gel,  $V = 10$  mL, pH 5.0).

solutions are acidic. Due to the increase of the basicity of the environment, metal ions are precipitated in the form of hydroxides. Conversely, in acidic pH region, nitrogen group of amide in copolymers are slightly protonated, which causes decrease in metal ion uptake. Also,  $pK_a$  value of sulphonic acid is around  $-2$ .<sup>15</sup> Therefore, at pH 5.0 value, all sulphonyl groups of copolymers are ionized forms so as to capture the metal ions easily. Another reason for choosing the pH value of 5 is that copolymers reach the highest swelling value at this pH. In order to evaluate the effect of initial metal ion concentration on adsorption characteristics of hydrogels, a series of experiments were conducted. Figure 7 and 8 show the adsorption behaviours of hydrogels in different initial concentrations of Co<sup>2+</sup> and Ni<sup>2+</sup>. It can be seen that the amount of adsorbed Co<sup>2+</sup> ions on NMMAAm gel increased with a slight increase of initial Co<sup>2+</sup> concentration. The amount of adsorbed Co<sup>2+</sup> ions reached 19 mg/g, which was a maximum value for NMMAAm hydrogel. As shown in the figure, the amount of Co<sup>2+</sup> removed from aqueous solution

**Figure 8.** Adsorption isotherms for Ni<sup>2+</sup> ( $m = 0.01$  g gel,  $V = 10$  mL, pH 5.0).

increased with an increasing amount of VSA content in the hydrogel. The maximum amount of adsorbed metal ion on NMMAAm-VSA hydrogel (1:3 mole ratio) reached to a value of 98 mg Co<sup>2+</sup>/g gel in 1000 mg/L initial metal concentration. The amount of adsorbed Ni<sup>2+</sup> on NMMAAm gel increased with the increase of initial Ni<sup>2+</sup> concentration and this value reached to a maximum value around 64 mg/g. Like Co<sup>2+</sup> ion, the amount of adsorbed Ni<sup>2+</sup> ion increased with an increasing amount of VSA content in the hydrogel. NMMAAm-VSA hydrogel (1:3 mole ratio) has had maximum adsorption capacity, which reached to 82 mg/g in 1000 mg/L initial metal concentration. A remarkable thing at this point is that the amount of adsorbed Ni<sup>2+</sup> ions on the NMMAAm hydrogel is not too different from the values of copolymers. Maximum adsorption capacity is nearly equal to other three type hydrogels that have a composition ratio of 1:1, 1:2, 1:3. The results of batch experiments showed that NMMAAm-VSA copolymers were more effective than NMMAAm hydrogels to remove Co<sup>2+</sup> and Ni<sup>2+</sup> ions from aqueous media. The reason why there is a differentiation between them is

that homopolymer contained –OH and –NH groups, copolymers also contained –SO<sub>3</sub><sup>–</sup> groups in addition to these two groups. Thus, the interactions between metal ions and –SO<sub>3</sub><sup>–</sup> groups increased and more metal ions were removed by copolymer from aqueous solutions. Similar results were observed in the Ozay's *et al.* study.<sup>23</sup> Generally, it was observed that nearly all hydrogels were more effective in removal of Co<sup>2+</sup> ions than removal of Ni<sup>2+</sup> ions at the whole range of the studied concentration and certain temperature. The main reason is that this comes from the periodical properties of both Co<sup>2+</sup> and Ni<sup>2+</sup>. It is known that the ionic radius of Ni<sup>2+</sup> ions is larger than that of Co<sup>2+</sup> ions.<sup>24</sup> When the complex formation between polymeric ligands and metal ions has been discussed, it was concluded that metal ions with smaller radii interacted more easily with polymeric ligands. On the other hand, the Ni<sup>2+</sup> ion has more electronegativity than the Co<sup>2+</sup> ions, which tends to have less interaction with –SO<sub>3</sub><sup>–</sup> groups. In addition to difference in their sizes, degree of hydration and the value of the binding constant with the adsorbent can also be regarded as the

**Table 2.** Parameters of Langmuir isotherm of Co<sup>2+</sup> and Ni<sup>2+</sup> on hydrogels

Co <sup>2+</sup>	NHMMA:VSA	NHMMA:VSA	NHMMA:VSA	NHMMA:VSA
	(1:0)	(1:1)	(1:2)	(1:3)
q <sub>e</sub> (mg/g, experimental)	–	–	78	98
q <sub>max</sub> (mg/g, theoretical)	–	–	84.75	106.28
K <sub>L</sub>	–	–	2.69 × 10 <sup>–3</sup>	7.41 × 10 <sup>–3</sup>
R <sup>2</sup>	–	–	0.98	0.98
Ni <sup>2+</sup>	NHMMA:VSA	NHMMA:VSA	NHMMA:VSA	NHMMA:VSA
	(1:0)	(1:1)	(1:2)	(1:3)
q <sub>e</sub> (mg/g, experimental)	–	–	76	82
q <sub>max</sub> (mg/g, theoretical)	–	–	99.01	86.21
K <sub>L</sub>	–	–	3.30 × 10 <sup>–3</sup>	9.13 × 10 <sup>–3</sup>
R <sup>2</sup>	–	–	0.96	0.98

– R<sup>2</sup> values are smaller than 0.96.

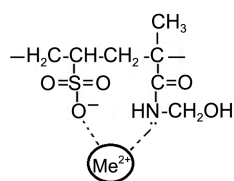
**Table 3.** Comparison of adsorption capacities of some adsorbents in the literature

Adsorbent	q <sub>e</sub>		Ref.
	Co <sup>2+</sup>	Ni <sup>2+</sup>	
NMMAAm-VSA (1/3 mole ratio)	98 mg/g	82 mg/g	This study
Poly(2-acrylamido-2-methyl-1-propansulfonic acid), p(AMPS)	101.78 mg/g	95.81 mg/g	[22] <sup>a</sup>
Magnetic p(AMPS)	110.07 mg/g	105.48 mg/g	[22] <sup>a</sup>
Calcined modified kaolinite	5.3 mg/g	5.2 mg/g	[26] <sup>b</sup>
Calcined modified montmorillonite	15.8 mg/g	15.6 mg/g	[26] <sup>b</sup>
Amberlite IRC 748	0.59 mol/L	0.62 mol/L	[27] <sup>c</sup>
EDTA-modified silica gel*	20.0 mg/g	21.6 mg/g	[28] <sup>d</sup>
DTPA-modified silica gel**	16.1 mg/g	16.7 mg/g	[29] <sup>d</sup>
Poly( <i>p</i> -chloromethyl styrene-ethylene glycol dimethacrylate), poly( <i>p</i> -CMS-EGDMA)	78.5 mg/g	98.3 mg/g	[30] <sup>e</sup>
Hexagonal templated zirconia	0.70 mmol/g	0.90 mmol/g	[31] <sup>f,g</sup>
Magnetic chitosan-diacetylmonoxime Schiff's base resin, (CSMO)	60 ± 1.5 mg/g	47 ± 1.5 mg/g	[32] <sup>h</sup>

<sup>a</sup>initial ion concentration: 500 mg/L, approximately 0.2 g dry absorbents. <sup>b</sup>clay 2 g/L; initial metal ion concentrations 50 mg/L; pH: Co<sup>2+</sup> 5.8, Ni<sup>2+</sup> 5.7; 303 K. <sup>c</sup>temperature 25 °C, initial solution concentration 2.5 g/L, pH 5.0. <sup>d</sup>initial concentration of 10 mg/L were 2 g/L of dose, pH 3, 50 rpm of agitation speed and 4 h of contact time. <sup>e</sup>pH 6.0; adsorption time: 48 h; amount of adsorbent: 0.02 g; initial ion concentration: 20.0 mM. <sup>f,g</sup>adsorption time: 60 min; amount of adsorbent: 0.1 g; initial ion concentration: 9.64 × 10<sup>–2</sup> mmol/dm<sup>3</sup>. <sup>h</sup>pH 5.0, amount of adsorbent: 0.03 g, adsorption time: 8 h. \*ethylene-diaminetetraacetic acid. \*\*diethylenetriaminepentaacetic acid

reason for differences of the amount of the adsorbed metal ions.<sup>25,26</sup> It is possible to find various studies in the literature for removal of  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  ions from aqueous systems by using different adsorbents.<sup>27-33</sup> Adsorption results using different adsorbents for removal of  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  have been listed in Table 3. As a result, it can be easily seen that the maximum amount of adsorbed  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  was relatively higher than most of the study in the literature.

Another remarkable thing about Figure 7 and Figure 8 is the shape of curves. The adsorption isotherms of  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  on hydrogels correspond to Langmuir type according to the Giles classification.<sup>34</sup> In Langmuir type isotherm, the initial portion provides information about the availability of the active sites to the adsorbate and the surface signifies the monolayer formation. In addition, it is used to describe chemical adsorption on a set of separate localized adsorption sites. Monolayer adsorption occurs on the hydrogel's surface during the adsorption process. This result has also been supported with evaluation of the data according to the Langmuir isotherm equation (Table 2). After  $R^2$  values in the Table 2 were investigated, it was observed that the results reached nearly 1.00  $R^2$ . Langmuir isotherm was observed in adsorption of the metal ions from solution.<sup>35</sup> As for the mechanism of adsorption; at pH 5.0 value, sulphonyl groups get ionized, and nitrogen group of amide structure in hydrogel is not positively charged, but has un-pair electrons. Because of the reasons mentioned above, we used acidic desorption agents (HCl,  $\text{HNO}_3$ , etc.) to reuse hydrogels, and desorption of the adsorbed all metal ions was assigned by using UV-Vis measurements. Results have not been included in the article. In the light of all these explanations, it is possible to say that adsorption mechanism has been formed with electrostatic interactions between metal ions and  $-\text{SO}_3^-$ ,  $-\text{NH}$  groups of hydrogel, and the adsorption has come out physically from Langmuir plots. Finally, it was offered by this study that the main mechanism could be as follows:



### Conclusion

In this study, NMMAAm and NMMAAm-VSA hydrogels were prepared by irradiation in air at ambient temperature in a  $^{60}\text{Co}$ - $\gamma$  source. Gel fraction values decreased with the increase of VSA content but swelling behaviour of hydrogels, in deionized water and at different pHs, increased with increase of VSA content. A significant change in swelling has been observed for all co-polymeric hydrogels at pH range of 2.0-13.0 due to the different interactions between functional groups. Two maxima have been obtained from swelling studies, one is at pH 4 and the other is at pH 11. Both homo- and co-polymeric hydrogels were used for removal of  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  from aqueous solutions. The

results of batch experiments showed that NMMAAm-VSA copolymers have been more efficient than NMMAAm hydrogels for removal of  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  ions from aqueous systems. As a result of this study, it can be stated that NMMAAm-VSA hydrogels can be used for removal of heavy metal ions from waste water as an adsorbent due to their high sorption capacity.

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