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Use of pH-thermosensitive hydrogels for nickel ion removal and recovery

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Abstract

N-isopropylacrylamide / itaconic acid hydrogels were prepared in this study, varying the proportion of itaconic acid in the pregel mixture. The kinetics of the hydrogel swelling at 4 °C was determined, obtaining the kinetic parameters, in accordance with the second-order kinetic model. Similarly, the capacity to absorb water in terms of temperature was determined, along with the transition temperature of the samples. The influence of temperature on the capacity of the hydrogels to absorb nickel from aqueous solutions at 5% of NiCl₂ and its subsequent recuperation was determined.

Keywords: *hydrogels, metals remover, recovery metals, pH-sensitive, thermosensitive.*

1. Introduction

Over recent years, the remediation of water contaminated with heavy metals has been carried out through the application of various methods^[1-6], using both chemical and physical processes. Various studies have analyzed the possibility of using hydrogels for the retention and removal of heavy metals from contaminated water^[7-11], reporting good results in terms of the removal process. However, there is no information available on either a process for recovering heavy metals from used polymer matrices or the possible reuse of these matrices. The costs of the remediation of contaminated water can be reduced through matrix reuse, provided that the material used for the removal of the metals is, as with the metals recovered during various industrial processes. Poly(N-isopropylacrylamide) (NIPA) is a thermo-responsive polymer that has a lower critical solution temperature (LCST) of 32 °C^[12] in water. Below the LCST^[13,14], polyNIPA and water are completely miscible; above the LCST, phase separation occurs. As a consequence of this transition, crosslinked polyNIPA hydrogels exhibit a volume phase transition at around this value. This temperature is known as the volume phase transition temperature (T_{VPT}), which is characterized by a sudden decrease in the capacity to absorb water and occurs at around 32 °C. The addition of acid groups to the NIPA polymer chain has been found to increase both the capacity to absorb water and raise the transition temperature^[15]. Therefore, this study aims to analyze the possibility of using thermosensitive and pH-sensitive hydrogels for the removal and recovery of nickel ions from aqueous solutions, by placing the hydrogels in aqueous nickel solutions at below transition temperature, and, once equilibrium is attained, raising the temperature to above T_{VPT} in order to recover the nickel removed.

2. Materials and Methods

2.1 Materials

N-isopropylacrylamide (NIPA) with a purity of 99%, from Aldrich. Itaconic acid (IA) with a purity of 99%, from Aldrich. The initiator used was potassium peroxydisulfate (K₂S₂O₈),

at 99% purity, from Aldrich. N,N, methylenebisacrylamide (NMBA) was used as a cross-linking agent with a purity of 99% (TCI). The accelerator used was N, N, N, N, tetramethylethylenediamine (TMEDA) from Tokyo Kasei. Bidistilled water was used in all the experiments.

2.2 Synthesis of hydrogels

Aqueous monomer solutions to 10 percent by mass (NIPA and IA, modifying the proportion of acid) were prepared in 20 mL glass containers in nitrogen atmosphere, to which was added 1% cross-linking agent in relation to the monomers, as well as NaOH solution for the complete neutralization (stoichiometric ratio) of the acid content of each sample. Once the solution had been formed, nitrogen was bubbling for one minute, 2% of initiator and 3% of accelerator was added in relation to the monomers (ensuring that all samples had a final monomer/water ratio of 10/90), the container was closed and sealed with parafilm, and left to react for 24 hours at 25 °C. The diagram of the polymerization reaction is shown in Figure 1

2.3 Cleaning

Once the reaction had finished, the samples were left to dry, firstly for three days at room temperature and then in a vacuum oven at 40 °C. This was carried out to avoid rupturing the samples due to sudden drying. The dry samples are placed in distilled water at 25 °C and, once they have attained equilibrium swelling (at around 7 days)^[11], they are placed in a temperature controlled bath at 40 °C for 2 days to remove from the samples the material that had not been added to the network. The water was then changed and the process repeated, until no signs were observed of turbidity in the wash water at 40 °C. The turbidity of wash water is an indicator of the presence of monomers and oligomers that contain NIPA. Once the process had been completed, the samples were left to dry, as described above, with their weight before and after the cleaning process used to determine the conversion level during the polymerization reaction.

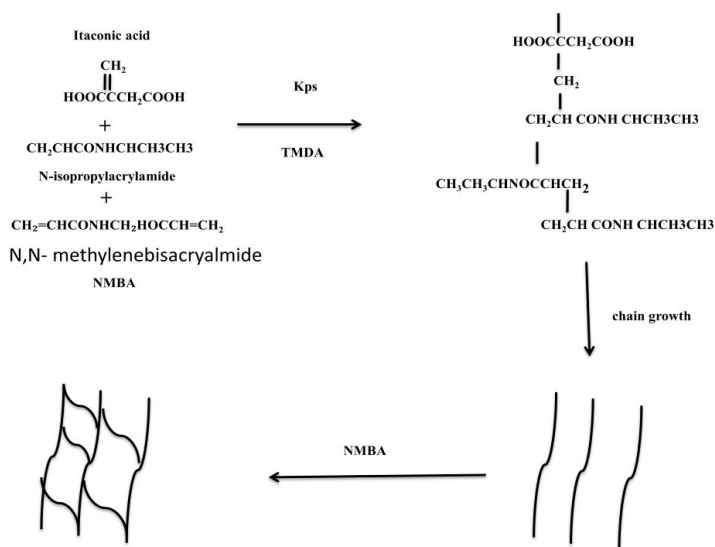


Figure 1. Scheme of the polymerization reaction of the synthesized hydrogels.

2.4 Swelling kinetics

To determine the swelling kinetics, the dry samples are weighed and placed in water at 4 °C. The samples are weighed at different times, with their surface dried using absorbent paper. The swelling kinetics are determined using the difference between the weight of the dry and swollen sample. This process is repeated until the weight of the swollen sample does not change, which determines the equilibrium swelling (H_{∞}), to the temperature of the experiment, with the swelling determined by means of the following equation^[16]:

$$H = \frac{m_t - m_0}{m_0} = \frac{\text{weight of hydrogel} - \text{weight of xerogel}}{\text{weight of xerogel}} \quad (1)$$

2.5 Equilibrium swelling in relation to temperature

Once the samples attained the equilibrium swelling at 4 °C, the samples were placed in a controlled temperature bath at 30 °C and, once they had reached the equilibrium swelling (which was determined using the process described above), the temperature was raised. The temperatures used in this study ranged from 4 to 46 °C. The transition temperature (T_{VP}) was determined using the equilibrium swelling curves versus the temperature, measuring the change in the water content in terms of equilibrium and temperature.

2.6 Nickel absorbing capacity

The xerogels are placed in 5% nickel (II) chloride aqueous solutions at 4 °C until the equilibrium swelling is reached (the time is determined by the swelling kinetics obtained previously) (a ratio of 300 grams of solution was used per gram of xerogel, for all experiments). Once this occurred, the samples were withdrawn from the medium and weighed, and a sample then taken from the residual solution to determine the concentration of Ni^{+2} . Using the Genesys 10 U.V. spectrophotometer from the Thermoelectron Corporation, the samples are returned to the solution and

placed in a controlled temperature bath at 30 °C, upon which the process described above is repeated, the temperature of the bath is raised to 40 °C, and the quantity of nickel removed is determined. This process is repeated for solutions with a pH of 3 (which is regulated by adding HCl) and a 5% NiCl_2 weight. All experiments were carried out in systems without agitation.

3. Results and Discussions

Swelling kinetics has been studied by various authors using the following equation^[17-19]:

$$\frac{dW}{dt} = K(W_{\infty} - W)^2 \quad (2)$$

Where:

$$W = \frac{m_t - m_0}{m_t} = \frac{\text{weight of hydrogel} - \text{weight of xerogel}}{\text{weight of hydrogel}} \quad (3)$$

Which, on being integrated with $W = 0$ in $t = 0$, the following was obtained:

$$W = \frac{KW_{\infty}^2 t}{1 + KW_{\infty} t} \quad (4)$$

On combining Equations 1-3, the following was obtained:

$$\frac{t(H+1)}{H} = \frac{(H_{\infty}+1)^2}{KH_{\infty}^2} + \frac{H_{\infty}+1}{H_{\infty}} t \quad (5)$$

Which is rearranged as:

$$\frac{t(H+1)}{H} = mt + b \quad (6)$$

With which H can be obtained in relation to time, with the following equation:

$$H = \frac{t}{t(m-1)+b} \quad (7)$$

With this expression, it is possible to determine the kinetic parameters with which the speed of water absorption and equilibrium swelling are obtained. Figure 2 shows the comparison between the experimental data and the theoretical prediction obtained with Equation 7, in which a good description of the experimental data is observed, thus confirming the standard deviation between the experimental data and the theoretical prediction, with said deviation presented in Table 1.

Transition temperature is determined by calculating the change in equilibrium swelling in relation to the temperature, with the temperature at which this change acquires the absolute maximum value being determined as the transition temperature (Table s1 of Supplementary material). The kinetic parameters and the equilibrium swelling are presented in Table 1. It can be observed that, on increasing the concentration of itaconic acid, the capacity of the hydrogels to absorb water increases (Figure 3). The yield obtained from the polymerization reaction of the samples was greater than 98% in all cases, as does the transition temperature of the samples (Figure 4 and Figure s1 of Supplementary material). This is due to the increase of the carboxylic groups, which, in turn, increases the hydrophile groups, thus absorbing a greater amount of water^[15,19,20].

Table 2 shows the decrease in the capacity of the hydrogels to absorb nickel solutions in relation to the capacity to absorb water, which is explained by the interactions of the nickel ions with the carboxylic groups, avoiding the association between the water molecules and these groups, reducing the capacity to absorb solution from the hydrogels. Similar results have been previously reported^[21], from which it is possible to speculate on the benefits of adding hydrogels, instead of xerogels, to the nickel solutions in order to determine whether the capacity to absorb ions increases. In the hydrogels, the polymer chains are found to be extended, while the xerogel chains expand. The risk of elongating the chains to their maximum length could be reduced or avoided, depending on the quantity of solution that is being penetrated and the presence of nickel ions. On the other hand, it is possible to establish the nickel removal process depending on the prevailing climate in the area from where the water to be decontaminated is found, with the hydrogels (or xerogels) placed at low (lower than 10 °C) or medium temperatures (higher than 15 °C). For the recovery of the nickel removed, the loaded gels can be placed at greater temperatures for those hydrogels with a lower itaconic acid content in the matrix, while those hydrogels that have a greater proportion

of itaconic acid are placed in pH 3 solutions and greater temperatures.

In this regard, an analysis must be undertaken of the minimum amount of solution with a pH of between 3 and 1 (taking into account of the possible degradation of material) that must be added to provoke the deswelling of the hydrogel and the amount of recovered nickel. It

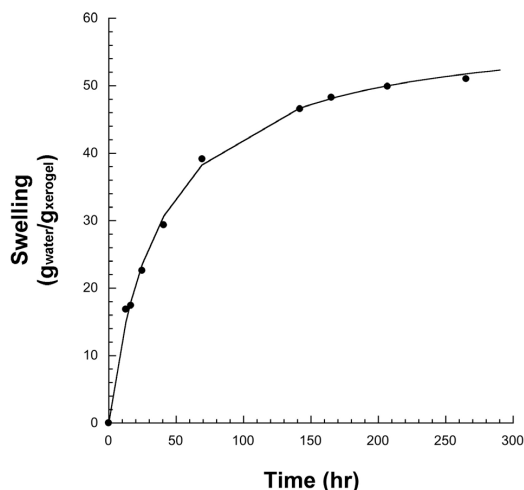


Figure 2. Comparison between experimental data and the second order swelling kinetic model for the NIPA/IA 99/1 sample with the experimental data (●), and the theoretical prediction (-).

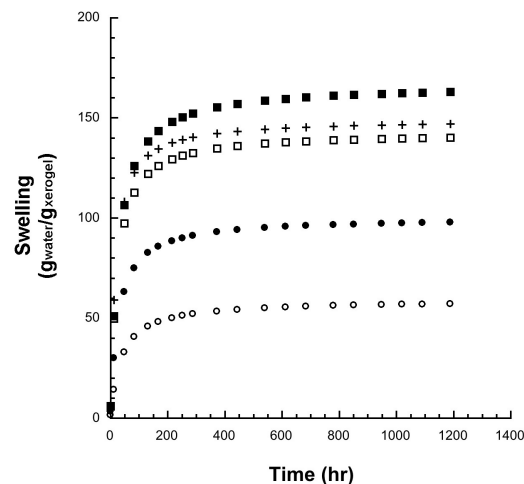


Figure 3. Swelling Kinetics of hydrogels depending on the proportion of NIPA/IA 99/1 (○), 98/2 (●) 97/3(□) 96/4 (+) y 95/5 (■).

Table 1. Equilibrium swelling and kinetic data of the hidrogeles synthized at 4 °C.

NIPA/IA % weight	99/1	98/2	97/3	96/4	95/5
Slope (m)	1.017	1.010	1.007	1.006	1.007
H_{∞} (g _{water} /g _{xerogel})	59.140	102.260	142.644	161.784	150.042
Dev std	0.582	0.770	2.248	2.916	2.837
Intercept (b)	38.374	16.810	9.426	9.780	7.331
K g _{hydrogel} /(g _{water} -min)	0.027	0.061	0.108	0.104	0.138
Transition temperature	38 °C	42 °C	44 °C	44 °C	44 °C

has been observed that when the pH of the solution is regulated (adding HCl to obtain a pH of 3), the capacity of the hydrogels to absorb solution is seen to be reduced, owing to the fact that the acid groups are not ionized and, with this, the availability of spaces in the network

for the capture of water and metal ions is also reduced (Table 2). So it is known that increasing the temperature increases the solubility and therefore Ni^{2+} prefers to be in water and not in the hydrogel. Table 3 shows that on reducing the concentration of nickel ions in the solution, the capacity to absorb nickel solution is increased, as does the percentage of nickel ion removal, which corroborates that the presence of nickel ions reduces the active spaces for water absorption.

With this, the space is opened to develop the process of removing metal ions, firstly by placing the hydrogels in the nickel ion solutions. Then, when the hydrogels become saturated with the metal, they are removed from the medium and placed in solutions with a pH of 3 or more, and/or at temperatures greater than 40 °C, at which the metal ions will be displaced from the hydrogel. The use of this procedure was intended to obtain metal saturated solutions and to explore the possibility of reusing the hydrogels. To determine the magnitude of the degradation of the hydrogels, all the samples were placed in the solutions at 5% of NiCl_2 at 4°C and, when they attained equilibrium swelling they were placed in a temperature controlled bath at 40 °C on four separate occasions. In all cases, similar swelling levels and Ni^{2+} ion absorption were obtained, with the loss of hydrogel mass determined in each experiment, which was less than 1% in all cases.

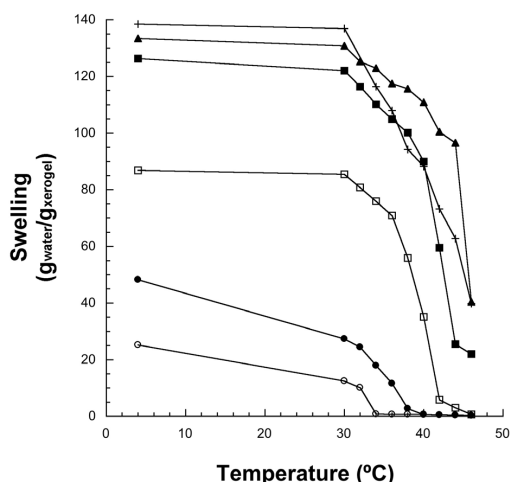


Figure 4. Equilibrium swelling in relation to temperature depending on the proportion of NIPA/IA 100/0 (○), 99/1 (●), 98/2 (□), 97/3 (■), 96/4 (+) and 95/5 (▲).

Table 2. Equilibrium swelling, mass of Ni^{2+} absorbed from the hydrogels when they are placed in 5% NiCl_2 solutions depending on the proportion of NIPA/IA at different temperatures and pH levels.

NIPA/IA % weight	100/0	99/1	95/5	90/10	85/15
W_{∞} water 4 °C	25.235	59.140	150.042	306.792	393.695
W_{∞} water 30 °C	13.165	27.35	130.820	249.482	265.648
W_{∞} water 40 °C	0.3950	0.60	110.81	207.680	227.276
W_{∞} Ni 4 °C	17.108	29.20	32.70	27.40	36.47
W_{∞} Ni 30 °C	3.382	10.11	19.50	15.69	28.57
W_{∞} Ni 40 °C	0.860	1.41	3.13	1.41	4.52
$g_{\text{Ni}}/g_{\text{xerogel}}$ 4 °C	0.318	0.645	0.77	0.88	1.201
$g_{\text{Ni}}/g_{\text{xerogel}}$ 30 °C	0.175	0.210	0.55	0.41	0.811
$g_{\text{Ni}}/g_{\text{xerogel}}$ 40 °C	0.05	0.069	0.139	0.20	0.608
W_{∞} Ni pH 3 4 °C	-	27.708	24.409	26.593	41.007
W_{∞} Ni pH 3 30 °C	-	1.580	6.958	12.927	27.4334
W_{∞} Ni pH 3 40 °C	-	0.622	2.120	1.077	2.566
$g_{\text{Ni}}/g_{\text{xerogel}}$ 4 °C	-	0.278	0.844	1.358	0.981
$g_{\text{Ni}}/g_{\text{xerogel}}$ 30 °C	-	0.351	0.487	0.331	0.677
$g_{\text{Ni}}/g_{\text{xerogel}}$ 40 °C	-	0.161	0.151	0.159	0.142

Table 3. Equilibrium swelling of the hydrogels for the NIPA/IA 85/15 hydrogel, placed in NiCl_2 solutions according to the salt concentration.

Concentration	4 °C		30 °C		40 °C	
NiCl ₂	W	g _{Ni} /g _{xerogel}	W	g _{Ni} /g _{xerogel}	W	g _{Ni} /g _{xerogel}
3.000%	30.956	1.429	22.388	1.205	12.012	0.380
2.500%	30.973	1.259	22.770	1.152	13.476	0.353
1.000%	32.092	0.500	24.513	0.417	17.293	0.138
0.500%	33.551	0.252	26.614	0.213	19.241	0.050
0.350%	52.757	0.215	42.153	0.142	31.578	0.018
0.200%	57.767	0.122	48.763	0.081	38.611	0.007
0.100%	71.048	0.090	57.933	0.028	48.558	<0.005

4. Conclusions

It was found that the addition of itaconic IA increased the capacity to absorb water. The capacity to absorb Ni ions was determined using aqueous NiCl₂ solutions with a composition of 5%. In all samples, the greatest capacity to absorb nickel was found at 4 °C. The possible use of these materials was determined for the recovery of nickel from industrial effluent and its recovery as a raw material, on removing the nickel from the solution at low temperatures and subsequently subjecting the saturated hydrogel to high temperatures. The low temperature depends on the proportion of itaconic acid in the sample. We can, therefore, establish that a low temperature would be 4 °C for the hydrogels with a 1 to 4% acid content. A temperature of 30 °C would be low for those hydrogels with a 5 to 15% acid content, these materials are left at this temperature to absorb the metal ions, with the loaded and saturated hydrogels then withdrawn from the medium and placed in the high temperatures, which would be 40 °C for the hydrogels with a low acid content and 46 °C for those hydrogels with a higher acid content. Small quantities of acid solution are added in order to obtain a pH value of between 1 and 3 in the medium.

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Supplementary Material

Supplementary material accompanies this paper.

Figure s1. Fraction of water released from the hydrogels in relation to temperature as a function of the proportion of NIPA/IA 100/0 (○), 99/1 (●), 98/2 (□), 97/3 (■), 96/4 (+) and 95/5 (▲), taking the equilibrium swelling of 4°C as a point of reference.

Table s1. Change in the fraction released in relation to temperature, which was calculated using $(F_{32^{\circ}\text{C}} - F_{30^{\circ}\text{C}}) / (32^{\circ}\text{C} - 30^{\circ}\text{C})$ at 32°C and in the same manner for the rest of the temperatures.

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