PREPARATION AND CHARACTERIZATION MAGNETIC HYDROGEL

KİRAZ Uğur[1], TEBER Sena[1], PEKER Hakan[1], SALLAN Furkan Cahit[1], NARİN Güler[2], KILIÇ Eylem[1]

[1] Usak University University, Faculty of Engineering, Department of Material Science and Nanotechnology Engineering, 64200, Usak, Turkey, E-Mail: eylem.kilic@usak.edu.tr
[2] Usak University University, Faculty of Engineering, Department of Chemical Engineering, 64200, Usak, Turkey, guler.narin@usak.edu.tr

Corresponding author: Kılıç, Eylem, E-mail: eylem.kilic@usak.edu.tr

Abstract: Every year more than 100,000 kinds of commercially available dyestuff are produced. Most of industrial dyes have synthetic origin, which are applied in many industries such as textiles, rubber, paper, plastics, leather, petrochemicals etc. The textile industry is one of the major consumers of dyestuff and the effluent from textile industries carries a large number of dyes and other additives which are added as auxiliary chemicals. During the dyeing process some of dyestuff does not bind and approximately 10-15 % of them remains in the wastewater effluents. The release of synthetic dyes to the environment cause serious environmental problems and detrimental effects to human health. Therefore development of an effective treatment method for removing dyes from wastewater is of great significance. In this study poly(vinyl) alcohol hydrogels containing different amounts of magnetic particles were prepared and characterized for dye adsorption from wastewater. The magnetic particles synthesized by co-precipitation methos were dispersed in aqueous poly(vinyl) alcohol solutions. The solutions were then physically crosslinked by the freezing-thawing method. The hydrogels prepared were characterized for their drying, swelling and gelation properties. It was found that the hydrogels has high water absorption capacity (equilibrium degree of swelling: 200–214% and equilibrium water content: 66–68%) and high crosslinking degree (95%) almost independent from their magnetic particle content. They gained magnetic property after addition of the magnetic particles in the polymer matrix.

Key words: poly(vinyl) alcohol, swelling behaviour, freeze-thaw, magnetic hydrogel

1. INTRODUCTION

Magnetic hydrogels are a type of functional hydrogel with magnetic properties, which enables recovery of the composite in a magnetic field following its application. Due to their relatively facile recovery they are used in removal of numerous pollutants such as heavy metals [1], fluoride, [2] and more recently dyes [3]. Most of industrial dyes have synthetic origin, which are toxic, carcinogenic, and teratogenic, they are widely used in industries such as textile and leather. Therefore development of an effective treatment method in removing dyes from wastewater is of great importance [4].

The aim of this work was to prepare and characterize composite poly(vinyl) alcohol magnetic hydrogels containing different amounts of magnetic particles (2.1, 4.0, 6.2, and 8.1 wt % of dry films) for dye removal applications.

2. EXPERIMENTAL

2.1 Materials

For the synthesis of magnetic particles $FeSO_4.7H_2O$ (CAS. No: 7782-63-0), $FeCl_3$ (CAS No: 7705-08-0) and NaOH (CAS No:1310-73-2). Polyvinyl alcohol (PVA) (CAS No: 9002-89-5, Density: 0.4-0.6 g/cm^3, %87.8 purity) was used in order to prepare magnetic hydrogels.

2.2 Preparation of magnetic particles (MP) and magnetic hydrogels

The co-precipitation method was chosen as a method for synthesizing of the magnetic particles. 4.6 grams of $FeCl_3$ and 3.4 g of $FeSO_4·7H_2O$ were dissolved in 400 mL deionized water. The temperature was increased to 70 ºC and solution was stirred with a speed of 1200 rpm to form a homogeneous solution. Then 5 M ammonia solution (100 mL) was added to the solution drop-by-drop and stirred at 70 ºC for 24 hours, with a final pH of 13. The color of the solution changed from light brown to black after mixing implying the formation of Fe_3O_4. Precipitated Fe_3O_4 particles were washed by surplus amount of deionized water repeatedly until pH 7 was achieved. The final products were dried in a static oven at 70 ºC for 48 h, and the Fe_3O_4 magnetic particles were finally obtained (Fig. 1a).

Aqueous solutions of PVA were prepared by dissolving 2 g of PVA powder in 20 mL deionized water at 90 ºC in a water bath under magnetic stirring. Different amounts of the synthesized magnetic particles (MP) (0.05, 0.10, 0.15 and 0.20 g) were added to the PVA solutions corresponding to 2.1, 4.0, 6.2 and 8.1 wt% MP in the dry films, respectively. Thereafter, the solutions were continuously stirred at 90 ºC for about 15 minutes and were cast in separate polyethylene petri dishes. The solutions were crosslinked by the freezing-thawing method by instantaneous freezing at -20 ºC for 16 h and then thawing at room temperature for 8 h. After the three freezing-thawing cycles, circular specimens with 27 mm in diameter were cut off the films using a cork borer. The films were dried in a static oven at 37 ºC until constant mass. The PVA film without MP was prepared and tested as control. The compositions of the films prepared are given in Table 1. They gained magnetic property after addition of the magnetic particles in the polymer matrix (Fig. 1, b1–b4).

Table 1: Compositions of magnetic hydrogel films

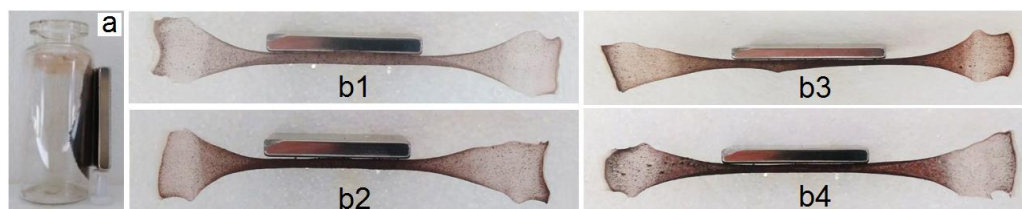| Films	MP amount added to PVA solutions (g/20 mL solution)	MP content of dry films (wt %)
0	0	0
1	0.05	2.1
2	0.10	4.0
3	0.15	6.2
4	0.20	8.1

*Fig. 1: Photos of the magnetic particles (a) and magnetic hydrogels
(b1: Film 1, b2: Film 2, b3: Film 3, b4: Film 4) under magnetic field.*

2.2 Characterization of magnetic hydrogels

The hydrogels with different compositions were characterized for their drying, swelling and gelation properties. Drying kinetics was investigated by measuring mass loss at 40 ºC until constant mass. Swelling kinetics experiments were conducted using 50 mL deionized water at 25 ºC, in a thermostated water bath. The mass of the films during drying and swelling were recorded as a function of time. Percent equilibrium degree of swelling (*EDS*) and equilibrium water content (*EWC*) of the films were calculated as,

$$EDS(\%) = (m_f - m_i) \times 100 / m_i \tag{1}$$

$$EWC(\%) = (m_f - m_i) \times 100 / m_f \tag{2}$$

where m_i and m_f are the initial (dry) and final masses of the films, respectively. The swelling tests were performed on three specimens for each film and the average *EDS* and *EWC* values were reported. Dissolution test was carried out in order to examine the stability of hydrogels upon swelling and fractional dissolution of uncrosslinked PVA. Following the swelling tests, the discs were dried at 40 ºC in a static oven until constant mass. Percent gelation degree was calculated as:

$$\text{Gelation degree}(\%) = m'_f / m_i \times 100 \tag{3}$$

where m_f' is the mass of the film after the soluble part was removed and m_i is the initial (dry) mass the film.

3. RESULTS AND DISCUSSION

The change in the mass of the films with time during drying process at 40 ºC is shown in Fig. 2. The mass loss has almost completed within the first 6 hours. The presence of MPs in the film did not affect diffusion kinetics of water through the film. Fig. 3 presents the swelling kinetics of films. The mass of all films increased rapidly within the first 4 h and then stabilized over the next 17 h period.
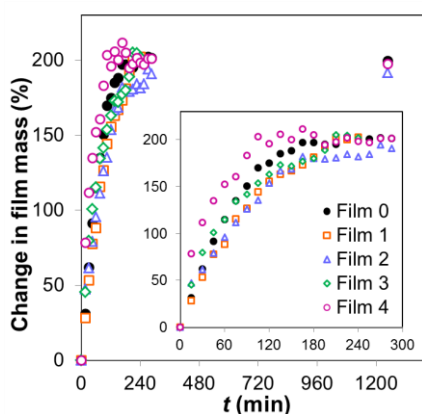

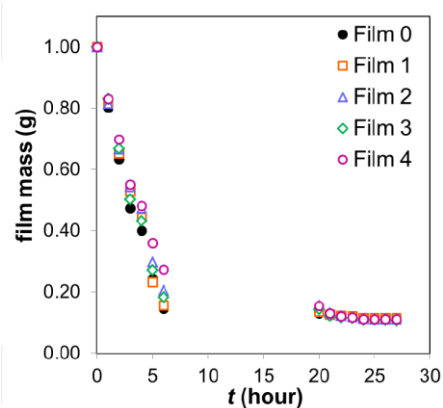*Fig. 2: Film mass change with time during drying at 40 ºC*   *Fig. 3: Swelling kinetics of the hydrogels*

Kinetics of the water absorption by the hydrogels can be expressed as:

$$M_{wt}/M_{w\infty} = kt^n \qquad \textbf{(4)}$$

where $M_{w\infty}$ and M_{wt} represent the amount of water in the film at time t and at equilibrium, respectively, k is a constant characteristic of the system, and n is an exponent which represents transport modes inside the film and provides information about the transport mechanism. A value of $n \leq 0.5$ indicates a Fickian diffusion mechanism (the rate of diffusion is much lower than the rate of relaxation), a value of $0.5 \leq n \leq 1$ indicates that diffusion is anomalous or Fickian and $n = 1$ implies case II (relaxation-controlled transport, diffusion is very fast contrary to the rate of relaxation). The constants n and k were calculated from the slope and intercept of the $\ln(M_{wt}/M_{w\infty})$ versus $\ln t$ curves were given in Fig. 4
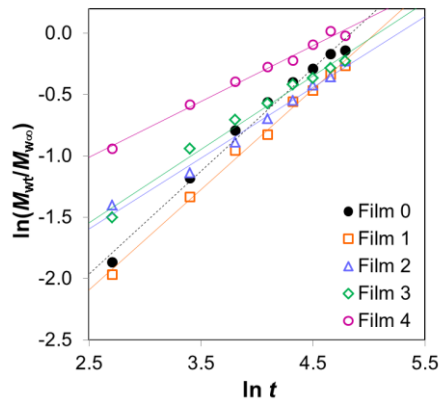
| Films	r^2	slope (n)	intercept (lnk)	k
0	0.989	0.839	-4.055	0.017
1	0.994	0.818	-4.135	0.016
2	0.987	0.577	-3.034	0.048
3	0.985	0.598	-3.039	0.048
4	0.989	0.455	-2.146	0.117

Fig. 4: Diffusion kinetics of water in films (first 120 min of immersion)

The calculated n value for Film 4, which is smaller than 0.5 indicated that the diffusion of water in this film is governed by a Fickian diffusion mechanism. The n values for the other films are between 0.5 and 1 indicating that diffusion is anomalous or Fickian. The diffusion coefficients for water in the swollen films were calculated by the following equation.

$$\frac{M_{wt}}{M_{w\infty}} = 4\sqrt{\frac{Dt}{\pi d^2}} \qquad \textbf{(5)}$$

where l is the thickness of the film measured by a micrometer and D is the diffusion coefficient of the water molecules from the film.

From the $M_{wt}/M_{w\infty}$ versus $t^{1/2}$ plots shown in the calculated diffusion coefficients and the regression coefficients (r^2) are given in Fig. 5. The diffusivity of water molecules in the films were in the range of 3.5–20.9×10^{-5} cm^2/s. The presence of magnetic particles did not change the swelling kinetics of the films remarkably.
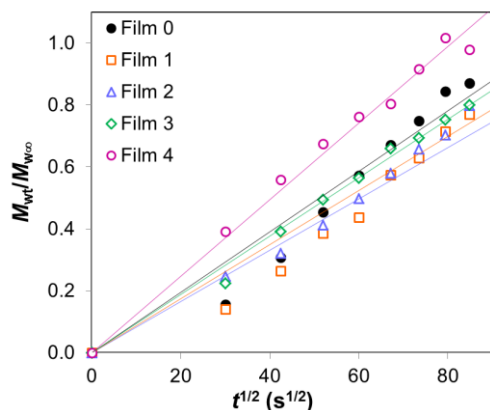
Films	MP content of dry films (wt %)	r^2	D (cm²/s)
0	0	0.966	2.09×10^{-4}
1	2.1	0.962	5.43×10^{-5}
2	4.0	0.987	3.51×10^{-5}
3	6.2	0.994	9.47×10^{-5}
4	8.1	0.990	8.09×10^{-5}

Fig. 5: $M_{wt}/M_{w\infty}$ *vs* $t^{1/2}$ *plots for diffusion of water in films (first 120 min of immersion)*
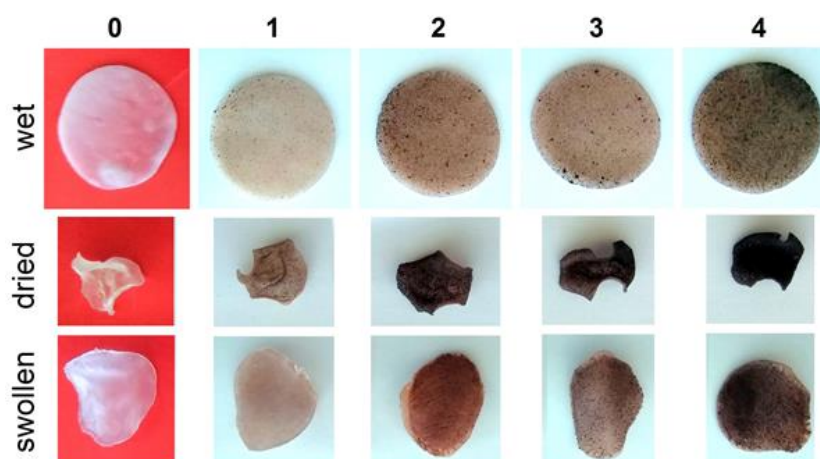

Fig. 6: *Wet, dried and swollen magnetic PVA hydrogel samples with increasing magnetic particle (MP) content (0: Film 0, 1: Film 1, 2: Film 2, 3: Film 3, and 4: Film 4)*

The volume of the films increased appreciably during the swelling test without disintegration as shown in Fig. 6. The pure PVA film has excellent transparency, while the films have become more and more opaque by the addition of MPs in increasing amounts. The transparent nature of the pure PVA film indicates the homogeneous network structure. The opacity of the blend films might be attributed to the increased crystallinity and microphase separation, which occurs in the early stage of the gelation process [5]. Fig. 7 shows dependence of the *EDS* and *EWC* of the films on their MPs content. The *EDS* values were in the range of 200–214 % of the dry mass. The *EWC* values were in the range of 66–68 %. Neither *EDS* nor *EWC* of the films were affected by the amount of MPs added.
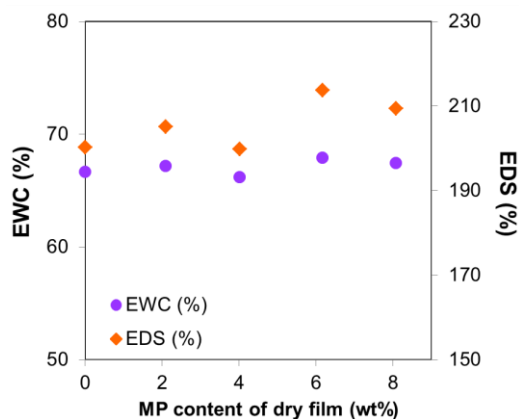
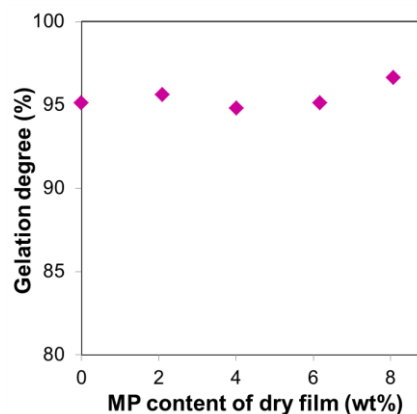*Fig. 7: Effect of MP content of the film on EDS and EWC*

Fig. 8: Effect of MP content on gelation degree

5. CONCLUSIONS

It was found that the hydrogels have high water absorption capacity (equilibrium degree of swelling: 200–214% and equilibrium water content: 66–68%) and high crosslinking degree (95%) almost independent from their magnetic particle content. They gained magnetic property after addition of the magnetic particles in the polymer matrix.

REFERENCES

[1] G. A. Mahmoud, "*Adsorption of copper (II), lead (II), and cadmium (II) ions from aqueous solution by using hydrogel with magnetic properties*", Monatsh. Chem., 2013, 144, pp.1097–1106.

[2] S. Dong, Y. Wang, "*Characterization and adsorption properties of a lanthanum-loaded magnetic cationic hydrogel composite for fluoride removal*", Water Res., 2016, 88, pp.852–860.

[3] M. Pooresmaeil, Y. Mansoori, M. Mirzaeinejad, A. Khodayari, "*Efficient removal of methylene blue by novel magnetic hydrogel nanocomposites of poly(acrylic acid)*" Advances in Polymer Technology, 2016, 37 (1), pp.1-13.

[4] E. Varzaru, I. Dumitrescu, C.E. Mitran, G.O. Iordache, *"Investigation Of Different Reducing Agents Of Azo Dyes From Textile Materials"* Annals of The University of Oradea Fascicle of Textiles, Leatherwork, 2017, 1(21), pp.125-130.

[5]   J.O. Kim, J.K. Park, J.H. Kim, S.G. Jin, C.S. Yong, D.X. Li, J.Y. Choi, J.S. Woo, B.K. Yoo, W.S. Lyoo, J.A. Kim, H.G. Choi, "*Development of polyvinyl alcohol-sodium alginate gel-matrix-based wound dressing system containing nitrofurazone*" Int J Pharm, 2008, 359, pp.79–86.