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Synthesis and Characterization of Hydrogel Nanocomposites based on (N- Isopropyl Acryl Amide– Acrylic Acid)/ LDH

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ABSTRACT

In this research, a novel hydrogel nanocomposites was developed by combining of N-isopropyl acryl amide, acrylic acid, as monomer, and different amounts (1, 3 and 5 wt.%) of unmodified and modified layered double hydroxide (LDH) in condition of room temperature. First, LDH was prepared via reaction of magnesium nitrate and aluminum nitrate. Then, LDH modified by using sodium dodecyl benzene sulfate. The measurement of swelling rate indicated that the absorption capacity of hydrogel had inverse relationship with the increase of LDH nanoparticles so that with the increase LDH/hydrogel ratio, water absorbs of hydrogel reduced. Scanning electron microscopy (SEM) revealed the continuous presence of nanoparticles in the hydrogel nanocomposite. Structural confirmation was achieved through Fourier-transform infrared spectroscopy (FT-IR), X-ray diffraction, and thermogravimetric analysis (TGA).

1. Introduction

Hydrophilic polymeric networks are called hydrogels that comprise the cross-linking swelling in contact with water but not dissolved. Hydrogels can take various physical forms including sheets, micro particles, nanoparticles, epithelium structures, and film [1]. Hydrogel nanocomposites were synthesized using organic/inorganic structures in hydrogels, which can cause improving physical, chemical, electrical, and biological properties and swelling/deswelling [2]. In recent years, types of hydrogel nanocomposite studied and developed such as carbon-based nanomaterials[3], polymeric nanoparticles [4], and inorganic nanoparticles [5]. Layered double hydroxide (LDH) has various applications one of them is used in the form of nanoparticles to improve the properties of hydrogel nanocomposites [6]. Hydrogels nanocomposite containing LDH was prepared with uncharged biopolymer for chromate removal [7]. Some hydrogel nanocomposite/LDH were used for the Controlled release of drugs such as diclofenac [8], also thermo-responsive hydrogels composite based on MgAl-LDH-CuS nano sheet used for

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therapy of multimode starvation via nir-responsive angiogenesis inhibitor releasing capability [9]. Various methods for the synthesis of hydrogel nanocomposite/LDH were reported such as the preparation of polyacrylamide-based hydrogel nanocomposite/LDH using the convenient green method [10]. Another usage of hydrogel nanocomposite/LDH is in agriculture it is used as a controlled-release nitrogen-phosphorus fertilizer [11].

In this report, we have done a synthesis of a novel hydrogel nanocomposite based on co-monomers. LDH concentration effects was studied on properties of hydrogel based on co-monomers such as N-isopropyl acrylamide and acrylic acid during a radical polymerization reaction.

2. Experimental

2.1. Materials and methods

N, N'-Methylenebisacrylamide crosslinking agent with 99% purity was obtained from Sigma-Aldrich Company. Other materials contain *N*-isopropyl acrylamide, acrylic acid, ammonium persulfate, sodium dodecyl benzene sulfate and sodium hydroxide were obtained from Merck Company. Magnesium nitrate hex hydrate and aluminum nitrate Nonahydrate were purchased from Sigma-Aldrich Company.

Infrared spectrum obtained by using Galaxy Series FT–IR spectroscopy. The thermogravimetric analysis performed using TA tools (TGA Q 5000). XRD spectra obtained by using Philips instrument and SEM images obtained from Philips XL 30 equipment.

2.2. Synthesis of LDH

In a three-neck flask, solution of 0.3M concentration was prepared via adding of 100mL of distilled water, magnesium nitrate and aluminum nitrate (2:1 ratio). This solution must have pH between 10-10.5 (pH controlled with adding NaOH solution, 3.0 M) together with stirring and it was heated up to about 50°C. After it stirred for an hour, the solution held at the same temperature for 24h. Then, the contents filtered and rinsed with distilled water to remove NaOH, and the sediments kept in distilled water.

2.3. Modifying LDH

Modified LDH prepared by adding 1.0g of LDH into the beaker with distilled water and mixed. Moreover, solution of the modifier (sodium dodecyl benzene sulfate, 1.0g in H_2O) dispersed in the ultrasonic device at 50°C for 10 minutes. Afterward, solution of LDH added and the mixture stirred for 10 minutes. Constantly dispersing and stirring for 15 minutes performed for several times. It stirred for 18 hours at 70°C. The modified LDH filtered and rinsed with distilled water.

2.4. Preparation of hydrogel nanocomposites

To preparation of hydrogel nanocomposites, the dispersible material was added to the polymeric solution to amount of 1, 3 and 5 wt.% to monomers. After mixing of the required values of acrylic acid, N-isopropyl acryl amide and methylene bis-acryl amide, initiator and the modified LDH solution added and the resulting suspension was mixed for 2 h. hydrogel nanocomposite was washed by distilled water for remove impurities.

2.5. Swelling properties of hydrogels

In order to study of swelling rate , dried hydrogel nanocomposite was settled in the beaker comprising 30.0mL of double distilled water at 37°C for measurement of swelling rate, the swelled hydrogel nanocomposite weight measured during at time regular intervals of 8 hours, then, by repeating the measurement after 24 hours the amount of equilibrium swelling was determined. The swelling rate calculated based on the Eq. (1) as follows:

$$\mathrm{ESR}=\frac{W_{st}-W_d}{W_d}\times 100 \quad (1)$$

where W_{st} is the weight of the swelled sample at time t and W_d is the initial weight of the dried sample.

3. Results and discussion

3.1. FT-IR result

The infrared spectrum of a hydrogel based on N-isopropyl acrylamide and acrylic acid is shown in Fig. 1. Peaks observed at 950cm^{-1} are associated with the C-H bond. In the range of 1000 to 1260cm^{-1}, these peaks are related to the stretching vibrations of the C-O ester bonds. A peak at 1384.8cm^{-1} corresponds to the C-CH_3bond, while the peak at 1737.7cm^{-1} indicates the stretching of the C=O bond, which is characteristic of the ester carbonyl group. The peak at 3433.1cm^{-1} represents the stretching vibration of the OH group.

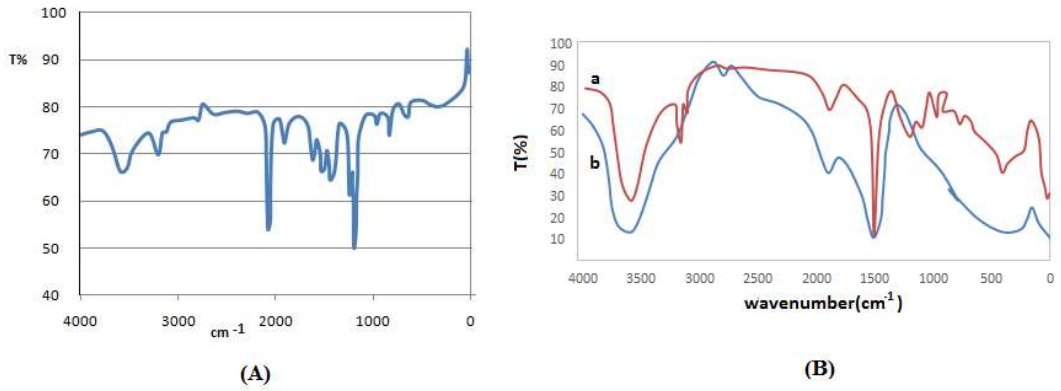

Fig.1. (A) FT-IR spectrum of hydrogel based on *N*-isopropyl acryl amide – acrylic acid, (B) FT - IR spectrum of (a) modified LDH and (b) unmodified LDH

In Fig. 1(B), a shown the infrared spectrum of unmodified LDH. Peaks observed at 1382.9cm^{-1} belong to tension of the nitrate group and in 3467.8 related to tension of OH. In Fig. 1(B), b the infrared spectrum of modified LDH is shown that the OH bond has absorption for LDH in 3467.8cm^{-1}. The absorption observed about 2925.8 and 3000cm^{-1} is derived from hydrogen belong aliphatic and aromatic respectively. Sharp absorbed bonds in 1382.9cm^{-1} is for CH aliphatic for dodecyl branch and the bond absorbed with less intense in 1637.5cm^{-1} are resulted from symmetric and asymmetric relations of stretching of C=C group for aromatic ring. The absorption observed in 1184.2cm^{-1} bond is for the sulfonate group.

3.2. XRD result

As indicated in Fig. 2(a) and Fig. 2(b), the X-ray diffraction (XRD) pattern of modified layered double hydroxide differs from that of unmodified layered double hydroxide. The XRD pattern of unmodified LDH shows sharp and high-intensity peaks at 12, 23, 35, 40, 46, 60, and 61. In contrast, the modified LDH pattern displays peaks at 8, 16,

38, and 39 that are more pronounced than those of the unmodified substance. This difference suggests a significant interaction between the polymeric matrix and the LDH.

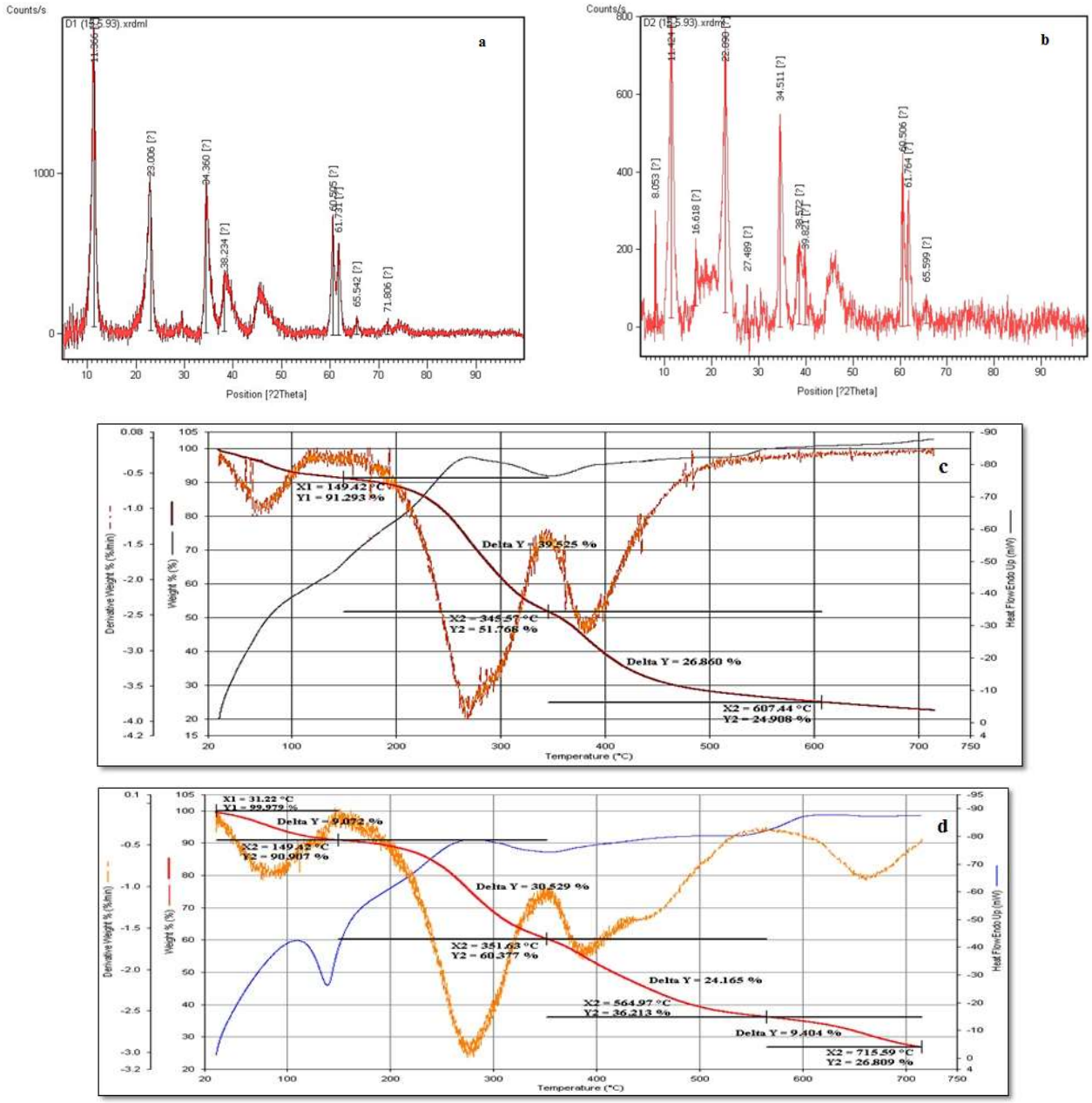

Fig. 2. (a) XRD pattern of nanocomposite with unmodified LDH, (b) XRD pattern of nanocomposite with modified LDH, (c) TGA curve for hydrogel without LDH, (d) TGA curve for hydrogel with LDH

The addition of a modifier has changed the distance between the layers and enhances the composition. As shown in Figs. 2(a) and 2(b), the presence of a modifier in LDH causes disruptions in the XRD structure. Fig. 2(c) demonstrates that the polymer without LDH retains 22.0% water when heated to 700°C. In comparison, Figure 2(d) shows that the polymer containing 0.5g of LDH retains 28.0% water at the same temperature. This illustrates that the presence of 0.5g of LDH enhances water retention at elevated temperatures, contributing to greater strength. Specifically, Fig. 2(d) indicates that at 150°C, the hydrogel nanocomposite retains 91.5% moisture and about 51%

moisture at 345°C. At 351°C, the hydrogel nanocomposite retains 60% moisture, which is an improvement over the hydrogel without LDH.

3.3. SEM analysis

Fig. 3 presents SEM pattern of the hydrogel. Without LDH, the particle size is in the micrometer range, while the addition of varying concentrations (wt.%) of LDH results in a more efficient reduction of particle size in the hydrogel nanocomposite (shown in b, c, and d). With 1% LDH, the particle size is reduced to 48-57nm, but with higher concentrations of LDH, the particle size increases, reaching 72nm at 5%. Conversely, the porosity is reduced.

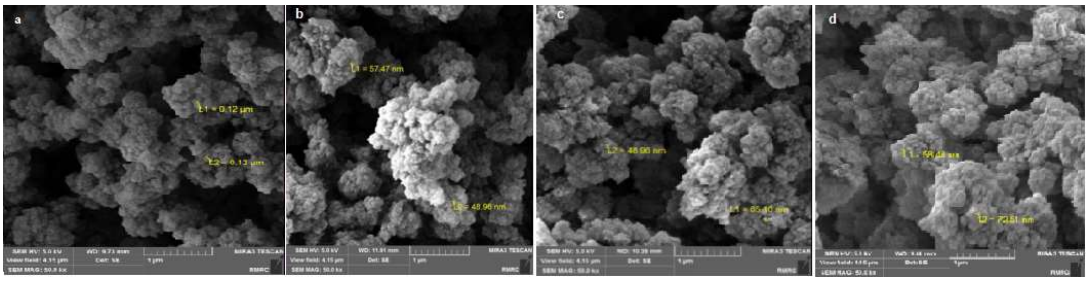

Fig. 3. SEM patterns (a) hydrogel without mLDH, (b) hydrogel nanocomposite with mLDH (1.0 wt.%), (c) hydrogel nanocomposite with mLDH (3.0 wt.%), (d) hydrogel nanocomposite with mLDH (5.0 wt.%)

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3.4. The effect LDH concentration on the swelling rate

In Fig. 4, it was observed that with increasing concentrations of nanoparticles from 1 to 5 wt.%, the cross linking increased and the swelling rate decreases. Reducing the number of units between bonding of the polymeric chains cause inverse effect on elastic properties that the requirement volume reduced for water molecules penetrate into network. Hydrogel nanocomposite with 5% LDH has less swelling rate but it has resistance and released less water with rise of temperature.

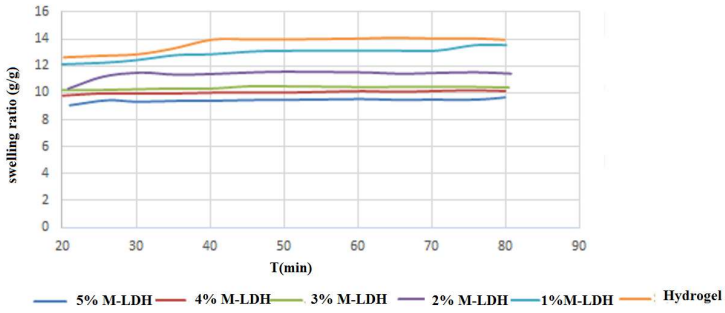

Fig.4. Concentration effect of LDH on swelling rate of hydrogel nanocomposite

4. Conclusion

A hydrogel nanocomposite based on poly (N-isopropyl acrylamide–acrylic acid) and layered double hydroxide (LDH) was prepared through the polymerization of two monomers, a cross-linker, and an initiator in water (H_2O). The LDH used includes both unmodified and modified forms, with sodium dodecyl benzene sulfate serving as the modifying agent. To analyze the properties of the hydrogel nanocomposites, Fourier-transform infrared

spectroscopy (FTIR), X-ray diffraction (XRD), thermogravimetric analysis (TGA), and scanning electron microscopy (SEM) were employed to assess characteristics such as resistance, porosity, and swelling behavior. The results indicate that unmodified LDH exhibits lower porosity compared to modified LDH. Furthermore, the swelling behavior of the hydrogel nanocomposite shows that the addition of modified LDH nanoparticles enhances moisture retention. As the temperature increases, the hydrogel loses less water, making it more effective for water management applications.

References

[1] Ahmed, E.M., 2015. Hydrogel: Preparation, characterization, and applications: A review. Journal of Advanced Research, 6(2), 105-121. https://doi.org/10.1016/j.jare.2013.07.006
[2] Karchoubi, F., Afshar Ghotli R., Pahlevani, H., Baghban Salehi, M., 2024. New insights into nanocomposite hydrogels; a review on recent advances in characteristics and applications. Advanced Industrial and Engineering Polymer Research, 7(1), 54-78. https://doi.org/10.1016/j.aiepr.2023.06.002
[3] Sui, B., Li, Y., Yang, B., 2020. Nanocomposite hydrogels based on carbon dots and polymers. Chinese Chemical Letters, 31(6), 1443-1447. https://doi.org/10.1016/j.cclet.2019.08.023
[4] Alacid, Y., Esquembre, R., Montilla, F., Martínez-Tomé, M.J., Mateo, C.R., 2023. Fluorescent nanocomposite hydrogels based on conjugated polymer nanoparticles as platforms for alkaline phosphatase detection. Biosensors, 13(3), 408. https://doi.org/10.3390/bios13030408
[5] Liu, X., Chang, M., Zhang, H., Ren, J., 2022. Reinforcement effects of inorganic nanoparticles for PAM-g-carboxymethyl Xylan nanocomposite hydrogels. Macromolecular Materials and Engineering, 307(10), 2200251. https://doi.org/10.1002/mame.202200251
[6] Sehat, S., Aliabadi, H.A.M., Mahdian, S., Kashtiaray, A., Sadat, Z., Mahdavi, M., Eivazzadeh-Keihan, R., Maleki, A., Madanchi, H., 2024. A natural nanocomposite based on gelatin-collagen hydrogel and silk fibroin embedded with ZnFe LDH for biological applications. Process Biochemistry, 147, 22-30. https://doi.org/10.1016/j.procbio.2024.08.008
[7] Gwak, G.-H., Kim, M.-K., Oh, J.-M., 2016. Composites of quasi-colloidal layered double hydroxide nanoparticles and agarose hydrogels for chromate removal. Nanomaterials, 6(2), 25. https://doi.org/10.3390/nano6020025
[8] Barkhordari, S., Alizadeh, A., 2021. Fabrication of pH-sensitive chitosan/layered double hydroxide (LDH)/Fe3O4 nanocomposite hydrogel beads for controlled release of diclofenac. Polymer bulletin, 79, 5533–5548. https://doi.org/10.1007/s00289-021-03761-3
[9] Liu, X., Hu, T., Jia, Y., Yang, S., Yang, Y., Cui, Z., Wang, T., Liang, R., Tan, C., Wang, Y., 2024. A MgAl-LDH-CuS nanosheet-based thermo-responsive composite hydrogel with nir-responsive angiogenesis inhibitor releasing capability for multimode starvation therapy. Journal of Nano biotechnology, 22(1), 127. https://doi.org/10.1186/s12951-024-02384-w
[10] Wu, L., Hu, Z., Chen, G., Li, Z., 2015. A convenient green preparation of layered double hydroxide/polyacrylamide nanocomposite hydrogels with ultrahigh deformability. Soft Matter, 11, 9038-9044. https://doi.org/10.1039/C5SM02232K
[11] Roy, A.S., Pillai, S.K., Ray, S.S., 2022. Layered double hydroxides for sustainable agriculture and environment: An overview. ACS Omega, 7(24), 20428–20440. https://doi.org/10.1021/acsomega.2c01405