Thiadiazole Derivative Impregnated on Cross-Linked Hydrogel for Water Retention and Adsorption of Nickel Ions for Sustainable Environment

Anwar Mohsen Sagban and Ayad Sulaiman Hamad
Department of Chemistry, College of Education for Pure Sciences, University of Tikrit, 34001 Tikrit, Salah Al-Din, Iraq
anwar.mohsen.sagban@ec.edu.iq, ayadsulaiman@tu.edu.iq

Keywords: Acrylic Acid, Azobisisobutyronitrile, Hydrogel, MBA, Adsorption.

Abstract: In this study, free radical copolymerization was used to prepare a hydrogel of poly (acrylic acid-co-2-amine -5-(3,5-dinitrophenyl)-1,3,4-thiadiazol) (poly-AA-ANT). The poly-AA-ANT hydrogel was characterized using Fourier transform infrared spectroscopy FTIR, Thermogravimetric analysis (TGA), and scanning electron microscopy (SEM), X-ry diffraction. The swelling of poly-AA-ANT was performed by using two solvents (water and methanol) each alone and found that the swelling ability in methanol was higher than for water. The removal of Ni^{2+} was conducted by immersing the poly-AA-ANT in a solution of Ni^{2+} and after a periol of time the residual we measured by atomic absorption spectrophotometer. The percentage of removal was 93.8%. The poly-AA-ANT hydrogel had a high swelling ratio of 546%. penetration rate of the poly-AA-ANT hydrogel coupled with the high swelling rate exposed to the internal adsorption sites. The high-water holding capacity of Poly-AA-ANT improved the moisture holding limit of soil for irrigation up to 24 days. systems as a result, Poly-AA-ANT has become an important addition to irrigation systems.

1 INTRODUCTION

Nickel is a widely distributed metal in the environment and has many industrial and commercial uses. The public may be exposed to Nickel in air, water, and food. Most nickel in the human body comes from drinking water and food [1]. Nickel is nutritionally essential for many species of animals, microorganisms, and plants, and therefore deficiency or toxicity symptoms can occur when nickel is ingested in too little or too much. Although several cellular effects of nickel have been documented, no deficiency has been described in humans [2]-[7]. Environmental contamination with toxic metals arises from industries and agricultural waste. Many industries, such as metal plating facilities, mining operations, and tanneries, dispose of waste that contains heavy metal ions. Because of their importance, heavy metals have been widely studied. These toxic metals can cause cumulative toxicity, cancer, and brain damage when present at levels above permissible levels. Removal of heavy metals such as cadmium, lead, copper, nickel, and mercury has become very important for environmental remediation [8]. The World Health Organization has recommended strict controls on the levels of various heavy metals in wastewater [9]. In recent years, polymer gels have played an important role in the adsorption of heavy metal ions because they can swell in water and achieve high adsorption [10]

Heavy metal pollution has become a global environmental issue and a major concern due to the toxic, bio accumulative and non-degradable nature of heavy metals. Therefore, this heavy metal must be removed from aquatic wastewater before being discharged into water bodies. Therefore, many technologies have been used to remove heavy metals from wastewater, such as ultrafiltration, reverse osmosis, coagulation, adsorption, electro-precipitation and chemical precipitation [11]-[15]. Among all these strategies, adsorption is frequently applied for removal by taking advantage of its simple operation, high removal rate, low cost and excellent regenerability [16]. Adsorbents are the material basis of adsorption technology; therefore, the development of new adsorbents is a research focus for wastewater treatment. Ion3 hydrogel is a polymeric material with a three-dimensional network structure [17] that can absorb large amounts of water and retain a certain amount of water compared to other similar materials such as cloth, cotton, and sponge [18-19]. Heavy metals,

unlike organic pollutants, are non-degradable and tend to accumulate in living organisms, which may cause serious problems for human health and wildlife [20]. Therefore, it is very necessary to remove these toxic heavy metals from water and soil. Ni^{2+} is widely used in industrial applications such as batteries, electroplating, and coins [21-23]. Ni2+ belongs to the so-called essential metals and is identified as a component of many enzymes, participating in vital metabolic reactions [24].

2 MANUSCRIPT PREPARATION

2.1 Materials and Reagents

3,5-dinitrobenzoic acid(C7H4O6N2,99), thiosemicarbazide(CH5N3S), phosphorous ox chloride (POCL3) acrylic acid (C3H4O2, 98%), Azo bis isobutyronitrile(98%), benzene(C6H6,99%), Nikel chloride nitrogen gas and nickel ion (Ni^{+2}) (99%) were used.

2.2 Instrumentation

The infrared spectra of the compound and poly-AA-ANT were measured in the range of (4000-400) cm-1 using an IR Affinity (SHIMADZU) instrument using a (KBr) disk in the frequency range. The 1H-NMR was measured using a Broker Ultra Shield, 500 MHz, using DMSO-d6 solvent and TMS reference for the compound. A (Rheometric Scientific TGA-1000) instrument was used to record the TGA of the prepared polymer, and a (ZEISS) scanning electron microscope (SEM) was used to measure the prepared poly-AA-ANT, and the absorbance of poly-AA-ANT recorded on a (SHIMADZU-1700) dual UV-Vis spectrometer was measured in the presence of a quartz cell using KOH solvent, and the UV-Vis spectra were measured on a (SHIMADZU 1800 UV) spectrometer.

2.3 Stepwise Synthesis of Poly-AA-ANT Hydrogel

2.3.1 Synthesis of 2-Amine -5-(3,5-Dinitrophenyl)-1,3,4-Thiadiazol

3,5 dinitro benzoic acid (0.01 mol) was refluxed with thiosemicarbazide (0.01 mol) in (10 ml) POCl3 in a 100 ml round bottomed flask. The reaction was then heated for three hours, after that (30 ml) of distilled water was added to it and the mixture was heated for four hours. The mixture was then neutralized using (10%) potassium hydroxide (KOH), the solution was filtered, the resulting precipitate was washed several times with distilled water, and the precipitate was left to dry.

2.3.2 Synthesis of poly-AA-ANT Hydrogel

The polymer were prepared using the solution polymerization technique and the free radical polymerization method by dissolving 2-amine -5-(3,5-dinitrophenyl)-1,3,4-thiadiazol (0.5g) in acrylic acid (5ml), completely dissolving it with occasional heating, then benzene (30ml) was added to the mixture with continuous stirring, methylene bisacrylamide (1g) was added to the mixture. At this point, N2 gas was pumped into the mixture and the gases were removed using a Schlenk device. The mixture was refluxed using a water bath at (75) oC. When this temperature was reached, the initiator azo bisiso butyro nitrile (AIBN) (0.008) was added with stirring rite (300rpm). After a while, the polymer began to form, and it was observed that (N_2) gas was released resulting from the disintegration of the initiator. After the reaction ended, methanol was added to isolate the polymer from the benzene. To complete polymer formation.

2.4 Swelling Studies of Poly(AA-ANT) Hydrogels

(0.5) g of dried hydrogel (Wd) was immersed in 20 mL of distilled water at room temperature. The hydrogel was left to swell until a constant weight was achieved. Then hydrogel was removed from the solution and the final of the hydrogel (Ws) was weighed and recorded. The swelling percentage of hydrogel was calculated by using through (1). Table 1 shows the swelling percentage in water for 24 h, Table 2 shows the swelling percentage in methanol after 24 h, and Figures 1 and 2 show the swelling percentage in water and methanol. as:

$$\%\, Swelling\ degree = \frac{Ws-Wd}{Wd} \times 100. \qquad (1)$$

2.5 Removal of Ni^{2+} Ion

A stock solution of 1000 mg/L Ni2+ was prepared. A standard solution of 5 mg/L was then prepared from this stock solution. Approximately 0.1 g of the hydrogel was immersed in 20 ppm of (5 mg/L) Ni^{2+} solution. After 24 hours, the hydrogel was removed from the solution. The remaining Ni^{2+}

Table 1: Percentage of swelling in water after 24 hours' poly-AA-ANT.

No	Swelling						Percentage of swelling
	0 h	3h	6 h	9 h	12 h	24 h	
poly-AA-ANT	0.5	0.63	0.76	1.99	2.56	3.23	546%

Table 2: Swelling ratio of polymers prepared in methanol poly-AA-ANT.

No	Swelling						Percentage of swelling
	0 h	3h	6 h	9 h	12 h	24 h	
poly-AA-ANT	0.5	0.59	0.68	0.80	1.13	2.34	368%

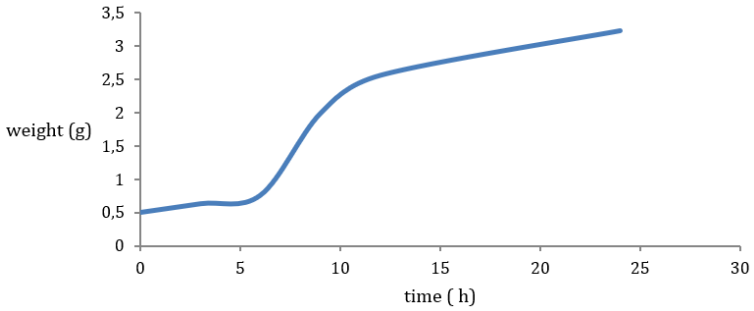

Figure 1: Swelling of poly-AA-ANT in water after 24h.

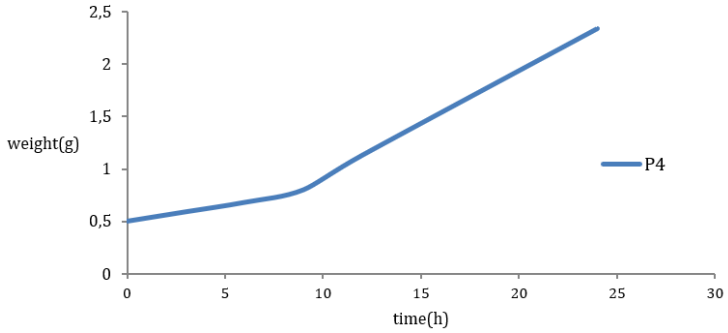

Figure 2: Swelling of poly-AA-ANT in methanol after 24 h.

Table3: The residual and the percentage of adsorption of Ni(II) using poly-AA-ANT hydrogel.

No.	Residual	Absorption rate %
poly-AA-ANT	1.225	%93.8

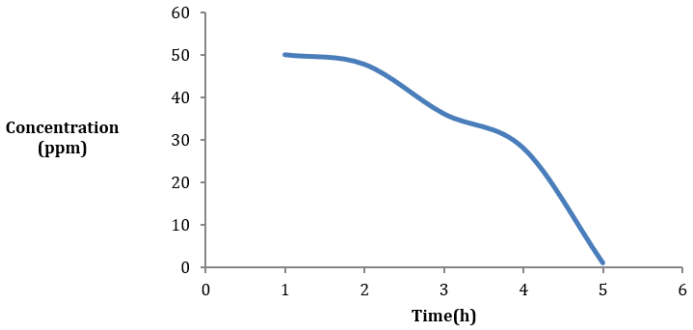

Figure 3: Removal of Ni^{2+}Ion of poly-AA-ANT.

concentration was monitored using atomic absorption spectroscopy. The Ni2+ removal ratio was calculated using (2), where Ci and Cf are the initial and final concentrations (mg/L) of the Ni2+ solution, respectively, as shown in Table 3. Figure 3 shows the nickel ion removal ratio.

$$(\%)Percentage\ removal\ = \frac{Ci-Cf}{Ci} \times 100. \quad (2)$$

2.6 Water-Retention Study of Poly-AA-ANT Hydrogel

The poly- hydrogel water preservation analysis was performed in soil collected from University, Diyala, where 20 g soil and 2 g poly- hydrogel were homogenized in a plastic container, 30 mL water was added gradually, and the weight (W1) wasdetermined using a weighing machine. The container was weighed every day (W2) and kept at room temperature until there was no consistency in weight loss. The water loss ratio (W %) of soil samples was calculated through the standard (3).

$$W\ \% = \frac{W1-W2}{30} \times 100. \quad (3)$$

3 RESULTS AND DISCUSSION

In this study, the reaction between 5,3-dinitrobenzoic acid and AAc in the presence of MBA as a cross-linking agent resulted in the formation of a hydrogel. In the initiation step, radical polymerization occurred by hydrolysis and hydrogen abstraction from the AAc chain [25]. Grafting of AAc onto the backbone of 3,5-dinitrobenzene at the active site occurred. Then the propagation reaction occurred continuously while the cross-linking agent built a cross-linking bond between the growing chains [26] .

3.1 Characterization

FTIR spectra of hydrogel were recorded by using Perkin Elmer Spectrum in the range of 4000–400 cm−1. The sample was completely dried before FTIR analysis. The thermal degradation of hydrogel was conducted by using thermogravimetric analyser TGA. Temperature used was up to800 °C with a heating rate of 10°C/ min under nitrogen atmosphere. SEM at appropriate magnification was used to observe morphology of the sample.

3.1.1 FTIR

The prepared compound was identified by FTIR spectrum, where the absorption bands (3510-3441cm-1) were observed, which belong to the (NH_2) band, the band at (3109) cm-1, which belongs to the aromatic (C-H) group, and the band (1620) cm-1 which belongs to the (C=N) group. As for the aromatic (C=C) band, it appeared at (1543) cm-1. Figure 4 shows the infrared spectrum of the compound.

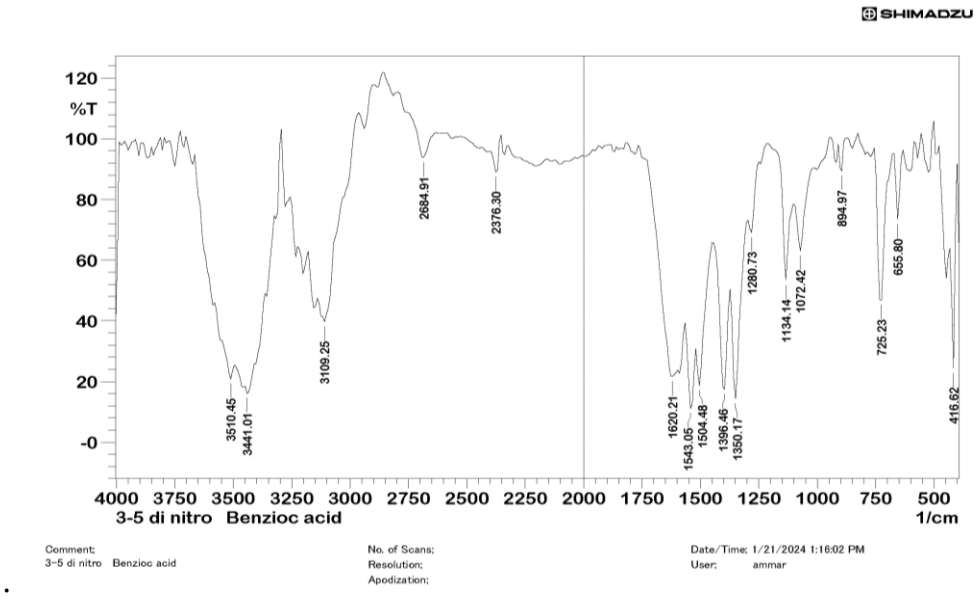

Figure 4: FT-IR Spectrum of 2-amine -5-(3,5-dinitrophenyl)-1,3,4-thiadiazol

3.1.2 1H-NMR Spectroscopy

7.70 ppm associated with the (-NH_2) group (S,2H), the aryl ring showed a vibration at 7.01 ppm associated with the proton (a) as in (d,1H), (b) a chirality at 9.02 ppm as in (t,1H), (c) a vibration at 8.06 associated with (t,1H) and (d) at 8.05 (a,1H) Figure 5 shows the nuclear resonance spectrum of the compound 2-amino-5-(2-chloro phenyl)-1,3,4-thiadiaozle.

3.1.3 FTIR of Polymer

The FTIR spectrum assures the formation of the poly(acrylic) through the presence at a stretching vibration at (3436) cm-1 related to O-H group and anther band at (2939) cm-1 which is attributed to the asymmetric and symmetric stretching vibration for (CH_2) group and consequently the signal at (2252) cm-1 is related to C≡N group. Finally, the peak at (1728) cm-1 is attributed to (C =O) stretching vibration Figure 6 shows the infrared spectrum of the polymer.

3.1.4 TGA Analysis

Study was conducted on the polymer to understand the thermal stability from room temperature to 800oC. Figure 7. The degradation occurred in three steps where the first degradation appeared at 100 ºC related to the removal of moisture resulted from the interaction with COOH group in the polymer. The second step of degradation occurred at 200 ºC. The third step appeared at 400 ºC which involved the scission of C-C bond in the polymer.

3.1.5 SEM Analysis

Scanning Electron Microscopy (SEM) is a sophisticated imaging technique used to observe the surface morphology and topography of samples at high magnifications. Unlike optical microscopy, which uses visible light, SEM employs a focused beam of electrons to interact with the sample, producing detailed images that reveal structural and compositional information. Figure 8 shows the SEM picture for poly-AA-ANT and the holes are presents these holes may be due to the cross linked.

3.1.6 XRD Analysis

XRD patterns of thiadiazole and poly-AA-ACT hydrogel are described in the 2θ range of 5º–90º Figure 9. The thiadiazole spectra showed fundamental diffraction peaks at 19.5º, 26.2º, 30.4º, 34.5º, 48.1º, and 52.3º corresponded to (111), (220), (311), (400), (511), and (440), respectively. Which demonstrated the crystalline characteristic of thiadiazole. The grafting of thiadiazole on polymer showed major transformation in the XRD pattern of poly-AA-ANT hydrogel. The hydroxyl groups of acrylic acid were affected by thiadiazole, which destroyed the crystalline structure and transformed it toamorphous composition.

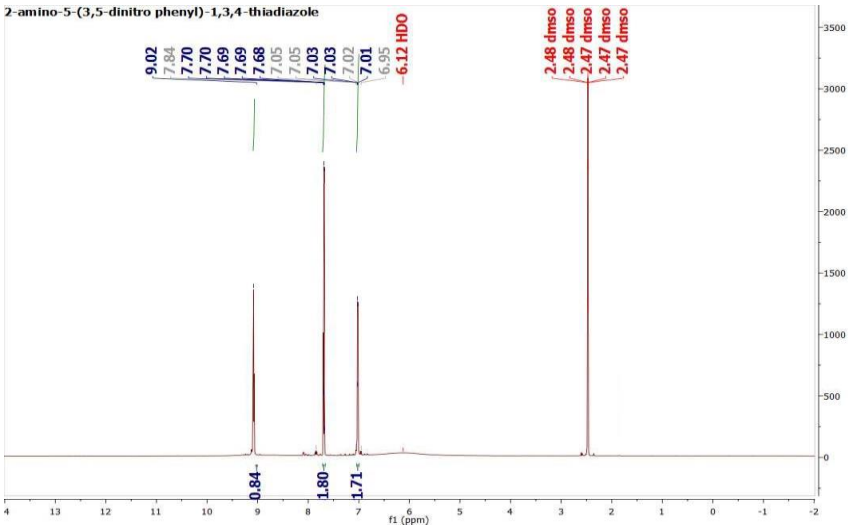

Figure 5: 1H-NMR Spectrum of 2-amine -5-(3,5-dinitrophenyl)-1,3,4-thiadiazol.

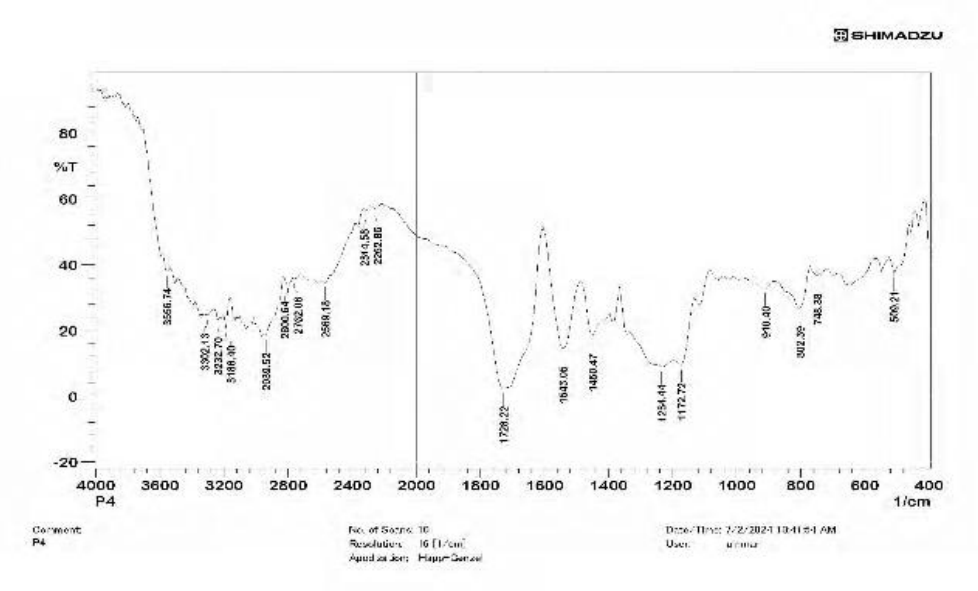

Figure 6: FT-IR Spectrum of poly-AA-ANT.

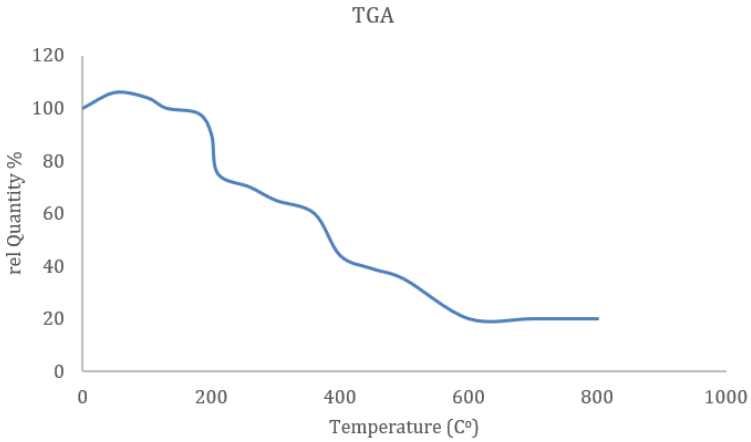

Figure 7: TGA of poly-AA-ANT.

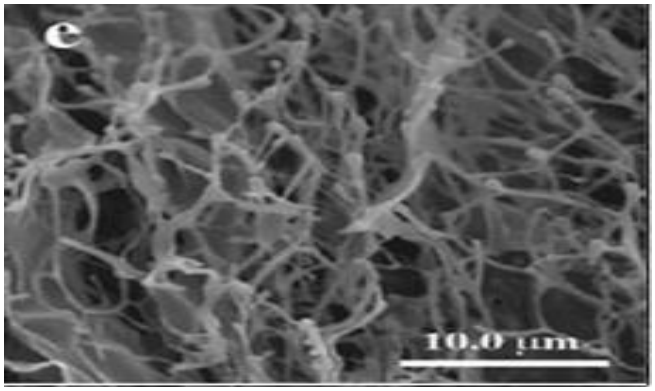

Figure 8: SEM morphology of poly-AA-ANT.

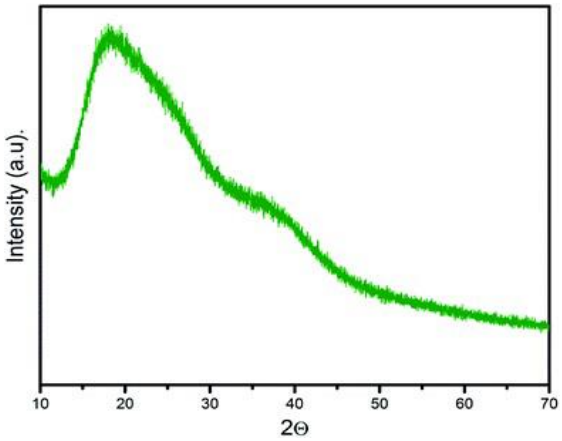

Figure 9: XRD of the poly-AA-ANT.

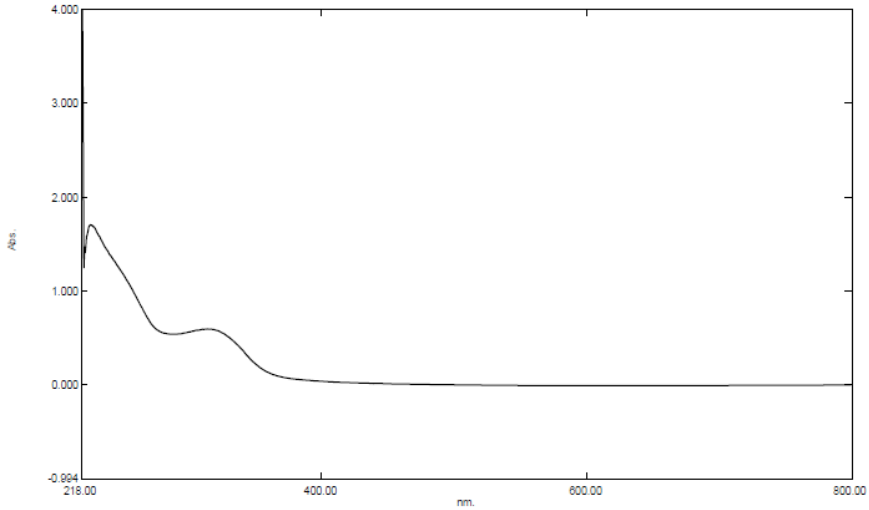

Figure 10: Shows IR short for the retained of 2-amine -5-(3,5-dinitrophenyl)-1,3,4-thiadiazol.

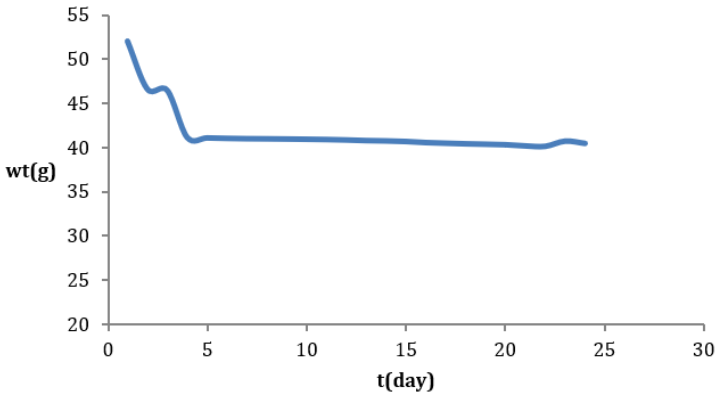

Figure 11: Water retention of soil.

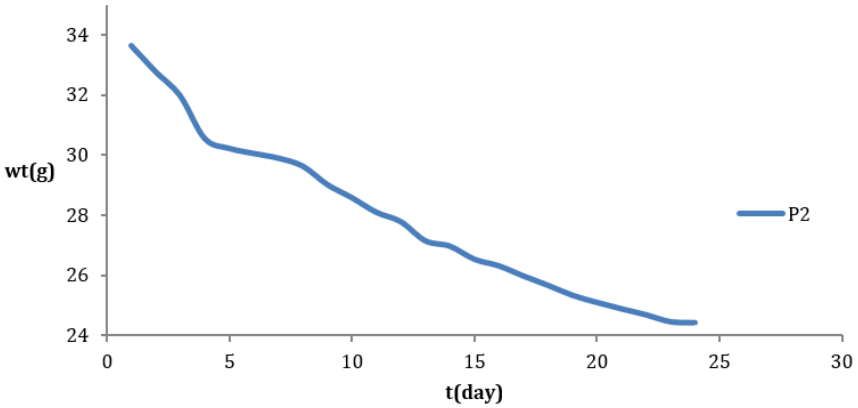

Figure 12: Water retention of poly-AA-ANT-soil.

3.1.7 5-(2-Chloro Phenyl)-2-Amino-1,3,4-thiadiazole Retention

Identification of 1,3,4-thiadiazole complex loaded on polymer using UV-visible technique. A buffer solution of pH = 8 was prepared, then 0.1 g of the polymer was weighed. This amount was added to 20 ml of the buffer solution and left for an hour. After that, the solution was filtered and the filtrate was placed in a UV-visible spectrometer, where the maximum absorption of the decomposed thiadiazole compounds was measured. This indicates that these compounds are loaded on the polymer. Figure 10 shows IR short for the retained shows IR short for the retained of 2-amine -5-(3,5-dinitrophenyl)-1,3,4-thiadiazol

3.2 Water-Retention Study of Polymer

Water retention analysis was performed using polymer in soil collected from University of Diyala, in Diyala province. 20 g of soil and 2 g of polymer were taken in a plastic container and 30 ml of water were added gradually. The weight (W1) was determined using a weighing machine. The container was weighed every day (W_2) and kept at room temperature so that there was no stability in weight loss. The percentage of water loss (W%) for soil samples was calculated using the standard formula. Figure 11 shows water retention using soil and Figure 12 shows water retention using the polymer poly-AA-ANT.

4 CONCLUSIONS

The polymerization with impregnation process was used to synthesize a novel polymer (poly-AA-ANT) Hydrogel that has been used for the adsorption of Ni(II) Ione from water. The swelling tendency was (546%) in water and (368%) in methanol. The adsorption which is the highest of Ni(II) ions was (%93.8) compared to the reported Ni(II) adsorption data. The prepared poly (AA-ANT) showed 1.2 times better soil -water retention. penetration rate of the poly-AA-ANT hydrogel coupled with the high swelling rate exposed to the internal adsorption sites. The high-water holding capacity of Poly-AA-ANT improved the moisture holding limit of soil for irrigation up to 24 days. systems as a result, Poly-AA-ANT has become an important addition to irrigation systems.

REFERENCES

[1] M. Cempel and G. J. Nikel, "Nickel: a review of its sources and environmental toxicology," Polish Journal of Environmental Studies, vol. 15, no. 3, 2006.

[2] V. Bencko, "Nickel: a review of its occupational and environmental toxicology," Journal of Hygiene, Epidemiology, Microbiology, and Immunology, vol. 27, no. 2, pp. 237-247, 1983.

[3] L. J. Casarett, Casarett and Doull's Toxicology: The Basic Science of Poisons, New York: McGraw-Hill, 2008.

[4] P. P. M. Muniyan, "Effect of nickel on certain biochemical parameters in selected tissues of Cirrhinus mrigala."

[5] E. O. Uthus and R. A. Poellot, "Dietary folate affects the response of rats to nickel deprivation," Biological Trace Element Research, vol. 52, pp. 23-35, 1996.

[6] J. J. Scott-Fordsmand, "Toxicity of nickel to soil organisms in Denmark," Reviews of Environmental Contamination and Toxicology: Continuation of Residue Reviews, pp. 1-34, 1997.

[7] L. Anah and N. Astrini, "Isotherm adsorption studies of Ni (II) ion removal from aqueous solutions by modified carboxymethyl cellulose hydrogel," in IOP Conference Series: Earth and Environmental Science, vol. 160, p. 012017, IOP Publishing, 2018.

[8] A. Ewecharoen, P. Thiravetyan, E. Wendel, and H. Bertagnolli, "Nickel adsorption by sodium polyacrylate-grafted activated carbon," Journal of Hazardous Materials, vol. 171, no. 1-3, pp. 335-339, 2009.

[9] C. K. Ahn, Y. M. Kim, S. H. Woo, and J. M. Park, "Removal of cadmium using acid-treated activated carbon in the presence of nonionic and/or anionic surfactants," Hydrometallurgy, vol. 99, no. 3-4, pp. 209-213, 2009.

[10] F. Boudrahem, A. Soualah, and F. Aissani-Benissad, "Pb (II) and Cd (II) removal from aqueous solutions using activated carbon developed from coffee residue activated with phosphoric acid and zinc chloride," Journal of Chemical & Engineering Data, vol. 56, no. 5, pp. 1946-1955, 2011.

[11] W. Q. Fu, Y. Wen, W. J. Tang, and Z. Y. Yao, "Cu (II) removal from aqueous solution by ultrafiltration assisted with chestnut shell pigment," Water Conservation Science and Engineering, vol. 7, no. 4, pp. 419-428, 2022.

[12] Z. Chen, W. Wei, H. Chen, and B. J. Ni, "Recent advances in waste-derived functional materials for wastewater remediation," Eco-Environment & Health, vol. 1, no. 2, pp. 86-104, 2022.

[13] M. Simić, J. Petrović, T. Šoštarić, M. Ercegović, J. Milojković, Z. Lopičić, and M. Kojić, "A mechanism assessment and differences of cadmium adsorption on raw and alkali-modified agricultural waste," Processes, vol. 10, no. 10, p. 1957, 2022.

[14] M. Petrović, T. Šoštarić, M. Stojanović, J. Petrović, M. Mihajlović, A. Ćosović, and S. Stanković, "Mechanism of adsorption of Cu^{2+} and Zn^{2+} on the corn silk (Zea mays L.)," Ecological Engineering, vol. 99, pp. 83-90, 2017.

[15] Z. Chen, W. Wei, W. Zou, J. Li, R. Zheng, W. Wei, and H. Chen, "Integrating electrodeposition with electrolysis for closed-loop resource utilization of battery industrial wastewater," Green Chemistry, vol. 24, no. 8, pp. 3208-3217, 2022.

[16] S. Bolisetty, M. Peydayesh, and R. Mezzenga, "Sustainable technologies for water purification from heavy metals: review and analysis," Chemical Society Reviews, vol. 48, no. 2, pp. 463-487, 2019.

[17] Y. Wang, W. Wang, X. Shi, and A. Wang, "A superabsorbent nanocomposite based on sodium alginate and illite/smectite mixed-layer clay," Journal of Applied Polymer Science, vol. 130, no. 1, pp. 161-167, 2013.

[18] A. Pourjavadi, A. M. Harzandi, and H. Hosseinzadeh, "Modified carrageenan 3. Synthesis of a novel polysaccharide-based superabsorbent hydrogel via graft copolymerization of acrylic acid onto kappa-carrageenan in air," European Polymer Journal, vol. 40, no. 7, pp. 1363-1370, 2004.

[19] T. Wan, R. Huang, Q. Zhao, L. Xiong, L. Qin, X. Tan, and G. Cai, "Synthesis of wheat straw composite superabsorbent," Journal of Applied Polymer Science, vol. 130, no. 5, pp. 3404-3410, 2013.

[20] S. Pandey and S. Tiwari, "Facile approach to synthesize chitosan based composite-characterization and cadmium (II) ion adsorption studies," Carbohydrate Polymers, vol. 134, pp. 646-656, 2015.

[21] K. S. Kasprzak, F. W. Sunderman Jr, and K. Salnikow, "Nickel carcinogenesis," Mutation Research/Fundamental and Molecular Mechanisms of Mutagenesis, vol. 533, no. 1-2, pp. 67-97, 2003.

[22] H. Dumrul, A. N. Kursunlu, O. Kocyigit, E. Guler, and S. Ertul, "Adsorptive removal of Cu (II) and Ni (II) ions from aqueous media by chemical immobilization of three different aldehydes," Desalination, vol. 271, no. 1-3, pp. 92-99, 2011.

[23] V. K. Gupta, A. Rastogi, and A. Nayak, "Biosorption of nickel onto treated alga (Oedogonium hatei): application of isotherm and kinetic models," Journal of Colloid and Interface Science, vol. 342, no. 2, pp. 533-539, 2010.

[24] M. Sadeghi, "Synthesis of a biocopolymer carrageenan-g-poly(AAm-co-IA)/montmorilonite superabsorbent hydrogel composite," Brazilian Journal of Chemical Engineering, vol. 29, pp. 295-305, 2012.

[25] A. Ashri, N. Amalina, A. Kamil, S. Fazry, M. F. Sairi, M. F. Nazar, and A. M. Lazim, "Modified Dioscorea hispida starch-based hydrogels and their in vitro cytotoxicity study on small intestine cell line (FHS-74 Int)," International Journal of Biological Macromolecules, vol. 107, pp. 2412-2421, 2017.