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THIADIAZOLS-FUNCTIONALIZED HYDROGEL NETWORKS: SYNERGISTIC EFFECTS ON HEAVY METAL IONS ADSORPTION AND MECHANICAL ROBUSTNESS

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ABSTRACT: Heterocyclic impregnated cross-linked hydrogels are advanced materials of increasing importance in the industrial, environmental and medical fields, driving the development of improved hydrogel structures. This research aims to prepare hydrogels based on the polymerization of acrylic acid grafted with 1,3,4-thiadiazole derivatives and cross linked diallyl phthalate, and their structures were proved by using FTIR and NMR spectroscopy, thermal stability was evaluated using TGA, surface structure using SEM, and crystalline properties using XRD. Swelling behaviour at two different temperatures were (25° C and 70° C). The solubility in various media and solvents was investigated and pClT-g-AAc-C-DAP showed best swelling activity at both temperatures and all hydrogels were insoluble. The adsorption efficiency of heavy metal ions (Fe(II), Cu(II), Cd(II), Ni(II) and Co(II)) was tested using atomic absorption spectroscope (AAS), with hydrogels demonstrating outstanding performance where dNT-g-AAc-C-DAP was better adsorbent for Ni(II) with percentage of removal 92.15%, pClT-g-AAc-C-DAP was the highest with Co(II) of 93.9%, pNT-g-AAc-C-DAP was the highest for Fe(II) of 94.4%, dNT-g-AAc-C-DAP was the highest for Cu(II) of 93.3% and pClT-g-AAc-C-DAP was the highest for Cd(II) of 94.8%. Tensile strength tests of composites composed of hydrogels with PVC showed a significant improvement in stress and strain and dNT-g-AAc-C-DAP exhibited. The results indicate the suitability of these materials for adsorption applications and enhancing mechanical properties industrially and environmentally.

KEYWORDS: thiadiazole, acrylic acid, diallyl phthalate, crosslinked hydrogels, metal ion adsorption, mechanical properties.

1 INTRODUCTION

Heterocyclic compounds are aromatic rings containing one or more rather than carbon atoms [1,2]. Among the most common heterocyclic atoms are nitrogen, oxygen, and Sulphur, while some rings contain other atoms such as phosphorus, iron, magnesium, and selenium [2-4]. These compounds are fundamental to classical organic chemistry, and research interest in them is growing due to their diverse applications in industry, medicine and antimicrobials [5-7]. Thiadiazols belong to the azole family of compounds, designated by the Hantzsch-Widmann nomenclature system. They are five-membered heterocyclic rings containing one sulphur atom and two nitrogen atoms, with the molecular formula $C_2H_2N_2S$. The ring exhibits aromatic properties due to two double bonds and a lone electron pair on the Sulphur atom, which contributes to its stability. Four structural isomers exist, differing in the positions of the heteroatoms: 1,2,3-thiadiazole, 1,2,4-thiadiazole, 1,2,5-thiadiazole, and 1,3,4-thiadiazole. These isomers are not interchangeable with each other [8]. The thiadiazol nucleus is an important heterocyclic nucleus and is used as a building block in many chemical structures, alongside similar rings such as oxadiazole, pyrrole, and triazine [9]. The 1,3,4-thiadiazole isoform was first described in 1882 by Hermann Emil Fischer, and its study was later developed by Oskar Busch and colleagues [10]. Heinrich Kohn and Ludwig Freund described the properties of its cyclic system in 1890 [11], and its true structure was definitively established in 1956 by Rudolf Gerdil and others [12].Thiadiazols are widely used as building blocks and synthetic intermediates in organic and medicinal chemistry, and they have numerous industrial applications, including in the production of hydrogels, plastics, and dyes [13,14]. 1,3,4-thiadiazole is considered the most important of the isoforms in practical applications due to its structural stability and distinctive chemical properties [15,16]. Hydrogels are essential materials in numerous industrial and everyday applications, thanks to their diverse properties and the ability to be precisely tuned and adapted to specific usage requirements. Thermal conductivity is a critical property of hydrogels, directly impacting on the efficiency and performance of the materials and composites they are used in. Pure hydrogels typically exhibit low thermal conductivity and high insulation properties, with thermal

conductivity (κ) often ranging from 0.1 to 0.5 W/m. K [17]. This property makes them commonly used in coatings and thermal insulation applications [18]. Over the past few decades, research interest in studying the properties of polymer-based composite materials has increased, with many studies focusing on the effect of the filler ratio, the nature of the interfacial interactions between the matrix and the reinforcing material, and the microstructure of the composite, with the aim of improving thermal conductivity and enhancing its efficiency in future industrial applications [19,20]. Hydrogels are used in several fields, including solid-state batteries, nanocomposites, thermal conductivity modelling, antibacterial properties, and 3D printing [21-25]. The hydrogels also called a hydrogel This hydrogel insoluble in water due to chemical or physical bonds within its structure. Instead, it accumulates water molecules within the hydrogel network. This is because the hydrogel contains hydrophilic groups such as -OH, -SO3, H, CONH2, and -CONH. This allows water to be absorbed into the system. Both natural and synthetic hydrogels can be used to form hydrogels [26]. Acrylic acid is an unsaturated carboxylic acid consisting of a phenyl group bonded to a carboxyl group. The super sorbent it is used for is characterized by its high solubility, enabling it to remove dyes and heavy metals under various solution conditions. Numerous studies have indicated the use of poly (acrylic acid) in the treatment of organic pollutants and metal ions such as zinc, nickel, magnesium, copper, and lead. Several different methods and techniques for preparing poly (acrylic acid) have also been documented [27]. Polyacrylic acid (PAA) derivatives are used industrially in ion exchange, adhesives, dispersants, superabsorbent, and other applications. Their applications often rely on linear or cross-linked structures, while the effect of structural branching remains incompletely understood despite its importance in surface and ion interactions. Therefore, there is growing interest in preparing structurally controlled branched PAAs due to their superior performance in some applications compared to linear systems [28]. Human health and the environment face increasing risks from exposure to harmful organic and inorganic compounds. Heavy metals are among the most dangerous pollutants because they cause toxic effects even at very low concentrations [29-32]. Therefore, developing effective methods for removing these metals is a crucial research objective. Several techniques have been developed for removing heavy metal ions, such as chemical precipitation, ion exchange, electrochemical methods, and adsorption [33-35]. Adsorption is considered one of the most efficient and flexible methods due to the ability to control the properties of the adsorbent material and modify its surface. Furthermore, the ease with which adsorbents can be renewed and reused under moderate conditions contributes to reducing costs and increasing practical feasibility. Recent studies have focused on hydrogels and nanocomposites as effective adsorbents. The adsorption of heavy metals is a crucial process for mitigating the impact of these pollutants, given their high toxicity and ability to react with solid surfaces even at low concentrations. Environmental pollution from heavy metals results from a range of industrial activities such as metal plating, mining, paint production, and automotive radiators, as well as agricultural sources including fertilizers and pesticides [36]. The presence of these metals in the environment is of great concern due to their high toxicity and harmful effects on human health and ecosystems, especially when permissible levels are exceeded [37]. In this context, the removal of heavy metals from wastewater has become a key focus of water treatment research, with several methods being used, such as chemical precipitation, membrane filtration, and ion exchange, with adsorption being preferred as an economical and effective solution for removing these metals [38-41]. Hydrogels are materials with long molecular chains that determine their mechanical behaviour, including elasticity, yield strength, and fracture resistance, which depend on their molecular structure, crystallinity, and chain cross-linking [42]. Mechanical performance is influenced by testing conditions such as stress rate, temperature, and loading type. Improving hydrogels with Fibers or nanoparticles can also increase tensile strength, stiffness, and impact resistance [43]. Advances in hydrogel membranes have contributed to elucidating the mechanisms of deformation and failure at the micro and nanoscales, which is important for engineering and biomedical applications [44].

2 MANUSCRIPT PREPARATION

2.1 Materials and reagents

The chemicals used in this study were of analytical purity as received from the suppliers without any further purification unless otherwise stated. The materials included: benzoic acid ($C_7H_6O_2$, 97%, solid, Fluke), 2-chlorobenzoic acid ($C_7H_5ClO_2$, 97%, solid, BDH Chemicals), 4-chlorobenzoic acid ($C_7H_5ClO_2$, 98%, solid, HI Media Laboratories), 4-nitrobenzoic acid ($C_7H_5NO_4$, 98%, solid, Merck Group), and 3,5-dinitrobenzoic acid ($C_7H_4N_2O_6$, 99%, solid, BDH Chemicals). Phosphorus oxychloride ($POCl_3$, 99%, liquid, Central Drug House), thiosimicarbazide (CH_5N_3S, 98%, solid, Merck Group), potassium hydroxide (KOH, 97%, solid, CDM Chemical), and methanol (CH_3OH, 99.9%, liquid, Scharlau) were also used. Metal salts were used, namely cobalt chloride ($CoCl_2$, 97%), ferric chloride (FeCl2, 99%), nickel chloride ($NiCl_2$), 99%), and copper chloride ($CuCl_2$, 98%) from BDH Chemicals, in addition to cadmium chloride ($CdCl_2$, 99%) from CDH. Acrylic acid ($C_3H_4O_2$, 98%, liquid), benzene (C_6H_6, 99%, liquid), hydrochloric acid (HCl, 98%, liquid), and dimethyl sulfoxide (C_2H_6OS, 97%, liquid) were also used from Central Drug House, while diallyl phthalate ($C_{14}H_{14}O_4$, 97%, solid), azobisisobutyrontrile (AIBN) ($C_8H_{12}N_4$, 98%) were obtained from Merck Group, dimethylformamide (C_3H_7NO, 99%, liquid) from Merck Group, and tetrahydrofuran (C_4H_8O, 99%, liquid) from BDH Chemicals. Nitrogen gas (N_2, 98%) from a local source and polyvinyl chloride (PVC, $(C_2H_3Cl)_n$, 99%, solid, MOH) were also used.

2.2 Instrumentation

A range of analytical instruments were used to evaluate the spectral and physical properties of the synthesis compounds and hydrogels. Fourier transform infrared (FTIR) spectroscopy was performed using a SHIMADZU Affinity IR spectrometer with a KBr disk method in the 400–4000 cm^{-1} range at the Department of Chemistry, College of Education for Pure Sciences, University of Diyala. UV-Vis absorbance of the compounds and hydrogels was measured using a SHIMADZU-1700 dual spectrophotometer with a quartz cell at the same department. The mineral content of the samples was determined using an AA500 atomic absorption spectrometer and its accessories, also at the Department of Chemistry. For thermal evaluation, a thermogravimetric analysis (TGA) of the hydrogels was performed using a Rheometric Scientific TGA-1000 at the Faculty of Science Laboratory, University of Tehran, Iran. The 1H-NMR spectrum of the compounds was measured using a Bruker Ultra Shield 500 MHz spectrometer with DMSO-d6 solvent and a TMS reference at the Central Laboratory, Kashan University, Iran. X-ray diffraction (XRD) was recorded using a Philips PW1730 spectrometer from the Netherlands, with a Cu-Kα beam at a wavelength of 0.15406 nm, a voltage of 30 kV, and a current of 20 mA within an angular field of 2θ = 10–80°, at Kashan International University, Iran. A Zeiss scanning electron microscope (SEM) (FE-SEM): TESCAN ,MIRA3 ,Czechia was used to perform spectroscopic analysis of the prepared hydrogels.

2.3 Synthesis of 2-amino-5- (substituted phenyl)-1,3,4-thiadiazole derivatives reaction

Equimolar amounts of substituted benzoic acid (0.01 mol) and thiosimicarbazide (0.01 mol) were mixed in a 100 mL sphere flask and dissolved in 10 mL of phosphorus oxychloride ($POCl_3$). The reaction mixture was heated for 3 hours. Then, 30 mL of distilled water was carefully added, and heating continued for an additional 4 hours. The mixture was allowed to cool to room temperature and then gradually adjusted with 10% potassium hydroxide (KOH) solution until the pH of the solution was close to pH=6. The resulting precipitate was filtered, washed several times with distilled water to remove impurities, and then allowed to dry at room temperature to obtain the final product [45].

2-amino-5-(4-nitrophenyl)-1,3,4-thiadiazole (A1): m.p 120-148, colour Dark yellow, yield 90%, IR 3302-3186(νNH2), 3093(νC–H), 1643(νC=N), 1589-1504(νC=C), H-NMR (DMF-d6) δ ppm 6.7(2), 7(2), 7.2(2).

2-amino-5-(2-chlorophenyl)-1,3,4-thiadiazole (A2): m.p 190-195, colour yellow, yield 90%, IR 3278-3116(νNH2), 3039(νC–H), 1635(νC=N), 1581-1458(νC=C), H-NMR (DMF-d6) δ ppm 6.2(2), 7.5(2), 7.6(1), 7.2(1).

2-amino-5-(4-chlorophenyl)-1,3,4-thiadiazole (A3): m.p 117-123, colour light brown, yield 92%, IR 3286-3163(νNH2), 3086(νC–H, 1635(νC=N), 1573-1427(νC=C), H-NMR (DMF-d6) δ ppm 6.7(2), 7.6(2), 7.8(2).

2-amino-5-(1-phenyl)-1,3,4-thiadiazole (A4): m.p 212-215, colour light yellow, yield 85%, IR 3275-3086(νNH2), 3062(νC–H), 1613(νC=N), 1581-1458(ν C=C), H-NMR (DMF-d6) δ ppm 7.2(2), 7.9(1), 8.3(2), 7.4(1).

2-amino-5-(3,5-Dinitrophenyl)-1,3,4-thiadiazole (A5): m.p 160-212, colour Acid green, yield 96%, IR 3356-3271(νNH2), 3093(νC–H), 1635(νC=N), 1566-1427(ν C=C), H-NMR (DMF-d6) δ ppm 6.4(2), 7.5(2), 7.6(1).

2.4 Synthesis of pNT-g-AAc-C-DAP, oClT-g-AAc-C-DAP, pClT-g-AAc-C-DAP, PT-g- AAc-C-DAP, dNT-g-AAc-C-DAP hydrogels.

The hydrogels were synthesis using solution polymerization by dissolving 0.5 g of the 1,3,4-thiadiazole substituents (A1–A5) in 5 mL of acrylic acid until completely dissolved, using heating where necessary to ensure full dissolution. Benzene (30 mL) was then added to the mixture with continuous stirring to achieve a homogeneous medium, followed by the addition of 5 mL of diallyl phthalate as a crosslinking agent. Nitrogen gas (N_2) was then passed through the mixture using a Schlenk line to remove dissolved oxygen and create an air-free environment. The reaction mixture was heated in a water bath at 70° C, and at this temperature, 0.008 mol of the starter (AIBN) was added. After approximately 30 minutes, hydrogel formation began, and the release of nitrogen gas (N_2) was observed because of the thermal decomposition of the starter. Upon completion of the reaction, methanol was added to the reaction medium to isolate the hydrogel from the benzene and dissolve the unreacted monomers, resulting in complete hydrogel precipitation. The product was then separated and dried to obtain the final hydrogel.

pNT-g-AAc-C-DAP: colour yellow, yield 99%, IR 3400-2400(νOH),3132(νNH2),3024(νCHaromat), 2997-2889(νCHalfa),1732-1635(νC=O), 1597(νC=N).

oClT-g-AAc-C-DAP: colour pale yellow, yield 99%, IR 3300-2400(νOH), 3197(νNH2), 3151(νCHaromat), 3012-2877(νCHalfa), 1728-1720(νC=O), 1597(νC=N).

pClT-g-AAc-C-DAP: colour white, yield 94%, IR 3400-2600(νOH), 3155(νNH2), 3097 (νCHaromat), 3001-2900(νCHalfa), 1732 (νC=O), 1597 (νC=N).

PT-g-AAc-C-DAP: colour white, yield 97%, IR 3300-2400(νOH), 3140(νNH2), 3086 (νCHaromat), 2900-2823(νCHalfa), 1732(νC=O), 1581(νC=N).

dNT-g-AAc-C-DAP: colour brown, yield 99%, IR 3400-2700(νOH), 3132(νNH2), 3097 (νCHaromat), 3020-2889(νCHalfa),1728-1600 (νC=O), 1581 (νC=N).

2.5 Solubility of Hydrogels

0.1 g of the hydrogels were weighed and added to 20 mL of each solvent separately to study its solubility behaviour. The solvents used included dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), N, N-dimethylformamide (DMF), benzene, water, methanol, and acetone, in addition to 10% (w/v) potassium hydroxide solution and 10% (w/v) hydrochloric acid solution. The samples were left in the different solvents for 24 hours at room temperature without stirring. It was observed that hydrogel was insoluble in all the solvents and solutions, indicating the formation of a highly chemically stable, three-dimensional cross-linked hydrogel network.

2.6 Swelling

The swelling behaviour of the hydrogels were determined by immersing 0.5 g of the hydrogel in 20 ml of distilled water and methanol separately. Swelling was measured based on the change in weight at 0, 3, 6, 9, 12, and 24 hours at room temperature, as well as at 70°C. The swelling ratio was calculated using the standard equation.

$$\text{Swelling percentage } \% = \frac{\text{Ws} - \text{Wd}}{\text{Wd}} \times 100$$

Table 1. Swelling percentage of the synthesis hydrogels in water.

No.	Time (h)					
	0	3	6	9	12	24
pNT-g-AAc-C-DAP	0	51	58	62	68	82
oClT-g-AAc-C-DAP	0	62	82	89	129	164
pClT-g-AAc-C-DAP	0	9	12	15	18	24
PT-g-AAc-C-DAP	0	64	67	72	79	87
dNT-g-AAc-C-DAP	0	43	46	49	53	59

Table 2. Swelling percentage of the synthesis hydrogels in methanol.

No.	Time (h)					
	0	3	6	9	12	24
pNT-g-AAc-C-DAP	0	121	133	138	143	157
oClT-g-AAc-C-DAP	0	262	279	285	289	318
pClT-g-AAc-C-DAP	0	13	18	25	28	31
PT-g-AAc-C-DAP	0	132	146	152	165	175
dNT-g-AAc-C-DAP	0	218	226	248	259	264

Table 3. Swelling ratio of the synthesis hydrogels in water at 70 °C.

No.	Time (h)					
	0	3	6	9	12	24
pNT-g-AAc-C-DAP	0	24	89	163	256	323
oClT-g-AAc-C-DAP	0	38	69	146	185	226
pClT-g-AAc-C-DAP	0	27	38	47	75	94
PT-g-AAc-C-DAP	0	56	75	146	174	215
dNT-g-AAc-C-DAP	0	42	57	69	84	119

Table 4. Swelling ratio of the synthesis hydrogels in methanol at 70 °C.

	T(h)					
No.	0	3	6	9	12	24
pNT-g-AAc-C-DAP	0	47	97	147	193	372
oClT-g-AAc-C-DAP	0	46	86	147	218	427
pClT-g-AAc-C-DAP	0	57	96	164	94	212
PT-g-AAc-C-DAP	0	49	93	174	228	316
dNT-g-AAc-C-DAP	0	83	153	196	247	351

2.7 Preparation of Standard Solutions of Heavy Ions

Standard solutions of Ni^{2+}, Cd^{2+}, Fe^{2+}, Co^{2+}, and Cu^{2+} ions were synthesis from 1000 ppm base solutions and diluted to 20 ppm using the dilution equation ($V_1C_1 = V_2C_2$).

2.7.1 Adsorption of Heavy Metal Ions

0.1 g of hydrogels were immersed in 20 mL of each metal solution at a concentration of 20 ppm for 24 hours. The residual concentration was measured using atomic absorption spectrometry, and the removal percentage was calculated using the equation:

$$\text{Adsorption percentage } \% = \frac{\text{Ci} - \text{Cf}}{\text{Ci}} \times 100$$

Ci: initial concentration
Cf: final concentration

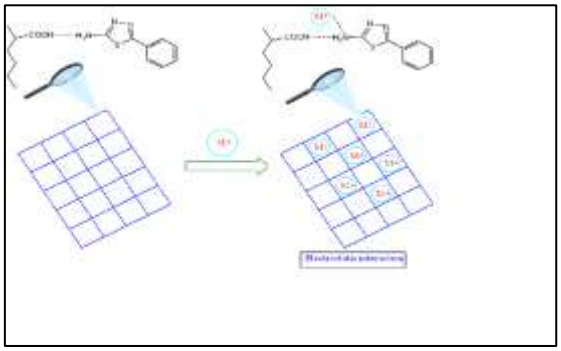

Figure 1: Mechanism of heavy metal adsorption in hydrogel

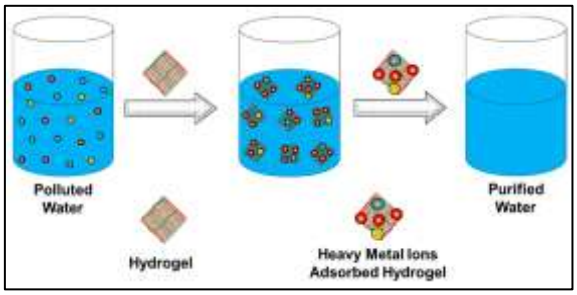

Figure 2: Schematic representation of the removal of heavy metal ions from contaminated water by hydrogel absorbent materials.

Table 5. The adsorption percentages of heavy metals ions by the hydrogels.

No	Fe (II)	Co (II)	Ni (II)	Cu (II)	Cd (II)
pNT-g-AAc-C-DAP	94.40	91.15	89.85	85.80	92.05
oClT-g-AAc-C-DAP	88.85	93.50	89.25	91.75	88.10
pClT-g-AAc-C-DAP	86.20	93.90	87.05	92.60	94.80
PT-g-AAc-C-DAP	92.30	86.80	90.10	88.55	91.45
dNT-g-AAc-C-DAP	88.95	89.35	92.15	93.30	89.90

2.8 Study of the mechanical properties of the synthesis hydrogel

(0.1 g) of the synthesis hydrogels were weighed and added to a solution of polyvinyl chloride (PVC) containing (1 g) of dimethylformamide (DMF). The solution was heated with continuous stirring for one hour to ensure homogeneous dispersion of the hydrogel within the hydrogel solution. The mixture was then poured into suitable Molds and allowed to cool and allow the solvent to evaporate. After the Molds were formed, the strain and stress properties were measured using a tensile strength meter.

Table 6. Tensile stress of hydrogel samples at different deformation stages.

No.	Stress				
	1	2	3	4	5
pNT-g-AAc-C-DAP	38.97	47.17	53.33	60.51	68.71
oClT-g-AAc-C-DAP	56.41	60.51	64.61	68.71	72.82
pClT-g-AAc-C-DAP	41.02	45.12	50.25	54.35	61.53
PT-g-AAc-C-DAP	51.28	55.38	60.51	66.66	71.79
dNT-g-AAc-C-DAP	56.41	60.51	62.56	69.74	74.87

Table 7. Tensile strain and elongation percentage of polymer.

No.	Strain				
	1	2	3	4	5
pNT-g-AAc-C-DAP	0.04	0.054	0.059	0.06	0.08
oClT-g-AAc-C-DAP	0.04	0.081	0.088	0.1	0.11
pClT-g-AAc-C-DAP	0.04	0.06	0.07	0.08	0.09
PT-g-AAc-C-DAP	0.05	0.08	0.11	0.12	0.16
dNT-g-AAc-C-DAP	0.106	0.127	0.153	0.194	0.269

3 RESULTS AND DISCUSSION

2-Amino-5-(substituted phenyl)-1,3,4- thiadiazol- (A1-A5)

The synthesis of the hydrogels involved the reaction of an appropriate carboxylic acid with thiosimicarbazide in the presence of POCl3 followed by reflux of water to form compounds (A1-A5). (A1-A5) were dissolved in acrylic acid followed by the addition of DAP, then the hydrogels were achieved by the addition of AIBN. (pNT-g-AAc-C-DAP, oClT-g-AAc-C-DAP, pClT-g-AAc-C-DAP, PT-g-AAc-C-DAP, dNT-g-AAc-C-DA). The adsorption of heavy metal ions was studied for (Cu (II), Fe (II), Ni (II), Co (II), Cd (II)). The mechanical properties of the hydrogels were studied after the preparation of composites by mixing them with calculated amount of PVC through the calculation of strain and stress. The results of swelling in water and methanol (25º C and 70º C) Show a high degree of cross-linking due to diallyl phthalate.

3.1 Characterization

3.1.1 X-ray diffraction (XRD)

X-ray diffraction (XRD) was used to study the crystal structure of the synthesis hydrogel. Diffraction patterns were recorded within the range of (10–70) ° using a Siemens D500 and Cu Kα radiation. The results shown in Figures 3. indicate the absence of sharp peaks, with a broad peak appearing at an angle of 2θ within the range of (16–22) °, indicating that the synthesis hydrogel has an amorphous nature, which is consistent with previous studies [45].

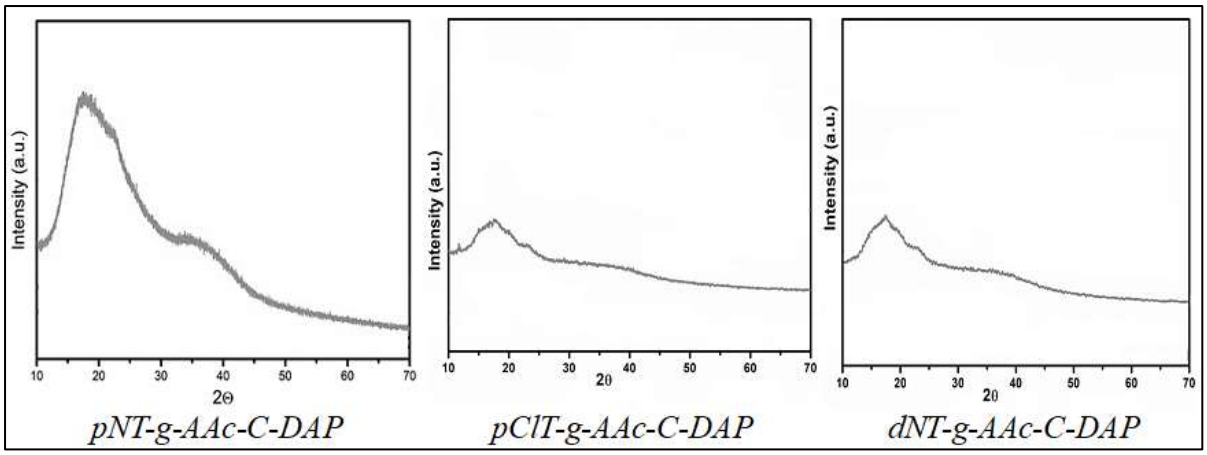

Figure 3. XRD pattern of [a] pNT-g-AAc-C-DAP hydrogel [b] pClT-g-AAc-C-DAP hydrogel and [c] dNT-g-AAc-C-DAP hydrogel

3.1.2 scanning electron microscopy (SEM)

The external appearance of the surface of a hydrogel was imaged using a scanning electron microscope. Figures 4. show the surface morphology of the hydrogel, which is characterized by an amorphous shape. The hydrogel showed a rough and porous surface. The porosity increased the surface area, which helped to increase the number of adsorption sites per unit area, with improved adsorption properties. Also, the pores increase the ability of the hydrogel to absorb and retain water, depending on its porosity and average pore size [46].

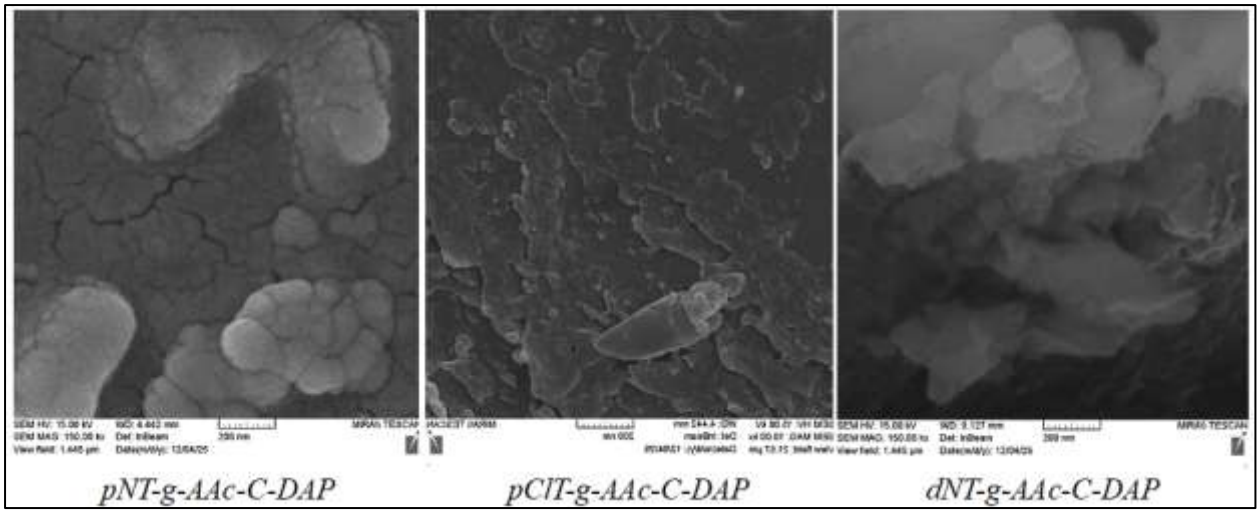

Figure 4. SEM morphology of [a] pNT-g-AAc-C-DAP hydrogel [b] pClT-g-AAc-C-DAP hydrogel and [c] dNT-g-AAc-C-DAP hydrogel**.**

3.1.3 thermal properties of hydrogels (TAG)

Study was conducted on the hydrogel to understand the thermal stability from room temperature to 800° C. Figure 5. The degradation occurred in three steps where the first degradation appeared at 100° C related to the removal of moisture resulted from the interaction with COOH group in the polymer. The second step of degradation occurred at 200° C. The third step appeared at 400° C which involved the scission of C-C bond in the hydrogel [47].

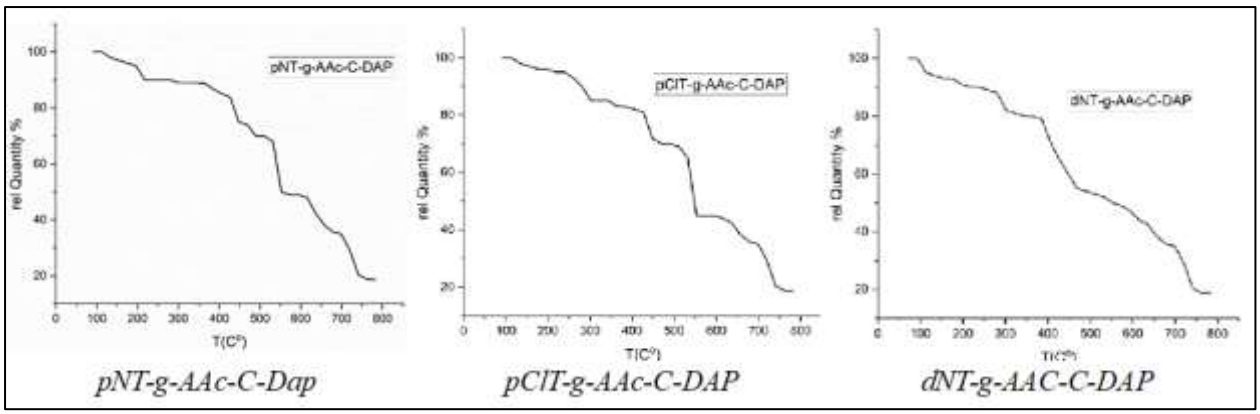

Figure 5. TGA pattern for (a) pNT-g-AAc-C-DAP hydrogel (b) pClT-g-AAc-C-DAP hydrogel and (c) dNT-g-AAc-C-DAP hydrogel.

4 CONCLUSIONS

The following work involved a successful synthesis of new cross-linked hydrogels impregnated with 1,3,4-thiadiazole derivatives that were characterized by multiple techniques shown above. The solubility test in different solvents and media assures the formation of stable three-dimensional networked structure. The swelling behavior demonstrated a reliable percentage indicating the presence of porous structure for the studying of adsorption of heavy metal ions. The performance of the hydrogels synthesized was high to the divalent heavy ions (Fe, Ni, Cd, Co and Cu) due to the strong chelation sites of 1,3,4-thiadiazole presented in the hydrogel chains making these hydrogels effective in water treatment especially these who contaminated with heavy metal ions. Finally, the study of mechanical properties after the addition of the synthesized hydrogels after mixing them with PVC and Polystyrene indicates that the PVC and polystyrene gained higher rigidity in all composites.

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