The influence of polyamide dendrimers on properties of PVA/PAA hydrogel films

Asma Abdalgader
University of Tripoli
Wael Elhrari (wael@prc.ly)
Libyan Polymer Research center
Ali Elejmi
University of Tripoli

Research Article

Keywords: polyamide dendrimers, polyvinyl alcohol, polyacrylic acid, hydrogel, metal adsorption

Posted Date: March 24th, 2023

DOI: https://doi.org/10.21203/rs.3.rs-2723212/v1

Additional Declarations: No competing interests reported.

Version of Record: A version of this preprint was published at Journal of Polymers and the Environment on July 4th, 2023. See the published version at https://doi.org/10.1007/s10924-023-02963-2.

Abstract

Polyamide dendrimers, poly(vinyl alcohol) (PVA), and poly(acrylic acid) (PAA) were heat-treated for hydrogels films preparation. The effect of the dendrimers periphery type (OH, NH_2), dendrimers content, and generation number on the properties of the hydrogels and adsorption performance at different pHs have been examined. Chemically bonded dendrimers into the hydrogel showed a high swelling ratio and high gel content compared to a neat film of PVA/PAA. The incorporation of dendrimers increases the swelling ability of the hydrogel. The highest swelling obtained was at low dendrimers content and high generation numbers G6-OH and G6-NH_2. The diffusion of water within the hydrogel follows the Fickian character. Combining the polyamide dendrimers into the hydrogel films showed potential use in metal chelating and the adsorption of Ni^{2+}, Zn^{2+}, Fe^{2+}, and Cu^{2+} ions onto the hydrogel. The adsorption results have shown dependency on pH, generation number, and dendrimers content. The adsorption increases at pH 6, high generation number, and high dendrimers content regardless of the periphery. The hydrogel containing G6-OH had high swelling and metal ion adsorption.

Introduction

Polymer gels are widely used for various applications, including medical applications, drug delivery, and tissue engineering [1–4]. In addition polymer gels are used in membrane separation techniques, where the adsorption techniques are utilized due to their high efficiency and availability [5–8].

Polyvinyl alcohol and polyacrylic acid are generally used as hydrogel polymers for various applications due to their outstanding properties, including good film-forming, high hydrophilicity, good chemical resistance, and the ability of swelling, and biocompatibility [2,9–13].

PVA/PAA hydrogel shows adsorption capacity of heavy metal from aqueous solutions due to the high electrostatic attraction and chemical bonding affinity of carboxyl and hydroxyl groups [14].

Several research groups have focused their studies on PVA/PAA hydrogel system for adsorption studies [5,10,15] Jinyeong Kim et al. investigated hydrogel system of PVA/PAA nanofibers containing thiol silica particles prepared by heat treatment. The adsorption of Cu(II) shows a maximum adsorption capacity of 125.47 mg/g [16]. Hongsik Byun et al.[17] studied the swelling behaviour and drug release of PVA/PAA films, the water contents reached equilibrium after 30 h, the time decreased with increased PAA content in the hydrogel the water content increased with increasing pH of the solution. Yahya Al-qudah et al.[18] used PVA/PAA cross-linked via γ radiation for the removal of heavy metal ions from aqueous solutions, they found the hydrogel adsorption capacity in order of Zn^{2+}>Co^{2+}>Mn^{2+}.

In PVA/PAA hydrogel system, the abundant–OH and –COOH groups showed a high affinity toward heavy metals. Accordingly, the introduction of primary and secondary amine groups into the hydrogels enhances the water uptake and metal chelating capability.

The dendrimers are a new branch of the polymer family, which are well-defined in size, shape, molecular weight, and monodispersity were first introduced by Vogtle and Tomalia [19,20]. Because of their unique architecture which starts from focal point and ended with numerous terminal groups on the surface which could be modified for various applications [21,22]. Therefore, the addition of dendrimers into the hydrogel films expected somehow changes the behaviour of the formed films; water uptake, swelling ability, and metal adsorption. Polyamide dendrimers based on tetraethyl-1,1,3,3-propane tetra carboxylate as a core and reaction of 1,6-diamino hexane, adipoyl chloride and tris(hydroxymethyl) aminomethane were synthesized via a multi-step divergent approach. Various generations were obtain start from G0 to G6. These polymers were characterized and studied in details elsewhere [23]. The synthesized dendrimers with different periphery resulted in a different number of terminal groups on the surface of the dendrimer molecule due to the reaction condition [23]. The primary amine and hydroxyl groups in the polyamide dendrimers will facilitate the attachment of the dendrimers into the hydrogel films through esterification or amidification reactions. The amine groups are expected to play role in enhancing the interactions of heavy metals to the hydrogel films.

In this paper, the influence of incorporating the polyamide dendrimers into hydrogel film on the characteristics of the hydrogel films has studied. The factors under study are generation numbers, dendrimers content and periphery type. The resulting features of the hydrogel films under investigation are the swelling behaviour, water uptake and the adsorption of ion metals. Three different generations of dendrimers G2, G4 and G6 with two different periphery NH_2, OH at three concentration of 1%, 2% and 3% attached into PVA/PAA (1 wt%/ 5wt%) hydrogel films were studied.

Experimental

Materials

Poly (vinyl alcohol) (Mw = 15,000 g/mol), from (Riedel-de Haen), polyacrylic acid (Mw = 500000–1000000 g/mol), from Fluka, pH buffer solutions 4,6,10 Fixanal (Riedel-dehaeh), deionized-water, dimethyl slufoxide (DMSO), 99%, and polysaccharide (dextran) from (Alfa Aesar). Copper and Iron standard solution from (spectrosol, BDH), zinc and nickel standard solution from (Fluka). Generation (2, 4, and 6) terminal OH and NH_2, were synthesized according to procedure described in reference [23].

Synthesis Of Films From G2, G4, And G6 Oh, Nh With Pva / Paa:

All prepolymers and the dendrimers (G2-OH / G4-OH / G6-OH / G2-NH_2 / G4-NH_2/G6-NH_2) were dissolved separately in DMSO then, the mixing with a specific amount (1% PVA, 5% PAA and (1, 2, 3% of dendrimers)). The solutions were then poured into a Petri dish previously treated with a thin layer of polysaccharide (5% dextran to facilitate the removal of the film). The solvent was allowed to evaporate on a heater for 5 min, and then, the glasses were heated at 120 ^{o}C in an oven for 5 days. After heating, they allow reaching room temperature then rinsed with water to delaminate the films.

To extract un-reacted polymers, the films were washed in increasing concentrations of ethanol-water solution mixtures (20, 50, 60, and 80%) for 2h and 100% ethanol overnight. The formulations are given in Table 1.

Table 1 Hydrogel chemical composition

Dendrimer	Number of terminal OH	Number of terminal NH_2	Dendrimer (wt%)	PAA (wt%)	PVA (wt%)
G2	12	12	1	5	1
			2	5	1
			3	5	1
G4	36	12	1	5	1
			2	5	1
			3	5	1
G6	108	36	1	5	1
			2	5	1
			3	5	1

Characterizations Of Hydrogels Films

Gel content.

Films samples were dried by placing them in the oven at 50 ^{o}C until a constant weight was obtained. The gel content was significantly calculated using the following formula:

Gel content (%) = $\frac{\mathrm{Wd}}{\mathrm{W0}} \times 100$ (1)

Where W_d and W_0 are the dried sample films after and before extraction, respectively.

Swelling (%)

The measured of swelling by hydration immersing disc of film samples (10 mm diameter, average thickness of 0.5 mm). Samples were withdrawn at different times, and the excess of water was carefully removed from the surface with absorbent paper and then weighed. The effect of pH on swelling behavior was studied at room temperature.

The swelling was calculated as indicated in equal 2:

Swelling (%) = $\frac{W_s - W_0}{W_0} \times 100$ (2)

Where, W_s is the wet mass and W_o is the initial mass.

Metal ions adsorption studies.

Metal ion's adsorption has studied in a solution of 100 ppm of Cu^{2+} ,Zn^{2+}, Ni^{2+}, and Fe^{2+} were prepared in distilled water. The pH was adjusted by adding 0.1 M of NaOH or HCl solution to a designed value. 3 ml of different metal ions solutions, were added and covered the films incubated with a known amount of dried films and allowed to balance at different pH. The film was taken off at desirable time intervals and the residual concentrations of metal ions were determined by UV-VIS GBC scientific equipment model Cintra 2020 spectrophotometer scan wave number from 200–1200 nm. The mount of metal ions adsorption per unit mass of films was calculated by using following equation:

$$qe = \frac{(C_o - C_e)\,V}{W}$$

3

Where, qe is the adsorption capacity of the hydrogels (mg/g); C_o and C_e are the concentrations of the initial and equilibrium metal ions solution (mg/L), respectively, V is the volume of the aqueous solution (L) and W is the mass of dray films (g).

Results And Discussions

Water sorption and Gel content:

The impact of dendrimers on the hydrogel films formation was examined, the gel content was measured for all films with different dendrimers generations number and different dendrimers content. The hydrogel films prepared from PVA/PAA shown gel content of 93% and water sorption of 71.07%. However, these films were degraded after 3 hr soaking in water, while the films with dendrimers were workable even after 96 hr. Therefore, the highest gel content obtained for all films was (96.4%) G6-OH and (95.7%) G6-NH_2. However, the films with 3% G4-NH_2 and 3% G2-OH contained the lowest gel content values (89.8, 88.8%) respectively. The water sorption results of the hydrogels were determined. The result show a decreased in water sorption with the increase of dendrimers content in the hydrogel. On the other hand, an increase in water sorption was observed with the increase in the generation number of the dendrimers. This behaviour illustrated clearly with dendrimers with OH periphery. In contrast, hydrogel with dendrimers having NH_2 as periphery showed different behaviour, the water sorption was increased with an increase in the dendrimers content. The effects of generation number of dendrimers with NH_2 periphery on water sorption were no clear. The results show that the addition of dendrimers into hydrogel film has significant

effect on the hydrogel films. However, no significant effect of the periphery on gel content was observed as shown in Table 2.

Table 2
Gel content and water sorption (%) of films from 1% PVA/ 5% PAA with different polyamide dendrimers content.

Film composition 1%PVA/5%PAA	Gel content (%)	Water sorption (%)	Film composition 1%PVA/5%PAA	Gel content (%)	Water sorption (%)
1%G2-OH	92.4	76.95	1%G2-NH2	93.8	82.92
2%G2-OH	93.3	74.31	2%G2-NH2	89.8	83.22
3%G2-OH	88.8	58.93	3%G2-NH2	90.5	92.04
1%G4-OH	91.7	88.25	1%G4-NH2	95.7	84.82
2%G4-OH	90.9	82.51	2%G4-NH2	92.5	90.64
3%G4-OH	93.9	78.04	3%G4-NH2	89.8	80.08
1%G6-OH	93.9	87.13	1%G6-NH2	95.7	82.60
2%G6-OH	96.4	83.40	2%G6-NH2	92.9	80.77
3%G6-OH	96.3	76.95	3%G6-NH2	95.6	90.47
1%PVA/5%PAA				93.0	71.07

Swelling properties

The ability of swelling is the most important parameter that evaluating the properties of hydrogels. The media of swelling, the dendrimers content, the periphery of dendrimers and the contact time were investigated.

Effect of times on the swelling.

Figure 1 show the swelling behaviours of dendrimers terminal OH versus time, the variables in the figures were dendrimers content, the study performed at pH 6. From the figures, all hydrogel films had shown rapid swelling behaviour regardless of pH media. The hydrogel films with the lowest dendrimers content have shown the highest swelling (%), while the hydrogel films with highest dendrimers content have shown lowest swelling. The reduction in the swelling (%) of the hydrogel films with increase in dendrimers content is due to the increase in crosslink networks in the films because of dendrimers structure, were the generation G6 for instance had 108 –OH groups as periphery, generation G4 had 36 -OH groups and G2 had 12 –OH groups as periphery. These number of –OH groups will make different and reacts with surrounding COOH of PAA resulting in restrict the movements of the chains thus, water diffusion is restricted as result, of the ability of the films to swell decreased.

Hydrogel films containing dendrimers ended with NH_2 as the periphery showed different behaviour to OH dendrimers. Figure 2 shows the swelling behaviours of hydrogels films containing NH_2 dendrimers as periphery at different dendrimers content and at pH 6. All hydrogel films had shown rapid swelling behavior regardless of pH media. The swelling (%) of G2-NH_2 are lowest and G6-NH_2 are the highest, even though the number of the NH_2 periphery in G2 and G4 are the same yet the hydrogel film with G4-NH_2 shown high swelling (%), that could be due to the structure of the dendrimers G4-NH_2 had 12 NH_2 but the length of the arm are longer, which facilitate the movement of the polymers chains, thus improve the swelling.

In general, the greater the percentage of the terminal-OH dendrimers in the hydrogel films, the less the swelling (%). On the other hand, in terminal NH_2 dendrimers, the swelling increases with the increase of the dendrimers content, and at the higher generation the more swelling.

Effect of pH on the swelling

The effect of pH on the swelling was examined by changes in the pH from pH 4 to pH10 the results are shown in Figure 3. It was observed that the swelling (%) increases with an increase in pH. This behavior were in agreement with the results of many research papers who studied the swelling of PVA/PAA [18, 24]. At pH 4 the obtained swelling of the films was the lowest compared to another pH, which could be due to the formation of temporary complex structure, physical crosslink between unreacted terminal groups of dendrimer (OH or NH_2) with OH of PVA and COOH of PAA [18]. As the pH increases above the pka value of PAA, which is 4.7, the fragmentation of COOH groups into carboxyl ions reduces the hydrogen bonds along the network chains thus, adds more mobility, and this leads to the swelling (%) increases with increasing pH. As the generation number of dendrimers increases the swelling (%) increases. At pH 10 the films had shown the highest swelling (%) of all films, as the generation number of dendrimers increases the swelling increases, NH_2 periphery shows to have the highest swelling values.

Effect of dendrimers content on swelling

Figure (4) shows the effect of dendrimer content on the swelling. The swelling (%) decreases as the dendrimer content increases in the hydrogel film due to the increase of the cross-linked network, which reduced the swelling ability of the films. The increase of cross-linked networks stood clear in the case of the dendrimers with terminal OH. The number of terminal OH increases with increase the generation number as shown in Table 1. On the other hand, the terminal NH_2 dendrimers do not increase as the terminal OH dendrimers. As a result, fewer cross-link networks occur.

The nature of water diffusion into hydrogels films was determined by used Fickian's law according to the following equation:

$$F = \frac{Wt}{W\infty} = kt^n$$

$$LnF = Lnk + nLnt$$

Where k is the front factor of the swelling rate, n is the exponent of swelling and W_∞ and W_t are the water intakes by the swollen hydrogel at time t and the equilibrium time, respectively.

A double-log plot of the swelling (%) versus time provides a value of n, which defines the nature of the solvent diffusion process, which is Fickian, non-Fickian diffusion kinetics or super caseii model. When $n \leq 0.5$, the mechanism is Fickian-type the diffusion absorption is controlled. But where $n = 1$ relaxation control occurs, leading to zero releases. When the value of n is between 0.5-1, where n = release follows the non-Fickian diffusion the system will be diffusion and relaxation controlled [18]. Table. 3. Shown the (n) values are ≤ 0.5 for all the hydrogels films examined which means that the water diffusion in hydrogels is usually of Fickian nature. In this case, it is believed that water molecules may simply spread across the polymer network via diffusion processes.

Table 3. Swelling kinetic parameters for films from 1% PVA/ 5% PAA with different polyamide dendrimers content.

1%PVA/5%PAA/polyamide dendrimers	n	K	1%PVA/5%PAA/polyamide dendrimers	n	k
1% G2-OH	0.37	0.50	1% G4-NH_2	0.56	0.49
2% G2-OH	0.22	0.48	2% G4-NH_2	0.53	0.48
3% G2-OH	0.23	0.43	3% G4-NH_2	0.12	0.47
1% G2-NH_2	0.1	0.48	1% G6-OH	0.09	0.51
2% G2-NH_2	0.05	0.49	2% G6-OH	0.06	0.49
3% G2-NH_2	0.3	0.46	3% G6-OH	0.02	0.45
1% G4-OH	0.09	0.48	1% G6-NH_2	0.1	0.48
2% G4-OH	0.1	0.48	2% G6-NH_2	0.19	0.46
3% G4-OH	0.5	0.50	3% G6-NH_2	0.09	0.49

By comparing the results of the films containing PVA/PAA with different proportions of PAA results obtained from Al-qudah [18], films prepared using gamma rays radiation, and the results of Lee [25] for the

film consisting of PVA/PAA and in different proportions of PAA prepared using UV rays radiation, comparing their results with ours obtained of polyamide dendrimers were prepared by induction (bulk) polymerization. The finding was all following Fickian of permeability, which confirms that the presence of polyamide dendrimers in the films does not affect the permeability of the film. On other hand in terms of durability, films of PVA/PAA polyamide dendrimers showed an increase in transformative strength and thus, the swelling could be measured at different pH levels for longer periods compared to films made from only PVA/PAA, as the latter cannot be measured for a period of more than 3 hr at most.

Adsorption Studies of metal ions on prepared films.

Effect of pH on adsorption solution.

Figure 5 illustrates the adsorption capacity of hydrogel films PVA/PAA without dendrimers for Zn^{2+}, Ni^{2+}, Cu^{2+}, and Fe^{2+} ions in their individual solutions at different pH. The pH values ranged from 2, 4, and 6 for metal ions. The results showed that the change in pH value of the medium resulted in a significant change in the amount of adsorption capacity of the ions Zn^{2+} , Ni^{2+} , Cu^{2+}, Fe^{2+}. The chelating properties of the hydrogels films functional groups are affected by the pH. The adsorption capacities of the four metal ions increased as the initial pH value of the solution increases, also the adsorption quantities illustrate sharp increases for pH from 2 to 6. At pH > 6, precipitations of hydroxide may to occur simultaneously, and could not lead to an accurate interpretation of adsorption. In the case, at low pH condition, the main effective adsorption sites of hydrogel films; (OH, COOH) both groups easily protonated, which reduce its adsorption therefore, low ion adsorption will take place. Although, at high pH conditions, proton functional groups will be taken off leading to an increase in adsorption activity, which resulted in higher ion adsorption.

Effect of polyamide dendrimers generation and content on adsorption of metal ions in solution.

The effect of dendrimer generation on the metal adsorption was carried out using different metal ions, Figure 6 shown an increase in dendrimer content into film companied with increase in generation number resulting in increase in the adsorption. It is clear that an increase in the dendrimer content and increase in the generation number in the hydrogel film is accompanied by an increase in the adsorption of ion metal to maximum value. This due to the ability of dendrimers capsulate the metal ions within its prose structure [26-30]. The results showed that in the initial stages of immersion, the adsorption of metal ions was rapid. This could be due to a large number of vacant active sites were available for adsorption in the initial stage.

At pH2 the trend in both figures are the same, but at G2-OH, there is an increase in metal uptake as the dendrimers content increases in the film, when generation number increased to G4-OH enhancement in metal uptake was observed. On the other hand, at G6-OH there is no enhancement in metal uptake was observed, but still an increase in metal uptake as dendrimers content increases. It is clear from the figures, that the metal ion adsorptions have different response to the film, Cu^{2+} ion shows to have lowest

value compared with others followed with Fe^{2+} then Zn^{2+} and lastly Ni^{2+}. It must be stated here this behavior occurred in all films with different dendrimers content and generation. So that polyamide dendrimer PVA/PAA film prefer to adsorb Ni^{2+} ion on Cu^{2+} ion in other word, the films have selectivity toward Ni^{2+} ion then Zn^{2+}, Fe^{2+} and then Cu^{2+}.

This observation was similarly occurred with dendrimers with NH_2 and other generation as shown in Figure 6. This behavior of selectivity was reported by [31].

It is observed from Figure 6, that in high generations, the adsorption of metal ions increases compared to lower generations, due to the large number of functional groups that are related to the metal ions and the formation of complexes, as well as due to the large number of internal voids that have the ability to retain the metal ions. The adsorption of Ni^{2+}, Zn^{2+}, Fe^{2+} and Cu^{2+} metal ions and comparison of adsorption of metal ions were studied in the case of the presence of the polyamide dendrimer or not. The films adsorption capacity is found for Ni^{2+}, Zn^{2+}, Fe^{2+} and Cu^{2+} metal ions in order from $Ni^{2+} > Zn^{2+} > Fe^{2+} > Cu^{2+}$.

Conclusion

The hydrogel films of PVA/PAA polyamide dendrimers were successfully prepared by thermo induction esterification amidification reactions. The prepared hydrogel shown to have high swelling (%) and high gel content compared to a neat film PVA/PAA. Hydrogel film contains G6-OH and G6-NH_2 was the highest gel content. The lowest dendrimers content had the highest swelling (%) that was observed in dendrimers with OH periphery. The behaviour of water diffusion through the hydrogel films followed the Fickian character. The adsorptions of metal ions were depending on pH, generation number and dendrimers content. The adsorption increase at pH 6, high generation number and high dendrimers content regardless of the periphery. The hydrogel films show to have selectivity toward Ni^{2+} ion then Zn^{2+}, Fe^{2+} and then Cu^{2+}. The addition of polyamide dendrimers has shown to enhance the properties of PVA/PAA films.

References

1. Wu L et al (2020) Strong and tough PVA/PAA hydrogel fiber with highly strain sensitivity enabled by coating MWCNTs.Compos. Part A Appl. Sci. Manuf.138,
2. Cheng Y et al (2020) High strength Polyvinyl alcohol/Polyacrylic acid (PVA/PAA) hydrogel fabricated by Cold-Drawn method for cartilage tissue substitutes.J. Biomater. Sci. Polym. Ed.31,
3. Diken ME et al (2020) Synthesis, characterization, and their some chemical and biological properties of PVA/PAA/nPS hydrogel nanocomposites: Hydrogel and wound dressing. J Bioact Compat Polym 35:203–215
4. Yan, Yu et al (2022) A Tough, Slippery, and Anticoagulant Double-Network Hydrogel Coating. Appl Polym Mater 4:5941−5951

5. Zhang S, Shi Q, Christodoulatos C, Meng X (2019) Lead and cadmium adsorption by electrospun PVA/PAA nanofibers: Batch, spectroscopic, and modeling study. Chemosphere 233:405–413
6. Hardian R, Pogany P, Lee YM, Szekely G (2021) Molecular sieving using metal-polymer coordination membranes in organic media. J Mater Chem A 9:14400–14410
7. Alammar A et al (2020) Architecting neonicotinoid-scavenging nanocomposite hydrogels for environmental remediation.Appl. Mater. Today21,
8. Kunalan S, Palanivelu K, Sachin EK, Teplyakov DA (2022) S. V. V. Thin-film hydrogel polymer layered polyvinyltrimethylsilane dual-layer flat-bed composite membrane for CO2 gas separation.J. Appl. Polym. Sci.139,
9. Chen Q, Zhu L (2012) PVA/PVAm hydrogel membranes for removal of metal ions from aqueous solution. Appl Mech Mater 130–134:1507–1510
10. He J, Chen JP (2014) Cu(II)-imprinted poly(vinyl alcohol)/poly(acrylic acid) membrane for greater enhancement in sequestration of copper ion in the presence of competitive heavy metal ions: Material development, process demonstration, and study of mechanisms. Ind Eng Chem Res 53:20223–20233
11. Li Z et al (2022) Fabrication of a novel electrospun polyvinyl alcohol/polyacrylic acid nanofiber adsorbent loading with montmorillonite or zeolite for uranium (VI) removal. J Radioanal Nucl Chem 331:297–307
12. Hu Z et al (2021) pH-responsive antibacterial film based polyvinyl alcohol/poly (acrylic acid) incorporated with aminoethyl-phloretin and application to pork preservation.Food Res. Int.147,
13. Zhan F, Yan X, Li J, Sheng F, Li B (2021) Encapsulation of tangeretin in PVA/PAA crosslinking electrospun fibers by emulsion-electrospinning: Morphology characterization, slow-release, and antioxidant activity assessment.Food Chem.337,
14. Jinhua X et al (2020) Phosphate functionalized poly(vinyl alcohol)/poly(acrylic acid) (PVA/PAA): an electrospinning nanofiber for uranium separation. J Radioanal Nucl Chem 326:475–486
15. Bessbousse H, Verchère JF, Lebrun L (2012) Characterisation of metal-complexing membranes prepared by the semi-interpenetrating polymer networks technique. Application to the removal of heavy metal ions from aqueous solutions. Chem Eng J 187:16–28
16. Kim J, Kang T, Kim H, Shin HJ, Oh SG (2019) Preparation of PVA/PAA nanofibers containing thiol-modified silica particles by electrospinning as an eco-friendly Cu (II) adsorbent. J Ind Eng Chem 77:273–279
17. Byun H et al (2008) Swelling behavior and drug release of poly(vinyl alcohol) hydrogel cross-linked with poly(acrylic acid). Macromol Res 16:189–193
18. Al-qudah YHF, Mahmoud GA, Abdel Khalek MA (2014) Radiation crosslinked poly (vinyl alcohol)/acrylic acid copolymer for removal of heavy metal ions from aqueous solutions. J Radiat Res Appl Sci 7:135–145
19. Tomalia DA et al (1985) *A New Class of Polymers: Starburst-Dendritic Macromolecules*.Polymer Journalvol. 17

20. George R, Newkome ZYGRB (1985) V. K. G. Cascade molecules: A new approch to micelles.J. Org. Chem2003–2004
21. Lyu Z, Ding L, Tintaru A, Peng L (2020) Self-Assembling Supramolecular Dendrimers for Biomedical Applications: Lessons Learned from Poly(amidoamine) Dendrimers. Acc Chem Res 53:2936–2949
22. de Araújo RV, Santos SdaS, Ferreira EI, Giarolla J (2018) New Advances in General Biomedical Applications of PAMAM Dendrimers.Molecules23,
23. Abdalgader A, Elejmi A, Elhrari W, Abdoorhman Z (2021) Synthesis and antibacterial property of polyamide dendrimers based on tetraethyl–1,1,3,3–propanetetracarboxylate. J Polym Res 28:462
24. CUDEMAN LINDAF N. A. P. *Preparation and Characterization of pH-Sensitive, Interpenetrating Networks of Poly (vinyl alcohol) and Poly(acrylic acid)*
25. Lee YM, Kim SH, Cho CS (1996) Synthesis and swelling characteristics of pH and thermo-responsive interpenetrating polymer network hydrogel composed of poly(vinyl alcohol) and poly(acrylic acid). J Appl Polym Sci 62:301–311
26. Scott RWJ, Wilson OM, Crooks RM (2005) Synthesis, characterization, and applications of dendrimer-encapsulated nanoparticles. J Phys Chem B 109:692–704
27. Ottaviani MF, Valluzzi R, Balogh L (2002) Internal structure of silver-poly(amidoamine) dendrimer complexes and nanocomposites. Macromolecules 35:5105–5115
28. Balogh L, Swanson DR, Tomalia DA, Hagnauer GL, McManus AT (2001) Dendrimer-Silver Complexes and Nanocomposites as Antimicrobial Agents. Nano Lett 1:18–21
29. Rajesh R, Venkatesan R (2012) Encapsulation of silver nanoparticles into graphite grafted with hyperbranched poly(amidoamine) dendrimer and their catalytic activity towards reduction of nitro aromatics. J Mol Catal A Chem 359:88–96
30. Štofik M, Strýhal Z, Malý J (2009) Dendrimer-encapsulated silver nanoparticles as a novel electrochemical label for sensitive immunosensors. Biosens Bioelectron 24:1918–1923
31. Muller J et al (2021) Complexation properties of water-soluble poly(vinyl alcohol) (PVA)-based acidic chelating polymers.Sep. Purif. Technol.255,

Figures

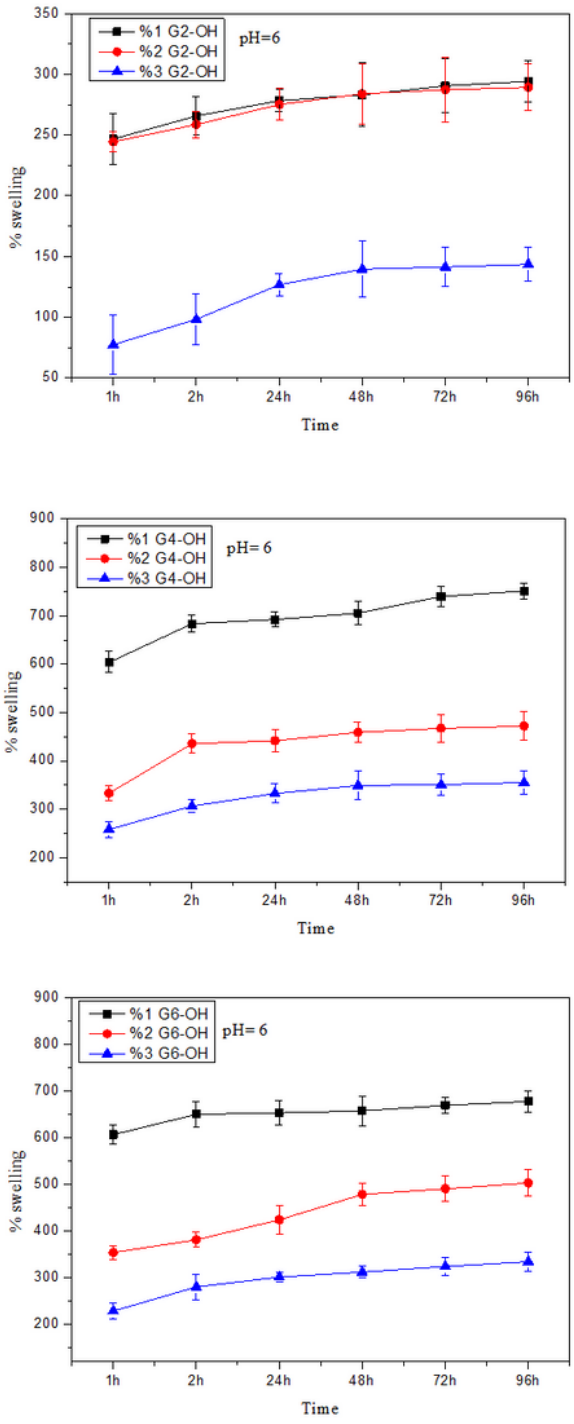
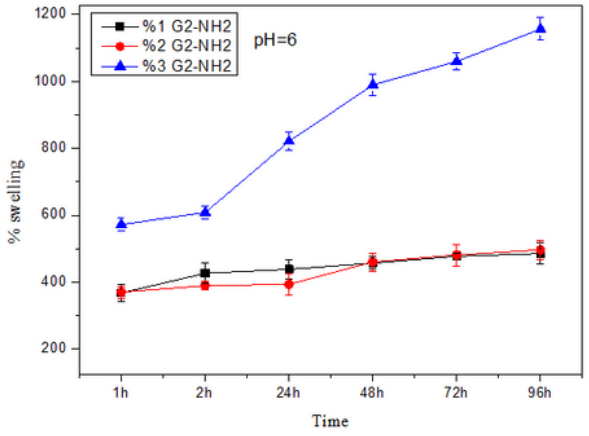
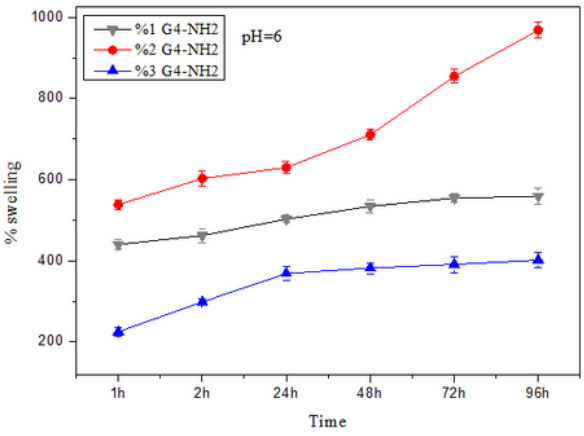


Figure 1

Effect of time on the swelling (%) of polyamide dendrimers PAA/PVA films with OH periphery at three dendrimers content 1,2 and 3% at pH 6.





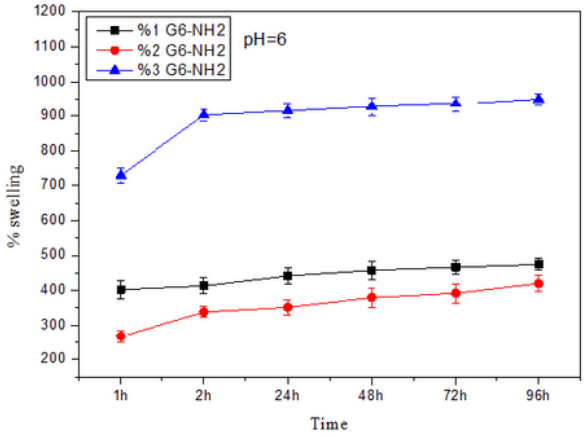


Figure 2

Effect of time on the swelling (%) of polyamide dendrimers PAA/PVA films with NH_2 periphery at three dendrimers content 1,2 and 3% and at pH 6.

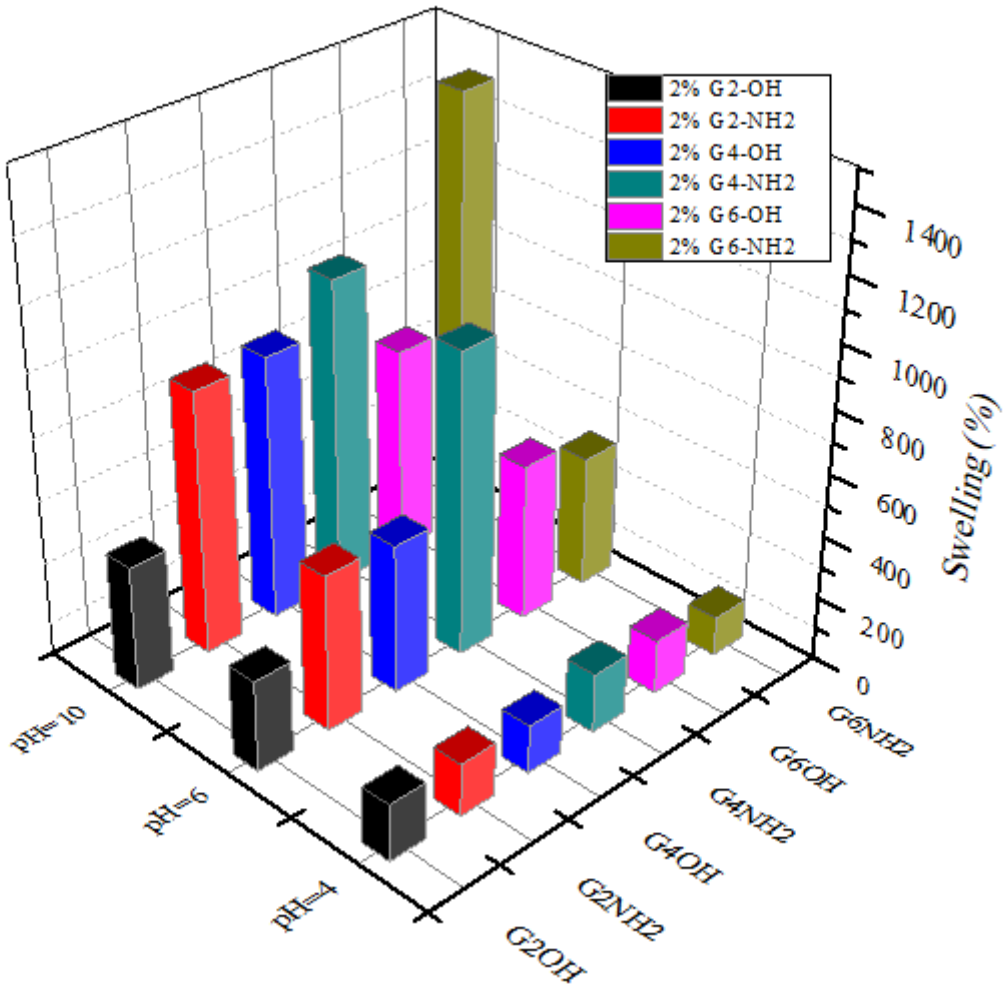


Figure 3

The effect of pH on the swelling for dendrimers PAA/PVA films

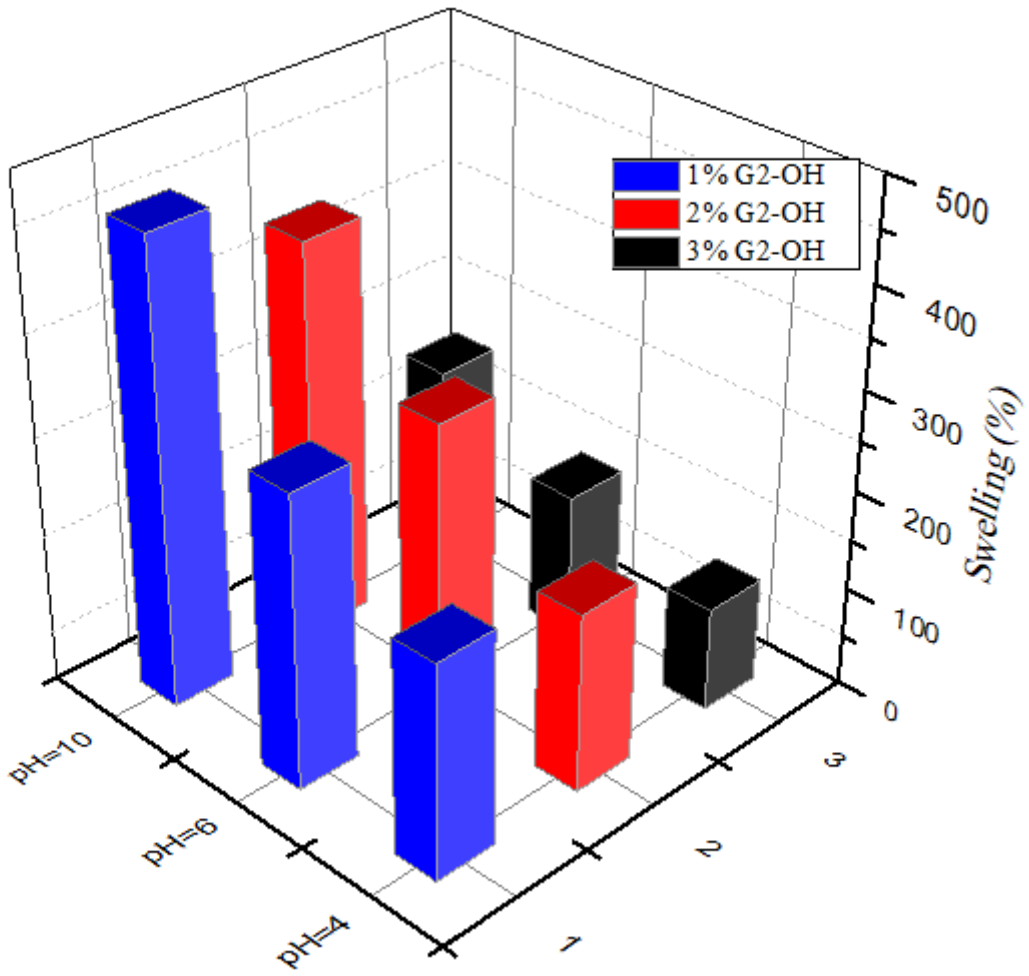


Figure 4

The effect of dendrimer content on the swelling

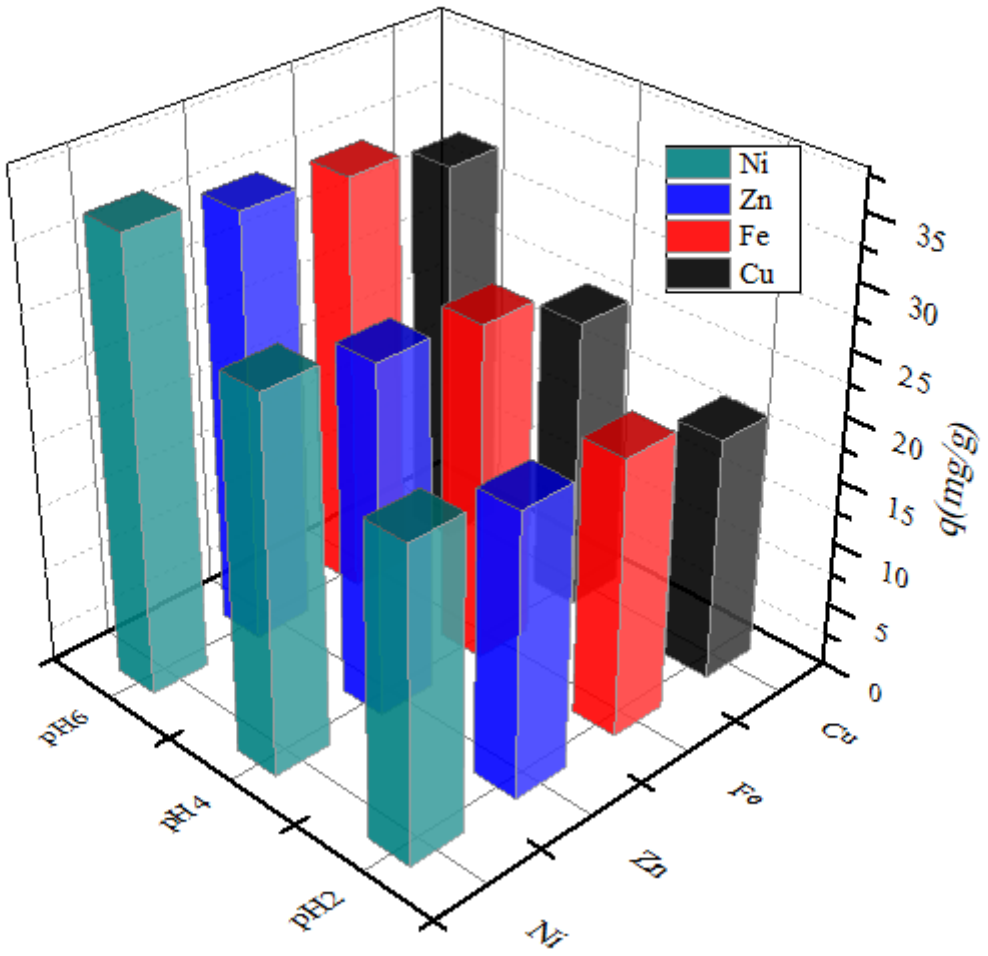


Figure 5

Effect of pH on the adsorption of Ni^{2+} , Zn^{2+} , Fe^{2+}, and Cu^{2+} ions onto PVA/PAA films , the initial metal ion concentration 100 mg/l.

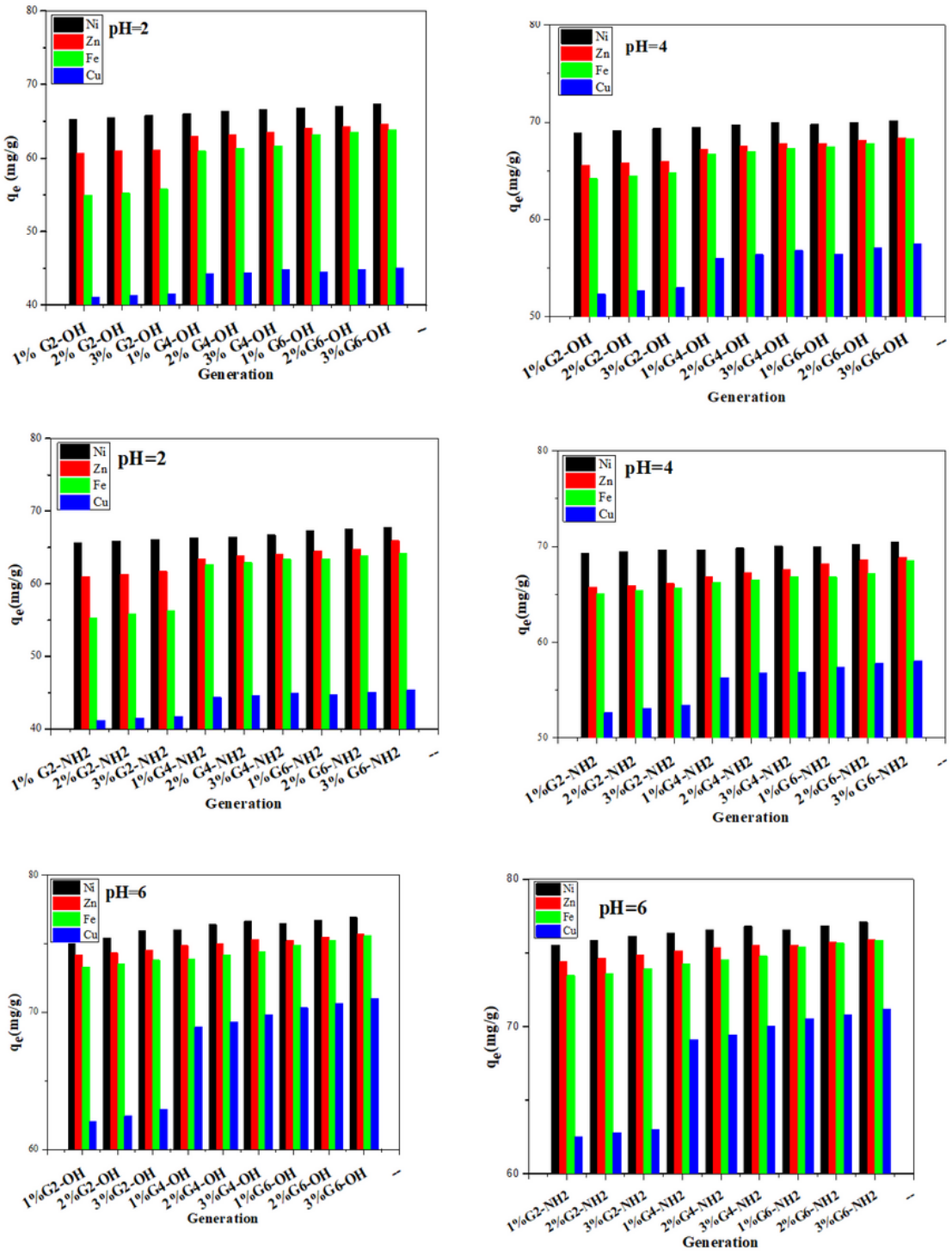


Figure 6

Effect of polyamide dendrimer content and generation number on the adsorption of Ni^{2+}, Zn^{2+}, Fe^{2+}, and Cu^{2+} ions , the initial metal ion concentration 100 mg/l.