Journal of Applied Sciences and Nanotechnology, Vol. 2, No. 4 (2022)

Journal of Applied Sciences and Nanotechnology

Journal homepage: https://jasn.uotechnology.edu.iq/

Effect of Crosslinking Agent (Zinc Chloride) on the Swelling Ratio and Water Retention Capacity of Polyacrylate and Polyvinyl Alcohol

[1,2]Saja A. Kadhim*, [1]Awham M. Hameed, [1]Rashed T. Rasheed

[1]Department of Applied Sciences, University of Technology – Iraq

[2]Educational Rusafa Directorate II, Ministry of Education – Iraq

Article information

Article history:
Received: February, 10, 2022
Accepted: June, 15, 2022
Available online: December, 10, 2022

Keywords:
Superabsorbent polymer,
Zinc chloride,
Swelling ratio,
Water retention capacity

Corresponding Author:
Saja A. Kadhim
*as.18.49@grad.uotechnology.edu.iq

Abstract

In this study, using potassium polyacrylate (KPA), polyvinylalcohol (PVA), and zinc chloride as cross-linking agents, successfully synthesized novel superabsorbent polymers. Different weight ratios of KPA and PVA were used to prepare the polymers using polymerization solution. So, polymers with different weight ratios made from PVA and KPA. Superabsorbent polymers (SAPs) were produced using a simple approach at ambient temperature. By comparing absorption peaks, Fourier transform infrared spectroscopy (FTIR) and UV analysis were utilized to investigate the molecular interactions. The morphology of superabsorbent polymers was investigated by scanning electron microscopy (SEM). According to FT-IR, UV, and SEM results, the superabsorbent polymers (Zn-KPA and Zn-PVA) were prepared successfully. A comparison of Zn-KPA and Zn-PVA SAPs was conducted. The effects of cross-linking on water absorption were investigated. The Zn-PVA superabsorbent polymer has a maximum swelling capacity of 407%, while the swelling ratio of the Zn-KPA was 304%. Thus, these prepared superabsorbent polymers could be used for agricultural applications such as water storage. With increasing zinc chloride content and time, superabsorbent polymers' swelling capacity has considerably improved.

DOI: 10.53293/jasn.2022.4703.1138, Department of Applied Sciences, University of Technology

1. Introduction

Superabsorbent polymer (SAP) is a hydrophilic material with 3-D networks formed by chemical or physical bonds. SAP has many advantages, including the ability to absorb large amounts of water (100 to 1000 times its dry weight) in a short period (10 – 30 min) without dissolving and having a high-water storage capacity [1-3]. SAP is widely utilized in a variety of industries, including medical, agriculture [4, 5], commodities, environmental pollution remediation, and others [6, 7]. SAPs made from natural polymers like cellulose, chitosan, and starch have the benefit of being biodegradable. However, because of their low water absorption rate, they must be employed in larger quantities [8, 9]. SAPs made from synthetic polymers, such as polyacrylic acid (PAA), polyacrylamide (PAM), and polyvinyl alcohol (PVA), on the other hand, have cheap costs, extended service lives, and a high-water absorption rate [10, 11]. In this work, SAPs have been synthesized using potassium polyacrylate (KPA) and polyvinyl alcohol (PVA). Polyacrylic acid (PAA) is a perfect backbone for producing superabsorbent polymers [13] due to its superior water absorbance, retention ability, biocompatibility, inertness, and non-toxicity [12]. It is used for paints and cosmetics, emerging applications, drilling fluids, and metal quenching [13]. In addition, polyvinyl alcohol (PVA) is an artificial hydrophilic polymer with medium water retention ability that is non-toxic and non-carcinogenic [14]. It is used to make paper, textile warp sizing, thickening, and various paints as beads or water solutions [18]. Even though SAPs have been extensively explored, enhancing their qualities, improving the theory, and increasing the controllability of their structural attributes are still major concerns. The synthesis and characterization of carboxymethylcellulose sodium salt (CMCNa) and hydroxyethyl cellulose (HEC)-based biodegradable hydrogels employing citric acid (CA) as a crosslinker is covered by Das, Dipankar, et al, (2021). The appropriate distribution of cellulose nanocrystals (CNCs) in the hydrogel matrix, as well as the optimal usage of crosslinkers, can result in a promising hydrogel material that can absorb and release water in a regulated manner, improving the use of the available water resources for agricultural purposes [19]. It has been shown in another study by Zhiguo Wang, et al., (2020) that superabsorbent polymer was obtained using free radical grafting solution polymerization of acrylamide (AM), acrylic acid (AA), and N, N'-dimethyl-N-ethyl ethacryloxyl ethyl ammonium bromide (DMAEA-EB) onto konjac glucomannan (KGM) with potassium persulfate ($K_2S_2O_8$) as initiator and N, N'-methylenebisacryl amide (MBA) as a crosslinker. Where, KAAD can be employed as a functional material in building, textiles, pharmaceutics, and other industries due to its high superabsorbent features [20]. In this study, SAPs have been synthesized using industrial polymeric materials such as potassium polyacrylate (KPA), polyvinyl alcohol (PVA), and zinc chloride as cross-linking by the solution polymerization method. The ability of SAP to absorb and retain water has been examined. These superabsorbent polymers could be employed for agricultural purposes like water storage. Successful solution polymerization was observed using FTIR and UV spectra. The morphology of superabsorbent polymers was studied using scanning electron microscopy (SEM).

2. Experimental Procedure

2.1. Materials

Potassium polyacrylate (C3H3KO2)n (99.9%, apparent density of 0.56 ml/g, monomer residual less than 500, potassium 21.60%, MAS Group Inc., China), Polyvinyl alcohol (C2H4O) n (the average molecular weight of 67, 000, degree of polymerization 1, 400, Me Scientific Engineering Ltd., UK), Zinc chloride ($ZnCl_2$), (purity 99.9%; made in Belgium). Sodium hydroxide (NaOH) (99.9%; BDH Company).

2.2 Preparation of Super Absorbent Polymers

2.2.1 Preparation of Zinc polyacrylate (Zn-KPA) SAPs

Stock solution of potassium polyacrylate (KPA) solution (2.174 % w/v) was synthesized by dissolving 5 g of KPA in distilled water (230 ml). Weights of (0.3, 0.4, 0.5, 0.6) g of $ZnCl_2$ were added separately to every 25 ml of stock solution and stirred over a magnetic stirrer for 30 min, at 70°C. The reaction was done according to Figure 1. The insoluble compound was collected by removing the water and dried at 25°C for 48 hours.

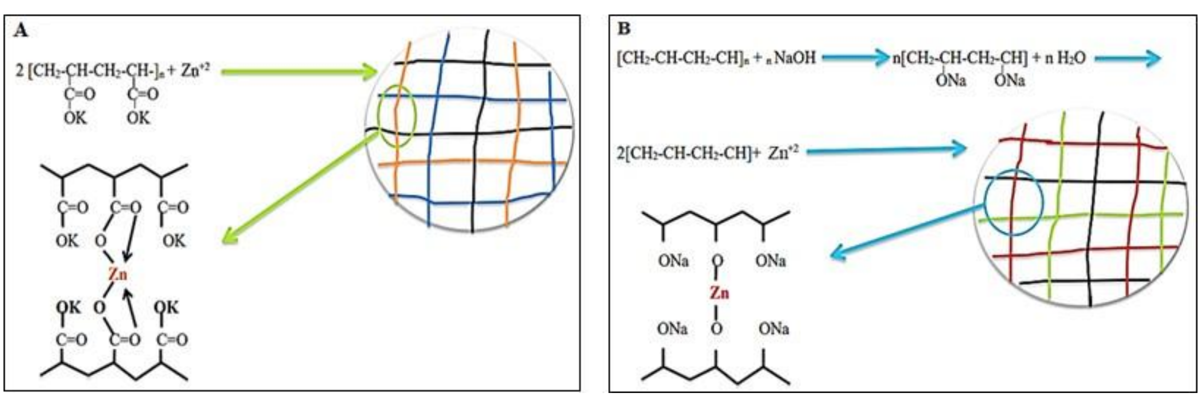

Figure 1: **A** (Zn-PA) SAP reaction, **B** (Zn-PVA) SAPs reaction.

2.2.2 Preparation of Zinc Polyvinyl alcohol (Zn-PVA) SAPs

Polyvinyl alcohol (PVA) solution (2.174 % w/v) was synthesized by dissolving 5 g of polymer material in a basic solution (25 ml) which consists of NaOH: distilled water at (8:100) ratio. Weights of (0.2, 0.4, 0.6, 0.8, 1 and 1.2) g of $ZnCl_2$ were added separately to the solution and stirred onto a magnetic stirrer for 30 min at 70°C. The reaction was done according to Figure 2. After that the prepared complex was emptied in a petri dish and dried at 25 °C for 48 hours.

2.3 Analytical Methods

TENSOR-27/ FTIR spectrometer - Bruker Optics Company- Germany was used in the wavenumber range of (4000–400) cm^{-1}). A TU-1901 spectrometer was used to record the UV-Vis spectra (Purkinje General Instrument, Beijing, China). Scanning electron microscopy (SEM) was used to test the morphological properties of superabsorbent polymers using (FESEM Zeiss Sigma 300- HV Germany with EHT=5KV, Mag=100 KX).

2.3.1 Swelling Ratio of SAPs

Swelling kinetics refers to the time needed for zinc polyvinyl alcohol (Zn- PVA) or zinc polyacrylate (Zn-KPA) complexes to reach their maximum swelling capacity. To carry out this experiment, different weights of dry complexes (Zn-PVA or Zn-KPA) at weights of salt (0.2, 0.4, 0.6, 0.8 and 1) g. These complexes were cut into small pieces, weighed, and immersed in the distilled water for 24 hours for (Zn- KPA) complex, and 9 hours for (Zn-PVA) complex, at 25 °C. The swollen specimens were removed and weighed after being cleaned with filter paper to remove excess water from the surface. Each weight was measured three times to get an average value. The degree of swelling is calculated using the equation below [21]:

$$\textbf{Swelling Ratio (\%)} = [(W_S - W_D)/W_D] \times 100\% \qquad (1)$$

Where W_S (g) is the wet specimens after filtration, and W_D (g), is the dried specimens.

2.3.2 Water Retention Capacity of SAPs

The water retention of superabsorbent polymers was examined utilizing the following procedure. Small pieces of SAPs swelled to saturate into distilled water. SAPs were wiped with filter paper and placed in Petri dishes at ambient temperature. After a constant period, time (6 hours for KPA and 3 hours for PVA), the weight of the SAPs was recorded. This procedure was repeated until the weight remained unchanged. The amount of water retention is calculated using the equation below [22]:

$$\textbf{Water retention capacity \%} = (W_T - W_D / W_S - W_D) \times 100\% \qquad (2)$$

Where W_T denotes the weight of SAP at time "T", W_D denotes the weight of dry SAP, and W_S denotes the weight of SAP when fully swelled.

3. Results and Discussion

3.1 FTIR Analysis

The nature of the bond creation was discovered using FTIR spectroscopic analysis. FTIR absorption spectra of KPA and Zn-KPA containing 0.3 g of $ZnCl_2$ superabsorbent polymer produced using the solution polymerization process are shown in Figure 3. The broadband at 3439 cm^{-1} is due to O-H stretching. C-H stretching, carbonyl group (C=O) stretching, ν_{asym} (COO-) stretching, C-H bending, and ν_{asym} (COO-) stretching of KPA were attributed to the peaks at (2924, 1695, 1602, 1522, and 1105) cm^{-1}, respectively [23-25]. The FTIR characteristic peaks of the Zn-KPA spectrum (Figure 3), showed a large shift from 1695 cm^{-1} to 1550 cm^{-1} ($\nu_{asym}(COO^-)$, This might be due to the strong interaction between the KPA's carboxyl group and Zinc, and a high wavenumber shift from 1602 cm^{-1} to 1535 cm^{-1} ($\nu_{C=O}$ stretching) with a decreasing peak intensity. The downshift of this peak is due to the electrostatic attraction between the Zn^{+2} cation and the carbonyl group, which is the highest reactive group of KPA, these results indicate the carboxyl groups are corporation as a bidentate ligand [26].

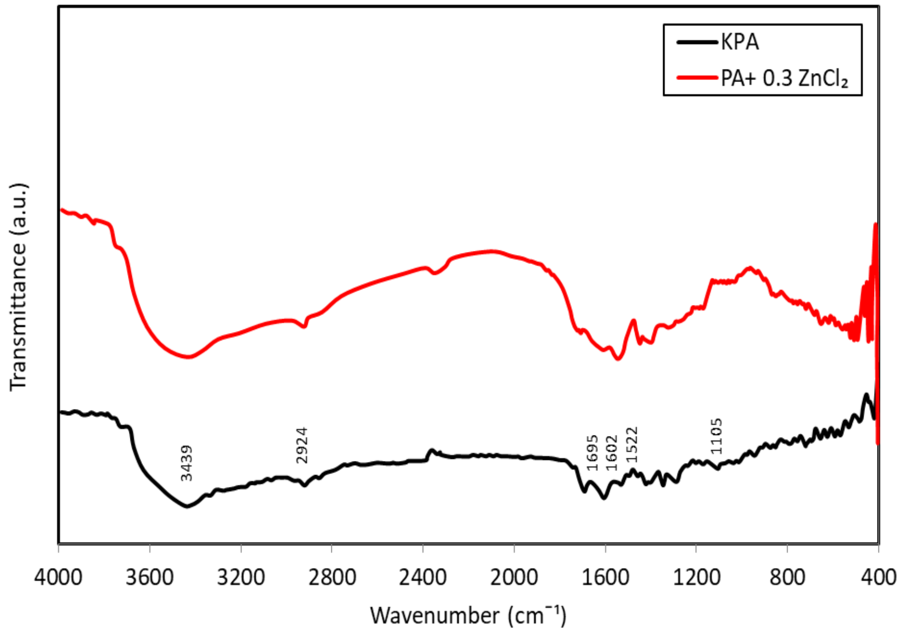

Figure 3: FTIR spectra of PAA and Zn-PA (0.3 g of $ZnCl_2$).

Furthermore, some of the peaks disappeared due to the Zn-O stretching vibration [27]. FTIR spectra of PVA and the Zn-PVA (0.8 g of $ZnCl_2$) super absorbent polymer can be seen in Figure 4. The main peaks of PVA were observed at (3392, 2922, 1599, 1413 and 1101) cm^{-1} are attributed to the O–H stretching vibration of the hydroxyl group, asymmetric stretching vibration of C-H, C-C stretching, bending vibration of $-CH_2$, and stretching vibration of C–O, respectively.

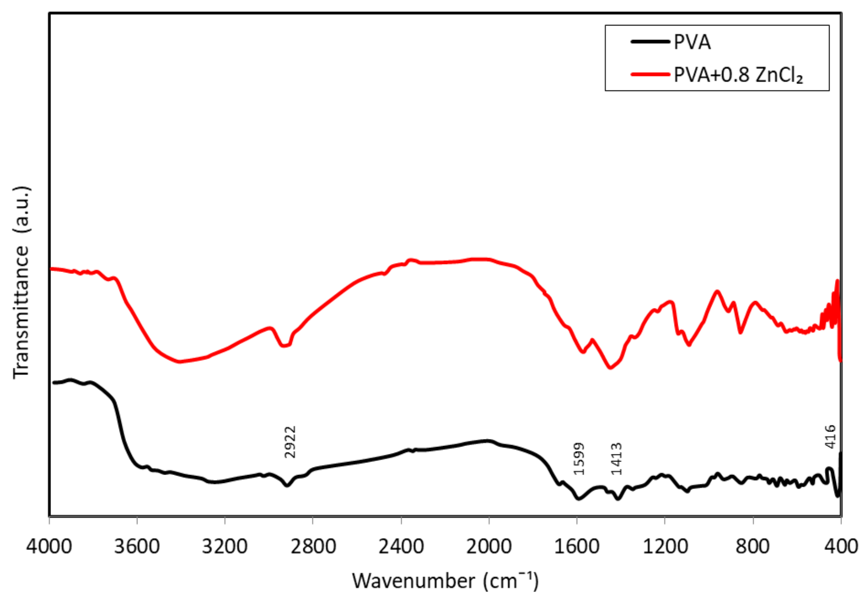

Figure 4: FTIR spectra of PVA and Zn-PVA (0.6 g of $ZnCl_2$).

The FTIR characteristic peaks of the Zn-PVA spectrum (Figure 4), showed a bottom shift from 1599 cm^{-1} to 1570 cm^{-1} due to the strong interaction between the PVA's hydroxyl group and zinc, and a high wavenumber shift from 1413 cm^{-1} to 1448 cm^{-1} with a decreasing peak intensity due to the electrostatic attraction between the Zn^{+2}cation and the hydroxyl group. as well as, the new peaks at (914, and 858) cm^{-1} are attributed to the Zn–O stretching vibration [28, 29].

3.2 UV-Vis Spectroscopy

UV-Vis spectroscopy gives useful information on the reflectance, absorbance, and transmittance of polymeric materials. [30]. It is well known that PVA and KPA are very important polymers because they have excellent optical properties, such as great translucency. The UV absorbance spectra of KPA, Zn-KPA (0.3 g of $ZnCl_2$) and PVA, Zn-PVA (0.8 g of $ZnCl_2$) dispersion are depicted in Figures 5 and 6 respectively. The absorbance spectra of KPA and PVA show a distinct peak at 260 nm, which can be attributed to the presence of carbonyl in the carboxylic group and n-π* in KPA and PVA, respectively [31].

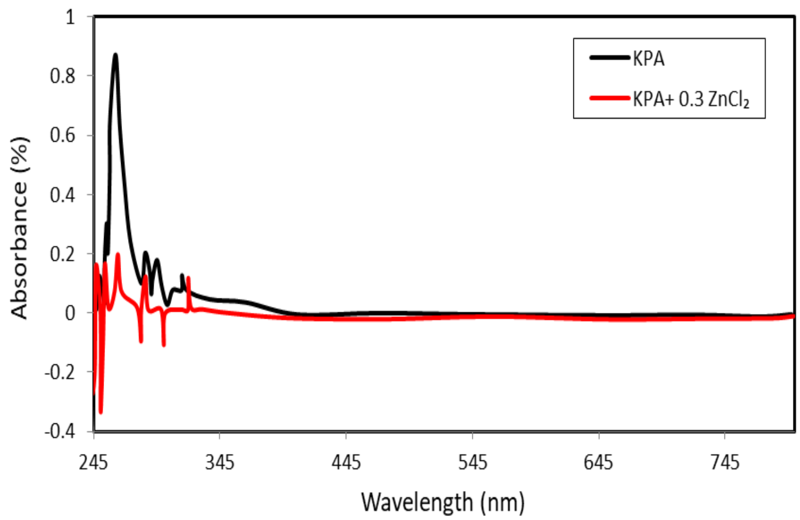

Figure 5: UV-vis spectra of KPA and Zn-PA (0.3$ZnCl_2$).

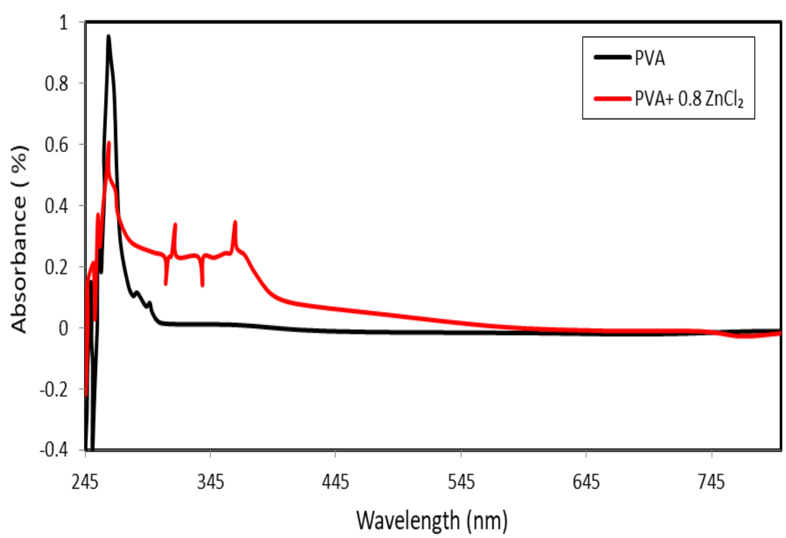

Figure 6: UV-vis spectra of PVA and Zn-PVA (0.8 g of $ZnCl_2$)

The absorption peak of KPA increases to 265 nm and to 261 nm for PVA with the addition of zinc chloride, respectively [31]. Zn-PVA and Zn-KPA super absorbent polymers reveal all the bands that are spotted in neat KPA and PVA with a minor distortion in the placement of the bands and some of the bands disappear due to the interaction between the polymer and salt. Hence, the UV–Vis spectra revealed that the absorption was mainly in the UV area, with a small visible wavelength range as the samples were colorless and semi-transparent. This result agrees with Deshmukh K, *et al* who studied the UV spectra of polymer blends depending on cationic polyamine and anionic polyvinyl alcohol [32].

3.3 SEM of SAPs

Figure 7(A and B) shows SEM micrographs of KPA and (Zn-KPA) respectively. It can be noticed that KPA has a heterogeneous surface and regular fibrous structure with the presence of agglomerate indicates that it is suitable for water absorption. Figure 7B shows the dispersion of the Zn^{+2} ions in the composition of the SAP. Where zinc chloride reacts with KPA and forms groups of small balls structures [33, 34].

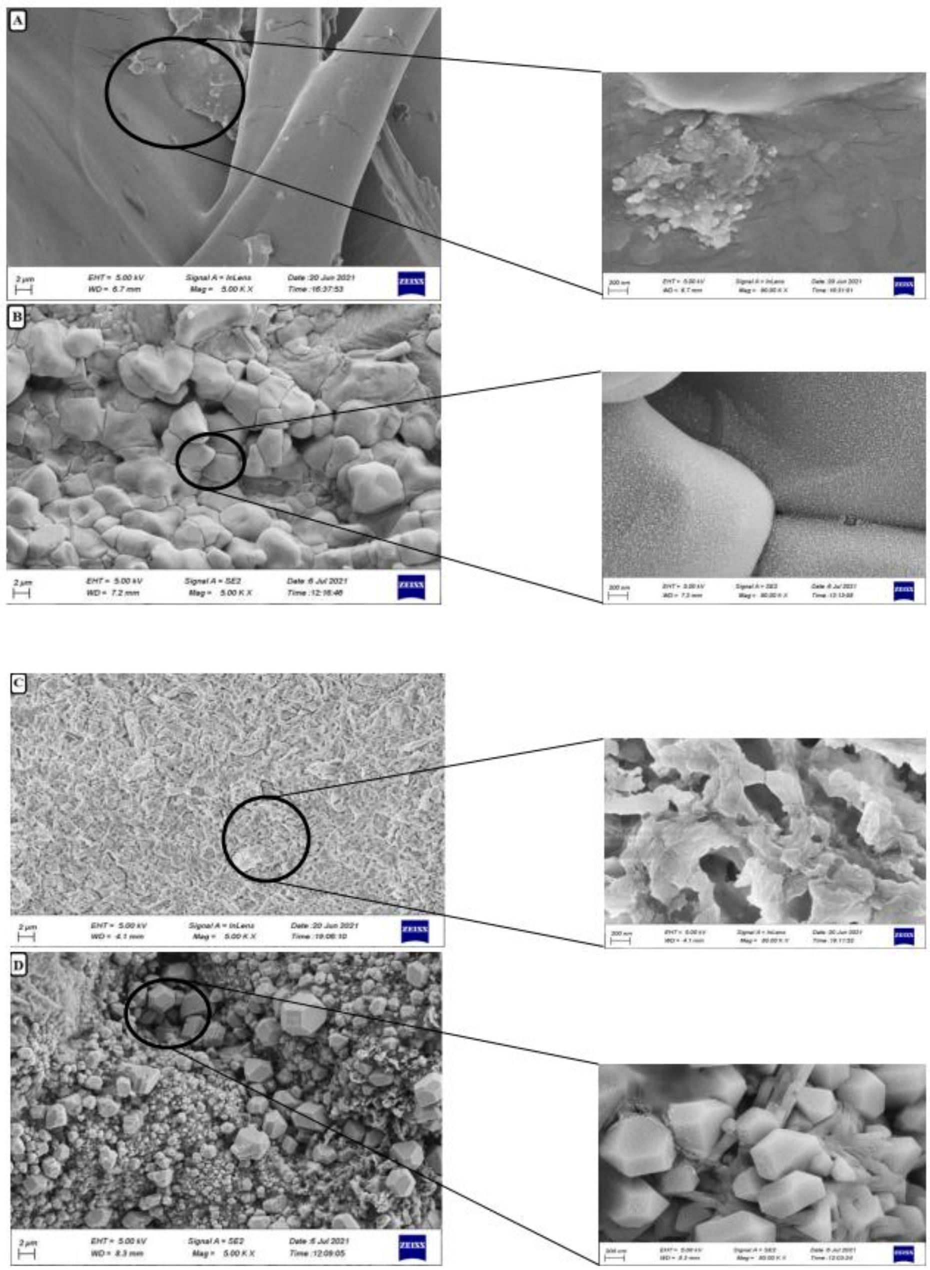

Figure 7: SEM micrographs of (A) KPA, (B) Zn-PA (0.3 g of $ZnCl_2$)) (C) PVA and (D) Zn-PVA (0.8 g of $ZnCl_2$).

The texture of the KPA and the Zn-KPA containing 0.3 wt. of $ZnCl_2$ differed noticeably. These variations confirm the influence of the Zn^{+2} ions on the absorption of water molecules. It can be said that the polymer structure has become similar to the structure of a porous sponge that can absorb more water. SEM images of PVA and (Zn-PVA) are seen in Figure 7 (C, and D) respectively, especially at low magnifications, PVA appears porous and has a spongy structure, and this becomes clearer at higher magnifications. The pores appear interconnected, overlapping, and open type as well as being uniformly scattered with nano or macro dimensions [35]. When zinc chloride is added (Figure 7D) a microscopic structure is generated that looks like small balls and has less porosity. When compared to structures without aluminum chloride, the composition seems denser and less regular in the distribution of pores. Zinc chloride acts as a catalyst, increasing the rate of cross-linking during the polymerization process, so allowing for the creation of a more cohesive molecular structure with a greater viscosity.

3.4 Swelling Ratio

The swelling ratio of KPA and Zn-KPA can be seen in Figures 8 and 9. The water absorbency increased with the immersion time while, decreased with the $ZnCl_2$ content increased from 0.3 g to 0.6 g for KPA and increased with the $ZnCl_2$ addition from 0.2 g to 0.8 g for PVA. It is seen that 0.3 g of Zn-PA and 0.8 g of Zn-PVA provided the highest swelling capacity of 305 % and 407 % respectively.

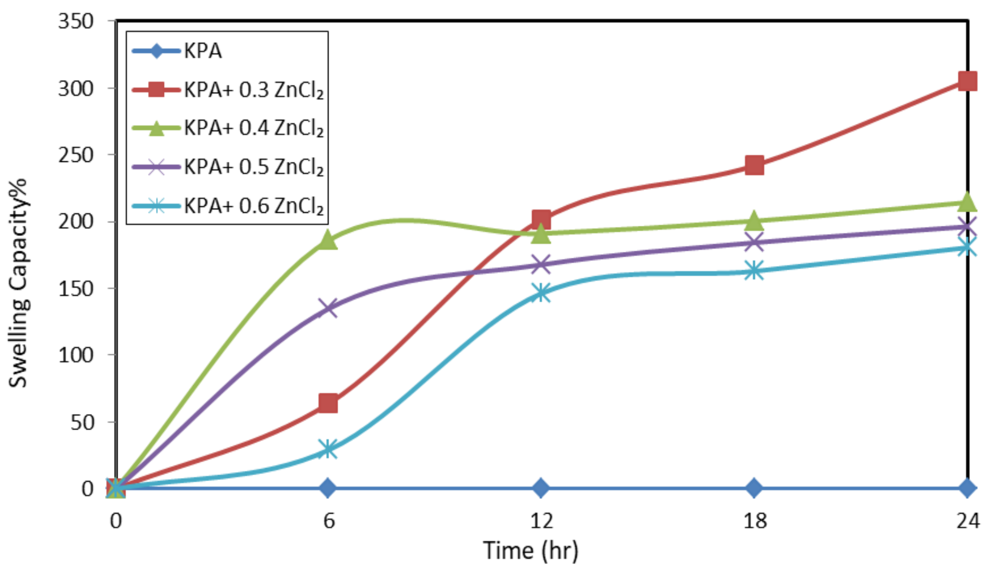

Figure 8: Swelling Ratio (%) of KPA and (Zn-KPA) SAPs.

The cross-links between the polymer chains form a three-dimensional network that keeps the SAPs from dissolving in water and the swelling process from continuing forever. This phenomenon is caused by the elastic retraction forces of the polymeric network [36]. The retraction forces are in balance, and the chains tend to swell to indefinite dilution. Cross-linking happens most often during the polymerization reaction step of SAP manufacturing. SAP particles that have been cross-linked can considerably increase both flow and absorption against pressure. SEM showed particle agglomeration, and there are pourers. The physical explanation behind of this phenomenon are formation the cross-linkage between polymer chains. During the swelling process, cross-linking agents protect the form of the particles. This results in a less tightly packed gel with air spaces, allowing the fluid to flow freely in a pattern with high permeability [36]. However, when the $ZnCl_2$ content was above 0.3 for KPA and above 0.8 g for PVA, the superabsorbent polymer was more rigid and could not absorb more water, due to an overabundance of cross-linker, resulting in a denser network structure and poorer water absorbency [22].

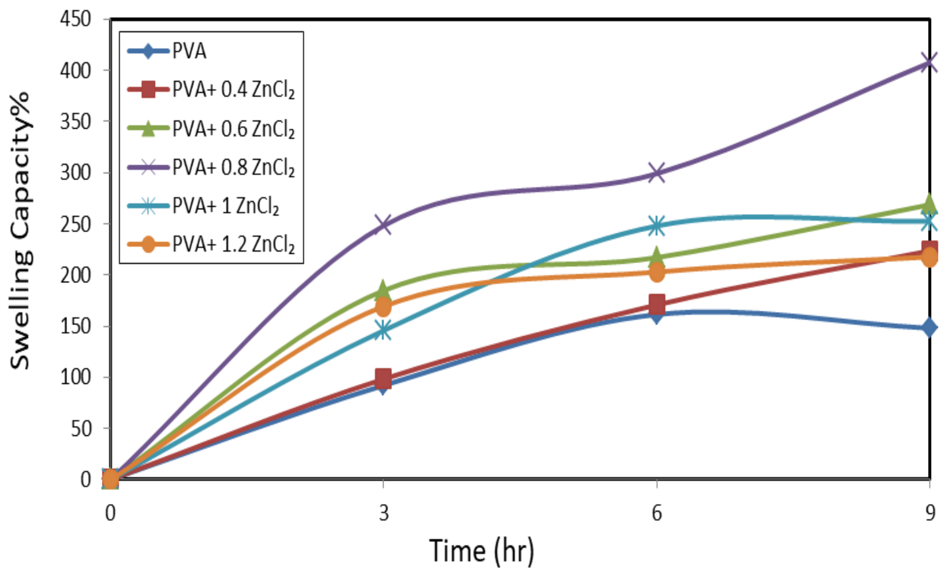

Figure 9: Swelling Ratio (%) of PVA and (Zn-PVA) SAPs.

3.5 Water retention Capacity

The water retention capacity of SAPs was calculated, and the findings are given in Figures 10 and 11. With time, the data showed a reduction in water retention. The graph (Figures 10 and 11) shows that Zn-KPA SAP had a greater water retention equilibrium than Zn-PVA. Water retention might be caused by hydrogen bonds and Van der Waals forces between water molecules and the SAPs [37]. With the addition of zinc chloride, the water retention capability of Zn-KPA increases. At room temperature and after 48 hours, the water retention capacity of KPA-(0, 0.3, 0.4, 0.5, and 0.6) $ZnCl_2$ were 0, 21.55, 34.22, 36.7 and 40.9% respectively, and the water retention ratio of PVA-(0, 0.4, 0.6, 0.8, 1, and 1.2) $ZnCl_2$ were 0, 4.05, 15.15, 20, 20.09 and 22.81% respectively. The network structure of KPA SAP is more compact than that of PVA SAP, Physical entanglements and water retention properties were increased as network density increased [38].

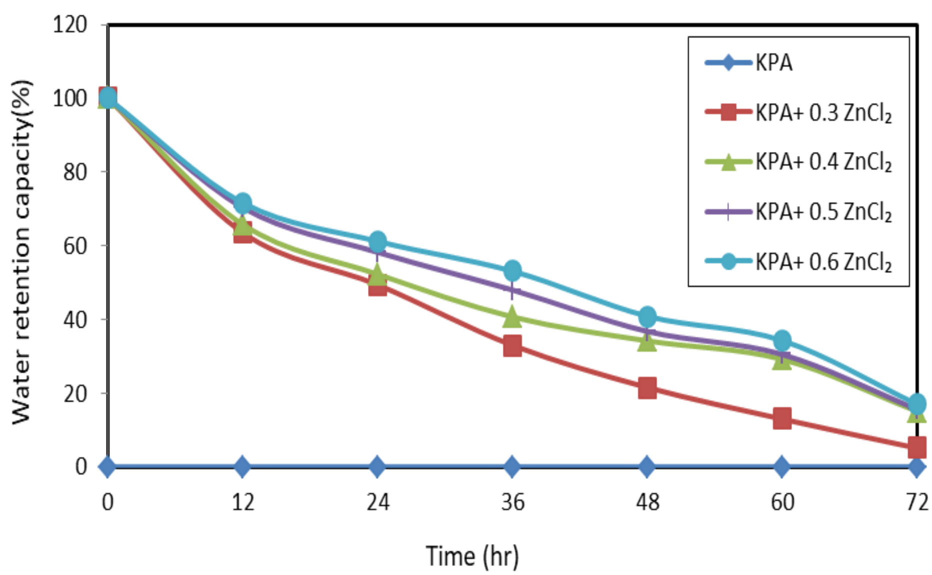

Figure 10: Water retention capacity (%) of KPA and (Zn-KPA) SAPs.

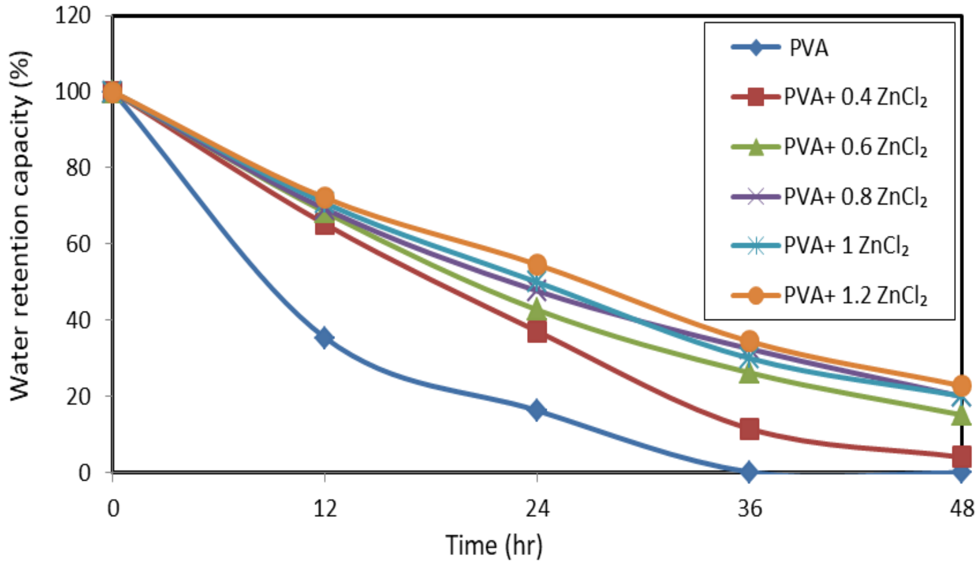

Figure 11: Water retention capacity (%) of PVA and (Zn-PVA) SAPs.

4. Conclusions

Zn-KPA and Zn-PVA superabsorbent polymers were produced by the solution polymerization of potassium polyacrylate or polyvinyl alcohol with zinc chloride to investigate the swelling ratio and Water retention capacity. By comparing the two complexes, the highest swelling ratio was obtained for Zn-PVA SAP equal to 407 % while, the swelling ratio of the Zn-KPA was 304%. As a result, the SAPs that have been created can be employed in agricultural applications. Zn-KPA SAP performed superior in terms of water retention agent than Zn-PVA SAP in distilled water. The water retention ratio of polymer increased with increasing the zinc chloride $ZnCl_2$. According to FT-IR, UV, and SEM results, the superabsorbent polymers (Zn-KPA and Zn-PVA) were prepared successfully.

Conflict of Interest

The authors declare that they have no conflict of interest.

References

[1] F. L. Buchholz, A. T. Graham. "Modern superabsorbent polymer technology". New York: Wiley- VCH; [chapters 1–7], 1998.

[2] F. A. Aouada, M. R. De Moura, E. De Abreu Menezes, A. R. De Araújo Nogueira, and L. H. C. Mattoso, “Hydrogel synthesis and kinetics of ammonium and potassium release, ” *Rev. Bras. Cienc. do Solo*, vol. 32, no. 4, pp. 1643–1649, 2008.

[3] Li, Yuhui, Huang, Guoyou, Zhang, Xiaohui, Li, Baoqiang, Chen, Yongmei, Lu, Tingli, Lu, Tian Jian, Xu, Feng. “Magnetic hydrogels and their potential biomedical applications, ” *Adv. Funct. Mater.*, vol. 23, no. 6, pp. 660–672, 2013.

[4] E. M. Ahmed. “Hydrogel: Preparation, characterization, and applications: A review, ” *J. Adv. Res.*, vol. 6, no. 2, pp. 105–121, 2015.

[5] S. M. H. Bukhari, S. Khan, M. Rehanullah, and N. M. Ranjha, “Synthesis and Characterization of Chemically Cross-Linked Acrylic Acid/Gelatin Hydrogels: Effect of pH and Composition on Swelling and Drug Release, ” *Int. J. Polym. Sci.*, vol. 2015, 2015, doi: 10.1155/2015/187961.

[6] A. Jackson, J. Souza, A. W. Dominghetti, M. Stella, and T. T. Rezende, “Water-retaining polymer and seedling type when planting irrigated, ” *Crop Science.*, vol.47, no. 2, pp. 334–343, 2016.

[7] N. Thombare, S. Mishra, M. Z. Siddiqui, U. Jha, D. Singh, and G. R. Mahajan, “PT Effect on water retention capacity of soil SC, ” *Carbohydr. Polym.*, vol.18, no.9, pp.169-178, 2018.

[8] Z. Khedaer, D. Ahmed, and S. Al-Jawad, “Investigation of Morphological, Optical, and Antibacterial Properties of Hybrid ZnO-MWCNT Prepared by Sol-gel,” *J. Appl. Sci. Nanotechnol.*, vol. 1, no. 2, pp. 66–77, 2021.
[9] R. Saleh, O. Salman, and M. Dawood, “Physical Investigations of Titanium Dioxide Nanorods Film Prepared by Hydrothermal Technique,” *J. Appl. Sci. Nanotechnol.*, vol. 1, no. 3, pp. 32–41, 2021.
[10] D. Hassan and M. Zayer, “Study and Investigation of the Effects of the OTA Technique on the Physical Properties of the ZnO Thin Films Prepared by PLD,” *J. Appl. Sci. Nanotechnol.*, vol. 1, no. 4, pp. 32–43, 2021.
[11] T. -H. Yang, “Recent Applications of Polyacrylamide as Biomaterials, ” *Recent Patents Mater. Sci.*, vol. 1, no. 1, pp. 29–40, 2010.
[12] L. Chang, L. Xu, Y. Liu, and D. Qiu, “Superabsorbent polymers used for agricultural water retention, ” *Polym. Test.*, vol. 94, no.7, p. 107021, 2021.
[13] N. J. Hameed, A.J. Haider[a), *and* R. E. Hawy “Optical properties study for PS/PMMA blend as laser active medium”, AIP Conference Proceedings vol.2123, no.2, pp.22, 2019.
[14] A. Kemmochi, T. Tamura, Y. Shimizu, and Y. Owada, “A novel hydrogel sheet prevents postoperative pancreatic fistula in a rat model, ” *J Hepatobiliary Pancreat Sci*, vol. 28, no.9, pp. 192–201, 2021.
[15] B. H. Musa and N. J. Hameed, “Effec1.Musa BH, Hameed NJ. "Effect of crosslinking agent (glutaraldehyde) on the mechanical properties of (PVA/Starch) blend and (PVA/PEG) binary blend films, "*J. Phys. Conf. Ser.*, vol. 1795, no. 1, 2021.
[16] A.J. Haider, F.I. Sultan, “Structural, morphological and random laser action for dye-Zno nanoparticles in polymer films”. *International Journal of Nanoelectronics and Materials* , vol.11, no. 1, pp.97–102, 2018.
[17] Z. Song *et al.*, “Laboratory and field experiments on the effect of vinyl acetate polymer-reinforced soil, ” *Appl. Sci.*, vol. 9, no. 1, pp.2, 2019.
[18] Buthaina A. I., Nahida J. H, jáafr Hussain koaer, "Hydrogel and Poly Vinyl Alcohol /Chitosamine Chloride Blends Preparation and Study of Their Properties for Medical Uses", *Engineering and Technology Journal*., Vol.32, no.6, pp. 54-70, 2014.
[19] D. Das, P. Prakash, P. Rout, S. Bhaladhare, “Synthesis and Characterization of Superabsorbent Cellulose-Based Hydrogel for Agriculture Application” *Starch/Staerke.*, vol. 73, no.1, pp.1-2, 2021.
[20] Z. Wang, L. Wu, D. Zhou, P. Ji, and X. Zhou, “Synthesis and Water Absorbing Properties via Grafting Polymerization Method, ” *Polymer.Sci. Ser.*, vol.62, no.7, pp.238–244, 2020.
[21] A. K. Sonker, K. Rathore, R. K. Nagarale, and V. Verma, “Crosslinking of Polyvinyl Alcohol (PVA) and Effect of Crosslinker Shape (Aliphatic and Aromatic) Thereof, ” *J. Polym. Environ.*, vol. 26, no. 5, pp. 1782–1794, 2018.
[22] S. Fang *et al.*, “Synthesis of chitosan derivative graft acrylic acid superabsorbent polymers and its application as water retaining agent, ” *Int. J. Biol. Macromol.*, vol. 115, no.7, pp. 754–761, 2018.
[23] J. E. Tackett, Appl. *Spectrosc.*, 44 (9), 158, 1990.
[24] J. Zufía-Rivas, P. Morales, and S. Veintemillas-Verdaguer, “Effect of the sodium polyacrylate on the magnetite nanoparticles produced by green chemistry routes: Applicability in forward osmosis, ” *Nanomaterials*, vol. 8, no. 7, pp.1-13, 2018.
[25] L. Li, L. Fu, X. Ai, J. Zhang, and J. Zhou, “Design and Fabrication of Temperature-Sensitive Nanogels with Controlled Drug Release Properties for Enhanced Photothermal Sterilization, ” *Chem. - A Eur. J.*, vol. 23, no. 72, pp. 18180–18186, 2017.
[26] D. Minerals, P. O. Box, “An Infrared Study of a Polyacrylate Flocculant Adsorbed on Hematite, ” *Langmuir.*, vol.14, no. 3, pp. 6512–6517, 1998.

[27] V. A. Guo, M. Muhammad, F.Wang, WWang, N. Guo, Y.Wei, "platform for hydrophobic anticancer drug delivery, " *Journal of Materials Chemistry B*., vol.1, no.5, pp. 5273–5278, 2013.
[28] W. Du, L. Jiang, M. Shi, X. Zhang, "The modification mechanism and the effect of magnesium chloride on poly (vinyl alcohol) films, " *RSC Advances.*, vol.9, no.3, pp.1602–1612, 2019.
[29] A. R. Polu, R. Kumar, and H. W. Rhee, "Magnesium ion conducting solid polymer blend electrolyte based on biodegradable polymers and application in solid-state batteries, " *Ionics (Kiel).*, vol. 21, no. 1, pp. 125–132, 2015.
[30] S. H. Deshmukh, D. K. Burghate, S. N. Shilaskar, G. N. Chaudhari, and P. T. Deshmukh, "Optical properties of polyaniline doped PVC-PMMA thin films, " *Indian J. Pure Appl. Phys.*, vol. 46, no. 5, pp. 344–348, 2008.
[31] N. Limpan, T. Prodpran, S. Benjakul, S. Prasarpran, "Food Hydrocolloids In fl uences of degree of hydrolysis and molecular weight of poly (vinyl alcohol) (PVA) on properties of fi sh myo fi brillar protein / PVA blend fi lms, " *Food Hydrocolloids.*, vol. 29, no.7, pp. 226–233, 2012.
[32] K. Deshmukh, J. Ahmad M. B. Hägg, "Fabrication and characterization of polymer blends consisting of cationic polyallylamine and anionic polyvinyl alcohol, " *Ionics*., vol.20, no.10, pp.957–967, 2014.
[33] D. Qiao, H. Liu, L.Yu, X. Bao, "Preparation and characterization of slow-release fertilizer encapsulated by starch-based superabsorbent polymer, " *Carbohydr. Polym.*, vol. 147, no.8, pp. 146–154, 2016.
[34] A. Bortolin, F. A. Aouada, L. H. C. Mattoso, C. Ribeiro, "Nanocomposite PAAm/methyl cellulose/montmorillonite hydrogel evidence of synergistic effects for the slow release of fertilizers, *Food Chem*., vol. 61, no.3, pp. 7431–7439, 2013.
[35] H. Tu, Y. Yu, J. J. Chen, X. W. Shi, J. L. Zhou, H. B. Deng, Y. M. Du, "Highly cost-effective and high-strength hydrogels as dye adsorbents from natural polymers: chitosan and cellulose", P*olymer Chemistry*, vol.*8, no.19, pp. 2913-2921*, 2017.
[36] A. Mohammadinezhad, G. B. Marandi, M. Farsadrooh, and H. Javadian, "Synthesis of poly(acrylamide-co-itaconic acid)/MWCNTs superabsorbent hydrogel nanocomposite by ultrasound-assisted technique: Swelling behavior and Pb (II) adsorption capacity, " *Ultrason. Sonochem.,* vol. 49, no. Ii, pp. 1–12, 2018.
[37] F. Wu, Y. Zhang, L. Liu, and J. Yao, "Synthesis and characterization of a novel cellulose-g-poly (acrylic acid-co-acrylamide) superabsorbent composite based on flax yarn waste, " *Carbohydr. Polym.*, vol. 87, no. 4, pp. 2519–2525, 2012.
[38] Y. Zhou, S. Fu, L. Zhang, and H. Zhan, "Superabsorbent nanocomposite hydrogels made of carboxylated cellulose nanofibrils and CMC-g-p (AA-co-AM), " *Carbohydr. Polym.*, vol. 97, no. 2, pp. 429–435, 2013.