Synthesis, Characterization and Swelling behavior of superabsorbent hydrogel, H-Na-PCMSA-g-PAN

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In recent years, increasing interest in polysaccharides based superabsorbent hydrogels has been developed mainly due to high hydrophilicity, biocompatibility, non-toxicity, and biodegradability of biopolymers. In this article we reviewed the literature survey on the studies in superabsorbents based on sodium alginate and its derivatives. This article further describes the synthesis, characterization and superabsorbing properties of the novel hydrogel first time synthesized from alkaline hydrolysis of polyacrylonitrile grafted sodium salt of partially carboxymethylated sodium alginate. The swelling measurements of the synthesized hydrogel have been carried out in various saline solutions and the hydrogel is found to exhibit salt resisting properties. The swelling kinetics of the hydrogel has also been studied and its values of the various swelling characteristics are reported.

Keywords: sodium salt of partially carboxymethylated tamarind kernel powder; acrylonitrile; graft copolymerization; superabsorbent hydrogels; swelling behavior

1. Introduction

1.1. Hydrogel and its Importance

Superabsorbent hydrogels (SHs) are three-dimensional cross-linked hydrophilic, linear or branched polymers with the ability to absorb large quantities (several hundred to a thousand times of their own dry weight) of water, saline or physiological solutions\textsuperscript{1,2}. Because of their excellent response to changing environment conditions such as temperature, pH and solvent composition, SHs are widely used for many applications which include agriculture\textsuperscript{3,4}, biomedical area as antibacterial materials\textsuperscript{5}, tissue engineering\textsuperscript{6}, biosensors\textsuperscript{7,8}, drug delivery systems\textsuperscript{9,10}, coal dewatering\textsuperscript{11}, wound dressing\textsuperscript{12}, contact lenses\textsuperscript{13}, hygienic products\textsuperscript{14}, waste water treatment\textsuperscript{15} and metal-ion removal\textsuperscript{16}. The global demand for SHs is increasing and has reached about 1.9 million metric tons in 2015 and further will reach 3.48 million metric tons in 2020\textsuperscript{17}.

The ability of hydrogels to absorb water arises from hydrophilic functional groups attached to the polymeric backbone, while their resistance to dissolution arises from cross-links between network chains.

SHs can be roughly divided into natural-based and full synthetic ones. Despite the advantages of hydrogels made from synthetic polymers like acrylic acid, vinyl alcohol, acrylamide etc. there are also severe limitations such as toxicity of residual monomers that are usually present in the gels and nonbiodegradability to this type of material. Because of these shortcomings, natural-based SHs have attracted much attention in recent years. On the other hand polysaccharides constitute the majority of the natural-based SHs because of their exceptional properties, i.e. biocompatibility, biodegradability, renewability and nontoxicity. The polysaccharides in their native form are not able to produce hydrogels with good stability and therefore SHs may be prepared using chemical or physical crosslinking approach or both\textsuperscript{18,19}. Graft copolymerization of vinyl monomers onto polysaccharides followed by crosslinking of their chains is also regarded as one of the efficient methods for the synthesis of polysaccharide-based SHs\textsuperscript{20}.

Many investigations have been carried out in this manner for the synthesis of SHs through graft copolymerization of vinyl monomers onto polysaccharides such as starch\textsuperscript{21-39}, carboxymethyl starch\textsuperscript{40}, cellulose\textsuperscript{42-49}, carboxymethyl cellulose\textsuperscript{50-54}, hydroxyethyl cellulose\textsuperscript{55}, sodium salt of partially carboxymethylated tamarind kernel powder\textsuperscript{56}, chitosan\textsuperscript{57-61}, carrageenan\textsuperscript{62}, gelatin\textsuperscript{63}, konjac glucomannan\textsuperscript{64}, maize bran\textsuperscript{65}, xyloglucan\textsuperscript{66}, agar\textsuperscript{67}, guar gum\textsuperscript{68,69}, sodium salt of partially carboxymethylated guar gum\textsuperscript{70}, sodium salt of partially carboxymethylated pyrillum\textsuperscript{71,72} and loofah fiber\textsuperscript{73}.

Sodium alginate (SA) is an industrially important marine polysaccharide product extracted from brown seaweeds. Alginates are unbranched copolymers of (1→4) linked β-D-mannuronic acid (M) and α-L-guluronic acid (G) residues\textsuperscript{74}. SA due to its excellent physical and chemical properties, it is widely used in food processing, medical and pharmaceutical industries, as well as in textile industries. Among the physicochemical properties, gelation in the presence of multivalent metal cations is important. However, ionic-crosslinked alginate gels show low absorbercies due to high crosslink density. Therefore, “chemically” crosslinking of alginate salts would be better than “ionic” crosslinking due to facile control of crosslinking degree and higher crosslink length.
1.2 Hydrogels Based on Sodium Alginate (SA)

A comprehensive literature survey reveals that some literature reports are available on the synthesis, characterization and swelling behavior of the superabsorbent hydrogels based on sodium alginate.

Pourjavadi et al.\textsuperscript{75} have prepared a series of highly swelling superabsorbent hydrogels based on sodium alginate-graft-poly(methyl acrylamide) and measured the absorbency of these hydrogels in salt solutions.

Pourjavadi et al.\textsuperscript{76} have synthesized a novel superabsorbent composite based sodium alginate and the inorganic clay kaolin via the graft copolymerization of acrylic acid in an aqueous medium with methylene bisacrylamide as a crosslinking agent and ammonium persulphate as an initiator. The swelling behavior of alginate-g-poly(sodium acrylate)/Kaolin superabsorbent hydrogel composites was studied in different salt media and the swelling kinetics of the hydrogel was studied.

Wang et al.\textsuperscript{77} have prepared a pH-sensitive semi-IPN superabsorbent hydrogel composed of sodium alginate-g-poly(sodium acrylate) network and linear poly(vinyl pyrrolidone) by free radical solution polymerization in the presence of an initiator ammonium persulfate and crosslinker N-N-methylene bisacrylamide. The swelling properties of the superabsorbent hydrogel were studied in different buffer solutions.

Marandi et al.\textsuperscript{78} have synthesized the superabsorbent hydrogel based on sodium alginate-poly(sodium acrylate)-co-acrylamide and studied the swelling behavior of the hydrogel in different buffer as well as salt solutions.

Pourjavadi et al.\textsuperscript{79} have synthesized a novel sodium alginate-g-poly(acrylic acid)/alumina composite and characterized it by FTIR and SEM techniques. The swelling kinetics of the hydrogels was studied in various solutions with pH values ranging from 0-14.

Yin et al.\textsuperscript{80} have synthesized a series of hydrogel by graft cross-linked copolymerization of sodium alginate and acrylic acid using N,N-methylene- (bisacrylamide) as a cross-linker. They have studied the swelling kinetics of the hydrogels in different buffer solutions and observed the overshooting effect in acidic medium.

Yang et al.\textsuperscript{81} have prepared a novel composite of α-methyl methacrylate grafted sodium alginate and hydroxyapatite and investigated the compositions and chemical groups of materials by IR, XRD and NMR techniques.

Wang et al.\textsuperscript{82} have prepared a novel sodium alginate-g-poly(acrylic acid)/sodium humate superabsorbent and studied the swelling behaviour in solutions of various pH and investigated the swelling kinetics in different saline solutions.

Phang et al.\textsuperscript{83} have prepared an alginate-based superabsorbent polymer, alginate-g-poly[acylamide-co-(itaconic acid)-g-(acrylic acid)] and examined its thermal and microbial degradation properties.

Yadav et al.\textsuperscript{84} have prepared a superabsorbent nanocomposite, alginate-g-(AMPS/MMT) and studied its swelling behavior in various cationic as well as anionic salt solutions. The superabsorbent composite was also characterized using FTIR, Rheology, TGA, XRD and SEM techniques.

A Taleb et al.\textsuperscript{85} have synthesized the nanocomposite, calcium alginate/organophilic montmorillonite and characterized it successfully using XRD, IR, TGA and TEM techniques.

A. Rashidzadeh and A. Olad\textsuperscript{86} have prepared a superabsorbent nanocomposite, sodium alginate-g-poly(acrylic acid-co-acrylamide/sodium montmorillonite) and studied slow-released fertilizer formulation encapsulated on prepared superabsorbent nanocomposite. The superabsorbent composite was also characterized using FTIR, TGA, XRD and SEM techniques.

Mohammad and Mojgan\textsuperscript{87} have prepared sodium alginate-poly(sodium acrylate-co-acrylamide) superabsorbent hydrogel by hydrolyzing the physical mixture of sodium alginate and polyacrylonitrile by sodium hydroxide solution and the influence of various reaction variables were systematically optimized to achieve a hydrogel with high swelling capacity (518g/g) in distilled water.

Erizal et al.\textsuperscript{88} have synthesized a poly(acrylamide-co-acrylic acid)-sodium alginate superabsorbent hydrogels via crosslinking gamma radiation. The influence of irradiation dose and sodium alginate concentrations on swelling capacity of hydrogels was also studied. The hydrogels were found to be sensitive to the ionic strength of the medium. The copolymers were characterized by FTIR and SEM techniques.

Sadeghi et al.\textsuperscript{89} have synthesized a novel alginate based superabsorbing hydrogel through graft copolymerization of acrylamide (AAm) onto the substrate in the presence of a crosslinking agent. The crosslinked alginate-poly(AAm) graft copolymer was then partially hydrolyzed in alkaline medium to yield a superabsorbent resin. The structure of the superabsorbing resin was confirmed using FTIR, SEM and TGA techniques.

Rashidzadeh et al.\textsuperscript{90} have prepared a novel slow release fertilizer hydrogel nanocomposite via free radical copolymerization of sodium alginate, acrylic acid, acrylamide and clinoptilolite using N-N-methylene bisacrylamide as a crosslinker and ammonium persulphate as a initiator. The swelling behavior of hydrogels in solutions of various pH and various saline solutions such as sodium chloride, potassium chloride, aluminium chloride and FeCl\textsubscript{3} as well as the swelling kinetics were investigated. The potential application of hydrogel was verified through sorption and fertilizer releasing from the hydrogel with and without clinoptilolite zeolite.

Mirdarikvande et al.\textsuperscript{91} have synthesized a novel alginate-based composite superabsorbent hydrogel through crosslinking graft copolymerization of acrylic acid onto alginate in presence of kaolin, using ammonium persulphate as a free radical initiator in the presence of methylene bisacrylamide as a crosslinker. The composite hydrogel structure was confirmed using FTIR, TGA and SEM techniques.
Thakur et al.\textsuperscript{92} have prepared the hydrogel by graft copolymerization of acrylic acid onto sodium alginate in the presence of a crosslinking agent (MBA), a free radical initiator potassium persulphate (KPS) and titanium dioxide (TiO\textsubscript{2}) nanopowder and found that the hydrogel exhibited a high swelling capacity of 412.98g/g. The batch adsorption experiments were also carried out for the removal of methylene blue (MB) cationic dye from aqueous solution using the synthesized hydrogel.

1.3 Hydrogels based on Sodium salt of Partially Carboxymethylated Sodium Alginate (Na-PCMSA)

A comprehensive literature survey further reveals that Lin et al.\textsuperscript{93} have synthesized the hydrogels composed of etherified sodium alginate, sodium acrylic acid and polyvinyl alcohol by aqueous solution polymerization. The pH- and salt responsiveness of the hydrogels were determined in various pH buffer solution as well as salt solutions of different ionic strength.

However, there is no published report, except this, regarding the synthesis of a superabsorbent hydrogel via alkaline hydrolysis of the graft copolymer of sodium salt of partially carboxymethylated sodium alginate containing polyacrylonitrile. Therefore, in the present work the optimally synthesized graft copolymer sample of sodium salt of partially carboxymethylated sodium alginate containing polyacrylonitrile (%G = 376.82, %GE = 96.46)\textsuperscript{94} has been hydrolyzed in an alkaline medium to form the superabsorbent hydrogel, H-Na-PCMSA-g-PAN. Considering the great importance of external saline solutions on water absorbency of superabsorbents and extending their applications, especially for agriculture and hygiene products, the swelling behaviour of the superabsorbent hydrogel has been studied in low conductivity water as well as different saline solutions. The swelling kinetics of the hydrogel has also been investigated.

2. Results and Discussion

2.1. Synthesis of Superabsorbent Hydrogel

The saponification of the optimally synthesized graft copolymer of sodium salt of partially carboxymethylated sodium alginate containing polyacrylonitrile sample was carried out by treating it with aqueous 0.7N sodium hydroxide solution at 90-95°C. Figure 1 represents the mechanism of crosslinking during conversion of nitrile groups of graft copolymer of sodium salt of partially carboxymethylated sodium alginate containing polyacrylonitrile into carboxamide and sodium carboxylate groups. As shown in the figure, in the first step, the hydroxide ions abstract hydrogen from the –OH group of the substrate leading to the formation of the corresponding alkoxide anions. Then, these sodium salt of partially carboxymethylated sodium alginate alkoxide anions (i.e. macroalkoxides) initiate crosslinking reaction between some adjacent polyacrylonitrile pendant chains leading to the formation of deep orange-red color intermediate with naphthyridine cyclic structures, including imine, -C=\text{N}-, conjugated bonds with evolution of ammonia\textsuperscript{95,96}. Thus, the intermediate having a conjugated polyimine structure then gets further saponified with residual sodium hydroxide solution to form hydrophilic carboxamide (\text{CONH}_2) and carboxylate (\text{CO}_2^-) groups. The disappearance of the conjugated system with formation of the hydrophilic groups was indicated when color of the system got changed from red to light yellow. This sharp change in color was used as a marker to halt the alkaline treatment. In this way, the starting hydrophobic graft copolymer sample was converted into a hydrophilic gel i.e. superabsorbent hydrogel.

![Figure 1: Mechanistic pathway of the conversion of the nitrile groups to carboxamide (A) and sodium carboxylate anions (B) during the course of alkaline hydrolysis of polyacrylonitrile containing graft copolymer of sodium salt of partially carboxymethylated sodium alginate.](image)

2.2. Swelling behavior in water and salt solutions

The swelling behavior of the superabsorbent hydrogel could be significantly affected by various factors of the external solutions such as its valences and ionic strength. The presence of ions in the swelling medium has a profound effect on the swelling behavior of the superabsorbent hydrogels. The underlying principle behind the ionic dependence of
swelling is well explained by the Donnan Equilibrium theory (Figure 2). According to this theory, the balance between the osmotic pressure of the swelling system and elastic response of the polymeric network that controls the extent of swelling. The osmotic pressure results from the difference in concentration of mobile ions between the interior of the hydrogel network and the external solution. The fundamental feature within the hydrogel, bringing about the unequal distribution, in the present case, is the presence of the ionizable, carboxylate groups (anionic sites) attached to the polymeric network.

In the present work, the swelling behavior of the “anionic” superabsorbent hydrogel has been studied by carrying out its absorbency measurements in low conductivity water, 0.15M salt (Sodium Chloride, Calcium Chloride, and Aluminium Chloride) and simulated urine (SU) solutions at different timings. The photographs of dry and swollen samples of superabsorbent hydrogels are shown in Figure 3.

![Diagram of Donnan Equilibrium theory](image)

**Table 1:** Swelling ratio [S(g/g)] values of the superabsorbent hydrogel sample in low conductivity water and different salt solutions (0.15 M) at different time intervals.

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Low Conductivity Water</th>
<th>NaCl</th>
<th>CaCl₂</th>
<th>AlCl₃</th>
<th>SU *</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>55.99</td>
<td>17.43</td>
<td>13.80</td>
<td>8.86</td>
<td>14.65</td>
</tr>
<tr>
<td>1.0</td>
<td>99.34</td>
<td>26.31</td>
<td>21.12</td>
<td>16.49</td>
<td>22.46</td>
</tr>
<tr>
<td>1.5</td>
<td>111.39</td>
<td>35.65</td>
<td>24.88</td>
<td>23.67</td>
<td>32.20</td>
</tr>
<tr>
<td>2.0</td>
<td>123.84</td>
<td>40.07</td>
<td>34.37</td>
<td>26.27</td>
<td>36.28</td>
</tr>
<tr>
<td>2.5</td>
<td>135.06</td>
<td>45.90</td>
<td>35.58</td>
<td>31.72</td>
<td>38.98</td>
</tr>
<tr>
<td>3.0</td>
<td>142.40</td>
<td>51.40</td>
<td>42.16</td>
<td>37.89</td>
<td>44.07</td>
</tr>
<tr>
<td>3.5</td>
<td>202.39</td>
<td>56.83</td>
<td>60.05</td>
<td>39.96</td>
<td>46.12</td>
</tr>
<tr>
<td>4.0</td>
<td>216.92</td>
<td>72.50</td>
<td>61.66</td>
<td>42.21</td>
<td>66.46</td>
</tr>
<tr>
<td>6.0</td>
<td>233.03</td>
<td>75.67</td>
<td>66.52</td>
<td>55.63</td>
<td>69.85</td>
</tr>
<tr>
<td>8.0</td>
<td>237.05</td>
<td>77.85</td>
<td>68.97</td>
<td>55.47</td>
<td>71.82</td>
</tr>
<tr>
<td>10.0</td>
<td>245.03</td>
<td>81.17</td>
<td>73.55</td>
<td>56.80</td>
<td>76.26</td>
</tr>
<tr>
<td>12.0</td>
<td>242.51</td>
<td>81.05</td>
<td>78.83</td>
<td>56.01</td>
<td>79.71</td>
</tr>
<tr>
<td>16.0</td>
<td>242.11</td>
<td>78.60</td>
<td>77.89</td>
<td>54.10</td>
<td>77.35</td>
</tr>
<tr>
<td>24.0</td>
<td>239.37</td>
<td>76.92</td>
<td>77.45</td>
<td>51.77</td>
<td>75.25</td>
</tr>
</tbody>
</table>

*Simulated Urine composition: 0.85g calcium chloride dihydrate, 1.14 g magnesium sulfate heptahydrate, 8.20g sodium chloride, 20.0 g urea and 1000 mL low conductivity water.
Table 1 represents the values of the swelling ratios (S) determined for the superabsorbent hydrogel at various time intervals in different swelling media. The kinetic swelling curves of the superabsorbent hydrogel in low conductivity water, 0.15M sodium chloride, 0.15M calcium chloride, 0.15M aluminium chloride and 0.15M simulated urine (SU) solutions are represented in Figures 4(a) – 4(d) respectively.

![Swelling curves](image)

**Figure 4**: Kinetic Swelling curves of superabsorbent hydrogel in (a) Low Conductivity Water, (b) 0.15M sodium chloride, (c) 0.15M calcium chloride, (d) 0.15M aluminium chloride and (e) 0.15M SU solutions.

As shown in Figure 4(a) the swelling of the anionic hydrogel is found to be increased steadily and continuously with time in low conductivity water up to 10 h beyond which it almost levels off. The hydrophilic groups such as carboxylate and carboxamide groups absorb the penetrating water through the formation of hydrogen bonds. The swelling is driven by repulsion of ionic and hydrophilic groups inside the network and osmotic pressure difference between the hydrogel and the external solution. It can be seen from Figure 4(a) that the hydrogel absorbs 55.99 g/g gel water quickly even within half an hour. Therefore, at this point (30 mins), the hydrogel absorbs water with a rate of about 1.97 g/g.min. However, the swelling ability of the anionic hydrogel in different salt (sodium chloride, calcium chloride and aluminium chloride) solutions, having same concentration (0.15M), as well as in simulated urine is found to be
decreased dramatically at all different timings in comparison with the values measured in low conductivity water [cf. Figures 4(b) to 4(e)]. This well known undesired swelling loss, which is commonly being observed in the swelling of ionic hydrogels\textsuperscript{33} is attributed to a “charge-screening” effect of the additional counter ions (cations) causing a non-perfect anion-anion electrostatic repulsion\textsuperscript{97}. The water-absorption properties are expected to result from osmotic pressure and interaction through hydrogen bonding of the carboxylate and carboxamide groups of the polymeric network with water molecules. When low conductivity water is used as swelling agent, the absorption capacity is found to be higher. At the swelling equilibrium, the chemical potential of water in the polymer network will be equal to that of the water surrounding to it. However, when a certain amount of salt (sodium chloride or calcium chloride or aluminium chloride or simulated urine, as in the present study) in low conductivity water is used as a swelling agent then the attraction of the strong electrostatic forces exist between the fixed anionic sites or the negatively charged carboxylate groups on the polymer chain and the cations (counter ions) of the salt, as a result of which these cations, by screening the fixed charges on the polymer chain, reduce the electrostatic repulsion tremendously as compared with what it would be in their absence [cf. Figures 4(b) to 4(e)]. Thus, because of the strong electrostatic forces the concentration of the cations (e.g. Na\textsuperscript+ or Ca\textsuperscript{2+} or Al\textsuperscript{3+}) will be higher inside the hydrogel than outside (Figure 2) as a result of which the osmotic pressure outside the hydrogel will decrease drastically and consequently the absorbency values will be diminished [cf. Figures 4(b) to 4(e)].

The effect of different cations with a common anion (Cl\textsuperscript-) on the absorbency of the superabsorbent hydrogel can also be explained from the results of Figures 4(b) to 4(c). It can be seen from this figure that the absorption capacity of the hydrogel decreases with an increase in the charge of the metal cation (Al\textsuperscript{3+} < Ca\textsuperscript{2+} < Na\textsuperscript+) in the solutions having the same concentration (0.15M). This can be attributed to the complexing ability arising from the coordination of the multivalent cations with carboxylate groups of the hydrogel to induce the formation of intramolecular and intermolecular complexes. This leads to an increase in the crosslinking density, which makes network shrink\textsuperscript{98}. This behavior is also in agreement with the results reported by Gugliemelli et al.\textsuperscript{99} on the viscosity of hydrolyzed starch polyacrylonitrile dispersions in various saline solutions. They showed that the viscosity of the dispersion decreased with an increase of the counter ion valency. Thus, in the case of aluminium chloride, due to the high complexing ability of the Al\textsuperscript{3+} ions with the carboxylate groups of the hydrogel, the crosslink density of the network ultimately increases but it may hinder the approach of the water molecules leading to the lowering of the water uptake compared to that of sodium chloride [cf. Figure 4(b)]. This ‘ionic crosslinking’ phenomenon mainly occurs at the surface of the particles and as a result, in the present case, the hydrogels are found to be rubbery and very hard to the touch when they swell in Ca\textsuperscript{2+} or Al\textsuperscript{3+} solutions, so that it cannot swell well. In contrast to this, the hydrogel particles are found to be swollen in sodium chloride and water, exhibiting lower gel strength to the touch. Similar results are also reported in the literature\textsuperscript{56, 61, 101}.

Thus, in the present work [Table 1 and Figures 4(a)-(d)] an encouraging and promising results have been obtained with regard to the swelling behavior of the superabsorbent hydrogel, in different swelling media i.e. absorbency in water, 0.15M sodium chloride, 0.15M calcium chloride, 0.15M aluminium chloride and 0.15M simulated urine solutions which are found to be 245.03 g/g gel, 81.17g/g gel, 77.89 g/g gel, 56.80 g/g gel and 79.71g/g gel respectively.

The dimensionless salt sensitivity factor \( f \) was calculated for 0.15M salt solutions according to the equation:\textsuperscript{22}:

\[
f = 1 - \frac{S_{\text{salt}}}{S_{\text{water}}}
\]

where \( S_{\text{salt}} \) and \( S_{\text{water}} \) are the values of the swelling ratio in a given saline solution and low conductivity water, respectively. Thus, the values of \( f \) calculated for the superabsorbent hydrogel in 0.15M different salt and simulated urine solutions at different timings are recorded in Table 2. The influence of increasing cation charge on the ultimate absorption for the superabsorbent hydrogel can be evident upon comparing the average salt sensitivity values (Table 2). It can be seen from this table that due to ionic crosslinking by multivalent cations (Ca\textsuperscript{2+} and Al\textsuperscript{3+}), the average salt sensitivity values of the superabsorbent hydrogel are found to be higher in 0.15M calcium chloride and aluminium chloride solutions in comparison with univalent cation Na\textsuperscript{+} in 0.15M sodium chloride solution. The average salt sensitivity value in the case of simulated urine solution is also found to be higher compared to 0.15M sodium chloride solution as the solution contains multivalent cations (Mg\textsuperscript{2+} and Ca\textsuperscript{2+}) in addition to univalent cation (Na\textsuperscript{+}). Thus, lower the cationic charge; the lower will be the average salt sensitivity. In other words, this low average salt sensitivity value is attributed to the low charge screening effect in the hydrogel when the swelling media is 0.15M sodium chloride solution. Similar results are also reported in literature\textsuperscript{86, 61, 101}.
Table 2: Dependency of the dimensionless salt sensitivity (f) of the superabsorbent hydrogel to the type of swelling media at different time intervals.

| Time (h) | f_{NaCl} | f_{CaCl_2} | f_{AlCl_3} | f_{SU} | Average Salt Sensitivity
|----------|----------|------------|------------|--------|-------------------------
| 0.5      | 0.689    | 0.754      | 0.842      | 0.738  |
| 1.0      | 0.735    | 0.787      | 0.834      | 0.774  |
| 1.5      | 0.680    | 0.777      | 0.788      | 0.711  |
| 2.0      | 0.676    | 0.723      | 0.788      | 0.707  |
| 2.5      | 0.660    | 0.737      | 0.765      | 0.711  |
| 3.0      | 0.639    | 0.704      | 0.734      | 0.691  |
| 3.5      | 0.719    | 0.703      | 0.803      | 0.772  |
| 4.0      | 0.666    | 0.716      | 0.805      | 0.694  |
| 6.0      | 0.675    | 0.715      | 0.761      | 0.700  |
| 8.0      | 0.672    | 0.709      | 0.766      | 0.697  |
| 10.0     | 0.669    | 0.700      | 0.768      | 0.689  |
| 12.0     | 0.666    | 0.675      | 0.769      | 0.671  |
| 16.0     | 0.675    | 0.678      | 0.777      | 0.681  |
| 24.0     | 0.679    | 0.676      | 0.784      | 0.686  |

\( f_{NaCl} = 0.679 \)  
\( f_{CaCl_2} = 0.718 \)  
\( f_{AlCl_3} = 0.785 \)  
\( f_{SU} = 0.709 \)

\( ^{a} \)calculated as per salt sensitivity factor (f) equation(1), on the basis of the Experimental Equilibrium Swelling Ratio (g/g gel) values for different swelling media.

2.3. Swelling Kinetics

In practical applications, for a hydrogel both a higher swelling rate and a higher swelling capacity are required. Figures 4(a) – 4(e) represent the kinetic swelling curves of the superabsorbent hydrogel in different swelling media [low conductivity water, sodium chloride (0.15M), calcium chloride (0.15M), aluminium chloride (0.15M) solutions and simulated urine (0.15M)].

In order to evaluate the mechanism of the swelling process of hydrogels, several kinetic models are used to test the experimental data. However, in the present work, for evaluating the dynamic swelling properties of the superabsorbent hydrogel a simple kinetic analysis based on the second order kinetics model was adopted and accordingly the second order equation can be expressed as per the following equation:

\[
\frac{dS}{dt} = k_S (S_{eq} - S)^2
\]

(2)

where \( S_{eq} \), \( S \) and \( k_S \) denote the equilibrium swelling (theoretical), swelling at any time, and swelling rate constant respectively. The integration of the above equation over the limits \( S = S_0 \) at \( t = t_0 \) and \( S = S \) at \( t = t \), gives

\[
t/S = A + Bt
\]

(3)

where \( B = 1/S_{eq} \) is the inverse of the maximum or equilibrium swelling, \( A = (1/k_S S_{eq}^2) \) is the reciprocal of the initial swelling rate of the hydrogel \( (r_i) \), and \( k_S \) is the swelling rate constant.

For analyzing the experimental results of the present work in terms of the above kinetic model, the plots of \( t/S \) versus \( t \) were plotted for the hydrogel in different swelling media. The plots were found to be linear with good linear correlation coefficient (Table 3), indicating that the swelling behavior of the hydrogel in the different swelling media follows the pseudo second order model. Figures 5 (a) to 5 (e) represent such type of plots of \( t/S \) versus \( t \) obtained for the superabsorbent hydrogel in water, sodium chloride, calcium chloride, aluminium chloride and simulated urine (0.15 M) solutions as swelling media. The values of the initial rate of swelling \( (r_i) \), swelling rate constant \( (k_S) \), and theoretical equilibrium swelling \( (S_{eq}) \) were calculated from the slope and intersection of the lines obtained in the graphs for the hydrogel in different swelling media. The results are summarized in Table 3. The value of the initial swelling rate \( (r_i) \) is found to be higher i.e. 2.72 [(g/g gel)min] when low conductivity water was used as swelling media in comparison with its values obtained for other swelling media i.e. different salt solutions (0.15M) and simulated urine. The value of \( r_i \) is also found to be decreased with increase in the ionic strength (cation charge) of the swelling media except the case of aluminium chloride solution.

However, this observed decrease in the value of the initial swelling rate \( (r_i) \) with an increase in the ionic strength (cation charge) of the salt solution (Table 3) is attributed to the decrease in the osmotic pressure difference between the gel network and the corresponding external solution. The values of the experimental equilibrium swelling ratio for different swelling media are reported in Table 3 along with the corresponding time required to achieve these swelling ratio values. As per the following equation the equilibrium water content (EWC\%) values were also calculated for the hydrogel in different swelling media and are included in Table 3.
EWC = \frac{\text{Weight of water in hydrated gel}}{\text{Total weight of hydrated gel}} \times 100 \quad (4)

Figure 5: Plots of t/S versus t for the superabsorbent hydrogel in (a) low conductivity water, (b) 0.15 M sodium chloride, (c) 0.15 M calcium chloride, (d) 0.15M aluminium chloride and (e) 0.15M simulated urine.
Table 3: Swelling Characteristics for the Superabsorbent hydrogel in different swelling media.

<table>
<thead>
<tr>
<th>Swelling media</th>
<th>Experimental Equilibrium swelling ratio (g water/g gel)</th>
<th>b</th>
<th>EWC (%)</th>
<th>d</th>
<th>Ionic Strength (mole-ion dm⁻³)</th>
<th>kₜ x 10⁵</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>low conductivity water</td>
<td>245.03 ± 0.58 (10) 333.33</td>
<td>99.59</td>
<td>2.72</td>
<td>---</td>
<td>2.45</td>
<td>0.990</td>
<td></td>
</tr>
<tr>
<td>NaCl (0.15M)</td>
<td>81.17 ± 0.59 (10) 90.91</td>
<td>98.78</td>
<td>0.87</td>
<td>0.15</td>
<td>10.50</td>
<td>0.988</td>
<td></td>
</tr>
<tr>
<td>CaCl₂ (0.15M)</td>
<td>77.89 ± 0.63 (16) 90.91</td>
<td>98.73</td>
<td>0.53</td>
<td>0.45</td>
<td>6.47</td>
<td>0.985</td>
<td></td>
</tr>
<tr>
<td>AlCl₃ (0.15M)</td>
<td>56.80 ± 0.23 (10) 62.50</td>
<td>98.27</td>
<td>0.56</td>
<td>0.90</td>
<td>14.33</td>
<td>0.980</td>
<td></td>
</tr>
<tr>
<td>Simulated Urine (SU)</td>
<td>79.71 ± 0.36 (16) 90.91</td>
<td>98.72</td>
<td>0.62</td>
<td>0.18</td>
<td>7.55</td>
<td>0.985</td>
<td></td>
</tr>
</tbody>
</table>

Values are recorded as mean ± standard deviations.

a Time required to achieve Experimental Equilibrium Swelling Ratio value;
b Theoretical Equilibrium Swelling Ratio;
c Equilibrium Water Content;
d Initial Swelling Rate;
e $\mu = \sum \frac{m_i z_i^2}{2}$, where $\mu$, $m_i$ and $z_i$ are the ionic strength, the ionic concentration and charge on each individual ion, respectively; &
f Swelling Rate Constant

3. Characterization

3.1. Infrared spectroscopy

The IR spectrum of graft copolymer of sodium salt of partially carboxymethylated sodium alginate containing polyacrylonitrile is shown in Figure 6(a). The spectrum shows the absorption bands of sodium salt of partially carboxymethylated sodium alginate as well as an additional absorption band at ~2245 cm⁻¹, which can be attributed to $-\text{CaN}$ stretching mode.

Figure 6: FTIR spectra of (a) optimally synthesized graft copolymer of sodium salt of partially carboxymethylated sodium alginate containing polyacrylonitrile and (b) the superabsorbent hydrogel.
Figure 6(b) represents the IR spectrum of hydrogel. The disappearance of the nitrile sharp peak at approximately 2245 cm\(^{-1}\) and appearance of the two distinct bands at approximately 1562 cm\(^{-1}\) and 1411 cm\(^{-1}\), indicating the respective presence of C=O asymmetric stretching and symmetric stretching modes of the carboxylate anion and the absorption band appeared at approximately 1671 cm\(^{-1}\) indicating C=O stretching in carboxamide functional groups are the measure proofs for the conversion of the nitrile groups into carboxamide and carboxylate groups after alkaline hydrolysis of the graft copolymer. The presence of these highly hydrophilic groups is the main responsible factor for imparting super swelling behavior of the saponified graft copolymer i.e. hydrogel.

3.2. Scanning Electron Microscopy

As the textural characterization of a superabsorbent polymer is important to understand its swelling behavior, the surface appearance and structure of graft copolymer of sodium salt of partially carboxymethylated sodium alginate containing polyacrylonitrile and the hydrogel were observed using Scanning Electron Microscopy. These micrographs are shown in Figures 7(a) and 7(b). It can be seen upon comparing the micrographs that the morphology of the graft copolymer [Figure 7(a)] is observed to be totally different morphology [Figure 7(b)] as the graft copolymer was treated in the alkaline medium to yield the superabsorbing hydrogel [Figure 7(b)]. The hydrogel [Figure 7(b)] exhibits porous structure. It is supposed that these pores are the regions for the permeation of water into the polymeric network, and ultimately it helps in enhancing the water absorbency of the hydrogel.

![Figure 7: Scanning Electron Micrographs of (a) optimally synthesized graft copolymer of sodium salt of partially carboxymethylated sodium alginate containing polyacrylonitrile (500X) and (b) the superabsorbent hydrogel, H-Na-PCMSA-g-PAN (500x).](image)

Figures 8(a) to 8(b) also shows the scanning electron microscopy pictures of the lyophilized hydrogel samples swollen in different swelling media. It also becomes evident that from this figure that the hydrogel exhibits porous structure.

![Figure 8: Scanning Electron Micrographs of the lyophilized hydrogel samples swollen in (a) low conductivity water, (b) 0.15M aluminium chloride solution and (c) 0.15 M simulated urine for 24 h and then frozen all the samples in liquid nitrogen and lyophilized.](image)

4. Conclusions

This review article provides the report on the comprehensive literature survey with regard to the studies in hydrogels based on sodium alginate and its derivatives. However, in view of the availability of scanty reports on the
hydrogels synthesized from sodium salt of partially carboxymethylated sodium alginate, an attempt has been made to prepare a novel superabsorbing hydrogel through grafting of acrylonitrile onto sodium salt of partially carboxymethylated sodium alginate, followed by alkaline hydrolysis of the graft copolymer to achieve an in situ crosslinked hydrogel network with high capability of water absorption in different swelling media. The observed promising results make it worth to prepare hydrogel suitable for utilization as diaper as well as adsorbent material. The results regarding the absorbency measurements of the hydrogel in low conductivity water, 0.15M different salt solutions and simulated urine have been explained successfully on the basis of the “charge screening” effect and “ionic cross-linking” phenomenon. The experimental data clearly suggested that the swelling process of the hydrogel obeys second-order kinetics in different swelling media. The swelling characteristics as well as equilibrium water contents have also been investigated for the superabsorbent hydrogel in different swelling media.

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References


