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A REVIEW OF THE SYNTHESIS AND MODIFICATION OF PVA-ALGINATE AS BINDER OF METAL ATOM

(Ulasan Tentang Sintesis dan Pengubahsuaian PVA-Alginat Sebagai Pengikat Atom Logam)

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Abstract

PVA-alginate hydrogel is formed by mixing PVA and alginate with a simple method and then dropping it into a cross-linking agent that leads to rapid gelation. The PVA-alginate hydrogel can be synthesised in water due to the high solubility of starting material. Both compounds have hydroxyl group (-OH) in their structure that helps in terms of solubility and is consequently classified as an inexpensive, safe, and environmentally friendly synthesis method. Although its starting material is soluble in water, the PVA-alginate hydrogel is lessened. This is because the formation of hydrogen bonding of -OH in the PVA-alginate structure reduces its ability. Meanwhile, the presence of carboxyl ion ($-COO^-$) in the PVA-alginate hydrogel structure acts as an active site for the metal ion to bind. Some researchers modified the PVA-alginate hydrogel to improve the binding effect to metal by increasing the active sites of metal. The PVA-alginate hydrogel can act as a metal ion binder to remove heavy metals such example from transition metal elements in wastewater that are considered harmful to the ecosystem. This review provides an overview of PVA-alginate hydrogel design and its modification to improve the binding properties, and cross-linking. Finally, the limitation of PVA-alginate and its modification were revealed with suggestions for future research in the catalytic study.

Keywords: PVA-alginate, metal binder, metal

Abstrak

Hidrogel PVA-alginat dihasilkan melalui percampuran PVA dan alginat dengan mengunakan kaedah yang mudah dan kemudian dititiskan ke dalam agen penghubung silang untuk mempercepatkan gelatin. Hidrogel PVA-alginat boleh disintesis dalam air kerana keterlarutan bahan permulaan yang tinggi. Kedua-dua sebatian mempunyai kumpulan hidroksil (-OH) dalam strukturnya yang membantu dari segi keterlarutan dan seterusnya dikelaskan sebagai kaedah sintesis yang murah, selamat dan mesra alam. Walaupun bahan permulaannya mempunyai sifat larut dalam air, PVA-algina berkurangan disebabkan pembentukan ikatan hidrogen -OH

dalam struktur hydrogel PVA-alginat mengurangkan keupayaannya. Sementara itu, kehadiran ion karboksil (-COO^-) dalam struktur PVA-alginat bertindak sebagai tapak aktif untuk pengikat ion logam. Sesetengah penyelidik mengubah suai hydrogel PVA-alginat untuk meningkatkan kesan pengikatan kepada logam dengan meningkatkan tapak aktif logam. Hidrogel PVA-alginat boleh bertindak sebagai pengikat ion logam untuk membuang logam berat contohnya daripada unsur logam peralihan dalam air sisa yang dianggap berbahaya kepada ekosistem. Kajian ini memberikan gambaran keseluruhan reka bentuk hidrogel PVA-alginat dan pengubahsuaiannya untuk meningkatkan sifat mengikat dan pautan silang. Akhirnya, batasan hidrogel PVA-alginat dan pengubahsuaiannya telah didedahkan dengan cadangan untuk penyelidikan dalam kajian pemangkin pada masa depan.

Kata kunci: PVA-alginat, pengikat logam, logam

Introduction

Heavy metals are emitted from mining, metallurgy, and manufacturing from the consumption of natural resources through the development of industry and agricultural activities. Low or trace-level concentrations of heavy metals in water are harmful to ecosystems. Industrial wastewater such as Ni, Pb, Hg, Cd, Cr, and As can interfere with the functioning of living creatures by binding with their vital cellular components. The clean-up of the contaminated water is very challenging because toxic metals are non-biodegradable [1,2]. Therefore, methods for the removal of heavy metal ions from wastewater are of great significance.

Chemical precipitation, coagulation, solvent extraction, membrane processes, electrochemical, ion exchange, and adsorption are methods for the removal of heavy metals [3]. Adsorption is the process of adsorbent as a binder that content active functional that bounded to the metal ions. Binding is a simple process, with high efficiency, and a low-cost method. Moreover, binding is an environmentally, and efficient binder used to bind heavy metals. Examples of biopolymers binder (alginate, chitosan, and cellulose hydrogels) are widely used for the removing heavy metals [4].

Alginate is widely used in research because it can be obtained in natural resources (the cell wall of brown algae) [5]. It is non-toxic and biodegradable of linear biopolymers. It has a rich carboxyl and hydroxyl functional group [4]. The presence of the carboxyl functional group has excellent form to bind with heavy metals in wastewater. The composition of alginate and cross-linking ions determines the binding strength and properties of alginate beads [5]. However, the mechanical strength, stability, and heat resistance of alginate beads are relatively low; hence their applicability is limited [1].

In research the polymer blend method is used to improve physicochemical properties of alginate. Poly(vinyl alcohol) (PVA) polymer is used to blend with alginate, it is a non-toxic, synthetic, high-strength polymer and environmentally friendly [6,7]. PVA contains a hydroxyl (-OH) group that can form hydrogen bond with -OH of alginate to form PVA-alginate (Figure 1) [8]. The produced PVA-alginate is physically stronger and more durable than alginate alone, in spite of the fact that both polymers are soluble in water [9]. Also, the chemical and physical properties of PVA-alginate can be improved by the addition of cross-link agent in the structure, such as calcium chloride ($CaCl_2$) [10-14] or the combination of $CaCl_2$ and boric acid [15-17].

PVA-alginate needs modification to improve its binding properties [18]. The aim of this review is to study the synthesis and modification of PVA-alginate to improve the binding properties. Modification of PVA-alginate is by using Polyaniline (PANI), Fe_2O_3 nanoparticles, γ-Fe_2O_3 nanoparticles, γ- Fe_2O_3-TiO_2, zeolite, zeolite-polyethylene oxide and carbon corncob- Zoogloea sp. MFQ7. The review also concentrates on suitable cross-links used to synthesis and modified PVA-alginate such as $CaCl_2$, $CaCl_2$-$B(OH)_3$ and glutaraldehyde.

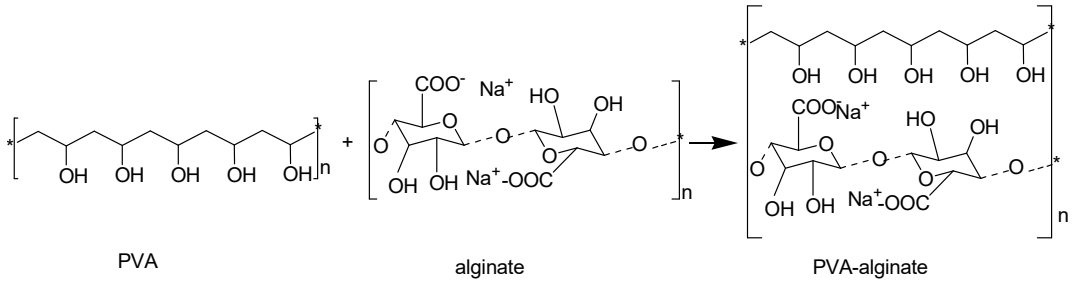

Figure 1. Chemical structure of PVA, alginate and PVA-alginate blended

Synthesis and Modification

In this paper, the PVA-alginate was synthesized by reaction between PVA and alginate. The discussion was continued with modification of PVA-alginate mixed either organic or inorganic or both compounds to take advantage of improving the binding properties. Then, capability of PVA-alginate as a binder with the transition metal was also scrutinized.

PVA has a lot of hydroxyl groups, which form hydrogen bonds with the water molecules and make it very soluble in water. The molecular weight and degree of PVA hydrolysis determine its solubility. The molecular weight is proportional to degree of hydrolysis. Meanwhile, the degree of hydrolysis is inversely correlated with its solubility. Due to the formation of intra- and inter- molecular hydrogen bonds between the hydroxyl groups amongst PVA (Figure 2), higher degree of hydrolysis was present and blunt its solubility in water. In contrast, inter- and intra- molecular hydrogen bonds are reduced due to the lower degrees of hydrolysis of steric hindrance brought on by a high concentration of hydrophobic acetate groups. Therefore, the solubility of PVA molecules in water molecules increased because the interaction of PVA and water increased [19,20].

Alginate is also soluble in water due to the presence of -COO^- and -OH functional group in the structure that can form a hydrogen bond with water. The molecular weight determines the solubility of alginate and its directly proportional to viscosity and degree of hydrolysis. The alginate has high viscosity because of the formation of a hydrogen bond due to the protonation of carboxylate groups in the backbone of alginate (Figure 3) [21]. To break the hydrogen bond between PVA and alginate during preparation by using water as a solvent is through heating [22], stirring [5], microwave [23] and distillation [22] process to form a homogenous PVA-alginate as shown in Table 1. Glycerin [7] and ferrofluids [23] are also used as solvent together with water. Preparation of PVA-alginate involves a single step (Number 10-13) or a few steps (Number 1-9). Form of PVA-alginate produced are beads [3,15], and fiber [22]. The temperature usually used is from 25 °C to 100 °C and duration to prepare PVA-alginate is 1 hours-24 hours.

Lee Te Chuan et al. [15] prepared PVA-alginate as binder of Cr^{6+}. PVA was dissolved in water and then heated with microwave for 1 minute, while alginate was also dissolved in water and stirred until dissolved. The PVA and alginate was blended until homogenous. PVA-alginate is a good binder of Cr^{6+}, where by 100% Cr^{6+} was bound to PVA-alginate. Li et al. [30] modified PVA-alginate in their study by using Polyaniline (PANI). Polyaniline (PANI) synthesized from phenylamine (PAN) was dissolved in acidified water and added with ammonium persulfate (APS). PANI obtained was added to PVA-alginate (Figure 4) because PANI contain many amine and imine functional groups, which is a good binder to metal. Amine and imine in PANI cause PANI to have three oxidation states, which are leucoemeraldine, emeraldine, and pernigraniline. During transition of PANI, electron donations occur from leucoemeraldine or emeraldine state to pernigraniline state. PVA-alginate-PANI was bound to Cr^{6+} at 95.25%.

Table 1. Preparation of PVA-alginate

No.	Step	PVA and/or Alginate	Solvent	Method	Temperature, °C	Hours	References
1	1	PVA	Water	Distillation	75-85	6	[22]
	2	Alginate	Water	Heat and stir	Not stated	Until dissolve	
	3	Mixed PVA-alginate		Stir	25	2	
2	1	PVA	Water	Microwave	100	0.017	[15]
	2	Alginate	Water	Stir	25	Dissolve	
	3	Mixed PVA-alginate		Stir		Homogenous	
3	1	PVA	Water	Heat	95	Dissolve then cools	[24]
	2						
	3	Add alginate			50	Dissolve	
4	1	PVA	Water	Stir	25	4	[23]
	2			Microwave		0.07	
	3	Alginate	Ferrofluid	Stir	25	Homogenous	
	4	Mixed PVA-alginate					
5	1	PVA	Water	Heat	80	4	[25]
	2			Microwave		0.07	
	3	Alginate	Water	-	-	-	
	4	Mixed PVA-alginate					
6	1	PVA	Water	Heat and stir Cool	80	2	[26]
	2			Stir			
	3	Alginate	Water		25	24	
	4	Mixed PVA-alginate					
7	1	PVA	Water	Heat	80	5	[18]
	2			Microwave	-	0.07	
	3	Alginate	Water	Stir	25	dissolve	
	4	Mixed PVA-alginate					
8	1	PVA-alginate	Water	Heat	90	1	[8]
	2			Stir	25	-until no burble	
9	1	Alginate	Water	Stir	25	Dissolve	[27]
	2	Add PVA		Heat and stir	80-85	3	
10	1	Alginate	Water	Stir	25	Dissolve	[5]
	2	Add PVA		Stir	25	dissolve	
11	1	PVA-alginate	Water	Heat and stir	90	dissolve	[28]
12	1	PVA-alginate	Water	Heat and stir	100	1	[6]
13	1	PVA-alginate	Water and glycerin	Heat and stir	95	Complete dissolved	[7]
14	1	PVA-alginate	Water	Heat	Not stated	Dissolve	[29]

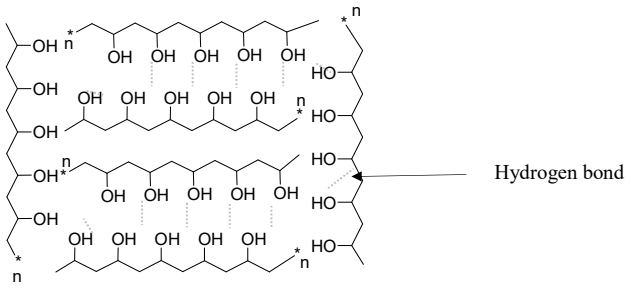

Figure 2. Hydrogen bond form between PVA

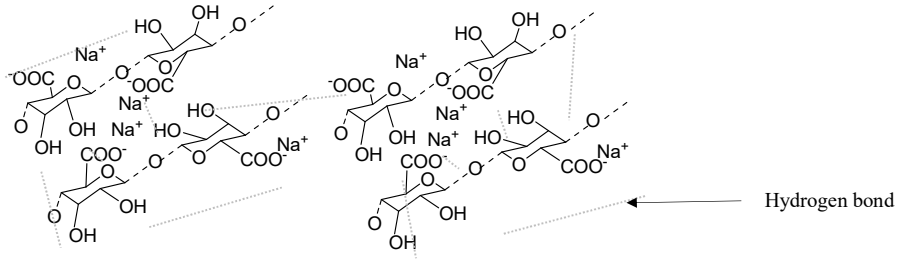

Figure 3. Hydrogen bonds formed between alginates

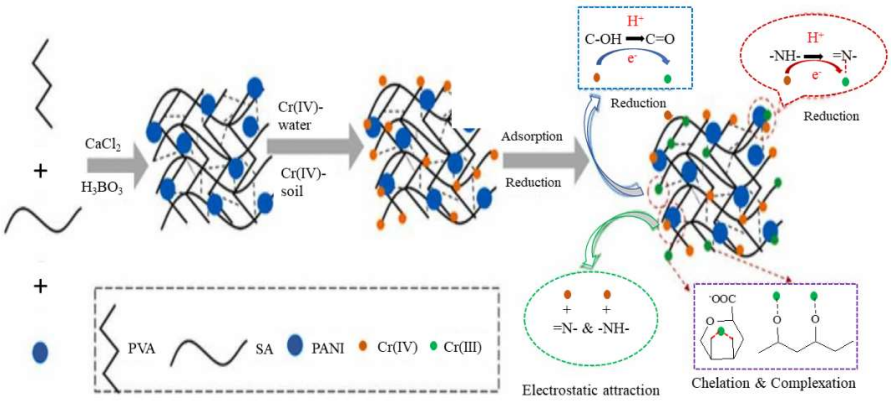

Figure 4. PVA-alginate-PANI as binder of Cr (VI) and Cr (III) [30]

Nie et al. [31] modified PVA-alginate by adding Fe_2O_3 which has surface that functionalize easily to bind with metals. Moreover, Fe_2O_3 have magnetic properties and superparamagnetic which leads to very high utilization in many fields. However, Fe_2O_3 nanoparticles are toxic causing limited usage. To reduce toxicity, they are blended with other polymers, proteins, silica or surfactant [32]. Nie synthesized Fe_2O_3 with green tea waste to reduce toxicity. Green tea was chosen because it is easy to find and many utilizations produce a lot of wastes. In addition, green tea waste contains a lot of hydroxyl groups and benzene rings known as polyphenols. Polyphenols are good as metal binders and have powerful reducibility. Fe_2O_3 was synthesized using

reflux $FeCl_2 \cdot 4H_2O$ and $FeCl_3$ dissolved in water and then added with ammonium hydroxide and heated. The Fe_2O_3 produced was added to green tea waste to obtain Fe_2O_3 nanoparticles. Fe_2O_3 was dissolve in water then added with PVA and alginate produce PVA-alginate- Fe_2O_3 nanoparticles. PVA-alginate-Fe_2O_3 nanoparticles (Figure 5) that were bound with Cr^{6+} and Cu^{2+} were 52.12 % and 59.78%, respectively. Result from three studies showed that the Cr^{6+} was excellently bound to PVA-alginate without modification.

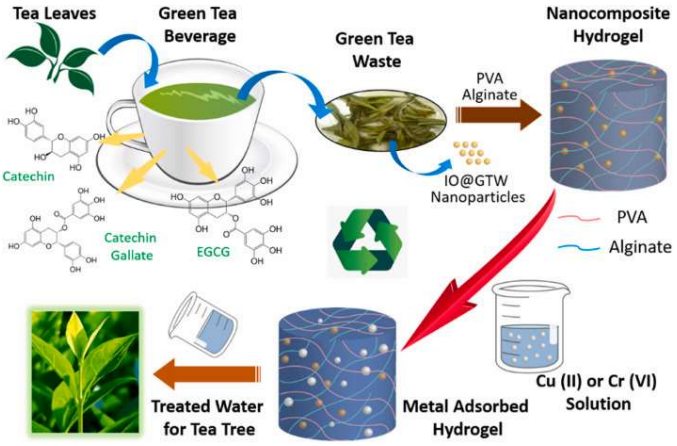

Figure 5. Synthesis of iron oxide nanoparticles by using green tea waste. Iron oxide nanoparticles were blended into PVA-alginate hydrogel to form PVA-alginate-Fe_2O_3 nanoparticles as a binder of Cu^{2+} and Cr^{6+} in an aqueous solution. The treated water was re-used for tea cultivation [31]

Zohreh Majidnia and Fulazzaky [3] also synthesized γ-Fe_2O_3 nanoparticles, magnetite (Fe_3O_4) precipitate which were acidified by using nitric acid form iron (III) nitrate nanoparticles. Then they were oxidized at 90 ºC. Then, γ-Fe_2O_3 nanoparticles were coated with trisodium citrate to remove all charges. The γ-Fe_2O_3 nanoparticles were blended with PVA-alginate to bind with Cs (I). PVA-alginate- γ-Fe_2O_3 nanoparticles that was successfully bound to Cs (I) was 91.8 %. In the study PVA-alginate also blended with titania (TiO_2) nanoparticles.

TiO_2 nanoparticles is non-toxic, have good stability, chemical and biological inert, with a larger surface area with relates to high binding properties (metal and non-metal) [33]. Zohreh Majidnia and Fulazzaky [3] prepared TiO_2 from titanium isopropoxide combined with acetyl acetone with presence of ethanol as solvent. The prepared solution was added with urea solution to deionized water via continuous stirring. The solution obtained was heated by using a furnace until yellowish white TiO_2 nanoparticles were obtained. The study found that PVA-alginate blended with TiO_2 able to bind to 90.1% Cs (I). They also prepared PVA-alginate blend with γ-Fe_2O_3 nanoparticles and TiO_2 nanoparticles. PVA-alginate- γ- Fe_2O_3-TiO_2 was successfully bound with 93.1% Cs (1). Therefore, PVA-alginate modified with Fe_2O_3 was suitable to bind more with Cs(I) that larger sized compared to Cr^{6+} small sized metal.

Ebrahimi et al. [22] synthesized PVA-alginate by reflux through distillation and stirring while alginate was heated and stirred. Then, PVA and alginate was blended until homogenous. PVA-alginate was used to bind with Cd^{2+} and it was found that 47.5% of Cd^{2+} could bind with PVA-alginate. Isawi [9] used the heating and stirring method to blend PVA and alginate. Then, zeolite was added to PVA-alginate due to its high binding properties because it is commonly used in the industry as a binder in ion-exchange separation and gas purification, molecular sieve, and soil modifier. Zeolites have a larger surface area with a small pore size. Moreover, it owes a

cage-like configuration which cause only medium size of metal ions to bind with zeolite. The larger surface area of zeolite is due to its structural form which is a three-dimensional tetrahedral framework in which each oxygen atom is shared by two tetrahedra, known as hydrated micro-porous alumino-silicate constituents [9].

Zeolite has a neutral charge caused by only Si in the structure. Substitution of Al in zeolite to replace Si causes its charge to be negative and need other metal ions (positive charge) to balance the charge, showing that it is very suitable to be a binder. Isawi [9] found PVA-alginate-zeolite (Figure 6) could bind to Pb^{2+}, Cd^{2+}, Sr^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+}, Mn^{2+}, and Li^{2+} at 99.5%, 99.2%, 98.8%, 97.2%, 95.6%, 93.1%, 92.4%, and 74.5% respectively, under pH 6. Meanwhile binding with Fe^{3+} and Al^{3+} that occurred at pH 5 were 96.5 % and 94.9 %, respectively although the binding process just allocated PVA-alginate-zeolite in solution that contained metal with shaking. Tabatabaeefar et al. [34] also used PVA-alginate-zeolite to bind with Ni^{2+} and Co^{2+} under pH 5.5 and reported that the percentages of Ni^{2+} and Co^{2+} bound were 83.7 and 84 %, respectively. A study done by Ebrahimi, et al. [22], Isawi [9] and Tabatabaeefar et al.[34] showed that larger size metals (Pb^{2+}, Cd^{2+}, Sr^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+}, Mn^{2+}, Fe^{3+} and Al^{3+}) bound excellently with PVA-alginate-zeolite. Meanwhile small size metals (Ni^{2+} and Co^{2+}) were less efficiently bound to PVA-alginate zeolite.

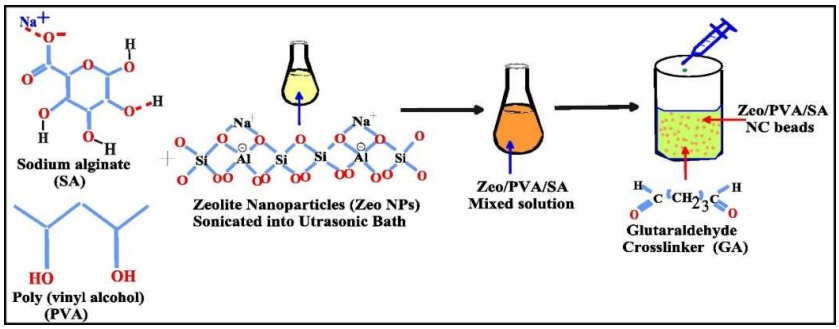

Figure 6. PVA-alginate-zeolite [9]

Although PVA-alginate-zeolite is suitable for metal binding, the large pore size on the surface of PVA-alginate-zeolite causes a barrier to the larger sized metals. Adding polyethylene oxide makes PVA-alginate-zeolite bind to the bigger sized of metals, especially metals located at the bottom of the periodic table that have a larger size. Polyethylene oxide can form cavities when added to PVA-alginate-zeolite, and thus form PVA-alginate-zeolite-polyethylene oxide (Figure 7). Fazel Zahakifar et al. [35] produced PVA-alginate-zeolite-polyethylene oxide to bind with U^{6+}. PVA and polyethylene oxide (PEO) were dissolved in a water in separate container and then heated until homogenous. Then, alginate was dissolved in water and heated until homogenous and added with zeolite. The alginate-zeolite was added to PVA-PEO. PVA-alginate-zeolite-polyethylene oxide produced was successfully bound either 81.4% of U^{6+}. Zahakifar et al. [36] also used PVA-alginate-zeolite-polyethylene oxide in their study and found 65.2 % of thorium (Th) (IV) was successfully bound with PVA-alginate-zeolite-polyethylene oxide.

Bacteria are also good in combining with PVA-alginate to bind with metal. Wang et al. [28] utilized corncob from agricultural waste. Corncob was heated by using a furnace to form carbon corncob. Carbon corncob is used for Zoogloea sp. MFQ7 bacterium to do microbial activity in anaerobic form and convert Mn^{3+} to Mn^{2+} (Figure 8). PVA and alginate were dissolved in water and heated. The cooling PVA-alginate was added with carbon corncob- Zoogloea sp. MFQ7. PVA-alginate-carbon corncob- Zoogloea sp. MFQ7 synthesized was used to bind Mn^{2+}, whereby 72.74% Mn^{2+} was successful bound.

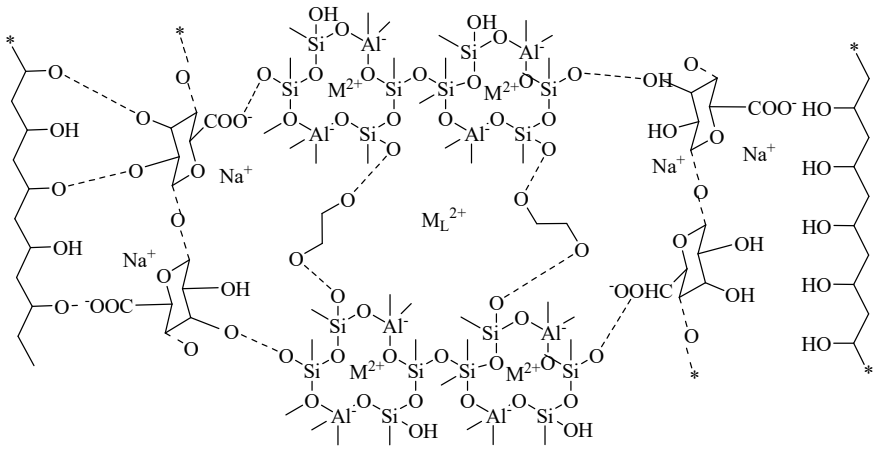

Figure 7. PVA-alginate-zeolite-polyethylene oxide (Note: M^{2+}= metal ion and $M_L{}^{2+}$= large metal ion)

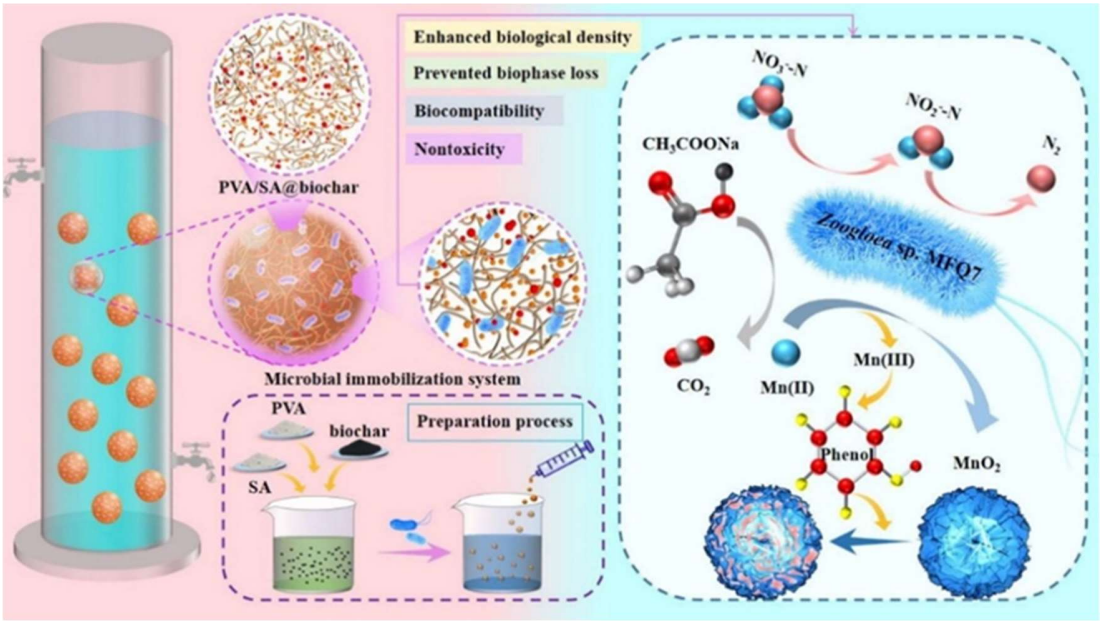

Figure 8. PVA-alginate-carbon corncob- Zoogloea sp. MFQ7 [28]

Table 2 lists modifiers to modify PVA-alginate as a binder of metals. Each modifier has criteria and is very selective to help PVA-alginate as a metal binder. PVA-alginate alone is a suitable binder for metal atoms. The surface area of PVA-alginate increases upon modification with the modifier to increase the selectivity and percentage of binding metals. The combination of PVA-alginate with modifier also increases the character of PVA-alginate as a binder towards bigger metal atoms. Usually, the best pH value condition used by researchers during the binding process is between pH 4-8 which, influence the percentage of binding PVA-alginate and modifier to metals ions.

Table 2. List of modifiers to modified PVA-alginate as a binder of metals

Modification	Metal Bind	Percentages of Binding (%)	Cross-Link	References
-	Cd^{2+} } pH5	47.5	Heat	[22]
-	Cr^{6+}	100	Boric acid, $CaCl_2$ and Na_2SO_4	[15]
Green tea waste and Iron oxide	Cr^{6+}	52.12	$CaCl_2$	[31]
	Cu^{2+} } pH 4	59.78		
Maghemite	Cs^{+} } pH 8	91.8	$CaCl_2$ H_3BO_3	[3]
Titania		90.1		
Maghemite-titania		93.1		
Polyaniline	Cr^{6+}	95.25	$CaCl_2$ H_3BO_3	[30]
zeolite nano	Pb^{2+}	99.5	Glutaraldehyde	[9]
particles	Cd^{2+}	99.2		
	Sr^{2+}	98.8		
	Cu^{2+} pH6	97.2		
	Zn^{2+}	95.6		
	Ni^{2+}	93.1		
	Mn^{2+}	92.4		
	Li^{2+}	74.5		
	Fe^{3+} pH5	96.5		
	Al^{3+}	94.9		
Zeolite	Ni^{2+} pH5.5	83.7	Heat	[34]
	Co^{2+}	84		
Polyethylene oxide and zeolite	U^{6+} } pH5	81.4	Heat	[35]
Polyethylene oxide and zeolite	Th^{4+} } pH5	65.2	Heat	[36]
Zoogloea sp. MFQ7 And glacial acetic acid	Mn^{2+}	72.7	$CaCl_2$	[28]

Cross-link

The combination structure of PVA and alginate are physically robust, in spite of the fact that both polymers are soluble in water [9]. To reduce the solubility and increases the physical and chemical properties of PVA-alginate by the addition of a cross-link agent in the structure. Chen et al. [37] reported that, chemical cross-linking was widely used to alter the physical properties of polymeric materials. Linking of polymer chains through chemical linkages gives a more rigid material structure and potentially a better-defined shape. The chemical cross-linking of polymers was not only limited to bulk materials, but also led to the creation of micro- or nano-sized organic particles which occurred as a covalent or ionic cross-link. List of chemical cross-links of PVA-alginate are calcium chloride ($CaCl_2$) [10-14] or the combination of $CaCl_2$ and boric acid [15-17] and glutaraldehyde [9,34]. Physical cross-link PVA-alginate is a freeze-thawing process [22,34,35].

Calcium chloride ($CaCl_2$) is the commonly used cross-linker to solidify PVA-alginate. Solidification occurs based on adsorbent via ion exchange, and chelation provides the resulting PVA-alginate gel with a significant structural strength. The ion exchange occurs when calcium ions take the place of sodium in the alginate of PVA-alginate. A polyvalent ion binding reaches the cross-linking with two carboxylic functional groups on adjacent polymer chains. Besides, this reaction can be accompanied by the chelation of calcium ions at the hydroxyl and carboxyl functional groups of sodium alginate chain [38]. Wang [39] found that the best per cent of $CaCl_2$ cross-linker used was 2 % because the function of Ca^{2+} enlarged the material suction space.

The formation eggbox model (each calcium atom is coordinated to the carboxylates and hydroxyl groups of four G monomers from two adjacent chains of alginate) was extensity studied (Figure 9) [40].

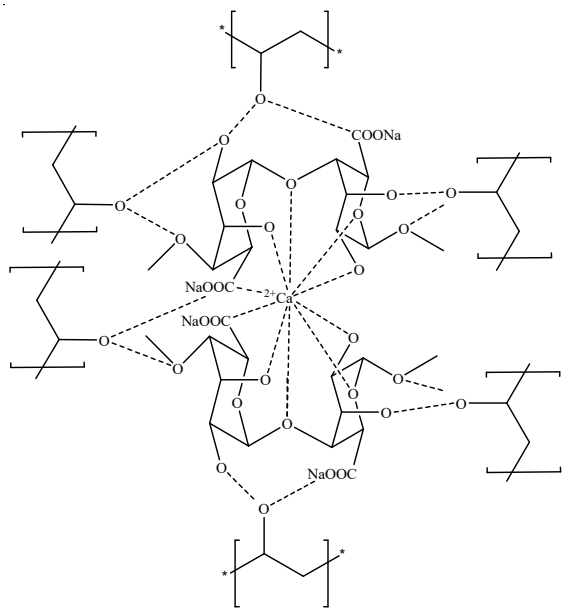

Figure 9. The reaction mechanism of $CaCl_2$ cross-linker with PVA-alginate

Mixed calcium chloride ($CaCl_2$) and boric acid ($B(OH)_3$) which were utilized as cross-linker to obtain spherical beads, prevented agglomeration during the PVA-alginate cross-linking process and improved surface properties (Figure 10). Boric acid was used to assist the cross-link between PVA polymer with tetrahydroxyborate ions ($B(OH)^{4-}$) cross-linked with the hydroxyl group (OH) on adjacent chains. The cross-link between two hydroxyls (PVA) and one borate ion is known as “di-diol” complexation. Boric acid is an electron acceptor (Lewis acid); it has an empty p orbital attracted to lone pair of the hydroxyl group of PVA. At the same time, calcium replaces the position of sodium in alginate, whereby two carboxyl’s in alginate bond to calcium. Since the crosslink process between PVA-alginate by boric is slow, it is not used as a stand-alone cross-linker as a consequence of agglomeration problem that trigged the polymer rigid to break up [41].

Glutaraldehyde is an organic compound with formula $(CH_2)_3(CHO)_2$. It consists of a five-carbon chain doubly terminated with formyl (CHO) groups. It is most widely used as a cross-link because it is inexpensive and easily available [43]. Moreover, it has good mechanical performance and stable chemical properties [44]. Glutaraldehyde has highly reactive bifunctional agent of aldehyde groups located at both ends, while able to bond to hydroxyl, imidazole group, amine, thiols and phenols [45]. The cross-linking occurs between aldehyde groups of glutaraldehyde and hydroxyl groups of alginates [9, 34] and PVA polymers [44] (Figure 11).

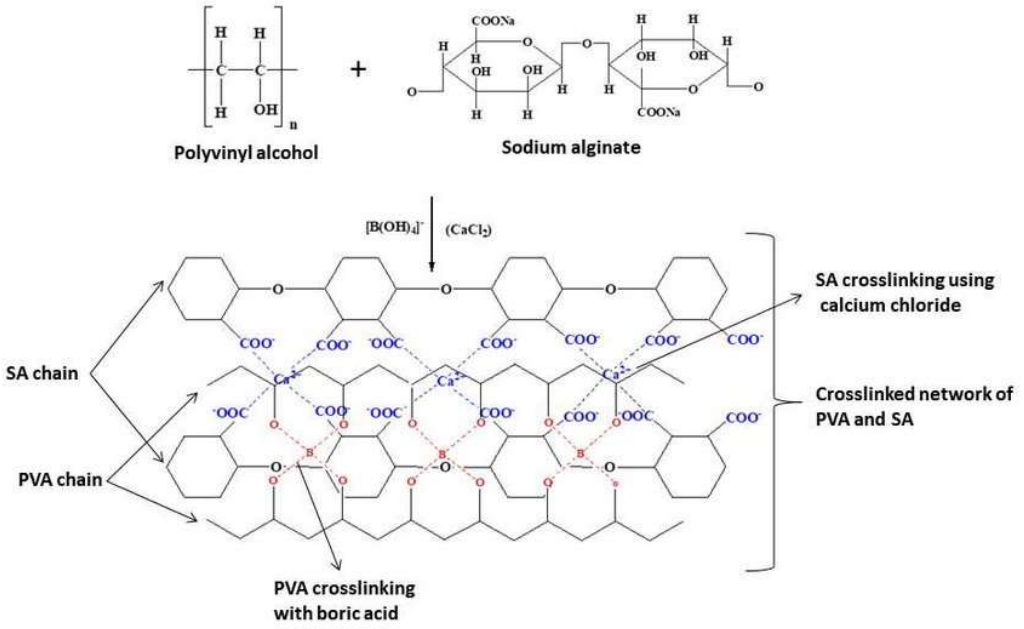

Figure 10. The reaction mechanism of $CaCl_2$ and $B(OH)_3$ cross-linker with PVA-alginate [42]

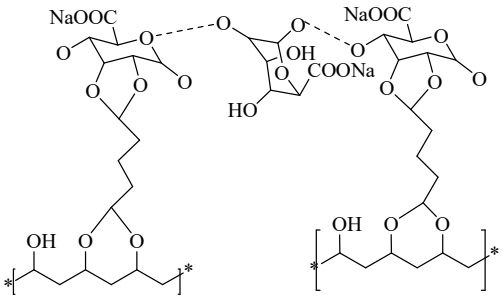

Figure 11. The reaction mechanism of Glutaraldehyde cross-linker with PVA-alginate

Freeze-thawing is a physical cross-link PVA-alginate which is widely used for pharmaceutical and biomedical applications. It is non-toxic, chemical free and biocompatibility [46]. In the freeze-thaw method, the concentration of polymer is increased due to bulk solvents or low molecule solutes freezing (crystallization). The network structure formed because chain space in the polymer was minimized and enabled the chains to align and connect to each other during the freezing process [47]. During thawing process, the polymer assembles and cross-link between the polymer due to defrosting solvent [48, 49] (Figure 12). Gel of PVA-alginate by freeze-thawing has high water uptake and is rubbery [46]. Therefore, chemical cross-link especially $CaCl_2$ as a cross-linker is preferable because it is easy to solidify and the structure strength of PVA-alginate is used as a metal binder.

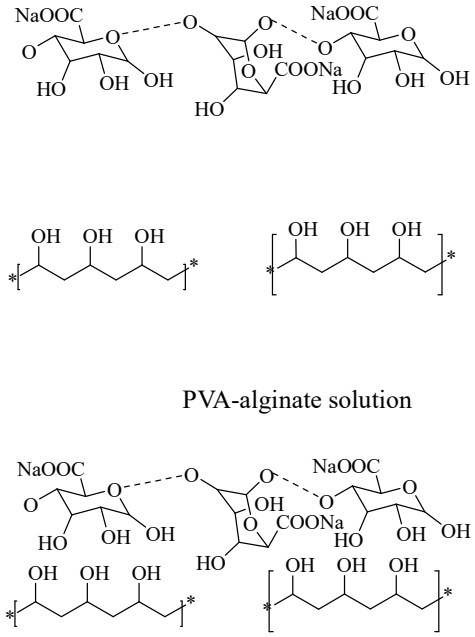

Figure 12. The reaction mechanism of freeze-thawing cross-linker with PVA-alginate

Conclusion

In this study, the synthesis and modification PVA-alginate binder were summarized. These binders have shown excellent binding performance towards metal ions. Highlights in this finding are: (i) PVA-alginate are good binder to small metal with low cost and an environmentally friendly binder, (ii) zeolites are good modifiers of PVA-alginate but only with a large sized of metal ion, (iii) PVA-alginate- zeolite- polyethylene suitable binder of larger sized of metal ion, (iv) $CaCl_2$ cross-linking agent are good to solidify PVA-alginate. Suggestions for future study are that PVA-alginate polymer is a good metal catalyst support for catalytic study of the carbon-carbon coupling reaction because it is a good metal binder and have good structural strength.

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