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Synthesis and applications of inverse vulcanized polysulfides from biocrosslinkers

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ABSTRACT

Elemental sulfur, an industrial by-product from petroleum industries worldwide, has drawn sufficient attention to researchers. The limited scope of application has caused a colossal surplus amount of elemental sulfur stacked in the open places. Several polysulfide synthesis processes, including condensation, free-radical process, and ionic copolymerization technique, were used but resulted in unstable products. A new polymerization technique, termed inverse vulcanization, has been introduced, which enabled different types of crosslinkers for polysulfide production and their scopes to explore numerous applications. The current paper concisely reviews the evolution and advances of using vegetable oils and plant extracts in inverse vulcanization to produce polysulfides. The alluring applications and properties have also been discussed briefly.

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1. Introduction

Sulfur is just 0.052 wt% of the Earth's crust. But the availability of elemental sulfur is increasing day by day and surpasses 70 million metric tons every year [1]. Elemental sulfur was available from ancient times and had many uses also. The uses have evolved with the time being. Some of the essential uses of elemental sulfur include pesticide and medicinal purposes, components of explosive and gunpowder, rubber vulcanization, sulfuric acid synthesis [2]. Sulfur was also at the heart of the significant search of Alchemy for decades, with a fallacious desire to turn metals into gold [3]. Sulfur is the oldest known and nontoxic element to humans. It is also a stable and cheap feedstock with high purity under ambient conditions with non-hygroscopic nature. These characteristics enticed the ancient chemists to make sulfur a suitable reagent for organic chemistry [4]. Petroleum oil refineries, the natural gas processing industry, or fossil resources generate a large amount of detrimental and unwanted sulfur, which is transformed into elemental sulfur. Amongst the sources, 98% of global elemental sulfur generation is caused by the refineries and overwhelming the market demand [5]. Sulfur has many applications. It is now mostly used in the manufacture of sulfuric acid. The high capacity for

per weight alkaline metal storage has turned sulfur into a promising material for rechargeable battery cathodes [6]. There is also high transparency of sulfur-rich materials in the IR region, which enables their application in optical IR materials.

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Moreover, sulfur has insecticidal properties to be used in the agro-industries. Besides these, sulfur is used to manufacture food preserving agents, Portland cement, surfactant, pharmaceuticals, detergent, ammonium sulfate, disintegration agents, matches [7]. Elemental sulfur has plentiful allotropes for its tantalizing properties, but the routes of direct sulfur synthesis are much limited for some drawbacks. A variety of copolymerization techniques have been introduced directly from elemental sulfur to the production of polysulfides, including free-radical, condensation, and ionic copolymerization. Pyun and the coworkers developed a novel route for the high sulfur content polymer to surmount the problems and produce chemically processable and stable polysulfide with a moderate amount of divinylic comonomer di-isopropenyl benzene (DIB), called inverse vulcanization [8]. The reaction path is given in Fig. 1. The general approach for inverse vulcanization is to dissolve the linker monomers directly into liquid sulfur and raise the molten solution beyond the floor temperature (159 °C) for the ROP of elemental sulfur. Molten sulfur is not only the solvent itself but also performs as a monomer and initiator. The polymerization process is simple and extensively atom efficient, which is an outstanding illustration of green chemistry. Moreover, this

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Fig. 1. Preparation of inverse vulcanized stable polysulfides [8]

solvent-free and facile technique enabled the kilogram scale polymer preparation [9]. Inverse vulcanization has also facilitated a wide range of crosslinkers including organic and inorganic materials [7]. Inverse vulcanized polysulfides have been used in several sectors. Polysulfides have been used in Li-S or Na-S rechargeable batteries for their substantial higher capacity value [10]. Nanoparticles have been induced in the polysulfides, which enhanced the optical and material properties [11]. The polysulfides have significant uses for heavy metal treatment such as mercury [12,13], gold [14], iron [15], palladium. Control released fertilizers have been produced from the inverse vulcanized polymer [16,17].

Oils and fats extracted from the plant source are considered as vegetable oils. The practice of using unsaturated vegetable oils and plant extract to prepare polysulfides has been seen from ancient times. Factice, a gel-like modifier, formulated with up to 25% sulfur and used to produce various pencil erasers and rubbers. Another remarkable example was ebonite, a hard and resilient building material where ~30–50% sulfur was heated with natural rubber in the presence of linseed oil [18]. Vegetable oils are produced on a scale of million tons all over the world. According to the statistics by the Foreign Agricultural Service of the US Department of Agriculture, the estimated amount of vegetable oil consumption in 2020/21 is 207.93 million metric tons [19]. In Fig. 2, the graph



Fig. 2. Prediction of globally consumed vegetable oil by types (million metric tons) in 2020/21 [19].

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shows the consumption of different types of vegetable oils. They are obtained chiefly from seeds or beans. The seed processing is accomplished by pressing or hexane extraction. Seeds contain oils in varying amounts.

In the current work, a comprehensive discussion will be done on using different vegetable oils and plant extracts as biocrosslinkers for the inverse vulcanization. The chemistry between the elemental sulfur and triglycerides with challenges during inverse vulcanized polysulfide preparation will be included. Moreover, the scopes of the produced polysulfides from these biocrosslinker classes will be reviewed.

2. Vegetable oils and plant extracts as crosslinker

Inverse vulcanization is a new technology of polysulfide synthesis where crosslinkers play a crucial role. Because of undergoing extreme temperature (\sim 185 °C) during the inverse vulcanization, the thermal stability of the crosslinker monomer is essential. The molecular weight of the produced polymer, thermal stability, shape persistent nature, and other vital properties vary according to the different crosslinkers. But still, there are many ambiguities to explain the dramatic change of different characteristics where the crosslinkers are very close in terms of unsaturation degree and molecular mass [20].

2.1. Vegetable oils

Triglycerides containing fatty acid chains control almost all the chemical and physical characteristics of vegetable oils. The presence of unsaturated double bonds of the vegetable oils makes them suitable to be the monomers of the inverse vulcanization process. A list of the used vegetable oils till now for inverse vulcanization is given in Table 1.

The first example of using vegetable oils for inverse vulcanized polysulfides was found in 2016. Sunflower, linseed, and olive oil were used to get the polysulfides at 160 °C under continuous rapid stirring for 50 to 70 min [18]. Although these three different vegetable oils have no similar fatty acid compositions, they showed almost the same characteristics with 80% sulfur content. The complete conversion of sulfur got disrupted while the sulfur content was raised over 80% [18]. Another research group formulated rubbery polysulfides from sunflower, olive, and canola oil at 180 °C [12]. The reaction time varied due to the different gel points of the selected vegetable oils.

The most used vegetable oil for inverse vulcanized polysulfides is canola oil [15,23-25]. Chalker and his team have done an exhaustive investigation on canola oil based polysulfides. They synthesized the copolymers at 180 °C for 50%, 60%, and 70% sulfur content. They prepared a porous version of the polysulfides in the presence of NaCl porogen, which improved the surface area of the polymers [12,15,24]. They also hypothesized heating the reaction mixture in both household and laboratory microwaves to meet the demand of the polysulfide quantity. It turned out a successful experiment that reduced the synthesis process's drastic time change, which can scale up the product amount [15]. Later on, the same team experimented with kilogram scale production of polysulfides next year with canola oil and successfully synthesized polysulfides with 98% vield and consumption of 87% alkene [24]. The copolymer was termed as "low-density polysulfide" and had the hydrophobic property as well. Chalker and his team investigated a post inverse vulcanization reaction compression molding [25]. The rapid and straightforward process needs only a hot press where about 100 °C the composite material can show some tunable and functional mechanical characteristics. Chalker and his team later investigated to prepare a sorbent by mixing activated

Table 1

List of the used vegetable oils with fatty acid percent composition for inverse vulcanization [21,22].

Vegetable oil	linoleic	oleic	palmitic	linolenic	stearic
Canola	22.2	64.4	2.5	8.2	1.0
Sunflower	64.4	21.4	6.1	-	5.3
Soybean	63.7	20.2	6.0	5.0	5.2
Olive	16.0	64.0	14.0	2.0	2.0
Linseed	17.0	22.0	5.0	52.0	3.0
Cottonseed	38.0	41.0	18.0	1.0	2.0
Corn	59.8	26.7	10.6	0.9	2.0
Rubber seed	39.6	24.6	10.2	16.3	8.7

carbon and canola oil based polysulfides which successfully prevented leaching by confining the heavy metal pollution with the dynamic S-S bond of the composite [23]. A comparison between canola and other vegetable oil based inverse vulcanized polysulfides like castor and rice bran oil was tested later [26]. Canola oil based copolymer showed the highest yield (97%) compared to rice-bran oil (94%) and castor oil (84%). The unreacted alkene amount for canola, rice bran, and castor oil based copolymers were respectively 14%, 7%, and 23%. The vegetable oil based polysulfides have excellent wettability due to the presence of hydroxylated ricinoleic acid. Chalker and his team also prepared canola oil based polysulfides at 180 °C with NPK fertilizer components (NH₄)₂SO₄, CaHPO₄, KCl [16].

Soybean oil was used to synthesize a new type of sulfur fertilizer where a conveniently accessible sulfur structure could be found for the oxidizing microorganisms (*A. niger*) [17]. The rubbery-like polymer was found at 165 °C within 40 min. The comparison of using high sulfur amount during the inverse vulcanization showed satisfactory results for 50 wt% S copolymer. While 90% sulfur content provided an inhomogeneous two-phased material, 50% sulfur content polymer had a smooth uniform surface. Recently, a mixture of several vegetable oils, including soybean (59%), canola (21%), sunflower (10%), rice (3%), peanut (3%), corn (3%), sesame (0.6%), linseed (0.4) was used to prepare both porous and non-porous polysulfide at 180 °C [14]. The oil mixture enabled the multiple uses of the polysulfide for wastewater treatment.

Corn oil was explored to prepare inverse vulcanized polysulfide through heating at 170 °C for 60 min and varying the sulfur content from 50 to 80% [27]. But only 50 and 60 wt% S copolymer gave the homogeneous polymer, and further increased sulfur content resulted in a dense polymer which is also a sign of incomplete conversion. The same research team investigated the use of rubber seed oil at 160 °C as a potential crosslinker for inverse vulcanization and used RSM to optimize the reaction parameters [28]. Cottonseed oil was examined as a potential crosslinker for inverse vulcanized polysulfide [13]. The polymer was prepared at 150 °C, and micromolecular modifiers were introduced during the postmodification process into the plant rubber copolymer to increase the adsorption capacity.

2.2. Plant extracts

Besides vegetable oils, several plant extracts and unconventional plant oils have been explored to prepare inverse vulcanized polysulfides. Limonene is an inexpensive by-product obtained around 70 thousand tons per year from the citrus industry [29,30]. A 50 wt% sulfur copolymer was prepared using limonene as bio-crosslinker heating for 90 min at 170–180 °C [31]. A red wax-like coating or desired solid mold was found by cooling at room temperature for heavy metal sorption. Hasell and his team also produced limonene-based sulfur copolymers at 175 °C [32,33]. The team identified some drawbacks of the S-limonene copolymer. The resultant polymer was not shape-persistent due to its low molecular weight, which was resolved by introducing dicyclopentadiene (DCPD) [33]. The new polymer showed moderate tensile and flexural strength.

Diallyl sulfide (DAS), diallyl disulfide (DADS), and myrcene have also been used to obtain the inverse vulcanized polysulfides [34-36]. DAS and DADS are found from the onion and garlic essential oil and responsible for their pungent odor [36,37]. Myrcene is extracted mainly from thyme oil which is a natural terpene [36,38]. S-DAS copolymer was synthesized at 170 °C varying 50-90 wt%, resulting in a highly flexible polymer film [35]. Jenkins and her team prepared garlic essential oil (DAS, DADS) based polysulfides through the inverse vulcanization by heating it at 180 °C for 60 min [34]. They reported a substantial adhesion decrease at 80% sulfur content. Hasell and his team used 175 °C for obtaining a rubbery sulfur copolymer from garlic essential oil [39]. Both teams explored the solubility of the resultant polymer, which turned out an insoluble polymer.

Algae oil obtained from B. Braunii containing unsaturated hydrocarbon botryococcene has been explored as a suitable crosslinker for the inverse vulcanization [40]. The copolymer was produced at 185 °C by varying the sulfur content from 50 to 90 wt%. Cardanol provides benzoxazine, an inexpensive crosslinker obtained from the cashew industries and used for polysulfide synthesis at 185 °C [41,42]. Being a low viscous monomer, cardanol benzoxazine tackles the elevation of viscosity during copolymerization. The long unsaturated alkyl chain creates supplementary reaction sites and extra thermal stability as well. Eugenol allyl ether extracted from Syzygium aromaticum, commonly known as clove oil, has been used to produce inverse vulcanized polysulfide [43]. The mixture was heated for 60 min at 180 °C and resulted in a dark red glassy polymer. Hasell and his team explored perillyl alcohol as a bio crosslinker for inverse vulcanization at 175 °C [44] and 180 °C to produce a microporous polymer in addition with farnesol, another plant extract, and other organic crosslinkers including DIB and DCPD [45]. The reaction mixture was heated for 25 min to get a ruby red copolymer with better T_g and sulfur stabilizing property [44]. Perillyl alcohol is extracted from essential plant oils like lemongrass, peppermint, sage and lavender and can also be obtained from bioreactor [46,47]. They also synthesized Ssqualene copolymer maintaining the same reaction procedure [44]. Squalene is a natural terpene primarily found in aquatic animals but now can be synthetically extracted from fungus [48]. Hasell group also used farnesene and farnesol as bio-crosslinker to synthesize inverse vulcanized polymer at 175 °C for 45 min [32]. The resulted polymer was a solid product of black color. Both comonomers are extracted from plant sources, including peaches, apple coating, Asiatic crop species like perilla, some species of Gardenia, potato tree, acacia tree. Some essential oils like chamomile, citronella, lemongrass, ambrette seeds, neroli, musk, cyclamen, rose, tolu, tuberose, and balsam are sources of farnesol [49,50]. The research group also explored terpinolene, a cyclic structured monoterpene, as an alternative crosslinker to reduce the feedstock stock extracted from some commercially available cannabis chemovars [33,51]. In the study, terpinolene was blended with either any of the following organic crosslinkers like DIB, DCPD, and ethy-

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lene glycol dimethyl acrylate (EGDMA) to influence the ductility of the polymer.

3. The chemistry between elemental sulfur $\left(S_{8}\right)$ and the biocrosslinkers

Polysulfides are compositionally classified based on three categories which had covered all known polymers till 1985: higher polysulfides or hyperstoichiometric (RS_{2+x}), stoichiometric disulfides (RS_{2.0}), and lower polysulfides or hypostoichiometric (RS_{2-x}) [52]. Most of them typically lead to ill-defined outcomes. Despite having the potential indication of excessive sulfur utilization, the resultant polysulfides from different polymerization methods had either lower sulfur incorporation rate into the final products or formed polymeric materials of minimal processability and property tuning [2]. A ring-opening polymerization (ROP), initiated by high temperatures typically above 159 °C, forms a polysulfide chain with further addition of other crosslinkers. Heating beyond it, sulfur quickly transforms into a one-dimensional metastable elastomer. While temperature exceeds 200 °C, the chain length reduces despite the increase of polysulfide amount. After getting back to room temperature, the polysulfides and the other rings turn into the cyclic sulfur structure [53]. The inverse vulcanization process solved the problems of obtaining a high sulfur content copolymer where sulfur is heated to obtain the ROP first and the crosslinker monomers are slowly added to the reaction mixture to get the desired high sulfur content polymers [1,2,10,54]. The triglycerides of each vegetable oils consist of a different fatty acid composition depending on its source, and C=C of the fatty acid breaks down to react with elemental sulfur during ROP [21]. From spectroscopic analysis, the reaction of the alkenes in triglycerides has been revealed, like the evidently observed C-H sp² bond stretch of the triglycerides has not been seen in any polysulfides [15,18,26]. A standard route of reaction between elemental sulfur and vegetable oils during inverse vulcanization is sketched down in Fig. 3, where R represents the different triglycerides according to the vegetable oil source. The alkene functional groups present in different triglycerides are responsible for the requisite points to crosslink during inverse vulcanization. The Z stereochemistry of these alkenes, which imparts strain to the olefin, was expected to facilitate a rapid response to sulfur radicals formed in inverse vulcanization [12]. However, there is no extensive and defined information on the reaction mechanisms of the vegetable oil based inverse vulcanized copolymers due to the structural complexity of the crosslinkers and unspecified reaction mechanism [55]. But it is proven that introducing vegetable oil crosslinkers have produced a superior polymer. The reaction mixture exhibits two stages for all vegetable oil based polymers. At first, a two-phased mixture is formed, which later became a single-phase liquid and subsequently resulted in a dark brown or red rubber. Chalker group attributed the difference of the total reaction time required for different vegetable oil based polymers to the unsaturation amount of the vegetable oils to attain their gel point [12]. Thermogravimetric analysis (TGA) has confirmed two significant mass losses of all vegetable oil based polysulfides [12,15,18,26,27]. The thermal decomposition of weak S-S bond and unreacted sulfur content causes the initial significant mass loss. The bond cleavage of C-S and the excess triglycerides are responsible for the other consequential mass loss. From several studies showed that the use of porogen (NaCl) increased the porosity and the surface area [14,15,39]. The emission of H₂S gas at high temperature (>200 °C) also created a porous surface of the resulted copolymers [21].

Both vegetable oils and plant extracts are abundant and costeffective comonomers. But the use of various plant extracts instead of vegetable oils becomes more reasonable to some extent as they have significant sulfur stabilizing percentage (up to 90 wt%) against S₈ depolymerization compared to the vegetable oils (up to 25–30 wt%) [44]. The plant extracts contain the alkene group that actively participated in the ROP during inverse vulcanization. The number of unsaturation like C=C has a linear relation with stable high sulfur content polymer [34,36,44]. Fig. 4 describes the reaction path of the plant extracts as crosslinkers in inverse vulcanization. Plant extract based crosslinkers produce low molecular weight copolymers [33,35,42]. They exhibited a major mass loss during TGA, while vegetable oil base copolymers showed two major losses. The major loss is similar to the first major loss of the vegetable oil based polysulfides discussed earlier. The gradual mass loss other than the first major loss indicated retaining the feed ratios in the ultimate copolymer products [40,43,44]. Generally, all of the polysulfides produced from plant extracts are highly shape persistent except farnesene [21,55,56]. Jenkins and her team observed the insoluble nature of the polysulfides derived from plant extracts and identified the two factors behind the phenomenon [34]. The factors are crosslinking and sulfur content. The molecular weight of the polymer also has a reciprocal relationship with solubility. Yet, the team has not fully described the impacts of the factors behind insolubility.

4. Applications of polysulfides synthesized from biocrosslinkers

After introducing the inverse vulcanization technique, the petroleum-based crosslinkers have used first to synthesize the polysulfides. Later on, the vegetable oils and plant extracts have replaced the conventional crosslinkers as they have similar properties. Moreover, they are abundant and inexpensive. So, these new bio crosslinkers based polymers are applied in various fields. In Fig. 5, a graphical illustration describes the applications of the polysulfides at a glance.

Inverse vulcanization has enabled the use of high sulfur content polymers. Sulfur has been used as potential material for preparing the cathode material of the Li-S battery. Sulfur is an alluring cathode material for its high capacitance. But complex electrochemistry and extremely low conductivity of sulfur cause high solubility of the Li-S polymers in the electrolyte, which is why the batteries have low cyclability [57,58]. As cathodic materials for Li-S batteries, high-sulfur content polymers are primarily distinguished by improved cycling capacity retention. The high sulfur content, above 80%, exhibited a decrease rate in the dissolution of active material into the electrolyte. The mechanical integrity reten-



Fig. 3. The reaction path between triglycerides of vegetable oils and elemental sulfur in inverse vulcanization [26].

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Fig. 4. The reaction path between the plant extracts functional groups and elemental sulfur in inverse vulcanization [44].



Fig. 5. Uses of bio-crosslinkers based sulfur copolymers.

tion of the cathode material might be one reason for the better cyclability of the polysulfides compared to only sulfur. The polysulfides also showed high coulombic efficiencies [18,36,41]. The biocrosslinkers based polysulfides have been used vastly for heavy metal removal and remediation of oil spills. Mercury [12,13,26,31,32,39,44,45], palladium [31], iron [15], lead [23], gold [14] and oil spill [24] are removed using high sulfur content copolymer adsorbent. The polysulfide adsorbent prepared from the bio-crosslinkers showed an excellent adsorbent capacity for heavy metals. The triglycerides and diene of the vegetable oils and the plant extracts portion played the key role during the sorption and studies showed that these polysulfide sorbent were highly selective to capture the heavy metals both from water and soil

[26,39]. Some triglycerides increase the wetting and uptake rate of the heavy metals as well [26]. The oil spill like crude oil and diesel fuel was efficiently remediated from both oil-polluted fresh and sea water using the sorbents and the sorbent could be use multiple times which is a real advantage [24]. Soybean oil based polysulfides have been successfully utilized for control released fertilizers [16,17]. They exhibited a high sulfur oxidation rate upto 368% which is remarkable higher than the elemental sulfur. The nutrients release was able to be controlled in such way that fertilizer wastage was reduced and a better plant health was observed [16]. Sulfur films with high flexibility and freestanding nature were prepared from inverse vulcanization where smooth uniform surface was found for the conversion of uneven crystalline S₈ into amorphous polysulfides [35]. The flexibility and elasticity of the films have been verified by the low young modulus and high tensile extension. The film flexibility might be caused by the low aliphatic carbon chains which rotated freely. It helped these films obtaining a low T_g. Garlic extract based (DAS, DADS, GEO) polysulfides were used to prepare strong adhesive which showed 3 times bond strength compared to commercial glues which was justified by single lap shear test [34]. Polymer composites from vegetable oils have been produced which have shown some excellent composite characteristics including excellent insulation and flame resistance, high tensile strength [59], repairable and reusable properties [25,60] acid resistance [61]. Table 2 shows the various applications of the bio crosslinker based inverse vulcanized polysulfides with their sources.

5. Conclusion

The recent pursue of using bio crosslinker instead of petroleumbased commoners for inverse vulcanization has unlocked a successful chapter for polysulfide production. But there are some drawbacks as well where the proper attention should be put for further development. The temperature control and the adjustment of continuous stirring rate are the key factors during the synthesis process as they directly influence the polysulfide properties. The crosslinking process of vegetable oil and plant extract with elemental sulfur, including the mechanism, thermodynamics, and kinetics, has not been clearly understood. Though the process is

Table 2

List of the investigated applications of the inversed vulcanized polysulfides with their crosslinker names.

Investigated application	Crosslinker name	Reference
Li-S battery	DADS, myrcene	[36]
	linseed, olive, and sunflower oil	[18]
	cardanol benzoxazine	[41]
	eugenol allyl ether (clove oil)	[43]
Mercury removal	Limonene, squalene, perillyl alcohol	[31,32,44]
	myrcene	[32]
	Farnesene	[32]
	farnesol	[32,45]
	Garlic oil	[39]
	Canola, sunflower, and olive oil	[12]
	Canola, rice bran, and castor oil	[26]
	Cottonseed oil	[13]
Iron removal	Canola oil	[15]
Palladium removal	Limonene	[31]
Lead removal	Canola oil	[23]
Gold removal	Vegetable oil blend	[14]
Oil spill removal	Canola oil	[24]
Fertilizer	Soybean oil	[17]
	Canola oil	[16]
Adhesive	Canola oil, DAD, DADS, GEO	[34,62]
Sulfur film	DADS	[35]
Composite and reparable polymer	Canola, sunflower, linseed oil	[25,44,59,61,62]
	Lignin	[60]

entirely nontoxic, temperature above 200 °C may lead to H₂S release. Despite the drawbacks, bio crosslinker for inverse vulcanization is a process of waste valorization where industrial wastes are converted to wealth. So, the scope of the bio crosslinker based sulfur copolymers should be explored more. Assessing the antibacterial properties, synthesis of thermally healable and high refractive indexed polymers might be the future scopes of the high sulfur content polymers. Although the polysulfides showed excellent healing and repairable properties with post modification facilities, the scope for exploring of the biodegradability is an important indication for future research. Intensive investigations can increase the multiple uses of sorbents for heavy metal removal and increase efficiency and recyclability. Exploring the optimum reaction conditions of inverse vulcanization with bio crosslinker can expand intriguing research areas for material science.

CRediT authorship contribution statement

Abdulah Nayeem: Conceptualization, Methodology, Writing original draft, Writing - review & editing. Mohd Faizal Ali: Supervision, Project administration, Funding acquisition. Jun Haslinda Shariffuddin: Conceptualization, Writing - review & editing, Validation, Supervision, Project administration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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