Modified (green) biopolymer Chelates for Industrial Waste Treatment: A step towards environmental sustainability

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ABSRACT

Numerous investigations are conducted to examine the effects of industrial effluents on the environment as industrial processes produce a lot of hazardous waste, which is often incorporated into the ecosystem. There is an urgent need to raise awareness of the necessity to treat different effluents effectively before releasing them into any public water body. The myriad dangerous contaminants contained in wastewater from diverse industrial sectors pose a threat to human health, marine life, and agriculture. The treatment of industrial waste is a crucial environmental issue, and there is ongoing research into practical and sustainable solutions. This study investigates the creation and use of modified (green) biopolymers as a potentially effective method for treating wastewater. The green biopolymers can be assessed as "greener" alternatives to harmful chemicals and the products that may result from their degradation. Natural sources of biopolymers provide environmentally safe substitutes for traditional chemical treatments. These biopolymers may be modified in a variety of ways to display improved adsorption capabilities, which makes them useful instruments for eliminating pollutants from wastewater. This research highlights the potential of modified biopolymers to help create a healthier and more sustainable environment by providing an overview of their synthesis processes and useful applications in industrial waste treatment.

Keywords: *Biopolymers, chelates, ion exchange, industrial waste treatment, environmental sustainability*

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1. Introduction

1.1 Need of Industrial Waste Treatment: One of the most important issues facing developing countries in the current period is the management of industrial effluent [1, 2]. At different locations, industrial effluent is immediately poured into a neighbouring field, a drain system, an internal cesspit or a natural drain [3]. Some of these industrial waste water discharges get little to no treatment prior to disposal. Receiving water bodies deteriorate in part due to the quality of industrial wastewater discharges. This is due to the potential for improperly or incompetently handled industrial waste water discharges to encourage eutrophication in water bodies and provide an ideal habitat for bacteria that can contaminate the water with poisons. In order to comply with the rules and legislation controlling wastewater, it is crucial to treat it appropriately before releasing it [4]. In emerging countries, urbanisation and industrialization have lately harmed the environment [5]. Effective intervention methods are required to reduce the harm that industrial wastewater effluents do to the environment and public health. Consistent monitoring, sufficient and appropriate treatment, careful planning, and appropriate legislation are needed to achieve the uncontaminated release of industrial effluent into receiving water bodies [6]. Heavy metal pollutants (As, Cd, Hg, Pb, Zn, Cr. etc.) are among the primary contaminants in industrial wastes that are responsible for severe human illnesses, like- devastating incidents of mercury poisoning have been reported in Nigeria, Japan and Iraq in the past times [7-9]. Therefore, the environment and public health may suffer greatly from the discharge of trash into water bodies if appropriate treatment and management strategies are not followed. A wide range of aquatic bacteria that create toxins that harm human health as well as the ecology at large can be found in wastewater.

1.2 Importance of Green Chemistry in Industrial Waste Treatment: Environmental pollution is not limited to the release of reactive chemicals into the environment; humankind is also continuously creating new synthetic compounds. Despite the fact that man has benefited much from synthetic chemicals, many of these substances are known to be hazardous in trace doses, occasionally when combined with other pollutants, or as breakdown products after being discharged into the environment. Chemical spills also tend to accumulate over time [10]. The term "green chemistry" was coined by Anastas and Warner at the US Environmental Protection Agency and refers to the adoption of a set of rules that forbid the use of hazardous substances in the creation, manufacture, and use of chemical compounds. The most appealing notion for attaining sustainability is "Green Chemistry" [11, 12]. A strategy for chemical engineering and investigation known as "green chemistry" encourages the development of materials and processes that lessen the use and production of hazardous substances. Green chemistry attempts to generate healthier and more effective chemicals while choosing the safest, most efficient way to synthesise them in order to decrease waste and remove hazards at the design stage [13]. Green chemistry promotes the creation of innovative technologies in order to fully realise the promise of renewable resources. It is clear that chemical pollution contributes to the likelihood of a worldwide ecological collapse and in this scenario the role of green chemistry is humongous.

2. Biopolymers

Biopolymers, sometimes referred to as the "building blocks of nature," are found in all living things, including microbes, plants, and animals. Biopolymers include entities like proteins (polymers of amino acids), carbohydrates and glycosylated molecules, metabolites, genetic material (polymers of nucleic acids), and other structural compounds [14]. Out of the three types of biopolymers viz. polynucleotides, polypeptides, and polysaccharides, the polysaccharides are of main focus when it comes to industrial waste treatment. Polysaccharides comprise the bulk of biomass. These are polymeric carbohydrates with a lengthy chain made up of head-to-tail glycosidic bonds that join monosaccharide molecules [15]. The degree of polymerization (DP) of most polysaccharides ranges from 200 to 3000. The architectures of polysaccharides vary between species and between varieties within a species. Polysaccharides show more diversity than other biopolymers because the plant or microbe that makes them develops under varied circumstances, and they change not only in structure owing to genetic differences across different species and kinds [16]. Unlike synthetic polymers, biopolymers have a basic structure composed of repetitive monomer units arranged in a certain sequence and are generally well-defined structurally. They are readily available and easily manufactured in huge quantities. They are a dependable supplier of inexpensive, non-toxic, biodegradable, and ecologically friendly polymeric materials [17].

3. Ion-exchange resins

One of the first accounts of the exchange of cations dates back to a little over a century ago, when agricultural scientist J. T. Way observed that some soils were more capable of collecting ammonia from fertilisers than others [18]. Ion exchange is the name for the reversible chemical reaction that occurs when dissolved ions are exchanged for new ions that have the same electrical charge or one that is comparable. Ion exchange sites are located throughout the polymer matrix, where the network of polymers is connected to "functional groups" that contain ions that are negatively or positively charged (cations or anions). These functional groups are easily attracted to ions that have the opposite charge. Updegraff and Cassidy [19] synthesised vinyl hydroquinone and its polymer, which are polymers with electron exchange characteristics. An insoluble resin including catechol-O and O-diacetic acid (as a chelating group) was produced by Blasius and Kynast [20]. High zirconium ion selectivity was demonstrated by this resin, which was able to distinguish Zr(IV) ion from a wide range of other cations. There are several types of ion-exchange resins. These resins are related to chelating resins and are specialised due to their chelating capabilities. Petrie et al. [21] used hydroxamic acid as the chelating ingredient to create an ion exchange resin. The ion-exchange method may remove up to ppb (parts per billion) in extremely high volumes of waste management; nevertheless, compared to other processes, it is a rather expensive operation [22]. It is possible to ascertain the ion exchange capability of the ion exchanger with clarity by means of an analytical analysis of its composition. The total number of ions taken up per unit volume or per unit mass of the exchanger under the specified conditions, given in milli moles or milli equivalents, is referred to as "loading." The specific experimental configuration that is utilised to determine the ion uptake value is always referred to as "loading." Loading can, of course, correspond with ion exchange capacity [23]. Figure 1 depicts a general categorization of ion-exchangers.

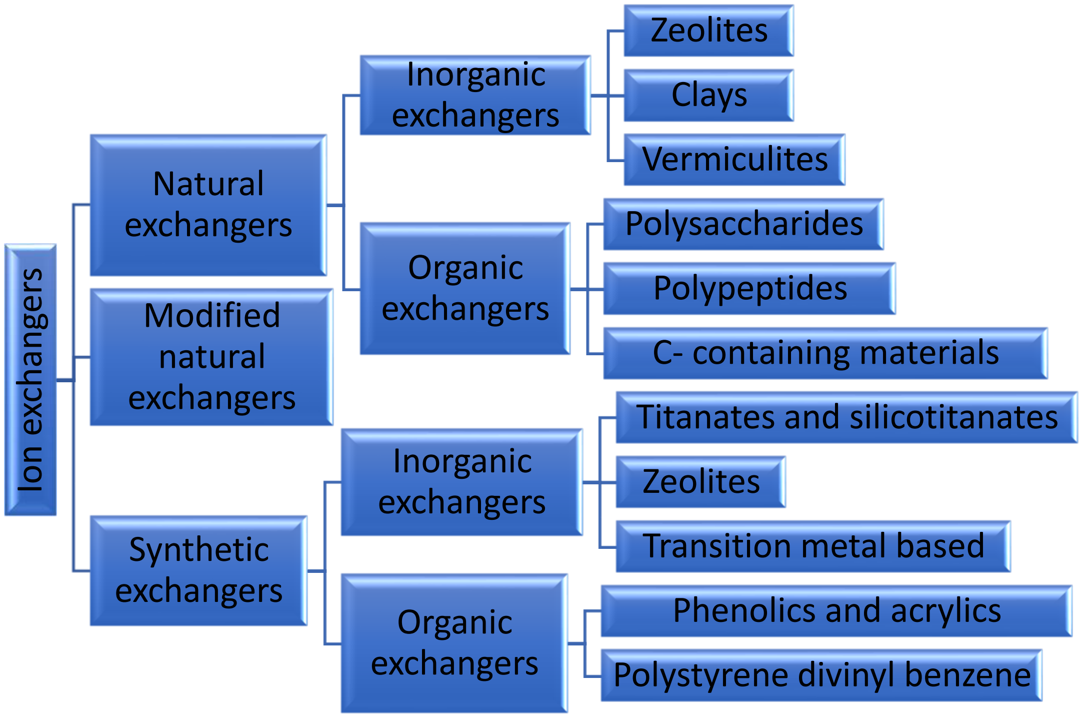

Fig- 1: General categorization of ion-exchangers

4. Chelating resins/ Chelates

A mineral ion or a cation is integrated into a complex ring structure by an organic or inorganic molecule (also known as a chelating agent, chelator, or chelant). This process is known as chelation. The Greek word "chelos," which means "claw" (chelates), gave rise to the term "chelation". Typically, chelating compounds contain nitrogen, sulphur, and/or oxygen as electron-donor atoms (also known as "ligand" binding atoms) [24]. -S-S, -SH, =NH, -NH2, -OPO3H, -OH, or >C=O are examples of functional groups that can constitute the "ligand" binding atoms [25, 26]. With the help of bidentate or multidentate ligands, the metal ion and two or more ligand atoms attached to the metal form chelate rings [27]. A monodentate ligand has a lower affinity for a metal ion than a multidentate ligand due to the chelate effect. Because chelating agents have a chelating action, these chemicals have enormous uses in the fields of clinical (human health), agricultural (fertilisers), and environmental detoxification. Ion-exchange resins can also include chelating resins. Most chelating resins consist of a polymer matrix and a chelating group. Most chelating resins are made of polymers, especially copolymers that bind to metal ions through reactive functional groups [28]. Ion exchange resins with chelating groups exhibit superior selectivity [29]. There are two types of chelating resins: synthetic and natural. Some of the common naturally occuring chelating resins are citric acid; gluconic acid; fulvic acid; amino acids; and mannitol. A resin is called a "bio-resin" or "green resin" if some or all of its core monomers come from biological sources. Bio-resins are very desirable substitutes for most polymers [31]. When biodegradable bioresins are disposed of, they may be easily broken down by microorganisms, making them organic, renewable, and water-based materials. Furthermore, the faster, less costly, and simpler commercial and industrial procedures used to recycle biodegradable polymers make them much easier to recycle.

A detailed examination of polymeric resins employed in hydrometallurgy for metal segregation and water/wastewater treatment has revealed that the pH of the solution and the characteristics of the resin's functional group determine how selectively it may adsorb materials. The primary functional atoms in functional groups (like- N, S, P, and O) and ion-exchange properties are analysed and the resins are arranged based on these features. The selection of an appropriate chelating resin for metal absorption and separation is guided by the results of this study [32, 33]. The selection criterion is dependent on both the kind of treatment and the concentration of metal ions.

5. Applications of modified biopolymer chelates for industrial waste treatment (reviewed over past 3 decades)

Some authors claim that ion exchange is the oldest known scientific phenomena in human history. Although the Bible and Aristotle's works provide descriptions that support this claim, two English agricultural chemists, J. T. Way and H. S. Thompson, are recognised for having made the first scientific mention of ion exchange in 1850. These scientists were the first to discover on their own that ammonium ions were taking the place of calcium ions in soils, and they also reported this finding in the 1850 issue of the Royal Agricultural Society of England's Journal [34]. The reversible exchange of cations between natrolite and chabazite, two naturally occurring zeolite minerals, was shown in 1858 by C. H. Eichorn. The study of inorganic substances capable of "base" exchange was based on this finding. Rivas et al. [35] used radical polymerization of 2, 2 bis (acrylamido) acetic acid to produce a water-insoluble metal ion complexing resin. A range of new chelating polymers containing pyridyl and bipyridyl donor groups have the potential to bind hazardous heavy metal ions, such as Cu (II) and Hg (II), instead of Co (II), Ni (II), and Cd (II), as demonstrated by Talanova et al. [36]. Chelation resins have proven to be quite successful in selectively absorbing trace heavy metals from water samples, as demonstrated by a research by Saha et al. [37]. Wang et al. [38] investigated the adsorption of Cr (III), Cu (II), Pb (II), and Cd (II) ions using a bifunctional ion-exchange resin. Wang et al. [39] mixed imidinodiacetic acid and glycidyl methacrylate at 60°C to produce the hydrophilic acrylate monomer with the binding group. The iminodiacetic acid chelating group on acrylate monomer was utilised to make the microbeads using the process of inversion suspension polymerization. The adsorption of Cd (II) and Pb (II) on microbeads was pH dependent, and the adsorption of Cr (III) and Cu (II) followed the Langmuir adsorption isotherm, but not the other way around. These are only a few of the observations that support these theories. Kabay et al. [40] eliminated boron from the geothermal effluents of Kizildere Geothermal Power Station, Denizli, using Diaion CRB 02 N-glucamine-type chelating resins. Prior to the sorption of the next cycle, a 5% sulfuric acid solution was used to elute the boron from the resin, and a 4% sodium hydroxide solution was used to renew the resin. We carried out a column-mode experiment to recover boron from acidic eluates. For this, a weak base ion exchange resin known as Diaion WA 30 was used to remove boron from H2SO4 solutions collected in the field. Mendes and Martins investigated the sorption of nickel and cobalt (in acid leach liquor) on the scale of numerous experimental parameters, i.e. time, beginning metals concentration, the ratio of Ni/Co concentrations, and pH of the aqueous solution [41]. For these investigations, they employed four distinct chelating (ion exchange) polymeric resins. During column tests, Diniz et al. [42] employed a chelating resin called Dowex M-4195 to extract Cu, Ni, Co, Pb, Fe, and Mn from a $MnCl_2$ leach solution. The results demonstrated that contaminants could be eliminated to a level that met the quality requirements needed to produce manganese compounds with $MnCl_2$ solution. In order to selectively adsorb Hg2+, a research team led by Sun and Qu et al. [43, 44] synthesised two types of chelating resins: one with poly(2-hydroxy ethylmercaptomethylstyrene) and diethanolamine, and the other with 2-amino-pyridine (on macroporous cross-linked polystyrene beads) via an S-containing spacer. Individual studies on the application of new chelating resins with iminodiacetate groups for removing heavy metal ions from aqueous solutions have been reported by Dinu et al. [45] and Zainol and Nicol [46]. Monier et al. [47] developed cross-linked magnetic chitosan-diacetyl monoxime Schiff's base resin to investigate the adsorption of heavy metal ions. Xiong et al. [48] used a straightforward method to create a novel, strongly adsorbent chelating resin with ethylenediamine functionalization. The resin may be used to preconcentrate and selectively separate Cu2+ ions from water and food samples, as well as to determine whether metal ions were present in tea samples. Dowex M-4195 (chelating resin) was employed for recovering heavy metal ions from severe acidic industrial waste water by Gao et al [49]. In some common very acidic conditions, heavy metal recovery was made possible by the resin even in the absence of sufficient neutralisation preparation. Kalaivani et al. [50] have reported on studies on the absorption of heavy metals (by adsorption) utilising chelating resins, synthesised using distinct functionalization routes, employing poly (6-(ethoxybenzothiazole acrylamide). Zhu et al. [51] successfully synthesised a novel dual-primary-amine chelating resin for the selective extraction of Ni (II) and Cu (II) from saline solutions. Bahy and Bahy [52] investigated the adsorption of Mn (II), Ni (II), and Cu (II) using a chelating resin made by co-polymerizing acrylonitrile with N,N′-methylene bisacrylamide (which was followed by amidoximation reaction with hydroxyl amine at high pH settings). The resin was successfully rejuvenated using nitric acid. Wang et al. [53] created a resin that was easy to regenerate, could be used up to six more times without experiencing a significant reduction in adsorption capacity, and demonstrated adsorption capabilities (for Pb2+) that were not substantially affected by the presence of coexisting ions. This resin was also used to remove dangerous Pb2+ ions during the water treatment process. Shaaban et al. [54] created a novel chelating resin that is nanoscale in size. The first stage involved copolymerizing N-methacryloxy phtalimide with methylene bisacrylamide using a suspension polymerization process, which produced ultrafine poly (N-methacryl oxyphtalimide-co-methylene bisacrylamide). The second stage involved producing chelating resin by reacting triethylene tetramine with poly (N-methacryl oxyphtalimide-co-methylene bisacrylamide). The FT-IR, SEM, TEM, Brunauer-Emmett-Taller (BET), and TGA analyses of the produced chelating resin demonstrated its ability to remove Ni (II), Cu (II), and Co (II) from aquatic materials. A study was proposed by Addala and Belattar [91] to assess the adsorbing capacity (by batch approach) of a chelating ion exchange resin modified by iminodiacetic acid group towards Pb (II) and Cd (II) by varying the quantity of lead and cadmium at different contact durations and a given pH. In the second stage, this adsorbent support was used in a column under dynamic circumstances to extract Pb (II) specifically from industrial effluents. After that, the exchange material was recycled to see if it could be used again and how well it removed the unwanted substance. Though it has weak flocculation, is difficult to recover from, and is difficult to reuse in applications, conventional dithio carbamate is an excellent metal-trapping agent. In order to address these problems, Yan et al. [56] conducted a research and created a novel and efficient chelating agent in the form of a magnetic dithio carbamate chelating polymer. This resin was used to adsorber EDTA-Cu from wastewater, and the copper absorption procedure was assessed. Better sedimentation performance and an impressive 99.19% copper sorption capacity were shown by the resin. El-Nemr et al. evaluated the copper adsorption properties on the chelating resins Amberlite IRC-86 [57]. In a different investigation, Hussain et al. [58] evaluated the sorption of Pb (II), Cu (II), and Cd (II) ions using chitosan, a biodegradable natural polymer, treated with salicylaldehyde to create salicylaldehyde functionalized chitosan nanoparticles. In a research, Rahman et al. [59] assessed the chelating resins' ability to adsorb different heavy metals from diverse aqueous samples. Recently, a number of studies have been provided that summarise the many kinds of chelating resins and their production methods, as well as the methods for selectively removing the intended hazardous metal ions from a variety of solutions. The great performances of chelating resins have been evaluated by researchers (Chu et al., [60]; Al-Mosawi et al., [61]; Lin et al., [62]), who have also listed the various mechanisms for adsorption involving heavy metal ions and chelating resins, in addition to the variables impacting the adsorption processes. Saiyad et al [63] and Palanisamy [64] have recently reviewed biopolymers for their effectiveness in waste water treatments and environmental sustainability.

6. CONCLUSION

Pollution remains a major hazard to human health despite the enormous strides that have been made subsequently towards cleaning up the environment. The problems are particularly severe in developing countries, where a large population is exposed to traditional sources of pollution, including indoor air pollution from biomass fuels, inadequate waste management, bad sanitation, contaminated water supplies, and industrial emissions.
Thousands of chemicals are used extensively around the world, and either during use or processing, they might all have a negative impact on the environment. Only a small percentage of them have had their toxicity and potential health risks assessed. Most of the knowledge that is lacking relates to the sources and mechanisms of action of these chemical hazards.
Pollution and human well-being have a complex and erratic connection. Chemical innovations are vital, but they can bring about unexpected undesirable side effects and new environmental problems, which makes using "greener" chemicals necessary. When creating bio-adsorbents, biopolymers are a dependable supply of affordable, non-toxic, biodegradable, and ecologically acceptable polymeric materials. These bio-adsorbents' chelating and ion-exchange capabilities can be used to cleanse industrial effluent. Thus, this review can be of huge help in fabricating novel modified biopolymers to abate pollution from industrial waste so as to develop environmental sustainability.

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