



Review

Carbohydrate biopolymers, lignin based adsorbents for removal of heavy metals (Cd^{2+} , Pb^{2+} , Zn^{2+}) from wastewater, regeneration and reuse for spent adsorbents including latent fingerprint detection: A review

B.G. Fouda-Mbanga, E. Prabakaran, K. Pillay*

Department of Chemical Sciences, University of Johannesburg, Johannesburg, South Africa



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ABSTRACT

Living organisms are created by carbohydrate biopolymers such as chitosan, carboxymethyl cellulose, alginate and lignin. These carbohydrate biopolymers have been extensively used for environmental applications because they are bio-degradable, bio-compatible, non-toxic and inexpensive. Recently, carbohydrate biopolymers have been used to prepare different nanocomposite adsorbents for treatment of wastewater. These adsorbents explored the removal effectiveness of inorganic pollutants from aqueous solution. This review article discusses the synthesis and application of chitosan, carboxymethyl cellulose, alginate and lignin nanocomposites as adsorbents for heavy metals. Toxic metals can be efficiently absorbed by cross-linkers, distributed in aqueous solutions of divalent heavy metal ions to examine their polymer absorption capacity. These nanocomposites were used for the adsorption of highly toxic metals such as Cd^{2+} , Pb^{2+} and Zn^{2+} in water. To make heavy metal ion uptake more effective, more functionalization has been implemented such as blending, grafting, or mixing with different nanomaterials with an extra functional group. The integration of the second part into the main polymer chain not only adds functionality but also increases mechanical efficiency, one of the core criteria for adsorbent recyclability. The remediation method of metal ions from wastewater is cheaper as long as the adsorbent is reused. Furthermore, they exhibited good performance for the reuse of spent adsorbents after adsorption-desorption processes including latent fingerprint detection with nanomaterials by using the powder dusting method. Chitosan, carboxymethyl cellulose, alginate and lignin based nanocomposites have demonstrated better adsorption activities due to great physical and chemical properties for the chelation of heavy metals such as Cd^{2+} , Pb^{2+} and Zn^{2+} from water and also higher regeneration with various eluents after several desorption-adsorption cycles. In addition, reuse of the spent adsorbents in latent fingerprint detection with different nanomaterials is discussed. Finally, this review article makes recommendations for future studies in light of environmentally favourable and economical applications.

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1. Introduction

The definition of heavy metals is an ongoing discussion and may be quite ambiguous, yet an element can be classified as a heavy metal if its density is very much higher than that of water and it is of natural origin and primarily occurs in the earth's crust (Nickel (Ni) and water). The main heavy metal pollutants present in surface waters are Lead (Pb^{2+}), Zinc (Zn^{2+}), Cadmium (Cd^{2+}), Copper (Cu^{2+}), Nickel (Ni^{2+}), Arsenic (As^{3+}), Cobalt (Co^{2+}), Iron

(Fe^{3+}), Manganese (Mn^{2+}), Mercury (Hg^{2+}), Chromium (Cr(VI)), Silver (Ag^+), Gold (Au^{3+}), Palladium (Pd^{2+}), Platinum (Pt^{3+}), Uranium (U(VI)), Cesium (Cs^+) and Rubidium (Rb^+). Among them, Cu^{2+} , Cr(VI) , Mn^{2+} , Ni^{2+} , Fe^{3+} , Cd^{2+} , Pb^{2+} and Zn^{2+} ions are highly toxic in nature especially in wastewater. The current trends in the adsorption of heavy metals such as Cd^{2+} , Pb^{2+} and Zn^{2+} ions have been chosen for discussion in this article since they are existing components of the earth's crust and found in the environment due to parent rock corrosion with a concentration less than 1000 ppm. They have relatively higher solubility in water than most other heavy metals, large quantities of these heavy metals are taken in by living organisms and these metals are extensively used in industries and result in a highly polluted environment [1].

* Corresponding author.

E-mail address: kriveshinip@uj.ac.za (K. Pillay).

Although some heavy metals such as zinc, barium, lead, silver are important to human health when they are under the regulatory limit (Zn < 5 ppm; Ba < 2 ppm; Pb < 0.015 ppm; Ag < 0.001 ppm) as recommended by the environmental protection agency (EPA); most of these heavy metals are considered to be harmful at different levels and excessive exposure to them can be fatal [2].

Heavy metal exposure may occur either through air, surface water, or food. The presence of heavy metals in surface water sources in many areas is often caused by human operations, mainly by mining, automobile emissions, and the employment of heavy metals containing compounds utilized in manufacturing. The wastewater created by industries is unleashed into the environment, mainly in the watercourses. In water of industrial operations, there are few origins of anthropogenic heavy metals including electroplating, metal smelting, chemical and manufacturing industries [3]. Homemade, commercial, and agricultural wastewater contains high metal concentrations that are frequently disposed off in many developed countries into the atmosphere [4]. Zheng discovered that metals like mercury and lead are stored in the soil around the reservoir after they are unleashed into the air by heavy air emissions from automobiles and factories (G [5]). Weathering and volcanic eruptions are other natural phenomena that lead to heavy metal emissions in certain parts of the world. Therefore, water contamination by heavy metals often relies on the location's geographical, biological, and industrial activity.

The risks of the entry of these heavy metals into the food chain are well documented. Thus, preparing and extracting as many as possible from wastewater before letting them into the atmosphere is highly necessary. Owing to the introduction of more strict laws and regulations on wastewater handling and discharge over the past decades, heavy metals have become key pollutants for the environment, and treatment methods to extract heavy metals from wastewater are of great concern and significance. Different methods have been used to remove heavy metals from wastewater including physical, chemical and biological techniques. These also include ultra-filtration, precipitation, oxidation and solvent extraction with electrolytic methods, membrane filtration, ion exchange, biological systems and adsorption methods. Here, biological methods have been shown to have lower heavy metal removal capacity from aqueous solution. Physical and chemical processes were effective for the removal of heavy metal ions in water samples with the adsorption method. The advantages and disadvantages of the adsorption method are given in Table 1.

However, the use of some of these conventional methods presented inherent disadvantages such as high operational costs and complexity, energy-intensive, production of large amounts of secondary contaminants such as sludge, fouling, low efficiency in removing trace levels of contaminants, large quantities of chemicals needed, susceptibility to pH, pre- and post-treatment. For this reason, attention has been focused on adsorption because of its low cost and ease of operation. Several materials have been studied as potential adsorbents to meet the industrial demands for safe and efficient low cost biomaterials. Such adsorbents are categorized into two types: traditional and non-conventional. Traditional adsorbents, including alumina, zeolite, AC, silica gel and bauxite, have been used on a small scale. In non-conventional

adsorbents, the most frequently used is agricultural and industrial waste, natural materials and biomass for removal of heavy metals. Large quantities of metal ion polluted wastewater are discharged into the environment from various industries. Heavy metal ions such as Cd²⁺, Cr(VI), Cu²⁺, Ni⁺, As³⁺, Pb²⁺, and Zn²⁺ are highly toxic in nature, which are released from chemical industries. They have shown better solubility in water and also intake by living organisms. The heavy metal ions tend to accumulate in the human body [6]. They are the cause of serious human health problems [1]. Hence the need for removal and treatment of heavy metals from wastewater prior to discharge in the environment is therefore a matter to consider.

The adsorption process has not effectively removed heavy metal ions from inorganic effluents. Inorganic effluents containing heavy metal ions are eliminated by using various methods such as electrochemical, chemical precipitation and ion exchange. These methods presented some disadvantages such as incomplete removal, huge amount of energy needed and large quantity of toxic sludge produced [7]. Nowadays, the adsorption method has improved the quality treatment of effluent waste and wastewater treatment due to low-cost adsorbents having good binding abilities with heavy metals [8]. A great number of adsorbents have been utilized for the removal of heavy metals. However, the key drawbacks of these adsorbents are their poor capacity to adsorb, weak connections with metallic ions, and their complexities in removing and regenerating some of them from water. Ion-exchange resins can significantly extract metal ions; however, they have low selectivity and display a significant level of swelling associated with poor mechanical stability [9]. Hence, attention in the past has been on carbohydrate biopolymers.

Carbohydrate biopolymers are generated from renewable resources of plants and chemicals synthesized from starch and sugar [10]. Due to their unique structure, physico-chemical properties, chemical stability, great sensitivity and high selectivity arising from the inclusion of chemical reactive groups such as hydroxyl, acetamide or amino functions in polymer chains, these biopolymers provide a relevant and desirable route to sorbents. In addition, these materials are plentiful, reusable, biodegradable and capable of binding a large range of molecules physically and chemically [11,12]. A diversity of carbohydrate biopolymers has been used extensively as adsorbents for the removal of heavy metals in wastewater. Among them, Chitosan, Lignin, Carboxymethyl cellulose and Alginate based adsorbents have been extensively used due to their low cost, efficiency, biocompatibility and biodegradability. They contain different functional groups such as amine, hydroxide, phenolic hydroxyl, methoxyl carboxylic acid and also good hydrophilicity. These functional groups of biopolymer based adsorbents enhance the removal efficiency of heavy metals from water samples due to chelating metal ions producing the complex.

Chitosan is naturally a carbohydrate biopolymer with heteropolymers of D-glucosamine and N-acetyl-D-glucosamine moiety. It is prepared from the deacetylation of chitin. Chitosan was applied in various applications such as biomedical and industrial due to non-toxicity, biocompatibility, biodegradability, high mechanical strength and physical-chemical properties. Chitosan is a major [13]

Table 1
Advantages and disadvantages of adsorption method.

| Advantages | Disadvantages |
|---|---|
| Flexibility, simplicity, easy operation, low cost and high efficiency to heavy metal pollutants | It was removing heavy metals from water with is precipitation as insoluble hydroxide in base medium |
| It creates excellence effluent treatment and wastewater. | Major disadvantages is discharge of precipitated hydroxide to environment |
| Adsorbents can regenerated and reused by suitable desorption methods. | It is a bit reversible Characteristic during adsorption |
| Adsorption method used to remove low concentration of heavy metals from waste water solution. | Adsorption process does not show the efficient removal of heavy metal ions from Inorganic effluents and by using chemical precipitation |

building group of amines and binds with heavy metal ions from wastewater by using adsorption methods. Chitosan is generally used as an adsorbent for the elimination of heavy metal ions from water samples and it has amine and hydroxyl groups used to absorb the heavy metal ions from wastewater [14]. It was applied in the removal of heavy metal ions from aqueous solution with pH 6–6.5 due to the cationic nature of Chitosan and cationic nature of heavy metal ions [13].

Cellulose is also a carbohydrate biopolymer and it is obtained from the D-glucose derivative of $\beta(1\rightarrow4)$ glycoside bonds. Cellulose is of a hydrophilic nature, biodegradable, biocompatible and insoluble in water. Cellulose is present in Plants leaves, cotton, wood and is an easily accessible low cost material. Cellulose based nanocomposites have shown good adsorption for the removal of heavy metal ions and chelation from water samples [15]. Cellulose based composites and nanocomposite materials were mostly used in wastewater treatment to minimize the influence of heavy metals in water. It has been produced in large quantities from agricultural waste and contains hydroxyl groups which are suited for the removal of heavy metal ions from aqueous solution [16]. It is prepared from different biomaterials due to low cost and easy modification. Hydroxyl groups have shown low adsorption removal capacities and hence it needs to be modified with other materials such as carboxyl, amidoxime, amide, ethylenediamine-tetraacetic acid (EDTA) sulfur as an anionic ligand and triethylenetetramine. These modified cellulose based adsorbents are extensively applied in heavy metal ion removal (Pb^{2+} , Cu^{2+} , Zn^{2+}). Modified cellulose showed good adsorption capacity and better removal of heavy metals ions from water samples than unmodified samples.

Alginate is a co-polymer with a linear chain and is also connected with two units of mannuronic acid and guluronic acid [17]. It is obtained from algae and some bacteria. It has been applied in wastewater treatment due to its low cost, biodegradability, non-toxicity and biocompatibility [18]. Generally, dry alginate yields a lower adsorption capability because of low porosity, loose network, weak water resistance property and low diffusion of heavy metal ions [19]. Hence, the most of highly porous aerogels and high porous based alginate materials are applied for the removal of heavy metal ions from wastewater. Alginate also follows two types of mechanism in removing heavy metal ions and

these include adsorption and ion exchange [20]. The higher adsorption capacity activity of ionotropic metal alginates was used to eliminate the heavy metal ions [21]. The polyelectrolyte is incorporated onto alginates to improve the chemical stability, selective adsorption of heavy metals and enhance the adsorption of heavy metal ions [22].

Lignin is one of the natural carbohydrate biopolymers, which contains lignocelluloses biomass and it also exists as a three dimensional networking structure which contains functional groups such as carboxyl, phenolic hydroxyl, methoxy and aliphatic groups. Lignin is prepared on a large scale in biorefinery industries and is also used in various applications such as dispersants, plasticizer adhesives and adsorbents [23]. Normally, lignin demonstrated low adsorption capacity due to less attraction with heavy metal ions [23]. Lignin is functionalized with amine and sulfonic groups to enhance the removal of heavy metals from water [24–26]. It was modified with different materials such as lignin-grafted nanocomposites [27] or lignin-based nanotraps [26], chitosan-lignin composites [28], chitin-lignin hybrids, lignin-based hydrogels, ion-exchange resins [24], lignin-based microspheres to effectively remove heavy metals ion from aqueous solution. It was also co-polymerized due to an increase in surface area, increase in diffusion, and dispersion and improved adsorption activity with modified functional groups (Y. [25]).

In this review, the removal of heavy metals of Cd^{2+} , Pb^{2+} , Zn^{2+} from aqueous solution by carbohydrate biopolymers of chitosan, carboxymethyl cellulose and alginate and lignin based adsorbents is discussed. The regeneration of the various adsorbents after desorption-adsorption cycles with different desorption reagents is also reviewed. This also includes reuse applications of the spent adsorbents to reduce secondary pollution and decrease toxicity. Finally, this review article has described latent fingerprint detection with different nanomaterials as a reuse application. The general view of this review article is shown in Fig. 1.

2. Carbohydrate biopolymers based adsorbents

Adsorption of pollutants with sustainable carbohydrate biopolymers and their changed appearances is one of the most recent advances in adsorption technology [23]. Carbohydrate biopolymers have currently been investigated for their adsorption

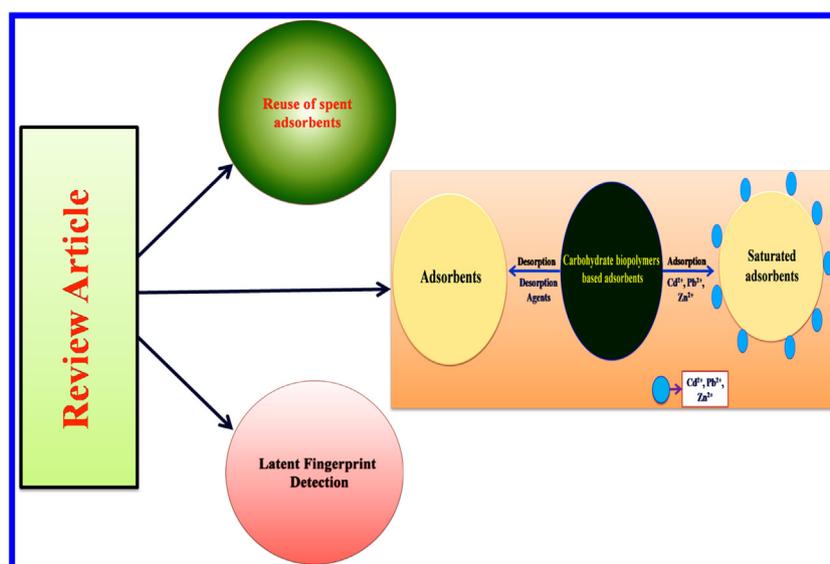


Fig. 1. The general view of the review article.

properties as environmentally safe, biocompatible and biodegradable tools due to the existence of a large proportion of N and O functional groups which in turn possess a higher affinity for heavy metal ions. Living organisms (plants, animals, bacteria, fungi and yeast) synthesize a wide range of biopolymers such as deoxyribonucleic acid (DNA), ribonucleic acid (RNA), proteins, cellulose, chitin, starch, etc. (S [29]). Table 2 displays reported studies for the remediation of Cd²⁺, Pb²⁺, Zn²⁺ using biopolymers as adsorbents. The discussion below places some emphasis on studies which have been conducted using these various carbohydrate biopolymers and the importance of functional groups in carbohydrate biopolymers in heavy metal adsorption.

2.1. Chitosan based adsorbent for heavy metals removal

The use of chitosan nanofibre based adsorbents is an excellent means of removing heavy metal ions from water. Chitosan beads were grafted with 4-aminobenzoic acid to extend the polymeric network for better adsorption of heavy metal ions due to large binding sites. 4-aminobenzoic acid grafted cross-linked chitosan (FGCX) was also used and various parameters such as pH, dosage, initial concentration, contact time, ionic strength and shaker speed were studied. Different isotherm models such as the Langmuir and DKR isotherm models were fitted to the adsorption data. It was observed that while some metals were in agreement with Freundlich and Temkin models; others followed the Langmuir model. This biosorption was feasible and spontaneous with endothermic adsorption. The FGXC adsorbent was suited for the pseudo-second-order kinetic model for adsorption of heavy metal ions and it is also followed the intra-particle diffusion model. The FGXC adsorbent removed the metal ions by chemisorption, ion exchange and electrostatic interactions. This biosorbent was also tested on industrial wastewater for the elimination of metal ions [31].

Cross-linked chitosan microspheres were modified with polymethacrylic acid (PMAA/CCS) for better adsorption of Cd²⁺ ions from wastewater. PMAA was easily grafted on CCS microspheres

due to the availability of carboxylic groups on the surface of CCS with atom transfer radical polymerization (ATRP). The PMAA/CCS nanocomposite adsorbed Cd²⁺ at an optimum pH of 5 which showed enhanced removal of Cd²⁺ ions from aqueous solution within 1 h. This was better than that observed for pure CCS composite where the adsorption took about 7 h for completion. This nanocomposite gave a maximum adsorption capacity of 1.3 mg g⁻¹. It was also regenerated with dilute HNO₃ for another cycle of adsorption of Cd²⁺ ions for reuse without changing the structural integrity of the adsorbent [35].

Poly (acrylic acid) grafted with glutaraldehyde-chitosan nanocomposite adsorbent (PAACS) was prepared to eliminate Pb²⁺ from wastewater samples by using the adsorption method. This adsorbent achieved an adsorption capacity of 734.3 mg g⁻¹ at pH 5.0. The PAACS nanocomposite was highly selective for the adsorption of Pb²⁺ from aqueous solution [25].

The copolymerization of chitosan and PVA (polyvinyl alcohol) was grafted with a maleic anhydride composite to form hydrogen bonds with the amino group. It was used in the adsorption of Pb²⁺ from aqueous solution. This composite contained various functional groups such as amino, OH and NH₂-CH=O (peptide) in PVA. These functional groups contained electronegative heteroatoms which are highly suitable for the chelation of Pb²⁺ from solution and the adsorbent showed an adsorption capacity of 90 mg g⁻¹.

Zn²⁺ is a heavy metal in water and also causes severe environmental problems. It accumulates in tissues and creates various diseases in humans and animals. Here, biopolymers of chitosan increases the adsorption of Zn²⁺ from aqueous solution due to acetyl and amine groups. A comparative study of chitosan nanoparticles with microparticles for the adsorption of Zn²⁺ ions in aqueous solution was reported. The adsorption was investigated as a function of various parameters such as initial concentration of Zn²⁺ ions, pH, contact time and temperature for the removal of Zn²⁺ ions. The particle size determined by DLS was 190.84 nm for chitosan nanoparticles. The optimum pH was 7 and 5 for chitosan microparticles and nanoparticles, respectively. The maximum removal efficiency of Zn²⁺ ions was 90.80 % and 99.10 % for chitosan

Table 2
Adsorption of Cd²⁺, Pb²⁺, and Zn²⁺ using biopolymers as adsorbents.

| Adsorbents | Results | Comments | Ions | References |
|---|---|--|--|------------|
| Arginine cross-linked chitosan-carboxymethyl cellulose beads | -Optimum pH 6.5 -Second order well describes the kinetic. -Langmuir isotherm well described the sorption. -Optimum capacities to adsorb of 182.5 and 168.5 mg g ⁻¹ . | Reuse of the adsorbent, regeneration studies not explored. | Pb ²⁺ and Cd ²⁺ | [30] |
| Modified ligand in single bed | -Langmuir and Dubinin-Kaganer-Radushkevich (DKR) well described isotherm data. -Spontaneous and endothermic process. | -Effect of coexisting ions and application of the adsorbent on real water samples not conducted. | Cd ²⁺ , Pb ²⁺ , Zn ²⁺ | [31] |
| multi functionalized polyacrylonitrile onto Arabic gum grafts | -Optimum pH 5 and 6 for Pb ²⁺ and Cd ²⁺ . -Utmost capacities to adsorb of 1017 and 413 mg g ⁻¹ for Pb ²⁺ and Cd ²⁺ respectively. -Sorption was best explained by the 2 nd order kinetic and Langmuir isotherm. | -Adsorbent demonstrates good selectivity. -Regeneration studies were reported. | Pb ²⁺ and Cd ²⁺ | [32] |
| Cellulosic biopolymer | -Sorption was best described by Langmuir model. -Second order well described the kinetic. -Maximum adsorption capacities of 16.85, 44.42, and 67.24 mg g ⁻¹ for Zn ²⁺ , Cd ²⁺ , and Pb ²⁺ independently. -Sorption was exothermic. | -Application on real water samples not investigated. Regeneration studies not investigated. | Pb ²⁺ , Cd ²⁺ , Zn ²⁺ | [33] |
| Chitosan and nanochitosan | -pH 7 and 5 as optimum. -90.80% and 99.10 % adsorption observed. -Utmost adsorption capacities to adsorb of 196.07 and 370.37 mg g ⁻¹ , respectively. -Pseudo-second-order well depicted the kinetics. | -Nanochitosan compared to Chitosan particles had higher removal efficiency for Zinc metal ions due to nano-size and larger surfaces area -Effect of competition ions and applications on real water samples was not explored. | Zn ²⁺ | [34] |

microparticles and chitosan nanoparticles, respectively. Maximum capacity of adsorption by chitosan macro and nano size particles was 196.07 and 370.37 mg/g, respectively. Adsorption kinetics followed a pseudo second order model. Nanochitosan compared to chitosan particles had a higher removal efficiency for Zinc metal ions due to the nano-sized particles, larger adsorption surfaces and more functional groups [34].

Chitosan (CS) was incorporated into polymethacrylic acid (PMA) which served as cross linker for hallosite nanotubes (HNT) (CS-PMA/HNT). The CS-PMA/HNT was used as an adsorbent for the removal of Pb^{2+} and Cd^{2+} metals in single and binary water samples. Here polymethacrylic is not only forming a nano-composite with CS and HNT, but also increases the adsorption capacity of heavy metals of Pb^{2+} and Cd^{2+} from aqueous samples. This nanocomposite displayed a maximum adsorption capacity of (357.4/89.4 mg/g) for Pb^{2+} and 341.6/85.4 mg/g for single component and (31.7/78.4 mg/g) and (303.6/77.3 mg/g) for the binary mixture in the water samples at pH 6.0. CS-PMA/HNT nanocomposite demonstrated that the adsorption experimental data fitted the pseudo second order kinetics for the removal of Pb^{2+} and Cd^{2+} as single and binary systems. The Freundlich isotherm model was in favour for single systems of metals Pb^{2+} and Cd^{2+} and modified Langmuir-Freundlich model for mixtures in wastewater samples. This nanocomposite therefore showed heterogeneous adsorption with interactive adsorption metals from the water samples [36].

Ethylene diamine tetra acetic acid (EDTA) was incorporated onto magnetic graphene oxide (mGO) functionalized with chitosan and it contained chelated amine groups. This nano-biocomposite was successfully used as an adsorbent for the removal of Pb^{2+} and Cd^{2+} ions in single and binary systems in solution. The single system exhibited better adsorption behavior for Pb^{2+} and Cd^{2+} ions with adsorption capacities of 2.33 and 1.05 mg/g, respectively at pH 5 with 0.3 g/L dosage. The pseudo-first order kinetic model fitted well the adsorption kinetic models of Pb^{2+} and Cd^{2+} . The adsorption process was spontaneous and endothermic. The CS/EDTA-silane/mGO nanocomposite showed higher adsorption of Pb^{2+} than Cd^{2+} due to the lower radius of Pb^{2+} . At higher concentrations of binary metals non-interactive and interactive effects depended on increasing concentration of Pb^{2+} ions and Cd^{2+} ions in aqueous solution. Additionally, the binary systems of Pb^{2+} and Cd^{2+} in water minimizes the adsorption capacity for Cd^{2+} with limiting effects on the adsorption behavior for Pb^{2+} . The CS/EDTA-silane/mGO nanocomposite resulted in better magnetic adsorption of Pb^{2+} and Cd^{2+} in binary systems than single systems [37].

Chitosan was added to 3-aminopropyltriethoxysilane (APTES) to make mesoporous silica (AMS). It has shown a high surface area of 511.77 m²/g with pores size (3.38 nm) and pore volume (0.036 cm³/g). The adsorption of Cd^{2+} and Pb^{2+} with the help of mesoporous silica was applied in aqueous solution. Various parameters such as contact time, pH, concentration of Pb^{2+} and Cd^{2+} and electrolyte concentrations were used to observe the mechanism of adsorption at the solid/solution interface. The Langmuir adsorption isotherm was fitted to the experimental results. The adsorption of Cd^{2+} and Pb^{2+} was best described by pseudo-second order kinetics. Higher concentrations of the background solution, NaNO₃ (0.0001 to 0.01 mol/L) did not reduce the adsorption of Pb^{2+} and Cd^{2+} ions in aqueous solution. X-ray Photoelectron Spectroscopy (XPS) analysis revealed that Cd^{2+} and Pb^{2+} was bound to the oxygen of AMS solid. Moreover, the adsorption capacity of Cd^{2+} and Pb^{2+} were 11.54 mg/g and 8.59 mg/g, respectively [38].

The synthesis of chitosan/sporopollenin microcapsules was performed by the cross linking of chitosan and sporopollenin. The microcapsules were applied in the removal of heavy metals from wastewater. The adsorption ability was evaluated as a function of

various parameters such as pH, temperature and adsorption time. The Chitosan/sporopollenin composite demonstrated maximum adsorption capacities of 1.34, 0.99, 0.77, 0.71, and 0.58 mmol/g, for Cu(II), Cr(III), Cd(II), Zn(II), and Ni(II) respectively. It showed a higher intake of Cd^{2+} and Zn^{2+} ions and lower adsorption efficiency for Cr(III) and Cu(II) in aqueous solution. This composite could therefore be used for the removal of target metal ions from wastewater [39].

Chitin nanofibers (CNF) were prepared by grinding and compressing a suspension of chitin microparticles (CMPs) and additionally a freeze drying method was utilized [19]. CNF with CMPs was modified into nanofibrils without alteration of chemical structure and crystalline structure. It was used as an adsorbent for the removal of Cd^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Pb^{2+} , and Cr^{2+} ions with adsorption capacities of 330.15, 134.72, 141.08, 134.03, 303.49, and 16.28 mg/g, respectively. This chitin composite had a rigid structure, good adsorption activity and also improved binding with metal ions in aqueous solution. This rigid composite did not dissolve in water and other solvents, and showed high surface area and good pores size of CNFs. These parameters increased the adsorption capacity of the various heavy metals ions [40].

2.2. Carboxymethyl cellulose (CMC) based adsorbent for removal heavy metals

Carboxymethyl cellulose coated with polyacrylamide composite (CMC/PAM) was synthesized for heavy metal ions adsorption from aqueous solution. This composite was made of hydrogels for strong adsorption of Cu^{2+} , Pb^{2+} and Cd^{2+} ions and this also favored the Langmuir adsorption model and pseudo-second-order kinetic model. Cu^{2+} ions loaded on CMC/PAM composite was regenerated and resulted in the formation of CuNPs on CMC/PAM hydrogel composite for the catalytic reduction of 4-nitrophenol to 4-aminophenol with better efficiency [41].

The synthesis of a carboxymethyl cellulose coated Fe₃O₄ (CMC-Fe₃O₄) nanocomposite was performed by impinging a stream-rotating packed bed. This method of preparation of CMC-Fe₃O₄ nanocomposite produced a large scale quantity of CMC-Fe₃O₄ nanocomposite which was a good adsorbent for the removal of Pb^{2+} ions from water. It exhibited a better adsorption capacity for Pb^{2+} than pure Fe₃O₄ and an adsorption capacity of 152.0 mg g⁻¹ was reported for CMC-Fe₃O₄. The results revealed that the adsorption of Pb^{2+} , was well fitted to Langmuir isotherm model and pseudo-second order kinetic model. This nanocomposite was tested for continuous adsorption and desorption cycles for the reusability and stability of the adsorbent after the adsorption of Pb^{2+} ion from wastewater [42].

Carboxymethyl cellulose (CMC) with nanoscale zero-valent iron (nZVI) (CMC-nZVI) nanocomposite was prepared by a novel impinging stream-rotating packed bed (IS-RPB) and was used as an adsorbent for elimination of Pb^{2+} . This CMC-nZVI was characterized with different instrumental techniques such as transmission electron microscopy (TEM), dynamic light scattering (DLS), X-ray powder diffraction (XRD), thermogravimetric analysis (TGA) and Fourier transform infrared (FTIR) spectroscopy. Pb^{2+} loaded on CMC-nZVI nanocomposite was investigated by XPS. The effect of removal of Pb^{2+} was determined as a function of different parameters such as pH, initial concentration of Pb^{2+} and contact time. This nanocomposite showed an adsorption capacity of 1237.32 mg.g⁻¹ at pH 6.0 for Pb^{2+} which was better than that observed for nZVI (838.84 mg.g⁻¹). The adsorption data of both CMC-nZVI and nZVI were described by the Langmuir isotherm model ($R^2 = 0.999$ (1376.07 mg g⁻¹ and 900.90 mg g⁻¹). Both sets of adsorption data also fitted the pseudo second-order kinetic model for adsorption of Pb^{2+} , which showed a correlation coefficient of $R^2 = 0.999$. The nZVI and CMC-nZVI nanocomposites were also

tested for the effect of co-existing cations such as Na^+ , Cu^{2+} , Ni^{2+} and Cd^{2+} on Pb^{2+} removal efficiency [43].

Magnetic carboxymethyl chitosan nanocomposites (CMC magnetic nanocomposites) were prepared by a co-precipitation method. CMC magnetic nanocomposites provided better and fast removal of heavy metals of Cu^{2+} , Pb^{2+} , and Zn^{2+} from aqueous solutions. CMC magnetic nanocomposite contained a lot of binding sites compared to pure chitosan and it also enhanced the adsorption capacity of heavy metal ions when compared to pure chitosan. The adsorption data revealed that the Freundlich adsorption isotherm best described the process. The recyclability and reusability of this adsorbent was also improved. CMC magnetic nanocomposite was also applied in industrial wastewater treatment to produce clean drinking water [44].

The surface of nanospheres was present in various micropores and nanopores and it demonstrated good adsorption ability for Pb^{2+} ions from water with a maximum adsorption capacity 139.38 mg/g. The carboxymethyl cellulose nanofibers showed a higher adsorption behavior and was also a good adsorbent. Carboxycellulose was converted into oxidized carboxycellulose nano-fibers by using nitric acid and sodium nitrate with an oxidation method. It showed a higher surface area and addition of carboxyl groups to enhance the adsorption of Pb^{2+} . The metal loaded adsorbents of oxidized carboxycellulose nanofibers were determined with FT-IR and X-ray diffraction characterization. Hence, using the Langmuir Model, the study reported a maximum adsorption capacity of 2270 mg/g at room temperature and pH 7 with a lead concentration of 5000 ppm.

Cellulose fibers were prepared from pineapple leaves and these were modified with ethylenediaminetetraacetic acid (EDTA) and carboxymethyl (CM) groups to make Cell-EDTA and Cell-CM respectively. These were used as adsorbents for the removal heavy metal ions (Pb^{2+} and Cd^{2+}) from water. They have shown higher adsorption ability than pure cellulose fibers at pH 1–7 with maximum adsorption capacity of 41.2 mg/g and 33.2 mg/g for Cell-EDTA and 63.4 and 23.0 mg/g for Cell-CM for Pb^{2+} and Cd^{2+} respectively. The adsorption experimental data was fitted to the pseudo-first-order model kinetic model and the pseudo-second-order model was favoured for adsorption of Pb^{2+} and Cd^{2+} ions. Cell-CM and Cell-EDTA depended on the Langmuir adsorption isotherm model and the desorption of Pb^{2+} and Cd^{2+} was achieved with HCl for the regeneration and stability studies of cell-EDTA and Cell-CM adsorbents. Both Cell-EDTA and Cell-CM adsorbents were used in a binary mixture of Pb^{2+} and Cd^{2+} with different ratios, in which Pb^{2+} was more favourably adsorbed than Cd^{2+} . The selectivity of Pb^{2+} was better with Cell-CM adsorbent than Cell-EDTA. The modified cellulose adsorbents increased the adsorption of the heavy metals Pb^{2+} and Cd^{2+} [45].

Carboxymethyl cellulose (CMC) hydrogel beads were effectively arranged utilizing epichlorohydrin (ECH) as a cross linking agent in the suspension. There was an ether linkage between ECH and CMC, which provided distinct evidence of the formation of hydrogel beads on the FTIR spectrum. This hydrogel demonstrated that the binding of metal particles onto oxygen groups enhanced the crystallinity of the material which was supported by X-ray characterization. The pore size was determined by using scanning electron microscope images. The adsorption of heavy metals were investigated at optimized pH and it was fitted to the Freundlich and Langmuir isotherms models to identify the adsorption ability of the adsorbent. There were very acceptable correlation coefficients of linearized conditions for the Langmuir model, which demonstrated that the sorption isotherm of the hydrogel beads for metal particles can be fitted to the Langmuir model. The maximum adsorption capacity of the hydrogel for metal particles is 6.49, 4.06, and 5.15 mmol/g for Cu(II), Ni(II), and Pb(II), respectively [46]. Epichlorohydrin cross-linked carboxymethyl cellulose fibers

(ECMCF) were prepared and ECMCF fibers were obtained with tiny fibrous shapes and particle sizes of 20–90 μm . These had a rough and porous surface. This character of ECMC increased the adsorption performance for the removal of Cd^{2+} from water. These showed higher sorption at pH 6.0 and the adsorption capacity was 150.60 ± 10.47 mg/g [47].

2.3. Alginate composite based adsorbent for removal heavy metals

An activated carbon–calcium alginate composite (ACAA-Ca) was used for the adsorption of Pb^{2+} ions from aqueous solution. This adsorption was conducted to remove Pb^{2+} in NaCl medium with ionic strength (0.1–0.75 mol/L) and also tested for the Differential Pulse Anodic Stripping Voltammetry (DP-ASV) technique after Pb^{2+} was loaded on the ACAA-Ca composite. The ACAA-Ca composite favoured the Langmuir and Freundlich isotherm models to fit the results of Pb^{2+} removal from aqueous solution. The pseudo first order, pseudo second order and Vermeulen kinetics were suited for the adsorption of Pb^{2+} in aqueous solution. Calcium alginate (AA-Ca) improves the adsorption capacity of activated carbon (AC) in the ACAA-Ca composite where the maximum adsorption capacities were 15.7 and 10.5 mg g^{-1} , respectively [48].

Polyvinyl alcohol/sodium alginate (PVA/SA) beads were prepared by using a mixture of polyvinyl alcohol (PVA), sodium alginate (SA) and the glutaraldehyde which was used as cross-linking agents. Then zeolite nanoparticles (ZeoNPs) were coated on PVA/SA to form Zeo/PVA/SA nanocomposite beads for the adsorption of heavy metals from wastewater. Zeo/PVA/SA nanocomposite beads were investigated with different instruments like FT-IR, XRD, particle size analyzer (PSA) and SEM). These nanocomposite beads were used as adsorbents for the elimination of heavy metal ions. The adsorption data fitted the pseudo-first-order model and Langmuir model. Furthermore, thermodynamics studies were carried out for the various metal ions and the outcomes showed that the process was endothermic and spontaneous. This adsorbent was optimized at pH 6.0 to show the maximum adsorption capacity of heavy metal ions. Reusability was conducted for 10 cycles, which slightly decreased the adsorption capacity of heavy metal ions [49].

Composite nanofibers using poly (vinyl alcohol) (PVA) and sodium alginate were prepared to remove cadmium metal ions from aqueous solution. These fibres were synthesized by the electro-spinning of mepoly (vinyl alcohol) (10 % wt)/sodium alginate (2% wt) instead of producing the nanofibers from the resulting solutions. The formation of fibres was confirmed by scanning electron microscopy (SEM). The poly (vinyl alcohol)/sodium alginate nanofibers was selected with a ratio of 40/60 as the adsorbent. The synthesized adsorbent was used to remove cadmium metal as a function of various parameters such as initial metal ion concentration, pH, temperature, contact time and stirring speed, and optimum values of the parameters were obtained. The results of the adsorption process were adapted to fit the experimental data. The Langmuir model was better, and the maximum adsorption capacity through this model was obtained as 93.163 mg/g of the adsorbent. Since the performance of an adsorbent depends on the duration of the adsorption process, the kinetics of adsorption results indicated that the experimental values showed a better fit to the pseudo-second-order model. Finally, the thermodynamic perspective was examined, and the process was found to be endothermic and spontaneous [50].

Calcium alginate was used for the removal of heavy metal ions from aqueous solution. This biosorbent was tested by Fourier Transform Infrared Spectroscopy. This adsorption process was conducted as a function of various parameters such as effect of pH, initial concentration, different dosage and contact time. The influence of adsorption parameters were used to detect the

maximum adsorption capacity of heavy metal ions from aqueous solution. The experimental data were analyzed with Langmuir, Freundlich, Koble-Corrigan and Redlich-Peterson models. The kinetic data of the biosorption process was evaluated using pseudo-first and pseudo-second order equations. The Webber and Morris model was employed to interpret metal ion diffusion on the calcium alginate surface [51].

Sodium alginate coated on magnetic nanoparticles ($\text{Fe}_3\text{O}_4\text{NPs}$) was prepared by using a reverse co-precipitation process to form spherical structures with Ca^{2+} ions as a cross linker for alginate. It formed magnetic alginate activated carbon (MAAC) beads for the effective removal of Cd^{2+} ions. The adsorption behaviour of MAAC beads was investigated with the effect of pH, contact time, dosage of adsorbent, agitation and speed of rotation on Cd^{2+} ion removal from water. The percentage removal of Cd^{2+} was 90 % with MAAC beads at pH6. The maximum adsorption capacity of Cd^{2+} 150 mg/g. This adsorbent was best fitted by the isotherms models of Freundlich and Temkin than the other models of Langmuir and Dubinin-Radushkevich equations. MAAC beads experimental data recorded good removal efficiency and easy regeneration from wastewater [52].

The sorption of cadmium (Cd) and lead (Pb) by calcium alginate beads (CAB) from aqueous solutions in batch systems was investigated. CAB was also tested for its adsorption activity with various parameters such as kinetic and thermodynamic parameters. The adsorption kinetic model was fitted with the pseudo-second-order and Elovich models to indicate the adsorption kinetic rate of Cd^{2+} and Pb^{2+} ions, in which Pb^{2+} sorption showed a higher kinetic rate constant than Cd^{2+} sorption due to good attraction between the alginate beads and lead cations. The Langmuir-Freundlich (L-F) and Dubinin-Radushkevich (D-R) isotherm models were suitable for the adsorption of Cd^{2+} and Pb^{2+} by CAB. The adsorption capacity of Cd^{2+} (27.4 mg/g) and Pb^{2+} (150.4 mg/g) at 25 °C increased with high temperature, and the adsorption process was endothermic and spontaneous. CAB showed higher adsorption activity at pH between 6 and 7 [53].

Different alginate gel based adsorbents were used for the adsorption of heavy metals and these included beads, capsules and gels. Among them, alginate capsules showed the highest adsorption of Pb^{2+} ions with an adsorption capacity of 1560 mg/g. The alginate gel was synthesized by a thin film method and adsorption equilibrium was reached within 10 min. The metal loaded alginate gel rapidly desorbed the metal with HNO_3 and could be reused 10 times for recycling. The dried alginate gel showed high performance for heavy metal removal from wastewater samples [54].

A hydroxyapatite-alginate/gelatin nanocomposite has been utilized as an adsorbent for the removal of Pb^{2+} and Cd^{2+} . The adsorption capacity of the hydroxyapatite-alginate/gelatin nanocomposite was investigated under the influence of various parameters such as adsorbent dosage, adsorbate concentrations and contact time. The pseudo-second order equation and Langmuir isotherm model were suited for the adsorption of heavy metals ions with hydroxyapatite/alginate composite adsorbent. The adsorption capacity of hydroxyapatite-alginate composite and hydroxyapatite/Alginate/gelatin composite were determined by using Langmuir isotherm models with 550 and 361 mg/g for Pb^{2+} and Cd^{2+} and 616 and 388 mg/g for Pb^{2+} and Cd^{2+} . This nanocomposite reduced the adsorption capacity due to the hinderance caused by heavy metals in the aqueous medium. Thus the preparation of ceramic/polymer composites for wastewater treatment was proposed [55].

Kaolin/sodium alginate-grafted poly (acrylic acid-co-2-acrylamido-2-methyl-1-propane sulfonic acid) (KL/SA-g-P(AA-co-AMPS)) was prepared by using intercalation graft polymerization of KL, SA, AA, AMPS and ammonium persulfate as an oxidizing agent. *N,N'*-methylenebisacrylamide was used as a cross-linker.

The composite was applied for the adsorption of metals ions. The KL/SA-g-P(AA-co-AMPS) composite was investigated for its adsorption ability of heavy metals such as (Pb^{2+}), (Cd^{2+}), and (Zn^{2+}). This composite displayed maximum adsorption capacities 834.7, 69.9, and 139.8 mg g^{-1} , for Pb^{2+} , Cd^{2+} , and Zn^{2+} ions respectively. The adsorption of Pb^{2+} and Zn^{2+} ions fitted the Freundlich model while the adsorption of Cd^{2+} ion fitted both the Langmuir and Freundlich models. The KL/SA-g-P(AA-co-AMPS) composite exhibited chelation with Pb^{2+} ions and ion exchange as mechanisms of adsorption for Zn^{2+} and Cd^{2+} ions. Finally, KL/SA-g-P(AA-co-AMPS) hydrogel gave a higher adsorption capacity for the removal of heavy metal ions from wastewater. Additionally the hydrogel composite was regenerated and reused in polluted water treatment [56].

2.4. Lignin composite based adsorbent for the removal of heavy metals

Lignin derivatives such as ligninosulfonate was separated by using a sulfite pulping method from biomass with Na^+ , Mg , NH_3 , SO_2^{2-} and $\text{Ca}(\text{OH})_2$ [57]. 6.5 % of elemental sulphur is contained in lignin sulfonate. This lignosulfonate was used for the removal of heavy metal ions from aqueous solution. Hence, Lignosulfonate grafted with Na-Alginate with cross linking agent epichlorohydrin was used. Batch experiments were carried out for the adsorption of Pb^{2+} ions with a maximum adsorption capacity (27.1 mg g^{-1}) at pH 5.0, 30 °C. This adsorbent activity was tested with the intraparticle diffusion equation and the Langmuir isotherm model for monolayer coverage. Furthermore, ligninosulfonate can be filled in a column for the elimination of Pb^{2+} ions from aqueous solution [58].

The lignin macromolecule naturally contains a certain fraction of oxygen containing functional groups namely carboxyl and hydroxyl. Chemical reactions may increase the amount of oxygen containing groups, which may improve lignin's hydrophilicity and polyelectrolyte activity. The oxidative alteration of an organosol lignin was obtained when wheat straw was added to oxygen. The oxidation was conducted in the presence of a polyoxometalate (POM) $\text{H}_3[\text{PMo}_{12}\text{O}_{40}]$ with O_2 and H_2O_2 . After the oxidative modification, the COOH and aliphatic OH groups on lignin increased significantly, whereas the lignin skeleton was maintained. The saturated adsorption amounts of the modified lignin for Cd^{2+} and Pb^{2+} ions were enhanced 3-fold and 2-fold to 35.9 mg/g and 155.4 mg/g, respectively, at pH 5.0 and 20 °C [59].

Carboxymethylated formic lignin was applied for the extraction of Pb^{2+} ions yielding a maximum adsorption capacity of 107.5 mg/g at pH 6.0 and 67.7 mg/g for Cd^{2+} ions at pH 5.0. The results were fitted by the Langmuir adsorption isotherm model, which depended on monolayer coverage adsorption. Furthermore, the adsorbent capability increased at lower pH values and decreased at higher pH values at higher ionic strength [24].

Thiol capped on lignin adsorbents was selected for the adsorption heavy metal ions from aqueous solution. Thiol groups reduced the water solubility, hydrophobic nature and regenerated the adsorbent easily after adsorption. The synthesis of the modified lignin-based adsorbent (LBA) with thiol moiety showed a high adsorption capacity of 72.4 mg/g at pH 6.0, 25 °C for Cd^{2+} ions and also high selectivity of 8.6-fold higher than pure lignin. The pseudo-second-order and Langmuir isotherm model were suited for the adsorption kinetics and adsorption isotherms, respectively. This indicated a chemical sorption between LBA and Cd^{2+} ions with monolayer adsorption on the LBA surface [60].

The adsorption mechanism of Cd^{2+} from the aqueous solution with lignin (Lig) and calcined lignin with various amounts of Lig200, Lig400, Lig600, Lig800, and Lig1000 were prepared. The characteristics, including specific surface area and pore volume of adsorbents were investigated and the adsorption capability along with the effect of temperature, contact time and effect pH on the

adsorption of Cd^{2+} ions was evaluated. The characteristics of the adsorbent surface were related to the adsorption capability of Cd^{2+} ions from the aqueous phase, and the correlation coefficients between the adsorbed amount and specific surface area and total pore volumes were 0.872 and 0.960, respectively. Furthermore the adsorption capacity using Lig800 (91.3 mg/g) was higher than other adsorbent samples. The adsorption mechanism was elucidated to investigate the binding energy and elemental distribution before and after Cd^{2+} ions adsorption. Finally, the desorption capability of Cd^{2+} ions from Lig800 using a hydrochloric acid solution was demonstrated. Results obtained herein suggest that Lig800 is a potential candidate for the removal of Cd^{2+} ions [61].

The effective removal of metal ion adsorbents from the biomass sources of modified lignin to offer these adsorbents as replacements for existing commercial materials has been proposed. The initial concentrations were increased up to 12.7 ppm for Pb^{2+} , Cd^{2+} and Zn^{2+} in order to reach the plateau values which represent saturation of the active points which are available for interaction with the metal ions. The maximum adsorption capacities were reported as 11.3, 17.5, and 7.7 mg/g for Zn^{2+} , Pb^{2+} , and Cd^{2+} , respectively on lignin. The maximum adsorption capacity of lignin is higher than 20 mg/g for Cu^{2+} ion. The maximum adsorption percentage is 96.7% for Pb^{2+} for 4 h at 330 K and is 95.0% for Zn^{2+} for 10 h at 290 K. The adsorption of all heavy metal ions first increased with pH and almost reached a plateau value around 4.0 for Cu^{2+} , 4.5 for Zn^{2+} and 5.0 for Pb^{2+} . High adsorption at higher pH values implies that metal ions interact with lignin by ion exchange [62].

Due to their restricted functional sites, the adsorption of heavy metals on raw biosorbents was discovered to be less efficient. Functional groups such as carboxylate, hydroxyl, sulphate, phosphate, amide or amine have been found to be accountable for significant metal bindings on the biosorbents [63]. The intrinsic sorption property of all biosorbents is based on the concentration and configuration of effective groups on the sorbing surfaces. Biosorbents do not exhibit strong sorption, because the number of these effectively binding groups is typically low [64].

Ghimire et al. [63] in their work highlighted the necessity of utilizing functionalized biosorbents for the removal of heavy metals such as Cd^{2+} and Zn^{2+} . In their studies the functionalized biosorbents demonstrated good selectivity, and adsorption capacities. However, investigation of the cost effectiveness and application in wastewater treatment were not reported [63]. In another study, Zhan and co-workers [22] emphasized the efficiency of sodium alginate chemically modified with polyethylimine as an adsorbent. The modified adsorbent displayed a greater adsorption capability to Cd^{2+} , Zn^{2+} and Pb^{2+} which may be due to the adsorbent surface and the porous structures to large quantities of carboxylic and amino groups. Regeneration studies were reported. However the effectiveness of the cost was not investigated.

Sulphonated lignin (SL) was obtained from grass (which was not used before as a precursor of activated carbon (AC)) and dissolved in water, SL was activated with ZnCl_2 , KCl, $\text{Fe}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$ at different concentrations of salt 10%, 20%, 30% w/w with temperatures at 600 and 700 °C at 1 h, and 2 h respectively. The heavy metal ions Cd^{2+} , Cu^{2+} and Zn^{2+} were removed from aqueous solution under optimized conditions. The sulphonated lignin-based activated carbons (SLACs) exhibited large surface area, high pore and large microspore volume with less dehydrating salt concentrations (10% w/w) at 700 °C, 2 h. The various SLACs were prepared with Zinc chloride, potassium chloride and ferric sulphate and they were characterized with various instrumental techniques. The activated carbon of SLACs were investigated for adsorption and removal efficiencies of Cd^{2+} , Cu^{2+} and Zn^{2+} ions from aqueous solutions. The salts increased the porosity, microporosity, surface area and water solubility. The activation mechanism produced the porosity and the dehydrating effect of ZnCl_2 , hydrolysis reaction with

KCl and redox reaction conducted by $\text{Fe}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$. They were employed to produce the water soluble SL and also to act as a better precursors for the synthesis of activated carbon [65].

Lignin xanthate resin (LXR) was prepared by using alkaline lignin and carbon disulfide with two step reactions. LXR formation was confirmed with various instrumental techniques. The porous nature of LXR was shown. LXR was used to remove Pb^{2+} ions from aqueous solution as a function of different parameters which included the effect of pH, dosage, kinetics and temperature. LXR demonstrated a higher adsorption capacity (4.8 higher) than alkaline lignin at 30 °C due to the addition of xanthate and porous structure. LXR indicated a spontaneous reaction for adsorption of Pb^{2+} due to the negative value of ΔG° and the positive value of ΔH° indicated an endothermic adsorption. It delivered a higher adsorption capability, feasibility and biocompatibility and eco-friendly reaction for the wastewater treatment process [66].

Amino-rich magnetic lignin (M-Lignin-PEI) was successfully prepared with a reversed-phase suspension cross linking reaction. The adsorption of Pb^{2+} was evaluated by using M-Lignin-PEI with various parameters like initial pH, dosage, concentration of Pb^{2+} and contact time. The M-Lignin-PEI showed superior adsorption capacity and removal efficiency for Pb^{2+} ions with corresponded to 96.60 mg/g and 99.73%, respectively. It showed good magnetic properties and consequently was easily separated from the solid-liquid interface. This adsorption process favored a pseudo-second-order kinetic model and also fitted the Langmuir model with monolayer adsorption. It was also regenerated and desorbed with HNO_3 acid after adsorption of Pb^{2+} ions in aqueous solution. M-Lignin-PEI was repeatedly recycled with five adsorption-desorption cycles and the adsorption efficiency was 85%. It was used in industrial applications for wastewater treatment [67].

Lignin and calcined lignin at various temperatures of (200 °C, 400 °C, 600 °C, 800 °C and 1000 °C) were synthesized and they were used for the adsorption of Cd^{2+} from aqueous solution. These adsorbents showed good specific surface area, pore volume and superior adsorption of Cd^{2+} as a function of temperature, time and pH. These adsorbents showed great adsorption capabilities for Cd^{2+} ions from wastewater samples. Among them, Lig800 °C exhibited the highest adsorption capacity (91.3 mg/g). Lig800 °C was regenerated with good desorption capability using HCl as the desorbing solution. Lig800 °C therefore showed great potential for the removal of Cd^{2+} ions from wastewater [61].

Modified lignin (FAL) was fabricated with trimercapto-s-triazine trisodium salt as modifier to enhance surface area. The modified FAL has demonstrated two types of electrostatic and coordination bonds to increase the removal of Pb^{2+} ions at pH 3–6. A large amount of Pb^{2+} ions were adsorbed at higher pH with modified FAL as well as adsorption capacity of Pb^{2+} 20.0 mg/g (pH 0.2), 28.2 mg/g (pH 1.2), 65.1 mg/g (pH 3.0), and 73.7 mg/g (6.0) at 25 °C. The modified FAL showed high removal of Pb^{2+} ions and it displayed a good interaction between FAL and Pb^{2+} with adsorption processes [68].

The heavy metal ions Pb^{2+} , Cu^{2+} , Cd^{2+} , Zn^{2+} , and Ni^{2+} were isolated by adsorption onto lignin from waste paper industry. This type of lignin showed a higher affinity for adsorption of metal ions Pb^{2+} , Cu^{2+} , Cd^{2+} , Zn^{2+} , and Ni^{2+} , in which the maximum intake of Pb^{2+} ions was observed when compared to the other metal ions which followed in the order $\text{Cu}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+}$. The adsorption process was suited to the pseudo-second-order kinetic model and the Langmuir isotherm fitted well with the equilibrium data. The heavy metal ion adsorption was mostly dependent on pH and ionic strength. The adsorption mechanism described the surface complexation modeling due to two different sites of carboxylic and phenolic groups. The phenolic group on lignin has enhanced the higher affinity for removal of heavy metals ions when compared to carboxylic sites [69].

Lignin-Based Magnesium Hydroxide Nanocomposite (LH-MH) was formed by $\text{Mg}(\text{OH})_2$ and lignin. The crystallinity, size and morphology were confirmed with XRD, TEM and SEM characterization. The LH-MH material demonstrated better adsorption behavior for Ni^{2+} , Cd^{2+} , and Pb^{2+} with single and multi-component systems in water. The experimental equilibrium data was fitted with Langmuir and Sips isotherm models. The LH-MH nanocomposite achieved the adsorption of nickel, cadmium, lead and magnesium with an ion exchange process. It was recovered with HCl, NaOH and MgCl_2 after the adsorption of heavy metals. LH-MH therefore worked effectively for the adsorption of toxic heavy metals from aqueous solution [70].

2.5. Tragacanth gum and composite based adsorbents for the removal of heavy metals

Tragacanth gum is an inexpensive polysaccharide that is readily found in numerous countries in the middle east [71,72]. This biopolymer and its composites have been used lately for the removal of heavy metals from wastewater. Iranian tragacanth gum grafted polyamidoxime (ITG-g-POA) was utilized for the removal of Zn^{2+} , Cr^{3+} , Co^{2+} and Cd^{2+} . The uptake process was pH dependent and took place at pH 6; the kinetic adsorption followed the pseudo-second order while the sorption isotherm was best described by the Temkin isotherm model. The optimum adsorption capacities obtained from Langmuir model were 100.0, 76.92, 71.42 and 66.67 (mg g^{-1}) in the order of $\text{Co}^{2+} > \text{Zn}^{2+} > \text{Cr}^{3+} > \text{Cd}^{2+}$ independently. The above outcomes showed that the selective order of the adsorption capacity is caused by the formation of stable chelating ring between the bidentate amidoxime ligand and metal ion [73].

A novel attractive biosorbent, hydrogel beads were synthesized from the biopolymer tragacanth gum, graphene oxide and polyvinyl alcohol through a gelation approach. This biosorbent was applied in aqueous solution for the removal of Pb^{2+} ion. The pseudo second order kinetic model well depicted the rates of adsorption and the experimental data were well suited with the Langmuir isotherm model with the optimum adsorption capacity of 81.78 mg g^{-1} . This biosorbent was recycled and no important activity loss after 3 cycles was observed [74]. Tragacanth gum/graphene oxide composite was prepared and used for the removal of heavy metals such as Pb^{2+} and Cd^{2+} . The pseudo first order kinetic model best described the process and Langmuir model suited well the sorption. The maximum adsorption capacity found was 142.50 and 112.50 mg g^{-1} for Pb^{2+} and Cd^{2+} . It was noticed that the percentage removal declined after some adsorption/desorption cycles [75].

2.6. The impact of functional group in carbohydrate biopolymer for heavy metal adsorption

The high affinity of biosorbents towards metal ions is owed to their surface chemistry, which consists of many reactive functional groups characterized by their unique hydrogen bonding, which is the effective tool for remediation heavy metals from wastewater [76,77]. These functional groups are capable of binding heavy metal ions by the substitution of hydrogen bonding with the existing metal in solution, or by the formation of metal ion-complexes through the hydrogen bond of the functional group with the given metal ion [78]. Functional groups like carboxylate, hydroxyl, sulphate, phosphate, amide, and amine groups onto the biosorbents have been reported to be responsible for appreciable metal binding [79–81]. Increasing the binding groups involves the substitution of specific functional groups on the biosorbent's surface with desirable functional groups by various chemical modification methods, such as the amination of giving functional groups, carboxylation of hydroxyl and amine groups,

phosphorylation of hydroxyl groups, saponification of ester groups, halogenation and oxidation. Raw biosorbents comprise several functional groups, and only certain groups are responsible for targeting metal ions, while the other groups could interfere with the metal ions. Hence, the elimination of inhibiting groups is important for enhancing biosorption, and usually involves decarboxylation and deamination [78,82]. All biosorbents have an intrinsic sorption property which is dependent on the concentration and types of functional groups on the sorbent surfaces [63]. As the density of these effective groups for metal binding is generally low, biosorbents do not show a high sorption capacity [64].

3. Regeneration application for the spent adsorbents

Although, little attention is currently paid to the disposal and recycling processes [83] the review also focuses on biopolymer based adsorbents for the elimination of heavy metals from aqueous solution and regeneration of used adsorbents for reuse applications after the adsorption of heavy metals. The reuse and disposal of used adsorbents were historically discharged into the environment after recovery or without removal of heavy metals but this produced secondary pollution in water samples [84]. The metal loaded adsorbents contaminated the environment and were also toxic to humans. Thus, the reused adsorbent was supposed to be recycled after recovery of the heavy metals and reused in other applications to minimize the toxic nature in water and the surrounding environment. The main focus of future studies should therefore be on heavy metals removal using biopolymer based adsorbents and reuse applications of the metal loaded adsorbents. A few studies of this nature are discussed below but many of these have focused mostly on adsorption-desorption cycles.

3.1. Regeneration of chitosan spent adsorbents

The adsorption-desorption method was a very essential process for the recovery of the adsorbent after adsorption of heavy metals ion from aqueous solution [85]. The nanocomposite chitosan/poly(ethylene glycol)/poly(acrylic acid) (CS/PEG/PAA) hydrogel containing hard Lewis base adsorption sites which included amino groups, hydroxyl groups, ether linkage, carboxylate ions was prepared by the glow-discharge electrolysis plasma (GDEP) technique. CS/PEG/PAA hydrogen adsorbent was exposed to both adsorption-desorption processes in the removal of heavy metal ions of Pb^{2+} and Cd^{2+} ion in water. EDTA-4Na eluent (0.015 M) was used to regenerate the adsorbent after adsorption of the heavy metal ions. The CS/PEG/PAA adsorbent showed selective adsorption of Pb^{2+} with coexistence of Cd^{2+} ions after four adsorption-desorption cycles. It did not decrease the adsorption capability after 4 cycles. CS/PEG/PA revealed a higher adsorption capacity for Pb^{2+} ions than for Cd^{2+} ions due to better reusability and good selectivity. This nanocomposite showed easy separation, better recovery and good purification for Pb^{2+} ions in aqueous solution. Therefore, CS/PEG/PAA exhibited great regeneration ability and can be effectively applied in wastewater treatment [86].

Chitosan coated perlite beads were desorbed after the adsorption of Cd^{2+} ions with 0.1 N HCl. It effectively released the Cd^{2+} ions three times. The desorption completely removed the metal ions from the beads and addition of 0.5 M ethylenediamine tetra acetate (EDTA) solution was carried out to complete saturation of Cd^{2+} in 100 mg/L of Cd^{2+} solution. These beads delivered good reusable capacity and good spent adsorbents after the removal of Cd^{2+} ions from aqueous solution [87]. Regeneration and desorption are crucial for commercial adsorbents. Activated Carbon-Chitosan Complex (ACCA) was regenerated after the adsorption of Pb^{2+} and Cd^{2+} ions in water. It showed high

desorption percentages and retention rate of heavy metals of Pb²⁺ (88 %) and Cd²⁺ (78 %) after five cycles. Finally, ACCA could be used as a better adsorbent for the removal of Cd²⁺ and Pb²⁺ in wastewater samples [88].

The practical application of regeneration and repeatability is an essential study for the use of the adsorbent. Magnetic modified chitosan used for the adsorption of Zn²⁺ from aqueous solutions (CMMC) has revealed good adsorption and desorption properties. The regeneration and reusability of CMMC was conducted and showed great desorption capabilities after the adsorption Zn²⁺ ion from aqueous solution. The desorption of Zn²⁺ ions removed from the CMMC beads were conducted with various eluents buffers with 0.1 M HCl, 0.1 M HNO₃ and 0.5 % CH₃COOH which resulted in 97.2 %, 82.1 % and 70.0 %, removal respectively. Among them 0.1 M HCl showed the optimum eluent buffer for the effective removal of Zn²⁺ from CMMC beads [89].

3.2. Regeneration of carboxymethyl cellulose spent adsorbents

The cellulose-based hydrogels (C-g-AA) possess excellent adsorption capabilities for metal ions. The regeneration and desorption process was investigated with heavy metal ions from wastewater samples. The desorption process was conducted with 0.1 mol/L HNO₃ and 0.1 mol/L NaOH respectively to eliminate heavy metal ions on C-g-AA hydrogel. The reuse of C-g-AA hydrogel was conducted for three cycles after adsorption of heavy metals with 0.1 M HNO₃ as the desorbing solution. 95 % removal of the heavy metal ions on the adsorbent was first observed and 87 % desorption after further desorption-adsorption cycles. However, 85 % adsorption capacity of heavy metals was observed after three cycles of regeneration. The C-g-AA hydrogel was suitable for efficient removal of heavy metal ions from aqueous solution [90].

The recyclability of the biosorbent was measured at 30 °C. 100 g of biosorbent was added into 500 mL of 500 mol/L of heavy metals ions solutions for 210 min, respectively, and then removed from the solutions. The regeneration of sugarcane cellulose-based adsorbents was performed with 500 mL of 1.0 M HNO₃ under agitation 30 °C at 120 min. The desorption-adsorption process of a cellulose based biosorbent was conducted by immersing the biosorbent into HNO₃ at 120 min after five regeneration cycles. The biosorbent exhibited a higher adsorption capacity for the removal of 268 mg/g, 160 mg/g and 43 mg/g heavy metals, respectively at 500 mol/L, which demonstrates the high sorption capacity of the biosorbent (F. [91]).

3.3. Regeneration of alginate spent adsorbents

The adsorbent, Fe₃O₄@SiO₂@PEI-NTDA, was synthesized by the immobilization of an amine and anhydride onto magnetic

Fe₃O₄@SiO₂ nanoparticles with polyethylenimine (PEI) and 1, 4, 5, 8-naphthalenetetracarboxylic-dianhydride (NTDA) for the elimination of Pb²⁺ and coexisting Cd²⁺, Ni²⁺, Cu²⁺, and Zn²⁺ ions from aqueous solutions. This adsorbent showed a higher adsorption capacity of 285.3 mg g⁻¹ for Pb²⁺ from water due to electrostatic interactions and chelation, at pH 6.0. The adsorbent was successfully recovered after 6 cycles of desorption-adsorption methods with 2 M HCl for 144 h due to high stability and better reusability. Hence, Fe₃O₄@SiO₂@PEI-NTDA NPs is suited to remove heavy metals from aqueous solution [92]. High-molecular alginates were obtained by using Djiboutian brown seaweeds, *Sargassum* sp. (S) and *Turbinaria* (T) and sodium salts in 31.0 and 42.7 %. This alginates were coated on Aerosil 200 silica, amine-functionalized and carboxylic acid groups to increase the strength and formation composite (Alg.(T/S)+SiO₂) Alg.(T/S)+SiO₂NH₂) and Alg.(T)+SiO₂CO₂H). These adsorbents were used to remove Pb²⁺ from wastewater and it was also successively regenerated after successive cycles of desorption-adsorption with 0.5 M HCl. Hence, Alg.T + SiO₂ was used as a good adsorbent due to fast adsorption of heavy metals and better desorption of Pb²⁺ ions in from aqueous solution [93].

3.4. Regeneration of lignin spent adsorbents

The regeneration of biomass derived porous carbon was obtained by using different desorption agents such as HNO₃, EDTA, NaNO₃ and Na₂CO₃ with 0.1 M. The desorption was carried with HNO₃ with high concentrations and it damaged the structure of adsorbent. Hence, 0.1 M Na₂CO₃ was supported for desorption process for the removal of Pb²⁺ and Cd²⁺ on biomass porous carbon adsorbent with desorption efficiencies 96 % and 92 %, respectively after five cycles of adsorption-desorption. This adsorbent showed potential as a great adsorbent for the removal of Pb²⁺ and Cd²⁺ from aqueous solution [94].

The low-cost adsorbents furfural and phenolic resin were also subjected to desorption-adsorption process analysis. This adsorbent could remove the heavy metals Cd²⁺, Ni²⁺, Pb²⁺, Cu²⁺ and Zn²⁺ from aqueous due to the availability of lignin, cellulose and hemicellulose in the adsorbent. It exhibited higher adsorption capacities of 18.3, 98.2, 34.8, 45.1 and 14.7 mg/g for heavy metals Cd²⁺, Pb²⁺, Zn²⁺, Cu²⁺ and Ni²⁺ respectively in wastewater at pH 5–7. These metals were effectively recovered from the adsorbent after desorption with 1 M HNO₃ as a regeneration solution so that, it could be applied in wastewater treatment (Y. [95]). Table 3 summarizes the regeneration method of carbohydrate biopolymers adsorbents.

Table 3
Regeneration methods of selected carbohydrate biopolymers adsorbents.

| Adsorbent | Regeneration method | Pollutant | Capacity mg/g | References |
|--|---|-----------|---------------|------------|
| Nanocellulose fibrils | 0.5 M HCl/0.5 M HNO ₃ | Cd(II) | 9.7 | |
| | | Pb(II) | 9.42 | |
| EDTA modified microfibers | 0.5 M HCl | Pb(II) | 227.3 | |
| | | Cd(II) | 83.75 | |
| Chitosan with epichlorohydrin and triphosphate | 0.1 M HCl and HNO ₃ | Pb(II) | 166.94 | [85] |
| | | Cd(II) | 476.1 | |
| ZnO nanoparticles coated with chitosan | 0.01 M EDTA | Pb(II) | 135.1 | [96] |
| | | Cd(II) | 476.1 | |
| Alginate beads with attapulgate | 0.2 M HCl | Cd(II) | 160 | [97] |
| | | Cd(II) | 2042 | |
| Alginate with PAMPS | NaCl | Pb(II) | 843 | [98] |
| | | Cd(II) | 2042 | |
| Carboxymethylβcyclodextrin polymer with EP | 0.01 M HNO ₃ /0.1 M Na ₂ EDTA/0.02 M H ₃ PO ₄ | Cd(II) | 27.7 | [99] |
| | | Pb(II) | 64.5 | |
| Chitosan/Ag NPs/Cu NPs/CNTs Multifunctional Nano-Composite | 0.1 M EDTA | Cd(II) | N/A | |
| | | Pb(II) | N/A | |

4. Reuse applications for the spent adsorbents

Reuse applications for the spent adsorbents are very important for reducing the toxicity as well as control of secondary pollution. The following discussion highlights some reuse applications which have been reported in the literature.

4.1. Steam treatment by using spent adsorbents

Recovery of steam may take place at higher or lower temperatures. High thermal steam reuse is conducted in ambient surroundings to prohibit oxidative steam reactions between the sorbent and adsorbate that might as well lead to calcination and degradation of the adsorbent permeable system. For similar purposes shallow thermal steam reuse of air flow that is less expensive than ambient flow can be implemented. In the warming up process carbon is produced by dehydration, thermal desorption, incineration and carbonisation of non-volatile compounds and pyrolytic residues gasification in the midst of small quantities of oxidant like water vapour at high temperatures (650–850 °C). Choice of vapor temperature depends on the heat efficiency of the adsorbent and the boiling point of organic and inorganic adsorbent solvency. For organic compounds, steam temperature is usually considered at 30–50 °C above the adsorbate boiling point [100].

4.2. Catalyst application by using spent adsorbents

This application can be useful for reusing metal loaded adsorbents and avoiding unleashing of the adsorbent into environment. Studies of reusing metal loaded adsorbents for this purpose were reported. He et al. [101] employed spent chromium adsorbents as catalysts for eliminating methylmercaptan. The findings indicated that extremely poisonous Cr (VI) exposure may end up inactivated due to the formation of Cr₂S₃. Furthermore, the catalysts acquired from the chromium-loaded spent adsorbent display greater potential than other catalysts which have been developed. In the meantime, the analysis of the impact of certain chemical species shows that spent chromium adsorbents have potential in catalysis. In addition, the spent reutilised adsorbents may be recovered for recycling. Fanourakis et al. [102] explored the reuse of different nanoadsorbents as photocatalysts for the removal of pharmaceutical pollutants. The outcome revealed that the different sorbents demonstrated high capacities to adsorb even though they were not tested on real water samples.

4.3. Cement application by using spent adsorbents

Verbinnen et al. [103] reutilized spent adsorbents for oxyanions and heavy metal pollutants in the generation of ceramics. It was demonstrated that the tested elements had higher concentrations in spiked sludge than in the unspiked one. Agarwal [104] studied the leaching behaviour of cement solidified by fly ash for heavy metal extraction. The results revealed that the leaching of pollutants such as zinc and lead ions was not feasible due to strong binding forces between the positive ions and the negative particles present in fly ash.

4.4. Fertilizers and soil conditioners by using spent adsorbents

Few studies on the reuse of spent adsorbents as fertilizers and soil conditioners were reported. However few studies were reported on the reutilisation of spent adsorbents in fertilisation and soil conditioning. A common adsorbent employed as metal loaded adsorbent is biochar. Yao et al. [105] reported the removal of phosphate ions from aqueous solution and its application as a slow release fertilizer. The results demonstrated the potential use of biochar as a fertilizer for soil improvement. Wang et al. [106] utilized wheat straw based adsorbents for ammonium and phosphate ion recovery and reused this adsorbent as a release adsorbent. In their outcome, they concluded the spent adsorbent was able to increase soil humidity content and the rate of dehydration of soil humidity and was inexpensive and sustainable for horticultural and agricultural applications.

4.5. Latent fingerprint detection

Latent fingerprint detection is another application that can be explored for the reuse of the spent adsorbent. Successful reuse of the spent adsorbents will solve the issue of secondary pollution and crime. The production of latent fingerprints is essential for the identification of individuals in forensic science. In the past, powder dusting, silver nitrate soaking, iodine fuming and ninhydrin spraying were the well-known and widely used techniques in latent fingerprint studies [107]. Table 4 gives a summary of the traditional techniques used in latent fingerprint detection presenting the major advantages and disadvantages of each one.

Different fine powders or nanoparticles (NPs), like SiO₂, magnetic powders, TiO₂, AgNPs, etc., that bind to sebaceous deposits in latent LFPs because of hydrophobic interactions. However, powders with an appearance-only color signal cannot be applied to substrates with identical background colours. Fine

Table 4
Latent fingerprint detection by using various nanomaterials.

| Techniques | Advantages | Disadvantages | References |
|-----------------------|---|---|------------|
| Powder dusting method | -High resolution. -High fluorescent intensity. -Ease to operate -Low cost | -Limited shelf life. -Poor contrast. -developed impressions affected by underlying patterns on the surface. | |
| Iodine fuming | -Use similarly at home for crime and lab testing. -Non-destructive. | -More lasting discoloration. -Photographic documentation does not last due to sublimation. | [108] |
| Silver nitrate | -Simple and effective | -Considered obsolete by many researchers. -The age of fingerprint restricted to a week. | [109] |
| -Ninhydrin | -Ninhydrin interacts with amino acids frequently found in residues from fingerprints. -Clear ridge visibility. -Better finger impression. -Non-destructive | -Decrease in contrast due to background stains. | |

powders with a good luminescence are therefore basically more useful.

Historically, the iodine fuming method has been known as one of the very first approaches available to the investigator to produce latent fingerprints. Therefore, fingerprints that need refuming with iodine to visualize or immediately after treatment to keep them stable are considerable. Recognizing this problem as a major flaw in iodine fuming, techniques were established to prolong the visible life of iodine-smoked latent prints [110].

The silver nitrate technique is one of the oldest methods of detecting latent fingerprints on porous items like paper, cardboard and wood. The technique focuses on the reaction of silver ions with the chloride content of sweat residue. The reaction product, silver chloride, is relatively unstable and, when exposed to ultraviolet radiation or sunlight, decomposes into finely divided silver, visualizing the ridges as a dark hue, usually black or brown.

The ninhydrin method is now commonly used in developing latent fingerprints present on the surface of porous materials (e.g., paper, cardboard, raw wood, and plasterboard). This technique was first proposed in the mid-20th century [111].

Traditional methods have proven useful in fingerprint application, hence in fighting crime. However, they are not always effective and have displayed disadvantages like poor sensitivity, high background interferences, low contrast and low selectivity (M. [112]). To confront this challenge, attention has been shifted to nanoparticles, fluorescent nanomaterials, and rare-earth up conversion fluorescent nanomaterials (UCNMs).

4.5.1. Fluorescent nanomaterials in latent fingerprint

Nanomaterials such as magnetic nanoparticles, semiconductor quantum dots and their composites, metals and their oxide nanoclusters, and carbon dots have been greatly attractive in latent fingerprint detection because of their good magnetic properties, sole dependency on size photoluminescence with stable emission, high quantum yield and good biocompatibility [113].

Table 5 summarizes reported studies using fluorescent nanomaterials for fingerprint application. This table outlines as well the efficiency of the materials compared to traditional methods as well.

Zhao et al. [118] prepared novel non-toxic CDs/SiO₂ nanoparticles. The synthesized CDs powder demonstrated excellent affinity, sensitivity and selectivity. The fluorescence colour may be changed as per the light sources increasing excitation wavelength, which renders it appropriate only for those with fluorescence on various backgrounds. CDs/SiO₂ is more efficient in terms of ridge details, sensitivity, steadiness and considerably fewer background interference when compared with commercial luminescent

powders. In addition, it was proposed that the fluorescence colour may be modified to change the excitation wavelength of the light source, making it useful even for the ones with various fluorescence colored backgrounds. CDs/SiO₂ was more successful in terms of ridge specifics, flexibility, stability and substantially fewer background interference when compared with commercial fluorescent powders.

The resulting interactions between quantum dots and fingerprint residues depend first of all on factors such as adsorption and electrostatic attraction. Due to the high oxidation quality of the quantum dots, the fluorescence produced by them can decrease dramatically over a short period of time, resulting in decreased contrast and poor long-term preservation of fingerprints. Quantum dots may be combined or covered with protective material to make more stable nanomaterials to fix this problem [119].

4.5.2. Nanoparticles for latent fingerprint application

Nanoparticles including metal nanoparticles, metal oxide nanoparticles and composites have been employed for latent fingerprint application in the past. Table 6 displays reported studies on latent fingerprint using nanoparticles.

The nanoparticles as seen from above can be good labeling agents and therefore are useful in latent fingerprint detection. However, the detection methods have their drawbacks which include contamination of reagents, need of expensive built equipment and prolonged imaging time [122].

4.5.3. Rare earth fluorescent nanomaterials in latent fingerprint detection

Rare Earth Upconversion Fluorescent Nanomaterials have drawn interest in researchers for latent fingerprint over the past because of the benefits of small particle size, large surface area, high quantity output, high fluorescent intensity, low emission peak and good optical stability [123]. They are suitable for the production of latent fingerprints in recent years, as well as successful fluorescent labels (M. [124]; M [5]). Due to the use of rare earth fluorescent nanomaterials to produce latent fingerprints, high performance, contrast, high selectivity and low background interference, the papillary ridge of fingerprints on different smooth substrates could be easily identified under the excitation wavelength of 254 nm UV light (M [124]). Additionally, material luminescence is highly dependent on their electronic band structure. Rare Earth (RE) element ions have an extreme luminescence in the divalent/trivalent state due to 4f electron transitions. Hence, RE elements luminescence is almost independent of the host matrix. However, the energy levels of RE elements may primarily be determined by the symmetry of the crystals, and

Table 5

A summary of nanomaterials used in latent fingerprint.

| Materials | Observations | References |
|--|---|------------|
| Green emitting carbon dots(G-CDs) | -Fluorescent fingerprint images have clear and systematic ridges. -Enough minutiae features and strong fluorescence intensity. | [114] |
| Nanohybrid composed of green- and red-emanating quantum dots | -Robust for imaging -Exhibition of light fluorescence color. | [115] |
| CdTe QDs capped with mercaptosuccinic acid (MSA) CdTeMontmorillonite(CdTe-COONH ₃ NH ₃ ⁺ QDs) and CdTe@SiO ₂ quantum dots (QDs) | -Clear images can last up to months. -High enhancement -Detection and identification of finger ridges. -More effectiveness with high resolution. -More accurate fingerprint ridges -Less interfering background. | [116] |
| CdS QDs coated chitosan and CdS/polymer nanocomposites | -Clear detection under a Rofin Polilight at 450 nm. -Retention of clear fingermarks observed. | |
| nitrogen doped carbon dot (N-CDs) | -Good images -bright patterns of unique features were detected. -Photoluminescence increases with increase in pH. | |
| N-CDs/ZnONPs Nanocomposite | Display excellent sensitivity and validity. | [117] |

Table 6

A summary of nanoparticles used in latent fingerprint.

| Materials | Observations | References |
|--|---|------------|
| AuNPs | -Patterns not conductive due to lack of interaction with fingerprint residue | [120] |
| CeO ₂ NPs, TiO ₂ NPs, FeO ₃ NPs, ZnONPs, V ₂ O ₅ NPs, SnO ₂ NPs CeO ₂ NPs, TiO ₂ NPs | -Good finger impression -High contrast -Bright ridges -Low background interference | |
| ZrO ₂ /CuO nanocomposite | -Enhance fingerprint displayed A well resolved ridge flow. -Pattern configuration with clear resolution. -Levels 1 and 2 were observed | [121] |

Table 7

Summary of Rare Earth upconversion materials utilized for latent fingerprint.

| Materials | Comments | References |
|---|---|------------|
| YVO ₄ :Eu and LaPO ₄ :Ce, Tb | Excellent results observed. | [126] |
| Tb doped gadolinium aluminate nanophosphors (GdAlO ₃ :Tb ³⁺) | -Yield a correct picture of the entire fingerprint with excellent accuracy and contrast. -Highly efficient -Fast | [127] |
| SrGa ₁₂ O ₁₉ :Mn ²⁺ | -Strong chemical stability -Can last up to months | [128] |
| NaYF ₄ :Yb,Er,Gd fluorescent upconversion nanorods (UCNRs) | -All 3 levels of LFP could be obtained favourably selectivity. -Great performance with excellent sensitivity. -Low background, high contrast, and low toxicity. | [129] |
| Yttrium aluminate nanophosphor (YAlO ₃ :Sm ³⁺) | -Additionally, an acid yellow 7 (AY ₇) was used to detect the blood fingerprints left on the eight substrates utilised for comparison. -Images lasting up to 30 days when illuminated at 365 nm. -High contrast and selectivity | [130] |

this depends on the host material. The use of the right material is therefore a very important factor in achieving improved optical properties [125]. Table 7 depicts a summary of Rare Earth upconversion materials utilized for latent fingerprint.

In spite of all the materials reported on latent fingerprint detection, reports on heavy-metal loaded spent adsorbents in this application are till date still lacking. Hence, studies in which heavy metal ions are loaded onto biopolymers and reused in latent fingerprint detection should be initiated.

5. Conclusion

Overall, the occurrences, source of exposure and industrial uses of cadmium lead and zinc metal were accentuated. It is obvious that these pollutants are problematic to humans and all other living organisms. Numerous approaches and techniques for the remediation of the above mentioned heavy metals have been emphasized. Adsorption has proven to be the most adequate technique and therefore the preferable one and was discussed in detail for the heavy metals of interest (cadmium, lead and Zinc). Different sorts of adsorbents for cadmium, lead and zinc ions remediation have been discussed. The removal of Cd²⁺, Pb²⁺, and Zn²⁺ ions by carbohydrate biopolymers based chitosan, carboxymethyl cellulose and alginate and lignin materials has been extensively discussed. It was seen that carbohydrate biopolymers are alternative ways to remove heavy metals when compared to conventional methods. These carbohydrates biopolymers possess functional groups that can adsorb metal ions through interactions like chelation and electrostatic interactions Further advantages and disadvantages of carbohydrate biopolymers based adsorbents have been described for the adsorption of heavy metals from wastewater. In this review article details on the regeneration of adsorbent after desorption with several cycles has also been

discussed. This article has also provided details on the reuse applications of spent adsorbents to minimize secondary pollution and to reduce the toxicity of releasing heavy metal load adsorbents into the environment. Finally, reuse of the metal-loaded adsorbent in latent fingerprint detection for social and environment development has been proposed as a future research perspective.

Declaration of Competing Interest

The authors report no declarations of interest.

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