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REVIEW

Critical Assessment of Polyaniline-based Biocomposites for Removal of Toxic Heavy Metals from Aqueous Media

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Polyaniline (PANI) is useful for the adsorption of hazardous substances because of its multiple N-containing functional groups, high adsorption capacity, superior selectivity and chemical durability. Although it is cheap and easy to synthesize, PANI has low processability and mechanical strength, which can be overcome by preparing composites of PANI with biomass waste. Biomass waste is a rich source of useful biopolymers, judicious use of which can also solve the problem of biomass-waste management. Furthermore, biomass waste provides excellent support and possesses functional groups, which help to synergistically remove potentially toxic elements (PTEs) from wastewaters. Composites of PANI have shown tremendous potential in the removal of PTEs from wastewaters. More recently, the focus of studies have been on PANI-based inorganic composites. Considering the environmental impact of these materials, use of PANI-based biosorbents would be more economical, environmentally friendly and promising. This review discusses the mechanisms of removal of PTEs by PANI biocomposites, factors affecting adsorption, characteristics and role of different biomass materials in the removal of PTEs, their advantages and limitations. This article also discusses the potential use of waste microbial biomass-polyaniline composites, which has not been fully explored thoroughly. The vast potential for future research has also been acknowledged, though much more study is needed before this method can be used to its full potential.

Keywords: Polyaniline, Metal ions, Biocomposites, Adsorption, Synergistic effect, Environment-friendly, Mechanism, Biosorbent.

INTRODUCTION

Electro-conductive polyaniline (PANI) is an inexpensive and environmentally-stable material with abundant nitrogen containing amine and imine functional groups. PANI has been used to efficiently remove toxic metal ions due to its unique doping-undoping mechanisms, redox activity and nitrogen containing functional groups. According to Alipour *et al*. [1], the adsorption process of PANI is attributed to the conductivity of its electrons and ions, since metal ions can be trapped through electrostatic interactions. PANI is also used in sensors, anti-corrosion additives, EMI shielding, supercapacitors, *etc*. [2]. It can also remove anionic pollutants from wastewaters [3-5] and can be regenerated [6].

Among the different polymers like polyaniline, polypyrrole, polythiophene, polyphenylene and polyacetylene used for the syntheses of composite adsorbents, polyaniline has been the most preferred one, due to various reasons, such as low monomer cost, high electrical conductivity, biocompatibility, easy synthesis and high mechanical and chemical stability [7]. However, the poor mechanical strength and insolubility of PANI in water or solvents are the main drawbacks [8]. Another problem associated with PANI for removing potentially toxic elements (PTEs) using batch and flow systems is the excessive pressure drop, owing to its small particle size [9]. Moreover, an additional step for separation of the adsorbent is necessary after completing the adsorption process. These drawbacks can be solved by converting PANI into its composites with either organic or inorganic components. These components include metal oxides [5,10], clay [11], polymers [12,13], metal-organic frameworks [14], zeolites [15], layered double hydroxides [16], carbon-based materials [17,18], biomaterials and biopolymers [19,20] and silica-containing sorbents [21]. One of the disadvantages of using materials like silica, clay minerals and zeolites is the disposal of residual metal sludge that poses practical problems [22]. Hence, biomass waste is proposed as an alternative method because it is environmentally safe, non-toxic, biodegradable, economical and readily available [6,23].

There has been an impetus for adopting sustainable and green technologies in recent years. In this context, biomass waste rich in cellulose, hemicellulose, lignin, *etc.* can be used. These biopolymers have different functional groups, which can be used to remove PTEs from wastewaters. Biopolymers themselves have been used for the removal of heavy metal ions. According to a recent review [24], the hydroxyl, carboxyl and amino functional groups present in biomass assist in the removal of heavy metal ions through ionic exchange and electrostatic attractions. The primary constituents of biomass are cellulose, hemicellulose and lignin. Biomass waste containing only lignin and cellulose shows a relatively low selectivity and mechanical resistance in removing PTEs [25]. The specific properties, advantages and limitations of different biomasses have been discussed subsequently in the text. Chemical pretreatment of biomass using acids, alkalis or oxidizing agents leads to hydrolysis of biomass, cleavage of interchain hemicellulosic bonds and decrease in lignin proportion [24]. This helps to increase its porosity and surface area, consequently leading to increased adsorption capacity. Another promising alternative is to combine these biopolymers with PANI. PANI already has many amine and imine functional groups and the biopolymer can provide structural support to the complex. Thus, a highly efficient relatively homogenous composite with excellent mechanical strength and performance can be obtained by combining PANI with biomass wastes [9,26,27]. However, research and development on PANI-biomass waste composites as adsorbents for removing PTEs from wastewaters have been limited. This is probably due to the emergence of other alternative adsorbents in the market. Nevertheless, research shows there exists a synergy between PANI and the biomaterial for the removal of PTEs.

In recent years, there have been several reviews on PANI. For example, Eskandari *et al.* [6] described the applications of PANI-based materials in the removal of metals, which included inorganic and bio-based components. Samadi *et al.* [22] reviewed the properties and applications of PANI-based adsorbents for the removal of different pollutants from wastewaters. Zare *et al.* [28] discussed other nano-adsorbents based on PANI and its derivatives to remove metal ions and dyes. A review by Jiang *et al.* [29] elaborated the use of PANI-based adsorbents to remove Cr(VI) from aqueous solution. Recent reviews have also explained the importance of polyaniline based composites for the removal of dyes and heavy metals from wastewaters and aqueous solutions [30,31]. To the best of our knowledge, present review is the first one dedicated entirely to removing potentially toxic elements (PTEs) using PANI-based biosorbents. The mechanisms of removal of PTEs by PANI, factors affecting the adsorption of PTEs, their advantages, properties and limitations have been discussed. Future prospects and scope of using PANI-based biosorbents for the removal of PTEs have also been proposed.

There are different mechanisms involved in the removal of PTEs using PANI. The reaction and its efficiency depend on the PTEs to be removed. Chromium(VI) exists either as $Cr_2O_7^{2-}$, $HCrO_4^-$ or CrO_4^{2-}. Amongst them, $Cr_2O_7^{2-}$ and $HCrO_4^-$ are present in acidic conditions (pH 2-6), whereas CrO_4^{2-} occurs in alkaline conditions (pH > 6) [32]. Hence, Cr(VI) can be removed at low pH. In contrast, PTEs like Cd(II), Pb(II) and Zn(II) present as cations can be removed at pH values higher than those required for Cr(VI). Under acidic conditions, PANI remains in the protonated state, whereas under alkaline conditions, PANI remains in its unprotonated form. Therefore, the mechanisms involved in the removal of different PTEs vary. The main mechanism of adsorption was reported to be the electrostatic interactions between polyaniline composite and the metal ion [30]. The mechanisms responsible for the removal of PTE using PANI-based biosorbents are listed in Table-1. The schematic representation of PTE removal using PANI is shown in Fig. 1.

Factors affecting the adsorption of PANI based biocomposites

Synthesis of PANI: Depending on its oxidation state, PANI can exists in three forms-leucoemeraldine (fully reduced state), emeraldine (a neutral state with 50% oxidized and 50% reduced groups) and pernigraniline (fully oxidized state). Generally, the emeraldine form is used as an adsorbent since the pernigraniline form is susceptible to decomposition [22]. Preliminary studies have shown that the undoped emeraldine base in PANI-based biocomposites is more efficient in removing Cr(VI), Cd(II) and Pb(II) [unpublished results]. Also, polyaniline was reported to be in the emeraldine form in the nanocomposites used for the remediation of heavy metal ions [7]. The different factors that govern the morphology and consequently the adsorption of PANI in PANI-based biocomposites are monomer aniline concentration, oxidant used and its concentration, type of dopant and the time and temperature of polymerization. The factors affecting the rate of adsorption by PANI-based biosorbents are summarized in Fig. 2.

The amount of PANI coated onto the biomaterial increases with increase in aniline concentration, which consequently increases adsorption. For example, Cr(VI) removal by PANI-cellulose composite increased with increase in aniline concentration [26]. With increase in ammonium persulfate/H_2O_2 (oxidant) concentration, the removal of PTEs increased before it declined. This trend was due to the over-oxidation of aniline, which led to the poor reduction of Cr(VI) to Cr(III). Moreover, over-oxidation leads to a decrease in the deposition of PANI on cellulose fibers [26]. The nature of the counter-ion in the dopant also influences the adsorption process. The -NH group in PANI flanked by phenylene groups on either side undergoes protonation and deprotonation during the adsorption process.

TABLE-1
BIOMASS MATERIALS USED AS COMPOSITES WITH POLYANILINE FOR THE REMOVAL OF PTEs, OPTIMAL pH CONDITIONS FOR ADSORPTION, THEIR ADSORPTION CAPACITIES AND REPORTED MECHANISMS OF ADSORPTION

Biomass material	Metal ions	Optimal pH conditions	Adsorption capacity or removal efficiency (mg/g or %)	Mechanism of adsorption	Ref.
Cellulose acetate (phytic acid dopant)	Hg(II); Cr(VI)	pH = 5; pH = 2	280; 94	Complexation; Electrostatic attraction and redox mechanism	[8]
Polyaniline-bacterial extracellular polysaccharide nanocomposite	Cr(VI)	–	97.3%	Electrostatic attraction	[52]
PANI/bacterial cellulose (BC) mat	Cr(VI)	pH = 7	100%	–	[101]
Prussian blue/ polyaniline@cotton fibers	Cu(II)	pH = 5	93.4% (31.93 mg/g)	Chemisorption	[53]
Saw dust	Cu(II); Cd(II)	pH = 5	208 mg/g; 136 mg/g	–	[9]
Calcium alginate	Cu(II); Pb(II)	pH = 5	79 mg/g; 357 mg/g	Synergistic effect of surface complexation and ion exchange	[27]
Rice husk	As(V)	pH = 10	34 mg/g	Complexation of As ions with the nitrogen of -N=C- groups	[33]
Chitin	Pb(II); Cd(II)	pH = 6	7 mg/g; 6 mg/g	Complexation/chelation	[37]
Saw dust	Pb(II)	pH = 5	24 mg/g	Ion exchange between Pb(II) and amine group of anilinium ion	[62]
Saw dust	Mn(II)	pH = 10	58.824 mg/g	–	[63]
Saw dust	Cr(VI)	pH = 10	97%	Ion exchange between dichromate and chloride ion of polymer	[64]
Cross-linked chitosan	Cr(VI)	pH = 4.2	179 mg/g	Electrostatic attractions	[32]
Activated carbon from orange peels	Pb(II)	pH = 4	6.81 mg/g	–	[35]
Chitin	Cr(VI)	pH = 4.2	24 mg/g	Electrostatic adsorption coupled reduction	[36]
Sodium alginate	Cr(VI)	–	73 mg/g	Electrostatic interactions	[54]
Alginate-montmorillonite/ polyaniline composite	Cr(VI)	–	29.89 mg/g	–	[55]
Bee carcass waste/polyaniline/ polyethylene glycol	Cr(VI)	pH = 2	50.56%	–	[56]
Hydrolyzed pectin-grafted-polyaniline	Cu(II), Ni(II), Pb(II) and Cd(II)	pH = 5	90% (Pb(II))	Electrostatic interactions	[1]
Rice husk ash	Hg(II)	pH = 9	–	–	[38]
Saw dust	Cd(II)	pH = 6	430 mg/g	–	[57]
Ethyl cellulose	Cr(VI)	pH = 1	38 mg/g	Electrostatic attraction	[40]
Chitosan	Pb(II); Cd(II)	pH = 6; pH = 6	13 mg/g; 12 mg/g	Electrostatic attraction and complexation	[43]
Polyaniline-graft-chitosan beads	Cu(II)	pH = 5	100 mg/g	–	[44]
Starch-montmorillonite	Cr(VI)	pH = 2	208 mg/g	–	[102]
Saw dust	Hg(II)	pH < 4	–	Complex formation; chelation	[58]
Saw dust	Pb(II)	pH < 4	–	Complex formation; chelation	[59]
Saw dust/PEG	Cr(VI)	pH = 2	3 mg/g	–	[20]
Lignin		pH = 4	25 mg/g	Electrostatic attraction	[66]
Humic acid	Cr(VI)	pH = 5	150 mg/g	–	[29]
Humic acid	Hg(II)	pH = 4-7.5	671 mg/g	–	[69]
Rice husk	Pb(II); Cd(II)	-	200 mg/g; 106 mg/g	–	[72]
Jute fiber	Cr(VI)	pH = 3	63 mg/g	Electrostatic attractions	[74]
Kapok fiber	Cr(VI)	pH = 4.5	66 mg/g	Formation of strong chemical bonds between the adsorbate and adsorbent	[77]
Kapok fiber	Pb(II)	–	63.6 mg/g	–	[78]
Biochar of waste grape fruit endothelium	Cr(VI)	pH = 3	100%	High porosity and electrostatic interaction in C–Fe–PAN	[79]
Rice husk ash	Zn(II)	pH = 3	24 mg/g	–	[80]
Rice husk ash	Cu(II); Cd(II)	–	–	Anion exchange, chemical oxidation, chelation are possible mechanisms	[81]
Jute fiber	Cd(II); Cr(VI)	pH = 5	140 mg/g; 50 mg/g	Complexation; Electrostatic attraction and redox mechanism	[76]

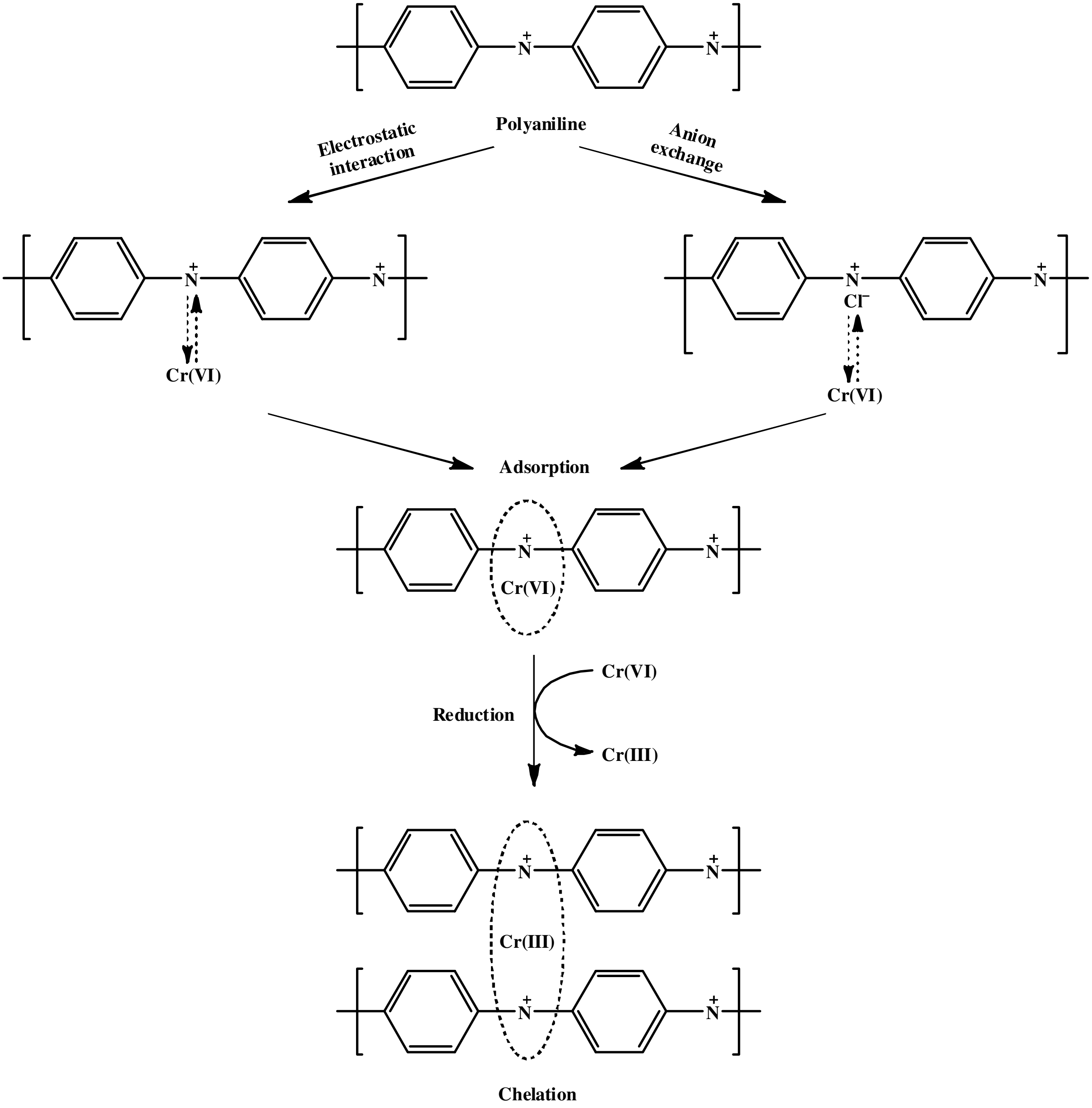

Fig. 1. Mechanisms involved in the removal of PTE from aqueous solution

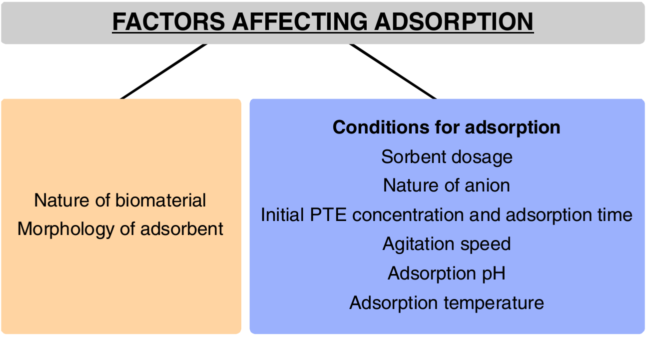

Fig. 2. Factors affecting the rate of biosorption of heavy metals by PANI-based biosorbents

Along with protons, there is the inflow of anions to maintain charge neutrality [33]. Since the redox state of PANI is regulated by an acidic dopant, such as HCl, its concentration affects the efficiency with which PTEs are removed [26]. With increase in HCl concentration, the efficiency of PTE removal increases steadily before reaching a plateau. The temperature for polymerization reaction influences the detoxification efficiency of Cr(VI) contaminated water. With increase in temperature from 0 to 25 ºC, the detoxification efficiency of Cr(VI)-contaminated water decreases. With further increase in temperature up to 60 ºC, polymerization decreases [26]. It indicates that the time for polymerization influences the degree of polymerization or oxidation of the monomer. After an optimal reaction time of 2 h, over-oxidation of PANI occurs that has a negative impact on detoxification [26].

Factors influencing adsorption: The different functional groups present on the sorbent (biomass and PANI) are responsible for the adsorption of PTEs. Many factors influence the adsorption capacity of PTEs, which mainly include the nature and morphology of the adsorbent and the conditions for adsorption, such as time and temperature, sorbent dosage, presence of other ions, *etc*.

Nature and morphology of the adsorbent: Polyaniline, in its different morphological forms, such as powder, film, nanoparticles (nanorods and nanofibers) and solid particles has been applied effectively for the removal of Cr(VI) ions [30]. The functional groups on the adsorbent are the sites where adsorption occurs and hence, they are primarily responsible for removing PTEs. It is suggested that more the functional groups on the adsorbent more is its efficiency. Therefore, the nature of the adsorbent and its morphology govern the adsorption of metal ions. For example, crosslinked-chitosan-grafted-PANI composite (CCGP) showed better adsorption, as compared to chitosan-grafted-PANI composite (CGP) [32]. The crosslinking agent, glutaraldehyde, in the CCGP composite, also contributes to the removal of Cr(VI) ions. Furthermore, the nature of the biomaterial used in the PANI-based biocomposites impacts the removal of PTEs from their aqueous solutions. For example, chitin has better efficiency for removal of PTEs than cellulose, whereas hemicellulose has better removal efficiency than chitin [34]. Biomass derived from plants is composed of cellulose, hemicellulose and lignin and their proportions vary depending on plant species. Hence, biomass with higher hemicellulose content would have better efficiency for removing PTEs than biomass with less hemicellulose content. Composites of PANI with activated carbon of different agricultural wastes have been tested to remove Pb(II) ions [35]. It was found that the efficiency of the PANI composite derived from activated carbon of orange peels was more than those of PANI and PANI composites with activated carbon derived from sources such as peach stones, banana peels, apricot stones and pomegranate peels. The higher efficiency is probably due to the uniform distribution of small particles of PANI on the surface of orange peels.

Conditions for adsorption: Generally, the removal efficiency of PTE increases with an increase in sorbent dosage up to a specific value, after which there is no significant change. However, the number of metal ions adsorbed per unit weight of the sorbent decreases [33,36]. The adsorption in natural water occurs in the presence of many anions, such as chloride, nitrate, bicarbonate, sulfate, *etc*. The presence of common anions decreased the selectivity for Cr(VI) removal by PANI-coated chitin (PCC) and sodium alginate PANI nanofibers due to competition between chromate ions and other anions for adsorption sites [5,36]. The authors also found that bicarbonate ions had a negative impact on the removal of Cr(VI) because it increased the solution pH from 4.2 to 7.9. Karthik & Meenakshi [37] indicated that the presence of Cu(II), Zn(II), Co(II) and Ni(II) ions decreased the adsorption of Pb(II) and Cd(II) by the PANI chitin composite. Generally, the adsorption of PTEs increases with an increase in time until equilibrium is reached. The two factors, initial PTE concentration and adsorption time are interdependent on each other. It was found that for a lower initial concentration of Cr(VI) ions, the time required to attain adsorption equilibrium in CGP composite and CCGP composite was less. In contrast, for higher Cr(VI) concentration, the time required was more [32]. It is also reported that the agitation speed affects the rate of adsorption. An increase in the speed of the magnetic stirring (up to 400 rpm), increased the removal of Hg(II) ions by PANI-rice husk ash composite [38]. Higher agitation speed increased repulsive forces on the sorptive sites of the sorbent and adsorption decreased. The adsorptive capacities of Cu(II) and Cd(II) on PANI-saw dust composite increased from 74 mg/g to 87 mg/g and 70 mg/g to 81 mg/g, respectively, when the temperature was raised from 293 K to 333 K [9]. The increase in adsorption capacity with rise in temperature suggests that adsorption of PTEs is an endothermic process [39]. In contrast, based on the values of ΔG^o, ΔH^o and ΔS^o, adsorption of Cr(VI) on PANI coated chitin was deemed a spontaneous and exothermic process [36]. Amongst all the other factors, solution pH is perhaps the most crucial factor influencing adsorption. The pH influences the surface charge of the adsorbent, ionization, speciation of the adsorbate and the solubility of metal ions in solution [35]. Most of the studies reported that acidic pH led to maximum metal adsorption, whereas few studies showed that maximum adsorption was achieved at neutral pH [30]. Electrostatic interactions influence pH, wherein the carboxylate, amino and hydroxyl groups exist in the protonated form at lower pH. The Cr(VI) removal is maximum for both CGP and CCGP at pH 2, since the $-NH_2$, -NH- and =NH groups in the composites remain protonated and assist in the removal of $HCrO_4^-$ ions through electrostatic attraction [32]. However, for As(V), maximum adsorption occurred at pH 10 [33]. Adsorption of arsenic was due to the complexation between As(V) and nitrogen atoms in the -N=C- groups. It is reported that PANI-ethyl cellulose composite could remove 100% of Cr(VI) ions at pH 1, whereas at pH 11, only 40% of Cr(VI) ions could be removed [40].

Synthesis of PANI-based biocomposites: Different PANI-based biosorbents have been prepared and tested for their ability to remove metal contaminants. The biomaterials are of both animal and plant origin. In some cases, biochars or activated carbon made from these sources have been used. These compounds contain functional groups that can participate in the metal-binding process. There are many studies on the synthesis of PANI-based biocomposites, but only few of them have been tested to remove metals. The advantages and limitations of these biomass components and are discussed below:

Chitin and chitosan: Chitin is a long-chain polysaccharide consisting of *N*-acetyl glucosamine residues. Chitin is obtained from the exoskeletal waste of crustaceans, such as lobsters, crabs and shrimps. About 1-100 Gt of chitin is generated annually from seafood processing [41]. Chitin co-exists with calcium carbonate and proteins and chemical processes are required to obtain chitin. Chitosan is obtained by partial deacetylation (above 60%) of chitin. Adsorption increases with increase in the degree of deacetylation, due to increase in the number of amino groups and changes in crystallinity. Hence, adsorption capacity of chitosan is more than that of chitin [42]. Karthik & Meenakshi [32,36], in a series of studies, demonstrated the effectiveness of PANI/chitin and PANI/chitosan in the removal of Cr(VI). In both cases, after the sorption of Cr(VI) ions onto the polymer, Cr(VI) changes to the non-toxic Cr(III) species. This is attributed to the amine and imine groups present in PANI. These composites have also been tested for removal of Pb(II) and Cd(II) ions from their aqueous solutions and it follows a pseudo-second-order kinetic reaction [37,43]. FTIR spectral analysis show that the –OH and $-NH_2$ functionalities of the composites interact with Pb(II) and Cd(II), which causes their removal. A pH of 6, is optimal for the removal of Pb(II) and Cd(II), wherein electrostatic attractions between positively charged ions and negatively charged adsorbent surface and complexation are responsible for sorption. At lower pH, ion exchange is involved, wherein the hydrogen ions of protonated amino groups are exchanged with the positively charged metal ions. Polyaniline-graft-chitosan beads showed the maximum adsor-ption of 100 mg/g for Cu(II) ions at 45 ºC at pH 5 [44]. The desorption of Cu(II) ions of up to 97.1% could be achieved from the adsorbent using 0.5 M HCl. The use of chitin for the removal of metals has some limitations since it is insoluble, has low strength and problems with separation and mass loss after sorption reactions [45]. The advantages of using chitosan-based composites are that they have better adsorption and are stable in an acidic medium [46]. Chitin, on the other hand, undergoes hydrolysis in an acidic medium. The drawbacks are that chitosan is expensive and requires multiple steps to obtain [47]. Moreover, low mechanical strength, poor stability, low porosity, high crystallinity and resistance to mass transfer of chitosan make chemical and structural modifications necessary for chitosan to be used as an adsorbent [48]. The PANI-composite with functionally modified chitosan is expected to enhance the adsorption capacity further. The use of chitin/polyaniline composite is limited to a specific range.

Starch, cellulose, cellulose derivatives, sodium alginate, dextrin and pectin: Starch, cellulose, alginic acid, dextrin and pectin are abundant, biodegradable and eco-friendly compounds. The hydroxyl functional groups in these complexes do not possess high metal adsorption capabilities and hence they are modified with other functional groups, such as carboxyl, amide, amine, *etc.* [49]. Blending with other compounds, possessing the required functional groups or their composites provide the required adsorption sites. For example, starch-montmorillonite-PANI composite (St-Mt/PANI) synthesized by *in situ* polymerization of aniline on the starch-montmorillonite composite surface could remove 208 mg/g of Cr(VI) from solution [50]. Starch can be chemically modified to introduce chelating groups, which are expected to improve the overall properties and adsorption capacity. Starch contains amylose and amylopectin, which have different structures and molecular weights depending on the plant species [51]. Additionally, the morphology of starch is responsible for its interactions with water and other components, which affects the properties in the polyaniline composite.

Cellulose and its derivatives have poor adsorption efficiencies and removal rates of PTEs [6]. In spite of having many hydroxyl functional groups, high crystallinity and strong intermolecular hydrogen bondings between the hydroxyl groups make the hydroxyl groups less accessible to metal ions [42]. However, their composites with amine-containing polymers like PANI show higher adsorption of PTEs [6]. PANI-coated ethyl cellulose (PANI/EC) is very effective in the removal of Cr(VI) from aqueous solution at acidic pH [40]. Introduction of PANI increases the hydrophilicity of the composite and facilitates reduction of Cr(VI) to Cr(III). The Cr(III) ions in the solution are adsorbed to the surface of PANI/EC. Similarly, PANI/cellulose fiber composite shows synergistic effects between PANI and cellulose in detoxifying and removing the toxic Cr ions from the solution [26]. Li *et al.* [8] synthesized PANI/cellulose acetate composite membrane (PANI-PA/CA) doped with phytic acid, which showed excellent adsorption of Hg(II) and Cr(VI) ions. The optimal pH values for removal of Hg(II) and Cr(VI) were 5 and 2, respectively. This is because the removal of Hg(II) ions involve complexation between mercury and nitrogen-containing functional groups. In contrast, the removal of Cr(VI) is a result of electrostatic attractions and redox reactions. Although cellulose is very abundant and has shown promising results for detoxification of Cr(VI) ions, the effect seems restricted to very few PTEs. A nanocomposite of polyaniline-bacterial extracellular polysaccharide, synthesized by *in situ* polymerization of aniline using ammonium peroxydisulfate oxidant could remove 97.3% of Cr(VI) from aqueous solution [52]. Recently, prussian blue/polyaniline@ cotton fibers, wherein polyaniline was doped with phytic acid, were tested for the removal of Cu(II)ions under weakly acidic conditions (pH 5) and the removal efficiency was found to be 93.4% with adsorption capacity of 31.93 mg/g [53]. Chemisorption was reported to be responsible for adsorption of the Cu(II) ions, which involved sharing/exchange of electrons between adsorbate and adsorbent.

Recently, a nanocomposite prepared using PANI and dextrin could successfully remove 52%, 48% and 26% of Cu(II), Pb(II) and Cd(II) ions, respectively [28]. The active protonated sites on the PANI-dextrin composite are the sites where adsorption occurs.

Sodium alginate is a natural, biodegradable and non-toxic polysaccharide possessing carboxyl and hydroxyl functional groups, which are beneficial for removing PTEs. However, it has low mechanical stability, which prevents it from being used as an adsorbent. Sodium alginate-PANI nanofibrous composite material could successfully adsorb and remove 73 mg/g of Cr(VI) at 303 K [54]. Alginate-montmorillonite/polyaniline composite, showed adsorption capacity of 29.89 mg/g for Cr(VI) ions in an endothermic process [55]. In another study, a composite of PANI with calcium alginate (PANI/CA) was used for testing the removal of Pb(II) and Cu(II) [27]. The synergy between the two components enables its use over a wide pH range (3-7), wherein adsorption of the composite is higher than those of individual components in the above pH range. The adsorption efficiency increased with pH, which is attributed to the ionization states in carboxylate, hydroxyl and amino functional groups.

A composite of bee carcass waste and polyaniline with polyethylene glycol additive showed good Cr(VI) removal of 50.56% at pH = 2, as against bee carcass and waste that showed 23.52% removal of Cr(VI) [56]. Pectin is a complex heteropolysaccharide present in the lamellae and cell walls of terrestrial plants. It mainly consists of esterified D-glucuronic acid molecules linked by α(1-4) linkages. Nanogel composite of hydrolyzed pectin-grafted-polyaniline was synthesized by oxidation polymerization and tested for the removal of Cu(II), Ni(II), Pb(II) and Cd(II), wherein the composite showed selectivity for Pb(II) ions and could remove up to 90% of Pb(II) ions at pH 5 [1].

Sawdust: Sawdust is a waste product of timber or wood industry and mainly converted to briquettes and used as fuel. A more ecologically viable option is to use sawdust as a biosorbent. Sawdust contains cellulose, hemicellulose and lignin and their proportions in hardwood or softwood vary. Sawdust coated with PANI was tested for removing a variety of metal ions, such as Cu(II), Cd(II), Hg(II), Pb(II), Cr(VI) and Ag(I) from aqueous solutions [9,57-61]. However, in all these studies, whether sawdust is derived from hardwood or softwood is not indicated. It is known that softwood contains a higher percentage of hemicellulose compared to hardwood. Because hemicellulose shows better adsorption of PTEs, it can be anticipated that sawdust from softwood would adsorb more PTEs. This would supplement PANI with more functional groups for the adsorption of PTEs. Positron annihilation measurements helped understand the adsorption mechanism of Pb(II) on PANI nanocomposite with sawdust [62]. The nitrogen atoms between the benzenoid and quinoid rings were sites for Pb(II) adsorption. The concentration of voids increased with an increase in sawdust from 3% to 5%, after which it decreased gradually up to 10%. The composite with 5% sawdust showed the highest removal efficiency of Pb(II) at pH 5. Polyaniline-sawdust nanocomposite was tested for the removal of Mn(II) ions at pH 10 and the maximum adsorption achieved was 58.824 mg/g [63]. Sawdust coated with polyaniline could remove Cr(VI) ions with 97% efficiency from solution at 20 ºC and pH 2 [64]. Increase in temperature was found to decrease the removal efficiency. Composite of PANI with polyethylene glycol (PEG) and sawdust could effectively remove Cr(VI) [20]. The introduction of PEG into PANI expected to change the molar mass, surface morphology, electrochemical properties and consequently the uptake of Cr(VI). This shows that ternary composites are promising adsorbents for removing PTEs, wherein the components and their proportions can be optimized for better results.

Lignin: Lignin is an abundantly produced sustainable and natural polymer but it is either burned or land-filled. Lignin is made of phenyl propane units, such as coumaryl, sinapyl and coniferal alcohols, occurring in different proportions in different types of wood (angiosperm and gymnosperms) [65]. Lignin is commonly present along with cellulose and hemicellulose. Owing to their different chemical compositions, lignin shows variations in adsorption of metal ions although it has low metal adsorption capacity. Lignin has two main functional groups, carboxyl and phenol, of which phenol groups show better affinity to metal ions [42]. Deprotonation of the functional sites could be the mechanism of adsorption of metal ions by lignin. Further, the introduction of oxygen/nitrogen/sulfur-containing functional groups highly increases the adsorption of PTEs to lignin. Seo *et al*. [66] studied the adsorption of Cr(VI) on lignin-PANI composite. The authors reported that despite the low removal efficiency of Cr(VI) by lignin, the lignin-PANI composite could remove Cr(VI) due to different reduction and adsorption reactions. The amine groups in PANI are responsible for reduction of Cr(VI) to Cr(III), whereas lignin and PANI are responsible for adsorption of Cr(III) ions. A hierarchical polyaniline-enzymatic hydrolysis lignin (PANI-EHL) composite showed strong reactive sorption of silver ions, wherein, EHL played a vital role in the chelation of silver ions [67].

Humic acid: Humic acid is an organic substance produced by microbial decomposition of animal and plant remains. Humic acids possess many functional groups, such as carboxylic, enolic, alcoholic and phenolic groups, which bind metal ions. A composite prepared by polymerizing aniline with humic acid, showed an adsorption capacity of 150 mg/g of Cr(VI) at pH 5 [29]. In addition, humic acid prevents the aggregation of PANI during the synthesis and modifies the morphology and adsorption capacity in the composite [68]. A polyaniline-sorbent could successfully adsorb 671 mg/g of Hg(II) from aqueous solution in a wide pH range of 4.0-7.5 in a batch humic acid process [69]. According to Li *et al*. [68], ionic strength and competing anions had an effect of the adsorption of Hg(II) and Cr(VI) ions.

Rice husk: The outer covering of the rice grain is called rice husk and it is a waste material obtained from rice milling. It is made up of cellulose (35%), hemicellulose (25%), lignin (20%), silica (17%) and protein [70]. The global production of rice is 400-550 million metric tons, about 10% of which is rice husk [71]. Hence, it is potentially a cheap and readily available material that can be used to remove PTEs. Composites of rice husk with PANI were prepared by two different methods to study its effect on the adsorption of for Pb(II) and Cd(II) ions [72]. In the first method, aniline was oxidatively polymerized onto rice husk in the presence of ammonium persulfate in acidic medium. In second method, the rice husk was soaked in formic acid solution of PANI. The composite prepared by soaking the rice husk in PANI indicated better removal of Pb(II) ions than the composite prepared by oxidative polymerization of aniline. This effect was, however, more negligible for Cd(II) ions. This is an indication that the method of preparation of the composite influences the adsorption capacity.

Jute fiber: Jute is a lignocellulosic fiber, widely grown in Asia; its mechanical properties are comparable to glass fibers [73]. Annually, about 3.6 Mt of jute fibers is produced. This low-cost, renewable and biodegradable material can be made into composites with PANI and used to remove PTEs from wastewaters. The surface of jute fiber was coated with short-chain PANI segments in the presence of the chain-terminating agent 1,4-phenylenediamine. The composite could efficiently remove Cr(VI) ions [74]. Cr(VI) ions could be removed at pH 3 through electrostatic interactions between $HCrO_4^-$ and NH_3^+ of polyaniline and the maximum adsorption was 4.66 mg/g [75]. Huang *et al*. [76] used jute fibers to adsorb aniline from water and then polymerize the adsorbed aniline. The PANI/jute composite was then applied for removing PTEs from water.

Kapok fiber: Kapok fiber has a hollow tube-like structure consisting of cellulose, xylan and lignin. A composite prepared by modifying the kapok fiber with PANI could control the growth orientation of PANI and efficiently adsorb Cr(VI) [77]. Furthermore, the presence of Cu(II) and Ni(II) ions in the solution did not affect the removal rate of Cr(VI) ions. Recently, a polyaniline-kapok fiber nanocomposite was synthesized by *in situ* polymerization of aniline in acidic conditions using ammonium persulfate oxidant [78]. This nanocomposite showed adsorption capacity of 63.6 mg/g for Pb(II) ions and the process was endothermic and spontaneous.

Biochar, activated carbon and ash: Biochar of grapefruit endothelium, used to prepare a composite with iron and PANI, was tested to remove Cr(VI) [79]. The removal of Cr(VI) was nearly 100%, which is due to the high porosity of adsorbent and synergistic effects of iron on PANI. Moreover, Cr(VI) could be reduced to the less toxic Cr(III) species when Fe(II) was oxidized to Fe(III). In an interesting study, PANI composites with activated carbon derived from different agricultural waste product, such as orange peels, banana peels, pomegranate peels, apricot stones and peach stones, were prepared in the presence of phosphoric acid [35]. They were tested for the removal of Pb(II). The PANI composite with orange peels show the best adsorption capacity due to the uniform distribution of PANI on its surface.

Ghorbani *et al.* [38,80] determined the ability of rice husk ash coated with PANI to remove Zn(II) and Hg(II) from aqueous solutions. The monolayer adsorption process had a capacity to adsorb 24.3 mg/g Zn(II) [80]. The adsorption efficiency for removal of Hg(II) ions was 95% at pH 9, compared to 72% and 78% for PANI and rice husk ash, respectively [38]. Similarly, a study was conducted to investigate the efficiency of rice husk ash coated with PANI to remove PTEs and anions [81]. It was found that the rice husk ash in the biocomposites has an important role in the removal of PTEs, but was not effective in increasing the removal of anions.

Highly potential but poorly explored avenues for remediation: Microbes offer a low cost, high performance and sustainable potential system for removal of heavy metals. Bacteria, cyanobacteria, lichens, micro- and macro-algae, micro- and macro-fungi and unicellular fungi have been explored for removal and recovery of heavy metals. Live or dead cells of wild or engineered microbes can be applied as free or immobilized biomass to treat the heavy metal polluted aqueous wastes. The first report on microbial biosorption of heavy metals dates back to 1980, which opened new areas for treatment of polluted water [82]. Removal of heavy metals by bacteria involve binding of metal ions with functional groups on cell surface, interaction with exopolysaccharide secretions, intracellular impounding of metal ions by importer proteins, metallochapherons and metallothionines. Electrostatic interactions, ion displacement, interaction of metal ion with amines, hydroxyl, phosphonate, carboxyl groups in bacterial cell wall play a role in the removal of arsenic, cadmium, lead, mercury from aqueous solutions [83]. Species of *Bacillus*, *Pseudomonas*, *Azotobacter*, *Arthrobacter*, *Alcaligens*, *Rhodococcus*, *Strenotrophomonas*, *Corynebacterium*, *Desulfovibrio* are some of known bacteria tested for the removal of heavy metals. Predominantly studied bacterial extracellular polymers and their selectivity for specific metal ions offer non-toxic, renewable and biodegradable biomaterials for removal of trace elements from water [84]. Recently, the extracellular polysaccharide, succinoglycan and its production by *Agrobacterium*, *Sinorhizobium* and other soil bacteria have gained importance. Many fungi are reported to have ability to remove metals from contaminated environment. Biosorption potential of various macrofungi (*Lepista*, *Lepiota*, *Armillaria*, *Boletus*, *Amanita*, *Ganoderma*, *Agaricus* and *Termetes*) [85] filamentous fungi (*Aspergillus*, *Mucor*, *Penicillium*, *Fusarium*, *Trichoderma* and *Cunnighummella*) and unicellular yeasts (*Candida* and *Saccharomyces*) [86-88] have also been reported. The role of functional groups, components of fungal cell walls and selective binding of metal ions were studied using highly sensitive and selective instruments like SEM, X-ray spectroscopy, NMR spectroscopy and X-ray photoelectron spectroscopy by various researchers [89]. Cell wall polymers may show selectivity for binding of specific metal ions. *Chlorella*, *Chondrus*, *Glocerallia*, *Ascophyllan* mixtures were found to be better biosorbents in multimetallic system, which offered a good system for treatment of effluents or the real solutions [90]. Algal cell wall contains alginic acid, fucoidan, cellulose, pectin, agar, carrageenan, xylan, mannan, glucan and chitin that possess various functional groups. Absence of nutrient media, no stringent efforts to maintain live pure cultures, no toxicity on metal accumulation in cell, high sorption desorption efficiency, easy recovery and reuse of biomass are some of the practical advantages of employing immobilized microbial biomass. Basic aspects of chemical engineering like better mechanical strength and higher porosity can be offered by a variety of synthetic polymers as well as natural polymers. Filaments of *Penicillium chrysogenum* were crosslinked with HCHO and heated to obtain reduced particle size of 0.3-0.75 mm, which showed high efficiency of removal of uranium of about 10% [91]. Smart materials prepared by precipitation of magnetic nanoparticles on biomass showed improved adsorption and removal of various xenobiotics. Biomass based composites prepared by co-immobilization of *B. cereus* with activated carbon into alginate beads and immobilization of yeast cells (*Saccharomyces cerevisiae*) were found to be better biosorbents [92]. Silica nanosols comprising of silicate matrix and algal polysaccharides were widely reported for biosorption of heavy metal ions [93,94]. Chitosan based immobilized algal sp. for the removal of phosphates and nitrates [95], polyamide-chitosan blended nanofibers [96], magnetic nanocomposites (MCNCs), such as magnetite (Fe_3O_4)–dextran, Fe_3O_4–chitosan and Fe_3O_4–alginate, have been demonstrated as new remedies in biosorption of metal ions [97]. Cell surface of saccharomyces cells were derivatized by anchoring of metal specific peptides and proteins that were capable of binding metal ions [98].

In 1990, the first microbial biosorbent was commercialized and since then many have been introduced. Many examples, such as BIO-FIX, Algasorb, B V Sorbex, AMT-Bioclaim^{TM}, Tsezos, *etc.* have been prepared from bacteria, algae, sphagnum, peat moss and fungi. These biotechnological tools have been found useful for the treatment of high-volume low-concentration complex effluents for recovery of heavy metals.

Millions of tons of microbial biomass are generated by food industry and fermentation industry. The wasted biomass can be channelized and used for metal removal. However, microbial biomass showed problem in desorption, as strong treatments with acid or alkali solutions affect cell surface structure and properties. Therefore, biosorption process has not accomplished the expected success. Chelating chemicals like EDTA, carbonates and bicarbonates have been used as desorption agents, however, the desorption capacity reduces after a couple of adsorption desorption cycles [99]. In recent decades, polymeric adsorbents have emerged as potential alternatives to traditional adsorbents in terms of their vast surface area, adjustable surface chemistry, perfect mechanical rigidity, pore size distribution and feasible regeneration under mild conditions. Commonly, polymeric materials can effectively adsorb many pollutants. PANI coated microbial biomass can provide a matrix having functional groups. Intra-technological approaches can be combined with biosorption to design environment friendly systems with better efficiency and attain success at industrial scale up [100]. The disposal of exhausted biomass is a principally major issue that remains unanswered. Landfill, incineration, electrowinning of biomass for recovery of sorbed metals is suggested. Polyaniline coating offers electrical conductivity, low cost and environmental stability. Additionally, biomass based may demonstrate selectivity for binding specific metal ions. Preferential binding of gold and silver ions over cadmium, chromium, nickel, zinc was observed in *Cladosporium* strains [89]. Taking into consideration all the above factors, it would be interesting to study the combination of microbial waste biomass with polyaniline to prepare composites, which could solve the mentioned shortcomings. This would not only provide an economically viable solution of remediation, but would also make use of waste biomass and tackle the problem of its disposal. The focus on the use of waste microbial biomass-polyaniline has been limited. In one study, mats of cellulose derived from *Acetobacter xylinum* were coated with PANI and this PANI/bacterial cellulose mat was tested for the removal of Cr(VI) ions from water [101]. This method was more practical, since removal of Cr(VI) ions was at neutral pH, as compared to other methods which were conducted at acidic pH. The steps involved in the removal of chromium ions were reported to be adsorption of Cr(VI) ions on the adsorbent surface, reduction of Cr(VI) to Cr(III) and the desorption of Cr(III) from the adsorbent surface. This study demonstrates the potential use of this method.

Advantages of PANI-based adsorbents in the removal of heavy metal ions from wastewaters: The advantages as well as the limitations of PANI-based biosorbents for the removal of PTEs are summarized in Fig. 3. The advantages of PANI are PANI, with its abundant amine and imine functional groups, is economical and easy to synthesize. In addition, it has high adsorption capacity and good selectivity and also possesses environmental stability. The use of biopolymers is a sustainable, economically and ecologically viable, green synthesis method of PANI-based biocomposites. Additionally, biopolymers contain many functional groups, which also play a role in PTE removal. The components of the biocomposites, PANI and the biopolymer show synergistic effects in the removal of PTEs [26,27]. In addition to the removal of PTEs, these biocomposites are also helpful in removing other organic pollutants, dyes, anions, colour, *etc.* from wastewaters [81,102,103]. They can be recycled and reused multiple times. After the adsorption of PTEs, precious or useful metal ions can also be recovered by the sequential desorption process. After desorption of PTEs, these biosorbents can be reused as supercapacitors, humidity sensors, *etc.*

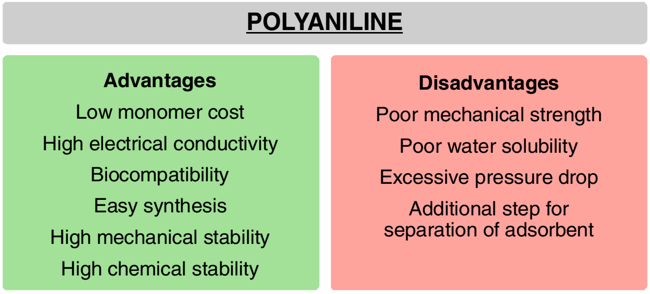

Fig. 3. Advantages and disadvantages of using PANI for removal of heavy metals from wastewaters

Scope of future research and assessment: PANI-based biosorbents, due to their eco-friendliness, low costs and sustainability, have many advantages over other adsorbents. However, research in this field has not progressed as expected. There remains further scope to develop the adsorption capacity in PANI-based biosorbents that are proposed as follows: binary composites of PANI with biomass have been extensively researched. However, there are very few examples of ternary composites of PANI. Therefore, the properties and advantages of the three components can be further investigated. Biochar and activated carbon have porous structures and large surface areas, which are very suitable for removing PTEs. They can be prepared from almost any type of biomass. There are numerous references on the synthesis of biochar and activated carbon from a wide range of biomass sources. However, comparatively very few of their composites with PANI have been tested for their heavy metal removal capabilities. Composites of biochar or activated carbon with PANI have a large potential for removing PTEs. Most studies have been undertaken on pure metal ion solutions and not on real wastewater systems containing a complex mix of contaminants. PANI-based adsorbents can simultaneously remove different contaminants, such as dyes, organic compounds, anions, *etc.* [81]. However, there are few comprehensive reports on the removal of multiple contaminants at the same time. pH conditions for the removal of PTEs at the site could be different from the optimal pH conditions required to remove the metal ions. So, the adsorbents must be tailored to be efficient for the removal of PTEs under actual conditions. Morphological features and hierarchical structures of the adsorbent influence adsorption. For example, calcium alginate coated with PANI having milli/nano-hierarchical structure has a higher efficiency for removal of Cu(II) and Pb(II) than the individual components of the biocomposites [27]. However, the removal efficiency increased when the micrometer-sized calcium alginate beads were used instead of millimeter-sized ones. Hence, more studies can be conducted to understand the effects of morphology on the adsorption of PTEs. More the surface area and porosity of the adsorbent, more is its adsorption capacity. Also, chemical pretreatment of biomass is known to increase the porosity and surface area of biomass [24]. Hence, studies should be focused on optimization of chemical treatment of biomass to increase its porosity as well as maintaining its other properties. Further coating with PANI would provide better bioadsorbents. Most studies have focused only on the removal of Cr(VI). However, there are other PTEs and effective remediation needs are sought. Investigations can be conducted to increase adsorption capacities by functionalizing the biocomposites. This is particularly important since removing different metal ions involve different mechanisms and different pH conditions. The adsorption capacity of PTEs depend on the method the PANI-based biosorbent is prepared. So far, this aspect has been overlooked and more studies on process optimization are required. Activated carbon has been obtained from different agricultural wastes such as bagasse, tea waste, coconut shell, peanut hull, *etc.* However, PANI-composites of only a few have been prepared and tested for the removal of PTEs. Biosorbents are likely to release certain substances, which could further lead to complicated chain reactions and finally have a negative impact on the environment [104]. Studies should be conducted to assess the safety of such biosorbents.

There should be more focus on reuse, recycle and disposal of biomass after its use. Improper disposal of biosorbents would not solve the cause of utilization of waste bioresources for useful purposes.

Conclusion

Polyaniline (PANI)-based biocomposites have tremendous potential and advantages for the removal of potentially toxic elements (PTEs). Composites of PANI with different biopolymers and biowaste materials like cellulose, starch, chitin, chitosan, sawdust, *etc.* have been prepared and show promising applications for the removal of PTEs. However, there is tremendous scope for research on PANI-based biosorbents, particularly using waste microbial biomass. Wastewater treatment and biowaste utilisation both benefit from the usage of PANI and biowastes, as the former serves as a cost-effective adsorbent while the latter offers a sustainable solution.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. A. Alipour, M. Lakouraj, V. Hasantabar, H. Tashakkorian and M. Mohseni, *Carbohydr. Polym. Technol. Appl.*, **2**, 100151 (2021); https://doi.org/10.1016/j.carpta.2021.100151
2. M. Beygisangchin, S.A. Rashid, S. Shafie, A.R. Sadrolhosseini and H.N. Lim, *Polymers*, **13**, 2003 (2021); https://doi.org/10.3390/polym13122003
3. H.J. Kim, S. Im, J.C. Kim, W.G. Hong, K. Shin, H.Y. Jeong and Y.J. Hong, *ACS Sustain. Chem. Eng.*, **5**, 6654 (2017); https://doi.org/10.1021/acssuschemeng.7b00898
4. J. Ding, Y. Pan, L. Li, H. Liu, Q. Zhang, G. Gao and B. Pan, *Chem. Eng. J.*, **384**, 123232 (2020); https://doi.org/10.1016/j.cej.2019.123232
5. C. Cui, X. Sun, C. Zhou, Y. Liu, H. Xiong, Y. Li and J. Han, *Colloids Surf. A Physicochem. Eng. Asp.*, **616**, 126336 (2021); https://doi.org/10.1016/j.colsurfa.2021.126336
6. E. Eskandari, M. Kosari, M.H. Davood Abadi Farahani, N.D. Khiavi, M. Saeedikhani, R. Katal and M. Zarinejad, *Sep. Purif. Technol.*, **231**, 115901 (2020); https://doi.org/10.1016/j.seppur.2019.115901
7. H. Hajjaoui, A. Soufi, W. Boumya, M. Abdennouri and N. Barka, *J. Compos. Sci.*, **5**, 233 (2021); https://doi.org/10.3390/jcs5090233
8. R. Li, L. Liu and F. Yang, *J. Hazard. Mater.*, **280**, 20 (2014); https://doi.org/10.1016/j.jhazmat.2014.07.052
9. D. Liu, D. Sun and Y. Li, *Sep. Sci. Technol.*, **46**, 321 (2010); https://doi.org/10.1080/01496395.2010.504201
10. M. Bhaumik, V.K. Gupta and A. Maity, *J. Environ. Chem. Eng.*, **6**, 2514 (2018); https://doi.org/10.1016/j.jece.2018.03.047
11. H. Soltani, A. Belmokhtar, F.Z. Zeggai, A. Benyoucef, S. Bousalem and K. Bachari, *J. Inorg. Organomet. Polym. Mater.*, **29**, 841 (2019); https://doi.org/10.1007/s10904-018-01058-z
12. S.A. Vali, M. Baghdadi and M.A. Abdoli, *J. Environ. Chem. Eng.*, **6**, 6612 (2018); https://doi.org/10.1016/j.jece.2018.09.042
13. S. Kamarudin, Z.A.A. Rahman, M.S.A. Rani, M. Mohammad, N. Mohammed and Z. Yaakob, *Polym. Bull.*, **79**, 1699 (2022); https://doi.org/10.1007/s00289-021-03585-1
14. Y. Lai, F. Wang, Y. Zhang, P. Ou, P. Wu, Q. Fang, Z. Chen and S. Li, *Chem. Eng. J.*, **378**, 122069 (2019); https://doi.org/10.1016/j.cej.2019.122069
15. X. Du, D. Zhang, X. Ma, W. Qiao, Z. Wang, X. Hao and G. Guan, *Electrochim. Acta*, **282**, 384 (2018); https://doi.org/10.1016/j.electacta.2018.06.025
16. M. Dinari and S. Neamati, *Colloids Surf. A Physicochem. Eng. Asp.*, **589**, 124438 (2020); https://doi.org/10.1016/j.colsurfa.2020.124438
17. M. Ramezanzadeh, M. Asghari, B. Ramezanzadeh and G. Bahlakeh, *Chem. Eng. J.*, **337**, 385 (2018); https://doi.org/10.1016/j.cej.2017.12.102
18. R. Kumar, M.A. Barakat, M.A. Taleb and M.K. Seliem, *J. Clean. Prod.*, **268**, 122290 (2020); https://doi.org/10.1016/j.jclepro.2020.122290
19. H. Hosseini and S.M. Mousavi, *J. Clean. Prod.*, **278**, 123817 (2021); https://doi.org/10.1016/j.jclepro.2020.123817
20. M.R. Samani and D. Toghraie, *J. Environ. Health Sci. Eng.*, **17**, 53 (2019); https://doi.org/10.1007/s40201-018-00325-y
21. E.A. Abdel-Galil, A.S. Tourky and A.E. Kasem, *Appl. Radiat. Isot.*, **156**, 109009 (2020); https://doi.org/10.1016/j.apradiso.2019.109009
22. A. Samadi, M. Xie, J. Li, H. Shon, C. Zheng and S. Zhao, *Chem. Eng. J.*, **418**, 129425 (2021); https://doi.org/10.1016/j.cej.2021.129425
23. Y. Wei, Y. Yan, Y. Zou, M. Shi, Q. Deng, N. Zhao, J. Wang, C. You, R. Yang and Y. Xu, *Electrochim. Acta*, **310**, 45 (2019); https://doi.org/10.1016/j.electacta.2019.04.067
24. D.T.C. Nguyen, T.V. Tran, P.S. Kumar, A.T.M. Din, A.A. Jalil and D.N. Vo, *Environ. Chem. Lett.*, **20**, 1421 (2022); https://doi.org/10.1007/s10311-021-01377-7
25. H. Yakisik and U. Özveren, *J. Turkish Chem. Soc. Sec. Chem.*, **8**, 289 (2021); https://doi.org/10.18596/jotcsa.635073
26. X. Liu, W. Zhou, X. Qian, J. Shen and X. An, *Carbohydr. Polym.*, **92**, 659 (2013); https://doi.org/10.1016/j.carbpol.2012.09.083
27. N. Jiang, Y. Xu, Y. Dai, W. Luo and L. Dai, *J. Hazard. Mater.*, **215-216**, 17 (2012); https://doi.org/10.1016/j.jhazmat.2012.02.026
28. E.N. Zare, A. Motahari and M. Sillanpää, *Environ. Res.*, **162**, 173 (2018); https://doi.org/10.1016/j.envres.2017.12.025
29. Y. Jiang, Z. Liu, G. Zeng, Y. Liu, B. Shao, Z. Li, Y. Liu, W. Zhang and Q. He, *Environ. Sci. Pollut. Res. Int.*, **25**, 6158 (2018); https://doi.org/10.1007/s11356-017-1188-3
30. S. Senguttuvan, P. Senthilkumar, V. Janaki and S. Kamala-Kannan, *Chemosphere*, **267**, 129201 (2021); https://doi.org/10.1016/j.chemosphere.2020.129201
31. A. Nasar and F. Mashkoor, *Environ. Sci. Pollut. Res. Int.*, **26**, 5333 (2019); https://doi.org/10.1007/s11356-018-3990-y

32. R. Karthik and S. Meenakshi, *Int. J. Biol. Macromol.*, **67**, 210 (2014); https://doi.org/10.1016/j.ijbiomac.2014.03.035
33. M.S. Lashkenari, B. Davodi and H. Eisazadeh, *Korean J. Chem. Eng.*, **28**, 1532 (2011); https://doi.org/10.1007/s11814-011-0014-8
34. Y.C. Lin and S.L. Wang, *Chem. Eng. J.*, **181-182**, 479 (2012); https://doi.org/10.1016/j.cej.2011.12.005
35. S.G. Mohammad, D.E. Abulyazied and S.M. Ahmed, *Desalination Water Treat.*, **170**, 199 (2019); https://doi.org/10.5004/dwt.2019.24694
36. R. Karthik and S. Meenakshi, *Int. J. Biol. Macromol.*, **72**, 235 (2015a); https://doi.org/10.1016/j.ijbiomac.2014.08.022
37. R. Karthik and S. Meenakshi, *Sep. Sci. Technol.*, **51**, 733 (2016); https://doi.org/10.1080/01496395.2015.1130060
38. M. Ghorbani, M.S. Lashkenari and H. Eisazadeh, *Synth. Met.*, **161**, 1430 (2011); https://doi.org/10.1016/j.synthmet.2011.05.016
39. P. Baruah and D. Mahanta, *Bull. Mater. Sci.*, **39**, 875 (2016); https://doi.org/10.1007/s12034-016-1204-0
40. B. Qiu, C. Xu, D. Sun, H. Yi, J. Guo, X. Zhang, H. Qu, M. Guerrero, X. Wang, N. Noel, Z. Luo, Z. Guo and S. Wei, *ACS Sustain. Chem. Eng.*, **2**, 2070 (2014); https://doi.org/10.1021/sc5003209
41. M. Yadav, P. Goswami, K. Paritosh, M. Kumar, N. Pareek and V. Vivekanand, *Bioresour. Bioprocess.*, **6**, 8 (2019); https://doi.org/10.1186/s40643-019-0243-y
42. R. Zhang and Y. Tian, *J. Leather Sci. Eng.*, **2**, 24 (2020); https://doi.org/10.1186/s42825-020-00038-9
43. R. Karthik and S. Meenakshi, *Chem. Eng. J.*, **263**, 168 (2015); https://doi.org/10.1016/j.cej.2014.11.015
44. E. Igberase, P. Osifo and A. Ofomaja, *J. Environ. Chem. Eng.*, **2**, 362 (2014); https://doi.org/10.1016/j.jece.2014.01.008
45. D. Zhou, H. Wang and S. Guo, *Sustainability*, **13**, 6460 (2021); https://doi.org/10.3390/su13116460
46. V. Janaki, K. Vijayaraghavan, B.-T. Oh, K.-J. Lee, K. Muthuchelian, A.K. Ramasamy and S. Kamala-Kannan, *Carbohydr. Polym.*, **90**, 1437 (2012); https://doi.org/10.1016/j.carbpol.2012.07.012
47. V. Janaki, B.-T. Oh, K. Shanthi, K.-J. Lee, A.K. Ramasamy and S. Kamala-Kannan, *Synth. Met.*, **162**, 974 (2012); https://doi.org/10.1016/j.synthmet.2012.04.015
48. N.A.A. Qasem, R.H. Mohammed and D.U. Lawal, *NPJ Clean Water*, **4**, 36 (2021); https://doi.org/10.1038/s41545-021-00127-0
49. B.G. Fouda-Mbanga, E. Prabakaran and K. Pillay, *Biotechnol. Rep.*, **30**, e00609 (2021); https://doi.org/10.1016/j.btre.2021.e00609
50. A. Olad, M. Bastanian and H. Bakht Khosh Hagh, *J. Inorg. Organomet. Polym. Mater.*, **29**, 1916 (2019); https://doi.org/10.1007/s10904-019-01152-w
51. Y.I. Cornejo-Ramírez, O. Martínez-Cruz, C.L. Del Toro-Sánchez, F.J. Wong-Corral, J. Borboa-Flores and F.J. Cinco-Moroyoqui, *CYTA J. Food*, **16**, 1003 (2018); https://doi.org/10.1080/19476337.2018.1518343
52. V. Janaki, M.-N. Shin, S.-H. Kim, K.-J. Lee, M. Cho, A.K. Ramasamy, B.-T. Oh and S. Kamala-Kannan, *Cellulose*, **21**, 463 (2014); https://doi.org/10.1007/s10570-013-0100-7
53. X. Wang, Q. Li, D. Yang, X. An and X. Qian, *Coatings*, **12**, 138 (2022); https://doi.org/10.3390/coatings12020138
54. R. Karthik and S. Meenakshi, *Int. J. Biol. Macromol.*, **72**, 711 (2015b); https://doi.org/10.1016/j.ijbiomac.2014.09.023
55. A. Olad and F. Farshi Azhar, *Desalination Water Treat.*, **52**, 2548 (2014); https://doi.org/10.1080/19443994.2013.794711
56. S.A. Hosseini, M.R. Samani and D. Toghraie, *Sci. Rep.*, **11**, 19117 (2021); https://doi.org/10.1038/s41598-021-97518-7
57. M. Mansour, M. Ossman and H. Farag, *Desalination*, **272**, 301 (2011); https://doi.org/10.1016/j.desal.2011.01.037
58. R. Ansari and F. Raofie, *E-J. Chem.*, **3**, 35 (2006); https://doi.org/10.1155/2006/523275
59. R. Ansari and F. Raofie, *E-J. Chem.*, **3**, 49 (2006); https://doi.org/10.1155/2006/378619
60. R. Ansari, A. Aliakbar and M. Masoudi, *J. Polym. Mater.*, **2**, 75 (2005).
61. R. Ansari and A. Fallah Delavar, *J. Iran. Chem. Soc.*, **5**, 657 (2008); https://doi.org/10.1007/BF03246147
62. N.J. Al-Thani, J. Bhadra, D. Abdulmalik, I. Al-Qaradawi, A. Alashraf and N.K. Madi, *Desalination Water Treat.*, **57**, 27374 (2016); https://doi.org/10.1080/19443994.2016.1167128
63. M. Qomi, H. Eisazadeh, M. Hosseini and H.A. Namaghi, *Synth. Met.*, **194**, 153 (2014); https://doi.org/10.1016/j.synthmet.2014.04.016
64. H. Esfandian, M. Jafari, M. Alizadeh, H.T. Rahmati and R. Katal, *J. Vinyl Additive Technol.*, **18**, 250 (2012); https://doi.org/10.1002/vnl.20310
65. Y. Ge and Z. Li, *ACS Sustain. Chem. Eng.*, **6**, 7181 (2018); https://doi.org/10.1021/acssuschemeng.8b01345
66. J.H. Seo, C.S. Choi, J.H. Bae, H. Jeong, S.H. Lee and Y.S. Kim, *BioResources*, **14**, 9169 (2019); https://doi.org/10.15376/biores.14.4.9169-9182
67. Z.W. He, Q.F. Lü and J.Y. Zhang, *ACS Appl. Mater. Interfaces*, **4**, 369 (2012); https://doi.org/10.1021/am201447s
68. Q. Li, L. Sun, Y. Zhang, Y. Qian and J. Zhai, *Desalination*, **266**, 188 (2011); https://doi.org/10.1016/j.desal.2010.08.025
69. Y. Zhang, Q. Li, L. Sun, R. Tang and J. Zhai, *J. Hazard. Mater.*, **175**, 404 (2010); https://doi.org/10.1016/j.jhazmat.2009.10.019
70. D.S. Malik, C.K. Jain and A.K. Yadav, *Appl. Water Sci.*, **7**, 2113 (2017); https://doi.org/10.1007/s13201-016-0401-8
71. S.O. Mezan, K.M. Hello, A.H. Jabbar, M.Q. Hamzah, A.N. Tuama, M.S. Roslan and M.A. Agam, *Int. J. Psychosoc. Rehabil.*, **24**, 4532 (2020).
72. T. Pham, T.T. Mai, M. Bui, T.X. Mai, H. Tran and T. Phan, *Adv. Nat. Sci. Nanosci. Nanotechnol.*, **5**, 015010 (2014); https://doi.org/10.1088/2043-6262/5/1/015010
73. M.A. Ashraf, M. Zwawi, M. Taqi Mehran, R. Kanthasamy and A. Bahadar, *Fibers*, **7**, 77 (2019); https://doi.org/10.3390/fib7090077
74. P.A. Kumar, S. Chakraborty and M. Ray, *Chem. Eng. J.*, **141**, 130 (2008); https://doi.org/10.1016/j.cej.2007.11.004
75. P.A. Kumar and S. Chakraborty, *J. Hazard. Mater.*, **162**, 1086 (2009); https://doi.org/10.1016/j.jhazmat.2008.05.147
76. Q. Huang, D. Hu, M. Chen, C. Bao and X. Jin, *J. Mol. Liq.*, **285**, 288 (2019); https://doi.org/10.1016/j.molliq.2019.04.115
77. Y. Zheng, W.B. Wang, D.J. Huang and A.Q. Wang, *Chem. Eng. J.*, **191**, 154 (2012); https://doi.org/10.1016/j.cej.2012.02.088
78. R.B. Gapusan and M.D.L. Balela, *Mater. Chem. Phys.*, **243**, 122682 (2020); https://doi.org/10.1016/j.matchemphys.2020.122682
79. J. Gao, Z. Wu, L. Chen, Z. Xu, W. Gao, G. Jia and Y. Yao, *Mater. Lett.*, **240**, 147 (2019); https://doi.org/10.1016/j.matlet.2018.12.116
80. M. Ghorbani, H. Eisazadeh and A.A. Ghoreyshi, *Iran. J. Energy Environ.*, **3**, 66 (2012); https://doi.org/10.5829/idosi.ijee.2012.03.01.3343
81. M. Ghorbani and H. Eisazadeh, *Compos. B Eng.*, **45**, 1 (2013); https://doi.org/10.1016/j.compositesb.2012.09.035
82. Y.-S. Yun, K. Vijayaraghavan and S.W. Won, Eds.: P. Kotrba, M. Mackova and T. Macek, Bacterial Biosorption and Biosorbents, In: Biosorption of Metal Ions, Springer Dordrecht: Heidelberg, London, New York (2011). https://doi.org/10.1007/978-94-007-0443-5
83. K. Vijayaraghavan and Y.S. Yun, *Biotechnol. Adv.*, **26**, 266 (2008); https://doi.org/10.1016/j.biotechadv.2008.02.002
84. M. Muthu, H.-F. Wu, J. Gopal, I. Sivanesan and S. Chun, *Polymers*, **9**, 721 (2017); https://doi.org/10.3390/polym9120721
85. N. Das, *Nat. Prod. Radiance*, **4**, 454 (2005).

86. J. Wang and C. Chen, *Biotechnol. Adv.*, **24**, 427 (2006); https://doi.org/10.1016/j.biotechadv.2006.03.001
87. P. Perego and S.B. Howell, *Toxicol. Appl. Pharmacol.*, **147**, 312 (1997); https://doi.org/10.1006/taap.1997.8271
88. A. Kapoor and T. Viraraghavan, Eds.: J. Wase and C. Forster, Biosorbents for Metal Ions, Taylor & Francis: London, pp. 67-85 (1997).
89. A.V. Pethkar, S.K. Kulkarni and K.M. Paknikar, *Bioresour. Technol.*, **80**, 211 (2001); https://doi.org/10.1016/S0960-8524(01)00080-3
90. E. Romera, F. González, A. Ballester, M.L. Blázquez and J.A. Muñoz, *Technol.*, **98**, 3344 (2007).
91. K. Stamberg, J. Stamberg, J . Katzer, H. Prochazka, P. Nemec, P. Hulak and R. Jilek, GB Patent 1417901 (1975).
92. P. Staroñ and J. Chwastowski, *Materials*, **14**, 7482 (2021); https://doi.org/10.3390/ma14237482
93. U. Soltmann, S. Matys, G. Kieszig, W. Pompe and H. Bottcher, *J. Water Resource Prot.*, **2**, 115 (2010); https://doi.org/10.4236/jwarp.2010.22013.
94. M. Gandhi, N. Viswanathan and S. Meenakshi, *Int. J. Biol. Macromol.*, **47**, 146 (2010); https://doi.org/10.1016/j.ijbiomac.2010.05.008
95. S. Fierro, M. del Pilar Sanchez-Saavedra and C. Copalcua, *Bioresour. Technol.*, **99**, 1274 (2008); https://doi.org/10.1016/j.biortech.2007.02.043
96. R. Nirmala, R. Navamathavan, H.-S. Kang, M.H. El-Newehy and H.Y. Kim, *Colloids Surf. B Biointerfaces*, **83**, 173 (2011); https://doi.org/10.1016/j.colsurfb.2010.11.026
97. C.-A. Ghiorghita, M.V. Dinu, M.M. Lazar and E.S. Dragan, *Molecules*, **27**, 8574 (2022); https://doi.org/10.3390/molecules27238574
98. K. Kuroda, M. Ueda, S. Shibasaki and A. Tanaka, *Appl. Microbiol. Biotechnol.*, **59**, 259 (2002); https://doi.org/10.1007/s00253-002-1014-8
99. S.P. Mishra, *Curr. Sci.*, **107**, 601 (2014).
100. E.F. Kankeu and A.F.M. Bafubiandi, *Afr. J. Biotechnol.*, **13**, 1756 (2014); https://doi.org/10.5897/AJB2013.13311
101. K. Jahan, N. Kumar and V. Verma, *Environ. Sci. Water Res. Technol.*, **4**, 1589 (2018); https://doi.org/10.1039/C8EW00255J
102. F. Mashkoor and A. Nasar, *Groundw. Sustain. Dev.*, **8**, 390 (2019); https://doi.org/10.1016/j.gsd.2018.12.008
103. M. Ahmad, A. Hussain, M. Anjum, T. Hussain, A. Mujahid, M. Hammad Khan and T. Ahmed, *Open Chem.*, **18**, 843 (2020); https://doi.org/10.1515/chem-2020-0137
104. W. Liu, Y. Dong, H. Lin and Y. Shi, *Water Air Soil Pollut.*, **232**, 429 (2021); https://doi.org/10.1007/s11270-021-05378-8