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Application of nano-biocomposites for remediation of heavy metals from aqueous environment : An Overview

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Abstract: Water contamination due to toxic heavy metals still remains a severe environmental problem. Several adsorbents have been reported to remove heavy metal ions from aqueous medium. In recent years, nano-biocomposites which integrate the advantageous properties of both biopolymers and nanoparticles have received an increasing attention as adsorbents for removal of various pollutants due to their nanosized structural and functional properties. This article gives an overview on remediation of heavy metals from aqueous environment using nano-biocomposites. A brief summary on nano-biocomposites and their applications towards remediation of heavy metals have been highlighted.
Keywords: Adsorption, biopolymers, heavy metals, nano-biocomposites, remediation.

1. Introduction

Toxic heavy metal pollution is of significant environmental and occupational concern because of the tendency of heavy metals to enter the food chain[1].Several conventional techniques such as chemical precipitation, filtration, chemical oxidation or reduction, electrochemical treatment, reverse osmosis, ion exchange and evaporation have been used to remove heavy metals from dilute solutions[2]. However, these techniques frequently face some problems for reaching legal discharge levels. The major problems associated with these processes include high operating cost and generation of secondary metabolites[3, 4]. So, there is a need to search for a cost effective and eco- friendly alternative technique for removal of heavy metals from aqueous environment.

Adsorption technique being very economical, simple, versatile and effective has been widely preferred for the removal of heavy metals from aqueous environment[5].

The biopolymers are represented as attractive adsorbents because of their chemical stability, particular structure, physico-chemical characteristics, high reactivity and selectivity towards heavy metal ions showing the presence of various reactive chemical groups in polymer chains[6]. In recent years, biopolymers have attracted more and more interest due to increasing environmental concern, since they are biodegradable and nontoxic to the environment. Biopolymers can be classified as natural biopolymers such as carbohydrates and protein (e.g. starch, cellulose, chitosan, alginate, soy protein, collagen and casein), chemically synthesized biodegradable polymers (e.g. poly-lactic acid (PLA), polygycolic acid (PGA), polyvinyl alcohol (PVA), poly butylene succinate (PBS), poly (ε-caprolactone) (PCL) and microbial polyesters (e.g. polyhydroxybutyrate (PHB), polyhydroxyalkanoates (PHA)[7].

Metallic nanoparticles (NPs) also exhibit unique chemical and physical properties and are massively enrolled towards the removal of pollutants because of their limited size and a high density on their edge surface sites. NPs are biologically, thermally and chemically stable and can be used safely[8]. Nanoparticles are classified based on the number of dimensions in the nanometer range such as isodimensional nanoparticles (e.g. silica, metal and metal oxide nanoparticles), two dimensions in nanometer range (e.g. carbon nanotubes (CNT), cellulose nanowhiskers) and one dimension in nanometer range (e.g. layered silicate clays)[9].

For certain applications, biopolymers cannot be fully competitive because some of their properties are too weak. Therefore, to extend their applications, the biopolymers have been associated with nano-sized fillers which could bring a large range of improved properties (stiffness, permeability, crystallinity and thermal stability) resulting the formation of nano-biocomposite[7]. These 'nano-biocomposites' have received increasing attention as potential adsorbents towards reducing environmental pollution which incorporates the advantages of both biopolymers and nanoparticles. This article gives a brief overview on application of nanobiocomposites for the removal of toxic heavy metals from aqueous environment.

2. Adsorbents for heavy metal removal

There are reports on the use of activated carbon[10], zeolites[11], functionalized polymers[12], chitosan[13], lignocelluloses[14], clay minerals[15]to serve as effective adsorbents for the treatment of wastewater containing heavy metals. In addition, nano-meter sized functionalized carbon nanotubes[16], nano-alumina[17], hydroxyapatite nanoparticles[18]also showed the high adsorption efficiency towards metal removal because of large surface area and high reactivity. Moreover, nano-materials including zero valence metal, magnetic nanoparticles etc. are impregnated onto conventional biopolymers like alginate[19], cellulose[20], chitosan[21], gum arabic[22] and polysaccharides[23]and have also been explored for the removal of heavy metals.

3. Nano-biocomposites

Nano- biocomposites are obtained by adding nanofillers to biopolymers, resulting in very promising materials since they show improved properties with preservation of the material biodegradability, without showing eco-toxicity. Such materials are mainly destined to biomedical applications and different short term applications e.g. packaging, agriculture or hygiene devices. They represent a strong and emerging answer for improved and eco-friendly materials[7]. Recently, the application of nano-biocomposites has become a novel approach for environmental applications such as removal of heavy metals, dyes and herbicides[24]. Biopolymers based nano-biocomposites have been reported for the removal of metallic ions from wastewater[22].

Nano-biocomposites are generally prepared following two methods; (a) direct compounding and (b) in-situ synthesis. In direct compounding, nanoparticles and biopolymer matrix are prepared separately and then mixed or compounded by fusion or mechanical forces. This method has been used broadly because of its ease in operation, comparatively low expense and suitability for massive production. The nanoparticles are having a high tendency to form large aggregates during fusion, which greatly reduces the advantage of its smaller dimensions. To overcome this limitation, several surface treatment have been followed during synthesis and also alterations in compounding conditions such as temperature, time and shear force in order to achieve fine dispersion of nanoparticles in biopolymer matrices[25].

The synthesis of multi-walled carbon nanotubes/chitosan nano-biocomposite by direct compounding method was reported by Salam et al.[26] in which two suspensions were made separately and then were mechanically mixed which showed a great efficiency for the removal of cadmium, copper, zinc and nickel from the aqueous solution. Under in situ synthesis, metal ions which served as nanoparticle precursors were preloaded within biopolymer matrix and uniformly distributed. Then, precursors were subjected to the corresponding gas or liquid containing OH^-, S^{2-} etc. to synthesize the target nanoparticles. Wu et al.[27],reported in situ synthesis of zero-valent copper-chitosan nano-biocomposite using $Cu(SO_4)_2.5H_2O$ as a precursor which was applied for the removal of hexavalent chromium. Pandeyet al.[28]reported the synthesis of organic-inorganic hybrid of chitosan and nanoclay and this nano-biocomposite was applied for the removal of chromium from aqueous solutions showing an uptake of 357.14 mg/g. A novel triethylene-tetramine grafted magnetic chitosan composite was synthesized via combination of chitosan and magnetic nanoparticles and used for the removal of Pb(II) ions from aqueous solution[29]. An uptake of 370.63 mg/g of Pb(II) was noted under optimized conditions (pH=6, T= 298K, t= 1.5h, C_0=200 mg/L and adsorbent dosage= 500 mg/L).

Nanoparticles (NPs) incorporated in nano-biocomposite can serve as catalysts and redox active media due to their high reactivity, large surface area, electrical and catalytic property. These properties have attracted great attention in designing highly efficient catalytic materials for purification of contaminated water. The common catalytic nanoparticles used include zero valence metal such as (Fe^0, Zn^0 , Cu^0) [30,31,32], bimetallic nanoparticles such as Zn/Pd[33], Fe/Pd[34], Fe/Al[35], Fe/Ni [36]and nanosized semiconductor materials such as nano-CdS[37], ZnO [38]and TiO_2[39]. Immobilization of nanoparticles onto polymer matrix such as biopolymers[40], porous resins[41], polymeric membranes[42] and ion exchangers[43] has been reported to solve the environmental problems to considerable extent owing to their ability in reduction of particle loss and prevention of particle agglomeration. It has been reported that nanoparticles (zero valence metal and bimetallic) such as Zn^0, Fe^0, Cu^0, Fe/Pd, Pd/Zn etc. are very efficient in removing various contaminants including heavy metals. The reactivity of some nanoparticles is considerably very high, for example nanoscale zero valent iron (nZVI) has the ability to self-ignite when exposed to air. Therefore, supporting the nanoparticles to matrix is required to conserve their chemical property by inhibiting the oxidation process until they come in contact with the pollutants being targeted.

Table1 summarizes the role of nano-biocomposites for the removal of heavy metals from aqueous environment.

Table 1.Nano-biocomposites used for the removal of heavy metals from aqueous media

NPs	Biopolymer matrix	Target heavy metal	Mechanism of metal removal	Adsorption capacity (mg/g)/ Removal %	References
Fe^0	Chitosan-carboxymethyl-β-cyclodextrin	Cu(II) Cr(IV)	Adsorption	250.0 mg/g 200 mg/g	1
Fe_3O_4	Chitosan	Pb(II)	Adsorption	370.63 mg/g	29
Fe_3O_4	Poly(γ-glutamic acid)	Cr(III)	Adsorption	24.60 mg/g	44
Fe_3O_4	TiO_2 coupled chitosan	Cd(II)	Adsorption	256.41 mg/g	47
Fe_3O_4	Cyclodextrin	Cu(II)	Adsorption	47.2 mg/g	23
Carbon nanotubes (CNT)	Chitosan	Cu(II), Cd(II), Zn(II), Ni(II)	Adsorption	100% 97% 96% 94%	26
Nano-clay (Cloisite 10A)	Chitosan	Cr(VI)	Adsorption	357.14 mg/g	28
Fe^0	Carboxymethyl cellulose	Cr(VI)	Reduction	94%	3
Fe^0	Chitosan	Cr(VI)	Reduction	82%	45
Cu^0	Chitosan	Cr(VI)	Reduction	99%	27
Magnetite	Chitosan	Pb(II), Cu(II), Cd(II)	Adsorption	95.3% 89.1% 92.1%	46
Iron oxyhydroxide	Cellulose	As(III), As(V)	Adsorption	99.6 mg/g 33.2 mg/g	20

4. Conclusion

The environmental applications of nano-biocomposites are interesting. This review presents the current status of nano-biocomposites towards heavy metal removal from water environment. The main preparation strategies for nano-biocomposites for metal removal have been discussed. The reported performances of nano-biocomposites are quite encouraging. Since industries are concerned with sustainable developments, and the production cost of biopolymers is decreasing, strong developments of biopolymers-based nanobiocomposites is possible in near future. Extensive research should be carried out to promote the large scale use of nano-biocomposites for the effective removal of heavy metals from wastewater.

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