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ECOFRIENDLY ADSORBENTS APPLICATIONS FOR THE REMOVAL OF CHROMIUM AND CADMIUM: AN OVERVIEW

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Abstract: Heavy metals like cadmium and chromium in industrial effluent streams pose a serious environmental problem. Chitosan provides high surface area and a specific affinity for adsorption of these metals from aqueous system. Chitosan has been reported to be an efficient heavy metal scavenger due to amino group. The nano-composite chitosan beads can be used in packed bed reactors. Chitin is the most abundant natural biopolymer. Hence de-acetylation of chitin to chitosan and subsequent chemical modifications needed to enhance the bioadsorbents can also be effectively reused for the treatment. Chitosan occur naturally in the environment in large quantities and run second in abundance to cellulose. Ecofriendly chitosan nano-composites provide high surface area and a specific affinity for heavy metal adsorption from aqueous systems. Thus, Chitosan have the potential to reduce and to solve some environmental pollution problems for creating Greener environment and chitosan is renewable polymers.
Keywords: Bioremediation, Chitosan, Cadmium, Chromium, Heavy metal
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INTRODUCTION

Industrial wastewater effluents, bearing heavy metals, pose a serious problem for the environment. Cadmium is widely used in several industries including metallurgy, surface treatment, dye synthesis or electroplating (Benguella *et al*., 2002). Cadmium has been well recognized for its negative effect on the environment where it accumulates readily in living systems through food chain and reported to cause renal disturbances, lung insufficiency, bone lesions hypertension, cancer. Chromium compounds find their way to the environment mainly through tanning and electroplating industries. Cadmium has been well recognized for its negative effect on the environment where it accumulates readily in living systems through food chain and is reported to cause renal disturbances, lung insufficiency, bone lesions, cancer and hypertension (Bailey *et. al.,* 1999). Chromium essentially exists in two forms namely Cr (VI) and Cr (III). Cr (III) is proved to be biologically essential to mammals as it maintains an effective glucose, lipid and protein metabolism. In contrast, Cr (VI) can diffuse as CrO_4^{2-} or $HCrO_4^-$ through cell membranes and can oxidize biological molecules with toxic results. Major toxic effects of Cr (VI) are chronic ulcers, dermatitis, and corrosive reaction in nasal septum and local effects in lungs (Kumar *et al*., 2009). In fact there are several tanneries and electroplating industries in India which generates toxic chromium and cadmium wastes in their industrial wastewater. In view of the toxicity of chromium and cadmium and their presence in various tanneries and electroplating industries effluents causing water pollution is essentially required (Hanbay *et al.,* 2008). In this review, heavy metals in industrial effluent streams pose a serious environmental problem, and ecofriendly chitosan nano-composites provide high surface area and a specific affinity for heavy metal adsorption from aquesous systems. To meet the environmental regulations, effluents contaminated with heavy metals in water must be treated before discharge. Chromium, especially in hexavalent form and cadmium are toxic to humans even if present in ppb range. Various removal techniques like chemical precipitation, oxidation/reduction, ion exchange and membrane sorption and carbon adsorption are widely used for the removal of toxic heavy metals from the waste streams. Some of the limitations of these methods are safe disposal of toxic sludge formed from chemical precipitation and the cost of ion exchange resins/activated carbon (Miliot *et al*., 1997; Guibal, *et al.,* 2004). The low cost adsorbents are useful their wide applications in removal of heavy metals from waste water. There are number of adsorbents like, bioadsorbent, activated carbon, chitosan, xanthate, clay, derived plants and carbon nanotubes have been used for removing the heavy metals from wastewater. The present review describes the potential and limitation of each of adsorbents in removing the heavy metals.

1. Bioadsorbents: Adsorbents derived from low-cost agricultural wastes can be used for the effectual removal of chromium, cadmium and various organic pollutants from aqueous water streams (Volesky *et al*., 1993; Williams *et al*.1998). Its Low cost, high efficiency, low sludge generation of biosorbent, no additional nutrient requirement, and the possibility of metal recovery make it suitable over conventional treatment methods such as chemical precipitation, membrane filtration, electrolysis, ion exchange etc. (Pehlivan *et al.,* 2008). Different low cost biosorbents such as wool, sawdust, olive cake, pine needles, almond shell, coal, cactus, walnet shell, coir pith etc. have been widely used for the treatment of chromium, cadmium and organic pollutants containing wastewaters (Namasivayam and Rangnathan,1993). Some researchers are used algae such as Chlorella *emersonii* (Arkipo *et al*., 2004), *Sargassum muticum,* Ascophyllum *sargassum*, (Volesky and Holan, 1995), *Ceramium virgatum*, *Aspergillus niger* (fungus) (Barros *et al*., 2003) as a biosorbents for effective cadmium and chromium removal from waste waters.

2. Activated Carbon: Activated carbon is widely used by many researches to remove heavy metals like chromium, cadmium and organic pollutants from water. Activated carbon adsorption is attractive choice of researchers for chromium, cadmium, other heavy metals removal and organo pollutants, because of its high surface areas and the presence of a wide spectrum of surface functional groups like carboxylic group (Mohanty *et. al.,* 2005).

Now a day's Researchers are still studying the use of activated carbon for removing chromium (Candela *et. al*., 1995; Sharma *et. al*. 1996), cadmium (Leyva-Ramos *et. al*., 1997) many researchers are used different types of powdered activated carbon AC from various raw materials to remove Cr(VI). They reported that at pH of 1.0, the retention of Cr (VI) was affected by its reduction to Cr (III) (Candela *et. al*., 1995). In the year 1994, Sharma and Foster studied the removal of Cr(VI) from aqueous solution on granular activated carbon. Sharma and Foster reported the good adsorption capacity of Cr (VI) was achieved at a pH range of 2.5-3.0 (Sharma and Foster, 1994). Further, (Selomulya *et al.,* 1999) used different types of activated carbons, produced from coconut shell, wood and dust coal for the remove of Cr (VI) from synthetic wastewater (Selomulya *et al*., 1999).

3. Xanthate: Adsorbents which contain sulfur groups having a high affinity for heavy metals and organic pollutants removal. Some sulfur-bearing compounds include thiocarbamoyl, thiols, dithiocarbamates, dithiophosphates and xanthates. Xanthates are formed by reaction of organic hydroxyl-containing substrate with carbon disulfide. Xanthates are quite selective for heavy metals like chromium, cadmium and organic pollutants like malathion removal (Takahashi *et al.,* 1971; Robert Wing *et al*., 1974).

4. Clay: Clay is also one of the adsorbents for removal of heavy metals and organo pollutants from water streams. There are three basic species of clay found in eco system that are smectites (such as montmorillonite), kaolinite, and micas, among all of these, montmorillonite has the highest cation exchange capacity and too low occurring cost then activated carbon (Virta, 2002). Number of studies conducted by researchers (Bhattacharya *et al*., 2006) by using montmorillonite clays and found good adsorption capacities for removing chromium, cadmium, other heavy metal ions and organic pollutants.

5. Dried plants: Dried plants are a class of natural adsorbents which are widely studied as an alternative adsorbent for chromium and cadmium and various organo pollutants removal. The efficiency of heavy metals and organic pollutants adsorption on this material was basically depend on various parameters such as particle size of crushed plants, solution concentration and pH. Some common examples of crushed dried plants are *Launeaar borescens, Asphodelus microcarpus, Withania frutescens, Asparagus albus, Euphorbia echinus*, *Carpobrotuse* and *Senecio anthophorbium* (Muthukumarana, 2011). These plants grow in the Agadir area and can be effectively play the role of adsorbent for pollutants such as chromium and cadmium and organic pollutants with high adsorption efficiency.

6. Nano-materials: The heavy metals ions mainly chromium and cadmium and organic pollutants cause severe health issues, and must be eliminated from the environmental system. Presently, nano-materials are attractive candidate now a days and increasing attention towards researchers. Several research groups worked on nano-materials and its applicability towards various application especially environmental remediation applications. The introduction of different types of nano-materials for water treating process that gives the great outcomes. Several nano-adsorbents such as metal NPs, CNTs, have excellent sorption properties and successfully applied in removing heavy metal ions, organic and biological contaminants (Hu *et al.,* 2005; Shi *et al.,* 2013). Metal nanoparticles have been attracting intensive interest because of their outstanding properties and potential applications in the areas of catalysis, magnetism, electronics, etc. Recently, carbon nanotubes and nanoparticles are widely used in the membrane science.

7. Carbon Nanotubes: Carbon nanotubes (CNTs) are types of the allotrope of carbon which are having tubular nanostructure, having length-to-diameter ratio of up to 132,000,000:1 (Sheng *et al*., 2010). Carbon nanotubes have been extensively studied over the past few years due to their exceptional properties, amazing structure and extensive technological applications (Sherigara *et al*., 2003). The applicability of CNT for the remediation of contaminants increases because of their large surface area, porous structure, and strong interaction between CNTs and metal ions (Chen, *et al*, 2009; Long and Yang, 2001; Di *et. al*., 2004; Wang *et al.,* 2007) and organic pollutants (Du *et. al*., 2008; Krystyna Pyrzynska, 2011). Extensive studies were carried out on adsorption of heavy metal ions, pharmaceuticals and organic pollutants on various types of CNTs. Gupta et al. published the synthesis of carbon nanotubes/magnetic iron oxide composite (Gupta *et al*., 2011).

8. Chitosan: Chitosan is a most widely used adsorbent for the removal of a broad range of toxic heavy metals and organo-pollutants. Now days, chitosan is attracting an increasing attention of researchers, as it is an effective scavenger for heavy metals and organo-pollutants. Chitosan can produce chemically from chitin and is found naturally in some fungal cell walls (shrimp, crabs, shellfish etc.). Chitosan is low-cost and plentiful in environment and having good efficiency for the removal of heavy metal contaminants and organic pollutants from aqueous streams. It was reported that chitosan binds five to six times more than chitin due to the free amino groups exposed during de-acetylation (Yang and Zall, 1984). The physiology of chitosan can be changed depend on the application, however it is commonly found in powdered state, which can be converted into beads form (Chen and Chung, 2006) and used to remove contaminate from water in both batch and dynamic mode. It is reported that the interaction between chitosan and hexavalent Cr (VI) and found good adsorption capacity of chromium at pH 4 (Udaybhaskar *et. al*., 1990) studied the chemically joining effects of chitosan (Schmuhl *et al.,* 2001). Lee *et al*. (2005) prepared chitosan-based polymeric surfactants (CBPSs) and used it for the removal of Cr(VI) from aqueous streams. Removal efficiency of Cr (VI) depended on several factors like solution pH, CBPS dose, and ionic strength and found good adsorption capacity for Cr (VI) than other modified chitosans (Lee *et. al*., 2005). Study of (Sankararamakrishnan *et. al*., 2006) used cross linked chitosan with glutaraldehyde, xanthate group, and chemically modified chitosan beads (CMCB) and flakes (CMCF) for the removal and recovery of hazardous chromium (VI) and found that the sorption mainly depends on both pH and concentration (Sankararamakrishnan *et. al*., 2006). Many studies are also available in literature for the cadmium removal using chitosan (Hsien and Rorrer, 1995; Guibal *et. al*., 1999; Lv *et. al*., 2008) and other investigators are studied on organo pollutants removal using chitosan from aqueous streams.

CHARACTERSTICS OF ECOFRIENDLY CHITOSAN

Chitin is one of the abundantly available biopolymer and consists of 2-acetamido-glucopyranose units linked by β-1, 4 linkages. Its deacetylated product, chitosan, has been reported to be an efficient heavy metal scavenger due to amino group (Lu *et. al*., 2011). The nano-composite chitosan beads can improve the metal uptake capacity and thus can be used in packed bed reactors. In a developing country like India, there is an urgent need for the development of new types of low cost and easily available materials of biological origin materials/processes for the wastewater treatment. Next to cellulose, chitin is the most abundant natural biopolymer (Guibal, 2004). Hence de-acetylation of chitin to chitosan and subsequent chemical modifications needed to enhance the adsorption capacity, will lead to a variety of new ecofriendly low cost efficient adsorbents for green environment.

FUNCTIONS OF ECOFRIENDLY CHITOSAN

Chitosan is obtained on an industrial scale by the alkaline de-acetylation of chitin, one of the most abundant biopolymers next to cellulose. Chitin, is a high molecular weight linear polymer of 2-acetamido-2-deoxy-D-glucopyranose units linked together by β-1, 4-glycosidic bonds. Chitosan, the N-de-acetylated product of chitin represents copolymers of 2-amino 2-deoxy-D-glucopyranose and 2-acetamido-2-deoxy-D-glucopyranose where the degree of deacetylation is greater than 60%. Both chitin and chitosan are becoming increasingly important natural polymers because of their unique properties like biodegradability, biocompatibility and bioactivity. In addition to attractive physical and mechanical properties, the presence of acetyl glucosamine and glucosamine units contributes to existence of heterogeneity of the polymer (Merrifield *et. al.,* 2004).The nitrogen atom in the amine group holds free electron doublets that can bind metal cations by chelation mechanisms. Amine groups can be easily protonated in acidic solutions and can retain heavy metal anions and organic compounds such as dyes by electrostatic attraction (Guibal *et. al*., 1998).

CONCLUSION

The efficient removal is important matter and it is a widely-studied of toxic metals from wastewater is an area. A number of technologies have been developed over the years to remove toxic metals from wastewater. Physical treatment can also be used to remove small concentrations of hazardous substances dissolved in water that would never settle out. One of the most commonly used techniques involves the process of adsorption, which is the physical adhesion of chemicals onto the surface of a solid. The effectiveness of the adsorbent is directly related to the amount of surface area available to attract the molecules or particles of contaminant. Chitosan is a biopolymer, which is extracted from crustacean shells or from fungal biomass. The high porosity of this natural polymer results in novel binding properties for metal ions such as cadmium, copper, lead, mercury and water purification processes. When chitosan is spread over oil spills it holds the oil mass together making it easier to clean up the spill. Water purification plants throughout the world use chitosan to remove oils, grease, heavy metals, and the fine particulate matter that cause turbidity in wastewater stream. Chitosan have the potential to reduce and to solve some environmental pollution problems for creating Greener environment and chitosan is renewable polymers. Some of the properties which are commercially attractive are polymeric, including natural decomposition, non-toxic to both the environment and human being, with no side-effects or allergenic effects if implanted in the body. Chitosan occur naturally in the environment in large quantities and run second in abundance to cellulose.

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