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Removal of Cadmium Ions from Water / Waste Water Using Chitosan - A Review

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ABSTRACT

The removal of Cd^{2+}ions from wastewaters is gaining wide interest from both environmental and economic viewpoints due to its serious hazardous impact on humans, animals and plants. Various adsorbents have been used viz., activated carbons, plant or lignocellulosic wastes, clay, biopolymers etc. Chitosan, a crustacean waste has gained wide attention as an effective biosorbent due to its low cost and high contents of amino and hydroxyl functional groups. Chemical modifications leading to the formation of chitosan derivatives, grafting chitosan and chitosan composites are extensively studied and widely reported in the literatures. The aim of this review is to summarize the sorption efficiencies of chitosan and its derivatives in the removal of Cd^{2+} ions from electroplating effluents and synthetic waters. A comparison on the chitosan derivatives prepared by five different methods as reported by researchers (thiocarbomyl, PVA blend, xanthate, Nano based and grafting) and an outline of their potential applications in the adsorption of Cd^{2+} ions are dealt in this paper. Amongst the mentioned composites reported, chitosan grafted with γ- cyclodextrin is found to possess better chelating ability in sequestering Cd^{2+} ions.

INTRODUCTION

Water pollution due to toxic metal ion from industrial discharges has been a major cause of concern. The current pattern of industrial activity and urbanization alters the natural flow of material and introduces hazardous wastes into the environment [1]. The environmental pollution due to heavy metal contaminations leads to bio-accumulating tendency, in turn pose great threat to human life [2,3]. Among the toxic heavy metals, Cadmium, Lead, Mercury are called, "the big three' due to their major impact [4].

The removal of Cadmium is gaining wide interest from both environment and economical view point due to its serious impact on humans, flora and fauna. The source of human exposure to cadmium includes atmospheric, terrestrial and aquatic routes [5,6]. There are several industries that are responsible for pollution with high level of cadmium ions.

The major sources of pollution are from the industries viz., metal plating, Cd-Ni batteries, phosphate fertilizers, mining, pigments, stabilizers, metallurgy, ceramics, photographs, textile printing, lead mining, sewage sludge, alkaline batteries and electroplating [7,8]. Even though, the electrochemical industries consume less water in comparison with other industries, the effluents of the former contain high concentration of cadmium and cyanides [9].

METAL TOXICOLOGY

Cadmium is a non-essential element and highly toxic to organisms at very low dosages. There are reports of nausea and vomiting at the level of 15mg/ L [10,11].

The health implications in human include renal damage, emphysema, kidney dysfunction, hepatic damage, hypertension, destruction of testicular tissue and RBC [12-14].

Cadmium damages cells by strong affinity to glutathione and sulfhydryl group in proteins and displacement of zinc, iron from proteins [15]. Cadmium may cause mutations even at low levels by inducing oxidative DNA damage and decreasing genetic stability which results in enhanced probability of mutations and consequently cancer initiation [16-18]. The permissible limit of Cd^{2+} ion is given in **Table 1.**

Table 1. Water quality standards.

Standards	Cd(II) ion	
	Drinking water (mg/L)	Wastewater (mg/L)
WHO[25]	0.003	0.1
ISI[23]	0.01	0.3
EPA[6]	0.05	0.3
CWQG[2]	0.001	0.05

The strange disease that appeared in the downstream basin on chronic cadmium poisoning of the Jinzu River, Japan around 1912 was called by locals "itai-itaibyo" ("itai" being what Japanese people said when inflicted with pain and "byo" literally meaning disease).

This name had come in because of the way victims cried out " ouch-ouch " under the excruciating pain they endured. It first impaired kidney function and progressively caused osteomalacia. Victims suffered from calcium deficiency as with the occurrence of old age, malnutrition', hormone imbalance and during pregnancy or breast feeding. Women were mostly afflicted with pain across their entire body and more severe cases suffered broken bones while trying to move on their own [19-21].

METHODS

The conventional methods being, reduction, precipitation, ion exchange, filtration, electrochemical treatment, membrane technology, reverse osmosis, evaporation etc. These methods may be extremely expensive or ineffective when metals are dissolved in large volume of solution at relatively low concentration [6]. Among all the treatment processes adsorption is a potential way of trapping heavy metal ions, due to its advantages viz., low energy consumption, easy availability, eco- friendly and low cost [22,23].

Though, the use of commercially activated carbon is well known for the removal of heavy metals, due to their large specific surface area and adsorption capacity, their high cost and sludge formation are the major limitations [24,25].

BIOPOLYMERS

Natural biopolymers are industrially attractive because of their capability of lowering transition metal-ion concentration to parts per billion levels. Natural materials that are available in large quantities or certain waste from agricultural operations may possess the potential to be used as low cost adsorbents, as they represent unused resources, widely available and are ecofriendly.

Recently, numerous approaches have been made for the development of cheaper and more effective adsorbents containing natural polymers. Among these, polysaccharides such as chitin and starch and their derivatives (chitosan, cyclodextrin) deserve particular attention.

These biopolymers represent an interesting and attractive alternative as adsorbents because of their particular structure, physico-chemical characteristics, chemical stability, high reactivity and excellent selectivity towards aromatic compounds and metals, resulting due to the presence of chemically reactive groups (hydroxyl, acetamido or amino functions) in their polymer matrix.

CHITOSAN

Chitosan is the second most available biopolymer in nature next to cellulose and it is made up of cationic amino polysaccharide copolymer of β-(1-4)-linked D-glucosamine and N-acetyl-D-glucosamine units. It is obtained by the alkylation and partial deacetylation of chitin [26] **Figure 1.**

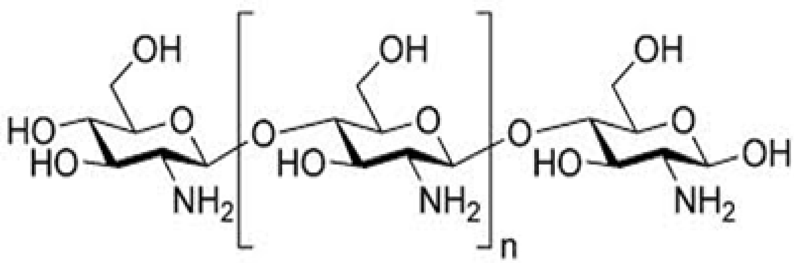

Figure 1. Chitosan.

Nowadays, Chitosan is being exploited in several major areas including pulp and paper, textiles, medical cosmetics, biotechnology, agriculture, food industries, chemical production, separation and environmental applications. Chitosan is mostly used in a variety of solid forms such as, beads, flakes and membranes. The amine groups are able to adsorb the metal ions especially group (III) transition metals through several mechanisms which include like (chemical interaction) chelation and (electrostatic interaction) like ion exchange [27].

The world's marketing for seafood crustaceans discard 50% of them as shell waste. Conversion of waste into useful adsorbent has contributed not only to the treatment of heavy metal contaminated environment but also minimizes the generated solid wastes.

Chitosan is highly stable and difficult to degrade which can be obtained as 10-20% w/w from the waste sea food shells by suitable chemical processing. They have been known for their metal adsorption properties since 1970's and are described as excellent metal adsorbents by many investigators due to their hydrophilicity, natural abundance, non-toxicity, biocompatibility, biodegradability, antibacterial property and remarkable affinity for many proteins [28].

Chitosan is readily soluble in acid solution therefore it should be engineered to a suitable physical modification. This helps to reduce the crystalline nature of polymer and expand the polymeric networks to the three dimensional, leading to enhance diffusion of large size molecules [29]. Use of functionalized Chitosan on removal of various pollutants is of special interest for better adsorption. Presence of sulphur containing groups like xanthate, dithiocarbamate, mercaptoacetyl group, thiols, thio urea, thiocarbamoyl etc., have been found to enhance the capacity of Chitosan.

EXPERIMENT AND DISCUSSION

The present work reviews the methodology of 5 different modifications of chitosan are reported by, D. Chauhan [30], A.K. Mishra [31], N. Sankaramakrishnan [32], Mahendrakumar [33] and SeyedMasoudSeyedi [34] for the removal of Cd^{2+} from electroplating effluents and synthetic waters.

Various methods employed by the authors have focussed on enhancing the efficiency of chitosan in terms of diffusion coefficient, adsorption kinetics, the solid to liquid ratio, selective functionalization and thermal stability.

The experimental conditions suggested by the workers for modified sorbents have been listed in **Table 2.** The enhanced adsorption capacity of 833.3mg/g for γ- cyclodextrin grafted chitosan (graft copolymerization of Chitosan with γ-cyclodextrin in presence of per sulfate/ascorbic acid redox system) is attributed to the selective functionalization of γ- cyclodextrin at 6th position in chitosan as reported by A.K. Mishra [30]. The percentage grafting inclined the adsorption efficiency as by activating the sorption sites on grafts. Accordingly, the adsorbent possessed higher degree of thermal stability and potential of reusability up to 9 cycles. The optimum pH 8.5 for Cd^{2+} removal by grafted chitosan may be attributed to the fact that in acidic medium, the cadmium species exists as hydrated Cd^{2+} [$(Cd(H_2O)_6{}^{2+}$, $Cd(H_2O)_4{}^{2+}$], which finds difficult to get adsorbed as compared to the species($Cd(OH)^+$) existing in the alkaline medium. Moreover, in acidic medium H^+ ions compete for the binding sites of the adsorbent [31].

Table 2. Cadmium adsorption onto modified chitosan composites.

No	Author	Nature of solution / Synthesis Effluent	Optimum "concn. (mg/L)"	Chitosan / deacetylation %	Cross linking reagent	Modified chitosan	pH/ Equilibration time " (hrs)"
1.	A.K. Mishra and A.K. Sharma, [31]	$Cd(NO_3)_2$. $4H_2O$	100	Flakes / 85	γ- cyclodextrin	Ch-graft-γ-cyclodextrin	8.5/ 4.5
2.	D.Chauhan [30]	Electroplating industry, Kanpur City, UP, India ; $Cd(NO_3)_2 \cdot 4H_2O$	75	Flakes / 85	Glutaraldehyde / Thiourea	Thio Carbomyl-chitosan	7.5 / 4
3.	N.Sankaramakrishnan [32]	Electroplating industry, Kanpur City, UP, India ; $Cd(NO_3)_2 \cdot 4H_2O$	100	Flakes / 85	Glutaraldehyde / NaOH, CS_2	Xanthated chitosan	8 / 16
4.	Mahendrakumar [33]	$Cd(NO_3)_2 \cdot 4H_2O$	50	Beads / 100	Glutaraldehyde / PVA Toluene, chlorobenzene	chitosan-PVA blend beads	6/ 7
5.	SeyedMasoudSeyedi [34]	$CdCl_2$. $2H_2O$	50	Beads / 90	sodium triphosphate, NaCl	Nano chitosan	4.6 / 1

D. Chauhan [31], reported that the cadmium-thiocarbomyl chitosan system is pH dependent, where in higher pH values are not resorted to due to the precipitation of Cd^{2+} ions as hydroxides. The low uptake capacity of Cd^{2+} ions and lower pH values could be attributed to the protonation of amino groups and unavailability of the amine groups for complexation with cadmium. Another aspect could be attributed to the competition of H^+ ions compete with Cd^{2+} ions to same binding sites on the adsorbent.

N. Sankaramakrishnan [32], observed that, introduction of xanthate group in chitosan flakes (cross linking with glutaraldehyde and carbondisulfide under alkaline condition) increased the adsorption capacity at about four times against that of plain flakes. Xanthate group being a soft base and tends to form stable complexes with metals (such as Cd^{2+}, Pb^{2+} and Cu^{2+}). The optimum pH for the removal of Cd^{2+} ions was found to be 8.0. At pH8 cadmium predominantly exist as Cd $(OH)^+$ species. Hydroxyl metal complexes are known to adsorb with a higher affinity than the completely hydrated metals because the formation of OH group on the metal reduced the free energy requirement for adsorption [34]. Therefore, it seems that the adsorption of Cd^{2+} ions can be related to the change in the availability of Cd $(OH)^+$.

Mahendrakumar [33], ensured that, the preparation of Chitosan – Poly (vinyl alcohol) beads (suspension of Chitosan – Poly (vinyl alcohol)aqueous solution in a mixture of toluene and chloro benzene followed by cross linking with Glutaraldehyde) enhanced the chemical stability with reduced swelling behavior. This is because with the increase in pH from 2, de protonation of chitosan amino groups take place and hence the adsorption of Cd^{2+} increased. According to the author, all adsorption studies were carried out in low acidic medium (pH 6.0).

Nano chitosan is found to be influenced by pH factor, the range being 2-7, beyond which it may be related to Cd $(OH)_2$ formation in Cd^{2+} removal as reported by Seyed Masoud Seyedi [34]. Also nano chitosan possess high rate of adsorption driven by temperature, due to the reduction in the binding energy.

The application of sorption on the commercial scale requires proper quantification of the sorption equilibrium for process simulation. Langmuir and Freundlich equation has been frequently used to give the sorption equilibrium. The Langmuir equation is applicable to homogeneous sorption wherein the sorption of each sorbate molecule on to the surface has equal sorption activation energy. Freundlich isotherms describe the homogeneity of the system, reversible adsorption nature and not restricted to the monolayer formation.

The isothermal constants and correlation coefficients for adsorption of Cd^{2+} from the electroplating effluents and synthetic waters under varying modifications are listed in **Table 3.**

Table 3. Isothermal constants and correlation coefficients.

S.No	Adsorbent	Langmuir Isotherm			Freundlich Isotherm		
		Q_{max} (mg/g)	B (mL/mg)	R^2	K_f	1/n	R^2
1	Ch-g-γ- CD [31]	833.33	0.0089	0.9923	33.65	0.4820	0.9747
2.	Thio Carbomyl chitosan [30]	666.70	0.0582	0.9667	6.46.	0.6711	0.9806
3.	Nano Chitosan [34]	358.00	0.0445	0.9944	15.70	0.5617	0.9884
4.	Xanthated chitosan N.Sankaramakrishnan [32]	357.14	0.0660	0.9774	29.83	0.0872	0.8255
5.	Chitosan –PVA Blend [33]	106.40	0.0290	0.9970	23.06	0.6900	0.9830

From the isothermal constants and correlation constant values **(Table 3)**, it is obvious that the Langmuir model yielded the best fit with the better R^2 values than the Freundlich model. This implies that Langmuir isotherm is the most suitable equation to describe the adsorption equilibrium of Cd^{2+} onto chosen chitosan composites.

The highest Q_{max} of Ch-g-γ- CD [30] proved to be very effective adsorbent as compared to other composites mentioned in this paper. The hydrophobic nature of γ-CD provides maximum metal binding sites to the Ch-g-γ- CD. The grafted chains may be the reason for the removal of metal ions from wastewater than the parent polymer.

Xanthate chitosan [32] is found to be better than the nano chitosan [34], even though the Q_{max} values are almost same. It may be due to the higher pH maintained in xanthate chitosan experiment. Also, the xanthate chitosan adsorption had been carried out for industrial effluent rather in the case of nano chitosan its only synthetic solution. This is the another valid point to consider xanthate chitosan to possess better sorption capacity as compared to nano chitosan.

Sulphur has a very strong affinity to most of the heavy metals with the formation of a stable metal- sulphur complexes (may be of HSAB principle). The sulphur containing xanthate [32] and thiocarbomyl chitosan [31] treat the industrial effluent, but thiocarbomyl chitosan shows high Q_{max} value due to the presence of nitrogen and oxygen with sulphur.

A large Q_{max} difference between Ch-g-γ- CD[30] and Ch- PVA[33] blend is observed. The chemistry behind which shall be that in case of Ch- PVA, the glutaraldehyde cross linking blend converts $-NH_2$ group into the salt resulting in lesser adsorption and thence the Q_{max} value.

CONCLUSION

An extensive study on the adsorption of heavy metals using chitosan and its composites has been carried out worldwide since 1970. This review paper has chosen a few chitosan derivatives (employed by researchers) as potential sorbents in the removal of Cd^{2+} ion. This is because, although chitosan itself is known for its metal adsorption property, the cross-linking improves the mechanical strength and selectivity of the chitosan composites. Among the chitosan composites compared in this paper, chitosan grafted polymer was found to possess better chelating property in the effective removal of Cd^{2+} ions with a Q_{max} value of

833.33mg/g. The comparison of the derivatives, being the objective of the paper shall have a great room in the hope that chitosan composites can be applied to remove one of the toxic "big three" (Cd^{2+} ion) commercially.

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