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Modifications of Chitosan with Different Functional Groups and Their Applications to Adsorption: A Review

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Abstract: *Chitosan obtained by deacetylation of second most abundant natural biopolymer 'Chitin' is found as the most reasonable material in the adsorption due to presence of the amino functional groups as well as hydroxyl groups in its molecule. These functional groups act as adsorbent sites for various types of organic like dyes, pesticides, phenols, drugs etc. as well as inorganic pollutants like heavy metal ions and others. The amino and hydroxyl groups on chitosan can be modified (grafting, cross-linking, etc.) to enhance physical, mechanical and adsorption qualities of this material. Related to the knowledge obtained from research papers published previously in literature, scientists have done many modifications of chitosan molecule by reacting with suitable reagents that react with the functional groups on this molecule to increase number of binding sites and adsorption capacity. This review compiles the research work of the last few years showing modifications in chitosan and its adsorption capacity towards various pollutants in water bodies.*

Keywords: *Chitosan, grafting, cross-linking, modification, adsorption, contaminants, dyes, heavy metals, adsorption capacity.*

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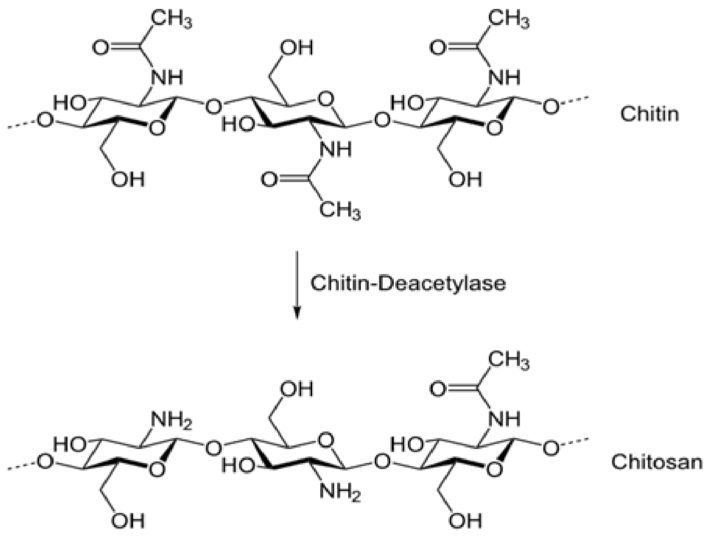
I. Introduction

Among three basic natural resources on earth i.e. air, water and soil, water is the most necessary component without which one cannot servive and is essential for all activities related to mankind but now a days, we are not getting clean and sufficient amount of water. This may be due to rapid expansion of industrialization and population. So scarcity of good drinking water in developing countries is of great concern. Nearly three-fourth of the fresh water of Indian water bodies is now changed into being tasteless and unfit for consumption. Not only India, but other countries are also suffering from the same problem. Basically, the contaminants add into ground water from three main sources- sewage disposal, agricultural runoff from agricultural land, where farmers make use of chemical as well as biofertilizers, insecticides, pesticides and industrial effluents [1-4].

This makes the water unfit for drinking and bathing. More than 1000 substances have been proved as contaminants in freshwater bodies and the list of those includes acidic and basic materials, some anions (e.g. nitrates, sulphide, chloride, cyanide etc.), strong detergents and soaps, domestic waste and manure, heavy metals (cadmium, iron, cobalt, zinc, lead etc.), farm nutrients, organic toxic components and radio nuclides etc. Heavy metal contamination of ground water is a major environmental problem due to their strong toxicity of some even at low concentration. Therefore, various water purification techniques like filtration, coagulation, precipitation, ion exchange, adsorption, reverse osmosis, chemical oxidation, electro dialysis etc. have been used for removal of these pollutants [5-7]. All mentioned methods except adsorption are operative with the release of very toxic by-products and are noticed as very costly. So, Adsorption comes out as a better substitute because of its low operating cost and formation of no side products. Adsorption is a process when any gas or liquid solute gets collected over the liquid or solid surface (adsorbent) forming a layer of adsorbate. This accumulation of adsorbate over adsorbent surface may occur due to some physical or chemical interactions. Many natural and synthetic adsorbents have been used in water treatment [7-8].

In recent years, researchers are showing great interest in using natural polymers as adsorbents as these materials are not very expensive. In fact these are easily available and also ecofriendly in use. There are many biopolymers which are proved as good adsorbents due to presence of functional groups like hydroxyl and amino groups that acts as binding sites for various types of contaminants present in water and helps in easy removal of these toxic materials. After adsorption, the adsorbent can be regenerated back using suitable reagents which make this technique superior over others. Among various biopolymers, Chitosan obtained by deacetylation of chitin is found as the most applicable material in the adsorption due to presence of the amino functional groups as well as hydroxyl groups in its molecule.



These functional groups act as adsorbent sites for various types of organic as well as inorganic pollutants. The amino and hydroxyl groups on chitosan can be modified (grafting, cross-linking, etc.) to enhance physical, mechanical and adsorption qualities of this material. Grafting increases the number of binding sites for adsorption of contaminants [7-10].

II. Review of Literature

After large literature review, it is conceived that among so many methods used for waste water treatment, adsorption process found best to remove certain categories of contaminants, especially nonbiodegradable. Activated charcoal is widely used as an adsorbent in wastewater treatment, but it remains an expensive material due to its high cost. Numerous cost effective adsorbents are mostly natural modified adsorbents, agricultural waste materials e.g. Rice straw, wheat bran, sugarcane baggage, onion etc., industrial by products waste and many micro-organism species [5-7]. Various industrial adsorbents such as fly ash, blast furnace sludge, slurry waste material, lignin, coffee pulp, sugar beet pulp material, waste material of tea factories have been investigated for the elimination of heavy metals and many organic substances. Among biosorbants, algae are one of the autotrophic organisms that has been tested and used as biosorbent material to adsorb toxic heavy metals. Its low cost, easy availability with more metal sorption capacity makes it more beneficial biosorbent. Fungi and yeast are other biosorbents that are used in the removal of heavy metal contaminants. They can be grown easily and produces large biomass; it shows good metal binding properties because of presence of cell wall material in large quantity. Above all are natural polymer based adsorbents [11-15].

2.1 Natural polymer based adsorbents.

In recent years, researchers are showing great interest in the syntheses of adsorbants, those are based on use of natural polymers (Cellulose, Lignin, Chitin, Chitosan etc.). It is due to their large abundance, comparatively less expensive and eco-friendliness. Structural features of Chitosan prove it as one of the most effective material for adsorption.

Chitosan is a polysaccharide obtained by deacetylation of chitin. Chitin is characterized as second most abundant natural biopolymers. It is mainly found in marine culture i.e. especially in the crustaceans, molluscs, insects and cell walls of some micro-organisms. Chitosan is found as the most reasonable material in the adsorption due to presence of the amino functional groups as well as hydroxyl groups in its molecule. These functional groups can be subjected to grafting i.e. conversion into other functional groups that may have more number of binding sites or sites having better adsorption capacities. Chitosan molecule is highly soluble in water as well as in acidic medium that inhibits its use as adsorbent in these medium. In order to get rid of this problem, chitosan is treated with certain reagents to create crosslinking between polymer chains that widen its area of application.

2.1.1 Adsorption of Metal ions

Chitosan and its derivatives obtained on modification by grafting have very good donor atoms like oxygen, nitrogen etc. to coordinate with metal ions. However, these molecules act as effective adsorbents for various metal ions. Table 1 summarized the recent research work on modification of chitosan by grafting as well as cross linking. Few derivatives are composites of chitosan with other effective adsorbants and their adsorption capacity with different heavy metals.

Table1. Adsorption of metal ions over chitosan based adsorbents

Chitosan Derivatives as Adsorbents	Metal ions Adsorbed	Adsorption Capacity(mg/g)	Reference
Chitosan with Histidine Modification	Ni(II)	56	[16]
Chitosan with Xanthate Modification	Co(II)	18.5	[17]
Carbon Nanotubes with Chitosan Modification	U(VI)	71	[18]
3,4-Dimeyhoxybenzaldehyde grafting of Chitosan	Cd(II)	216.4	[19]
Chitosan with Ethylene-1,2-diamine	Pb(II) & Zn(II)	32 & 20	[20]
Chitosan and Graphene oxide Composite	Cr(VI)	81.9	[21]
Tetraethylenepentamine grafted Chitosan	UO_2(II)	486	[22]
Carboxymethylated Chitosan	Fe(III)	9.3	[23]
Chitosan with Ethylenediamine Modification	Pb(II)	121	[24]
Chitosan grafted with Glycine	Co(II)	83	[25]
Chitosan with Glutaraldehyde crosslinking	Hg(II)	662	[26]
Epichlorohydrin crosslinked Chitosan	Cu(II)	146	[26]
Chitosan with EDTA	Co(II)	80	[27]
Chitosan with N-Butylacrylate	Cr(VI)	17	[28]
Citosan with Citric Acid crosslinking	Pb(II)	102	[29]
Chitosan modified with Triethylene tetramine	Th(IV)	133	[30]
Chitosan modified with Diethylene triamine	U(VI)	65	[31]
Chitosan with Ketoglutaric acid	Cd(II)	201	[32]

2.1.2 Adsorption of dyes

Dyes represent another problematic group. Basically, activated charcoal is used as decoloriser to remove dyes from wastewater, but it is very costly. Then some other cost effective sorbents like waste material from industrial effluents, agricultural wastes and biosorbents were investigated. Along with these low-cost adsorbents chitosan and modified chitosan proved to be a promising adsorbent for dyes also. Literature studies reveal that these natural polymer based adsorbants have outstanding removal capabilities for certain dyes. Table 2 presents few chitosan based adsorbents for dyes.

Table 2: Adsorption studies of Dyes over chitosan based adsorbents

Modified Chitosan Adsorbent	Dye	Adsorption capacity (mg/g)	Reference
Graphite oxide and Chitosan composite	Reactive Blue 5	277	[33]
Chitosan with Cyclodextrin	Methylene Blue	2789	[34]
Chitosan and SBA-15 composite	Acid Red18	201	[35]
Polymethylmetha-acrylate grafted Chitosan	Reactive Blue19	1498	[36]
Chitosan bentonite composite	WASC	102	[37]
Reactive red 120 grafted Citosan	Lysozyme	117	[38]
Chitosan Zeolite composite	Burnt orange liquid dye	305	[39]
Polypropyleneimine grafted Chitosan	Reactive Blue 5	6250	[40]
Chitosan grafted with diethylenetriamine	Acid orange 7	6.1	[41]
Carbon nanotubes and Chitosan composite	Congo Red	263	[42]

Chitosan and modified ball clay composite	Methylene Blue	260	[43]
Graphite oxide and Magnetic Chitosan nanocomposite	Reactive Blue 5	391	[44]

2.1.3 Adsorption of other organic species

Chitosan composites also proved as good adsorbent for many organic species other than metals and dyes like pesticides, herbicides etc. Table -3 summaries few records of modified chitosan and their adsorption capabilities.

Table-3: Adsorption studies of some organic pollutants using modified chitosan adsorbents

Modified Chitosan Adsorbents	**Organic Pollutants**	**Adsorption Capacity (mg/g)**	**Reference**
Chitosan with Glutaraldehyde cross- linking	4-nitrophenol	57.5	[45]
Magnetic Chitosan	Diclofenac	191	[46]
Chitosan with cross-linking of cyclodextrin	Phenol 4-chlorophenol 2,4,6-trichlorophenol	60 70.5 376	[47]
N-(2-Carboxybenzyl) grafted Chitosan	Pramipexole	307	[48]
Chitosan and Graphite oxide composite	Dorzolamide	334	[49]

2.2 Regeneration of Adsorbent

Regeneration of modified chitosan after pollutants adsorption is one of the areas in which researcher are showing much interest world widely. The regeneration of adsorbent is one of the cost effective process which low down the cost of adsorbent and open the possibility of recovering the pollutants from surface of adsorbent. Literature studies reveal that various types of desorption agents has been used for regeneration of adsorbents. These desorption agents are as

a) Acid solution as HCl, HNO_3 in aqueous form as desorption agent
b) Basic solution as NaOH, Na_2CO_3in aqueous form as desorption agent
c) EDTA solution as desorption agent

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