The Pharma Innovation Journal 2016; 5(1): 92-95

www.ThePharmaJournal.com

The Pharma Innovation

ISSN: 2277- 7695
TPI 2016; 5(1): 92-95

www.thepharmajournal.com
Received: 12-11-2015
Accepted: 13-12-2015

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Eco friendly chitosan: An efficient material for water purification

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Abstract
Chitosan is a versatile bio polymer with unique structural features. It binds effectively with fine suspended particles, pollutants, bacteria, heavy metals etc. The biocompatible and biodegradable nature of chitosan makes it a potential candidate for water purification purpose. Over the last few years, the research on biomaterials like chitosan has opened new possibilities to develop water purification systems with non toxic in nature and no residual impact on the environment. The polymer chain with abundant -NH_2 and–OH groups acts as multiple bonding sites to interact with various molecules. The chemical composition of chitosan clearly shows that it is a natural polysaccharide (a simple polymeric sugar) which is completely non-toxic for living organisms.

Keywords: Chitosan, Coagulant, Anti microbial, Natural polymer

1. Introduction
Water is a life sustaining drink and is essential for the survival of all living organisms. However, there are toxic contaminants present in water that cause many life threatening health risks. So, water should be protected from contamination for public health cause and environmental reasons. The potable water obtained from raw resources requires a crucial step of removal of turbidity present in the form of suspended and colloidal materials. Along with this, removal of organic compounds, bacteria, algae and colour is also an important step in surface water treatment process. These steps dramatically reduce the risk of waterborne diseases. Rapid development of industries in the past century has increased the level of heavy metals in our food and water system [1]. Therefore, efficient removal of these pollutants/contaminants from water is a major environmental concern. There are various types of commercially available organic/inorganic synthetic polymers for water treatment purpose [2, 3]. These polymers have good anti-microbial activity and superior flocculation efficiency. However, they do have residual impact on the environment. These polymers are synthetic in nature and are often non-biodegradable. This is the reason that a sustainable and environment friendly material for water purification purpose has become a considerable interest in the field of research.

Chitosan is a natural linear biopolymer extracted from the exo skeleton of the sea crustaceans (crabs, prawns, lobsters, shrimps etc.). It is a sea food waste which is produced in abundance at coastal areas. However, this humble looking material possesses outstanding combination of properties required for water purification, food industries, cosmetics, biomedical applications [4, 5]. In addition to this, chitosan is inexpensive, biodegradable and nontoxic for mammals [6]. Chitosan is natural water coagulant/flocculent and is able to reduce turbidity, colour, clay particles etc. from water. Additionally, considerable savings in chemicals and sludge handling is achieved by using a natural coagulant like chitosan [7]. Chitosan is also effective in removal of organic pollutants, heavy metals, bacteria etc. The U.S. Environment Protection Agency (EPA) has given an official authorization to chitosan for drinking water purification.

2. Structure of Chitosan
Chitosan is a linear biopolymer (Fig. 1), having beta $1 \rightarrow 4$ linked units of poly (d-glucosamine) (80%) and poly (*N*-acetyl-d-glucosamine) (20%). Chitosan is extracted from chitin by removal of acetate moiety through hydrolysis (deacetylation) under strong alkaline conditions (Fig. 2).

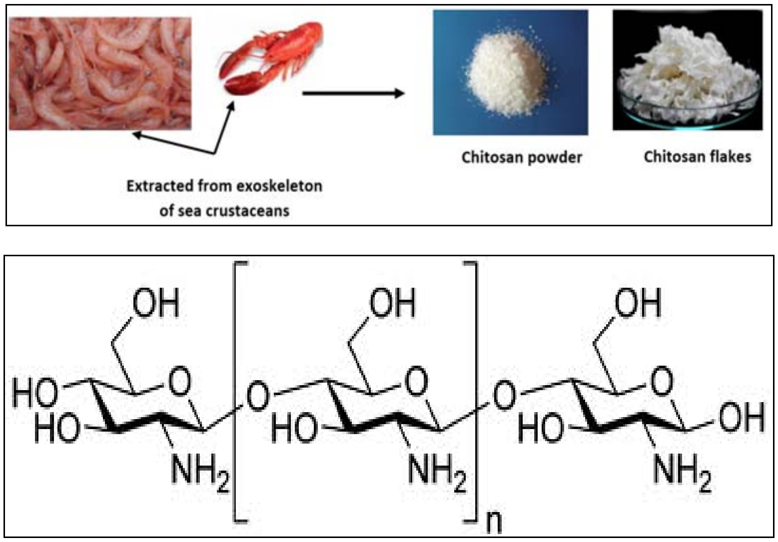

Fig 1: Chitosan, a polysaccharide with β-(1-4) linked glucosamine units

The available glucosamine and acetyle glucosamine units in the chitosan depend upon the degree of deacetylation of chitin. The degree of deacetylation (number of $–NH_2$ and $-CH_3CONH_2$ groups) controls properties such as solubility, acid base behaviour etc. The Scanning Electron Micrograph (SEM) of chitosan particle is shown in Fig. 3a. The amine groups present in the chitosan becomes protonated when dissolved in an aqueous medium below pH 6.0. Under this condition, chitosan turns into a linear polycationic electrolyte with high positive charge density. The Transmission Electron Micrograph (TEM) of chitosan dissolved in 1% acetic acid solution is shown in Figure 3b.

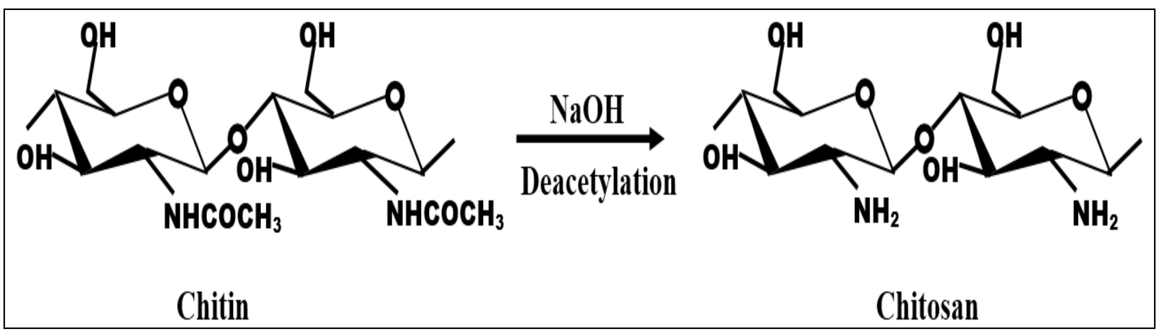

Fig 2: Deacetylation process by which chitosan is obtained from chitin.

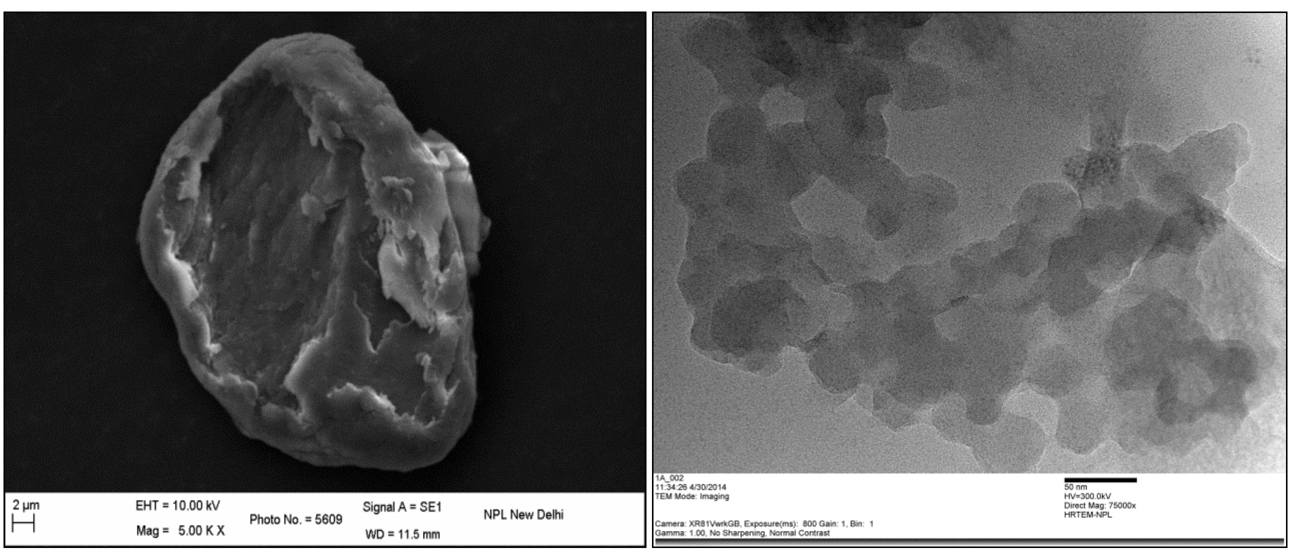

Fig 3 (a): SEM micrograph of chitosan particle. (b) The TEM micrograph of the chitosan after dissolution in 1.0% acetic acid solution.

3. Physical and Chemical Properties of Chitosan
Various naturally occurring polysaccharides like pectin, agar, dextrin, cellulose etc. are acidic in nature, whereas, chitosan is highly basic in nature because of the presence of protonated amine groups (NH_3^+) along the polymer chain. Fig. 4 illustrates the conversion of $-NH_2$ groups of chitosan into $-NH_3^+$ groups. The polycationic nature of the chitosan is the basic reason for its unique properties like metal chelation, ability to form films, ability to bind with microbial cells, viscosity, solubility in various media, optical and structural characteristics etc.

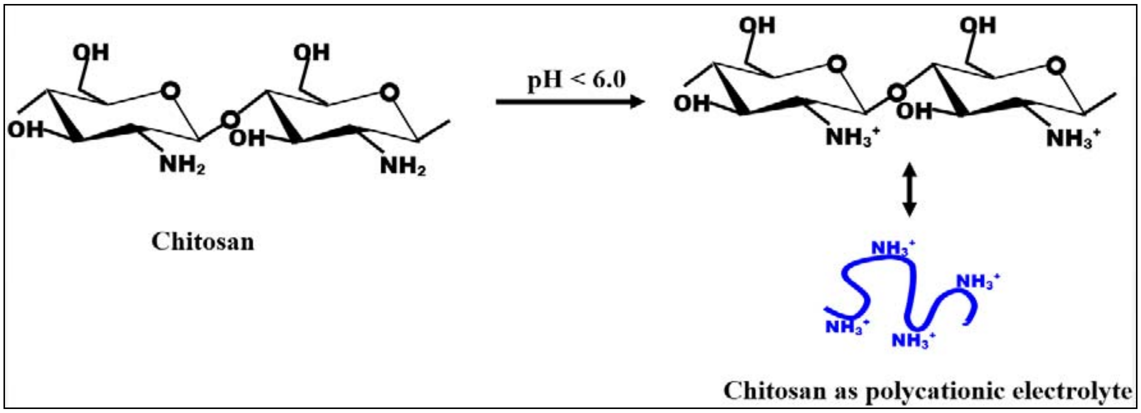

Fig. 4. Conversion of chitosan to a polycationic electrolyte at pH < 6.0.

In chitosan, there exist one $-NH_2$ group and two –OH groups in each glycosidic unit. Because of the presence of these two reactive groups, chitosan exhibit useful chemical and biological properties. This unique structural arrangement is the reason of the rigid crystalline structure of chitosan due to inter/intra molecular hydrogen bonding.

4. Chitosan for Water Purification
4.1. As a coagulant
Removal of fine suspended particles from water is the preliminary step of water filtration/purification process. The poly cationic nature of chitosan carries positive charges along the polymer chain. A long chain polymer like chitosan can effectively coagulate natural particulates and colloidal materials, which are negatively charged. Electrostatic interaction, adsorption, charge neutralization, inter-particle bridging as well as hydrophobic flocculation works here [8]. Thus chitosan helps in agglomeration/flocculation of the particles (Fig. 5). These particles settle down in water and easily filtered. Flocculation through chitosan is easy, simple to carry out, cost effective and free from toxic chemicals.

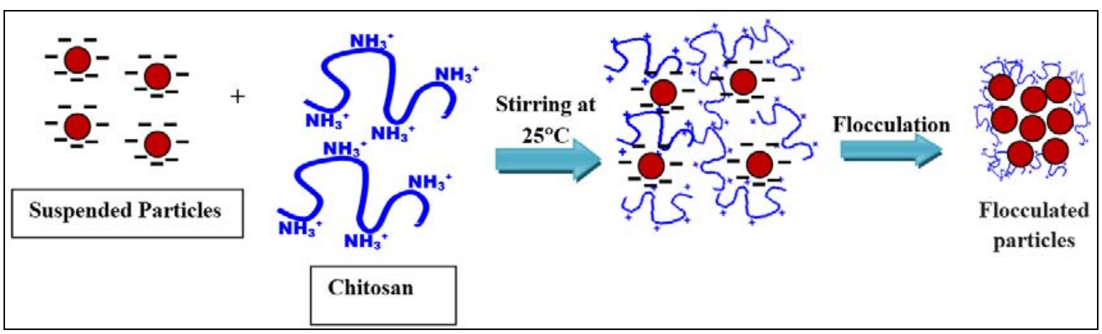

Fig 5: Mechanism of flocculation of particles using chitosan.

4.2. Removal of heavy metals
Heavy metals like Copper, Nickel, Mercury, Lead, Zinc, Arsenic etc. are extremely toxic and are bio persistent in nature. Chitosan has a tendency to bind/chelate with metal ions like cadmium, copper, lead, mercury etc. The amine groups present along the polymer chain are strongly active with metal ions [9]. At pH close to neutral (when $-NH_2$ groups are not protonated), chitosan reacts with metal ions as follows (eq. 1).

$$M^{n+} + RNH_2 \longleftrightarrow M(RNH_2)^{n+} \qquad (i)$$

The amine groups form coordinate bonds with the metal ions (as shown in Fig. 6) by the donation of free electrons present on nitrogen and oxygen in the amine groups and hydroxyl groups, respectively, to the vacant orbitals of the metal. The metal binding efficiency of chitosan depends on the availability of the amine groups (high degree of deacetylation) for interaction with metal ions, chain length, extent of inter/intra molecular hydrogen bonding etc.

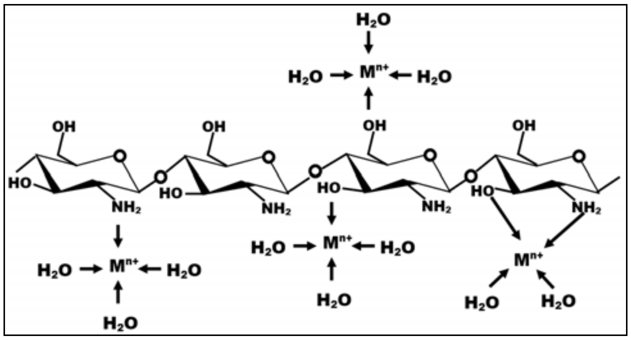

Fig. 6. Mechanism of removal of metal ions by chitosan.

4.3. Removal of organic compounds
Chlorine is used as disinfectant for drinking water. However, chlorinated hydrocarbons such as trichloromethane, di-chlorobenzene and chlorophenol are also formed as by products. These chlorinated hydrocarbons are carcinogenic in nature. Chitosan can effectively eliminate trichloromethane from water as the amine groups present along the chitosan chain integrates with the halides in water. Chitosan can also effectively adsorb organic matters such as phenols, polychlorinated biphenyls, pesticides, surfactants etc.

4.4. Efficient removal of bacteria
Chitosan (positively charged) can be used to design reverse osmosis/ultrafiltration membranes to filter, adsorb and kill the microorganisms (negatively charged) in a natural way. Antimicrobial effects of chitosan are attributed to its flocculation and bactericidal activities. Roussy *et. al.* [10] has reported a bridging mechanism for bacterial coagulation by chitosan. Chitosan molecules bind on the microbial cell surface (Fig. 7) and form an impervious layer around it. Thus they alter the cell permeability and causes leaking of the intracellular constituents and ultimately death of the microbial cell.

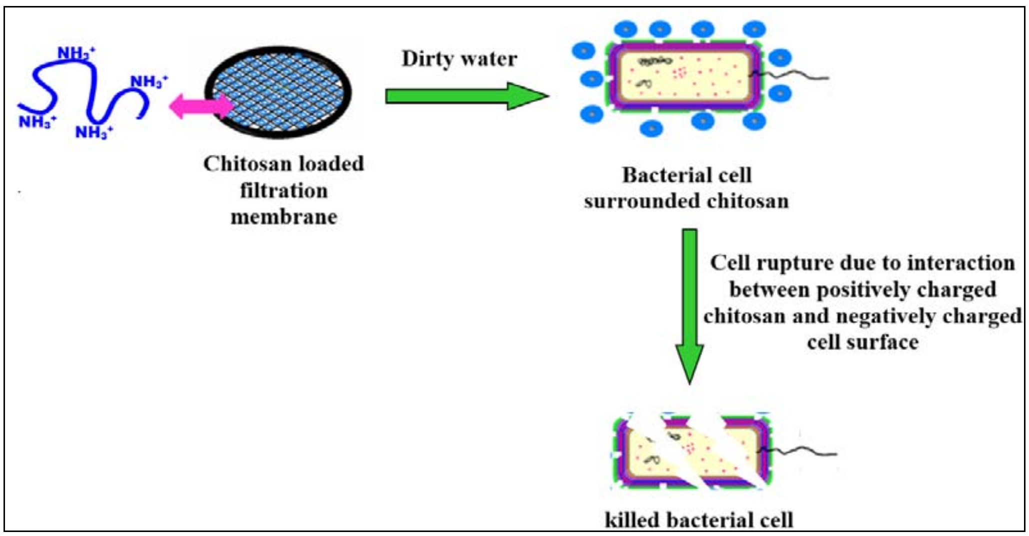

Fig 7: Mechanism of killing of bacterial cell by chitosan.

5. Conclusion and Future Prospects
The article illustrates the importance of chitosan in the field of water filtration/purification. Chitosan is a natural, nontoxic, biodegradable, biocompatible polymer suitable for water purification purpose. Apart from this, chitosan based nano materials can be explored to evaluate their potent in wide range of promising applications. Different methods can be adopted to synthesize chitosan based nano composites/nano hybrids with more advanced water purification capabilities. In addition to this, modifications in chitosan can be carried out to tailor different properties like cationic, anionic, hydrophilicity etc. The amine groups and hydroxyl groups of chitosan chain can be modified chemically to form nano particles, nano sheets, hydrogels etc. with unique properties.

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