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# Blended Composites of Chitosan: Adsorption Profile for Mitigation of Toxic Pb (II) Ions from Water

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Vrushali Kinhikar

Additional information is available at the end of the chapter

## Abstract

An environmental pollution is the unfavorable alteration of surrounding toxicity due to heavy metals, organic pollutants, radioactive materials, pesticides, dyes, pigments, fatty/oil impurities and minerals that are responsible for crucial ecological and health concerns. The indiscriminate industrial and anthropological activities render water resources unsuitable for consumptions. Percolations of synthetic pollutants in water are responsible for detrimental effects on aquatic flora and fauna. Environmental contamination of water poses the major challenge to develop efficient water treatment techniques based on usage of biopolymers. Hence, chitosan (de-acetylated chitin: $\beta$-(1 → 4) D-glucosamine) biosorbent is preferred which is cheap, biodegradable, and biocompatible for the mitigation of few heavy metals from water. Chitosan's flexible skeleton was modified by doping few organic/inorganic moieties to yield biocomposites for adsorption of varied pollutants. In this chapter, the batch adsorption of toxic Pb (II) ions from water using graphite doped chitosan composite (GDCC) as an adsorbent is discussed. Maximum Pb (II) ions adsorption capacity was 6.711 mg/g (from Langmuir) at optimum pH 6 with dosage of 1 g/L in 120 min. Biosorption mechanism is emphasized in context with wastewater cleanup procedures.
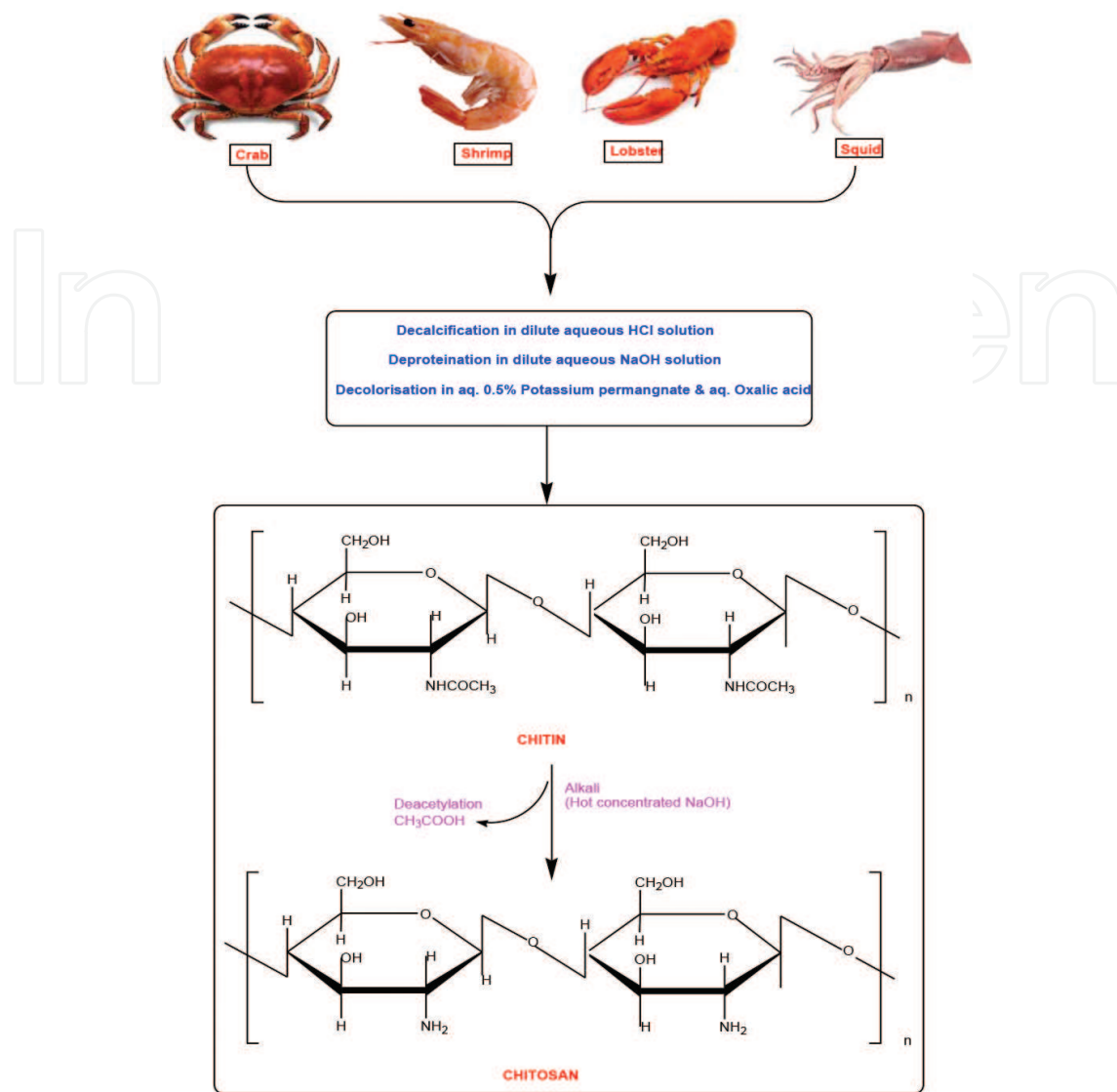
**Keywords:** chitosan, graphite, GDCC, Pb (II) ions, water, adsorption

## 1. Introduction

Chitin (pronounced as Kite-in) is the precursor of chitosan (pronounced as Kite-o-san) was first discovered in 1811 by a Frenchman named Henri Braconnot as a result of extraction

**Figure 1.** Chemical structures of chitin and chitosan.

from the fungus. Later on in the year 1820, it was derived from the skin of insects. In 1859, C. Roughet obtained "modified chitin" from chitin treated with alkaline sodium hydroxide solution. However, in 1894, F. Hoppe-Seyler treated chitin with different alkaline solution of potassium hydroxide at 180°C and the product called as Chitosan [1]. In 1902, Frankel and Kelly recognized the chemical composition of chitin and chitosan, and in the 1950s, several researchers such as H. Sponsler and W.H. Dore have determined their chemical structures through X-ray experiments.

Chitosan is a hydrophilic natural polymer produced by alkaline deacetylation of chitin, which is the most abundant biopolymer occurring in nature, after cellulose and an exoskeleton part of crustaceans such as shrimp, lobsters, and crab shells [2]. Chitin and chitosan are commercially produced in countries like India, Japan, Poland, Norway and Australia. Chitin and chitosan are nitrogenous polysaccharides that consist of acetyl glucosamine and glucos-

amine units. Chemically these two polymers are β-(1–4)-2-acetamido-2-deoxy-*D*-glucan and β-(1-4)-2-amino-2-deoxy-*D*-glucan, respectively (**Figure 1**). The difference between the chitin and chitosan lies in the degree of deacetylation (DD) and their solubility in 0.1 M dilute acidic medium. If the degree of deacetylation of chitin falls to 50%, then it becomes soluble in aqueous acidic media such as acetic acid, propionic acid, and so on. [3]. The insolubility of chitosan in water, alkaline medium and organic solvents is due to the presence of hydrogen bonds between its molecules; however, the protonation of amine group renders its solubility in acidic solutions [4]. The DD affects the adsorption capacity of the chitosan. High DD generally results from the presence of high amounts of amino groups, and it can increase the adsorption capacity of chitosan by protonation [5].

Chitin and chitosan possess molecular weight up to several million g/mol. Commercially available chitosan has an average molecular mass ranging from 3800 to 500,000 g/mol and its degree of *N*-acetylation is 2–40% [6]. Deacetylation of chitosan ensures the presence of free amino groups that can be easily protonated in an acidic environment, making chitosan as cationic polyelectrolyte (pKa ≈ 6.5) and water soluble below the pH of 6.5 [7]. It shows high affinity for water pollutants adsorption due to the presence of amine ($-NH_2$) and hydroxyl (–OH) functional groups that act as chelating sites. This integral amine functionality (primary, secondary and tertiary) acquires positive charge in acidic condition and thus become sorption site for anions. Chitin and chitosan are of commercial interest due to their high nitrogen content (7.21%) compared to synthetically substituted cellulose (1.25%) and their excellent properties such as biocompatibility, biodegradability, non-toxicity and adsorptive abilities. It was found that chitosan is highly selective with respect to the uptake of metal ions. It shows an uptake of transition and post-transition metal ions and does not allow the sorption of alkali and alkali earth metal ions from the aqueous solution [8]. These selective adsorption properties have been used for environmental cleanup viz. uptake of heavy metals ions, pesticides, dyes/pigments, radionuclide, and so on from the polluted water resources.

## 2. Chitosan modification

Although of its several broad spectrum advantages, it has severe limitations viz. lower chemical and mechanical stabilities (due to hydrophilic nature), high pH sensitivity, and solubility in most organic acids, non-porosity and low specific surface area. These inadequacies limit its usage in wastewater treatment applications. Thereby to overcome all of these pitfalls and to tailor it for the specific wastewater treatment application, several attempts for its physical and chemical modification to achieve their biocomposites/nanocomposites have been conducted. The physical and chemical modification of chitosan was adopted to derive the desired adsorbent's characteristics and to improve its adsorption kinetic parameters feasible for pollutants removal.

**Physical modification** of chitosan has been carried out by various techniques to obtain accomplished polymer as powders, beads, flakes, nanoparticles, hydrogels, films, fibers

membranes, sponge, honeycomb, and so on (**Figure 2**). Chitosan beads and fibers of various porosities can be prepared by neutralization methods (**Figure 3**) where chitosan is treated with acetic acid and mixture added drop wise to 1 M NaOH by using microsyringe [9].
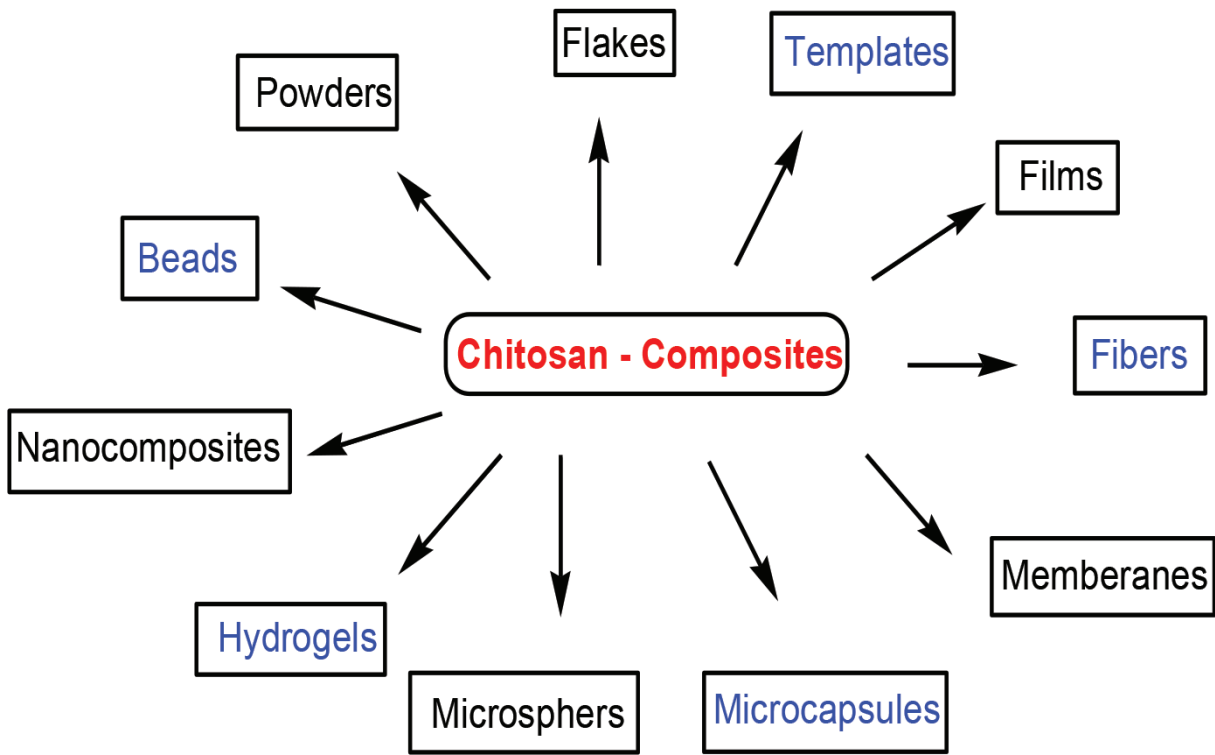


**Figure 2.** Various physical forms of chitosan bio-composites.
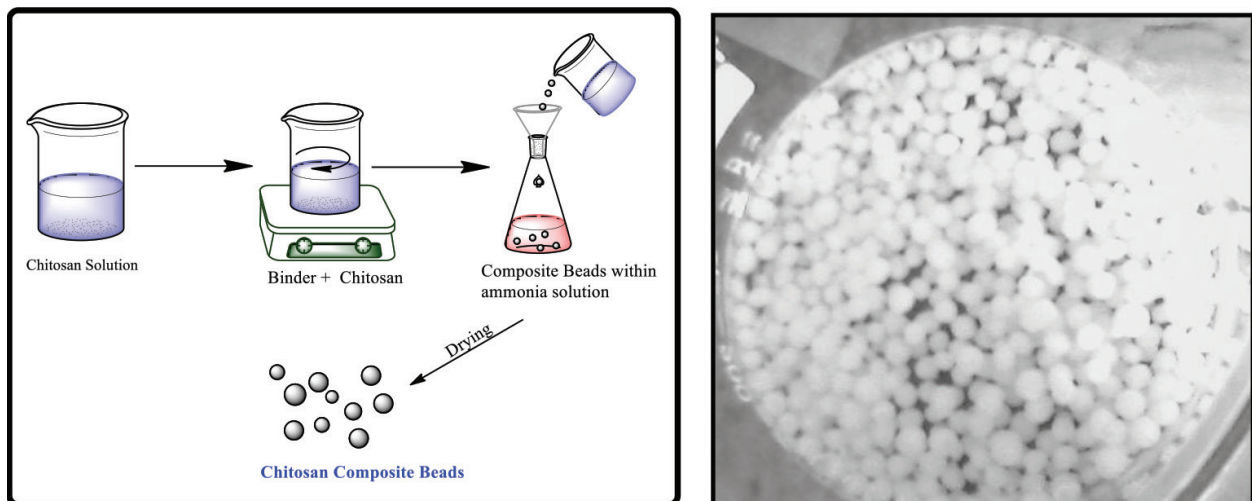


**Figure 3.** Synthesis of chitosan bio-composites beads.

Chitosan membranes can also be synthesized by treating chitosan with acetic acid where the solution is poured into a Petri dish and once the solvent evaporated, the membrane is neutralized with sodium hydroxide [10]. Moreover, chitosan sponges with different porosities can be prepared by freeze-drying techniques where chitosan solutions or gels are frozen followed by lyophilization [9]. One of the attractive ways of physical modification is to provide new desirable characters to chitosan and to synthesize chitosan-based biocomposites by mixing or blending of chitosan with the support or reinforcement matrix [11]. In blending, at least two polymers are mixed to obtain a new material with different physical properties [12]. At thermodynamic equilibrium, the two polymers of amorphous nature appear to be as a single phase or homogeneous on blending with a new set of improved properties from the individual components. The miscibility and compatibility between the blended polymers are decided by their mechanical and thermal properties [13]. The method of blending is effective in practical application due to its simplicity in operation and availability of various organic compounds and natural polymers. Blending permits the wide range of properties by union of both the components viz. chitosan and the reinforcement matrix to achieve physically and chemically stable biopolymers required for the specific applications.

**Chemical modification** is the application of various chemical treatments such as cross-linking, sulfonation, carboxymethylation, depolymerization, nitration, alkylation, sulfonation, phosphorylation, xanthations, Schiff's base formation, alkylation, acylation, hydroxylation and graft copolymerization. Various extensive novel chitosan derivatives can be obtained by chemical modifications. The chemical modification of chitosan has two main objectives: (1) to enhance the metal adsorption properties and (2) to improve the stability of chitosan in water or acidic medium. The chemical modification incorporates the various functional groups in the chitosan may involve the $-NH_2$ group at the C-2 position (specific reactions) or $-OH$ groups at the C-3 and C-6 positions (nonspecific reactions) [3]. The various cross-linking reagents such as glyoxal, formaldehyde, glutaraldehyde, epichlorohydrin, ethylene glycol, diglycidyl ether and isocyanates are commonly used to modify the chitosan but are not preferred due to their toxicity. Cross-linking decreases the adsorption efficiency particularly in case of chemical reactions involving amino groups, but it provides mechanical strength and enhances the stability of chitosan against acidic and basic solutions [14].

Graft copolymerization is also the promising method that allows the covalent bonding between the grafted functional groups onto the chitosan backbone. The objectives of grafting new functional groups on chitosan are to alter the pH range and adsorption sites so that to enhance adsorption selectivity for the target pollutant.

Enzyme-modified chitosan is also one of the attractive methods of chitosan modification due to the reaction specificity. The alteration of the surface and rheological properties of chitosan using hexyloxyphenol which was grafted onto chitosan mediated by tyrosinase [15] has been studied for the modification of chitosan to achieve desired characteristics for the particular applications (**Figure 4**).
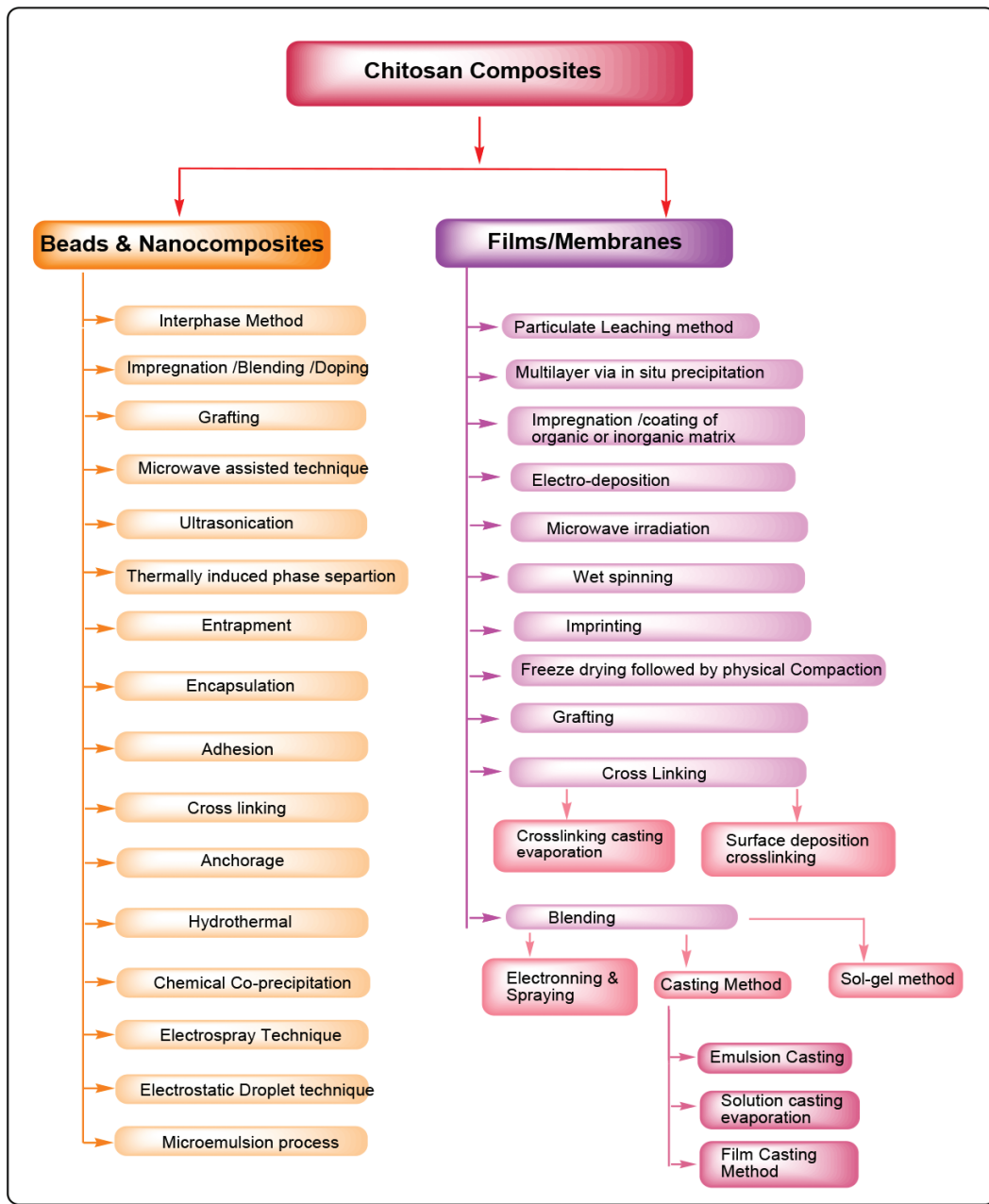
**Figure 4.** Various synthetic methods of chitosan biocomposites.

## 3. Applications of chitosan

Chitosan has wide and vast variety of applications ranging from biomedical and cosmetics products to agriculture and wastewater treatment [16]. The applications of chitosan in various fields and its specific properties responsible for specific applications are tabulated as follows (**Table 1**).

| Applications of chitosan | Properties of chitosan |
| --- | --- |
| Cosmetics | Fungicidal and Fungistatic in nature. Facilitates the interaction with common integuments (skin covers) and hair. Chitin, chitosan and its derivatives offers uses in three areas of cosmetics: Hair, skin and oral care. |
| Paper industry | Chitosan molecules greatly resemble those of cellulose the main constituent of plant walls. It is used in the production of toilet paper, packaging/wrapping paper and cardboard. |
| Textile industry | Antistatic and soil repellant properties of chitin derivatives are used in textile industries. |
| Food processing | Chitosan used in food industry as it is nontoxic to warm blooded animals. Microcrystalline chitin shows good emulsifying properties, superior thickening and gelling agent for stabilizing foods. |
| Agriculture | It acts as plant growth enhancer. |
| Photography | Scratch resistance, optical and film forming property. |
| Chromatographic separation | The presence of free –$NH_2$ group and primary and secondary –OH groups enables its use as chromatographic support by using HPLC. |
| Solid-state batteries | Solubility in acetic acid facilitates ionic conductivity. |
| LED application | Dyes containing chitosan gel have been used as potential component in laser and other light emitting devices (LEDs). |
| Biomedical applications | Such as artificial skin, artificial kidney, wound dressing, drug delivery system and space filling implants. Chitosan has been found to have an accelerator effect on the tissue engineering process owing to its polycationic nature. Chitosan used for burn treatment since it can form tough water absorbent, biocompatible films and shows excellent oxygen permeability. |
| Opthalmology | It possesses all the properties required for an ideal contact lens, optical clarity, mechanical stability, sufficient optical correction, gas permeability, wettability and immunological compatibility. |
| Pharmaceutical application | Since chitin and chitosan do not cause any biological hazard and are inexpensive, these polymers might be suitable for use in the preparation of commercial drugs. |

**Table 1.** Applications of chitosan and its composites in various fields.

# 4. Wastewater treatment application

The toxic heavy metal ions must be detained before its percolation into the water resources to protect the aquatic flora, fauna, human beings and consequently the environment.

To accomplish the increased stringent environmental regulations and maximum permissible limit of contaminants in water, a wide range of treatment technologies such as chemical precipitation, coagulation flocculation, flotation, ion exchange, membrane filtration, electrochemical treatment technologies, adsorption/bioadsorption [17], and so on are most frequently examined. Among the aforementioned technologies, adsorption has been preferred due to its flexible operation, generation of high-quality treated effluent and regeneration of
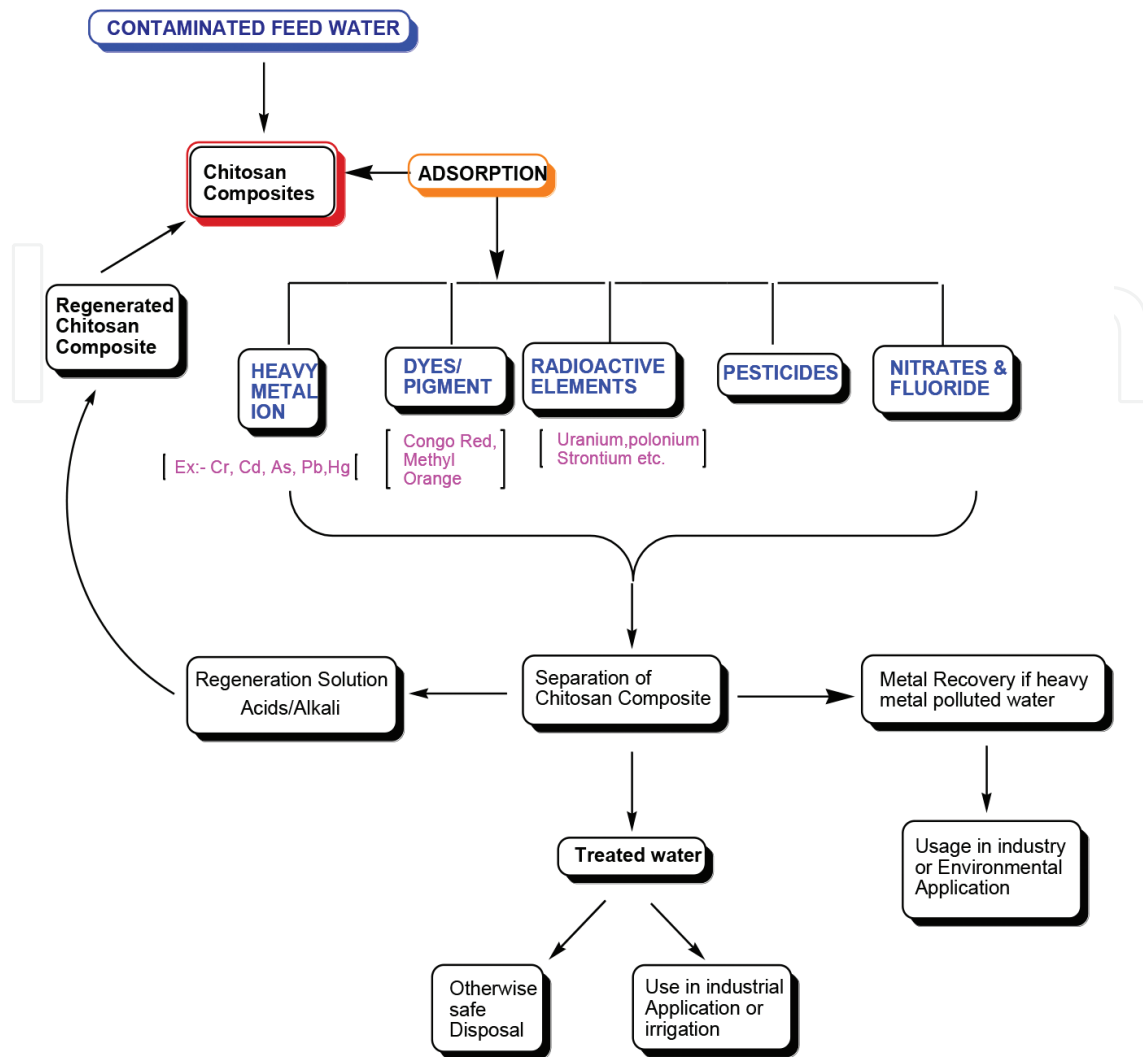
**Figure 5.** Schematic representation of chitosan composite/biocomposite in wastewater treatment application.

adsorbent by desorption. In chitosan, the integral –NH$_2$ and –OH functional groups acts as a chelating sites for the adsorption of various water pollutants viz. heavy metal ions, dyes/pigments, pesticides, and so on (**Figure 5**).

## 5. Heavy metal contamination status in India

The Central Pollution Control Board (**CPCB**) [18] carried out a major groundwater quality survey and the report recognized about 20 critical sites of ground water pollution in various states of India. CPCB found that industrial effluents are the primary and major cause for ground water pollution. The major heavy metals contamination sites including lead metal in Indian scenario are given in **Table 2**.

The heavy metal lead (Pb) was considered as father of all metals during Roman era. Much of its gratitude was due to its huge availability, consequently used in daily life by people across

| Sr. No. | Area | Industrial activities | Groundwater quality problems |
|---|---|---|---|
| 1 | Digboi (Assam) | Oil refinery | Fe and Mn ions were more than permissible limit. Ni, Zn, Cd, Cr, Pb were also reported. |
| 2 | Howrah (West Bengal) | Foundries and Electroplating | Heavy metals viz. Pb, Cd, Cr were very high and Zn, Cu, were within limit. Hg, Fe, Mn and pesticides were also very high, CN and phenolic compounds in traces. |
| 3 | Botharam Patncheru (AP) | Pesticides, Pharmaceuticals | Phosphates, Hg, As, Cd, Fe, Mn and Pb were beyond limit, Pesticides, coliform, TDS, were also exceeded the desirable limit. |
| 4 | North Arcot (TN) | Tanneries and dyeing units | Hg, Cd, Pb and As were in traces. Zn, Cu, Cr, Fe and Mn beyond limit at several locations. Total Coli form and fecal Coli form were also on higher side. |
| 5 | Ratlam, Nagda (MP) | Distillery Dye, Pharmaceuticals | TDS, Hg, Pb were on higher side. Pesticides and fecal Coli forms were also present. |
| 6 | Mandi Gobindgarh (Punjab) | Wooden, chemicals, electro-plating and other steel metals units. | Pb, Cu, Cd exceeded the desirable limit of drinking water. Phenol compounds and cyanide were also present on higher side. |
| 7 | Parwanoo (HP) | Ancillary, fruit proceeding plant, air pesticides. | The presence of Cd, Pb, Fe, and Mn was observed on higher side. Pesticides and phenol were above the toxic limit. |
| 8 | Kala Amb (HP) | Paper mills | Heavy metals like Cd, Pb and Mn and Phenol compound were higher than the toxic limit. Pesticides, Coli forms were also present. |
| 9 | Pali (Rajasthan) | Textile, dyes | Pb and Zn, F, TDS and Cl found higher. |
| 10 | Jodhpur (Rajasthan) | Textile, steel, engineering foundry, chemicals, oil, pulses and rubber. | Heavy metals such as Fe, Cr, Mn, Pb were also on higher side. Na, TDS exceeded the limit. |
| 11 | Angul Talcher | Thermal power station, fertilizers, chemicals, mining activities. | Cr, Fe, Cd, Pb & F, $NO_3$ all were found in concentration level exceeding standards limits. |

**Table 2.** Pb (II) ions contamination status in India.

all classes. The special attention needs to be given on its mitigation from contaminated water bodies. Lead was ranked second on the Comprehensive Environmental Response.

Compensation and Liability Act (1980) (CERCLA) Priority List of Hazardous Substances in 1999 and 2001 (after arsenic #1, and before mercury - #3). The priority list is prepared by the Agency for Toxic Substances and Disease Registry (ATSDR) and Environmental Protection Agency (EPA) and is based on the frequency of occurrence of particular contaminants at National Priorities List (NPL) sites and their potential threat to human health. Pb (II) ions can be found in effluents from battery recycling plants, lead mining and electronic assembly plants. Lead metal elucidates destructive effects almost on every organ

systems viz. nervous, blood circulation, reproductive, digestive, kidneys as become highly toxic and carcinogenic even at low concentration. World Health Organization (WHO) prescribed the maximum permissible limit (MPL) of lead metal in drinking water as 50 ppb initially during 1995 that was further decreased to 10 ppb in 2010. However, more recently, an EPA document recommended a zero lead value in a national primary drinking water standard [19].

In recent years, the chitosan blended biocomposites have been synthesized by impregnation with graphite [20], iodate [21] activated carbon of *Luffa cylindrica* [22], and so on and were utilized for Pb (II) ions mitigation from water. The choice of these materials was concerned with its high adsorption efficiency, safe and simple to use, easy to maintain, minimal production of residual mass, low capital cost and nontoxicity. The resultant adsorbents viz. graphite doped chitosan composite (GDCC), Iodate doped chitosan composite, and activated carbon of *Luffa cylindrica* doped chitosan biocomposite satisfy all these requirements during their usage as a bioadsorbents. In this chapter, the synthesis, characterization and batch adsorption of Pb (II) ions by using GDCC are explained.

## 6. Synthesis of graphite doped chitosan composite (GDCC)

Chitosan dissolved in acetic acid and heated at 50°C to obtain gel followed by the addition of powdered graphite in (1,1 w/w) ratio. Mixture was then agitated magnetically (800 rpm) at 27°C) for 5–6 h and dropped in aqueous ammonia to obtain beads. Finally, it was filtered, washed with double distilled water and dried in oven at 70–80°C. The GDCC was grounded, and the particle size recorded in range of 176–246 μm. (**Figure 6B**).



**(A)**                                  (B)
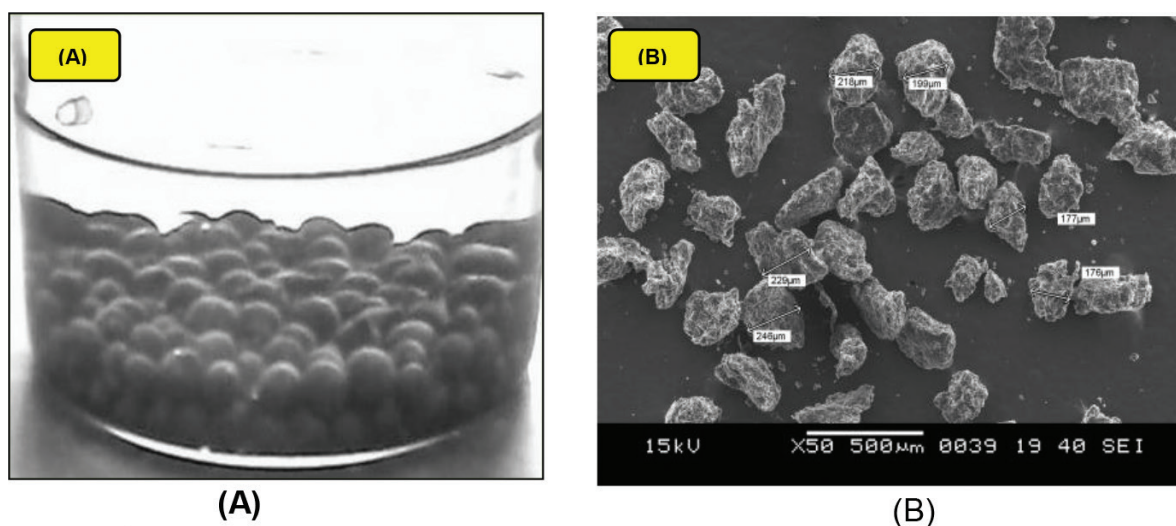
**Figure 6.** (A) GDCC beads and (B) SEM image of powdered GDCC, with particle size in range of 176–246 μm.

# 7. Results and discussion

## 7.1. Physicochemical characterization of GDCC

The results of the proximate and elemental analysis of GDCC is shown in **Table 3**

### 7.1.1. TGA and DSC analysis of GDCC

Thermogravimetric/Differential Scanning Calorimetry (TGA/DSC) was used to evaluate the thermal stability and to determine the decomposition temperature of the adsorbents. TGA and DSC analysis of chitosan (CS), Graphite (Gr), and Graphite doped chitosan composite (GDCC) are shown in **Figure 7(A)** and **(B)** respectively.

From TGA curve, it was observed that CS showed two steps of degradation. The initial degradation occurred at around 30–100°C and displayed 5% weight loss. This degradation may correspond to the loss of adsorbed and bound water or moisture vaporization. Initial decomposition around 100°C can be attributed to the strong water adsorptive nature of CS. The second decomposition stage was at 270°C and continued up to 312°C with 46.28%

| Adsorbent | Proximate analysis (%) | | | | Elemental analysis (%) | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Moisture | Volatile matter | Ash | Fixed Carbon | C | H | N | S | O |
| CS | 5.3 | | 6.2 | | 38.5 | 7.8 | 7.1 | 0.19 | 46.45 |
| GDCC | 7.2 | 55 | 4 | 33.8 | 57.69 | 3.78 | 4.03 | 0.23 | 34.27 |

**Table 3.** Proximate and elemental analysis of GDCC.
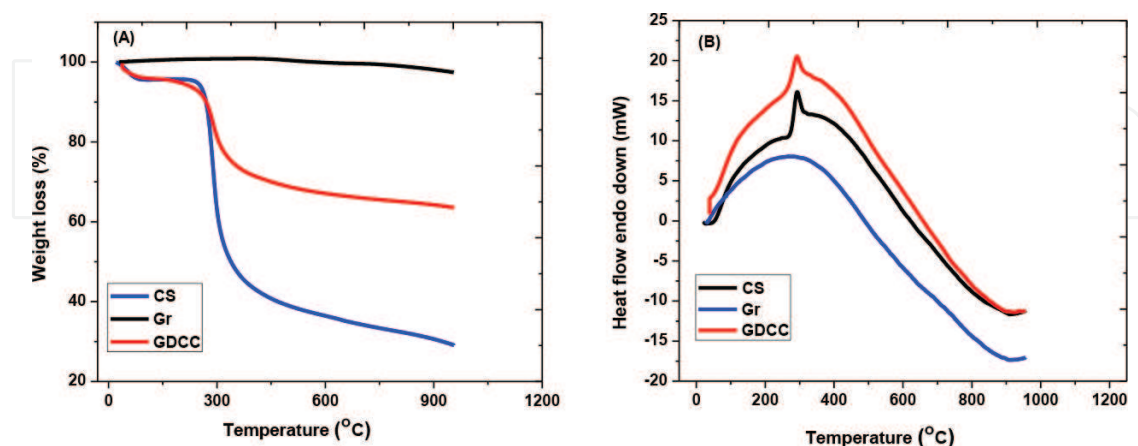


**Figure 7.** (A) Thermogravimetric analysis (B) differential scanning calorimetric analysis of chitosan (CS), graphite (Gr) and graphite doped chitosan composite (GDCC).
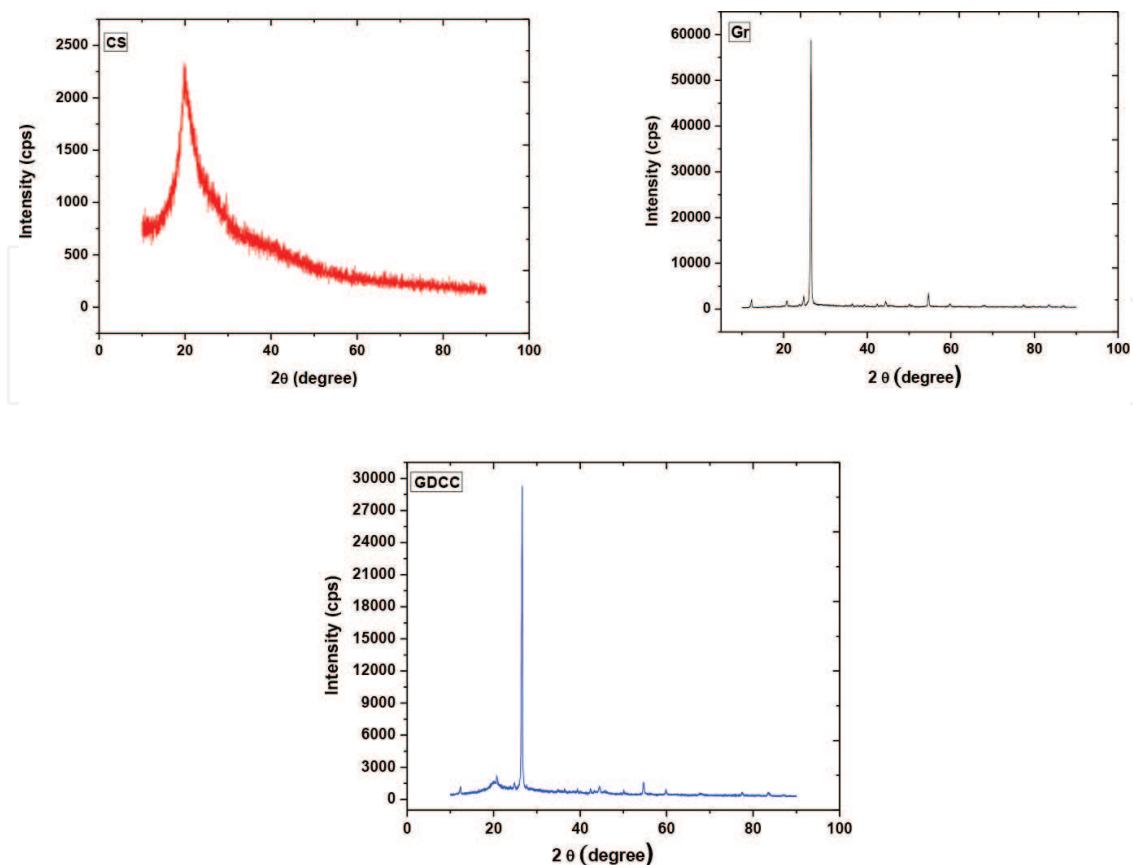
**Figure 8.** XRD analysis of chitosan (CS), powdered graphite (Gr) and GDCC.

weight loss. The temperature at which maximum degradation occurred was 288.35°C. At the end of 955.1°C, the total weight loss of CS was 70%. TGA analysis of powdered graphite shown high thermal stability up to 700°C and displayed only 2.5% weight loss at the end of 955°C.

TGA analysis of GDCC also exhibited two steps of degradation. First stage decomposition occurred between 38.01 and 200°C which showed about 5% weight loss due to evaporation of water. The second stage of decomposition showed a weight loss of 18.37% in the temperature range of 265.15–321.6°C. The temperature at which the maximum degradation occurred was 288.55°C. At the end of 955°C, the total weight loss was 35%. The TGA analysis revealed that with respect to powdered graphite, the GDCC became less thermally stable, whereas with respect to the CS, the composite became more thermally stable. These observations showed a good miscibility between CS and graphite to achieve GDCC or biocomposite.

The DSC curve of CS and GDCC both shows one exothermic peak at 292 and 291.37°C, respectively. For CS, the onset of exothermic peak was at 276.89°C and continued up to 311.49°C with $\Delta H = -149$ J/g and for GDCC the onset of exothermic peak was at 270.64°C and continued up to 311.86°C with $\Delta H = -60.1211$ J/g.
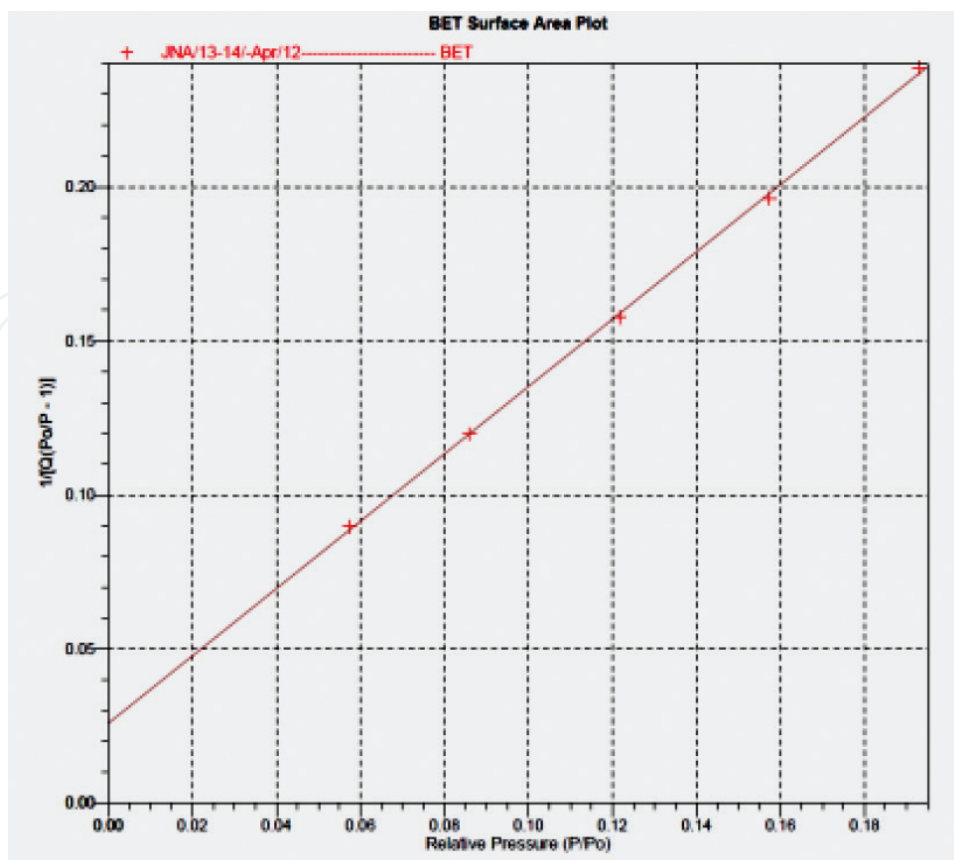
**Figure 9.** BET surface area plot of GDCC.

### 7.1.2. XRD analysis of GDCC

The XRD pattern of powdered graphite, chitosan and GDCC is shown in **Figure 8**. X-ray diffraction pattern of CS exhibited broad diffraction peak at $2\theta = 20°$ with d-spacing of 4.2 Å is characteristic of semi crystalline chitosan [23]. The peaks are broadened due to amorphous nature of chitosan polymer. The diffraction peak appeared at $2\theta = 26.5°$ which indicated d-spacing of about 3.35 Å is a characteristic of graphite peak [24]. The XRD pattern of the GDCC indicated the formation of homogeneous/single phase composite, and the peaks were obtained at $2\theta$ value 26.5°. The broad peak at around $2\theta = 20°$ which was due to CS decreased in intensity after doping with graphite which confirms that graphite is doped on the surface of chitosan. A predominant peak of graphite along with small peak of chitosan appeared in GDCC showed that the incorporation of graphite in matrix was successful and effectively provided a support to the chitosan.

### 7.1.3. BET surface area analysis of GDCC

The BET surface area plot of GDCC is shown in **Figure 9**. The BET surface area of GDCC adsorbent was 3.89 $m^2/g$, whereas for CS, it was 9.923 $m^2/g$. Thus, it was observed that the BET surface area of GDCC composite was decreased with respect to CS. During modification of

CS by graphite, the decreased surface area may be due to the blockage of internal porosities of CS by incorporated modifier, that is, powdered graphite to achieve GDCC composite. The adsorptive ability of GDCC for Pb (II) ions is good in spite of decreased BET surface area with respect to CS.

It is due to the participation of various functional groups such as –OH, C=O and –NH$_2$ on the adsorbents surface thereby adsorption occurred predominantly via chemisorption mechanism. Surface area is the physical parameter and the adsorptive capacity increases with increasing surface area for a pure physisorption process.

### 7.1.4. SEM analysis of GDCC before and after Pb (II) ions adsorption

The scanning electron microscopic images of chitosan and GDCC before and after Pb (II) ions adsorption are shown in **Figure 10(A-C)** respectively. **Figure 10(A)** revealed small amount of round voids and well-developed elongated bilobed porous structure in chitosan. The surface morphology of chitosan was drastically changed to flaky, smooth and porous nature with some voids/cavities after impregnation with graphite as in **Figure 10(B)**. The morphology of Pb (II) ions loaded GDCC exhibited accumulation of shiny, whitish, sharp needle shaped crystalline mass onto its surface due to the adsorption of Pb (II) ions (**Figure 10**C).
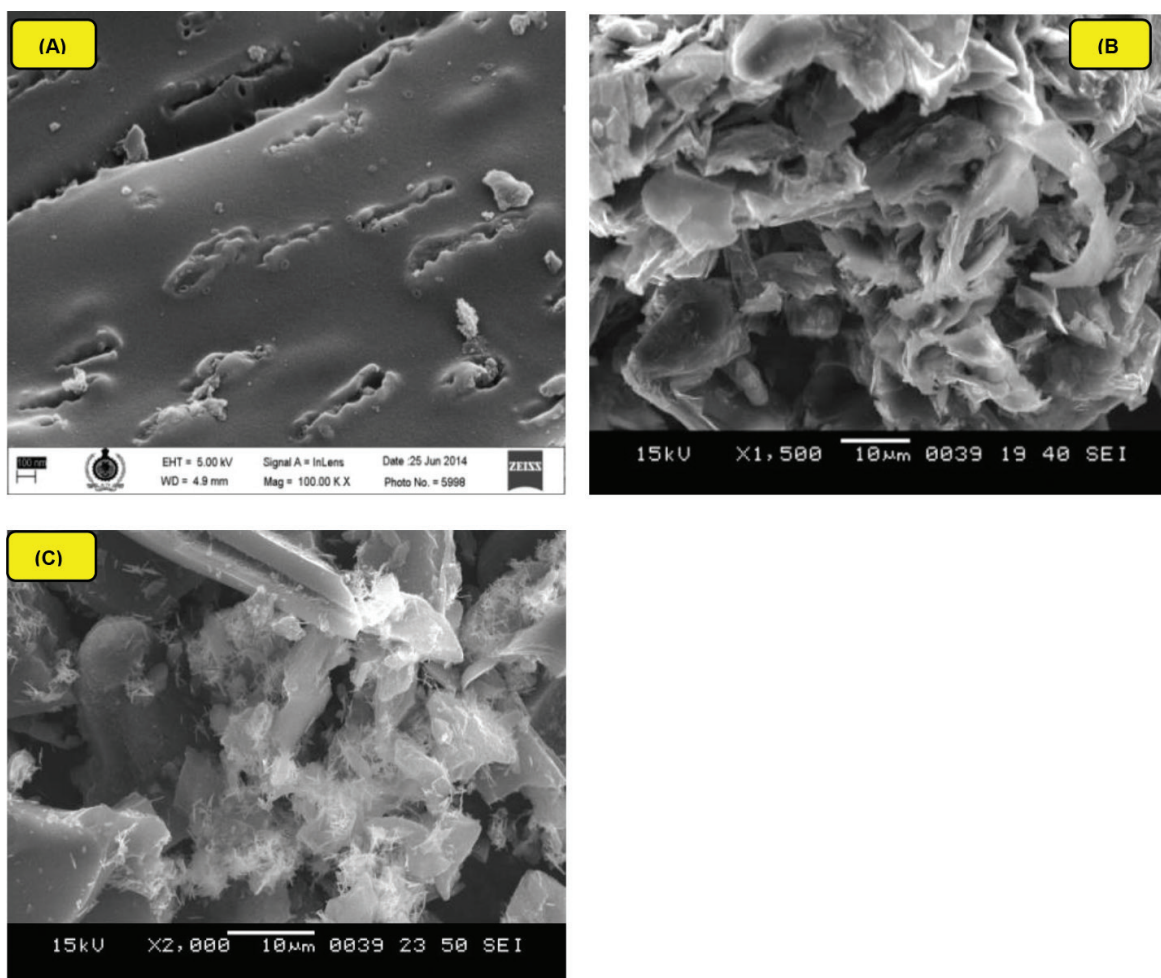


**Figure 10.** SEM image of (A) CS, (B) GDCC before adsorption, and (C) GDCC after adsorption.
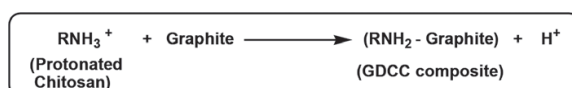
## 8. Adsorption mechanism

The bioadsorbents possess various functional groups like carboxyl, hydroxyl, amino, phosphate, and so on that can provide an active binding site for the adsorption of heavy metal ions. The mechanism of bioadsorption is quiet complicated due to assorted structure of the bioadsorbents. The factors that affect the efficient bioadsorption onto the surface of biosorbents are the availability of number of active binding sites, the affinity of pollutant for the bioadsorbent surface and the presence of variety of functional groups that can exhibit an acceptor-donor interaction with the heavy metal ions. The adsorption process is a combination of ion exchange, complexation, precipitation, and so on and greatly influenced by the solution pH. Similarly, in order to understand the adsorption mechanism, it is also necessary to determine the pH of point zero charge (pHpzc) of the adsorbent. pHpzc is of prime importance in the field of environmental science. It determines how easily and adsorbent adsorbs toxic ions. The difference between the initial pH (pHi) and final pH (pHf) values is plotted against initial pH (pHi). The point of intersection of the resulting curve at which difference between pH = 0 is noted as pH of point zero charge. The cationic adsorption is favored at pH > pHpzc while anionic adsorption is favored at pH < pHpzc [25] This is due to the fact that at low pH values, hydronium ions concentration increases that competes with cationic pollutants for the adsorption sites on the adsorbent. While at higher pH, hydroxide ions concentration increases and the adsorbent surface becomes negatively charged thereby increases the attraction between the cationic pollutants with the adsorbent surface. Thus, pH > pHpzc is favorable for the cationic adsorption. In anionic adsorption, solution pH should be less than the pH pzc so that the adsorbent surface becomes positively charged to enhance the anionic pollutants adsorption onto the adsorbent surface. The general adsorption mechanistic representation is shown in **Figure 11**.

On the basis of results obtained from the analytical and spectroscopic data, the schematic representation of Pb (II) ions adsorption mechanism onto GDCC is represented in scheme as below.

The amino group of chitosan plays a major role in removal of Pb (II) ions via adsorption as it acts as coordination site for metal ions. The amino group gets protonated in acidic medium due to reaction with H$^+$ ions and is chemically represented as below.

$$RNH_2 + H^+ \longrightarrow RNH_3^+$$
**Protonated Chitosan**

The FTIR analysis revealed the corresponding prominent changes of –NH bending vibrations after doping of graphite with chitosan indicated that –NH vibration is affected as a result of modification. Thus, the doping of graphite with chitosan results in formation of nonprotonated chitosan-graphite composite and is represented as follows.

$$RNH_3^+ + Graphite \longrightarrow (RNH_2 - Graphite) + H^+$$
(Protonated Chitosan)                    (GDCC composite)

The abovementioned relationship suggests that the acidic pH can enhance the complexation between chitosan and graphite.
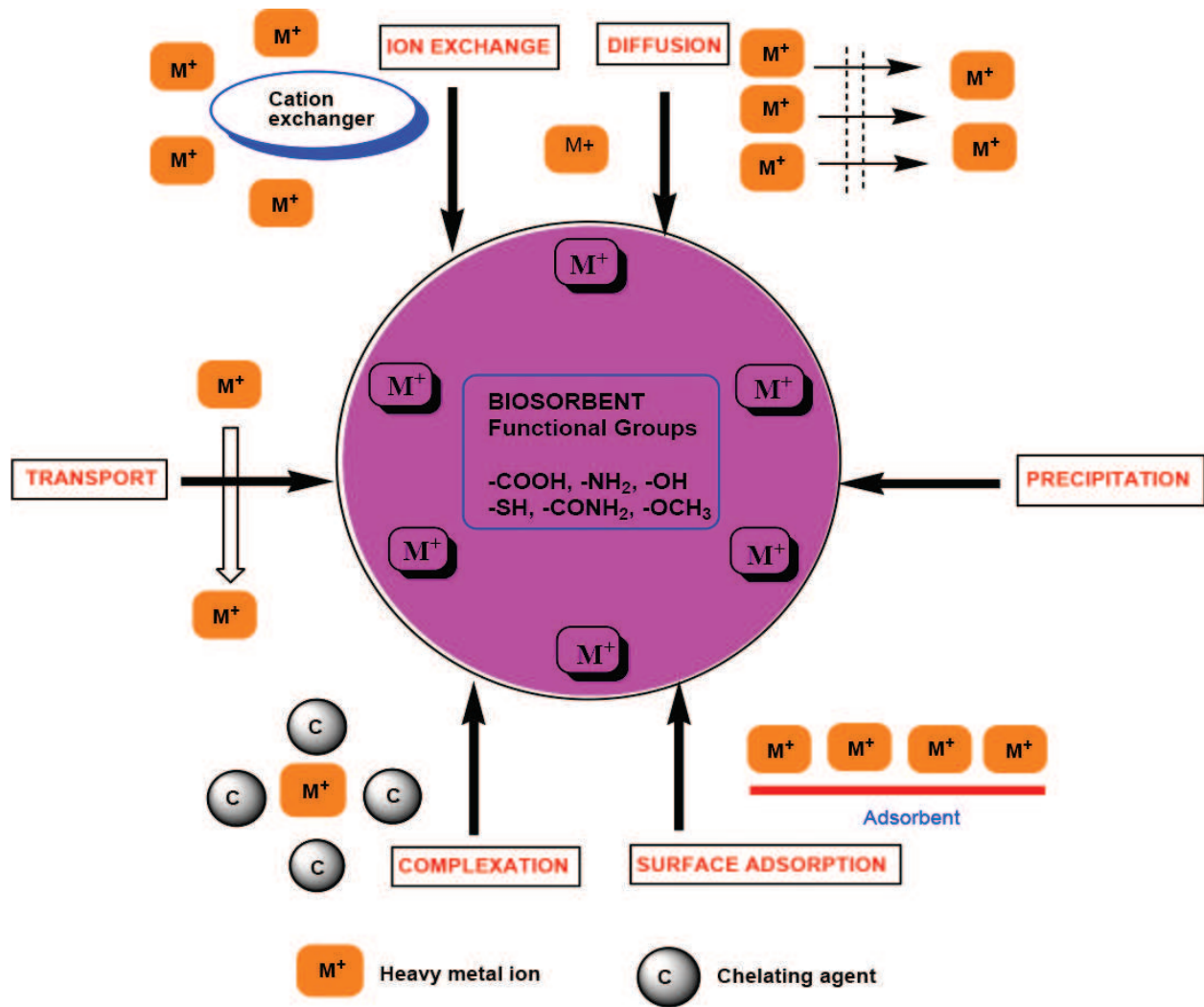
**Figure 11.** Plausible adsorption mechanism of heavy metal ions onto the adsorbent.

As chitosan acts as a chelating agent signifies nitrogen atom as the prominent adsorption site for Pb (II) ions adsorption. The chitosan-graphite complex binds with Pb (II) cation via the formation of coordination bond, and it is represented as follows:

$$(RNH_2 - Graphite) + Pb^{2+} \longrightarrow Pb - (RNH_2 - Graphite)^{2+}$$
$$OR$$
$$(Pb - GDCC)^{2+}$$
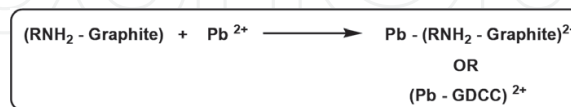
## 9. Adsorption kinetics

To study the mechanism and kinetics of Pb (II) ions adsorption, characteristic adsorption constants were determined using pseudo first order, pseudo second order and intraparticle diffusion models.
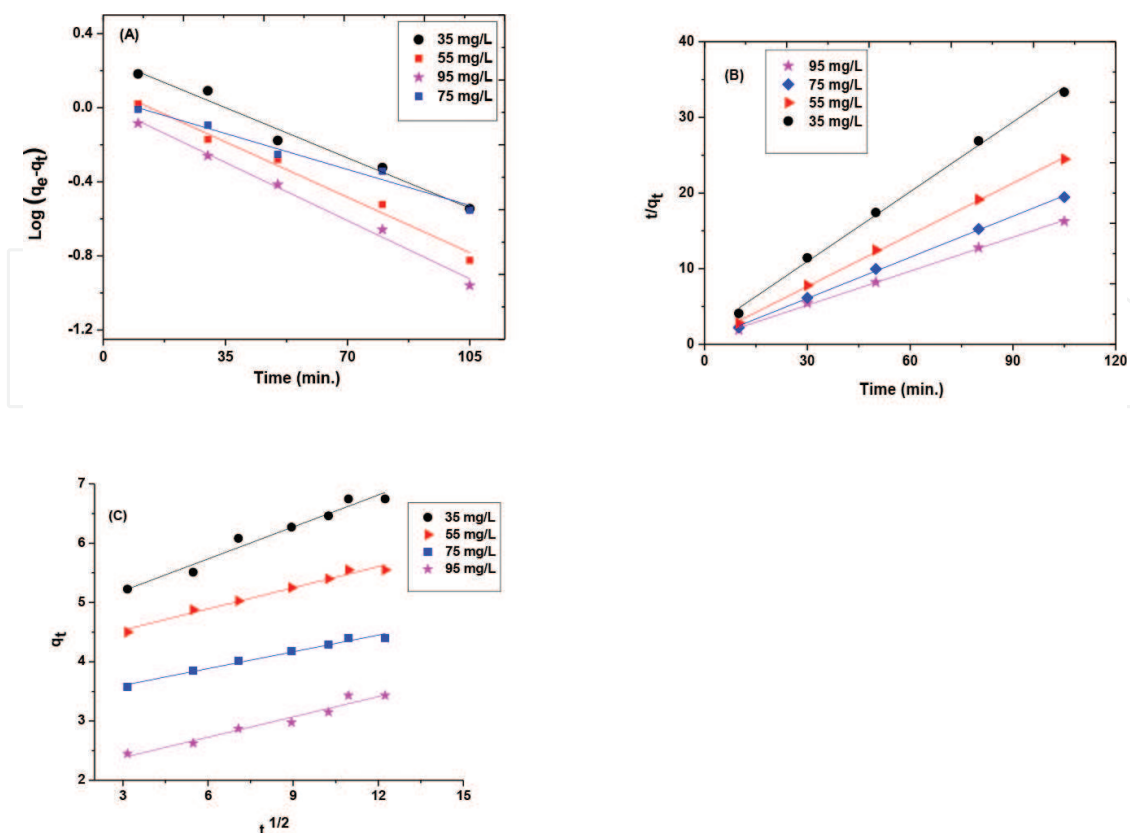
**Figure 12.** Linear plot of (A) pseudo first-order kinetics (B) pseudo second-order kinetics and (C) Weber-Morris Intraparticle diffusion model.

The Lagergren pseudo first-order plot, Ho presented Pseudo second-order kinetics plot and Weber Morris Intraparticle diffusion plot are shown in **Figure 12(A-C)**. Similarly, the kinetic parameters viz. rate constant ($k_1$ and $k_2$), equilibrium adsorption capacity ($q_e$) and correlation coefficient ($R^2$) are indicated in **Table 4**. Equilibrium adsorption capacity ($q_e$) and the pseudo first-order rate constant ($k_1$) can be obtained from the intercept and slope of plot between Log ($q_e-q_t$) against time t. Similarly, the equilibrium adsorption capacity (qe) and the pseudo-second-order rate constant $K_2$ were obtained from the slope and intercept of the plots of t/qt against t.

The linear correlation coefficient values of pseudo first order are comparatively lower than pseudo second-order kinetics mechanism. The calculated $q_e$ values are much higher than the experimental $q_e$ values for 35 to 95 mg/L Pb (II) ions concentration and thus does not represent the good fit of pseudo first order with the experimental adsorption data. Consequently, it can be concluded that the adsorption of Pb (II) ions onto GDCC is not better explained by the pseudo first-order kinetics mechanism. Results presented in the table clearly show that the correlation coefficient for pseudo second-order equation is higher than pseudo first order for all 35 to 95 mg/L concentrations of Pb (II) ions. Similarly, high $k_2$ of pseudo second order suggested that the metal could be rapidly sequestered by carbon functional groups, resulting in the system quickly reaching equilibrium. The calculated $q_e$ values from pseudo second order are much closer and in good agreement with the experimental $q_e$ values, which indicate that

| Pb (II) ions (mg/L) | Pseudo-first-order | | | $q_e$ (cal.) | Pseudo-second-order | | | Intraparticle diffusion model | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $K_1$ (min$^{-1}$) | $q_e$ (mg/g) | $R^2$ | | $K_2$ (g/mg$^{-1}$ min$^{-1}$) | $q_e$ (mg/g) | $R^2$ | $K_i t$ (mg/g min$^{0.5}$) | C (mg/g) | $R^2$ |
| 35 | 0.0115 | 1.1350 | 0.97 | 3.43 | 0.0545 | 3.2573 | 0.99 | 0.114 | 2.042 | 0.95 |
| 55 | 0.0207 | 1.0423 | 0.99 | 4.4 | 0.0628 | 4.4052 | 0.99 | 0.094 | 3.319 | 0.98 |
| 75 | 0.0184 | 1.3001 | 0.98 | 5.55 | 0.0505 | 5.5248 | 0.99 | 0.119 | 4.176 | 0.98 |
| 95 | 0.0161 | 1.8663 | 0.97 | 6.745 | 0.0324 | 6.7114 | 0.99 | 0.179 | 4.658 | 0.96 |

**Table 4.** Adsorption kinetics parameters for Pb(II) ions onto GDCC.

the adsorption of Pb(II) ions by GDCC follows pseudo second-order kinetics. The confirmation of pseudo second-order kinetics indicates that during the adsorption process, concentration of both adsorbent and adsorbate is involved in rate-determining step, which may be chemical adsorption or chemisorptions [26].

Intraparticle diffusion parameters are shown in **Table 4**. The intraparticle diffusion $k_i$ values were obtained from the slope of a plot of $q_t$ versus $t^{1/2}$. From figure, it follows that the correlation coefficient values are lower for varying Pb (II) ions concentration (35, 55, 75 and 95 mg/L) than pseudo second-order kinetics. Similarly, intraparticle diffusion plot is not linear, and the straight line does not pass through the origin, indicating that intraparticle diffusion was involved in adsorption but was not the only rate-controlling step.

# 10. Conclusion

The quality of water is an ever growing concern throughout the developing countries. The natural and manmade activities have a large impact on drinking water contamination that ultimately affects the human health, ecological balance and social and economic progress of countries. The chemical contamination due to heavy metal ions makes water unsuitable for drinking. Among the prominent chemical pollutants, arsenic, mercury and lead threatens health of billions of world population. It is very important for a rapidly developing country like India to be vigilant of these heavy metal problems and to ascertain preventive and remedial measures for their management. Sometimes modern and expensive remedial measures are problematic for a country like India, and hence the attempts have to be focused on the prevention and mitigation of the environmental pollutants. This chapter dealt with the mitigation of heavy metal Pb (II) ions from contaminated water using graphite doped chitosan composite (GDCC). Maximum Pb (II) ions adsorption capacity was 6.711 mg/g (from Langmuir) at optimum pH 6 with dosage of 1 g/L in 120 min. The choice of these materials was concerned with its good adsorption efficiency, safe and simple to use, easy to maintain, minimal production of residual mass, low capital cost and nontoxicity.

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## References

[1] Pastor A. Quitina y Quitosano: Obtención, caracterización y aplicaciones. Programa CYTED, CIAD, A.C., Fondo Editorial de la Pontificia Universidad Católica del Perú, Lima, Perú; 2004

[2] Arrascue ML, Garcia HM, Horna O, Guibal E. Gold sorption on chitosan derivatives. Hydrometallurgy. 2003;**71**:191-200

[3] Rinaudo M. Chitin and chitosan: Properties and applications. Progress in Polymer Science. 2006;**31**:603-632

[4] Aranaz I, Mengíbar M, Harris R, Pãnos I, Miralles B, Acosta N, Galed G, Heras Á. Functional characterization of chitin and chitosan. Current Chemical Biology. 2009;**3**: 203-230

[5] Piccin JS, Vieira MLG, Goncalves JO, Dotto GL, Pinto LAA. Adsorption of FD&C Red No. 40 by chitosan: Isotherms analysis. Journal of Food Engineering. 2009;**95**:16-20

[6] Tajik H, Moradi M, Rohani SMR, Erfani AM, Jalali FSS. Preparation of chitosan from brine shrimp (Artemia urmiana) cyst shells and effects of different chemical processing sequences on the physicochemical and functional properties of the product. Molecules. 2008;**13**:1263-1274

[7] Lavorgna M, Piscitelli F, Mangiacapra P, Buonocore G. Study of the combined effect of both clay and glycerol plasticizer on the properties of chitosan films. Carbohydrate Polymers. 2010;**82**:291-298

[8] Muzzarelli RA, Boudrant J, Meyer D, Manno N, DeMarchis M, Paoletti M. Current views on fungal chitin/chitosan, human chitinases, food preservation, glucans, pectins and inulin: A tribute to Henri Braconnot, precursor of the carbohydrate polymers science, on the chitin bicentennial. Carbohydrate Polymers. 2012;**87**:995-1012

[9] Krajewska B. Membrane-based processes performed with use of chitin/chitosan materials. Separation & Purification Technology. 2005;**41**:305-312

[10] Guibal E. Interactions of metal ions with chitosan-based sorbents: A review. Separation & Purification Technology. 2004;**38**:43-74

[11] Yu L, Dean K, Li L. Polymer blends and composites from renewable resources. Progress in Polymer Science. 2006;**31**:576-602

[12] Payne GF, Chaubal MV, Barbari TA. Enzyme-catalysed polymer modification: Reaction of phenolic compounds with chitosan films. Polymer. 1996;**37**:4643-4648

[13] Grizzuti N, Buonocore G, Lorio G. Viscous behavior and mixing rules for an immiscible model polymer blend. Journal of Rheology. 2000;**44**:149-164

[14] Chiou MS, Ho PY, Li HY. Adsorption of anionic dyes in acid solutions using chemically cross-linked chitosan beads. Dyes and Pigments. 2004;**60**:69-84

[15] Chen T, Kumar G, Haris MT, Smith PJ, Payne GF. Enzymatic grafting of hexyloxy-phenol onto chitosan to alter surface and rheological properties. Biotechnology and Bioengineering. 2000;**70**:564-573

[16] Dutta PK, Dutta J, Tripathi VS. Chitin and chitosan: Chemistry, properties and applications. Journal of Scientific and Industrial Research. 2004;**63**:20

[17] Xu HY, Yang L, Wang P, Liu Y, Peng M. Kinetic research on the sorption of aqueous lead by synthetic carbonate hydroxyapatite. Journal of Environmental Management. 2008;**86**:319-328

[18] Ground water pollution scenario in India. (Source: CPCB). http://nihroorkee.gov.in/rbis/india_information/ground%20water%20pollution.htm

[19] Current Drinking Water Standards, EPA. Office of Water, 2002. http://www.epa.gov/safewater/mcl

[20] Gedam AH, Dongre RS, Bansiwal AK. Synthesis and characterization of graphite doped chitosan composite for batch adsorption of lead (II) ions from aqueous solution. Advanced Materials Letters. 2015;**6**:59-67

[21] Gedam AH, Dongre RS. Adsorption characterization of Pb (II) ions onto iodate doped chitosan composite: Equilibrium and kinetic studies. RSC Advances. 2015;**5**:54188-54201

[22] Gedam AH, Dongre RS. Activated carbon from Luffa cylindrica doped chitosan for mitigation of lead(II) from an aqueous solution. RSC Advances. 2016;**6**:22639-22652

[23] Cardenas G, Miranda SP. FTIR and TGA studies of chitosan composite films. Journal of the Chilean Chemical Society. 2004;**49**:291-295

[24] Krishna Rao KSV, Naidu BV, Subha MCS, Sairam M, Aminabhavi TM. Novel chitosan-based pH-sensitive interpenetrating network microgels for the controlled release of cefadroxil. Carbohydrate Polymer. 2006;**66**:333-344

[25] Nomanbhay SM, Palanisamy K. Removal of heavy metal from industrial wastewater using chitosan coated oil palm shell charcoal. Electronic Journal of Biotechnology. 2005;**8**:43-53

[26] Ho YS, McKay G. Sorption of dye from aqueous solution by peat. Chemical Engineering Journal. 1998;**70**:115-124