Development of biopolymer supported composites/beads for nitrate and phosphate removal from water

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Abstract: To overcome the problems of blue baby syndrome (methemoglobinemia) and eutrophication (algae growth) caused by excess nitrate (NO_3^-) and phosphate (PO_4^{3-}), the numerous removal studies for $NO_3^-$and PO_4^{3-}have been investigated by the environmental researchers. In the present research work, the polymer supported composites/beads were developed and utilized for $NO_3^-$and PO_4^{3-}removal from water. The synthesized biopolymers based materials possess high adsorption capability with good removal capacity than their respective parent materials. The $NO_3^-$and PO_4^{3-}removal mechanism of biopolymers based materials was found to be ion-exchange, surface complexation and electrostatic attraction. The synthesized composites/beads can be reutilized upto several adsorption cycles which shows the cost-effective nature. The applicability of biopolymer supported composites/beads at field conditions was checked by collecting $NO_3^-$and PO_4^{3-}contaminated water sample from the nearby area of Dindigul district, Tamilnadu.

Keywords: Clays; Metal ions; Iron oxide, Graphene oxide; Biopolymers; NO_3^-/PO_4^{3-}adsorption

1 Introduction

Water is a lung of entire living species on the earth. Water is found all over but not everywhere drinkable that is why it is called as a precious resource. Water is a major

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component (∼ 65 %) of the human body which plays the virtual functions in body cells and tissues. Another unique feature of water is its capability to dissolve the variety of substances and so it is called as the universal solvent. The world water is distributed from various sources such as ocean (96.50 %), glacier (1.74 %), ground (1.70 %) in which fresh water (0.76 %) is found to be very lower. Hence to highlights the significance of fresh water and promotion for its sustainable management, the World Water Day is celebrated on March 22, every year. The pollutant is referred as any substance which causes adverse effects to the environment. The chemical nature, persistence and concentration have to determine the brutality of any pollutant. Though the different kinds of pollution such as water, air, soil, plastic, thermal, light, etc., are disturbing humans life cycle, the severe health effects are observed due to water pollution. Nowadays the water sources are deeply affected by numerous pollutants and hence the control of water pollution is very challenging task even in the developing countries.

2 Water scarcity and contamination

On the increase of population, disorganization of water resources, industrialization, etc., leads to the rapid scarcity of the drinking water system which is growing demand on the earth. In historical records, the water shortages were appeared from the year of 1800 itself. All over the world there are five countries namely Yemen, Libya, Jordan, The Western Sahara and Djibouti have faced the deepest water scarcity issues. According to the survey related to global water crises, about 844 million people are deficient in the access of basic drinking water probably more than 1 of every 10 people. In addition, about 800 children under the age group of 5 die from diarrhoea due to the poor quality of drinking water. Moreover, in the year of 2018 about 2.1 billion people still survive without safe drinking water at their homes. By 2030, about 700 million people could be dislocated by severe water scarcity. The world's population will have grown by an estimated 2 billion people and global water demand could be up-to 30 % higher than today. The deepest scarcity and rapid contamination of the drinking water sources may lead to the 3^{rd} world war in the near future.

The water should be free from physical (odourless, colourless, tasteless, etc.), chemical (should not contains inorganic substances) and biological (should not contains any micro-organisms) parameters. Nowadays it's deeply affected by various natural and man-made pollutants which lead to the cumulative effect on the entire living species. In worldwide about 80 % of the waste-water generated by society flows back into the environment directly without being treated. Some other chemicals such as solvents (tri and tetrachloroethene) and hydrocarbons found in water can cause health effects as well. Water-borne diseases are caused by pathogenic micro-organisms that are transmitted in water. This disease can be spread while bathing, washing or drinking water and by eating food exposed to contaminated water. The diarrhoea and vomiting are the most commonly reported symptoms of water-borne illness, other symptoms can includes skin, respiratory or eye problems. Hence, the standard water quality parameters are recommended by World Health Organization (WHO 1996) which is presented in Table 1.

Table 1. Standard water quality parameters

S.No.	Parameters	Tolerance limit	Remarks
1	Turbidity (NTU)	5	No relaxation
2	pH	6.5 to 8.5	May be exceeded upto 9.2
3	Nitrate (mg/L)	45	No relaxation
4	Phosphate (mg/L)	< 0.5	No relaxation
5	Sulphate (mg/L)	150	May be exceeded upto 500
6	Fluoride (mg/L)	0.6 to 1.2	May be exceeded upto 1.5
7	Chloride (mg/L)	250	May be exceeded upto 500
8	Iron (II) (mg/L)	0.3	May be exceeded upto 1.0
9	Chromium (VI) (mg/L)	0.05	No relaxation
10	Mercury (mg/L)	0.001	No relaxation
11	Lead (mg/L)	0.1	No relaxation
12	Cyanide (mg/L)	0.05	No relaxation
13	Phenol (mg/L)	0.01	May be exceeded upto 0.02
14	Mineral oil (mg/L)	0.01	May be exceeded upto 0.03
15	Total dissolved solids (mg/L)	400	May be exceeded upto 600
16	Total hardness (mg/L)	300	May be exceeded upto 700

3 Nitrate (NO_3^-) and phosphate (PO_4^{3-})

Nitrogen (N) and phosphorous (P) are belong to the p-block elements having an atomic numbers of 7 and 15 respectively in the periodic table. N and P are the significant nutrients which have a significant energy transport, contribution to biomass growth and agricultural fields (Aswin Kumar & Viswanathan 2017). It is also the main component of DNA which contains genetic instructions for the development and function of all the living organisms. N in the forms of nitrate (NO_3^-) or ammonium (NH_4^+) whereas P in a form of phosphate (PO_4^{3-}) are utilized as fertilizer in the agricultural fields. About 78 % of the air that we breathe is composed of N2 gas and in some areas of the United States, mainly the north-east, certain forms of N are commonly deposited in acid rain. The physico-chemical characteristics of NO_3^- and PO_4^{3-} are shown in Table 2.

Table 2. Physico-chemical characteristics of nitrate and phosphate

Physico-chemical characteristics	Nitrate	Phosphate
Primary salt	KNO_3 and NH_4NO_3	KH_2PO_4, $(NH_4)_3PO_4$ and $Ca_3(PO_4)_2$
Nature	White crystalline powder	White crystalline powder
Solubility	Readily soluble in water	Readily soluble in water
pH	~ 6.7	~ 6.3
Ionic radius (A°)	~ 1.46	~ 2.30
Uses	Fertilizer and soap industries	Fertilizer and soap industries

3.1 Sources and toxic effects of NO_3^- and PO_4^{3-}

The natural sources of NO_3^- and PO_4^{3-} are minerals/rocks whereas the anthropogenic sources are fertilizers/industrial activities, etc. The waste-water often contains the higher concentrations of inorganic nutrients such as NO_3^- and PO_4^{3-}. The waste-water treatment processes remove only around 50 % of N and 60 % of P. The concentrations of these major nutrients are still high in processed sewage as compared with the irrigation water from other sources. The high abundance of NO_3^- in ground water sources is a critical issue in many countries including New Zealand. The excess NO_3^- and PO_4^{3-} concentration in waste-water causes environmental pollution (Aswin Kumar & Viswanathan 2018). Some of the other chemicals which contribute to water pollution arise from agricultural run-off. One of the primary contaminants is NO_3^- and PO_4^{3-}. Although pesticides are also reported to considerably contribute to water pollution, they are not reported to cause severe health problems. The various sources, environmental and health effects of NO_3^- and PO_4^{3-} is shown in Table 3.

Table 3. Sources and effects of nitrate and phosphate

Nutrient	Sources		Effects
	Natural	Anthropogenic	
Nitrate	Minerals and rocks	Fertilizers, industrial waste water, manure, sanitary landfills, garbage dump, etc.	Blue baby syndrome (Methemoglobinemia) and eutrophication
Phosphate			Eutrophication

The chemical reduction of NO_3^- into NO_2^- in potable water could lead to the crucial health hazards when it reacts with haemoglobin. This reaction causes methemoglobinemia (blue baby syndrome) referring to the blue coloured skin of young children. In addition, the elevated NO_3^- content in drinking water is also a main reason for the causes of gastric cancer by reduced NO_3^- in the form of nitrosamines. The phenomenon of algae blooms of the aquatic region is often referred to as eutrophication (algae growth) caused by extreme NO_3^- and PO_4^{3-} species in water which leads to esthetic troubles such as the worsening of reservoirs, coastal region, rivers and lakes by depleted dissolved oxygen (DO) content in water (Aswin Kumar & Viswanathan 2019). The higher NO_3^-/PO_4^{3-} concentrations in water disturb the ecological balance and deteriorate its quality. The health and environmental effects of NO_3^- and PO_4^{3-} are shown in Figure 1.

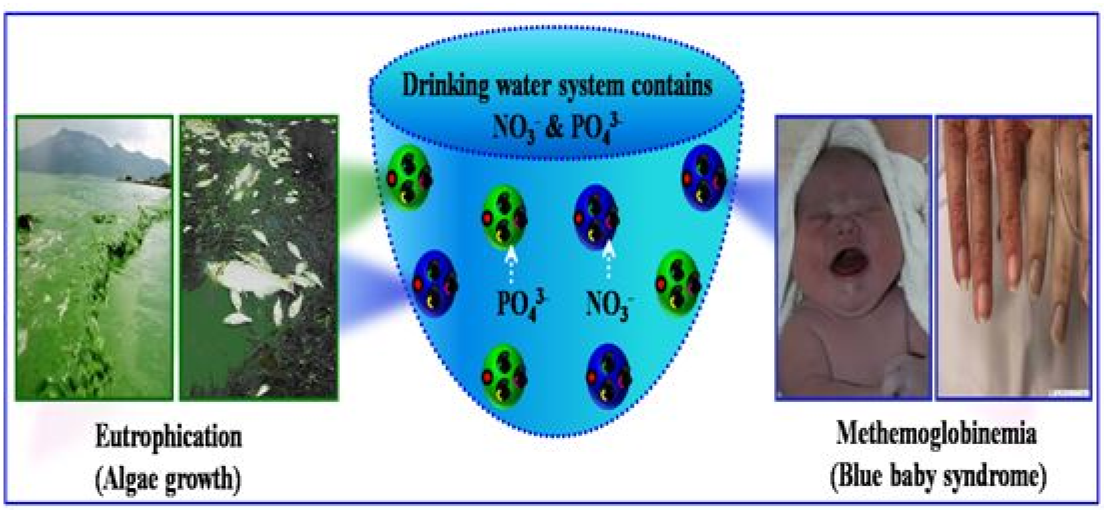

Figure 1. Health and environmental effects of NO_3^- and PO_4^{3-}

3.2 Needs for nitrate and phosphate removal

N and P are the significant nutrients for the growth, reproduction of plants and other living organisms. However, the drinking water contains the extreme NO_3^-species leads to the irreversible disease in young children called blue baby syndrome (methemoglobinemia). In addition, the elevated NO_3^-content in drinking water is also leads to gastric cancer. The extreme $PO_4^{3-}$and NO_3^-contents in water sources develop the algae blooms of aquatic region which is often referred as eutrophication. Hence, the tolerance limit of $NO_3^-$and PO_4^{3-}in drinking water is fixed as 40 and ¡ 0.5 mg/L respectively (Galalgorchev 1992). To provide the safe drinking water, the removal of excess $NO_3^-$and $PO_4^{3-}$from water is the best remedy.

4 Removal techniques of nitrate and phosphate from water

The worldwide environmental researchers have focused to apply the numerous techniques towards the removal of $NO_3^-$and $PO_4^{3-}$from drinking/waste-water. Though these techniques satisfies at first sight, each of them possesses some merits and as well as demerits which is listed in Table 4.

Table 4. Merits and demerits of various removal techniques of nitrate and phosphate

NO_3^- and PO_4^{3-} removal techniques	Merits	Demerits
Ion-exchange	It is efficient method for water softening	It is unsuitable for the contaminants which are not ionic species, ion-exchanger possess high operational cost and highly pH sensitive
Biological method	Raw sewage contains N and P can be removed	It is slow process and possess higher operational cost
Adsorption	Ions with low concentration can be removed and cost effective	Low selective and production of waste products
Membrane process	Easy operation and gets high quality effluents	High cost, low flow rate and possess limited screen size
Chemical precipitation	Simple, inexpensive & non-metal selective	Formation of secondary pollution, and poor settling time

Among the listed techniques $NO_3^-$and $PO_4^{3-}$by adsorption process was seems to be cost-effective, easily operative and suitable at field condition (Aswin Kumar & Viswanathan 2020).

5 Adsorption process

Adsorption is the adhesion of ions, atoms or molecules from a gas, liquid or dissolved solid to a surface of the material. Adsorption is classified into two types namely physical and chemical adsorption. The contribution of adsorbent material in adsorption system plays a most important role in determining the adsorption capacity of the adsorbent. The several parameters such as surface area, surface charge, mechanical strength, porosity, etc., enhance the adsorption nature of the adsorbent materials (Viswanathan & Meenakshi 2010a). Recently, the numerous adsorbent materials such as clays, iron oxide and biopolymer supported materials have been used for the removal of toxic ions from water (Gopalakannan *et al.* 2016a). The easy handle, applicable at wide range of pH condition, high performance, good removal capacity and low processing cost of the adsorption process makes it as applicable for drinking/waste-water treatment. Some demerits of the adsorption process are that the regeneration of the adsorbent requires steam/vacuum conditions and formation of waste product.

6 NO_3^- and PO_4^{3-} adsorption using biopolymers encapsulated inorganic materials

The significant adsorbent materials utilized for the removal of toxic ions from water and are summarized as follows:

6.1 Clay based materials

Clays are defined as fine grained minerals which generally contain metal ions/metal oxides with appropriate water contents. Clays are turned into hardened when dried or fired which is also distinguished from other fine powdered soils due to their different mineralogy and size. Clay is the ideal base materials of organic-inorganic composites. From ancient times, the numerous synthetic and commercial clay materials such as bentonite (Bent), hydrotalcite (HT), kaolin (KN), montmorillonite (MMT), hydrocalumite (HC), hydroxyapatite (HAp), etc., have been widely utilized for the water purification due to their attractive benefits such as low-cost, good ion-exchange capacity, chemical composition with micro porosity, layered structure and nanoscale size (Viswanathan & Meenakshi 2010b).

However, the uses of clays alone create pressure drops during filtration which weakens field applications. Hence biopolymers such as chitosan (CS) and alginate (Alg) was encapsulated with the clays to produce the clays based biopolymeric composites namely CSHT and AlgHT composites for NO_3^- and PO_4^{3-} removal. The synthesized CSHT and AlgHT composites remove NO_3^-/PO_4^{3-} *viz.*, electrostatic attraction, ion-exchange and inner sphere complexation as shown in Figures 2 and 3 respectively.

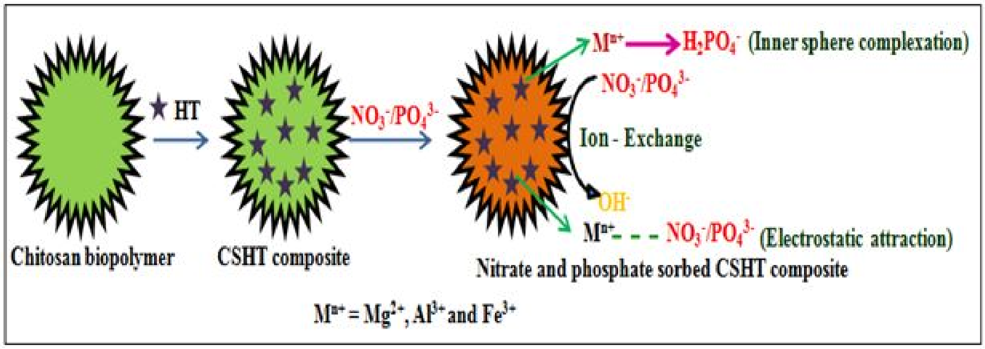

Figure 2. The feasible mechanism of nitrate and phosphate uptake by CSHT composite.

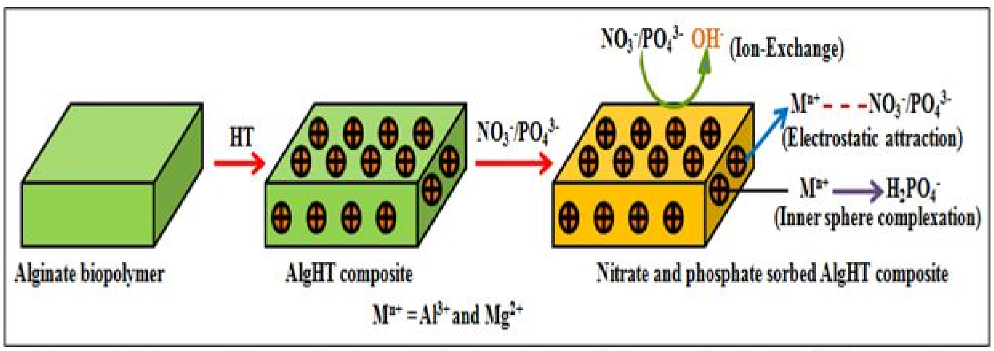

Figure 3. The possible mechanism of nitrate and phosphate sorption by AlgHT composite.

Likewise, to improve the sorption property of Bent clay, it is modified as composite form by encapsulating Bent with CS/Alg biopolymer namely CSBent and AlgBent composites for NO_3^- and PO_4^{3-} removal. The mechanism of CSBent and AlgBent composites was governed by electrostatic attraction, ion-exchange and inner sphere complexation as shown in Figures 4 and 5 respectively.

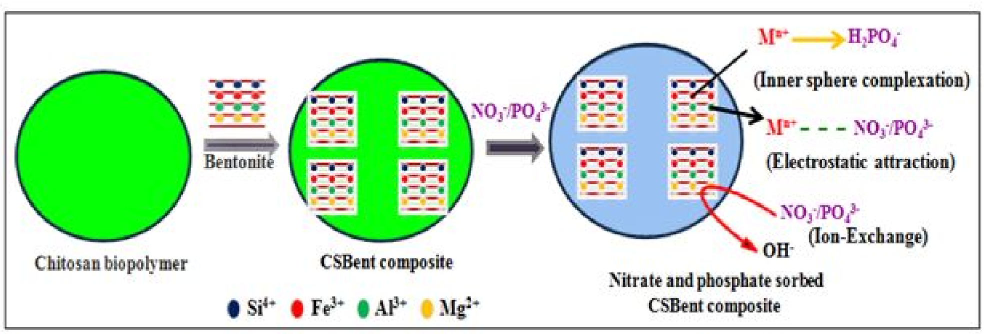

Figure 4. The feasible mechanism of nitrate and phosphate removal by CSBent composite.

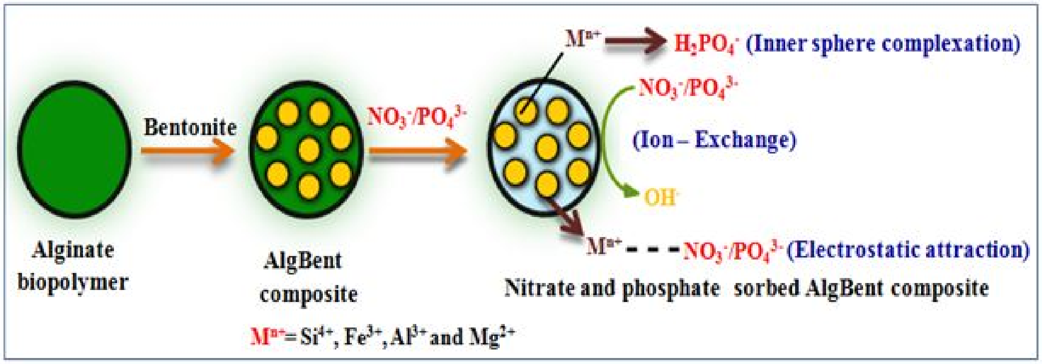

Figure 5. The feasible mechanism of nitrate and phosphate sorption by AlgBent composite.

6.2 Metal ion loaded materials

The metal has the tendency to become positively charged ions by losing their electrons present in the outermost orbit. If the positive charge character on the metal ion increases it behaves as Lewis acid means that it will ready to bind with Lewis bases like NO_3^- and PO_4^{3-}. The metal ions such as Zr(IV), La(III), Ce(III), *etc.*, have a good tendency to attract the negatively charged anions (NO_3^-, PO_4^{3-}, *etc.*,) towards it. In addition, the metal ions can easily co-ordinates with the functional groups of the biopolymers CS and Alg to form stable metal-polymer complex (Viswanathan & Meenakshi 2009). The modification of clays with cationic surfactants increases their basal spacing resulting in exposure of more adsorption sites and hence metal ion cross-linked biopolymeric clay composite materials were developed for the adsorption studies.

Xue-Pin *et al.* (2006) have developed metal-ion-loaded collagen fibers (MICF) namely Zr(IV)-ICF and Fe(III)-ICF for the removal of PO_4^{3-} from water. The Zr(IV) and Fe(III) ion contents (mmol/g) in Zr(IV)-ICF and Fe(III)-ICF were found to be 6.667 and 6.667 mmol/g respectively. Likewise, Biswas et al. (2007) have studied the orange waste gel (OWgel) loaded La(III), Ce(III) and Fe(III) composites for the removal of PO_4^{3-} from water.

Hence, the metal ions such as Zr4+, Ce3+, La3+, Al3+ and Mg2+ ions were cross-linked with CSBent, AlgHT respectively to obtain Zr@AlgHT, Ce@AlgHT, La@AlgHT, Al@AlgHT, Mg@AlgHT, Zr@AlgBent, Ce@AlgBent, La@AlgBent, Zr@CSBent, Fe@CSBent and Ca@CSBent composite beads for NO_3^- and PO_4^{3-} removal. The mechanism of metal ions loaded AlgHT, CSBent and AlgBent composite beads was governed by electrostatic attraction, ion-exchange and inner sphere complexation as shown in Figures 6, 7 and 8 respectively.

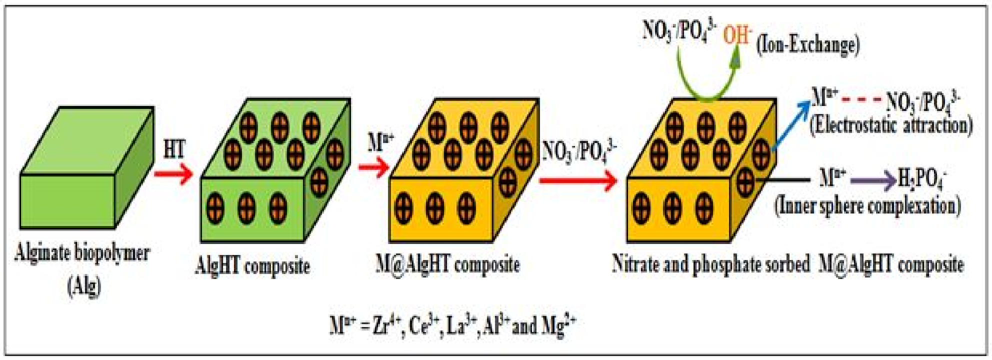

Figure 6. The mechanism of nitrate and phosphate sorption using M@AlgHT composite beads.

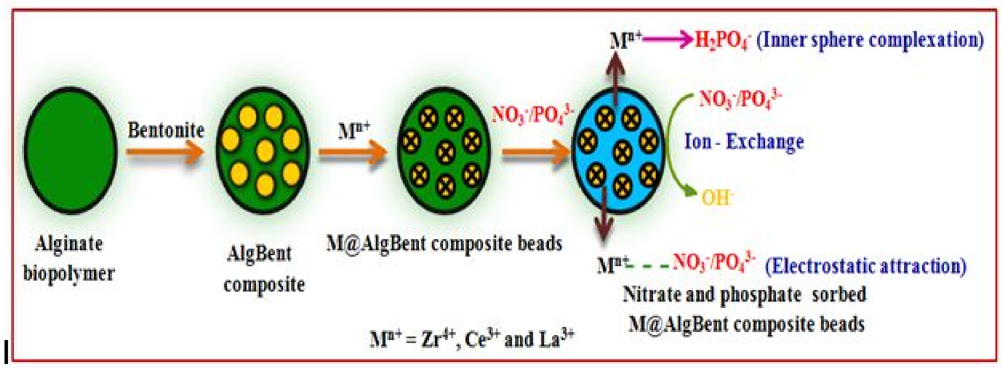

Figure 7. The mechanism of nitrate and phosphate sorption by M@AlgBent composite beads.

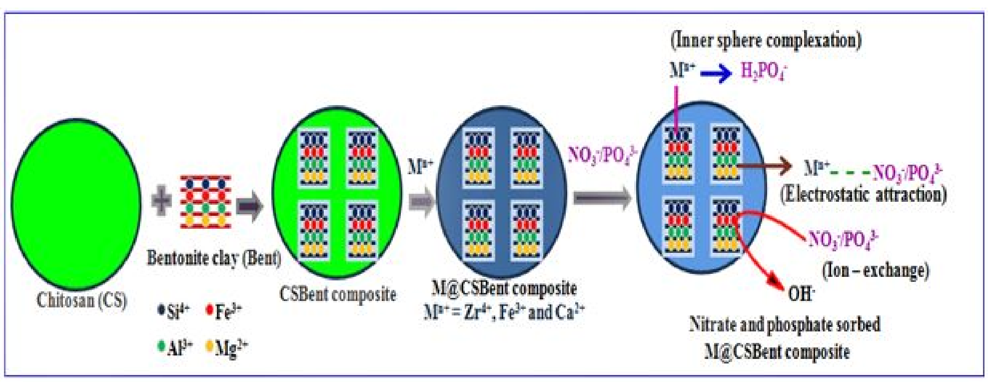

Figure 8. The possible mechanism of phosphate sorption by M@CSBent biocomposites.

6.3 Magnetic iron oxide supported materials

The magnetic separation technology provides the valuable approach towards NO_3^- and PO_4^{3-} adsorption due to the presence of active magnetic ferric (Fe^{3+}) ion in the magnetic iron oxide (Fe_3O_4). The vast quantity of toxic pollutants from water has been purified using Fe_3O_4 in a very diminutive period with applying low energy leads to fast decontamination. Moreover, the Lewis acidic nature of Fe^{3+} can easily attracts the Lewis bases. The active Fe^{3+} ion in Fe_3O_4 can easily form a complex with the functional groups of biopolymers such as CS and Alg to produce a stable Fe^{3+}-polymer complex adsorbent for the removal of anionic toxic pollutants. Moreover, the magnetically supported materials can be easily withdrawn using an external magnet and hence the centrifugation or filtration is not required for magnetic supported materials. Hence Fe_3O_4 supported hybrid composite materials have been investigated for the removal of anionic pollutants especially NO_3^- and PO_4^{3-} from drinking/waste-water.

Shi et al. (2011) have studied the activated carbon (AC) loaded Fe_3O_4(AC/Fe_3O_4) composite for PO_4^{3-} removal and the adsorption capacity of 98.39 mg/g was observed. It was found that the higher surface area of the synthesized AC/Fe_3O_4 composite leads to enhanced PO_4^{3-} removal. Wang et al. (2016) have studied rectorite (REC) assisted Fe_3O_4-CTAB (REC/Fe_3O_4-CTAB) composite for the removal of both NO_3^- and PO_4^{3-} from water. REC is an interstratified natural clay mineral composed of a regular stacking of dioctahedral mica and smectite like layer. Likewise, Ammavasi & Mariappan (2018) have developed Fe_3O_4 fabricated LDH/cellulose (Fe_3O_4@LDH/Cel) composite for the removal of F^- from water. However the adsorption nature was found to be decreased at basic pH condition due to OH^- ions which occupies the active sites of composites surface instead of F^- ions. Dewage *et al.* (2018) have synthesized α-Fe_2O_3 and Fe_3O_4 dispersed on Douglas fir biochar for NO_3^- and F^- removal from water in which the good adsorption capacities of 15 and 9 mg/g respectively was observed within 5 min. The result shows that the incorporation of α-Fe_2O_3 and Fe_3O_4 into biochar forms a magnetic hybrid biochar/α-Fe_2O_3/Fe_3O_4 composite which contains active α-Fe_2O_3 and Fe_3O_4 surface sites. Hence, Fe_3O_4 coated GelHT composite namely Fe_3O_4@GelHT composite was synthesized and utilized for NO_3^- and PO_4^{3-} removal which follows electrostatic attraction, ion-exchange and inner sphere complexation as shown in Figure 9.

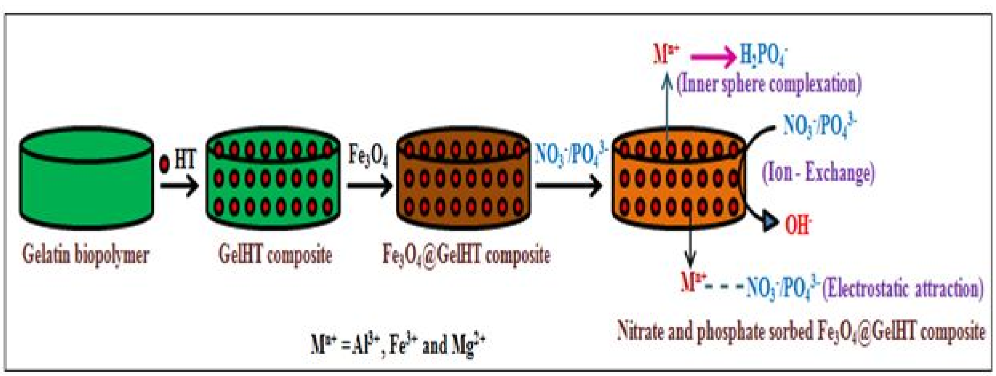

Figure 9. The mechanism of nitrate and phosphate sorption using Fe_3O_4@GelHT biocomposite.

6.4 Functionalized polymeric materials

The significant efforts have been focusing in the development of highly efficient adsorbents toward toxic ions removal. Functionalization is the process of adding fresh functions or properties to the adsorbent by modifying the surface chemistry of the adsorbent materials. In recent year, the numerous functional groups such as amine (-NH_2), carboxylic acid (-COOH), thiol (-SH), shiff base, etc., have been considered as the significant functional groups which prominently improves the surface reactivity of the adsorbents for the removal of numerous pollutants such as heavy metals, NO_3^-, F^-, PO_4^{3-}, SO_4^{2-}, ClO_4^-, etc.

Sowmya & Meenakshi (2013) have developed the efficient and regenerable quaternary - NH_2 modified CS beads (QCB) for the removal of $NO_3^-$and $PO_4^{3-}$from water. The reaction of cross-linked CS beads with glycidyl trimethyl ammonium chloride (GTMAC) gives the strong anion-exchange ability beads with N-quaternary group which makes QCB as the good candidate for adsorption process. The prepared QCB possess the good adsorption capacity of 67.5 and 59 mg/g towards $NO_3^-$and PO_4^{3-}respectively. Moreover, the regeneration studies of QCB were also performed and up to 10 cycles, about 99.00 and 97.50 % of adsorption efficiency for respective $NO_3^-$and $PO_4^{3-}$was maintained.

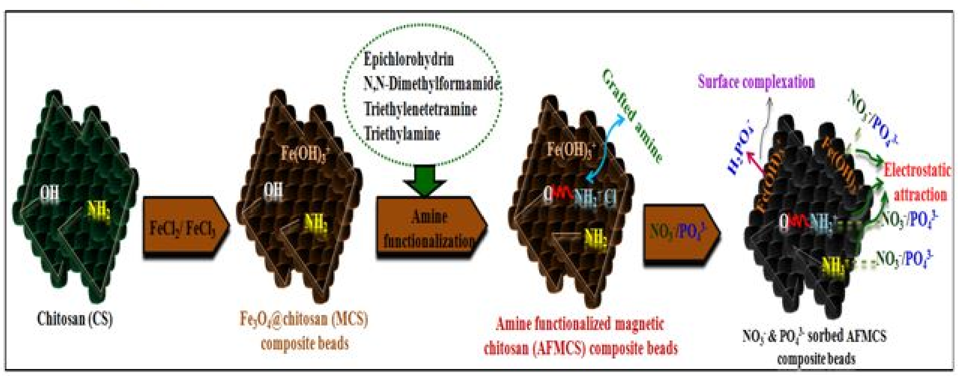

Figure 10. The mechanism of nitrate and phosphate removal by AFMCS composite beads.

Sowmya & Meenakshi (2014) have focused to prepare quaternized chitosan-melamine-glutaraldehyde resin (QCMGR) for the effective removal of $NO_3^-$and $PO_4^{3-}$from water. Melamine having three primaries NH−2 groups which is easily cross-linked with aldehyde. The adsorption study was carried out by both batch and as well as column methods. It was observed that $NO_3^-$and $PO_4^{3-}$was adsorbed effectively on QCMGR by replacing Cl^- ions at the quaternary ammonium group by ion-exchange mechanism which leads to the good removal capacity of 97.5 and 112.5 mg/g toward $NO_3^-$and PO_4^{3-}respectively. Hence, amine functionalized magnetic chitosan (AFMCS) composite beads were synthesized and utilized for $NO_3^-$and PO_4^{3-}removal from water. The possible mechanism of AFMCS composite beads toward NO_3^- and PO_4^{3-} was found to be electrostatic attraction and complexation mechanism which is shown in Figure 10.

6.5 Functionalized graphene oxide supported materials

Recently the materials with higher reactivity and specific surface area possess the incredible potential for waste-water treatment. Graphene oxide (GO) is a hydrophilic carbon materials having the oxygen rich functional groups such as alcohols (R-OH), epoxides (C-O-C), COOH and ketone (C=O) which leads to the more active sites and make it as an effective adsorbent for toxic ions removal. However, due to the interactions of adjacent layers in GO leading to the lower adsorption nature than expected. To outweigh these problems, the functionalization of GO has been developed for the removal of numerous toxic ions from water. The functionalized GO based materials have advantages such as large surface area, thermally stable, suitable pore size and surface modification. The adjustable surface nature of GO allows it for the various heteroatom functionalization such as sulfur (S), N, O, etc.

Sakulpaisan *et al.* (2016) have studied the Titania (Ti_2O_3) functionalized GO (T-F-GO) composite for the removal of PO_4^{3-} from water. T-F-GO composite was synthesized by solvothermal method and the interaction between the surface -OH groups of Ti_2O_3 and the surface -COOH of GO was occurred which gives T-F-GO composite.

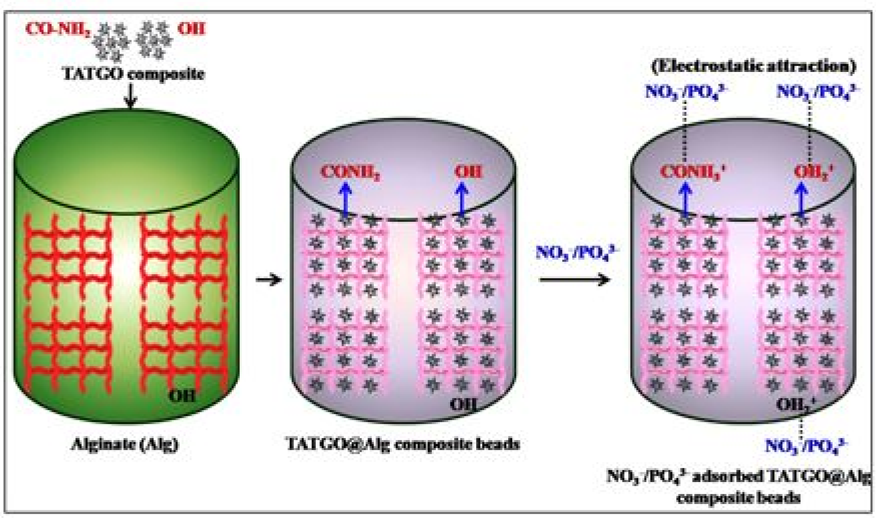

Figure 11. The possible mechanism of TATGO@Alg composite beads for NO_3^- and PO_4^{3-} removal.

The nitrogen rich organic framework namely triaminotriazine (TAT) acts as an adsorbent for the various toxic ions removal. However, TAT possesses the soft powdered nature which develops the pressure drops during filtration. To overcome this problem the chemically modified TAT was developed in recent years. Hence TAT functionalized GO (TATGO) encapsulated Alg namely TATGO@Alg composite beads were synthesized and utilized for NO_3^- and PO_4^{3-} removal from water. The TATGO@Alg composite beads remove both NO_3^- and PO_4^{3-} via., electrostatic attraction as shown in Figure 11.

7 Contribution to the Society

Nitrogen and phosphorus are the necessary key factors liable for improving the nutrients of plants, higher animals and also links the food chain of all the living organisms. Conversely, the extreme level of nitrate ionic strength in drinking water instigates the irrevocable disease in young children called methemoglobinemia (blue baby syndrome). This is occurred in human due to the rapid oxidation of Fe^{2+} of haemoglobin into Fe^3+ of methemoglobin which disbanding the oxygen co-ordination site causes the blue colorization of the skin in toddlers. In addition, nitrite in drinking water is also recuperating the dangerous disease called gastric cancer. Conversely, the surplus NO3- and PO43- contents in water lead to the eutrophication of drinking water sources which comprises the abundant of aquatic species. The tolerable limits of NO_3^- and PO_4^{3-} in drinkable water are 40 and ¡ 0.5 mg/L respectively.

The persistent usage of NO_3^- and PO_4^{3-} has attended the researchers to expand the proficient approaches of confiscating both nitrate and phosphate from the affected aquatic system. To overcome these problems, we have prepared the various biopolymer assisted nanomaterials/composites by hydrothermal method for NO_3^- and PO_4^{3-} removal from water. The advantages of the prepared biopolymeric nanomaterials/composites such as biodegradable, biofunctional, biocompatible and eco-friendly help the society to provide the safe life.

8 Conclusions

The synthesized biopolymer assisted composites/beads were utilized for NO_3^- and PO_4^{3-} removal from water. The biopolymers encapsulated materials possess the higher removal capacity towards nitrate and phosphate as compared with their parent adsorbent materials. In most cases, the mechanism of NO_3^- and PO_4^{3-} removal was governed to be electrostatic attraction and surface complexation. The synthesized biopolymer encapsulated materials can be reused for several cycles which show the cost-effective nature.

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