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Biosorption for Removal of Nitratesand Phosphates: A Review

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ABSTRACT: Although notable progress is being made by researchers in the development of tenable and advanced water treatment technologies, stillhuge population and increasing water demand present challenges for water field researchers.Among multitude of pollutants, removal of nitrates and phosphates,is one of the most threatening issues of global water contamination. For this, biosorption has been used and analysed extensively. In this review, all different sorbent materials, particularly for nitrates and phosphates, are hereby listed and discussed. A brief proposal has also been made about the development of combination of sorbent materials, for both nitrates and phosphates, so that after usage, these materials can be recycled and reused as a source of nitrates and phosphates for various useful purposes.

Keywords- Biosorption, Biosorbent, Nitrates, Phosphates.

1. INTRODUCTION

India is continuously struggling to meet its water requirements due to its large population and increasing demand. On an average 1486 m^3 water is available per capita annually [1].According to World Resources Institute, India is the 13th most water stressed country [2]. Due to increasing population in India and improper disposal of domestic and industrial waste in water bodies and rivers, there is much decline in fresh water availability. As India is the world's 10th most industrialized country [3], it contributes high percentage of organic, inorganic and toxic pollutants in polluting precious water resources [4]. Untreated wastewater is indiscriminately disposed into streams, which leads to many health problems and poor water quality of the water bodies and groundwater. Nearly six lakh children lost their lives in 2010 due to water borne diseases in India; which is 30% of the global total [5]. Globally, about 2 million tons of waste are released in water bodies on daily basis which take in waste from domestic, industrial and agricultural fields [6]. We see for the above-described points, there is much needed value of wastewater treatment.

1.1 Nitrates and phosphates in waste water

Researchers have reported a number of different microbial populations, organic and inorganic contaminants in sewage waste water.This review hereby focusses particularly on nitrates and phosphates as both of these are more often used in fertilizers production, poultry farming etc, thus phosphorus and nitrogen concentration are very high in wastewater from agricultural, domestic and industrial field.Nitrates once ingested get reduced to nitrites so possess health problems especially in infants causing methaemoglobin formation resulting in asphyxia [7]. Its high concentration in water also affects thyroid gland in pregnant women [8]. Also, nitrates get easily converted in carcinogenic substances such as N-nitroso compounds by reacting with other chemicals [9]. Phosphate is one of the main causativechemicals, responsible for eutrophication of our precious natural water bodies. Orthophosphate is found as most widely present species of phosphate in municipal and industrial wastewater [10]. According to U.S. Environmental Protection Agency(USEPA), phosphorus concentration in water should be less than 50 mg L^{-1} [11,12].

1.2 Removal of nitrates and phosphates

A number of methods are used for nitrates and phosphates removal as for example, ion exchange resins, precipitation, reverse osmosis, chemical reduction, bioreactor process, magnetic nanoparticles-based method, electrodialysis etc [13,14,15,16,17]. These methods have limitations such as low efficiency, narrow range of applicability, high requirement of reagents, generation of toxic wastes during production of regents. Among all these, biosorption method seems to be the most effective alternative for removal and recovery of nitrates and phosphates from wastewater due to its simplicity, high efficiency, ease of implementation, recovery rate, economical characteristics. Also, for and during biosorption no other pollutants are generated [18].

1.3 Significance of recovery of nitrates and phosphates

Future uses of nitrates and phosphates after removal and recovery from wastewater (if a cost- effective technique which is operational at large scale is developed) are as following [19].

- use as fertilizer for soil conditioning

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- use in detergents, cosmetics manufacturer industries
- use in animal feed preparation
- use as a potting material

2. DISCUSSION

2.1 Biosorption and biosorbent

Biosorption is the method in which biological materials are used to remove unwanted substances from aqueous solution via adsorption. It is a reversible and quick process in which biosorbate ions binds to the functional groups existing on biosorbent surface [20].

2.2 Biosorbents for nitrates and phosphates

A number of biosorbent materials are being developed with a broad range of applications in removal and recovery of nitrates and phosphates through biosorption.

2.2.1 Biosorbents for Phosphates Removal

Chemically modified ground giant reed has been studied and reported for phosphate sorption [21]. Its sorption capacity was reported 55.7 mg/g. The suitable pH range for this process was 5-10. Anion exchange resins made from chemically modified soyabean hulls were also considered [22]. Chemically modified sawdust of a fibre crop Aleppo pine is reported for phosphate sorption [23]. Algal species such as, Kappaphycus alverezii, Chlorella vulgaris and Scenedesmus dimorphus are reported for phosphate removal and recovery from wastewater [24]. Cultured Staphylococcus xylosus treated with Fe (III) were used for phosphates biosorption, showed monolayer sorption and impressive recovery rates. Biogenic iron oxide produced by iron oxidising bacteria has been reported for removal of phosphates from aqueous solutions [25].Biochar materials developed by using chemically modified orange peel powder can effectively remove phosphates from water [26]. Activated oyster shells are found to have high phosphate removal capacity [27]. Peat has come as a potential sorbent for phosphate removal from aqueous solutions as it has large surface area and is highly porous and also is abundantly available, so is economical to use [28]. Also, after usage, phosphate rich peat can be used as a source of phosphorus for soil conditioning. Biosorbents have been made from agricultural wastes and by-products called AWBs for removal of phosphates from water [29]. Silica based sorbents also known as Nanostructured Silicates have also been used for phosphate sorption [30]. Corn stalk-based resin having biosorption capacity 40.48 mg/L and Zr (IV) loaded orange waste gels having biosorption capacity 175mg/L were also reported for phosphate reduction in wastewater samples [31,32].

2.2.2 Biosorbents for Nitrates removal

Carbon based adsorbents were studied and unsatisfactory results were reported for nitrate sorption [33]. However, carbon nanotubes, powdered activated carbon, commercial granular activated carbon, show high adsorption of nitrate [34]. Red mud after activation is found to give better results for nitrates removal [35]. A number of novel bacterial strains are being isolated and used for nitrate removal from waste water samples [36, 37,38,39,40]. Chitosan is found as an effective biosorbent for nitrate removal from groundwater, but at the same time it results in turbidity in water [41]. Zeolite coated with chitosan showed maximum results for nitrates removal and best results were observed at 303-313 K [42].Many modifications are also done regarding chitosan beads using epichlorohydrin (ECH) and sodium bisulphate which resulted in enhancing the biosorption capacity. 104.0 mg/g adsorption capacity was recorded when sodium bisulphate conditioned chitosan beads were used in acidic environment. Fixed bed design was incorporated to support the biosorbent during the process [43].These chitosan derived biosorbents show economic and many other advantages. 92.1 mg/g biosorption capacity was reported during laboratory studies [44]. The reason for fine adsorption results was due to interaction between Nitrates (anions) and amine groups (positively charged). Egg shells were also taken for reducing nitrates from waste water samples and these egg shells showed significant nitrate removal capacity [45].Although, seeds of amla, potato flakes, husk of banana, wheat, rice etc were used for nitrate removal of nitrates, but only potato flakes gave significant results in nitrate removal, given contact time of 40 minutes, 51.42% nitrate reduction was observed [46]. A microalga, *Trentepohlia Aurea* was also used for sorption of nitrate from wastewater [47].Chinese reed and bamboo powder are among the novel biosorbents for nitrates sorption. Lignocellulosic agricultural waste materials (LCM) and sugarcane bagasse (BG) are been described well for nitrates removal from aqueous solution by several researchers [48]. Modified wheat straw was studied for nitrates removal from wastewater and fine results were reported [49]. Similarly, rice straw was used and tested as a source of activated carbon in nitrate recovery from artificial water samples [50].

2.2.3 CommonBiosorbent MaterialsforRemoval of Nitrates and Phosphates

Phosphate and nitrate removal from wastewater, seem relatable,in some ways [51]. Cross-linked chitosan beads are a leading example of common biosorbent for common biosorbent for both nitrates and phosphates [52]. Its sorption capacity and feasibility of the experiment can be modified and increased, like by protonation of amino group present in chitosan.

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Table 1. Basic parameters used to study for the development of a specific biosorbent

S. No	Name	Significance	References
1.	Biosorption capacity	Indicates the concentration of sorbed biosorbate	[53]
2.	Biosorption efficiency	Refers to the percentage of Biosorption	[54]
3.	• Gibbs free energy change • Enthalpy change • Entropy change	To determine spontaneity of the process	[55]
4.	Isotherm Models • Langmuir • Freundlich • Langmuir- Freundlich • Reddlich-Petterson	To understand mechanism of the process	[56]
5.	Kinetic Models • Pseudo-first order • Pseudo-second order • Intra-particle diffusion	Fordesigning of the adsorption system	[57]
6.	Spectrometric analysis (FTIR)	For characterization of the biosorbent	[58]

CONCLUSION

Nitrates and phosphates are the main pollutants found in domestic and industrial waste water. Main advantages of using biosorption over other conventional methods includes elimination of veryminute quantities of contaminants, cost effectiveness, high efficiency, easy biosorbent regeneration and no additional pollutants formation during the process [59]. Also, non-biodegradable waste can be used in supporting and carrying the biosorbent during treatment. Nanotechnology is being used to upgrade biosorbents for increasing the process efficiency. Researchers are working on Genetically engineered microbial biosorbents having specific affinity and other features for enhancement of biosorption efficiency and its applicability, so in future, more advanced and relevant technologies are hoped to be developed and to be used in waste water treatment [60]. Particular attention is needed to be given to develop more advance material which can be used as a common biosorbent for both nitrates and phosphates removal and recovery from wastewater, so that these can be recycled and used in fertilizer industries. Biosorption should be made operational at domestic level, community level and small industries level, so that recovered nitrates and phosphates loaded on biosorbent can be used in agricultural fields for enhancing soil fertility and in other areas. At large scale with real wastewater sample, main problem is the presence of other pollutants, so more research needs to be done regarding recovery of the phosphates and nitrates at large scale after biosorption. High chemical oxygen demand (COD) of real wastewater samples also create problem. Storage problem which may arise in case of reusability should be emphasized upon. Sorbent beds should be made for assessment of the refined sorbent [61].Biosorption offers a number of advantages over other methods but commercial adoption of biosorption is still lacking in case of nitrates and phosphates.

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