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Strategies for Nitrate removal from aqueous environment using Nanotechnology: A Review

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ABSTRACT

Nitrate is a water pollutant whose removal from water is necessary to lessen pollution and prevent damage to life. Several conventional techniques such as adsorption, ion exchange process, reverse osmosis, electrochemical, chemical, and biological methods have been developed for removal of nitrate, however they have several limitations such as requirement of post-treatment, less efficiency, and high installation costs. The field of Nanotechnology has observed tremendous growth in the past and has many environmental applications such as the use of nanomaterials for soil and water remediation, filtration of pollutants, water purification, biosensors, and in desalination. Recently, Nanotechnology has emerged as an excellent alternative for nitrate removal over conventional techniques. Nanomaterials due to their small size have large surface area and thus have high reactivity which, enables them to be used as reducing agents and adsorbents. This review focuses on the use of different nanomaterials especially nanoparticles, nanotubes, nanofibers, nanoshells, nanoclusters, and nanocomposites for removal of nitrate from an aqueous system. The limitations of using such nanomaterials for removal of nitrate and possible techniques to overcome these limitations have been discussed as well.

1. Introduction

Water pollution is a major issue with several consequences on life on earth. It is mainly caused by the industrial pollution and anthropogenic activities [1]. In the past 200 years, there have been significant changes in the global nitrogen cycle. There is now increasing mobility and availability of nitrogen over large areas of earth. Apart from this, inorganic nitrogen such as nitrates (NO_3^-) enter the environment, especially in aquatic systems through different anthropogenic activities such as agricultural and urban runoff, usage of pesticides, organic or inorganic compounds, improper treatment of industrial wastes, leaching of waste in groundwater, and sewage effluents [2–7]. Nitrate concentrations above acceptable limit, as given in international standards, in various water sources is a major environmental concern all over the world. This ion is found naturally and is the most stable form of combined nitrogen for oxygenated systems. It also serves as an essential source of nitrogen for plants. It is a widespread contaminant as it is highly water soluble [8]. It also affects several drinking supplies, and is known to cause eutrophication [9,10]. At elevated levels, it is known to cause many health complications such as methemoglobinemia [11], diabetes [12] and is also known to cause outbreak of infectious diseases. They also adversely affect freshwater and marine animals, with freshwater fishes being more susceptible to elevated nitrate levels in water [13]. It also significantly affects cattle through nitrate poisoning [14]. Nitrate removal from environmental sources such as surface water bodies and ground water is thus essential for preventing such issues.

Several techniques have been established for removal of nitrate from waste water. Adsorption [15–19], Ion exchange process [20], electrochemical methods [21–23] reverse osmosis, [24] biological methods [25–29], and chemical methods [30] are some of the conventional techniques implemented. However, these techniques have several limitations. Conventional adsorption techniques require proper selection of the adsorbent such that it is robust and can work under variable environmental conditions. Estimation of the adsorption efficiency, reusability, and disposal of the adsorbents with nitrate are also some of the major issues [16]. Ion exchange techniques require post-treatment and are sensitive to various contaminants present in the water [31]. Reverse osmosis is also sensitive to contaminants other than nitrate. It requires a specific amount of pressure and is also prone to biofouling. Biological and chemical methods cause toxicity in the water. Also, installation of such techniques can be expensive. Nanotechnology can serve as an alternative for these conventional techniques.

Nanotechnology is a field which deals with modification, design, and application of nanoscale objects (10^{-9} m). It has various

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applications in food safety, medicine, cosmetic industries, and electronics. Nanomaterials are synthesized through top down or bottom-up approach out of which, bottom up approach is a widely preferred technique as it offers greater size control and prevents the contamination of nanomaterials [32,33]. They have excellent thermal, mechanical, optical, structural, and morphological properties which enable them to be used in different environmental applications. In environment, nanotechnology has been used in groundwater remediation and filtration of waste water to lessen its negative impacts on the ecosystem [34,35]. It has also been used in energy production [36,37], pollution treatment and dye removal [38–40].

In this review, nitrate removal using nanotechnology has been discussed. It is a comprehensive compilation of papers from past 12 years that have used nanotechnology for nitrate removal. They have been accessed through SciFinder, Google Scholar, and ScienceDirect. The criteria for the selection of the papers was such that they reported the use of different nanomaterials, either with or without modification, for the removal of nitrate from aqueous environment. The nanomaterials used for nitrate removal possessed different reducing and adsorbing capabilities for nitrate. This review is novel and such kind of work, which solely focuses on the use of nanotechnology for nitrate removal has not been reported previously.

2. Mechanisms of nitrate removal

Nitrate in nature is usually formed as a denitrification product of nitrogen. It is highly soluble in water and is unreactive. Fertilizers and other waste products that consist of nitrogen are decomposed to give ammonia followed by further oxidation to nitrate and nitrite. Nitrate is usually present in air, water, and food and is taken up by plants to synthesize organic nitrogenous compounds [41].

Despite being unreactive, it can be microbially reduced to form nitrogen gas (N_2), and nitrogen monoxide (N_2O). Commonly used reducing agents include active metals, ammonia, borohydride, formate, hydrazine, hydroxylamine, hydrogen, and Iron. Active metals reduce nitrate to ammonia or nitrite in a basic solution, while ammonia in an acidic solution reduces nitrate to nitrogen or nitrous oxide at high pressure and temperatures. Sodium borohydride forms nitrite and ammonia in the presence of metal alloys. Nitrate reduction can take place through energy methods such as electrochemical, thermal, or photocatalytic methods. However, simple chemical reduction reactions in aqueous solutions cannot efficiently remove nitrate [42]. Effective reduction takes place in the presence of powerful catalysts. Nanomaterials, due to their small surface area have high catalytic properties and thus, have excellent reducing potential. Nitrate on reduction releases ammonia (NH_3), nitrogen gas (N_2), nitrite (NO_2^-), and ammonium (NH_4^+). The products formed differ based on the type of the nanomaterial used.

Another common mechanism in nitrate removal is adsorption. In adsorption method, nitrate molecule is attached on the surface either through physisorption or chemisorption. Nanomaterials that have excellent adsorption properties possess two main properties: their innate surface area and external functionalization [43]. High surface area, adsorption activity, location of atoms on surface, lack of internal diffusion resistance, and high surface binding energy are also some of the factors that determine the adsorption capability of the nanomaterial [44,45]. The adsorption capability of a nanomaterial is found through different isotherm and kinetic models. Table 1 shows the different nanomaterials used for nitrate removal, along with the isotherm and kinetic models used. The nanomaterials that have been used for nitrate removal are nanoparticles, nanotubes, nanoclusters, nanoshells, nanofibers, and nanocomposites (Fig. 1). The reducing capacity and adsorption efficiency may vary with each nanomaterial. Fig. 2 shows the removal mechanisms of nitrate through different nanomaterials.

3. Nanomaterials for nitrate removal

Nanomaterials used till date for removal of nitrate are nanoparticles, nanotubes, nanofibers, nanoclusters, and nanocomposites. Fig. 3 gives a classification of the nanomaterials used for nitrate removal. Table 2 shows the different nanomaterials used for nitrate removal along with parameters such as initial nitrate concentration, pH, adsorbent dose, and temperature. It also compares the nitrate removal efficiencies of different nanomaterials. Table 3 shows the removal mechanisms of nitrate by the nanomaterials and the nitrate determination method.

3.1. Nanoparticles

Nanoparticles are in the range of 1–100 nm and can be metallic, semiconductor, or polymeric. They have various environmental applications such as microbial detection and monitoring, source recovery, and chemical degradation or environmental remediation. They can effectively remove a wide variety of contaminants as well [46]. They can be used as reducing agents, or as adsorbents for various contaminants in soil or water. Due to their small size, large surface area and excellent catalytic activity, nanoparticles are emerging as an alternative to conventional treatments for removal of nitrate from wastewater. They had been used either as a standalone system in the aqueous solution, with or without coating, or were immobilized on different supports. Fig. 4 shows the different supports used for immobilization of nanoparticles.

3.1.1. Nanoscale zero valent particles (NZVI)/Iron nanoparticles

Nanoscale Zero Valent Iron (NZVI) has gained attraction worldwide due to their excellent catalytic activities, and large surface area [47,48]. These properties enable them to be used as a reducing agent. Some studies reported here have used NZVI as adsorbents as well.

Bare NZVI, i.e. NZVI which have been directly synthesized from its source without any modification are widely used for nitrate removal. In a study, NZVI had been synthesized through a natural reduction process of hydrothermal and natural goethite. Normally, NZVI synthesis is an expensive process, however, when synthesized with natural sources such as natural and hydrothermal goethite, the process becomes significantly cheaper. On comparison of NZVI synthesized with natural and hydrothermal goethite, with ordinary zerovalent iron, it was found that ordinary NZVI showed a 90% removal rate at pH 1, but the removal rate drastically decreased to 10% at pH 6, while NZVI obtained from natural and hydrothermal goethite showed a removal rate of 95.1% and 91.3% respectively at pH 1, and this rate decreased to 72.4% and 83.5% at pH 8. Increasing the initial nitrate concentration also affected the nitrate removal rates. NZVI synthesized from natural goethite showed an increase in formation of ammonia with increase in time, while very low concentration of nitrite was formed. Some of the nitrate was reduced to nitrogen gas as well. NZVI synthesized using natural and hydrothermal goethite was a cheap alternative and it showed much better nitrate removal rates than ordinary zerovalent iron [49]. Freshly synthesized NZVI, dried NZVI, and dried and sonicated NZVI have also been used for removing high concentrations of nitrate. Nitrate reduction using these NZVIs were done at various conditions such as pH, initial concentrations of nitrate, and adsorbent dose. There was barely any influence of pH on the reduction of nitrate, as the reduction had occurred at an unspecific pH. The NZVIs reduced nitrate to ammonium and nitrite. However, the amount of nitrite produced was less and had reduced with time. In case of fresh NZVI, rapid nitrate reduction had occurred, with 1 mg/mL of nitrate; reduced within a minute. In this case, nitrite production increased to 5% in 20 min. In case of dried and sonicated NZVI, the nitrite produced was nearly 7% [50]. In another study, bare NZVIs had been doped with gold, copper and silver nanoparticles and were used for simultaneous removal of nitrate and cadmium (Cd) contamination. Here, the reactivity of NZVI to the co-contaminants and by-product formation was evaluated, and it