Removal of Nitrate from Water by Adsorption – A Review

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Abstract

Nitrogen is present in atmosphere and is essential for all living things. However excess nitrate-nitrogen present in water can lead to adverse effects on living beings. Nitrate is the most common anion to be found in groundwater. Water quality monitoring in various states and countries conducted in groundwater survey around the world showed varying concentrations of nitrate. Most of the places, the concentration is within USEPA standards of 10mg/L nitrate-nitrogen (45mg/l nitrate according to Bureau of Indian Standards). However, some isolated cases showed spike in nitrate concentration in water mostly due to presence of wastewater disposal sites, landfills and septic/solid disposals. Consumption of nitrate contaminated water can affect livestock and humans especially babies and pregnant women such as methenaglobemia in infants. Various treatments have been found for removing ground nitrate from groundwater. Most cost effective and efficient method is adsorption.

Keywords: nitrate, water, adsorption, zeolites, removal

I. INTRODUCTION

Water, a transparent chemical substance, covers almost 71% of earth and plays one of the most vital role in the biotic component sustaining on earth. Origin of water on the planet of earth is not fully understood till now, with different hypotheses on the possibilities of accumulation of water on the earth. Water on earth is of constant amount, recycling through various processes of transpiration, precipitation, evaporation, condensation and runoff. Most of the water, about 97% is salt water in seas and oceans, a fraction as water vapour, with only 3.5% is freshwater. Out of the freshwater, 69% is in the form of ice and only less than 0.7% is easily available in lakes, rivers and groundwater [2].

The consumption of water by countries depends on their standard of living and degree of industrialisation. Sources of water are mostly surface water including lakes, rivers, streams etc. But with need of more and more water, groundwater sources are being explored for larger scale.

II. NITRATE IN WATER

Nitrate is polyatomic ion of nitrogen present in water and soil. It is very soluble and produces colourless, odourless and tasteless water. It is very important for plants and hence nitrate is available in fertilizers applied to the plants. Nitrate is very water soluble and excess nitrate percolates through soil media and reaches groundwater table. Some of the geological formations also contain nitrate ions which increases groundwater nitrate in such locations. The nitrate ions in water vary in different places some places exceeding the drinking water standards.

A. Global and Indian Scenario of nitrate contamination

The water quality assessment carried out in various states and countries by government agencies have presented data of various anionic contaminations in groundwater. Molecular, atmospheric nitrogen may be transformed into organic nitrogen by nitrogen fixing bacteria and algae. Therefore, natural waters may contain dissolved nitrogen gas (N), ammonia (NH3), in addition to ionic forms such as ammonium (NH4), nitrite (NO2), nitrate (NO3) as well as organic nitrogen compounds.[5]

Table – 1
Number of Indian States with Contaminated Groundwater. [19]

Chemical contaminant	*Number of Indian states*
Arsenic (> 0.05 mg/L)	*10*
Fluoride (>1.5mg/L)	*20*
Heavy metals (Lead >0.1mg/L ; Cadmium>0.003mg/L ; Chromium> 0.05 mg/L.)	*15*
Iron (>1mg/L)	*24*
Nitrate (>45mg/L)	*21*

Around the world, various countries have conducted water survey and found exceeding concentration of nitrate. Many of the states with nitrate pollution are developing or underdeveloped with developing parts of already developed countries. Majority of European countries shows nitrate levels higher than 50mg/l NO3-N. West and Central America have 10-30mg/l NO3-N in most

parts. In China, most regions shows highest of 30mg/l and lowest of 2-5 mg/l. It is mainly due to huge quantities of fertilizers used in the country. In Australia, the nitrate contamination is widespread with formation of clusters of regions exceeding 50mg/l NO3. Some parts have more than 100mg/l in the country. In Namibia, Bostwana and South Africa, the highest contamination of nitrate is in central part exceeding 500mg/l NO3.[2]

In India, more than 21 states are contaminated with nitrate in groundwater exceeding 45mg/l. Churu, Jaipur, Meerut, Nagpur, Gondia, Hyderabad are some of the cities having high nitrate contaminations. Aurangabad, Buldana, Jalgaon, Nagpur, Amravati, Wardha in Maharashtra state has 250-380mg/l of nitrate in various wells. Most of the wells and sources of drinking water have not yet been tested to provide accurate number of places contaminated with high nitrate pollution.[6]

B. Sources of Nitrate Pollution of Groundwater

Most of the contamination in groundwater comes from excessive use of the fertilizers and faulty septic tanks. Some percentage also comes from the plant metabolism process of fixation. The sources can be said as below:

- Decaying plant or animal material.
- Agricultural fertilizers and nutrients.
- Domestic sewage, septic tanks.
- Areas of high density animal confinement.
- Geologic materials containing soluble nitrogen compounds.
- Natural cycle of nitrogen by plants by the process of 'nitrogen fixation'.

C. Effects of nitrate pollution on health and environment

Consumption of excess nitrate contaminated water does not lead to sudden adverse effects. Also due to its colourless tasteless property, identifying the polluted water is difficult. Nitrate, when consumed, reacts with haemoglobin & reduces the oxygen in the body. Baby blue syndrome (methemoglobinemia) is most common ill affect of nitrate consumption of more than 45mg/L affecting infant of less than 6 months.

Some of the serious diseases that are documented in various studies are chronic inflammatory, blue-baby cancer, enema of eyelids, tumour, congestion of nasal mucous membranes and pharynx, stuffiness of the head and gastrointestinal, muscular, reproductive, neurological and genetic malfunctions caused by nitrate. [20]

Excess nitrate contaminants present in ponds, lakes and rivers lead to eutrophication. Eutrophication is a phenomena where due to the availability of nutrients like nitrate and phosphate, there is an abundant growth of algae which renders it unsuitable as a source of drinking water.

D. Drinking water standards for nitrate

The permissible limits for nitrate in drinking water are different under different institutions. Also nitrate is expressed as nitrate (NO3) and nitrogen nitrate (N-NO3), measured in microgram per litre (mg/L) or parts per million (ppm).

Table – 2
Drinking Water Standards for Nitrate [8], [24]

Contaminant	*Maximum Contaminant Level*
Nitrate (NO3)	*USEPA:* *MCL= 10.0 mg/L* *MCLG(goal) = 10.0 mg/L (N-NO3)*
	Health Canada MAC: 10 mg/L (N-NO3)
	WHO Guideline: 50 mg/L (NO3)
	IS 10500 -2012: 45mg/l (NO3)

III. PRESENT TECHNOLOGIES FOR REMOVAL OF NITRATE

Many studies have been carried out for the removal of nitrate from groundwater for making it potable. However, some of the methods fall short of being reliable and cost effective.

Reverse osmosis is one of the fine methods to remove any of the foreign constituent from water, making it potable. However, it requires a unit of storage tanks, sediment filter unit, a membrane, etc, which can spike up the cost for treatment. Also, reverse osmosis generates nearly 10% of reject water from the total feed water. This fact makes it unsuitable in the regions of limited source supply.

Distillation is one of the age old method of purifying water, however it requires huge amount of energy to generate sufficient water for drinking purpose. Similarly to reverse osmosis, it is slow process and expensive.

Electrodialysis is another novel and effective method of removing nitrate from groundwater. But the treatment for large supply of water can be costly affair.

Adsorption and ion exchange is one of the most effective, simple and reliable method of treatment of nitrate contaminated groundwater. Certain resins can provide very high removal rates. The adsorbents or ion exchange resins can be regenerated which these methods cost effective and waste conscious.

Another method of nitrate removal is biological denitrification. However, this method requires initial food supply to sustain biological activity, thus not very suitable for groundwater.

IV. ADSORPTION – NOVEL METHOD FOR NITRATE REMOVAL FROM WATER

Adsorption is a phenomenon of adhesion of ions or molecules from one phase in to another. It is a surface phenomena where the ions are adhered to the surface of another media in mono or multilayer. Adsorption depends on the surface charge of the media used to adhere the ions called as adsorbent and the charge of ions to be adhered called as adsorbate.

Adsorption is most widely researched and still evolving process in water and wastewater treatment. The property of adsorption which makes it so novel process is its suitability of moulding as per requirement. Most common materials such as activated carbon, clays, and zeolites as well as waste materials like fruit feels, seeds, husks, etc can be used as adsorbent. Also very simple working and understanding of chemistry behind the process made it popular in research areas.

Nitrate is a polyatomic compound of nitrogen with three molecules of oxygen and one molecule of nitrogen bonded by an ligand. Most of the nitrate is in the form of ammonium nitrates or magnesium nitrates which are found in commonly used agricultural fertilizers. The cations in the salts are adsorbed by the clay particles having negative surface charge. This negative charge repulse the anions like nitrate. Thus the nitrate readily mixes with pore water. For removing nitrate from water, adsorbents with positive surface charge are employed which gives more removal efficiency. Materials with Al and Fe ions are more efficient to remove anion due to their amphoteric nature. They can remove cations and anions depending on the environment like pH. Anions like PO4 and arsenate can be removed by using compounds with ligand bonds.

Zeolites are another novel material for removal of impurities and pollutants from water. Zeolites are naturally occurring crystalline materials with sodium aluminosilcate frameworks. Common natural zeolites have cations like Na or Ca on the surface which acts as adsorbing site or exchange site depending on cation or anion is to be removed. Suitable surface modification with cationic surfactants can increase the active sites for removal of nitrate.

V. LITERATURE REVIEW

Table – 3
Literature Review on Various Papers Regarding Adsorption.

Sr.No	*Material*	*Concentration (mg/l)*	*Dose (g/L)*	*pH*	*Contact time*	*Frendluich Adsorption capacity (mg/g)*	*Langmuir Adsorption capacity (mg/g)*	*Removal efficiency (%) Adsorption Capacity (mg/g)*	*Ref.No.*
1.	*Chloridric acid treated CL zeolite.*	*100*	*1.6*	*5*	*180*	*-*	*2.66*	*37%*	*1*
2.	*Al –Cli*	*400*	*0.5*	*-*	*240*	*-*	*-*	*9.676mg/g*	*9*
	Fe-Cli							*16.15mg/g*	
	Mn-Cli							*10.53mg/g*	
	Mg-Cli							*18.08mg/g*	
3.	*MO- CAC*	*12*	*1*	*-*	*20*	*-*	*40.9±1.6*	*49%*	*11*
	MO-RHA						*31.5±2*	*28%*	
4.	*Natural Clinopilotite*	*6.5*	*1*	*9.5*	*60*	*-*	*1.30*	*-*	*17*
5.	*ZVI Zeolite*	*33.5*	*3*	*6.2*	*864*	*-*	*-*	*70%*	*20*
6.	*Acid Activated Bentonite clay*	*250*	*2*	*5*	*90*	*-*	*8.68*	*80%*	*23*
7.	*10% Ni/Fe EG*	*60*	*1.3*	*6*		*-*	*-*	*98.4%*	*25*
8.	*Unmodified Zeolite*	*100*	*0.1*		*5.5*	*144*	*0.44*	*2mg/g*	*18*
	Ze-ZVI						*3.75*	*22.92mg/g*	
9.	*SBA-16 mesoporous silica*	*250*	*2*	*5*	*-*	*1.47*	*49.02*	*51.1 mg/g 40%*	*21*
10.	*Perlite*	*100*	*0.7*	*5*	*120*	*-*	*-*	*36.63mg/g 91.01%*	*15*
11.	*Rice hull zeolite -Water washed*	*69*	*0.2*	*240*	*-*	*-*	*-*	*99.11*	*7*
	-Acid washed							*99.26%*	
12.	*Surface modified natural CLI*	*50*	*1.5*	*6.5*	*144*	*-*	*-*	*97%*	*14*
13.	*Banana peel adsorbent*	*200*	*0.05*	*6*	*30*	*-*	*-*	*80%*	*4*
14.	*Fe-Z*	*300*	*1*	*5.5*	*144*	*-*	*-*	*5.6 mg/g*	*10*
	Mn-Z							*3.9mg/g*	

	Mg-Z							*3.2 mg/g*	
15.	*Annona squamosa bark*	*100*	*1*	*2*	*300*			*99%*	*12*
16.	*Chitin*	*100*	*1*	*6.7*	*2*	*0.2*	-	*35%*	*13*
17.	*ZnCl2-Activated carbon*	*40*	*7.5*		*2*	*6.24*	-	*10.3mg/g*	*3*
18.	*Clay*	*300*	*1.5*	*5.1*	*180*	*215.69*	-	-	*14*

VI. CONCLUSION

Nitrate being a ubiquitous, important as well as polluting ion which cannot be eliminated completely from earth, it is vital to effectively mitigate it under the safe standards. Many researches and studies have been carried out for removal of nitrate from water. Various modifications of the available techniques and materials have also been studied.

In our present study, a locally available natural zeolite is studied for removal of nitrate from groundwater. Also suitable surface modification is also researched to effectively increase the efficiency of removal of nitrate.

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