Section A-Research paper

A Review on Nitrate Removal from Water by Adsorption

Dr. Maaz Allah Khan
Department of Civil Engineering
U.I.E.T.Babasaheb Bhimrao Ambedkar University, India

Kaushlesh Kumar Shah
Department of Civil Engineering
K.M.C. Language University.

Abstract

All life depends on nitrogen, which is present in the atmosphere. However, too much nitrate-nitrogen in water can have a negative impact on living things. The most frequent anion to be found in groundwater is nitrate. Nitrate concentrations were monitored for water quality in different states and nations as part of a global groundwater survey. The concentration is often within the USEPA's 10 mg/L nitrate-nitrogen (45 mg/l nitrate, according to Bureau of Indian guidelines) guidelines. However, in a few isolated instances, water nitrate concentrations spiked, primarily as a result of the existence of landfills, septic systems, and solid waste disposal facilities. Consuming nitrate-contaminated water can have negative effects on humans, animals, and pregnant women. One such effect is methenaglobemia in young children. Different therapies have been used..

Keywords: nitrate, water, adsorption, zeolites, removal

I. INTRODUCTION

Water, a clear chemical that makes up nearly 71% of the planet, is essential to the survival of the biotic components on earth. With numerous theories regarding the potential for water to accumulate on earth, the origin of water on the planet of Earth is still not entirely known. Earth's water supply is constant and is recycled through a number of processes, including transpiration, precipitation, evaporation, condensation, and runoff. The majority of water, or 97%, is salt water found in seas and oceans. Freshwater makes up about 3.5% of the total. Less than 0.7% of the freshwater is readily accessible in lakes, rivers, and groundwater, while 69% of the freshwater is in the form of ice [2].
Countries' water use is based on

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

Consuming excessive amounts of nitrate-contaminated water does not immediately have negative effects.
The fact that the polluted water is tasteless and colourless further makes it difficult to recognise.When nitrate is ingested, it intera cts with haemoglobin and lowers the body's oxygen levels.The most frequent adverse effect of nitrate ingestion of more than 45 mg/L on infants younger than 6 months old is baby blue syndrome (methemoglobinemia).Numerous studies have identified a nu mber of serious diseases, including chronic inflammation, bluebaby cancer, eyelid enema, tumours, nasal and pharyngeal congest ion, head congestion, and gastrointestinal, muscular, reproductive, neurological, and genetic defects brought on 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 the phenomena of ions or molecules sticking together when they move from one phase to another. The ions are stuck to the surface of another medium in mono or multilayers in this surface phenomenon. Adsorption is dependent on the surface charge of the adsorbent, the material employed to adhere the ions, and the charge of the ions being adhered, or adsorbate.

The most extensively studied and continually developing technology for treating water and wastewater is adsorption. The capacity of adsorption to be moulded to meet requirements is a characteristic that makes it such a new process. Most common materials like activated carbon, clays, and zeolites can be utilised as adsorbents, as can waste products such fruit skins, seeds, and 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.*	*102*	*1.6*	*5*	*180*	-	*2.66*	*37%*	*1*
2.	*Al –Cli*	*401*	*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*	*11*	*1*	*-*	*20*	-	*40.9±1.6*	*49%*	*11*
	MO-RHA						*31.5±2*	*28%*	
4.	*Natural Clinopilotite*	*6.4*	*1*	*9.5*	*60*	-	*1.30*	-	*17*
5.	*ZVI Zeolite*	*32.5*	*3*	*6.2*	*864*	-	-	*70%*	*20*
6.	*Acid Activated Bentonite clay*	*247*	*2*	*5*	*90*	-	*8.68*	*80%*	*23*
7.	*10% Ni/Fe EG*	*61*	*1.3*	*6*		-	-	*98.4%*	*25*
8.	*Unmodified Zeolite*	*108*	*0.1*		*5.5*	*144*	*0.44*	*2mg/g*	*18*
	Ze-ZVI						*3.75*	*22.92mg/g*	
9.	*SBA-16 mesoporous silica*	*251*	*2*	*5*	*-*	*1.47*	*49.02*	*51.1 mg/g 40%*	*21*
10.	*Perlite*	*10*	*0.7*	*5*	*120*	-	-	*36.63mg/g 91.01%*	*15*
11.	*Rice hull zeolite -Water washed*	*67*	*0.2*	*240*	*-*	-	-	*99.11*	*7*
	-Acid washed							*99.26%*	
12.	*Surface modified natural CLI*	*51*	*1.5*	*6.5*	*144*	-	-	*97%*	*14*
13.	*Banana peel adsorbent*	*190*	*0.05*	*6*	*30*	-	-	*80%*	*4*
14.	*Fe-Z*	*301*	*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.

REFERENCES

[1] Ali Azari, et al, Nitrate Removal from Aqueous Solution by using Modified Clinoptilolite Zeolite, Arch Hyg Sci Vol.3, No.1, (2014), pp 184-92
[2] Ashu Chaudhary et.al, Global Status of Nitrate and Heavy Metals in the Ground Water with Special Reference to Rajasthan, Chemical Science Review and Letters, vol. 4(14), (2015), pp643-661
[3] C Namasivayam and D Sangeetha, Removal and Recovery of Nitrate From Water by ZnCl2 Activated Carbon from Coconut Coir Pith, an Agricultural Solid Waste, Indian Journal of Chemical Technology, Vol (12), (2005),pp513-521
[4] Ch. Adisheshu Reddy et.al, Banana Peel as a Bioasorbent in Removal of Nitrate from Water, International Advanced Research Journal in Science, Engineering and Technology Vol. 2, Issue 10, (2015), pp 94-98
[5] Concept Note on Geogenic Contamination of Ground Water in India with a special note on Nitrate, Central Ground Water Board Ministry of Water Resources Govt. of India, (2013)
[6] Danila S. Paragas et al, Preparation, Characterization And Application Of Rice Hull Derived Zeolites In The Water Treatment, Journal Of Asian Scientific Research, 4(7), (2014), Pp 348-355.
[7] Hemant W. Khandareet et al, Scenario of Nitrate contamination in Groundwater: Its causes and Prevention, International Journal of ChemTech Research, Vol.5, No.4, (2013), pp 1921-1926
[8] IS 10500 : 2012, Bureau of Indian Standards, May 2016.
[9] Jelena Pavlovic et.al., Surface Modification of the Natural Clinoptilolite for its Potential Use for the Nitrate Removal from Water Media, Proceedings of the 5th Serbian-Croatian-Slovenian Symposium on Zeolites, pp 112-115
[10] Jelena K. Milenković et al, Modification Of Natural Clinoptilolite For Nitrate Removal From Aqueous Media, Journal of Serbian Chemical Society, (2014), pp 1309-1322
[11] John Barajas et al., Simultaneous Removal of Anions Using Moringa-Functionalized Adsorbents, IEEE Systems and Information Engineering Design Conference (2016), pp 12-15
[12] M Sumeetha and K. Ravindranath, Removal of Nitrates from Polluted Waters using Bio-Adsorbents,International Journal of Life Science Biotechnology and Pharma Research, Vol.(2), No.3,(2012),pp151-160
[13] M. Morghi et al, Removal of Nitrate Ions from Aqueous Solution using Chitin as Natural Adsorbent, International Journal of Research in Environmental Studies, Vol.(2),(2015), pp8-20
[14] Mahmond El Ouardi et al, Effective Removal of Nitrate Ions from Aqueous Solution using New Clay as Potential Low-Cost Adsorbent, Journal of Encapsulation and Adsorption Sciences, Vol.(5), (2015), pp178-190
[15] Mazyar Sharifzadeh Baei, Removal of Nitrate from Aqueous Solutions in Batch Systems using Activated Perlite: An Application of Response Surface Methodology, Asia-pacific Journal Of Chemical Engineering, (2015), PP 437-537
[16] Mike Masukume et al., Nitrate Removal From Groundwater Using Modified Natural Zeolite, Water Environment Technology, (2011), Pp. 292-297
[17] Mozhdeh Murkani et al, Evaluation of Natural Zeolite Clinoptilolite Efficiency for the Removal of Ammonium and Nitrate from Aquatic Solutions, Environmental Health Engineering and Management Journal, (2015), pp 17–22
[18] Saloome Sepehri, et al, Nitrate Removal From Aqueous Solution Using Natural Zeolite-supported Zero-valent Iron Nanoparticles ,Soil & Water Resource, 9-(4), (2014), Pp224–232
[19] Sandeep Pai and Prathamesh Mulye, Indiaspend.com, 11, March, 2016.
[20] Seunghak Lee, Development of a New Zero-Valent Iron Zeolite Material to Reduce Nitrate without Ammonium Release, Journal of Environmental Engineering (ASCE), Vol. 133, (2007), pp 6-12
[21] Thi Hai Linh Bui, Removal of nitrate from water and wastewater by ammonium-functionalized SBA-16 mesoporous silica, (2013).
[22] V. Sunitha, Nitrates in Groundwater: Health Hazards and Remedial Measures Indian Journal of Advances in Chemical Science, Vol.1, No.3, (2013), pp 164-170
[23] Wasse Bekele, et.al., Removal of Nitrate Ion From Aqueous Solution by Modified Ethiopian Bentonite Clay, IJRPC, Vol.4, No.1, (2014), pp 192-201.
[24] www.wqa.org, Water Quality Association, National Headquarters & Laboratory, Lisle, Illinois, (2013), dated 02.08.2016.
[25] Yue Jun-jie, et al, Expanded Graphite Applied in the Reactive Nano- Fe/Ni Composite as a Support for Reduction of Nitrate in Waters, IEEE (2010), pp 4-7