Research article Available online www.ijsrr.org ISSN: 2279–0543

International Journal of Scientific Research and Reviews

Nitrate Removal from Groundwater Using Crushed Lemon Peel and Activated Charcoal

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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. In some places, the concentration is more than USEPA standards of 10mg/L nitrate-nitrogen (45mg/l nitrate according to Bureau of Indian Standards) and was mostly due to presence of wastewater disposal sites, landfills and septic/solid disposals. Elevated concentrations of nitrate in surface and ground waters can cause eutrophication of natural water bodies, and in drinking water they can pose a threat to human health, especially to infants by causing 'blue baby' syndrome. Various treatments have been found for removing nitrate from groundwater. Adsorption technology is an attractive method to remove nitrate from water compared to other technologies in terms of simplicity, cost, design, operation and maintenance, and effectiveness. The use of low cost adsorbents like crushed lemon peel and activated charcoal is been investigated as a viable replacement for the current expensive method of removing nitrate. The main objective of the work is to investigate and implement a conceptual layout for an inexpensive and simple system focused on column based study. The ground water would be treated to reduce nitrate contents to permissible drinking water standards as stipulated by BIS: 10500: 2012 so that it can safely be used for drinking purposes by general public.

KEYWORDS

USEPA	United States Environmental Protection Agency
BIS	Bureau of Indian Standards
GAC	Granular Activated Carbon
MCL	Maximum Contaminant Level
MCLG	Maximum Contaminant Level Goal
WHO	World Health Organisation
MAC	Maximum acceptable concentrations
IS	Indian Standards

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INTRODUCTION

General background

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 water soluble and excess nitrate percolates through soil media and reaches groundwater table. The nitrate ions in water vary in different places some places exceeding the drinking water standards.Nitrate enters water bodies as a result of excessive use of fertilisers and contamination from animal waste and urine, sewer leakage, and industrial discharge. Once the nitrate enters the environment it is very difficult to remove it. The increasing level of nitrate contributes to potentially serious problems for people's health and the environment. It is therefore very important to prevent nitrate pollution by using cost-effective treatment methods that can remove large amounts of nitrate efficiently.

The major health concern of nitrate exposure through drinking water is the risk of methemoglobinemia, or "blue baby syndrome," especially in infants and pregnant women. It can also cause certain types of cancer, and other chronic health issues. Nitrate is naturally occurring at low levels in most waters, but it is particularly prevalent in groundwater that has beenimpacted by certain agricultural, commercial or industrial activities. Of specific concern are crop fertilization activities and discharges from animal operations, wastewater treatment facilities, and septic systems. The lack of affordable and feasible nitrate treatment alternatives can force impacted utilities to remove nitrate contaminated sources from their available water supply. In many instances, this action can severely compromise a water utility's ability to provide an adequate supply of safe and affordable potable water.

Nitrate in drinking water

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. Table 1 shows the number of Indian States with contaminated groundwater. In India, more than 21 states are contaminated with nitrate in groundwater exceeding 45mg/l.

Table 1 Number of Indian states with contaminated groundwater

Sl No.	Chemical Contaminant	Number of Indian states
1	Arsenic (> 0.05 mg/l)	10
2	Fluoride (>1.5mg/l)	20
3	Heavy metals Lead>0.1mg/l; Cadmium>0.003mg/l; Chromium> 0.05 mg/l.	15
4	Iron (>1mg/l)	24
5	Nitrate (>45mg/l)	21

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 and 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, tumor, congestion of nasal mucous membranes and pharynx, stuffiness of the head and gastrointestinal, muscular, reproductive, neurological and genetic malfunctions caused by nitrate. 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

Drinking water standards for nitrate

Various countries follow various standards depending upon their concerned scales. Table2 shows the drinking water standards for nitrate on a global scale. In India, we generally follow the BIS (Bureau of Indian Standards). And accordingly the maximum permissible level of nitrate allowed in drinking water is 45mg/l. In many places in India, even though the nitrate levels are less than the permissible limit, studies revealed that the population was badly affected by diseases like blue baby syndrome which are caused clearly due to nitrate.

Table 2 Drinking Water Standards for Nitrate

Sl. No.	Contaminant	Maximum Contaminant Level
1	Nitrate(NO_3)	USEPA: MCL= 10.0 mg/l MCLG(goal) = 10.0 mg/l (N-NO_3)
		WHO Guideline: 50 mg/l (NO_3)
		Health Canada MAC: 10 mg/l(N-NO_3)
		IS 10500 -2012: 45mg/l (NO_3)

OBJECTIVE

- Removal of nitrate using natural adsorbents from ground water and reduce the nitrate levels to maximum possible permissible levels
- To find out the most suitable combinations of crushed lemon peel and activated carbon for removal of nitrate from water
- To determine the effects of adsorbent concentrations, adsorbent dosage and rate of flow.
- Another objective of the project is to study about the adverse effects of nitrate content in water.
- To investigate the feasibility of crushed lemon peel and activated carbon for the removal of nitrates from wastewaters.
- To determine the removal efficiency of the adsorbent for various nitrate concentrations.

MATERIALS AND METHODS

Material selection and analysis

Activated charcoal and crushed lemon peel are used as adsorbents for removing nitrates from groundwater. Charcoal is activated both physically and chemically. Crushed lemon peels were collected from juice shops that are left waste and are sun dried and oven dried.

Activated charcoal

- Activated charcoal is a form of carbon processed to have small, low-volume pores that increase the surface area available for adsorption.
- Very cheap.
- Eco-friendly.
- Available in plenty

Lemon peel

Tones of lemon peels are discarded and send to garbage as useless materials and it is very significant and even essential to find applications and uses for these peels, as the management of wastes nowadays is becoming a very serious environmental issue. These waste peels are literally zero cost as they are thrown away by people and industries after use, non-hazardous and environment friendly bio-materials which can be used as adsorbents in groundwater treatment. Lemon peel contains a plant pigment polymetoxylated flavones and due to its water holding capacity it is used as nitrate removal bio adsorbent. The lemon peels were collected from houses and juice shops. It was washed thoroughly in plain water and then it was sundried for three days and was

then oven dried for one day. It was then crushed into small pieces using a hammer manually. It was sieved and the portion of lemon peel retained in the 1.18mm sieve was collected. Since the perforations in the glass column (apparatus) are of size 1mm, the sieve size was chosen as 1.18mm so that the crushed lemon peel does not pass through the perforations.

Selection of case study area

The case study area for this project was chosen as Eloor, a suburb of Kochi and a municipality in Paravur Taluk, Ernakulam District in the Indian state of Kerala, India. Demography of Eloor is represented in Fig 1. It is an industrial area situated around 13 kms north of the city.There are nearly 8,245 houses in Eloor and a population of 30,092 as per census 2001. The major industries include phosphate fertilizer plant, monazite industry, caustic soda unit, pesticide plant, aluminium and zinc smelter. In addition there are small industries that include, manufacturing petro-chemical compounds, pesticides, insecticides rare earth metals etc.From the various studies it was observed that the concentration of nitrates ranges between 2.0 to 23.3 mg/l (mean: 19mg/l) indicates that there may be possibility for leaching of nitrate to nearby groundwater sources.

Figure1Location map of Eloor suburb (Source: Google maps)

Experimental setup

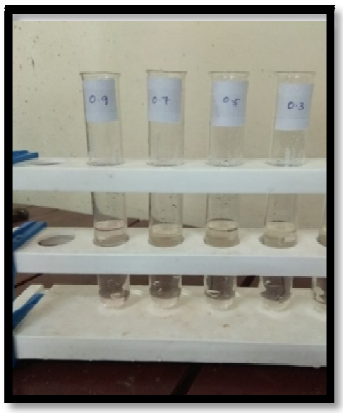
The nitrate standard samples of0.1mg/l, 0.3mg/l, 0.5mg/l and 0.7mg/l was to be prepared. 0.163g of Anhydrous KNO_3 was dissolved in distilled water and diluted to 100mli.e., 1000 ppm solution. 10 ml of this solution is taken and 90ml of distilled water was added to it to make up a solution of 100ml which means 100 ppm. Then take 10 ml of it and then again add 90ml of distilled water to make 100 ml (i.e., 10 ppm). Thus according to need of sample, different concentration of nitrate solutions can be prepared. 1ml of 10 ppm solution was added and 99ml of distilled water was added to it. This makes up a solution of 0.1mg/l. Now take 3ml from 10 ppm solution and then add

97 ml of distilled water to make up a solution of 100ml. This is 0.3mg/l solution. Similarly solutions of 0.5mg/l and 0.7mgl were prepared. Nutrient stock solutions were prepared according to standards of Strickland and Parsons 1979. The stock solution (100 ml) was taken in 250 ml conical flasks. Fig 3.7 shows the stock solution prepared for four different concentrations namely 0.1mg/l, 0.3mg/l, 0.5mg/l and 0.7mg/l respectively.

Adsorption test using spectrophotometer

Ten milliliters of each solutions (0.1mg/l, 0.3mg/l, 0.5mg/l and 0.7mg/l) was taken in four different test tubes. Two ml of sodium chloride solution was added into it and was stirred well. Then 10ml of sulphuric acid was slowly poured into each test tubes and kept in water bath for few minutes so that the test tubes cools down since heat is liberated due to the chemical reaction. Then 0.5ml Brucinesulphanilic acid solution is addedand mixed well. After thorough mixing the samples are placed in a boiled water bath for twenty minutes at 95^{o}Cas shown in Fig 4. After twenty minutes the samples were taken out of the water bath and was allowed to cool down completely. The final colour development after cooling the solution in water bath is shown in Fig 3

Figure 2 Solutions before boiling (Source: Author)Figure 3 Solutions after boiling (Source: Author)



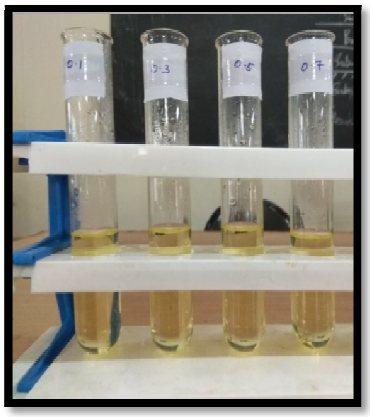


Figure 4 Solutions in water bath (Source: Author)

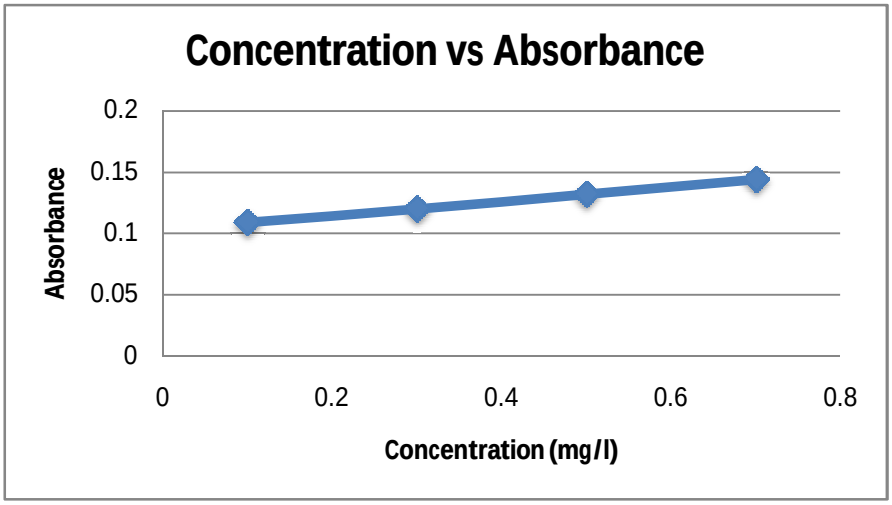
The spectrophotometer was used to obtain absorbance readings of standards. Reference solution used was a blank solution and test was performed as per standard procedure.

The absorbance corresponding to varying concentrations were noted down and is shown in Table 3. The calibration curve plotted using the absorbance reading and concentration is given in Fig 5

Table 3Absorbance reading corresponding to various concentrations

CONCENTRATION (mg/l)	ABSORBANCE
0.1	0.108
0.3	0.120
0.3	0.132
0.4	0.144

Figure 5 Concentration v/s Absorbance



Reactor setup

The reactor setup consists of two glass columns provided with perforations on each one as shown in Fig6 The adsorbents; crushed lemon peel and activated charcoal are placed one each on the perforated plate. The samples containing nitrate was pumped into the glass column using a submersible pump at different flow rates from the suction tank. The water was then allowed to flow through each layer and the filtered water was collected at the delivery tank. The concentration of nitrate before and after the treatment was analyzed and the corresponding absorbance was noted down using a spectrophotometer. The experiment was repeated at different flow rates and different layer thickness.

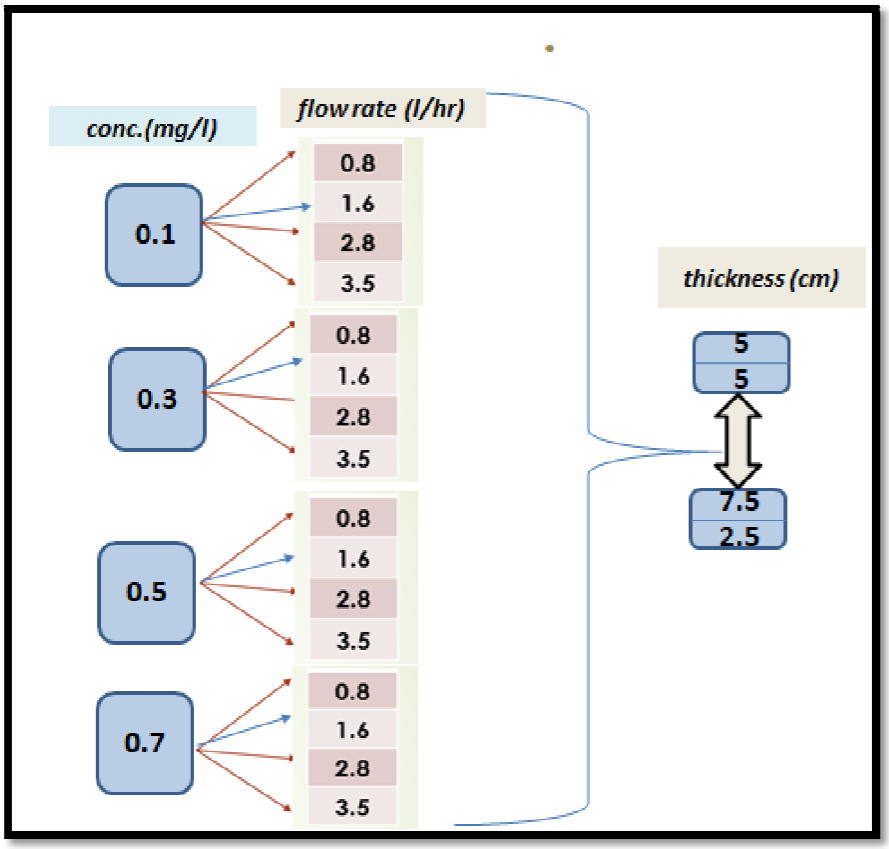
Figure 6 Reactor setup (Source: Author)

Combination of the parameters

Four different solutions of the required concentrations (0.1mg/l, 0.3mg/l, 0.5mg/l and 0.7mg/l) were prepared and were diluted to four liters so that it could be passed through the apparatus. All the four solutions were passed at four different flow rates (0.8 l/hr, 1.6 l/hr, 2.8 l/hr and 3.5 l/hr) under equal layer thickness. All the results were studied separately and the test combinations were observed and they were again tested under varying thickness.

Then graphs were plotted with concentrations versus absorbance for different flow rates and layer thickness and the best possible combination was selected. Then the samples were collected from the case study are, tested by the most suitable combination obtained and the concentration of nitrate was examined.

Figure7 Proposed combinations of concentrations, flow rates and adsorbent thickness



RESULTS AND DISCUSSIONS

The solutions of four different concentrations (0.1mg/l, 0.3mg/l, 0.5mg/l and 0.7mg/l) were prepared and they were diluted to four liters so that it could be passed through the glass columns (apparatus). To determine the best possible combination that gives the maximum efficiency under the combinations of varying flow rate and concentrations, each of the standard samples prepared were studied separately. The observations are listed below

Table 4 Treatment efficiency under varying concentrations at a flow rate of 0.8 l/hr.

Material	Initial concentration (mg/l)	Flow rate (l/hr)	Absorbance	Final concentration (mg/l)	Efficiency (%)
Activated charcoal +crushed lemon peel	0.1	0.8	0.103	0.024	75.7
	0.3	0.8	0.106	0.065	78.3
	0.5	0.8	0.108	0.100	80
	0.7	0.8	0.111	0.141	79.9

Table 5 Treatment efficiency under varying concentrations at a flow rate of 1.6 l/hr.

Materials	Initial concentration (mg/ l)	Flow rate(l/hr)	Absorbance	Final concentration (mg/l)	Efficiency (%)
Activated charcoal + crushed lemon peel	0.1	1.6	0.104	0.034	65.6
	0.3	1.6	0.108	0.097	67.8
	0.5	1.6	0.110	0.148	70.4
	0.7	1.6	0.114	0.208	70.3

Table 6 Treatment efficiency under varying concentrations at a flow rate of 2.8 l/hr.

Materials	Initial concentration (mg/ l)	Flow rate (l/hr)	Absorbance	Final concentration (mg/l)	Efficiency (%)
Activated charcoal + crushed lemon peel	0.1	2.8	0.104	0.042	58
	0.3	2.8	0.109	0.124	59.5
	0.5	2.8	0.114	0.195	61
	0.7	2.8	0.118	0.272	61.2

Table 7 Treatment efficiency under varying concentrations at a flow rate of 3.5 l/hr.

Materials	Initial concentration (mg/ l)	Flow rate (l/hr)	Absorbance	Final concentration (mg/l)	Efficiency (%)
Activated charcoal + crushed lemon peel	0.1	3.5	0.105	0.048	52.3
	0.3	3.5	0.110	0.138	54.1
	0.5	3.5	0.115	0.224	55.3
	0.7	3.5	0.121	0.312	55.5

From the tables it is clearly observed that as initial concentration increases, absorbance values increases, thereby indicating an increase in the treatment efficiency on a gradual basis. The relationship between concentration and absorbance is plotted in the graphs as shown below.

Figure 8 Concentration v/s absorbance at a flow rate of 0.8 l/hr

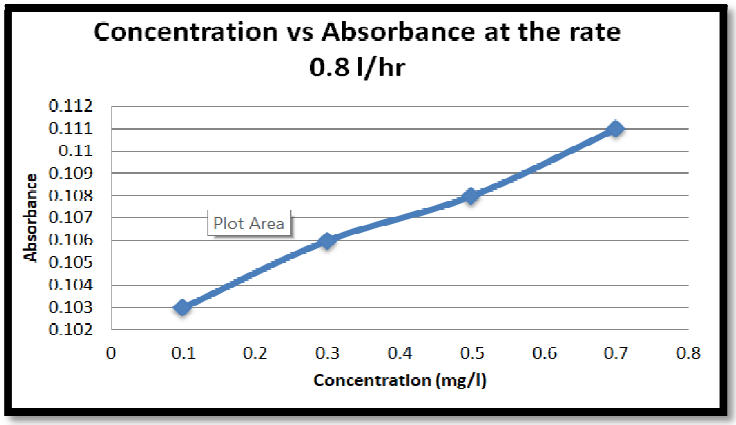


Figure 9 Concentration v/s absorbance at a flow rate of 1.6 l/hr

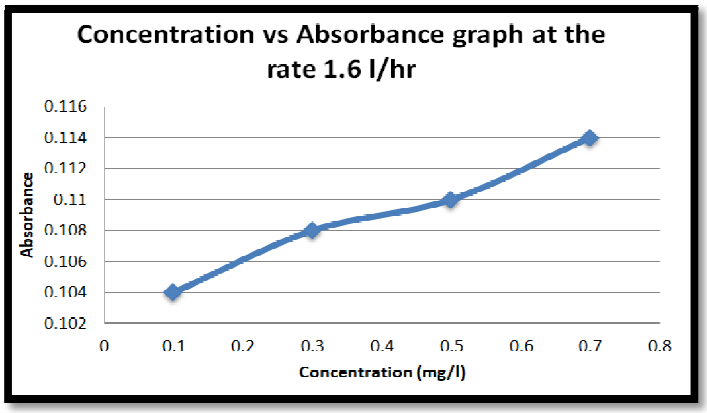


Figure 10 Concentration v/s absorbance at a flow rate of 2.8 l/hr

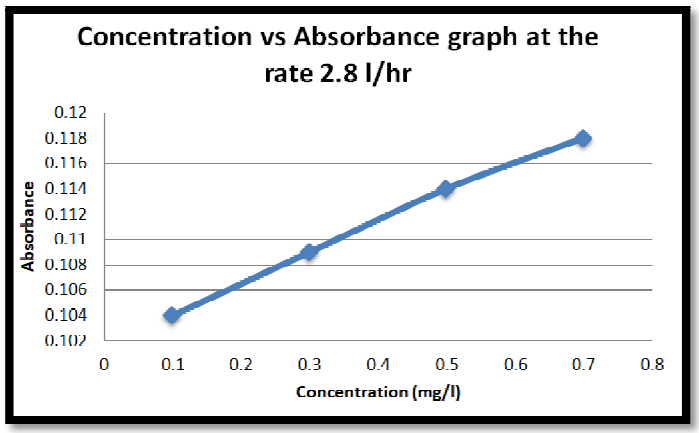
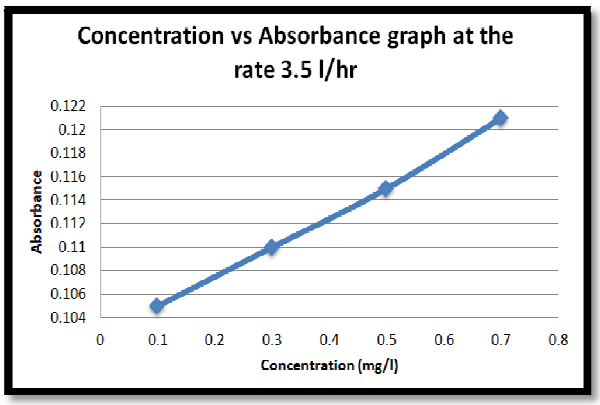


Figure 11 Concentration v/s absorbance at a flow rate of 3.5 l/hr



The treatment efficiency range was high for the flow rate of 0.8 l/hr. The consolidated findings are as listed.

Table 8 The consolidated table derived from efficiency and concentration

Concentration (mg/l) ➡	0.1	0.3	0.5	0.7
Flow rate (l/hr) ⬇	Efficiency (%)			
0.8	75.7	78.3	80	79.9
1.6	65.6	67.8	70.4	70.3
2.8	58	58.7	61	61.2
3.5	52.3	54.1	55.3	55.5

From the consolidated table it was found that maximum efficiency is obtained at a concentration of 0.5mg/L at a flow rate of 0.8 L/hr which is 80% and a minimum efficiency of 52.3% is obtained at a flow rate of 3.5 L/hr, and a concentration of 0.1 mg/L. Similarly, the graphs plotted between concentration and efficiency is shown.

Figure 12 Concentration v/s efficiency at a flow rate of 0.8 l/hr

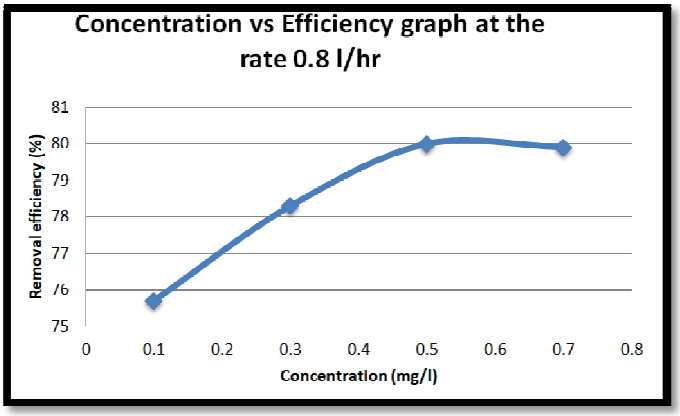


Figure 13 Concentration v/s efficiency at a flow rate of 1.6 l/hr

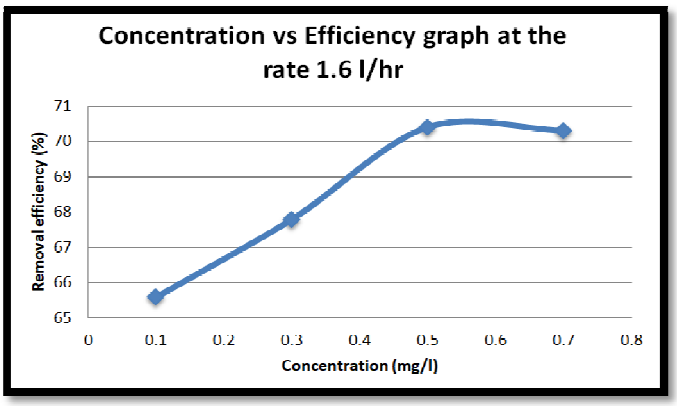


Figure 14 Concentration v/s efficiency at a flow rate of 2.8 l/hr

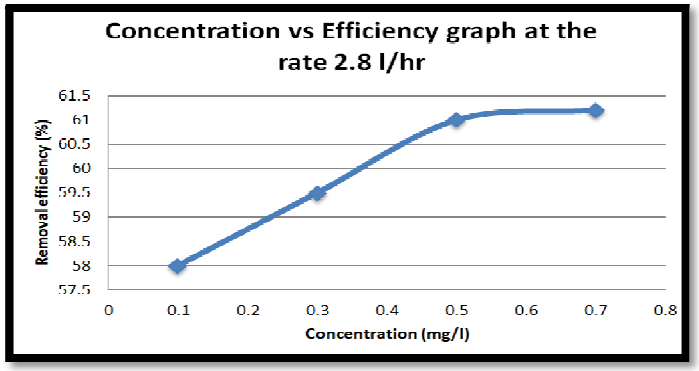
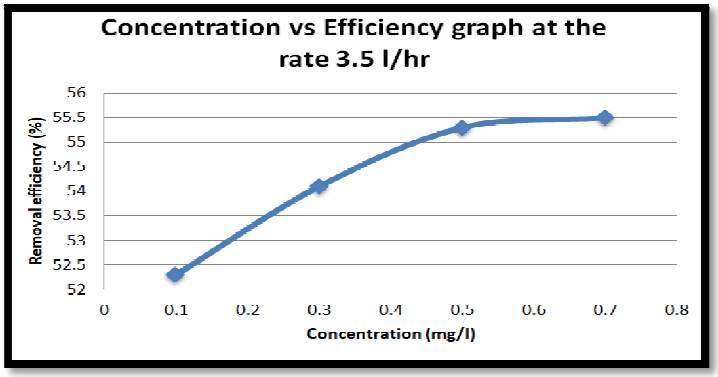


Figure 15 Concentration v/s efficiency at a flow rate of 3.5 l/hr



From the graphs it can be concluded that as concentration increases, efficiency also increases gradually. The maximum efficiency is at 0.5mg/l and then it becomes somewhat constant. The same observation is visible at all flow rates. After obtaining the maximum and minimum efficiencies the individual adsorption efficiency of the adsorbents were analysed separately. It is shown in the table below.

Sample collection

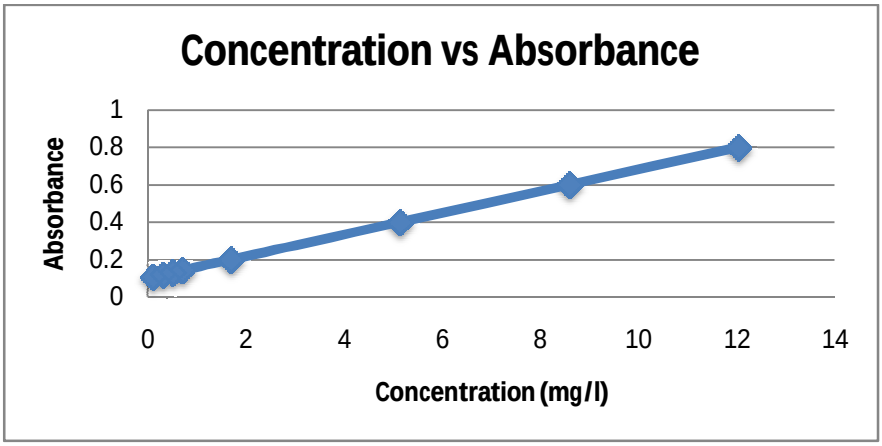
The sample was collected from North Eloor, Kochi (10.0697° N, 76.3029° E).Around 20 liters of groundwater was directly collected from the wells

Figure 16 Procurement of the sample from well

Test for nitrates were then performed and corresponding concentrations were calculated from concentration v/s absorbance curve.

Figure 17 Color of solution before treatment Figure 18 Color of solution after treatment

Figure 19 Concentration v/s Absorbance



The absorbance value for the ground water sample collected was 0.8 and the value is not within the limits of the plotted calibration curve. Hence the graph was extrapolated and the corresponding concentration obtained was 12.03 mg/l, which is more than the USEPA and WHO limits. The sample was tested at a flow rate of 0.8 l/hr and an additional parameter, thickness was also introduced. The analysis was first conducted with equal thickness, and then the thickness was varied.

Table 9Treatment efficiency for varying thickness of adsorbents

	Flow rate	Material	Layer thickness (cm)	Initial conc. (mg/l)	Final conc. (mg/l)	Efficiency (%)
SAMPLE	0.8	Activated charcoal	5	12.03	2.41	80
		Crushed lemon peel	5			
	0.8	Activated charcoal	7.5	12.03	2.11	82.5
		Crushed lemon peel	2.5			
	0.8	Activated charcoal	2.5	12.03	2.77	77
		Crushed lemon peel	7.5			

The maximum efficiency obtained was 82.5% which was the best possible result obtained under the combination of crushed lemon peel and activated charcoal.

CONCLUSION

The increasing level of nitrate nitrogen contributes to potentially serious problems for people's health and the environment. It is therefore very important to prevent nitrate pollution by using cost-effective treatment methods that can remove large amounts of nitrate efficiently. Our

study was focused on Eloor, a suburb of Kochi and a municipality in ParavurTaluk, Ernakulam District in the State of Kerala, India. It is an industrial area situated around 13 kms north of the city. From the previous studies conducted it was found that the concentration of nitrates ranges between 2.0 to 23.3 mg/l (mean: 19mg/l) indicates that there may be possibility for leaching of nitrate to nearby groundwater sources. The experimental studies clearly suggests that abundantly available and low cost natural adsorbents like crushed lemon peel powderandactivated charcoal are very effective in removing nitrate from ground water. Activated charcoal is found to be more promising for the removal of nitrate.

From all the observations made, it can be concluded that an upward linear curve was obtained from the calibration curve in which absorbance increases with concentration. For equal layer thickness maximum efficiency (80%) was obtained for a concentration of 0.5 mg/l at the rate of 0.8 l/hr. Initial concentration of the collected sample was obtained as 12.03 mg/l. After treatment final concentration was obtained as 2.11 mg/L (82.5% Efficiency). This clearly indicates that the combination of crushed lemon peel and activated charcoal is highly effective in removing nitrate from groundwater at lower costs. The efficiency of lemon peel would have nearly doubled if it was activated using acids. However activation is not done because during the time of disposal so that an analysis of the lemon as waste disposed as municipal solid waste was intended to be tried as an absorbent. Also, the acid treated lemon peel could adversely affect the environment which still means the disposal of the natural adsorbents are quite eco-friendly. Activated charcoal can be treated and reused again, whereas lemon peel can be usefully disposed in to landfills, can be used up for land treatment, can be incinerated or even be used for biogas generation, as it is completely pure and natural. Maximum efficiency (82.5%) was obtained for the layer thickness 7.5 cm (activated charcoal) and 2.5 cm (crushed lemon peel). Hence activated charcoal and crushed lemon peel can be suggested as two promising, eco-friendly and low cost adsorbents for the efficient removal of nitrate from groundwater.

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