Removal of Nitrate from Simulated Waste Water using Selective Filter Media

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Abstract –The Studies adopted for improving the water quality by removing nitrate. The study carries by using selective filter media which are locally available and inexpensive. Media combinations of charcoal with brick bats (i.e, Setup I), rice husk ash with pebbles (i.e, Setup II) were used. To assess their effectiveness the laboratory scale model constructed filled with above combinations. The effect of various parameters on removal of nitrate were also studied. Set up I gives the nitrate removal efficiency 45.29%The setup II is seen to produce an optimum degree of nitrate attenuation, the average removal efficiency of bed obtained is 67.26%.

***Key Words*:** nitrate, charcoal, brickbats, rice husk ash, pebbles

1.INTRODUCTION

There are so many uses of water in day today life which are increasing in applications. It includes agricultural, industrial, household, recreational and environmental activities and these activities generates the wastewater. Any addition to undesirable substances to ground water caused by human activities is considered to be added contamination. Contamination may occur to a lesser magnitude when compared to pollution, but it also may render the contaminated medium unusable or make it slightly hazardous to life. Movement of water and dispersion within the aquifer spreads the pollutant over a wider area. The contaminants in ground water comes from leaking sewers, landfills, industrial areas storage, oil storage, fertilizers and pesticides spreading on land, etc. They are listed in annexure table1. The contaminants are of organic or inorganic type. There are many problems with ground water contamination that are increasing because of the large and growing number of toxic compounds using in industrial and agricultural. Also the treatment options for ground water pollution are costly, non-effective, so the ground water contamination is the serious problem, as the ground water is difficult to treat.

Nitrate is a problem as a contaminant in drinking water (primarily from groundwater and wells) due to its harmful biological effects. High concentrations can cause methemoglobinemia, and have been cited as a risk factor in developing gastric an intestinal cancer. Due to these health risks, a great deal of emphasis has been placed on finding effective treatment processes to reduce nitrate concentrations to safe levels. An even more important facet to reduce the problem are prevention measures to stop the leaching of nitrate from the soil. Some suggest that reducing the amount of fertilizers used in agriculture will help alleviate the problem, and may not hurt crop yields. Other new developments in leach pits and slurry stores help to control the nitrate that comes from stored manure. By installing these prevention methods and reducing the amount of fertilizer used, the concentration of nitrate in the groundwater can be reduced over time. Treatment processes, such as ion exchange can have an immediate effect on reducing levels in drinking water. These processes do not remove all the nitrate, but can help to bring the concentration down to the suggested level of 10mg/L.

Sources of Nitrate in water and wastewater:

Although there are many sources of nitrogen (both natural and anthropogenic) that could potentially lead to the pollution of the groundwater with nitrates, the anthropogenic sources are really the ones that most often cause the amount of nitrate to rise to a dangerous level. Waste materials are one of the anthropogenic sources of nitrate contamination of groundwater. Many local sources of potential nitrate contamination of groundwater exist such as, sites used for disposal of human and animal sewage; industrial wastes related to food processing, munitions, and some polyresin facilities and sites where handling and accidental spills of nitrogenous materials may accumulate. Septic tanks are another example of anthropogenic source nitrogen contamination of the groundwater. Many areas of the United States and other countries have reported significant contamination of groundwater from septic tanks. Ground water contamination is usually related to the density of septic. In densely populated areas, septic systems can represent a major local source of nitrate to the groundwater. However in less populated areas septic systems don't really pose much of a threat to groundwater contamination.

When natural sources contribute a high concentration of nitrate to the groundwater it is usually as a result of anthropogenic disturbance. One example of this is the effect of forested areas on the leaching of nitrate to the groundwater. Natural, mature forests conserve nitrogen but human disturbances can lead to nitrate pollution of the groundwater. However, while this is a potential problem for groundwater, forests represent a very small source of nitrogen compared to agriculture.

Health Effects of Nitrate:

Heavy metals are major pollutants in marine; ground and industrials, and even in treated waste water. The presence of these metals in the environment has been a great concern because of their toxic nature and other adverse effects on receiving waters. Among these heavy metals are chromium, beyond the permissible quantities can cause various chronic disorders in human beings. It is well known that heavy metals can damage nerves, liver and bones, and they also block functional groups of essential enzymes [1]. Tannery waste characteristically contains a complex mixture of both organic and inorganic pollutants. For example, in related studies, chlorinated phenols and chromium were found to be closely associated with the tannery waste [2].

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areprevention measures to stop the leaching of nitrate from the soil. Some suggest that reducing the amount of fertilizers used in agriculture will help alleviate the problem, and may not hurt crop yields. Other new developments in leach pits and slurry stores help to control the nitrate that comes from stored manure. By installing these prevention methods and reducing the amount of fertilizer used, the concentration of nitrate in the groundwater can be reduced over time. Treatment processes, such as ion exchange can have an immediate effect on reducing levels in drinking water. These processes do not remove all the nitrate, but can help to bring the concentration down to the suggested level of 10mg/L.

Nitrate can cause severe problems, including eutrophication and infection diseases, such as cyanosis and cancer of the alimentary canal [4]. Also all forms of chromium can be toxic at high levels [3]. The conventional treatments used for groundwater include coagulation and flocculation is not effective for the removal of nitrates. Ion-exchange, deionization, reverse osmosis, electrocoagulation are the methods widely used for removal of nitrates and chromium which have disadvantages like expensive, non-availability of materials easily, sludge formation, the waste stream from reverse osmosis process is exceptionable. Overall the methods adopted for removal of nitrate and chromium generates some environmental pollution and therefore, there is need of the clean technology which can be provided easily by using filter media available locally and naturally.

2. Body of Paper

The evaluation of nitrate removal efficiency for different concentration will be done in future. But now samples of different concentrations of nitrate are not easily available, hence KNO3 is dissolved in distilled water and prepare solutions of different concentration for experimental setup.

Material and method include the information regarding the experimental setup, filter media and method adopted for estimation and analysis of nitrate and chromium.

Experimental Setup:-

In this connection, studies were conducted to explore avenues low cost treatment for nitrate reduction in water using selective filter media. Media combinations of rice husk ash with pebbles, charcoal with brickbats and bagasse ash with bauxite were used, as they are known to have a very high potential for adsorption of natural and manmade pollutants. A laboratory scale physical model study was constructed using a acrylic glass sheet column of size 0.40 m × 0.30 m × 1.50 m with coarse and fine layers of sand. The all portion of the column used was of acrylic glass 6 mm thick, so that the filter media could be clearly visible. The bottom portion of the sheet was fitted with strainer for collection of samples. A strainer was placed at bottom, which serves as soil retainer and prevents small particles from leaching out of the column. A perforated plate was placed at the top to effect the uniform spreading of the solution over the entire area.

After the column was filled with sand and other media, distilled water was applied for saturation of soil and media over a period of one day. After the complete draining of distilled water using different concentrations of nitrate, the experiment was started; the chemical compound used was potassium nitrate. Simulated solution of nitrate of varying concentration was induced to the column containing charcoal and brick bats from the overhead placed tank. The inlet flow is 3000L/m2/day which is given by the inlet pipe connected to the overhead tank of capacity 50 lit at terrace, tank and constant head was maintained by using overflow outlet connected with the pipe. The samples were collected at the bottom at every 30 min interval and analyzed for nitrate concentration. Graphs were plotted for "percentage reduction versus time" and "percentage reduction versus initial concentration " Similar procedure was repeated for another filter media in which rice husk ash with pebbles and bagasse ash with bauxite were used instead of charcoal and brick bats.

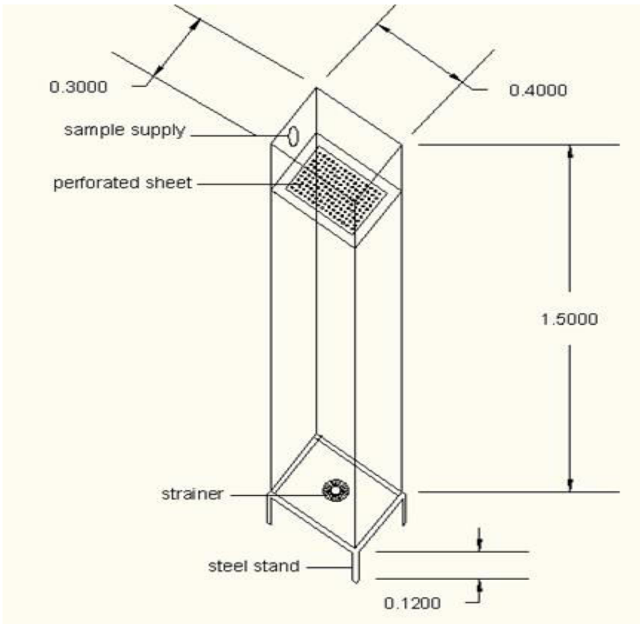

Fig-1: Schematic view of experimental setup

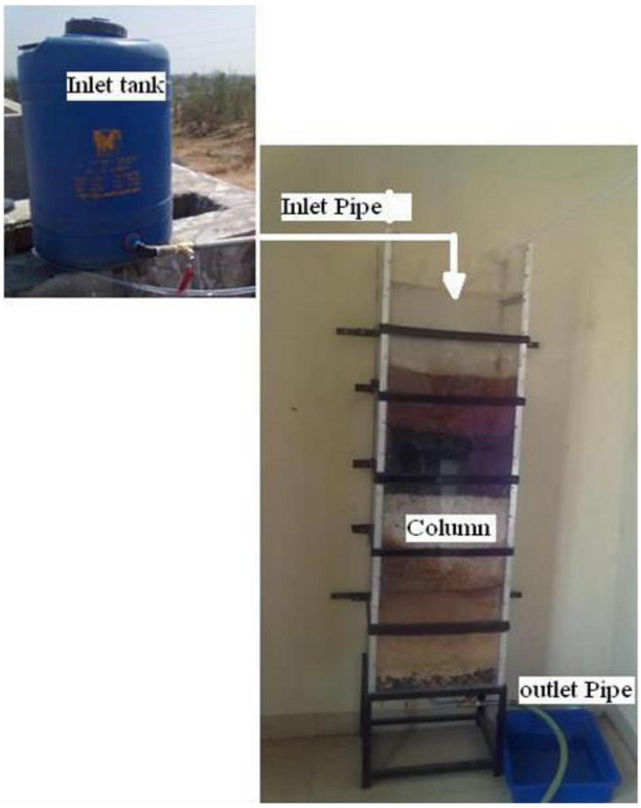

Fig- 2: View of experimental set up I

Fig- 3: View of experimental setup II

Sr. no.	Filter media	Volume occupied (m3)	Height of bed (cm)	Required quantity kg	Size (mm)	Cost per Kg (Rs)	Total cost (Rs)
1	Fine sand	0.036	30	55	0.2-1.0	5	275/-
2	Course sand	0.036	30	72	4.0-8.0	6	432/-
3	Charcoal	0.024	20	5	0.2-5	15	75/-
4	Brick bats	0.024	20	46	0.5-5	1	46/-
			Total Cost				828/-

Table-1: Filter media specifications for setup I

Sr. no.	Filter media	Volume occupied (m^3)	Height of bed (cm)	Required quantity kg	Size (mm)	Cost per Kg (Rs/-)	Total cost (Rs/-)
1	Fine sand	0.036	30	55	0.2-1.0	5	275/-
2	Course sand + rice husk ash	0.036	30	36+10	0.5-8.0	6+20	416/-
3	Pebbles	0.012	10	5	10-40	5	25/-
4	Course sand	0.036	30	48	4.0-8.0	6	288/-
						Total cost	1004/-

Table-2: Filter media specifications for setup II

Information Related to Filter Media:-

Sand: Sand, either fine or coarse, is generally used as filter media. The size of the sand is measured and expressed by the term called effective size. The effective size, i.e. D10 may be defined as the size of the sieve in mm through which ten percent of the sample of sand by weight will pass. The uniformity in size or degree of variations in sizes of particles is measured and expressed by the term called uniformity coefficient. The uniformity coefficient, i.e. (D60/D10) may be defined as the ratio of the sieve size in mm through which 60 percent of the sample of sand will pass, to the effective size of the sand.

Gravel: The layers of sand may be supported on gravel, which permits the filtered water to move freely to the under drains, and allows the wash water to move uniformly upwards.

Brick bats: The layers of brick bats are supported on charcoal bed. Brick bats are proved to be most economical filter material for the removal of pollutants with the cheap availability.

Charcoal: These are used as a adsorbent material in filter media. Which are having the great area for attachment of pollutants by the various forces.

Rice husk ash: This is also the adsorbent material having large sides for the adsorption of pollutants and gives the effective removal efficiency.

Removal Mechanisms:

Filtration:

Filtration is the process of passing water through material to remove particulate and other impurities, including floc, from the water being treated. These impurities consist of suspended particles (fine silts and clays), biological matter(bacteria, plankton, spores, cysts or other matter)and floc. The material used in filters for public water supply is normally a bed of sand, coal, or other granular substance. Filtration processes can generally be classified as being either slow or rapid. Filtration process involves some type of filter media, over which water flows. This filter media blocks passage of contaminants through physical obstruction, chemical adsorption, or a combination of both processes. Material construction of the filter media varies widely, but the most effective medias are made from carbon or a combination of carbon with other elements.

Modern filtration technology allows water filters to remove more and more contaminants through the chemical process of adsorption. In the adsorption process, contaminants are encouraged to break their bond with water molecules and chemically adhere to the filter media. Generally, water goes through several stages of filtration to ensure that each filter media will remove the ultimate number of contaminants. Water normally passes through a water filter at a relatively low speed, in order to ensure adequate contact time with the filter media. Once the water has passed through the required stages of filtration, it emerges as pure drinking water, free from contamination.

Adsorption:

The term adsorption refers to a process wherein a material is concentrated at a solid surface from its liquid or gaseous surroundings. If the attraction between the solid surface and the adsorbed molecules is physical in nature, the adsorption is referred to as physical adsorption. Generally, in physical adsorption, the attractive forces are vander Waals forces, and as they are weak, the resulting adsorption is reversible in nature. On the other hand, if the attraction forces between adsorbed molecules and the solid surface arise due to chemical bonding, the adsorption process is called chemisorption. In view of the higher strength of the bonding in chemisorption, it is difficult to remove chemisorbed species from the solid surface. The second, and in many cases the most

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important mechanism of filtration, is adsorption. Adsorption is the gathering of gas, liquid, or dissolved solids onto the surface of another material

Coagulation takes advantage of the mechanism of adsorption when small floc particles are pulled together by vander Waal's forces. In filtration, adsorption involves particles becoming attracted to and "sticking" to the sand particles. Adsorption can remove even very small particles from water.

Adsorbents:-

The most important property that a good adsorbent should possess is a porous structure resulting in high surface area. In addition, the time taken for adsorption equilibrium to be established should be as small as possible so that it can be used to remove contaminants in lesser time. Thus, for removal of pollutants, one looks to adsorbents with high surface area and porosity and showing fast adsorption kinetics. Following table shows the different type of adsorbent which shows the nitrate removal efficiency as well as additional environmental benefits in terms of removal pollutant present in water.

Estimation of Nitrate:

Following methods are available for determine of nitrate

1. Ultraviolet spectrophotometric method
2. Ion chromatographic method
3. Nitrate electrode method
4. Cadmium reduction method (NO^-_3 is reduced NO^-_2)
5. Devarda's alloy method (reduction to ammonia) (UNEP/WHO, 1996).
6. Nitrate can also be determine colorimetrically by disulphonic acid method and brucine Method.

Estimation of nitrate by ultraviolet (UV) spectrometric screening method:

An ultraviolet (UV) technique measure the absorbance of nitrate at 220 nm, which is suitable for screening uncontaminated water (low in organic matter). A second measurement made at 275 nm, may be used to correct the nitrate value (because 275 nm is not absorbed by nitrate, but absorbed by other matter). The nitrate calibration curve follows Beers low upto11mg NO_3-N/L.

Apparatus:

100 mL beakers, measuring cylinder, Spectrophotometer, for use at 220 nm and 275 nm with matched silica cell of 1cm or longer Path.

Reagent:

1. **Stock nitrate solution (1mL= 100µg NO_3-N):-** Dry potassium nitrate (KNO_3)in an oven at 105^{0}c for 24h. Dissolved 721.8 mg in water and dilute to 1000mL. Preserve with 2 ml chloroform per L. This solution is stable for at least 6 months.
2. **Intermediate nitrate solution (1 mL = 10 µg NO_3-N) :-** Dilute 100 mL of stock nitrate solution to1000 mL with water. Preserve with 2 ml chloroform per L. This solution is stable for at least 6 months.
3. **Hydrochloric acid solution, 1N :-** Dilute 83 mL of conc. HCL to 1L

Procedure:

1. **Treatment of sample:**

Take 50 mL of clear sample and (filter it, if necessary) add 1 mL HCL solution and mix thoroughly.

2. **Preparation of standard curve:**

Prepare nitrate calibration standards in range of 0 to 7 mg NO_3-N/L. Dilute the following volumes of intermediate solution i.e. 0,1,2,4,7,10,15,20,25,30 and 35 to 50mL with distilled water. Treat the standards in same manner as sample.

3. **Spectrophotometric reading:**

Read absorbance against water set at zero absorbance. Use a wave-length of 220 nm to obtain NO_3-N reading and a wavelength of 275 nm to determine interference due to dissolved organic matter

Calculation:

1. For sample and standards, subtract two times the absorbance reading at 275nm from the reading at 220nm to obtain absorbance due to NO_3-N only.
2. Construct a standard curve by plotting absorbance due to nitrate against NO3-N concentration.
3. Obtain sample concentration directly from the standard curve.

(Note:- if correction value is more than 10% of the reading at 220 nm, do not use this method.)

Results of standard graph preparation:

As per the method of nitrate determination by spectrophotometer the results are prepared for getting the standard graph of nitrate detection.

Absorbance (A)	*Nitrate concentration (mg/L)*
0.038	*1*
0.1125	*2*
0.2691	*5*
0.385	*7*
0.5658	*10*
0.8361	*15*
1.1104	*20*
1.3995	*25*
1.6368	*30*
1.9432	*35*
2.1464	*40*
2.5513	*50*

Table-3: Results of standard graph

By the above table standard graph is plotted below for the determination of nitrate concentrations in solutions.

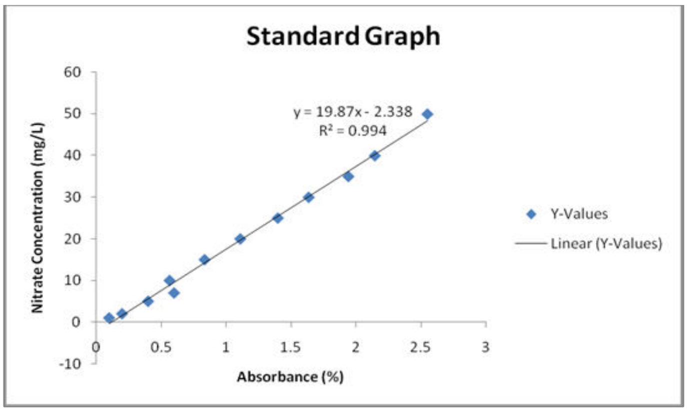

Chart-1: Standard graph of nitrate

The above graph gives the nitrate concentration in feed as function of absorbance. The graph obtained is straight line with the equation of line. This graph is used for the further results which are taken on the filter column.

Requirement of Equipments:

1. UV spectrophotometer
2. pH meter
3. Pipette
4. Measuring cylinder
5. 100ml beakers
6. Weighing machine

Results of nitrate removal by experimental setup:

Results of setup I for:

The next step of the study is to check the removal efficiency of the nitrate for different filter media. So the various concentrations of nitrate as shown in table no. is feed to the bed at 3.5 hrs contact time and readings are taken at every 30 min time interval.

Sr. No.	Initial conc. (mg/L)	30 (min)	60 (min)	90 (min)	120 (min)	150 (min)	180 (min)	210 (min)
1	35	0.61	10.2	21.4	27.2	28.4	29.8	30.87
2	40	15.47	14.62	16.6	21.4	27	26.14	25.5
3	45	29.68	28.61	27.97	25.88	25.23	26.14	25.5
4	50	6.1	12.43	19	32.13	36.5	34.3	30.4
5	60	18.1	23.8	31.7	36.5	36.5	36.8	37.4
6	70	18.4	35.9	38.6	41.8	40.8	43.7	44.6

Table-3: Variation in nitrate concentration using charcoal (0.2-5mm) and brick bats(0.5-5mm).

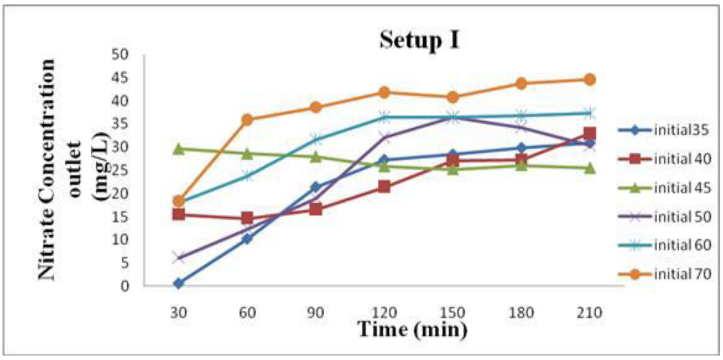

Chart-2: Nitrate reduction in set up-I

The above graph is plotted as nitrate concentration (mg/L) is function of time (min.) which is shown in figure 5. Here the nitrate concentration in inlet water was at initial stage decreased greatly and slowly increased due to the adsorption in beds. The graph shows that the lowest removal efficiency was obtained at a nitrate concentration of 35 mg/L and the maximum removal was obtained at a nitrate concentration of 50 mg/L.

Sr. No.	Initial conc. (mg/L)	30 (min)	60 (min)	90 (min)	120 (min)	150 (min)	180 (min)	210 (min)
1	35	98.25	70.87	38.85	22.28	18.85	14.85	11.8
2	40	61.32	63.5	58.5	46.5	32.5	34.65	36.25
3	45	38.5	36.42	38	36.67	43.93	41.91	43.33
4	50	87.7	75.14	62	35.74	27	31.4	39.2
5	60	69.83	61.16	47.16	39.16	39.16	38.67	42.16
6	70	73.71	64.87	64.48	64.17	64.17	63.5	63.62

Table-3: Percentage adsorbed of nitrate concentration using charcoal (0.2-5mm) and brick bats(0.5-5mm).

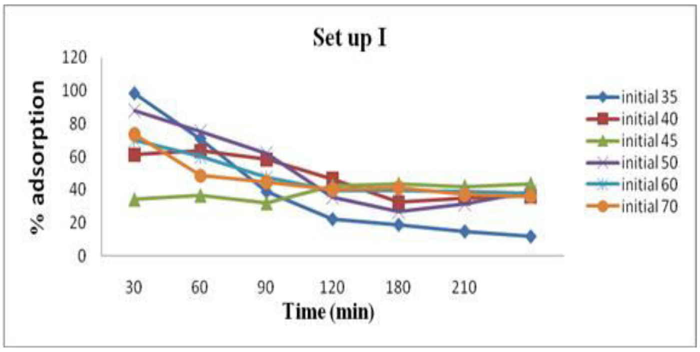

Chart-3:% *adsorbed* in the Set up-I

The Chart-3 is plotted as % adsorbed is the function of time (min). The graph gives the idea about the reduction of nitrate in the solution. Initially the reduction percentage was high and as time passes it was decreased. The maximum reduction % is obtained at a nitrate concentration of 50 mg/L which was 51%. And the lowest % reduction was obtained at a initial nitrate concentration of 30 mg/L which is 39.39%.

Results of setup II for nitrate removal:

Results taken on the set up II are as shown in table-4at a contact time of 3.5 hrs. This setup gives the best results, the removal efficiency obtained by this bed is about 67.26%.

Sr. No.	*Nitrate conc. (mg/L)*	*30 (min)*	*60 (min)*	*90 (min)*	*120 (min)*	*150 (min)*	*180 (min)*	*210 (min)*
1	30	0.01	9.6	10.4	11.4	12.3	15.2	15.6
2	40	*5.4*	*3.2*	*4.6*	*11.7*	*13.8*	*21.6*	*23.5*
3	45	*1.6*	*21.5*	*28.9*	*31*	*28.8*	*32*	*34.8*
4	50	*5.9*	*4.9*	*6.8*	*10.6*	*12.2*	*13.3*	*13.8*
5	60	*6.3*	*8.8*	*13.3*	*20.5*	*20.5*	*21.3*	*21.8*
6	70	*10.6*	*14.6*	*15.2*	*20.7*	*23.5*	*26*	*30.7*

Table-4: Variation in nitrate concentration using setup II

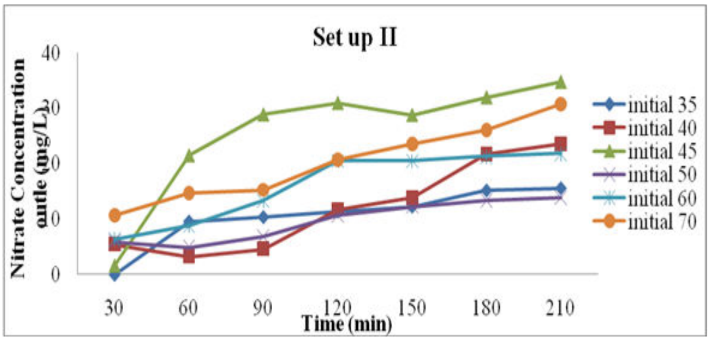

Chart-4: Nitrate reduction in set up-II

The Chart-4shows the nitrate concentration (mg/L) is the function of time (min). The graph shows the removal of nitrate with respect to time, as time is increases removal of nitrate is decreases. The maximum nitrate removal is obtained at a nitrate concentration of 50 mg/L which is 40.4 mg/L in average and that of minimum obtained at a 45 mg/L which is only 18.32 mg/L. This bed gives the maximum removal efficiency.

Sr. No.	*Nitrate conc. (mg/L)*	*30 (min)*	*60 (min)*	*90 (min)*	*120 (min)*	*150 (min)*	*180 (min)*	*210 (min)*
1	30	99.96	68	65.33	62	46	49.33	48
2	40	*86.5*	*92*	*88.5*	*70.75*	*65.5*	*46*	*41.25*
3	45	*96.44*	*52.22*	*37.55*	*31.11*	*35.82*	*28.88*	*22.67*
4	50	*88.2*	*90.2*	*86.4*	*78.8*	*75.6*	*73.4*	*72.4*
5	60	*89.5*	*85.33*	*77.83*	*65.83*	*65.83*	*64.5*	*63.67*
6	*70*	*84.85*	*79.14*	*78.28*	*70.42*	*66.42*	*62.85*	*56.14*

Table-5: Percentage adsorbed of nitrate concentration using setup-II

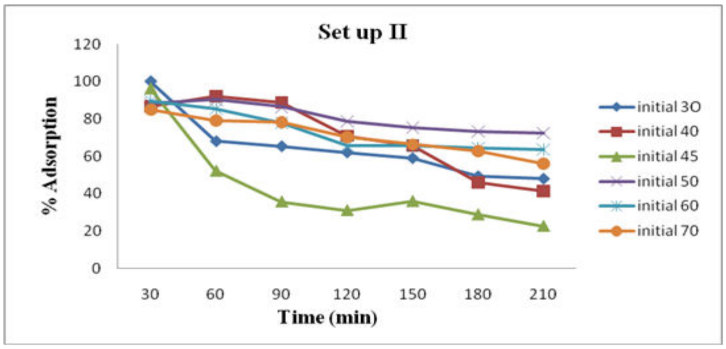

Chart-5: *% adsorbed* in the set up II

The Chart-5is plotted as % adsorbed is the function of time (min). The graph gives the idea about the reduction of nitrate in the solution. Initially the reduction percentage was high and as time passes it was decreased. The maximum adsorption % is obtained at a initial nitrate concentration of 50 mg/L which was 80.71% and that of minimum was obtained by initial nitrate concentration of 45 mg/L. which was 43.3%.

3. CONCLUSIONS

The present study focuses on the cost effective ecofriendly technique of the removal of the very harmful pollutants in water and wastewater. The filter media used in the experimental setup gives the different removal efficiencies for different concentrations of NO3. So the final conclusion for the study is as follows:

1. Set up I gives the nitrate removal efficiency 45.29%. The maximum removal is obtained at a nitrate concentration of 50 mg/L which is 51.18% from setup I. The lowest removal efficiency is obtained for initial nitrate concentration of 35 mg/L which is 39.39% from setup I.
2. The setup II is seen to produce an optimum degree of nitrate attenuation, the average removal efficiency of bed obtained is 67.26%. The maximum removal efficiency is achieved at the nitrate concentration of 50 mg/L from the setup II which is 80.71%. The lowest removal efficiency is observed at a nitrate concentration of 45mg/L from the setup II which is only 43.3%.

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