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NITRATE REMOVAL FROM WATER USING MEMBRANE BIOREACTOR METHOD BY *spirulina* ALGAE

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ABSTRACT

Contamination of water resources with nitrate as the primary contaminant is the most serious environmental problem in several rural regions worldwide. Consumption of underground drinking water with nitrate concentration of 100-200 mg/l is considered as a general hygienic potential risk, especially in children, resulting in diseases such as blue baby syndrome. The aim of this applied analytical study is to investigate Nitrate removal from water using membrane bioreactor method by spirulina algae. The percentage extraction of nitrate was studied under various parameters (nitrate concentration, PH, time and changes in electrical conductivity) with spirulina algae from water. With increasing pH from 7 to 8, increased extraction. In general, change the pH from 7 to 8 and changing the concentration of 50 mg/l to 300 mg/l can nitrate removal rate from 59% to 87% by Spirulina algae change. Also, electrical conductivity increases with increasing pH. According to the results we can say that the best extraction was in conditions of pH=8, treatment time of 9 days and concentration of feed 50 mg/l.

Keywords: Nitrate, water pollution, biological absorption, spirulina algae, membrane bioreactor

1. INTRODUCTION

Nitrate is one of the potential pollutants present in water bodies when nitrogenous compounds are completely oxidized by aerobic degradation. More concentrations of nitrate in drinking waters cause Methemoglobin in infants. In the intestinal tract of infants, bacteria converts the nitrate ion to nitrite ion, which reacts with a wide range of secondary and tertiary amines and amides to produce p-nitroso compounds, most of these compounds are potent Carcinogens. In stomach where acidic conditions prevail, the reactions occur quite rapidly affecting the ability of blood cells to absorb oxygen. This causes slow suffocation of the infants, which may lead to death. Because of the oxygen deprivation, the infant will often take on a blue or purple tinge in the lips and extremities and hence the name, blue baby syndrome [1-5]. There are many sources identified as potential source of nitrogen contamination. They are both natural and anthropogenic origin [1, 6-8]. Anthropogenic sources, most often, cause the amount of nitrogen compounds in waters to rise to dangerous levels. Improper disposal of waste materials, human and animal sewages, industrial wastes related to food processing and munitions, accidental spilling of nitrogenous materials and leakage of Septic tanks are some of the examples [9]. Ground water contamination is usually related to the density of septic systems. In densely populated areas, septic systems turn to be major local source of nitrogen compounds to the groundwater. Another potential source of nitrate contamination is the run offs from the agricultural fields using excessive fertilizers in the nearby areas and from the leaches of manure stores. Many efforts have been envisaged by the various groups of researchers [1, 10] throughout the Globe in reducing nitrogen-nitrate concentration in polluted waters by evoking physicochemical phenomenon such as Ion Exchange [11, 12]. Biochemical de-nitrification [12-14], Reverse Osmosis [15, 16], Electodialysis [16], Catalytic denitrification [17], algae spirulina and membrane bioreactor. These methods have one or other disadvantages and more over, these methods involves complicated procedures and expenditure. A universally acceptable procedure is still eluding the researchers. Immersed heterotrophic membrane bioreactor (MBR) produced high quality product water when NO_3^- contaminated water was made to flow through the lumen of tubular microporous membranes. NO_3^- diffused through the membrane pores. Denitrification took place on the shell side of the membranes [35].

The MBR achieved over 99% NO_3^- removal at an influent concentration of 200 mg NO_3^- /L. Biological denitrification had been considered the most effective process for nitrate removal in comparison to other treatment process, like electrodialysis, ion exchange, and reverse osmosis [18-20], biological treatment removes nitrate under anoxic conditions, denitrifying bacteria are capable of using the oxygen bound in nitrate as a terminal electron acceptor and nitrogen is released as gaseous N_2[21]. In addition, biological denitrification is the only process that directly targets nitrate and does not shift the concentration of other ions. For these reasons, biological treatment represents a cost effective alternative. Nevertheless it suffers from certain disadvantages[22]. Many bacteria belonging to different genera can grow anaerobically by reducing ionic nitrogenous oxides to gaseous products. Nitrates or nitrites served as the terminal electron acceptors instead of oxygen and resulted in generation of ATP. Such denitrification was dissimilatory nitrate reduction. When electrons are transferred from the donor to the acceptor, the organism gains energy which was applied for the synthesis of a new cell mass and the maintenance of the existing cellmass. The enzymes associated with denitrification are synthesized under anaerobic or partially aerobic conditions. Nitrate reduction to nitrogen gas occurred as:

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$$

Each step was catalyzed by an enzyme system. Dissimilatory reduction of nitrate to nitrite was important for most bacteria, since the process involved energy conservation by increased substrate level phosphorylation reaction. Since denitrification was a respiratory process, an oxidisable substrate was needed as an energy source. Limitation of biological denitrification was possible bacterial contamination and presence of residual organics [23]. Spirulina named as Tecuitlatl by Aztecs, this means stone's excrement during 16th century. Later, due to outbreak of contagious disease, new customs were adopted by people such as new foods, religious, political and social changes, and the topic of Tecuitlatl came to an end. It was not known till when man began to use microalgae, but at present this resources can be so called," green tendency. Spirulina (Arthrospira) belongs to the oxygenic photosynthetic bacteria that cover the groups Cyanobacteria and Prochlorales[24]. The main purpose of this study is to investigate the effects of the primary operational factors on the efficacy of the algae spirulina and membrane bioreactor in treating nitrate-contaminated sample. These

factors are included current pH, time, Pressure and Nitrate Concentration.

2. MATERIAL AND METHODS

2.1. Preparation of Samples Containing Nitrate

Sodium nitrate was used for preparation of the solution according to the rules of an oral solution 500 mg/l was built. For this removed nitrate concentration by algae is measured with a spectrophotometer, Should draw a calibration curve with different concentrations. Thus, four different concentrations of 20, 50, 100 and 300 mg/l of each sample (Fig. 1) were prepared and absorption by the spectrophotometer, then uptake curve was plotted versus concentration. The curve correlation coefficient was 0.995, the show attracted a linear relationship with concentration. However, this diagram helps to calculate the concentration of each unknown sample (Fig. 2).

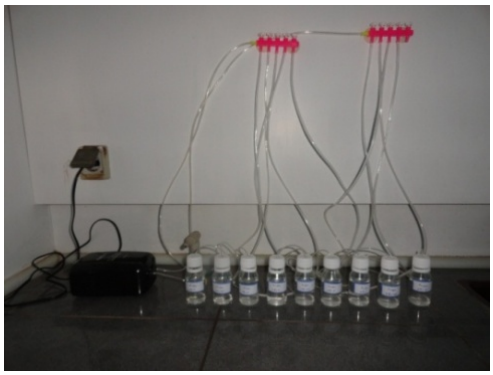

Figure 1: Samples contain difference concentration and pH.

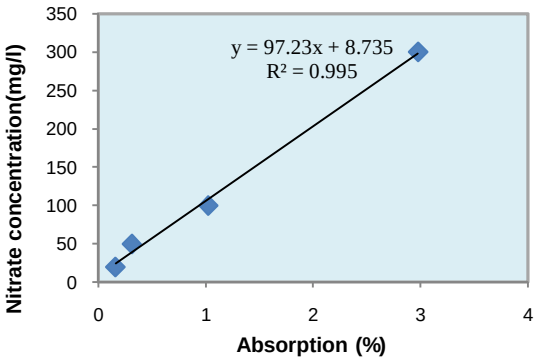

Figure 2: Calibration curves at different concentrations of nitrate solution.

2.2. Treated Samples Containing Nitrate

For treatment of samples per container of 50 cc of nitrate solution at three different concentrations 50, 100 and 300mg/l was poured and algae were added to each sample. The amount of algae in all the tests, 2 ml of each sample was injected. Then pH of each sample set with acids and bases in the level of 7, 7.5 and 8. The samples in intervals of 3, 6, 9 days, algae were exposed. At each time interval the amount of nitrate removed with a syringe and

measured by a spectrophotometer. The concentration of each sample after purification by algae derived calibration curve was calculated using linear equations.

2.3. Optimal Treatment of Treated Samples Using Membrane Bioreactor

According to the results, a solution that was more algae removal rate was chosen as the optimal solution. The optimal solution in the membrane bioreactor (Fig. 3) tanks were dumped in three pressure ranges 10, 12, 14 Bar passed through the membrane. Solution by membrane bioreactor filtration membrane module output was collected, then the filtered solution by syringe was removed at any pressure value. The removal of nitrate membrane was measured with a spectrophotometer. The pressures are selected according to the type of membrane used.

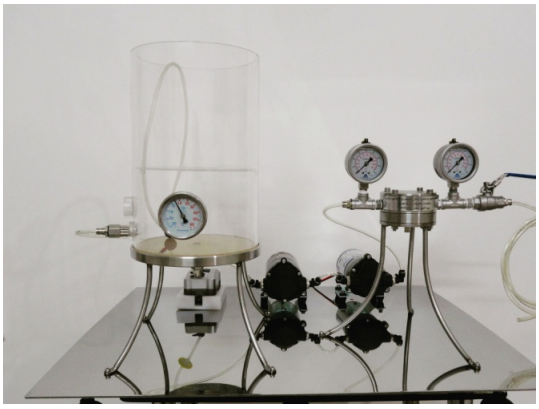

Figure 3: Membrane bioreactor

2.4. Analytical Methods

All tests are performed in triplicate, and the mean data values are reported. The samples are tested for nitrate, pH after electrochemical by using spectrophotometer (Agilent Cary 8454, Germany), TDS-meter (JENWAY, Germany), pH-meter (Metrohm, Germany), respectively. Nitrate is determined according to procedure detailed in standard methods [25]. The percentage nitrate removal is calculated according to the following Eqn (1):

$$R(\%) = 1 - (C / C_0) \times 100 \quad (1)$$

Where the percentage of nitrate removal (R, percentage) and the nitrate value before and after treatment (C_0 and C, mg/L) expressed.Kinetics reaction models are calculated according to the following Equns (2) and (3):

$$\ln C_t = \ln C_0 - K_{1t} \quad (2)$$

$$1 / C_t = K_{2t} + 1 / C_0 \quad (3)$$

Where C_0 and C_t are the concentration of nitrate at the beginning and after time t of the reaction, respectively. K_1 and K_2 are the first, and second order reaction constants, respectively. Values of K_1 and K_2 can be calculated from the slope of the plots

ln C_t versus t, and $1/C_t$ versus t, respectively.

2.5. Design of Experiments

In order to evaluate the effect of different factors and determine the impact of each of these factors on nitrate removal tests, the full factorial experimental design method was used. The answers given in the survey, the percentage of nitrate uptake by the algae. Other operating parameters that affect the nitrate removal process by algae and bioreactors include: pH solution contaminated with nitrates, conductivity, timing for the removal of nitrate by algae. In full factorial method, each of the parameters in the least (-1), maximum (+1) and a point in the center of the case was investigated. The investigation factors, along with the levels of each of them is shown in Table 1.

Table 1: Factors of the type of response surface methodology full factorial.

Factors	Factor levels		
	-1	0	+1
A: Concentrations of pollutants (ppm)	50	100	300
B: pH (µs/cm)	7	7.5	8
C: Time (day)	3	6	9

3. RESULTS AND DISCUSSION

3.1. Extraction Nitrate Optimal Solution by Membrane Bioreactor

3.1.1. Pressure Effect on Nitrate Extraction by Membrane Bioreactor

As seen in Figure 4, nitrate removal rate by increasing the pressure increased. Some researchers have studied this phenomenon, because it increases the pressure was increased polarization. In this case we can say that the sodium cation ionic radius is very small and therefore have little hydration energy, and thus can enter the membrane holes are the holes in the membrane some of them remain. In this case, the adsorption of particles on the membrane surface forces between them depends on the electrostatic and van der Waals forces play an important role. With increasing pressure, constant surface forces as it moves through sodium ions and then nitrate (for electric balance solution) does not substantially change, but because solvent by increasing the pressure has increased, the amount of the solution is increased, resulting in higher nitrate is removed. When the pressure is increased to a large extent can be stripped off the cations adsorbed in the pores, and they bring with them to the exit as they will go nitrate [26-28]. According to Figure 4, the results showed that the highest nitrate removal at a pressure of 14 bar equal to 99 percent.

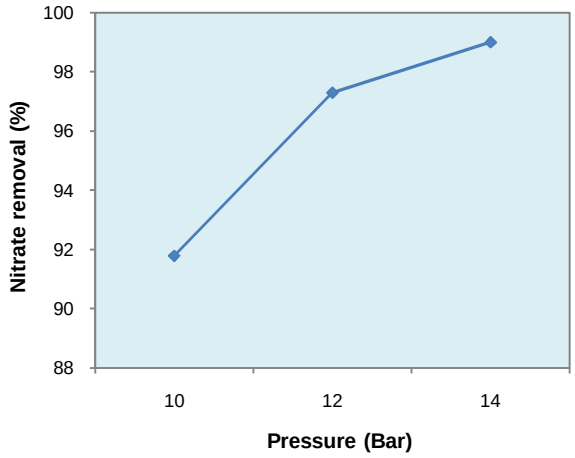

Figure 4. The effect of pressure on the extract nitrate optimal solution by membrane bioreactor.

3.2. Extraction of Nitrate From Water Using Spirulina Algae

3.2.1. Effect of Nitrate Concentration (50, 100, 300mg/l), pH and Time on Nitrate Extraction

The percentage extraction of nitrate was studied under various parameters (nitrate concentration, pH and time) with spirulina algae from feed. The results are presented in the Graph No: 1, 2 and 3. However, many studies are available on spirulina algae. As was observed with increasing concentration of nitrates in feed from 50 to 300mg/l, the extraction was reduced by spirulina algae, because spirulina algae has the ability to absorb a certain amount of nitrate. As the concentration was increased degree of extraction declined, but the percentage of extraction with increasing treatment time trending. Because spirulina algae is a biological absorption, and the more it is exposed to a solution containing nitrate, can absorb more of it [23, 25, 29]. This process continues until all the living tissue of algae full of lead nitrate solution. With increasing pH from 7 to 8, increased extraction (Graph 1, 2, 3). This is because the increase of pH to a certain extent can enhance algae growth, this makes algae can absorb greater amounts of nitrate. In general, change the pH from 7 to 8 and changing the concentration of 50 mg/l to 300 mg/l can nitrate removal rate from 59% to 87% by Spirulina algae change. According to the results we can say that the best extraction was in conditions of pH=8, treatment time of 9 days and concentration of feed 50 mg/l. This result isn't in agreement with Koparal and Ogutveren who have observed higher removal rate at lower pH values [30]. It probably is due to method types. Otherwise this result is in agreement with other researchers [31].

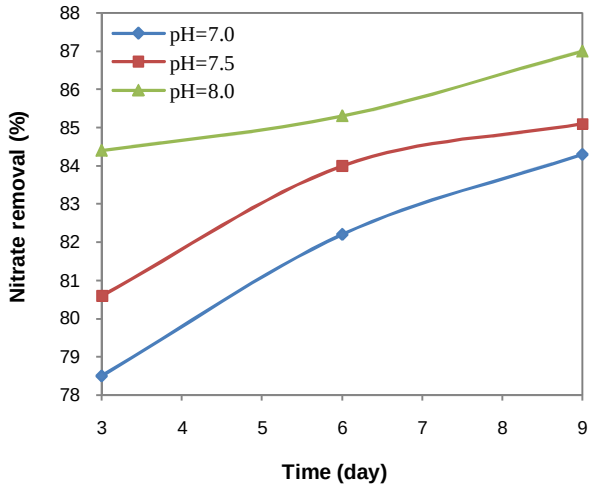

Figure 1: Effect of nitrate concentration (50mg/l), pH and time on nitrate extraction.

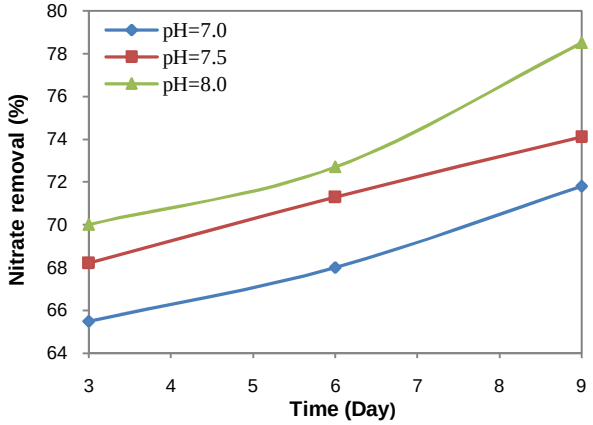

Figure 2: Effect of nitrate concentration (100mg/l), pH and time on nitrate extraction.

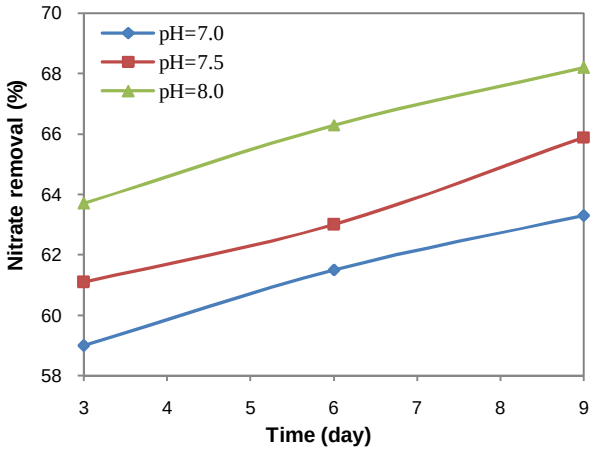

Figure 3: Effect of nitrate concentration (300mg/l), pH and time on nitrate extraction.

Researchers shown that influence of process parameters such as pH, current density and time were studied and the optimal conditions of operation were found to be at pH 8, at 0.89 mA/cm2 for 7h. It is possible to remove nitrate bellow the limit

of the drinking water standard using this method [32]. Otherwise, researchers indicated that the optimum condition for Nitrate removal by means of modified zeolite as adsorbent is pH=5, contact time of 180 minutes and adsorbent amount of 16 g/l. The investigation of isotherm and kinetic equations indicated that Nitrate adsorption follows Langmuir and pseudo first order, respectively [33]. Data indicate that zeolite efficiency in Nitrate adsorption is decreased by changing pH from 3 to 9. The minimum and maximum efficiency of zeolite in Nitrate adsorption is in pH=9 and pH=5, respectively. In acidic pHs, production increase of available protons that are able to be added to zeolite surface has increased absorbability. However, in alkaline pHs, because of negative charge and OH ion, a repelling force is created between adsorbent and Nitrate that decreases the absorbability [34, 35]. In a study of [36] the maximum efficiency of Nitrate removal was 90% that was observed in pH=5 and Nitrate primary concentration of 500 mg/l.

3.2.2. Effect of Nitrate Concentration (50, 100, 300mg/l), pH and Time on Changes in Electrical Conductivity

Electrical conductivity increases with increasing pH. Because sodium and hydroxide ions into the solution, which can further increase the electrical conductivity. Effect of pH was studied by conducting electrolysis at pH 7, 7.5 and 8 by keeping time for 9 h. According to Figure 4, 5, 6, which corresponds to the lowest concentration of nitrate solution, by increasing the pH from 7 to 8, electrical conductivity vary of 270.8 to 350.4 in 9 days. Similar observations were also reported by some researchers [37].

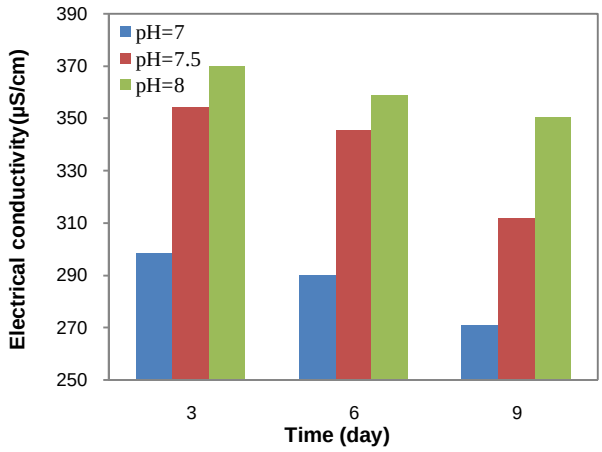

Figure 4. Effect of nitrate concentration (50mg/l), pH and time on changes in electrical conductivity

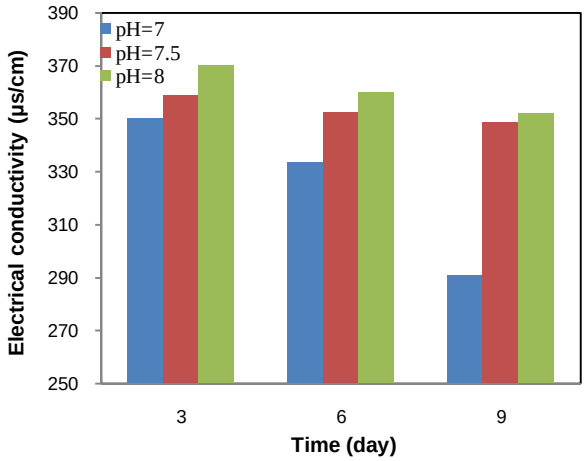

Figure 5. Effect of nitrate concentration (100mg/l), pH and time on changes in electrical conductivity.

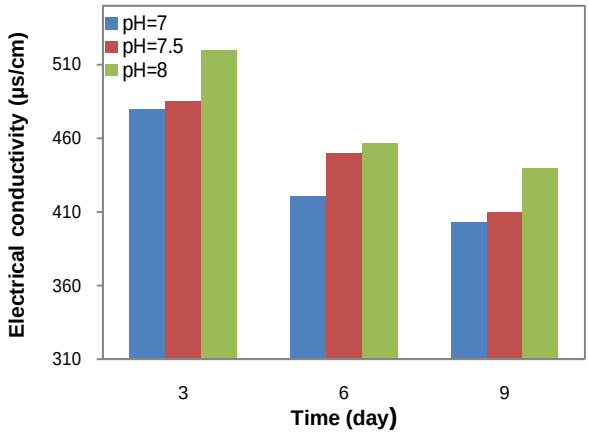

Figure 6: Effect of nitrate concentration (300mg/l), pH and time on changes in electrical conductivity.

4. CONCLUSION

Many researchers have tried to find a cheaper and convenient ways to treat water contaminated with nitrate and industrial wastewater, as an alternative to costly waste water treatment such as chemical precipitation, ion exchange techniques, electrodialysis, remove microbial method, activated sludge, solvent extraction and other methods usual. Considering the results of the use of spirulina algae as an absorbent for the removal of nitrate was considered. The use of spirulina algae of concentration in 50 ppm, pH = 8, retention time of 9 days, 87% of the nitrate removal yielded. According to the results we can say that the best extraction was in conditions of pH=8, treatment time of 9 days and concentration of feed 50 mg/l. So for the highest degree of nitrate removal to be viewed by Spirulina algae must feedstock containing nitrate in optimal condition was removed.Following the work of membrane bioreactor was used, so the optimum nitrate solution through the membrane separation process is very good

in the nitrate contamination of the solution so that the use of nitrate membrane separation rate of 87% to 99% improved.

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