



Reduction of Nitrate Level using Low cost Adsorbents

E. Kowsalya*, Mayukh Gangopadhyay, S. Sharmila, L Jeyanthi Rebecca

¹Department of Industrial Biotechnology, Bharath University, Tamilnadu, India.

Abstract : Nitrogen are present in the form nitrate and nitrite in Industrial effluent or waste water like Dairy Industry, Fertilizer Industry etc. The use of low cost adsorbent has been investigated as a replacement for the current expensive method of removing nitrate from waste water. The objective of this work is the study of adsorption of nitrate containing solution, by using low cost adsorbent Casurinas Dried Leaf (Sample I) and Activated Carbon (Sample II). Nitrate solution with known concentration had been prepared. Then liquid phase adsorption has been carried out by using these two adsorbent and result has been investigated by batch mode. A colorimeter is used to estimate the Nitrate Concentration by the colour formation undergone by PDA method. Parameters such as adsorbent dose, effect of time have been observed through Batch Adsorption. In present study, it is observed that adsorption showed 25% adsorption for Sample I by using it at the amount of 1g to 4g and for sample II it is quite higher, 91% by using it in 0.1mg dose and shows maximum 96.4% adsorption when 0.4g is added.

Introduction

Nitrate is present remarkably in various industrial waste water such as, Dairy Industry, Fertilizer Industry etc. In fact, nitrate is a reactive form of N, the dominant form of nitrogen pollution in surface and ground water. Many communities rely on ground water for drinking water and thus nitrate contamination is a matter of serious health concern. Consuming water with high level of nitrates may lead to significant health issues, including methemoglobinemia (also called blue baby syndrome), certain types of cancer, and other chronic health issues. (Agricultural Sustainability Institute at UCDAVIS).

Now a days there are different process of removing nitrate from waste water such as: protonation, impregnation of metals and metal oxides, grafting of amine groups, organic compounds including surfactant coating of alumina-silicate minerals, and heat treatment are used. Also Adsorption is an efficient and economical method using in removal of dyes from industrial effluents. In this process, a substance (soluble dye) from the liquid phase (wastewater) is transferred to the surface of a solid, highly porous material (adsorbent), to which it binds physically or chemically⁽¹⁾. The adsorption technique is preferable to other waste water treatment techniques in terms of efficiency, low cost, simplicity, ease of operation, and inactivity towards toxic substance. Moreover, the specific advantage of method is that the adsorbent can be chosen from a large variety of material. These adsorbent, used in batch or dynamic condition, can be naturally occurring material (wood, peat, coal, chitin and chitosan, biomass, clays, etc.), as well as industrial/agricultural waste sorby products (flyash, redmud, blast furnace slag, dye hydroxide sludge, sawdust, bark, lignin, sunflower stalks, maize cob, rice husk, hazelnutshell, olivestones, seashell, etc.)⁽²⁾

The use of spent tea & Ground nut powder as a Adsorbent Shows the degree of reduction of dye component degree of reduction up to 86-94%⁽³⁾. the adsorption by using low cost materials in decontamination

processes was carried out⁽⁴⁾. In recent years, sever allow-cost materials such as industrial by-products and agricultural wastes have been used as plant biomass precursor for the Zn (II)removal as well as other metal ions from water systems⁽⁵⁻⁷⁾also The adsorption study of Nickel(II) on Passiflora foetida seeds⁽⁸⁾, phenol on Acacia Nilotica branches⁽⁹⁾, Fe(III) on hibiscus sabdaritta stem⁽¹⁰⁾, acid blue113 on varagu millet husk⁽¹¹⁾. Removal of Cu(II) by Orange peel adsorbent⁽¹²⁾was studied by so many researchers .In this Project we concentrate our work on the removal of Nitrate using low cost adsorbent. The nitrate adsorption capacity for Surfactant-modified activated carbon(SMAC) increased with increasing the CPC loading (SMAC)The SMAC exhibited much higher nitrate adsorption capacity than that of the unmodified activated carbon⁽¹³⁾.The percentage of nitrate ion removal from aqueous solution using this clay was determined to be 80% at an optimum condition of initial concentration⁽¹⁴⁾.So in this project we have worked out the use of two adsorbents Casurina leaves powder,and Activated Carbon for the removal of Nitrate content in a waste water sample.

Preparation of Adsorbent:

Casurinas fresh leaves were collected and dried in sunlight for one week. Then the dried leaves were washed thoroughly 3-4 times with both tap water and distilled water. Then the leaves are placed in hot air oven for 10 minutes to remove the water and moisture. Atlast this leaves are put in a grinder to prepare powder and at last powder had poured in a container and thus Sample I is prepared. Activated carbon was first washed with distilled water and then it was dried in air Atlast it was kept in container and SAMPLE II was prepared.



Fig1: Sample I



Fig2: ii) Sample II

Casuarina dried leaves),(Activated Carbon)

Preparation of Absorbate:

721.8 mg of anhydrous KNO_3 was dissolved in distilled water and diluter to 1 liter. 10 ml of this solution contains 1 mg of nitrate. Thus according to need of sample different concentration of nitrate can be prepared.

PDA Reagent:

25 g of crystal white phenol was dissolved in 150 ml of conc. H_2SO_4 was heated on water bath for 2 hours. This is called phenol disulphonic acid which is capable to form colour with nitrate.



Fig 3: Formation of yellow colour by the effect of PDA Reagent

Estimation of Nitrate:

10 ml of nitrate solution was taken and it was made upto 50 ml, thus its concentration is 1mg/50 ml. Like that 20 ml, 30 ml, 40 ml, and 50 ml of nitrate solution had taken and made upto 50 ml which gives nitrate concentration 2mg/50 ml, 3mg/50 ml, 4 mg/50 ml and 5mg/50 ml respectively. Now those solutions are evaporated over a hot plate till formation of residue, which was dissolved in 3 ml of phenol disulphonic acid. Reaction was allowed to stand for 10 minutes and then 15 ml of distilled water was added. Later 7 ml of ammonia soln. was added and the final volume was made upto 50 ml. intensity of the yellow colour as percentage transmission was measured at 410 nm. Valuation of NO₃ was obtained in reference calibration curve and the value was computed in the following formula.

$$\frac{mg}{L} \text{ Nitrate } N = \frac{mg \text{ Nitrate } N}{ml \text{ sample}}$$

Thus by taking 50 ml of effluent sample in a beaker same process had been undergone and the yellow colour formation was checked through the colorimeter to find the amount of nitrate present in the effluent from the nitrate standard graph.

Batch Adsorption Studies

50 ml of effluent sample was taken and two adsorbents, Dried Casuarina Leaves and activated carbon sample added to determine the adsorption by the effect of Initial Nitrate Concentration, Adsorbent Dose and Contact Time of adsorbent. Each time 50 ml of effluent sample had been taken and required amount of adsorbent had been added with it. After that the solutions were agitated at a constant speed and temperature using rotary shaker. Then the solutions were kept under centrifuge for 20 minutes at 7000+ rpm. The supernatant had been separated and PDA method had been processed and yellow colour formation was checked through the colorimeter. The colorimeter reading is compared in standard nitrate graph to determine the decrease of nitrate in the solution. The percentage deduction of nitrate is calculated by the following,

Formula:

$$\% \text{ Nitrate reduction} = ((C_0 - C_f) / C_0) * 100$$

Where, C₀= initial Nitrate concentration (mg/L), C_f= final Nitrate Concentration(mg/L)

Effect of Adsorbent

By the O.D. value of Potassium Nitrate sample, we came to know that our effluent sample contains 5mg/50 ml concentration of nitrate. Now in this effluent sample 1g, 2g, 3g & 4g casuarina dried sample are added and 0.1g, 0.2g, 0.3g & 0.4g Activated Carbon sample has been added in different conical flask. Same like above, they were kept in rotary shaker for an hour, the solutions were centrifuged at 7000+rpm for 20 minutes

and supernatants were separated. The colour formation of these has been observed by undergoing PDA method and colorimeter reading has been taken.

Effect of Time:

Nitrate solution of concentration 5mg/50ml were taken in 3 conical flasks and 2g of casuarina leaves sample were added with each. Same as these effluents were taken in 3 anther conical flask and 0.2g of activated carbon sample were added. These all are kept in the rotary shaker for different time intervals of 20, 40 and 60 minutes. After agitation the solutions were centrifuged at 7000+ rpm 20 minutes and supernatant were separated. Then through colorimeter we judged the amount of nitrate reduction through the PDA Method discussed above.

Result and Discussions

Effect of Adsorbent Dose:

For the Potassium Nitrate sample of 5mg/50 ml concentration.

Table1- Effect of adsorbent dose on nitrate reduction from effluent(5mg/50ml) for sample I

Adsorbent Dose	% Reduction
1 gram	28
2 gram	28
3 gram	28
4 gram	28

Table 2:Effect of adsorbent dose on nitrate reduction from effluent(5mg/50ml) for sample II

Adsorbent Dose	% Reduction
0.1 gram	91
0.2 gram	93
0.3 gram	96
0.4 gram	96.4

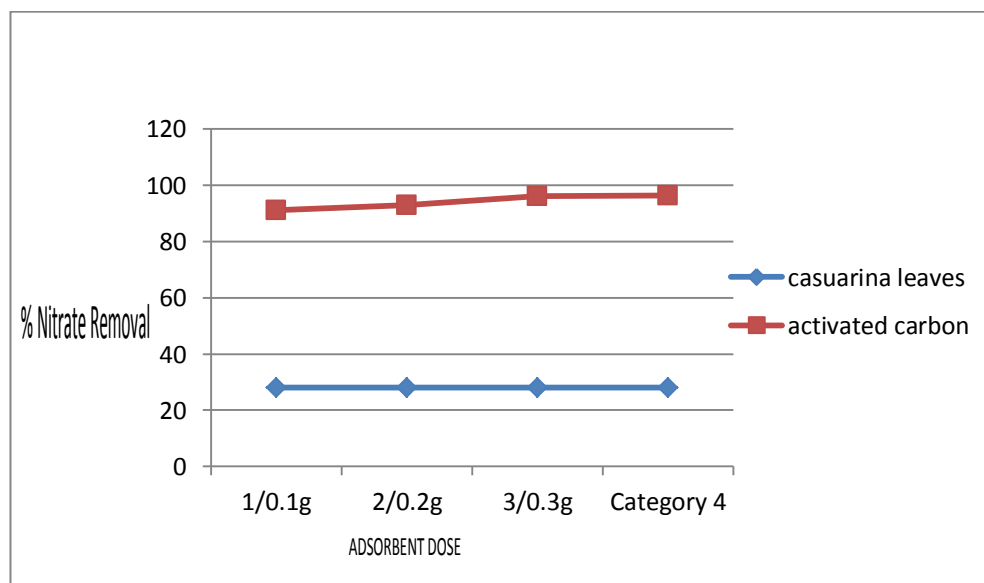


Fig4: Effect of adsorbent dose on nitrate concentration

An increase in adsorbent dosage resulted in a corresponding increase in the percentage removal of nitrate from water⁽¹⁵⁾

By this graph it is clear that adsorbent dose does not affect the adsorption of nitrate by using Casuarina Dried leaves where, activated carbon had shown more adsorption with increase of doses. And according to the value, activated carbon shows maximum reduction of Nitrate (96.4% highest)

Effect of Time:

Table 3- Effect of time on Adsorption of effluent with at constant adsorbent dose 2g for sample I

Time	% Reduction
20 mins	10
40 mins	20
60 mins	28

Table 4: Effect of time on Adsorption of effluent with at constant adsorbent dose 2g for sample II

Time	% Reduction
20 mins	60
40 mins	92
60 mins	96.4

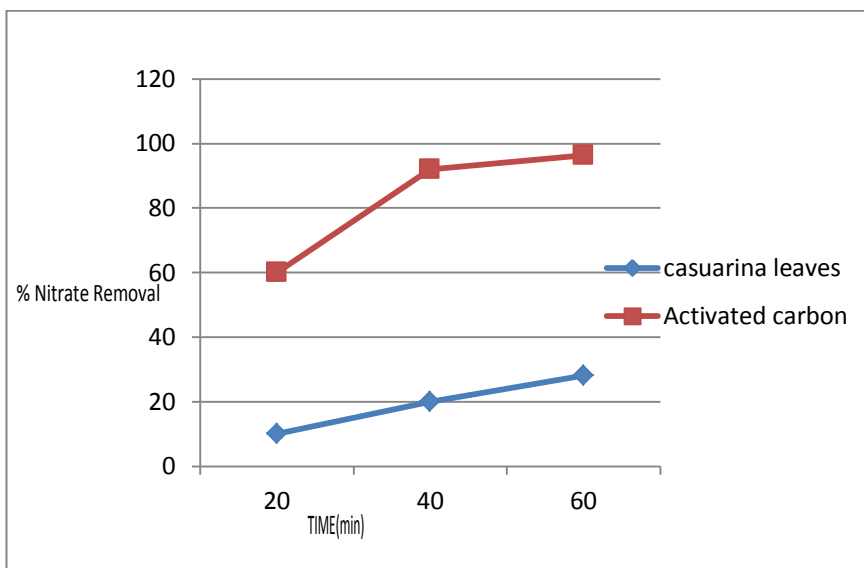


Fig 5: Effect of Time on Nitrate Concentration by constant adsorbent dose.

From this graph we can tell that adsorption by using casuarina dried leaves and activated carbon increase with time. Thus it shows maximum 96.4% reduction of nitrate through Activated carbon where Casuarina Dried leaves shows maximum 28% reduction of Nitrate.

Conclusion

Thus by these project we had verified the adsorption power of two different adsorbent. Nitrate is one of the most dangerous pollutants. By experimental results, we came to a decision that Activated Carbon is no doubt very strong adsorbent which gives maximum upto 96.4% nitrate reduction. In the other side, casuarina dried leaf sample gives maximum 25% nitrate reduction. In compare to activated carbon, it is less efficient adsorbent but activated carbon is comparatively costly, where casuarina tree is very common species, and it is

definitely very cheap. Casuarina leaves sample can be used as Adsorbent in a larger scale by little modification with other combination material. In future we want to undergo this research by recovering the amount of nitrate from the adsorbent, and to investigate the result in many other different parameters such as pH, rpm of centrifuge, initial nitrate concentration etc.

References

1. Crini, G., (2006). "Non-biodegradable low-cost adsorbent for dye removal. A review," *Bioresour Technol.* 97(9), 1061-1085.
2. Bozlur, R.M., Shibata, S., Diba, C.F., Uono, M. (2012). "Low cost biodegradable adsorbent material for the removal of dissolved dyes from aqueous solutions: An economical process," *IACSIT Intern. J. Eng. & Technol.* 2(5), 468-473.
3. E. Kowsalya, Sharmila S, Jeyanthi Rebecca L, Yogesri K. Ground Nut Shell and Spent Tea: An Ecofriendly Low Cost Adsorbent, *Int. J. pharm. Sci. Rev. Res.*, 31(1), March-April; 2015 Article No. 27, Pages 132,
4. Mohamed Chiban, Amina Soudani and Fouad Sinan "Removal of Nitrate Ions by using Low-Cost Adsorbents: Equilibrium Isotherm, Kinetics and Thermodynamic Study" pp. 31-48.
5. Zaharia, C. (2008). Environmental Legislation, Politehnia Publishing House, Iasi, Romania.
6. Latif, A., Noor, S., Sharif, Q.M., and Najeebullah, M. (2010). "Different techniques recently used for the treatment of textile dyeing effluents: A review," *J. Chem. Soc. Pak.* 32(1), 115-124.
7. Suteu, D., Zaharia, C., Muresan, R., and Popescu, A. (2009). "Using of industrial waste materials for textile waste water treatment," *Environ. Eng. Manage. J.* 8(5), 1097-1102.
8. Velumani K, Kumar P E, Sivakumar V, "Novel Adsorbent prepared from *Passiflora foetida* seeds for the adsorption of Nickel(II) in aqueous solution." *Int. J. ChemTech Res.*, Vol 9., No.7, pages 574-586, 2016.
9. Bhajan Dass, Pushpajha, "Activated carbon of *Acacia nilotica* branches for adsorption of phenol". *Int. J. ChemTech Res.*, Vol 8, No.12, pages 269-279, 2015.
10. P. Manivannan, S. Arivoli, Raja Mohamed, "Equilibrium and Thermodynamics studies on the removal of Fe(III) on Activated Hibiscus sabdaritta stem nanoparticle". *Int. J. ChemTech Res.*, Vol 8., No.10, pages 346-354, 2015.
11. Valliammai, K.S Nagaraja, B. Jeyaraj, "Removal of acid blue 113 by Activated carbon of varagu millet husk". *S Int. J. Chemtech Res.*, Vol 8., No.12, pages 329-341, 2015.
12. Srinivas Tadepalli, K.S.R. Murthy, N.N. Rakesh, "Removal of Cu (II) and Fe (II) from Industrial waste water using orange peel as adsorbent in batch mode operation". *Int. J. ChemTech Res.*, Vol 9., No.5, pages 290-299, 2016.
13. Zheng WJ1, Lin JW2, Zhan YH2, Fang Q2, Yang MJ2, Wang H2 "Removal of nitrate from aqueous solution using cetylpyridinium chloride (CPC)-modified activated carbon as the adsorbent". [Article in Chinese]
14. Wasse Bekele, Gezahegn Faye and Nestor Fernandez "Removal Of Nitrate Ion From Aqueous Solution By Modified Ethiopian Bentonite Clay" 1) Chemistry Department, College of Natural Sciences, Jimma University, Ethiopia. 2) Inorganic Chemistry Department, Faculty of Chemistry, University of Havana, Cuba.
15. Mike Masukume, Maurice S. Onyangol, Ochieng Aoyi and Fred Otieno "Nitrate Removal From Groundwater Using Modified Natural Zeolite". Department of Chemical and Metallurgical Engineering, Tshwane university of Technology-South Africa
