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Use of Different Bioadsorbents for the Nitrate Removal from Water

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Abstract: Our life is very precious and water is one of the most important natural resource for the existence of our life. For the last two decades; there is an increased interest in the study of nitrate in the ground water. Earlier the nitrate concentration in the ground water was very low nearly 5ppm. However due to pollution the nitrate concentration in the water has increased considerably. In the environment, nitrogen is found in different forms like Nitrate (No₃-), Nitrite (No₂-), and Ammonia (NH₃) and Nitrogen gas (N₂). Nitrate pollution of water is mainly due to excessive use of fertilizers, human sewage and livestock manure. Nitrates presence in the potable water beyond permissible limits is the major issue today for the people living in the western Rajasthan. It is affecting their health badly. Infants, less than six months can be victim of nitrate poisoning "Methemoglobinemia". (blue baby syndrome), Beside this gastric cancer, hypothyroidism, hormonal imbalance disorder, birth malformations and growing hypertension in the human beings is also attributed to the increased concentration of nitrate in the water. Therefore our prime objective was to remove nitrate from the contaminated water by an affordable and easy method. In this paper we have used activated charcoals of dried and fresh biomass of different bio adsorbents to remove nitrate from contaminated water. With the increase in pH the % removal efficiency was found to first increase and then decrease for different bioadsorbents.. As bio adsorbents dose was increased from 0.1 to 0.5 gm, there was a general increase in the nitrate removal efficiency. There was an increase in the nitrate removal efficiency with the increase in the temperature. Normal contact time was 30 to 40 minutes for the maximum adsorption. The order for nitrate removal was Bael leaves >Mausambi Peel >Khejri leaves>orange peel>Lemon Peel>Ashok leaves. We used biochar of Bael leaves for further studies and it showed significant capacity for the nitrate removal. By kinetic study it was found to follow pseudo second first order kinetics and the analysis for isotherm equilibrium data using Freundlich, Langmuir and Tepkin equations by linear methods showed that it fitted well with all the three equations. Due to the high efficiency and economic consideration adsorbents technique is best among different methods and biochar of Bael leaf was found to be a great option for nitrate removal.

Keywords: Ground water, Nitrate, bio adsorbents, adsorption, Methemoglobinemia

I. INTRODUCTION

In almost all parts of the world, ground water pollution is a growing concern. In India ground water is one of the main source for potable water.. The commonly observed contaminants such as Nitrates and heavy metals etc. are added to our water resources by various human activities including domestic sewerage; agricultural practices and industrial effluents. Most of the organic and inorganic contaminants of nitrogen undergo transformation into nitrates by the nature known as nitrogen cycle.[1-2]

Nitrate is essential compound for normal health & hygiene. It is normally found in food stuff, leafy vegetables & proteins including purified pyrimidine & urea. It exists in different forms viz: - Nitrate (No₃-), Nitrite (No₂-) Ammonia (NH₄⁺). The ultimate product of biological nitrification is Nitrate.

In the agricultural sector increased use of nitrogen fertilizer is the major reason for nitrate contamination [3]. In spite of this poorly treated or untreated human and animal wastes are also responsible for contamination. Non-point sources are also responsible for nitrate contamination [4-7] and which are also hard to detect. Factors such as dissolved oxygen, electron donor availability, precipitation, thickness, source availability irrigation, ground water flow etc. are also control distribution of nitrate in ground water. Blue baby syndrome (Methemoglobinemia) especially occur in infants is due to increase in the concentration of nitrate in water & it is due to high solubility of nitrate in water [8-9]. High concentration also causes gastric & intestinal cancer [10-11]. According to WHO 45 ppm is the permissible limit of Nitrate for human consumption. According to W.H.O. the guideline value for nitrate-nitrogen is 10 ppm (mg/L of nitrate -nitrogen) [12-13]. The Indian council of medical research has recommended a highest desirable level of 20ppm of nitrate-nitrogen in the drinking water while maximum permissible level recommended for drinking water is 50 ppm.

There are many techniques which are useful to reduce nitrate contamination and are based upon physicochemical & biological processes.[14]. These include membrane separation adsorption ion exchange [15-16], biological treatment, biochemical

denitrification [17-20]. Adsorption appears the most appropriate among these methods of separation because they are economically viable in developing country like India. Rest of the methods involve a lot of procedure and are costly also. Due to its simple operation, low energy consumption & a short treatment cycle it is a best technique. Selection of appropriate nitrate adsorption material is very necessary for better result. Activated carbon is generally considered as one of the best adsorbent for the nitrate removal [21]. In the present work we have used bio chars of locally available leaves and peels and used them as bio adsorbent for nitrate removal from water. Various parameters like contact time, adsorbent dose, initial nitrate concentration and effect of temperature have been investigated.

II. MATERIAL AND METHOD

The reagents used were of AR grade. Stock solution of nitrate was prepared by dissolving 1.62 g of anhydrous potassium nitrate in 1000 ml of distilled water in a volumetric flask. Standard solution of desired concentration was prepared by further dilution of the stock solution. We have done comparative study of different bio adsorbents charcoal for the nitrate removal and found out the best adsorbent for the nitrate removal. Bael leaves (Aegle marmelos), Khejri leaves (Prosopis cineraria), Ashok leaves (Saraca ashoka), Lemon peel (Citrus lemon), Orange peel (Citrus sinensis) & mausmi peel (Citrus limetta) were used as bioadsorbents.

A. Material Development

Bael is a medicinal tree. Its use in skin, eye treatment stomach related problems are very evident. Due to porosity of Bael peel, orange peel powder, they adsorb nitrate from aqueous solution. Mausambi peel powder has good water holding capacity and it can be expressed by number of grams of water held by 1 gram of sample. It is mainly used by juice processing industry and peels are thrown away as a waste. Lemon peel contains a plant pigment polymethoxylated flavones and due to its water holding capacity it is used as nitrate removal bio adsorbent. Khejri plays an important role in the economy of arid and semi-arid zone of Rajasthan. Fresh leaves were obtained from trees and peels from domestic waste. Biomass were washed thoroughly for 2-3 times in tap water & after that in distilled water. Then leaves and peel were sundried for 3-4 days, then were put into a bag and were crushed manually. After that powder was sieved to get various particle size. Now the dried leaf and peel powder were heated in a muffle furnace at 500°C for 1-2 hours. The biochar so obtained was activated by acid and base treatment.

- 1) Acid treatment: 4 gm of leaf biomass charcoal powder sample was taken in a 100 ml flask and 40ml of 1N HNO₃ was added to it. The mixture was gently heated on burner for few minutes, after the boiling started, the treated bio char was washed with distilled water until maximum colour was removed and clear water was obtained.
- 2) Alkali treatment: 4 gm of leaf biomass charcoal powder sample was taken in a 100 ml flask and 40ml of 5N NaOH was added to it. Then mixture was gently heated on burner until boiling started. Treated biomass was washed with distilled water washing was done until maximum colour was removed and clear water obtained. The charcoal powder so obtained was porous and micro porous particles provided suitable binding sites for nitrate ions.[22]

All the experiments were carried out using acid and base treated biochars. It was observed that's % removal efficiency of nitrate was better ore in the case of acid treated biochar. So in all the experiments we have used acid catalysed biochars obtained from biomass. Fig.1 shows various dried leaves and peels powder used for our experiments. Table one represents sources from where we have collected our samples of biomass.

TABLE I BIOADSORBENTS AND SAMPLING SITES

S.NO.	Adsorbent	Sampling Site
1	Bael Leaves	Field
2	Ashok Leaves	Field
3	Khejri Leaves	Field
4	Orange Peel Powder	From Domestic Waste
5	Lemon Peel Powder	From Domestic Waste
6	Mausmi Peel Powder	From Domestic Waste



Fig. 1 Dried and Powdered Peel and Leaves samples

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B. Batch study

100 ppm nitrate solution was taken in a 100 ml of stopper bottle. From this 50 ml of solution was taken and 0.2 gm of adsorbent was added to the solution. At room temperature batch adsorption experiments were carried out and 30 minutes to 3 hours contact time was maintained. The solution was kept still so that adsorbent can get settle easily and pH was adjusted using 1M NaOH or 1M HCl solution using pH meter. The supernatant was separated with a wattmann filter paper number [42, 43].



Fig. 2 Bio chars of various bio adsorbents

In the Figure 2 we have shown pictures of various charcoals obtained from different bioadsorbents. It also shows pictures of various solutions prepared during our experiments. In the Table II we have compared % removal efficiency of six different biochar prepared from leaves and peels.

Table II Percentage removal of nitrate with different adsorbents

S.NO.	Adsorbent	Initial conc. Of nitrate in mg\l	Final conc. in (mg\l)	Amount adsorbed in mg\l	% Removal
1	Bael leaves	100	11	89	89%
2	Mausmi peel powder	100	16	84	84%
3	Orange peel powder	100	20	80	80%
4	Khejri leaves	100	18	82	82%
5	Lemon peel powder	100	21	79	79%
6	Ashok leaves	100	28	72	72%

III. RESULTS & DISCUSSION

Bael, ashoka , khejri leaves , orange peel, lemon peel and mausambi peel charcoal powder were selected as adsorbent for the present study. Sampling site is tabulated in table 1. From table 2 it is observed that order of adsorption is bael, mausambi, orange, Khejri, alemon and ashoka powder respectively. On the basis of above results among all the bio adsorbents , Bael leaves biochar was selected for further studies to check the effect of contact time , concentration , adsorbent dosage & temperature.

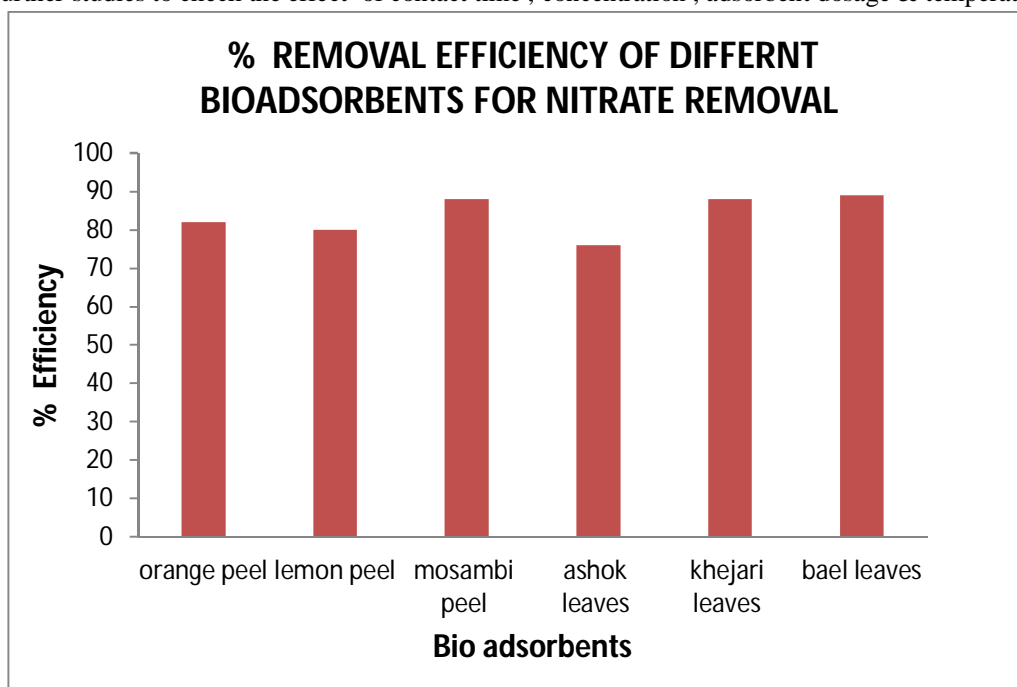


Fig.:3 comparative study of various bioadsorbents for nitrate removal efficiency

C. Effect of pH

We have compared nitrate removal efficiency of biochar of six different bioadsorbents at different pH.. It was observed that % nitrate removal efficiency was different for each biocharas shown in the fig:4. When pH variations were carried out in each of these bioadsorbents, percentage removal of nitrate decreased with the increase in pH from 2 to 10. pH was adjusted using 0.1 M HCl 0.1 M NaOH. It is due to neutralization of negative charge by greater hydrogen ion concentration at lower pH. Due to strong electrostatic interaction between sorbate-sorbent they show high adsorption capacity at lower pH.[24]

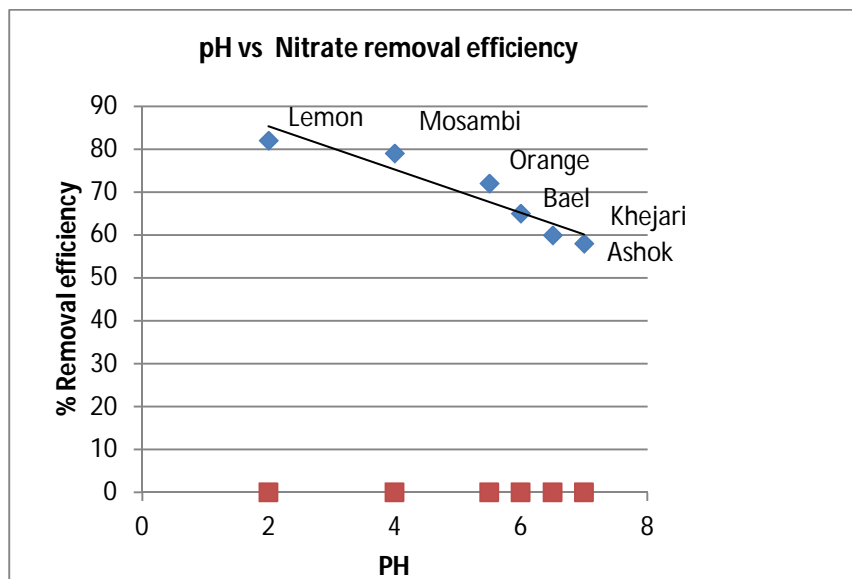


Fig.4 Comparative study of nitrate removal efficiency of different bioadsorbents at different pH

D. Effect of adsorbent dose

Adsorbent doses also influence the sorption equilibrium. Effect of adsorbent dose on percentage removal of nitrate is shown graphically. Experiments were performed with varying amounts of adsorbent ranging from 0.1 to 0.5 g/100 ml at optimum pH value. Adsorption of nitrate increased with the increase in the adsorbent dose up to a particular level and then reached at an equilibrium. At higher dose probably due to the overlapping of active sites and reducing of the net surface area adsorption is decreased. [25] Hence 0.3 g of bioadsorbents in 100 ml of nitrate solution was considered as an optimum dose & was used for further study.

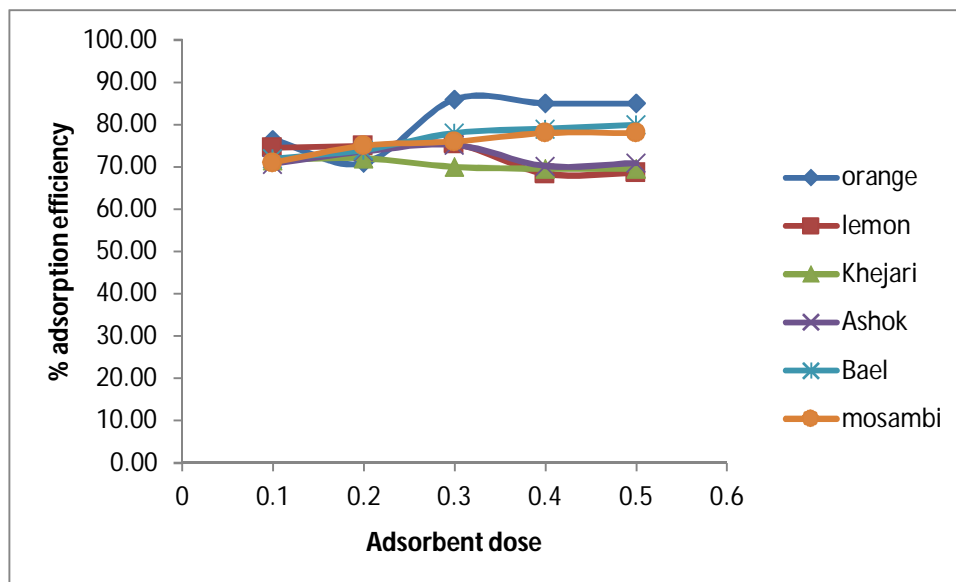


Fig. 5 comparative study of % removal of nitrate with change in adsorbent dose.

E. Effect of contact time

It is found that exclusion of nitrate ion increases with the increase in contact the time to some level at optimum pH & dose [28]. Further increase in contact time does not increase the nitrate ion uptake due to sorbent-sorbent interaction or due to deposition of nitrate ion on the available adsorption sites on adsorption material. Approximate after 60 minutes it reaches to the equilibrium and line in the figure becomes parallel to the time axis, it can be explained on the basis that they reach at a saturation point due to

decrease in the adsorption sites. The highest efficiency of nearly 80% was observed for time of 60 min for Bael biochar. Hence 60 min contact time was selected as optimum contact time for further experiments.

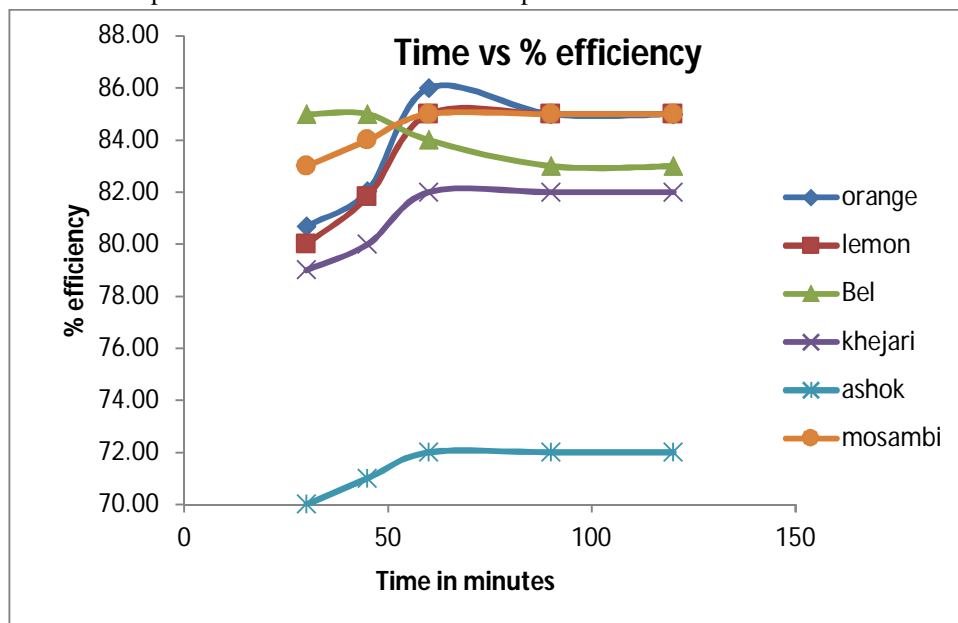


Fig:6 Comparative study of different bioadsorbents for nitrate removal vs contact time

Figure 6 shows that maximum nitrate removal is achieved in the 30-45 minutes contact time. It is continued till 60 minutes and then % removal efficiency is decreased.

F. Effect of initial nitrate concentration

Effect of initial nitrate concentration is studied by varying nitrate concentration in the nitrate sample with a constant amount of bio adsorbent of 0.1 g. The amount adsorbed per unit mass showed increase with rise in the concentration of nitrate initially. Graph shows that nitrate removal efficiency of adsorbent increases first and then decreases because of the fixed dose of adsorbent capacity gets saturated at high concentration. Due to filled active sites of adsorbents & pore volume, removal of nitrate increases initially as number of available adsorption sites are high & as these sites are occupied decreases with the increase in the nitrate concentration [26-27].

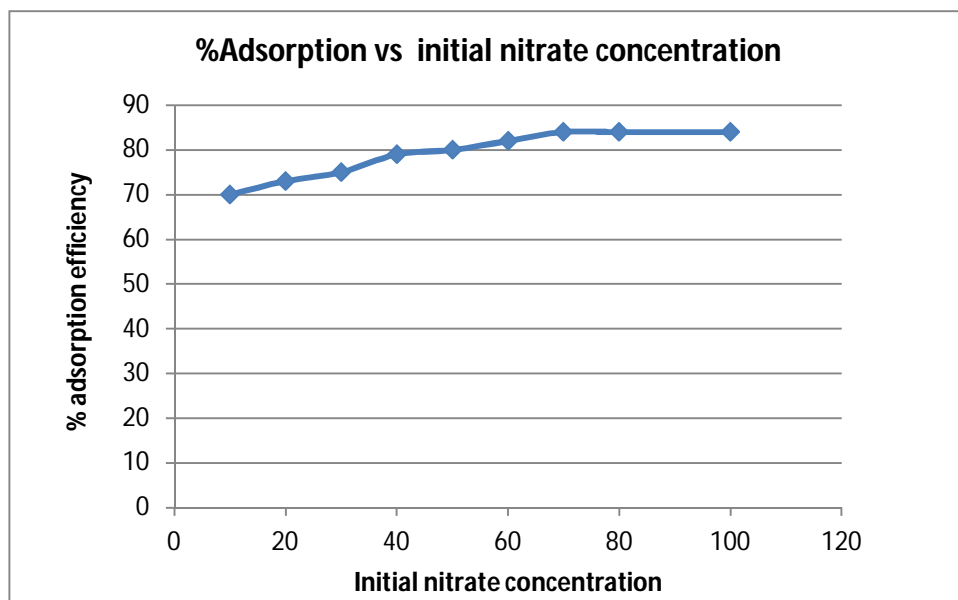


Fig. 7 Initial nitrate concentration variation with % removal efficiency with the Aegle Marmelos leaves biochar

As best results were obtained by the use of Bael leaves biochar for the % nitrate removal efficiency. Further studies were carried out with the biochar of Bael leaves.

G. Effect of temperature

With the increase in temperature the %removal of nitrate increases .The increase in sorption with temperature may be attributed due to increase in the number of active site available for sorption on the adsorbents [29]

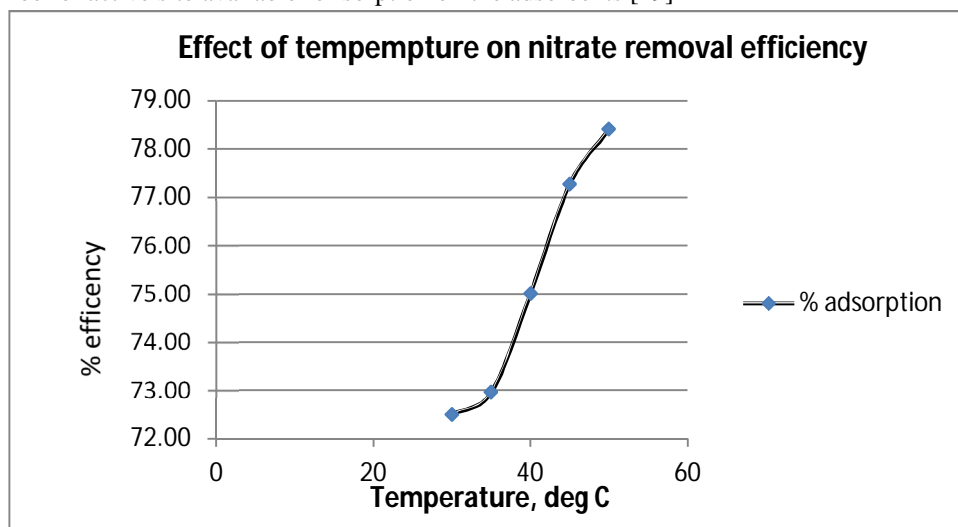


Fig. 8 Effect of temperature on the nitrate removal efficiency of Aegle marmelos biochar

Adsorption mechanism

The data has been correlated with Freundlich, Templin and Langmuir models.

Freundlich Isotherm

General form of isotherm is $q=KfC^{1/n}$ & the linear form of Freundlich equation is represented as follows: $\log x/m = \log Kf + 1/n \log Ce$ and the linear form of Freundlich equation is represented as follows[30]:

$$\log x/m = \log Kf + 1/n \log Ce \quad (1)$$

Where x is the amount of (solute) nitrate adsorbed in mg.

m : is the mass or weight of adsorbent in grams.

Ce: - is the residual concentration of nitrate at equilibrium in mg/l.

Kf: is a Freundlich constant which is a measure of adsorption capacity and

1/n is a measure of adsorption intensity. This adsorption isotherm is based on the physico-chemical adsorption on heterogeneous surface. The plot of $\log x/m (q_e)$ versus $\log Ce$ of equation (1) should result in a straight line. From the slope & intercept of the plot, the values of n & Kf were calculated.

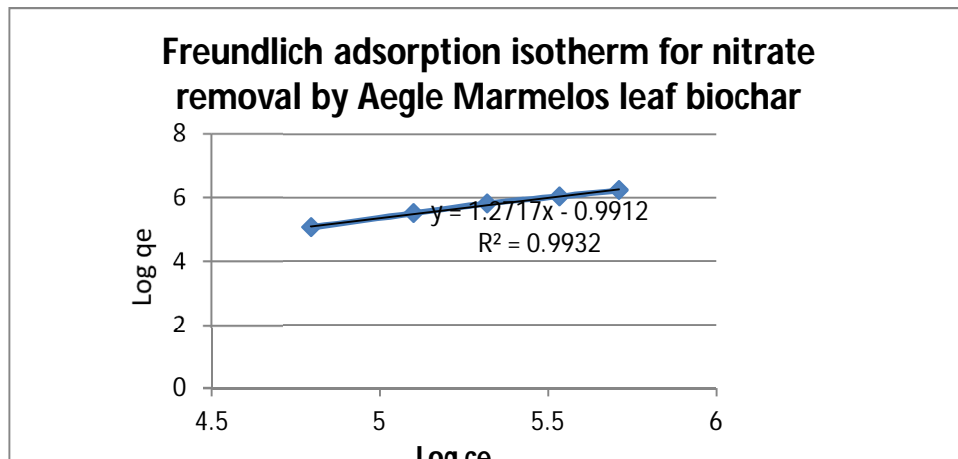


Fig. 9 Freundlich adsorption isotherm for Aegle marmelos leaf biochar

Langmuir isotherm

The Langmuir isotherm commonly written as:

$$q_e = q_0 b C_e / (1 + b C_e)$$

Where: Q_e is the amount adsorbed (mg/g) and C_e is the equilibrium concentration of adsorbate (mg/l), related to capacity & energy of adsorption respectively and the linear form of the Langmuir isotherm can be expressed as:-

$$1/q_e = (1/q_0) + 1/b q_0 C_e$$

Where: $1/q_e$ is plotted against $1/C_e$, a straight line with slope $1/b Q_0$ is obtained which shows that the adsorption follows the Langmuir isotherm as shown in figure :-

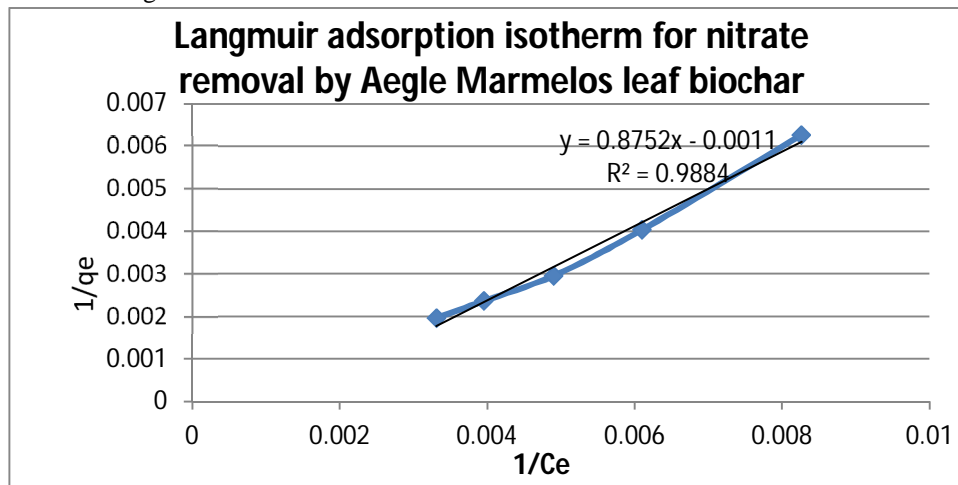


Fig. 10 Langmuir adsorption isotherm for Aegle marmelos leaf biochar

The Langmuir constants b & Q_0 are calculated from the slope & intercept with y-axis.

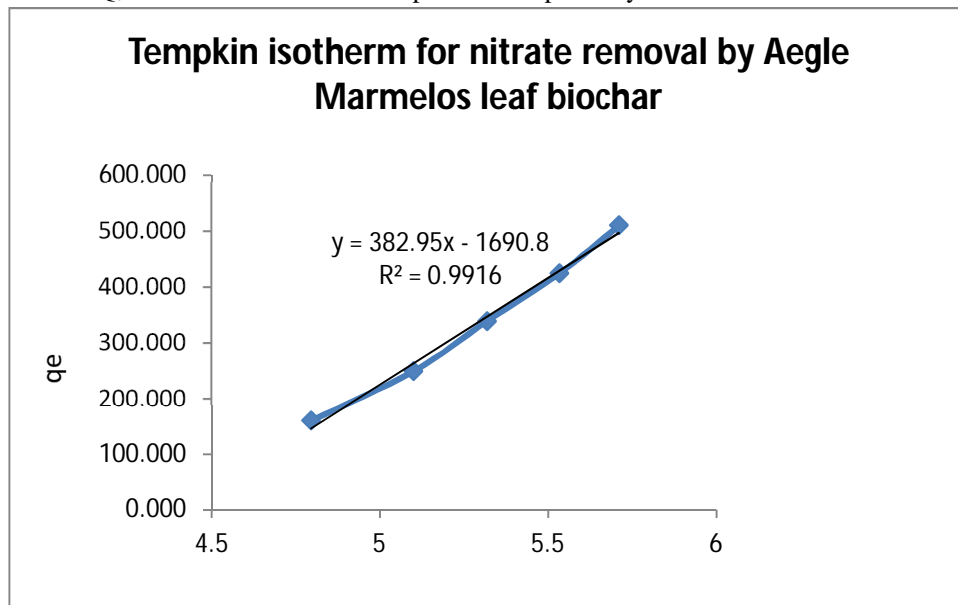


Fig. 11 Tempkin adsorption isotherm for Aegle marmelos leaf biochar

The adsorption studies were in accordance with Freundlich, Langmuir and Tempkin equations. The value of R^2 were 0.99, 0.988 and 0.99 .

IV. CONCLUSION

Comparative study of various bio adsorbents for the nitrate removal was done. Performance of bio adsorbent depended upon pH, temperature, dose of adsorbent & contact time of the adsorbent. Biochar of Bael leaves powder was found to be most promising

for the removal of nitrate on synthetic waste water assuming as an industrial waste % removal efficiency was around 80 .At 6.5 pH maximum nitrate removal was obtain & contact time of 60 minutes was sufficient . There was an increase in the removal efficiency with the increase in the temperature. Best results were obtained at biochar concentration of .3mg/l. The equilibrium data obtained also fitted well with Langmuir & Freundlich adsorption isotherm and by kinetic study it was found to follow pseudo second order kinetics. Bael leaves are easily locally available in any season. They are cheap & economic too & do not harm our environment .The present research work may find application of the biochar of Bael leaves in the development of sustainable ,eco-friendly & house hold water treatment system for the removal of nitrate .

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