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Adsorption of Nitrate using Laterite soil, Black Cotton Soil and Fuller's Earth

Dr. Shashikant R.Mise[1], Pooja[2], Ramesh Bashetty[3]

[1]Professor, Department of Civil Engineering, PDA College of Engineering, Kalaburagi-585102, India.
[2]PG student, Department of Environmental Engineering, PDA College of Engineering, Kalaburagi-585102, India.
[3]PhD student, Department of Environmental Engineering, PDA College of Engineering, Kalaburagi-585102, India.

Abstract – Adsorption technique is one of the most common method used for treatment of polluted water, but seeking for the low cost adsorbent is the objective of this study. Nitrate is generated by discharge of untreated waste such as agricultural run off, aerial deposition, acid rain, muncipal solid waste, leachate from dumping of sewage sludge. An attempt for naturally available low cost effective adsorbent is made by utilizing Laterite soil, Black cotton soil and Fullers earth. Kinetics of adsorption is found to follow first order reaction and the adsorption rate of Nitrate are 6.37mg/g, 7.41mg/g and 8.12mg/g by Laterite soil, Black cotton soil and Fullers earth respectively. Adsorption behaviors are found to follow Freundlich, and langmuir isotherms. For Column tracer experiment the values of Freundlich coefficient K_f, Freundlich Isotherm constant 1/n, Distribution coefficient K_{fd} and Retardation factor "R" for Laterite soil are 1.210, 0.931, 1.032, 2.070 and for Black cotton soil are 1.10, 0.966, 1.192, 2.560 and for Fullers earth are 0.890, 1.10, 2.522 respectively. The result of the Column Experiment follows Freundlich Isotherm.

Key Words: Nitrate, Adsorption, Fullers earth, kinetics, Isotherms

1. INTRODUCTION

Water is one of the most essential elements on earth. Every living being needs water for its survival. When we look at the water available on earth, we find that a mere 2.5% of fresh water is available to humans. While 68.7% of this accounts for glaciers and ice cap, we are left with 30.1% of ground water and just 1.2% of surface water. The requirement of the fresh water in various sectors such as domestic, irrigation, industry and others increases significantly all over the world. Thus, water liability, both in terms of quality and quantity, has declined to such an extent to the rapid increase in the population and industrialization.

The wastewater streams released from industries are contaminating the fresh water available in nature, resulting in depletion of the fresh water and increasing the water pollution. Large amounts of nitrate may cause eutrophication, which means an excess of nutrients resulting in oxygen deprivation and fish deaths.

Water pollution by Nitrate is of considerable concern, as this is used in a variety of applications including fertilizer in agriculture, oxidizing agents and are usually present in high concentrations in the liquid wastes which are released directly into the Environment without any pre-treatment.

Nitrates are not generally considered toxic, but at high concentration the body may convert nitrates to nitrite. Nitrites are toxic salts that disrupt blood oxygen transport by disrupting hemoglobin to methemoglobin conversion. This causes nausea and stomachaches for adults. For young infants it may be extremely risky, and also cause Blue baby syndrome

1.1 OBJECTIVES

To evaluate a feasible and economical low cost treatment of Nitrate present in synthetic sample by Black cotton soil, Laterite soil and Fullers earth which are naturally available adsorbents.

- To study the physical properties of adsorbents like Black cotton soil, Laterite soil and Fullers earth
- Adsorbing capacity of Black cotton soil, Red soil and Fullers earth on adsorption of Nitrate as a function of contact time, adsorbent dosage and pH.
- To study Sorption kinetics.
- To study Isothermal patterns.
- To study column experiment.

1.2 LITERATURE REVIEW

Shashikant.R.Mise, Rameshshetty(2013): In this research, adsorption of Nitrate on Red soil has been studied through using batch adsorption techniques. Main objectives of this study are, to study the physical properties of Red soil, detection of Nitrate removal by adsorbent as a function of contact time, adsorbent dosage and pH, to study sorption kinetics. The results of this study showed that the Optimum contact time, dosage and pH for adsorption of Nitrate on Red soil reached to equilibrium after 130mins, with removal efficiency of (86%), 1400mg

as optimum dosages. Higher adsorption of Nitrate was observed at higher pH, obtained at pH 6.0, the rate of adsorption of Nitrate obeys first order rate equation. The obtained results of the batch experiments are best fit to Langmuir and Freundlich adsorption isotherms. From the experimental analysis it is concluded that Red soil shows good removal efficiency.

Andrzej Gierak and Iwona Lazarska(2017): In this study the results of the investigations of the adsorption process of nitrate, nitrite, and ammonium ions on carbon adsorbent with the application of the solid phase extraction method to isolate and enrich the investigated ions from aqueous solutions of the concentration below 1mg/L. For the determination of the concentration of the analyzed ions, they applied the ion chromatography method. The sorption capacity for the tested adsorbents as well as the efficiency of the enrichment of the investigated ions were determined.

2. MATERIALS AND METHODOLOGY

Laterite soil: It is a soil and sedimentary rock type rich in iron and aluminum, and is commonly considered to have formed in hot and wet tropical areas. Nearly all laterites are of rusty-red colouration, because of high iron oxide content. They develop by intensive and long-lasting weathering of the underlying parent rock. Tropical weathering (laterisation) is a prolonged process of chemical weathering which produces a wide variety in the thickness, grade, chemistry and ore mineralogy of the resulting soils. The majority of the land area containing laterites are between the tropics of Cancer and Capricorn.

Black cotton soil: Black soil is also called as Black cotton soil as its colour is black Generally, Black cotton soil is found in the central, western and southern states of India, including Karnataka. Black cotton soil is one of major soil deposits of India. They are very tenacious of moisture and exceedingly sticky, when wet. Due to considerable contraction on drying large and deep cracks are formed. These soils contain abundant iron and high quantities of lime, magnesia and alumina. Black soils are poor in nitrogen, phosphorus and organic matter. The soils are generally rich in montmorillonite and bi elliptic group of clay minerals

Fullers earth: It is a clay material that has the capability to decolorize oil or other liquids without chemical treatment. Fuller's earth typically consists of palygorskite or bentonite. Modern uses of fuller's earth include absorbents for oil, grease, and animal waste (cat litter) and as a carrier for pesticides and fertilizers. Minor uses include filtering, clarifying, and decolorizing; active and inactive ingredient in beauty products; and as a filler in paint, plaster, adhesives, and pharmaceuticals

Table1: Physical Characteristics of Adsorbents

Sl.No	Chacterstics	Units	Laterite soil	Black cotton soil	Fullers earth
1	Moisture content	%	3.3	6.29	8.21
2	pH values	------	7.6	7.1	7.8
3	Specific gravity	------	2.79	2.08	1.80
4	Bulk density	gm/cc	1.12	1.36	0.920
5	Colour	------	Red	Black	Light gray
6	Surface area	m2 /g	523	607	720

RESULTS AND DISCUSSION

Effect of contact time: The adsorption is strongly influenced by the contact time, for the study of effect of contact time 100mL of 10mg/L Nitrate solutions are mixed with 1gm of adsorbents and stirred on Gyro shaker. The samples are filtered and analyzed for Nitrate concentrations using UV spectrophotometer pectrophotometer respectively. The removal efficiency of Nitrate by Laterite soil, Black cotton soil and Fullers earth are found to be 86%, 74%, and 68% with optimum contact time of 130 minutes, 80 minutes , 90 minutes respectively as shown in Chart 1

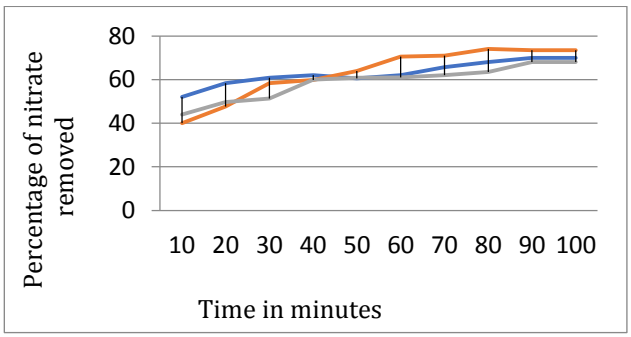

Chart -1 Effect of Contact Time on Nitrate Removal by Laterite soil, Black cotton soil and Fullers earth

Effect of optimaum Ph: To determine the optimum pH 100 mL of 10mg/L Nitrate solutions are taken in the respective conical flasks. Optimum dosage of adsorbents are added. The pH of the flasks is adjusted. The flasks were shaken for optimum contact time. After stirring, the samples are filtered and analyzed for the residual Nitrate concentration. The optimum pH for Nitrate removal by Laterite soil, Black cotton soil and fullers earth are 1.5, 1.5 and 2 with removal efficiency of 86.0%, 80.0% and 78.5% respectively as shown in chart -2.

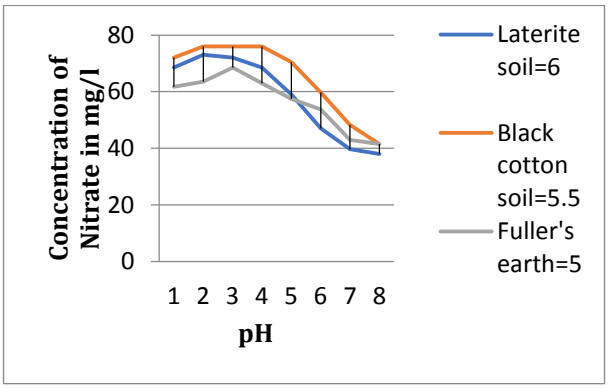

Chart -2 Effect of pH on nitrate Removal by Laterite soil, Black cotton soil and fullers earth

Effect of optimum dosage: To determine the optimum dosage of adsorbent, various dosages of adsorbents are added to 100mL of 10mg/L concentration of Nitrate solutions to the respective conical flasks. The solution in the conical flask was subjected to stirring for optimum contact time and the dosage varies. The samples are filtered and analyzed for residual concentration of Nitrate. The dosage which gives minimum residual concentration is chosen as optimum dosage. The optimum dosage for Nitrate removal by Laterite soil, Black cotton soil and fullers earth are 1000mg, 1200mg and 1400mg with the removal efficiency of 71.0%, 78.0% and 66.0% respectively.

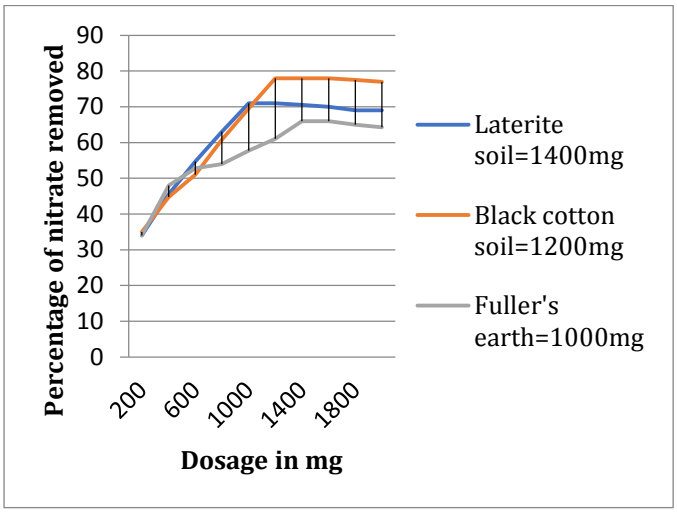

Chart -3 Effect of Adsorbent Dosage on nitrate removal by Laterite soil, Black cotton soil and fuller's earth

Table -2 Optimum Contact Time, Optimum Dosage and Optimum pH of Nitrate Removal by Naturally Available Adsorbents

Parameters	Laterite soil	Black cotton soil	Fullers earth
Optimum contact time (in minutes)	130	90	80
Optimum dosage (in mg)	1400	1200	1000
0ptimum ph	6	5.5	5.0

Sorption Kinetics: The kinetics of Nitrate removal is performed at ambient temperature at different time interval of adsorption. The batch sorption kinetic data for the adsorption of the Nitrate is tested for the first order reaction for Laterite soil, Black cotton soil and Fullers earth respectively. parameters are as shown in table 3 for all the adsorbents. The rate equation for the first order reaction is given by levenspiel.

Ln Ca/Co = K*T

K = rate constant

Table-3 Parameters of Freundlich, Langmuir isotherms

	Freundlich Isotherm		Langmuir Isotherm		
	1/n	K	a	b	R
Laterite Soil	0.179	0.01567	0.012	0.098	0.0550
Black cotton soil	0.432	0.00785	0.046	0.046	0.0384
Fullers earth	0.587	0.0036	0.044	0.059	0.0095

Adsorption isotherm studies

Modeling the equilibrium data is a fundamental for the industrial application of adsorption since it gives information for designing and optimizing operating procedure. The adsorption equilibrium data are conveniently represented by adsorption isotherms, which correspond to the relationship between the mass of the solute adsorbed per unit mass of adsorbent qe and the solute concentration for the solution at equilibrium Ce.

In order to successively represent the equilibrium adsorptive behavior, it is important to have a satisfactory description of the equation state between the two phases composing the adsorption system. Three kinds of isotherms equations were tested to fit the experimental data. The Isotherm constants are presented in table 4

Langmuir equation: Ce /qe = (Ce /qmax) + [1/ (qmax *b)]

Freundlich equation: log qe = log K_f + (1/n) log Ce

K_f = Coefficient of Freundlich Isotherm

Where qe is the amount adsorbed at equilibrium (mg/g) and Ce is the equilibrium concentration of metal ions in solution (mg/L). The other parameters are different isotherm constants, which can be determined by regression of the experimental data. In the Langmuir

equation, qmax (mg/g) is the amount of adsorbate per unit weight of adsorbent to form a complete monolayer on a sorbate surface.

Column Tracer Experiments

To observe the retention and leaching of Nitate through respective adsorbent column, Perspex glass columns of 5.5cm diameter were used. The length of the adsorbent filled in the columns is chosen based on texture and compaction

A series of column tracer experiments have been performed with Nitate on different adsorbents obtaining retardation coefficients. Results obtained by Column tracer method are interpreted using Freundlich isotherm formulae describing the adsorption isotherms. For all adsorbents of Nitrate adsorption, the best fit is obtained for the Freundlich isotherm as shown in the chart 4, and table 3 described by the formula:

$$Cads = K_{fd} \times Caq^{*}1/n$$

Where,

Cads = balance concentration of the studied compound in the carbon bed;

Caq = balance concentration of the studied compound in the water;

K_f and n = coefficients of the Freundlich adsorption isotherm.

Substitute distribution coefficient (determined using the Freundlich isotherm)

KdF for a given value of balance concentration of ion adsorbed in the solution equals

$$K_{df} = K_f Caq 1n\ Caq = K_f Caq(1/n-1)$$

For the distribution coefficient determined on the basis of the adsorption isotherm, the retardation has been defined as

$$R=1 +\rho\ d n\ K_{dF}$$

From the table 2 it is clear that follows Freundlich isotherm and proves to be a favourable adsorption as 1/n values are less than unity. It obeys Langmuir isotherm as separation factor 'R' is lesser than 1 and greater than 0 (0<R<1)

Table -4 Data showing the values of Freundlich Coefficients

Adsorbent	KF(Coefficient of Freundlich Isotherm)	1/n (Coefficient of Freundlich Isotherm)	KFd (Distribution coefficient)	R(Retardation coefficient)
Laterite soil	1.210	0.931	1.032	2.070
Black cotton soil	1.10	0.966	1.192	2.560
Fullers earth	1.420	0.890	1.10	2.522

From the table 3 it is clear that follows Freundlich isotherm and proves to be a favourable adsorption as 1/n values are less than 1

3. CONCLUSIONS

- From the kinetic study rate of reaction follows first order and the adsorption rate of Nitrate are .37mg/g, 7.41mg/g and 8.12mg/g by Laterite soil, Black cotton soil and Fuller's Earth sand respectively.
- From the Isotherm constants it is concluded that adsorption process obeys Freundlich Isotherms.
- For Column tracer experiment the values of Freundlich coefficient KF, Freundlich Isotherm constant 1/n, Distribution coefficient K_{Fd} and Retardation factor R for Laterite soil are 1.210, 0.931, 1.032, 2.070 and for Black cotton soil are 1.10, 0.966, 1.192, 2.560 and for Fullers earth are 0.890, 1.10, 2.522 respectively.
- The result of the Column Experiment follows Freundlich Isotherm as 1/n<1

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BIOGRAPHIES

1) Dr. Shashikant R. Mise
Professor, PDA College of Engineering kalaburagi

2) Pooja
PG Student

3) Ramesh Bashetty
Ph.D Student