REMOVAL OF NITRATES FROM WASTEWATER USING SOILS AS ADSORBENTS-BATCH & SORPTION KINETIC STUDY

Ramesh Bashetty[1] , Dr. Shashikant R. Mise[2] , Mallikarjun.S. D[3] , Dr. Siddangowda[4]

[1]Ph.D Research Scholar, Environmental engineering division, Civil Engineering Department PDA College of Engineering. Kalaburagi 585102 (K.S)

[2]Professor PG Environmental Engineering Course, PDA College of Engineering. Kalaburagi 585102 (K.S)

[3]Ph.D Research Scholar, Environmental engineering division, Civil Engineering Department, PDA College of Engineering. Kalaburagi 585102 (K.S)

[4]Professor, Civil Engineering Department, Government Engineering College, Raichur 585401 (K.S)

ABSTRACT

The adsorption of nitrate on Fuller's earth, Laterite soil, and Black cotton soil has been studied in this study at room temperature. This review's main objectives are to focus on the real characteristics of Laterite, Black cotton, and Fuller's earth soils, as well as the finding that nitrate evacuation by adsorbents is influenced by contact time, adsorbent dosage, and pH. The data and test results show that nitrate ejection increases as contact time increases and reaches equilibrium at a particular moment. With adsorption effectiveness of 70%, 74%, and 68%, respectively, the optimal contact times for the expulsion of nitrate by Laterite soil, Black cotton soil, and Fuller's earth are 55, 50, and 45 minutes.

The results of the investigation into adsorbent dosage optimisation show that increasing the amount of dose applied increases the amount of nitrate that is expelled from the systems. With expulsion efficacy of 71.0%, 78.0%, and 66.0%, respectively, the recommended dosages for nitrate evacuation by Laterite soil, Black cotton soil, and Fuller's earth are 1200 mg, 1400 mg, and 1000 mg. Nitrate adsorption is essentially pH subordinate. The optimal pH values for nitrate evacuation by Fuller's earth, Black cotton soil, and Laterite soil are 7, 6.5, and 6, respectively, with expulsion proficiency of 68%, 76%, and 64%.

Further the sorption kinetics was also carried out keeping the batch conditions constant to observe that the Nitrate adsorption using Fuller's earth, Laterite soil and Black Cotton soil follows first order rate equation.

Keywords: *Nitrate, Adsorption, Contact time, Dosage, pH, WHO, Sorption Kinetics, Electro coagulation.*

1.INTRODUCTION

Untreated waste discharge, including leachate from sewage sludge disposal, acid rain, aerial deposition, municipal solid waste, and agricultural runoff, produces nitrate.

To eliminate nitrate from water and wastewater, a number of treatment systems have been developed. Chemical precipitation, reverse osmosis, ion exchange, membrane separation, ultrafiltration, filtration, electrocoagulation, solvent extraction, sedimentation, Electrodialysis, evaporation, cementation, dilution, air stripping, steam stripping, and flocculation are examples of common techniques. The most popular technique has historically been reduction and chemical precipitation.

The wastewater Industry-generated streams are compromising the natural freshwater supply, which causes freshwater depletion and increases water pollution. A high nitrate level can lead to eutrophication, which is an overabundance of nutrients that causes oxygen deprivation and fish mortality. Since nitrate is employed in many different applications, such as fertiliser in agriculture, and since oxidising agents are typically found in high concentrations in liquid wastes that are released into the environment without any pre-treatment, water pollution from nitrate is a serious concern.

In general, nitrate is not regarded as harmful. However, the body may change nitrate into nitrite at high concentrations. Toxic salts called nitrites interfere with haemoglobin's conversion to methaemoglobin, which impairs blood oxygen transport. Adults have nausea and stomachaches as a result. It can cause blue baby syndrome and be quite dangerous for young babies.

2.Literature review

2.1NITRATE'S SOURCE

Although nitrate in water can come from a variety of sources, industrial discharges are typically thought to be the main culprit. Road runoff, aerial deposition, agricultural runoff, acid rain, and leachate from sewage sludge disposal are the other sources of nitrate in surface water. [25]

2.2 NITRATE:

Almost all nitrate salts are soluble in water, and nitrate is a polyatomic ion with the chemical formula NO3. Nitrates are frequently found in fertilisers and explosives. Anhydrous potassium nitrate is a typical illustration of an inorganic nitrate salt. Figure 2.1 displays anhydrous potassium nitrate in powdered form.

Figure 2.1Anhydrous Potassium Nitrate

2.3 Use of an absorbent FeMgMn-LDH that resembles hydrotalcite for the selective removal of nitrate from aqueous solutions (Hongguang Zhou and Yanmei Yang et al.,2020)

This study examined the adsorption properties of FeMgMn-LDH, a type of possible environmental remediation material that was created via a co-precipitation process, for nitrate. With a high buffer capacity (final pH stayed between 9 and 10) and excellent reversibility, the produced FeMgMn-LDH is demonstrated to be a promising adsorbent for the removal of anions. It can also remove nitrate ions selectively by an anion-sieve action.

At 25 °C, the highest nitrate adsorption is 10.56 N- mg g^{-1}. With an adsorbent dosage of 5 g/L in actual water, the removal rate of nitrate ions can reach 86.26%. $CO_3^{2-} > PO_4^{3-} > SO_4^{2-}$ is the order of competition of coexisting anions on nitrate adsorption by FeMgMn-LDH. The nitrate adsorption process on the FeMgMn-LDH is spontaneous and exothermic, as indicated by the negative values of $\Delta G0$ (from − 27.796 to − 26.426 kJ mol^{-1}) and $\Delta H0$ (− 6.678 kJ mol^{-1}). Electrostatic attraction and ion exchange are the primary adsorption mechanisms by which FeMgMn-LDH removes nitrate from aqueous solutions.[1]

2.4. Industrial solid waste for Nitrate adsorption features and challenges N.K. (Soliman and A.F. Moustafa,2020)

Waste from industrial operations, including any solid materials that are rendered unusable during a production process, is referred to as industrial solid waste (ISW). According to the ISW, there is a global environmental crisis that needs to be addressed in order to lessen its impact and environmental load. One intriguing, viable, and affordable alternative idea for ISW management is the adsorption of heavy metals from industrial effluents using ISW.

Potential benefits of the ISW include its availability, high efficiency, low cost, and green alternative source status. The complicated process of nitrate adsorption onto ISW is influenced by a number of variables, such as the initial concentration of metal ions, contact time, solution pH, temperature, and adsorbent dose. This paper examines the variables of temperature, pH, adsorbent dosage, and contact time that influence heavy metal adsorption onto ISW. The following are the main conclusions of this review:

- At the beginning of the adsorption process, the percentage of heavy metal ions removed is large; however, it progressively declines until it achieves equilibrium.
- The process of heavy metal adsorption is significantly impacted by temperature.
- Each metal ion has a certain pH value at which metal ion adsorption is at its highest.
- Because the adsorbent's surface area and number of active sites increase with increasing adsorbent dosage, catalytic activity often rises as well.
- Optimising the conditions for heavy metal adsorption onto ISW will be made easier with an understanding of the elements that influence this process.

2.5 Adsorption Study for the Removal of Nitrate from Water Using Local Clay, Abdessamadbattasand AbdelaliElGaidoumi et al., (Feb 2019)

The study focused on using local clay to adsorb nitrate ions and remove them. The effects of contact time, adsorbent properties, beginning nitrate concentration, solution pH, concentration, and adsorbent granulometry were investigated in a number of batch tests. Freundlich's model is satisfied by local clay, according to adsorption isotherm research. The reaction's rate is governed by pseudo-second-order kinetics. At an acidic pH, local clay effectively adsorbs nitrates. Under ideal circumstances, the adsorption capacity was determined to be 5.1 mg/g.

The adsorption yield decreases with the initial nitrate concentration and rises with the adsorbent dose. X-ray fluorescence (XRF), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electronics microscopy (SEM), and specific surface area (BET) measurements were used to characterise the local clay. The study's findings suggested that local clay is a valuable resource for eliminating nitrates from aqueous solutions, which can be applied to water treatment without requiring any chemical changes.

3.0 OBJECTIVES Sorption kinetics refers to the rate at which a substance, such as a contaminant or nutrient, is absorbed or adsorbed by another material, like soil or sediment. The main objectives of this study Includes:

1. To assess the viability and affordability of treating nitrate, which is present in synthetic samples, using naturally occurring adsorbents such as Fuller Earth, Black cotton soil, and Laterite soil.

2. To research the physical characteristics of adsorbents such as Fuller's Earth, Black cotton soil, and Laterite soil.

3. The effect of Laterite, Black cotton, and Fuller's earth soils on nitrate adsorption as a function of pH, adsorbent dosage, and contact time.
4. To determine reaction rate by providing insight into the rate at which a solute is adsorbed onto a solid-liquid interface.
5. To understand sorption mechanism which involves mass transfer, diffusion, and reaction on the adsorbent surface.
6. To Evaluate adsorbent performance of an adsorbent.

4.MATERIAL AND METHODOLOGY

4.1 Selection of Suitable Adsorbents

Laterite soil is a type of sedimentary stone and dirt that is rich in iron and aluminium. It is typically thought to have formed in hot, humid tropical climates. As seen in Fig. 1, almost all laterites have a tarnished red colouration due to their high iron oxide content. They are produced by elevating and surviving the parent rock that is buried. A lengthy process of substance enduring known as tropical enduring (laterisation) produces a wide range of following soils in terms of thickness, grade, science, and metal mineralogy. The majority of the laterite-containing land area lies between the Cancer and Capricorn rainforests. Figure 4.1 illustrates the availability of laterite soil in India.

Figure-4.1:LateriteSoil

Black cotton soil:

Due to its generally dark tone, black soil is also known as black cotton soil. It is found in Karnataka and other parts of India's central, western, and southern regions. As seen in Fig. 4.2, black cotton soil is one of India's important soil stocks. When wet, they are extremely sticky and remarkably resilient to moisture. Large and deep fractures are formed as a result of widespread compression during drying. As seen in fig., these soils have significant concentrations of lime, magnesia, and alumina along with an abundance of iron. Black soils have low levels of natural matter, phosphorus, and nitrogen. The majority of the dirts are rich in bielliptic mud mineral accumulation and montmorillonite. Figure 3 illustrates the availability of black cotton soil in India.

Figure -4.2: Black cotton soil

Fuller's earth: This dirt substance can decolorize oil or other fluids without the need for compound treatment. As seen in Fig. 4.3, Fuller's earth often consists of bentonite or palygorskite. These days, more full soil is used as a transporter for pesticides and manures, as well as sponges for oil, oil, and animal waste (cat litter). Sifting, clarifying, and decolorizing are minor applications; inert and dynamic fixing filler in paint, masonry, glues, and medications.

Figure-4.3:Fuller'searth

4.4 BATCH ADSORPTION STUDY

4.4.1 Determination of Optimum Contact Time

Since contact time has a significant impact on adsorption, 100 mL of 10 mg/L nitrate solutions are combined with 1 gramme of adsorbents and shaken on a Gyro shaker to examine the impact of contact time. A UV spectrophotometer and an atomic absorption spectrophotometer are used to filter the samples and determine their nitrate contents, respectively.

4.4.2 Determination 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. For the best contact duration and dosage variations, the solution in the conical flask was stirred. The samples are filtered and analyzed for residual concentration of Nitrate. The dosage which gives minimum residual concentration is chosen as optimum dosage.

4.4.3 Determination of Optimum pH

100 mL of 10 mg/L nitrate solutions are taken in the corresponding conical flasks to get the ideal pH. The right amount of adsorbents is added. The flasks' pH levels are changed. For the ideal duration of contact, the flasks were shaken. The samples are stirred, filtered, and their residual nitrate concentration is measured. The ideal pH is the one that yields the lowest residual concentration.

4.5 SORPTION KINETICS

There are often two stages to the adsorption kinetics: a fast removal phase and a much slower phase prior to the equilibrium being reached. It is important to (i) know all the molecular specifics of the reaction, including the energetic and stereo chemistry, and (ii) have a fair understanding of the reaction mechanism, including all the elementary steps, in order to arrive at an unambiguous rate rule. The efficiency of the adsorption process is directly controlled by the adsorption kinetics, which are determined by the rates at which metal ions are absorbed by the adsorbent.

It is possible to think of the movement of metal ions from the liquid phase to the solid phase as a reversible reaction in which the two phases achieve equilibrium. To estimate the rate constants, the batch adsorption data was analysed using a batch adsorption kinetic model.

5. RESULTS AND DISCUSSIONS

5.1 SORPTION KINETICS

5.1 DETERMINATION OF OPTMUM CONTACT TIME

To investigate the impact of contact time, 100 mL of a 10 mg/L nitrate solution is placed in a 250 mL conical flask, combined with 1 gramme of adsorbent for each flask, and shaken on a Gyro shaker for 5, 10, 15, 20, 25, 30, 40, 45, 50, 55, and 60 minutes. UV visible spectrophotometric analysis is used to filter the samples and determine any remaining nitrate quantities. In the adsorption process, contact time is very important.

Figure 4.1 display the experimental values of Nitrate, respectively. It can be seen from the tables that different adsorbents have varying contact times. Sharp increases in the initial stage and declines close to equilibrium are characteristics of the adsorption curves. This is mostly because of the vast surface area that is available and the adsorption sites that are open and active in the beginning. Later, the adsorbent becomes saturated, and the removal efficiency falls close to equilibrium. Plots of the percentage of nitrate removal against time are shown. The figures show that there is little increase in adsorption after equilibrium and with additional time. Laterite soil, Black cotton soil, and Fuller's earth have been reported to remove nitrate 70%, 73%, and 68% of the time, with the best contact times being 55, 50, and 45 minutes, respectively.

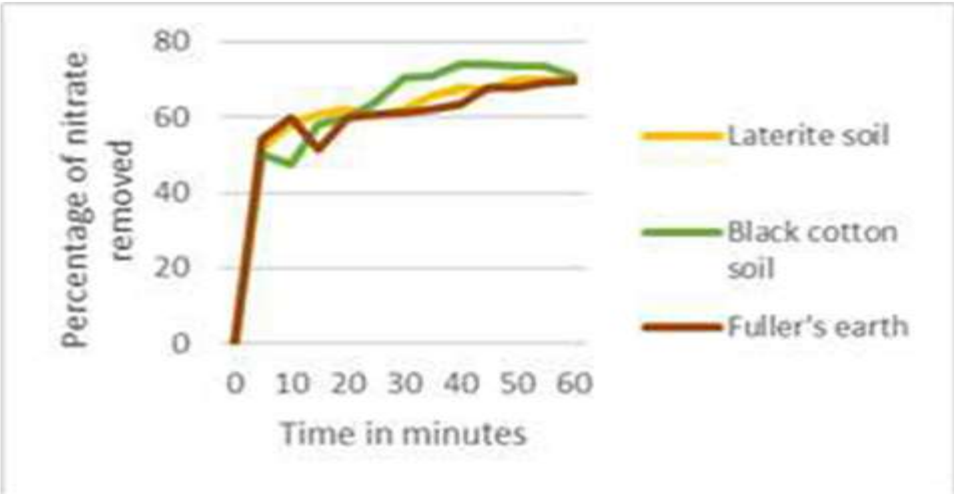

Fig-5.1 Effect of Contact Time on Nitrate Removal by Low-cost adsorbents

5.2 DETERMINATION OF OPTIMUM DOSAGE

Different adsorbent dosages are introduced to 100mL of a nitrate solution with a concentration of 10mg/L in the corresponding 250mL conical flasks in order to ascertain the ideal adsorbent dosage. For the best contact time, the solution in the conical flask was stirred, and the dosage ranges including 200 mg, 400 mg, 600 mg, 800 mg, 1000 mg, 1200 mg, 1400 mg, 1600 mg, 1800 mg, and 2000 mg.

Adsorption is the process by which a solute is continuously transferred from solution to adsorbent until the residual solution concentration and the material adsorbed by the adsorbent surface remain in equilibrium throughout a constant contact time. Figure 4.2 respectively display the experimental values of nitrate.

The graph shows that the amount of nitrate in the samples first drops off dramatically and then reaches its maximum as the dosage of adsorbents increases. This is mostly because there are a lot of surface areas and adsorption sites available. Adsorbents eventually become saturated, which lowers their removal efficiency. The optimum dosage is defined as the dosage at which the maximum removal is achieved. Even after increasing the dosage of the adsorbent, not much change is seen after this. With removal efficiencies of 71.0%, 78.0%, and 66.0%, respectively, the ideal dosages for nitrate removal by Laterite soil, Black cotton soil, and Fuller's earth are 1200 mg, 1000 mg, and 1400 mg.

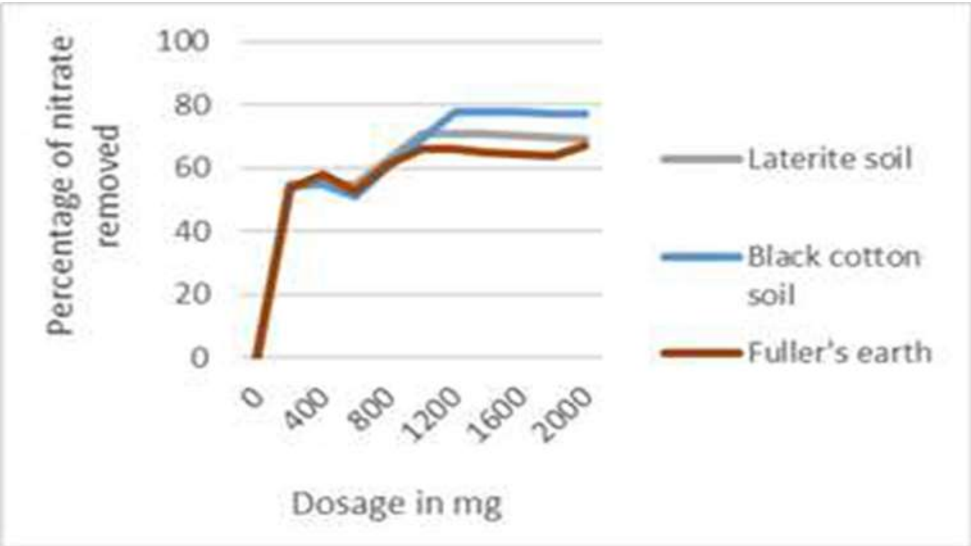

Fig-5.2Effect of Dosage on Nitrate removal by Low-Cost Adsorbents

5.3 DETERMINATION OF OPTIMUM PH

To ascertain the ideal pH in 250 mL conical flasks, 100 mL of solutions containing 10 mg/L nitrate are taken. Adsorbents are added to the appropriate flasks in the right dosage. For nitrate, the pH of the flasks is changed between 5.5, 6, 6.5, 7, 7.5, 8, and 8.5. For the ideal duration of contact, the flasks were shaken. The samples are stirred, filtered, and their residual nitrate concentration is measured. The flasks that contain nitrate and have the highest clearance percentage are chosen as having the ideal pH. The degree to which naturally occurring adsorbents can remove nitrate at varying pH values depends on the pH of the solution. In addition to surface area, ideal time, and ideal dosage, pH also affects how much nitrate is removed. Figure 4.3 both display the experimental value of nitrate. It has been found that nitrate is eliminated more successfully in the high pH range. The ideal pH values for Laterite soil, Black cotton soil, and Fuller's earth to remove nitrate are 7, 6.5, and 6, respectively, with removal efficiencies of 68.7%, 76.0%,and63.5%.

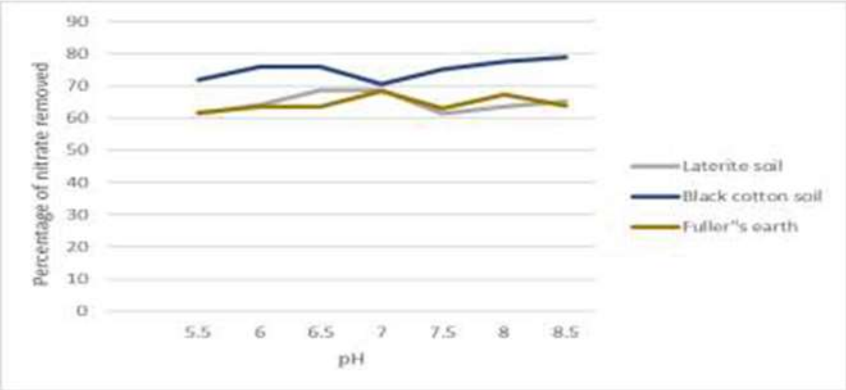

Fig5.3 Effect of pH on Nitrate Removal by Low-Cost Adsorbents

Table 5.1: Optimum Contact Time, Optimum Dosage and Optimum pH for Nitrate Removal by Low-Cost Adsorbents

PARAMETERS	**LATERITRSOIL**	**BLACKCOTTON SOIL**	**FULLERS EARTH**
CONTACTTIME (Inminutes)	55	50	45
DOSAGE (Inmilligram)	1200	1000	1400
pH	7	6.5	6

5.4 SORPTION KINETICS

The kinetics of nitrate removal were conducted at several adsorption time intervals while maintaining constant temperature. For the first order reaction, the batch kinetic data for the nitrate's adsorption was examined. Leven Spiel provides the rate equation for the first order reaction.

LnCa/Co= K*T

i.e.,2.303log10 a/(a-x)=K*T

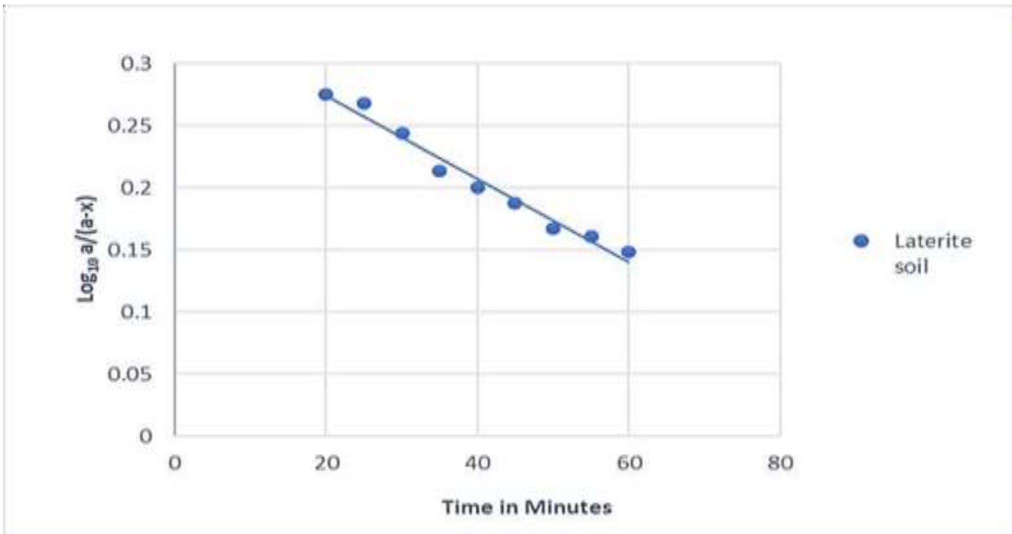

Fig 5.4 Reaction Rate Constants for Nitrate Removal by Laterite soil

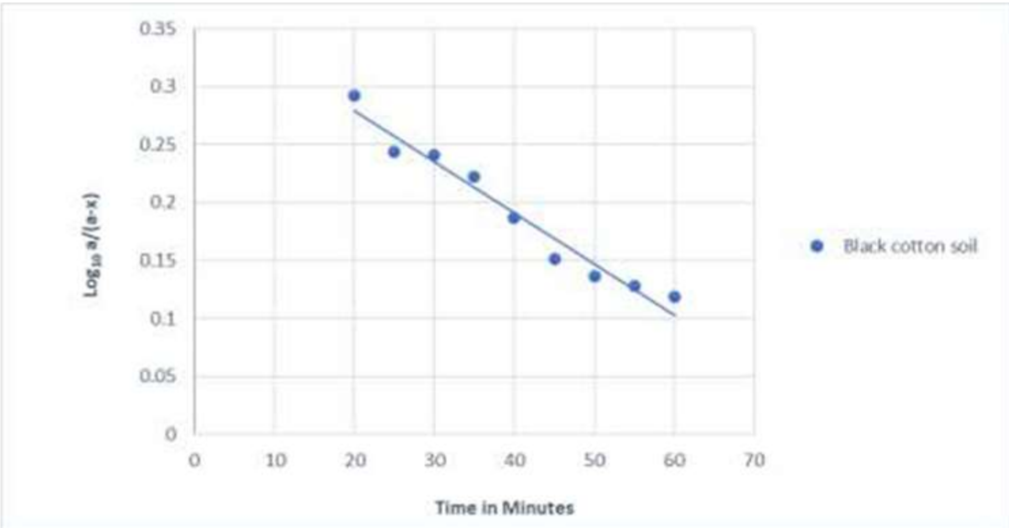

Fig5.5 Reaction Rate Constants for Nitrate Removal by Blackcotton soil

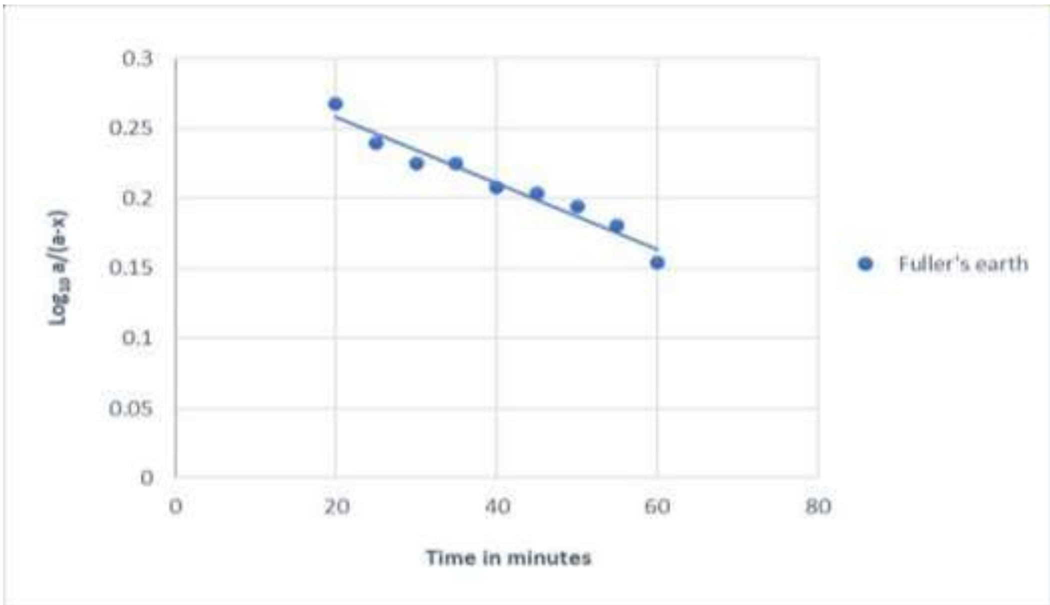

Fig 5.6 Reaction Rate Constants for Nitrate Removal by Fuller's earth

Table 5.2 Reaction Rate Constants for Low-Cost Adsorbents for Nitrate Removal

Adsorbent	"K" valuesfrom Calculation	"K" valuesfrom Graph
Lateritesoil	0.014	0.018
Blackcotton soil	0.018	0.021
Fuller'searth	0.011	0.012

6.0 CONCLUSIONS

Based on the experimental study following conclusions are drawn

1. It's evident from the soil characteristics that Laterite soil, Black cotton soiland Fuller's earth good adsorbent for removingNitrate and these adsorbents are easily and cheaply available.
2. The batch study of adsorption of Nitrate with Laterite soil, Black cotton soil and Fuller's earth was studied byestimating the effect of contact time on the percentage removal of nitrate. The data and results from the experiment reveal that removal of nitrate increases with increase in contact time and attains equilibrium at particular time. The optimum contact time for the removal Nitrate by Laterite soil, Black cotton soil and fuller's earth are found to be 55 minutes, 50 minutes and 45minutes with removal efficiency of 70% 73% and 68% respectively.

3. The result of experiment on optimization of dosage of adsorbent reveals that, increasein amount of dosage added, increases the removal of from the solution.
4. The optimum dosage for nitrate removal by Laterite soil,Black cotton soil and fuller‘s earth are 1200mg,1000mg,1400mg with the removal efficiency of71.0%, 78.0%and 66.0% respectively.
5. The adsorption of Nitrate are mainly pH dependent. The optimum pH for nitrate removal by Laterite soil, Black cotton soil and Fuller‘s earth are 7,6.5,6 with removal efficiency of 68.7%,76% and 63.5% respectively.
6. From the batch study it can be concluded that nitrate removal efficiency of Black cotton soil > Laterite soil >Fuller‘s earth.
7. The rate of Adsorption of Nitrate obeys first order rate equation.

REFERENCES;

1. Hongguangzhou, youlintan, weigao, yuezhangand yanmei yang:―havestudiedthe selective nitrate removal from aqueous solutions by a hydrotalcite like absorbent femgmn-ldh‖ Scientific report Vol 10. (30 September 2020).

2. N.k.soliman,a.f.mustafa―industrial solid waste for Nitrate adsorption features and

challenges: are view journal of material research and technology vol.9.(2020)pp5-10

3. J. w. palko, d. i. oyarzun, b. ha, m. stadermann, j. g. santiago: ―nitrate removal from water using electrostatic regeneration of functionalized adsorbent‖ LLNL-JRNLVol 770-745 (march 28, 2019)
4. Jaslinikhsan, setifani: ―an isotherm model of the adsorption of nitrate ions on the surface of silica from sugarcane bagasse ‖Journal of Chemical Technology and Metallurgy,vol 54 (march 2019) pp 5-10
5. Yifruwaktoleberkessa,seidtikumeretaandfekadufufafeyisa:―simultaneousremoval of nitrate and phosphate from wastewater using solid waste from factory‖ appliedwater science journal.vol.3 (february 2019) pp 28