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M.Sc. THESIS ON

ADSORPTION OF NITRATE ANION FROM AQUEOUS SOLUTION BY NATURAL COAL FROM DEDO DISTRICT, JIMMA ZONE, SOUTH WEST ETHIOPIA

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List of abbreviations

AC   Activated carbon

PpmParts per million

RpmRevolution per minute

FTIRFourier Transform Infrared

UV Ultra violet

Abstract

Nitrate anion is colorless, odorless and has no taste and is not detectable in drinkingwater without testing. Nitrate is one of the most important pollutants of urban and rural drinking water. Recently, the use of different technologies to remove these contaminants is investigated. In this study,the investigatedperformance of natural coal mineral originated from Jimma zone (Dedo district), as natural, low-cost, alternative and eco-friendly adsorbent forremoval of nitrates ions from aqueous solution within a batch process. The natural coal was characterized byFourier Transform Infrared (FTIR). The effects of variousexperimental parameters were examined such as contact time, pH, temperature, initial concentration of pollutant, andadsorbent mass. The removal of nitrate was 67.36% at natural coal pH 2 using1 g/l of adsorbent in 50 ml of nitrate solution having initial concentration of 1000 mg/L. Adsorption kinetic study revealed that the adsorption process followed second order kinetic. Theoretical correlation of the experimental equilibrium adsorption data for the Nitrate- natural coal system was properly explained by the Langmuir isotherm model. The pH heavily affected the adsorption capacity,and the percentage removal was found to decrease with increase in pH.The negative value of ΔH° and ΔG° indicates that the adsorption process is spontaneous and exothermic in nature. A decrease in randomness is indicated by negative values of entropy change.The obtained results indicated that this natural coal was very good adsorbent for nitrate ion, interesting alternative material with respect to more costly adsorbent used, and could be used as a highly efficient adsorbent for the separation of nitrate from drinking or waste water

Keywords: Nitrate anion, Acid Activated Natural Coal,Adsorption, Water treatment,kinetics,equilibrium,Freundlich Isotherm, Langmuir Isotherm,and Batch Experimental Method.

1.Introduction

1.1 Background of the study

Water is an undeniable fact in the species life. Whereas water submerge more earth surface but only about 2.66% of the total globalwater resources (groundwater, lakes and rivers, polar ice and glaciers) are fresh water [1].

Diminution of the water quality can be attributed to water pollutionsor contaminations. Water pollution is generally defined as any physical, chemical, or biological alteration in water quality that has a negative impact on living organisms. On the other hand, pollution can be defined as the transfer of any substance to the environment[2].

Nitrate is one of the water pollutants which create throughirregular use of the fertilizers in a relatively small land area. Nitrateis nontoxic in the concentrations lower than 50 mg/ L but abovethis concentration it is toxic. This pollutant can be fatal for infantsunder 6 months of age. Nitrate through the convert to nitrite reactswith the hemoglobin in blood and converts the hemoglobin intomethaemoglobin which does not carry oxygen to cell tissues. Thisphenomenon results in a bluish color of infant's skin so calledmethaemoglobinemia or the blue baby syndrome [3,4].

Nitrate contamination in groundwater has become an ever increasing and serious environmental threat since 1970s [5]. The excessive application of fertilizers in agriculture causes the infiltration of large quantities of thision into underground and surface water[6]. Nitrate, due to its high water solubility [7], is possibly the most widespread groundwater contaminant in the world, imposing a serious threat to drinking water supplies and promoting eutrophication [8, 9]. Elevated levels of nitrate in drinking water can cause many health problems such as gastric cancer, which results from the reduction of nitrate to nitrosamines in the stomach [10]. In addition, methemoglobinemia or blue baby syndrome, a serious health risk, occurs when nitrate is converted to nitrite, which then reacts with the hemoglobin to cause blueness of the skin of newborn infants[11]. After ingestion of plants or water high in NO_3^-, acute poisoning may occur within 30 minutes to 4 hrs.incattle.

Thus, the problem occurs very quickly and often the cattle are observed to be normal one day and dead the next day [12].reviewed the epidemiologic evidence for the linkages between drinking water NO_3^- and the risk of specific cancers, adverse reproductive outcomes, and other health outcomes in the context of the current regulatory limit for nitrate in drinking water[13]. Nitrate contaminated water supplies have also been linked to outbreaks of infectious diseases in humans [14].Literature survey reveals thatNO_3^- ion also causes diabetes and is a precursor of carcinogen [15, 16]. US Environmental Protection Agency (EPA) has set the maximum contamination level as 44 mg/l of NO_3^-[17].

Nitrate contamination in ground and drinkingwater caused concerns on a global scale. In the lastdecade, nitrate concentration has increased both in groundand surface water at a rapid rate.The increasing use ofnitrogen fertilizers in agriculture sector is the reason forthe contamination caused by nitrate. Other factors such assewage, urban and agricultural

runoffs, untreatedwastewater disposal, industrial wastewater, septic system leachate, waste disposal site leach ate, agriculturalfertilizer, and nitrogen compounds added to the air throughindustry and cars also give rise to the pollutants in waters[18, 19]. Due to its high solubility,nitrate is the most likely cause of the contamination inground waters across the globe, and a potential threat towater resource, as well as increasing eutrophication.

Nitrate ions can be removed by different methods such aschemical reduction [20], biological DE nitrification [21], reverse osmosis, electro dialysis [22], ion exchange [23],and physical adsorption. The sorption process is an easy method and findinga cheap sorbent with high capacity of removal is very important. In general, adsorption is a process of collecting soluble substancesfrom solution to a suitable interface. Different materialscan be used for the nitrate adsorption such as ion-exchange resins,sepiolite and activatedsepiolite by HCl, activated carbon, bamboo powder charcoal, amine-modified coconut coir, modified wheat residue, and modified rice hull. All these materials have greatexternal surfaces and have a capacity for nitrate extraction fromwater. External surface is the main property of adsorbent materialsbecause adsorption is an interface process between water and solidmaterial.

Adsorption, in general, is the process of collecting soluble substances that are in solution on a suitable interface. Natural coals have been widely used as adsorbents for pollution control

due to their high uptake ability, non-toxicity and large potential for ion exchange.The main aim of our study is to determine the adsorption capacity of locally available natural coal materialsoriginated from Jimma Zone, OromiyaRegion (Dedo District) and to remove nitrate from its aqueous solution. Hence, the effect of various parameters on the adsorption process has been investigated: contact time, solution pH, andmass of adsorbent and nitrate concentration [24].

Adsorption is a widely used as an effective physicalmethod of separation in order to elimination or loweringthe concentration of wide range of dissolved pollutants (organics, inorganic) in an effluent. It is big news thatactivated carbon (AC) is a well-known adsorbent that canbe used efficiently for removal of a broad spectrum ofpollutants from air, soil and liquids. Adsorbents areusually porous solids, and adsorption occurs mainly onthe pore walls inside particles. Examples are activatedcarbon (adsorbs mainly organics), silica gel and activatedalumina (adsorb moisture), zeolites and molecular sievesand synthetic resins. Among them, AC is more efficientadsorbent for elimination of many pollutants (organic,inorganic, and biological) of concern in water andwastewater treatment [25].

In the recent years, it has been increasingly used for the prevention of environmental pollution and anti-pollutionlaws have increased the sales of AC for control of air andwater pollution. AC is a broad-spectrum agent thateffectively removes toxic and bio-refractive substancessuch as insecticides, herbicides, chlorinatedhydrocarbons, heavy metal ions, and phenols, typicallypresent in many water supplies. AC in fact is amicrocrystalline, non-graphitic form of carbon withporous structure that has been processed to develop itsinternal porosity [26, 27].

AC has a high degree of porosity, anextensive surface area, and a high degree of surfacereactivity. Its large specific surface area of $(500 - 2000m^2/g)$ is in fact the most important physical property ofAC which allows the physical adsorption of gases orvapors and dissolved or dispersed substances fromliquids. It has large number of very fine pores

(Microspores) gives the AC a large inner surface, whichis the basis of its remarkable adsorption properties.Consequently, they are effective adsorbents for manypollutant compounds (organic, inorganic, microbial andbiological) of concern in water and wastewater treatment [28].

Active refers to adsorption activity: a carbon that is activated has a high capacity for adsorption. The carbon may be produced from practically any source, including vegetable, animal, petroleum, coal, and peat. Activated carbon (AC) is manufactured in different ways. The physical and chemical properties of AC depend on the source material and the manufacturing process [26].

Much of the variability in activated carbons is due to the variety of source materials, which differ profoundly in their structure and chemical composition. Coconut shell, a popular source for the production of AC for gas phase applications, produces a uniformly porous material with a high percentage of microspores. Carbons produced from hardwood are noted for their greater variability in pore size with a larger percentage of mesopores. Bone char is another popular source of AC. The presence of calcium and phosphate and a relatively low percentage of carbon (10%) give these material unique sportive properties, due in part to its coarse pore structure and low percentage of carbon. Peat, petroleum and coal have become important sources for AC production, and they too produce AC of unique character. Each of these source materials is highly variable. Therefore, given the same manufacturing technique and the same type of source material there still may be variable performance in the resulting AC [29, 27].

Various methods have been used to produce activated carbon. These may be classified into two categories: thermal activation which relies on high temperatures ($700^{o}C$) and employs steam or CO_2; and, chemical systems which dehydrate the feed stock. Chemical activation with phosphoric acid is used to digest sawdust, wood shavings, or peat. Each method has advantages and disadvantages. The chemical techniques give very high yield of an extremely adsorptive material, but the resultant AC requires further treatment to develop sufficient mechanical strength for certain applications [30].

1.2. Statement of the Problem

Nitrate contamination in ground and surface water has become an ever increasing and serious environmental threat.Wide industrial activities, agriculture and services activities such as untreated waste water disposal into the environment, the indiscriminate use of chemical andthe excessive application of fertilizers in agriculture causes the infiltration of large quantities of thision into underground and surface water. Nitrate, due to its high water solubility, there is a highpossibility for thewidespread ground and surface water contamination throughout the world. This imposing a serious threat in drinking and surface water supplies andpromoting eutrophication. Elevated levels of nitrate in drinking water can cause many health problemssuch as gastric cancer, which results from the reduction of nitrate to nitrosamines in the stomach. In addition,methemoglobinemia or blue baby syndrome, a serious health risk, occurs when nitrate is converted to nitrite,which then reacts with the hemoglobin to cause blueness of the skin of newborn infants[3, 4].

The high content of nitrate ion in waste water is the problem of the community. Therefore, numerous techniques for the removal of nitrate ion from water samples have been used. These include biological de-nitrification, chemical reduction, reverse osmosis, electro dialysis, and ion exchange, but adsorption has been shown to be an economical and effective alternative for removing ionsfrom water. Adsorption, in general, is the process of collecting soluble substances that are in solution on a suitable interface. So,this study is proposed based on the fact that, the natural coal have been used as adsorbents for removal of nitrate ion due to their high uptake abilitynon-toxicity and large potential for ion exchange[31].

1.3. Objective of the Study

1.3.1. General Objective

> ➢ To assess the adsorption capacity of locally available natural coal materials originated from Dedo District, Jimma Zone and to remove nitrate anion from its aqueous solution.

1.3.2 Specific Objectives

- ➢ To determine the removal of nitrate anion from aqueous solution by the adsorption of activated natural coal**.**
- ➢ To prepare and characterize activated carbon from natural coal for the removal ofnitrate ion from waste water.
- ➢ To determine the equilibrium parameters using batch adsorption experimental data.

1.4.Significance of the Study

Nitrate can occur naturally in surface and groundwater at a level that does not generally cause health problems. High levels of nitrate in well water often result from improper well construction, well location, overuse of chemical fertilizers, or improper disposal of human and animal waste. Sources of nitrate that can enter your well include fertilizers, septic systems, animal feedlots, industrial waste, and food processing waste. Wells may be more vulnerable to such contamination after flooding, particularly if the wells are shallow, have been dug or bored, or have been submerged by floodwater for long periods of time.

Excessive nitrate in the water impose a danger to human health and contribute to eutrophication. To solve this problem it is necessary to find the way how to remove nitrate ion from waste water. Even if there are many methods for the removal nitrate ion, the activated natural coal is an easy method and locally available cheap materials to remove nitrate ion from waste water. Moreover, it is necessary to create awareness for the surrounding community as well for others in a tangible way how much natural coal is useful not only used for fuel but also used as adsorbent for the removal of nitrate ions and other waste materials from water.

Extensively used in waste water treatment by using cost effective or low cost adsorbent to remove toxic nitrate from waste water.

2. Review of Related Literature

2.1. History of nitrates

Nitrate is a polyatomic ion whose molecular formula is NO^-_3 and its molecular mass is 62.0049 grams per mole. This ion is derived from nitric acid [32]. Nitrate ions such as ammonium ions are not attached to soil particles, so moves along water movement in soil and enter groundwater and surface waters. Wide industrial activities, agriculture and services activities such as untreated waste water disposal into the environment, the indiscriminate use of chemical and animal fertilizers in agriculture make entrance of different combinations particularly nitrate ion to water resources (surface and underground). Nitrates in surface water are seen with small amounts, but found in groundwater at higher levels.

Water quality standard for humans is usually based on the protection of children's health. Nitrate, in particular, causes outbreaks of infectious diseases such as cancer of the alimentary canal and cyanosis among children. Excess nitrate in drinking water may cause blue-baby syndrome, which results from the conversion of hemoglobin into methaemoglobin, which cannot carry oxygen [33].

The maximum contaminant level for nitrate set by the world health organization (WHO) and the US environmental protection agency (USEPA) for drinking water are 50 and 45 mg/l of nitrate respectively [34]. In this study, the initial concentration of nitrate solution in all samples exceeds the limit of 50 mg/lit. Nitrates alone do not make disease, but all the dangers of nitrates for health are related to its conversion to nitrite. Side effects of high nitrates cause harmfulness to health as two forms to the body complications of methemoglobinemia or blue baby syndrome are created in infants and young children by consumption of water contaminated with nitrates. [35] In addition the possibility of carcinogenic water contaminated with nitrate has also been reported. Nitrosamine is a compound that is formed also in environments containing high nitrate and are known as carcinogens matters. These compounds are one of the causes of gastrointestinal cancer particularly gastric cancer in humans. [36]

Pollution of water resources by excessive presence of nitrogen compounds such as nitrate, nitrite and ammonium, is a real health and environmental problem. The heavy utilization of artificial fertilizers and the uncontrolled discharges of raw have been known to cause the Penetration of large nitrate and phosphate quantities into the ground and surface waters [37].

Nitrate excess in drinking water may cause blue disease in babies calledmethemoglobinemia in newborn infants as well as other illnesses[38].The most important environmental problems caused by nitrogen and phosphorus compoundsare eutrophication of watersupplies and infectious disease [39]. These components which are involved in theeutrophication of surface waters and the presence of highlevels of nitrate and nitrite ions in drinking water has anadverse risk to human health [40].

Several purification techniques based on thephysicochemical and biological processes are used toremove or reduce the amount of toxic pollutants found inwater and wastewater. These include methods of ionexchange, biological treatment, membrane separationand adsorption[41].Among these methods the adsorption appears the mostappropriate [42]. Activated carbon isgenerally considered a universal adsorbent for theremoval of various aquatic pollutants especially organicpollutants.

2.1.Activated carbon

A considerable amount of production of activated carbon is intended for the removals of pollutants from many different industrial wastewaters. The main property of activated carbon is the large porous surface areas that gives it high capability for retaining chemical materials from liquids and gases and make it versatile adsorbents. Therefore, activated carbon has been used widely in many   industrial fields. Also, activated carbon is used as a catalyst and catalysis supports for environmental issues such as separation, decomposition[43].

The utilization of activated carbon depends on its form and the media in which they are used in (liquids or gases).

The main application of activated carbon in the liquid medium is related to industrials processing such as chemical process, petroleum refining, solvent recovery, metal recovery, chemical and pharmaceutical industries[43, 44]. Also, activated carbon is used for water treatment and wastewater from industrial process especially to eliminate organic pollutant such as pesticides, heavy metals, odors, taste, bacteria and detergent [45, 43].

In gaseous medium, activated carbon applications are related to purification of gases such as airpollutions treatment, volatile organic compounds, separations, deodorization [46, 47]. Generally, the powder form is used in liquid media, whereas the granular form is used in both media. The application of activated carbon usually depends on their properties[48].

Activated carbon is manufactured from a wide kind of carbon-rich materials. These materials include coal, wood, peat, coconut shells, bones and fruit stones. Nowadays, new materials are under investigation to be used as a source of activated carbon. Theoretically, any organic materials with a high percentage of carbon could be activated to reinforce its sorption characteristics. Virtually, the best candidates for activated carbon are materials which possess organic origins. Nowadays, 60% of activated carbon productions come from coal [49].

The prevalent use of specific raw materials as a source of activated carbon is clearly bounded by the supply of those materials. Cost and the ability of activated carbon to satisfy all kinds of application. As a result, natural materials are the best candidate in the manufacture of Activated Carbon due to their good availability, being environmentally friendly, cheap and renewable materials. Lignocelluloses biomass can be considered as a massive source because it is an agriculture waste.Also, environmental problem such as water, air, accumulations pollution could be solved if the Lignocelluloses biomass byproducts wastes were converted to have additional worth as activated carbon, followed by coal. Also, coconut shell and peats are used to produce activated carbon but they are less available and more expensive in cost [50].

Generally, activated carbon is manufactured by two essential activation methods, including physical (thermal) activation and chemical activation

The characteristics of activated carbon involves; pore size distribution, shapes of the pores and surface chemistry which effectively depends on the nature of carbonaceous precursor, activation methods and activation conditions [50]. Physical or thermal activation is one of the activation methods and consist of two steps. First step is called carbonization. Carbonization is the conversion of carbonaceous precursor to char in the absence of oxygen at high temperature[51], followed by the second step which is called gasification. The resulted char is exposed to high temperature in the presence of gases such as carbon dioxide (CO_2) or steam [52].

Chemical activation is the second activation method which is carbonization and activation of the acquired char by soaking it in chemical agents such as alkaline metal oxide or acids [53, 29]. The selection of activation method plays very important roles because it determines the effectiveness of the characteristics of activated carbon such as porosity, surface area, sorption properties and activated carbon yields [29].

Chemical activation is the most popular method in recent times. Chemical activation is much easier and simpler than physical activation because both carbonization and impregnation process is carried out at the same time. Rich carbon content materials are produced as a result of the pyrolysis process with high porosity structure. Chemical agents such as H_3PO_4, HCl, HNO_3, $ZnCl_2$, KOH, NaOH, K_2CO_3 and Na_2CO_3 can be used in chemical activation [60]. The chemical agents to activate lignocelluloses materials are usually phosphoric acid and zinc chloride which is used because it has not been formerly carbonized. Whereas, carbonized materials such as coal or chars, usually sodium hydroxide has been used as activating agent. All chemical agents used during the activation stage act as a dehydrating agent and are removed during thermal decomposition. The main aim of using chemical agent is to obtain highly developed porous structure and to reduce the creation of tar [26].

The product and properties of activated carbon depend on some factors such as degree of impregnation and pyrolysis condition.

Degree of impregnation also called impregnation ratio is the main important factor in the chemical activation that affects the porosity of resulting products directly.It can be defined as a ratio of the chemical agent weight to the startingmaterials weight. There are two mechanisms of the product based on the impregnation ratio. Microspores and Mesopores.Microspores activated carbon structures are formed when the starting material is activated with asmall ratio of chemical agents and therefore the size of pores are usually small.

Whereas, by increasing the impregnation ratio of chemical agents, widening pore size activated carbon were formed which are called mesopores structure [48].

The properties and production of activated carbon also depend on the pyrolysis conditions such as pyrolysis temperature, soaking time and atmosphere. Pyrolysis temperature is an important factor that should be taken into account alongside the nature of the raw materials. Chemical activation is a one step process. The extent of temperature varies between (450 – 900˚C) based on the nature of starting materials. Some studies showed that an increase in pyrolysis temperature led to increase mesoporous activated carbon structures product and decrease in micro porous structure. Also, the Surface area of the product is affected and thus porous structures were discarded. Soaking time is a critical factor of pyrolysis condition it can be defined as the appropriate period of time to burn the sample at definite temperature. It is possible that an increase in the duration of soaking time leads to reduction of both the total pore volume and surface area due to collapse of the smaller pores [54].

Chemical activation has advantages if it compared with physical activation process. These advantages include: low energy and cost process. Also, the product had better characteristics of porous structures. In addition, it has a large surface area and higher carbon yields due to prevention of formation of volatile compounds and tar because of the dehydrogenation properties of the chemical agents [48]. The properties and production of activated carbon also depend on the pyrolysis conditions such as pyrolysis temperature, soaking time and atmosphere. Pyrolysis is an important factor that should be taken into account alongside the nature of the raw materials. Chemical activation is a one step process.

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The main purpose of the activation process is to reinforce the pores structure. Physical activation is one of the activation methods that play a significant role in the production of activated carbon especially in the determination of the size and effectiveness of the pores. Physical activation usually consists of two steps: Carbonization and activation [47].

3. Materials and Methods

3.1 Chemicals

Chemicals that was used for this study include:-Potassium nitrate (KNO_3), Sigma- Aldrich, Natural coal,Sodium hydroxide, NaOH (SIGMA),Distilled water for washing purposes,Phosphoric acid, H_3PO_4(85%) from Aldrich- Germany,Hydrochloric acid, HCl (Aldrich) and double distilled water for the preparation of standard solution.

3.2 Apparatus and Instrument

UV Spectrophotometer(T80 + UV/VIS spectrometer),Hot plate, Volumetric pipettes: 2.5 and 10 mL, Calibrated pipette, Fume hood,Volumetric flask: (50, 100, 500, and 1000) mL, Funnel. Boiling flasks (250 mL), Erlenmeyer's flasks (250 mL), Burettes (50mL), Titrimetric flasks, Pipettes, Holders for funnels, Holders for burettes, Filter paper No 1 or 42, Glazed paper for weighing, Spoon, Rubber stoppers,Oven, Mortar and pestle,Magnetic stirrer,Mechanical shaker, and Electronic balance were used.

3.3. Experimental Procedure

3.3.1. Preparation of nitrate solution

All experiments of the study wereconducted in the laboratory of chemistry department ofJimma University,in Jimma town.For preparationofthe standard solution of nitrate, analytical gradepotassiumnitrate(KNO_3) was used.To prepare a nitrate standard solution withconcentrations of 1000 mg/L, 7.3 g potassium nitratewas dissolved in distilled water in 1000 mL volumetric flask and finally the volume was made to 1000 mL with distilled water.Theadjustment of the pH of nitrate solution, 0.01 MHCland 0.01 M NaOH wasused.All experimentswere employed using double distilled water, and the concentration of nitrate ion was determined by UV-Visspectrophotometer at a wavelength of 307 nm.

3.3.2. Preparation of Natural coal.

Activated carbon was obtained from natural coal, from Dedo District,Jimma Zone. It wascollected andwashed withdistilled water, dried in an oven for 24 hours at 110°C, ground in a ball mill and sieved to particlesize range of 0.3-0.6 mm. One gram of natural coal was soaked for twenty four hours in 100 mL of a solution prepared from 3 M phosphoric acid. Then chemically activated natural coal was neutralized with solution NaOH and, extensively washed with deionized water. Then the prepared, dried andpowdered form of natural coal was heated at 450-900°C in the absence of oxygen and inert atmosphere in order to prepare carbonized natural coal. Then the carbonized material was used for adsorption.To evaluate the surface modification of natural coal,FTIR analyses was performed.The outer microstructure of the activated carbon beforeand after chemical treatment surface was evaluated [55].

Figure.1:Activated Carbon from natural coal.

Table 1: Chemical characteristics of natural coal

Total elements(%)		Ash chemistry/ oxides(%)	
Carbon	51.51	Fe_2O_3	6.85
Hydrogen	4.42	Al_2O_3	34.17
Nitrogen	0.96	CaO	1.42
Sulfur	0.56	MgO	0.71
Oxygen	12.51	SiO_2	54.56
		SO_3 0.90	

Source: Raw data taken from Dilbi Coal Mining Share Company, (2008) with letter permission

3.3.3.Analysis

The concentrations of nitrate in the solutions before and after equilibrium weredetermined by UV/VIS spectrometer (T80 + UV/VIS spectrometer) with detecting wavelength at 307 nm [56]. The pH ofsolution was measured with a Hanna pH meter using a combined glass electrode. The shaking was carried out in a wrist action shaker.

3.3.4. Adsorption experiment

Batch adsorption experiments were performed by contacting 1 g of the selectednatural coal powder with 50 mL of the aqueous solution of different initial concentrations (10 to 100 mg/L) at natural solution pH (2.0). The experiments were performed in wrist action shaker for a period of 3 hours at 200 rpm using 100 mLErlenmeyer flasks containing 50 mL of different nitrate ionconcentrations at atemperature of (20^0C). Continuous mixing was provided during the experimental period with a constant agitation speed of 200 rpm for better mass transfer with high interfacial area of contact. The remaining concentration of nitrate anion in eachsample after adsorption at different time intervals was determined by UV.Visspectroscopy after filtering the adsorbent with Whatman filter paper No. 42 to make it adsorbent free. The nitrate ion concentration retained in the adsorbent phase was calculated.

The effect of adsorbent dosages (0.5 – 3.5 g/L) on the equilibrium adsorption of nitrate ionon the selected natural coal powder was investigated by employing with initial concentration of 50 mg/L at a temperature (20 ^{0}C). For these experiments, the flasks were shaken with natural solution pH (2.0) (natural solution means the actual solution in which it was prepared by dissolving the salts into the water) and agitation speed (200 rpm) for the minimum contact time required to attain equilibrium. The adsorption isotherm was found by agitating nitrate ionsolution of different initial concentrations with the known amount of natural coal powder till the equilibrium was achieved. The kinetics of adsorption was determined by analyzing adsorptive uptake of the nitrate ion from the aqueous solution at different time intervals.

3.3.5. Nitrate removal process

In this study, adsorption tests were done by batch method into 100 mL Erlenmeyer flask and 50 ml nitrate solution volume preformed withwrist action shaker at 200 rpm. To conduct experiments in discrete conditions, various parameters such as contact time, pH, temperature, adsorbent dosage and initial concentration of nitrate were investigated.In all studies, various parameters except initial concentration of nitrate solution, the initialconcentration of 50mg/L nitrate were used. All tests were repeated three times and average of them was reported in this paper.

4. Result and Discussion

4.1. Natural coal characterization by FTIR

FT-IR spectra help identify functional groups on theadsorbent surface and hence explain the adsorption mechanism.FTIR spectroscopy was carried out to analyzethe effect of acid attack and the change that have taken place in the structure of natural coal as the result of modification byphosphoric acid activation. Samples measured on PerkinElmer, Spectrum 65 FT-IR in the range 4000-400 cm^{-1}using KBr pellets.
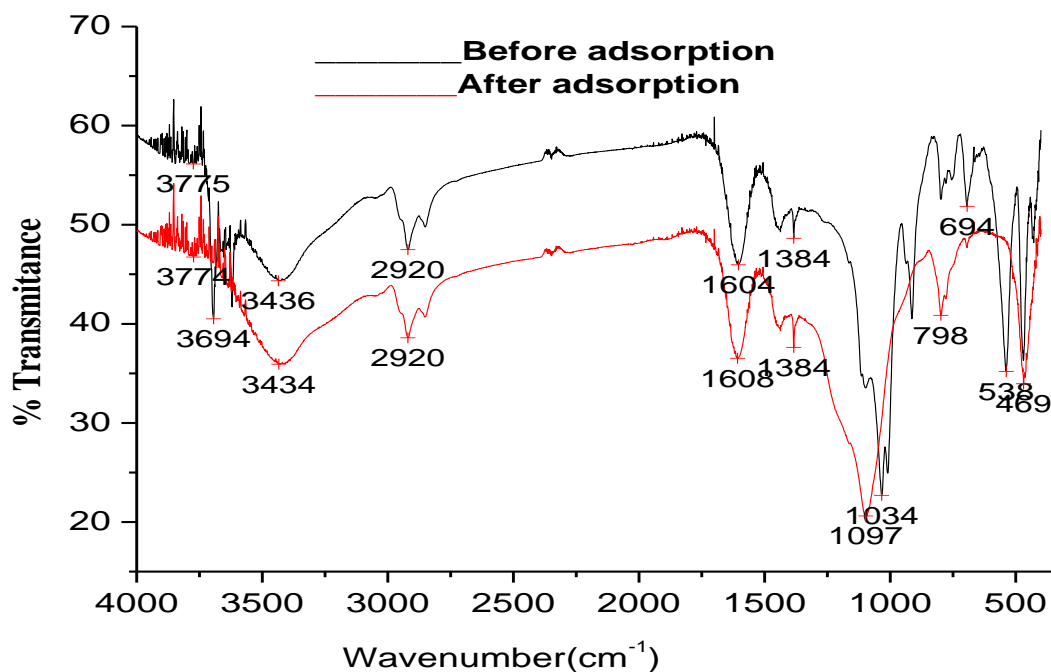

Fig.2FT-IR spectra of natural coal before after adsorption.

In **Figure 2**, The spectrum of the original natural coal exhibits absorption bands at 3775 cm^{-1} assigned to the stretching vibrations of the OH groups for the water molecules adsorbed on the natural coal surface,and the band 3694 and 3436 cm^{-1} are the inner OH stretching vibration and the outer stretching vibration of carboxylic acid, The band at 2920 cm^{-1} representing symmetric and asymmetric stretching vibration of methylene and methyl group. The absorption bands in the region of 1384 and 1604 cm^{-1} corresponds to carbon - nitrogen single bond and nitrogen – oxygen double bond stretching vibrations. The absorption bands in the region of 1034 cm^{-1}corresponds toC -O stretching vibration. And finally 538 cm^{-1}, and 694 cm^{-1}representing Al –O –Si, skeletal vibration and Si – O stretching vibration.

As a regard to the FT-IR spectrum of the nitrate loaded natural coal and its comparison with activated natural coal before adsorption, there is a decrease in peak at 3775 cm^{-1} in natural coal to 3774 cm^{-1}. Also, this peak becomes weak and broader after the adsorption. These decreases can be ascribed to the interactive adsorption of nitrate onto surface of natural coal. In addition, the spectrum of activated coal after adsorption show an increasing in the peak at 694, 1034 and 1604, cm^{-1} as it is compared with the natural coal before adsorption spectrum due to the bonding between natural coal structure and nitrate.Similarly after adsorption, the intensity of the band at 3436 and 538 cm^{-1}decreases due to the removal ofoctahedral cations, causing the loss of water and hydroxyl groups coordinated to them. As well as theformation of three–dimensional networks of amorphous Si– O–Si units and the adsorption interactive between nitrate and natural coal. Few band positions did not changed by the modification, suggesting that the basic natural coal structure did not collapse.

4.2. Spectrophotometric method of nitrate anion analysis

The average (of replicates/triplicates) was expressed along with the standard deviation.

Table2. Standard calibration curve for nitrate anion at 307 nm.

Concentration (mg/L)	Absorbance			Average
Blank	0.00	0.00	0.00	0.00
10	0.095	0.099	0.097	0.097
20	0.200	0.208	0.210	0.206
30	0.310	0.297	0.305	0.304
40	0.380	0.389	0.392	0.387
50	0.450	0.449	0.460	0.453

According to the absorbance taken for the different concentrations of standards, is found to be proportional to concentration. Thus as concentration is increased absorbance also increased linearly, at Table 2 andFigure 3,This standard graph can also be used to estimate the nitrate concentration of samples at any given absorbance.
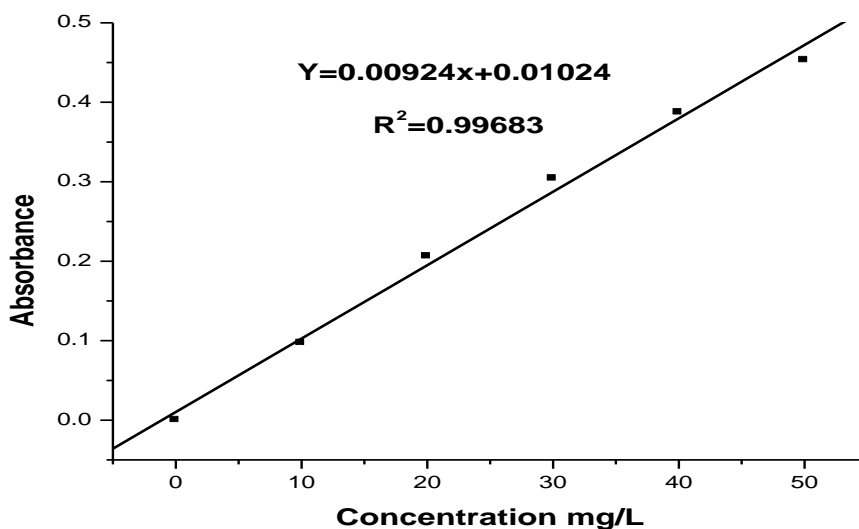
Fig. 3: Standard calibration curve for nitrate ion

4.3. Nitrate adsorption experiments

4.3.1. Effect of contact time

Contact time is an important parameter to determine the equilibrium time of adsorptionprocess. To determine equilibrium time, 1.0 g of adsorbent (natural coal) was mixed with nitrate solutions (50 mL, 100 mg/L) with pH 3. Experimental determination of nitrate ion was then done after the mixture was shaken by rotary shaker which was operated by 200 rpm at 20°C and for the desired time. The experiment was done for contact time of 30, 60, 90, 120, 150, 180, 210, 240 and 270 minutes and the result is shown as indicated below in **Figure 4**, nitrateadsorption onto activated natural coal increaseswhen increasing treatment time starting from''0 to 180'' min. However, the increase was notsignificant for longer contact times. This trendcould be attributed to the fact that at the initialtime between 0-180 minutes there exist anumber of vacant sites on the adsorbent butafter 180 minutes these sites became filled withthe adsorbate molecules which at a pointbetween 180 and 240 minutes the repulsiveforce between solute molecules and bulkphase becomes significant and the vacantsites remain constant with time.

Within first 180 minutes, nitrate adsorption process is fast and since 180 minutespassage, a significant increase is not observed in nitrate due to the saturation of the adsorbent surface of Nitrate and adsorption rate reaches equilibrium after 210 minutes. Because after 180 minutes, nitrate adsorption is low and is not economical, optimum contact time is 180 minutes that for activated natural coal, and the removal was 67.58 percent.Thisobservation agrees with the literature reported by[57].

Fig. 4: Effect of contact time on nitrate removal by acid activated natural coal, (initial concentration 50 mg/L, dose 1g/100 mL,time 30 -270 min, 200 rpm at 20^0C and pH 2)

4.3.2. Effect of pH

The effect of initial solution pH on nitrate removal is illustrated in **Figure 5**. The initial pH values were adjusted by adding 0.1 M of HCl or NaOH.Adsorption of nitrate by activated natural coalwas investigated in the pH range 1-5. After the desired pH was fixed for nitrate solution (50 mL, 100 mg/L), 1.0 g of adsorbent was mixed and the mixture was then shaken at 20 °C for 180 minutes and nitrate analysis was made.

The result shows that higher adsorption capacity is observed at lower pH values (acidic media) and it has adecreasing tendency as the pH increased. This is because natural coal becomes progressively deactivated, loses its positive surface charges and its adsorbent capacity towards the nitrate anion decreases.It is evident from the figure that the percentage removal of nitrate decreased from 67.15% to 18.86% for increase in pH from 2 to 10. Thus, the high adsorption capacity at low pH is mainly due to the strong electrostatic interaction between the positively charged sites of adsorbent (presence of H^+) and the anions. However, lower sorption of the nitrates ions at alkaline pH could be attributed to the abundance of OH^- ions which was compete with the pollutant for the same sorption sites.Thisobservation agrees with the literature reported by[57].
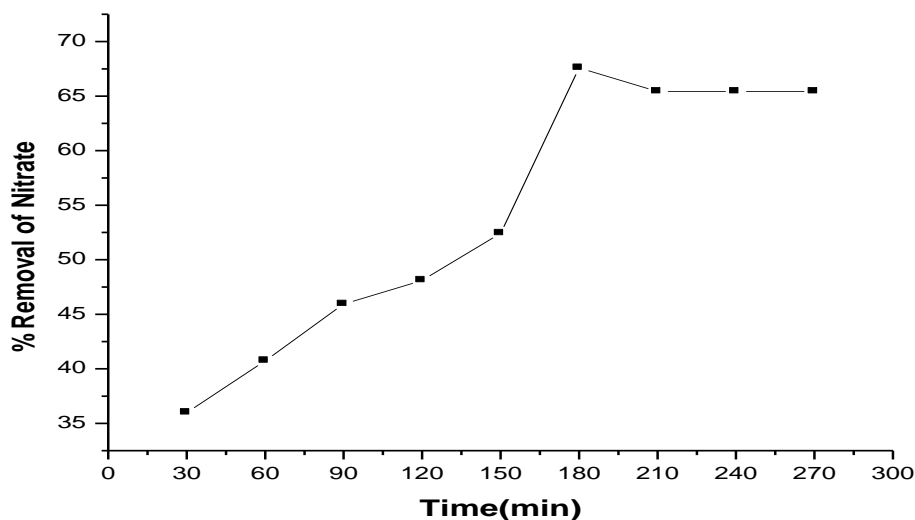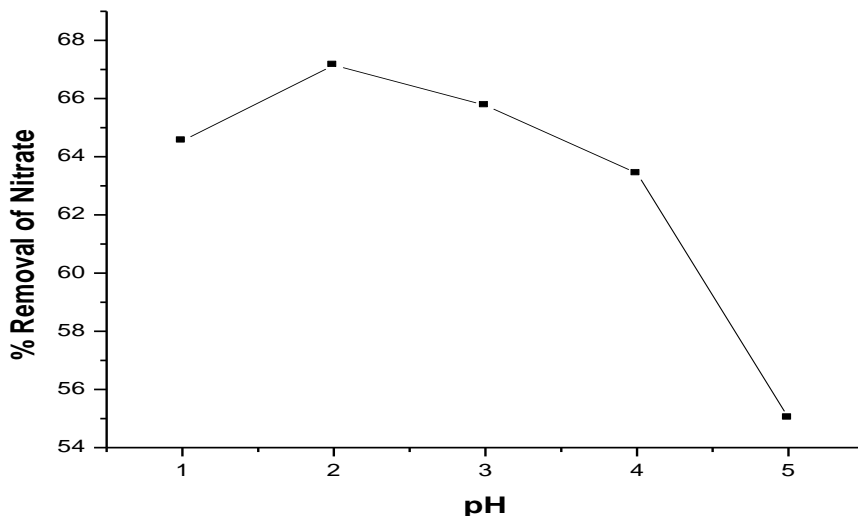

Fig. 5: Effect of pH on nitrate anion removal by acid activated natural coal, (initial concentration50 mg/L, dose 1g/100 mL contact time 180 min, 200 rpm at 20°C)

4.3.3. Effect of Temperature

Results of effect of temperature on nitrate removal efficiency are shown in **Figure6**.Temperature affects the adsorption rate by altering the molecular interactions and the solubility of the adsorbateand thus affects adsorption. To find an optimum temperature,the adsorption was done at a temperature of 20, 25, 30, 35, 40, 45, 50, 55, and 60^0C. The other Parameters were made constant; adsorbent (1.0 g), nitrate solution (50 mL, 100 mg/L),

Contact time (180 minutes) and pH 2.The result showed that the percentage of nitrate adsorption increased when the temperature increased to 20^0C. However, when the temperature further increased, the adsorption decreased, as shown in the graph.

Fig. 6: Effect of temperature on nitrate removal by acid activated natural coal (initial

Concentration 50 mg/L, dose 1g/100 mL contact time 180 min, 200 rpm pH 2.)

4.3.4. Effect of adsorbent dosage

Different amounts of natural coal that means from (0.5 – 3.5g) was placed into conical flasks, then nitrate solutions (50 mL, 100 mg/L) with pH 3 was added to it. The mixture was then shaken for 180 minutes at 20 °C. As indicated in **Figure 7**, removal of nitrate increased with increase in adsorbent mass. This is to be expected because for a fixed initial solute concentration, increase in total dose present a greater surface area and increase adsorption potential**.** However, it isobserved that as the adsorbent mass increases, there was no change in percentage removal possibly due to overlapping of active sites at higher dosage[58].
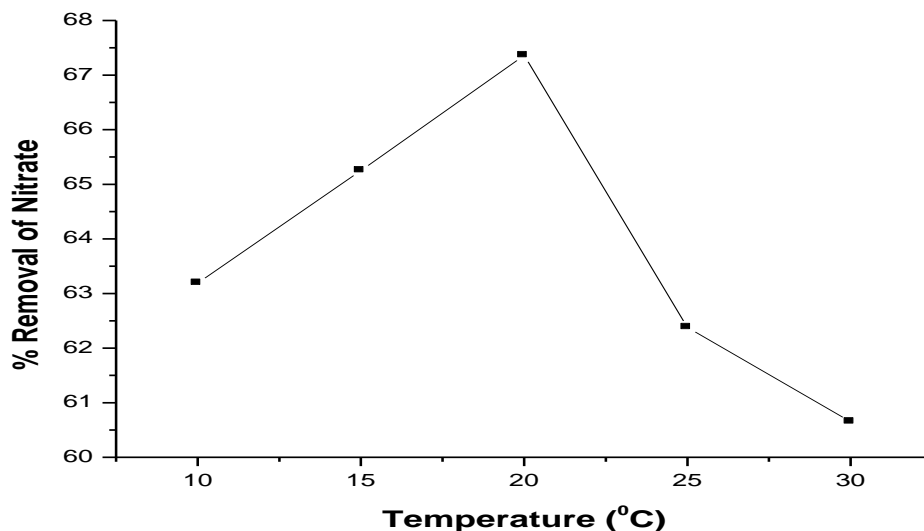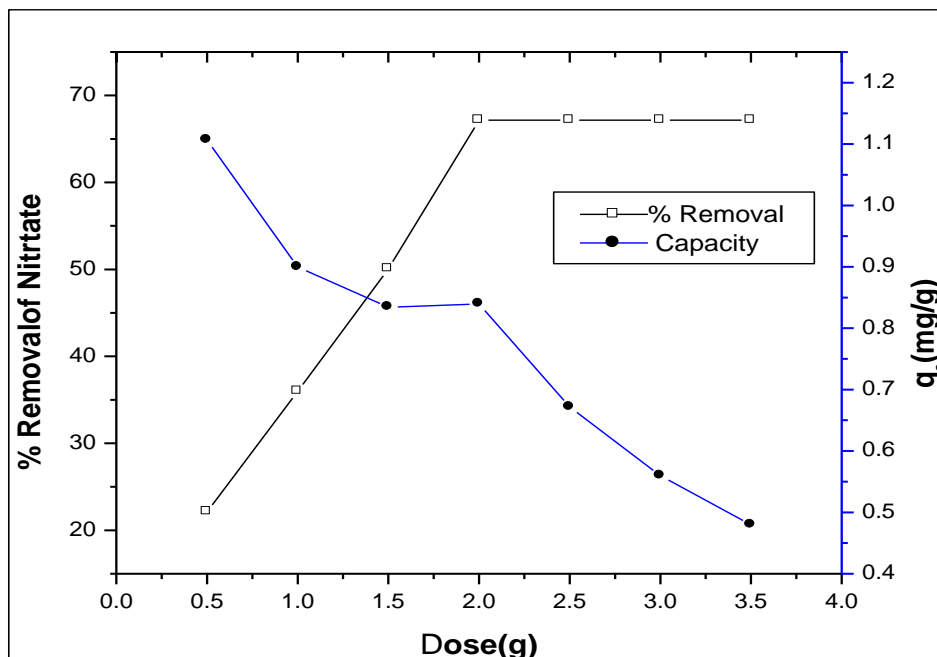
Fig. 7: Effect of mass of adsorbent on nitrate removal by acid activated natural coal(Initialconcentration 50 mg/L, contact time 180 min, 200 rpm, pH 2 and temperature 20 ^{0}C)

4.3.5. Effect of initial nitrate concentration

The influence of initial nitrate concentration on adsorption percentage was estimated **Figure 8**. The initialconcentration of nitrate solution was varied from 50 mg/L to 110 mg/L with pH 2 were added to optimum adsorbent dose (1 g). Each mixturewas then shaken at 20 °C for 180 minutes. After that the initial and final nitrate concentrations were recorded.The result obtained is presented in graphical form as percentage removal versus initial nitrate concentration. It is evident from the graph that the percentage removal of nitrate decreased from 67.16% to 17.38% for initial nitrate concentration of 50 mg/L to 110 mg/L. It is due to the limitation of adsorption sites on the natural coal surface. This can be explained as follows:

Withincrease in the initial nitrate concentration the amount of adsorbate species in the solution increases, but the amount of adsorbent remains constant and hence the percentage removal decreases with increase in initial nitrate concentration. The higher uptake of nitrate at low concentration may be attributed to the availability of more active sites on for lesser number of adsorbate species.Similar results has been reported by [59]on equilibrium sorption of Pb(II) and nitrate ions from aqueous solution using chemically modified rice husk.
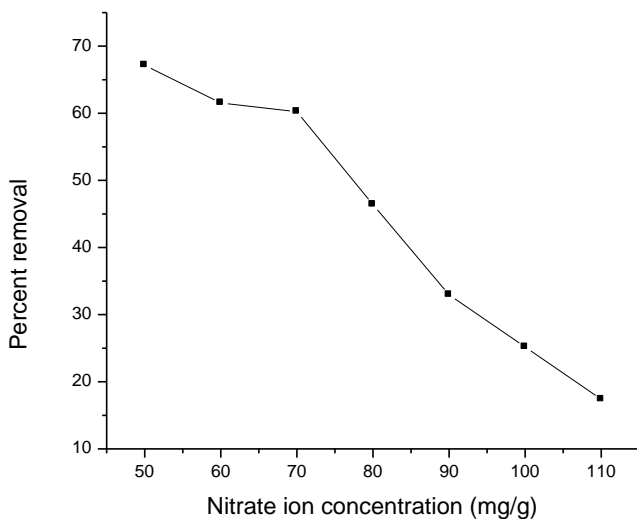
Fig. 8: Effect of nitrate ion concentration on nitrate removal by acidactivated natural coal

(Dose1g/100 mL, pH 2, contact time 180 min, 200 rpm at 20 ^{0}C)

4.4. Adsorption isotherms

The relationship between the amount ofadsorbed substance (qe) and the concentration ofthe substance in liquid phase (Ce) at temperatures T is adsorption isotherm [60, 61]. The most popular theories to explain the adsorption process that had been expressed include:

- Langmuir and Freundlich equation.

In order to determine the adsorption isotherms, Langmuir and Freundlichisotherm linear forms were used to analyze nitrate adsorption.For the determination of adsorptionisotherms,

a series of stoppered 100 ml Erlenmeyer flasks were used and each flask was filled with 50 mL of nitrate solution of varying initial concentration (50 to 110 mg/L). A fixed amount of adsorbent (1 g) was then added into each flask. The flasks were kept on a rotaryshaker at a fixed rate that was 200 rpm, for 3 hours that was sufficient to establish the equilibrium. After this period, the mixture was allowed to settle and the supernatant solution was filtered off using What man filter paper No. 42 and the equilibrium concentrations of nitrate was measured by the UV spectrophotometer. The amount of the nitrateadsorbed at equilibrium (qe, mg g-1) and the removal percentage (R %) was calculated according to the expressions:

$$q_e = \frac{(C_0 - C_e)}{m} V \quad (1)$$

$$R\% = \left[\frac{C_0 - C_e}{C_0}\right] 100 \quad (2)$$

Where: C_0 and $Ce$are the initial and equilibrium nitrate concentrations (mg/L), respectively, V is the solution volume (L), and m is the mass of adsorbent (g).

In this work, two models were used to describe the relationship between the amount of nitrate adsorbed, $qe$and its equilibrium concentration, Ce. These were Langmuir, and Freundlichadsorption isotherms.

4.4.1. The Langmuir isotherm

The Langmuir model is based on the assumption that the maximumadsorption occurs when a saturated monolayer of solute molecules is present on the adsorbent surface, the energy of adsorption is constant and there is no migration of adsorbate molecules in the surface plane. The Langmuir isotherm is given by:

$$q_e = \frac{q_m K_l C_e}{1+K_L C_e} \quad (3)$$

The constants in the Langmuir isotherm can be determined by plotting ($1/q_e$)
Versus ($1/C_e$) and making use of above equation rewritten as:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_L} \frac{1}{C_e} (4)$$

Where q$m$and $K_L$are the Langmuir constants, representing the maximumadsorption capacity for the solid phase loading and the energy constant related to the heat of adsorption respectively.

Further, the essential characteristics of the Langmuir isotherm can be described by aseparation factor R, which is defined by the following equation

$$R_L = \frac{1}{1+bC_i} (5)$$

Where Ci is the initial concentration of nitrate (mg/L) and R_L is the Langmuirconstant (in g/L). The value of separation factor R_L, indicates the isotherms shape and the nature of the adsorption process is unfavorable (R $_L$>1), linear (R $_L$ =1), favorable (0 < R $_L$< 1) and irreversible (R_L= 0).

4.4.2. The Freundlich isotherm

The Freundlich isotherm model is an empirical relationship describing the adsorption of solutes from a liquid to a solid surface and assumes that different sites with several adsorption energies are involved.

Freundlich adsorption isotherm is therelationship between the amounts of nitrate adsorbed per unit mass of adsorbent, q_e,and the concentration of the nitrate at equilibrium, C_e.

$$q_e = K_f C_e^{\frac{1}{n}} \qquad\qquad (6)$$

The logarithmic form of the equation becomes,

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \qquad\qquad (7)$$

Where $K_f$and$n$are the Freundlich constants, the characteristics of the system.$K_f$and n are the indicators of the adsorption capacity and adsorption intensity, respectively. The ability of Freundlich model to fit the experimental data was examined. For this case, the plot of log $C_e$vs. log $q_e$was employed to generate the intercept value of $K_f$and the slope of n.

Table 3. Effect on Adsorbate concentration on percent removal of nitrate ion and calculation of adsorption isotherms

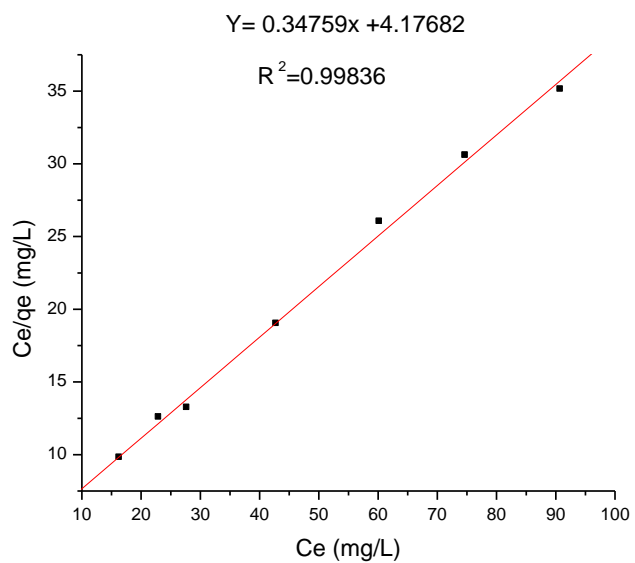| Nitrate conc. (mg/L)	Ce	qe	Percent removal	Ce/qe	logCe	log qe
50	16.42	1.68	67.16	9.77	1.22	0.23
60	23.07	1.84	61.54	12.54	1.36	0.26
70	27.83	2.11	60.24	13.19	1.44	0.32
80	42.89	2.26	46.38	18.98	1.63	0.35
90	60.33	2.32	32.96	26.00	1.78	0.37
100	74.82	2.45	25.18	30.54	1.87	0.39
110	90.88	2.59	17.38	35.09	1.96	0.41

Fig. 9: Langmuir plot for nitrate adsorption onto activated natural coal at 20 ^{0}C
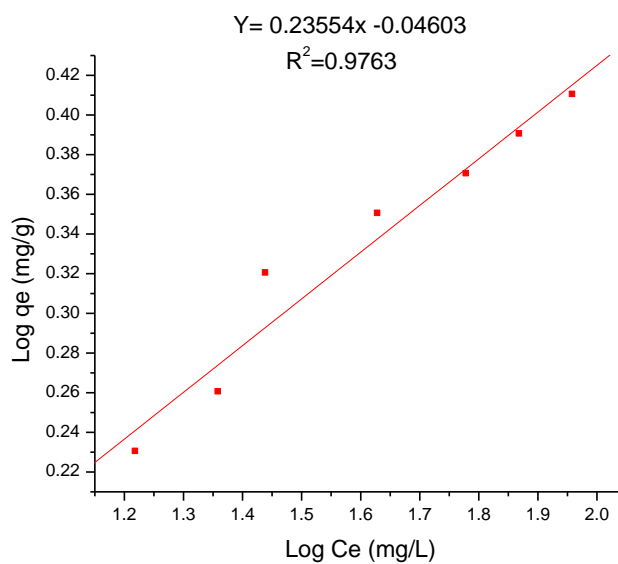
Fig.10: Freundlich plot for nitrate adsorption onto activated naturalcoal at 20^{0}C

Table 4: Freundlich and Langmuir Isotherm data

Langmuir Isotherm				Freundlich Isotherm		
Parameter						
R_L	q_m(mg/g)	K_L (L/mg)	R^2	K_f (mg/g)	n	R^2
0.0016	2.87	11.98	0.99836	1.12	4.24	0.9763

From **Table 4,**it can be seen that the value of n = 4.24 that it is in range set by Freundlich Model which is between 1 and 10 showing favorable adsorption of nitrate onto the activated natural coal prepared in this work. At the same time, the separation factor R_L= 0.0016, is in the range $0 < R_L < 1$, which indicates a favorable adsorption process. In view of correlation coefficient, R^2, values for Langmuir more close to 1 than the value for Freundlich models and thus the data best fit with Langmuir model.optimum conditions of contact time (3 hours), acid activated natural coal (1.0 g), initial nitrate concentration (50mg/L), pH 2, and temperature (20 ^{0}C). With the help of Langmuir and Freundlich models, adsorption isotherms of nitrate ions removal efficiency from aqueous solution by acid activated natural coal were studied and the data best fit into the Langmuir model. Similar results reported By[61].Thenatural coal obtained from Dedo district, Jimma zone is alternativea very good materials for purification ofnitrate ions from waste water.

4.5. Adsorption Kinetics

In order to investigate the controlling mechanism of adsorption processes such asmass transfer and chemical reaction, the pseudo-first-order and pseudo-second order equations are applied to model the kinetics of nitrate adsorption onto natural coal powder. The pseudo-first-order rate equation is given as [60]:

$$\log(q_e - q_t) \;=\; \log q_e - \frac{K_{ad}}{2.303}\, t \quad (8)$$

Where q_t and q_e are the amount adsorbed (mg/g) at time, t, and at equilibrium respectively and k_1 is the rate constant of the pseudo-first-order adsorption process (min^{-1}). Straight line plots of $\log(q_e - q_t)$ against time were used to determine the rate constant, k_1, and correlation coefficients, R^2. The values of k_1 and calculated equilibrium adsorption capacity, q_e, calc. can be obtained from the slope and intercept, respectively, of the linear plot of $\ln(q_e - q_t)$ versus t.

Table5. Effect of nitrate ion adsorption calculation on the kinetics study

Time (min)	Abs.	Ce (mg/g)	Initial (Con. mg/g)	Percent removal	qt	qe	Log (qe – qt)	t/qt
30	0.306	32.00	50	35.98	0.0179	0.0338	-0.801	1667.46
60	0.284	29.63	50	40.74	0.0203	0.0338	1.693	2945.17
90	0.260	27.03	50	45.94	0.0229	0.0338	1.639	3918.21
120	0.250	25.95	50	48.10	0.0240	0.0338	1.619	4989.20
150	0.230	23.78	50	52.43	0.0262	0.0338	1.579	5721.59
180	0.160	16.21	50	67.58	0.0337	0.0338	1.471	5326.67
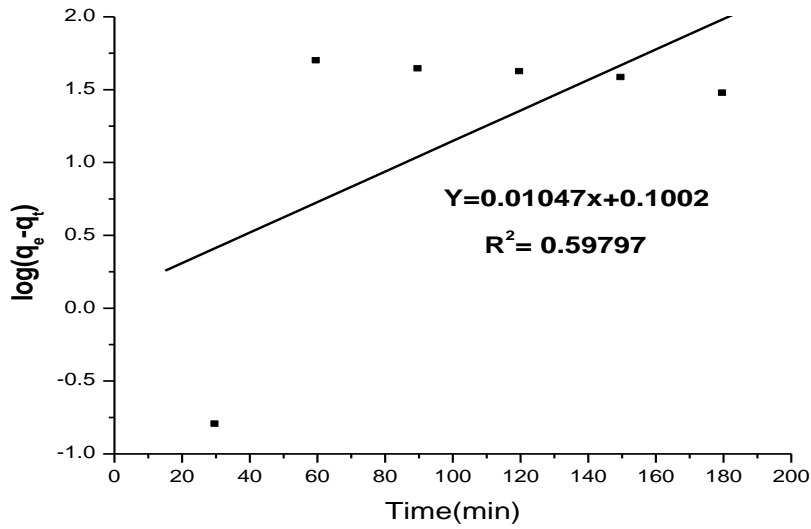
Fig. 11: Graph of pseudo - first order rate for nitrate ion.

A pseudo-secondorder equation based on adsorption equilibrium capacity may be expressed in the form

$$\frac{1}{q_t} = \frac{1}{q_e^2\,K_2} + \frac{t}{q_e} \quad (9)$$

Where q_e and q_t are the amounts of nitrate adsorbed (mg g^{-1}) at equilibrium and at time t (min),respectively, and k_2(g min^{-1} mg^{-1})is the rate constant of pseudo- second-orderadsorption equation [62].
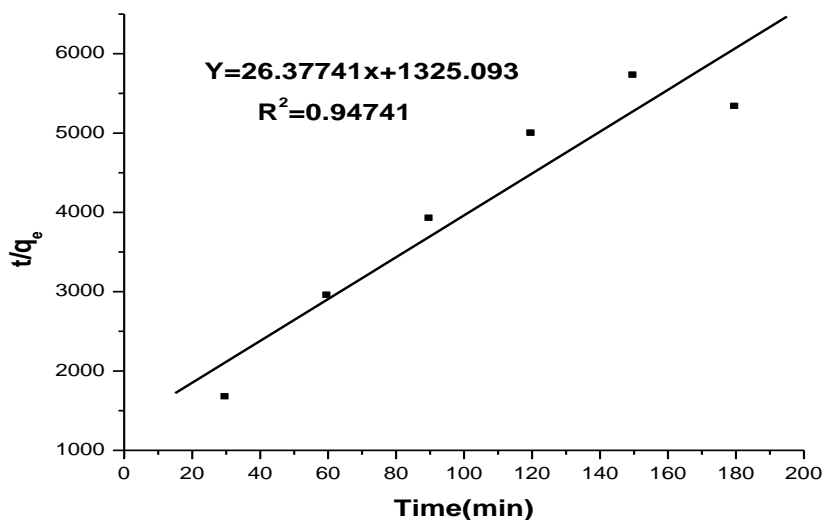
Fig. 12: Graph of pseudo second – order for nitrate ion

Table6. Adsorption kinetics of pseudo- first and second- order model for
Nitrate adsorption by activated natural coal.

Parameter	Pseudo – first order			Pseudo –second order		
Concentration (mg/g)	K_1 (min)$^{-1}$	qe(mg/g)	R^2	K_2(gmg^{-}min^{-1})	qe (mg/g)	R^2
50	0.024	1.02	0.5979	1.31	10.038	0.9474

Straight line plots of log(qe - qt) against t, were used to determine the rate constant, k_1, and correlation coefficients, R^2, for nitrate concentrations, as shown in Fig. 10. With the coefficient of 0.5979 (for 50 mg/L), it was seen that adsorption of nitrate ion on activated natural coal powder did not follow pseudo first-order kinetics compare with the correlation coefficient of pseudo second-order kinetics.

The pseudo-first-order and pseudo-second-order rate constants determined from **Figures. 11** and **12** are presented in Table 6 along with the corresponding correlation coefficients.

The plot of t/qt versus t for pseudo-second-order model **Figures. 12** yields very good straight lines (correlation coefficient, $R^2 > 0.9474$) as compared to the plot of pseudo-first order. Which relies on the assumption that chemisorption may be the rate-limiting step. In chemisorption (chemical adsorption), the nitrate ions stick to the adsorbent surface by forming a chemical (usually electrostatics) bond and tend to find sites that maximize their coordination number with the surface [63].

4.6. Thermodynamics parameters for the adsorption

Thermodynamic parameters show the feasibility and spontaneity of adsorption process. The parameters namely standard change in Gibb's free energy (ΔG o), standard change enthalpy (ΔHo) and standard change entropy (ΔS o). In general these parameters indicate that the adsorption process is spontaneous or not and exothermic or endothermic. The standard enthalpy change ($\Delta H°$) for the adsorption process may be: (i) positive value indicates that the process is endothermic in nature, or (ii) Negativevalue indicates that the process is exothermic in nature and a given amount of heat is evolved during the binding of nitrate ion on the surface of activated natural coal. The positive value of standard change ($\Delta S°$) indicate an increase in the degree of freedom (or disorder) of the adsorbed species. These parameters were determined from given equations.

$$\ln K_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (10)$$

$$K_c = \frac{C_a}{C_e} (11)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 (12)$$

where Kc, C_0, Ce, R, T are the equilibrium constants, amount of nitrate ion (mg/L) adsorbed on the adsorbent per liter (L) of the solution at equilibrium, general gas constant (8.31 J/mol.K) and absolute temperature (T) respectively.

34

Similarly ΔG^o, ΔHo and ΔS^o are the change in Gibb's free energy (KJ/mole), enthalpy (KJ/mol) and entropy (J/mol.K) respectively. The plots of logqe/Ce versus 1/T for the adsorption of nitrate ion on activated natural coal are shown in **Figure. 13**. The adsorption enthalpy (ΔH^o) and entropy (ΔS^o) were determined from slope and interceptof Fig. The values of Gibb's free energy (ΔG^o) were negative for adsorption of nitrate ion on activated natural coal at all temperatures studied. Its values are found to be decreased with increasing the temperature as represented in Table 8.

The negative value of enthalpy (ΔH^o) indicates that the adsorption of nitrate ion onto activated natural coal is an exothermic process. Similarly, the negative values of entropy (ΔS^o) represent decrease in randomness at the nitrate interface during the adsorption of nitrate ion onto activated natural coal. The negative values of ΔG^0 at the three temperatures show that the adsorption process is spontaneous and the degree of spontaneity decreases with increasing the temperature. And also, the decreasing in ΔG^o values with increasing temperature shows a decrease in feasibility of sorption at higher temperature.

Table7. Thermodynamic graft for determination of enthalpy, entropy and free energy of Nitrate anion.

Tem. (^{0}C)	Average Abs.	Ce	con	% removal	qe	qe/ce	logqe/ce	1/T
20	0.161	16.31	50	67.36	1.68	0.1030	-0.98	0.05
25	0.184	18.80	50	62.38	1.56	0.0829	-1.08	0.04
30	0.192	19.67	50	60.65	1.51	0.0767	-1.11	0.033
35	0.200	20.53	50	58.92	1.47	0.0716	-1.14	0.028
40	0.210	21.61	50	56.76	1.41	0.0652	-1.18	0.025
45	0.226	23.35	50	53.29	1.33	0.0569	-1.24	0.022
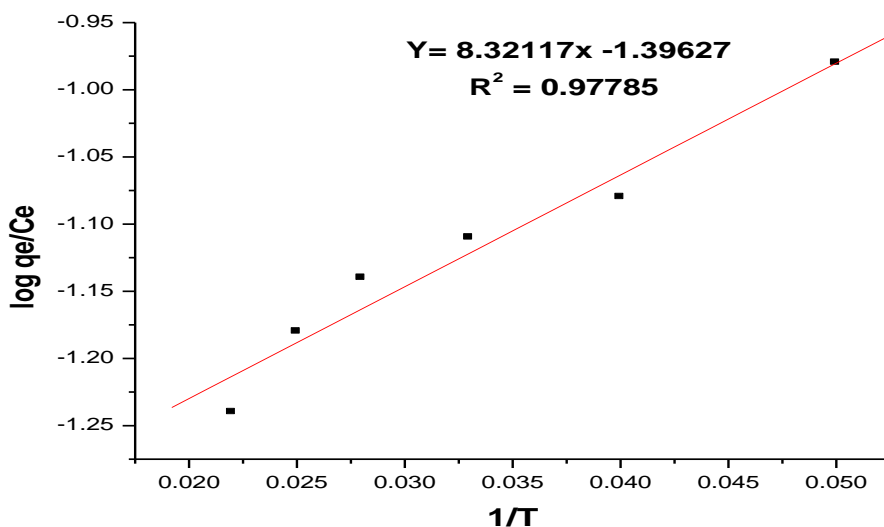
Fig. 13: Graph of thermodynamics adsorption of nitrate ion on activated natural coal.

Table8. Thermodynamic parameters for adsorption of nitrate ion on activated natural coal.

Parameters		ΔG (KJ/mol)		
ΔH (KJ/mol)	ΔS (J/mol)	293K	298K	303K
-69.18	-11.60	-3398.8	-3456.8	-3514.8

From the **Table8.**It has been observed that with increase in temperature, adsorption capacity decreases. This implies that for the initial nitrate concentration of each solution, the adsorption is exothermic in nature. The negative values of ΔH^o indicate exothermic and ΔG^o indicate that the adsorption process is spontaneous in nature. A decrease in randomness is indicated by negative values of entropy change. The magnitude and sign of ΔS^o gives an indication whether the adsorption reaction is an associative or dissociative mechanism. A negative value of ΔS^o suggests that the adsorption process involves an associative mechanism. The adsorption leads to order through the formation of an activated complex between the adsorbate and adsorbent. Also a negative value of ΔS^oreflects that no significant change occurs in the internal structures of the adsorbent during the adsorption process.

5. Conclusion and Recommendation

5.1. Conclusion

This study investigated the adsorption characteristics and suitability of natural coal mineral as potentialadsorbent for the removal of nitrate anion from aqueous solutions using batch technique. The results showed that this natural coal could be used as potential adsorbent and it was highly effective adsorbent for the removal of nitrates anions from aqueous solutions. The batch study parameters,contact time, pH of solution, mass of adsorbent, and initial solution concentration were found to be effective on the adsorption processes. The adsorption equilibrium was attained within 3 hours. From the studies conducted, it was established that pseudo-second-order kinetic model described the kinetic rate. The percentage removal was found to decrease with increase in pH. The increase in adsorbent dosage increased the percent removal of nitrate due to the increase in adsorbent surface area in adsorbent dosage. The equilibrium data fitted well the Langmuir isotherm equation and this adsorbent showed large uptake capacity of nitrate (qe, cal = 10.03 mg/g) compared to Freundich isotherm model, which is (1.02 mg/g). Natural coal is a potential candidate as a highly efficient adsorbent for remediation of nitrate contaminated water owing to its exceptional uptake capacity as well as high selectivity for this anionic contaminant.

The negative value of ΔH^o and ΔG^o indicate that the adsorption process is exothermic and spontaneous in nature respectively. A decrease in randomness is indicated by negative values of entropy change. The magnitude and sign of ΔS gives an indication whether the adsorption reaction is an associative or dissociative mechanism. A negative value of ΔS suggests that the adsorption process involves an associative mechanism.

5.2.Recommendation

To increase the adsorption capacity of the natural coal it is important to increase surface area of the natural coal by treating different chemicals. In addition to that legislation help to encourage the development and use of natural coal as adsorption methods for nitrate treatment, for the surrounding community as well as for the region.

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Appendixes

Appendix 1: Data for time effect and absorbance

Time (min)	Abs. trial 1	Abs. trial 2	Abs. trial 3	Abs. average	Percent Removal
30	0.300	0.306	0.312	0.306	35.98
60	0.284	0.286	0.282	0.284	40.74
90	0.260	0.261	0.259	0.260	45.94
120	0.240	0.248	0.262	0.250	48.10
150	0.230	0.230	0.230	0.230	52.43
180	0.155	0.160	0.165	0.160	67.58
210	0.172	0171	0167	0.170	65.42
240	0.168	0.167	0.175	0.170	65.41
270	0.172	0.173	0.165	0.170	65.38

Appendix 2: Data for pH effect and absorbance

pH	Abs. trial 1	Abs. trial 2	Abs. trial 3	Abs. average	Percent Removal
1	0.358	0.370	0.364	0.364	64.55
2	0.320	0.326	0.326	0.324	67.15
3	0.281	0.283	0.282	0.282	65.77
4	0.238	0.240	0.248	0.242	63.43
5	0.200	0.200	0.206	0.202	55.03
6	0.167	0.163	0.156	0.162	42.58
7	0.185	0.186	0.184	0.185	35.13
8	0.198	0.198	0.210	0.202	24.95
9	0.216	0.217	0.221	0.218	20.64
10	0.242	0.241	0.243	0.242	18.86
11	0.245	0.241	0.244	0.242	16.09

| 12 | 0.246 | 0.240 | 0.240 | 0.242 | 14.11 |

Appendix 3:Data for temperature effect and absorbance

Tem .(^{O}C)	Abs. trial 1	Abs. trial 2	Abs. trial 3	Abs. average	Present Removal
10	0.240	0.240	0.240	0.240	63.19
15	0.232	0.232	0.232	0.232	65.25
20	0.221	0.223	0.234	0.226	58.92
25	0.210	0.209	0.211	0.210	62.38
30	0.190	0.193	0.199	0.194	60.65
35	0.160	0.160	0.163	0.161	67.36

Appendix 4: Data for dosage effect and absorbance

Dosage	Abs. trial 1	Abs. trial 2	Abs. trial 3	Abs. average	Percent Removal
0.5	0.361	0.359	0.390	0.370	22.13
1.0	0.299	0.298	0.321	0.306	35.98
1.5	0.240	0.240	0.243	0.241	50.05
2.0	0.160	0.168	0.158	0.162	67.15
2.5	0.159	0.159	0.168	0.162	67.13
3.0	0.162	0.160	0.164	0.162	67.05
3..5	0.166	0.161	0.159	0.162	67.00

Appendix5: Data for initial concentration effect and absorbance

Initial Conc.	Abs. trial 1	Abs. trial 2	Abs. trial 3	Abs. average	Percent Removal
50	0.158	0.158	0.170	0.162	67.16
60	0.179	0.178	0.207	0.224	61.54
70	0.188	0.190	0.204	0.267	60.24
80	0.257	0.258	0.259	0.407	46.38
90	0.300	0.330	0.330	0.568	32.96
100	0.355	0.355	0.358	0.703	25.15
110	0.390	0.398	0.388	0.850	17.38