DEBRE BIRHAN UNIVERSITY

COLLEGE OF NATURAL AND COMPUTATION SCIENCES

DEPARTMENT OF CHEMISTRY POST GRADUATE PROGRAMM

Local Clay as Adsorbent for the Removal of NH_3-N, PO_4-P, NO_3-N and H_2S from Brewery Wastewater

A Thesis Submitted to school of Graduate Studies, Department of Chemistry Debre Birhan University in partial Fulfillment of the Requirements *for the attainment of* the Degree of Master of Science in Analytical Chemistry

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As members of Examining Board of the Final M.Sc. thesis open defense, we certify that we have read and evaluated the thesis prepared by Limat Teferi, entitled "Investigation of Local Clay as Adsorbent for the Removal of NH_3-N, PO_4-P, NO_3-N and H_2S from Brewery Wastewater" and recommended that it can be accepted as fulfilling the thesis requirements for the Degree of Master of Science in Analytical Chemistry

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Declaration

I, the undersigned, declare that this thesis entitled “*Investigation of Local Clay as Adsorbent for the Removal of* NH_3*-N,* PO_4*-P,* NO_3*-N and* H_2S *from Brewery Wastewater*” is my original work, and has not been presented by any other person for an award of a degree in this or any other University, and that all resources of materials used for this thesis have been duly acknowledged.

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Acronyms

AC	Activated Carbon
ANOVA	Analysis of Variance
BOD	Biological Oxygen Demand
CIP	Clean In Place
COD	Chemical Oxygen Demand
DD	Donnan Dialysis
ED	Electrodialysis
GAC	Granular Acetic acid
h	initial rate of adsorption
K_f	Freundlich constant
k_L	Langmuir constant
K	equilibrium constant
MF	Micro Filtration
UF	Ultra Filtration
qe	adsorption capacity
Ce	equilibrium concentration
qt	adsorption capacity at time t
n	adsorption intensity

Abstract

Inorganic pollutants are considered a major cause for environmental problems. Several conventional treatment methods have been developed for removal of toxic environmental pollutants from waste waters. Currently, low cost, easily available materials gets greater attention towards for the removal of toxic pollutants from the environment due to their best adsorption capacity and simple preparation methods. Among the broad lists of adsorbent materials, local clay has been selected for this study for the removal of ammonia, phosphate, nitrate and hydrogen sulfide from brewery waste water. The adsorbent local clay was treated with NaCl, Na_2CO_3, citrate, HCl, H_2O_2 and KOH to remove organic and inorganic impurities. The treated clay was dried and grounded sieved using 63µm, 90µm and 1mm mesh size sieve. Stock solution of ammonia, phosphate, nitrate and H_2S were prepared and working solutions were obtained by several dilutions. Batch adsorption experiments on to clay were conducted for each species. The result revealed that maximum removal efficiency of local clay was 98.25%, 96%, 96.24% and 86.72% for ammonia, phosphate, nitrate and hydrogen sulfide at a pH of 7, 5, 2 and 7 respectively.The adsorption data of target species have been described by the Freundlich and Langmuir isotherm models. The adsorption process fitted to both Langmuir and Freundlich isotherms with some deviations and a maximum adsorption capacities of and 0.529, 0.44, 0.015 and 0.681 mg/g for NO_3, PO_4, NH_3 and H_2S respectively. Adsorption kinetics for NO_3^- and $PO4^{3-}$ followed pseudo first order with regression coefficient of 0.9996 and 0.998 respectively. While NH_3 and H_2S followed pseudo second order with regression coefficients of 0.997 and 0.996 respectively. Optimum operating conditions of 11 gm adsorbent dose, 120 minutes and pH of 7, 5, 2 and 7 for NH_3, PO_4^{3}-., NO_3^- and H_2S respectively, of these solution were applied to remove these species from real brewery waste water. The results showed that local clay reduced ammonia from its initial concentration of 0.764 mg/l to 0.377mg/l, phosphate from 6.834mg/l to 2.464mg/l, nitrate from 4mg/l to 1.2mg/l and H_2S from 2mg/l to 0.23mg/l. Therefore, it can be concluded that these clay has potential adsorptive capacity for the removal of NH_3, PO^{3-}_4, NO^-_3 and H_2S from aqueous solutions.

Key words: *Adsorption, NO_3-N, PO4-P, NH_3-N and H_2S, Isotherm models, kinetics, thermodynamics*

1. INTRODUCTION

1.1. Background

Industry is sustained by the extraction and processing of natural resources as raw materials. These same raw materials find their way into the environment in different forms as finished and waste products. Although the finished products are used for different activities, the waste products become a burden to the environment. This means that although industrialization is considered as the corner stone of the development strategies due to its significant contribution to the economic growth and hence human welfare, it may lead to serious environmental degradation. Among the beverage sub-sector today, beer brewing industry is a huge global business, consisting of several multinational companies and many thousands of smaller producers ranging from brewpubs to regional breweries. Beer is the fifth most consumed beverage in the world behind tea, carbonates, milk and coffee and it continues to be a popular drink with an average consumption of 23 liters/person per year [1].

Production of beer includes blending and fermentation of maize, barley malt and sorghum grits using yeast, which requires large volumes of water as the primary raw material. Traditionally, the amount of water needed to brew beer is several times the volume actually brewed. For instance, an average water consumption of 6.0 hectoliters is required to produce one hectoliters of clear beer [2]. Large volumes of water are being used by the industry for production of beer for two main purposes; as the main ingredient of the beer itself and as part of the brewing process for steam raising, cooling, and washing of floors, packaging, cleaning of the brew house during and after the end of each batch operation. The amount of waste water that is being discharged from the industry after the production of beer, also contributes to this large volume of water [3].

Brewing process is accompanied by the release of a great variety of contaminant each of which can determine the usability of the water for certain applications and can cause problems with effluent discharge. The main constituents include; Nitrogen, H_2S, NH_3 and Phosphorous. The constituents of the effluent fluid are present in large quantities and require some pretreatment before discharging the effluent fluid into a sewage system [4].

At increased concentration of the contaminants, effluent fluid can be harmful in the following ways:

i) Impaired respiration to humans.
ii) Nausea and reduction in appetite

Inorganic contaminates such as nitrogen indicates level of matter concentration. Decomposition as a function of time will reduce contaminants like sulphate in the concentration into sulfides and hydrogen by anaerobic bacteria action. Hence, as long as the effluent fluid keeps degrading, the hydrogen sulphide gas produced will cause bad odor to the waste water. Hydrogen sulfide is a pollutant that is commonly regarded as toxic. Inhalation of high concentrations of hydrogen sulfide can be lethal. Hydrogen sulfide mainly attacks the neural system and important organs, like the liver and the kidney [5].

The pollution of the aquatic environment with metals and anions may be either natural or anthropogenic origin. Several common treatment methods, including coagulation sedimentation, filtration, adsorption, chemical precipitation, ion exchange, classical solvent extraction, evaporation and biological methods are used for removal of inorganic contaminants from natural waters or wastewaters. Membrane processes such as reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF) and microfiltration (MF) in hybrid systems, Donnan dialysis (DD) and electrodialysis (ED) as well as in combination with extraction (liquid membranes) and bioreactors, are applied to remove inorganic micropollutants from aquatic environment [6]. However, these methods are not widely used, because economically not feasible, non regenerable, produces toxic waste and inefficient for low level contaminants. The need to find alternative inexpensive and effective methods for inorganic pollutants abetment from wastewaters becomes inevitable. Adsorption process is the best in comparison with other methods because of its ease of operation, uses low cost adsorbents and effective towards removal of organic and inorganic pollutants even at low concentration level [7]. Local clay is widely available, and it is effective towards adsorption of inorganic and organic pollutants.

The brewery plant generate large volumes of waste water with inorganic species such as nitrite, sulphide, ammonia etc, which are beyond the required level in the environment. In this research, local clay was used as an adsorbent to remove inorganic pollutants. The effectiveness of adsorption capacity of local clay as adsorbent towards ammonia, hydrogen sulfide, phosphate and nitrates have been investigated. These pollutants are selected because at higher concentration, they cause bad odor, affect aquatic life, impair health hazard to humans and animals etc. High concentration of H_2S results fatal disease, nitrogen and phosphate result eutrophication. A series of batch experiments were performed to characterize inorganic pollutant adsorption equilibrium on local clay.

This research reveals the significance of NH_3, H_2S, PO^{3-}_4 and NO^-_3 removal from wastewater streams and explains the adsorption potential of local clay, at different operation conditions such as pH, dose required, initial concentration of pollutants and contact time. In addition, adsorption isotherms, adsorption kinetics as well as models used to characterize adsorbent adsorption has been investigated.

1.2. Statement of the Problem

Rapid urbanization and industrialization cause the generation of high amount of waste water containing toxic pollutants such as ammonia, hydrogen sulfide, nitrites, phosphate etc. These pollutants has high risk on the environment and human health.

Ammonia pollution will cause chemical burn to the vegetation, absence of aquatic flora and fauna, shortness of breath, skin and eye irritation, respiratory irritant, chemical burns to the respiratory tract, skin and eyes, severe cough, chronic lung disease and aquatic life is highly affected. Hydrogen sulfide causes inflammation of the moist membranes of eye and respiratory tract, olfactory neuron loss, death etc. Nitrogen and phosphorus pollution causes eutrophication of lakes and rivers. The effects of eutrophication of waters are undesirable, because the aesthetic value of a lake is lowered through excessive growth of aquatic weeds and algae and production of floating algal scums which are a nuisance to those who used the water for recreational purposes. Other effects include undesirable odors and tastes, depletion of dissolved oxygen, destruction of aquatic life and impairment of water treatment operations such as clogging of filters by alga [7].

To reduce these problems of health risk , different treatment options such as chemical precipitation, ozonization, electrochemical treatment, membrane processes and ion exchange have been employed. But those technologies are extremely expensive, inefficient to very low concentrations, further toxic wastes, and creating yet another disposal problem. But adsorption is the most efficient, low cost and easy operation and recovery of the material used [6].

Among the materials that are used for adsorbents, natural clay is the best adsorbent due to its availability, low cost, efficient removal of pollutants from contaminated waste water and with no toxicity.

1.3. Objectives of the Study

1.3.1.General Objective

The main objective of this study is to investigate the potential adsorption capacity of local clay for the removal of NH_3-N, NO_3-N, PO_4-P and H_2S from brewery waste water.

1.3.2.Specific Objectives

The specific objectives of the study are:

- To study the adsorption capacity of local clay towards inorganic pollutants,
- To investigate the effects of different parameters such as pH, temperature, particle size, dosage of adsorbent, initial concentration of adsorbate and contact time on adsorption efficiency and removal capacity of local clay,
- To find the model that best fits with the adsorption process,
- To prepare the adsorbent(local clay) properly,.

1.4. Significance of the Study

The major motive for the removal of inorganic pollutants of brewery waste water are to make free the surrounding environment and to reduce their effect on human health due to direct exposure. The final out come of the study will benefit the surrounding society, the brewery and other industrial sectors due to the use of cheap, effective and easily operable technique to treat the contaminated waste before discharge.

For many industrial sectors including coal mining, fertilizer producers and gas and coke manufacturing industries that discharge ammonium ion, nitrite and hydrogen sulfide can be easily apply clay as adsorbent for the removal of these pollutants.

2. LITERATURE REVIEW

2.1. Source of Inorganic Pollutants in Wastewater

Environmental pollutants arise from a variety of sources that are constituent parts of the pollution process. The sources of the actual causative agents of environmental pollution can occur in gaseous, liquid, or solid form. The contamination of the environment by inorganic chemicals can occur from several process sources, and the effects of the chemical on the environment are determined by the chemical and physical properties of the chemical. Most toxic pollutants originate from human-made sources, such as mobile sources (such as cars, trucks, and buses) and stationary sources (such as factories, refineries, and power plants), as well as indoor sources (such as building materials and activities such as cleaning) [8].

Table 1. Examples of Inorganic Pollutants(8)

Pollutant	**Formula**	**Sources**	**Polluted Medium**
Sulfur dioxide	SO_2	Volcanoes, industry, vehicles	air
Nitrogen dioxide	NO_2	Volcanoes, Industry, Transports	Air
Carbon monoxide	CO	Transports	Air
Ammonia	NH_3	Industry, Agriculture	Air, soil
Hydrogen sulfide	H_2S	Industry, Anaerobic fermentation	Water, Soil,
Hydrogen chloride	HCl	Industry, Transports	Air
Hydrogen fluoride	HF	Industry	Air
Ammonium salts	$NH_4{}^+$	Farms, factories	Soil, water
Nitrate salts	NO_3	Farms, factories	Soil, water
Nitrite salts	NO_2	Farms, factories	Soil, water
Lead salts	Pb	Heavy industry Transports	Air
Mercury salts	Hg	Industry	Soil, water
Zinc salts	Zn	Industry	Air, water

2.1.1.Environmental Impacts of Inorganic Pollutants

Most important inorganic pollutants are trans boundary in so far as they do not recognize boundaries. In addition, many inorganic pollutants cannot be degraded by living organisms and therefore stay in the ecosphere for many years, even decades.

Inorganic pollutants also destroy biota and the habitat, and because of this, it is emphasized that inorganic pollutants can brought a serious long term global problem that affects more or less every country and, therefore, can only be solved by a coordinated set of actions and the necessary commitment of nations of the Earth (with no exceptions) to international environmental agreements [9].

An increase in the environmental availability of inorganic nitrogen usually boosts life production, firstly increasing the abundance of primary producers. However, high levels of inorganic nitrogen that cannot be assimilated by the functioning of ecological systems (i.e., N saturated ecosystems) can cause adverse effects on the least tolerant organisms [10].

Ammonium (NH_4^+), nitrite (NO_2^-) and nitrate (NO_3^-) are the most common ionic (reactive) forms of dissolved inorganic nitrogen in aquatic ecosystems. These ions can be present naturally as a result of atmospheric deposition, surface and groundwater runoff, dissolution of nitrogen-rich geological deposits, N_2 fixation by certain prokaryotes (cyanobacteria with heterocysts, in particular), and biological degradation of organic matter. Consequently, in addition to natural sources, inorganic nitrogen can enter aquatic ecosystems via point and non point sources derived from human activities [11,12].

High levels of ammonia, nitrite and nitrate, derived from human activities, can impair the ability of aquatic animals to survive, grow and reproduce, resulting in direct (acute or chronic) toxicity of these inorganic nitrogenous compounds [13].

High levels of nitrite in water is a potential factor triggering stress and cause high mortality in aquatic organisms. Environmental increase in nitrite impairs the function of several aquatic species. Aquatic animals are more toxic towards nitrite in toxication because nitrite in the ambient water, taken up across gill epithelium and accumulated to very high concentrations in the fish body fluids. Nitrite induced shortage of O_2 results in high stress levels leading to hyperventilation, elevated heart rate, and increased blood pressure in fish [14].

Another effect of the accumulation of nitrogen and phosphorus on the environment is occurrence of eutrophication. Where excess carbon is produced and accumulates, secondary effects of eutrophication often occur such as noxious algal blooms (including some toxic ones), decreased water clarity, and low dissolved oxygen. The ultimate symptom is a loss or degradation of habitat with consequences to marine biodiversity and changes in ecosystem structure and function, such as cycling of elements and processing of pollutants. Eutrophication is the increased accumulation of organic matter, usually as a result of increased nitrogen and phosphorus inputs, but could result from the supply of excessive decomposable organic carbon as well [15].

2.2. Characteristics of Brewery Waste Water

2.2.1. Description of Brewing Process

The brewing process uses malted barley and/or cereals, unmalted grains and sugar(corn syrups, adjuncts), hops, water, and yeast to produce beer. Most brewers in the world use malted barley as their principal raw material. Depending on the location of the brewery and incoming water quality, water is usually pretreated with a reverse osmosis, carbon filtration or other type of filtering system [16].

The brewing process which involves malting of grain, milling, mashing, wort cooling, fermentation, packaging, and pasteurization consume resources such as water, energy, grist materials, adjuncts and auxiliary materials such as Kieselguhr, bottles, cans, crown corks, glue, enzymes, antioxidants, foam stabilizers, colloidal stabilizers caustic soda and detergents for cleaning bottles and equipment [17].

Brewing is based on the standard of four processes of wort production,fermentation and maturation, beer processing and bottling. It is important to know the total consumption and discharge of organic load and waste water for environmental reasons [18].

The main water using areas of a typical brewery are brew house, cellars, packaging and general water use. Water use attributed to these areas includes all water used in the product, vessel washing, general washing and cleaning in place (CIP); which are of considerable importance both in terms of water intake and effluent produced [19].

2.2.2. Composition and Characteristics

Wastewater generated from beer manufacturing amounts to 65-70% of the water intake volume. The wastewater contains: maltose, dextrose, wort, trub, spent grains, yeast, filter slurry (Kieselguhr and lucilite), green beer and bright beer. Furthermore, brewery wastewater contains nutrients, nitrogen and phosphorus, which can result in adverse environmental impacts. Nitrogen primarily comes from malt, adjuncts and nitric acid used for cleaning [20].

Discharge of yeast also contributes to the amount of nitrogen in the wastewater. Phosphorus, which comes from cleaning agents, is usually found in concentrations ranging from 30-100 mg/l depending on water ratio and cleaning agents used [21].

2.3. Environmental Impacts of Brewery Wastewater

Untreated wastes from processing factories located in cities are discharged into inland water bodies resulting in stench, discolouration and a greasy oily nature of such water bodies. These wastes pose serious threat to associated environment including human health risks [22]. Industrial effluents contain toxic and hazardous materials from the wastes that settle in rivers as bottom sediments and constitute health hazards to the urban population that depend on the water as source of supply for domestic uses [23,24].

The primary environmental impacts that can be attributed to the production of beer are the result of noise, emissions to air, wastewater discharges and inefficient waste handling system. Potential adverse environmental problems that may be associated with the operation of these facilities include:[25]

Surface water pollution caused by the uncontrolled discharge of untreated wastewater can lead to depletion of dissolved oxygen in surface water and generation of noxious odors. Furthermore, wastewater may contain nutrients which stimulate aquatic plant growth and contribute to eutrophication.

Groundwater pollution results from leaking fuel and chemical storage tanks, and from the handling of fuel and chemicals around the facility can result in local groundwater pollution.

Occupational health and safety concerns tend to be related to exposure to excessive noise and contact with potentially dangerous substances or materials (such as ammonia, caustic and acid).

2.4. Treatment Methods of Brewery Wastewater

2.4.1. Wastewater Treatment Methods

Brewing industries are one of the major industrial users of water. The high organic content of brewery effluent classifies it as a very high strength waste in terms of chemical oxygen demand, from 1000 mg/L to 4000 mg/L and biochemical oxygen demand of up to 1500 mg/L. The treatment of brewery wastewater effluent is a costly task for the brewer in order to meet the government regulations and to practice environmentally friendly manufacturing [26]. The untreated effluent discharge from these industries is colored and highly intoxicating due to presence of alcohol and can be toxic to aquatic life in receiving waters, hence the need for the treatment of brewery wastewater effluent before being discharged into water courses. However, the current problems in water and wastewater treatment stem from the increasing pollution of waters by organic compounds that are difficult to decompose biologically because these substances resist the self purification capabilities of the rivers as well as decomposition in conventional wastewater treatment plants. Consequently, conventional mechanical-biological purification no longer suffices and must be supplemented by an additional stage of processing [27].

The effluent requirements for direct discharge to surface waters are set by the EEPA and World Bank as in the following way:

Table 2. Brewery effluent requirements for direct discharge to surface waters [19].

Parameters	Amount
PH	6-9
BOD_5(mg/L)	50
COD (mg/L)	<250
TSS (mg/L)	50
P (mg/L)	5
Ammonia nitrogen (NH_3-N) (mg/L)	10
Temperature (^oC)	≤ 30

To meet the above requirements the brewery waste discharge must be treated using different techniques. These treatment methods are; Physical, chemical and biological treatment processes.

1) Physical Treatment Processes

Among the first treatment methods used are physical unit operations, in which physical forces are applied to remove contaminants. Physical methods remove coarse solid matter, rather than dissolved pollutants. It may be a passive process, such as sedimentation to allow suspended pollutants to settle out or float to the top naturally. In general, these methods have yielded little success; most often resulting in incomplete contaminant removal and/or separation. Sedimentation has been found to be unsatisfactory even with the addition of coagulants and other additives [28].

2) Chemical Treatment Processes

Chemical pretreatment may involve pH adjustment or coagulation and flocculation. The acidity or alkalinity of wastewater affects both wastewater treatment and the environment. Low pH indicates increasing acidity while a high pH indicates increasing alkalinity. The pH of wastewater needs to remain between 6 and 9 to protect organisms. Waste CO_2 may be used to neutralize caustic effluents from clean-in-places (CIP) systems and bottle washers [29]. The waste CO_2 can also be used as a cheap acidifying agent for decreasing the pH of alkaline wastewaters before the anaerobic reactor, thus replacing the conventionally used acids.

Coagulation and flocculation are physicochemical processes commonly used for the removal of colloidal material or color from water and wastewater. In water and wastewater treatment, coagulation implies the step where particles are destabilized by a coagulant, and this may include the formation of small aggregates by Brownian motion. On the other hand, the subsequent process in which larger aggregates (flocs) are formed by the action of shear is then known as flocculation [30]. After small particles have formed larger aggregates, colloidal material can then be more easily removed by physical separation processes such as sedimentation, flotation, and filtration [30].

3) Biological Treatment Processes

It is based on the activity of a wide range of microorganisms,converting the biodegradable organic pollutants in the wastewaters. Brewery effluents having both chemical (with very high organic content) and microbial contaminants are generally treated by biological methods [31]. After the brewery wastewater has undergone physical and chemical pretreatments, the wastewater can then subjected to biological treatment. Compared to physicochemical or chemical methods, biological methods have three advantages: (1) the treatment technology is mature, (2) high efficiency in COD and BOD removal, ranging from 80 to 90%, and (3) low investment cost. However, though biological treatment processes are particularly effective for wastewater treatment, they require a high energy input [32].

Biological treatment of wastewater can be either aerobic (with air/oxygen supply) or anaerobic (without oxygen). Generally, aerobic treatment has successfully been applied for the treatment of brewery wastewater and recently anaerobic systems have become an attractive option [33].

Because the conventional method of beer brewery wastewater treatment is based on biological methods, it naturally leads to longer hydraulic retention time and is subject to failures due to shock loading and improper maintenance. Moreover, the biodegradation of flavonoids present in the brewery requires specific bacterial strains to achieve higher removal efficiencies [34].

a) **Aerobic Process:**

Conventional activated sludge treatment of wastes is often an effective and economically viable system for reducing organic pollutants in wastewater. Reductions of BOD & COD content of wastewaters following aerobic treatment [35].

Aerobic biological treatment is performed in the presence of oxygen by aerobic microorganisms(principally bacteria) that metabolize the organic matter in the wastewater, thereby producing more microorganisms and inorganic end-products (principally CO_2, NH_3, and H_2O). Aerobic treatment utilizes biological treatment processes, in which microorganisms convert nonsettleable solids to settle able solids [36].

The major limitations are that they produce a lot of sludge and are costly to operate. The main cost component being the aeration such limitation can be addressed by using anaerobic digesters [37].

b) Anaerobic treatment:

Anaerobic digestion constitutes an option to treat the brewery effluent. The anaerobic treatment system does not produce biological sludge is a key factor, as well as its ability to reduce chemical and biological oxygen demand (COD, BOD) and suspended solids at low hydraulic retention time. Up flow anaerobic sludge blanket (UASB) treats brewery organic wastewater with high efficiency in a sludge granular bed containing self-coagulated particles of anaerobic microorganisms as bio-catalysts [38]. Anaerobic wastewater treatment is the biological treatment of wastewater without the use of air or elemental oxygen. Anaerobic treatment is characterized by biological conversion of organic compounds by anaerobic microorganisms into biogas which can be used as a fuel-mainly methane 55-75 vol% and carbon dioxide 25-40 vol% with traces of hydrogen sulfide. In the Upflow Anaerobic Sludge Blanket (UASB) reactor, the wastewater flows in an upward mode through a dense bed of anaerobic sludge [36].

For large scale breweries with existing wastewater treatment on-site, conventional treatment methods have been employed anaerobic reactors (UASB) and activated sludge systems. These treatment systems generally do not lead to recycling of important nutrients in the waste, but instead produce relatively large quantities of low-value sludge and create disposal problems [37].

a) Ammonium Removal: Ammonia has a hazardous and toxic effect on human health and biotic resources also, only if the intake becomes higher than the capacity to detoxify and predefined permissible limits. Ion-exchange process has been used in various fields in recent years, including the ammonium ions removal from wastewater due to their many unique properties, such as high treatment capacity, high removal efficiency, low cost and fast kinetics. Natural adsorbent such as natural clays are one of the considerable and applicable adsorbents due to their low-cost, availabilities and easy applications in the removal of ammonia contaminants from environment [38].

ammonium nitrogen (NH_4-N) is a very common chemical form in aquatic ecosystems and its toxic effect on life is very high. Total removal or at least a significant reduction of NH_4^+-N is thus very important prior to disposal into streams, lakes, seas and land surface. Up to now, the main treatment methods to remove/reduce NH_4^+-N involve reverse osmosis, biological nitrification, denitrification, air stripping, chemical treatment, ion-exchange and super critical water oxidation. The easy operation technology, low energy input & cost, high safety makes the adsorption process a superior solution for ammonium stripping from aqueous systems.

Natural adsorbent such as natural clays are one of the considerable and applicable adsorbents due to their low-cost, availabilities and easy applications in the removal of ammonia contaminants from environment [39]. P.V. Haseena et al. Showed that the removal of ammonia nitrogen using chitosan bentonite film composite was effective. Bentonite has been used for the removal of various hazardous substances from water or wastewater [40].

b) Phosphorus Removal:

phosphorus is an impactful limiting element, which causes eutrophication in water bodies, ultimately leading to water degradation and demise of aquatic plants, animals together with other living microorganisms. The common forms of phosphorus present in aqueous solutions are orthophosphate, polyphosphate and organic phosphate They fall into three main categories: biological, chemical, and physical. Physical methods such as reverse osmosis and electrodialysis are too expensive, whereas others are ineffective, reaching only 10% removal efficiency. Enhanced biological treatment method can achieve 97% removal of total phosphorus, but operational difficulties make it unstable. Chemical techniques are the most effective and well-studied methods, including phosphate precipitation with different salts such as calcium and aluminium. However, the use of salts increases the costs, and the amount of sludge generated; therefore, this method has not been applied widely. Besides, phosphorus precipitation by metal salts makes the precipitate unrecoverable for potential processing into fertilizer .Another chemical technique, adsorption, has proven to be economical because the only cost associated with the adsorbents is transportation. Moreover, there is no sludge generated from the process [41].

c) Removal of H_2S:

The hydrogen sulfide in biogas stream stands as extremely toxic gas which causes corrosion, erosion, fouling for metal devices such as, cooking stoves, biogas plants and steam turbines. The presence of H_2S in combustion process results in formation of sulfur dioxide which is harmful for environment, and injurious for human and animal health as it causes irritation of mucous membranes, headaches, dizziness, nausea and sudden death. For these motives, substantial attention has been paid to removal of H_2S from industrial waste [42].

Few studies have proposed the utilization of waste ashes (coal ash, biomass ash), kaolin and modified crude clay, Penausende muscovite, laterite, montmorillonite , which are economically feasible for CO_2 and H_2S removal [43].

The removal techniques of H_2S from water include aeration, ion exchange, reverse osmosis, ozonation and chemical treatments. However, removal of H_2S by aeration is not necessarily ideal for all situations. It requires an acidic pH, long contact times and, by proxy, a high energy input. H_2S is difficult to remove in alkaline water because most of H_2S is present in the form of HS^- and H^+ ions. Both ion exchange and reverse osmosis are complicated and do not produce the desired results. Ozone oxidation of H_2S is very effective treatment but it is very costly to set up a treatment facility [44].

2.4.2. Inorganic Pollutant Removal Methods

There are different treatment systems available for the removal of hazardous inorganic chemicals that migrate to the environment, including, chemical coagulation, sedimentation, photochemical degradation, oxidation and adsorption. Because of the high cost, many of these conventional methods have not been widely applied at large scale [45,46,47].

1) **Biological processes:** This process do not always provide satisfactory results and partial elimination of inorganic nutrient is achieved, since many of the organic substances produced by the chemical industry are toxic or resistant to biological treatment.

2) **Chemical oxidation:** is generally expensive because the sludge formed during treatment tends to be more resistant to complete chemical degradation, and furthermore, they all consume energy and reagents. Advanced Oxidation Processes,

are among the most widely used technologies for industrial effluent treatment of water polluted by organic compounds characterized by their low biodegradability; complete mineralization of the organic contaminant can be achieved but their operational cost is relatively high. Capable of treating multiple analytes in a single step. Accelerating removal of pollutants via solar, UV Vis rays or ultrasonic radiation. Its weakness is formation of by products (chlorine or hypochlorite) and needs high energy costs for large scaling processes. Extra energy sources (solar, UV-Vis rays or ultrasonic).

3)Membrane technologies: Operated without phase changes or chemical conditioning. Low energy consumption. Its limitation is its short lifetime of membranes and process productivity. Huge volume of concentrate (which require further treatments) [48].

4) Fenton process: High removal rates of organic and inorganic, biodegradable and non biodegradable pollutants, ease of handling and low operational cost. Its limitation is production of residual sludge and requires large usage of chemical reagents.

Conventional removal of inorganic pollutants is done by ion exchange, solvent extraction, reverse osmosis, electrodialysis, precipitation, flocculation and membrane separation processes. However adsorption compared with other methods appears to be an attractive process due to its efficiency, cost effectiveness and the ease with which it can be applied in the management of inorganic pollutants containing wastewater. In recent years, a number of adsorptive materials, such as living and dead plants, microorganisms, agricultural and industrial by-products etc. were used in removal of inorganic pollutants from waste water [49].

2.5. Adsorption Process

Adsorption is the process by which a solid adsorbent can attract a component in water to its surface and form an attachment via a physical or chemical bond, thus removing the component from the fluid phase. The advantages of adsorption process are simplicity in operation, inexpensive compared to other separation methods and no sludge formation [50]. The adsorption process is generally classified as either; physisorption (physical adsorption), or chemisorption (chemical adsorption).

a) Physisorption (physical adsorption)

Adsorption in which the forces involved are intermolecular forces (van der Waals forces) of the same kind as those responsible for the imperfection of real gases and the condensation vapours, and which do not involve a significant change in the electronic orbital patterns of the species involved [51]. Physical adsorption is generally a multilayer process, not limited by the available solid surface area, reversible, more rapid, occurs on almost all solid surface.

b) Chemisorption (chemical adsorption)

Chemisorption (or chemical adsorption*)* is adsorption in which the forces involved are valence forces of the same kind as those operating in the formation of chemical compounds [51]. Chemisorption limited to the formation of a mono molecular adsorbed layer, has some activation energy, much slower than physical adsorption, may not be reversible.

2.5.1. Types of Adsorbents

There are different kinds of adsorbents for different adsorption purposes. The most known adsorbent are activated carbon, silica gel, clays, activated alumina and zeolites.

i) Activated Carbon

AC is a tasteless, solid, microcrystalline, non graphitic form of black carbonaceous material with a porous structure. ACs have a very porous structure with a large internal surface area ranging from 500 to 3895 m^2 g^{-1}, and making them versatile adsorbents with a wide range of applications [52]. The efficiency of any AC to absorb the targeted compounds (colour, ash, colloids) depends on several factors,such as carbon's porosity, surface area, pore size distribution, bulk density, surface chemistry, hardness, pH, particle size and density, amount of water-soluble minerals and its total ash content. Commercial production of AC depends on using raw materials, such as wood, refinery residuals, peat, coal (bituminous, sub bituminous, lignite and anthracite), coke, pitches, carbon blacks and nutshells [53]. The ACs from agricultural by products have the advantage of offering an effective, low cost and available replacement for the non-renewable coal based granular activated carbons (GACs), where they have similar or better adsorption efficiency [54].

ii) Activated alumina

Activated alumina is a filter media made by treating aluminium ore so that it becomes porous and highly adsorptive. It can also be described as a granulated form of aluminium oxide. Activated alumina removes a variety of contaminants that often co-exist with fluoride such as excessive arsenic and selenium. The medium requires periodic cleaning with an appropriate regenerate such as alum or acid in order to remain effective. Activated alumina has been used as an effective adsorbent especially for point of use applications. The main disadvantage of activated alumina is that the adsorption efficiency is highest only at low pH and contaminants like arsenites must be preoxidized to arsenates before adsorption. In addition, the use of other treatment methods would be necessary to reduce levels of other contaminants of health concern for the non-renewable coal-based granular activated carbons (GACs), where they have similar or better adsorption efficiency [55].

iii) Zeolite

Zeolites are highly porous aluminosilicates with different cavity structures that consist of a three dimensional framework and a negatively charged lattice. The negative charge is balanced by cations which are exchangeable with certain cations in solutions. High ion-exchange capacity and relatively high specific surface areas, and more importantly their relatively low prices, make zeolites attractive adsorbents [56].

Zeolites are three dimensional micro porous ,crystalline solid with well defined structures which contain aluminum, silicon and oxygen in their regular framework. Since they have pore size of several angstroms, zeolites are able to separate components of a mixture on the basis of a difference in molecular size (i.e. molecular sieving effect). The zeolite pore size is mainly determined by its unique structure, but it can also be affected by zeolite composition. In addition to the molecular sieving effect, zeolitic hydrophilic or hydrophobic nature is also a very important attribute of zeolites for prevaporation. Zeolite hydrophilic/hydrophobic property mainly depends on the Si/Al ratio, i.e., zeolitic hydrophilic property increases as the aluminum content in the zeolite framework increases and vice versa [57].

iv) Silica gel

Silica gel is a controlled dehydrated polymeric structure made from the coagulation of a colloidal solution of silicic acid with the formula $SiO_{2n}H_2O$. This amorphous material consists of spherical particles 2-20 nm in size, sticking together to form the adsorbent silica gel. This adsorbent is used in most industries for water removal due to its strong hydrophilicity of the silica gel surface towards water. Some of the applications of silica gel are: water removal from air, drying of non reactive gases, drying of reactive gases, adsorption of hydrogen sulfide, oil vapor adsorption and □ adsorption of alcohols [58].

2.5.2. Mechanisms of Adsorption

Due to the higher affinity of the adsorbent for the adsorbate species, the latter is attracted and bound there by different mechanisms. The process continues till equilibrium is established between the amount of solid-bound adsorbate species and its portion remaining in the solution. The degree of adsorbent affinity for the adsorbate determines its distribution between the solid and liquid phases. The adsorption process of the adsorbate molecules from the bulk liquid phase into the solid (adsorbent) phase is described by the following four steps:

1) The mass transfer of the adsorbate molecules across the external boundary layer toward the solid particle.

2) Adsorbate molecules are transported from the particle surface into the active sites by diffusion within the pore filled liquid and migrate along the solid surface of the pore.

3) Solute molecule adsorption on the active sites on the interior surfaces of the pores.

4) The molecule gets approached inside the pores of the adsorbent [59]. In general, the adsorbate transport occurs in the following steps. The first step involves the external diffusion (the substrates diffuse from the bulk solution to the external surface of the adsorbent), the second step was due to the transport of the solute across the boundary layer, and the third step involves transfer of compounds in the pores to the internal parts of the adsorbent and finally uptake of molecules by the active sites, and the fourth step involves adsorption and desorption of adsorbate [60]. Adsorption capacity depends on the physical and chemical characteristics of both the adsorbent and adsorbate, concentration of the adsorbate in liquid solution, experimental conditions such as temperature and solution pH, and the amount of time the adsorbate is in contact with the adsorbent (residence time) [50].

2.5.3. Factors Affecting Adsorption process

Because of the chemical structure of the adsorbate is quite varied, the adsorbate ability of interaction with microorganism depends on a number of factors such as the chemical structure, the characteristics of waste water or adsorbent structural specificity [61]. Other factors such as pH,temperature,ionic strength,adsorbent dose, adsorbent particle size etc.

1) Effect of pH:

pH is considered an important parameter in adsorption studies as it controls the adsorption at the adsorbent solution interface. It affects both the adsorbent and the adsorbate present in the solution [62].

Adsorbents can be viewed as natural ion-exchange materials that primarily contain weakly acidic and basic groups. The uptakes of adsorbate by most biomass types decrease dramatically as the pH of the adsorbate solutions decreases from pH 6.0 to 2.5 [63].

2) Effect of contact time

The rate of adsorption is higher at the early stage, due to a large available surface area of the adsorbent and presence of abundant active sites on the surface. The fast initial uptake is also due to the rapid accumulation of the adsorbate on the surface of the adsorbent. As these sites become exhausted or saturated with time, the sorption rate also decreases .The removal rate of adsorbate also increases with an increase in contact time [64].

3) Effect of Temperature

Many literature showed that when the temperature increased the adsorption capacity also increased. Therefore, higher temperature facilitated the adsorption. Thermodynamic parameters such as the free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS), can be evaluated from the variation of the thermodynamic equilibrium constant, K_o, with temperature [65]. The magnitude of ΔG, increased with increasing temperature, revealing that the degree of spontaneity increased at higher temperatures. The positive values of ΔS reflect an increased degree of disorderliness at the solid/liquid interface during the adsorption process [66].

Temperature also plays an important role in the adsorption of heavy metals. It has two major effects on the adsorption process. Increasing the temperature will also increase the rate of adsorbate diffusion across the external boundary layer and in the internal pores of the adsorbate particles, because liquid viscosity decreases as temperature increases. It also affects the equilibrium capacity of the adsorbate, depending on whether the process is exothermic or endothermic [61].

4) Effect of initial concentration of Adsorbate

The adsorption capacity of the adsorbent increased with increasing initial concentration of the adsorbate which can be attributed to an increase in electrostatic interactions involving sites of progressively lower affinity for the adsorbate up to the point of saturation [67]. Conversely, the percentage removal of the adsorbate decrease markedly with an increase in the initial concentration of the adsorbate. This phenomenon might be due to the rapid saturation of all adsorbate binding active sites of the adsorbent at a certain concentration of the adsorbate [68]. The adsorption process is highly dependent on initial concentration of adsorbate because at lower concentration, the ratio of the initial concentration of adsorbate to the available surface area is low (concentration /surface area) and subsequently the fraction adsorption of adsorbate increases. However, at higher concentration the availability of active sites for adsorption becomes less and hence the percentage removal of adsorbate decreases [69].

5) Effect of particle size

The particle size has an important role to play in the amount of the adsorbate adsorbed. with a decrease in the particle size, the amount of the adsorbate adsorbed also increases. The pore structure of the adsorbents affects the adsorption of the adsorbate in two ways: the size exclusion limits the adsorption of the adsorbates of a given size and shape (sieve effect), and the adsorption capacity may increase with the increase in the specific pore volume. The increase in the adsorption capacity is more significant for the increase in the surface area,through decrease in the particle size [68].

6) Effect of Adsorbent Dose

Removal efficiencies of adsorption increases with increase in adsorbent dose and reach a saturation level at higher doses for all adsorbents that can be related to an increase in contact surface area of adsorbent particles [70]. Adsorbent doses beyond the steady state do not improve adsorption due to availability of excess adsorption sites than that of sorbets, assuming that the number of adsorption sites per unit mass of adsorbents remains constant. At lower dosage of adsorbents, there are insufficient active sites that the adsorbate can easily occupy. However, at higher dosage, active adsorption sites are sufficiently available for the adsorbate to occupy [71].

2.6. Adsorption Isotherm Models

Empirical models are simple mathematical relationships, characterized by a limited number of adjustable parameters,which give a good description of the experimental behavior over a large range of operating conditions. The model used to describe the results should be capable of predicting adsorbate binding at both low and high concentrations [72].

2.6.1. Freundlich Model

The first mathematical equation fits to an isotherm was published by Freundlich and Kuster in 1907. Freundlich showed that adsorption from solution could be expressed by empirical formula: $q_e =$ □ $KC_e^{1/n}$

Where *K* (mg/g) (l/mg) 1/n and *n* are Freundlich constants related to adsorption capacity and adsorption intensity respectively [73].

2.6.2. Langmuir Model

In 1918, Irving Langmuir published a new model isotherm for gas or liquid adsorbed on solid, which retained his name.The Langmuir adsorption model is valid for single layer adsorption. It is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, that the energy of adsorption is constant,and that there is no transmigration of adsorbate in the plane of the surface [74].

The Langmuir isotherm equation is: $qe = \dfrac{qmbCe}{1 + bCe}$

The Langmuir isotherm is used most frequently to describe the adsorption isotherm which is limited by the assumptions of uniform energies of adsorption on the surface of adsorbent. It is based on four assumptions [75].

- ✓ The surface of the adsorbents is uniform, that is, all the adsorption sites are equivalent.
- ✓ There is no interaction between molecules adsorbed on neighboring sites.
- ✓ All adsorption occurs through the same mechanism.
- ✓ Molecules are adsorbed at the define sites on the adsorbent surface.

The important characteristics of a Langmuir isotherm equation can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, *Rs,* which is defined by the following equation [76]: $Rs = \frac{1}{1 + bCo}$

The separation factor as described above was calculated using the Langmuir model constants. This separation factor yields the type of isotherm as Rs>1 unfavorable, Rs=0 linear, 0<Rs<1 favorable [77].

2.7. Kinetics of Adsorption Process

Kinetics studies provide the important information about the possible mechanism of adsorption that involves the diffusion (bulk, external, and intra particle) and chemical reactions [78]. Kinetic models can be chosen depends on the nature of adsorbent, type of solutes, and experimental conditions of the process.

Many different kinetic models have been used including zero order, first order or pseudo first order, second order or pseudo second order and third order to describe the kinetics of adsorption. Among these models the three models such as pseudo first order, pseudo second order, and Weber Morris intraparticle models are widely used [79].

The pseudo first-order linear Lagrange equation, describes the kinetics of the adsorption process as follows [80].

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t$$

Where q_e (mg/g) and q_t (mg/g) are the amount of adsorbate adsorbed at equilibrium and at *t* time respectively and k_1 is the rate constant of this first order model.

Pseudo second-order equation can be written in linear form as follows [81].

$$\frac{1}{qt} = \frac{1}{k2qe2} + \frac{t}{qe}$$

Where the slope and intercept of (t/q_t) versus t are used to calculate the pseudo second-order rate constant, k and adsorbate adsorbed at equilibrium, q_e. This model used to explain the probability of overall adsorption properties was suited to chemically adsorption mechanism. Chemically, adsorption process usually involves monolayer adsorption because of specific bonding between adsorbates and the surface of adsorbent [82].

The intraparticle diffusion model used to show the adsorptions are by intraparticle mixing. Linear equation for intraparticles diffusion model as follows;

$$q_t = k_i t^{1/2} + c$$

Where k_i is the intraparticle diffusion constant and c is intercept [83].

Dynamics of the adsorption process can further evaluated by using various diffusive models. These models are based on the assumption that the step that limit the rate of adsorption are related with diffusion of molecules: (a) transfer (diffusion) of the adsorbate molecules to the border film of the adsorbent, (b) diffusion of the molecules into the inside of the pores of the adsorbent, (c) binding of the molecules of the adsorbate to the active sites of the adsorbent. The Weber–Morris intraparticle diffusion model has been widely used to describe these three phases [84].

2.8. Thermodynamics of Adsorption Process

Adsorption is a spontaneous process with the change of the values of the thermodynamic functions [40]. In order to understand its mechanism such thermodynamic parameters can be calculated as: the change of free enthalpy (the Gibbs free energy) $\Delta G°$, change of enthalpy $\Delta H°$, and of entropy $\Delta S°$ [85].

$$\Delta G° = -RT\ln K_0$$

If the value of free enthalpy is known, then the spontaneity of the process can be

calculated: If $\Delta G<0$ the process develops spontaneously, If $\Delta G=0$ the system is in equilibrium. The calculation of $\Delta H°$ and $\Delta S°$ is possible due to the dependence described by: $\Delta G° = \Delta H^0 - T\Delta S^0$

The following equation shows the dependence between the equilibrium constant K_0, and ΔH° and ΔS°.

$$-RT\ln K_0 = \Delta H^0 - T\Delta S^0 \rightarrow \ln K_0 = -\Delta H^0/RT + \Delta S^0/R$$

The presentation of the dependence in the form of the graph $K_0=1/T$ facilitates the calculation of thermodynamic parameters.

The rate of adsorption depends on the temperature in which the process develops as described by the Arrhenius Eq.:

$$k = A\exp[-Ea/(RT)]$$

The logarithmic form of those equations allows for calculating activation energy. If its value is greater than 4–6 kJ mol^{-1}, it reveals the chemical mechanism of the binding of the sorbate (chemisorption). If Ea is smaller than 4 kJ mol^{-1}, sorption takes place as a result of weaker physical interactions [86].

2.9. Clay as an Adsorbent

Clays are among the cheapest, abundant, environmentally friendly, ion exchangeable and non-toxic adsorbents that can be used to substitute the expensive commercial activated carbon in tackling environmental pollution problems. Clays are composed of the octahedral (Al^{3+}, Fe^{2+}, Fe^{3+}, or Mg^{2+}) and tetrahedral (Si^{4+}) structures depending on the type of clay. Pillaring or basal plane spacing (001) is carried out to expand the silica layer of clay through intercalation of cations from common sources such as hydroxyl aluminum, iron, titanium, gallium, chromium and zirconium. Pillaring of clays helps in transforming them into micro porous and mesoporous materials and the pillars are stabilized through calcinations [87].

2.9.1. Structure and composition of Clay

A simple classifcation of clay minerals divided into four main groups: kaolinite group, illite group, smectite group, and vermiculite. Kaolinite group includes kaolinite, dickite, nacrite, and halloysite; formed by the decomposition of orthoclase feldspar (e.g. in granite). Illite group also includes hydrous micas, phengite, brammalite, celadonite, and glauconite (a green clay sand); formed by the decomposition of some micas and feldspars; predominant in marine clays and shales. Smectite group also includes montmorillonite, bentonite, nontronite, hectorite, saponite and sauconite [88].

The atomic structure consists of octahedral or alumina sheets and tetrahedral or silica sheets. The octahedral sheet is basically a combination of closely packed six hydroxyls or oxygen enclosing a metal atom (aluminum, magnesium, iron or other atom). The basic building block of all clay minerals is the same; they consist of two basic structures: the tetrahedral and octahedral sheets which are stacked together in certain ways. The variation of the basic structures makes the composition of major clay minerals (smectites, kaolin, palygorskite, sepiolite) is very different [89].

The structure and composition of smectite are different with kaolinite, therefore both of these clays possess different physical and chemical properties. Smectites are one of the largest and most important classes of the phyllosilicate clay mineral group. The Equidimensional smectite group includes sodium montmorillonite, calcium montmorillonite, beidellite (aluminum montmorillonite) and vermiculite, while elongate smectite includes nontronite (iron montmorillonite), saponite (magnesium Montmorillonite), and hectorite (lithium montmorillonite) [90].

2.9.2. General Uses of Clay

Bentonite clay, or Montmorillonite, is really just aged volcanic ash. Bentonite clay is amazing at absorbing toxins from the body. There are many benefit of bentonite to human being: Aides allergies; Helps with skin problems; Recovery from vomiting and diarrhea; Helps with acid reflux and bloating; Speeds healing of the skin; Offers immune system support; Cleanses toxic metals from the body; Removes fluoride; Absorb the effects of harmful chemicals etc. Some of the examples of bentonite clay uses to human health are provided. Bentonite clay has many use to humans to prepare the following such as, shampoo, deodorant, facial mask, toothpaste, detox bath, cuts & scraps,food poisoning, burns, bug bites and digestive issues [89].

Because of its great adsorbing capacity, now days modified bentonite based composite offer a fascinating alternative platform for use as adsorbents in wastewater remediation applications [88].

2.9.3. Adsorption of inorganic Pollutants on Clay

Bentonites clay offers an attractive and inexpensive option for the removal of inorganic and organic contaminants. Clay can remove approximately 70 % of the waste of water in a water removal system and the remaining 30 % can be removed using activated carbon. The fate and mobility of adsorbates are greatly affected by their strong interaction with natural clay and oxide minerals that are widely present in the natural environment [91]. Clays play an important role in the environment by acting as a natural scavenger of pollutants by taking up cations and anions either through ion exchange or adsorption or both. Thus, clays invariably contain exchangeable cations and anions held to the surface. The prominent cations and anions found on clay surface are Ca^{2+}, Mg^{2+}, H^+, K^+, NH_4^+, Na^+, SO_4^{2-}, Cl^-, PO_4^{3-}, and NO_3^-. These ions can be exchanged with other ions relatively easily without affecting the clay mineral structure [92]. The principal use of adsorbent clays is in decolorizing oils. Special uses are in insecticides and fungicides, fertilizers, water softeners, adsorbent carbon, ceramic materials, drilling muds, molding sands, cements, and as catalysts in cracking and reforming oil products [93].

3. MATERIALS AND METHODS

3.1. Materials and Equipment

The main raw material used for as an adsorbent during the experiment was local clay. The equipments used were UV Vis spectrophotometer(9100 UVVis, S/N20-1650-01-0421, AC 95-200/(50-60) Hz.150), pH meter (Mettler Toledo AG, S/N B510679227, Swizerland), Hach DR 900 colourimeter(), COD digester(DR200, S/N 16090co589, China), electronic balance, oven, different mesh size sieves, centrifuge

3.2. Chemicals and reagents

Analytical grade reagents used were 0.1N NaOH, 0.1N HCl, 89% phenol, 1M Na_2CO_3, 0.5M citrate and 2M NaCl, 30% H_2O_2, ammonium molybdate, ammonium meta vanadate, sodium nitroprusside, tri sodium citrate, sodium hypochlorite, nitricol and DPD oxalate photometer reagent, ethanol (95%) and distilled H_2O.

The experiment began on January 2019 until May 2019, a total of five months were spent for the laboratory work in Debrebrihan university and Dashen brewery. Ammonia and phosphate analysis were done in both Debrebirhan university chemistry laboratory and Dashen Brewery quality control laboratory, and nitrate and hydrogen sulfide analysis was done in Dashen brewery waste treatment laboratory. Real sample analysis were all done in Dashen brewery waste treatment and quality control laboratory.

3.3. Experimental Methods

3.3.1. Preparation of Local Clay

The adsorbent i.e local clay was collected from the district of ANKOBER,40km away from Debre Birhan. The adsorbent was dispersed in distilled water for 24hrs to remove impurities. After this, the dispersion was centrifuged for 30min at 3000 rpm. To eliminate organic and inorganic compounds, the washed clay was again dispersed in distilled water and heated to 80^oc in the presence of 1M Na_2CO_3, 0.5M citrate and 2M NaCl. Carbonates were removed by treating with 1M HCl and chlorides were removed by washing several times with distilled water. Organic compounds can be completely removed by 30% H_2O_2 at 70^oc. The purified clay was dried to 150^oc in an oven and the saturated with K^+.

The dried adsorbent was crushed using mortar and pistil. The grounded clay was sieved using different mesh size sieves such as 63µm, 90µm and 1mm and used for the analysis of different parameters of the adsorption process.

3.3.2. Adsorbent Characterization

1) X-Ray Diffraction (XRD):

XRD analysis is based on constructive interference of monochromatic X-rays and a crystalline sample were analyzed with an X’Celerator scintillation detector operating at 30 mA and 40 kV from 10^o to 80^o with a scanning rate of $h4^o.min^{-1}$. The analysis was done at Adama Science and Technology University.

2) FT-IR Analysis:

The vibrational behavior of the respective samples was examined by using Fourier transformer infrared spectroscopy(PEIR SUBTECH SPECTRUM ASCII PEDS), in the range 400-4000 cm^{-1} with resolution of 4 cm^{-1}, using FTIR spectrometer. The samples were analysed in powder form.

3.3.3. Preparation of Stock Solution

Standard ammonia solution, KH_2PO_4, KNO_3 and ZnS were used for the preparation of stock solutions. Stock ammonia (1000ppm) was prepared by taking 2ml of 25% ammonia solution in to 1000mL of distilled water. Stock KH_2PO_4 solution(50ppm) was prepared by dissolving 0.2195gm of KH_2PO_4 to 500ml distilled water and KNO_3 solution(1000ppm) was prepared by taking 3.6gm in to 500ml distilled water. Different working solutions were prepared from stock solutions by several dilutions at different concentrations. All chemical reagents were analytical grade reagents obtained from Dashen brewery quality department and local market in Addis Ababa.

3.3.4. Sampling and Characterization of Wastewater

Working solutions for calibration were prepared by serial dilution of the stock solution for each analyte. The initial and final concentrations of the analytes, in the filtrate were determined by using UV/VIS spectrophotometer at a wavelength of 400nm for phosphate and at 640nm for ammonia and the others were analyzed using Hach DR 900 photometer.

3.3.5. Batch Adsorption Experiment

In order to understand the adsorption behavior a number of batch studies were conducted to investigate the effect of adsorbent dose, contact time, pH, initial concentration, temperature and particle sizes.

Different concentration of the adsorbent were prepared starting from 2g, 5g, 7g, 9g and 11g to study the effect of dose of the adsorbent. The effect of pH was studied by varying the pH from 2-11 by adjusting HCl and NaOH. Initial adsorbate concentration of 1ppm, 5ppm, 10ppm, 15ppm, 20ppm, 25ppm, 30ppm and 40ppm, contact time (30-120 min) and temperature (30-80^{o}c) was studied. For each analysis 2 gram of adsorbent was employed. The filtrate was filtered using whatman filter paper. The analysis of the filtrate (i.e the amount of NH_3 and PO_4 left unadsorbed) were analyzed using UV-Vis spectrophotometer and NO_3 and H_2S was determined using Hach DR 900 photometer. The system is equilibrated by shaking at 200rpm and the contents of the flasks at room temperature so that adequate time of contact time between adsorbent and the adsorbate is maintained. All the analyses have been carried out according to the Standard Methods.

NH_3 analysis was conducted using phenate method by UV-Vis spectrophotometer at a wavelength of 640nm. PO_4 was determined by spectrophotometrically using vanado molybdate method. The adsorption capacity q_e was calculated as: $qe = \frac{(Co - Ce) \times V}{m}$, where qe adsorption capacity at equilibrium, V = volume of adsorbate solution (ml), m=mass of adsorbent(g), Co initial concentration in mg/L, Ce concentration at equilibrium (mg/L). The removal percentage (R %) is defined as the ratio of difference in adsorbate concentration before and after adsorption (Co–Ce) to the initial concentration of the adsorbate in aqueous solution (Co); $\%R = \left(\frac{Co - Ce}{Co}\right) \times 100$ [7]. The equilibrium adsorption isotherms of Langmuir and Freundlich isotherm models were studied and the fittest model was identified. The kinetics of the adsorption processes were studied using pseudo first order and pseudo second order rates of reaction. The thermodynamics of the adsorption process was also studied.

4. RESULT AND DISCUSSION

4.1. Characterization of Local Clay

4.1.1 XRD Analysis

XRD analysis of the raw sample of adsorbent local clay was achieved by X-ray diffraction in order to identify the main adsorbent minerals. The diffractogram of the adsorbent sample local clay in the following figure shows that this material is mostly composed of quartz with peaks located at 2θ angles:(19.86^0, 27.78^0, $35.01\ ^o$ and 61.87^o), confirms the presence of montmorillonite in the sample. cristobalite(22^o), hematite(24.25^o), quartz(23.74), feldspar(28.046), hematite(24.45 and 54.01) and other impurities present at an angle of 20.16^0, 20.38^0, 30.33^0, 33.22^0, 35.41^0, 35.63^0,

35.79^0, 42.21^0,, 61.87^0 and 62.22° this data is similar with the reported ones by different writers [94].

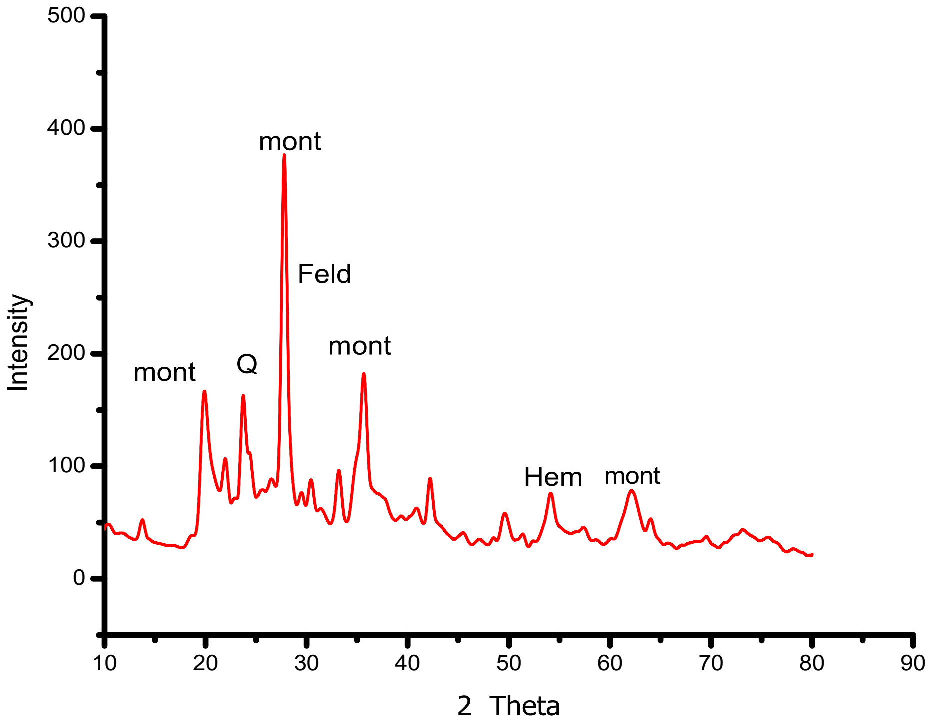


Fig. 1: XRD spectrum of adsorbent

4.1.2. FT-IR Analysis and Adsorption mechanism of Local Clay

The functional groups present on the adsorbent, local clay were characterized using PE IR subtech spectrum(Perkin Elmer). IR spectroscopy has significantly contributed to the understanding of the structure, bonding and reactivity of clay minerals. The examination for the IR spectra in the range 4000 - 400 cm^{-1} provides information on fundamental vibrational modes of the constituent units of these materials. The spectra of the samples show the presence of several functional groups. These spectra revealed a reduction, broadening, disappearance or appearance of new peaks after the process of adsorption. The shifts in the spectra revealed the effect of adsorption. The prominent bands after adsorption show that the prepared adsorbents will be effective in the removal of inorganic species. OH, stretching and bending vibrations occur in the spectral region of 3750-3500 cm^{-1}. The sharp band at 3426 shows O-H stretching which is similar with the reported. The spectral band at 3129 shows =C-H stretching, -C-H stretching, 1565 NH bending, 1398 organic sulfate stretching, 1178 shows CN stretching, 1037 shows Si-O stretching, 503 shows S-S stretching [95]. After the adsorption process takes place the spectral bands are different in some ways. The bands at 3635 cm-^{1} assigned non bonding O-H stretching and 3424 cm^{-1} and 1641cm^{-1} are H-O-H stretching and bending vibrations respectively, which fits within range reported at peaks 1620–1642 cm^{-1}, 1407 cm^{-1} indicates O-H bending primary alcohols or phenol, 1041 cm^{-1}and 538cm^{-1} shows stretching and bending of Si-O. 469 cm^{-1} shows Al-O bending or S-S stretching. Si-O and Al-O bending mode dominates in the range 600-400 cm^{-1} [96]. From the above information the local clay is similar with bentonite clay.

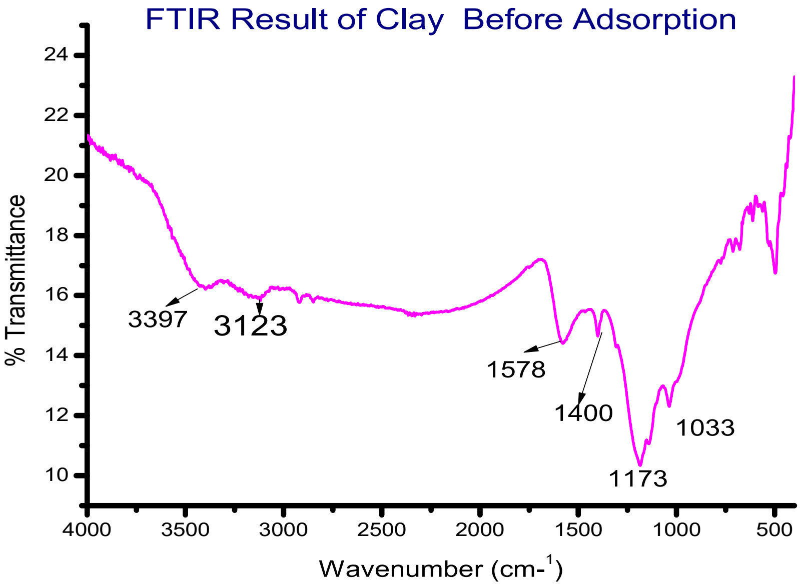


Fig.2. The IR spectra of clay before adsorption

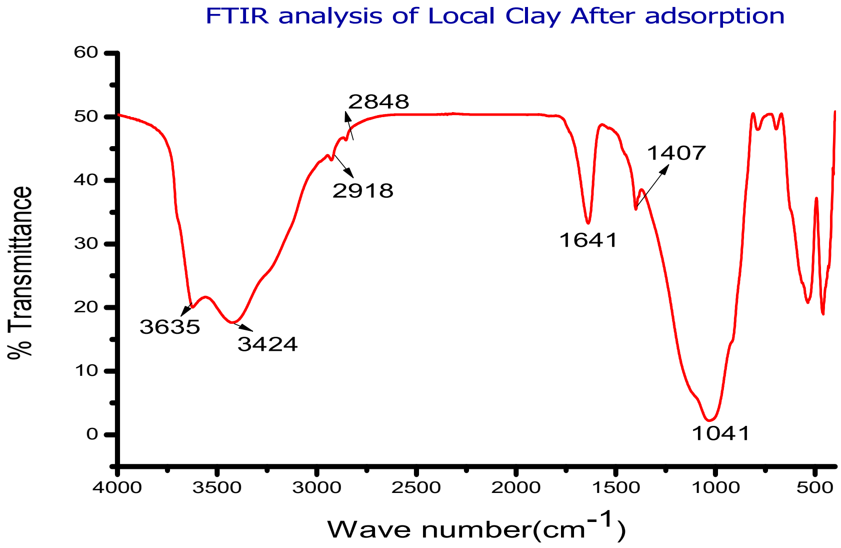


Fig.3. FT-IR spectra of local clay after adsorption

4.2. Effect of pH on Adsorption Process

pH of the solution is one of the most critical parameters that affect the chemical properties of absorbing and adsorbing surfaces. The solution pH would affect both aqueous chemistry and surface binding sites of the adsorbent [62].

The effect of pH on adsorption process of NH_3, PO_4^{3-}, NO_3^- and H_2S was studied in the range of 2-11. In the present study the effect of pH on the adsorption of ammonia showed increment as the pH increases and reached maximum from 32.64% to 98% at pH 7 , and decreases as the solution gets more basic. Solution pH affected equilibrium between the soluble NH_4^+ ions and dissolved molecular ammonia (NH_3) in water. In an acidic environment, ammonium was present as NH_4^+ [97]. The solution H^+ competed with NH_4^+ to adsorb on the clay, so that the adsorption of NH_4^+ ions on adsorbents decreased. When the pH increased to alkaline values, the nonvolatile NH_4^+ ion paired with OH^- in the solution, which led to the formation of molecular ammonia. As the number of exchangeable ions in the interlayer increased, the removal of ammonium increased. Thus the NH_4^+ adsorption was most favorable at neutral pH [97].

For PO_4^{3-} adsorption the effect of pH was studied starting from 2-11 and the adsorption increases as the pH increases from 2-5 and reached maximum value from 36.91% to 94.6% at pH 5 and slightly decreases as the solution becomes more basic due to the presence of more OH^- ions compete with phosphate ion for the available adsorption sites [98]. Similarly, NO_3^- maximum adsorption 96.24% takes place at pH 2 and decreases to 22% as the pH increases to 11. The pH of the solution is a very important parameter in the study of the adsorption of nitrate ions by clay. It is observed that the adsorption capacity qe reaches their maximum at pH 2 and decrease with the increase in pH. Usually, the influence of pH on anion exchange reaction was mainly due to the competition between the hydroxyl ions and anions. When pH of the solution increases, the surface becomes negatively charged and the adsorption capacity for nitrate decreases, because negatively charged surface sites on the adsorbent did not favor nitrate due to the electrostatic repulsion [99]. The maximum adsorption 86.72% for H_2S occurred at neutral pH (7). At low pH<3, H_2S exist as neutral H_2S and at pH 4-7 it exists as HS^- and H_2S, above pH >7 it exists as S^{2-}[100]. At high pH repulsion occurs with hydroxyl ions due to this adsorption decreases. The influence of pH on the adsorption of NH_3, PO_4^{3-} NO_3^- and H_2S is shown in the following Fig.4

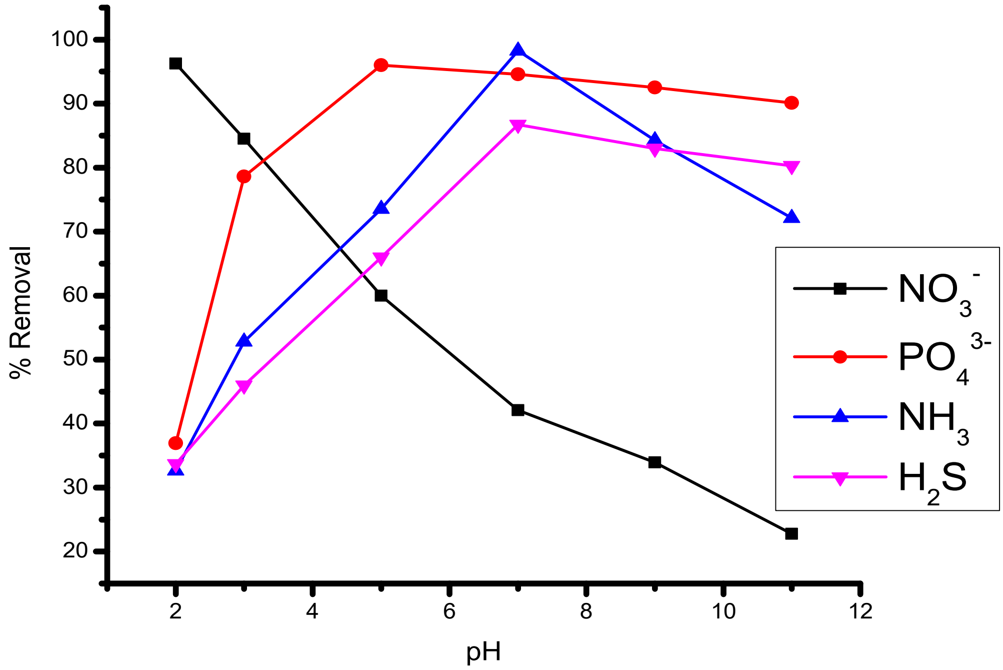


Fig. 4. Effect of pH on Adsorption of NO_3^-, PO_4,$^{-3}$ H_2S and NH_3

4.3. Effect of Adsorbent Dosage on Adsorption Process

The effect of dosage of clay on the adsorption of NO_3^-, PO_4^{3-}, H_2S and NH_3 increase with increase in dosage of adsorbent. This is due to as the adsorbent dose increases, the number of active sites for binding the adsorbate molecules on the adsorbent increases and thus more adsorbate was attached to their surface. Thus it results in the increment of adsorption efficiency until saturation [70].

The removal efficiency of NH_4^+ ions by local clay increases with increasing adsorbent dosage from 2 g to 11 g. It could be seen that the removal efficiency of NH_4^+ increases relatively rapidly when the adsorbent dosage increases from 2-7. This effect can be attributed to an increased number of active surface sites for the NH_4^+ adsorption thereby significantly enhancing the adsorption capacity. The adsorbent dose effect was investigated at room temperature for an initial concentration 30mg/l for each adsorbate with stirring at 200 rpm for 60 min. Figure 2 shows that the adsorption efficiency increases with increasing the adsorbent dose. The adsorption efficiency of NO_3^- increases from 30% to 91%, for PO_4^{3-} from 25.6% to 90.2%, for NH_3 from 22.72% to 92.61% .This can be explained by the increase in the number of active adsorption sites, and the availability of the adsorption sites increases the adsorption capacity. The adsorption yields vary from lower to higher percentage and better adsorption efficiency is observed for a concentration of adsorbent clay at 11g. But for H_2S the efficiency decreases from 98.4% to 54.16%. This may be due to as the initial stage of adsorption, the process is rapid so all the species may be adsorbed initially and as adsorbent dose increase more available active surfaces will be present.

For all H_2S, PO_4^{-3}, NO_3^- and NH_3 as adsorbent dosage increase, the removal efficiency increases. The result is shown in the following fig.2

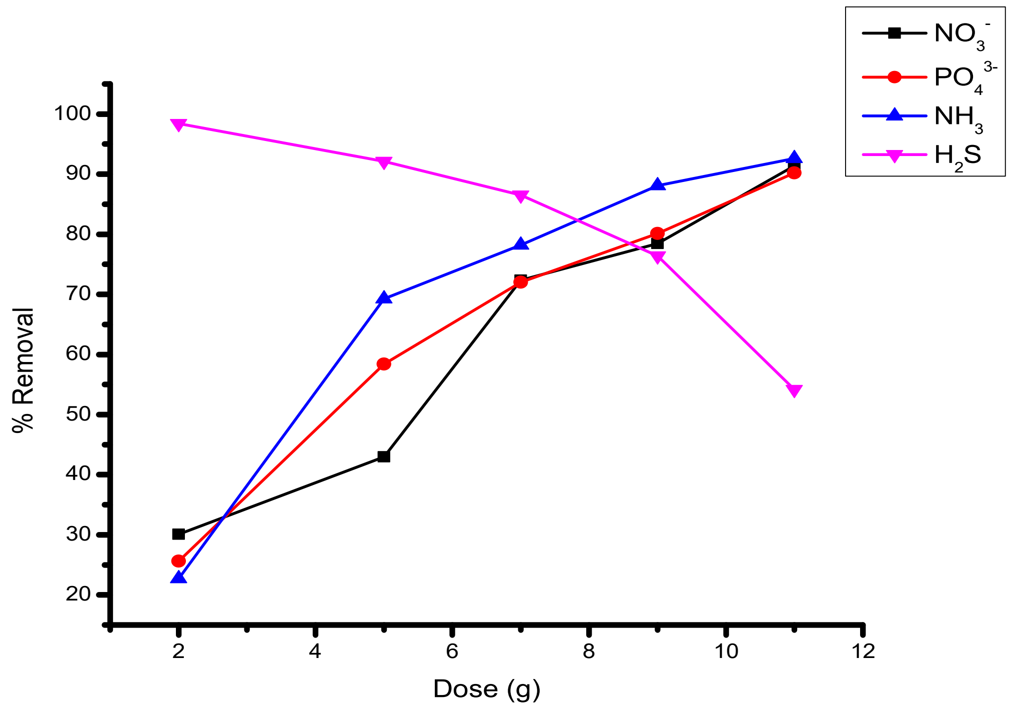


Fig. 5. Effect of adsorbent dose on Adsorption of Species on natural Clay

4.4. Effect of Initial Concentration of Adsorbate

The initial concentration of pollutant provides an important driving force to overcome all mass transfer resistance of the adsorbate between the aqueous and solid phases. Higher initial concentration results higher deriving force towards the pores and results higher adsorption capacity. The high adsorption at the initial concentration may be due to an increased number of vacant sites on the adsorbent available at the initial stage [101]. The initial concentration was conducted starting from 5, 10, 15, 20 and 25 ppm at 200rpm for 60min for all species and at their optimum pH. As the initial concentration increased, the removal efficiency of both phosphate and ammonia increased while the removal efficiency of NO^-_3 and H_2S decreased slightly. This may be due to the rapid saturation of vacant site for the adsorption of NO^-_3 and H_2S [101].

The results of effect of initial concentration is given in fig.6.

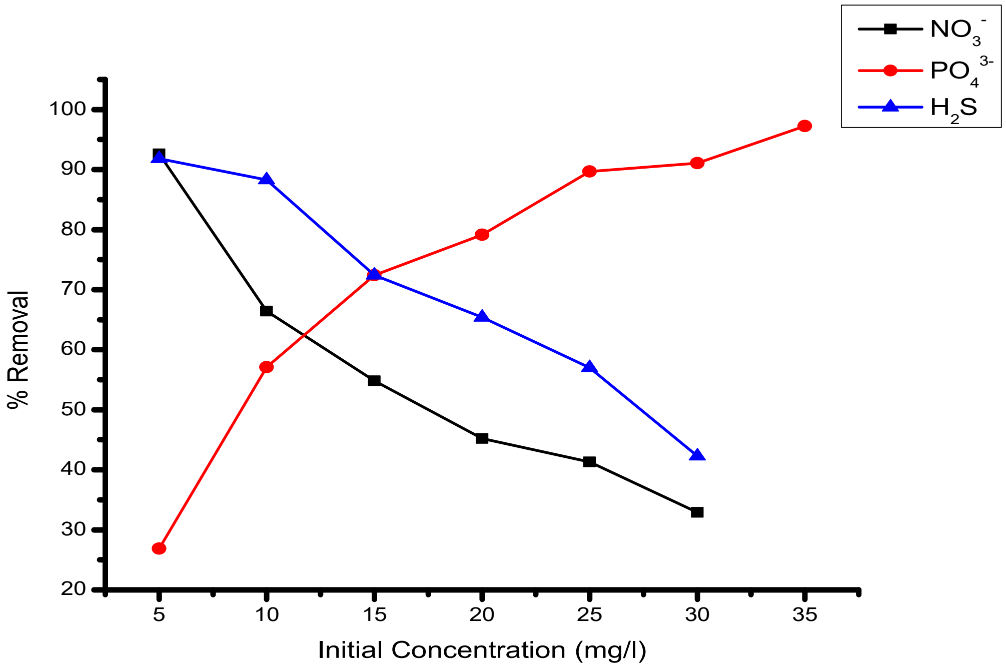


Fig.6. Effect of initial concentration on adsorption of NO_3^-, PO_4^{3-} and H_2S by clay

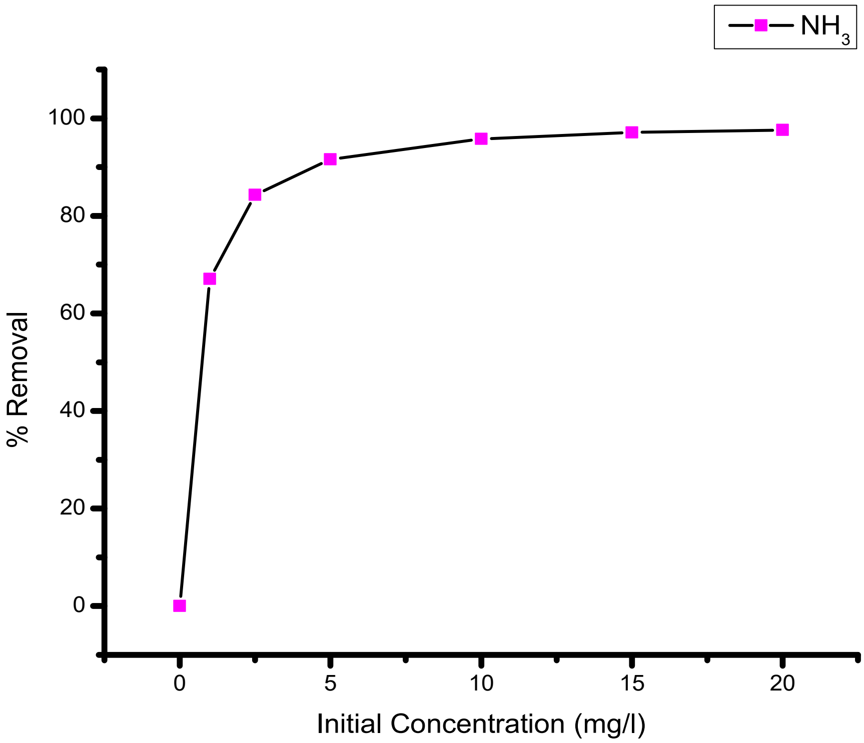


Fig.7. Effect of initial concentrations on adsorption of NH_3 on clay at 200rpm, T=25°C, t=60 min and pH 7

4.5. Effect of Contact Time

The contact time between adsorbate and adsorbent is one of the most important design parameters that affect the performance of adsorption processes. In the present study, the time variation was taken starting from 30, 60, 90 and 120 min. For the adsorption of ammonia the maximum adsorption percentage (88.68%) takes place at 60 min. This time is the saturation point for ammonia adsorption and further increase of time shows slightly constant.

The adsorption capacity of the nitrate ions increases with contact time and reaches a maximum value 96.58% at 90min. After 90min, the adsorption capacity decreases. This decrease can be explained by the saturation of the free adsorbent sites and may be due to an adsorbate release.

The maximum adsorption capacity of PO_4^{3-} and H_2S are 95.7% and 96.8% at 60 min and 30 min respectively. The result shows that H_2S adsorption is maximum at the initial stage of contact time and it becomes slightly decreasing. These may be due to the activity of functional groups on the surface of adsorbent. Large volumes of vacant site are available at the initial stages of adsorption and decreases as time goes on . This is due to the development of repulsive forces between the solute on the adsorbent and the solution[64].

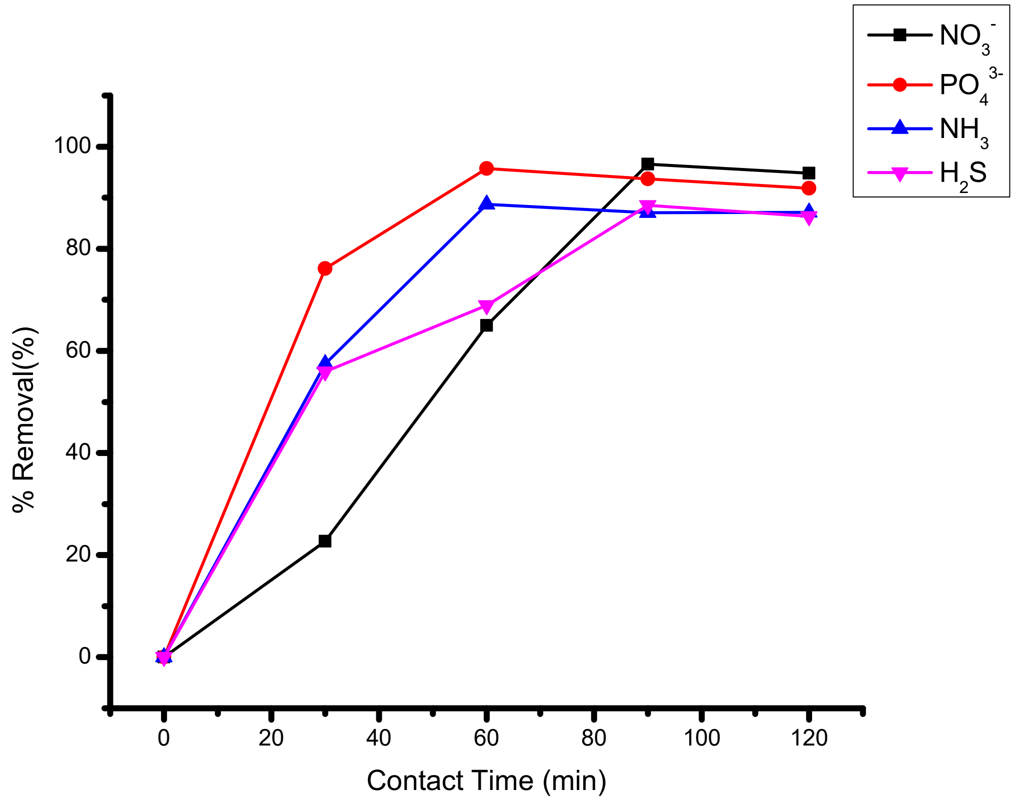


Fig. 8. Effect of contact time on the adsorption of NO_3^-, PO_4^{-3}, NH_3 and H_2S

4.6. Effect of Temperature

Temperature is an indicator for the adsorption nature whether it is an exothermic or endothermic process. The temperature range taken from 30, 45, 60, and 80°c for all species in this study.

In the present study the amount of ammonium removed onto solid surface increased from 65.4% to 90.6% with temperature increasing, since adsorption process is of a chemical nature (chemisorption). The H_2S adsorption increase with temperature and the adsorption capacity increase from 36.7% to 91.56%. The NO^-_3 adsorption increase from 38.8% to 87.96% the adsorption of PO_4^{3-} increase from 52.5% to 97.43% at their optimum pH, 60 min contact time and 200 rpm agitation speed. This shows that the adsorption process is an endothermic process. In such cases an increase of temperature can favour the reaction between the adsorbate and the adsorbent, thereby enhancing the capacity of adsorption [100].

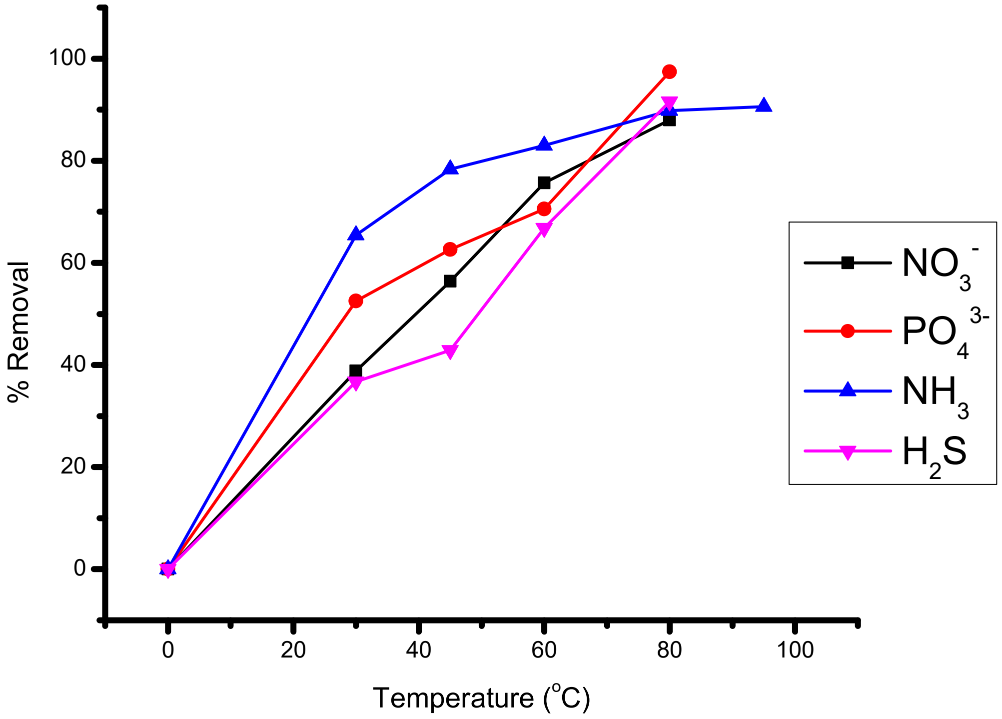


Fig.9. Effect of Temperature on NO_3^-, PO_4^{-3}, NH_3 and H_2S on natural clay

4.7. Effect of Particle Size

Particle size of adsorbent is another parameter that affects the adsorption process. The effect of particle size was studied using the 63µm , 90µm and 1mm sieve size at pH 2, 5, 7 and 7 for NO_3^-, PO_{4-}^{3}, NH_3 and H_2S respectively at t=60 min, agitation speed 200rpm and temperature at 30°c. As the particle size increases from 63µm to 90µm, the adsorption decreases as the particle size increases. This is due to small particle size has large surface area to accommodate more adsorbate species in all direction so adsorption becomes rapid and high amount of adsorbate will be adsorbed [68]. In the present study the effect of particle size was tested on adsorption of Ammonia and phosphate. These species showed the adsorption capacity was maximum at 63µm particle size and decrease at 90µm and further to 1mm . The amount of ammonia and phosphate adsorbed decreases from 99.98% to 98.99% and 99.18% to 94% as the particle size increases from 63µm to 1mm respectively.

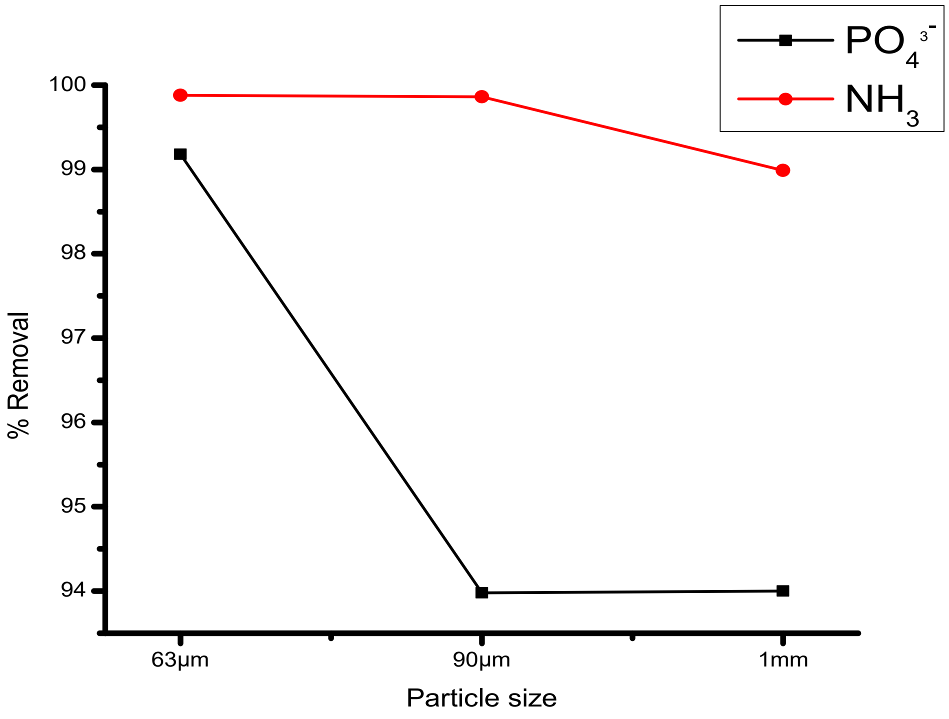


Fig.10. Effect of particle size on PO_4^{-3} and NH_3 adsorption

4.8. Adsorption Isotherms

Adsorption isotherms study can describe how an adsorbate interacts with the adsorbent. The isotherm provides a relationship between the concentration of adsorbate in solution and the amount of species adsorbed on the solid phase when both phases are in equilibrium [72].

The concentrations of NH_3, NO_3^-, PO_4^{3-} and H_2S in their equilibrium phase and that in the clay at a room temperature was studied to know the maximum adsorption capacity of the local clay for these species. To determine this maximum adsorption capacity of clay Langmuir and Freundlich isotherm models were used. Langmuir and Freundlich Isotherm Correlation coefficient and constants of the adsorption of these species on clay were obtained from the slope and intercept of the plot of amount of adsorbed species per unit mass, qe against equilibrium concentration of adsorbate remaining in solution Ce shown in Fig below. The different isotherm parameters from the different plots are given in Table 3 . The correlation coefficients (R^2) of Langmuir model for the adsorption of the NO_3^-, NH_3, PO_4^{3-}, and H_2S were 0.994, 0.941, 0.987, and 0.995, respectively, which were slightly higher for NO_3^- and H_2S than the R^2 values of

Freundlich model for the adsorption of PO_4^{3-} and NH_3, which is lower in Langmuir model. The result reveals that the adsorption of NO_3^- and H_2S is well fitted to the Langmuir model, this implies that the clay surfaces are homogeneous adsorption patches, on which monolayer coverage of the adsorbate were formed on the outer surface of the adsorbent i.e. clay. On the other hand, the adsorption of the adsorbate species NH_3 and PO_4^{3-} by clay is well fitted to Freundlich isotherm models with a correlation coefficient (R^2) of 0.956 and 0.999 respectively.

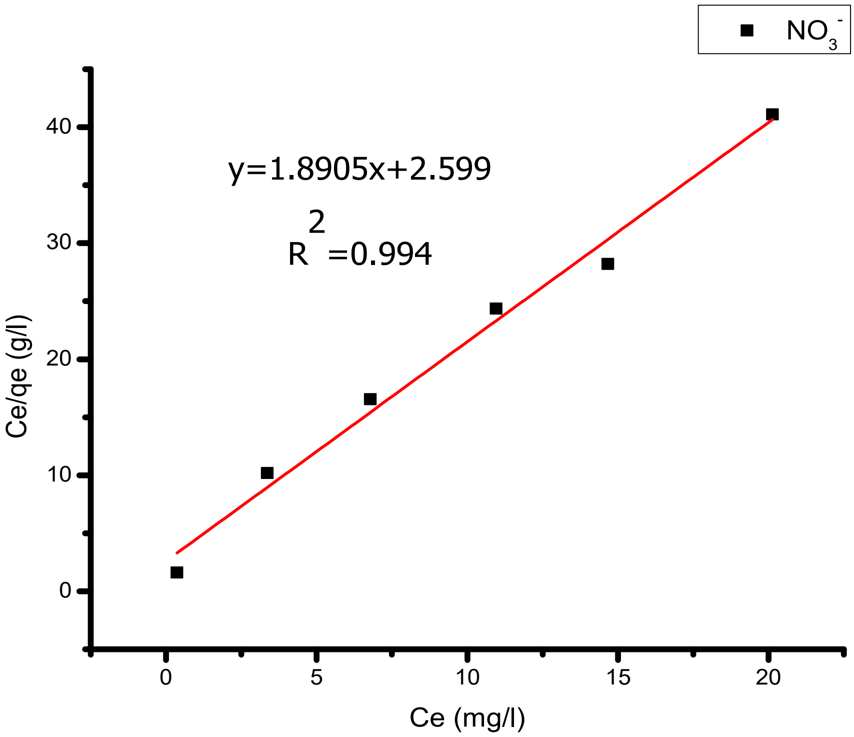


Fig.11. Langmuir isotherm for NO_3^- adsorption on local clay

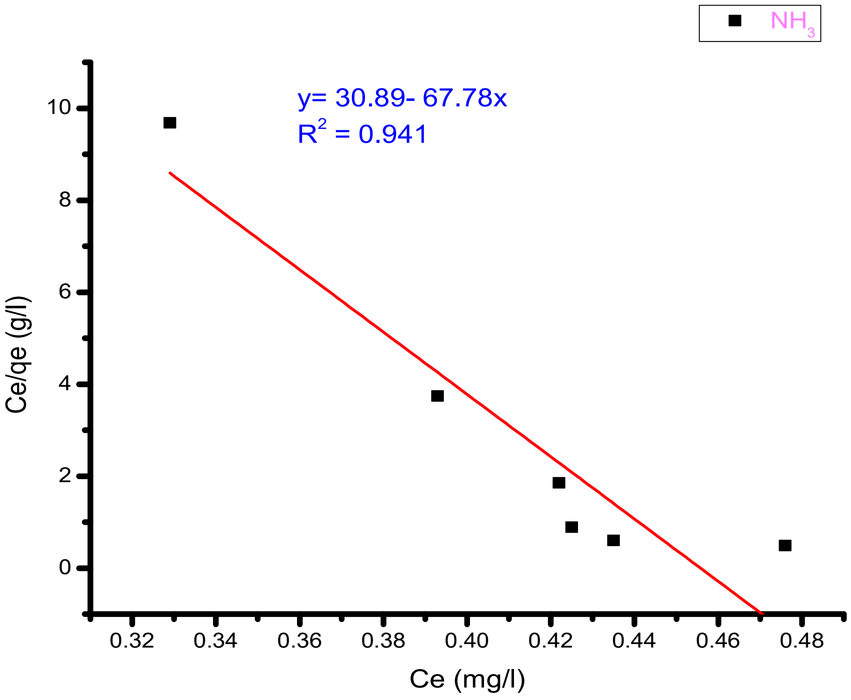


Fig.12. Langmuir isotherm for NH_3 adsorption on local clay

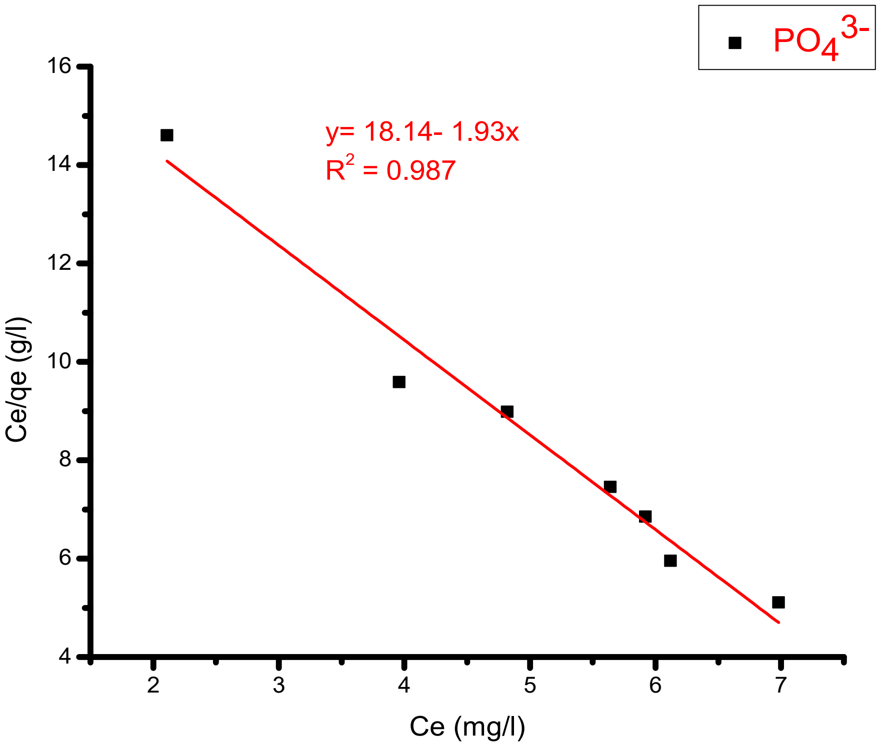


Fig.13. Langmuir isotherm for adsorption of Phosphate on clay

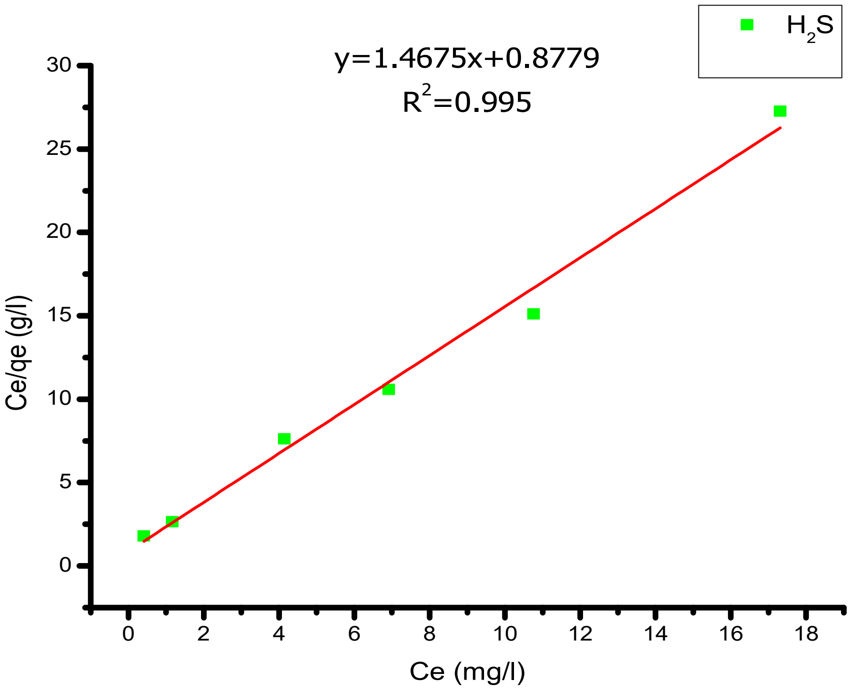


Fig.14. Langmuir isotherm for adsorption of H_2S on clay

Freundlich isotherm model constant parameters, Kf and n were determined by linear regression from the plot of ln(qe) against ln(Ce). Kf is the degree of adsorption; when Kf value is low it indicates minimal adsorption of adsorbates whereas the higher Kf value suggests greater adsorption ability [73]. For this case, Kf value was highest for NH_3 (1519 mg/g) and it was lowest for PO_4^{3-} (0.015 mg/g) indicating a non favorable adsorption according to Freundlich isotherm.

Adsorption intensity, n from Freundlich Isotherm was determined for both metal ions. When n>1, the adsorbate is favorably adsorbed on an adsorbent and it indicates the situation of adsorption intensity. From this it can be conclude that the were favorably adsorbed on clay. The value of n was lower for NH_3 (0.102) but was highest for NO_3^-(4.88) suggesting a maximum adsorption of NO_3^- and least of NH_3 according to Freundlich model. Two of the adsorbates(NO_3^- and H_2S) favored Langmuir model while two of the adsorbates (PO_4^{3-} and NH_3) favored Freundlich model.

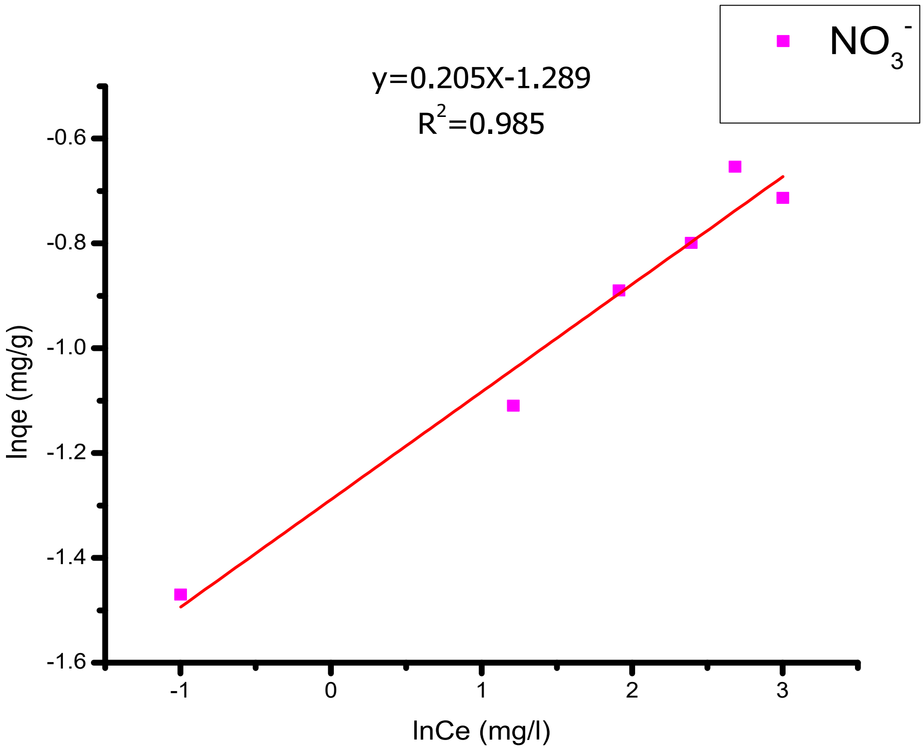


Fig. 15. Freundlich isotherm for the adsorption of NO_3^- on local clay

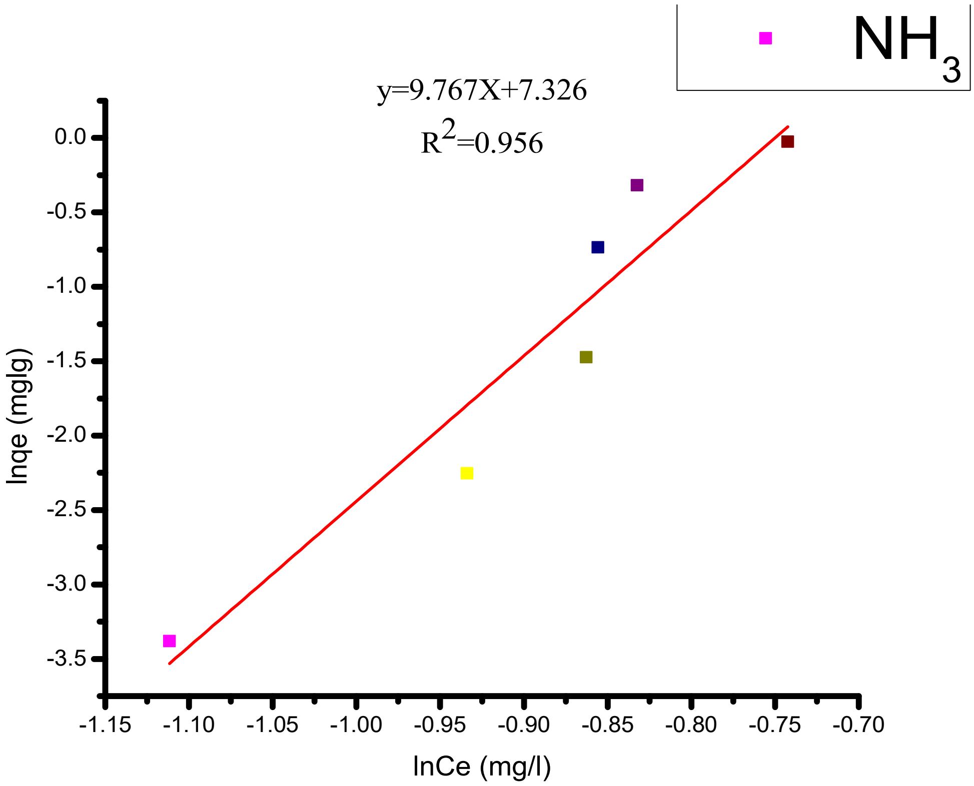


Fig. 16. Freundlich isotherm for adsorption of NH3 on clay

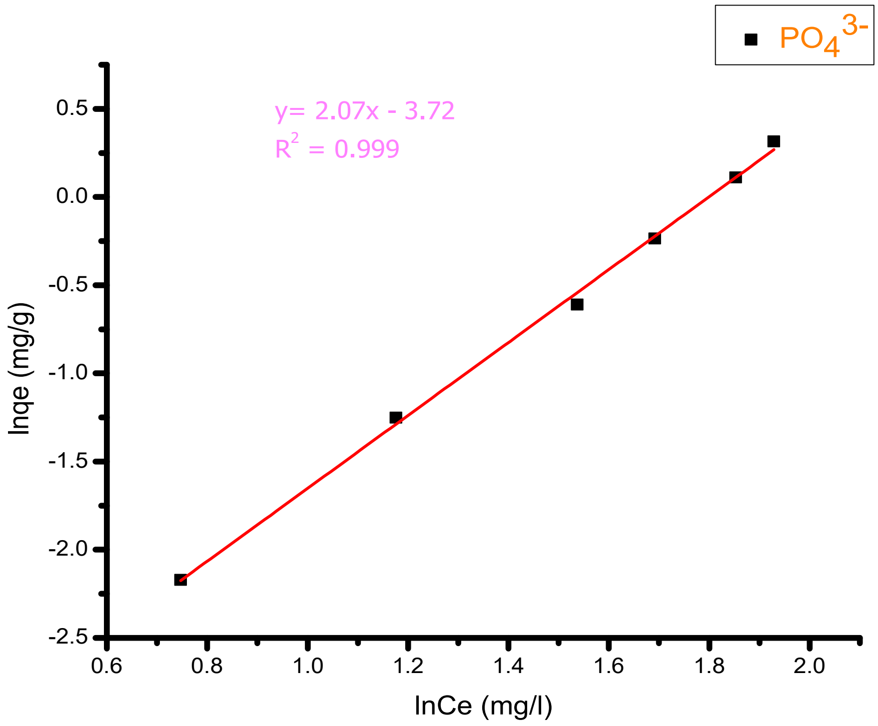


Fig. 17. Freundlich isotherm adsorption for PO4^{3-} adsorption on Clay

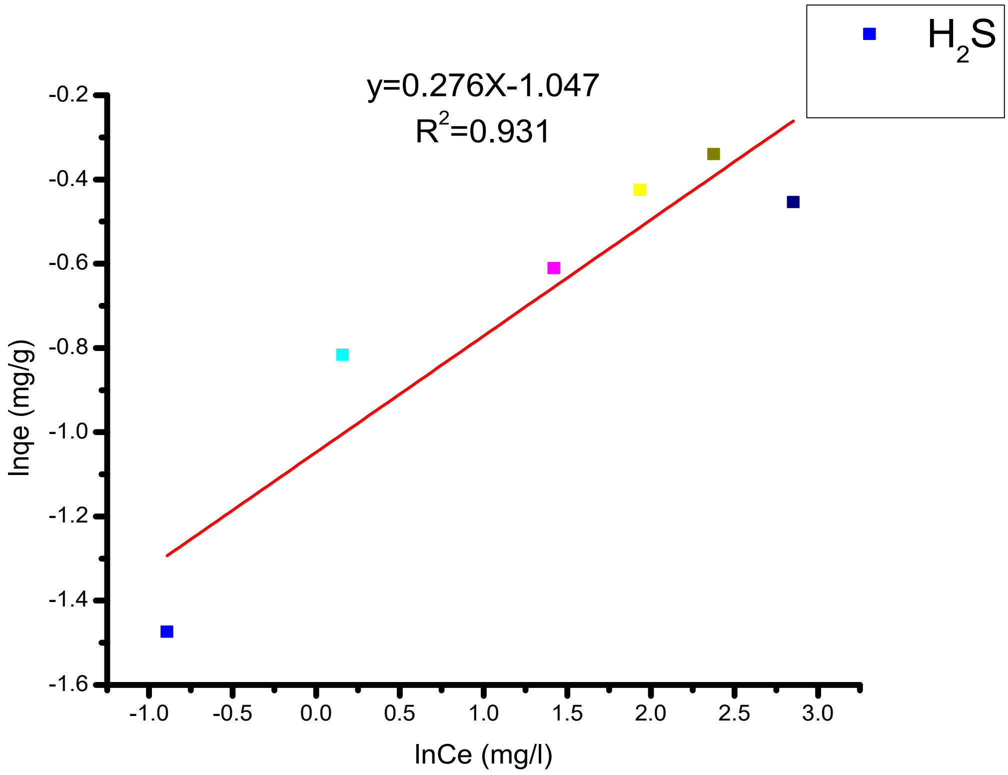


Fig.18**.** Freundlich isotherm for the adsorption of H_2S by clay

Generally, from Langmuir Isotherm model the value of maximum sorption capacity, q_m of clay for adsorption of H_2S were 0.68mg/g which is greater than the other adsorbates. The constant parameter K_L in Langmuir equation is related to the energy of adsorption and K_L values for adsorption of PO_4^{-3} was greater than the other three adsorbates..

Table.3. Langmuir and Freundlich Isotherm Correlation coefficient and constants of the adsorption of clay.

Adsorbate	Langmuir			Freundlich		
	qm (mg/g)	KL (L/mg)	R^2	n	kf	R^2
NO_3^-	0.529	0.727	0.994	4.88	0.276	0.985
PO_4^{3-}	0.44	5.16	0.987	0.4	0.015	0.999
NH_3	0.015	2.158	0.941	0.102	1519	0.956
H_2S	0.681	1.67	0.995	3.623	0.35	0.931

4.9. Kinetics of Adsorption

The removal efficiency of NH_4^+ on local clay increases with the increasing reaction time and reaches equilibrium in 30 min. The adsorption of NH_4^+ on local clay is very rapid and reaches equilibrium within 30 min. This may be attributed to the utilization of readily available adsorption sites of the local clay leading to a fast diffusion and rapid equilibrium attainment. When the adsorption of the exterior surface of the adsorbent reaches a saturation point, NH_4^+ ions enter into the pores of adsorbent and are absorbed by the interior surface of particles [79].

To further investigate the adsorption behavior, pseudo first order and pseudo-second order kinetics models were used to analyze the obtained data and can be summarized as follows:

Pseudo first and second order kinetic models have been tested to fit the data obtained from different adsorption experiments of NH_3, H_2S, NO^-_3 and PO_4^{3-} onto local clay. The pseudo first order plots of ln(qe-qt) versus t for all species adsorption did give approximate street lines in figure below and the rate constants (k_1) can be calculated from the slope and intercept. The experimental and calculated qe values, pseudo-first order rate constants and regression coefficient of determination (R^2) values are given in Table4. Since the plots show linearity and the R^2 values of NO^-_3, PO^{3-}_4, NH_3 and H_2S were found to be 0.9996, 0.988, 0.985 and 0.99999 respectively, the calculated qe values (qcal) was not in a good agreement with the experimental qe values (qexp).

A pseudo second order kinetic model was applied to fit the experimental data. It was plotted t/q against t and constant parameters of k_2 and h values were determined from the slopes and intercepts. The linear pseudo-second order equation showed good agreement of experimental data with correlation coefficients 0.999, 0.99999, 0.999 and 0.9999 for the adsorbates NO_3^-, PO_{4-}^{3}, NH_3 and H_2S respectively as shown in Table 4 and in the following Figure.

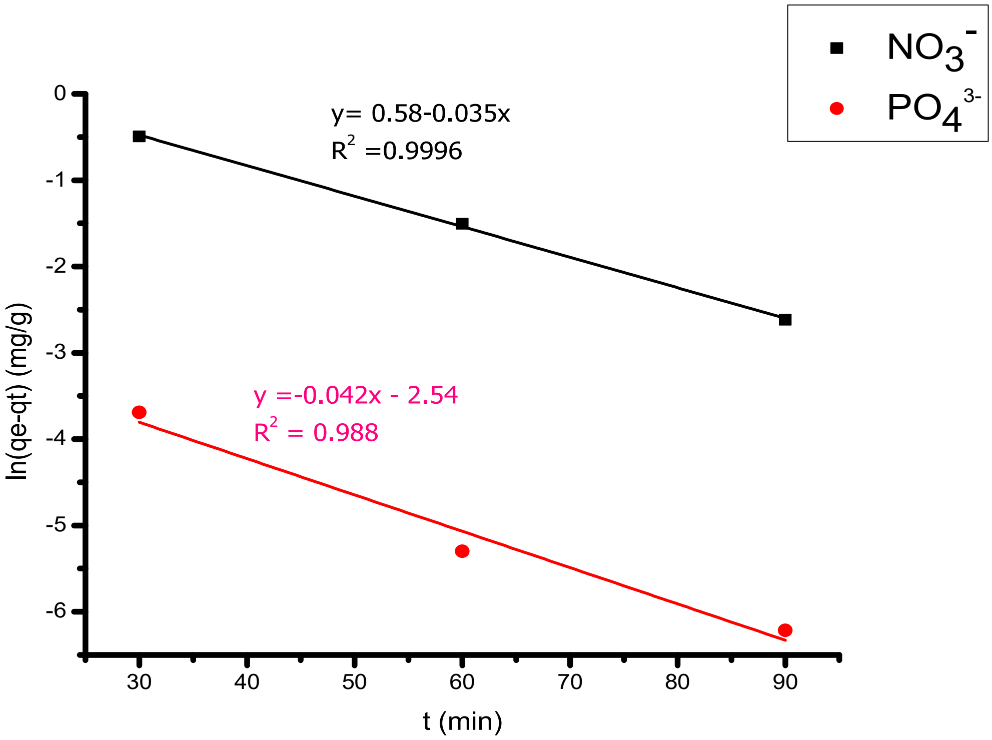


Fig. 19. Pseudo 1st order plot of adsorption of NO_3^- and PO_4^{-3}

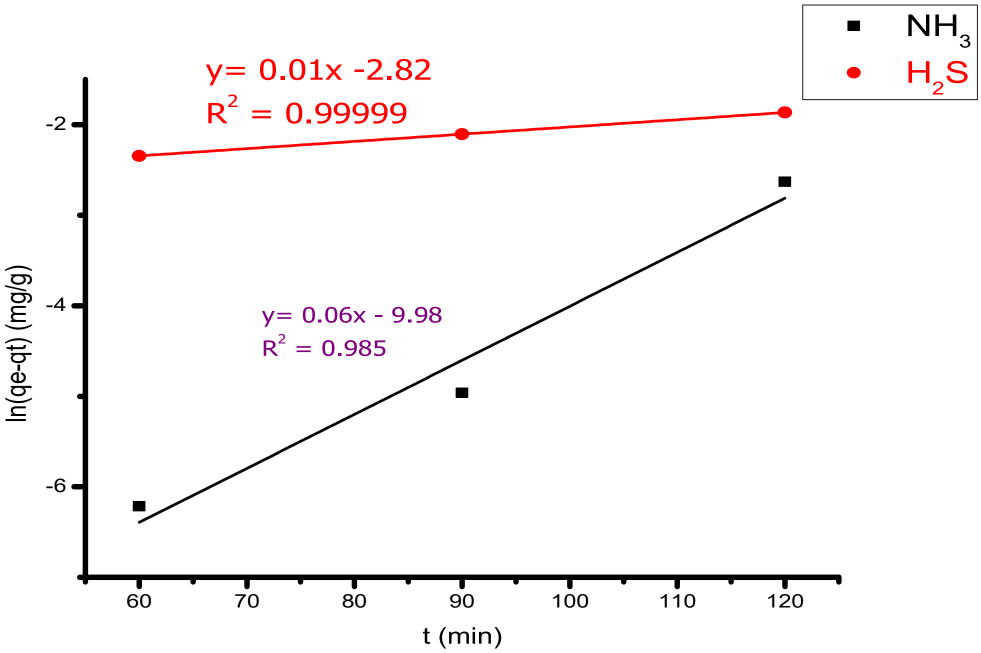


Fig. 20. Pseudo 1st order plot of adsorption of NH$_3$ and H$_2$S

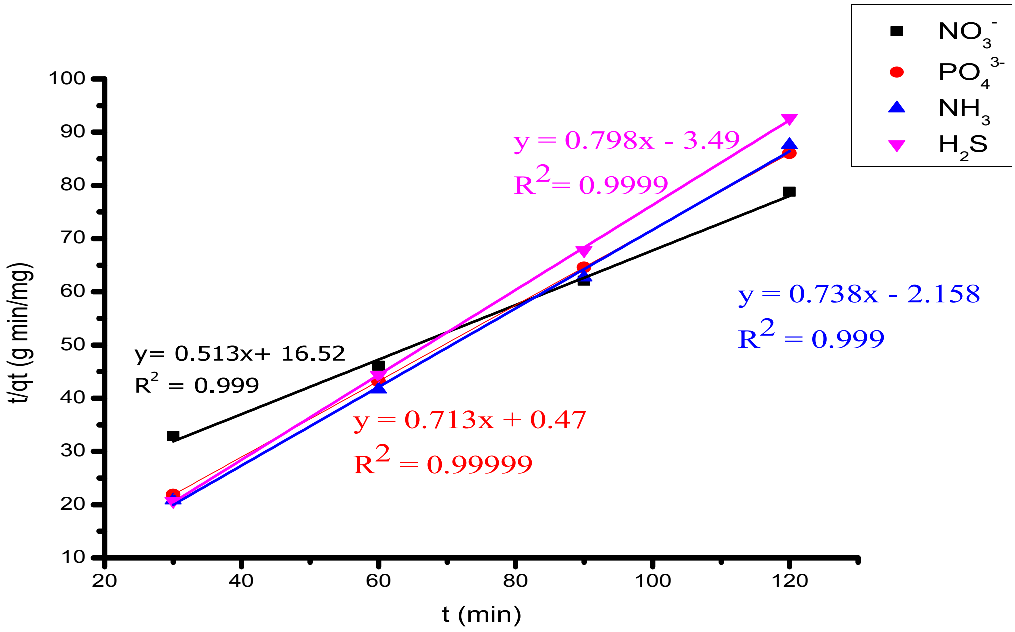


Fig.21. Pseudo 2nd order plot of NO$_3^-$, PO$_4^{3-}$, NH$_3$ and H$_2$S

Table 4. Pseudo 1st and 2nd order parameter values

Adsorbate	Pseudo 1st Order			Pseudo 2nd Order				qe(exp)
	R^2	k1	qe (mg/g)	R^2	h	K_2	qe (mg/g)	
NO_3^-	0.9996	0.035	1.79	0.999	0.134	0.016	1.95	1.523
PO_4^{3-}	0.988	0.04	0.79	0.99999	6.289	3.257	1.39	1.395
NH_3	0.985	0.059	0.000046	0.999	0.469	0.254	1.36	1.442
H_2S	0.99999	0.008	0.06	0.9999	0.287	0.184	1.25	1.45

4.10. Thermodynamics of Adsorption

Thermodynamic parameters are the actual indicators to determine where a process proceeds spontaneously and to ascertain if the process has any practical use The thermodynamic parameters that must be considered to determine the adsorption processes are the changes in standard enthalpy (ΔH^0), standard entropy (ΔS^0), and standard free energy (ΔG^0) due to transfer of unit mole of solute from solution onto the solid–liquid interface [85]. These parameters are related with the following equation:

$$\ln(qe/Ce)=\Delta S^o/R - \Delta H^o/RT$$

$$\Delta G^o= \Delta H-T\Delta S^o$$

$$\Delta G^\circ = - RT \ln Kc$$

Kc, the equilibrium constant, represents the ability of the adsorbent to retain the adsorbate and extent of movement of the adsorbate within the solution [85]. The Kc is the ratio of the equilibrium concentration of the adsorbate (qe) attached to adsorbent compared to the van't Hoff equation as equilibrium concentration in solution (Ce), and can be deduced from the following Eqn.

$$Kc = qe /Ce$$

$$\ln Kc = \Delta S^\circ/R - \Delta H^\circ/RT$$

The values of ΔH° (kJ mol-1) and ΔS° (J mol-1 K-1) can be obtained from the slope and intercept of a linear plot between ln Kc and 1/T intercept of a linear plot between ln Kc and 1/T. Kc indicates the capability of the clay to retain a solute and also the extent of its movement in a solution phase.

The positive value of ΔG° indicates the non spontaneous of nature of adsorption at low temperature. The negative value of ΔH° shows the exothemic nature of the adsorption process as temperature rises. The positive value of ΔS° shows the randomness of the adsorption process [86].

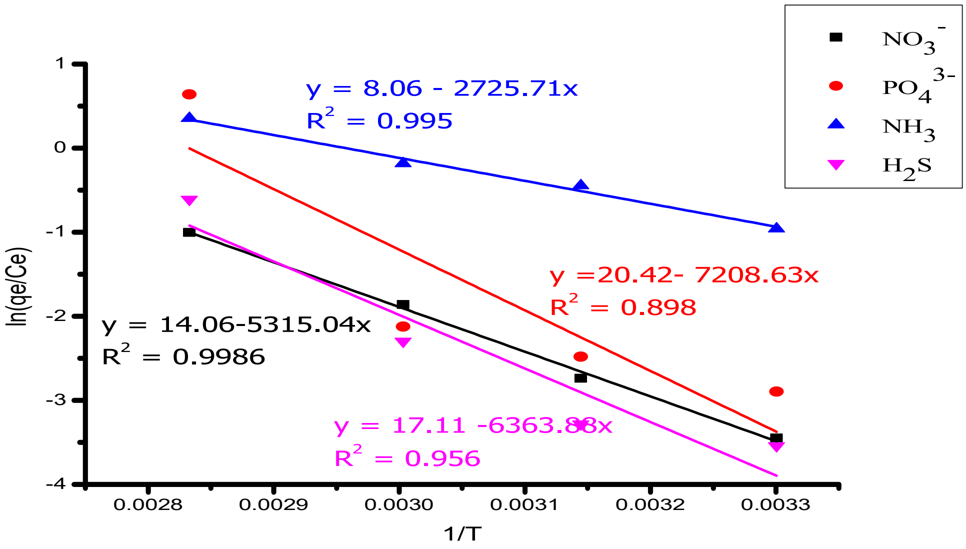


Fig.22. Thermodynamics effect of temperature on adsorption of NO_3^-, PO_4^{-3}, NH_3 and H_2S by local clay

Table.5. Thermodynamic parameters

Adsorbate	-ΔG° KJ/mole'				ΔH° (KJ.mol^{-1})	ΔS°(J.mol^{-1}.K^{-1})
	30°c	45°c	60°c	80°c		
NO_3^-	-79.61	-81.36	-83.11	-85.45	-44.2	116.89
PO_4^{3-}	-111.4	-113.92	-116.47	-119.86	-59.9	169.77
NH_3	-42.97	-43.97	-44.98	-46.32	-22.66	67.01
H_2S	-96	-98.74	-100.28	-103.12	-52.91	142.25

4.11. Data Analysis Using ANOVA

Two factors pH and initial concentration were selected for the study of their influence on the adsorption process. The pH was varied from 2, 3 and for NO3 and 5, 7 and 9 for the rest and initial concentration was taken from 10 to 20 ppm and contact time kept constant at 90 min. The most significant factor were identified using ANOVA analysis for each adsorbate.

ANOVA is a common statistical method that assays the significance and the adequacy of the total variation in a set of data into component parts associated with specific sources of variation for the target of trial hypotheses on the factors of the model. This technique was used to test the statistical significance of the proposed model. To measure how well the suggested model fits the experimental data, the statistical parameters of F-value, R^2 and p-value were evaluated. The ANOVA result is reported in the following Tables. From data in it can be found that the model was highly significant at 95% of confidence level for the adsorption of NO_3, NH_3 and H_2S and non-significant for PO_4 adsorption local clay due to its p or sig -value is lower than 0.0001 so another model may be devised. The p-value less than 0.05 indicates the significant of the source of variation. The interaction of pH and Co (initial concentration) is not significant at 0.05 level, since sig. value 1 is >0.05 for all species except NO^-_3. pH, Co and pH-Co interactions are significant variables for NO^-_3 adsorption. This implies pH, Co and the interaction of the two variables have significant effect on the removal of NO^-_3. pH is significant variable for NH_3, while pH and initial concentrations are significant variables for H_2S adsorption.

pH, contact time and the interaction of both factors are significance variables for H_2S adsorption.

The P-values were utilized as a tool to introduce the significant or non-significant variables. Each variation source with p-value less than 0.05 would be a significant one. pH and initial concentration are significant variables. This implies that the effect of pH and initial concentration has significant effect on the adsorption of and, while the interaction of pH and initial concentration is non-significant variable and has no significant effect on removal of the target species.

Table.6.ANOVA result of factors(pH and initial concentration) versus response(%Removal) on NO^-_3 adsorption

Tests of Between-Subjects Effects

Dependent Variable :% Removal

Source	Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	4056.471[a]	8	507.059	8.168	.000
Intercept	117709.700	1	117709.700	1.896E3	.000
pH	1889.961	2	944.981	15.222	.000
Initial Concentration	779.194	2	389.597	6.276	.009
pH * Initial Concentration	1387.317	4	346.829	5.587	.004
Error	1117.424	18	62.079		
Total	122883.595	27			
Corrected Total	5173.895	26			

a. R Squared = .784 (Adjusted R Squared = .688)

Table 7. ANOVA result of factors(pH and initial concentration) versus response(%Removal) on PO_4^{3-} adsorption

Tests of Between-Subjects Effects

Dependent Variable:%Removal

Source	Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	202.650[a]	8	25.331	.486	.850
Intercept	215304.086	1	215304.086	4.133E3	.000
pH	49.897	2	24.948	.479	.627
Co	57.361	2	28.681	.551	.586
pH * Co	95.392	4	23.848	.458	.766
Error	937.775	18	52.099		
Total	216444.511	27			
Corrected Total	1140.425	26			

a. R Squared = .178 (Adjusted R Squared = -.188)

Table 8. ANOVA result of factors(pH and initial concentration) versus response(%Removal) on NH_3 adsorption

Tests of Between-Subjects Effects

Dependent Variable:%Removal

Source	Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	426.775[a]	8	53.347	1.289	.309
Intercept	201543.552	1	201543.552	4.869E3	.000
pH	414.123	2	207.062	5.002	.019
Co	7.486	2	3.743	.090	.914
pH * Co	5.166	4	1.292	.031	.998
Error	745.053	18	41.392		
Total	202715.381	27			
Corrected Total	1171.828	26			

a. R Squared = .364 (Adjusted R Squared = .082)

Table 9. ANOVA result of factors(pH and initial concentration) versus response(%Removal) on H_2S adsorption

Tests of Between-Subjects Effects

Dependent Variable:%Removal

Source	Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	519.909[a]	8	64.989	2.172	.082
Intercept	151918.503	1	151918.503	5.077E3	.000
pH	244.576	2	122.288	4.086	.034
Co	275.333	2	137.667	4.600	.024
pH * Co	1.481E-5	4	3.704E-6	.000	1.000
Error	538.655	18	29.925		
Total	152977.067	27			
Corrected Total	1058.564	26			

Table 10. ANOVA result of factors (pH and time) versus response(%Removal) on H_2S adsorption

Tests of Between-Subjects Effects

Dependent Variable:%Removal

Source	Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	783.230[a]	8	97.904	6.400	.001
Intercept	151918.503	1	151918.503	9.932E3	.000
pH	244.576	2	122.288	7.995	.003
Time	538.655	2	269.327	17.607	.000
pH * Time	5.926E-5	4	1.481E-5	.000	1.000
Error	275.333	18	15.296		
Total	152977.067	27			
Corrected Total	1058.564	26			

a. R Squared = .740 (Adjusted R Squared = .624)

From the table we conclude that since the value of F much greater than sig. the pH and initial concentration have significant effect. From the two factors pH has high influence than initial concentration on the adsorption of NO^-_3

4.12. Adsorption Efficiency of Local Clay for Real Brewery Wastewater Samples

Laboratory experimental results were applied to real wastewater samples in order to move from the experiment to the application in real world. Waste water samples containing ammonia, phosphate, nitrate and hydrogen sulfide were obtained from brewery plant of Dashen which is located 5kmaway from Debrebirhan. currently the waste is treated using biological method which consume large amount of energy. This experiment was conducted to serve as an alternative method of waste treatment and all the species were tested.

Batch adsorption test was conducted for all analytes at their optimum points obtained from prior synthetic waste water batch adsorption experiment. The feasibility and efficiency of a adsorption process depends not only on the properties of the adsorbents, but also on the composition of the waste water. The samples were taken from three different sites and mixed together for batch adsorption process. The following table illustrates the results of parameters before and after adsorption was conducted.

Table 11. The amount of brewery wastewater parameters before and after adsorption

Effluent Parameters	Amount Before Adsorption	Amount After Adsorption
TSS(mg/l)	820	75
TDS(mg/l)	852.7	297
Conductivity(mS/cm)	2.28	0.16
COD(mg/l)	3360	920
BOD(mg/l)	1890	530
Turbidity(FAU)	702	81
NO_3-N(ppm)	4	1.2
PO_4-P(ppm)	6.834	2.464
NH_3-N(ppm)	0.764	0.377
H_2S(ppm)	2	0.23

To determine the amount of each target analyte masking agents were used to minimize the competitive species before and after adsorption.

For adsorption of wastewater containing ammonia, optimum parameters from batch synthetic wastewater adsorption were selected as; pH=7, contact time =60 min, and clay dosage of 2g.

The initial measured concentration of ammonia in wastewater was 0.764 ppm, for PO^{3-}_4 the optimum parameter selected was pH=5, contact time 60min, dosage 2g and its initial concentration was 6.834ppm. For NO^-_3 the optimum pH=2, contact time 90min, its initial concentration was 4ppm, While the optimum parameters for H_2S batch adsorption were; pH=7, contact time =90 min, and clay dosage of 2gm and its initial concentration in wastewater was 2ppm.

Table 12. Optimum condition for the adsorption of NO^-_3,PO^{3-}_4, NH_3 and H_2S

Parameter	Optimum Condition Parameters			Real Waste Water Parameters	
	pH	Contact time(min)	Adsorbent dosage(gm)	pH	Initial Concentration(mg/l)
NO^-_3	2	90	2	2	4
PO^{3-}_4	5	60	2	5	6.834
NH_3	7	60	2	6	0.764
H_2S	7	90	2	7	2

After adsorption of waste water containing each target species onto local clay, the removal efficiency for NO^-_3, PO^{3-}_4, NH_3 and H_2S were 70%, 63.95%, 50.65% and 88.5% respectively. The results were some how lower than the removal efficiency of synthetic waste water containing individual species. This is due to the presence of other competing species present in the sample. Taking into consideration of this result, almost more than half of the targeted species were removed by the clay from brewery waste water. The better way would be effective if effluents are discharged separately and treated before mixing all waste streams together. This adsorption technique eliminates the interference of other species for the adsorbent sites. The optimum conditions may be important and more effective for other waste water sources.

5. CONCLUSION AND RECOMMENDATION

5.1. Conclusion

The result of this study shows that local clay successfully used for the removal of inorganic pollutants from waste water. Natural clays present a major advantage of giving low cost recovery processes making them suitable for use in water purification and wastewater treatment.

The adsorption of NO^-_3, PO^{3-}_4, NH_3 and H_2S from aqueous solution by local clay was investigated. The effect of contact time, initial concentration, solution pH, temperature and adsorbent dose on the removal of these species has been studied. pH was found to be dominant factor as per analysis of ANOVA and optimal pH for NO^-_3, PO^{3-}_4, NH_3 and H_2S was 2, 5, 7 and 7, respectively. Isothermal data of the targetspecies adsorption by local clay indicated that, the adsorption process followed both the Langmuir and Freundlich models. Data analyzed from the models, showed the adsorption capacity of local clay for NO^-_3 was found to be higher than the others. From this, it can be concluded that the affinity of clay for $NO_3^-$is greater than that of the other species. The kinetics of adsorption was well represented by pseudo second order kinetic model.

These experimental studies on local clay were conducted in removing of NO^-_3, PO_4^{3-}, NH_3 and H_2S from brewery waste using clay as adsorbent. The results showed that the removal efficiencies for NO_3^-, PO_4^{3-}, NH_3 and H_2S from brewery wastewater were 70%, 63.95%, 50.65% and 88.5% respectively. This reduction in removal efficiency may be attributed to the presence of competitive species. The thermodynamic effect of temperature on the adsorption process was studied at different temperatures. The result show that as the temperature increases the adsorption process becomes non spontaneous and its randomness decreases. This reveals that the adsorption process is favorable at low temperature for adsorbates. The affinity to the adsorbent would be the governing mechanism for adsorption of these target species. The study revealed that the local clay is potentially useful material for the removal of NO^-_3, PO_4^{3-}, NH_3 and H_2S from aqueous solutions.

5.2. Recommendation

Based on the results gained from the study, the following suggestions have been made for future work.

Adsorption experiments can be carried out by treating local clay with different chemicals such as inorganic acids (hydrochloric acid, nitric acid sulfuric acid, tartaric acid, citric acid, thioglycollic acid), base (sodium hydroxide, calcium hydroxide, sodium carbonate), organic compounds (ethylenediamine, formaldehyde, methanol) and oxidizing agent (hydrogen peroxide). The multiple application of this adsorbent other than waste treatment can be assessed, evaluated, analyzed and tested.

A pilot-scale column adsorption with the developed adsorbent can be conducted for real wastewater. Using local clay as an adsorbent costs low and easily available, so it is beneficial to use this material as an alternative adsorbent.

In this study, local clay was applied to the removal of inorganic species. However to assess the range of applicability of this adsorbent;

- other toxic pollutants need to be tested
- The adsorbent being natural and low cost; can be increased it efficiency by acid and thermal activation.
- The use of this adsorbent can replace AC, most widely used adsorbent
- The batch adsorption of inorganic pollutants on local clay should be scaled up to continuous process for industrial purpose
- The reaction time was limited to 2hrs, therefore; the adsorption efficiency should be tested at higher contact time.

6. REFERENCE

[1] G. S. Simate, J. Cluett, S. E. Iyuke, E. T. Musapatika, S. Ndlovu, L. F. Walubita*, et al.*, "The treatment of brewery wastewater for reuse: State of the art," *Desalination,* vol. 273, pp. 235-247, 2011.

[2] A. M. Enitan, J. Adeyemo, S. K. Kumari, F. M. Swalaha, and F. Bux, "Characterization of brewery wastewater composition," 2015.

[3] H.-J. Choi, "Parametric study of brewery wastewater effluent treatment using Chlorella vulgaris microalgae," *Environmental Engineering Research,* vol. 21, pp. 401-408, 2016.

[4] U. Inyang, E. Bassey, and J. Inyang, "Characterization of brewery effluent fluid," *Journal of Engineering and Applied Sciences,* vol. 4, pp. 67-77, 2012.

[5] W. Feng, S. Kwon, E. Borguet, and R. Vidic, "Adsorption of hydrogen sulfide onto activated carbon fibers: effect of pore structure and surface chemistry," *Environmental science & technology,* vol. 39, pp. 9744-9749, 2005.

[6] M. Bodzek, "Inorganic micropollutants removal by means of membrane processes-state of the art," *Ecological Chemistry and Engineering S,* vol. 20, pp. 633-658, 2013.

[7] S. Saleh, K. B. Kamarudin, W. A. W. A. K. Ghani, and L. S. Kheang, "Removal of organic contaminant from aqueous solution using magnetic biochar," *Procedia engineering,* vol. 148, pp. 228-235, 2016.

[8] D. Briggs, "Environmental pollution and the global burden of disease," *British medical bulletin,* vol. 68, pp. 1-24, 2003.

[9] R. Riedel, D. Schlenk, D. Frank, and B. Costa-Pierce, "Analyses of organic and inorganic contaminants in Salton Sea fish," *Marine pollution bulletin,* vol. 44, pp. 403-411, 2002.

[10] J. A. Camargo and Á. Alonso, "Ecological and toxicological effects of inorganic nitrogen pollution in aquatic ecosystems: a global assessment," *Environment international,* vol. 32, pp. 831-849, 2006.

[11] N. N. Rabalais, "Nitrogen in aquatic ecosystems," *AMBIO: A Journal of the Human Environment,* vol. 31, pp. 102-113, 2002.

[12] K. Tilak, K. Veeraiah, and J. M. P. Raju, "Effects of ammonia, nitrite and nitrate on hemoglobin content and oxygen consumption of freshwater fish, Cyprinus carpio (Linnaeus)," *Journal of Environmental Biology,* vol. 28, pp. 45-47, 2007.

[13] E. E. Deane and N. Y. Woo, "Impact of nitrite exposure on endocrine, osmoregulatory and cytoprotective functions in the marine teleost Sparus sarba," *Aquatic toxicology,* vol. 82, pp. 85-93, 2007.

[14] C. Galitsky, N. Martin, E. Worrell, and B. Lehman, "Energy Efficiency Improvement and Cost Saving Opportunities for Breweries: An ENERGY STAR (R) Guide for Energy and Plant Managers," Lawrence Berkeley National Lab.(LBNL), Berkeley, CA (United States)2003.

[15] K. Bedu-Addo, W. G. Akanwariwiak, and I. F. Mensa-Bonsu, "Water Audit of Breweries: A Case Study of a Modern Brewery in Ghana," *Universal Journal of Environmental Research & Technology,* vol. 3, 2013.

[16] J. Wang, "China's national cleaner production strategy," *Environmental Impact Assessment Review,* vol. 19, pp. 437-456, 1999.

[17] A. Z. Gu, A. Saunders, J. Neethling, H. Stensel, and L. Blackall, "Functionally relevant microorganisms to enhanced biological phosphorus removal performance at full-scale wastewater treatment plants in the United States," *Water Environment Research,* vol. 80, pp. 688-698, 2008.

[18] A. T. Jaiyeola and J. K. Bwapwa, "Treatment technology for brewery wastewater in a water-scarce country: a review," *South African journal of science,* vol. 112, pp. 1-8, 2016.

[19] A. Gebeyehu, N. Shebeshe, H. Kloos, and S. Belay, "Suitability of nutrients removal from brewery wastewater using a hydroponic technology with Typha latifolia," *BMC biotechnology,* vol. 18, p. 74, 2018.

[20] P. Thiel and P. d. Toit, "The chemical composition of a brewery waste," *Journal of the Institute of Brewing,* vol. 71, pp. 509-514, 1965.

[21] A. G. Rao, T. S. K. Reddy, S. S. Prakash, J. Vanajakshi, J. Joseph, and P. Sarma, "pH regulation of alkaline wastewater with carbon dioxide: a case study of treatment of brewery wastewater in UASB reactor coupled with absorber," *Bioresource technology,* vol. 98, pp. 2131-2136, 2007.

[22] K. Bedu-Addo and W. G. Akanwarewiak, "Determination of the pollution loads of Brewery X and the impacts of the pollutant on the Sisai River," *Journal of Public Health and Epidemiology,* vol. 4, pp. 316-319, 2012.

[23] C. E. Canada, C. F. P. A. Office, F. R. A. Plan, and E. R. E. Corp, *Technical Pollution Prevention Guide for Brewery and Wine Operations in the Lower Fraser Basin*: Environment Canada, 1997.

[24] O. Olafadehan, O. Jinadu, L. Salami, and L. Popoola, "Treatment of brewery wastewater effluent using activated carbon prepared from coconut shell," *International Journal of Applied Science and Technology,* vol. 2, pp. 165-178, 2012.

[25] A. Taiwo, S. A. Amadi, and N. J. Amakama, *Adsorption and Treatment of Organic Contaminants using Activated Carbon from Waste Nigerian Bamboo* vol. 13, 2010.

[26] F. Ademiluyi, S. Amadi, and N. J. Amakama, "Adsorption and Treatment of Organic Contaminants using Activated Carbon from Waste Nigerian Bamboo," *Journal of Applied Sciences and Environmental Management,* vol. 13, 2009.

[27] M. Samer, "Biological and Chemical Wastewater Treatment Processes," ed, 2015, pp. 1-50.

[28] H. Huang, K. Schwab, and J. G. Jacangelo, "Pretreatment for low pressure membranes in water treatment: a review," *Environmental science & technology,* vol. 43, pp. 3011-3019, 2009.

[29] M. Kothiyal and G. Semwal, "Performance Evaluation of Brewery Biological Wastewater Treatment Plant. MOJ Eco Environ Sci 3 (1): 00058. DOI: 10.15406/mojes. 2018.03. 00058," *Performance Evaluation of Brewery Biological Wastewater Treatment Plant,* vol. 2, 2018.

[30] Y. Feng, X. Wang, B. E. Logan, and H. Lee, "Brewery wastewater treatment using air-cathode microbial fuel cells," *Applied microbiology and biotechnology,* vol. 78, pp. 873-880, 2008.

[31] C. L. Grady Jr, G. T. Daigger, N. G. Love, and C. D. Filipe, *Biological wastewater treatment*: CRC press, 2011.

[32] K. Vijayaraghavan, D. Ahmad, and R. Lesa, "Electrolytic treatment of beer brewery wastewater," *Industrial & engineering chemistry research,* vol. 45, pp. 6854-6859, 2006.

[33] F. Cakir and M. Stenstrom, "Greenhouse gas production: a comparison between aerobic and anaerobic wastewater treatment technology," *Water research,* vol. 39, pp. 4197-4203, 2005.

[34] M. McManus, "Wastewater Treatment Design for a Brewery," 2011.

[35] A. Ochieng, M. S. Onyango, M. Thokozani, S. Esmail, T. Leswifi, R. Sophia*, et al.*, "Water and Wastewater Management in Local Government: Skills Needs and Development," 2015.

[36] L. Fillaudeau, P. Blanpain-Avet, and G. Daufin, "Water, wastewater and waste management in brewing industries," *Journal of cleaner production,* vol. 14, pp. 463-471, 2006.

[37] M. Hultberg and H. Bodin, "Fungi-based treatment of brewery wastewater—biomass production and nutrient reduction," *Applied microbiology and biotechnology,* vol. 101, pp. 4791-4798, 2017.

[38] V. Gupta, H. Sadegh, M. Yari, R. Shahryari Ghoshekandi, B. Maazinejad, and M. Chahardori, "Removal of ammonium ions from wastewater: A short review in development of efficient methods," *Global Journal of Environmental Science and Management,* vol. 1, pp. 149-158, 2015.

[39] P. Haseena, K. Padmavathy, P. R. Krishnan, and G. Madhu, "Adsorption of Ammonium Nitrogen from Aqueous Systems Using Chitosan-Bentonite Film Composite," *Procedia Technology,* vol. 24, pp. 733-740, 2016.

[40] T. Nguyen, "Adsorption Of Phosphorus From Wastewater Onto Biochar: Batch And Fixed-bed Column Studies," 2015.

[41] I. Kandola, A. Pogrebnoi, and T. Pogrebnaya, "Oldoinyo Lengai Volcanic Ash for Removal of Hydrogen Sulfide and Ammonia from Biogas," *Journal of Materials Science and Chemical Engineering,* vol. 6, p. 78, 2018.

[42] D. Nguyen-Thanh, K. Block, and T. J. Bandosz, "Adsorption of hydrogen sulfide on montmorillonites modified with iron," *Chemosphere,* vol. 59, pp. 343-353, 2005.

[43] S. Edwards, R. Alharthi, and A. E. Ghaly, "Removal of hydrogen sulphide from water," *American Journal of Environmental Sciences,* vol. 7, p. 295, 2011.

[44] I. G. CARA and G. JITĂREANU, "Application of Low-Cost Adsorbents for Pesticide Removal," *Bulletin of the University of Agricultural Sciences & Veterinary Medicine Cluj-Napoca. Veterinary Medicine,* vol. 72, 2015.

[45] A. Barros, S. Prasad, V. D. Leite, and A. G. Souza, "The process of biosorption of heavy metals in bioreactors loaded with sanitary sewage sludge," *Brazilian Journal of Chemical Engineering,* vol. 23, pp. 153-162, 2006.

[46] K. Monika, "Use of various technologies, methods and adsorbents for the removal of dye," *Journal of environmental research and development,* vol. 6, pp. 879-883, 2012.

[47] S. Velizarov, J. G. Crespo, and M. A. Reis, "Removal of inorganic anions from drinking water supplies by membrane bio/processes," *Reviews in Environmental Science and Bio/Technology,* vol. 3, pp. 361-380, 2004.

[48] S. Das, "Biosorption of chromium and nickel by dried biomass of cyanobacterium Oscillatoria laete-virens," *International Journal of Environmental Sciences,* vol. 3, pp. 341-352, 2012.

[49] R. P. Kumar, S. Varanasi, and V. Purushothaman, "Investigation of the biosorption mechanisms of Methylene blue onto press mud through kinetic modeling analysis," *Indian Journal of Science and Technology,* vol. 3, 2010.

[50] B. Gu, J. Schmitt, Z. Chen, L. Liang, and J. F. McCarthy, "Adsorption and desorption of natural organic matter on iron oxide: mechanisms and models," *Environmental Science & Technology,* vol. 28, pp. 38-46, 1994.

[51] L. S. Oliveira and A. S. Franca, "Low-cost adsorbents from agri-food wastes," ed: Nova Science Publishers: New York, NY, USA, 2008, pp. 171-209.

[52] J. Mdoe, "Agricultural Waste as Raw Materials for the Production of Activated Carbon: Can Tanzania Venture into this Business?," *Huria: Journal of the Open University of Tanzania,* vol. 16, pp. 89-103, 2014.

[53] P. Ravichandran, P. Sugumaran, S. Seshadri, and A. H. Basta, "Optimizing the route for production of activated carbon from Casuarina equisetifolia fruit waste," *Royal Society open science,* vol. 5, p. 171578, 2018.

[54] E. Iakovleva and M. Sillanpää, *The use of low-cost adsorbents for wastewater purification in mining industries* vol. 20, 2013.

[55] S. Wang and Y. Peng, *Natural zeolites as effective adsorbents in water and wastewater treatment* vol. 156, 2010.

[56] B. Cekova, D. Kocev, E. Kolcakovska, and D. Stojanova, *Zeolites as alcohol adsorbents from aqueous solutions* vol. 37, 2006.

[57] O. R. Cevallos, "Adsorption Characteristics of Water and Silica Gel System for Desalination Cycle," 2012.

[58] M. Sulyman, J. Namiesnik, and A. Gierak, "Low-cost Adsorbents Derived from Agricultural By-products/Wastes for Enhancing Contaminant Uptakes from Wastewater: A Review," *Polish Journal of Environmental Studies,* vol. 26, pp. 479-510, 2017 2017.

[59] I. Michalak, K. Chojnacka, and A. Witek-Krowiak, "State of the art for the biosorption process--a review," *Appl Biochem Biotechnol,* vol. 170, pp. 1389-416, Jul 2013

[60] Y. Argun, A. Karacalı Tunç, U. Çalışır, N. Kılınç, and H. Irak, *BIOSORPTION METHOD AND BIOSORBENTS FOR DYE REMOVAL FROM INDUSTRIAL WASTEWATER: A REVIEW* vol. 5, 2017.

[61] M. Salman, M. Athar, U. Shafique, R. Rehman, S. Ameer, S. Zulfiqar*, et al.*, *Removal of formaldehyde from aqueous solution by adsorption on kaolin and bentonite: A comparative study* vol. 36, 2012.

[62] Y. Sag and T. Kutsal, "Recent trends in the biosorption of heavy metals: A review," *Biotechnology and Bioprocess Engineering,* vol. 6, p. 376, 2001/12/01 2001.

[63] E. Stephen, *Biosorption Kinetics of Heavy Metals from Fertilizer Industrial Waste Water Using Groundnut Husk Powder as an Adsorbent* vol. 2, 2017.

[64] G.Vijayakumar , R.Tamilarasan and M. Dharmendirakumar, "Adsorption, Kinetic, Equilibrium and Thermodynamic studies on the removal of basic dye Rhodamine-B from aqueous solution by the use of natural adsorbent perlite", *J. Mater. Environ. Sci.* 3 (1) , 157-170, 2012.

[65] B. Meroufel, B. Omar, B. Mohamed, Y. Benmoussa, and M. A. Zenasni, *Adsorptive removal of anionic dye from aqueous solutions by Algerian kaolin: Characteristics, isotherm, kinetic and thermodynamic studies* vol. 4, 2013.

[66] M. Rahman and K. Sathasivam, *Heavy metal biosorption potential of a Malaysian Rhodophyte (Eucheuma denticulatum) from aqueous solutions* vol. 13, 2016.

[67] R. Yadav, K. Upadhyay, and S. Maru, *Colour removal from paper mill effluent using activated Carbon* vol. 28, 2012.

[68] M. Ghauri, M. Tahir, T. Abbas, M. S. Khurram, and K. Shehzad, "Adsorption studies for the removal of ammonia by thermally activated carbon," *Science International,* vol. 24, pp. 411-414, 2012.

[69] A. M. Aljeboree, N. Radi, Z. Ahmed, and A. Alkaim, *The use of sawdust as by product adsorbent of organic pollutant from wastewater: Adsorption of maxilon blue dye* vol. 12, 2014.

[70] D. H. Ravuri and A. V. V. S. Swamy, *Physico-chemical key parameters, langmuir and freundlich isotherm and lagergren rate constant studies on the removal of divalent nickel from the aqueous solutions onto powder of calcined brick* vol. 4, 2012.

[71] E. Mekonnen, M. Yitbarek, and T. Soreta, *Kinetic and Thermodynamic Studies of the Adsorption of Cr(VI) onto Some Selected Local Adsorbents* vol. 68, 2014.

[72] R. Dhankhar and A. Hooda, *Fungal biosorption—an alternative to meet the challenges of heavy metal pollution in aqueous solutons* vol. 32, 2011.

[73] Z. Aksu and J. Yener, *A Comparative Adsorption/Biosorption Study of Mono-Chlorinated Phenols onto Various Sorbents* vol. 21, 2001.

[74] M. Ali, A.-E. Hussian, A. Abdel-Satar, M. Goher, A. Napiórkowska-Krzebietke, and A. M Abd El, *The isotherm and kinetic studies of the biosorption of heavy metals by non-living cells of chlorella vulgaris* vol. 21, 2016.

[75] A. Venkata AjayKumar, N. A. Darwish, and N. Hilal, *Study of Various Parameters in the Biosorption of Heavy Metals on Activated Sludge* vol. 5, 2009.

[76] W. Wei, Q. Wang, A. Li, J. Yang, F. Ma, S. Pi*, et al.*, *Biosorption of Pb (II) from aqueous solution by extracellular polymeric substances extracted from Klebsiella sp. J1: Adsorption behavior and mechanism assessment* vol. 6, 2016.

[77] M. B. Desta, "Batch Sorption Experiments: Langmuir and Freundlich Isotherm Studies for the Adsorption of Textile Metal Ions onto Teff Straw (Eragrostis tef) Agricultural Waste," *Journal of Thermodynamics,* vol. 2013, pp. 1-6, 2013.

[78] Z. Kariuki, J. Kiptoo, and D. Onyancha, *Biosorption studies of lead and copper using rogers mushroom biomass 'Lepiota Hystrix'* vol. 23, 2017.

[79] M. Ahmed, J. Zhou, H. Hao Ngo, and W. Guo, *Adsorptive removal of antibiotics from water and wastewater: Progress and challenges* vol. 532, 2015.

[80] A. Halim, M. T. Latif, and A. Ithnin, *Ammonia removal from aqueous solution using organic acid modified activated carbon* vol. 24, 2013.

[81] D. Suteu, A. Blaga, M. Diaconu, and T. Măluțan, *Biosorption of reactive dye from aqueous media using Saccharomyces cerevisiae biomass. Equilibrium and kinetic study* vol. 11, 2013.

[82] R. Saadi, Z. Saadi, R. Fazaeli, and N. Fard, *Monolayer and multilayer adsorption isotherm models for sorption from aqueous media* vol. 32, 2015.

[83] I. Tsibranska and E. Hristova, *Comparison of different kinetic models for adsorption of heavy metals onto activated carbon from apricot stones* vol. 43, 2011.

[84] D. Robati, *Pseudo-second-order kinetic equations for modeling adsorption systems for removal of lead ions using multi-walled carbon nanotube* vol. 3, 2013.

[85] L.-E. Liu, J. Liu, H. Li, H. Zhang, J. Liu, and H. Zhang, *Equilibrium, kinetic, and thermodynamic studies of lead (II) biosorption on sesame leaf* vol. 7, 2012.

[86] K. B. Fontana, G. Gonçalves, E. R. L. R. Watanabe, E. Lenzi, J. A. M. T. Pietrobelli, and E. Chaves, *Biosorption and Diffusion Modeling of Pb(II) by Malt Bagasse* vol. 2016, 2016.

[87] M. Auta and B. Hameed, *Modified mesoporous clay adsorbent for adsorption isotherm and kinetics of methylene blue* vol. s 198–199, 2012.

[88] S. Ismadji, F. Edi-Soetaredjo, and A. Ayucitra, "Natural Clay Minerals as Environmental Cleaning Agents," ed, 2015, pp. 5-37.

[89] S. Pandey and J. Ramontja, *Recent Modifications of bentonite Clay for Adsorption Applications* vol. 2, 2016.

[90] I. E. Odom, *Smectite clay Minerals: Properties and Uses* vol. 311, 1984.

[91] A. A. Adeyemo, I. O. Adeoye, and O. S. Bello, "Adsorption of dyes using different types of clay: a review," *Applied Water Science,* vol. 7, pp. 543-568, 2017/05/01 2017.

[92] A. A. Adeyemo, I. O. Adeoye, and O. S. Bello, "Adsorption of dyes using different types of clay: a review," *Applied Water Science,* vol. 7, pp. 543-568, 2017/05/01 2017.

[93] R. Srinivasan, "Advances in application of natural clay and its composites in removal of biological, organic, and inorganic contaminants from drinking water," *Advances in Materials Science and Engineering,* vol. 2011, 2011.

[94] A. Battas , A. El Gaidoumi, A. Ksakas, and A. Kherbeche, "Adsorption Study for the Removal of Nitrate from Water Using Local Clay", *The Scientific World Journal,* vol.2019, Feb 2019.

[95] J. Coates,"Interpretation of infrared spectra, a practical approach," *Encyclopedia of analytical chemistry: applications, theory and instrumentation,* 2006.

[96] F. O. Nwosu, O. J. Ajala, R. M. Owoyemi and B. G. Raheem, "Preparation and characterization of adsorbents derived from bentonite and kaolin clays", *Applied Water Science (2018) 8:195.*

[97] O. I. El-Shafey, N. A. Fathy, and T. A. El-Nabarawy, "Sorption of Ammonium Ions onto Natural and Modified Egyptian Kaolinites: Kinetic and Equilibrium Studies", *Advances in Physical Chemistry,* vol. 2014.

[98] J.K.Edzwald, D.C. Toensing, and M.Chi-Yew Leung, "Phosphate Adsorption Reactions with clay minerals", *Environmental Science and Technology*, Vol.10, no.5, May 1976.

[99] A. Ansary-Moghaddam, E.BAZRAFSHAN, P. Amirian, A.H. Mahvi, "Application Of Adsorption Process For Phenolic Compounds Removal From Aqueous Environments: A Systematic Review", *Global NEST Journal,* Vol 18, No 1, pp 146-163, 2016.

[100] F. Ayarib, S. Eturkia, N. Jedidia, and H. Ben Dhia,"Use of clay mineral to reduce ammonium from wastewater. Effect of various parameters", *SURFACE ENGINEERING AND APPLIED ELECTROCHEMISTRY* Vol. 48 No. 3 2012.

[101] O. A. Habeeb, R. Kanthasamy, G.A. Mohammed Ali and R.M. Yunus , "Isothermal Modelling Based Experimental Study Of Dissolved Hydrogen Sulfide Adsorption From Waste Water Using Eggshell Based Activated Carbon", *Malaysian Journal of Analytical Sciences,* Vol 21 No 2 (2017): 334 - 345

7. APPENDIXES

A. Experimental data

Table A1: NO_3^- and PO_4^{3-} adsorption results at different levels of pH, contact time and initial concentration with constant clay dose of 2g, temperature of 30°c and stirring of 200rpm

pH	NO_3^-			pH	PO_4^{3-}		
	Co	time	% Removal		Co	Time	% Removal
2	10	30	61.77	5	20	30	83.75
2	10	60	75.87	5	20	60	90.28
2	10	90	86.41	5	20	90	90.82

2	15	30	57.91	5	25	30	87.26
2	15	60	72	5	25	60	93.79
2	15	90	82.54	5	25	90	94.33
2	20	30	54.71	5	30	30	87.73
2	20	60	68.8	5	30	60	94.26
2	20	90	79.34	5	30	90	94.8
3	10	30	57.87	7	20	30	83.28
3	10	60	71.96	7	20	60	89.82
3	10	90	82.5	7	20	90	90.36
3	15	30	54	7	25	30	86.79
3	15	60	68.09	7	25	60	93.32
3	15	90	78.63	7	25	90	93.86
3	20	30	50.8	7	30	30	61.9
3	20	60	54.89	7	30	60	93.8
3	20	90	65.43	7	30	90	94.34
5	10	30	49.69	9	20	30	82.58
5	10	60	63.79	9	20	60	89.12
5	10	90	74.33	9	20	90	89.66
5	15	30	45.83	9	25	30	86.09
5	15	60	59.92	9	25	60	92.62
5	15	90	70.46	9	25	90	93.16
5	20	30	42.63	9	30	30	86.6
5	20	60	56.72	9	30	60	93.1
5	20	90	67.26	9	30	90	93.64

Table A$_2$: NH_3 and H_2S adsorption results at different levels of pH, contact time and initial concentration with constant clay dose of 2g, temperature of 30°c and stirring of 200rpm

	NH_3			H_2S			
pH	Co	Time	%Removal	pH	Co	time	%Removal
5	10	30	75.58	5	10	30	70.06
5	10	60	86	5	10	60	74.39
5	10	90	80.1	5	10	90	80.93
5	15	30	70.03	5	15	30	64.76
5	15	60	86.45	5	15	60	69.09
5	15	90	86.52	5	15	90	75.62

5	20	30	76.21	5	20	30	62.43
5	20	60	86.5	5	20	60	66.76
5	20	90	86.69	5	20	90	73.3
7	10	30	83.81	7	10	30	76.98
7	10	60	94.23	7	10	60	81.31
7	10	90	94.3	7	10	90	87.84
7	15	30	84.26	7	15	30	71.67
7	15	60	94.85	7	15	60	76.01
7	15	90	94.75	7	15	90	82.54
7	20	30	84.44	7	20	30	69.34
7	20	60	94.85	7	20	60	73.68
7	20	90	94.92	7	20	90	80.21
9	10	30	79.15	9	10	30	75.73
9	10	60	89.56	9	10	60	80.06
9	10	90	89.63	9	10	90	86.6
9	15	30	79.6	9	15	30	70.43
9	15	60	90.01	9	15	60	74.76
9	15	90	90.08	9	15	90	81.29
9	20	30	79.77	9	20	30	68.1
9	20	60	90.19	9	20	60	72.43
9	20	90	90.26	9	20	90	78.97

Co	Ce			qe				Ce/qe			
	NO_3^-	PO_4^{3-}	H_2S	NO_3^-	PO_4^{3-}	NH_3	H_2S	NO_3^-	PO_4^{3-}	NH_3	H_2S
5	0.369	2.11	0.41	0.23	0.1445	0.034	0.229	1.6	14.60207612	9.68	1.79
10	3.36	3.96	1.17	0.33	0.302	0.105	0.442	10.18	9.585798817	3.74	2.65
15	6.78	4.82	4.14	0.41	0.509	0.229	0.543	16.54	8.985507246	1.85	7.62
20	10.96	5.64	6.92	0.45	0.718	0.479	0.654	24.36	7.453671929	0.89	10.58

25	14.67	5.92	10.76	0.52	0.954	0.728	0.712	28.21	6.852846402	0.598	15.11
30	20.133	6.12	17.31	0.49	1.194	0.976	0.635	41.09	5.951557093	0.488	27.26
35	0	6.98	0	0	1.401	0	0	0	5.107604017	0	0

Table A3: data on Langmuir equilibrium adsorption isotherm models on adsorption of NO_3^-, PO_4^- and H2S on local clay

Co = initial concentration, Ce= equilibrium concentration, qe = adsorption capacity

Table A4: data on Langmuir and Freundlich equilibrium adsorption isotherm models on adsorption of NH_3 on local clay

NH_3					
C_0	Ce	qe	Ce/qe	lnCe	lnqe
1	0.329	0.034	9.68	-1.111697528	-3.381394754
2.5	0.393	0.105	3.74	-0.933945667	-2.253794929
5	0.422	0.229	1.85	-0.862749965	-1.474033275
10	0.425	0.479	0.89	-0.85566611	-0.736054682
15	0.435	0.728	0.598	-0.832409248	-0.317454231
20	0.476	0.976	0.488	-0.742337425	-0.024292693

Table A5: data on Freundlich equilibrium adsorption isotherms model on adsorption of NO^-_3, PO_4^{3-} and H_2S

lnCe			lnqe		
NO_3^-	PO_4^{3-}	H2S	NO_3^-	PO_4^{3-}	H2S
-0.996958635	0.746687947	-0.891598119	-1.47	-2.172	-1.474033275
1.211940974	1.17557333	0.157003749	-1.11	-1.252	-0.816445397
1.913977102	1.53686722	1.420695788	-0.89	-0.611	-0.610645959
2.394252282	1.691939134	1.93441577	-0.799	-0.236	-0.424647928

2.685804592	1.853168097	2.375835555	-0.654	0.11	-0.339677368
3.00236026	1.928618652	2.851284369	-0.713	0.315	-0.45413028

Table A$_6$:Pseudo first order kinetics of adsorption

time	Ct				qt			
	NO_3^-	PO_4^{3-}	NH_3	H_2S	NO_3^-	PO_4^{3-}	NH_3	H_2S
30	11.75	2.588	1.131	0.96	0.913	1.37	1.442	1.45
60	3.98	2.15	1.194	2.925	1.301	1.39	1.44	1.354
90	1.026	2.147	1.294	3.45	1.45	1.393	1.435	1.328
120	5.22	2.29	2.58	4.092	1.523	1.395	1.37	1.295

qe-qt				ln(qe-qt)			
NO_3^-	PO_4^{3-}	NH_3	H_2S	NO_3^-	PO_4^{3-}	NH_3	H_2S
0.61	0.025	0	0	-0.494296322	-3.688879454	0	0
0.222	0.005	0.002	0.096	-1.505077897	-5.298317367	-6.214608098	-2.343407088
0.073	0.002	0.007	0.122	-2.617295838	-6.214608098	-4.96184513	-2.103734234
0	0	0.072	0.155	0	0	-2.63108916	-1.864330162

Table A$_7$:Pseudo second order kinetics of adsorption

t	t/qt			
	NO^-3	PO_4^{3-}	NH3	H2S
30	32.85870756	21.89781022	20.80443828	20.68965517
60	46.11837048	43.16546763	41.66666667	44.31314623
90	62.06896552	64.60875808	62.71777003	67.77108434
120	78.79185817	86.02150538	87.59124088	92.66409266

Table A_8: Thermodynamic data of adsorption process

1/T	qe				Ce			
	NO_3^-	PO_4^{3-}	NH_3	H_2S	NO_3^-	PO_4^{3-}	NH_3	H_2S
0.00330033	0.583	0.787	1.327	0.551	18.35	14.25	3.4588	18.99
0.003144654	0.846	0.939	1.39	0.644	13.08	11.21	2.1674	17.13
0.003003003	1.135	1.058	1.415	1.002	7.3	8.83	1.7	9.97
0.002832861	1.32	1.46	1.449	1.374	3.6	0.77	1.0166	2.53

lnqe/Ce			
NO_3^-	PO_4^{3-}	NH_3	H_2S
-3.449197667	-2.896283937	-0.958000953	-3.539932995
-2.738320265	-2.479746037	-0.444224545	-3.280887865
-1.861241697	-2.121774681	-0.18349872	-2.297582581
-1.003302109	0.6398012	0.354409937	-0.610493109

Table A_9: Effect of pH, adsorbent dosage, initial concentration of adsorbate, contact time, temperature and particle size on adsorption process at optimum condition of each species separately at 200 rpm

pH	%Removal			
	NO_3^-	PO_4^{3-}	NH_3	H_2S
2	96.24	36.91	32.64	33.67

3	84.52	78.6	52.8	45.98
5	60	96	73.56	65.97
7	42.1	94.6	98.25	86.72
9	33.91	92.5	84.26	82.98
11	22.78	90.12	72.14	80.26

Dose	%Removal			
	NO_3^-	PO_4^{3-}	NH_3	H_2S
2	30.11	25.61	22.72	98.4
5	42.98	58.4	69.25	92.13
7	72.36	72	78.21	86.52
9	78.45	80.13	88.1	76.4
11	91.4	90.2	92.61	54.16

Initial Concentration	%Removal		
	NO_3^-	PO_4^{3-}	H_2S
5	92.62	26.89	91.8
10	66.4	57.1	88.31
15	54.8	72.41	72.4
20	45.2	79.15	65.42
25	41.32	89.67	56.98
30	32.89	91.09	42.3

35		97.23		
Contact Time	%Removal			
	NO_3^-	PO_4^{3-}	NH_3	H_2S
30	22.68	76.1	57.44	55.9
60	64.96	95.7	88.68	68.9
90	96.58	93.71	87.06	88.5
120	94.82	91.82	87.14	86.36
Temperature	%Removal			
	NO_3^-	PO_4^{3-}	NH_3	H_2S
0	0	0	0	0
30	38.83	52.5	65.41	36.7
45	56.4	62.62	78.32	42.9
60	75.68	70.54	82.98	66.78
80	87.96	97.43	89.82	91.56
95			90.61	
Effect of Size	%Removal			
	PO_4^{3-}		NH_3	
63µm	99.18		99.88	
90µm	93.98		99.86	
1mm	94		98.99	

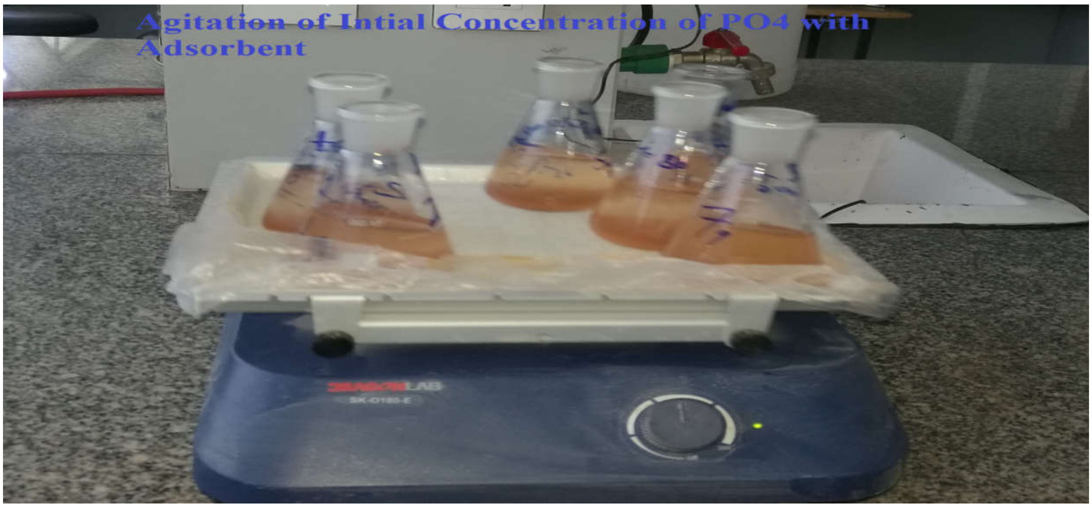
Table A10. Characteristic IR absorption frequencies of Local Clay functional groups

Wave number(cm^{-1})	Functional Groups	Types of vibration
3750-3500	OH	Stretching
3424	H-O-H	Stretching
3129	=C-H	Stretching
1641	H-O-H	bending
1568	-C-H	Stretching
1398	Organic SO_4	Stretching
1178	C=N	Stretching
1041	Si-O-Si	Stretching
1037	Si-O	Stretching
900-800	Al-OH, AlMgOH, Al-Al-OH	Al substitution by Mg, Stretching
583	S-S	Stretching
538	Si-O	bending
469	Al-O	bending

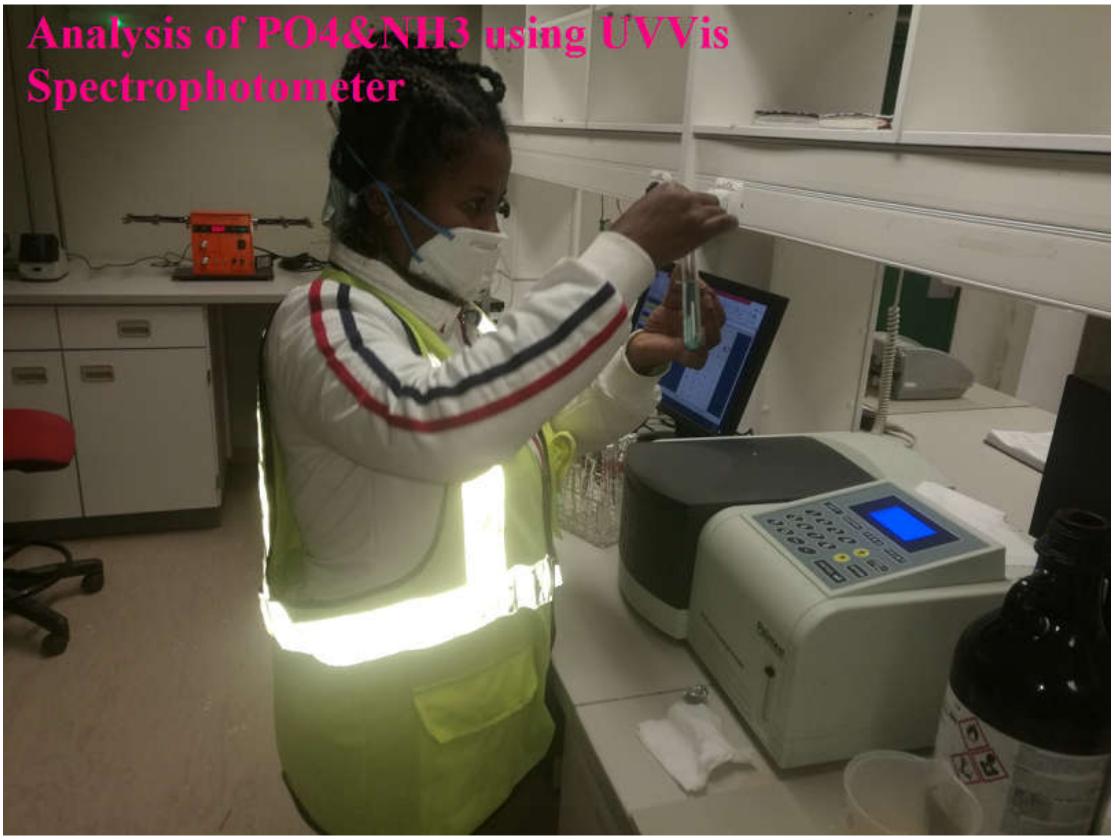
B. Laboratory Photos

Prepared Adsorbent with d/t sieve size

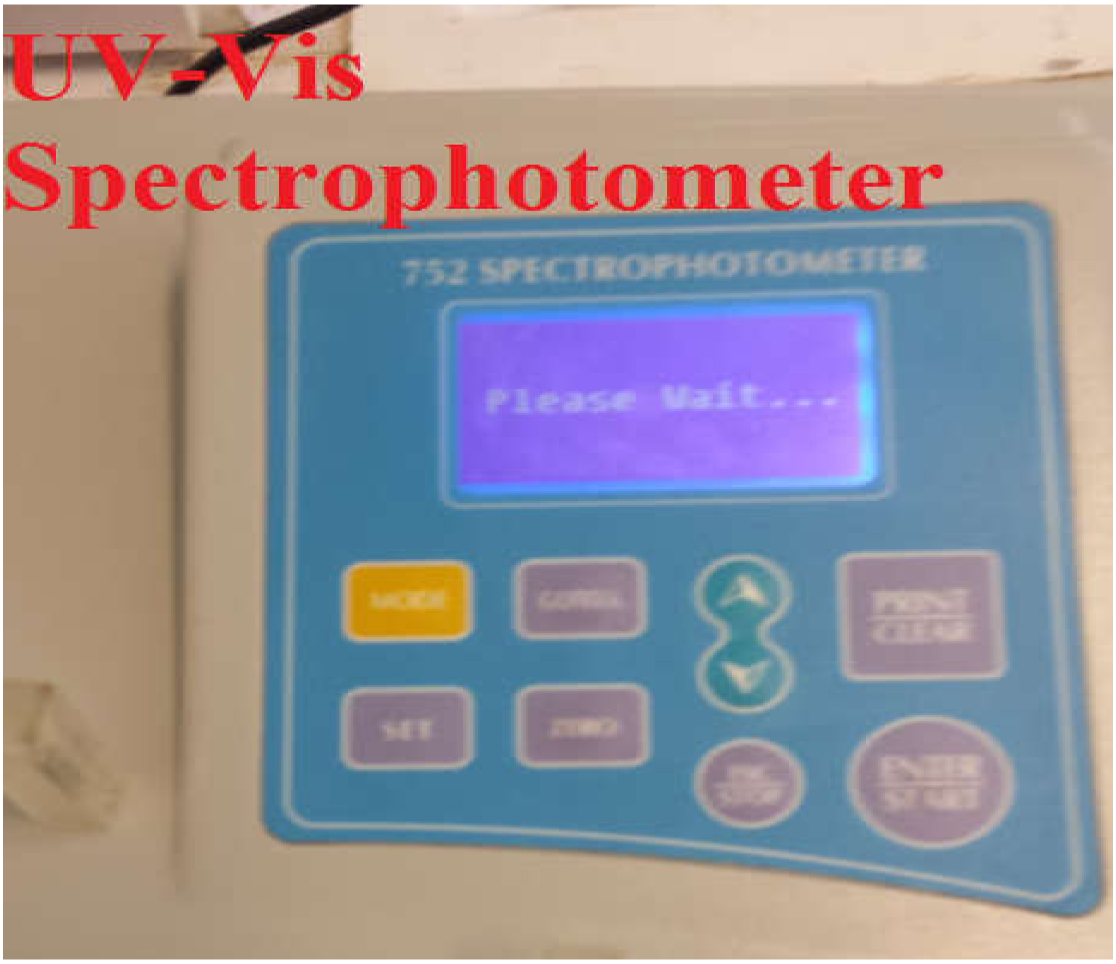
Conducting NH3 analysis Using photo meter



Agitation of Intial Concentration of PO4 with Adsorbent


Analysis of PO4&NH3 using UVVis Spectrophotometer


Hach DR900 photometer
and Electronic Balance



UV-Vis Spectrophotometer