INTRODUCTION
Drinking water free of toxic chemicals or having below the maximum acceptable level of concentration is crucial for health life. Currently, increased industrialization1, 2, 3, use of chemicals for various concerns2, agricultural1, 3 and domestic1 activities both in developing and developed countries have resulted ground and surface drinking water contamination with a number of toxic pollutants. It is reported that 60 % population of developing countries have no access to safe drinking water1. From the various water contaminants studied, nitrate is the most important1. Contamination of ground and surface water by nitrate is increased as a result of excessive use of nitrogenous fertilizers in agricultural activities4, 5 and disposal of untreated sanitary and industrial wastes4. Nitrate occurs naturally in soil containing nitrogen-fixing bacteria, decaying plants, septic system effluent, and animal manure6; thus, discharge nitrate into water and contaminate it. Nitrate, due to its high water solubility, is possibly the most widespread groundwater contaminant in the world1. Nitrate gets into the body of human with drinking water, food, drug and etc7. Drinking water is one of the main sources of exposure to nitrates in areas where its concentration is exceeding the maximum acceptable contaminant level for nitrate set by the World Health Organization (WHO) and US Environmental Protection Agency (USEPA) for drinking water are 50mg/L and 45mg/L respectively (USEPA, 2000, WHO, 2004)4, 5. Elevated nitrate concentrations in drinking water more than the maximum acceptable contaminant level are linked to health problem such as methemoglobinemia in infants and stomach cancer in adults1-7. Different nitrate ion removal techniques from water based on physicochemical or biological principles, were investigated and compared for...
technical and economical feasibility. Among the techniques; nano-particles of zero valent iron magnetic, anoxic packed reactor, aluminnum nano particle, ion exchange, reverse osmosis, chemical reduction, electrodialysis, distillation and biological processes have been reported to have good removal capacity of nitrate from water. Activated carbon with Zn and ZnSO₄ also showed increased removal efficiency of nitrate from aqueous solution which is due increasing of activated carbon positive charge impregnation by Zn and ZnSO₄. This phenomena increased anions adsorption such as nitrate.

Natural 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. Large specific surface area, chemical and mechanical stability, layerd structure, high cation exchange capacity (CEC), and so forth have made the clays excellent adsorbent materials. Being natural and their abundance presence makes them a low-cost green, nontoxic adsorbent which can be used for removal of different contaminants from water and making clean and pure drinking water available for developed and developing nations. Thus, clays invariably contain exchangeable cations and anions held to the surface. The prominent cations and anions found on clay surface are Ca²⁺, Mg²⁺, H⁺, K⁺, NH₄⁺, Na⁺, SO₄²⁻, Cl⁻, PO₄³⁻, and NO₃⁻.

Over the recent years, research on the modification of clay to increase their adsorptive capacity to remove other contaminants from drinking water other than metals is in progress. In most of the cases, they proved to be better or comparable with the existing commercial filter materials, adsorbents, and conventional methods used for decontamination of drinking water.

The desired changes in the adsorptive properties of a bentonite occurring as a result of acid activation depend considerably on acid leaching conditions. Several acid activation experiments under different operating conditions have been reported in the literature, in particular the choice of acid concentration, treating time and temperature. It is also important to take into account the mineral composition of starting materials from various deposits when developing leaching procedure.

Acid modified natural bentonites are the subject of many studies. The acid treatment of clay minerals is referred to as acid activation because it increases the specific surface area and number of active sites of the solids and this increases the adsorptive power of the activated clay mineral. While acid activation of bentonite, exchangeable cations (Na⁺, K⁺, Ca²⁺) replaced by H⁺ and partial dissolution of octahedral cations (Al³⁺ or Mg²⁺) occurred thereby leaving some vacancies. Nitrate ion removal capacity of Ethiopian acid activated bentonite clay from water was not studied. Bentonite clay with different geographical location is different in chemical composition (Table 2) and thus has different adsorption capacity towards toxic chemicals from water. Under this study, we presented nitrate ion adsorption capacity of acid activated bentonite clay of Ethiopia, Afar, Gewane area, from synthetic water via batch experimental method. The result suggested an efficient removal of nitrate ion from aqueous solution to the level of acceptable concentration set by WHO. Experimental data shown in Table 1 indicates that activated bentonite under this study showed an excellent adsorption capacity of NO₃⁻ and better than several form of activated carbon, including some commercial brands. This provides strong evidence for the potential of activated bentonite in technological applications of toxic anions’ removal from aqueous solutions.

### Table 1: Comparison of specific nitrate adsorption capacity by different materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Adsorption capacity (mg/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wheat straw charcoal</td>
<td>1.1</td>
<td>16</td>
</tr>
<tr>
<td>Mustard straw charcoal</td>
<td>1.3</td>
<td>16</td>
</tr>
<tr>
<td>CAC; retail outlet of Eureka Frobes Limited Aquaquard</td>
<td>1.22</td>
<td>16</td>
</tr>
<tr>
<td>Bamboo powder</td>
<td>1.25</td>
<td>17</td>
</tr>
<tr>
<td>CAC; Nacalai tesque, Model 079-39, Japan</td>
<td>1.09</td>
<td>17</td>
</tr>
<tr>
<td>Coconut activated by ZnCl₂</td>
<td>10.3</td>
<td>7</td>
</tr>
<tr>
<td>2M HCl activated Ethiopian bentonite</td>
<td>5.0</td>
<td>This work</td>
</tr>
</tbody>
</table>

### MATERIALS AND METHODOLOGY

**Bentonite Clay**

Bentonite clay has been brought from geological survey of Ethiopia that was extracted from Gewane area (Figure 1), Afar region, North eastern Ethiopia.
Fig. 1: Picture showing bentonite deposit at Gewane area, Afar region, Ethiopia

Table 2: Chemical compositions of Ethiopian bentonite

<table>
<thead>
<tr>
<th>Locality</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>MnO</th>
<th>TiO₂</th>
<th>P₂O₅</th>
<th>H₂O</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gewane</td>
<td>61</td>
<td>11.5</td>
<td>6.9</td>
<td>0.7</td>
<td>2.6</td>
<td>1.3</td>
<td>1.1</td>
<td>0.1</td>
<td>1</td>
<td>-</td>
<td>10</td>
<td>4.8</td>
</tr>
<tr>
<td>Warssia</td>
<td>49</td>
<td>13.4</td>
<td>8.71</td>
<td>3.87</td>
<td>2.79</td>
<td>1.1</td>
<td>1.31</td>
<td>0.1</td>
<td>1.61</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Gidicho</td>
<td>60.8</td>
<td>10.9</td>
<td>13.5</td>
<td>0.9</td>
<td>1.3</td>
<td>2.2</td>
<td>1.1</td>
<td>0.16</td>
<td>1.09</td>
<td>-</td>
<td>2.3</td>
<td>7.7</td>
</tr>
</tbody>
</table>

Chemicals and Instrumentation

Chemicals
The chemicals those were used for the study include mainly hydrochloric acid (HCl, 37%, RPE) potassium nitrate (KNO₃, 99%, NICE) obtained from Addis Ababa NEWAY PLC. All chemicals and reagents are Analytical grade used without purification.

Instrumentation
The main instruments used are FTIR Spectroscopy, UV-VIS Spectrophotometer, DR5000 Model, HANNA pH-meter 211, Water Bath Grant GLS 400 Model and Sieve.

METHODOLOGY

Modification and acid activation of raw Bentonite
The Clay sample was crushed by laboratory mortar and pestle and sieved with standard sieve 150 μm for the physical modification of raw bentonite. The sample was then stored in an air-tight container for further use.

Activation of Bentonite Clay
According to Jovanovic and Jonackovic acid activated bentonite clay with HCl over concentration range of 0.5-4 M was found to have increased surface area. The maximum surface area and optimum porosity is achieved by activation with 2M HCl and decrease with further increase in acid concentration. The increase in surface area at low concentration is attributed to cation exchange (i.e replacement of exchangeable cation by H⁺ ion) and removal of impurities like calcite. However, the decrease in surface area beyond 2M HCl is due to structural changes and the decomposition of samples. Under this study, 50 g sample of natural bentonite clay was soaked in 250 mL of 2M HCl acid at 80 °C for 3hours in shaking water bath. It was then filtered and washed several times with distilled water until the pH of the solution was 6. Finally it was dried at 105 °C in oven until it has constant mass, grounded to pass 150 μm and stored for further use.

Preparation of Nitrate Solution
Nitrate stock solution of 1000 mg/L concentration was prepared by dissolving 1.63 g potassium nitrate which was pre-dried at 105 °C for 24 hours in 100 mL distilled water. The solution was then diluted to 1000.00 mL scale in a volumetric flask. From this solution, different standard solutions of 250-500 mg/L were prepared by dilution; 50 mL of each of these solutions was used in every experiment. At the end of each experiment, 20 mL of the solution of adsorption was taken from each sample and was preserved with 0.04 mL of concentrated sulfuric acid 98% (w/w). These solutions were stored at 4 °C in polyethylene containers until nitrate concentration was measured.

To prevent the interference of hydroxide and carbonate ion with nitrate ion, HCl solution (1.00 mL, 1.00 M) was added to 50 mL clear nitrate solution sample. The solution was then mixed thoroughly. Standards were treated in the same manner as samples.

Adsorption Experiment
Nitrate adsorption onto activated bentonite clay was studied by batch experiment in a set
of 100 mL capped conical flasks. All used apparatus were thoroughly pre cleaned with distilled water. After the adjustment of initial pH solution of nitrate using buffer solutions, it was added into flask containing activated bentonite. The experimental flasks were shaken at 250 rpm using a temperature controlled water bath. The flasks were left under continued constant-speed shaking for the desired time. In all cases, experiments were carried out in triplicate and mean values were taken for calculation. Optimization of contact time, initial pH, temperature, adsorbent and adsorbate; adsorption isotherm were studied.

RESULTS AND DISCUSSION
Bentonite characterization by FTIR
FTIR spectroscopy was carried out to analyze the effect of acid attack and the change that have taken place in the structure of bentonite as the result of modification by acid activation. Samples measured on PerkinElmer, Spectrum 65 FT-IR in the range 4000-400 cm\(^{-1}\) using KBr pellets.

![FTIR spectra of the natural and acid activated Ethiopian bentonite](image)

The FTIR spectra of natural bentonite and acid activated bentonite were taken in the range of 4000-400 cm\(^{-1}\). FTIR spectroscopy is very sensitive to modification of the clay structure upon acid treatment as illustrated in Figure 2. The spectrum of the original clay exhibits absorption bands at 3435 and 1635 cm\(^{-1}\) assigned to the stretching and bending vibrations of the OH groups for the water molecules adsorbed on the clay surface, and a band at 3618 cm\(^{-1}\) representing the stretching vibration of the hydroxyl groups coordinated to octahedral Al\(^{3+}\) cations.\(^{13}\) The Si–O bands are strongly evident in the silicate structure of the original clay and can be easily recognized in the infrared spectrum by very strong absorption bands in the 1100–1000 cm\(^{-1}\) region. The most intensive band at 1035 cm\(^{-1}\) is attributed to Si–O in-plane stretching. The bands at 526 and 468 cm\(^{-1}\) correspond to Si–O–Al (octahedral) and Si–O–Si bending vibrations respectively. The natural clay spectrum also contains a band at 794 cm\(^{-1}\) which is attributed to cristobalite. The bands at 912, 873 and 839 cm\(^{-1}\) arise from the bending modes of the hydroxyl groups AlAlOH, AlFeOH and AlMgOH, respectively. Similar result was reported by Ajemba \(^{14}\), Motlagh et al.\(^{15}\).

The FT–IR spectra of the natural and acid activated clay samples reflect the structural modification which takes place due to acid activation. Leaching causes the decrease in intensity of the absorption bands at 912, 873 and 839 cm\(^{-1}\). This result suggests the partial depletion of Al, Mg and Fe from the clay structure, in accordance with the changes in chemical composition. The intensity of the bands at 3435 and 1635 cm\(^{-1}\) for water of hydration and the hydroxyl stretching band at 3618 cm\(^{-1}\) also shows decrease after acid activation. It is due to the removal of octahedral cations, causing the loss of water and hydroxyl groups coordinated to them. After acid leaching, the intensity of the band at 1035 cm\(^{-1}\) decreases due to the formation of three–dimensional networks of amorphous Si–O–Si units.

The band at 792 cm\(^{-1}\) associated with cristobalite not only survives the acid leaching but increase in intensity during the process. In addition, the transformation of the tetrahedral sheet was found at 792 cm\(^{-1}\). The acid activation leads to the formation of amorphous silica, indicated by the increased intensity of the peak, which may expose more adsorption sites.\(^{16}\) Most band positions did not change following modification, suggesting that the basic bentonite structure did not collapse.

Spectrophotometric method of nitrate ion analysis
Nitrate concentration was determined by a standard method called “Ultraviolet Spectrophotometric Screening Method”. This method followed exactly the procedure described in the standard methods for the examination of water and wastewater.\(^{24}\) Nitrate ion absorbance at 220 nm was measured against distilled water background and at 275 nm to determine interference with dissolved organic matter. Net absorbance due to NO\(_3^-\) ions was calculated by the following equation:

\[
\text{Absorbance due to } \text{NO}_3^- = \text{Abs}_{220} - [2 \times \text{Abs}_{275}] \ldots \ldots \ldots \ldots
\]
Experimentally, nitrate ion solution (100 mg/L NO$_3^-$) was prepared by diluting 100.00 mL of the stock solution prepared from KNO$_3$ with distilled water and further diluted to get standard solutions with concentrations in the range 0.0-7.0 mg/L NO$_3^-$. The data are indicated below in Table 3 and Figure 3.

### Table 3: Spectrophotometric data used for calibration curve

<table>
<thead>
<tr>
<th>Amount of nitrate (mg/L)</th>
<th>Absorbance at 220 nm</th>
<th>Absorbance at 275 nm</th>
<th>NO$_3^-$ absorbance (Abs220 -</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>0.152</td>
<td>0.01</td>
<td>0.132</td>
</tr>
<tr>
<td>2</td>
<td>0.257</td>
<td>0.011</td>
<td>0.235</td>
</tr>
<tr>
<td>3</td>
<td>0.38</td>
<td>0.012</td>
<td>0.356</td>
</tr>
<tr>
<td>4</td>
<td>0.491</td>
<td>0.014</td>
<td>0.463</td>
</tr>
<tr>
<td>5</td>
<td>0.582</td>
<td>0.015</td>
<td>0.552</td>
</tr>
<tr>
<td>6</td>
<td>0.689</td>
<td>0.017</td>
<td>0.655</td>
</tr>
</tbody>
</table>

As indicated above in Figure 4, nitrate adsorption onto activated bentonite increases when increasing treatment time starting from “0 to 90” min. However, the increase was not significant for longer contact times. This trend could be attributed to the fact that at the initial time between 0-90 minutes there exist a number of vacant sites on the adsorbent but after 90 minutes these sites became filled with the adsorbate molecules which at a point between 90 and 180 minutes the repulsive force between solute molecules and bulk phase becomes significant and the vacant sites remain constant with time. This observation agrees with the literature reported by Saravanane et al.

### Effect of pH

Adsorption of nitrate by activated bentonite was investigated in the pH range 2-10. The pH was varied as desired, by adding different buffer solutions (i.e acetate buffer for pH 2 - 5.6, phosphate buffer for pH 6 - 8.5 and ammonium buffer for pH 9 and 10). After the desired pH was fixed for nitrate solution (50 mL, 250 mg/L), 2.0 g of adsorbent was mixed with. The mixture was then shaken at 30 °C for 90 minutes and nitrate analysis was made.

Bentonite is a metal oxide adsorbent containing different metal oxide in the structure. In activation, hydroxylated surfaces of these oxides developed charge on the surface. The interaction between nitrate ion and metal oxide was modeled by assuming ligand exchange reactions as follows

\[
\text{MOH} + \text{H}^+ \leftrightarrow \text{MOH}^+ \quad \text{23}
\]

\[
\text{MOH}^+ + \text{NO}_3^- \leftrightarrow \text{MOHNO}_3 (\text{or} \quad \text{MNO}_3 + \text{H}_2\text{O}) \quad \text{23}
\]

where M represents metal ions (Al, Fe or Si). Similar results have been reported by Cengeloglu et al. for adsorption of nitrate by red mud. The result (Figure 5) shows that higher adsorption capacity is observed at lower pH values (acidic media) and it has a decreasing tendency as the pH increased. This is because bentonite becomes progressively deactivated, loses its positive surface charges and its adsorbent capacity towards the nitrate anion decreases.
Effect of Temperature
Temperature affects the adsorption rate by altering the molecular interactions and the solubility of the adsorbate and thus affects adsorption. To find an optimum temperature, the adsorption was done at a temperature of 20, 25, 30, 35, 40 and 45 °C. The other parameters were made constant; adsorbent (2.0 g), nitrate solution (50 mL, 250 mg/L), contact time (90 minutes) and pH (5).

The result showed that the percentage of nitrate adsorption increased when the temperature increased to 30 °C. However, when the temperature further increased, the adsorption decreased, as shown in Figure 6, probably desorption took place.

Effect of adsorbent dosage
Different amounts (0.25-2.50 g) of bentonite was placed into conical flasks, then nitrate solutions (50 mL, 250 mg/L) with pH 5 was added to it. The mixture was then shaken for 90 minutes at 30 °C.

As indicated in Figure 7, removal of nitrate increased with increase in adsorbent mass. This is to be expected because for a fixed initial solute concentration, increase in total dose present a greater surface area and increase adsorption potential. However, it is observed that as the adsorbent mass increases, there was no change in percentage removal possibly due to overlapping of active sites at higher dosage.

Effect of initial nitrate concentration
Nitrate solutions with different concentrations (250-500 mg/L NO₃⁻) with pH 5 were added to adsorbent samples (2.0 g each). Each mixture was then shaken at 30 °C for 90 minutes. Initial and final nitrate concentrations were recorded. The adsorption capacity at equilibrium $q_e$ (mg/g) was calculated according to equation:

$$q_e = \frac{(C_0 - C_e)V}{W}$$

where $C_0$ and $C_e$ (mg/L) are the liquid-phase concentrations of nitrate initially and at equilibrium respectively, $V$ is the volume of the solution (L) and $W$ is the mass of dry adsorbent used (g).

As can be seen from the result presented in Figure 8, nitrate removal efficiency decreases with increasing initial nitrate concentration. The decrease in removal efficiency at higher initial nitrate concentrations is due to the saturation of the most active sites of the adsorbent due to increased diffusion rate of nitrate to adsorption sites, tending to saturate them, and in turn, the ulterior utilization of less accessible or less active sites of the adsorbent. Similar results has been reported by Gupta et al on equilibrium sorption of Pb(II) and nitrate ions from aqueous solution using chemically modified rice husk.
Adsorption isotherms
In this study, Langmuir and Freundlich isotherm models were used to describe the relationship between the amounts of nitrate adsorbed and its equilibrium concentration in solution at 30 °C using adsorbate (2.0 g), nitrate solutions (250, 300, 350, 400, 450, 500 mg/L), pH (5) and contact time (90 minutes) has been studied and results are shown in Figure 10 & Figure 11.

Langmuir equation
It assumes a mono layer adsorption onto a uniform adsorbent surface with energetically identical sorption sites 30. The linear form of Langmuir isotherm equation is given by:

\[ \frac{C_e}{q_e} = \frac{1}{Q_o} + \frac{1}{Q_o b C_e} \]

where \( C_e \) is the equilibrium concentration of the adsorbate (mg/L), \( q_e \) is the amount of adsorbate per unit mass of adsorbent (mg/g), \( Q_o \) and \( b \) are Langmuir constants related to adsorption capacity and rate of adsorption. Further, the essential characteristics of the Langmuir isotherm can be described by a separation factor \( R_L \); which is defined by the following equation

\[ R_L = \frac{1}{1 + b C_o} \]

Freundlich equation
It describes equilibrium on heterogeneous surfaces and hence does not assume mono layer capacity. The well-known logarithmic form of the Freundlich isotherm expression is given by the following equation

\[ \log q_e = \log K_F + \frac{1}{n} \log C_e \]

Where \( C \) is the initial concentration of nitrate (in ppm or mg/L) and \( b \) is the Langmuir constant (in g/L). The value of separation factor \( R_L \), indicates the isotherms shape and the nature of the adsorption process is unfavorable (\( R_L > 1 \)), linear (\( R_L = 1 \)), favorable (0 < \( R_L < 1 \)) and irreversible (\( R_L = 0 \)) 31.

Table 4: Effect of Adsorbate concentration on percent removal of nitrate and calculation of adsorption isotherms

<table>
<thead>
<tr>
<th>Nitrate concentrations (mg/L)</th>
<th>( C_o )</th>
<th>( q_o )</th>
<th>% removal</th>
<th>( C_e q_e )</th>
<th>( \log C_e )</th>
<th>( \log q_e )</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>50</td>
<td>5.00</td>
<td>80</td>
<td>10</td>
<td>1.69</td>
<td>0.69</td>
</tr>
<tr>
<td>300</td>
<td>69</td>
<td>5.775</td>
<td>77</td>
<td>11.948</td>
<td>1.83</td>
<td>0.76</td>
</tr>
<tr>
<td>350</td>
<td>84</td>
<td>6.650</td>
<td>76</td>
<td>12.63</td>
<td>1.92</td>
<td>0.82</td>
</tr>
<tr>
<td>400</td>
<td>124</td>
<td>6.900</td>
<td>69</td>
<td>17.97</td>
<td>2.09</td>
<td>0.83</td>
</tr>
<tr>
<td>450</td>
<td>166.5</td>
<td>7.0875</td>
<td>63</td>
<td>23.49</td>
<td>2.22</td>
<td>0.85</td>
</tr>
<tr>
<td>500</td>
<td>200</td>
<td>7.500</td>
<td>60</td>
<td>26.67</td>
<td>2.3</td>
<td>0.875</td>
</tr>
</tbody>
</table>

Fig. 9: Adsorption isotherms of nitrate on the acid activated bentonite clay at 30°C
From Table 5 it can be seen that the value of $n = 3.68$ that it is in range set by Freundlich model which is between 1 and 10 showing favorable adsorption of nitrate onto the activated bentonite prepared in this work. At the same time, the separation factor $R_L = 0.13$, is in the range $0 < R_L < 1$, which indicates a favorable adsorption process.

In view of correlation coefficient, $R^2$, values for Langmuir more close to 1 than the value for Freundlich models and thus the data best fit with Langmuir model. Similar results reported by Djebbar et al. to explain the adsorption of phenol on natural clay.

### CONCLUSION

Natural bentonite clay has been activated by 2M HCl and the result obtained by FIT-IR spectroscopy characterization indicated the expected activation. Nitrate ions removal capacity of acid activated Ethiopian bentonite clay from aqueous solution was studied using batch experiment and the results obtained indicates that greater than 80% of nitrate ions has been removed from aqueous solution at optimum conditions of contact time (90 minutes), acid activated Ethiopian bentonite clay (2.0 g), initial nitrate concentration (250 mg/L), pH (5), and temperature (30°C). With the help of Langmuir and Freundlich models, adsorption isotherms of nitrate ions removal efficiency from aqueous solution by acid activated bentonite were studied and the data best fit into the Langmuir model. Thus, this work consider acid activated Ethiopian bentonite clay as being good alternative less expensive materials for purification of water from nitrate ions.

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