Effect of Acid Treatment on the Chemical Properties of Clays from Selected Sites in Murang’a and Nyeri counties, Kenya

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Abstract
Assessing improvement on the quality of clay has been conducted by treatment with different concentrations of hydrochloric and oxalic acid. This project intended to assess the effect of acid treatment on the elemental composition of clays from selected sites. The clays were leached using hydrochloric and oxalic acid separately at a concentration of 0.0, 0.1, 0.25, 0.5, 1, and 2M. The elemental composition of raw and acid-treated clays was determined using AAS. Elemental composition of the acid-treated clays, in oxide form were in the ranges of 40.80-65.16 % SiO$_2$, 7.16-30.33 % Al$_2$O$_3$, 0.33-7.62 %TiO$_2$, 0.24-2.65 % K$_2$O, 0.01-1.82 % MgO. The findings of this study showed that the quality of clays could be improved by acid treatment hence the clays can be used as a source of raw materials for industrial applications.

Keywords: Acid-treatment, Elemental, raw materials
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Introduction
Clay is a stony or earthy mineral aggregate composed of fine-grained minerals, which are plastic at appropriate water content and hardens up when fired [1,2]. Clays have a variable chemical composition that largely depends on parent rock from which they originated and the physical and chemical changes in the environment where they are found [3]. Clay has silica, alumina, and water as primary constituents; other constituents are iron, alkaline, and alkaline earth metals [4]. The industrial utilization of clay is closely related to its reactivity and surface properties and depends strongly on surface modification. Several ways are recommended in literature to enhance the properties of clay materials with thermo-chemical treatment [5,6] or chemical activation [7].

The presence of built-in impurities in clays has a huge impact on the utility of clays. Most clays contain high levels of iron oxides, acid treatment help improve properties and applications of clay [5,8]. Iron impurities removal and reduction are of great importance for the usability of clay in many of its applications especially where purity requirements are specifically high, in order to make high-quality ceramic products clay with low iron content, preferably less than 1% are desirable [9]. Approaches of minimizing iron in clays include froth floatation, gravity, and magnetic separation, reductive roasting, size separation by hydrocyclone, selective flocculation and acid treatment/leaching [10,11,12,13,14,15]. Chemical treatment methods such as acid activation improve surface and catalytic properties of clay by inducing changes in crystal structures of aluminosilicate minerals because of the dissolution of ions and/or structural rearrangement [16,10,5,8]. Hydrochloric acid is preferentially used because of the ease of titration of its slurry, ease of removal of the iron matrix, and titanium oxide insolubility, which is present in many types of clay [17]. However, other inorganic acids used include sulfuric acid [13,14,12]. Among the organic acids, Oxalic acid has shown the best efficiency in kaolin whitening with iron removals of 45-80% having been obtained [18], [14] Studied iron removal from clays by acid treatment, the findings of the study revealed that plasticity property of the acid-treated clays was restored by base treatment of the acid-treated samples [14], [15] Studied elemental and mineralogical composition of raw and acid-washed clays from Kano plains, the findings of this study revealed that iron oxides levels were reduced by acid treatment and the second finding was that acid treatment alters the mineralogical composition of clays and results to clay minerals interconversion [15]. This study was conducted with the aim of assessing the effect of treating clays with different concentrations of hydrochloric and oxalic acid on the elemental composition of clays. This paper, therefore, reports the findings of the effects of acid treatment on the elemental composition of acid-treated clays.

Materials and Methods
The purposive non-probability sampling design was used to select sampling sites. Samples were obtained from sites whose clays were being commercially for pottery. The clay deposits investigated were collected from Githima (0° 46’ 40” S, 37° 6’ 31” E), Kimathi (0° 40’ 0” S, 37° 10’ 28” E) and Ithanje (0° 36’ 30” S, 37° 6’ 46” E). The clay samples were collected at two depths that is 0.5 and 1.0 meter. In each site, the clay samples were obtained from three (3) points that were at least 100 meters apart. From each sampling point/depth 10 kg samples were collected and packed in newly cleaned plastic buckets which were then covered with their lids.

Weighed 0.1g of clay sample was placed in a 125-mL plastic beaker, 1.0 ml of aqua-regia was added then 3.0 ml of hydrofluoric acid was added and left to digest for 8 hours. 50 ml boric acid was added to allow further
digestion for one hour. This solution was topped to the 100 ml mark using distilled water. Samples were analyzed alongside the standards [13]. This was done using AAS at the department of Mines and Geology, Ministry of Petroleum and Mining. The results of the elemental analysis of the raw clay samples were given in the form of percentage weight (wt %) of SiO₂, Al₂O₃, Fe₂O₃, etc.

Weighed 100 g of each sample was put in a beaker and 200 ml of hydrochloric acid of different molarities (0.0M, 0.1M, 0.25M, 0.5M, 1M, and 2M) was added to each clay sample and the reaction allowed to proceed for 24 hours. Each of the mixtures obtained was subjected to filtration and the residue washed using distilled water to remove any acid-matrix. Rinsed residues were oven-dried then later cooled. The cooled samples were prepared for AAS analysis [3, 13].

Results and Discussion

Table 1 below shows variation in concentration of the various elements when the clays samples were treated with different concentrations of hydrochloric acid and oxalic acid.

### Table 1: Variation of the elemental composition of clays from selected sites with acid treatment

| Acid used | Site       | Acid conc | SiO₂ (%) | Al₂O₃ (%) | CaO (%) | MgO (%) | K₂O (%) | TiO₂ (%) | MnO (%) | Fe₂O₃ (%) | LOI (%) |
|-----------|------------|-----------|----------|-----------|---------|---------|---------|----------|---------|-----------|---------|
| HCl       | Githma     | 0.0 M     | 44.03±0.03 | 22.02±0.04 | 13.03±0.04 | 0.28±0.01 | 0.02±0.01 | 0.96±0.03 | 7.62±0.03 | 0.08±0.02 | 20.53±0.15 | 11.47   |
|           |            | 0.1M      | 44.96±0.03 | 22.15±0.04 | 13.13±0.04 | 0.29±0.01 | 0.02±0.01 | 0.97±0.03 | 7.63±0.03 | 0.08±0.02 | 20.54±0.15 | 11.47   |
|           |            | 0.25M     | 46.03±0.03 | 22.35±0.04 | 13.23±0.04 | 0.30±0.01 | 0.02±0.01 | 0.98±0.03 | 7.64±0.03 | 0.08±0.02 | 20.55±0.15 | 11.47   |
|           |            | 0.5M      | 47.03±0.03 | 22.53±0.04 | 13.33±0.04 | 0.31±0.01 | 0.02±0.01 | 0.99±0.03 | 7.65±0.03 | 0.08±0.02 | 20.56±0.15 | 11.47   |
|           |            | 1M        | 50.03±0.03 | 22.93±0.04 | 13.53±0.04 | 0.34±0.01 | 0.03±0.01 | 1.02±0.03 | 7.68±0.03 | 0.08±0.02 | 20.59±0.15 | 11.47   |
|           |            | 2M        | 52.03±0.03 | 23.33±0.04 | 13.73±0.04 | 0.36±0.01 | 0.03±0.01 | 1.04±0.03 | 7.71±0.03 | 0.08±0.02 | 20.62±0.15 | 11.47   |
| Oxalic acid | Ihanje     | 0.0 M     | 44.03±0.03 | 22.02±0.04 | 13.03±0.04 | 0.28±0.01 | 0.02±0.01 | 0.96±0.03 | 7.62±0.03 | 0.08±0.02 | 20.53±0.15 | 11.47   |
|           |            | 0.1M      | 44.96±0.03 | 22.15±0.04 | 13.13±0.04 | 0.29±0.01 | 0.02±0.01 | 0.97±0.03 | 7.63±0.03 | 0.08±0.02 | 20.54±0.15 | 11.47   |
|           |            | 0.25M     | 46.03±0.03 | 22.35±0.04 | 13.23±0.04 | 0.30±0.01 | 0.02±0.01 | 0.98±0.03 | 7.64±0.03 | 0.08±0.02 | 20.55±0.15 | 11.47   |
|           |            | 0.5M      | 47.03±0.03 | 22.53±0.04 | 13.33±0.04 | 0.31±0.01 | 0.02±0.01 | 0.99±0.03 | 7.65±0.03 | 0.08±0.02 | 20.56±0.15 | 11.47   |
|           |            | 1M        | 50.03±0.03 | 22.93±0.04 | 13.53±0.04 | 0.34±0.01 | 0.03±0.01 | 1.02±0.03 | 7.68±0.03 | 0.08±0.02 | 20.59±0.15 | 11.47   |
|           |            | 2M        | 52.03±0.03 | 23.33±0.04 | 13.73±0.04 | 0.36±0.01 | 0.03±0.01 | 1.04±0.03 | 7.71±0.03 | 0.08±0.02 | 20.62±0.15 | 11.47   |

*Values are means ± SD (n=3)

The SiO₂ content of Githma clay increased from 40.80 to 52.14 % as HCl acid strength increased from 0.0M to 2M. However, silica (SiO₂) content for the Githma sample treated with HCl acid fall within the standard range of 46-62 % SiO₂ content that is required for the production of good refractory materials [19]. LOI increased as well from 11.47 % to 16.45 % as HCl acid strength increased from 0.0M to 2M. LOI values for all Githma sample treated clays were within the acceptable range of 8-18 % LOI for refractory bricks [20]. Alumina composition in Githma sample treated with HCl decreased from 16.27 % to 11.86 % as HCl acid concentration increased from 0.0M to 2M. However, the values of alumina (Al₂O₃) content did not meet the requirement of 25-44 %Al₂O₃ for refractory bricks [20]. The composition of iron oxides in Githma sample treated with HCl decreased from 20.53 % to 8.54 % as acid concentration increased from 0.0M to 2M. However, all the samples treated with HCl have higher iron content that did not fall within the standard range of 0.5-2.4 % Fe₂O₃ for refractory bricks [20]. Magnesium oxide (MgO) content decreased with an increase in HCl acid concentration (0.0M to 2M) from 0.02 to below detectable levels. Potassium oxide (K₂O) content decreased from 0.96 to 0.72 % as acid strength increased from 0.0M to 2M HCl. Titanium oxide (TiO₂) content decreased from 7.62 to 5.82 % as acid strength increased from 0.0M to 2M HCl. Manganese oxide (MnO) content decreased from 0.08 to 0.01 % as acid strength increased from 0.0M to 2M. It is clear from the results in Table 1 above that as the acid strength increased from 0.0 M to 2M,
the levels of MgO, Al₂O₃, CaO, K₂O, and TiO₂ decreased progressively. However, the levels of SiO₂ and LOI increased as acid strength increased. This is in line with a report by Panda et al., [21] while studying the effect of acid treatment on Kaolin clay structure and chemical properties [21].

The silica content in the Githima clay sample treated with oxalic acid increased from 40.80 to 59.02 % as the acid concentration increased from 0.0M to 2M. However, all the values of the Githima sample treated with oxalic acid fall within the standard range of 46-62 % SiO₂ content that is required for the production of good refractory materials [19]. LOI values of Githima samples treated with oxalic acid increased from 11.47 to 20.42 % as the acid concentration increased from 0.0M to 2M. However, most of the LOI values for Githima samples treated with oxalic acid are within the standard range of 8-18 % LOI for refractory bricks [20]. The composition of iron oxide content decreases from 20.53 to 7.56 % with an increase in oxalic acid concentration from 0.0M to 2M. However, iron oxides content was high and did not fall within the acceptable range of 0.5-2.4 % Fe₂O₃ for refractory bricks [20]. The composition of alumina (Al₂O₃) as well decreased from 16.27 to 7.16 % as oxalic acid concentration increased from 0.0M to 2M. However, alumina content for all the samples is below the acceptable range of 25-44 % Al₂O₃ for refractory bricks [20]. Titanium oxide (TiO₂) levels decreased from 7.62 to 7.16 % as oxalic acid concentration increased from 0.0M to 2M. Potassium oxide (K₂O) content reduced from 0.96 to 0.24 % as oxalic acid concentration increased from 0.0M to 2M. Manganese oxide (MnO) content reduced from 0.08 to 0.01 % as oxalic acid concentration increased from 0.0M to 2M. Magnesium oxide (MgO) content was reduced from 0.02 % to below detectable levels. Calcium oxide (CaO) content was reduced from 0.52 to 0.28 %. From the results in Table 1 above it is clear that the elemental composition of Githima clay is significantly affected by treatment with acid (oxalic acid), the levels of SiO₂ and LOI increase as oxalic acid concentration increases. However, Fe₂O₃, Al₂O₃, MgO, CaO, MnO, TiO₂, and K₂O decrease with an increase in oxalic acid concentration.

The SiO₂ content of the Kimathi sample treated with HCl increased from 55.40 to 65.16 % as acid concentration increased from 0.0M to 2M HCl. However, most of the SiO₂ values fall within the acceptable range of 46-62 % for the production of good refractory materials [19]. LOI of the Kimathi sample treated with HCl increased as well from 12.20 to 15.02 % as acid concentration increased from 0.0M to 2M HCl. However, all LOI values for Kimathi acid-treated samples were within the standard range of 8-18 % LOI for refractory bricks [20]. The composition of iron oxides (Fe₂O₃) content decreased progressively from 3.90 to 3.57 % as acid concentration increased from 0.0M to 2M HCl. However, iron oxides content was high and therefore did not fall within the standard range of 0.5-2.4 % Fe₂O₃ for refractory bricks [20]. The composition of alumina (Al₂O₃) was reduced significantly from 22.40 % to 17.45 % as HCl concentration increased from 0.0M to 2M. However, no alumina (Al₂O₃) content values fall within the standard range of 25-44 % Al₂O₃ for refractory bricks [20] (Chester, 1973). Potassium oxide (K₂O) content was reduced from 2.65 to 2.16 % as HCl concentration increased from 0.0M to 2M. Magnesium oxide (MgO) content decreased as well from 1.82 to 1.43 % as HCl concentration increased from 0.0M to 2M. Calcium oxide (CaO) content decreased as well from 15.02 to 14.5 % as HCl concentration increased from 0.0M to 2M. Titanium oxide (TiO₂) content decreased from 0.62 to 0.43 % as HCl concentration increased from 0.0M to 2M. Magnesium oxide (MnO) content decreased from 0.06 to 0.02 % as HCl concentration increased from 0.0M to 2M. From Table 1 above, it is evident that Kimathi clay elemental composition is affected by treating with hydrochloric acid. The levels of most soluble metal oxides decreased with an increase in the concentration of the acid. Levels of Al₂O₃, CaO, MgO, K₂O, TiO₂, MnO, and Fe₂O₃ decreased progressively with an increase in HCl concentration. These findings are in agreement with findings by Eze et al., [3] while investigating the effect of acid treatment on the physicochemical properties of Kaolin clay obtained from a mine in Abia state, Nigeria [3].

The silica content of Kimathi clay increased from 55.40 to 65.00 % as oxalic acid concentration increases from 0.0M to 2M. However, most of the silica content values fall within the standard range of 46-62 % for refractory bricks [19]. Loss On Ignition (LOI) increased as well from 12.20 to 18.02 % with an increase in oxalic acid concentration from 0.0M to 2M. However, most of the LOI values fall within the acceptable range of 8-18 % LOI for refractory bricks. The composition of iron oxide (Fe₂O₃) reduced from 3.90 to 2.77 % as oxalic acid concentration increased from 0.0M to 2M. However, iron content values are higher than the recommended range of 0.5-2.4 % Fe₂O₃ for refractory bricks [20]. Alumina (Al₂O₃) content decreased from 22.40 to 12.92 % as oxalic acid concentration increased from 0.0M to 2M. However, alumina composition does not fall within the recommended range of 25-44 % for refractory bricks [20]. Titanium oxide (TiO₂) content decreased from 2.65 to 1.88 % as oxalic acid concentration increased. Magnesium oxide (MgO) content was reduced from 1.82 to 0.73 %. Manganese oxide (MnO) was reduced as well from 0.06 to 0.01 %. Titanium oxide (TiO₂) was reduced from 0.62 to 0.33 %. Generally, most of the metallic oxides in Kimathi clay samples are leached with oxalic acid, some of these oxides include Fe₂O₃, Al₂O₃, MnO, CaO, K₂O, MgO and TiO₂, these oxides decreases with increase in oxalic acid concentration. However, SiO₂ and LOI levels increase with an increase in acid strength.

The composition of silica (SiO₂) increased from 44.03 to 59.45 % as HCl concentration increased from 0.0M to 2M. However, most silica composition values fall within the recommended range of 46-62 % SiO₂ for the production of good refractory materials [19]. Loss On Ignition (LOI) increased as well from 10.84 to 13.87 % as Hydrochloric (HCl) acid concentration increased from 0.0M to 2M. However, all LOI values fall within the
By acid treatment include Fe. The acid treatment causes a reduction in the composition of most elements with a higher reduction being achieved at a higher concentration as shown in Table 1 above. The concentration of oxalic acid increased from 0.0M to 2M. However, most of the silica content values fall within the acceptable range of 8-18 % SiO2 for refractory bricks [20]. Alumina (Al2O3) composition decreased from 30.33 to 14.78 % as oxalic acid concentration increased from 0.0M to 2M. However, most of the alumina content values fall within the acceptable range of 25-44 % Al2O3 for refractory bricks [20]. Titanium oxide (TiO2) was reduced from 3.49 to 2.71 % as oxalic acid concentration increased from 0.0M to 2M. Manganese oxide (MnO) content decreased from 0.84 to 0.62 % as oxalic acid concentration increased from 0.0M to 2M. Manganese oxide (MnO) content decreased as well from 0.14 to 0.02 % as oxalic acid concentration increased from 0.0M to 2M. Manganese oxide (MnO) was reduced from 0.02 to below detectable levels. Treatment of Ithanje clay samples with oxalic acid shows that some of its metallic oxides are adversely affected. From the results, it is evident that oxalic acid leached some of the soluble metallic oxides such as Fe2O3, Al2O3, MnO, K2O, MgO and CaO. These results are similar to one found by Xavier et al., [8] while investigating the effect of acid treatment on clay palygorskite clay obtained from Guadalupe [8].

The composition of silica increased from 44.03 to 49.42 % as oxalic acid concentration increased from 0.0M to 2M. However, most silica content values fall within the recommended range of 46-62 % SiO2 for the production of good refractory materials [19]. Loss On Ignition (LOI) increased as well from 10.84 to 20.98 % as oxalic acid concentration increased from 0.0M to 2M. However, most of the LOI values fall within the acceptable range of 8-18 % Al2O3 for refractory bricks [20]. Alumina (Al2O3) composition decreased from 30.33 to 14.78 % as oxalic acid concentration increased from 0.0M to 2M. However, most of the alumina content values fall within the acceptable range of 25-44 % Al2O3 for refractory bricks [20]. Iron oxide (Fe2O3) composition reduced from 10.40 to 7.91 % as oxalic acid concentration increased from 0.0M to 2M. Titanium oxide (TiO2) content decreased from 3.49 to 2.71 % as oxalic acid concentration increased from 0.0M to 2M. Potassium oxide (K2O) content decreased from 0.84 to 0.62 % as oxalic acid concentration increased from 0.0M to 2M. Manganese oxide (MnO) content decreased as well from 0.14 to 0.02 % as oxalic acid concentration increased from 0.0M to 2M. Manganese oxide (MgO) was reduced from 0.02 % to below detectable levels. Treating Ithanje clay samples with oxalic acid shows that some of its metallic oxides are adversely affected. From the results, it is evident that oxalic acid leached some of the soluble metallic oxides such as Fe2O3, Al2O3, MgO, CaO, and TiO2; their levels were reduced with increase in acid strength. However, SiO2 and LOI levels increased with an increase in acid strength.

The results of acid treatment indicate that the chemical composition of the clays changed substantially. As the concentration of the acid increased, there was a marked increase in the dissolution of all soluble cations [8]. The acid treatment causes a reduction in the composition of most elements with a higher reduction being achieved at a higher concentration as shown in Table 1 above. Wachira [14] did a study on effects of acids (sulphuric, hydrochloric and oxalic acid) treatment on the iron composition of clays from Murkurwe-ini and found that the levels of SiO2 and LOI increased after acid treatment while there was a reduction of Fe2O3, MgO, Na2O, Al2O3, TiO2, and CaO, these findings are in agreement with the results in Table 1 [14].

Loss On Ignition (LOI) of the clays increased after acid treatment. This is due to an increase of amorphous silica that made water adsorption higher [21].

Figure 1 below gives a more simplified but comprehensive summary of the comparison of iron removal from the clay samples from the selected sites between the two acids (hydrochloric and oxalic acid). Oxalic acid was found to be more effective at the same acid concentration than hydrochloric acid and this was in agreement with the previous report by Calderon et al., [18]. The findings were in line with the report by Wachira [14] while studying iron removal of clays and restoration of clays’ plasticity [14].
Results of the elemental composition of clays from the three selected sites (Table 1 above) show that the clays are affected significantly by acid treatment, therefore this justifies the hypothesis that the elemental composition of clays from selected sites in Murang’a and Nyeri counties are affected by acid treatment.

Conclusion
From the results, it is evident that hydrochloric and oxalic acid removes impurities such as iron oxides from clays by the dissolution of metallic compounds having deleterious effects on applications of clays. Increasing the acid concentration from 0.0M to 2M HCl increases the acid attack on the clay structure which results in more bond breaking and the formation and subsequently, more metallic oxides are leached from clay.

This study has also established that the quality of the clay is noticeably improved by acid treatment by reducing its iron content and other metallic oxides having a negative effect on clay applications for industrial materials. Clays with iron content less than 1% find applications in high-grade ceramics, paper industry, catalysis, filler material, and on white cement.

Acid treatment can be used to improve properties of clays from Githima, Kimathi, and Ithanje hence the clays can be used as a source of raw materials for industrial applications.

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