Addis Ababa University

School of Graduate Study

Department of Chemical Engineering

SELECTION OF CLAY ADSORBENTS AND DETERMINATION OF THE OPTIMUM CONDITION FOR DEFLUORIDATION OF GROUND WATER IN RIFT VALLEY REGION

By
Ahmedin Hassen

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Advisor

Dr. Berhanu Assefa and Dr.-Ing. Nurelegne Tefera

Department of Chemical Engineering
Addis Ababa University
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Approved by the Examining Board:

Ato Alemayehu Ambaw ____________________
Chairman, Department Head

Dr. Berhanu Assefa ____________________
Advisor

Dr. Ing. Nurelegne Tefera ____________________
Advisor

Dr. Ing. Belay Weldeyes ____________________
External Examiner

Ato Teshome Worku ____________________
Internal Examiner

Signed Declaration

I declare that the thesis for the M.Sc. degree at the University of Addis Ababa, hereby submitted by me, is my original work and has not previously been submitted for a degree at this or any other university, and that all reference materials contained therein have been duly acknowledged.

Name: Ahmedin Hassen

Signature: ____________________

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Abstract: People in several regions of the Rift Valley of Ethiopia are suffering from skeletal and non-skeletal fluorosis as result of consuming water containing excessive fluoride. Defluoridation of drinking water using variety of material has been suggested by different researchers. This study assesses the fluoride adsorption characteristics of clays collected from different areas in Ethiopia. Bombawoha clay, Combolcha clay and Muger clay 2 were found to have the better potential as fluoride adsorbents.

The effect of contact time, amount of adsorbent dose, pH, particle size, heat treatment of adsorbent and initial concentration of fluoride was investigated. The adsorption was rapid during the first one hour. The adsorption efficiency of fluoride was increased with adsorbent dosage. The defluoridation capacity was appreciable with in acidic pH range. Clay adsorbents treated in the range between 400 to 600^oC gave better fluoride removal. The fluoride adsorption efficiency depends directly with initial fluoride concentration. The adsorption data were well fitted to the Langmuir isotherm model with adsorption capacity of 0.136, 0.168, and 0.191 for Bombawoha clay, Combolcha clay and Muger clay 2 respectively.

Laboratory scale column were conducted and showed good removal of fluoride. At breakthrough the three clay samples Bombawoha clay, Combolcha clay and Muger clay 2 showed 0.1248, 0.235, 0.239 mg/g of adsorption capacity, 1.64, 1.1, 1.02 mg/L of residual fluoride and 300, 500, 500 mL of breakthrough volume respectively.

Contents

List of Tables

List of Figures

1 Introduction

1.1 Background

Pure water is scarce and is not easily available to all. Deprived sections of the society consume contaminated water and get sick periodically, often resulting in epidemics. The water may be contaminated by natural sources or by industrial effluents. One such contaminant is fluoride. Fluoride is an ion of the element fluorine. Fluorine is the most highly reactive element of halogen family. Most fluoride associated with monovalent cations such as NaF and KF is soluble in water, while the one formed with divalent cations such as CaF_2 and PbF_2 is generally insoluble. Fluoride is "more toxic than lead and less toxic than arsenic" and is an accumulative toxin [1].

Fluoride in drinking water could be beneficial or detrimental for health depending on its concentration and total amount ingested. The presence of fluoride is beneficial for calcification of dental enamel, in particular for children under eight years old. However, excess fluoride intake causes dental and skeletal fluorisis [47].

The drinking water standards for fluoride ion specified by various authorities are given in Table-1. Contrary to the standard value, the evidences in India show that even about 0.50 mg/l of fluoride ion in drinking water is causing mild, moderate and severe forms of dental fluorosis. Instead, Coster has reported that a family in Northern Tanzania had been using ground water containing fluoride between 10 and 14 mg/l for several generations without any harmful effects [37].

The occurrence of high fluoride concentrations in groundwater and the risk of fluorosis associated with using such water for human consumption is a problem faced by many countries, notably India, Sri Lanka, China, the Rift Valley countries in East Africa, Turkey, and parts of South Africa [40].

Table 1. The drinking water standards for fluoride ion specified by various Authorities [16, 17, 37].

Authority	Limit of fluoride concentration (mgL^{-1})
WHO (International Standard)	0.5
US Public Health	0.7-1.2
South African Bureau of Standards	1.0
Ethiopia (QSAE, 2001)	1.5
Ethiopia(MoWR-proposed, 2002)	3.0

Ethiopia is one of the 23 countries where the population suffers from the consumption of fluoride rich drinking water [35]. People in several areas of the Ethiopian Rift Valley are consuming water with up to 33 mg/l of fluoride [26]. So it is required to implement appropriate water treatment procedures using local resources that are accessible to the rural community with technically simple, cost effective, and easily transferable technology. In this study, we investigate the possibilities of utilizing clay as a low cost deflouridation adsorbent.

1.2 Fluorosis

The relationship between fluoride and fluorosis was first noted in the early part of the 20th century when it was observed that residents of certain areas of U.S.A. developed brown stains on their teeth. In the 1930's it was observed that the prevalence and severity of this type of mottled enamel was directly related to the amount of fluoride ingested [13]. Optimum fluoride concentration in drinking water may be defined as a one that arrest the prevalence of dental carries without causing a significant amount of fluorosis [37].

1.2.1 Symptoms of fluorosis

Dental fluorosis, which is characterized by discolored, blackened, mottled or chalky-white teeth, is a clear indication of overexposure to fluoride during childhood when the teeth were developing. These effects are not apparent if the teeth were already fully grown prior to the fluoride overexposure; therefore, the fact that an adult may show no signs of dental fluorosis does not necessarily mean that his or her fluoride intake is within the safety limit [10]

Chronic intake of excessive fluoride can lead to the severe and permanent bone and joint deformations termed as skeletal fluorosis. Early symptoms include sporadic pain and stiffness of joints: headache, stomach-ache and muscle weakness can also be warning signs. The next stage is osteosclerosis (hardening and calcifying of the bones), and finally the spine, major joints, muscles and nervous system are damaged. Whether dental or skeletal, fluorosis is irreversible and no treatment exists. The only remedy is prevention, by keeping fluoride intake within safe limits [19].

Research of several investigators during the last 5–6 years has proven that life-long impact and accumulation of fluorides causes not only human skeletal and teeth damage, but also changes in the DNA-structure, paralysis of volition, cancer, etc [25].

1.2.2 Distribution of Fluorosis

Worldwide

The latest information shows that fluorosis is endemic in at least 25 countries across the globe. The total number of people affected is not known, but a conservative estimate would number in the tens of millions. In 1993, 15 of India's 32 states were identified as endemic for fluorosis [42]. In Mexico, 5 million people (about 6% of the population) are affected by fluoride in groundwater. Fluorosis is prevalent in some parts of central and western China and caused not only by drinking fluoride in groundwater but also by breathing airborne fluoride released from the burning of fluoride-laden coal. Worldwide, such instances of industrial fluorosis are on the rise [19].

Ethiopia

Both dental and skeletal fluorosis is prevalent in the rift valley region of Ethiopia because of high fluoride waters that originate from springs and boreholes [26].

An extensive study was done among 1,456 individuals in 14 communities in the central Rift Valley and reported dental fluorosis prevalence rates was between 69% and 98% (mean 84%) in the groups sampled. Slight, no significantly higher rates were found in young males (82.5%) as compared to young females (81%), in the age group 10-14 years. In a similar study from the Ethiopian Rift Valley, showed prevalence of dental fluorosis in permanent anterior teeth, ranging from 34% to 75% in 8-year-old children residing in various villages of the Wonji-Shoa Sugar Estate and 77% among adults (20-25 years old) [26].

1.3 The origin and distribution of fluoride in Ethiopia

Concentrations of fluoride greater than the WHO guideline value of 1.5 mg/l have been found in groundwaters from several parts of Ethiopia, but are recognized to be highest in the Rift valley zone [26]. Concentrations often greater than 10 mg/l are found in waters from the Rift valley. A recent analysis of the water samples from this region (along the roads from Addis to Awasa and from Addis to Nazareth) by the Chemical Engineering Department of Addis Ababa University (AAU) shows that the fluoride concentration ranges on average from 5 to 25 mg/litre [18].

Moderately high (unacceptable) concentrations have also been found in groundwaters from volcanic rocks in the highlands. Concentrations in groundwaters from the ancient basement rocks are typically low (e.g. Mekele area.) [11].

Unusually low fluoride concentrations have been reported in groundwaters from wells and springs in the Rift Valley town of Arba Minch and the nearby escarpments in southern Ethiopia. This is apparently due to inputs of low-fluoride runoff from the highlands or from nearby rivers or lakes [26].

The problematic fluoride concentrations were derived from hot springs (high temperature) and by weathering of the volcanic bedrocks (presence of alkalinity (HCO_3) [3]. Fluoride concentrations above 5.0 mg/l in the Rift Valley were found mostly in hot springs (100% of all sources), lakes (78%), shallow wells (54%) and boreholes (35%) and the lowest concentrations (below 1.5 mg/l) in springs and rivers [20].

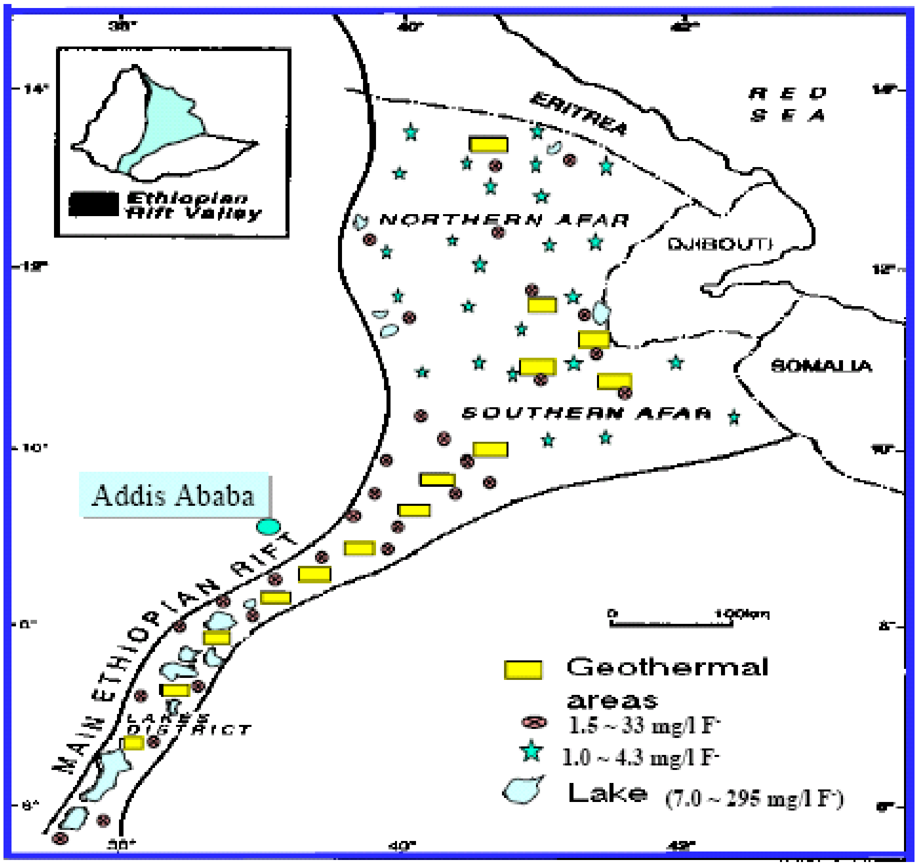

Fig.1 Fluoride distribution with in the Rift Valley of Ethiopia [17].

1.4 Motivation of the research

Since groundwater forms a major source of drinking water in the rift valley area, both dental and skeletal fluorosis are important public health problems in this area, in addition to its social and economic problems.

So far most of the ground water treatment methods can not be applied in most developing countries, including Ethiopia, because the population is too poor to afford buying or paying for materials used by the methods for removing fluoride. Therefore, the viable option is to look for low cost processes that can be built using local expertise and based on locally available and cost-effective fluoride coagulants or adsorbents.

1.5 Objective of the research

The general objective of this research is therefore was to investigate locally available clay adsorbents for deflouridation of rift valley ground water.

The specific objectives of this research were

- Characterization of commonly available clay adsorbents
- Study of the capacity of clay adsorbents for defluoridation
- Selection of the best adsorbent among studied clay adsorbents for removal of fluoride and determination of optimum operating conditions.

2 Literature Review

2.1 Commercial Deflouridation Methods

The process of removal of fluoride is generally termed as defluoridation. Numerous commercial methods have been described employing various materials for the fluoride removal since 1930 [35]. Defluoridation methods using organic or inorganic substances in many laboratories and field studies nowadays are summarized as follows:

2.1.1 Adsorption method

There is a natural tendency for components of a liquid or a gas to collect often as a monolayer but sometimes as a multilayer at the surface of a solid material. This phenomenon is called adsorption [24].

At present, adsorption treatments on natural and synthetic materials offer the best prospects for the selective removal of fluoride from natural mineral waters [44]. Here are some of the commercial adsorbents used in the adsorption and ion exchange method.

Activated Alumina (Al_2O_3), Activated bauxite (Hydrate of $Al(OH)_3$), Zeolite ($NaO_2.Al2O_3).nSiO_3.XH_2O$), Activated carbon, Charcoal .

Among the most frequently encountered commercial sorbents the case of Activated Alumina is reviewed as follows.

Activated Alumina (AA)

Alumina (Al_2O_3) is practically insoluble in water. The solubility in acid and alkali depends upon previous heat treatment, strong reagents do not easily attack it, and Alumina needs to be activated for the defluoridation process. There are different grades of activated alumina. The suitability of the grade for defluoridation depends upon the porosity and surface area of the alumina. Other considerations, which are also of importance, include the life of the activated alumina for defuoridation purposes [46].

The defluoridation capacity of activated alumina is independent of temperature. The adsorption of activated alumina obeyed Langmuir's adsorption isotherm indicating that the force of adsorption is governed by chemisorption. However, fluoride removal by AA may also take place with decreasing pH and the extent of chemisorptions increase at a much higher rate. AA also adsorbs bicarbonate ions. Thus, the defluoridation capacity of AA decreases at increased concentration of bicarbonate. But chloride and sulphate ions have no effect on fluoride removal capacity. AA can be regenerated by 2% hydrochloric acid, 2% sodium hydroxide and 1% sulphuric acid. Fluoride removal efficiency is typically above 95% [25, 40, 46].

A disadvantage of this process is that the regeneration steps result in an aqueous solution containing fluoride. On the other hand, if the spent alumina is discarded, the cost of the defluoridation increases. Apart from that, spent alumina may leach out fluoride ions when it comes in contact with alkali [25].

2.1.2 Precipitation Methods

These processes are based on the formation of insoluble fluorides following the action of suitable reagents, which precipitate and can then be separated from the water by decantation. The reagents used in such treatments are calcium or aluminium salts (decarbonation with lime, flocculation with sulphates of alumina) [37]. It is unlikely that precipitation treatments by addition of salts could be used to treat natural mineral waters. Because the treatment requires relatively large quantities of chemical reagents, which are often difficult to remove. Hence, the quality and original mineral content of the water will not be preserved [41].

Precipitation Using Lime and Alum

Since the early 1960s, the National Environmental Engineering Research Institute (NEER), Nagger, has been involved in research and development activities on the defluoridation of water. One of the technologies, which have been successfully transferred from the laboratory to the field, is the Nalgonda Technology. The first community defluoridation plant for removal of fluoride from drinking water was constructed in the district of Nalgonda in Andhra Pradesh, in the town of Kathri, thus, the name of the technology. In this technology, raw water is mixed with adequate lime and alum. The amount of lime depends on the alkalinity of the raw water. If the raw water has adequate alkalinity, the addition of lime is not required. Alum solution is added after the addition of lime, stirred gently for 10 minutes and the flocs formed are allowed to settle. This process of floc formation and settling requires an hour. In rural areas where the people practice domestic defluoridation, the advice given is to mix the water with lime and alum and leave it overnight, so that the next morning the clean supernatant is decanted for use and is safe for consumption. In the Nalgonda technique, besides fluoride, turbidity, colour, odour, pesticides and organic substances, if any, are also removed. Bacterial contamination is also reduced significantly [46].

The addition of lime or sodium carbonate ensures adequate alkalinity for effective hydrolysis of aluminium phosphate to aluminium hydroxide (that is, floc formation) and as a result, aluminium does not remain in the treated water [46].

Precipitation with calcium compounds

Many methods of precipitation of fluorides with salts of calcium, aluminium and iron are reported in the literature [29, 30]. Precipitation processes are governed by the solubility of a forming salt. The most common method of treatment is the precipitation of calcium fluoride using calcium from either lime or calcium chloride [39].

The fundamental problem that exists using lime arises from the low solubility of the calcium hydroxide. It therefore requires excess of reagent to complete precipitation. The relatively high solubility of the calcium fluoride does not allow a complete removal of F-. An additional difficulty with lime precipitation is the poor settling characteristics of the precipitate [40].

2.1.3 Membrane processes

Membrane processes such as reverse osmosis (RO), nanofiltration (NF) and electrodialysis are recently developed methods for F^- removal from water. All elements in water can be reduced by membrane. Thus this method is claimed to be the best water purification process available. But 30 % of raw water is lost in the process [41].

Reverse osmosis process is well-known in the industrialized world like the U.S.A and Europe for the removal of ions and soluble materials from sea and brackish water. The study by Lhassani et al. indicates that F^- can be removed using nanofiltration [22]. Berhanu investigated the performance of different RO and NF membrane for fluoride removal and achieved more than 90% removal [g]. However, the technology is not affordable by the rural community.

2.1.4 Ion exchange treatments

Ion exchange treatment uses charged anion resins to catch fluoride ions in the water. The products most widely used are tricalcic phosphates (bone char, bone ash or animal black, bone powder, synthetic apatite), and Synthetic resins [41].

Ion exchange on tricalcic phosphate takes place between a hydroxyl and a carbonate ion from apatite and a fluoride ion, thus forming insoluble fluoroapatite that can be easily decanted. Tricalcic phosphate is marketed in the form of powder but may also be formed *in situ* through a reaction between phosphoric acid and calcium chloride or lime [41, 46].

Ion exchange treatments are at present not very successful and difficult to carry out:

- The use of tricalcic phosphates is limited by the relatively low adsorption capacity and average mechanical properties (friability).
- At present, there are few fluoride exchange resins on the market and they still have limited exchange capacity.

2.2 Deflouridation using low cost materials

The removal of fluoride from water using commercial materials by adsorption, membrane separation, and ion exchange techniques are expensive for developing countries. By virtue of which the search for a low cost deflouridation materials was essential.

Different low cost materials have been used in Tanzania and India. In these countries, the people have been using locally produced aluminum sulfate at household level in order to remove the fluoride from their drinking water. The process involves simple coagulation by mixing a given dose of aluminum sulphate and filtering using cloth. The process is cheap; however, it increases the concentration of aluminum ion in the treated water, which has other health risks. In India, Bulusu et al. [15, 48] developed another technique based on the addition of an alkali (lime) and aluminum sulfate. Also this method is claimed be cheap. In Sri Lanka, a filter bed has been built from selected low temperature burnt clay (silicates, aluminates and hematite) at cost of $ 20 and used for the separation of fluoride in household water [38]. It is reported that it has reduced the fluoride content to acceptable level during its two-month of operation. In Turkey, burnt locally available raw alumina was used for a preliminary test. It gave about 78 % removal of fluoride while the commercial activated alumina removed about 92 % [4]. Omueti and Jones studied the adsorption of F^- by Illinois soils. They reported that at low concentrations F^- adsorption onto soils was described by both Langmuir and Freundlich isotherms. It was also suggested that F^- adsorption onto soils was due to the presence of the amorphous aluminium hydroxides [36]. Zevenbergen et al. studied the defluoridation of water using the Ando soil of Kenya. It was concluded that the use of Ando soils appears to be an economical and efficient method for defluoridation of drinking water [56]. Bjorvatn et al. studied the defluoridation of water using soil samples from Ethiopia. It was reported that five soil samples from highland areas around Addis Ababa reduced the fluoride content of the water from about 15 to 1 $mg.L^{-1}$. From this study, it was concluded that the highland soil may be useful for removal of excessive F^- from drinking water [7].

Other materials such as spent bleaching earth, spent catalyst; rare earth oxides, bone charcoal, seeds of the ***drumstick plant*** (Moringa oleifera) and activated carbon were studied as F^- adsorbents [40]. Mahramanlioglu et al. investigated the adsorption of F^-

using spent bleaching earth. They found that the removal of F^- depends on the contact time, pH and adsorbent concentration [32]. Lai and Liu studied the F^- removal from water with spent catalyst. Their findings showed that spent catalyst could be utilized as adsorbent for F^- removal. Its adsorption capacity was comparable to that of activated alumina [27]. Raichur and Basu studied the adsorption of F^- onto rare earth oxides. Rare earth oxides showed great potential for F^- removal from water [43]. Researchers from Indian University of Roorkee studied the deflouridation capacity of drumstick plant and they stated that the defluoridation efficiency of the seeds of drumstick could possibly be related to calcium and magnesium levels in the plants though there is no linear correlation between them [46]. Lu et al. investigated the removal of F- using red mud. The removal of F^- using red mud was found to be 82% [31]. Chaturvedi et.al. also studied the defluoridation of water by adsorption on fly ash. This study also showed that low Fluoride concentration, high temperature and acidic pH favor the adsorption of F^- [10].

In different parts of the world, other geomaterials such as kaolinite, bentonite, lignite and different types of other clays and hydrous aluminum silicates have been tested for their adsorption capacity of fluoride. Promising adsorbing capacity for fluoride is reported, in particular for kaolinite (from Sri Lanka) and for heat-treated clay, composed of quartz, illite, geothite and feldspar (from China). Their performance depends on the operating temperature and the size of the material and pretreatment used (e.g. the degree of burning of the materials) [45, 48]. The above defluoridation materials have not yet been commercialized.

In Ethiopia, aforementioned geomaterials are locally available in large amount. However, the quality could be different. Some preliminary study was conducted on alum and heat-treated clay material [2, 33]. The performance of kaolinite and other clay types was investigated in this work.

2.3 Clay adsorbents

2.3.1 Principles of adsorption

Adsorption is a process that occurs when a gas or liquid or solute (called adsorbate) accumulates on the surface of a solid or more rarely a liquid (adsorbent), forming a molecular or atomic film (adsorbate). Adsorbent solids are usually used in granular form, varying in size from roughly a 2 mm in diameter to as small as 0.05 mm. The solid must possess certain engineering properties depending upon the application to which they are put. If they are used in a fixed bed through which a fluid is to flow, for example, they must not offer too great a pressure for flow nor must they easily be carried away by the flowing stream. Adsorption is a very general phenomenon, and even common solids will adsorb gases and vapors at least to a certain extent. But only certain solids exhibit sufficient specificity and adsorptive capacity to make them useful as industrial adsorbents [44].

Some substances adsorb fluoride ion by its surface, and it can exchange its negative ions such as OH-group for fluoride ions. This process depends on suitable condition (pH, temperature, flow rate, time, grain size of malarial, etc.) [46]. The most common criteria for selection of suitable sorbents are: cost of the medium and running costs, ease of operation, adsorption capacity, potential for reuse, number of useful cycles and the possibility of regeneration [40].

An ion exchange mechanism whereby F^- is exchanged with OH groups in the mineral structure is generally assumed to be the rate determining step in the adsorption process. This ion exchange process can be presented by the following equilibria,

$$MOH^{2+} + F^- \leftrightarrow MF + H_2O$$
$$MOH + F^- \leftrightarrow MF + OH^-$$

Where MOH and MOH^{2+} : metal oxides like Al oxides

Easily exchangeable OH- groups are those found in metal hydroxides or hydrated metal oxides such as aluminium or iron oxides, although it is known that not all structural forms of metal oxides have exchangeable OH^- groups with F^-, notably magnetite (Fe_4O_6) and corundum (α-Al_2O_3). Lattice OH- groups such as found in aluminiumsilicates, for example kaolinite, have a low tendency to be replaced by F^-[21].

The extent of adsorption is proportional to specific area. Specific area can be defined as that portion of the total area that is available for adsorption. Surface area is related to the grain size of the adsorbent. The choice of particle size is made by considering two sets of factors: 1) ease of mass transfer from the fluid to the surface, creation of as much interfacial surface area as possible and reduction of antiparticle diffusion path length, all of which favor smaller particles; and (2) maintenance of a low pressure drop, which favors larger particles [24].

Because hydrogen and hydroxide ions are adsorbed quite strongly, the adsorption of other ions is influence by the pH of the solution. In general, adsorption of typical pollutant from water is increased with decreasing pH [53]. The pH of the system is a very important parameter and determines the degree of protonation of the OH^- exchange sites and the degree of protonation of F^-. The pH will therefore determine the specific charge of an exchange site and therefore ultimately also the adsorption tendency of the substrate [40].

Adsorption processes are normally exothermic, thus the extent of adsorption generally increases with decreasing temperature. From a small number of investigations it can be seen that temperature affects several factors which are important in the adsorption from solution. For completely miscible systems, selective adsorption generally decreases with rise in temperature. It is the expected effect for an exothermic process, and is compatible with a decrease in magnitude [44].

The physicochemical nature of the adsorbent can have profound effects on both rate and capacity for adsorption. Where as Solubility, molecular sizes, and charge (Ionic species) are considered in the case of adsorbate [6].

Adsorption isotherms can be used to obtain information about the mechanism of adsorption. It can also be useful in determining adsorption capacities and Langmuir constants. Langmuir constants are useful in comparing adsorption characteristics of different substrates. In many studies, linear Langmuir adsorption curves or F- adsorption onto metal oxide surfaces have been found [9]. In this study adsorption isotherms for the selected clays were determined.

2.3.2 Adsorption characteristics of Clay

The term “clay” is applied both to materials having a particle size of less than 2 micrometers and to the family of minerals that has similar chemical compositions and common crystal structural characteristics. The characteristics common to all clay minerals derive from their chemical composition, layered structure, and size. Most clay has the ability to soak up ions (electrically charged atoms and molecules) from a solution and release the ions later when conditions change [52].

Clays are potentially good adsorbers of anions since they contain crystalline minerals such as kaolinite, smectite and amorphous minerals such as allophane and other metal oxides and hydroxides, which could adsorb anions such as F^- [2].

The structure of the clay plays a very important role in determining the charge on the clay surface and type of exchange that can occur with ions in solution. In general the more negative the surface the better the sorption will be for positively charged metal ions. The pH parameter plays a dominant role in determining the adsorption capacity as pH modifies the charges on the clay minerals. Charges are generally positive under acid conditions and negative in an alkaline environment. An acid pH will favour adsorption of negatively charged ions while alkaline conditions will enhance adsorption of positively charged ions [40].

2.3.3 Clay deposit in Ethiopia

The following four groups of clay deposits are studied by the Geological survey of Ethiopia.

Kaolin

Exploration in Bombowha and Kombolcha areas proved about 300,000 tones of kaolin at each of these localities. Moreover, recently it is reported that several hundred thousand tons of good quality kaolin is known to be hosted by the kaolinised granites of Bombowha area. Alumina is generally above 35% in the Bombowha kaolin with other elements such as iron (<1%) and total alkali and titanium accounting for less than 3%. On the other hand the kombolcha kaolin bears a relatively lower alumina (33.24%), and higher total alkali and iron, averaging 2.54% and 2.63% respectively [51].

Bentonite

Bentinitic clay resources are found in the Afar region. They are located near the main road. The total resources in this region is estimated to 170 million ton and the chemical composition is in the range of 50-60% silica, 11-14% alumina, 7-9% iron and less than 1.3% sodium and potassium oxides. The Gindcho Island in the Lake Abaya in the rift valley is another source of bentonitic clay [51].

Structural clay

These clays occur in the vicinity of Addis Ababa between Debre Birhan and Debresina, and at mulo and zega weden between Debrezeit and kalitti, at sululta at rift valley lakes region, and at Awzeit, Debre Tabor, and Kerker in Gonder region of northern Ethiopia. It has an average composition of 49.46% silica, 13.05% iron oxide, and 17.24% alumina [51].

2.3.4 Adsorption studies using clay

Many studies report on the fluoride adsorption capacities of clays and soils and their potential use as sorbents. Chaturvedi studied fluoride removal using China clay. The results show that low F^- concentration, high temperature and acidic pH are factors favouring the adsorption of F^-. It was concluded that the alumina constituent of the China clay is responsible for F^-adsorption [9]. Defluoridation systems using suitable South

African clays, processed in various ways, as adsorbents. This study assessed the fluoride adsorption characteristics of clays collected from different areas, where a high fluoride concentration in groundwater is a problem. Bauxitic clays were found to have the best overall potential as fluoride adsorbents. Simple chemical activation using 1% Na_2CO_3 solutions and dilute hydrochloric acid could enhance adsorption capacity of certain clay types [40]. Several researchers have studied the removal of F^- using fired clays. Hauge et al. studied the defluoridation of drinking water using pottery. The study investigated the effect of firing on F^- adsorption. The results show that clays fired at temperature up to 600°C gave higher F^- adsorption [21]. Moges et al. studied the defluoridation of water using fired clay chips in Ethiopia. Their findings indicated that F^- adsorption is affected by factors such as initial concentration, mass of adsorbent and the pH of the solution [33].

Natural clays present a major advantage due to their abundance in nature (locally available). Since these clay minerals are widely available in Ethiopia, it can be used as an alternative defluoridating material. Therefore, in this thesis the fluoride adsorption capacity comparisons have been made for different Ethiopian clays. The optimum operating conditions for those clay types with better adsorption capacity have also been determined.

3 Experiments

3.1 Clay sampling

- In this study eight different clay samples were collected (Table 2) and the corresponding adsorption capacities investigated.

Table2 Compositions of the Clay samples [48, 50, 51, 52].

Components	Harer Clay 1	Amercha Clay	Harer Clay 2	Combolcha Clay	Bombawoha Clay	Muger Clay 1	Muger Clay 2	Mesobo Clay
Silica (SiO_2)	63.3	63.3	63.3	47.4	46.2	66.85	40.18	65
Alumina (AlO_3)	19.68	22.6	17.45	33.2	38.2	19.05	22.63	20.5
Titania (TiO_2)	0.05	0.03	0.02	0.62	0.06	1.41	--	--
Ferric Oxide (Fe_2O_3)	3	4.52	1.5	2.79	0.94	6.72	20	1.5
tLime (CaO)	<0.01	<0.01	<0.01	0.7	0.08	1.95	1.33	--
Magnesia (MgO)	1.1	--	--	0.3	0.15	--	0.8	--
Potash (K_2O)	3.8	2.4	2.8	1.3	0.37	3.01	--	1.5
Soda (Na_2O)	0.3	0.5	0.7	0.2	0.05	--	--	2.4
Phosphorus penta oxide (P_2O_5)	0.04	0.035	0.038	<0.02	0.04	--	--	--
Manganic Oxide (MnO_2)	--	--	--	0.1	0.03	--	--	--
Barium Oxide (BaO)	--	--	--	--	0.01	--	--	--
Strontium (Sro)	--	--	--	--	0.01	--	--	--
Loss on Ignition (LOI)	6.45	--	--	12.1	13.8	8.4	11.39	--

3.2 Analytical Methods for the Determination of Fluoride

3.2.1 Reagent and Standard Solutions

Standards at a required concentration range were prepared by appropriate dilution of the stock solution, a 1000 mg F^-/L sodium fluoride with distilled water.

The ionic strength adjustment buffer (TISAB) was prepared following a recommended procedure, except that EDTA (ethylenediaminetetraacetic acid) replaced CDTA (cyclohexanediaminetetraacetic acid) [5] as follows: 57 mL of glacial acetic acid, 58 g of sodium chloride, 7 g of sodium citrate and 2 g of EDTA were added to 500 mL distilled water, allowed to dissolve, pH adjusted in the range of 5.2 to 5.5 using 5 M sodium hydroxide, and then made up to 1 L in a volumetric flask with distilled water.

3.2.2 Instrumentation

Fluoride ion selective electrodes were used for routine determination of F^-. A pH-ISE-conductivity meter (Model 250) was employed. The pH was measured with the same meter using pH glass electrode.

The liquid phase fluoride concentration was measured as follows (according to the procedure described in the instrument's manual)

- Samples or standards and TISAB were placed in a glass beaker with volumetric ratio of 50:1mL and the solution was stirred using magnetic stirrer.
- The fluoride ion selective electrode was immersed in the solution.
- The reading was made just after five minutes in order to attain stable value.

The fluoride ion selective electrode was calibrated prior to each experiment. The precision of the measured value was determined by measuring 8 replicate standard fluoride solutions of 5 mg/L with the pre-calibrated instrument.

The statistical tool, Meet MINITAB 14 students release for windows, has been employed to analyze the generated data during experimentation. In this respect the confidence limit (CL) for all average (mean) values has been evaluated, one-way analysis of variance (ANOVA) with multiple comparisons of the means have also been determined and accordingly the graphs for the residual values verses the fitted values, normal probability, and order of the data have been plotted.

3.3 Determination of Adsorption Capacities

Preliminary tests were conducted in order to investigate the fluoride adsorption capacities of clay samples collected. From this study, clay samples with better adsorption capacity were selected.

The fluoride adsorption capacity and efficiency from the residual fluoride concentration was calculated by the following equations. [5]

$$\% \text{ Adsorption} = \frac{C_o - C_t}{C_o} * 100 \qquad \text{-----------------------------------} (3.1)$$

$$\text{Adsorption capacity } (q_e) = \frac{C_o - C_t}{m} * v \qquad \text{-----------------------------} (3.2)$$

Where C_o = initial fluoride concentration

C_t = residual fluoride concentration at time t

m = mass of adsorbent

v = volume of the solution used in the batch

q_e = adsorption capacity (mg of fluoride removed/g of adsorbent)

Three clay samples namely, Combolcha clay, Bombawoha clay and Muger clay 2 that exhibited better adsorption capacity were selected in order to investigate the effect of different operating parameters on the fluoride adsorption potential of these clays. The investigation includes determination of adsorption isotherm curves and the effect of temperature, pH, contact time, and particle size in order to determine whether how significant change in adsorption capacity can be induced by these factors.

3.4 Adsorption Procedure (Batch process)

The batch experiments were conducted by mixing 50 mL of tap water collected from the Toga Village near Awassa with clay for 2 hr in 100 mL glass bottles at room temperature. After 2 hr mixing, the mixtures were centrifuged at 4000 rpm for 10 minutes and decanted before final fluoride analysis.

To ensure that F^- does not adsorb on the inner walls of the adsorption vessels, blank runs were performed. In this procedure a 50 mL of having 3 mg F^-/L standard solution was added to a 100 mL glass bottle and the F^- concentration measured after 2 hr and again after 24 h. No significant reduction in F^- concentration was found for both measurements.

3.4.1 Fluoride adsorption capacity of the clay samples

Adsorption capacities for different clay samples were determined using the same procedure described in section 3.2. Here 1 to 10 grams of each clay samples were analyzed.

3.4.2 Effect of Temperature

The selected clay samples were heated at different temperatures, range from 100 to 800°C in steps of 100°C, in a preheated furnace for 2 h. After heating clays were cooled and stored in desiccators. The adsorption capacities were determined for these temperatures using the same procedure as in section 3.4.

3.4.3 Effect of Contact Time

Using the batch adsorption procedure described in Section 3.4. But residual F^- concentrations were measured for different contact time of adsorption, 1, 2, 3, 4, 5, 6 hours in order to investigate the effect of contact time. In this section the kinetic of the adsorption data was also analyzed based on reaction kinetics of pseudo-first-order and pseudo-second-order mechanisms.

3.4.4 Effect of pH

In this section, the effect of pH was analyzed for the three selected clay types, namely Bombawoha clay, Combolcha clay and mugger clay 2. Initial pH of raw water was prepared in the range of 2 to 10. The desired PH was adjusted using 0.1M of NaOH and 1%HCl solution. Residual F^- concentrations were determined after two hours of contact time.

3.4.5 Effect of Adsorbent dose on Adsorption Capacity and Efficiency

Adsorption efficiency (i.e. percentage of adsorption) and adsorption capacity (i.e. mg of fluoride removed per gram of adsorbent) were analyzed using 1 to 10 gram of each of the three selected clay types.

3.4.6 Effect of Clay Particle Size

To investigate the effect of particle size of the clays four different ranges of particle size (i.e. < 0.5mm, 0.5-1.0mm, 1-1.25mm and > 1.25mm) were analyzed, available mesh size. Both raw and heated clay samples were considered. The same batch adsorption procedure was used as in section 3.4.

3.4.7 Effect of Initial Fluoride Concentration

The effect of initial fluoride concentration on the adsorption capacity was analyzed using different initial fluoride concentration ranging from 5 to 25 mg/l. Five grams of each of the selected clay was used at the same contact time of adsorption.

3.4.8 Adsorption Isotherm

Adsorption isotherms were determined for the selected clays. Untreated clay samples were considered at an initial raw water pH of 3 where maximum adsorption was observed. Adsorption isotherm has also been developed for Bombawoha clay sample heat treated at 600^{o}C. Data were generated by mixing a constant initial fluoride concentration of 5.8 mg/L (Toga water) with nine series of increasing dosages of all adsorbents ranging from 2 to 10 g. The adsorption process was carried out for a contact time of 24 h to ensure equilibrium.

3.5 Laboratory Column Experiment

Laboratory scale column were developed to compare the results obtained using the batch type adsorption.

Continuous flow defluoridation study was carried out using a column made from glass with internal diameter and effective bed height of 22 mm and 36 mm, respectively. A cotton pad was placed between the adsorbent and the stop cock to avoid the escape of particles. The column was packed with 10 g of the selected clays, Bombawoha clay, Combolcha clay and Muger clay 2 with particle size range of 0.5 - 2.5 mm. Tap water from Toga with initial fluoride concentration of 5.8 mgF^{-}/L and pH of 8.54 was allowed to flow down the column at a rate of 4 mL/min. Samples were taken at regular intervals of 25 minutes and the F^{-} concentration determined. Residual F^{-} concentration was plotted against time. Breakthrough times were determined graphically and used to calculate breakthrough volumes and adsorption capacities of the columns.

In addition, the column experiment was studied using the same procedure but for water solution at initial pH equals 3 using Combolcha clay sorbent. To analyze the effect of flow rate the column study was also conducted with influent flow rate of 2 mL/min.

3.6 Regeneration Procedure

Regeneration for exhausted clay packing was conducted. The efficiency of column regeneration with 0.1 M Na_2CO_3 and 1% HCl was studied for Muger clay 2 using packing of 10 g, flow rates of 4 $mL.min^{-1}$, and feed concentrations and pH of 5.8mgF^-/L and 3 respectively.

Regeneration removes the previously sorbed F^- from the surface. The addition of Na_2CO_3 releases F^- from the clay surface. The use of 1% HCl reactivates the surface for F^- adsorption [40].

4 Results and Discussions

4.1 Performance of fluoride meter

The precision of the analysis method was determined using 8 replicate measurements of 5 mg/L standard fluoride solution. The mean value and standard deviation (SD) were 5.02 and 0.047, respectively. Furthermore, the relative SD (0.935 %) was much lower than 5 %, which shows good replication of the experiment.

4.2 Fluoride adsorption capacity of the collected clay samples

The results for the percentage of F^- adsorbed for the clay samples collected are given in Fig. 2. Adsorption capacities range from about 5%, for some of clays which have got lower amount of Al and Fe oxides, to 85%, for clays with relatively higher amount of Al and Fe oxides, has been observed. The results show that higher adsorption capacity can be associated to clay samples with higher Aluminium and Iron oxide.

According to the results in the ANOVA analyses, the p-value (<0.001) indicates that the mean values for the capacities of the clay samples investigated are significantly different when the significance level is set at 0.05, which is a conventional value [14]. Further more the residual plot shows that the experimental design was randomized (Fig. 15, Annex 2). In this figure the three clay samples, Bombawoha, Combolcha, and Muger clay2 show higher mean values of fluoride adsorption efficiency.

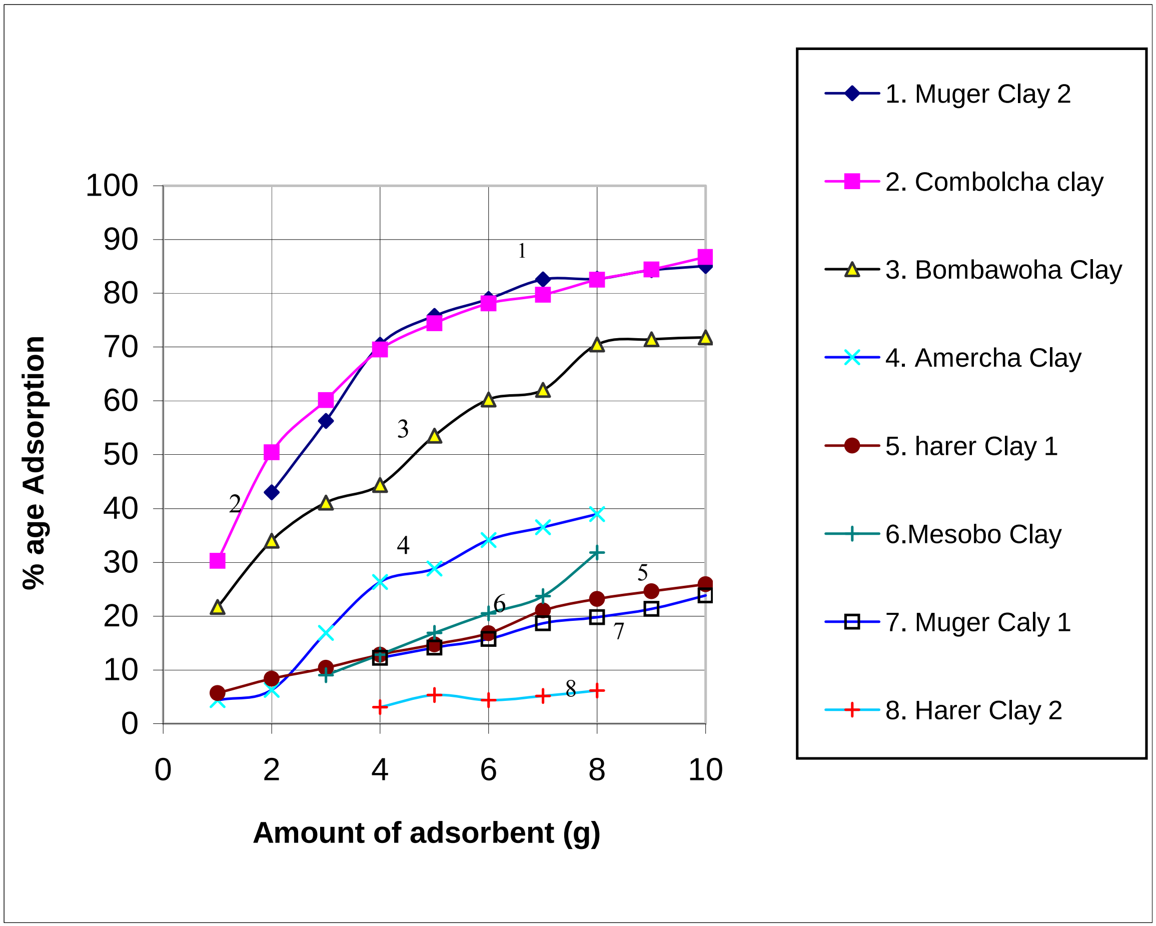

Fig. 2 Adsorption capacities of different clay samples (Average data for duplicate measurements).

4.3 Effect of temperature

Increasing in adsorption capacity was observed with increasing temperature up to 600°C and followed by a decrease at temperatures above 600°C as shown in Fig. 3. Similar results were obtained for clays with high concentrations of Al and Fe oxides in other works [21].

The result in the Fig.18 (Annex 2) shows there is a significant difference of the means for the studied temperature range except for the range 400 to 600°C. The significance level was set at 0.05.

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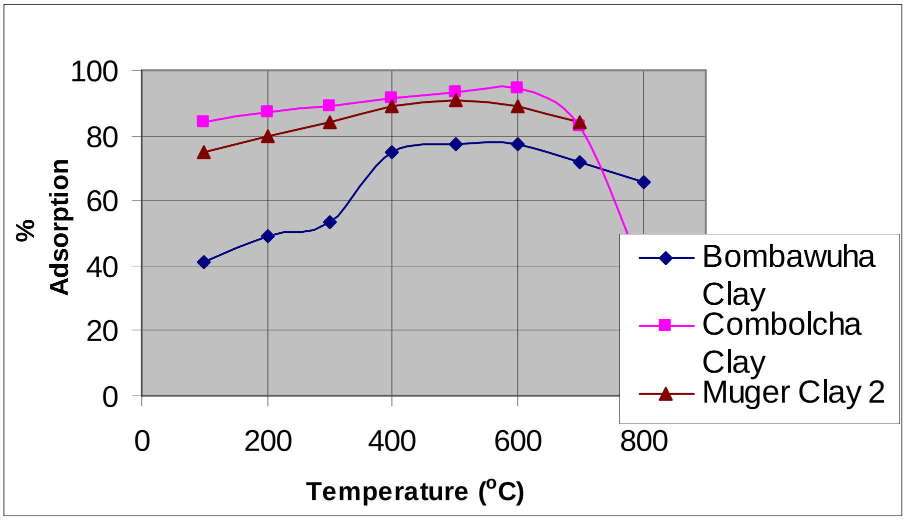


Fig. 3 Adsorption capacity of the selected samples with temperature using 5g of adsorbent. (Average data for duplicate measurements).

It is reported that aluminium oxides are converted to γ-Al_2O_3 upon heating of clay minerals up to 600^oC, and then contribute to improved adsorption characteristics. The decline in adsorption capacity above 600^oC can be attributed to the gradual conversion of aluminium oxide into α-Al_2O_3 and iron oxides to magnetites form of oxides that show little tendency to adsorb fluoride [40].

4.4 Effect of contact time

The adsorption efficiency at different contact time has been investigated and the results are plotted in Fig. 4.

The result showed that, the rate of adsorption of F^- was very fast initially. But after one hour the rate of decrease in residual fluoride became very slow. Beyond two hours the residual fluoride showed a slight increment. This means that adsorption was completed in the first two hours indicating that longer contact time has a negligible effect on the adsorption. Faster initial adsorption rate is possibly due to the availability of sufficient vacant adsorbing sites in presence of higher fluoride concentration gradient. Afterwards, the F^- uptake rate by the adsorbent decreased significantly due to limited vacant adsorption sites available.

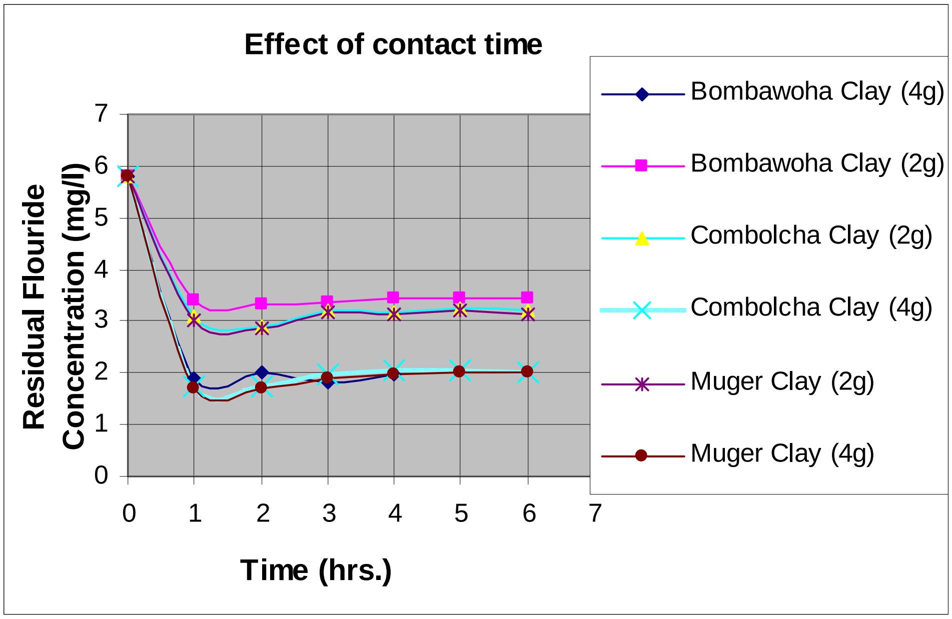


Fig.4 Residual fluoride concentration with time for selected clays different dose, Initial fluoride conc. =5.8 mg/l. (Average data for duplicate measurements).

The one way analysis of variance showed that (Fig. 19, Annex 2) significant difference of the means was observed only up to two hours of contact time. The randomness of the experiment was also observed in the residual plot.

The kinetics of the adsorption of fluoride was also studied based on reaction kinetics of pseudo-first-order and pseudo-second-order Lagergren model. Only pseudo-second-order Lagergren model were found to be better fit (Fig. 5).

Pseudo-second-order Lagergren model is generally expressed as [28]:

$$\frac{dq}{dt} = k_2 (q_e - q)^2 \text{ --------- } (4.1)$$

Rearranging equation (4.1),

$$\frac{dq}{(q_e - q)^2} = k_2 dt \text{ ------- } (4.2)$$

Where k_2 is the rate constant of second order sorption (g/mg.hr.)

q_e is the amount of adsorbed fluoride at equilibrium (mg/g)

q is the amount of adsorbed fluoride at any time t (mg/g)

t is the time of stirring (hr.)

Equation (4.3) is determined after integration and linearization of eqn (4.2) for the boundary conditions = 0 to t = t and $q = 0$ to $q = q_e$.

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} - - - - - - - - - - (4.3)$$

Fig. 5 shows that t/q versus t gave straight lines with the related correlation coefficients (R^2) were all above 0.99 which is well fitted with the pseudo second-order equation of Lagergren model.

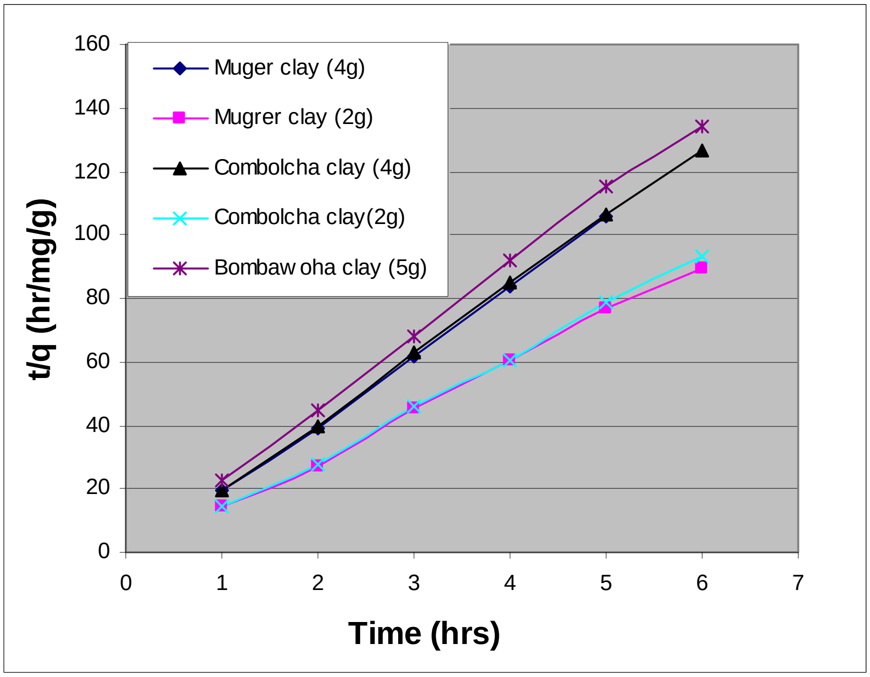


Fig. 5 Pseudo second order plot of fluoride adsorption kinetics for selected clays at different dose, Initial fluoride conc. = 5.8 mg/l. (Average data for duplicate measurements).

4.5 Effect of pH

It is well documented in literature that pH of water significantly affect fluoride uptake capacity. In order to see this effect experiments were conducted for the selected clays. Figure 6 shows the influence of initial solution pH on the fluoride removal efficiency of the three selected clay adsorbents.

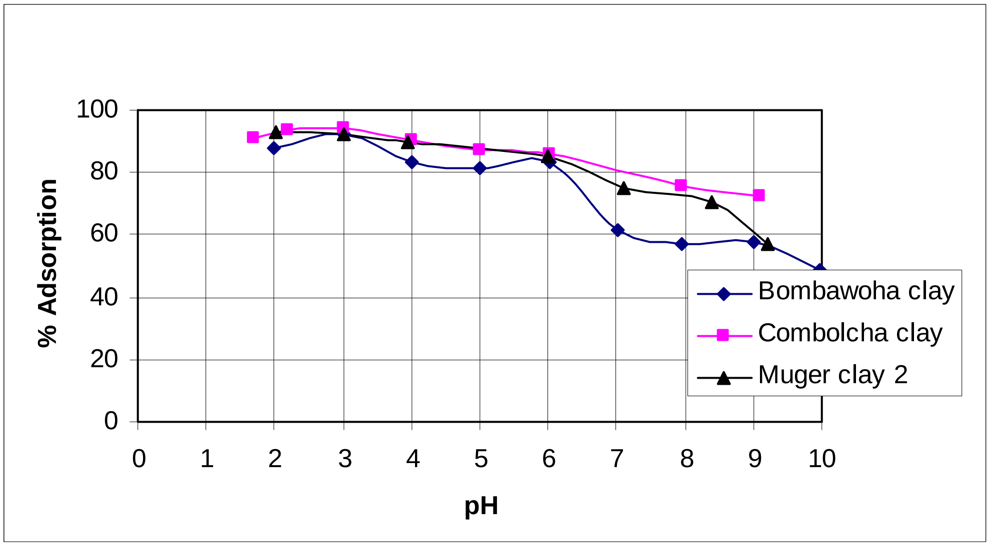
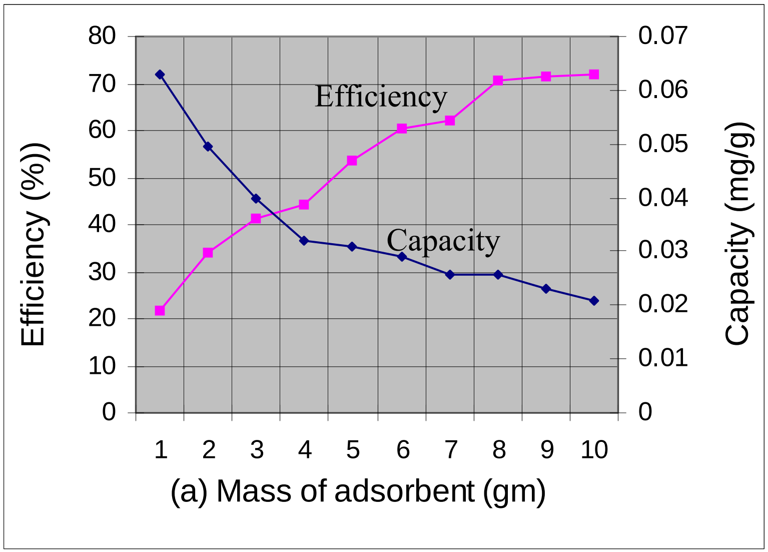


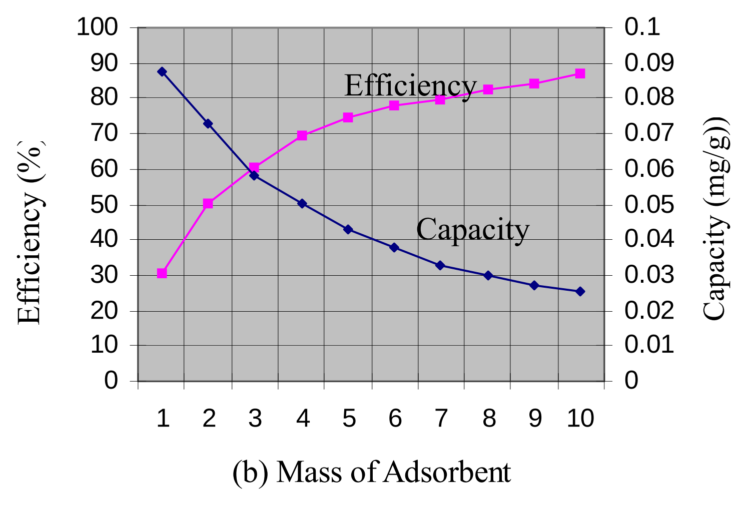
Fig. 6 Percentage adsorption with initial raw water pH for Bombawoha Clay, Combolcha Clay and Muger Clay 2 (mass of clay adsorbent = 5g).

The result (Fig.6) shows that higher adsorption capacity is observed at lower pH values (acidic media) and it has a decreasing tendency as the pH increased. Previous study revealed that the concentration of positively charged components of the clays (i.e. oxides of silicon, aluminium and iron) increases with decreasing pH and hence they can readily adsorb the negatively charged fluoride ion [40]. Thus, decrease in the adsorption capacity in the basic region is due to the decrease in positive charges of the clay and increase in competition of F^- with the OH^- as both have the same charge and ionic radii [55]. ANOVA shows that the mean value of adsorption efficiency is much higher in acidic solution than basic solution (Fig. 17, Annex 2).

4.6 Effect of Adsorbent dose on Adsorption Capacity and Efficiency

The experimental result shows that all the clay types exhibited decreased adsorption capacity and increased adsorption efficiency with increased adsorbent dosage (Fig.7). It seems that increasing of fluoride removal efficiency with an increase in adsorbent dosage was due to the increased in availability of F^- binding sites. See Fig. 16 (Annex 2) for the output of the statistical analysis. The decrease in capacity is due to the depletion of fluoride in the solution with increasing dose of adsorbent





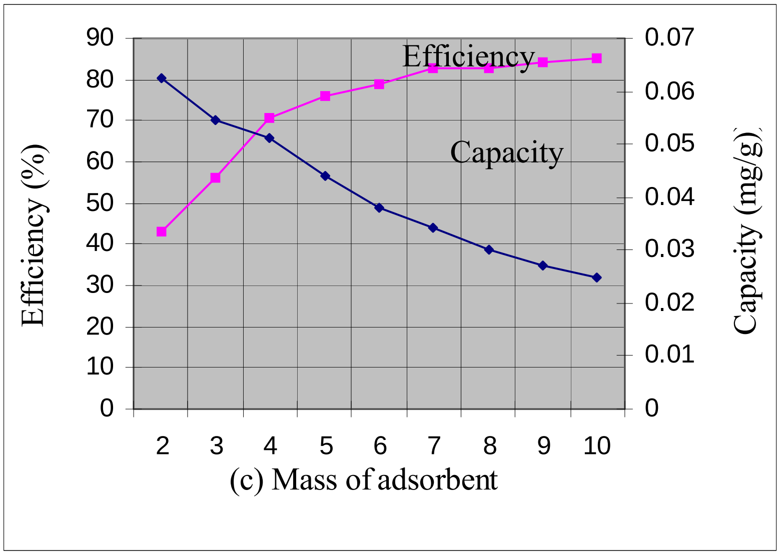


Fig. 7 Adsorption capacity and efficiency at different mass of clay.
(Average data for duplicate measurements)
(a) Bombawoha Clay, (b) Combolcha Clay and (c) Muger Clay 2.

4.7 Clay Particle size vs. adsorption capacity

It was clearly shown that (Table 3) particle size of 1 to 1.25 mm gave a better adsorption capacity in the case of Bombawoha clay. Where as for the other two clay types, Combolcha and Mugger clay 2 higher adsorption capacities have been achieved for fine particle size (<0.5mm). Significant change of adsorption capacity was observed for the heated clay with changing particle size. For unheated samples change in adsorption capacity with change in particle size is not significant that is probably due to the inherent dissolution dynamics, which does not allow the clay particles to maintain their original size during adsorption process. ANOVA shows that the mean values variation with particle size (Fig. 21, Annex 2).

Table 3 The Percentage of Adsorption vs. particle size for the three selected clay types. Mean values ± CL using 95% confidence interval. (Data for duplicate measurements).

Particle size (mm)	Bombawoha Clay		Combolcha Clay		Muger Clay	
	4gm untreated	4gm heated	4gm at untreated	4gm heated	4gm unheated	4gm heated
<0.5	44.74 ± 0.17	45.52 ± 0.00	70.00 ± 0.34	92.88 ± 0.03	44.14 ± 0.34	66.29 ± 0.17
0.5 - 1.00	46.12 ± 0.17	54.83 ± 0.34	66.47 ± 0.51	88.93 ± 0.00	41.38 ± 0.34	61.38 ± 0.34
1.00 - 1.25	50.86 ± 0.34	65.43 ± 0.84	65.09 ± 0.17	78.36 ± 0.17	39.66 ± 0.34	50.86 ± 0.00
>1.25	43.79 ± 0.68	54.66 ± 0.00	65.09 ± 0.17	73.79 ± 0.00	39.22 ± 0.17	41.72 ± 0.34

4.8 Effect of Initial Fluoride Concentration

The result of the experiment (Fig. 8) shows that, for a given mass of adsorbent, the fluoride removal capacity increases with increasing initial concentration. The increase in adsorption capacity with increase in initial fluoride concentration is due to increased diffusion of fluoride to adsorption sites and utilization of less accessible or less active sites of the adsorbent.

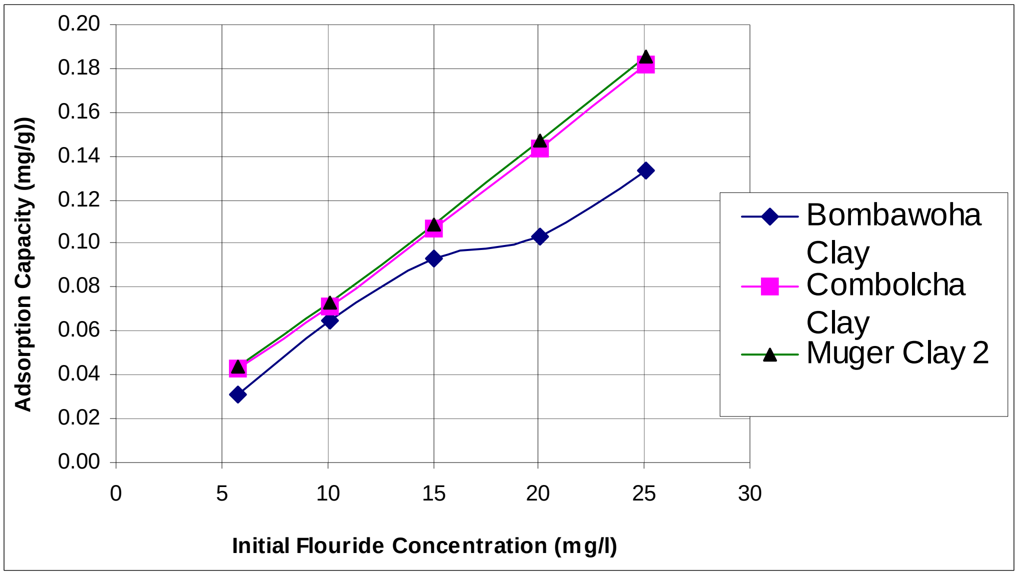


Fig 8 Effect of initial fluoride concentration on the adsorption capacity for the selected clay samples using 5g of adsorbent. (Data for duplicate measurements).

Fig. 20 (Annex 2) shows that there is significant variation of the mean values ($p< 0.001$) with initial fluoride concentration.

4.9 Adsorption Isotherm

Figure 9 shows adsorption isotherms, which show the relationship between the bulk aqueous phase concentration of adsorbate and the amount adsorbed at equilibrium condition.

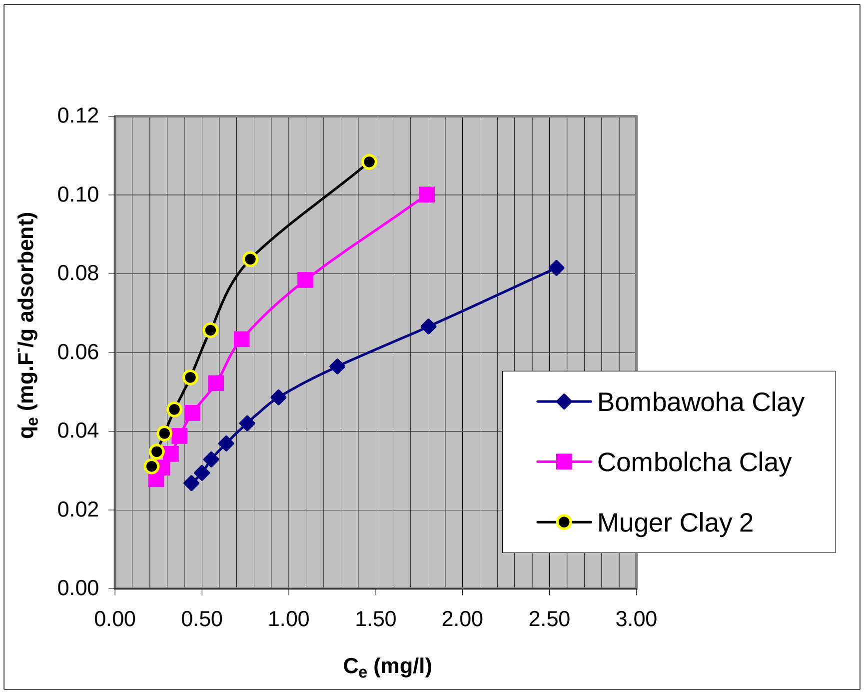


Fig. 9 Adsorption isotherms for the three selected clays
(Initial raw water pH=3 and F$^-$=5.8 mg/l, contact time=24h).

Many studies show, adsorption isotherm curves for F$^-$ adsorption onto metal oxide surfaces can be well represented by Langmuir model [23].

Langmuir derived the model based on some reasonable assumptions like uniform adsorption surface, monolayer adsorption, and constant temperature and also assumed equal rates of adsorption and desorption at equilibrium [5].

The Langmuir equation can be written as

$$\frac{Ce}{q_e} = \frac{1}{bQ} + \frac{Ce}{Q} \quad \text{------------------------------------} \quad (4.4)$$

Where:

q_e = the amount of fluoride adsorbed per unit weight of adsorbent (mg/g) at equilibrium

C_e = the equilibrium fluoride concentration (mg/L)

Q = the measurement of the adsorption capacity (mg/g) based on Langmuir isotherm

b= the Langmuir constant (l/mg)

Ploting C_e vs. C_e/q_e, the Langmuir constants, Q and b can be determined from the slope and intercept of the line.

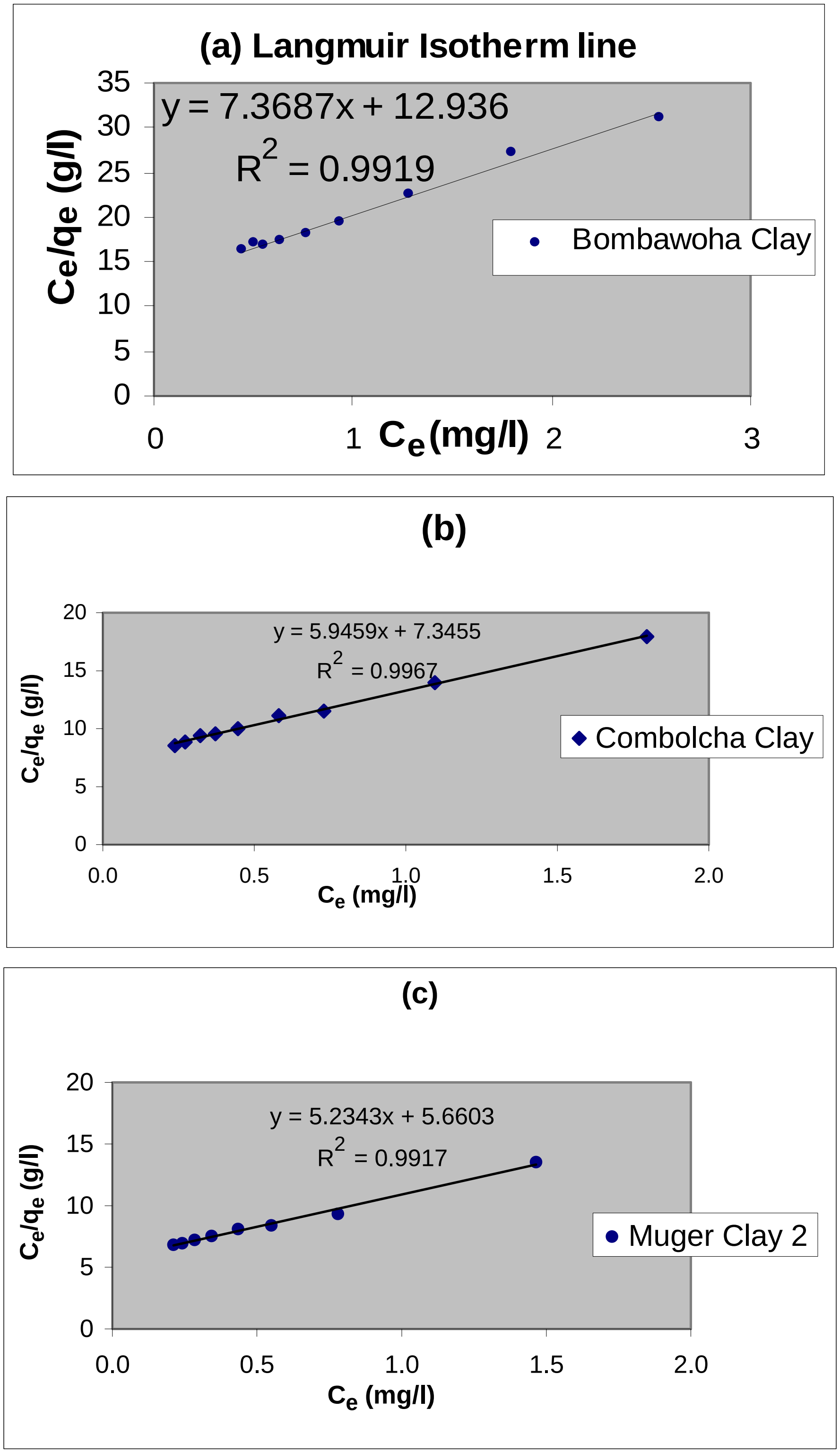


Fig. 10 Langmuir Isotherms for (a) Bombawoha clay, (b) Combolcha clay, and (c) Muger Clay (Initial fluoride conc.= 5.8 mg/l, contact time=24h).

The results shown in the Fig. 10 indicate that all experimental fluoride adsorption isotherm data have well fitted to the Langmuir isotherm, and the related correlation coefficients (R^2) were all above 0.99 (Fig. 10). Adsorption capacities (Q = inverse of slope of the Langmuir isotherm line) of 0.136, 0.168, and 0.191 (Table 4) were obtained for Bombawoha clay, Combolcha clay, Muger clay 2 and Bombawoha clay (heat treated at 600°C) respectively.

Table 4 Langmuir isotherm parameters

Adsorbent	Equation	Q (mg/g)	b (L/mg)	R^2
Bombawoha clay	$\frac{q_e}{Ce} = 7.3687C_e + 12.936$	0.136	0.57	0.9919
Combolcha clay	$\frac{q_e}{Ce} = 5.9459\ C_e + 7.3455$	0.168	0.81	0.9967
Muger clay 2	$\frac{q_e}{Ce} = 5.2343\ C_e + 5.6603$	0.191	0.92	0.9917

The adsorption capacity of different soils and clay types from other studies have been compared with the values obtained in this study. The values are presented in Table 5. The comparison gives rough indication of F^- adsorption trends for a wide variety of soils and clays from all over the world. The adsorption capacities obtained for all the three clay types fall in the range for those of acid soils, which showed the best values in the earlier studies [8].

Table 5 Comparison of F^- adsorption capacity data in mg/g for different soils and clays.

Adsorbent sample name and description	Adsorption Capacity (mg/g)	Reference
Bentonite clay South Africa	0.1	[40]
Bentonite clay Wyoming, USA	Trace	[8]
Alkaline soils USA	0.04-0.08	[8]
Kaolinite Clay South Africa	0.03	[40]
Acid soils USA	0.17–0.25	[8]
Acid soils Illinois, USA	0.13	[36]
Potter's clay, 30% Al2O3 1106 White St Thomas	0.12	[7]
Clay pots Ethiopia	0.07	[33]
Bombawoha Clay Ethiopia	0.136	This Thesis
Combolcha Clay Ethiopia	0.168	This Thesis
Muger clay 2 Ethiopia	0.191	This Thesis

4.10 Performance of Adsorption Column

Breakthrough curves for Bombawoha, Combolcha and Muger Clay 2 are shown in Figure 11. Initially, most of the F- was adsorbed, so the F- concentration in the effluent was low. As the adsorption continued, the effluent concentration increased, slowly at first but then suddenly.

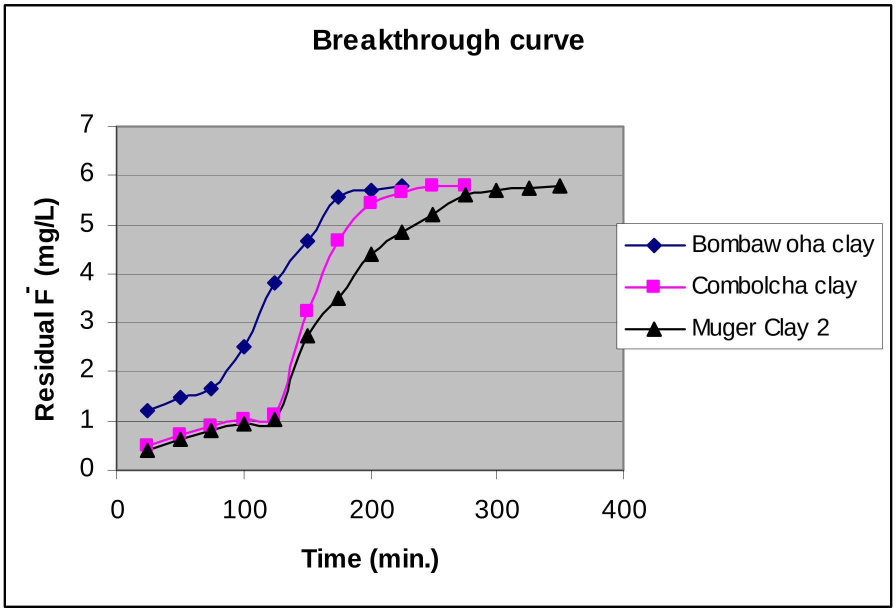


Fig 11 Breakthrough curve for the three clays (tap water influent concentration, mass of adsorbent, pH and flow rate of 5.8 mg/L,10g, 5.84 and 4 mL/min respectively)

Table 6 Breakthrough volumes, residual F^- concentrations at breakthrough and column capacities for a column packed with 10 g of clay sorbents. (Feed solution concentrations 5.8 mg/L, flow rate 4 mL/min.).

Clay type	Residual Flouride (mg/L)	Breakthrough time (min.)	Breakthrough volume (mL)	Adsorption capacity (mg/g)
Bombawoha	1.64	75	300	0.1248
Combolcha	1.1	125	500	0.235
Muger Clay 2	1.02	125	500	0.239

Table 6 compares the adsorption capacities and residual fluoride concentrations of the three clays for 10 g sorbent and a feed solution of 5.8 mg/L F^- passed through a column at 4 mL/min. The same trend of adsorption capacity is observed for the clays as in the batch procedure but with a higher adsorption capacity.

The increase in the capacity of adsorption could be as a result of better hydrodynamic condition which allows efficient contact between F^- and the adsorption sites

In order to investigate the effect of PH, the column experiment was run for water solution at pH equals 3 for Combolcha clay sorbent. The breakthrough curves and comparison of adsorption capacities for the two pH values (raw water pH=8.54 and 3) are shown in the Figure 12 and Table 7 respectively.

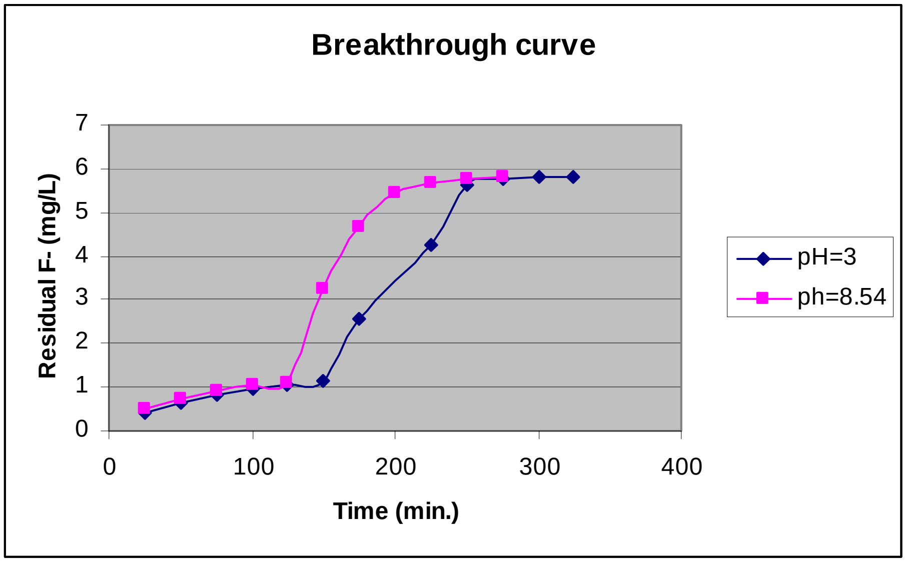


Fig 12 Breakthrough curve for Combolcha clay at two different pH values (tap water influent concentration=5.8 mg/L, flow rate =4 mL/min, 10g of sorbent).

Table 7 Breakthrough volumes, residual F^- concentrations at breakthrough and column capacities for a column packed with 10 g of Combolcha clay. (Feed solution concentrations 5.8 mg/L, flow rate 4 mL/min.).

Initial pH	Residual Fluoride (mg/L)	Breakthrough time (min.)	Breakthrough volume (mL)	Adsorption capacity (mg/g)
8.54	1.1	75	500	0.235
3	1.14	150	600	0.28

In order to investigate the effect of flow rate, the column experiment was also run for initial F^- concentration of 5.8 mg/L. As shown in the Fig 13 at lower flow rates of 2 mL/min, the adsorption was very efficient. When the flow rate increased, the breakthrough curve became steeper and the break point time and adsorbed F^-

concentration decreased. This behavior can be explained in terms of residence time. If the residence time of the solute in the column is longer, there will be higher chance to reach equilibrium. Thus, the removal efficiency will be higher.

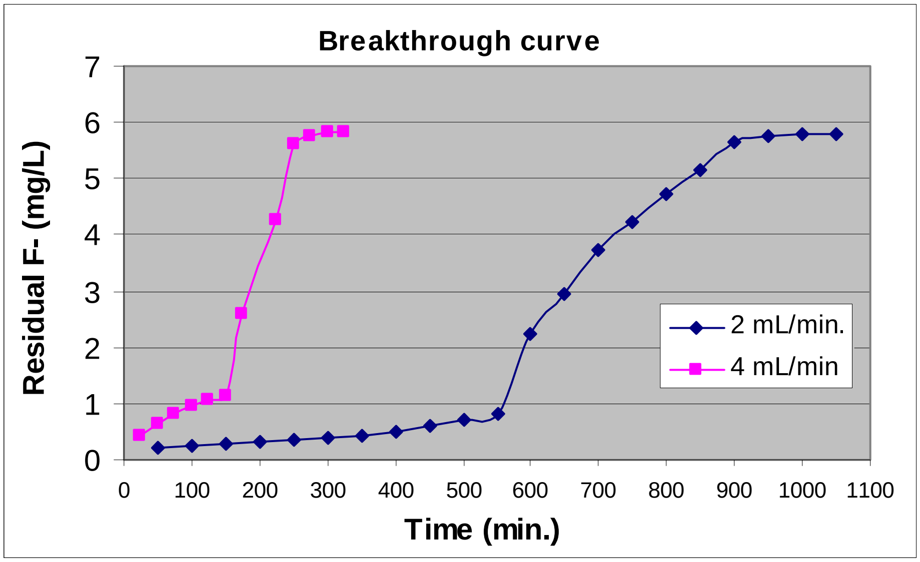


Fig 13 Breakthrough curve for Combolcha clay at two different flow rates (5.8mg/L feed solution and pH=3, 10g of sorbent).

4.11 Regeneration experiment

The results obtained after the first regeneration is shown in Figure 14 for Muger Clay 2. The column adsorption capacity and residual F^- concentration obtained after the first regeneration is given in Table 8. From the Table it is evident that even after one regeneration the breakthrough volumes and hence the adsorption capacities of the columns did slightly decline. Perhaps, the regeneration procedure should be optimized to bring back the original capacity.

Table 8 Breakthrough volumes, residual F^- concentrations at breakthrough and column capacities for a column packed with 10 g of Muger clay 2 after one step regeneration. (Feed solution concentrations 5.8 mg/L, flow rate 4 mL/min., pH=3).

Residual Flouride (mg/L)	Breakthrough time (min.)	Breakthrough volume (mL)	Adsorption capacity (mg/g)
1.05	100	400	0.19

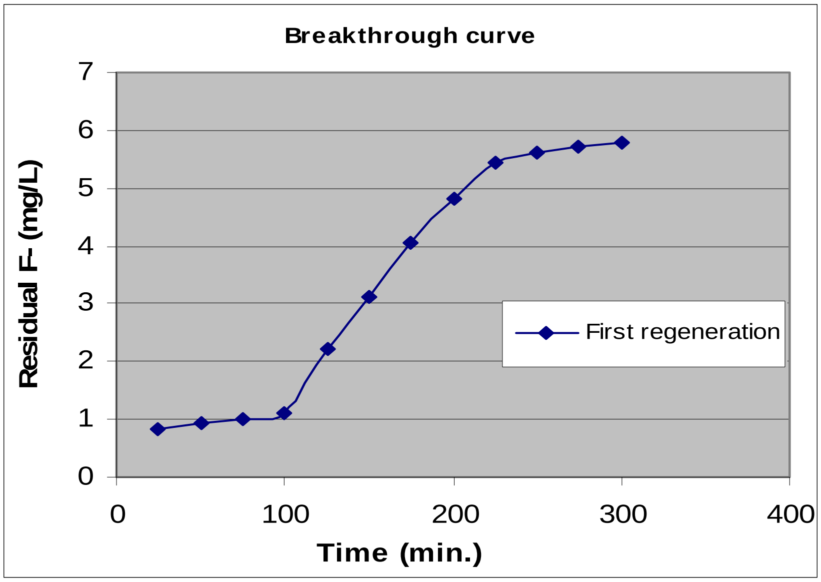


Fig. 14 Breakthrough curve for Combolcha clay after one regeneration (10 mg/L F$^-$ and pH =3 feed solution through a 10 g sorbent at a flow rate of 4 mL/min).

5 Conclusions and Recommendations

Conclusions

This study shows that clay types can differ in their adsorption capacities for F. Clay types consisting of the metal oxides of Fe and Al were found to have the better potential as sorbents for F- from aqueous solutions.

The pH of the solution was found to be the most important factor affecting adsorption potential. Results obtained show that better adsorption was achieved in the acidic range, pH = 3 to 6 with maximum adsorption potential at pH = 3.

Heat treatment at temperatures of up to 600°C was observed to increase F- adsorption. A decrease in F- adsorption was observed at temperatures above 600°C.

The concentration of fluoride also found to affect the defluoridation capacity of the adsorbent. The fluoride adsorption capacity was increased with increasing initial fluoride concentration.

The selected clays, Bombawoha clay, Combolcha clay and Muger clay 2 showed good adsorption capacities using laboratory scale defluoridation column. The regenerated column showed a slight decrease in the breakthrough volumes and the adsorption capacities with first regeneration.

The adsorption isotherm conformed to the Langmuir model in the range tested in this study. The kinetic studies showed that the adsorption reaction of fluoride removal can be well described by a pseudo second-order rate equation

The overall results obtained showed that three of the collected Ethiopian clay namely, Bombawoha clay, Combolcha clay and Muger clay 2 have good capacities for F- removal.

5.2 Recommendations and future works

In this paper only eight clay types are considered for the selection. So additional potential Ethiopian clay adsorbents should be identified and assessed with geologist and other related specialist.

In this study the structural characteristics of the clay is not taken into account. The relation between the structural characteristics of the clay and its affinity to adsorb fluoride should be studied as well.

Previous study showed that treatment of clay adsorbents by chemicals such as Aluminum and Iron chlorides gave better fluoride adsorption capacity [40]. To exploit this effect further study should be conducted on chemical treatment using the aforementioned chemicals and others.

The column experiments showed a better performance of the selected clays than the batch type. It is therefore recommended that these clay adsorbents should be studied further in full scale to determine optimum domestic defluoridation column parameters (bed height, flow rate, particle size).

The regeneration procedure should be optimized and safe disposal methods of exhausted adsorbents and regenerates should be identified.

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Annex 1

Summarized table for the data generated during experimentation. A 95% confidence interval (CI) value is used for the estimation of confidence level (CL).

Table 9 The percentage F^- adsorbed for the clay samples collected
(Mean ± CL values for duplicate measurements)

Mass of Clay (g)	Clay type			
	Bombawoha Clay	Harer Clay 1	Combolcha Clay	Harer Clay 2
1	21.72 ± 0.68	5.69 ± 0.68	30.26 ± 0.51	
2	34.05 ± 0.51	8.36 ± 0.51	50.43 ± 1.18	
3	41.12 ± 0.51	10.43 ± 0.51	60.17 ± 0.68	
4	44.40 ± 0.84	12.84 ± 0.51	69.57 ± 1.52	3.10 ± 0.68
5	53.53 ± 0.51	14.74 ± 0.17	74.40 ± 0.51	5.34 ± 0.34
6	60.26 ± 1.18	16.81 ± 0.17	78.10 ± 0.68	4.40 ± 0.84
7	62.07 ± 0.34	21.03 ± 0.34	79.74 ± 0.17	5.17 ± 0.00
8	70.52 ± 0.34	23.19 ± 0.51	82.50 ± 0.51	6.21 ± 0.34
9	71.47 ± 0.84	24.66 ± 0.68	84.40 ± 0.17	
10	71.81 ± 0.51	25.95 ± 0.17	86.72 ± 0.68	
Mass of Clay (g)	Clay type			
	Amercha Clay	Muger Clay 1	Muger Clay 2	Mesobo Clay
1	4.40 ± 0.51			
2	6.29 ± 0.51		43.02 ± 0.17	
3	16.90 ± 0.34		56.29 ± 0.51	5.28 ± 0.51
4	26.38 ± 0.34	12.24 ± 0.34	70.43 ± 0.51	5.06 ± 0.51
5	28.88 ± 0.84	14.14 ± 0.68	75.78 ± 0.51	4.82 ± 1.69
6	34.14 ± 0.34	15.78 ± 0.17	78.97 ± 0.34	4.61 ± 0.34
7	36.55 ± 0.00	18.71 ± 0.17	82.59 ± 0.34	4.43 ± 0.51
8	38.97 ± 0.34	19.83 ± 0.34	82.67 ± 0.84	3.16 ± 0.17
9		21.38 ± 0.34	84.31 ± 0.34	
10		23.88 ± 0.51	85.00 ± 0.17	

Table 10 Adsorption capacity for three Clay samples treated at different temperature (Mean ± CL values for duplicate measurements)

Clay type	Bombawoha Clay	Combolcha Clay	Muger Clay 2
Temperature (^oC)	% Adsorption	% Adsorption	% Adsorption
100	41.38 ± 0.34	83.75 ± 0.76	74.91 ± 0.51
200	48.02 ± 1.35	86.97 ± 0.86	79.83 ± 0.68
300	53.62 ± 0.68	88.66 ± 0.74	84.22 ± 0.51
400	75.00 ± 0.68	91.47 ± 0.51	89.26 ± 0.10
500	77.33 ± 0.84	93.36 ± 0.17	90.69 ± 0.51
600	77.16 ± 0.17	94.48 ± 0.34	88.67 ± 0.57
700	72.07 ± 0.68	83.04 ± 1.23	83.81 ± 0.03
800	65.43 ± 0.17	37.33 ± 1.18	

Table 11 Adsorption efficiency for different values of pH
(Mean ± CL values for duplicate measurements)

Bombawoha Clay		Combolcha Clay		Muger Clay 2	
PH_i	% Adsorption	PH_i	% Adsorption	PH_i	% Adsorption
2	87.53 ± 0.12	1.7	91.29 ± 0.51	2.01	92.96 ± 0.05
3	92.36 ± 0.10	2.2	93.79 ± 0.34	3.02	92.00 ± 0.14
4	83.19 ± 0.07	3	94.48 ± 0.00	3.96	89.94 ± 0.12
5.01	81.72 ± 0.00	4.01	90.33 ± 0.07	6	85.00 ± 0.68
6.01	83.28 ± 0.34	5.01	87.32 ± 0.05	7.1	75.00 ± 0.34
7.01	61.29 ± 0.17	6.02	85.69 ± 1.02	8.4	70.43 ± 0.51
7.95	57.16 ± 0.17	7.94	75.60 ± 0.17	9.2	57.33 ± 0.17
9.02	57.41 ± 0.00	9.1	72.50 ± 0.17		
9.97	48.45 ± 0.34				

Table 12 Adsorption Capacity (mg/g) for various initial fluoride concentrations (mg/l).
(Mean ± CL values for duplicate measurements)

Initial Fluorides Conc. (mg/l)	Bombawoha Clay	Combolcha Clay	Muger Clay 2
5.8	0.031 ± 0.005	0.043 ± 0.005	0.044 ± 0.003
10.1	0.064 ± 0.003	0.071 ± 0.006	0.073 ± 0.004
15.05	0.093 ± 0.003	0.107 ± 0.005	0.109 ± 0.002
20.02	0.103 ± 0.004	0.144 ± 0.002	0.147 ± 0.001
25.12	0.133 ± 0.001	0.181 ± 0.001	0.185 ± 0.003

Table 13 Residual fluoride concentration at different contact time for the selected clay samples (Mean ± CL values for duplicate measurements)

	Bombawoha clay		Combolcha clay		Muger Clay 2	
Time (hrs)	4gm	2gm	2gm	4gm	2gm	4gm
1	0.50 ± 0.02	3.41 ± 0.02	0.63 ± 0.05	0.69 ± 0.04	0.66 ± 0.02	0.67 ± 0.02
2	1.00 ± 0.05	3.34 ± 0.03	1.25 ± 0.03	1.38 ± 0.07	1.31 ± 0.02	1.34 ± 0.03
3	1.50 ± 0.04	3.37 ± 0.00	1.88 ± 0.01	2.06 ± 0.01	1.97 ± 0.04	2.02 ± 0.00
4	2.00 ± 0.00	3.44 ± 0.00	2.50 ± 0.03	2.75 ± 0.01	2.63 ± 0.03	2.69 ± 0.02
5	1.99 ± 0.00	3.46 ± 0.01	1.25 ± 0.04	1.88 ± 0.02	1.56 ± 0.00	1.72 ± 0.02
6	1.99 ± 0.00	3.33 ± 0.01	1.50 ± 0.03	2.25 ± 0.02	1.88 ± 0.03	2.06 ± 0.00

Annex 2

MINITAB 14 out puts for the experiments conducted in chapter 3.

Fig. 15 ANOVA analysis result and Residual plot for the experiment 3.4.1

One-way ANOVA: % Ads. Versus Clay types

```
Source     DF        SS       MS        F      P
Clay type   7  11294.13  1613.45  5012.07  <0.001
Error       8      2.58     0.32
Total      15  11296.70

S = 0.5674   R-Sq = 99.98%   R-Sq(adj) = 99.96%


                                  Individual 95% CIs For Mean Based on
                                  Pooled StDev
Level           N    Mean  StDev  --------+---------+---------+---------+-
Amercha clay    2  28.880  0.608              *)
Bombawoha clay  2  53.535  0.361                          (*
Combolcha Clay  2  74.400  0.368                                     *)
Harer caly2     2   5.345  0.247  (*
Harer clay1     2  14.745  0.120       *)
Mesobo clay     2  16.895  1.223        *)
Muger clay1     2  14.135  0.488       *)
Muger clay2     2  75.775  0.361                                     (*
                                  --------+---------+---------+---------+-
                                         20        40        60        80

Pooled StDev = 0.567
```

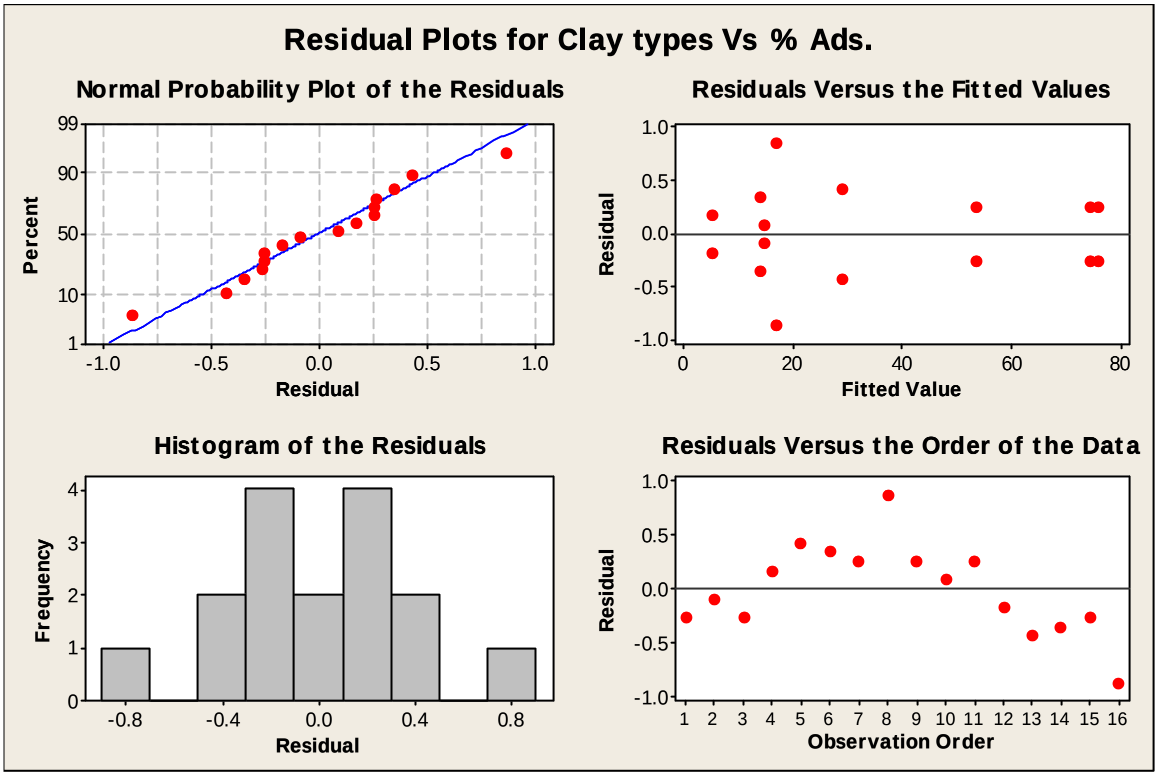


Fig. 16 a ANOVA analysis result and Residual plot for the experiment 3.4.5.

One-way ANOVA: Bombawoha clay (% Ads. versus dosage (g))

```
Source  DF        SS       MS        F      P
Mass     9  5378.077  597.564  2530.98  <0.001
Error   10     2.361    0.236
Total   19  5380.438

S = 0.4859   R-Sq = 99.96%   R-Sq(adj) = 99.92%


                         Individual 95% CIs For Mean Based on
                         Pooled StDev
Level  N    Mean  StDev  ------+---------+---------+---------+---
 1     2  21.725  0.488  *)
 2     2  34.050  0.368          (*
 3     2  41.120  0.368               *)
 4     2  44.400  0.608                 (*
 5     2  53.535  0.361                       (*
 6     2  60.260  0.849                            *)
 7     2  62.070  0.240                             *)
 8     2  70.515  0.247                                  (*)
 9     2  71.465  0.615                                   (*
10     2  71.810  0.368                                   (*
                         ------+---------+---------+---------+---
                              30        45        60        75

Pooled StDev = 0.486
```

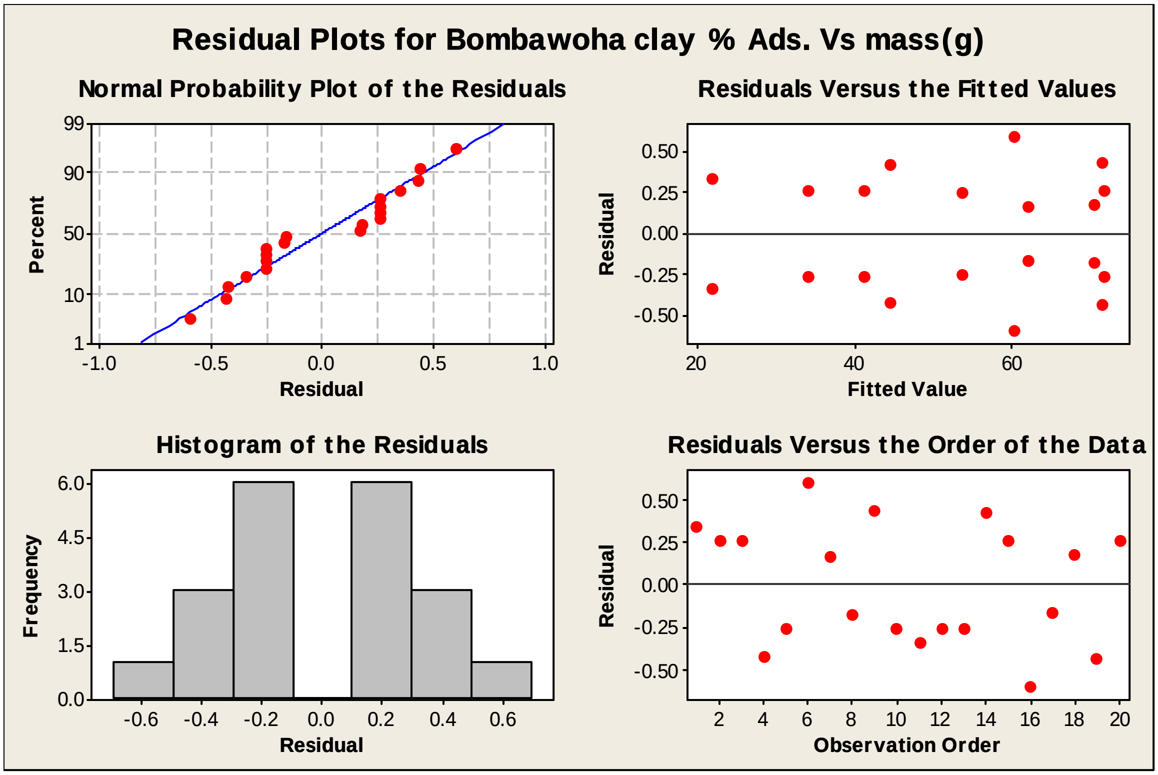


Fig. 16 b ANOVA analysis result and Residual plot for the experiment 3.4.5.

One-way ANOVA: Bombawoha clay (Ads. capacity versus dosage (g))

```
Source  DF         SS         MS        F      P
Mass     9  0.0031574  0.0003508  1185.20   <0.001
Error   10  0.0000030  0.0000003
Total   19  0.0031603

S = 0.0005441   R-Sq = 99.91%   R-Sq(adj) = 99.82%


                              Individual 95% CIs For Mean Based on
                              Pooled StDev
Level  N      Mean     StDev  ---+---------+---------+---------+------
 1     2  0.063000  0.001414                                     (*
 2     2  0.049500  0.000707                          *)
 3     2  0.039750  0.000354                 (*)
 4     2  0.032250  0.000354           (*)
 5     2  0.031100  0.000141          (*)
 6     2  0.028900  0.000141        (*)
 7     2  0.025800  0.000283      (*
 8     2  0.025800  0.000283      (*
 9     2  0.022950  0.000071   (*)
10     2  0.020950  0.000071  *)
                              ---+---------+---------+---------+------
                               0.024     0.036     0.048     0.060

Pooled StDev = 0.000544
```

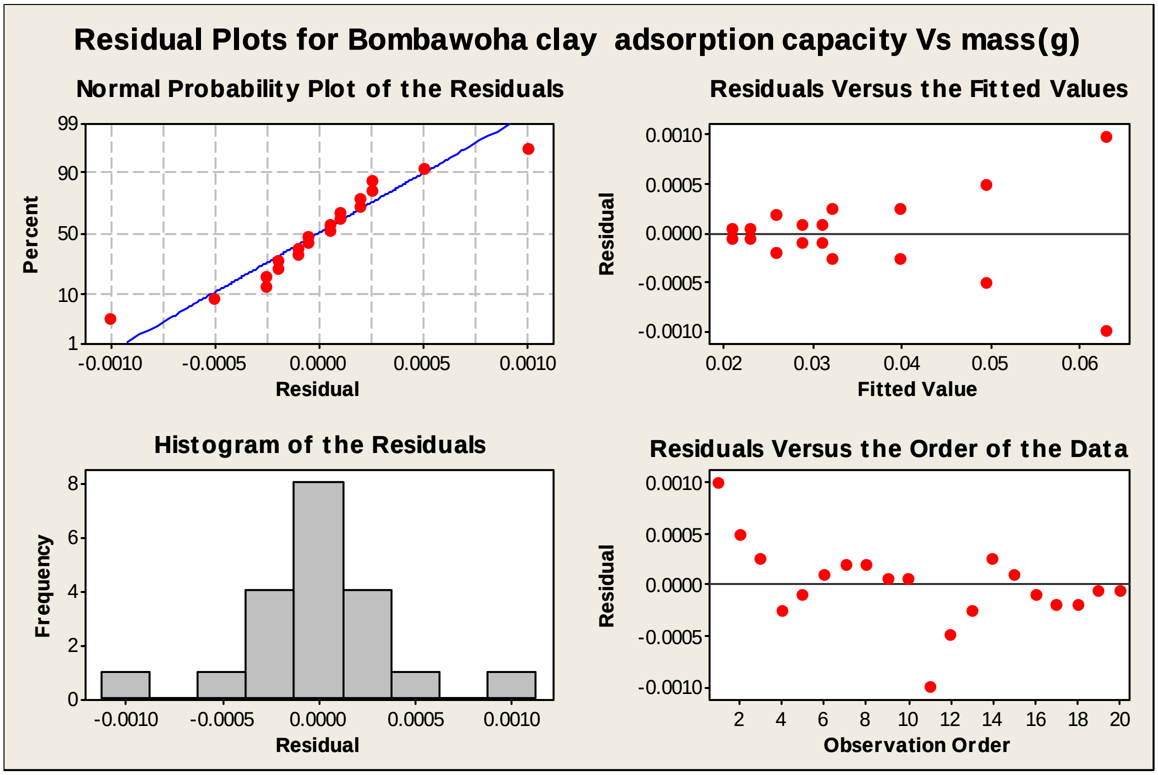


Fig. 16 c ANOVA analysis result and Residual plot for the experiment 3.4.5.

One-way ANOVA: Combolcha clay (% Ads. versus dosage (g))

```
Source  DF        SS       MS        F      P
Mass     9  5761.622  640.180  2085.35  <0.001
Error   10     3.070    0.307
Total   19  5764.692

S = 0.5541   R-Sq = 99.95%   R-Sq(adj) = 99.90%


                         Individual 95% CIs For Mean Based on
                         Pooled StDev
Level  N    Mean  StDev  +---------+---------+---------+---------
 1     2  30.260  0.368  *)
 2     2  50.430  0.849                (*
 3     2  60.175  0.488                       *)
 4     2  69.565  1.096                             *)
 5     2  74.400  0.368                                (*
 6     2  78.105  0.488                                  (*)
 7     2  79.745  0.120                                    *)
 8     2  82.500  0.368                                     (*)
 9     2  84.395  0.120                                       *)
10     2  86.725  0.488                                        (*
                         +---------+---------+---------+---------
                        30        45        60        75

Pooled StDev = 0.554
```

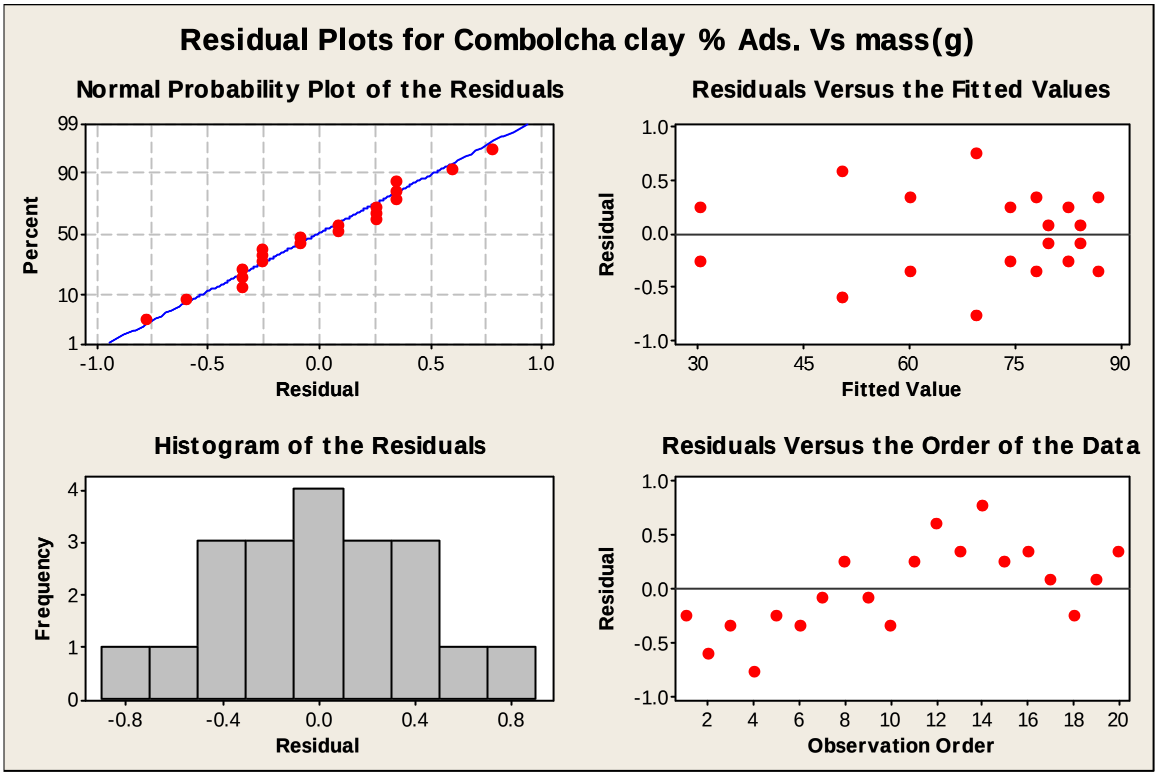


Fig. 16 d ANOVA analysis result and Residual plot for the experiment 3.4.5.

One-way ANOVA: Combolcha clay (Ads. capacity versus dosage (g))

```
Source  DF         SS         MS        F      P
Mass     9  0.0079318  0.0008813  1762.62  <0.001
Error   10  0.0000050  0.0000005
Total   19  0.0079368

S = 0.0007071   R-Sq = 99.94%   R-Sq(adj) = 99.88%


                              Individual 95% CIs For Mean Based on
                              Pooled StDev
Level  N      Mean     StDev  --------+---------+---------+---------+-
 1     2  0.088000  0.001414                               (*)
 2     2  0.073000  0.001414                        *)
 3     2  0.058500  0.000707                 *)
 4     2  0.050500  0.000707             *)
 5     2  0.043000  0.000000         *)
 6     2  0.038000  0.000000      (*)
 7     2  0.033000  0.000000    (*
 8     2  0.030000  0.000000  (*)
 9     2  0.027000  0.000000 (*
10     2  0.025000  0.000000(*
                              --------+---------+---------+---------+-
                                    0.040     0.060     0.080     0.100

Pooled StDev = 0.000707
```

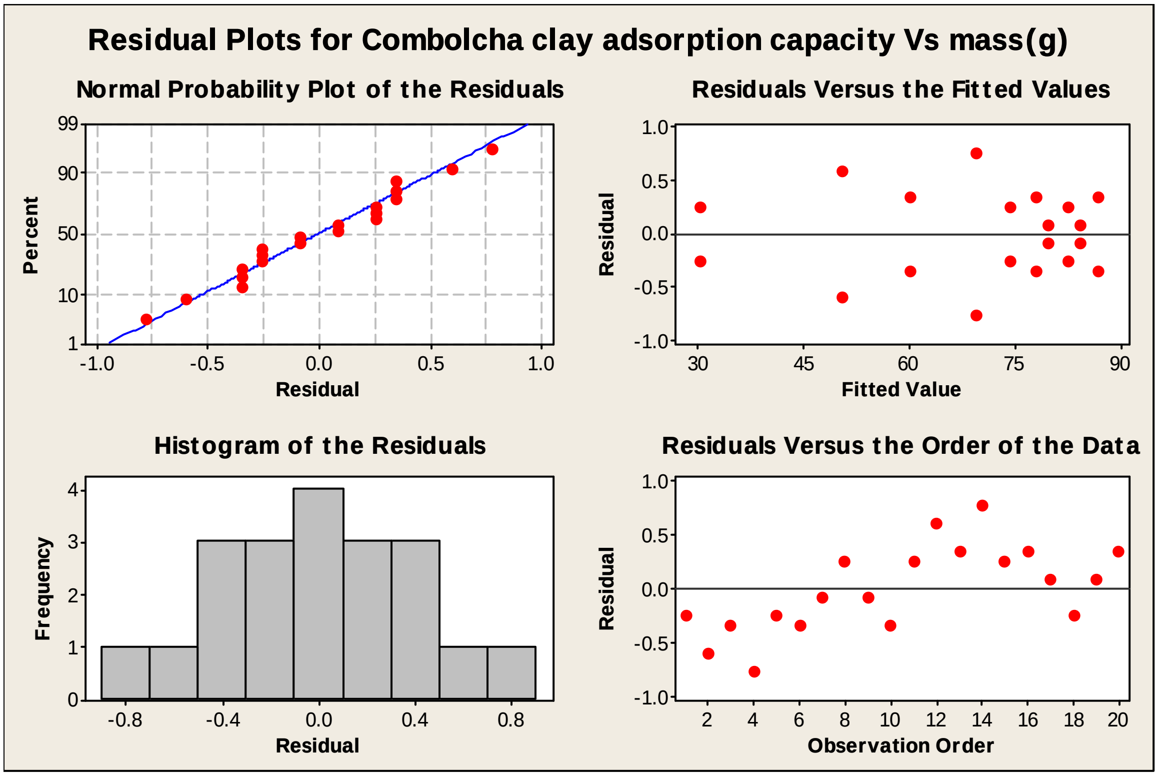


Fig. 16 e ANOVA analysis result and Residual plot for the experiment 3.4.5.

One-way ANOVA: Muger clay2 (% Ads. versus dosage (g))

```
Source  DF        SS       MS        F       P
Mass     8  3374.108  421.763  3875.51  <0.001
Error    9     0.979    0.109
Total   17  3375.087

S = 0.3299   R-Sq = 99.97%   R-Sq(adj) = 99.95%


                         Individual 95% CIs For Mean Based on
                         Pooled StDev
Level  N    Mean  StDev  -----+---------+---------+---------+----
 2     2  43.015  0.120  (*
 3     2  56.290  0.368             (*
 4     2  70.430  0.368                         (*
 5     2  75.775  0.361                              *)
 6     2  78.965  0.247                                (*
 7     2  82.585  0.247                                   (*
 8     2  82.670  0.608                                   (*
 9     2  84.310  0.240                                     *)
10     2  85.085  0.120                                     (*
                         -----+---------+---------+---------+----
                             48        60        72        84

Pooled StDev = 0.330
```

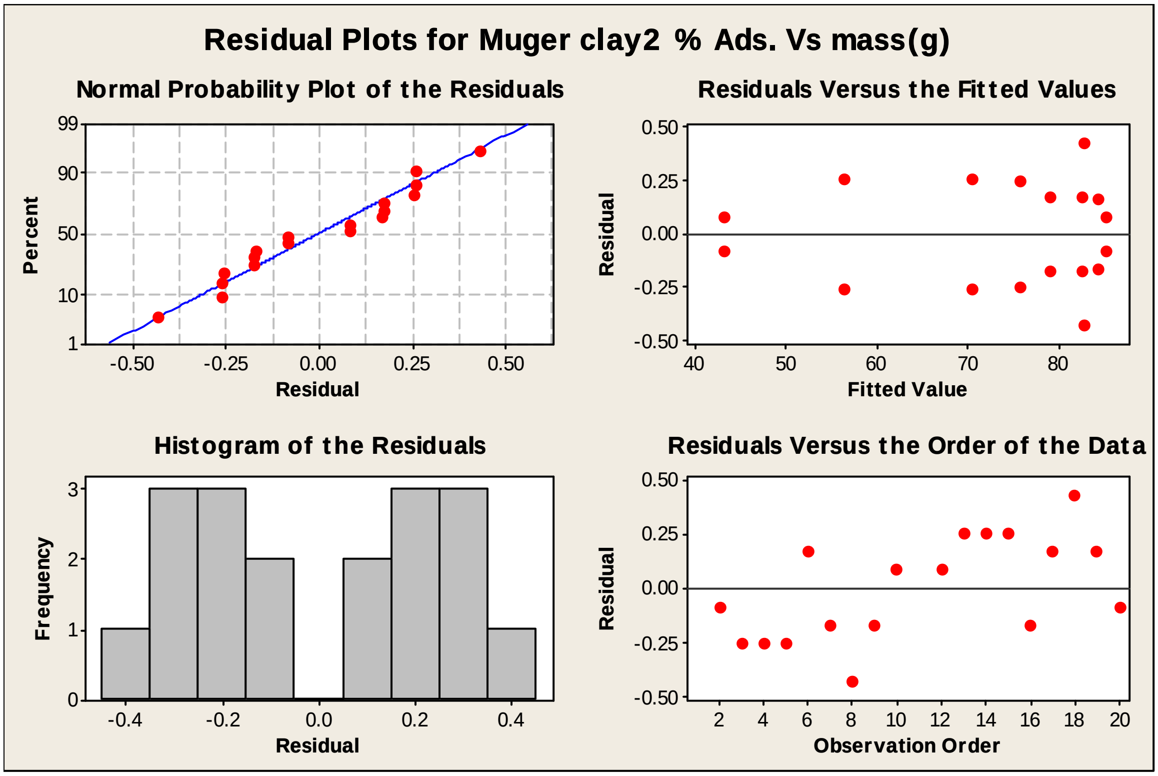


Fig. 16 f ANOVA analysis result and Residual plot for the experiment 3.4.5.

One-way ANOVA: Muger clay2 (Ads. capacity versus dosage (g))

```
Source  DF         SS         MS        F      P
Mass     8   0.0027670  0.0003459  3112.87  <0.001
Error    9   0.0000010  0.0000001
Total   17   0.0027680

S = 0.0003333   R-Sq = 99.96%   R-Sq(adj) = 99.93%


                              Individual 95% CIs For Mean Based on
                              Pooled StDev
Level  N      Mean     StDev  ------+---------+---------+---------+---
 2     2  0.062500  0.000707                                        (*
 3     2  0.054500  0.000707                                (*
 4     2  0.051000  0.000000                            (*)
 5     2  0.044000  0.000000                     (*)
 6     2  0.038000  0.000000               (*)
 7     2  0.034000  0.000000           (*)
 8     2  0.030000  0.000000       (*)
 9     2  0.027000  0.000000    (*)
10     2  0.025000  0.000000  (*)
                              ------+---------+---------+---------+---
                                  0.030     0.040     0.050     0.060

Pooled StDev = 0.000333
```

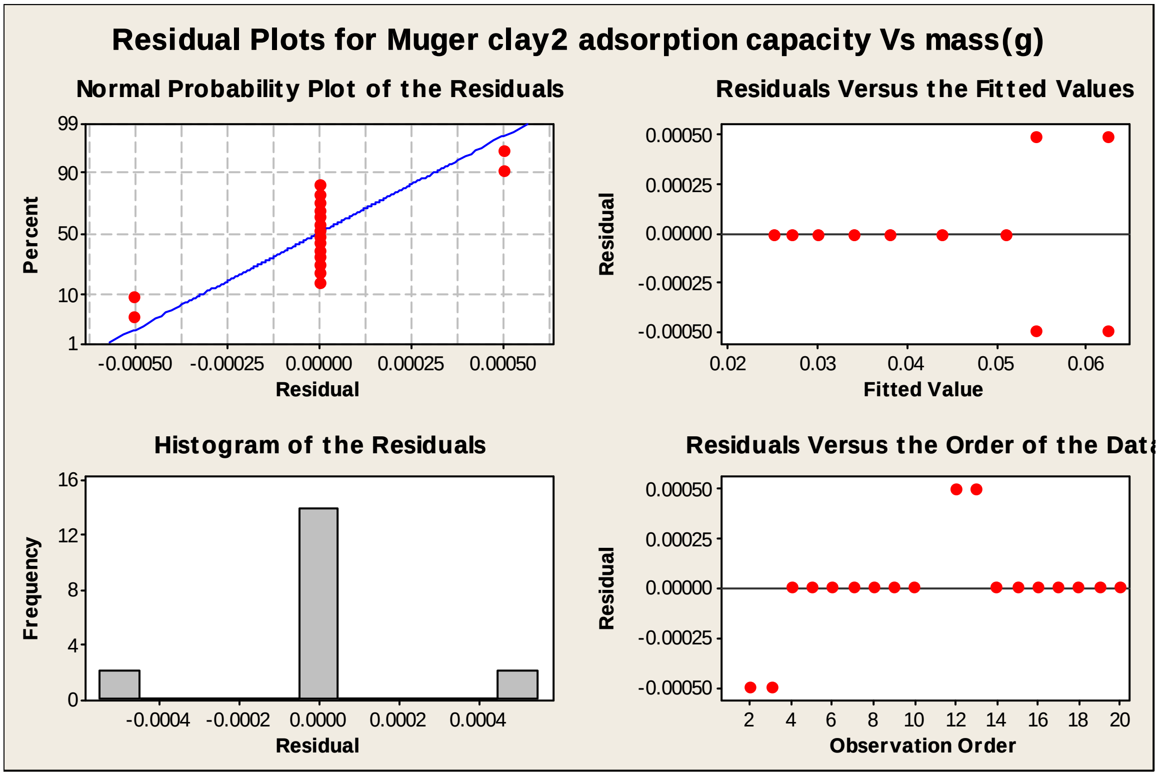


Fig. 17 a ANOVA analysis result and Residual plot for the experiment 3.4.4.

One-way ANOVA: Bombawoha clay versus pH

```
Source   DF        SS       MS         F      P
pH        8  4205.672  525.709  29215.07  <0.001
Error     9     0.162    0.018
Total    17  4205.834

S = 0.1341   R-Sq = 100.00%   R-Sq(adj) = 99.99%


                         Individual 98% CIs For Mean Based on
                         Pooled StDev
Level  N    Mean  StDev   +---------+---------+---------+---------
2.00   2  87.530  0.085                                    *
3.00   2  92.360  0.071                                        *
4.00   2  83.190  0.042                                *)
5.01   2  81.720  0.000                               *
6.01   2  83.275  0.247                                *)
7.01   2  61.295  0.120              *
7.95   2  57.155  0.120          (*
9.02   2  57.410  0.000           *
9.97   2  48.450  0.240   *)
                          +---------+---------+---------+---------
                         48        60        72        84

Pooled StDev = 0.134
```

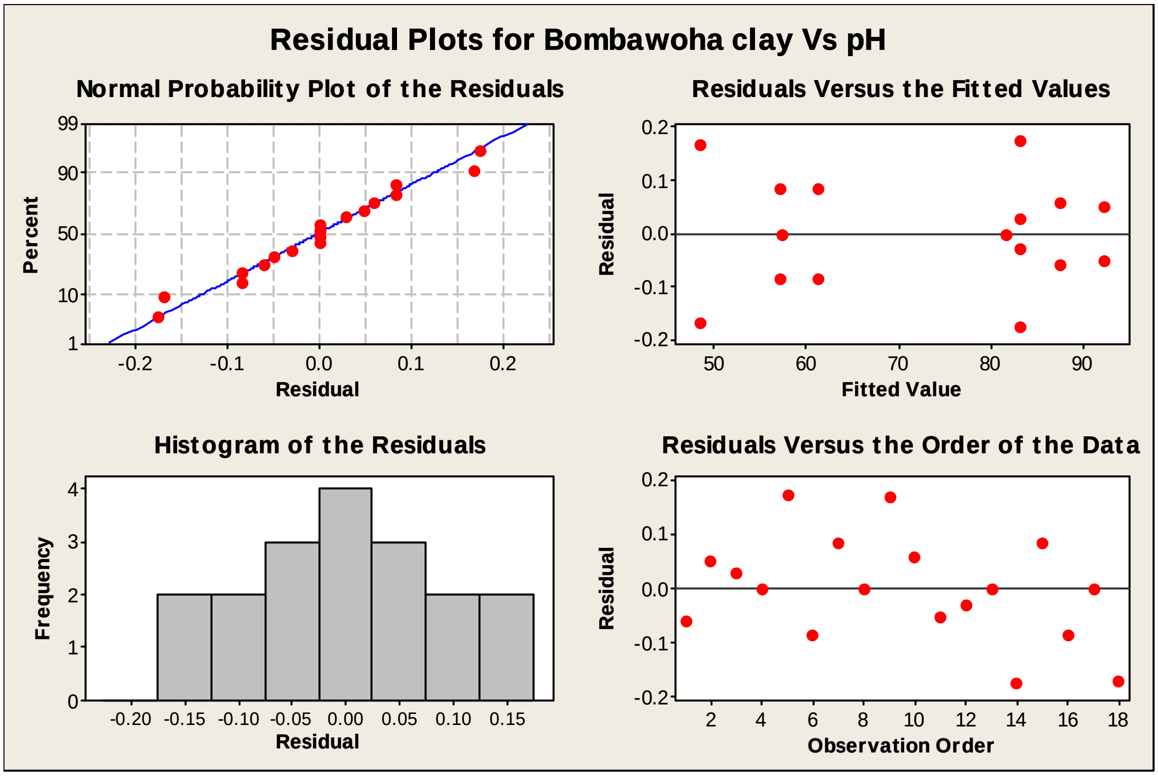


Fig. 17 b ANOVA analysis result and Residual plot for the experiment 3.4.4.

One-way ANOVA: Combolcha clay versus pH

```
Source   DF        SS        MS        F      P
pH        7  940.7370  134.3910  1393.37  <0.001
Error     8    0.7716    0.0964
Total    15  941.5086

S = 0.3106   R-Sq = 99.92%   R-Sq(adj) = 99.85%


                         Individual 95% CIs For Mean Based on Pooled
                         StDev
Level  N    Mean  StDev     +---------+---------+---------+---------
1.70   2  91.290  0.368                                    (*)
2.20   2  93.795  0.247                                        (*)
3.00   2  94.480  0.000                                          *)
4.01   2  90.325  0.049                                   (*
5.01   2  87.315  0.035                              (*
6.02   2  85.690  0.735                           (*)
7.94   2  75.605  0.120          (*)
9.10   2  72.500  0.127     (*)
                            +---------+---------+---------+---------
                         72.0      78.0      84.0      90.0

pooled StDev = 0.311
```

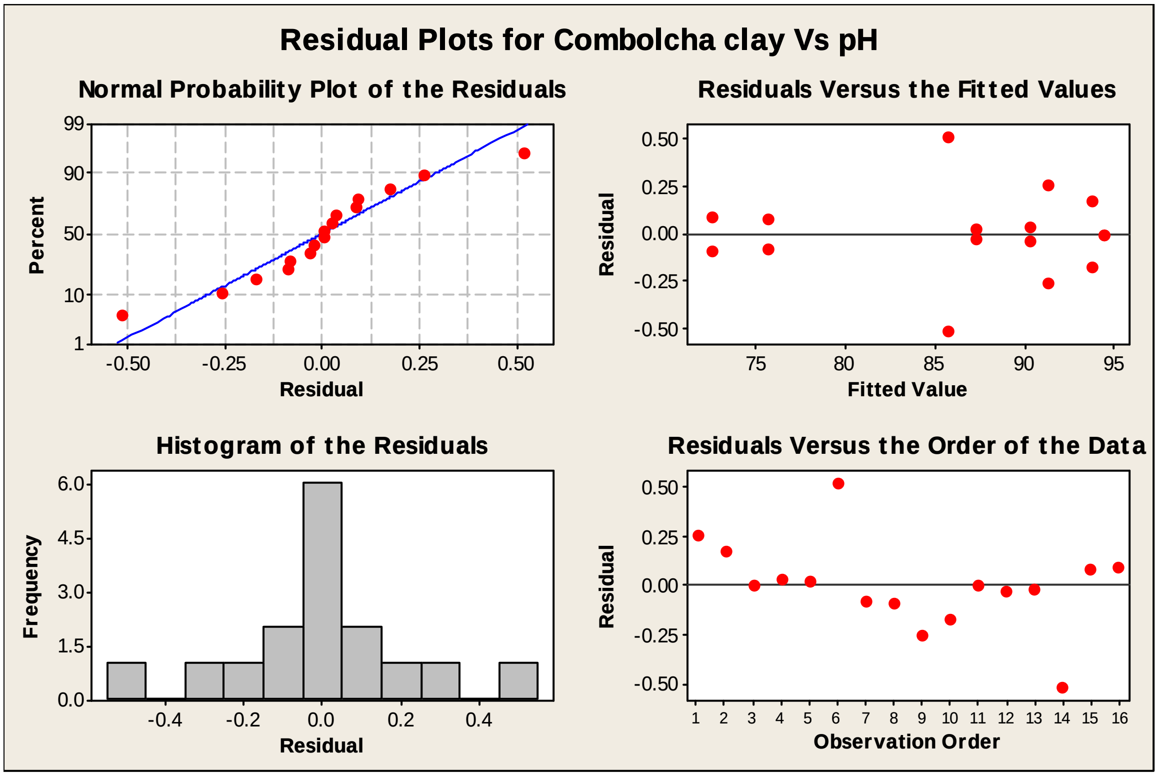


Fig. 17 c ANOVA analysis result and Residual plot for the experiment 3.4.4.

One-way ANOVA: Muger clay 2 versus pH

```
Source   DF        SS       MS        F      P
pH        6    2130.746  355.124  5440.73   <0.000
Error     7       0.457    0.065
Total    13    2131.203

S = 0.2555   R-Sq = 99.98%   R-Sq(adj) = 99.96%


                         Individual 95% CIs For Mean Based on
                         Pooled StDev
Level  N    Mean  StDev  ---+---------+---------+---------+------
2.01   2  92.955  0.035                                     *
3.02   2  92.000  0.099                                    *
3.96   2  89.940  0.085                                  *
6.00   2  85.000  0.481                             *
7.10   2  75.000  0.240                   *
8.40   2  70.430  0.368              *)
9.20   2  57.325  0.120  *)
                         ---+---------+---------+---------+------
                           60        70        80        90

Pooled StDev = 0.255
```

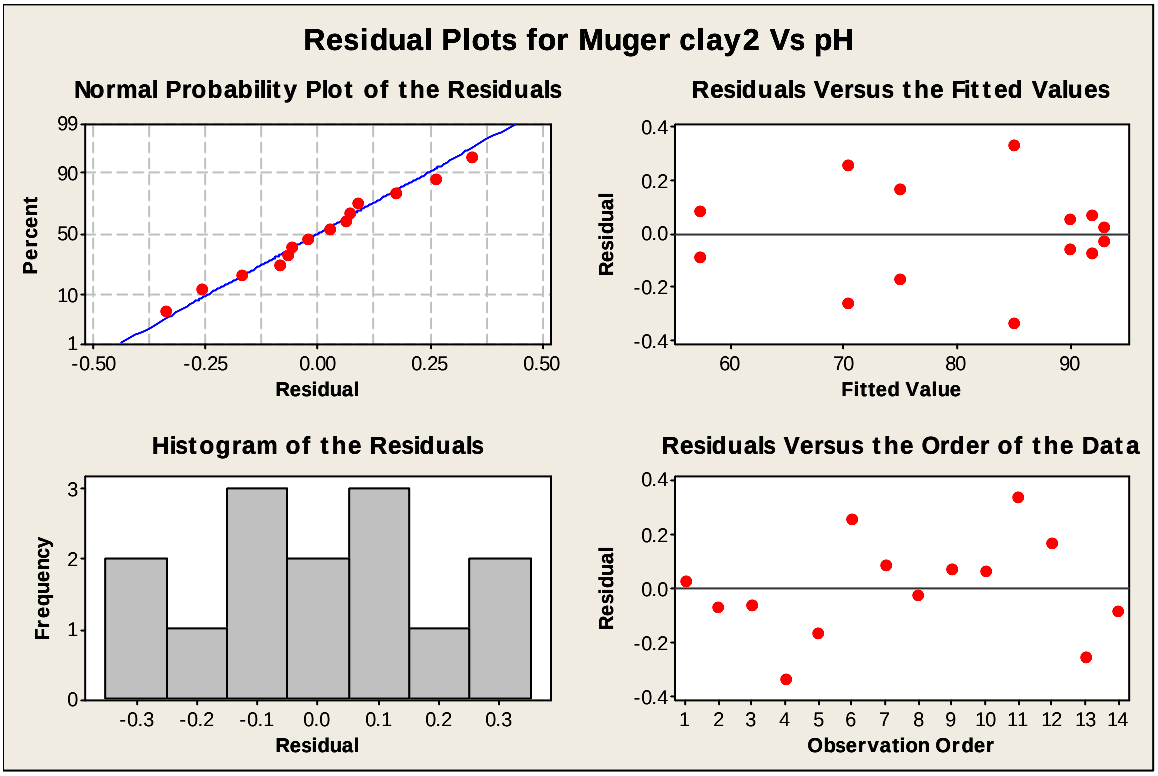


Fig. 17 a ANOVA analysis result and Residual plot for the experiment 3.4.2.

One-way ANOVA: Bumbawoha clay versus Temp.

```
Source   DF        SS       MS        F      P
Temp     7   2778.587   396.941  1499.48  0.000
Error    8      2.118     0.265
Total   15   2780.705

S = 0.5145   R-Sq = 99.92%   R-Sq(adj) = 99.86%


                         Individual 95% CIs For Mean Based on
                         Pooled StDev
Level  N    Mean  StDev  ---------+---------+---------+---------+
100    2  41.380  0.240  *)
200    2  48.790  0.976         (*)
300    2  53.625  0.488              (*
400    2  75.000  0.481                                  (*)
500    2  77.330  0.608                                    (*)
600    2  77.155  0.120                                    (*)
700    2  72.065  0.488                               (*)
800    2  65.430  0.127                         *)
                         ---------+---------+---------+---------+
                                 50        60        70        80

Pooled StDev = 0.515
```

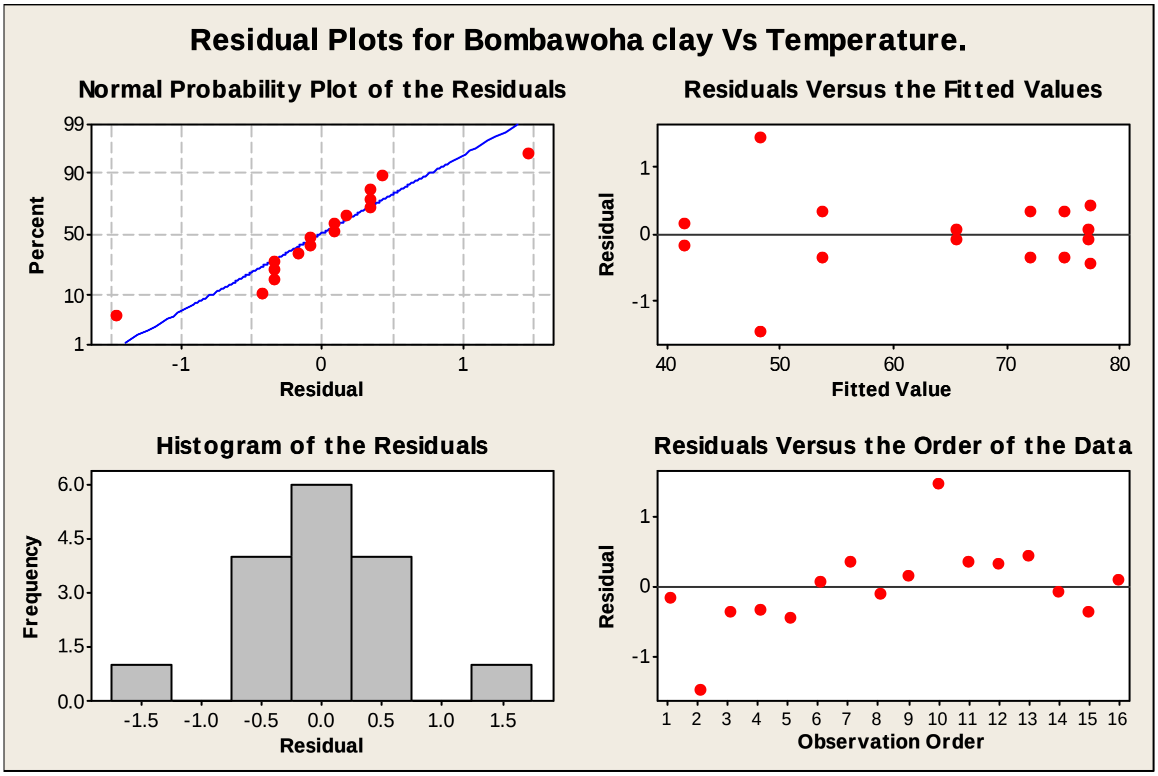


Fig. 18 b ANOVA analysis result and Residual plot for the experiment 3.4.2.

One-way ANOVA: Combolcha clay versus Temp.

```
Source    DF        SS       MS        F      P
Temp      7  4884.895  697.842  2064.43  0.000
Error     8     2.704    0.338
Total    15  4887.600

S = 0.5814   R-Sq = 99.94%   R-Sq(adj) = 99.90%


                         Individual 95% CIs For Mean Based on
                         Pooled StDev
Level  N    Mean  StDev  ------+---------+---------+---------+---
100    2  83.750  0.552                                 (*
200    2  86.970  0.622                                   (*)
300    2  88.655  0.530                                    (*)
400    2  91.465  0.361                                      (*)
500    2  93.365  0.120                                        *)
600    2  94.485  0.247                                        (*)
700    2  83.040  0.891                                 *)
800    2  37.325  0.856  (*)
                         ------+---------+---------+---------+---
                              45        60        75        90

Pooled StDev = 0.581
```

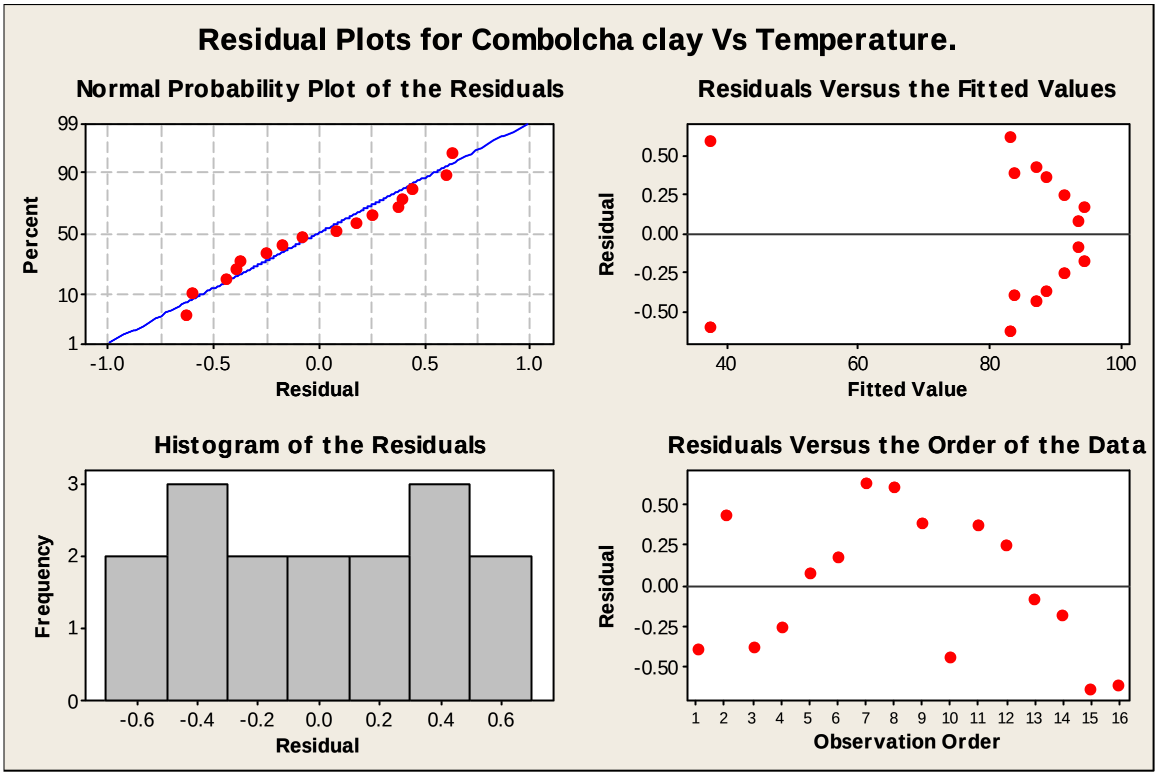


Fig. 18 c ANOVA analysis result and Residual plot for the experiment 3.4.2.

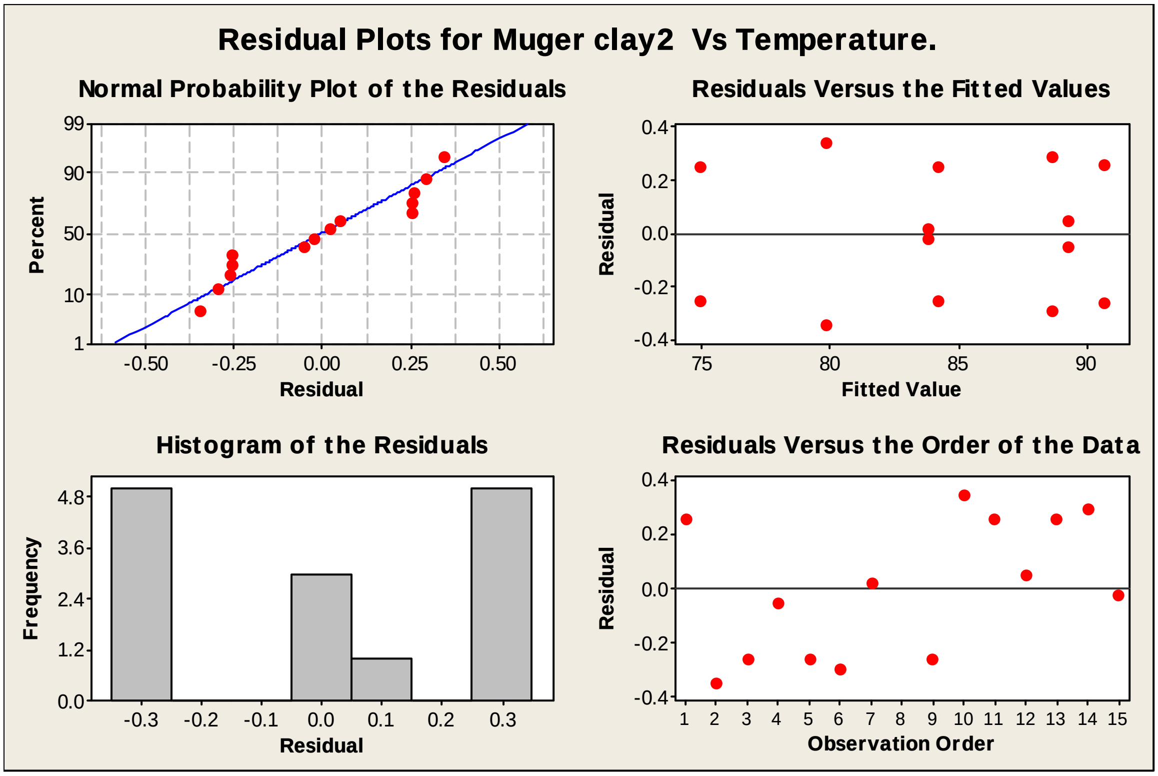
One-way ANOVA: Muger clay 2 versus Temp.

```
Source   DF        SS      MS       F      P
Temp      7  539.033  77.005  733.68  0.000
Error     8    0.840   0.105
Total    15  539.873

S = 0.3240   R-Sq = 99.84%   R-Sq(adj) = 99.71%


                         Individual 95% CIs For Mean Based on
                         Pooled StDev
Level  N    Mean  StDev    -+---------+---------+---------+--------
100    2  74.915  0.361    (*)
200    2  79.825  0.488              (*)
300    2  84.225  0.361                      (*-)
400    2  89.260  0.071                                (-*)
500    2  90.690  0.368                                   (*)
600    2  88.675  0.417                               (*)
700    2  83.810  0.028                      (*)
800    2  75.115  0.163    (*)
                           -+---------+---------+---------+--------
                         75.0      80.0      85.0      90.0

Pooled StDev = 0.324
```



Residual Plots for Muger clay2 Vs Temperature.

Normal Probability Plot of the Residuals

Residuals Versus the Fitted Values

Histogram of the Residuals

Residuals Versus the Order of the Data

Fig. 19 a ANOVA analysis result and Residual plot for the experiment 3.4.3.

One-way ANOVA: Bombawoha clay (2g) versus Time

```
Source  DF        SS        MS      F      P
Time     5  0.020542  0.004108  32.87  <0.001
Error    6  0.000750  0.000125
Total   11  0.021292

S = 0.01118   R-Sq = 96.48%   R-Sq(adj) = 93.54%


                          Individual 95% CIs For Mean Based on
                          Pooled StDev
Level  N    Mean   StDev   -+---------+---------+---------+--------
1      2  3.4100  0.0141                       (---*----)
2      2  3.3350  0.0212   (----*----)
3      2  3.3700  0.0000            (---*----)
4      2  3.4400  0.0000                              (----*----)
5      2  3.4550  0.0071                                  (----*----)
6      2  3.4250  0.0071                          (----*----)
                           -+---------+---------+---------+--------
                          3.320     3.360     3.400     3.440

Pooled StDev = 0.0112
```

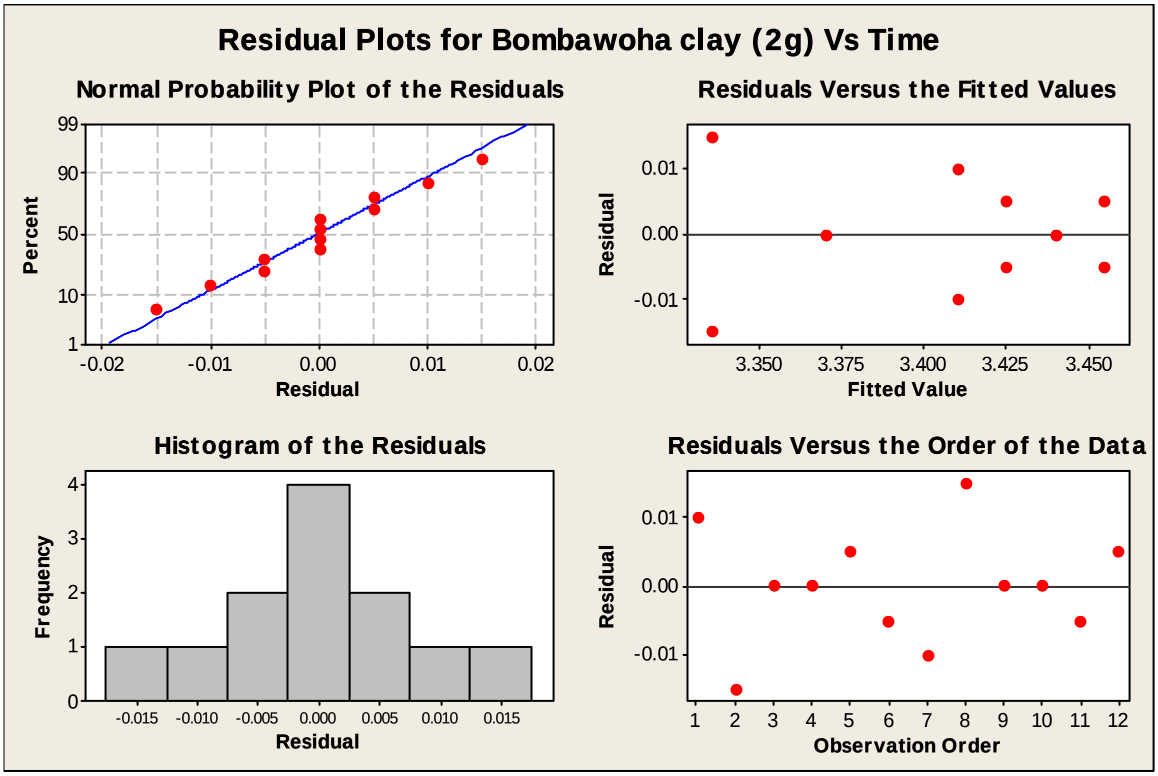


Fig. 19 b ANOVA analysis result and Residual plot for the experiment 3.4.3.

One-way ANOVA: Bombawoha clay (4g) versus Time

```
Source  DF        SS        MS      F      P
Time     5  0.047575  0.009515  25.37  0.001
Error    6  0.002250  0.000375
Total   11  0.049825

S = 0.01936   R-Sq = 95.48%   R-Sq(adj) = 91.72%


                          Individual 95% CIs For Mean Based on
                          Pooled StDev
Level  N    Mean   StDev  ---+---------+---------+---------+------
1      2  1.9100  0.0141             (----*----)
2      2  2.0050  0.0354                           (---*----)
3      2  1.8300  0.0283  (---*----)
4      2  1.9900  0.0000                        (----*----)
5      2  1.9900  0.0000                        (----*----)
6      2  1.9900  0.0000                        (----*----)
                          ---+---------+---------+---------+------
                           1.820     1.890     1.960     2.030

Pooled StDev = 0.0194
```

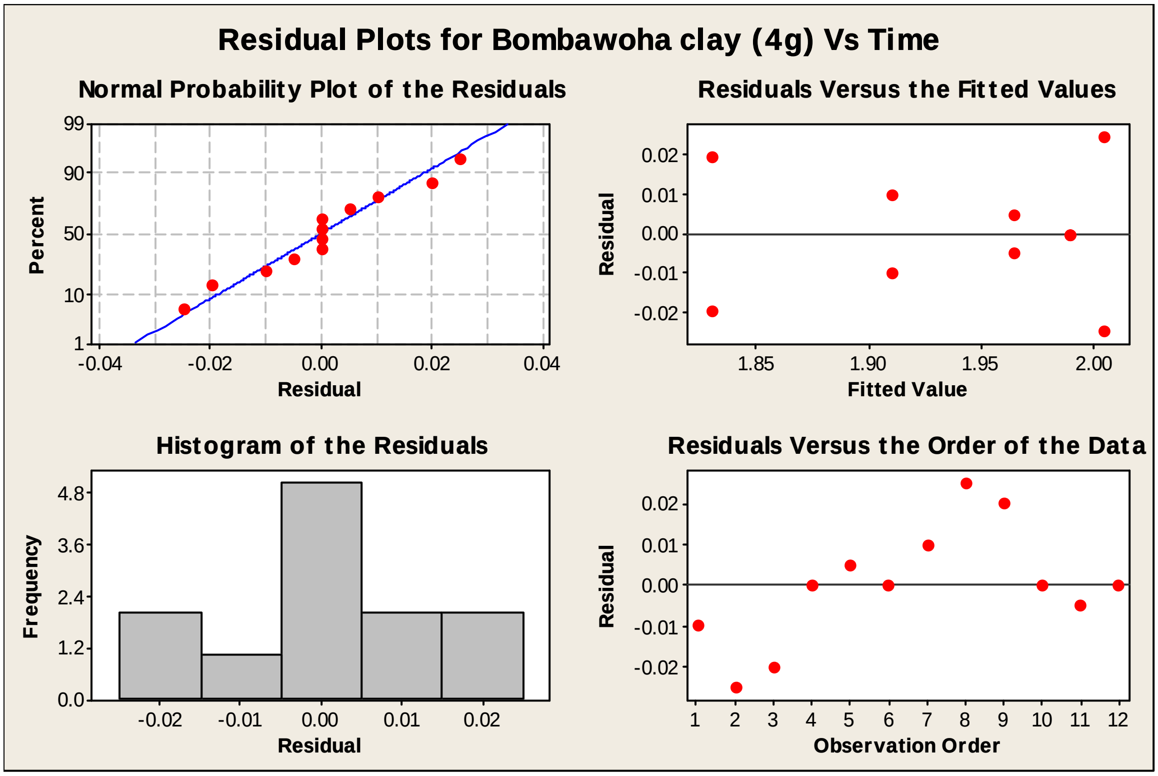


Fig. 19 c ANOVA analysis result and Residual plot for the experiment 3.4.3.

One-way ANOVA: Combolcha clay (2g) versus Time

```
Source  DF        SS        MS      F      P
Time     5  0.181375  0.036275  63.09  <0.001
Error    6  0.003450  0.000575
Total   11  0.184825

S = 0.02398   R-Sq = 98.13%   R-Sq(adj) = 96.58%


                          Individual 95% CIs For Mean Based on
                          Pooled StDev
Level  N    Mean   StDev  --+---------+---------+---------+-------
1      2  3.0750  0.0354                 (--*---)
2      2  2.8950  0.0212  (--*---)
3      2  3.2050  0.0071                            (--*---)
4      2  3.1650  0.0212                        (---*--)
5      2  3.2600  0.0283                                (---*--)
6      2  3.2250  0.0212                             (---*--)
                         --+---------+---------+---------+-------
                           2.88      3.00      3.12      3.24

Pooled StDev = 0.0240
```

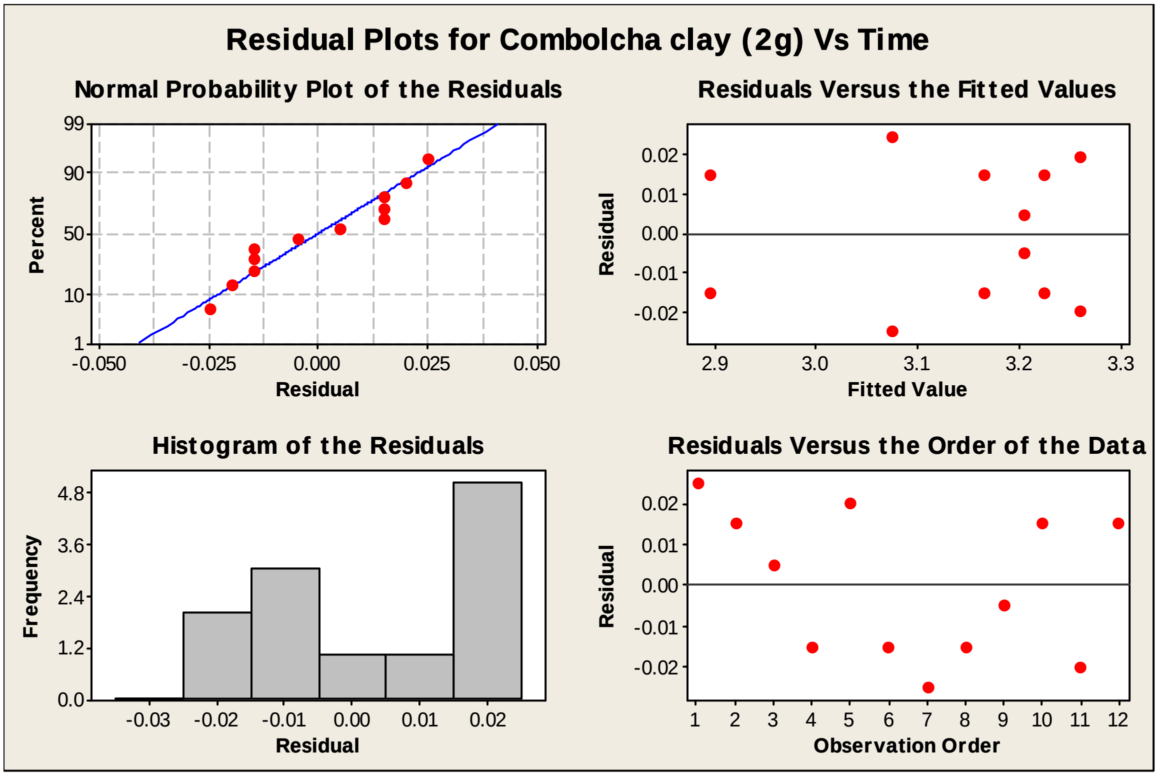


Fig. 19 d ANOVA analysis result and Residual plot for the experiment 3.4.3.

One-way ANOVA: Combolcha clay (4g) versus Time

```
Source  DF        SS        MS      F       P
Time     5  0.203142  0.040628  65.01  <0.001
Error    6  0.003750  0.000625
Total   11  0.206892

S = 0.025   R-Sq = 98.19%   R-Sq(adj) = 96.68%


                          Individual 95% CIs For Mean Based on
                          Pooled StDev
Level  N    Mean   StDev   +---------+---------+---------+---------
1      2  1.7400  0.0283    (---*---)
2      2  1.7550  0.0495     (---*----)
3      2  1.9850  0.0071                            (---*----)
4      2  2.0350  0.0071                                 (---*----)
5      2  2.0500  0.0141                                   (---*---)
6      2  2.0100  0.0141                               (---*---)
                           +---------+---------+---------+---------
                          1.70      1.80      1.90      2.00

Pooled StDev = 0.0250
```

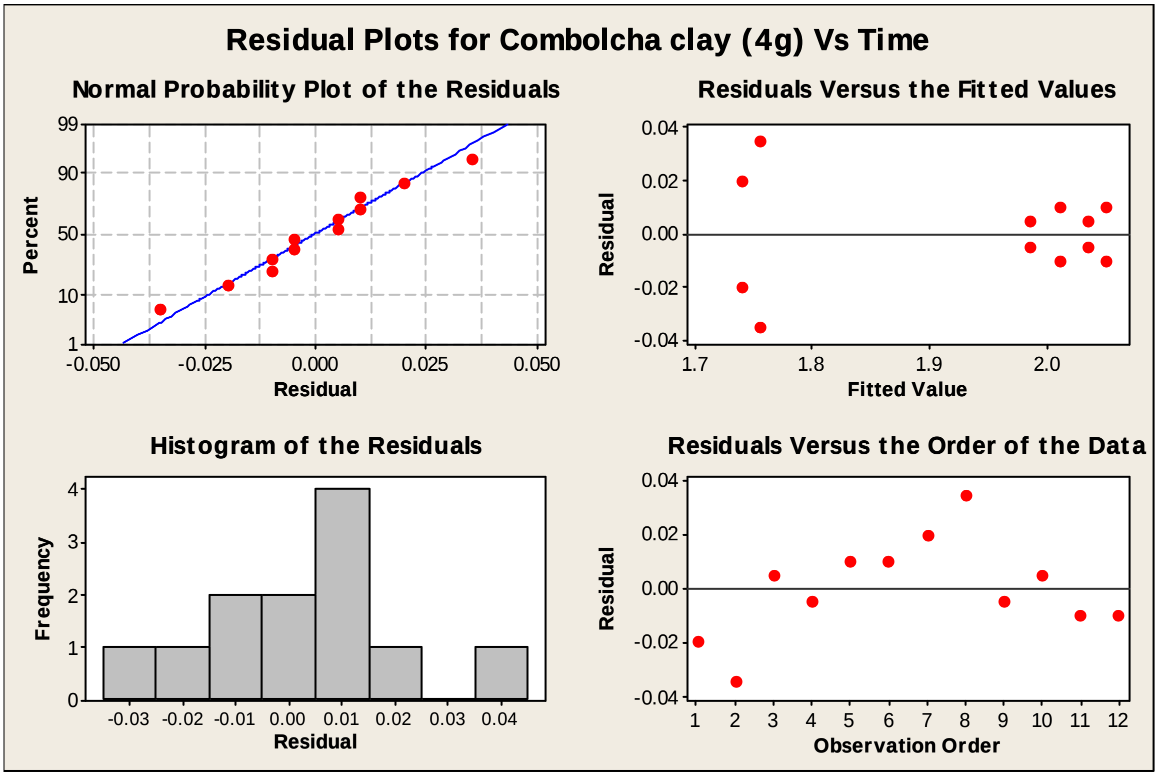


Fig. 19 e ANOVA analysis result and Residual plot for the experiment 3.4.3.

One-way ANOVA: Muger clay2 (2g) versus Time

```
Source  DF        SS        MS      F       P
Time     5  0.163800  0.032760  93.60  <0.001
Error    6  0.002100  0.000350
Total   11  0.165900

S = 0.01871   R-Sq = 98.73%   R-Sq(adj) = 97.68%


                                  Individual 95% CIs For Mean Based on
                                  Pooled StDev
Level  N    Mean   StDev  ----+---------+---------+---------+-----
1      2  3.0100  0.0141              (--*--)
2      2  2.8600  0.0141  (-*--)
3      2  3.1700  0.0283                           (--*--)
4      2  3.1450  0.0212                         (--*--)
5      2  3.2000  0.0000                              (--*-)
6      2  3.1250  0.0212                        (-*--)
                          ----+---------+---------+---------+-----
                            2.88      3.00      3.12      3.24

Pooled StDev = 0.0187
```

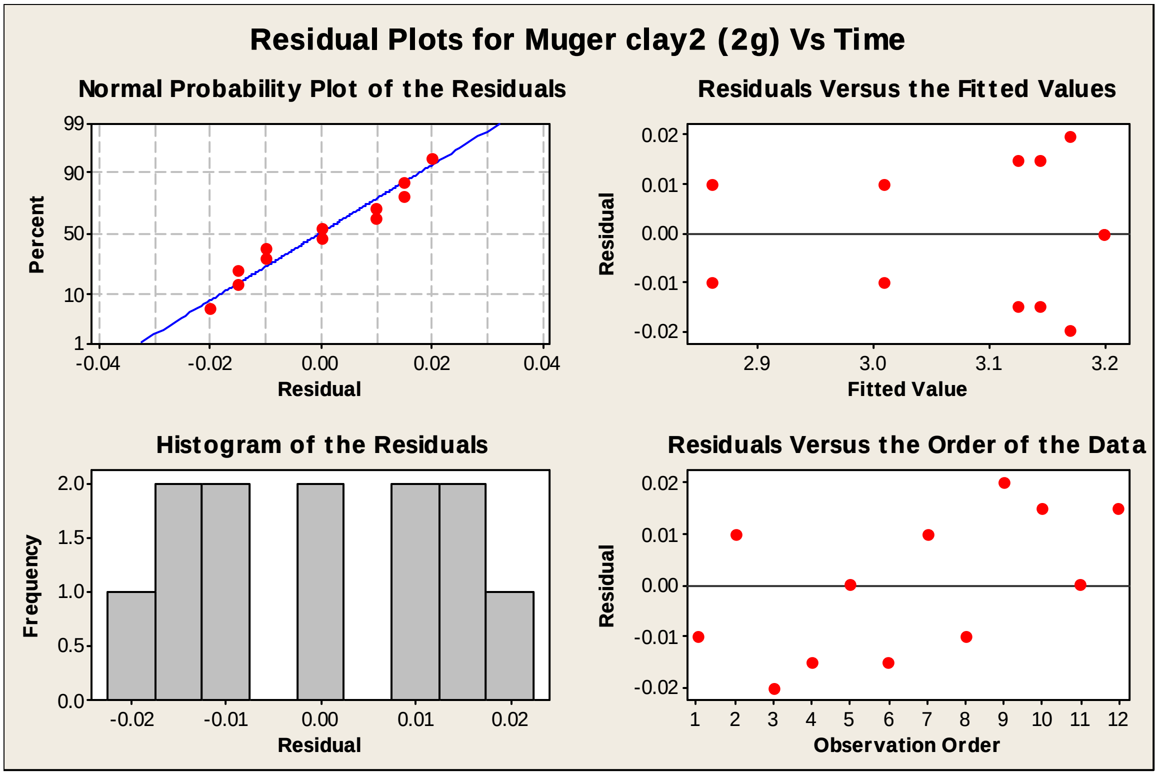


Fig. 19 f ANOVA analysis result and Residual plot for the experiment 3.4.3.

One-way ANOVA: Muger clay2 (4g) versus Time

```
Source  DF        SS        MS       F      P
Time     5  0.211175  0.042235  241.34  <0.001
Error    6  0.001050  0.000175
Total   11  0.212225

S = 0.01323   R-Sq = 99.51%   R-Sq(adj) = 99.09%


                          Individual 95% CIs For Mean Based on
                          Pooled StDev
Level  N    Mean   StDev  --+---------+---------+---------+-------
1      2  1.7000  0.0141  (-*-)
2      2  1.7150  0.0212   (-*--)
3      2  1.9000  0.0000                    (-*-)
4      2  1.9900  0.0141                             (-*-)
5      2  2.0100  0.0141                               (-*-)
6      2  2.0100  0.0000                               (-*-)
                          --+---------+---------+---------+-------
                          1.70      1.80      1.90      2.00

Pooled StDev = 0.0132
```

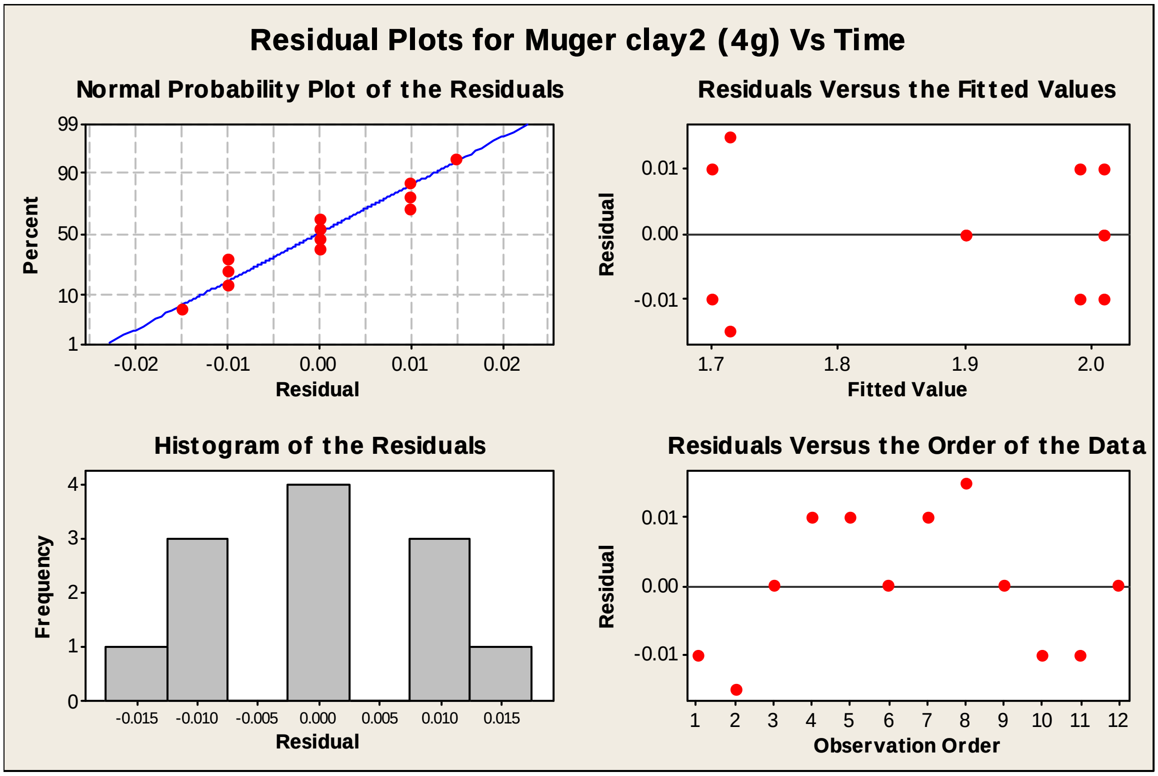


Fig. 20 a ANOVA analysis result and Residual plot for the experiment 3.4.7.

One-way ANOVA: Bombawoha clay versus initial fluoride conc.

```
Source  DF        SS       MS         F      P
Co       4  37.50644  9.37661  26600.31  <0.001
Error    5   0.00176  0.00035
Total    9  37.50820

S = 0.01877   R-Sq = 100.00%   R-Sq(adj) = 99.99%


                          Individual 95% CIs For Mean Based on
                          Pooled StDev
Level  N    Mean   StDev    +---------+---------+---------+---------
 5.80  2  1.4825  0.0035    *
10.10  2  2.9550  0.0212             (*
15.05  2  4.3450  0.0212                       *
20.02  2  5.6600  0.0283                                *
25.12  2  6.9750  0.0071                                        (*
                            +---------+---------+---------+---------
                          1.5       3.0       4.5       6.0

Pooled StDev = 0.0188
```

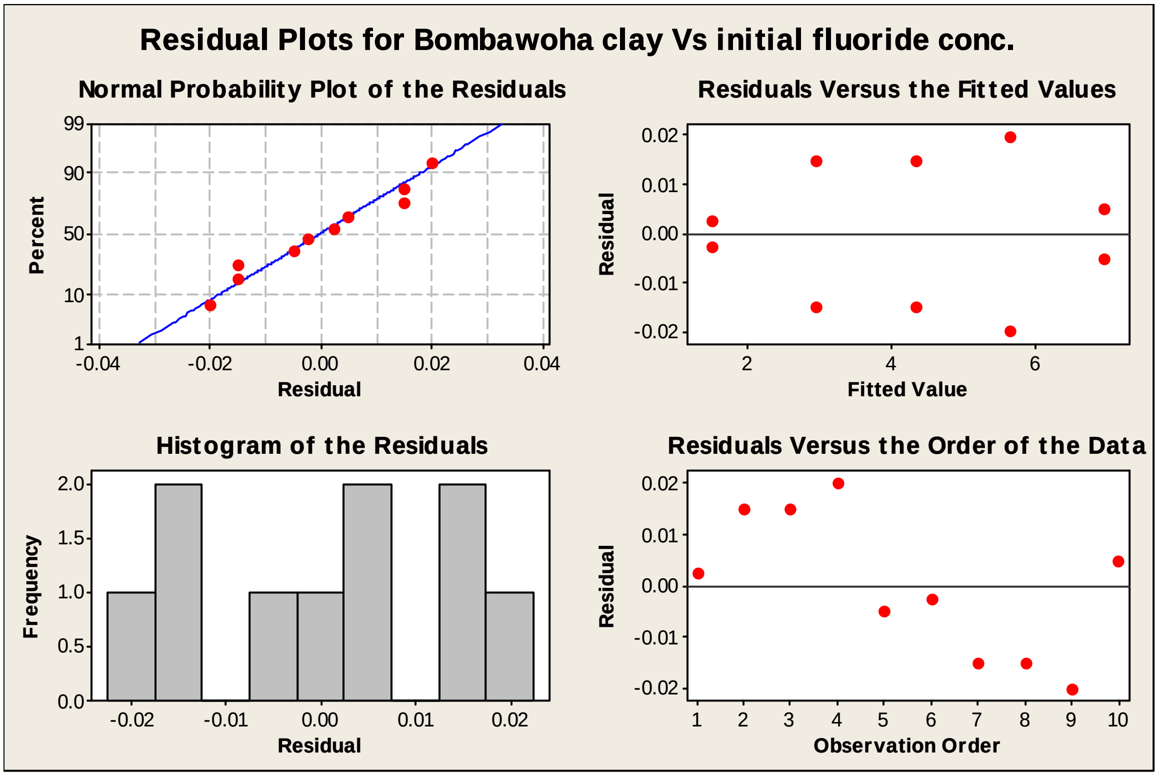


Fig. 20 b ANOVA analysis result and Residual plot for the experiment 3.4.7.

One-way ANOVA: Combolcha clay versus initial fluoride conc.

```
Source  DF        SS       MS         F       P
Co       4  122.7825  30.6956  46333.02  <0.001
Error    5    0.0033   0.0007
Total    9  122.7858

S = 0.02574   R-Sq = 100.00%   R-Sq(adj) = 100.00%


                           Individual 95% CIs For Mean Based on
                           Pooled StDev
Level  N      Mean   StDev  ---------+---------+---------+---------+
 5.80  2   2.6925  0.0035  *
10.10  2   3.6600  0.0424     (*
15.05  2   5.7550  0.0354            *
20.02  2   9.7400  0.0141                            *
25.12  2  11.7950  0.0071                                    *
                           ---------+---------+---------+---------+
                                  5.0       7.5      10.0      12.5

Pooled StDev = 0.0257
```

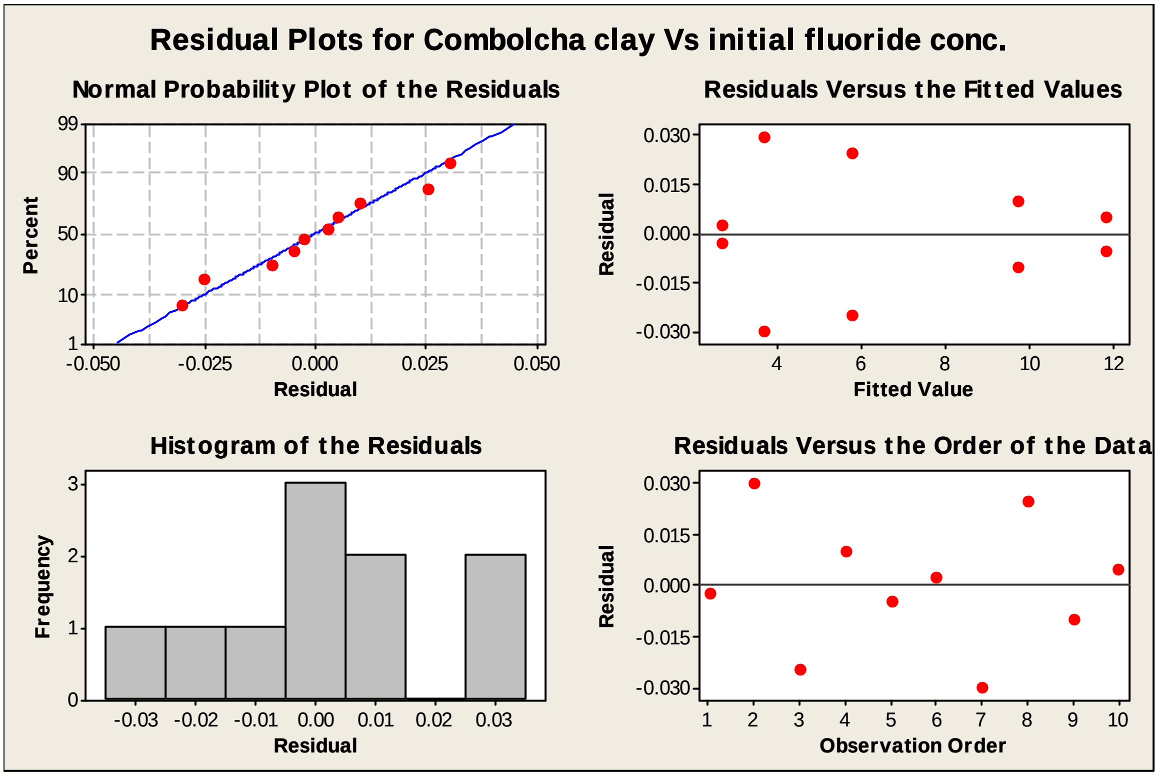


Fig. 20 c ANOVA analysis result and Residual plot for the experiment 3.4.7.

One-way ANOVA: Muger clay2 versus initial fluoride conc.

```
Source  DF        SS       MS         F      P
Co       4  33.14634  8.28659  21247.65  <0.001
Error    5   0.00195  0.00039
Total    9  33.14829

S = 0.01975   R-Sq =  99.99%   R-Sq(adj) = 99.99%


                          Individual 95% CIs For Mean Based on
                          Pooled StDev
Level  N    Mean   StDev   -+---------+---------+---------+--------
 5.80  2  1.4050  0.0212   *)
10.10  2  2.8300  0.0283             *
15.05  2  4.1600  0.0141                     (*
20.02  2  5.3150  0.0071                             *)
25.12  2  6.5950  0.0212                                      *
                           -+---------+---------+---------+--------
                          1.5       3.0       4.5       6.0

Pooled StDev = 0.0197
```

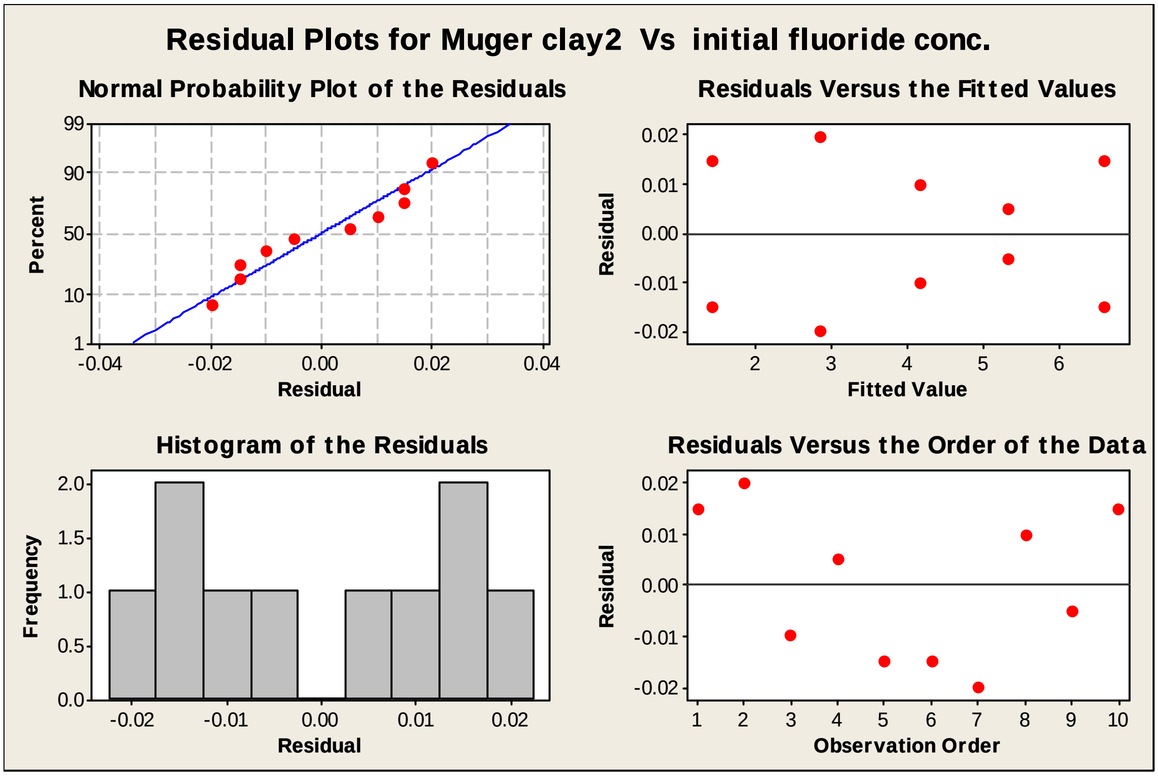


Fig. 21 a ANOVA analysis result and Residual plot for the experiment 3.4.6.

One-way ANOVA: Bombawoha clay (4g untreated) versus particle size

```
Source  DF       SS       MS       F      P
Size     3  58.9869  19.6623  240.89  <0.001
Error    4   0.3265   0.0816
Total    7  59.3134

S = 0.2857   R-Sq = 99.45%   R-Sq(adj) = 99.04%


                              Individual 95% CIs For Mean Based on
                              Pooled StDev
Level       N   Mean  StDev  -------+---------+---------+---------+--
(<0.5)      2  44.745  0.120       (-*-)
(0.5-1.0)   2  46.120  0.127            (-*--)
(1-1.25)    2  50.860  0.240                               (-*--)
(>1.25)     2  43.795  0.488   (-*-)
                              -------+---------+---------+---------+--
                                  45.0      47.5      50.0      52.5

Pooled StDev = 0.286
```

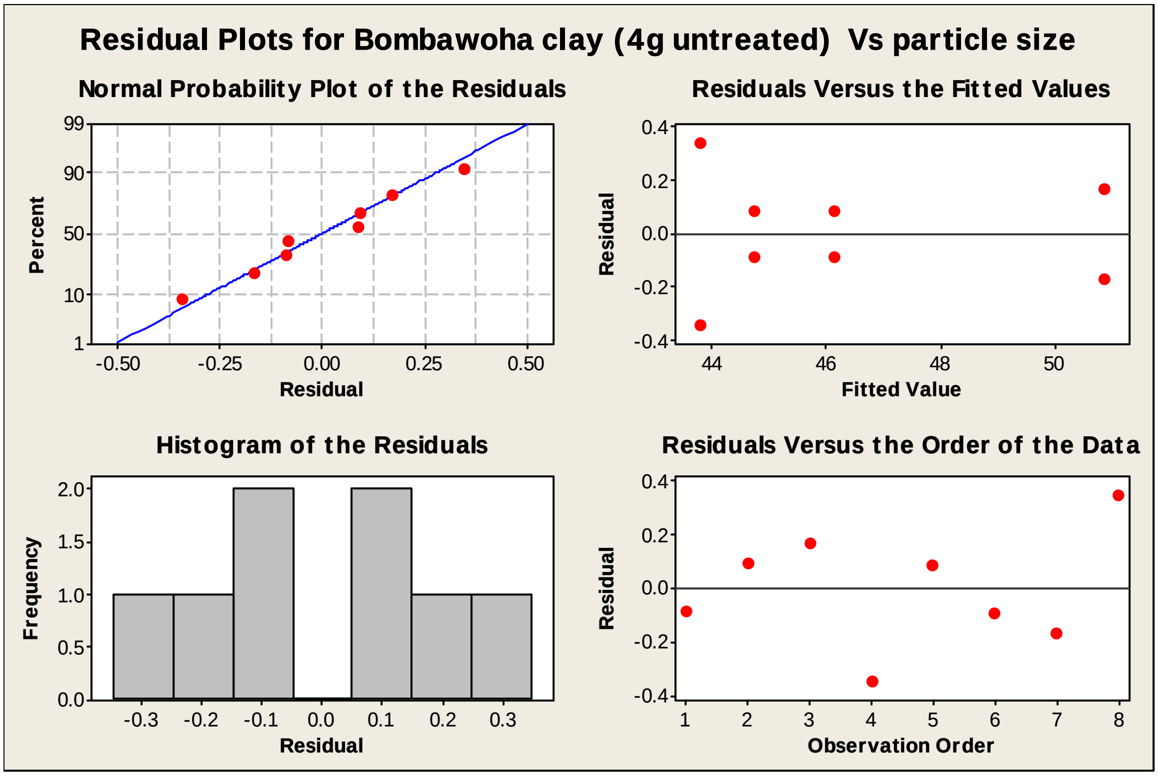


Fig. 21 b ANOVA analysis result and Residual plot for the experiment 3.4.6.

One-way ANOVA: Bombawoha clay (4g heated) versus particle size

```
Source   DF       SS      MS        F      P
Size     3  397.503  132.501  1239.48  <0.001
Error    4    0.428    0.107
Total    7  397.930

S = 0.3270   R-Sq = 99.89%   R-Sq(adj) = 99.81%


                              Individual 95% CIs For Mean Based on
                              Pooled StDev
Level      N    Mean  StDev  -----+---------+---------+---------+----
(<0.5)     2  45.520  0.000    (*)
(0.5-1.0)  2  54.830  0.240                  (*)
(1-1.25)   2  65.430  0.608                                    (*)
(>1.25)    2  54.660  0.000                  (*)
                              -----+---------+---------+---------+----
                                48.0      54.0      60.0      66.0

Pooled StDev = 0.327
```

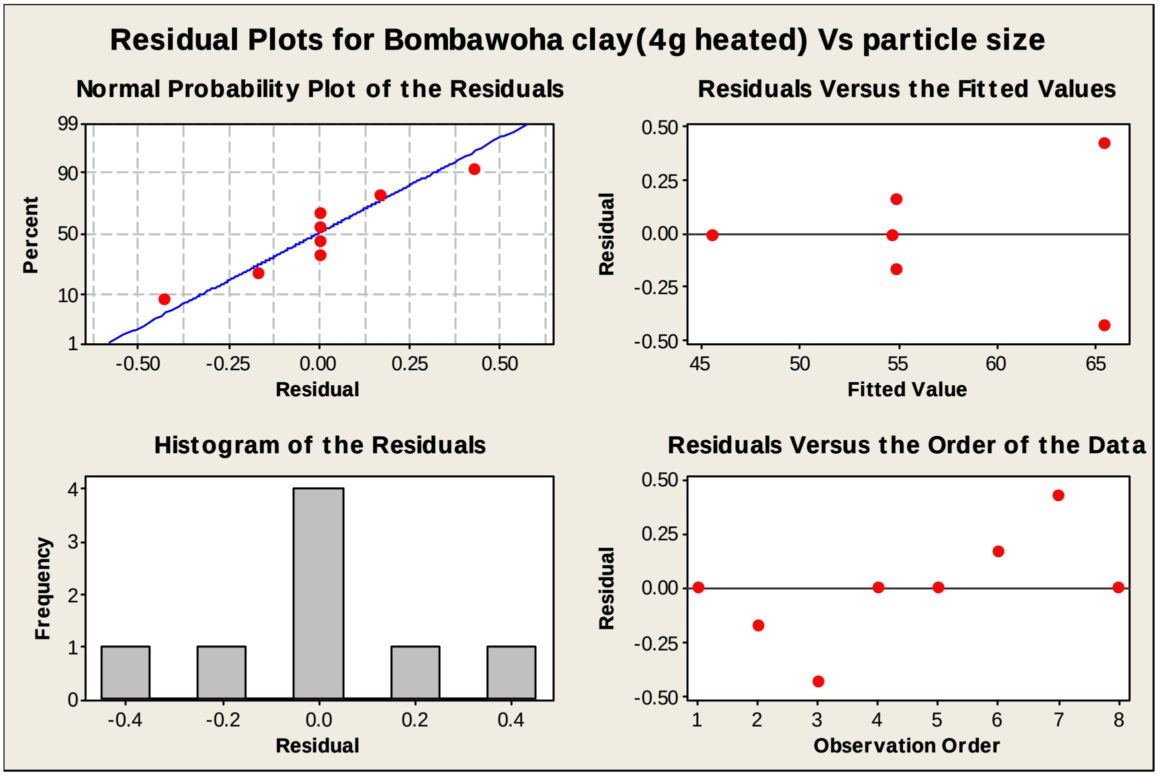


Fig. 21 c ANOVA analysis result and Residual plot for the experiment 3.4.6.

One-way ANOVA: Combolcha clay(4g untreated) versus particle size

```
Source  DF       SS       MS       F      P
Size     3  32.3097  10.7699  198.75  <0.001
Error    4   0.2168   0.0542
Total    7  32.5265

S = 0.2328   R-Sq = 99.33%   R-Sq(adj) = 98.83%


                              Individual 95% CIs For Mean Based on
                              Pooled StDev
Level      N    Mean   StDev  ---------+---------+---------+---------+
(<0.5)     2  70.000   0.240                                  (--*--)
(0.5-1.0)  2  66.465   0.361            (--*--)
(1-1.25)   2  65.085   0.120   (--*--)
(>1.25)    2  65.085   0.120   (--*--)
                               ---------+---------+---------+---------+
                                     66.0      67.5      69.0      70.5

Pooled StDev = 0.233
```

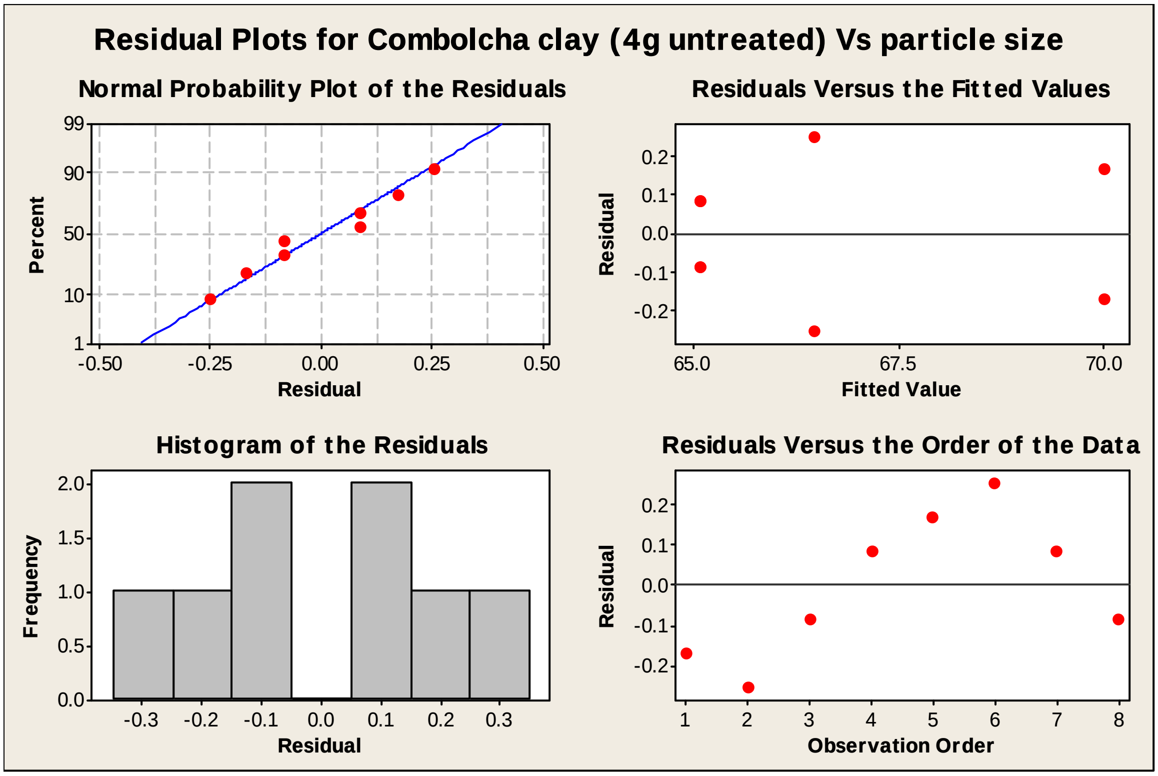


Fig. 21 d ANOVA analysis result and Residual plot for the experiment 3.4.6.

One-way ANOVA: Combolcha clay (4g heated) versus particle size

```
Source  DF        SS        MS         F      P
Size     3  476.2426  158.7475  41638.70  <0.001
Error    4    0.0152    0.0038
Total    7  476.2579

S = 0.06175   R-Sq = 100.00%   R-Sq(adj) =  99.99%


                                Individual 95% CIs For Mean Based on
                                Pooled StDev
Level        N    Mean   StDev  ---+---------+---------+---------+------
(<0.5)       2  92.8800  0.0283                                        *
(0.5-1.0)    2  88.9300  0.0000                                *
(1-1.25)     2  78.3650  0.1202           (*
(>1.25)      2  73.7900  0.0000  (*
                                 ---+---------+---------+---------+------
                                 75.0      80.0      85.0      90.0

Pooled StDev = 0.0617
```

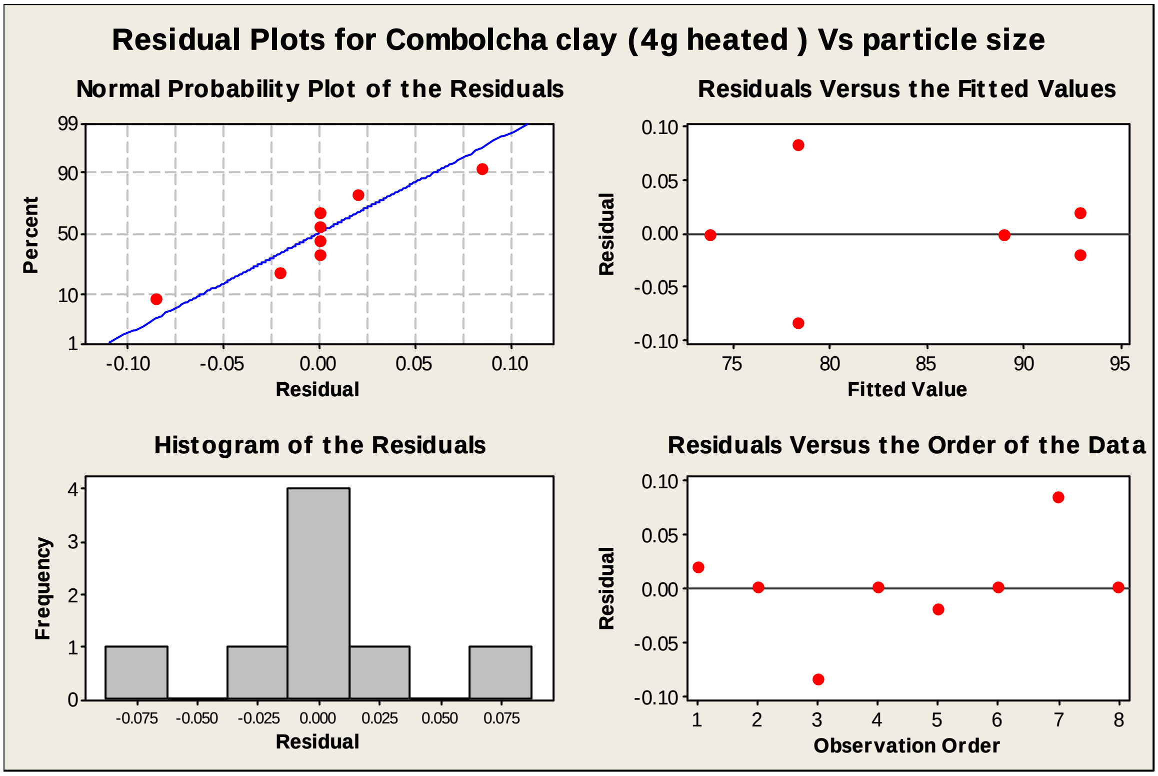


Fig. 21 e ANOVA analysis result and Residual plot for the experiment 3.4.6.

One-way ANOVA: Muger clay2 (4g untreated) versus particle size

```
Source  DF       SS      MS       F       P
Size     3  29.8473  9.9491  208.03  <0.001
Error    4   0.1913  0.0478
Total    7  30.0386

S = 0.2187   R-Sq = 99.36%   R-Sq(adj) = 98.89%


                              Individual 95% CIs For Mean Based on
                              Pooled StDev
Level       N   Mean  StDev  -+---------+---------+---------+--------
(<0.5)      2  44.140  0.240                                     (--*--)
(0.5-1.0)   2  41.380  0.240                   (--*--)
(1-1.25)    2  39.655  0.247        (-*--)
(>1.25)     2  39.225  0.120     (--*-)
                                -+---------+---------+---------+--------
                              39.0      40.5      42.0      43.5

Pooled StDev = 0.219
```

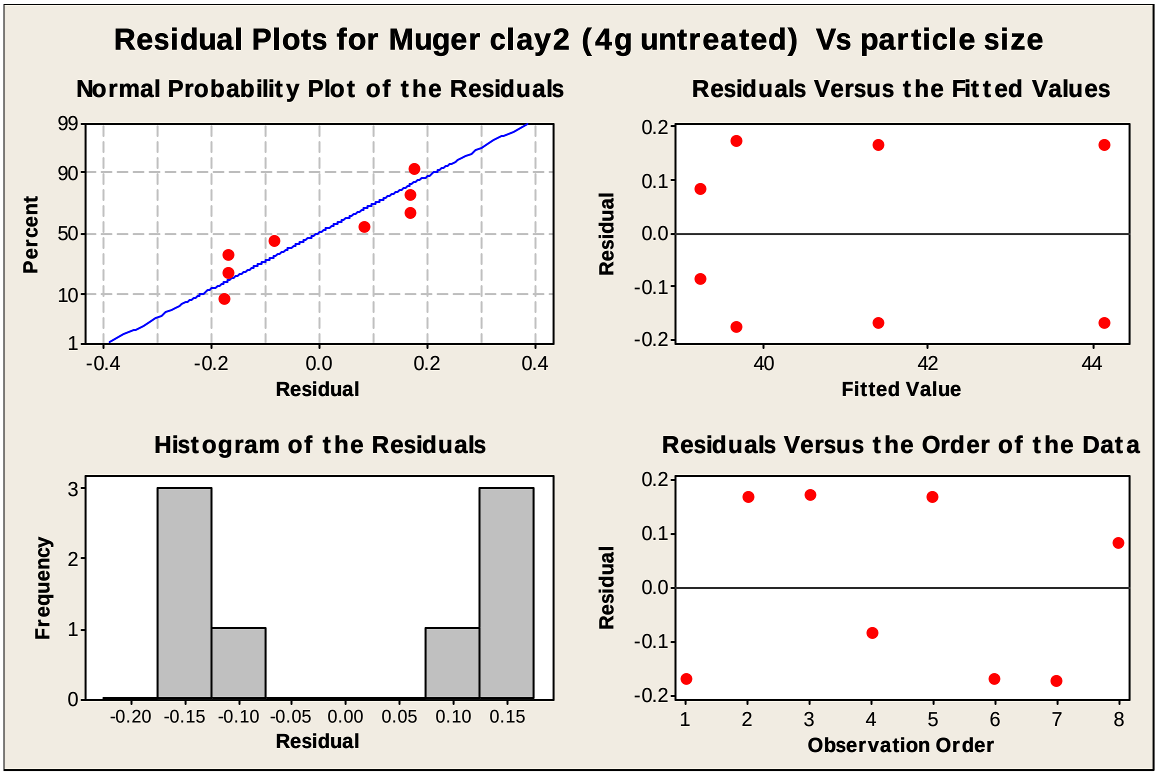


Fig. 21 f ANOVA analysis result and Residual plot for the experiment 3.4.6.

One-way ANOVA: Muger clay2 (4g heated) versus particle size

```
Source  DF        SS        MS        F       P
Size     3  723.2595  241.0865  7223.57  <0.001
Error    4    0.1335    0.0334
Total    7  723.3930

S = 0.1827   R-Sq = 99.98%   R-Sq(adj) = 99.97%


                              Individual 95% CIs For Mean Based on
                              Pooled StDev
Level       N    Mean   StDev   -+---------+---------+---------+--------
(<0.5)      2  66.295  0.120                                    (*
(0.5-1.0)   2  61.380  0.240                             (*
(1-1.25)    2  50.860  0.000                (*
(>1.25)     2  41.725  0.247     (*
                                 -+---------+---------+---------+--------
                              42.0      49.0      56.0      63.0

Pooled StDev = 0.183
```