

SILVER / ZEOLITE NANO COMPOSITE-BASED CLAY FILTERS FOR WATER DISINFECTION

Report to the
Water Research Commission

by

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EXECUTIVE SUMMARY

Safe water is essential to human health and the development of a country. In developing countries, eruptions of water-borne diseases such as cholera and typhoid fever are still out of control. In South Africa, between November 2008 to January 2009, 5341 patients were diagnosed and treated for cholera and 34 people died as a result of the disease. Rural communities are the most affected by these water-borne disease eruptions because of the lack of affordable and easy techniques to disinfect water from open water sources prior to human consumption. Clay filter pots have been employed to ameliorate the water quality in rural areas; several attempts have been made in order to improve the quality of these ceramic pots. Colloidal silver (used as a powerful disinfectant) is brush coated onto the Potters for Peace (PFP) pot, which leaches out over a period of time. Von Naegeli and others in 1893 discovered that the antibacterial activities of silver were due to the Ag^+ . A small amount of Ag^+ is released from the metallic surface when placed in contact with liquids. The result of the ongoing research will help to ameliorate the PFP pot model with the innovative use of the zeolites as an adsorbing platform for silver nanoparticles as a source of Ag^+ as disinfectant.

In this study, natural zeolite clinoptilolite Hard and Soft samples (HEC and SEC respectively) from the Ecca Holdings mine were pre-treated using 1 M HCl for four cycles under stirring condition, for 2 hours each cycle. This was to remove exchangeable cations as well as elements such as Ba, Sr and traces of many other toxic elements present in the as-received natural mineral samples, and reduce the competitive adsorption during the silver loading process. Acid pre-treatment effectively removed Na^+ and Mg^{2+} cations from the matrix of the natural zeolite but did not remove K^+ or Ca^{2+} from the exchange sites under the conditions applied. A calculated mass of silver to be loaded onto each zeolite sample (both acid treated and untreated) by the ion exchange procedure was varied to attain 3 different loadings of silver ions. NaBH_4 was then added as reductant to reach an $\text{AgNO}_3/\text{NaBH}_4$ ratio of 1:4. The ion exchange procedure was found to be problematic in terms of obtaining a specified metal loading and silver loadings varied from below 1 to above 14 mass %. However, in general, the silver content was higher in the acid pre-treated zeolites (HECT and SECT) than in the untreated zeolites (HEC and SEC). The Hard Ecca Clinoptilolite acid treated (HECT) sample which contained a higher percentage of clinoptilolite generally presented the highest results in term of the amount of silver that could be loaded under the applied conditions. Leaching of the silver from the zeolite samples (untreated and acid pre-treated clinoptilolite) was found to be inconsistent but in all cases was lower than $0.2 \mu\text{g/mL}$. The amount of silver available for inhibition of microbes in the zeolite samples prepared by ion exchange or their leachates was too low to kill the bacteria.

Because of the low loadings of silver obtained using the ion exchange procedure, the wet impregnation procedure was employed to load a greater amount of the Ag metal nanoparticles on the zeolite. The concentrations of silver ions applied to the acid pre-treated HEC clinoptilolite were 53.935; 539.35; 5393.5 and 10787 $\mu\text{g/mL}$ respectively. Impregnated silver ions were reduced on the acid treated natural clinoptilolite by four different reducing agents (ascorbic acid, formaldehyde, hydrazine monohydrate or sodium borohydride respectively). The percentage of silver leached out from wet impregnated samples was much greater in the non-reduced Ag/c clinoptilolite, of which up to 5.2% was observed to leach depending on the starting silver loading used, compared to that of the reduced Ag/c clinoptilolite samples where less than 1% of the loaded silver leached out per leaching run. The antibacterial effect of the silver nanoparticles depends on size; the smaller the silver nanoparticles are, the more easily they reach

the nuclear content of bacteria and bind with the bacterial DNA and the reducing agent should have a weak or a middle reduction power to obtain mono-dispersed, non-agglomerated silver nanoparticles. An equivalent antimicrobial activity was observed for the non-reduced sample as was observed in the case of the ascorbic acid reduced sample, hence the leaching was minimized by reduction of the silver salt to metal with ascorbic acid as reductant, yet still maintaining an equivalent antimicrobial property. The Ag/clinoptilolite nano composites reduced with formaldehyde, hydrazine monohydrate and sodium borohydride presented only a small inhibitory effect under the tested conditions even at high silver concentrations. Only the aqueous leachates of the non-reduced Ag/clinoptilolite presented an antibacterial effect, and this was in relation to the concentration of silver leached out into the water. The aqueous leachates of the reduced Ag/clinoptilolite did not present an antibacterial effect or presented only a slight antibacterial effect because the reduced silver did not leach into the water. This indicated that there was not a silver residual in the water after contact with the silver loaded zeolite which is positive in terms of minimal ingestion of silver by the water users and release to the environment.

The amount of clinoptilolite that can be loaded into the filter pot body during pot manufacture before it becomes weak was investigated. The ceramic filter pot was composed of the hard Ecce Holding clinoptilolite (EHC), white clay, red clay, bentonite and the milled grape residue. The combined bodies made with different percentage of clinoptilolite (20% and 50%) were fired at 900°C. The flow rate of the combined bodies when fired at 900°C with 20% of clinoptilolite was greater than that of the combined bodies containing 50% of clinoptilolite. This was ascribed to the degree of vitrification and should be further investigated at lower firing temperatures. The results of this study highlighted that Ecce Holding clinoptilolite can be loaded into the filter pot up to 50% before the pot becomes weak. The addition of the milled grape residue could correct the loss of porosity.

In summary, this research showed that natural, acid treated zeolites could indeed retard the excessive leaching of silver into solution whilst still giving an antimicrobial effect, when using wet impregnation as silver loading technique and reduction of silver salts using ascorbic acid. High loadings of silver could be supported stably on the zeolite. The treated water had a level of residual silver well below the WHO target thus would be safe for ingestion. The study also showed that clay pots could have zeolite incorporated to 50% without losing strength and porosity and thus flow could be tailored using milled grape residues. However the research still has some points, such as different ways to produce non-agglomerated silver nanoparticles upon the zeolites and the influence of the pot firing temperature on the silver/clinoptilolite nano composite characteristics, that need to be clarified; and further studies are necessary to investigate the optimum conditions under which the silver/zeolite loaded ceramic filter pot can be made and its longer term antibacterial efficiency, toxicity and ecological impact should be tested.

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LIST OF ABBREVIATIONS

AgNP	Silver nanoparticle
Asc. Ac.	Ascorbic acid
CFU	Colony Forming Unit
DNA	Deoxyribonucleic acid
EDS	Energy-Dispersive X-ray Spectroscopy
EHC	Ecce Holding Clinoptilolite
FTIR	Fourier Transform Infrared Spectroscopy
HEC	Hard Ecce Clinoptilolite
HECT	Acid treated Hard Ecce Clinoptilolite
ICP	Inductively Coupled Plasma
IZA	International Zeolite Association
LOI	Loss on ignition
MS	Mass Spectrometry
NTU	Nephelometric Turbidity Unit
PFP	Potters for Peace
POU	Point of Use
RPM	Revolution per Minute
SEC	Soft Ecce Clinoptilolite
SECT	Acid treated Soft Ecce Clinoptilolite
SEM	Scanning Electron Microscopy
SIPP	Silver Impregnated Porous Pot
SME	Small and Medium Enterprise
STEM	Scanning Transmission Electron Microscopy
UNICEF	United National Children's Fund
US EPA	United State Environmental Protection Agency
UWC	University of the Western Cape
WHO	World Health Organization
WRC	Water Research Commission
XRD	X-ray Powder Diffraction
XRF	X-ray Powder Fluorescence

INTRODUCTION

Access to clean drinking water constitutes a serious human health issue in developing countries. According to the World Health Organization (WHO), approximately one-sixth of the world population do not enjoy safe and clean water especially in the rural areas. Within the African continent, about 400 million inhabitants do not have access to safe drinking water. The rural areas account for a high percentage of water related infections with cases of water-borne diseases such as cholera and typhoid fever being on the increase. In most cases, the prevalence of these diseases is due to the anthropogenic activities such as pollution via release of toxic waste chemicals by mining industries without responsible waste treatment technique before discharge into open water source. Other factors include lack of affordable and easy techniques to disinfect water from open water sources prior to human consumption (WHO, 2008). In general, government interventions continue to suffer setbacks due to lack of 'political will' such as failed policies and corruption, lack of provision or maintenance of critical infrastructure and government insensitivity to creating an enabling environment in addressing the challenges for the provision of safe drinking water.

In addressing water quality problem, the use of local materials such as traditional filters has been employed. These filters are made by mixing the clay materials and some combustible organic compounds (Halem, 2006). Several attempts have been made in order to improve the quality of those ceramic water filters. Colloidal silver (used as a powerful disinfectant) is brush coated onto the Potters for Peace (PFP) pot, which leaches out over a period of time. It is envisaged that the use of the zeolites as an adsorbing platform and silver nanoparticles as a disinfectant can effectively contribute to ameliorate the deficiency of the PFP pot model. The preference of zeolites is because of their physico-chemical properties such as ion exchange capacity and the presence of pores and channels in their framework giving them the aptitude to serve as molecular sieves (Shameli et al., 2011; Davies and Etris, 1997).

The University of the Western Cape (UWC) has acquired limited funding from the Water Research Commission (WRC) to conduct research into developing silver loaded zeolites for application in a ceramic water filter based on the PFP models. The industry partners Red Seal trading as Nano Natura, ECCA Holdings, with UWC, the private sector and water purification specialists wish to conduct meaningful and applied research into filtration media to ascertain the effectiveness of utilizing natural low-tech filters to purify our scarce water resources. The PFP model has a proven track record. However the technology can be improved upon and its applications extended through the innovative use of zeolites and utilizing effective microorganisms in filtering grey, black effluent and brack water. Colloidal silver can potentially be incorporated into the filtration medium for slow release by loading it on to the zeolite mineral. The purpose of the project is to manufacture a natural, low technology, rural water filter based on the PFP model with adaptations to improve its effectiveness and to market it to rural households for top quality water filtration. The filtration technology that is being proposed can be adapted for the purification of potable, grey, brack and black water and may also be an effective medium to filter out contaminated water from agriculture and industrial waste. This system is appropriate for low or intermittent volume applications as in household use. The proposed system is unique and innovative in its ability to naturally filter (the mediums have nano size particles where 1 gram of the material has a surface area of at least 50 m²) and provides an extremely large surface area for effective disinfection of microorganisms and other pathogenic species. The incorporation of zeolite

into the clay mix will also play a further role in water purification through its ion exchange capacity to absorb ammonias, salts and heavy metals from effluent.

It has been shown in an associated WRC project that the natural zeolite clinoptilolite is effective in ammonia removal from waste water (WRC Project No. K5/1897). This current study will focus on the disinfection of water from biological contaminants using ceramic pot filters loaded with a silver/zeolite nano composite. The deliverable of this research could provide a cheap and effective way to render rural water sources safe for human consumption and limit the use of chemical disinfectants in the water treatment processes. This research is targeted at home and/or group use (houses have collective tanks) in trickle filters for potable, grey and black water applications.

PROBLEM STATEMENT

In the past, water filtration technology has been driven by chemical and highly capital intensive approaches. Reverse osmosis is a highly effective system but is energy and maintenance intensive and requires vast capital outlays. Reverse osmosis plants accumulate waste (+30 %) because the systems can only filter part of the water or effluent to be treated. The chemical approach requires a level of expertise and under resourced municipalities do not manage the process correctly. The potable water is mainly monitored for *Escherichia coli* counts. Harmful deflocculants are also used that may be detrimental to health.

Clean water is not the same as safe water hence rural communities in Africa use ceramic pot filters made with local clay material fired at high temperature. These ceramic pots serve a dual purpose of storage and coolant. Unfortunately, only a few reported cases of bacterial activity of these pots have been established with efficiency rate between 82 and 99 % (Halem, 2006). In as much as this is a good bacterial removal efficiency, water is safe only if it has no microorganisms. Hence new filters with silver coating have been found to be efficient for disinfection of water with a removal efficiency of *E. coli* of between 99 and 100%. For instance, colloidal silver (used as a powerful disinfectant) is brush coated onto the PFP pots. However, the colloidal silver leaches out into the water inconsistently and after using those filter pots repeatedly, is depleted; decreasing the efficiency of the filter (Lantagne, 2001). Silver could become a potential health risk to humans if its concentration in water is above 44 µg/mL (Panyala et al., 2008). PFP have targeted their product to individual households. This approach has many merits, mainly with maintenance, responsibility and sustainability. An owner will look after and maintain a unit more effectively than a communal one.

This study focused on an effective way to disinfect water using zeolites as silver carriers to improve and stabilize the bacterial removal efficiency of pot filters. Silver is generally known as a disinfectant in water treatment, also incorporated into ceramic pots (Momba *et al.*, 2010), and methods involving silver modified zeolites have earlier been suggested as a possible water disinfectant (Milán *et al.*, 2001; Inoue *et al.*, 2002). Therefore, this research focused on the use of silver nano particles in the disinfection of water in ceramic/zeolite pot filters. This investigation studied the following aspects:

1. The silver nanoparticles will be loaded by cation exchange and wet impregnation onto natural zeolite clinoptilolite.
2. The silver/zeolite nano composite will be mixed with clays that are used to make ceramic filters.

3. The mixture will be used to make ceramic filters with silver/zeolite nano composite and the disinfection properties of the resultant filter will be assessed at different flow rates.

OBJECTIVES

The silver/zeolite nano composite will be mixed with clay minerals to produce ceramic water filters. Therefore, the objectives of this project are:

- To increase the efficiency of the silver disinfection by use of nano silver. Nano silver possesses a high surface area, resulting in an improved disinfection
- To reduce the loss of silver from ceramic water filters since silver will be encapsulated in the zeolite framework. This will ensure improved sustainability of the filter
- To reduce the fouling of the filters by biofilm accumulation. The ceramic filters from Potters of Peace containing silver have shown to be affected by fouling because of leaching of silver, thereby allowing accumulation of biofilm.

The overarching aim of the research is that:

- Filters should be 'low tech' and be incrementally increased to address the volume and filtration requirements of each application.
- Filters should also be able to be maintained in rural environments with locally available resources.
- The filters should be affordable.
- The filters should add environmental value in the filtration process.
- The filters should be locally made as part of job creation programmes.

The focal point of this research is the use of silver nanoparticles in the disinfection of water in the ceramic pots filters. This will be achieved by:

- Incorporating silver ions into the zeolites by cation exchange or wet impregnation,
- Investigating the concentration of silver leached out into the water,
- Investigating the efficiency of silver antimicrobial activity in water,
- Investigating the quantity of zeolites that can be put into the pot before it becomes structurally weak.

Low volume filtration methods should also be researched, including: Physical filtration, microorganism filtration and the incorporation of zeolite into the filtration media mix to ascertain its ability to exchange ions (heavy metals exchange) and absorb ammonias and salts.

Impacts of the study

Society

This research will potentially guarantee access to potable waters in the rural areas. It will also provide jobs in several sectors including water purification, environmental industrial management, etc. Viable, technology advanced materials and processes that will be developed, may contribute significantly to the growth and competitiveness of potable water industry. The research will augment industrial sector achievements and productivity, leading to the creation of jobs and clean waters.

Economy

The research will vigorously stimulate interaction with local and international industry with regard to understanding industrial technological solutions to societal needs and requirements. The research thrust is thoroughly grounded, and provides function for development of novel methods, applications and products.

Health

Human health is considered one of the most pressing problems of the 21st century. This research will hopefully provide solutions to endemic microorganisms in the water and also remove trace metals depending on the percentage loading of zeolites and thus guarantee the supply of safe water for human consumption.

Environment

The major environmental concern associated with the use of clay filters is the possibility of arsenic leaching into the filtrate. This problem has been reported in clay filters from Cambodia but clay filters produced in Nicaragua and Ghana did not have such problem (Halem, 2006) and hopefully will not pose a problem in South Africa. Thus adequate screening for arsenic in additives for clay filters production will be given top priority. The materials are recyclable so disposal is environmentally friendly when the pot is no longer usable.

Industry partner profile, size, history, services and products

Ecca Holdings mines Bentonite and has established markets for the mineral. In the mining process Zeolite is removed as overburden that is currently being stockpiled; the current markets of Zeolite have been relatively stagnant.

Red Seal design studio has been operating for the past fifteen years in the Western Cape and is a design and product development organisation specialising in the establishment of markets and the creation of small and medium enterprises. It currently manufactures planters that contain Bentonite and Zeolite. Experience has been acquired in SME development when working in government parastatals for 10 years. Red Seal Design Studio, the industry partner situated in Barrydale (Western Cape), has established products for markets that are outsourced to independent community based producer groups for manufacture. Nano Natura has been established for two years and is dedicated to developing appropriate Nano technology in rural water filtration, packaging and effluent control. Red Seal has established a joint venture between the local mine ECCA Holdings, UWC Chemistry department to develop ranges of eco-friendly products under this empowering business model. This entity has been established as a collaborative effort between the local Western Cape zeolite mine (ECCA holdings), the University of the Western Cape and Nano Natura to utilize natural zeolites incorporated into ceramics and cellulose waste to manufacture products for job creation purposes. Zeolites are natural absorbents and micro filters and can be utilized in many applications. The products are manufactured by an independent community producer group who manufacture the products under licence agreements to Red Seal Design. Training of the producer group in management and manufacture is currently underway.

The choice of the materials used for the manufacture of silver/zeolite loaded clay filter pots was motivated by the fact that they are cost effective and locally available. Bentonite and natural

clinoptilolite come from Eccca Holdings Company. The milled grape residues come from local farms. These materials are well known and are used to make other type of pots such as plant pots.

Natural Zeolites are a by-product of the ECCCA Holdings mine and are incorporated into ceramics and cellulose waste to manufacture products for job creation purposes. Current projects underway are the development of a rural water filter based on an international business model that has been in existence for many years. It has become apparent that this technology can be applied to other areas to create both jobs and conserve the environment. Market surveys reveal that this technology can be applied to filtration and in fruit packaging as an absorbent to prevent fruit from degrading prematurely. This packaging contributes to the environment by adding conservation value to waste dump sites as well. Compostable and ceramic pots are currently being supplied by Red Seal to the horticultural industries and the main clients are Woolworths. Currently 6 people are employed in the project. New technology in air filtration and packaging has the potential to create a conservative estimate of 50 jobs in each project in year two and three. If exports can be arranged then these figures may double.

Increased energy and fuel costs have created an environment where transportation costs often exceed the value of the commodity, making it sometimes unviable. This is the case for zeolite and associated minerals when marketed in their raw form. For example the costs of transporting zeolite to Gauteng exceed R400 per ton. The answer lies in creating markets and establishing local enterprises for value-added industries, particularly in rural areas in the Western Cape where production costs are far lower than in urban environments. When value is added close to resources the transportation costs expressed as a percentage of overall costs make the end product more viable and more competitive. There is an international movement away from chemicals that are harmful to the environment, to a more natural approach that is conservation-minded. Zeolite and its many properties fall into this category. Stringent international independent audits are conducted on producers to ensure compliance with regulations that do not only pertain to the product but also to the down-stream effects of its operations with regard to pollution and the social contract that the organisation has with its workers. The above-mentioned opens up huge markets in alleviating pollution and purifying water and waste with Zeolite and its potential to be incorporated into other filtration media. There are many forms of Zeolite and it has a multitude of applications.

Target markets of industry partners

Agricultural applications

Successful trials have been conducted using the mineral to reduce ammonia levels in chicken houses to decrease the respiratory problems associated with high levels of ammonia. This in turn impacts on protein conversion rates. Zeolite's ability to absorb moisture has been investigated to create microclimates that are unfavourable for the growth of pathogens, moulds, and bacteria that thrive in humid conditions. This reduces the risk of infectious diseases. Down-stream multipliers have been investigated in the production of chicken compost, which has greater nutritional value after being 'loaded' with nitrogen through the ion exchange process by converting ammonias into nitrogen.

Zeolite's properties and functions in horse stable bedding are similar to broiler production but are more important in the horse racing industry where respiratory infections need to be minimised.

Small ceramic balls mixed with Zeolite have been developed with additions of organic matter that burn out in the process. The balls are being tested in air and water filtration.

Zeolite as a filtration medium.

Trials have been conducted on calcining the zeolite material in its raw state and blending it with clays and organic fillers that are carbonised in the process. This is targeted at the aquaculture industry as an entry level and to proceed to the filtration of grey, black and eventually potable water. A clay filter pot has been developed in conjunction with 'Potters for Peace', (an international organisation that has an international track record in many countries.) that specializes in rural, low volume household water filtration. Rural infant mortality rates are high due to harmful bacteria build-up in streams.

Zeolite in conserving water

Zeolite can be used to prevent the leaching of water and nutrients from the soil in the horticulture sector. Current trials have proven successful in saving up to 30% of water.

The mineral has been applied to farmlands to increase growth, condition the soil and to prevent unwanted nutrients leeching into the ground water. Trials conducted by the mine in the Overberg have proven successful in this regard.

High value, high tech, industries

The purpose of developing lower value industries is to acquire cash flow and funding for product development and research and to establish higher value industries in the next phase of product development.

LITERATURE REVIEW

According to the WHO/UNICEF Joint Monitoring Programme (WHO/UNICEF, 2006) there are 1.1 billion people around the world who still lack sustainable access to relatively safe drinking water. This includes people in rural, urban and peri-urban areas. According to the WHO a short-term solution to meet the basic need of safe drinking water can be found in household water treatment and safe storage (WHO, 2008). In South Africa, information provided by the Department of Water Affairs in 2007 puts the number of people who remain without access to clean water at 7.2 million. Point-of-use or household treatment methods can be used to provide an improved quality of drinking water to households in situations where centrally treated water supply is not available or the treated water supply is not of a potable quality. The most appropriate technology will depend on the situation, the quality of the raw water, the availability of the technology, the time frame in which it is to be used, as well as the customs, preferences and education levels of the local population.

Water treatment utilities mostly employ disinfectants such as chlorine based chemicals to kill microbes in bulk water treatment. However, chlorine requires well-treated water (turbidities < 1 NTU) to be effective as a disinfectant. Taking into account that the poor, rural communities – who do not have the luxury of treated water supply – are most affected by bacterial and other pathogen water related diseases, cheaper and user friendly household water treatment methods are constantly being sought to avert these problems. In the use of suitable home filters (such as ceramic pots) with built-in disinfectant, thereby avoiding the home addition of chlorine to water, the taste of the water is maintained and no disinfection by-products are formed.

Clay Materials

Clay refers to naturally occurring minerals composed mainly of fine grained minerals that make up colloid fraction (particle size of ~2 μm) which possess plasticity when exposed to water and harden when dried (Guggenheim, 1995). Clays and clay minerals have been mined since the Stone Age; today they are among important minerals used by manufacturing and environmental industries.

Origins

Clays also have other materials in them that do not impart plasticity and organic matter, formed over long periods of time by gradual chemical weathering of rocks, usually silicate bearing (Tehrani, 2005). Early formation of well-ordered clays in natural weathered volcanic glass of Precambrian origin was documented by Tazaki et al. (1989). Clays and clay minerals occur under a fairly limited range of geologic conditions. The environments of formation include soil horizons, continental and marine sediments, geothermal fields, volcanic deposits and weathering rock formations. Most clay minerals form where rocks are in contact with water, air or steam. All of these environments may cause the formation of clay minerals from pre-existing minerals. Extensive alteration of rocks to clay minerals can produce relatively pure clay deposits that are of economic interest (Blatt, 1980). There are three procedures of clay formation:

Erosion: the transport and deposition of clays and clay mineral produced by eroding older continental and marine rocks and soils are important parts of the cycle that forms sedimentary rocks. The ancient sedimentary rock record is composed of about 70% mudstones (which contain about 50% of clay-sized fragments). Today, sedimentary environments that contain muds cover about 60% of marine

continental shelves and 40% of deep ocean basins. Continental aquatic environments such as lakes, rivers, estuaries and deltas also contain high proportions of fine-grained sediments (Blatt, 1980).

Diagenesis: is the in-place alteration of a mineral to more stable forms, excluding superficial alteration. Common silicate materials such as quartz, feldspars and volcanic glasses, as well as carbonates, non-crystalline iron oxides and primary clay minerals are transformed during diagenesis into stable clay minerals mainly by dissolution and recrystallization. Bentonite beds usually form from altered volcanic ash, but other types of rock may also serve as sources (Blatt, 1980).

Weathering: weathering of rocks and soil is the primary way that clays and clay minerals form at the earth's surface today. The weathering process involves physical disaggregation and chemical decomposition that change original minerals to clay minerals. Factors governing rock weathering and soil formation include the initial type of rock, the ratio of water to rock, the temperature, the presence of organisms and organic material, and the time. Kaolinite is found in most weathering zones and soil profiles. Montmorillonites, which are chemically more complex than kaolinites, are common in the lower parts of weathering profiles, nearer the rock, where chemistry exerts a strong control on mineralogy (Blatt, 1980).

Some attempts have been carried out on the synthesis of clay minerals from their oxides. Modern studies of the formation of clay minerals in the laboratory begin with Noll's hydrothermal synthesis of montmorillonite, pyrophyllite, kaolinite and mica (Robertson, 1953).

Crystalline Structure

Clays are aluminosilicates with a layered crystalline structure and are subject to shrinking and swelling as water is absorbed and removed between the layers. They are composed mainly of silica, alumina and water, frequently with appreciable quantities of iron, alkalis and alkali earths (Ralph, 1968). Two structural units are involved in the atomic lattices of most clay minerals. One unit consists of closely packed oxygens and hydroxyls in which aluminium, iron and magnesium atoms are embedded in an octahedral combination so that they are equidistant from six oxygens or hydroxyls. The second unit is built of silica tetrahedrons. The silica tetrahedrons are arranged to form a hexagonal network that is repeated indefinitely to form a sheet of composition, $\text{Si}_4\text{O}_6(\text{OH})_4$ (Figure 1) (Ralph, 1968). Clays have a layered crystalline structure and are subject to shrinking and swelling as water is absorbed by and removed from the layers.

Properties

The characteristics common to all clay minerals derive from their chemical composition, layered structure and size. Clay minerals all have a great affinity for water. Some swell and may double in thickness when wet. Most have the ability to soak up ions from a solution and release the ions later when conditions change.

Plasticity

Plasticity is a property of clays or other minerals which combines the strength of the solid with the fluidity of a liquid. It allows the solid to be reformed without rupturing and allows the new form achieved to remain without any attempt to return to the original form. Plasticity is linked to the moisture content. The material becomes more plastic with the increase of the amount of water, but

there is an optimum point after which increasing of the amount of water gives too much fluidity. Clay materials have strength, a certain resistance and the plasticity which are summed up in the term of “workability” (Hamer, 1975).

Shrinkage test: it is the simplest way to know how plastic the material is. Each material and the combined body is mixed with the same amount of water and extruded in bars of about 100 mm in length. The bars are then measured from wet to dry to determine the shrinkage. The greater the shrinkage of the bar, the more plastic it is.

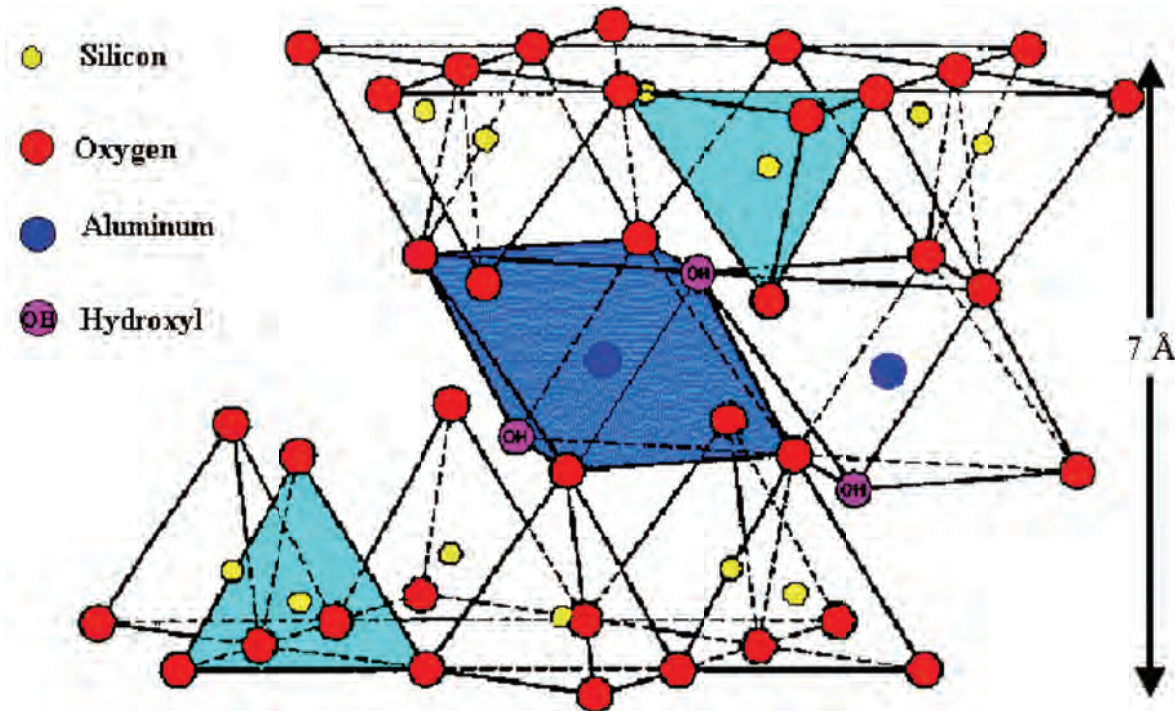


Figure 1: Inter-lamellar structure of Montmorillonite Clay (Delhom, 2000)

Surface Area

Clays have high surface areas that previously had been suggested as sites where concentration and catalysis can take place (Jiang *et al.*, 2004). The adsorption capabilities result from a net negative charge on the structure of minerals. This negative charge gives clays the capability to adsorb positively charged species. Their sorption properties also come from their high surface area and their high porosity. Montmorillonite clay has the largest surface area and the highest cation exchange capacity (Nayak, 2007).

Ion Exchange

The cation exchange capacity of the clay, as well as the size and charge of the cations determine the amount of swelling. The greatest amount of swelling is observed with small univalent cations such as Li^+ and Na^+ while polyvalent cations such as Ca^{2+} and Mg^{2+} present an incomplete swelling due to the strong interactions between the cation and water. When the inter-lamellar layer contains at least a single layer of water, theoretically, any cation can be exchanged irrespective of the size and charge (Gre'gorio, 2006).

Classification

Clays are generally classified in terms of the differences in the layered structures that make up the clay material (Table 1). Different classes of clays include smectites (beidellite, montmorillonite, nontronite, saponite and hectorite), mica (illite), kaolinite, serpentine, pyrophyllite (talc), vermiculite and sepiolite (Gre'gorio, 2006).

Table 1: Clay classification (Myriam *et al.*, 2005)

Charge (x) moles per half unit cell	Diocahedral	Triocahedral
1:1 Sheet	Kaolinite	Serpentine
0	$Al_2Si_2(O_5)(OH)_4$	$Mg_3Si_2(O_5)(OH)_4$
2:1 Sheet	Pyrophyllite	Talc
0	$Al_2Si_4(O_{10})(OH)_2$	$Mg_3Si_4(O_{10})(OH)_2$
Smectites		Octahedral substitutions
	Montmorillonite	Hectorite
0.2–0.6	$(Al_{2-x}Mg_x)Si_4(O_{10})(OH)_2(CEC)_x$	$(Mg_{3-x}Li_x)Si_4(O_{10})(OH)_2(CEC)_x$
		Tetrahedral substitutions
	Beidellite	Saponite
	$Al_2(Si_{4-x}Al_x)(O_{10})(OH)_2(CEC)_x$	$Mg_3(Si_{4-x}Al_x)(O_{10})(OH)_2(CEC)_x$
Micas	Illite	Vermiculite
0.6–0.9	$(Al_{1.75}R_x)Si_{3.5}Al_{0.5}(O_{10})(OH)_2K_{0.75}$	$(MgFe_3)(Si_{4-x}Al_x)(O_{10})(OH)_2Mg_x$
	Glauconite	Phlogopite
1	$(Al_{2-x}Fe^{3+}Fe^{2+}Mg)(Si_{3.75}Al_{0.25})(O_{10})(OH)_2K$	$Mg_3(Si_3Al)(O_{10})(OH)_2(K)$
	Muscovite	Biotite
	$Al_2(Si_3Al)(O_{10})(OH)_2K$	$(Mg,Fe^{2+})_3(Si_3Al)(O_{10})(OH)_2(K)$

Three types of clays are used for the ceramics such as the body of the filter pot: bentonite, white clay and red clay.

Bentonite: the main minerals in bentonites are smectite clays such as montmorillonite, beidellite, saponite and hectorite. Smectite clay is 2:1 layer clay mineral and has two silica tetrahedral sheets bonded to a central alumina octahedral sheet. All smectites have very high cation exchange when activated with strong acids (Onal *et al.*, 2002). Bentonite is an aluminosilicate mineral derived from weathered volcanic ash and largely composed of montmorillonite. It has a high surface area, high plasticity, and expands when wet. It can immobilize contaminant species through the processes of ion exchange, coordination or ion-dipole interactions (Bhattacharya *et al.*, 2008). In pottery, bentonite is used as a plasticizer to allow the material to flow through the mould, generating a strong bond between the clay particles. The clay bonding occurs when, under pressure, the excess clay flows through the mould and binds the material. Too much Bentonite also causes high shrinkage, resulting in cracks in the pot during the drying process. Bentonite is often mixed with water and then added to the mixture as

opposed to adding it as a dry powder. The dry powder can expand when hydrated, causing the body to crack. More than 75% of bentonite consumed in South Africa is produced by two open cast mines, Cape Bentonite mine owned by Ecce Holdings near Heidelberg in the Western Cape and the Ocean Bentonite mine owned by G & W Base & Industrial Minerals near Koppies in the Free State (Mabovu, 2011).

White clay: is mainly composed by quartz, montmorillonite and hematite (Mohsen, 2010). This clay is stoneware clay and vitrifies at higher temperatures. White Clay has excellent working properties and is extensively used in throwing clays that require more plasticity to form the ware (Hamer, 1975).

Red clay: is mostly constituted of kaolinite, quartz, montmorillonite, albite and hematite. Iron oxide, Fe_2O_3 is the main colorant in the clays, being responsible for the reddish colour after firing (Mohsen, 2010). Red brick clay vitrification temperature on its own is too low (Hamer, 1975).

In the pot manufacture, adding the three clays together is also good practice to balance out material inconsistency. The three clays have the advantage to be locally available and cost effective.

Uses

Clays and clay minerals have been mined since the Stone Age; today they are among important minerals used by manufacturing and environmental industries. Clays exhibit plasticity when mixed with water in certain proportions. When dry, clay becomes firm and when fired in a kiln, permanent physical and chemical changes occur. These reactions, among other changes, cause the clay to be converted into a ceramic material. Because of these properties, clay is used for making pottery items, both utilitarian and decorative (Hamer, 1975). Recent studies have investigated clay's absorption capacities in various applications, such as the removal of heavy metals from waste water and air purification (Dude et al., 2001). Recent research indicates that various animals visit clay licks periodically to eat from them, apparently because either the clay contains one or more antidotes for the various poisons in plants and seeds the animals eat, or because the clay coats the animals' guts to protect them from those substances. Several clays are used as gastrointestinal protectors (Wilson, 2003).

A traditional use of clay as medicine goes back to prehistoric times. An example is Armenian bole, which is used to soothe an upset stomach, similar to the way parrots (and later, humans) in South America originally used it. Kaolin clay and attapulgite have been used as anti-diarrheal medicines (Mohsen, 2010). The ingestion of clays leads to removal of toxic elements from the kidney, liver, heart and brain of rats (Bogdanov et al., 2009).

Clay Pot Manufacture

Clay materials and combustible organic compounds (milled grape residues) are mixed with water. Three types of clays are used for the body of the filter pot: bentonite, white clay and red clay. The mixture is hydraulically pressed into pots and fired at 900°C. This creates small pores that contribute to the filter porosity. The SME partner company, Red Seal, has spent two years research on developing of the clay press for filter pot manufacture so any further problems with clay pot making should be minimal. The hydraulic press being used has 30 tons per 25 mm x 25 mm surface pressure.

Steps

Mixing, pressing, drying and firing constitute steps of the pot manufacturing (Figure 2).

Mixing: Clay materials and milled grape residues are mixed with enough water to get the optimum moisture content, the mixture is call “body” when there is only one material mixed with water and “combined bodies” when there are two or more materials. Obtaining the correct moisture content is important because the workability of the body in the mold is related to the moisture content; this gives a pot which resists physical stresses after being pressed (Hamer, 1975).

Drying: is the removal of moisture. It is the establishment of the equilibrium moisture content between object and air. Wet clay dries by wetting the air around it; when the air holds as much water as the clay, the drying ceases. Three factors are involved in drying: temperature, which encourages the evaporation; humidity of surrounding air; and the movement of the air past the surface. These three factors can be controlled when the pots are covered. Warm, dry and breezy weather is more effective than cool, damp and still weather. An important effect of drying is shrinkage. Shrinkage or rather unequal shrinkage is responsible for drying cracks and warping (Hamer, 1975).

Firing: Clay disintegrates in water but is changed by firing into stone-like material, unaffected by water. The fired clay is called biscuit. There are five stages of a biscuit firing: water smoking, decomposition of the vegetable matter, ceramic change, burning out and progressive vitrification (Hamer, 1975).

1. *Water smoking:* The remainder of the pore water, which has been unable to dry out because of atmospheric humidity and pressure, is driven out by heating. The action takes place between room temperature (20°C) and the boiling point of water (100°C); this is considered to be completed by 120°C. During the water smoking there is water vapour escaping from the chamber.
2. *Decomposition:* Many types of clay contain vegetable matter which breaks down at approximately 200°C. This is the same action as occurs in a compost heap. This is not the burning out of the carbon, which occurs at higher temperatures.
3. *Ceramic change:* The bound water which is part of the crystal structure of clay is driven off; this causes the change from clay to pottery body, known as ceramic change. This begins very gently between 350°C and 450°C and increases to a maximum at 600°C. There is a slight shrinkage over the period of ceramic change.
4. *Burning out:* Carbon and sulphur are present in clays and remain to be burnt out by the process called oxidation. They combine with oxygen to form monoxide, dioxide and trioxide gases (CO, CO₂, SO, SO₂, SO₃). This process requires at least the dull red heat of 700°C and reaches the climax around 800°C. Most of the carbon has been burnt out by 900°C but some sulphur lingers until 1100°C or 1150°C.
5. *Vitrification:* This begins at 800°C when soda and potash within the body start to flux the free silica; which fills the pores between the alumino-silicate particles. The body shrinks during the vitrification. Above 1000°C, the fused alumino-silicate is able to form mullite. The temperature chosen depends upon the balance required of the properties of strength and porosity.

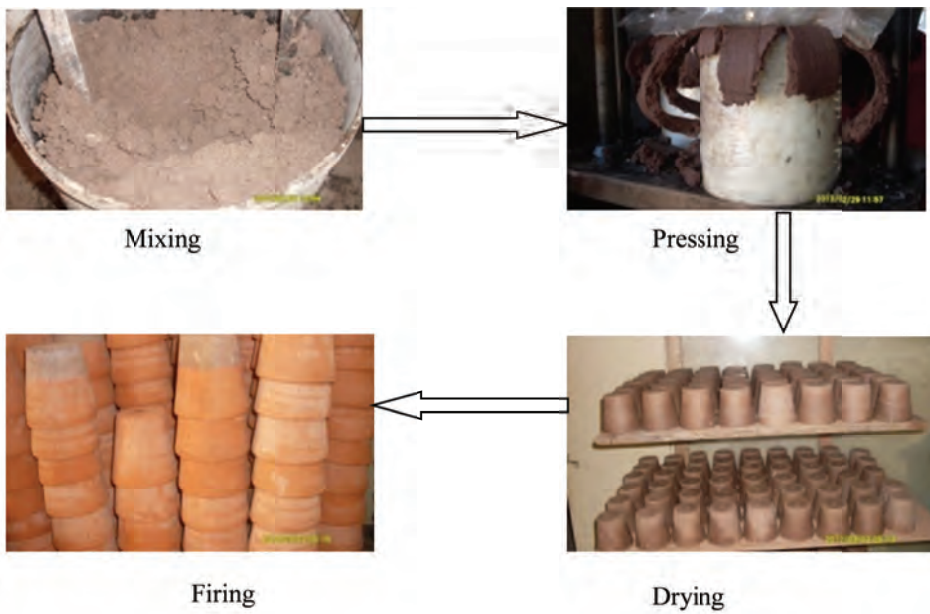


Figure 2: Steps of the pot manufacturing

Physical Filter Characteristics

Porosity

It is the ability of fired clay called “biscuit” to absorb water by capillary action. In plastic clay the interstitial spaces between the clay and other mineral particles are filled with water. After the ceramic change at 600°C these spaces become empty and the body becomes porous. The fired body or biscuit reaches its maximum strength with maximum porosity between 900°C and 1000°C. The vitrification phenomenon reduces the filter pot porosity (Hamer, 1975). At high temperature, all the waste organic materials in the body are burned; this creates small pores into the filter pot matrix and compensates the loss of porosity. There are three types of pores: interconnected, isolated and dead-end pores (Figure 3). The interconnected pores form a continuous phase within the porous medium and contribute to the flux across the filter. The isolated and the dead-end pores do not contribute to the flux across the filter (Halem, 2006).



Figure 3: Types of pores in the pot filter (Xiaolong, 2005)

The normal test for porosity is to take a warm sample of a biscuit and weight it accurately. It is then placed in boiling water for 5 minutes and left in the water as this is allowed to cool. Thereafter it is dried with a damp sponge and reweighed. The percentage of porosity is given by:

$$\text{Percentage of porosity} = \frac{\text{Weight after soaking} - \text{dry weight}}{\text{dry weight}} \times 100$$

Mechanism of filtration

The overall removal of impurities associated with the process of filtration can be summarized by: mechanical screening, sedimentation and diffusion (Figure 4).

Mechanical screening is the purifying process that includes removing the particles of suspended matter that are too large to pass through the filter pores.

Sedimentation removes particulate suspended matter of finer sizes than the pore openings by precipitation upon the surface of the clay material. Due to the larger density of the suspended matter than water it will follow a different path resulting from gravitational force.

Diffusion is the random motion of particles caused by collision with surrounding molecules, which could eventually lead to adsorption to the filter material (Halem, 2006).

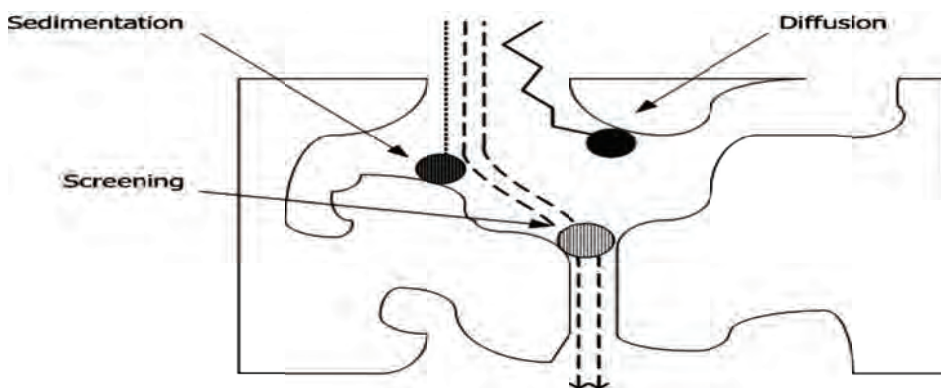


Figure 4: Mechanism of filtration (Halem, 2006)

Maturing Range

The maturing range is that part of a firing, usually considered as between two temperatures, where the body reaches its correct strength and compactness through vitrification. Below this range the body is under-fired, being too weak and porous. Above this range the body is over-fired and is likely to be so dense and glassy that it is brittle when cool. Most over-fired bodies also deform during firing by blistering and collapsing. Clays have different maturing ranges. Some red clays; which are rich in fluxes, mature in the range 950°C to 1050°C. Some ball clays mature in the region of 1150°C to 1200°C. It will be noticed that the range is not always the same length. Some fire clays have a very long maturing range, from 1200°C to 1400°C, whilst some special bodies may, by virtue of the active fluxes present, be matured in a range from 1090°C to 1100°C (Hamer, 1975).

Sintering

Sinter means to fasten together by mutual adhesion without apparent fusion. All ceramics, simple oxides or complex minerals pass through a stage of sintering before melting. There is no liquid (molten) phase involved and yet the individual particles stick to each other due to the phenomenon of electrical friction involving some rearrangement of structure at the surfaces. The result is that materials which start as powder become solid at a temperature which is only halfway to the melting point (Hamer, 1975).

Vitrification

Clays deform when they are over-fired. They collapse and might even melt, transforming to glass. At this point the silica and silicates of the clay have been successfully fluxed by alkaline oxides. Vitrification is the result of the fluxing of the feldsparoids and free silica in the body. This molten silicate flows into the interstices between the clay particles and attacks and begins to flux them by interaction. When the whole has cooled, the original clay particles are welded together by a glassy matrix which almost fills all the interstitial spaces. A vitrified body is usually accepted as having a small porosity. When the body has reached the point of being non-porous it is also so glassy that it fractures more easily (Hamer, 1975).

Vitrifiable clay is the clay which has a long maturing range and can therefore be fired successfully up to its vitrification point without deformation. This is necessary for the making of stoneware. The slow maturation is dependent upon the presence of suitable fluxes and anti-fluxes. The suitable fluxes are potash (K_2O) and soda (Na_2O) whose action starts at around $500^\circ C$ and progresses consistently. About 2 to 5% content is sufficient. Unsuitable fluxes are calcia ($1100^\circ C$), magnesia ($1170^\circ C$) etc. which have short active periods of fluxing. Alumina is the only suitable anti-flux; around 30% it will satisfactorily check a tendency to fuse too quickly. Stoneware clays, most ball clays and the least refractory fireclays could be called vitrifiable clays. Some red clays can also be vitrified but most have a tendency to bloat before densification is reached. Porcelain body is prepared vitrifiable clay (Hamer, 1975).

Pyrometric Cones

The pyrometric cones are made from ceramic minerals and are similar in composition to glazes. With heat the cones soften and eventually bend over, this action is called collapsing and squatting. If more heat were to be applied, the cones would melt into a glass. This can be viewed from the outside of the kiln through a spy-hole and by this means the potter has knowledge of what heat-work is taking place inside the kiln. Each cone is given a number corresponding to a temperature at which it will collapse through heat-work if that temperature is arrived at through a specified cycle. Cones are therefore more accurate than electric pyrometers which only measure temperature without relation to time. It is common practice when firing by visible cones to set three cones next to one another. One cone will be the one for the correct firing temperature and the others will be the consecutive ones above and below this. Thus there is a warning of about $20^\circ C$ when the first cone collapses and the potter knows that he must watch the second or firing cone in order to be accurate. The third should remain standing as proof that the kiln was not over-fired (Figure 5). The cone should be set at an angle of about 70° from the horizontal which ensures that it will collapse in that direction only (Hamer, 1975).



Figure 5: Collapse and squatting of pyrometric cones
<http://www.ortonceramic.com/pyrometrics/arts/cones.shtml>

Cracks

Cracks are unwanted breaks in a piece of pottery. They are caused by physical stress and are the result of the expansion, contraction and shrinkage of the pot. They can occur at any stage of the manufacturing process from the drying of the body to the cooling of the biscuit (Hamer, 1975).

Zeolites

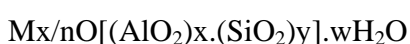
The term zeolite was first used by a Swedish mineralogist, Axel F. Cronstedt in 1756. From the Greek word zeolithos, “zeo” means to boil and “lithos” means a stone, this is due to the frothing features when heating zeolites (Breck, 1974). From 1777, various authors described the properties of zeolite minerals, including adsorption properties, reversible cation exchange and dehydration (Kulprathipanja, 2010).

Origins

Zeolites can be either natural or synthetic. The most abundant natural zeolite is clinoptilolite. Other natural zeolites are analcime, chabazite, erionite, ferrierite, heulandite, laumontite, mordenite and phillipsite. They are some of the most abundant mineral species on the earth (Nagy et al., 1998). Zeolite formation in nature requires a few hundred to tens of millions of years depending on the chemical environment. Zeolites come from the formation of igneous, metamorphic or sedimentary rocks; mainly through hydrothermal processes over geological time scales (Breck, 1974). They occur as minor constituents in vugs or cavities in basaltic and volcanic rock (Kulprathipanja, 2010). Synthetic zeolites are made by crystallization of sodium aluminosilicate gels prepared from pure sodium aluminate, sodium silicate and sodium hydroxide solutions (Kugbe, 2009; Vadapalli, 2010 and Somerset, 2008).

Crystalline Structure

Zeolites are alumina-silicates and are represented as MO_4 (M= Si and Al) with a 3-dimensional micro porous crystalline structure of interconnected framework of tunnels and cages. The silicon to aluminium ratio in zeolites varies and this directly determines their acidic properties. Also, zeolites contain water molecules alongside different cations, which are mainly from group I and II elements present in the porous structure of zeolites frameworks. The cations balance with the negative charge of the zeolite lattice (Figure 6).



Where

M = Exchangeable cation with the valence of n

w = Number of water molecules

y/x = Stoichiometric factor between 1-5 depending upon the structure

(x+y) = Total number of tetrahedra in the unit cell (Breck, 1974, Scott *et al.*, 2003; Weitkamp and Puppe, 1999).

Zeolites have high ion-exchange capacity and lattice stability (Shameli *et al.*, 2011). As the Si/Al ratio increases, the cation concentration and the ion exchange capacity decreases mainly in proportion to the lower aluminium content, thereby making the zeolite more hydrophobic (Van Bekkum *et al.*, 2007).

For over half a century, zeolites have played an important role in the development of modern processes in the chemical and petroleum industries. They are used in catalytic applications and separation processes (Scott C. *et al.*, 2003). Some investigations have shown that zeolites can be synthesized by using fly ash from coal combustion (Somerset *et al.*, 2008; Vadapalli *et al.*, 2010).

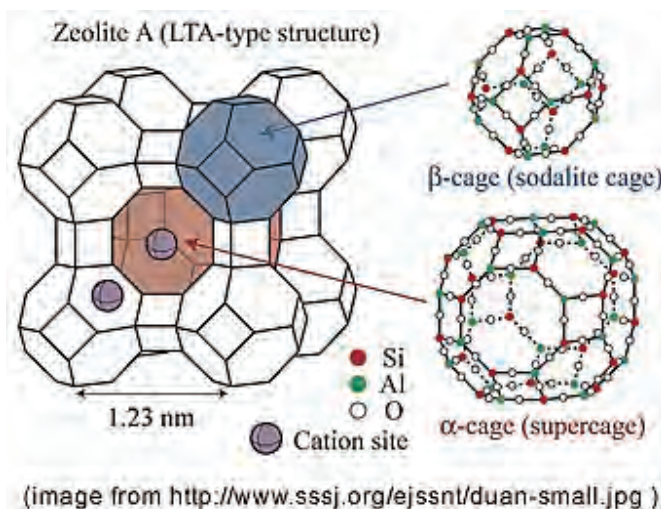


Figure 6: Schematic representation of zeolites (www.sssj.org/ejssnt/duan-small.jpg)

Properties

Colour

Natural zeolites are colourless but impurities such as Fe can give them colour. In synthetic zeolites, the presence of alkali or alkaline earth cations impact on the colour (Breck, 1974).

Porosity

Zeolites are porous aluminosilicates having a uniform pore structure. They exhibit pore sizes from 0.3 to 1.0 nm and pore volumes from about 0.10 to 0.35 cm³/g (Kulprathipanja, 2010). Water moves freely in and out of these pores but the zeolite framework remains rigid and does not swell unlike clays. Another special aspect of this structure is that the pore and channel sizes are nearly uniform, allowing the crystal to act as a molecular sieve at the Angstrom scale. The porous zeolites are host to water and other molecules, but only those of appropriate molecular size fit into the pores, creating the molecular sieving property (Scott *et al.*, 2003).

Ion Exchange

The cations in the zeolites are exchangeable with other cations giving zeolites an ion exchange property (Scott *et al.*, 2003). The Si in the structure has a valence of +4 making the SiO₄ tetrahedra neutral, while the AlO₄ tetrahedra are negatively charged because Al has a valence of +3, creating a Brønsted acid site due to the resulting charge imbalance in the framework structure, which imparts exchangeable sites to the zeolite structure. Therefore the ion exchange capacity of zeolites depends on its chemical composition. Ion exchange capacity is inversely proportional to the Si/Al ratio. The specific ion exchange capacity depends on the structure of the zeolite, the Si/Al ratio and the ions to be exchanged (Weitkamp and Puppe, 1999).

Classification

Zeolites can be classified on the basis of their framework structure (Nagy *et al.*, 1998). The International Zeolite Association (IZA) recommends the use of the three letter code for zeolites with various structures (Table 2).

Table 2: Examples of the three letter coding used by IZA

Zeolite name	Three letter code
Clinoptilolite	HEU
Heulandine	HEU
Faujasite	FAU
Gismondine	GIS
Gmelinite	GME
Boggsite	BOG
Mordenite	MOR

Natural Zeolite: Clinoptilolite

Clinoptilolite (HEU), which in Greek means “oblique feather stone”, is a member of the zeolite group of minerals. Clinoptilolite, a natural zeolite is currently mined as a waste product at Cape Bentonite Mine during the removal of bentonite clay. Annually about 23 000 tonnes are dumped but can be readily recovered. In South Africa, Clinoptilolite is presently mined commercially at Pratley mine; Vulture Creek in Ubombo, KwaZulu-Natal and the product is sold commercially for domestic fish keeping, as cat litter, for water purification and soil remediation.

Structure

An approximate empirical formula of clinoptilolite is $(Ca, Fe, Mg, Na)_3-6Si_{30}Al_6O_{72}.24H_2O$. It is in the chemical class of silicates, subclass of tectosilicates, group of zeolites and family of Heulandite. Clinoptilolite is a devitrification product of volcanic glass in tuffs. Tuffs are consolidated pyroclastic rocks. The devitrification occurs when the glass is in contact with saline waters. Both clinoptilolite and heulandite have the same tetrahedral framework, labelled HEU (Figure 7) (Frost, 2001).

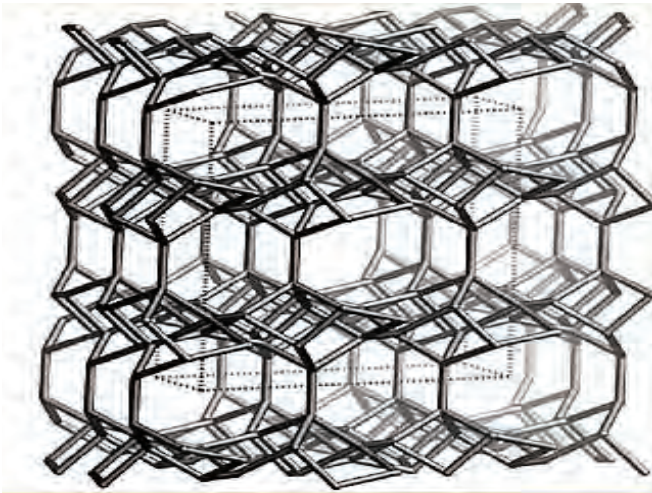


Figure 7: Clinoptilolite (HEU) Framework Model (Baerlocher *et al.* 2002)

Uses

Ames (1960) demonstrated the use of clinoptilolite as an ammonium scavenging agent for remediation of ammonium pollution and determined the ion selectivity for clinoptilolite. Nowadays clinoptilolite has found widespread environmental applications which attract the attention of many researchers. The major uses of clinoptilolite include water softening and purification, petrochemical cracking, gas and solvent separation, radioprotection, soil disinfection, soil improvement, food additives and biomedical applications (Bogdanov *et al.*, 2009).

Water and wastewater treatment: technologies using zeolites for water purification are based on their cation exchange property, through which dissolved cations are removed from water by exchanging with other, less problematic cations. Methods for removal of arsenate and arsenide from drinking water with zeolites have been reported. Clinoptilolite is a natural zeolite which is known for its ability to remove ammonium from polluted waters (Bogdanov *et al.*, 2009).

Adsorption and catalysis: zeolites may hold water up to 60% of their weight due to the high porosity and void volume of the crystalline structure. Zeolites assure a permanent water reservoir, providing prolonged moisture during dry periods. Natural zeolites can absorb CO, CO₂, SO₂, H₂S, NH₃, HCHO, Ar, O₂, N₂, H₂O, He, H₂, Kr, Xe, CH₃OH and many other gases and can be used to collect them or control odours (Bogdanov *et al.*, 2009).

Nuclear waste and fallout: the removal of nuclear wastes and fallout is one of the great priorities of zeolite applications. It was reported that clinoptilolite-Na can remove ¹³⁷Cs and ⁶⁰Co. Recent studies reported that zeolites can be used to remove U⁶⁺ (Bogdanov *et al.*, 2009).

Agriculture: in recent years attention has been paid to the development of substantial agriculture and hence the use of clinoptilolite as soil amendments has been applied to improve physical and chemical properties of soils (Bogdanov *et al.*, 2009).

Animal feed additive: the addition of zeolites improves the calorificity, digestion, appetite and animal's weight. Clinoptilolite acts as a mycotoxin binder, absorbing toxins which are dangerous to animals.

The addition of clinoptilolite to the diet of pig, poultry and cattle, improves their weight gain and increases feed conversion ratios (Bogdanov et al., 2009).

Biomedical application: the use of clinoptilolite for treatment of cancer-bearing mice and dogs led to improvements in the overall health status, prolongation of the life span and decrease of the tumour size in some cases. An immunostimulatory effect of natural clinoptilolite has been detected, and it is possible that this is the mechanism of its antimetastatic ability (Bogdanov et al., 2009).

Silver Nanoparticles

Nanotechnology is defined as the understanding and control of matter at dimensions between 1 and 100 nm, where unique physical properties make novel applications possible. The use of nanoparticles in several industries has led to many investigations. Nanoparticles exhibit dissimilar characteristics in comparison with their bulk metal states (Huwe et al., 2007). Silver, as a transition metal, has many applications in the fields of medicine, dentistry, clothing, catalysis, mirrors, optics, photography, electronics and food industries (Rai et al., 2009). Besides that, the incorporation of single nanoparticles into other substrates results in a system with novel properties (Shameli, 2011). Rai et al. (2009) regard silver nanoparticles as a new generation of antimicrobials. They do not demonstrate a bacterial resistance in comparison to the common antibiotics. However bacterial resistance to the silver nanoparticles may develop with continued use (Khan et al., 2011).

Synthesis of Silver Nanoparticles

Various methods are used to synthesize silver nanoparticles including photocatalytic reduction (Chang et al., 2006), chemical reduction (Shameli, 2011; Szczepanowicz, 2010; Qin et al., 2010), photochemical or radiation-chemical reduction, metallic wire explosion, sonochemical, polyols (Nersisyan et al., 2003), matrix chemistry (Ayyad et al., 2010), photoreduction (Courrol et al., 2007), reverse micelle-based methods (Xie et al., 2006) and biologically synthesized (Kalishwaralal et al., 2010; Sathishkumar et al., 2010; Zeiri et al., 2002).

Antimicrobial Properties of Silver

Application of silver in medicine and as a preservative dates back to 550-529 BC (Davies and Etris, 1997). Silver vessels have been used for preservation of water and fresh milk by the ancient Greeks, Romans and Egyptians by placing silver and copper coins in the casks containing water or fresh milk to retard the growth of microbes. Application of silver in medicine was pioneered in 1881 by Carl Crede by using 2% AgNO₃ in the eye of new born babies to prevent gonorrhoeal ophthalmia (Davies and Etris, 1997). Von Naegeli and others in 1893 discovered that the antibacterial activities of silver were due to the Ag⁺. A small amount of Ag⁺ is released from the metallic surface when placed in contact with liquids. In the early 1900's silver foil dressings were used for wounds. These dressings were used extensively until just after World War I when antibiotics were discovered. In the early 1970's the study of implanted silver wires and electrodes and silver-coated fabrics for the treatment of complex bone infections was researched at Veterans Administration Hospital in Syracuse, New York by Becker and others. Discovery of the wound healing properties of silver plated fabrics applied with the application of an electrical potential led to the commercial introduction of silver dressings for wound healing and burns. Silver sulfadiazine ointment is mostly used treatment for burns. The antimicrobial activity of silver led to the application of silver particles on cutting boards, table tops, washing machines and

refrigerators to prevent food poisoning. The cosmetic industry uses silver in perfume to kill bacteria that cause odour.

Several metal salts and compounds demonstrate strong antimicrobial properties, and silver alone shows both strong antimicrobial properties and low or no toxicity to humans. The colloidal state of silver proved to be the most effective because of lack of the caustic properties of salts (such as AgNO_3) and has proved to be very effective at very low concentrations. Around 1940, there were approximately four dozen different silver compounds on the market being used to treat every known infectious disease. With the advent of antibiotics, interest in silver, as an antimicrobial declined (Chopra, 2007). At that time, no antibiotic resistant strains of disease organism were known. Recently, with the development of antibiotic resistant strains of bacteria and viruses, there is renewed focus in the use of silver as an antibiotic. Nowadays, colloidal silver is sold as a trace mineral supplement without medical report over the counter. Silver is also used in the water purification systems of space craft, and in preventing the growth of algae and bacteria in swimming pools.

Mechanisms of Silver Antimicrobial Activity

The antimicrobial activity of silver depends on the concentration of the silver ion. AgNO_3 has been used in medicine to kill microbes because it dissociates readily, releasing free Ag^+ ion. The antimicrobial effects of silver compounds, such as colloidal (nano-) silver occur because of their oxidative properties when releasing Ag^+ . The microcidal action of Ag^+ involves *inter alia* the following (Hwang *et al.*, 2007; Davies and Etris, 1997):

Interaction with thiol (sulfhydryl, -SH) groups of enzymes and proteins. Many cellular functions of bacteria occur at the cell wall. Silver ions, when attached to the proteins controlling respiration and the ionic balance of the bacterial cell interfere with its functions, resulting in suffocation and death of the bacterium.

Silver also inhibits DNA replication by interfering with DNA unwinding. The mechanism for the antimicrobial action of silver ions is not well understood, but their effects on bacteria can be noticed by different bacterial changes: the DNA molecules can only replicate when they are in the relaxed state, they lose the replication ability when they are in the condensed form; when the silver ions penetrate inside the bacterial cell the DNA molecule turns to the condensed form and loses its replication ability leading to cell death (Liau *et al.*, 1997; Feng *et al.*, 2000)

The disinfectant properties of silver nano particles have been widely researched. Momba *et al.* (2010) provides an extensive summary of the disinfection properties of silver nano particles and conditions determining their efficiency. The disinfection efficiency appears to depend on the dose, size and shape of the nano particles, and on the target organism. In general, Gram-negative bacteria such as *E. coli* are more susceptible than Gram-positive species such as *Staphylococcus aureus*, possibly as a result in differences in the structure of their cell membranes. Gram-negative bacteria have a 2-3 nm layer of peptidoglycan between the cytoplasmic membrane and outer membrane whereas Gram-positive bacteria have a 30 nm thick peptidoglycan layer and no outer membrane. Morones *et al.* (2005) examined both the exterior and interior of four different species of Gram-negative bacteria (*E. coli*, *S. typhus*, *P. aeruginosa* and *V. cholerae*) after treatment with suspensions of silver nano particles using Scanning Transmission Electron Microscopy (STEM). Nano particles were observed to have attached both to the cell membranes and to have penetrated into the cytoplasm. The mean size of nano

particles both attached to and inside the cells was 5 nm with a standard deviation of 2 nm compared to the mean size of 16 nm with standard deviation 8 nm of free nano particles in the suspension used to treat the cells. The authors concluded that interaction between cells and nano particles primarily involved particles in the 1-10 nm range. In addition, Morones *et al.* (2005) further found that ~ 98% of the nano particles smaller than 10 nm exhibited octahedral and multiple twinned icosahedral and decahedral morphologies, all of which present mainly {111} surfaces, which have high atom density facets and which have been shown to favour silver reactivity. Morones *et al.* (2005) also suggested that these effects, as well as the high specific area of the particles, allowed nano particles in the 1-10 nm to bind with the cell membranes. Once attached, the nano particles caused structural changes to the membrane, making them more permeable and allowing the particles to enter into the cells. The nano particles caused dose dependent inhibition of subsequent cell growth. *E. coli* and *S. typhus* were more susceptible than *P. aeruginosa* and *V. cholerae* but no significant growth of any of the species was observed at nano particle concentrations which the authors calculated to correspond to approximately 2000 1-10 nm sized particles per cell. Nano particles in solution will release silver ions which may also contribute to antimicrobial effects. The authors found that nano particles freshly dissolved in 0.2 M NaNO₃ immediately released Ag⁺ at concentrations of ~108 µg/L but after 24 hours the concentration had dropped to ~ 20 µg/L. These concentrations are similar to those found in the filtrate from the first few runs of newly silver coated ceramic filters (Lantagne, 2001) and may contribute to biocidal effects. However, the response of cells to silver nano particles appears to be different to that of silver ions. Cells treated with silver nitrate show a low molecular weight region which is believed to be the cell conglomerating its DNA as a defense mechanism against toxic compounds when the cell detects a disturbance at the cell membrane. This phenomenon is absent from cells which have been penetrated by nano particles (Morones *et al.*, 2005).

Thus, exposure of bacteria to silver causes inhibited growth, suppresses respiration, metabolism and therefore results in death of the organism (Hwang *et al.*, 2007). The mechanism of silver disinfection of bacteria makes silver a broad spectrum biocide with no silver resistance towards it by the microbes.

Use of Nano Silver in Point of Use Water Treatment

Nano particles and nano structures have characteristic dimensions in the range 1-100 nm (Theron *et al.*, 2008). At this scale, materials often exhibit significantly different physical, chemical and biological properties, very large specific surface area and quantum effects which occur at the nano-scale. There is increasing interest in the potential use of nanotechnology in point of use (POU) water treatment devices particularly for use in the developing world with proponents suggesting that nanotechnology-based materials can be used to create cheaper, more durable and more efficient POU devices (Hillie *et al.*, 2006; Theron *et al.*, 2008). A number of devices and treatment methods incorporating nano materials are already commercially available and others are currently being developed. These include filters, filtration membranes, catalysts and nano particles for groundwater remediation. Since these technologies are very new, most of the information available on currently available devices comes from the manufacturers and there is little independent verification of their performance (Hillie *et al.*, 2006). Various concerns have been raised about the potential risks of using nano particles and materials in general, including potential environmental and human health effects as well as socio-economic and ownership issues and again, due to the newness of these technologies, there is little or no data addressing these topics (Hille *et al.*, 2006). A comprehensive review of the scientific literature on

potential and emerging applications of nanotechnology in water treatment is provided in Theron *et al.* (2008).

Incorporation of Silver onto Solid Matrices

Several researchers have experimented with imbedding silver nano particles in various solid matrices. Son *et al.* (2006) prepared ultrafine cellulose acetate particles containing imbedded silver nano particles with average diameter of 15.4 nm. These were reported to have high antibacterial activity against Gram – positive *S. aureus* and Gram-negative *E. coli*, *Klebsiella pneumoniae* and *P. aureginosa*. Jain and Pradeep (2005) coated silver nano particles onto polyurethane foam which they then tested for use as antimicrobial filter. Polyurethane was chosen because it is cheap, non-toxic and contains carbamate groups (-N(H)COO-) which were expected to bond with the nano particles. The silver nanoparticles were prepared by boiling silver nitrate solution with sodium citrate and cooling to precipitate the nano particles. Foam sheets were soaked overnight in the nano particle solution, thoroughly rinsed to remove adsorbed ions and then air dried. There was no loss of nano particles after four to seven washing and drying cycles indicating the nano particles were securely bonded to the foam. The microbial removal efficiency was tested by wrapping a 6 mm thick piece of foam twice around a 157 mm diameter 20 cm long ceramic candle filter and passing a suspension of *E. coli* through it at a rate of 0.5 L/min. Influent concentrations of 10^3 CFU/ml and 10^5 CFU/ml were used. Samples were collected at hourly intervals over a period of four hours. No *E. coli* were detected in any of the effluent samples. The authors did not report bacterial removal for the ceramic filter alone. Dankovich and Gray (2011) described a method to deactivate pathogenic bacteria by percolation through a paper sheet containing silver nano particles. The silver nano particles are deposited by the in situ reduction of silver nitrate on the cellulose fibres of an absorbent blotting paper sheet. The aim was to achieve inactivation of bacteria during percolation through the sheet, rather than removal of bacteria from the effluent by filtration. The silver nanoparticle containing (AgNP) papers were tested for performance in the laboratory with respect to bacteria inactivation and silver leaching as suspensions of bacteria percolated through the paper. The AgNP sheets exhibited antibacterial properties toward suspensions of *Escherichia coli* and *Enterococcus faecalis*, with log reduction values in the effluent of over log 6 and log 3, respectively. The silver loss from the AgNP sheets was minimal, with values under 0.1 mg/L (the current US EPA and WHO limit for silver in drinking water).

Use of Nano Silver/Ceramic Pots for Point of Use Water Treatment

Application of silver in water treatment dates back to ancient times. This led to the development of ceramic water filters containing silver by Potters for Peace (Figure 8) for water disinfection with no need for electricity or advanced technology.

These filters are made from clay materials, Clay is mixed with sawdust or other combustible organic compounds such as rice and coffee husks in 1:1 ratio. The mixture is mixed with water to make a paste and placed in a mould. The moulded pot is dried in open air and then kilned at 890°C, burning off the combustible organic material. This creates very tiny pores in the pot capable of excluding fungi, protozoa and bacteria from passing through (Bielefeld *et al.*, 2009).

After cooling the pots are either painted (inside and outside) or soaked in a solution of colloidal silver. The colloidal silver solution is made by diluting 3.2% of colloidal silver by approximately 125 times (Estrada, 2004; Bielefeld *et al.*, 2009). Table 3 highlights the average usage of grey water per day in households in Australia.

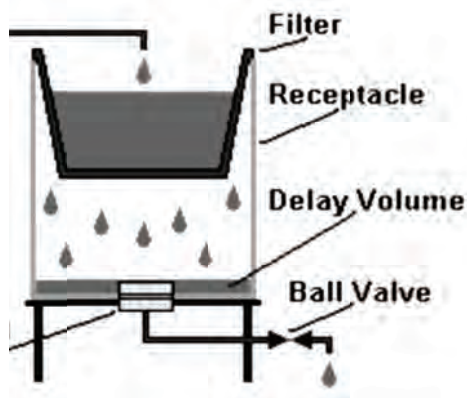


Figure 8: Ceramic filtering apparatus produced by Potters for Peace (Bielefeldt, 2009)

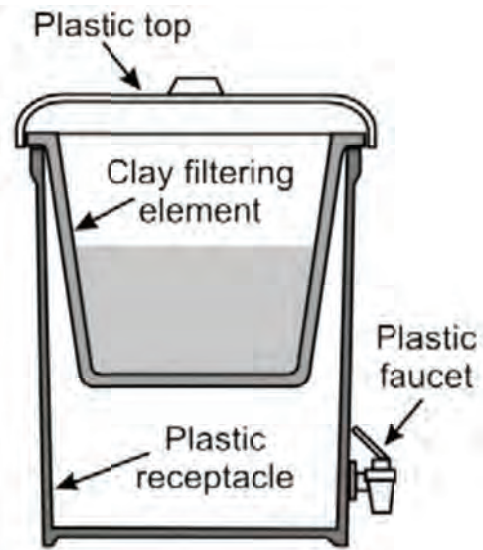


Figure 9: PFP filter pot design (Roberts, 2003)

Table 3: Average usage of grey water per day (Australia)

Waste water source	Total waste water		Total grey water	
	%	Litres/day	%	Litres/day
	Total		Total	
Toilet	32	186	-	-
Hand basin	5	28	8	28
Bath/shower	33	193	54	193
Kitchen	7	44	-	-
Laundry	23	135	38	135
Total	100	586	100	356

Potters for Peace (PFP) Filtration Unit

The PFP have a successful model in the development of a rural water filter that has been applied and tested over the past 15 years on many continents. The average pore size of ceramic water filters made by the PFP is 0.6-3 μm (Lantagne, 2001 and Campbell, 2005). The PFP filter has a throughput of 2 L per hour. The Potters for Peace international organization has conducted extensive research on the use of colloidal silver in the pots.

Mechanism for the Removal of Contaminants

The mechanisms for contaminant removal by silver impregnated water filters are; size exclusion and inactivation. Size exclusion removes larger microorganisms such as protozoa and some bacteria bigger than the filter pore sizes. Smaller bacteria and viruses may also be removed by adsorption and

inactivation by ionic silver. (Brady *et al.*, 2003; Huang *et al.*, 2008, Butkus *et al.*, 2004; Kim *et al.*, 2008).

New filters with fresh silver coating have been found to be very effective for disinfection of water. A removal efficiency of 99-100% for *E. coli* was established (Oyanedel-Craver and Smith, 2008; Brown, 2007). Over time, as many batches of water are treated, the silver leaches out of the pot into the water decreasing the efficiency of the filter. Most of the silver leaches out in the initial runs as shown in Table 4 (Lantagne, 2001).

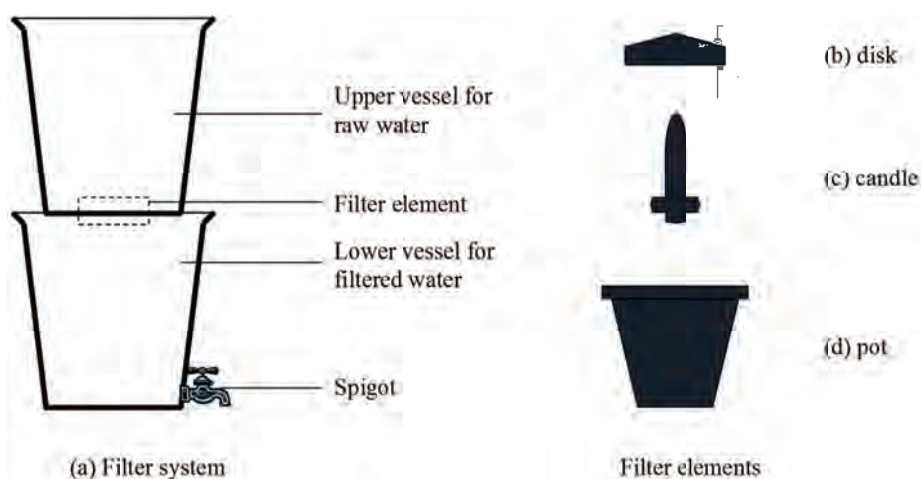
Table 4: Concentration (in mg/L) of silver leached out at different flow rates

Filter flow rate (L/h)	1	1.5	2
First run	44	61	29
Second run	11	19	18
Third run	12	21	15

However, ceramic filters without a silver coating achieved a high bacterial removal efficiency of 82-99% (Oyanedel-Craver and Smith, 2008; Lantagne 2001). Field studies in Nicaragua over six months on ceramic filters with silver coating showed a disinfection rate of 97.6 and 89.3% for *E. coli* and total coliform respectively (Hwang, 2007). Brown, 2007 found that sixty ceramic water filters in Cambodia maintained their disinfection efficiency over 45 months. Lantagne (2001) tested ceramic water filters that were being used for 1-3 years and analysed for the total removal of total coliforms, H₂S producing bacteria and *E. coli*. He found that, out of 24 filters, only 53% of the filters totally removed total coliforms, H₂S-producing bacteria, and *E. coli* respectively.

From the above discussion it can be concluded that the disinfection of bacteria in ceramic filters coated with colloidal silver is mainly due to size exclusion. The silver inactivation of microbes enhances this disinfection. The leaching out of silver from ceramic water filters explains the fact that new filters show enhanced disinfection compared to old filters or filters without silver coating. The enhanced efficiency of silver containing filters can be maintained if silver can be applied in a form that controls its solubility. Some researchers have found that silver deposited on carbon materials or zeolites can be used as disinfectants without adding silver into the treated water (Lv, 2009).

Momba *et al* (2010) summarized the Potters for Peace-type of clay pot units currently being employed internationally as home treatment devices, as well as the potentially viable options to use and their manufacturing processes. Further, they investigated which anti-bacterial nano particle coatings and/or mixes may be used to efficiently inactivate bacteria and viruses. Some of these units are illustrated in the Figure 10.



Their survey highlighted the following aspects with regard to ceramic home treatment devices.

Ceramic filters, whether produced commercially by companies in the developed world or by local potters in developing countries, have been shown to be effective in removing bacteria, in particular, *E. coli* and larger organisms such as protozoa and helminths, and in reducing the incidence of diarrhoea among users. However, they are not very effective for virus removal.

The mechanisms of removal/inactivation of pathogens are not well understood. Physical straining, sorption and inactivation by silver all appear to play a role. Removal efficiency by sorption mechanisms appears to decline over time as sites are exhausted. Routine cleaning will not regenerate sites within the filter walls. Testing limited volumes of water in new filters may therefore give an unrealistic impression of removal efficiencies, especially viruses. It is recommended that at least 100 L of water should be filtered through any given filter before determining removal efficiencies.

Plastic filtered water receptacles are easier to clean and disinfect than ceramic ones. Clean filter discharge of typical filter pots ranges from 1 to 3 L/h. The flow rate is assumed to be related to the porosity, pore size and structure as well as the dimensions of the filter element which in turn depend on the manufacturing process. However, the relationship between pore characteristics, discharge and removal efficiency has yet to be successfully quantified. The use of porous grog in the fabrication of filter elements is reported to improve flow characteristics. Using multiple candle filters instead of a single pot is another way to increase the flow of a filter unit. Filters should be regularly scrubbed to remove surface clogging to restore the flow rate. Filters appear to remain effective for seven or more years if properly used and maintained.

Removal efficiencies in the field are often lower than those obtained in laboratory studies. Typical removal efficiencies in the field are expected to be 2 log bacteria, 0.5 log viruses and 4 log protozoa. Education about water and sanitation issues and training in the proper use and maintenance of the filters is critical to their successful implementation. Filter effectiveness has further been found to correlate with frequent follow up visits to households by community or health workers. Both treated and stored raw water can easily be contaminated by improper handling so training must include safe

collection, handling and storage of water. Ceramic filter elements are fragile and easily broken if dropped. Broken filter elements is a major reason for disuse of the filters in field studies. Damaged spigots on the filter receptacle are another. It is therefore important that communities have access to replacement parts.

The mechanisms by which silver amendments to filters improve bacterial removal in ceramic filters are not well understood. Silver ions which leach from the filter may play a role but silver is not usually detected in the filtrate after the first six months of use. Silver coated onto inert surfaces has been shown to generate active oxygen species through a catalytic reaction with oxygen. This can kill viruses and bacteria on contact with the surface. The same phenomenon has been observed with other metals and metal oxides including CaO and MgO. The advantage of silver is that it does not alter the pH of the water. Combinations of silver with other metals such as copper and zinc may improve removal efficiencies through synergistic effects; however, this has never been tested in their application.

There are general concerns about the use, environmental fate and impact of nanotechnologies largely due to lack of data. Recent studies have shown that some types of carbon nanotubes have adverse effects in mammals and in beneficial microbial populations in wastewater treatment. The use of nano particles offers the possibility of enhanced reactivity compared to conventional coatings due to very high active surface densities. The biocidal activities of various types of nano particles have been tested, often in suspension with bacteria, which allows the particles to penetrate into the cells, but also when immobilised in inert matrices. Biocidal activity appears to correlate with smaller particles sizes (< 10 nm), prevalence of {111} crystal facets and even dispersion of the nano particles. Nano particles with demonstrated antimicrobial activity include silver, copper, magnesium and calcium oxide and their halogen adducts, titanium dioxide based photocatalysts and carbon nanotubes (in suspension). The conditions under which these particles have been tested usually do not reflect the conditions expected in ceramic filters (pH, concentration, photocatalytic effects, mobility of nano particles, contact time). However, silver nano particles deposited in polyurethane foam have been shown to be effective in inactivating bacteria at substantially higher flow rates than are achieved in current ceramic filter models (Jain and Pradeep, 2005).

From their laboratory studies Momba *et al* (2010) further noted the following findings: a synthetic Silver Impregnated Porous Pot (SIPP) ceramic unit for household water filtration, incorporating nano-silver and producing approximately 1 L/h of product water flow, was successfully fabricated. Based on the results of the experiments described, it was demonstrated that the new SIPP pots, in which nano-silver is impregnated into the clay during the firing process, were just as effective in removing bacterial contamination from influent water as the established PFP pots sourced from Kenya, but with unit water treatment cost advantages. Utilising the SIPP pot, an average *E. coli* removal rate of 1.2 logs (equivalent to 91.8% removal) could be displayed, up to a water production of 32 L. The more efficient bacterial performance of the SIPP pots as compared to the PFP pots were attributed to the embedded silver nano particles in the clay micropores. Since the embedded silver nano particles were harder to wash away, the resultant bactericidal activity of the pot was longer than that of PFP pots since the PFP pot only have painted colloidal silver on the inside and outside surface. The silver leached from the SIPP pot was, however, at a level of between 0.5 and 0.6 mg/L, higher than the WHO recommendation of 0.1 mg/L. Although the cost of the silver needed per pot is higher for the SIPP pot than the PFP pot, the SIPP pot is more cost-effective in terms of unit water treatment cost.

Overview of Selective Silver Loading Methods

This section covers a review of different techniques used to load silver nanoparticles on zeolite. The silver loading on the clinoptilolite was done using ion exchange and wet impregnation.

Ion Exchange

The ion exchange method of the metal loading on a support has the advantage of producing a highly dispersed catalytic component within the carrier. A cation salt containing the catalytic species can exchange with the exchangeable carrier charge balancing cations. Ion exchange is the most commonly used method for the metal loading on the zeolites. In practice, the pre-acid treatment of the zeolites ameliorates the metal loading (Haber et al., 1995).

Wet Impregnation

Impregnation consists of contacting a porous support substrate with a liquid containing the components to be deposited on the surface of the substrate. During the impregnation, many processes may take place at different rates. These include: the selective adsorption of species by Coulomb forces, the ion exchange between the charged surface and the electrolytes, the deposition of the species to be attached to the surface and the partial dissolution of the surface of the solid. The wet impregnation is employed when the quantity of metal ion to be introduced into the support substrate is greater than would be obtainable by ion exchange (Haber et al., 1995).

EXPERIMENTAL METHODS

This project is divided into three sections: section A gives the optimization of the silver loading in relation with the antibacterial activity; section B summarizes the investigation of the percentage of the natural zeolite clinoptilolite that can be put into the pot before it becomes weak; section C combines section A and section B, taking in account the optimum ratio of different materials used, to get the silver/zeolite nano composite-based clay pot filter. This deliverable will focus on sections A and B; section C will be part of our planned future work.

Section A: Silver Loading Optimization

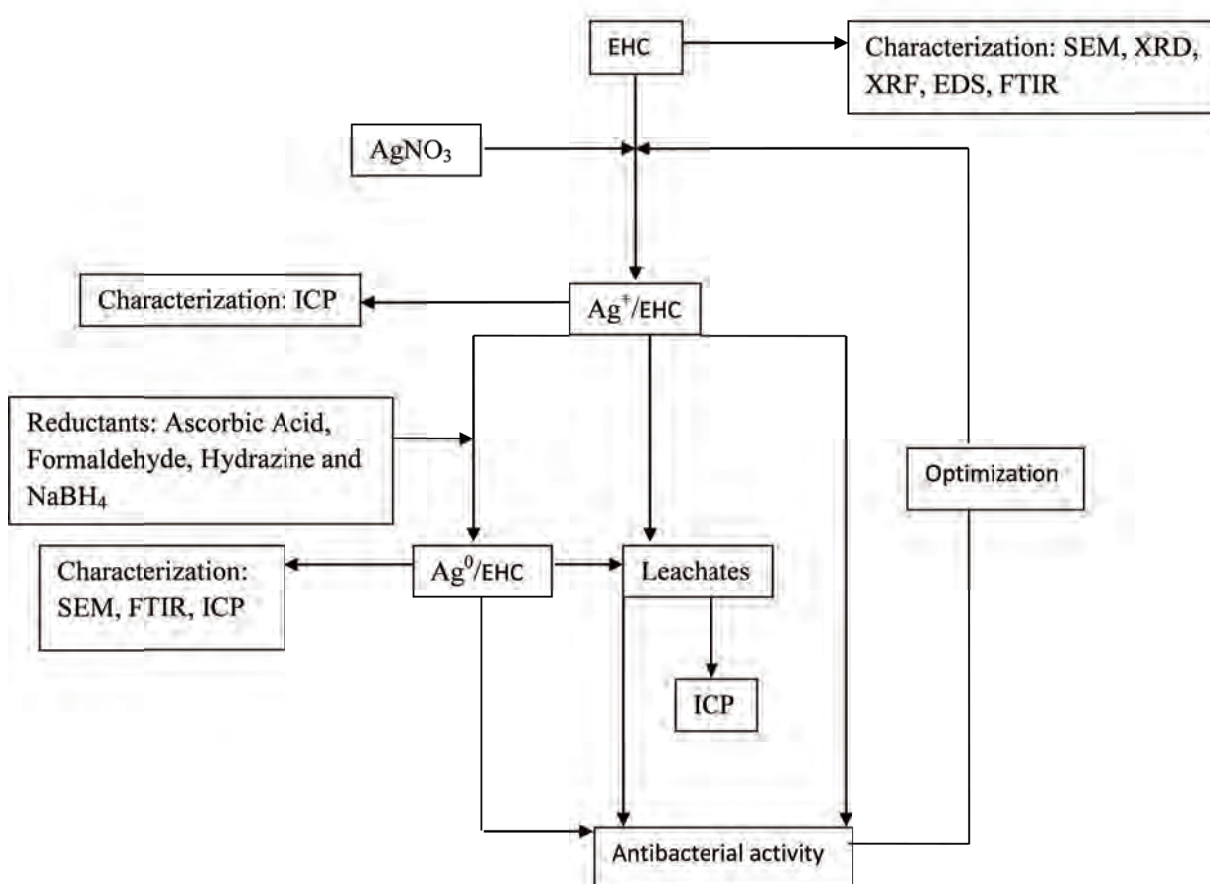


Figure 11: Diagram of different steps of the section A

In this section, the amount of loaded silver nanoparticles on the clinoptilolite (EHC in schematic) was investigated. The optimization of the silver loading in the clinoptilolite was investigated in relation to the antibacterial activity. The ion exchange and the wet impregnation process were compared to obtain the optimum concentration of silver loading on the clinoptilolite. The minimum amount of silver that has an antibacterial effect was investigated, before the loading processes were optimized.

Ion Exchange Process

Experiments

Two types of Ecce Holding clinoptilolites, the Hard Ecce Clinoptilolite (HEC) and the Soft Ecce Clinoptilolite (SEC), were used as silver carriers. To avoid or reduce cation competition while silver is loaded into the zeolite framework, HEC and SEC are pre-treated with HCl. Silver nitrate (AgNO_3) and sodium borohydride (NaBH_4) are used as silver precursor and reducing agent respectively in the case of the ion-exchanged materials.

Acid Pre-treatment of Clinoptilolites before the Silver Loading

Zeolites contain some cations such as Na^+ , K^+ , Mg^{2+} and Ca^{2+} , which can be in competition with Ag^+ during the loading process. In order to avoid this cationic competition, acid pretreatment was used to replace some of the exchangeable cations contained in the zeolite framework (Na^+ , K^+ , Mg^{2+} and Ca^{2+}) with H^+ to reduce the cation competition. 70 g of each zeolite (HEC or SEC) were treated with 750 mL of 1 M HCl for four (4) cycles under stirring condition, for 2 hours each cycle. Acid treated clinoptilolites (HECT and SECT) were washed with de-ionized water and centrifuged at 5000 RPM for 10 minutes. The measured pH values for the acid treated zeolite before and after rinsing with de-ionized water were between 0 and 4 respectively. All samples were oven dried overnight at 50°C . Four zeolite samples were used for the silver loading and were denoted as follows:

Untreated natural zeolites: Hard Ecce Holdings clinoptilolite sample (HEC), Soft Ecce Holdings clinoptilolite sample (SEC).

Acid treated zeolites: Hard Ecce Holdings clinoptilolite sample (HECT), Soft Ecce Holdings clinoptilolite sample (SECT).

Silver Loading

10 g of HEC, SEC, HECT and SECT were suspended in different volumes of 0.01 M of AgNO_3 . The calculated mass of silver to be loaded onto each zeolite sample (both treated and untreated) were 0.022 g, 0.031 g and 0.043 g of silver ions. Each mixture was stirred for 24 hours at room temperature to obtain the AgNO_3 /zeolite suspensions and to ensure the completion of the cation exchange process. 0.04 M of NaBH_4 was then added as reductant under continuous stirring to reach a constant AgNO_3 / NaBH_4 molar ratio of 1:4. The AgNO_3 / NaBH_4 mixture was contacted together for 1 hour. The obtained Ag/zeolite nano composites were washed with de-ionized water and dried overnight at 50°C (Shameli, 2011).

Silver Leaching

The leaching out of the silver into the water was investigated by shaking 2 g of each sample of Ag/zeolite nano composite in 20 mL of de-ionized water at a speed of 133 rpm and different duration of time for 10, 30 and 60 minutes interval. The Ag/zeolite mixture was filtered and the filtrate was analysed using ICP analytical technique to determine the amount of silver being leached.

Total acid Digestion of Zeolite

Total acid-digestion of the zeolite samples before and after silver loading was carried out in order to determine the total elemental composition present in HEC, HECT, SEC and SECT zeolites prior to the leaching experiment. 2 mL of concentrated hydrofluoric acid (HF) and 5 mL aqua regia were mixed with 0.25 g of zeolites in a Parr bomb at 200°C for 2 hours. The sample was allowed to cool after

which the excess HF in the digester was volatilized by the addition of 25 mL of saturated H₃BO₃ solution. The digestate was filtered through a 45 µm pore filter membrane and the solution was diluted to 50 mL with deionized water (Gitari et al., 2011).

Characterization Methods

Characterization refers to the use of techniques to investigate detailed structures and properties of a material. In this study, Scanning Electron Microscopy (SEM), Energy-Dispersive X-ray Spectroscopy (EDS), Fourier Transform Infrared Spectroscopy (FTIR), X-ray Fluorescence (XRF) and X-ray Powder Diffraction (XRD) were used to determine the surface morphology, mineral phases and crystalline structure as well as the functional group configuration of zeolite material. Other techniques employed include ICP-MS, ICP to determine the concentration of leached silver and the total amount of silver metal loaded into the zeolite framework.

Microbial Study

Six zeolite samples that had been loaded with silver (HEC+2.2 mg/g Ag; HEC+3.1 mg/g Ag; HEC+4.3 mg/g Ag; HECT+2.2 mg/g Ag; HECT+3.1 mg/g Ag and HECT+4.3 mg/g Ag) were tested for their antimicrobial activity on *E. coli* Epi 300. Two zeolite samples without silver loading (HEC and HECT) were used as negative controls. Three other controls, 1 µg/mL standard silver and two antibiotics (Erythromycin and Chloramphenicol), were used as positive standards in order to control the sensitivity of the bacteria. Tryptic Soy agar plates were used as media upon which the bacteria colonies were cultured (Shameli, 2011).

Sample preparation: 2 g of each sample was diluted in 20 mL of distilled water and the pH was measured. The diluted samples and the leachates (obtained in 8.1.1.1.3) were tested on *E. coli* Epi 300.

Medium preparation: Tryptic Soy agar medium was prepared by diluting 15 g of casein peptone, 5 g of soya peptone, 5 g of sodium chloride and 15 g of agar in 1 litre of distilled water. The pH of the solution was 7.3 at 25°C. The solution was sterilized in the autoclave at 121°C and 20 minutes. After cooling, the solution was poured into sterile petri dishes (Shameli, 2011).

Growth inhibition zones: 10 µL of *E. coli* was inoculated on the whole medium surface. A stain of 20 µL of each treatment (all samples as well as the 1 µg/mL standard silver solution respectively) was dropped on the central point of respective agar plates coated with the *E. coli* inoculums. The sterile paper disks impregnated with Erythromycin and Chloramphenicol were also placed as the separated control samples. The Tryptic Soy agar plates with bacterial suspension and the various treatments were sealed and incubated at 37°C overnight. After incubation, the diameter of the growth inhibition zones was measured. All tests were done in triplicate.

Investigation of the Antimicrobial Effect of Silver and Silver Nitrate

It was necessary to know the concentration of silver having an antibacterial effect before the loading process. This is why the standard silver solution and the silver nitrate at 5, 10, 20, 40, 80 and 160 µg/mL were tested on *E. coli* Epi 300; this was to obtain the minimum concentration of silver having an antibacterial activity. Two antibiotics (Erythromycin and Chloramphenicol) were used as positive standards in order to control the sensitivity of the bacteria. Tryptic Soy agar plates were used as mediums on which the bacteria colonies grew up.

Medium preparation: Tryptic Soy agar medium was prepared by diluting 15 g of casein peptone, 5 g of soya peptone, 5 g of sodium chloride and 15 g of agar in 1 litre of distilled water. The pH of the solution was 7.3 at 25°C. The solution was sterilized in the autoclave at 121°C and 20 min. After cooling, the solution was poured into sterile petri dishes (Shameli, 2011).

Growth inhibition zones: 10 µL of *E. coli* Epi 300 were spread on the whole medium surface. A stain of 20 µL of each treatment was dropped on the central point of an agar plate coated with the *E. coli* Epi 300. The two antibiotics were also placed on the surface of agar plate coated with *E. coli* Epi 300. The Tryptic Soy agar plates with bacterial suspension and the various treatments were sealed and incubated at 37°C overnight. After incubation, the diameter of the growth inhibition zones was investigated.

Silver Loading

The volume of the solution required was empirically determined to correspond to that beyond which the catalyst begins to look wet. The quantity of water to wet the clinoptilolite was measured using a burette (Kasongo, 2011). The clinoptilolite pore volume was 0.5 mL/g.

Ten grammes of Ecce Holding Clinoptilolite (HEC) were soaked with 5 mL of silver nitrate solution at different concentrations (0.01; 0.10; 1.00 and 2.00 mol/L). After being well mixed during a few minutes, the slurry obtained was oven dried at 70°C and crushed once dry. The silver ions were reduced on the clinoptilolite by adding 5 mL of a solution of reductant (ascorbic acid, formaldehyde, hydrazine monohydrate or sodium borohydride respectively) to reach a constant AgNO₃/reductant molar ratio of 1:2. The reduced silver/c clinoptilolite nano composite obtained was oven dried at 70°C and crushed.

Silver Leaching

The leaching out of the silver into water was investigated by shaking 2 g of each sample of Ag/zeolite nano composite in 20 mL of deionized water three times, during 30 minutes per run, at a speed of 133 rpm. The suspended mixture was filtered using a 0.45 µm membrane filter. The filtrates were analysed using the ICP analytical technique to determine the amount of silver being leached out into the water.

Antibacterial Activity

2 g of each sample was diluted in 20 mL of distilled water. The mixture obtained and the leachates were tested on *E. coli* Epi 300 following the method described above.

RESULTS AND DISCUSSION

Characterization

Fourier Transform Infra-Red Spectroscopy (FTIR)

Figure 12 compares the FT-IR spectra of HEC and HECT (A), SEC and SECT (B) at the range of wave numbers between 350 and 4000 cm^{-1} .

During the silver loading process of the treated zeolites (HECT and SECT), Ag^+ is only in competition with H^+ while it is in competition with Na^+ , K^+ , Ca^{2+} and Mg^{2+} during the silver loading process of the untreated zeolites (HEC and SEC); the acid pre-treatment could be an important step in the process to improve the amount of loaded silver. Apart from removing the charge balancing Group I and Group II cations (Na^+ , K^+ , Mg^{2+} , Ca^{2+}) from the porous structure of the zeolite, acid washing with HCl can cause dealumination of the zeolite (Van Bekkum, 2007).

Figure 12 shows that there is little difference between the peaks of treated zeolites (HECT and SECT) and untreated zeolites (HEC and SEC); this means the acid treatment did not destroy the zeolite composition and structure.

X-ray Powder Diffraction (XRD)

The increase of Si/Al ratio would lead to the decrease of the cation concentration and the ion exchange capacity (proportional to aluminium content). The typical Si/Al molar ratio for clinoptilolite is 2:5 (Van Bekkum, 2007). The quantitative XRD data shows that the percentage of the clinoptilolite mineral phase is greater in the HEC than in the SEC and the percentage of the quartz (SiO_2) is greater in the SEC than in the HEC (Figure 13); that means the Si/Al molar ratio is higher in the SEC than in the HEC and the HEC should have the best ion exchange capacity and the greatest cation capacity of the two natural zeolites.

Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray Spectroscopy (EDS)

Figure 14 shows the aggregated morphology of particles of the hard Eccla clinoptilolite (HEC) before and after the acid pretreatment for illustrative purposes. The EDS analysis graphs below show the effects of acid treatment; cations such as Na^+ and Mg^{2+} were removed and the quantities of K^+ and Ca^{2+} decreased after acid treatment.

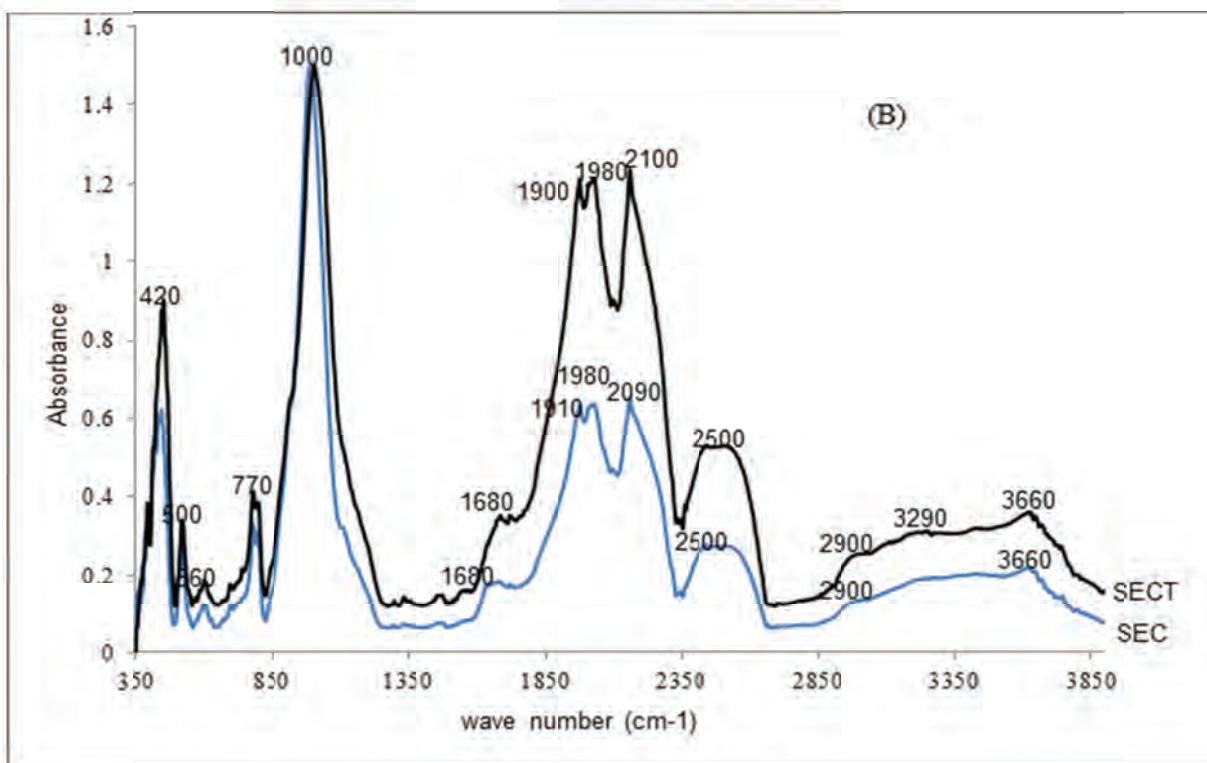
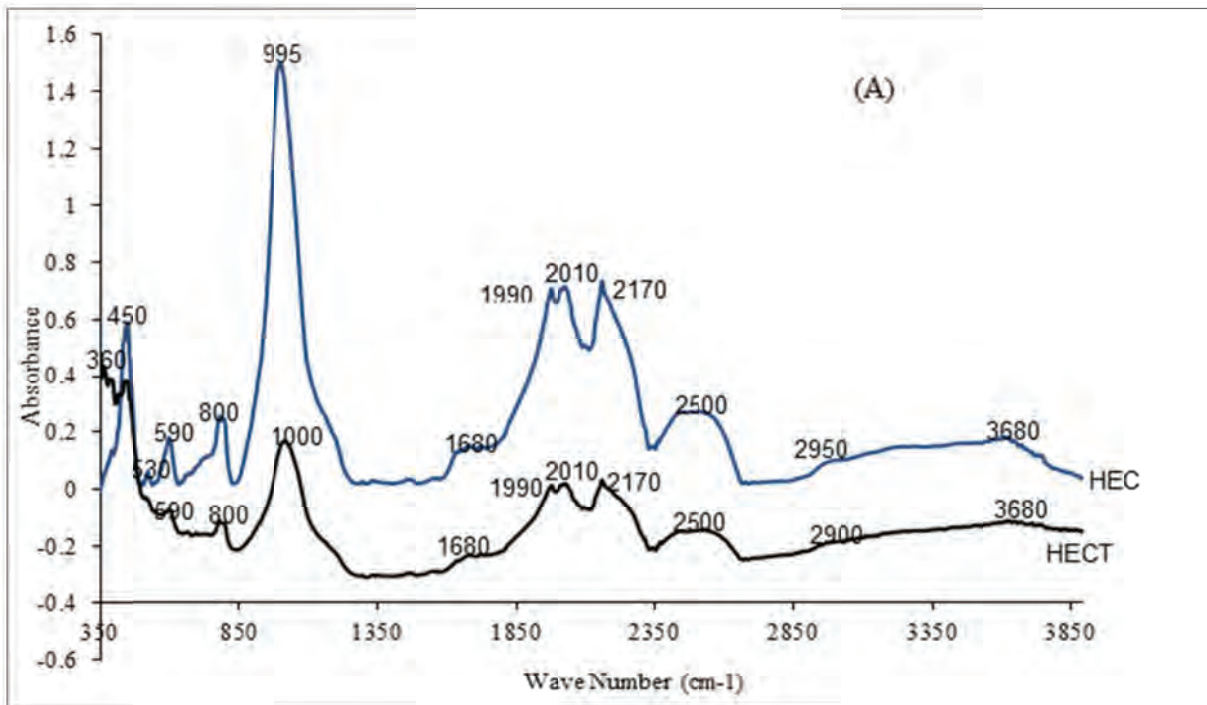


Figure 12: Comparison of FT-IR spectra HEC and HECT (A), SEC and SECT (B)

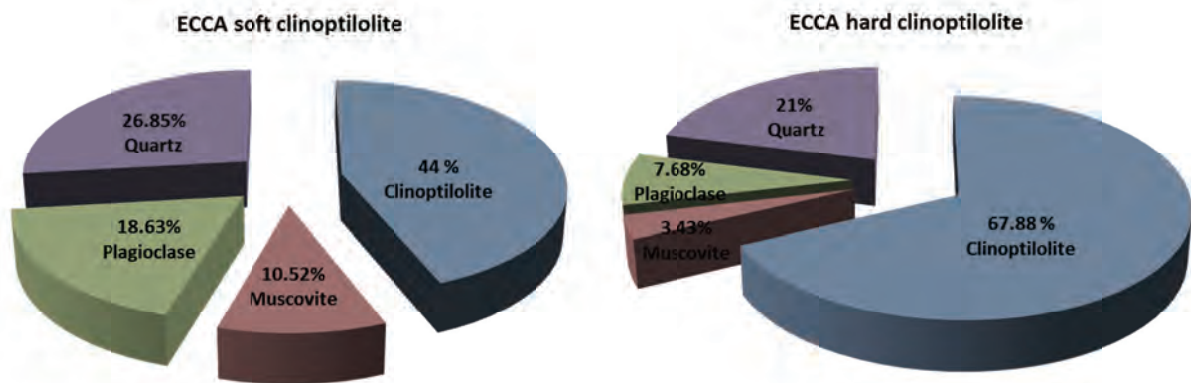


Figure 13: Quantitative X-Ray Diffraction data for SEC and HEC samples

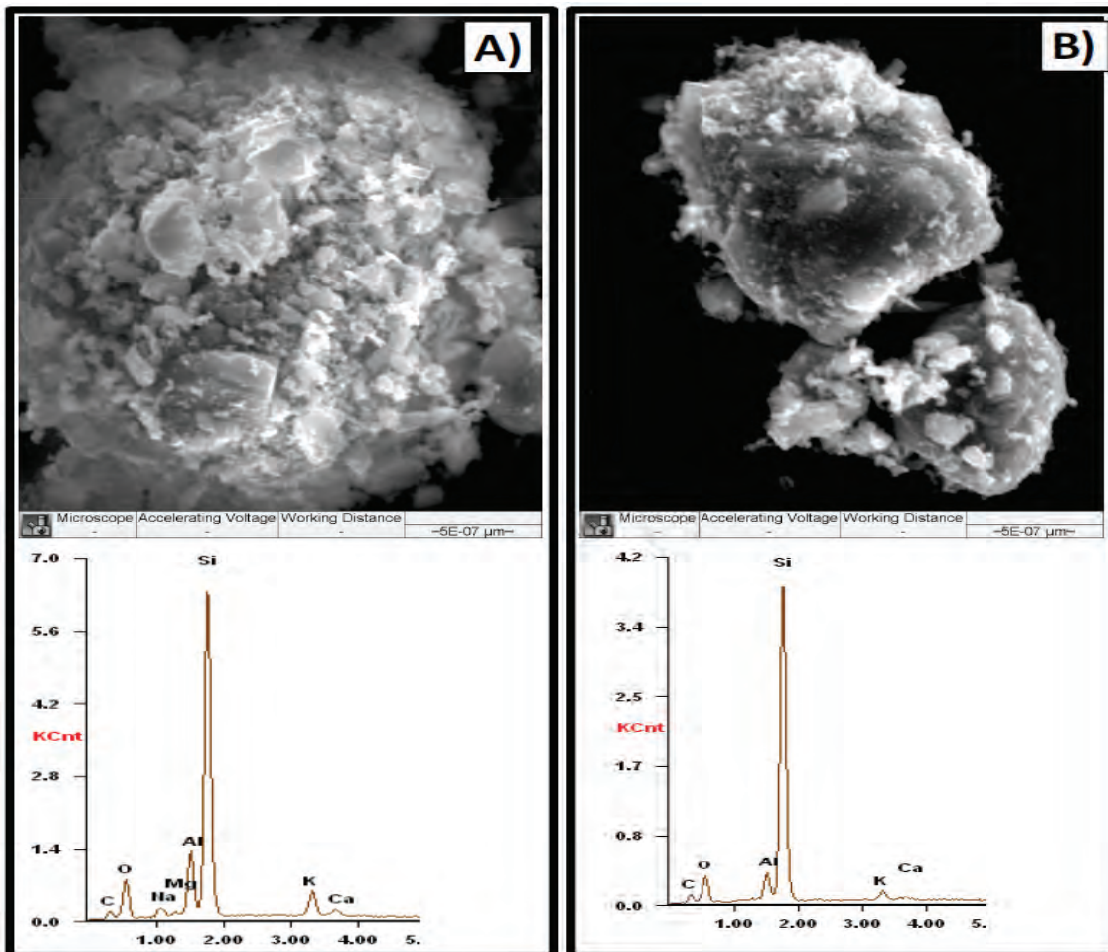


Figure 14: SEM-EDS of the Hard Ecce Clinoptilolites before (A) and after (B) acid treatment

A similar morphology was observed for all the zeolite samples used. A full quantitative characterization of these natural zeolite materials is given in Petrik and Ndungu (2012).

Table 5: EDS results of HEC, SEC, SECT and HECT

Sample	Na %	K %	Ca %	Mg %
HEC	2.42±0.03	4.15±0.30	1.00±0.04	0.87±0.02
HECT	ND	4.09±0.2	0.97±0.02	ND
SEC	1.81±0.05	2.75±0.6	0.88±0.07	1.53±0.04
SECT	ND	2.68±0.10	0.76±0.08	0.02±0.001

ND = Not detected

As shown in the Table 5, the acid pre-treatment effectively removed Na⁺ and Mg²⁺ cations from the matrix of the natural zeolite but did not remove K⁺ and Ca²⁺ from the exchange sites. Na⁺ and Mg²⁺ could be more easily removed from the HEC sample than from the SEC sample. The cation competition should be less in the HECT than in the SECT and the amount of the loaded silver should therefore be higher in the HECT than in the SECT.

X-ray Fluorescence (XRF)

X-ray fluorescence (XRF) analysis for major oxides in wt % for soft and hard ECCA Holdings samples was done in triplicate and the results are summarized in Table 6.

The major elements comprising the zeolite are Si, Al, Group I and II cations, and iron. It is noticeable that the Na content is the highest of the charge balancing cations present in the soft and hard samples (Table 6); while the EDS analysis shows that the amount of K is the highest. The EDS analyses is only determining the composition of a very small area of each sample while the XRF analyzes the entire sample; the results obtained by XRF are thus much more accurate than those obtained by EDS. The loss on ignition (LOI) is an indirect measure of the void volume of the zeolite indicating the relatively high porosity and water retention capacities of the zeolite samples. The HEC sample had a higher LOI than the SEC sample which corresponds to the relative amount of the clinoptilolite mineral phase as was determined by XRD, which analysis had showed that the hard sample had a higher amount of the zeolite phase present. These results show the relative inhomogeneity of the mineral deposit being mined as both the soft and hard sample were obtained from the same deposit. The trace elements are shown in Table 7.

Trace element analysis showed that there was a considerable amount of Ba, Sr as well as traces of many other toxic elements present in the as received mineral samples. Hence, confirming the need to thoroughly acid wash and remove soluble trace elements from these natural minerals to remove most leachable species prior to its use in a water filtration system.

Table 6: Elemental composition of the natural zeolite samples (major elements)

Sample	SEC %	HEC %
SiO ₂	66.519	71.762
TiO ₂	0.152	0.091
Al ₂ O ₃	12.323	10.187
Fe ₂ O ₃	1.471	0.325
MnO	0.004	0.010
MgO	1.466	0.568
CaO	0.975	0.848
Na ₂ O	2.175	2.506
K ₂ O	1.714	2.391
P ₂ O ₅	0.034	0.024
SO ₃	0.264	0.114
Cr ₂ O ₃	0.003	0.001
NiO	0.001	0.001
H ₂ O	5.788	2.650
LOI	6.674	8.291
Total	99.562	99.771

Inductively Coupled Plasma (ICP)

The silver/clinoptilolite nano-composites were analysed by ICP after digestion to determine the concentration of the silver nanoparticles loaded into the clinoptilolite framework. ICP analysis was also used to determine the concentration of silver leached out into the water. Table 8 summarizes the results of the metal loading onto the zeolite by ion exchange and the degree of leaching of the silver, and gives the concentration of silver loaded and leached out per g of zeolite. However, it is not certain at this point that the ICP data is fully replicable due to matrix effects in a high matrix environment such as occurs when a solid containing a high Si and Al content is digested and analysed by this technique and thus the µg/ml silver incorporated into the zeolite is not certain. ICP analysis of the leachates after leaching with water is more certain since the matrix is not present.

Table 7: Elemental composition of the natural zeolite samples (trace elements)

Trace elements	SEC (ppm)	HEC (ppm)
Mo	0.000	0.000
Nb	14.765	14.580
Zr	129.185	150.430
Y	19.310	18.085
Sr	908.655	559.015
Rb	37.280	27.920
U	7.820	4.180
Th	12.810	18.235
Pb	21.215	22.850
Zn	29.596	31.394
Cu	1.114	0.000
Ni	0.000	0.000
Co	0.000	0.000
Mn	180.470	38.934
Cr	27.641	21.194
V	13.578	6.387
Sc	8.061	4.127
Ba	2506.454	2711.833
S	497.825	676.042

According to Table 8, it was not possible to load all the silver onto the zeolites by ion-exchange and loading trends were inconsistent. Table 8 shows that levels of silver in leachates from silver loaded zeolites ranged between 0.01 to 0.1 µg/mL of leachate depending on the contact time.

Table 8 and Figure 15 show that silver has successfully been loaded into the zeolites; but the loading % results were inconsistent when using the ion-exchange method. Moreover a significant spread is observed in the data obtained from the ICP analysis following digestion of the solid material after silver loading, which indicates that the ion exchange procedure is problematic in terms of obtaining a specified metal loading or that the analysis is not trustworthy due to matrix effects that are problematic when doing ICP analysis of digested solids. However, in general, the silver content is higher in the acid pre-treated zeolites (HECT and SECT) than in the untreated zeolites (HEC and SEC); this could be because there is less competitive adsorption occurring during ion exchange with the acid pre-treated zeolites than was the case for the untreated zeolites. The Hard Ecça Clinoptilolite acid treated (HECT) sample generally presents the highest results in term of the amount of silver that could be loaded under

the applied conditions. ICP analysis could not confirm whether the silver is in the zeolite framework or on the surface.

Table 8: Concentrations of silver loaded and leached out per g of clinoptilolite

Sample	Mass of silver loaded per g of zeolite (mg/g)	Concentration of silver in zeolite samples by ICP ($\mu\text{g/mL}$)	Concentration of silver leached out into water by ICP ($\mu\text{g/mL}$)		
			10 min leach time	30 min leach time	60 min leach time
HEC	2.2	0.8232	0.052	0.0475	0.0697
	3.1	0.1832	0.1164	0.1146	0.1639
	4.3	0.9324	0.1769	0.1814	0.2058
HECT	2.2	2.4864	0.0119	0.0145	0.0149
	3.1	1.3996	0.1634	0.029	0.0379
	4.3	21.6732	0.0186	0.0224	0.0222
SEC	2.2	0.3704	0.0306	0.0186	0.0326
	3.1	0.4868	0.0623	0.047	0.0469
	4.3	1.0412	0.0695	0.07	0.0586
SECT	2.2	1.6048	0.047	0.0686	0.0958
	3.1	1.486	0.0684	0.1311	0.1101
	4.3	0.4408	0.1157	0.105	0.112

The leachates were analysed by ICP. Leaching (%) of silver from the zeolite on the base of the mass of silver actually loaded is shown in Figure 16.

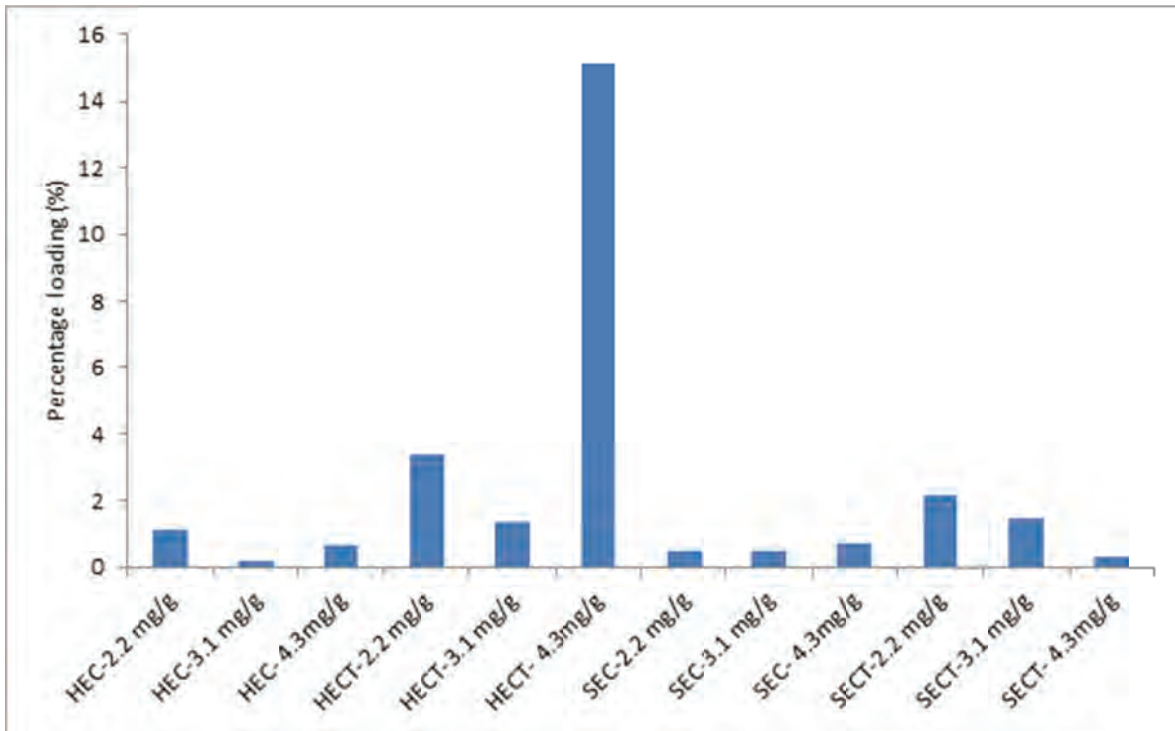


Figure 15: Actual loading (%) of silver as determined by ICP obtained in various zeolite samples on the base of the mass of silver loaded by ionexchange

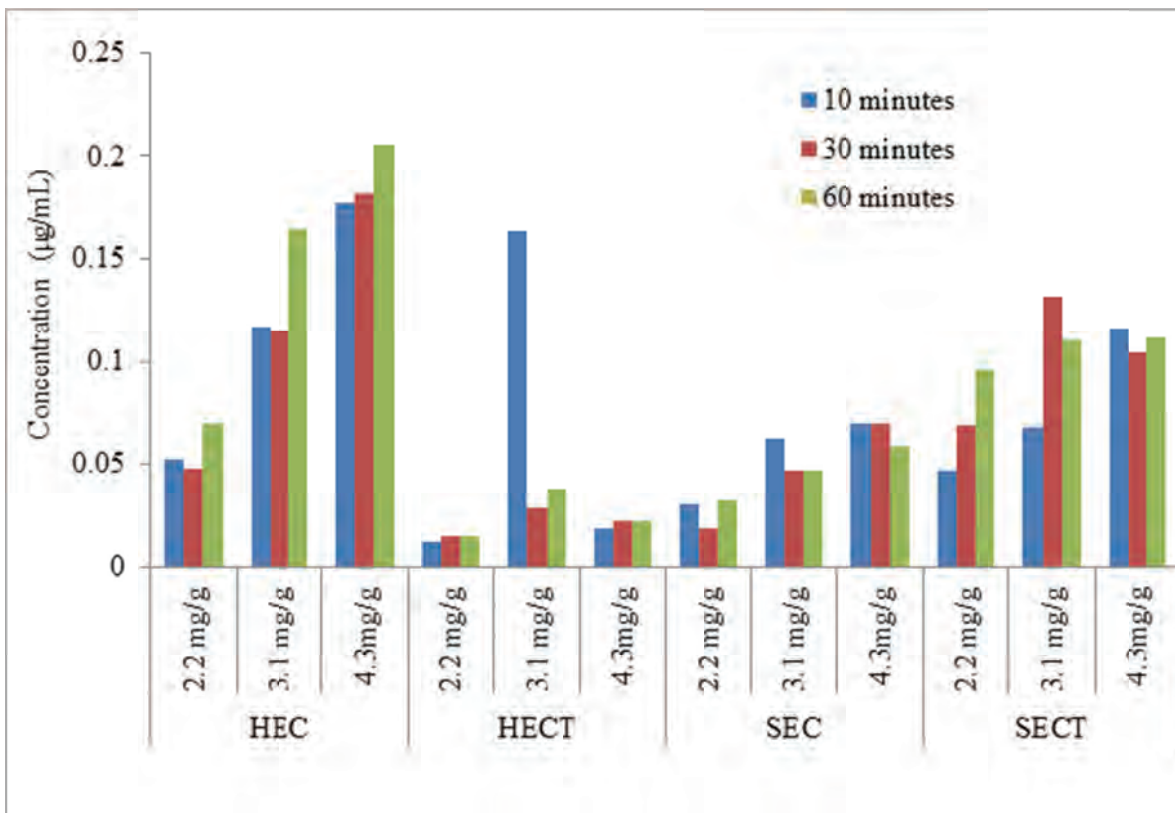


Figure 16: Level of silver in leachate (in µg/mL) from the zeolite on the base of the mass of silver theoretically loaded

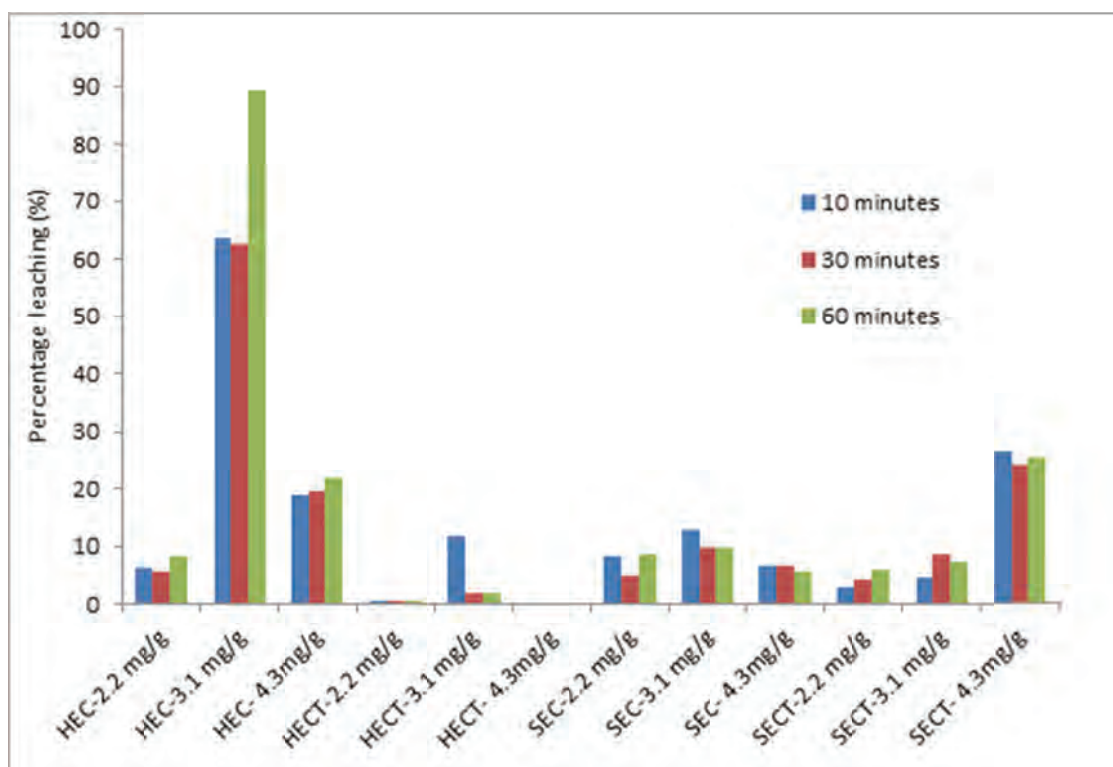


Figure 17: Leaching (%) of silver from the zeolite on the base of the mass of silver actually loaded as determined by digestion of the solid and ICP analysis

Silver levels detected in leachates from the zeolites ranged from 0.02 $\mu\text{g/mL}$. Figure 16 and Figure 17 show that the leaching was greatest from the Ecca Hard zeolite samples that had not been pre-treated with acid for all leaching times applied, whereas in the case of the HECT sample very low silver leaching was generally observed. On the other hand the SEC zeolite sample showed an inconclusive trend with the leaching % at nearly similar levels for both treated and untreated zeolite. Leaching for specific times, e.g. 30 minutes showed a correlation (Figure 16) with the amount (in $\mu\text{g/ml}$) of silver leached compared to the theoretical amount of silver loaded, with the higher loadings leaching more silver than the lower loadings. This trend is not obvious when the leaching is corrected according to the ICP data (Figure 17), giving the elemental analysis of the silver actually loaded. However, due to matrix effects caused in the flame during ICP analysis of the zeolite that was digested, the ICP data is not certain and currently the digestion and re-analysis of these samples are underway. The solids will also be re-analysed by XRF to ensure that matrix effects do not result in errors of analysis. In WRC Project No. K5/1897 it has been clearly demonstrated that removal of the charge balancing cations from natural clinoptilolite was a very complex procedure, requiring exhaustive exchange (up to 23 extractions with HCl acid) to remove all exchangeable cations and it is therefore postulated that the conditions applied to exchange out the charge balancing cations before silver loading in this study was not yet achieved at the optimum conditions.

Antimicrobial Activity

Figure 18 shows selected examples of the various treatment options using ion-exchange: the leached samples (A), the diluted samples (B), the 1 $\mu\text{g/mL}$ standard silver (C), and the two antibiotics (D), on

E. coli. The results demonstrated that only the two control samples (D) with the antibiotics, Erythromycin (3.00 ± 1.00 mm) and Chloramphenicol (13.67 ± 1.16 mm) placed upon the bacterial inoculums, had an antibacterial inhibitory effect, which confirmed that the bacteria used as inoculums were sensitive to the inhibition of the antibiotics as expected. The antibacterial effect of silver is well known (Shameli et al., 2011); therefore the lack of any inhibitory effect on the microbes by inoculums of $1 \mu\text{g/mL}$ of the standard silver inoculums demonstrated that the $1 \mu\text{g/mL}$ silver concentration was too low to have an inhibitory effect during the time of the experiment (overnight). The same was observed in the case of the diluted and leached samples, thus it is evident that the amount of silver available for inhibition of microbes in the prepared zeolite samples or their leachates was too low to kill the bacteria. Moreover this study showed that silver in leachates from ion-exchanged zeolites ranged between 0.01 to 0.1 $\mu\text{g/mL}$ of leachate, depending upon leaching time and silver loading, which was an order of magnitude lower silver concentration than needed for inhibition to occur.

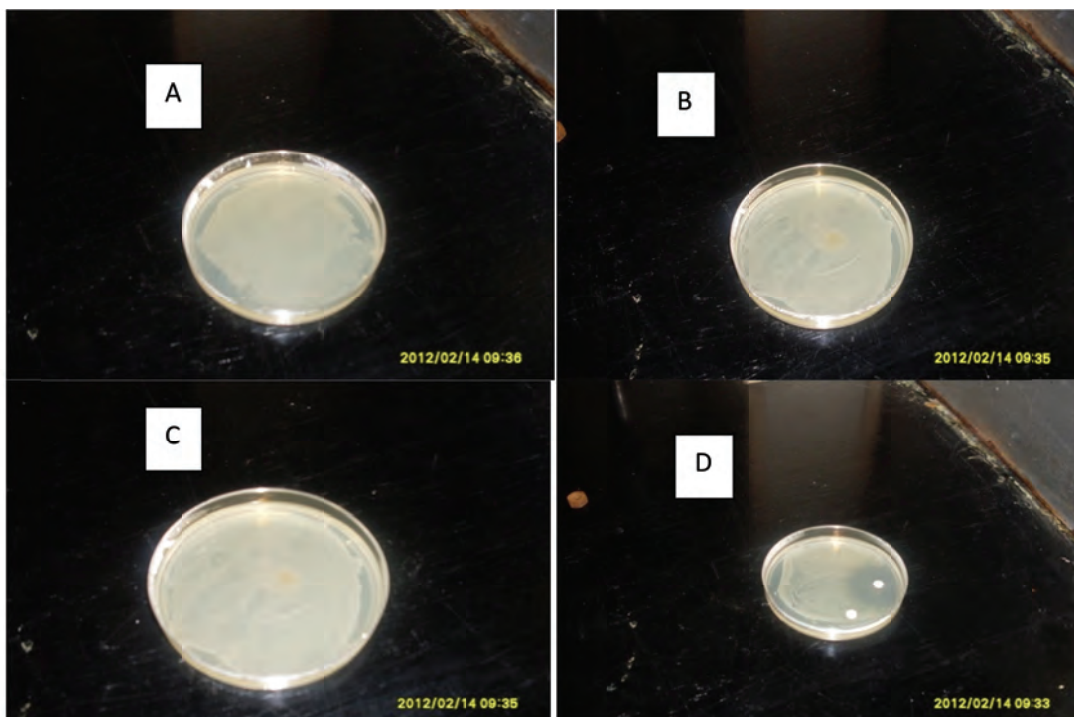


Figure 18: Comparison of the inhibition zone between the leached samples (A), the diluted samples (B), the $1 \mu\text{g/mL}$ standard silver (C) and the two antibiotics(D) on *E. coli*

According to Shameli (2011), the silver/zeolite nano-composites had an antibacterial effect. In that investigation, the amounts of silver per g of zeolite used (5; 10; 15; 20 and 50 mg/g of Ag per zeolite) was greater than what was used in this study (2.2; 3.1 and 4.3 mg/g of Ag per zeolite). Silver in leachates ranged between 0.01 to 0.1 $\mu\text{g/mL}$ of leachate, depending upon leaching time and silver loading. The commercial Na^+ -Y-zeolite powder $\leq 45 \mu\text{m}$ was used in their study while in this study the untreated and acid treated samples of natural Hard and Soft Ecca Clinoptilolite powders with a particle size $< 125 \mu\text{m}$ were used. A larger particle size would have an effect on the diffusional rate of silver out of the zeolite matrix and could have slowed leaching down. Moreover, the difference in silver loading could explain why the treatments used in this study did not have the expected antibacterial effect. Further experiments should be designed to mitigate these nuisance variables such as particle size.

Wet Impregnation Process

The concentration of silver loaded by ion exchange was too low (average of 1 µg/mL) to have an antimicrobial effect on *E. coli* Epi 300. The wet impregnation technique was therefore used to optimize the silver loading into the zeolite. According to Kasongo (2011), the wet impregnation is employed when the quantity of metal ion to be introduced into the support substrate is greater than would be obtainable by ion exchange. The volume of the solution required is empirically determined to correspond to that beyond which the catalyst begins to look wet.

As is shown in Figure 13, the HEC sample contained a higher percentage of clinoptilolite than SEC and HEC showed better results than SEC in term of loading and leaching (Figure 15 and Figure 16). This is why the HEC sample was used as silver carrier to optimize the silver loading by wet impregnation. Four reducing agents (ascorbic acid, formaldehyde, hydrazine monohydrate and sodium borohydride) with different reduction power are used to reduce the silver ions onto the HEC. This was to investigate the influence of the reducing agent on the silver leaching and the antimicrobial activities.

Investigation of the Antimicrobial Effect of Silver and Silver Nitrate

The concentrations of the silver loaded into the zeolites framework by ion exchange were too low to inhibit the bacterial growth. The wet impregnation method was therefore used to optimize the silver loading; but the concentration of silver which had an antibacterial effect was firstly investigated.

The standard silver and the silver nitrate at 5, 10, 20, 40, 80 and 160 µg/mL were tested on *E. coli* Epi 300. Table 9 summarizes the concentrations of the standard silver and the silver nitrate that have an inhibitory effect on *E. coli* Epi 300. Figure 19 shows how the treatments worked on *E. coli* Epi 300.

Table 9: The inhibitory effects of the standard silver and the silver nitrate on *E. coli* Epi 300

Concentration (µg/mL)	Standard silver	Silver nitrate
5	-	-
10	-	-
20	-	±
40	±	++
80	++	+++
160	++	+++

(-): No inhibitory effect; (+): Inhibitory effect.

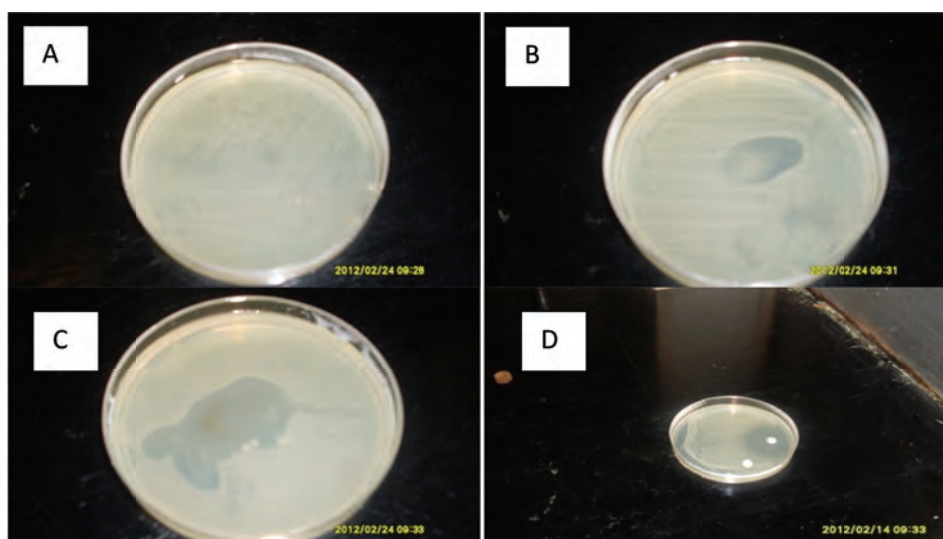


Figure 19: Inhibitory zones of standard silver and silver nitrate on *E. coli* Epi 300 at 10µg/mL (A), 40 µg/mL (B), 160 µg/mL (C) and the inhibitory zone of the positive controls (Erythromycin and Chloramphenicol) on *E. coli* (D)

Table 9 shows that the inhibitory effect of the silver nitrate starts at 20 µg/mL while the inhibitory effect of the standard silver starts at 40 µg/mL. At the same concentration silver nitrate is more effective than standard silver. According to Panyala et al. (2008), the silver nanoparticles, in higher concentrations than 44 µg/mL, are necrotic to cells; leading to rapid mammal cell membrane rupture. Our results indicate that the silver has the same effect on the bacterial walls at similar concentrations.

Silver Loading

The wet impregnation method was used to optimize the silver loading. Compared to the ion exchange method, wet impregnation was employed to load a greater amount of the Ag metal nanoparticles upon the zeolite, but the uniform distribution and the incorporation of the silver ions into the clinoptilolite framework are not guaranteed because the silver can accumulate on the external surface. 10 g of HEC were soaked with 5 mL of silver nitrate solution at different concentrations and the masses of silver ions loaded were 0.53935; 5.3935; 53.935 and 107.87 mg per gram of clinoptilolite. The silver ions were reduced on the clinoptilolite by 5 mL of the solution of the reducing agent (ascorbic acid, formaldehyde, hydrazine monohydrate or sodium borohydride) at the molar ratio Ag/reducing agent of 1:2.

Shameli (2011) used sodium borohydride (strong reducing agent) to reduce silver ions on the zeolite. According to Songping (2005), the reducing agent should have a weak or a middle reduction power to obtain mono-dispersed, non-agglomerated silver nanoparticles. The antibacterial effect of the silver nanoparticles depends on their size; the smaller the silver nanoparticles are, the more easily they reach the nuclear content of bacteria and bind with the bacterial DNA (Shameli, 2011). The influence of the reducing agent on the silver nanoparticles size was investigated using reducing agents with different reduction power (ascorbic acid, formaldehyde, hydrazine monohydrate or sodium borohydride). The effect of the different reducing agents on the colour of the silver-clinoptilolite was shown in Figure 20 below.

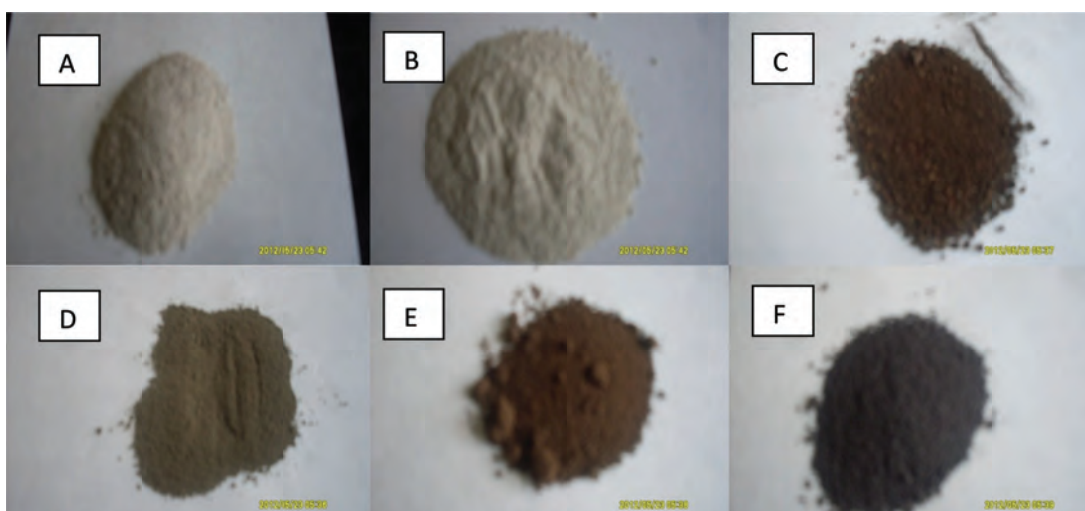


Figure 20: Photos of reduced silver zeolite composite; A = HEC, B = HEC + AgNO₃, C = HEC + AgNO₃ + Ascorbic acid, D = HEC + AgNO₃ + hydrazine, E = HEC + AgNO₃ + Sodium borohydride, F = HEC + AgNO₃ + Formaldehyde

The Ecce Holding Clinoptilolite is plastic when moist because of its high clay content. During the experiment, it was noticed that the clinoptilolite lost its plasticity after being reduced by strong reducing agents (formaldehyde, hydrazine or sodium borohydride) at high concentration. This could indicate that strong reducing agents modified the aluminosilicate structure. Those modifications were investigated by comparing the chemical bonds (Figure 21) and the crystal morphology (Figure 22) of the HEC before and after the loading and reduction with ascorbic acid, a weaker reductant.

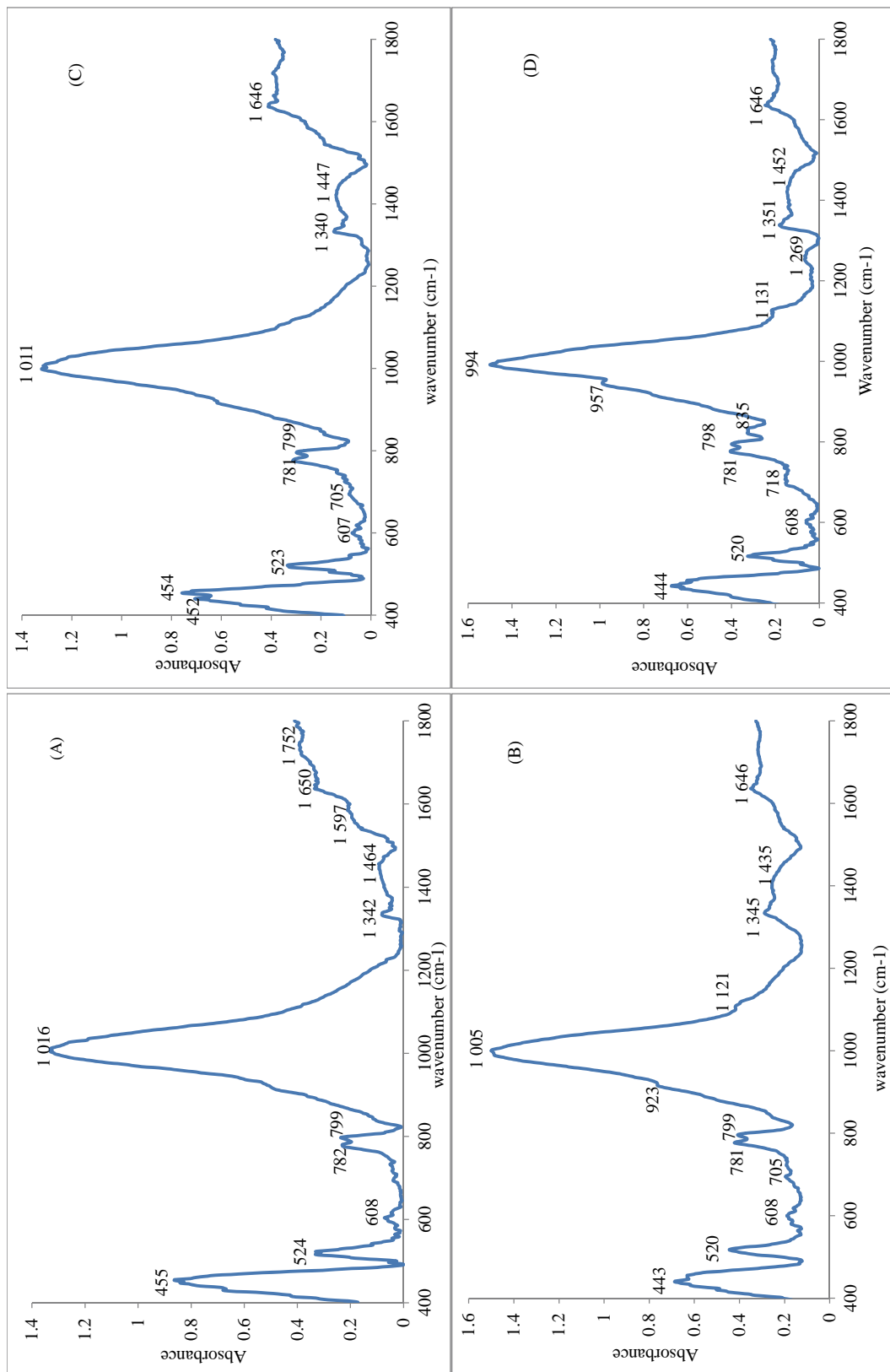


Figure 21: Comparison of FTIR of HEC (A), HEC+2 M AgNO₃ (B), HEC+2 M AgNO₃+Asc.Ac. (C), HEC+2 M AgNO₃+NaBH₄ (D)

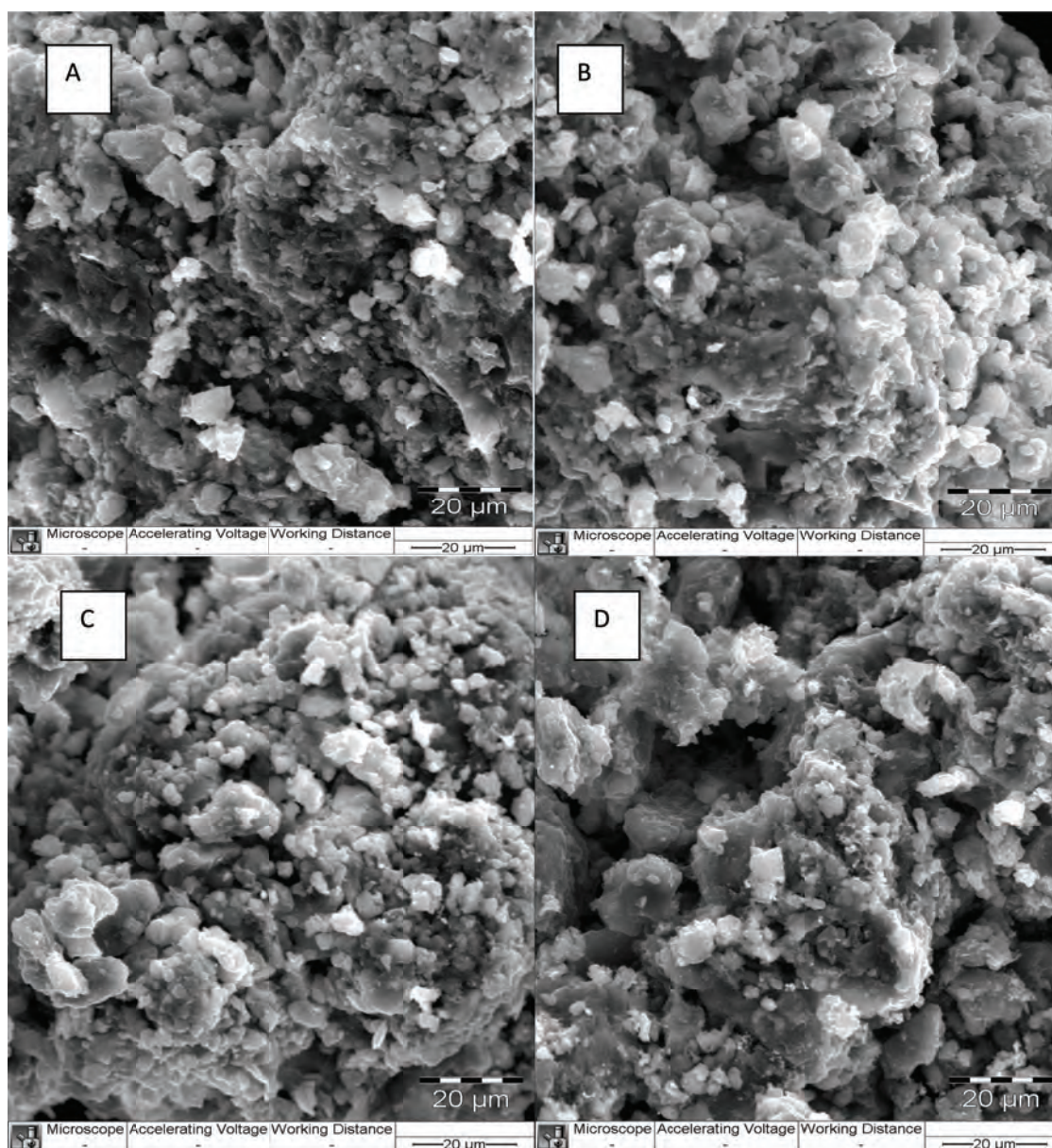


Figure 22: Morphology of crystals of EHC (A), EHC+ 2 M AgNO₃ (B), EHC+ 2 M AgNO₃+Asc ac. (C), EHC+ 2 M AgNO₃+NaBH₄ (D)

Scanning electron microscopy does not show any morphologic change after the silver loading and reduction. FTIR shows that there is no change to the characteristic peaks of aluminosilicates (between 440 and 800 cm^{-1} , and around 1000 cm^{-1}). There is a modification of peaks between 1345 and 1435 cm^{-1} due to the silver loading on the clinoptilolite. The reduction with the ascorbic acid did not modify the zeolitic structure, but the sodium borohydride reductant did, with appearance of peaks at 835, 957, 1131 and 1269 cm^{-1} indicating amorphous material. The peak at 1011 cm^{-1} shifted to 994 cm^{-1} due to the reduction with sodium borohydride. Shameli (2011) did not mention modifications caused by sodium borohydride. In their study reduction was done in the aqueous solution; while it was done on the dry Ag/c clinoptilolite in our study showing the modification of the zeolitic structure.

Silver Leaching

2 g of each sample (silver loaded or not) were suspended in 20 mL of distilled water. The mixture was shaken, during 30 minutes per each run (three replicates), at 133 RPM. After filtering, the leachates were analysed by ICP to investigate the concentration of silver that leached out in the extracted water (Table 10). The concentrations of silver ions applied to the Ag/clinoptilolite were 53.935; 539.35; 5393.5 and 10787 $\mu\text{g/mL}$ respectively.

Table 10: Concentration of silver leached out into the water

Sample	Time (min)	Concentration of silver ($\mu\text{g/mL}$)			
		53.935	539.35	5393.5	10787
Non-reduced Ag-clinoptilolite:	30	0.073 \pm 0.042	0.298 \pm 0.037	309.982 \pm 6.371	562.368 \pm 5.133
	60	0.065 \pm 0.010	0.411 \pm 0.115	146.947 \pm 4.898	242.290 \pm 7.483
	90	0.096 \pm 0.053	0.656 \pm 0.204	31.725 \pm 3.867	68.201 \pm 2.604
Ag-clinoptilolite reduced with;					
Ascorbic acid	30	0.157 \pm 0.096	0.028 \pm 0.013	0.013 \pm 0.007	0.015 \pm 0.005
	60	0.237 \pm 0.198	0.071 \pm 0.081	1.713 \pm 0.029	19.430 \pm 4.647
	90	0.133 \pm 0.058	0.688 \pm 0.059	4.013 \pm 0.619	23.282 \pm 3.063
Formaldehyde	30	0.085 \pm 0.120	0.246 \pm 0.221	35.798 \pm 2.364	50.084 \pm 3.171
	60	0.088 \pm 0.056	0.875 \pm 0.270	31.349 \pm 4.967	19.933 \pm 1.262
	90	0.032 \pm 0.046	0.580 \pm 0.056	10.115 \pm 0.295	13.523 \pm 4.892
Hydrazine monohydrate	30	0.021 \pm 0.029	0.280 \pm 0.010	0.058 \pm 0.036	0.0063 \pm 0.004
	60	0.024 \pm 0.035	0.098 \pm 0.020	1.724 \pm 1.114	0.224 \pm 0.068
	90	0.043 \pm 0.000	0.535 \pm 0.047	1.452 \pm 1.191	0.291 \pm 0.119
Sodium borohydride	30	0.024 \pm 0.033	0.051 \pm 0.034	0.025 \pm 0.035	0.306 \pm 0.191
	60	0.022 \pm 0.031	0.190 \pm 0.102	0.488 \pm 0.044	0.808 \pm 0.324
	90	0.019 \pm 0.007	0.418 \pm 0.031	2.091 \pm 0.315	2.050 \pm 0.416

Table 10 shows that only small quantities of silver leached out into the water during leaching studies of the wet impregnated samples. Figure 23 demonstrates that the percentage of silver leached out is much greater in the non-reduced wet impregnated Ag/clinoptilolite sample, of which 5.2% was observed to leach depending on the starting loading used, compared to that of the reduced samples where less than 1% of the silver leached out per run. This could be because the silver ion does not bond well to the zeolite substrate and is easily dissolved while the reduced silver is properly supported upon the zeolite matrix and is not soluble. The exact mechanism of disinfection will require further investigation.

In the non-reduced Ag/clinoptilolite, the concentration of the leached silver ions decreased from the first leachate run to the third one. There was not much change in the amount of silver ions leached out into the solution per run at low concentrations of silver ions (53.935 and 539.35 $\mu\text{g/mL}$). At those

concentrations, silver ions are well bound to the clinoptilolite. At high concentrations (5393.5 and 10787 $\mu\text{g/mL}$), there is an excess of silver ions which is not well bonded to the clinoptilolite. The excess of silver ions could be held inside the pores or just on the surface and was easily leached with water.

The concentration of silver leached out was very low for the reduced Ag/c clinoptilolite samples, even when the concentration of silver nanoparticles on the clinoptilolite was high (5393.5 and 10787 $\mu\text{g/mL}$). The concentration of the leached silver was not proportional to the concentration of the silver on the clinoptilolite and the concentration of the silver leached out did not change much from the first leachate run to the third one, except for the formaldehyde samples (Figure 23). The reduced silver nanoparticles were found to stay on the clinoptilolite much longer than the silver ion. From these results, it can be foreseen that the reduced silver on the clinoptilolite will be effective for a longer time, while the unreduced silver ion will have a short efficiency. Figure 24 gives the variation of the concentration of silver on the clinoptilolite after each run.

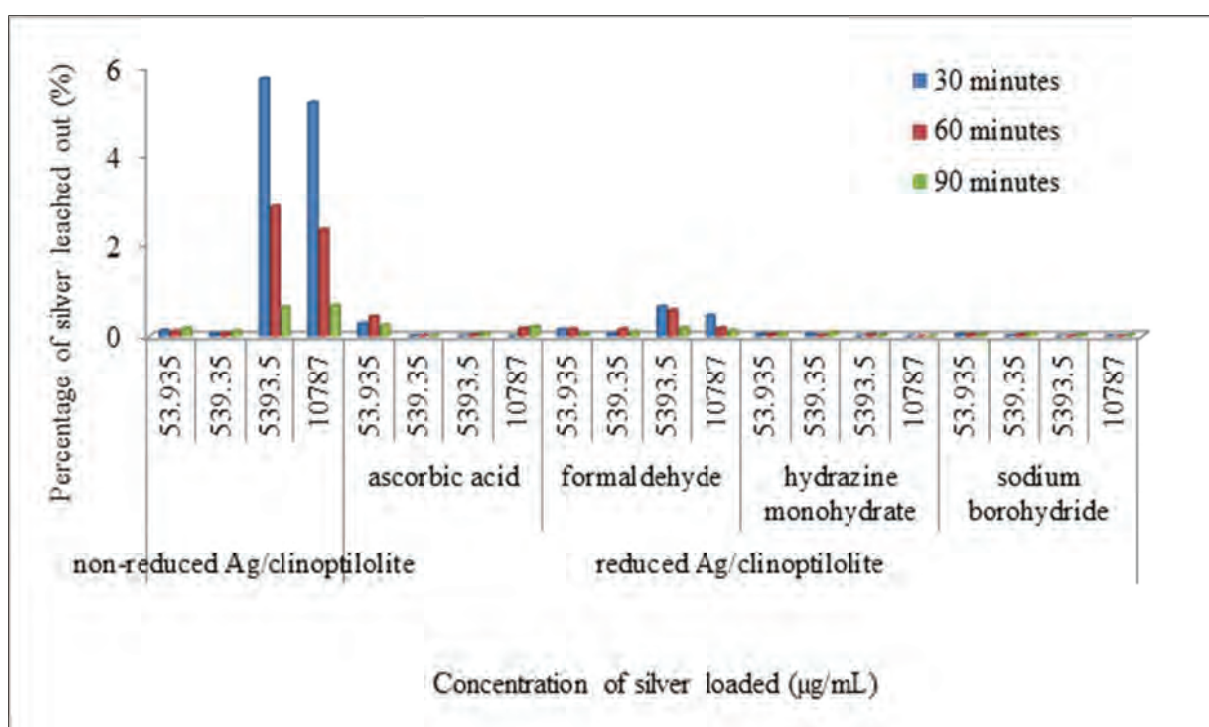


Figure 23: Percentage of the silver leached out into the water

From Figure 24, it is possible to predict the number of leaching runs (leaching 1 g of Ag loaded zeolite with 10 ml water each time) to completely leach the silver out from the matrix (Table 11).

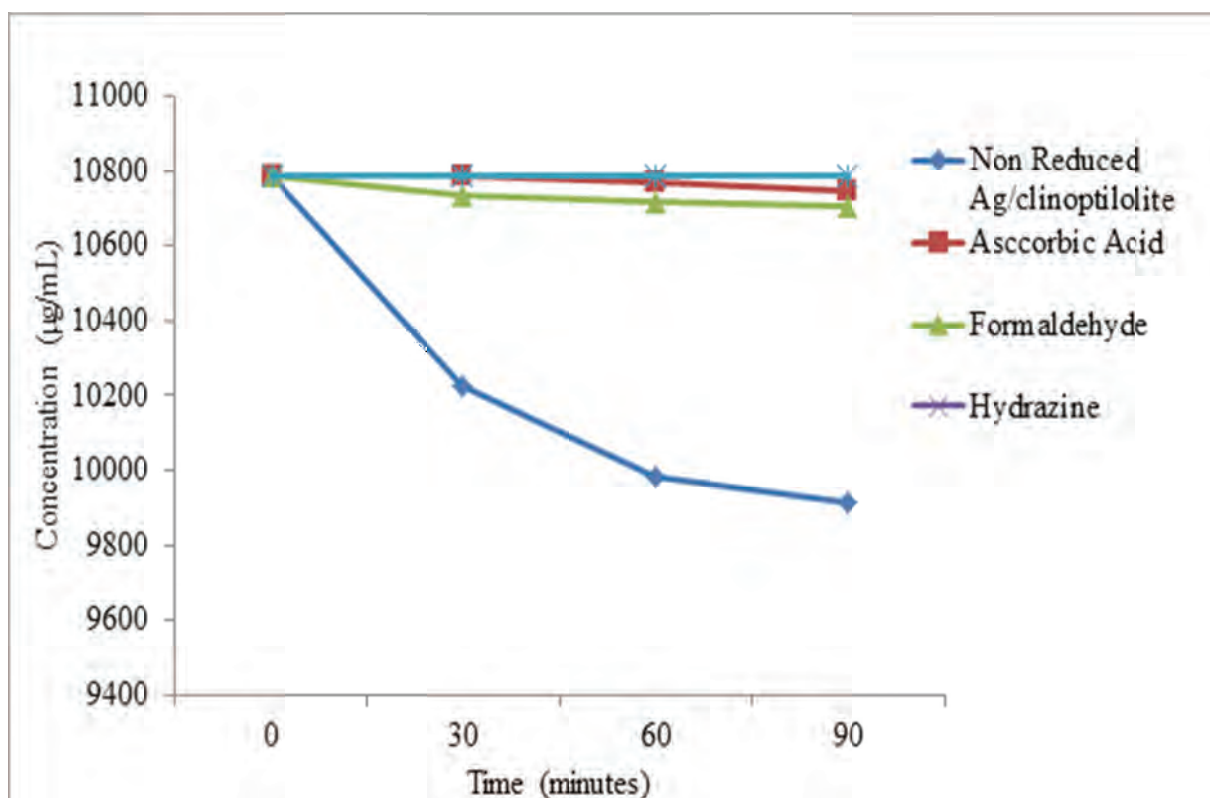


Figure 24: Variation of the silver concentration as a function of reductant type on the clinoptilolite for the three first leachate runs, starting with an initial concentration of 10787 µg/mL Ag loading by wet impregnation

Table 11: Prediction of the number of leaching runs required before all the loaded silver is leached, ending with only 50 µg/mL of residual silver on the clinoptilolite

Sample	Non-reduced Ag/c clinoptilolite	Reduced Ag/c clinoptilolite			
		Ascorbic acid	Formaldehyde	Hydrazine	Sodium borohydride
Initial silver concentration (µg/mL)	10787	10787	10787	10787	10787
Final silver concentration (µg/mL)	50	50	50	50	50
Number of runs	36.88	753.88	385.58	6179	10180.47

Table 11 shows that the sodium borohydride reduced silver zeolite material would leach most slowly and thus by implication last the longest; the other wet impregnated and reduced samples also leached more slowly than the silver salt, thus all the reduced samples would retain effective antibacterial activity for orders of magnitude longer usage if used in the filter pot than the unreduced silver salt. This also implies that a greater amount of silver salt would be leached into the filtered water from the unreduced silver zeolite which could then be ingested or land up in the environment, if the silver salt were not reduced. As can be seen in Table 12, an equivalent antimicrobial activity was observed for the non-reduced sample as was observed in the case of the ascorbic acid reduced sample, hence the leaching was minimized by reduction of the silver salt to metal with ascorbic acid as reductant, yet still maintaining an equivalent antimicrobial property.

The percentage of silver leached out into the water after the loading by ion exchange or by the wet impregnation technique was compared, with 0.8232 and 0.9324 mg/L concentrations of silver loaded by ion exchange; whereas it was possible to load between 53.935 and 539.35 mg/L of silver loaded by the wet impregnation technique and sodium borohydride used as reducing agent.

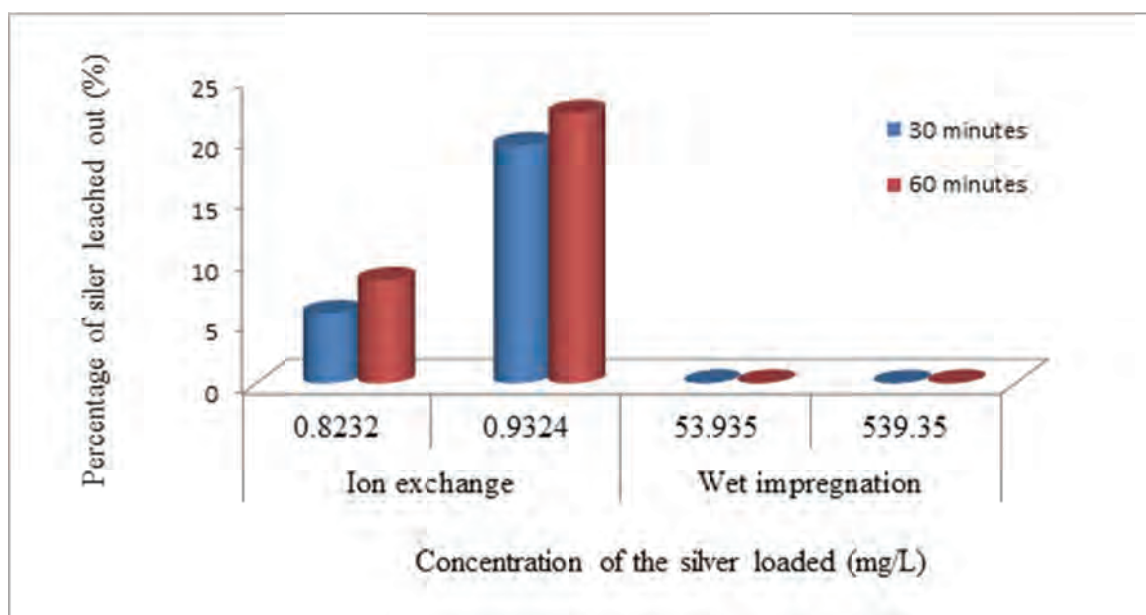


Figure 25: Comparison of the percentage of the silver leached out after the loading by ion exchange or by wet impregnation followed by reduction with sodium borohydride

In comparison to the ion exchange, the wet impregnation process allowed a greater amount of silver nanoparticles to be loaded. Figure 25 shows that the percentage of silver that leached out after the wet impregnation process is much lower than the percentage of silver that leached out after the ion exchange process. The leaching study showed that besides the fact that the wet impregnation allowed a greater amount of silver to be loaded, the amount of silver that can kill bacteria will be maintained for a longer period on the zeolite if silver is loaded by wet impregnation. There is a possibility for certain sizes of silver particles to be stopped by the 0.45 μm membrane filter and this could be another reason why the concentration of silver in the leachates from reduced Ag/clinoptilolite was very low.

In all cases the conclusion concerning the required maximum concentration of the silver (0.1 mg/L) in treated water as prescribed by WHO can only be measured after doing trials on the silver/clinoptilolite Nano composite-based clay filter pot, because at high firing temperature the ceramic vitrification change occurs. Forces that bind silver on the zeolite could thus be altered.

The non-reduced Ag/clinoptilolite powder is light in colour, but the addition of the reducing agent causes the Ag/clinoptilolite to change colour. The reducing agent or the high firing temperature used during pot manufacture may cause the silver nanoparticles to aggregate to one another and result in agglomerated silver particles (Songping, 2005). This would need to be further investigated.

Antibacterial Activity

The antibacterial activity of the Ag/clinoptilolite nano composites was carried out by diluting 2 g of each sample in 20 mL of distilled water. The mixture obtained was tested on *E. coli* Epi 300. Table 12 gives the results of the bacterial inhibition effect of the Ag/clinoptilolite nano composites on *E. coli* Epi 300. The antibacterial effect of the leachates was also investigated (Table 13).

Table 12 shows that the inhibitory effect increases with the increase of the silver concentration in the non-reduced Ag/clinoptilolite and the Ag/clinoptilolite nano composite reduced with the ascorbic acid. The Ag/clinoptilolite nano composites reduced with formaldehyde, hydrazine monohydrate and sodium borohydride presented only a small inhibitory effect even at high silver concentrations. Hence ascorbic acid proved to be the most effective reductant to use to get consistent trends of Ag release from wet impregnated samples.

Matsumura et al. (2003) compared the antibacterial activity of the silver/zeolite and silver nitrate and concluded that the silver ion bound to the zeolite matrix is involved in the bacterial action of silver/zeolite. According to Shamel (2011), the antibacterial effect of non-reduced Ag/zeolite is greater than that of reduced Ag/zeolite. The antibacterial effect of the reduced Ag/zeolite decreased with the increasing size of silver nanoparticle and the silver nanoparticle size increased with the increase of the concentration of the reducing agents. Silver nanoparticles have to be small enough to go through the bacterial walls and demonstrate their antibacterial activity by binding to the microbial DNA, avoiding bacterial duplication and preventing metabolic enzymes of the bacterial electron transport chain, causing their inactivation. Formaldehyde, hydrazine and sodium borohydride are strong reducing agents, ascorbic acid has middle reduction power (Songping, 2005). In our study, formaldehyde, hydrazine and sodium borohydride presented very small inhibitory effect. The question is: is that small inhibitory effect due to the big size of the silver nanoparticles or to some secondary reactions caused by the aluminosilicate modifications (Figure 20).

Some authors used dispersing agents such as sodium dodecylsulfate, which creates micellar solution with Ag^+ , to produce silver nanoparticles with size below 20 nm (Szczeponowicz, 2010). It may be interesting to investigate the influence of various dispersing agents on the silver nanoparticles size and the resultant antibacterial activity.

The antibacterial effect of the leachates from each combination was then tested on *E. coli* Epi 300 as shown in Table 13.

Table 12: the bacterial inhibition effect of the Ag/clinoptilolite on *E. coli* Epi 300

Sample	Concentration of silver (µg/mL)	Microbial growth inhibition
non-reduced Ag/clinoptilolite	53.935	±
	539.35	+
	5393.5	++
	10787	+++
Ag/clinoptilolite reduced with;		
ascorbic acid	53.935	-
	539.35	+
	5393.5	++
	10787	+++
formaldehyde	53.935	-
	539.35	+
	5393.5	+
	10787	+
hydrazine monohydrate	53.935	-
	539.35	+
	5393.5	+
	10787	±
sodium borohydride	53.935	-
	539.35	+
	5393.5	±
	10787	±

(-): No inhibitory effect; (+): Inhibitory effect.

Table 13 shows that only the leachates obtained from the non-reduced Ag/clinoptilolite presented an antibacterial effect, and this was consistent with the concentration of silver leached out into the water (Figure 22). The leachates of the reduced Ag/clinoptilolite do not present an residual antibacterial effect or present just a little bit antibacterial effect because the reduced silver did not leach into the water. The reducing agents could cause the silver nanoparticles to agglomerate. Some of the agglomerated silver particles may not go through 0.45 µm membrane filter. This indicated that there was not a silver residual in the water after contact with the zeolite which is positive in terms of minimal ingestion of silver by the water users and release to the environment.

Table 13: The antibacterial effect of the leachates on *E. coli* Epi 300

Sample	Concentration of silver (µg/mL)	Microbial growth inhibition			
		30 minutes	60 minutes	90 minutes	
non-reduced Ag/clinoptilolite	53.935	-	-	-	
	539.35	+	-	-	
	5393.5	++	+	±	
	10787	++	+	+	
Ag/clinoptilolite reduced with;	ascorbic acid	53.935	-	-	-
		539.35	-	-	-
		5393.5	-	-	-
		10787	-	±	±
	formaldehyde	53.935	-	-	-
		539.35	-	-	-
		5393.5	+	±	-
		10787	+	±	-
	hydrazine monohydrate	53.935	-	-	-
		539.35	-	-	-
		5393.5	-	-	-
		10787	-	-	-
sodium borohydride	53.935	-	-	-	
	539.35	-	-	-	
	5393.5	-	-	-	
	10787	-	-	-	

(-): No inhibitory effect; (+): Inhibitory effect.

Among the reduced Ag/clinoptilolite nano composites, the sample reduced with ascorbic acid presented the best inhibitory results. It is the only solid sample which presented a significant antimicrobial effect (Table 12); this can indicate that silver nano particles are smaller than in the case of the three other reducing agents. This would require further investigation.

Section B: Optimization of the Quantity of Clinoptilolite into Fabricating the Clay Pot

Ecca Holding Clinoptilolite samples were integrated into the clay body of the pot according to the following schematic (Figure 26).

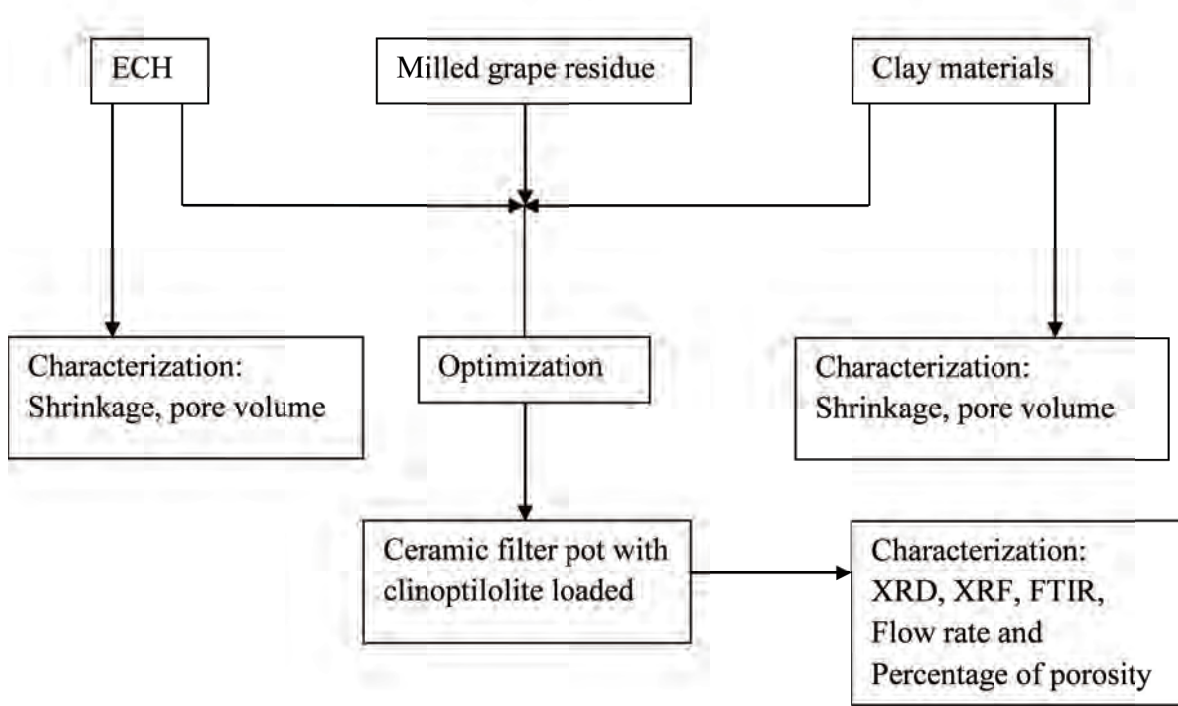


Figure 26: Diagram showing different steps of the section B

Experimental Method

The Ecca Holding Clinoptilolite has a high porosity and high clay content responsible for its plasticity. The amount of clinoptilolite that can be loaded into the clay filter pot before it becomes weak was investigated. The Table 14 gives the raw materials used to make filter pots and in different trials.

Table 14: Raw materials used to make filter pots and different trials done

Body trial	Percentage (%)						Total
	Bentonite	Red clay	White clay	Clinoptilolite	Milled residue	grape	
Zeolite body	-	-	-	100	-	-	100
Combined bodies1	5	10	15	50	20	-	100
Combined bodies 2	10	30	30	20	10	-	100

Results and Discussion

The ceramic filter pot was composed of the hard Ecce Holding clinoptilolite (EHC), white clay, red clay, bentonite and the milled grape residue according to the percentages given in the Table 14. The milled grape residue was used to create small pores in the pot after being burnt. The shrinkage and the pore volume of Ecce Holding clinoptilolite, white clay, red clay and bentonite were compared (Table 15).

Table 15: Shrinkage and pore volume of different raw materials

Materials	Shrinkage (mm)	Pore volume (mL/g)
Ecce Holding clinoptilolite	6	0.5
Bentonite	12	0.7
White clay	7	0.3
Red clay	4	0.25

Table 15 shows that bentonite had the highest shrinkage and pore volume. Ecce Holding hard clinoptilolite had shrinkage of 6 mm and this could be due to its clay content. Looking at the clinoptilolite plasticity, there should be a possibility to make a pot with Ecce Holding clinoptilolite alone. But the plasticity constituted an inconsistency because it caused physical stresses and cracks in the pot (Figure 27). Ecce Holding hard clinoptilolite had higher pore volume than white and red clays, so the higher the loading of the clinoptilolite, the higher the loading of silver that can be achieved in the pot.



Figure 27: Cracks due to physical stresses

In the pot manufacture, adding the four materials together is good practice to balance out material inconsistency. The four materials have the advantage to be locally available and cost effective. The combined bodies made with different percentage of clinoptilolite were fired at 900°C. The volumetric flow rate and the percentage of porosity of the pots containing 20% and 50% of Ecce Holding clinoptilolite were compared (Table 16).

Table 16: Volumetric flow rate and percentage of porosity of filter pots containing 20% and 50% of Ecce Holding hard clinoptilolite

Samples	Flow rate (L/h)	Percentage of porosity (%)
Combined bodies with 50% of clinoptilolite	0.2	29.93
Combined bodies with 20% of clinoptilolite	0.3	24.18

During the vitrification process, molten silicate flows into the interstices between the clay particles and attacks and begins to flux them by interaction. When the whole clay body has cooled, the original clay particles are welded together by a glassy matrix which almost fills all the interstitial spaces. A vitrified body is usually accepted as having a small porosity (Hamer, 1975). Table 16 shows that the flow rate of the combined bodies when fired at 900°C with 20% of clinoptilolite was greater than that of the combined bodies containing 50% of clinoptilolite. This was ascribed to the degree of vitrification and should be further investigated at lower firing temperatures. The vitrification process should be more important in the combined bodies with 50% of clinoptilolite than in the combined bodies with 20% of clinoptilolite. The addition of the milled grape residue can correct the loss of porosity. The influence of the milled grape residue on the volumetric flow rate of the pot was carried out: 00, 30, 40 and 50% (w/w) of the milled grape residue were added to the combine bodies containing 50% of clinoptilolite and Table 17 summarizes the results of the volumetric flow rate of different trials.

Table 17: influence of the milled grape residue on the volumetric flow rate

Percentage of the milled grape residue (%)	0	20	30	40	50
Flow rate (L/h)	0.002	0.2	0.32	0.51	1

Table 17 shows that the porosity could effectively be tailored using milled grape residues, and the desired flow rates could be achieved. PFP mixed clay materials with sawdust or other combustible organic compounds such as rice and coffee husks in 1:1 ratio to get a filter pot having a volumetric flow rate between 1.5 and 2 L/h (Halem, 2006).

The purpose of this project was to make pots that can effectively filter 1.5 L of water per hour. The flow rate can be optimized by changing the amount of the milled grape residue as is shown in the Table 17. But the pot may become weak with too high amount of the milled grape residue and this aspect requires further investigation to minimize fragility of the filter pots.

Characterization of the pot containing 20% of clinoptilolite was performed and is presented in this section.

X-ray Fluorescence was performed for elemental composition of the filter pots and Table 18 gives the major elements and Table 19 the trace elements containing in the filter pot containing 20% of clinoptilolite.

Table 18: Major elements contained in the filter pot with 20 % of clinoptilolite

Major elements	%
Al ₃ O ₃	17.19
CaO	0.88
Cr ₂ O ₃	0.01
Fe ₂ O ₃	7.07
K ₂ O	3.08
MgO	1.79
MnO	0.05
Na ₂ O	0.89
P ₂ O ₅	0.15
SiO ₂	66.09
TiO ₂	0.76
LOI	0.94
H ₂ O	0.04
Total	98.94

Table 19 shows the presence of trace elements in the pots of which some can be toxic if soluble and leached into solution. Those unwanted soluble elements should be washed away before the use of the pot, by letting water pass through the filter pot sufficient times.

Figure 28 gives the FTIR spectrum of the ceramic filter pot containing 20% of clinoptilolite. The filter pot was kilned at 900°C; Figure 28 shows that the temperature did affect bonds that characterize aluminosilicates. The same analysis should be done on the silver/c clinoptilolite nano composite-based clay filter pot to check the changes that could appear due to the exposure of the silver nanoparticles to high temperature.

X-ray Powder Diffraction results are given in Figure 29 showing the different mineral phases in the pot containing 20% clinoptilolite. Figure 29 shows the presence of montmorillonite which is mainly contained in the bentonite, the clinoptilolite and the white clay. Hematite is present and is responsible for the reddish colour of the pot as was shown in Figure 2. Kaolinite, Hematite and Albite are mainly present in the red clay (Mohsen, 2010). Figure 13 showed that Ecce Holding clinoptilolite also contained a significant amount of quartz. The clinoptilolite mineral phase was not detected in the XRD spectrum but this could be due to the relative abundance of the other mineral phases present in the other components of the clay mix and their peak intensities. Further studies are necessary to ensure that the zeolite was not destroyed during the heat treatment at 900°C. The temperature of firing should be optimized to prevent sintering of the zeolitic phase whilst maintaining the pot integrity.

Table 19: Trace elements contained in the filter pot with 20 % of clinoptilolite

Trace elements	ppm
Ni	50
Cu	BD
Zn	214
Ga	24
As	26
Rb	146
Sr	173
Y	47
Zr	274
Nb	19
Pb	27
Th	18
U	2
Ti	4537
V	149
Cr	91
Co	228
Ba	1102
La	66
Ce	121
Nd	50

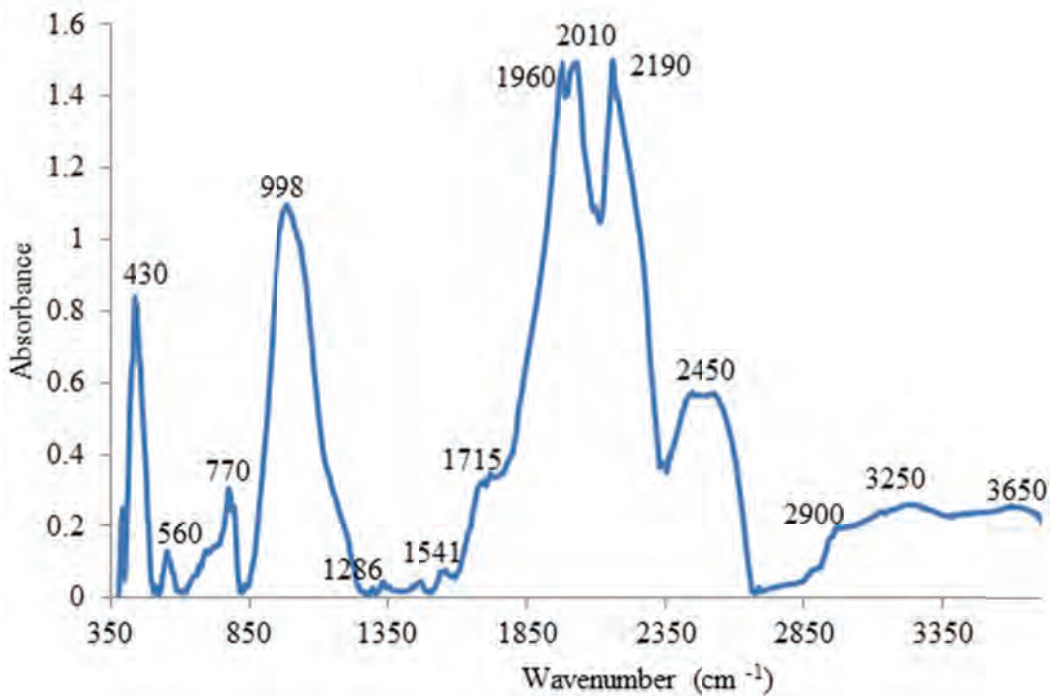


Figure 28: FTIR spectrum of the ceramic filter pot containing 20% of clinoptilolite

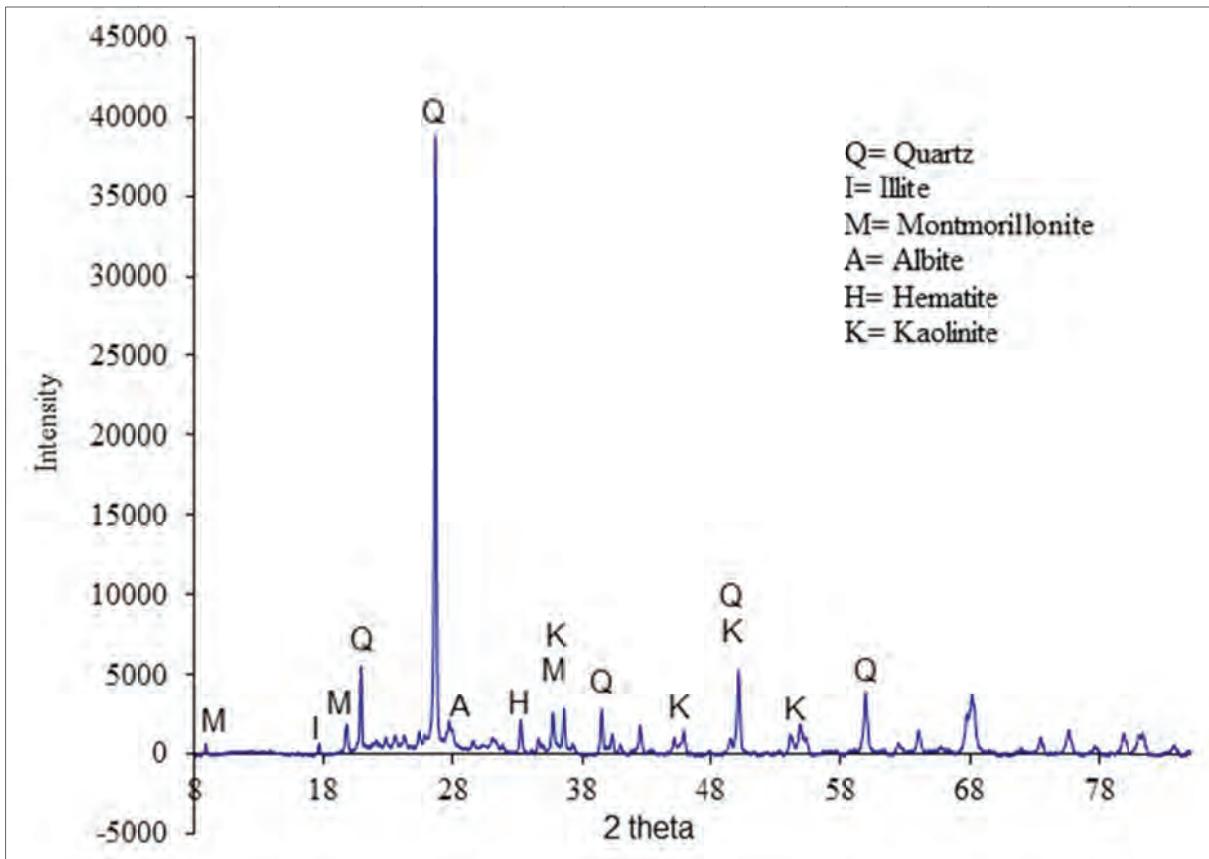


Figure 29: XRD spectrum of the ceramic filter pot containing 20 % of clinoptilolite

CONCLUSIONS

The mechanisms by which silver amendments to filters improve bacterial removal in ceramic filters are not well understood. The literature review revealed that silver ions which leach from the filter may play a role but silver is not usually detected in the filtrate after the first six months of use. In previous studies new filters show enhanced disinfection compared to old filters or filters without silver coating. The enhanced efficiency of silver containing filters can be maintained if silver can be applied in a form that controls its solubility. Silver coated onto inert surfaces has been shown to generate active oxygen species through a catalytic reaction with oxygen. This can kill viruses and bacteria on contact with the surface. Biocidal activity appears to correlate with smaller particles sizes (< 10 nm), prevalence of {111} crystal facets and even dispersion of the nano particles. Prior studies found that more efficient bacterial performance of the SIPP pots compared to the PFP pots were attributed to the imbedded silver nano particles in the clay micropores. Since the imbedded silver nano particles were harder to wash away, the resultant bactericidal activity of the pot was longer than that of PFP pots since the PFP pot only have painted colloidal silver on the inside and outside surface. The silver leached from the SIPP pot was, however, at a level of between 0.5 and 0.6 mg/L, higher than the WHO recommendation of 0.1 mg/L.

In this study natural clinoptilolite zeolite samples Hard and Soft samples (HEC and SEC respectively) of Clinoptilolite from the same Ecce Holdings mine, that were differing in the % of phase purity, were analysed and major and trace element analysis showed that there was a considerable amount of exchangeable cations as well as elements such as Ba, Sr and traces of many other toxic elements present in the as-received natural mineral samples. Hence, confirming the need to thoroughly acid wash and remove exchangeable cations and soluble trace elements from these natural minerals to remove most leachable species prior to their use in a water filtration system. This aspect has not been investigated by prior studies.

Natural clinoptilolite zeolite samples were pre-treated using 1 M HCl for four cycles under stirring condition, for 2 hours each cycle. Acid pre-treatment effectively removed Na^+ and Mg^{2+} cations from the matrix of the natural zeolite but did not remove K^+ or Ca^{2+} from the exchange sites under the conditions applied. In WRC Project No. K5/1897 it has been clearly demonstrated that removal of the charge balancing cations from natural clinoptilolite was a very complex procedure, requiring exhaustive exchange (up to 23 extractions with 0.1M HCl acid) to remove all exchangeable cations and it is therefore postulated that the conditions applied to exchange out the charge balancing cations from the natural clinoptilolite before silver loading in this study was not yet achieved at the optimum conditions.

A calculated mass of silver to be loaded onto each zeolite sample (both acid treated and untreated) by the ion exchange procedure was varied to attain 3 different loadings of silver ions. NaBH_4 was then added as reductant to reach a $\text{AgNO}_3/\text{NaBH}_4$ ratio of 1:4. When ion exchange procedures were applied to load silver upon the zeolite samples it was not possible to load all the silver onto the zeolites and loading trends were inconsistent. In general, the silver content was higher in the acid pre-treated zeolites (HECT and SECT) than in the untreated zeolites (HEC and SEC). The ion exchange procedure was found to be problematic in terms of obtaining a specified metal loading and silver loadings varied from below 1 to above 14 mass %. However, in general, the silver content was higher in the acid pre-treated zeolites (HECT and SECT) than in the untreated zeolites (HEC and SEC); this could be because there was less competitive adsorption occurring during ion exchange using the acid pre-treated zeolites than was the case for the untreated zeolites. This showed that the acid pre-treatment step impacts upon the amount of silver that can be loaded upon the natural zeolite due to competitive adsorption. During the silver loading process of the treated zeolites (HECT and SECT), Ag^+ is only in competition with H^+ , K^+ , Ca^{2+} while it is in competition with Na^+ , K^+ , Ca^{2+} and Mg^{2+} during the silver loading process of the untreated zeolites (HEC and SEC); optimizing the acid pre-treatment could be an important step in the process to improve the amount of loaded silver. The Hard Ecce Clinoptilolite acid treated (HECT) sample which contained a higher % of clinoptilolite generally presented the highest results in term of the amount of silver that could be loaded under the applied conditions. Thus the quality and phase purity of the natural zeolite also impacted upon the amount of silver that could be loaded, and the higher purity natural clinoptilolite sample was applied in further tests.

Silver levels detected in leachates from the silver ion exchanged zeolites after reduction ranged from 0.02-0.20 $\mu\text{g}/\text{mL}$. Leaching for specific times, showed a correlation with the amount (in $\mu\text{g}/\text{ml}$) of silver leached compared to the theoretical amount of silver loaded, with the higher loadings leaching more silver than the lower loadings. Leaching of the silver from the zeolite samples (untreated and acid pre-treated clinoptilolite) was found to be inconsistent but in all cases was lower than 0.2 $\mu\text{g}/\text{mL}$.

A standard silver solution and the silver nitrate salt were tested on *E. coli* Epi 300 at 5, 10, 20, 40, 80 and 160 µg/mL. The inhibitory effect of the silver nitrate solution started at 20 µg/mL while the inhibitory effect of the standard silver started at 40 µg/mL. Lack of any inhibitory effect on the microbes by inoculums of 1 µg/mL of the standard silver inoculum demonstrated that the 1 µg/mL silver concentration was too low to have an inhibitory effect upon *E. coli* Epi 300 during the time of the experiment. The same was observed in the case of the diluted and leached zeolite samples prepared by ion exchange, thus it is evident that the amount of silver available for inhibition of microbes in the zeolite samples prepared by ion exchange or their leachates was too low to kill the bacteria.

Because of the low loadings of silver obtained using the ion exchange procedure, the wet impregnation procedure was employed to load a greater amount of the Ag metal nanoparticles on the zeolite. The concentrations of silver ions applied to the acid pre-treated HEC clinoptilolite were 53.935; 539.35; 5393.5 and 10787 µg/mL respectively. Impregnated silver ions were reduced on the acid treated natural clinoptilolite by four different reducing agents (ascorbic acid, formaldehyde, hydrazine monohydrate or sodium borohydride respectively). The antibacterial effect of the silver nanoparticles depends on size; the smaller the silver nanoparticles are, the more easily they reach the nuclear content of bacteria and bind with the bacterial DNA and the reducing agent should have a weak or a middle reduction power to obtain mono-dispersed, non-agglomerated silver nanoparticles. It was noticed that the clinoptilolite lost its plasticity after being reduced by strong reducing agents (formaldehyde, hydrazine or sodium borohydride) at high concentration. The percentage of silver leached out from wet impregnated samples was much greater in the non-reduced Ag/c clinoptilolite, of which up to 5.2% was observed to leach depending on the starting silver loading used, compared to that of the reduced Ag/c clinoptilolite samples where less than 1% of the loaded silver leached out per leaching run. In the non-reduced Ag/c clinoptilolite, the concentration of the leached silver ions decreased from the first leachate run to the third one, showing that rapid leaching and depletion of the silver ions would occur if silver salts were not reduced in situ prior to use. The concentration of silver leached out was very low for the reduced Ag/c clinoptilolite samples, even when the concentration of silver nanoparticles on the clinoptilolite was high. The reduced silver nanoparticles were found to stay on the clinoptilolite much longer than the unreduced silver ion itself.

The inhibitory effect for *E. coli* Epi 300 increased consistently with the increase of the silver loading in the case of the non-reduced Ag/c clinoptilolite as well as in the case of the Ag/c clinoptilolite nano composite reduced with the ascorbic acid. Hence ascorbic acid proved to be the most effective reductant to use to obtain consistent trends of Ag release. The Ag/c clinoptilolite nano composites reduced with formaldehyde, hydrazine monohydrate and sodium borohydride presented only a small inhibitory effect under the tested conditions even at high silver concentrations. An equivalent antimicrobial activity was observed for the non-reduced sample as was observed in the case of the ascorbic acid reduced sample, hence the leaching was minimized by reduction of the silver salt to metal with ascorbic acid as reductant, yet still maintaining an equivalent antimicrobial property. Only the aqueous leachates of the non-reduced Ag/c clinoptilolite presented an antibacterial effect, and this was in relation to the concentration of silver leached out into the water. The aqueous leachates of the reduced Ag/c clinoptilolite did not present an antibacterial effect or presented only a slight antibacterial effect because the reduced silver did not leach into the water. This indicated that there was not a silver residual in the water after contact with the silver loaded zeolite which is positive in terms of minimal ingestion of silver by the water users and release to the environment.

The amount of clinoptilolite that can be loaded into the filter pot body during pot manufacture before it becomes weak was investigated. The ceramic filter pot was composed of the hard Ecce Holding clinoptilolite (EHC), white clay, red clay, bentonite and the milled grape residue. The shrinkage and the pore volume of Ecce Holding clinoptilolite, white clay, red clay and bentonite were compared and it was found that bentonite had the highest shrinkage and pore volume. Ecce Holding hard clinoptilolite had an intermediate shrinkage of 6 mm and this could be due to its clay content as this is not a pure phase mineral deposit. There should be a possibility to make a pot with Ecce Holding clinoptilolite alone, but at this stage the plasticity constituted an inconsistency because it caused physical stresses and cracks in the fired pots. The combined bodies made with different percentage of clinoptilolite were fired at 900°C. The volumetric flow rate and the percentage of porosity of the pots containing 20% and 50% of Ecce Holding clinoptilolite were compared. The flow rate of the combined bodies when fired at 900°C with 20% of clinoptilolite was greater than that of the combined bodies containing 50% of clinoptilolite. This was ascribed to the degree of vitrification and should be further investigated at lower firing temperatures. The results of this study highlighted that Ecce Holding clinoptilolite can be loaded into the filter pot up to 50% before the pot becomes weak. The addition of the milled grape residue could correct the loss of porosity. It was found that the porosity could effectively be tailored using milled grape residues, and the desired flow rates could be achieved. The purpose was to make pots that can effectively filter 1.5 L of water per hour. The flow rate could be optimized by changing the amount of the milled grape residue.

RECOMMENDATIONS FOR FURTHER WORK

The following topics of investigation are recommended.

- Determination of the size of reduced silver on the zeolite or in the aqueous solution and its antimicrobial activities;
- Different ways to produce non-agglomerated silver nanoparticles upon the zeolites such as the use of dispersing agents;
- The influence of the temperature on the Ag/c clinoptilolite nano composites in the manufacture of the silver/zeolite nano composite-based clay pot filter;
- The influence of the temperature on the silver/zeolite nano composite-based clay pot filters characteristics. Further studies are necessary to ensure that the zeolite was not destroyed during the heat treatment at 900°C. The temperature of firing should be optimized to prevent sintering of the zeolitic phase whilst maintaining the pot integrity;
- The antibacterial efficiency and toxicity of the silver loaded ceramic filter pots;
- The ecological impact of the silver and in the food chain.

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