

SYNERGYSTIC EFFECTS OF TITANIUM (IV) OXIDE MODIFIED CLAY FOR DISINFECTION AND PURIFICATION OF WATER

Ojok D O^{1*}, Wandiga S O¹, Abong'o D A¹

¹College of Biological and Physical Sciences, School of Physical Sciences, Department of Chemistry, University of Nairobi, P.O. Box 30197-00100, Nairobi, Kenya.

*Corresponding Author Email: dojok90@yahoo.com

ABSTRACT

Access to potable water is a problem facing developing countries worldwide. The spread of water related diseases is expected to grow worse in the coming decades with water scarcity occurring globally even in regions currently considered water rich. A study was carried out to assess the effectiveness of titanium oxide (TiO₂) modified clay filters in water purification. Clay soils used for the filter making and samples filtration were collected from Kenyatta University, Department of Ceramics and Got Ramogi in Thika and Bondo Sub-counties respectively. The chemical compositions of the clay samples were determined using X-ray fluorescence. Clay filters were molded and coated with TiO₂ (DEGUSSA P25, calcination at 600°C) and degradation of methyl orange was used to test its photo catalytic activity. The water parameters analyzed were turbidity, pH, total suspended solids, total dissolved solids, Escherichia Coliform (E.coli), pesticides and heavy metals. Results showed that modified clay filters reduced turbidity from 24.667 NTU to 0.0212 ± 0.0016 NTU, TSS from 276 ± 14.730 mg/L to 1.00 ± 0.328 mg/L. The E. coli colonies were reduced from 4310.83 ± 15.718 c.f.u/100 to 0.00 c.f.u/100ml and the spiked 1000ppm of lead, copper and organochlorine pesticides to below detection limits. Improved efficiency of the TiO₂ modified clay filters had the enhanced ability to reduce the contaminant levels in water.

Key words: Modified clay filters, DEGUSSA P25, photo catalyst activity, physico-chemical and biological parameters, water filtration

1. INTRODUCTION.

Many problems associated with lack of clean, fresh water are well known worldwide [1]. Report from WHO show that close to 1.8 billion people lack access to quality drinking water, while 2.6 billion have little or no sanitation [1]. Montgomery and Elimelech reported that 3,900 children die daily from water borne diseases [1].

Lima *et al* (2000) and Behrman *et al* (2004) reported that the leading causes of health disability are intestinal parasitic infections and diarrhoea causing water borne bacteria and enteric viruses [2; 3]. According to WHO (2004) estimate, around 4.0% of the global deaths and around 5.7% of the global diseases are caused by inadequate water, poor sanitation and hygiene, while around 4.2% of the disability adjusted years worldwide is attributed to other water-related diseases such as ascariasis and schistosomiasis. In addition, many countries especially in Africa experience the highest water disparities with over 50% of the water resources concentrated within a single basin [4].

By 1995, already 10 African countries including Kenya, Algeria, Burundi, Cape Verde, Djibouti, Egypt, Libya, Malawi, Rwanda and Tunisia experienced water scarcity. According to report from the UN, the situation is expected to worsen by 2025 [4]. It is now evident that sickness related to drinking contaminated water is one of the leading courses of human mortality and morbidity [5]. At the moment, about 75% of Africa's water resources come from ground water, whereas the surface and rain water constitute 25%. The greatest challenge is that, most of the water resources are heavily contaminated by high load of sediments, chemicals and microbiological pollutants.

Sobsey, 2002 in a paper presented at the UN meeting, in Geneva, on water management at home, observed that it would take decades before effectively treated conventional piped water system was connected to most households. He went ahead to suggest that people must collect water from the source and organise for its treatment at the consumption point [6]. The shortfall in the service provision has been addressed in the recently UN Passed sustainable Development goals (SDG, 2015) and the concluded Millennium Development Goals, which aim to reduce the percentage of people who cannot access safe water by 2015 [7]. Cases of waterborne diseases caused by drinking unsafe water are very high among the poor in developing countries. The most affected are the children, the elderly and immuno-compromised individuals, whose immunities cannot resist waterborne infectious diseases [8].

The data available from the International agencies [9], and local research activities [10], show that African water resources have elevated levels of microbiological pathogens like bacteria, viruses, protozoa as well as chemical contaminants such as pesticides, heavy metals and persistent organic pollutants among others [11]. Kenya is one of the African countries grossly affected by water quality and scarcity challenges [12]. Currently, the country is categorized as chronically water scarce with water supply of less than 647m^3 / persons per year, compared to global benchmark of 1000m^3 / person per year. Statistics projects a drop to 235m^3 / person per year in Kenya by 2025 [12]. Singh and Bengtson 2005 predicted an increase in demand which will be driven by the increased population growth [13]. They observed that the population increase is likely to put more stress on the existing water sources [13]. The challenges facing water quality and water quantity are great and of equal measure. Out of total Kenyan population of 40 million [14], urban population constitute 32.3%, whereas 67.7% constitute rural population. Kenya CBS (2009) went further to report that only 13.4% and 38.4% of the rural and urban populations respectively are using piped water. More than 86% of the rural communities have no access to clean water [15].

MATERIALS AND METHODS

Materials

UV Spectrophotometer model Shimadzu – Pharmaspec UV 1700, pH meter model IQ Scientific Inc. Turbidity meter (LaMotte Tc-3000), Furnace model (ELSKLO DESNA J.V, Type LNT-20. Serial No. 30), Atomic Absorption Spectroscopic (SpectrAA. 10. Labtec), Gas Chromatograph/Mass Spectrometry (VARIAN CP 3800) Solid Phase Extraction cartridges from Superlco Analytical™, Whatman filters paper No. 1, 3M microfilm test kits, Magnetic stirrer, 100ml Pyrex beakers, sampler vials and paster pipettes were used.

Chemicals. TiO₂ powder used was DEGUSSA P25, triple distilled water, lead nitrate Pb (NO₃)₂ of 99.5% purity, copper powder and nitric acid (HNO₃) analar grade of 97% purity, a mixture of 17 organochlorine pesticides (OCP) and HPLC grade, hexane HPLC grade 99.7% purity from Sigma Aldrich, (Germany) Dichloromethane (DCM) HP grade 99.7% purity from RFCL India and methanol HPLC grade 99.7% purity from RFCL India

2.1. Soil collection and characterization.

The soil samples used for filter making were obtained from Got Ramogi in Usigu location, Bondo Sub-county and from the Ceramic department at Kenyatta University. Soil samples (0-15 cm plough layers) were collected from five different points in Got Ramogi area, combined to make composite sample. The five sampling points were randomly selected within sampling site. A soil core was dug using hoe and scooped using a spade down to the depth of 15cm from the five different locations within the site and approximately 500 g of the scooped core taken. The cores were thoroughly mixed to give a composite sample. Triplicate samples of approximately 500 g were taken from the composite sample. Each sample was wrapped in a sterilized aluminium foil, labelled and placed in black plastic bag before transferring to a labelled self-sealing polythene bag and each placed in a plastic container with lid and stored temporarily in polyurethane cool-boxes prior to transportation to the laboratory for analysis and further storage. In the laboratory, samples were taken for characterization while the rest were stored at ≤ -19 °C and analysed within 7 days. Soil types, for making filters, were taken to the department of Mines and Geology (Ministry of Mining), Nairobi for XRF analysis.

2.3. Filter making

2.3.1 Clay processing

Got Ramogi soil is known to produce soil which is suitable for clay moulding. The soil from Kenyatta University was used by the department of ceramics to make various types of earthen wares. The collected clays were first dried under shade for one week, before being homogenized using a pestle and mortar. The soil samples were sieved using a 600µm mesh size sieve. Hagan *et al*, 2009 in his findings, pointed out that the particle size should not be emphasised as long as the soil to be used in filter making, is in powder form.

2.3.2 Saw dust processing

Saw dust was collected from Industrial Area in Nairobi County, dried at the roof top under sun in the Department of Chemistry, University of Nairobi, for 3 days and then sieved with a sieve of mesh size of 600µm. Dies, 2003 observed that the size of the combustible material influences the final pore size in the ceramic filter. Large particle size of the combustible makes the filter to become too porous and fragile.

2.3.3 Clay- saw dust mixing

Different percentage weight ratios of clay to saw dust (samples) were used to obtain the optimum percentage weight ratio for use. The ratios used were; 50: 50, 55: 45, 60: 40 and 65: 35. Dry mixing was thoroughly done for 30 min before water was added. This was to ensure that saw dust and clay were uniformly mixed. After addition of water, the mixture was properly kneaded then wedged to remove air which might have been lodged between the clay particles. Each of the samples was then divided into six equal pieces and the weight of each piece was measured.

2.3.4 Filters making

Filters were made on the potter's wheel under the guidance of a ceramic technician at Kenyatta University. 50: 50 and 55: 45, clay to saw dust percentage ratios were moulded with difficulty on the potter's wheel, since the two clays had lost most of their plasticity due to the presence of high percentage of sawdust in the mixtures. All sets of the clay filters were made in triplicates.

Clay filters were labelled while, still wet as GR1, GR2 and GR3 for natural clay filters, while TGR1, TGR2 and TGR3 for modified clay filters made of clay from Got Ramogi (GR). KN1, KN2 KN3 were labels for natural clay filters while TKN1, TKN2 and TKN3 were for the filters made from clay from Kenyatta University (KN).

2.3.5 Filters drying and kilning

The twelve filters were air dried for 6 days in the shade, weights were measured. Filters were kilned at 850 °C for 5 hours in a furnace (model ELSKLO DESNA J.V. Type LNT-20, Serial no. 30) at Ceramic department, Kenyatta University. After the kilning, the filters were soaked in 10 litres of distilled water for 16 hours to remove air and ash that were lodged in the pore spaces.

2.3.6 Flow rate testing

The filters were filled with water then placed on top of 1 litre Pyrex beakers into which water drained. All the water was allowed to drain into the beaker through the filter pores. The time which water took to drain into the beaker was recorded. The amount of water collected in the beaker was measured using a measuring cylinder then expressed to one hour.

2.3.7 Calcination of TiO₂ powder

Titanium (iv) oxide (TiO₂) powder used was DEGUSSA P25 (a Titania photo catalyst) from London Drug house. The photo catalyst was used without further purification. 50g TiO₂ was placed in a crucible then heated in a furnace at a temperature of 600°C for 1 hour, the ramp rate was 5°C/min.

2.4. Testing the photocatalytic activity of TiO₂.

2.4.1 Degradation of methyl orange by TiO₂

Effectiveness of the TiO₂ photo catalyst was tested by degrading methyl orange (MO) under solar radiation. 0.08g (80 mg) of TiO₂ was put in a 100ml water sample containing 15 ppm and 20 ppm MO. The mixture was first stirred in darkness on a magnetic stirrer in for 30 minutes then under solar radiation for up to 180 minutes. An aliquot of the mixture was drawn from the sample after 20 minutes interval, filtered using a glass wool inserted in a funnel, centrifuged, and taken to Shimadzu-pharmaspec UV 1700 UV spectrophotometer for the determination of its concentration at wavelength of 471nm. The samples were analysed both at 3pH and 7pH. Further tests were done on the Methyl orange degradation to determine hourly reduction of the concentration the dye. The above procedure was repeated with 0.03g, 0.05g, 0.10g

and 0.12g of TiO₂ separately to determine the optimum amount which would degrade high percentage of methyl orange. The percentage degradation of methyl orange by different mass of TiO₂ was calculated using the following formula:

$$\text{Percentage reduction} = \frac{(C_0 - C_t)}{C_0} \times 100$$

Where C₀ is the original concentration of the methyl orange and C_t is the final concentration after a given time (t).

2.4.2 Escherichia Coli (E.coli) test

This was done using 3M test kit. Water that was used for analysis was collected from Nairobi River in a 1L, sterilized glass bottle and taken to the analytical laboratory (University of Nairobi) for analysis. The bottle was first shaken before an aliquot of water sample was drawn from the bottle using Pasture pipette and carefully poured onto the 3M Test Kit. The kit was then placed in an incubator at a constant temperature of 37.2 °c for 24 hours to enable the E. coli colonies to grow. This initial test was done to determine the E. coli load in the water from Chiromo River.

0.08g of TiO₂ was stirred in 100ml of the water sample using a magnetic stirrer under solar radiation. An aliquot of the sample was drawn from the beaker then transferred to the 3M test kit at an hourly interval. The kit was then incubated in the same condition as used for the initial test and the results recorded.

2.5. Coating of filters using TiO₂

Coating was done on filters labelled TKN1, TKN2, TKN3, TGR1, TGR2 and TGR3. 0.08g of TiO₂ powder was placed in a 200ml beaker. 100ml water was added to the powder in the beaker. The suspension was then stirred on a magnetic stirrer for 1 hour to make the suspension homogeneous. The mixture was then poured in each clay filter. The mixture was then gently rolled on the inner surface of each filter to ensure that TiO₂ was uniformly spread on the surface of the filter. This also gave the photo catalyst enough time to penetrate into the pore surface. The filters were then dried under shade for two days, to allow TiO₂ to adsorb onto clay particles, before heating in an oven at a temperature of 600°C for one hour. Calcinations make the photo catalyst to be photo catalytically active. After heating, the filters were then left to cool before they were soaked in water for 24 hours to remove air and ash from the pore spaces. Filters made of clay from Kenyatta University were TKN1, TKN2 and TKN3 and those from Got Ramogi were TGR1, TGR2 and TGR3.

2.6. Water collection

Triplicate water samples for the determination of pesticide residues were collected from sampling site at Chiromo River next to Pesticide analytical laboratory (University of Nairobi) and Usenge beach in the Bondo (Lake Victoria), by grab sampling method into labelled 2.5 litre amber glass bottles. The water samples for pH, turbidity, total dissolved solids (TDS), total suspended solids (TSS), copper and lead analyses were collected in 1.0 L plastic container. Water samples for faecal coliform were collected in triplicate sterilized 1.0 L glass bottles. All the water samples were then temporarily stored in polyurethane cool boxes containing dry ice and taken to the laboratory for analyses.

2.6. Water analysis.

The parameters were analysed on water samples collected from Usenge in Bondo sub-county and Nairobi River. All the analyses were done at the department of Chemistry, University of Nairobi at an ambient temperature. The analyses of all the physico chemical parameters were done in triplicates. All the analyses

were first done prior to filtration to determine the state of the sample then after filtration to check on the efficiency of the filters.

pH measurement; The pH test was done in the Pesticide Analytical Laboratory, using pH was measured using a pH meter model IQ Scientific Instruments, Inc. San Diego, CA, U.S.A. The pH calibration was done using pH 4, 7 and 10 buffers.

Turbidity test; this was carried out in the laboratory using turbidity meter model LaMotte TC-3000e and recorded.

Total dissolved solids (TDS) measurement:

This was done by thoroughly shaking the water samples, and filtering 100ml of the samples through pre weighed Whatman filter paper No.1. The filtrate was then transferred into a clean pre weighed glass beaker and heated in oven at temperature of 103°C for 24hours to evaporate the water. The temperature of the oven was then adjusted to 180 °C for 8 hours. The beaker was removed from the oven and put in desiccators to cool then its weight was taken. TDS was calculated using method of Mackereth et.al (1989)[16].

Total suspended solids; 100ml of the water samples were shaken thoroughly to homogenize it. 100ml was then filtered through a pre weighed Whatman filter paper No.1. The residue retained on the filter was dried to a constant weight in an oven at 105°C, cooled in a desiccator then weighed. TSS was calculated as the weight of the residue per volume of the sample filtered, using the method of Mackereth et.al (1989).

E. coli test; this was done using 3M Test kit. Water used for the analysis was collected from Nairobi River in 2L amber bottles and taken to the Pesticides Analytical Laboratory for analysis.

An aliquot of raw water was drawn from the bottle using Pastuer pipette and carefully transferred into the 3M Test Kit. The kit was then placed in an incubator at a constant temperature of 37.2° C for 24 hours to enable the E. coli colonies to grow.

Heavy metal analysis. This was done on the water sample collected from Lake Victoria. 100ml of the water sample was digested with a mixture of HNO₃ and HCL (3:1) in a 500ml digestion flask at 100°C until the volume is reduced to 30ml.

Copper; 1g copper powder was dissolved in 50 ml of 5M HNO₃ analytical grade made to 1litre to make a concentration of 1000 ppm as a stock solution. From the stock solution, concentrations of 1 ppm, 5 ppm, 10 ppm, 20 ppm, 50 ppm, 100 ppm and 500 ppm were prepared. The atomic absorption spectroscopy (AAS) machine used was of model SpectrAA. 10. Labtec. The lamp current used for the analysis was 3 mA, it was at a wavelength of 324 nm and slit width was 0.5 nm. The fuel used on the machine was acetylene and air was the oxidant.

Lead; 1.5980g of Pb (NO₃)₂ analytical grades was dissolved in 100ml deionised water then diluted to 1000ml to obtain 1000 ppm stock solution. The following concentrations were prepared from the stock solution: 1 ppm, 5 ppm, 10 ppm, 20 ppm, 50 ppm, 100 ppm and 500 ppm.

The prepared water samples were filtered then taken for AAS analysis. The analysis was done at the Department of Geology and Mines, Ministry of Environment and Natural resources (Nairobi). The machine used was SpectrAA.10. Labtec model and was set at the following working condition: Lamp current was 8 mA, wavelength was 217 nm, slit width was 1.0 nm, and the flame used was acetylene while air was the oxidant.

Pesticide analysis. To test the effectiveness of photo catalyst coated clay filters against pesticides 0.5 ppm mixture of 17 organo- chlorine pesticides (OCP) pesticides in water. The pesticide mixture was first dissolved in acetone then dissolved in water. The OCP pesticide mixture contained α -HCH, β -HCH, δ -HCH, gamma-HCH, Heptachlor, Isodrin, Aldrin, Heptachlor epoxide, Endosulphan, pp-DDE, Dieldrin, Endrin, pp-DDD, Endrin aldehyde, pp-DDT and methoxychlor was used. Photocatalytic activation was done using

solar radiation. 100ml of the water sample was filtered then taken through pesticide extraction process another similar amount of water was used as a control and therefore was not passed through filtration process. 100 ml water spiked with the pesticide mixture, was filtered through each of the moulded clay filters, another 100 ml of spiked water was taken for extraction without being taken through the filtration process for validation purposes. The pesticides were extracted from the filtered water using Solid Phase Extraction procedure. Solid Phase Extraction (SPE) was performed using 1cm 18' packed super clean cartridges from Superlco Analytical™, U.S.A., with silica between two polyethylene layers. The SPE cartridges were first conditioned with 10 ml 99.7% HPLC grade hexane from Sigma Aldrich Germany, 10 ml 99.7% HPLC grade DCM from RFCL Ltd India and 10 ml 99.7% HPLC grade methanol also from RFCL Ltd, India. This was followed by flushing with 10 ml distilled water. The filtered water was run through the SPE cartridges and eluted with 30ml 99.7% HPLC grade hexane from Sigma Aldrich Germany.

The eluate was concentrated to near dryness in rotary evaporator and made to a final volume of approximately 1ml in isooctane and then transferred into 20ml glass vials using Pasteur pipettes. These concentrates were blown down under white spot nitrogen gas to a residual volume approximately 1ml and transferred into auto sampler vials using Pasteur pipettes ready for GC injections. Actual volumes in the auto sampler vials were determined gravimetrically using mass and density of isooctane. Analyses of all samples were conducted in splitless mode. VARIAN CP 3800 GC/MS for total ion counter (TIC) chromatograph instrument was used for the analyses of the residual concentration of the pesticides with time. The instrument was equipped with a DB5 MS capillary column of dimensions 30M x 0.25mm x 0.25µm and a temperature program with initial temperature of 80°C for 3 minutes, ramped to 250°C at 10°C/min with a hold time of 23 minutes. High purity helium gas (99.999%) was used as a carrier gas whereas white spot nitrogen was used as a makeup gas. A carrier gas constant flow rate of 1ml/min was maintained throughout all the analyses, whereas the makeup gas was maintained at a constant flow of 30 ml/min.

3. RESULTS AND DISCUSSION.

3.1 Soil characterization.

The chemical composition of clays varies within broad limits, being a “measure” of their general properties. This is due to the fact that the same oxide may be present in several mineral phases that show opposite influences on the ceramics [17]. As a consequence, two clays with similar compositions may show a different technological behaviour [17]. The results of chemical composition by weight (57.8 %) of SiO₂ for the Kenyatta University and Got Ramogi (56 %) of the clays under study (Table 1). The percentage weight given as oxides are composed of slightly higher percentage composition of SiO₂ but lower composition of Al₂O₃ in Kenyatta University than in Got Ramogi clay (Table 1). Kenyatta University clay had percentage weight (15.37%) while Got Ramogi had (20.51%) of Al₂O₃ values. The losses on ignition for the clays were 10.75% and 9.11% for Kenyatta University and Got Ramogi clays respectively. A loss on ignition generally entails the removal of water of crystallization and carbonaceous material through the application of heat [18]. Kenyatta University had highest lost on ignition (LOI) value of 10.75% (Table 1).

Table 1: Percentage, chemical composition by weight for Kenyatta University and Got Ramogi clays soils.

	Kenyatta University	Got Ramogi
Metal oxide	Percentage weight (%)	
SiO ₂	57.8	56
Al ₂ O ₃	15.37	20.51
CaO	1.11	0.36
MgO	1.9	0.18
Na ₂ O	2.34	1.59
K ₂ O	0.49	0.47
MnO	0.1	0.13
Fe ₂ O ₃	7.62	6.19
LOI	10.75	9.11

Garcia and Benea (2002) observed that clay particles are characterized by a high surface energy determined by the presence of negative charges; meanwhile, inside the structure, the neutrality of the molecules is preserved. As a consequence, the properties of clays are highly influenced by the surface phenomena; the degree of dispersion determines the increase of the specific surface, thus of the surface energy. In practice, when establishing the suitability of clays for filter making, the ceramic mass composition, their chemical composition, mineralogy, correlation and particle size distribution with the technological characteristics are important [19]. According to Weitkamp and Puppe (1999), Si in the structure has a valence of +4 making the SiO₂ tetrahedra neutral, while the Al₂O₃ tetrahedra are negatively charged because Al has a valence of +3, creating a Brönsted 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 [20]. The Si/Al ratios, for Kenyatta University and Got Ramogi clays are 3.8 and 2.7 respectively (Table 1). Got Ramogi clay with lower Si/Al ratio of 2.7 has higher ion exchange capacity than the Kenyatta University with the ratio of 3.8 [20].

3.2 Filter making process.

Clay- saw dust mixing.

Table 2: Plasticity levels of clay to saw dust mixtures used

Soil	Sawdust	Level of plasticity
50	50	<<plastic
55	45	<plastic
60	40	>plastic
65	35	>>plastic

Plasticity increases with the reducing portion of sawdust in the mixtures (Table 2). The less plastic mixtures which were from the soil to sawdust ratios of 50: 50 and 55:45 were not molded due to their lesser plasticity and porosity values (Table 2).

Clay filters. During the molding process, filters which had clay to saw dust ratios of 55:45 and 50: 50 could not be molded since the clay in the mixtures had lost their plasticity due to the high percentage of saw dust. Clay filters which had the mixture ratio of 60: 40 and 65: 35 were molded with ease (Table 2).

Table 3: Weight and percentage shrinkage of molded clay from Kenyatta University and Got Ramogi

Site	weight		Fired weight	% shrinkage before firing	% shrinkage after firing
	wet	dry			
Kenyatta University	1.67	1.433	1.42	14.2	15
Got Ramogi	1.67	1.495	1.489	10.48	10.78

The weight of each filter of clay from Kenyatta University was 1.67 kg (wet) and 1.433 kg (dry) under a shade for 6 days while those from Got Ramogi were 1.67 kg (wet) and 1.495 kg (dry) (Table 3). Kenyatta University moulded clay had the highest shrinkage before firing at 14.2% and 15% after firing while that from Got Ramogi had 10.48% and 10.78 % respectively (Table 3). The high values of shrinkage lead to the occurrence of hidden fissures (cracks or splits) and decrease of mechanical resistance. [21] The shrinkage and mechanical resistance are correlated with the mineralogical composition [21].

According to Hagan *et al* (2009), drying under shade is to remove the excess water which used to mould the clay. The initial drying enables the filters to hold their shape although they could still get wet when placed in water [22]. Hagan *et al* (2009) reported that firing process removed the excess water while further heating-is to remove water which was chemically bonded to the clay's alumina and silica molecules.

Flow rate analysis. The analytical flow rate for the selected filters 60:40 and 60:35 respectively were measured in ml per hour (mlhr^{-1}). Filter from clay - saw dust ratio of 65: 35 recorded very low flow rates of 30.6 ml hr^{-1} during the pre- test session and was not included for the further analysis. Filters made from clay - saw dust ratio of 60: 40 were used for further analysis. Kenyatta University clay filters showed the highest flow rates of 146 ml hr^{-1} and 144 ml hr^{-1} from the natural and modified filters respectively (Table 4) while Got Ramogi filters showed low flow rates of 112 ml hr^{-1} and 120 ml hr^{-1} from the natural and modified filters (Table 4). According to Kabegambe *et al*, (2011) filters with moderate flow rate are the most suitable, since filters which recorded very low flow rates cannot collect enough water for domestic use while those with very high flow rate may not filter all the contaminants. High flow rate is also a sign of micro cracks on the filters [23]. The above observation becomes the basis upon which Got Ramogi clay was selected for modification.

Table 4: Natural and modified clay filters flow rates

Sites and filters nature	Filter labels	Filter flow rate (mlhr ⁻¹)
Kenyatta University clay filters		
natural filter	KN1	146
	KN2	144
	KN3	142
modified filters	TKN1	144
	TKN2	141
	TKN3	145
Got Ramogi clay filters		
natural clay	GR1	114
	GR2	115
	GR3	112
	TGR1	117
	TGR2	120
modified filters	TGR3	116

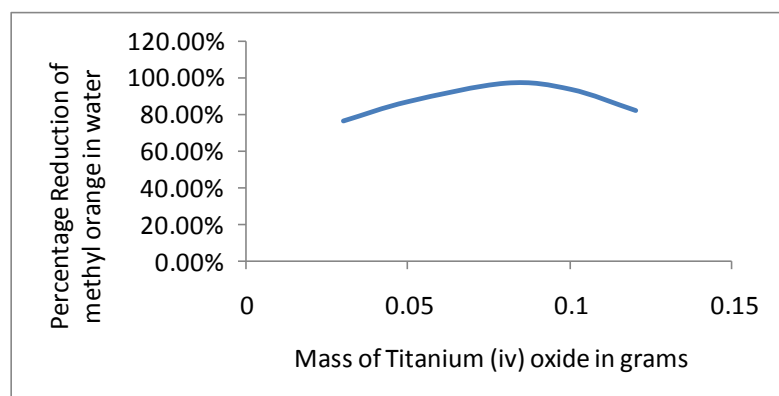
3.3. Testing the photocatalytic effectiveness of titanium (iv) oxide

Determination of the optimum amount of titanium oxide for reduction of methyl orange dye is shown in Table 5.

Table 5: The percentage reduction of methyl orange by varying amounts of titanium (iv) oxide.

Mass of TiO ₂ (g)	% reduction of methyl orange
0.03	76.67
0.05	87.21
0.08	97.23
0.1	92.88
0.12	82.34

The Photo catalytic effectiveness of reduction of organic pollutant (methyl orange dye) with titanium (iv) oxide showed the optimum of 97.23% with the weight of 0.08g of titanium oxide (Table 5). Weight of 0.03g TiO₂ showed the lowest level of methyl orange dye reduction. The weight of 0.08g of titanium oxide was chosen as the optimum weight for use (Figure 1).

**Figure 1: The percentage optimum amount of titanium (iv) oxide for the rapid degradation of methyl orange.**

In photocatalytic degradation reactions, the observed rate constant decreases with the increase of initial organic pollutant (methyl orange dye) concentration up to 0.12g (Figure 1). The highest degradation rate is 97.23% using 0.08g of titanium (iv) oxide. The results indicate that the percentage reduction of methyl orange increases by increasing the photo catalyst amount of titanium (iv) oxide to 0.08g then decreases (Figure 1). Konstantinou and Albanis, (2004) observed that increasing the photocatalyst amount increases the active sites [24]. They also observed that the reduced reaction of the photocatalyst was due to the deactivation of the activated molecules by collision with the inactivated molecules. Reduced light penetration and shielding by titanium (iv) oxide by the increased amount of the photocatalyst was also responsible for the reaction rate of the photocatalysts on the methyl orange. The main steps of the photocatalytic reaction occur on the surface of the catalyst, and therefore high adsorption capacity is associated with reaction favouring step [25]. The experimental research conducted by Rashid and El Amin (2007) deduced that photocatalytic reactions mostly follow Langmuir-Hinshelwood kinetic rate model, where all the active sites of the photocatalyst is occupied by methyl orange (pollutant) molecules. A further increase of the amount of the photocatalyst may result in decreased rate of reaction and observed rate constant [26].

The optimum concentration for the methyl orange dye degradation process

The concentration of 15 ppm shows the highest degradation rate at 240 minutes than 20 ppm at pH 3 (Figure 2).

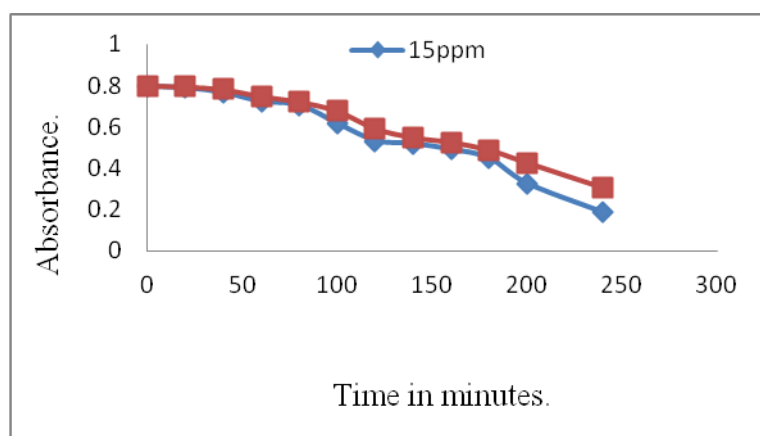


Figure 2: Degradation of 15 ppm and 20 ppm methyl orange dye at pH 3.

The concentration of 15 ppm methyl orange dye shows the highest degradation rate at 240 minutes than 20 ppm at pH 7 (Figure 3).

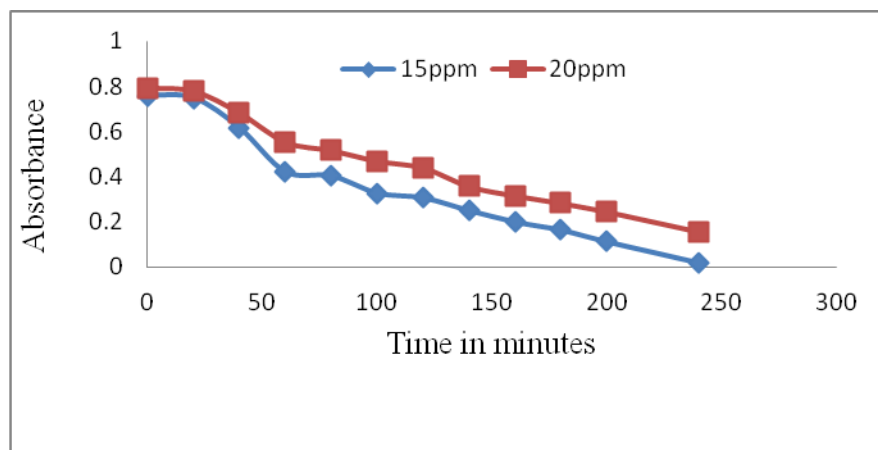


Figure 3: Degradation of 15 ppm and 20 ppm methyl orange dye at pH 7.

From Figures 2 and 3 concentration of 15ppm showed optimum degradation at 240 minutes at both pH 3 and 7 respectively.

The optimum pH for the degradation of methyl orange dye

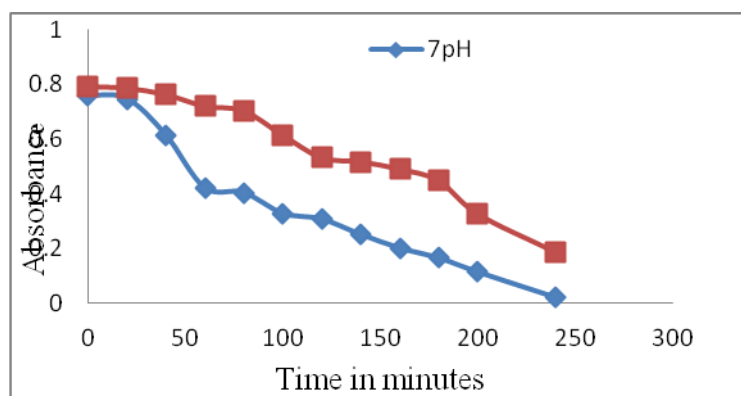


Figure 4: Degradation of 15 ppm methyl orange dye at pH 3 and 7

To obtain the optimum degradation pH, methyl orange at 15ppm and 20ppm were degraded at pH 3 and 7pH.

The rate of degradation of 15ppm was highest at pH 7 than the pH 3 at 240 minutes (Figure 4)

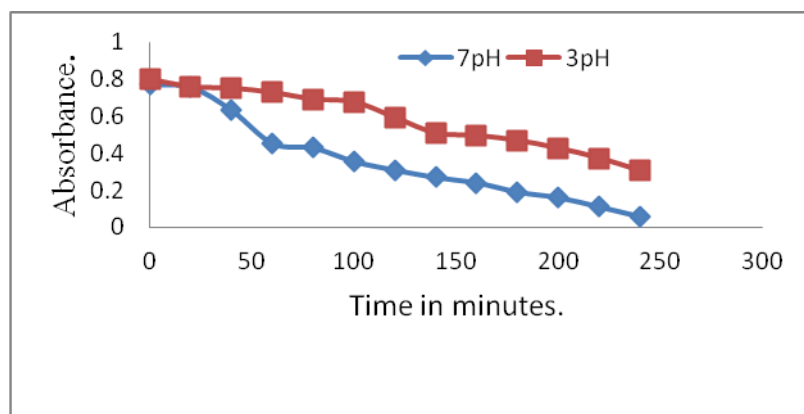


Figure 5: Degradation of 20 ppm methyl orange dye at both pH 3 and 7.

The concentration of 20ppm shows the highest degradation rate at the pH 7 than pH 3 at 240 minutes (Figure 5)

From Figures 4 and 5, pH 7 is the optimum pH value chosen for use in the analysis.

Working with the samples at 15 ppm at pH 7 gave the highest degradation rates as shown in Figures 2, 3 and 4. The optimum methyl orange dye at concentration of 15 ppm and pH 7 was chosen for the degradation process.

The optimum time for methyl orange degradation process

To obtain the optimum time for degradation, methyl orange at 15ppm and pH 7 was degraded at 60 minutes intervals (Figure 6)

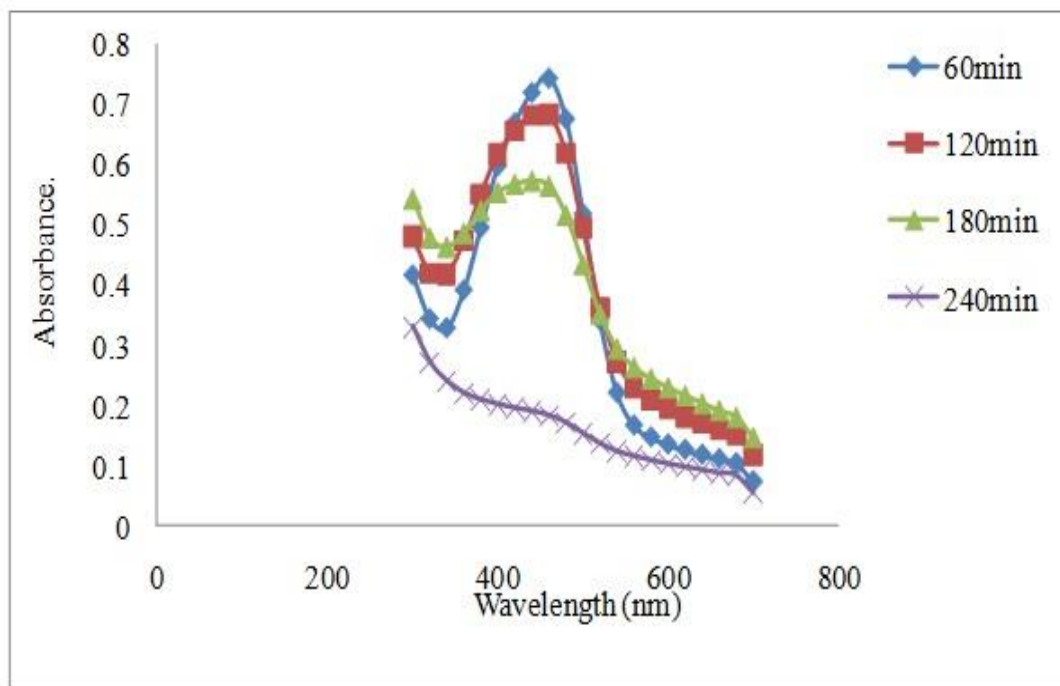


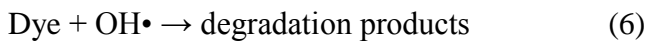
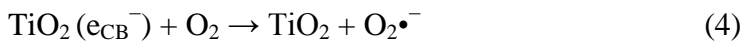
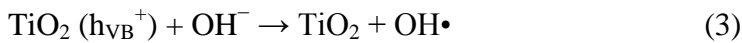
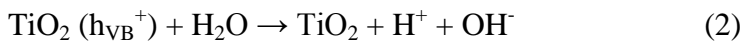
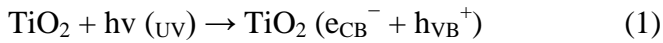
Figure 6: Degradation of 15ppm, pH 7 of methyl orange at 60 minutes interval.

Figure 6 shows the optimum degradation values for methyl orange at concentration of 15ppm, pH 7 pH and 240 minutes. 1 hour shows the least degradation time followed by 2 and 3 while 4 hours is the best degradation time for methyl orange dye (Figure 6).

Therefore 15 ppm at pH 7 in 4 hours are the optimum concentration, pH and time for the degradation of methyl orange dye in water sample

Chen and Liu (2007) described dyes as class of organic compounds used in the textile industry which are also known industrial pollutants. Chen and Liu (2007) observed that chemical stability of modern dyes make them resistant to the commonly used conventional biological methods used to treat industrial wastewater; this has resulted in the emission of coloured discharge from the treatment plants [27]. Dalton *et al* (2001) also supported the use of inorganic photocatalysts as cheap and effective way of removing organic compounds and pollutants [28]. Marinas *et al* (2001), Tanaka *et al* (2002) and Konstantinou and Albanis (2004) also supported the use of TiO_2 photocatalyst as an effective alternative means of removing organic pollutants from wastewater [29, 30, and 24]. According to the reaction mechanism proposed by Vinodgopal and Khamat (1994), methyl orange dye is degraded by conduction band electrons (e^-) and valence band holes (h^+) which are generated when light energy greater than its band gap energy ($E_g=3.2$ eV) radiates TiO_2 suspended in aqueous solution [31].

The photo-generated electrons can react with the dye leading to its complete degradation through reduction process, react with O_2 adsorbed on the Ti-surface or dissolved in water reducing it to superoxide radical anion O_2^\bullet [32]. Rashed and El- Amin (2007) used Hoffman *et al* (1995) illustration to explain that the photo generated electron holes can oxidize the organic molecule to form R^+ , react with OH^- or H_2O to form OH^\bullet radicals, which together with peroxide radicals are responsible for the TiO_2 photodecomposition of organic substrates [26]. Given below is a complete reaction mechanism proposed by Hoffman *et al* (1995) [32], showing the relevant reactions at the TiO_2 semiconductor surface causing the degradation of dyes.



According to observation made by [32], the resulting OH^\bullet radical, can oxidize most of methyl orange dye to the mineral end-products.

3.4. Coating the filters with TiO_2 .

TiO_2 particles were firmly adsorbed onto clay particles in the filters. When water sample was poured into the filters, TiO_2 particles were not dislodged from the clay surface. This shows that the coated filters are used for filtration without dislodging TiO_2 particles from the clay surface.

3.5. Results for the analysis of the physico-chemical parameters done on lab-water samples.

The results of pH, turbidity, total dissolved solids, total suspended solids and E. coli in the filtered water sample are shown in the Table 6.

Table 6: Levels of physico - chemical parameters in the filtered water samples.

Parameters	Filters				WHO guidelines
	KN	TKN	GR	TGR	
pH	7.52±0.058	7.1±0.100	7.48±0.015	6.77±0.051	6.5-8.0
Turbidity (NTU)	1.761±0.6629	0.870±0.295	0.395±0.048	0.0212±0.0016	5
TDS (mg/L)	334.222±3.372	332.89±0.214	296±5.321	291±8.320	1000
TSS (mg/L)	1.665±0.578	1.493±0.578	1.527±0.598	1.00±0.328	Nil
E. coli (cfu)	Nil	Nil	Nil	Nil	Nil

Source (WHO 1996).

Here KN refers to natural clay filter made using Kenyatta University clay, TKN is the TiO_2 coated Kenyatta University clay filter, GR is the Got Ramogi modified clay filter and TGR is the TiO_2 coated clay filter made from the soil from Got Ramogi.

Water filtration and pH analysis;

pH is the negative logarithm of the hydrogen ion concentration. The pH of the water sample was 7.93 ± 0.058 . pH of the water filtered by natural clay filter (KN) was 7.52 ± 0.058 while for the one filtered by the modified clay filters (TKN) from the same region was 7.1 ± 0.100 . Table 6 gives a comparison of the reductions of the pH by the four clay filters. Results for the pH of water filtered by Got Ramogi natural clay filter (GR) was $\text{pH } 7.099 \pm 0.009$. Modified clay filter (TGR) from the same region had $\text{pH } 6.77 \pm 0.0511$. The filtration by TGR reduces the pH of water. Table 6 shows the pH reduction by both the GR and TKN filters makes the water neutral (pH 7.1). The information given in table 6 shows that TKN and TGR gave

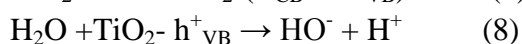
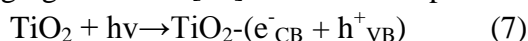
better pH reduction than KN and GR. The pH of the filtered water fall within the values recommended by WHO which is in the range of 6.5- 8.5 [33; 34].

The marginal change in pH of the water samples filtered by natural clay filters, KN and GR was due to the presence of H^+ ions in water. The slight increase of H^+ was caused by competition between metallic ions and dissolved salts, for the binding sites on clay structure [35]. On the clay structure was OH^- ion giving the clay a negative charge when the dissolved salts get into contact with the clay surface, the cation would be preferred to the H^+ ion. The presence of H^+ in water is responsible for the reduction of its pH [36].

When it comes to the pH of the water sample which had been filtered by modified clay filters, additional process involving photocatalysis comes into play [36]. When light photon of band gap 3.2 eV or more hits the surface of TiO_2 particle, the lone electron at the outer most energy level of the molecule is photoexcited to the higher energy level to form electron – hole pair (e^- , h^+) [38].

The water molecule was split by the valence hole (h^+) electrons on the TiO_2 surface to produce OH^- molecules and H^+ ions (equations 7 and 8). Some of the H^+ produced participates in further reactions producing hydrogen peroxide H_2O_2 and hydroperoxyl HO_2^{\cdot} Radicals

Reduction in the pH (Table 6) in the sample was attributed to presence of excess H^+ ions in the sample. H^+ ions were generated by splitting of water molecules by the photoinduced TiO_2 to produce OH^- which is a scavenging molecule [37]. The reaction process is illustrated by equation below.



The pH levels of water filtered by KN, TKN, GR and TGR clay filters fall within the range set by World Health Organisation and the Kenya Bureau of Standards for drinking water which is 6.5- 8.5 [33; 34].

Turbidity values;

Turbidity often refers to the presence of insoluble particulates in the targeted water sample [39].

The turbidity of the water sample was 24.667 ± 0.0577 Nephelometric turbidity unit (NTU). After sample was filtered by the natural clay filters, the turbidity reduced to 1.761 ± 0.6629 NTU by natural Kenyatta University clay filters (KN) while those filtered by modified one (TKN) had a turbidity of 0.870 ± 0.295 NTU. The turbidity of water samples filtered by natural clay filters (GR) was 0.395 ± 0.0481 NTU and those filtered by modified clay filters (TGR) from the same place was 0.0212 ± 0.0016 NTU (Table 6). The turbidity levels are in line with the WHO set standard for minimum turbidity level (Table 6) for domestic water of 5 NTU [33]. The results show that Got Ramogi modified clay filters have higher turbidity reduction capacity than the Kenyatta University clay filters.

Filtration can be used to reduce turbidity to below 5 NTU to allow maximum UV light utilization and photocatalytic reaction [40]. The results in Table 6 show that all the filters recorded turbidity of less than 1NTU which are by far below World Health Organisation maximum turbidity level of 5 NTU [33]. High turbidity, according to the observation made by Rincón and Pulgarin (2004), negatively affect the rate of photocatalytic disinfection. Chin et al, 2004 observed that TiO_2 does not reduce turbidity, but instead affects the optical properties and the penetration of UV light by scattering and absorbing the rays [41]. Therefore it is necessary to filter water first before subjecting it to photocatalytic treatment.

Total dissolved solids (TDS).

Dissolved solids in freshwater samples include soluble salts that yield ions such as sodium (Na^+), Calcium (Ca^{2+}), magnesium (Mg^{2+}), bicarbonate (HCO_3^-), sulfate (SO_4^{2-}), or chloride (Cl^-) [42]. The total dissolved solids in the water sample were 344 ± 8.7178 mg/L.

The total dissolved solid (TDS) of water filtered using natural clay filters from Kenyatta University was 332.889 ± 3.372 mg/L (Table 6). Water samples filtered by modified clay filters from the same place, had the total dissolved solids of 330.889 mg /L ± 3.372 mg/L. The total dissolved solids in the water filtered using Got Ramogi clay was 296 ± 5.321 mg/L modified clay filters from Got Ramogi had TDS of 291 ± 8.320 mg/L. The results in table 6 show that Got Ramogi natural and modified clay filters had higher ability to reduce TDS than the Kenyatta University clay filters for water samples. It is clear from the results that all the filters proved effective in removing dissolved solids from water.

Total suspended solids (TSS). The total suspended solids of the water sample were 276 mg/L ± 14.730 mg/L. The total suspended solids of the sample filtered by natural Kenyatta University clay filter were 1.667 ± 0.578 mg/L (Table 6). TSS of the water filtered by the modified clay filters from the same region were 1.493 ± 0.598 mg/ L .Total suspended solid of the water sample filtered by Got Ramogi natural clay filter were 1.527 ± 0.33 mg/L, while modified clay filters from the same region produced water with TSS of 1.00 ± 0.328 mg/L. From the results shown in Table 6, Got Ramogi modified clay (TGR) had better sample filtration for the TSS than the other three filters.

The analysis showed slight variation in the amount of suspended solids removed by natural clay and TiO_2 modified clay. Chong, 2010 observed that suspended solids also shield target pollutants from oxidation reactions and this result into lowered efficiency of the photocatalysts. It is therefore advisable that the water intended for photocatalytic treatment be filtered first.

3.6. The Escherichia coliform (E.coli) filtration and analysis

The *E. coli* count in the water sample which was 4310.83 ± 15.718 Colony forming units (c.f.u) was reduced to 0.0 c.f.u after filtration by all the three sets of filters. After filtration no *E. coli* colonies were detected in the filtered samples (Figure 7).

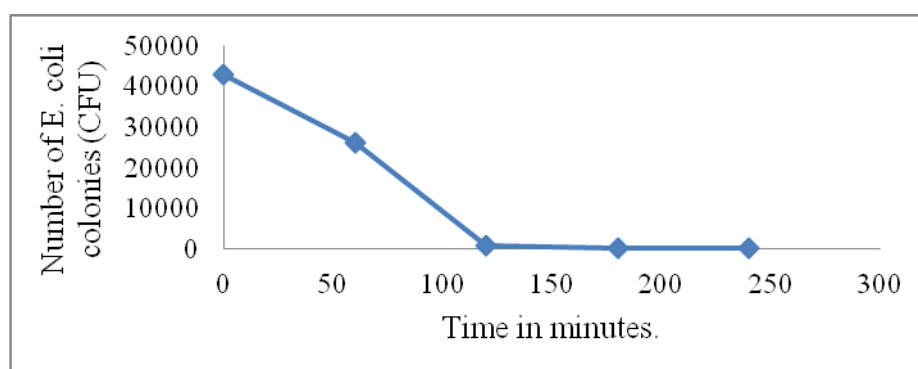


Figure 7: The reduction of Escherichia Coliform in a suspension of TiO_2 .

Figure 7 shows the colonies of the water sample before and after filtration. The absence of dark blue dots on the 3M test was an indication that the filtered water was free from *E. coli*. The results for all the filtered samples showed no *E. coli* colonies in the filtered water meaning that clay filtration was effective in eliminating *E. coli* (Table 6). However when an aliquot of the residues was removed from each of the filters and transferred to 3M petrifilm test kit then incubated, *E. coli* colonies developed on the test kit with

samples from natural clay filters (KN and GR) while samples from modified filters (TKN and TGR) had no *E. coli* colonies. This showed that *E. coli* were not only filtered out by the modified filter but were also destroyed. Huang et al. (2000) illustrated that TiO_2 photocatalysis caused initial oxidative damage to the cell wall, although the cells were still viable [43]. Wei *et al* (1994) added that photocatalytic action gradually increased the cell permeability by eliminating the protective cell wall of the *E. coli*, followed by the oxidative damage on the underlying cytoplasmic membrane [44]. Wei *et al* further reported that, if free TiO_2 particles entered into membrane-damaged cells, cell death could be accelerated. Cho *et al* (2004) concluded that the $\cdot\text{OH}$ radicals produced during the heterogeneous photocatalysis is the main reactive species responsible for *E. coli* elimination [45]. According to Maness *et al* (1999), lipid peroxidation reactions, which led to the loss of normal functions associated with an intact membrane, was the underlying death mechanism of *Escherichia coli* cells undergoing the UV irradiation in the presence of TiO_2 [46].

Copper filtration and analysis

Table 7: Levels of copper in the filtered water samples from natural and modified clay filters.

Concentration (ppm)	Concentrations in filtered water.			
	KN	TKN	GR	TGR
1	BDL	BDL	BDL	BDL
5	BDL	BDL	BDL	BDL
10	BDL	BDL	BDL	BDL
20	BDL	BDL	BDL	BDL
50	0.0116±0.0029	BDL	BDL	BDL
100	0.0200±0.0000	BDL	BDL	BDL
500	0.4367±0.0208	0.233±0.0306	0.2317±0.0198	BDL
1000	0.8867±0.0451	0.430±0.01	0.3527±0.0146	BDL

*BDL- Below detection limit.

From Tables 7 and 8, the filter clay KN, was not able to filter samples with ≥ 50 ppm (0.023% Cu) while TKN and GR did not filter ≥ 500 ppm (0.046%) of copper and lead respectively. There was no amount of copper detected in the filtration of ≤ 1000 ppm of copper sample using the modified clay filter TGR. Modified Got Ramogi clay (TGR) gave the best filtration levels for copper (Table 7) and lead (Table 8) concentrations.

Lead filtration and analysis.

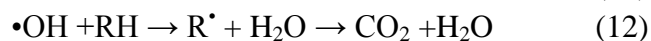
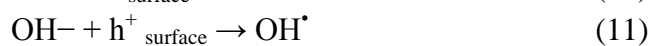
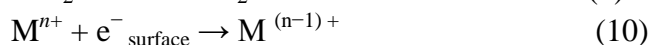
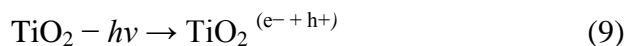
Table 8: Levels of Lead in the filtered water samples from natural and modified clay filters

Concentration (ppm)	Concentrations in filtered water			
	KN	TKN	GR	TGR
1	BDL	BDL	BDL	BDL
5	BDL	BDL	BDL	BDL
10	BDL	BDL	BDL	BDL
20	BDL	BDL	BDL	BDL
50	0.0110±0.0017	BDL	BDL	BDL
100	0.0233±0.0025	BDL	BDL	BDL
500	0.394±0.0309	0.3135±0.0153	0.3667±0.0208	BDL
1000	0.9356±0.0222	0.3533±0.0153	0.4567±0.0158	BDL

Chemical analysis done on the soil indicated that SiO_2 and Al_2O_3 forms a large proportion of the chemicals found in the soil (Table 1). Heavy metals are mainly removed from water by ion exchange and chemisorption [47]. Godelitsa (1999) reported the formation of stable inner complexes because the OH^- , which is the functional group, forms strong chemical bonds with metal ions outside the hydration envelopes of the metal [48]. Elevated concentrations ($\leq 50\text{ppm}$) of heavy metals in water were not totally removed by natural clay filters. This is probably due to the fact that the natural clay filter had attained its absorptive saturation level, [47]. Silica (SiO_2) has a structure composed of infinite three-dimensional framework of tetrahedron [49]. Each silicon atom forms four single bonds with four oxygen atoms located at the four corners of a tetrahedron. A surface functional group in silicates (57.8% in TKN and 56% in TGR) plays a significant role in the adsorption process [49]. Donald (1998) reported that it is oxygen atoms bound to the silica tetrahedral layer and hydroxyl groups which are associated with the edges of the silicate structural units [50]. Murray (1994) noted that the functional groups are the ones which provide surface sites for the chemisorption of transition and heavy metals [49]. The cations in the zeolites are exchangeable with other cations giving zeolites an ion exchange property [51]. The specific ion exchange capacity depends on the structure of the clays, the Si/Al ratio and the ions to be exchanged [21]. Dean and Robins 1947 reported that the presence of Al_2O_3 in the soil leads to rapid adsorption of heavy metals from water.

The surface hydroxyl groups dissociate in water and serve as Lewis bases towards metal cation (M^+). Such deprotonated sites (one or possibly two), forms complex with the heavy metal ions [49]. Abd- Allah (2007) reported that the excellent adsorption capacity of the clay is due to its high specific area and the ability of holding water in the interlayer sites [53]. Dean and Rubins (1947), in experiments of phosphate adsorption by kaolinite clays, reported that the relatively rapid adsorption of ions from dilute solutions is a property of the Al-OH groups at the crystal edges. This explains the higher efficiency that Got Ramogi clay filter displayed over Kenyatta University clay filter.

Heavy metals removal from water using modified clay filters is illustrated by the reaction mechanism which was proposed by Chen and Ray (2001) and Serpone and Pelizzetti (1989). Solar illumination on TiO_2 leads to the production of electron and electron holes which can either recombine to produce heat, or can be used to reduce or oxidize species in solution at the TiO_2 surface as indicated by equations (9 – 13) [54,55].



In equations (9) to (13), M represents the metal ions, R represents an organic species, and n is an integer. From the mechanisms and the available literature, it is clear that TiO_2 offers additional adsorption and chemisorption sites to the heavy metals to those on the clay structure.

A number of studies on heavy metal ion adsorption at the solid / liquid interface showed that it depends on parameters such as the system pH, the initial metal concentration, the amount of the adsorbent and the temperature [56; 57; 58; 59; 60].

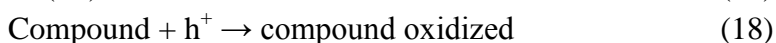
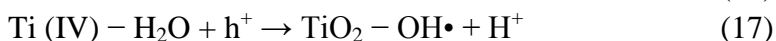
Filtration and analysis of pesticide residue levels in water samples.

Table 9: Organochlorine pesticide levels in filtered water sample.

Pesticide	Concentrations in ng/L (Validation results).	pesticides' residue levels from water sample filtered by TGR filters
Alpha-HCH	91.2048	BDL
Beta-HCH	910.5147	BDL
Delta-HCH	2512.479	390±108.45
Heptachlor	1098.245	BDL
Aldrin	657.2004	BDL
Heptachlor epoxide	531.139	BDL
Endosulphan 1	475.7729	BDL
PP-DDE	559.5298	BDL
Dieldrin	350.0299	BDL
Endrin	284.5042	BDL
PP-DDD	247.501	BDL
Endosulphan 2	269.896	BDL
Endrin aldehyde	366.2792	BDL
PP-DDT	451.2727	BDL
Endosulphan sulphate	BDL	BDL
Methoxychlor	60.47903	BDL

Table 9 shows the results of the 16 mixtures of the organochlorine pesticide (OCP) levels in water samples filtered by TGR filter. TGR filter is able to filter completely all the 15 OCP except Delta-HCH (Table 9). Mills and LeHunte (1997) reported that oxidation processes of the organic pollutants, by the generated reactive hydroxyl radicals ($\bullet\text{OH}$) using UV/ TiO_2 and UV/ H_2O_2 methods, can lead to degradation or mineralization of most pesticide contaminants [63].

Sepone and Pelizzetti (1989) reported that the electrons could either react with the organic substrate or react with adsorbed O_2 on the TiO_2 -surface or dissolved in water, to form superoxide radical anions $O_2^{\bullet-}$ [55]. Konstantinou et al (2002) reported that the created electron holes can either oxidise the organic molecule directly, or react with the OH^- ions and the H_2O molecules adsorbed at the TiO_2 surface, to form $OH\bullet$ radicals which together with other highly reactive oxidant species (peroxide radicals) are reported to be responsible for the heterogeneous TiO_2 photodecomposition of organic substrates [61]. The reaction mechanism at semiconductor surface causing the degradation of pesticides, which was proposed by [33], can be expressed as follows:



The $OH\bullet$ radical formed is a very strong oxidizing agent which can oxidize most of organic pesticides to the mineral end products. Substrates which are not reactive to hydroxyl radicals are degraded by TiO_2 photocatalysis whose rates of decay are highly influenced by the semiconductor valence band edge position [62].

The analysis of water samples from the Lake Victoria.

All the analysis on lake water samples was done using modified clay filters from Got Ramogi (TGR) clay. TGR clay filter was used since it has the superior ability in removing pollutants from water samples compared to modify filter clay soil from Kenyatta University.

The results for the physico-chemical analysis done on the unfiltered water samples collected from Lake Victoria are shown in the table below.

Table 10. Levels of physico-chemical, Escherichia coliform and heavy metals parameter in the filtered water from Lake Victoria.

Parameter	Original levels	Levels after filtration
pH	7.89±0.057	7.44±0.009
Turbidity (NTU)	14.067±0.115	0.379±0.031
TDS (mg/L)	122±14.574	116.876±6
TSS (mg/L)	55±1.528	0.052±0.002
E.coli (CFU)	2686±30.55	BDL
Copper (ppm)	0.015±0.007	BDL
Lead (ppm)	0.018±0.0113	BDL

Analysis done on the water sample collected from the same site had the following levels of organochlorine pesticides (Figure 8);

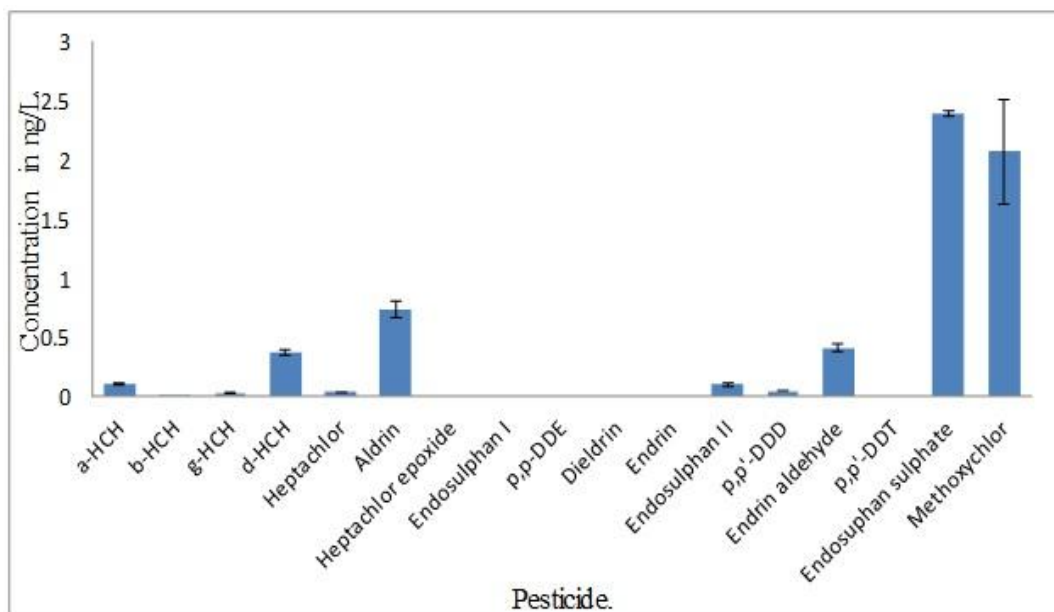


Figure 8; Organochlorine pesticide residue levels in the water sample from Lake Victoria.

All the OCP residues were not detected in the filtered water. The reaction mechanism in each of the analyzed parameters follow similar pathway to the ones analyzed in the lab water sample. The results of the analysis done on the filtered water samples from both the laboratory and Lake Victoria showed that modified clay filters are improved version of natural clay filters and are very effective in removing organo chlorine pesticides from water.

Conclusion

Results of the tests, done on the water sample, which was filtered by both natural and modified clay filters showed 100% removal of the *E. coli*. Natural clay filters can be used to remove ≥ 100 ppm lead and copper from water while modified clay filter is capable of removing even 1000 ppm copper and lead from water. WHO placed the minimum concentration of copper and lead in for household use to 2mg/L and 0.01mg/L. Analysis done on the OCPs in the filtered water sample collected from Lake Victoria showed that all the pesticides, which were earlier on detected, had been effectively removed by the modified clay filter. TiO_2 coated clay filters can be used to reduce the concentration of the organo-chlorine pesticides from water.

Acknowledgement

The authors wish to acknowledge Safe Global Water Consortium- USAID (SGWC-USAID) for funding this project.

Reference

- [1] Montgomery, M. A. & Elimelech, M. Water and sanitation in developing Countries: including health in the equation. *Environ. Sci. Technol.* 41, 17–24 (2007) | [Q](#) |.
- [2] Lima, A. A. M., S. R. Moore, M. S. Barbosa Jr, A. M. Soares, M.A. Schlepner, R.D. Neumann, C.L. Sears, J. P. Nataro, D.P. Fedorko, T. Wuhib, J. B. Schorling & R.L. Guerant. Persistent diarrhea signals a critical period of increased diarrhea burdens and nutritional Shortfalls: a prospective cohort study among children in northeastern Brazil. *J. Infect. Dis.* 181, 1643–1651 (2000) | [PubMed](#) | [ChemPort](#).

- [3] Behrman, J. R., Alderman, H. & Hoddinott, J. Hunger and malnutrition in Copenhagen Consensus—Challenges and Opportunities (London, 2004) OCL57489365 (London School of Hygiene and Tropical Medicine, 2004).
- [4] WHO, 1998. Guidelines for drinking-water quality, second edition, Addendum to Volume 2. P. 281-283. | [Article](#) |
- [5] United Nations Water / Africa, (2011). Vision for 2025: Equitable and sustainable use of socio-economic development, P8
- [6] Shannon, M., A, Paul W. Bohn, Menachem Elimelech, John G. Georgiadis, Marinas B. J, Mayes A.M. Science and technology for water purification in the coming decades (2008).
- [7] Sobsay M. D., (2002). Managing Water in the Home: Accelerated Health Gains from Improved Water supply, Geneva: World Health Organization.
- [8] UN (United Nations). 2000. *Millennium Declaration*. UN General Assembly: A/RES/55/2, 18 September 2000.
- [9] Brown, J. M. (2007). "Effectiveness of ceramic filter. Filtration for drinking water treatment in Cambodia". *PhD thesis, University of North Carolina, Chapel Hill*.
- [10] World Bank (2009) Climate Variability and Water Resources Degradation in Kenya: Improving Water Resources Development and Management. Working Paper No. 69. 34854.
- [11] Getenga, Z. M., F. O. Kefftgara, and S. O. Wandiga, (2004b) Determination of Organochlorine pesticides in soil and water from river Nyando Drainage System Within Lake Victoria Basin, Kenya. *Bull. Environ. Contam. Toxicol* 72 (2): 335-342 "
- [12] Wandiga S.O. (2001) Use and distribution of organochlorine pesticides. The future in Africa. *Pure Appl. Chem.* 73 (7): 1147-1155.
- [13] Singh, P. & Bengtson, L. The impact of warmer climate on melt and evaporation for the rainfed, snowfed and glacierfed basins in the Himalayan region. *J. Hydrol.* 300, 140–154 (2005)
- [14] Kenya CBS. (2009) Population of Kenya: Ministry of planning and Development census report, Nairobi, Kenya.
- [15] Kenya Water for Health Organization/United Nation development Program, Initiative report on the assessment of the capacity of water action to effectively participate in water sector reforms in Bondo District (2007). PP 10.
- [16] Mackerth F.J.H., Heron .J., Talling J.F., (1989): Water Analysis; Some Revised Methods for Limnologists, Scientific publication No. 36; 7-118.

- [17] Teoreanu, I., Ciocea, N., Bârbulescu, A., Ciontea, N. (1985), Tehnologia produselor ceramice si refractare, Editura Tehnică, Bucuresti, p.78-81
- [18] Amaakaven, V., T, Ali, E, A, Idu, F., U. (2014). The physico-chemical and mineralogical properties of Mbaruku clay and its suitability as an industrial raw material. *International journal*. eISSN: 2319-1163. pISSN: 2321-7308.
- [19] Garcia, M, Benea, M. Characterisation of some clays used for white ware ceramics II (2002). Technological characterisation. P. 77- 84.
- [20] Weitkamp, J., Puppe, L. (1999). Catalysis and zeolites: fundamentals and applications, Springer, New York.
- [21] Benea, M., Gorea, M. (2002), Characterization of some clays used for whiteware ceramics. I. Mineralogical composition, Studia Univ. "Babeş-Bolyai", Geologia, XLVII, 1, Cluj Napoca
- [22] Hagan, J.M., Harley, N., Pointing, D., Sampson, M., Smith, K., and Soam, V. 2009, *Resource Development International - Cambodia Ceramic Water Filter Handbook -, Version 1.1*, Phnom Penh, Cambodia.
- [23] Kabegambe, M., Kaahwa, Y., Obwoya, K., S. Percolation rate of water through filter for point of use, **2011**, KIST journal. Vol. 1(1) pp. 39-46.
- [24] Konstantinou I, Albanis T.A (2004). TiO₂-assisted Photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations. Appl. Catal. B: Environ. 49: 1–14. Kun, R., mogyórosi, I., Dékány. Appl. Clay sci. 32. 2006. 99-110.
- [25] Rashed, M. N., El- Amin, A.A., 2007. Photocatalytic degradation of methyl orange in aqueous TiO₂ under different solar irradiation sources. Research paper. P. 7.
- [26] Gomes da Silva, C., S, C. Synthesis, spectroscopy and characterisation of TiO₂ based photocatalysts for degradative oxidation of organic pollutants. 2008 PhD thesis.
- [27] Chen, S., F., Liu, Y., Z., 2007. Study on the photocatalytic degradation of glyphosate by TiO₂ photocatalyst. Chemosphere 67, 1010 – 1017.
- [28] Dalton, J. S, Janes, P. A, Jones NG, Nicholson JA, Hallman KR, Allen GC (2001). Photocatalytic oxidation of NO_x gases using TiO₂: A surface spectroscopic approach. Environ. Pollut.120: 415-422.
- [29] Marinas A, Chantal G, Jos - M. M, Amadeo FA, Ana A, Jean-Marie H (2001). Photocatalytic degradation of pesticide–acaricide formetanate in aqueous suspension of TiO₂ • Appl. Catal. B: Environ. 34(3): 241-25.
- [30] Tanaka K, Reddy KSN (2002). Photodegradation of phenoxyacetic acid and carbamate pesticides on TiO₂. Appl. Catal. B: Environ. 39(4): 305-310.

- [31] Vinodgopal, K, Kamat, P. Journal on Photochemistry Photobiol. A. 83 (1994) 141-148.
- [32] Hoffman M,R, Martin S, Choi W, Bahnemann DW (1995). Environmental application of semiconductor photocatalysis. Chem. Rev. 95: 69-96.
- [33] WHO 1996 Guidelines for drinking water quality international programme on chemical safety, **vol 2**. World Health Organisation, Geneva.
- [34] Kenya Bureau of Standards (KEBS) (1996). Kenya Bureau of Standards, KS 05- 459: part 1, p 6 ICS 13.060.20
- [35] Awan, M, A, Qazi, I, A, Imran Khalid (2003). Removal of heavy metals through adsorption using sand. Journal of Environmental Sciences Vol. 15, No. 3, pp.413-416.
- [36] Kohlmann, F., J. What is pH and how is it measured? A technical handbook for industry (2003). Lit. No G004.
- [37] Chong, M.N. (2010) Non-Photocatalytic Mineralization and Disinfection for water reclamation; From Catalytic Engineering to Process Optimization and Modeling.
- [38] Kabra K, Chaudhary R, Sawhney RL (2004) Treatment of hazardous organic and inorganic compounds through aqueous-phase photocatalysis: a review. Ind. Eng. Chem. Res 43: 7683–7696
- [39] Viesman Jr., Hammer, M. J., 1998. Water supply and pollution control. Addison Wesley Longman Inc. 6th Edition, California USA.
- [40] Gelover, S., Gómez, L. A., Reyes, K., Teresa Leal, M., 2006. A practical demonstration of water disinfection using TiO₂ films and sunlight, Wet. Res. 40, 3274-3280.
- [41] Rincón, A.G., Pulgarin, C., 2004. Effect of pH, inorganic ions, organic matter and H₂O₂ on E. coli K12 photocatalytic inactivation by TiO₂-implications in solar water disinfection. Appl. Catal. B: Environ. 51, 283e302.
- [42] Chin, M. L., Mohamed, A. R., Bhatia, S., 2004. Performance of photocatalytic reactors using immobilized TiO₂ film for the degradation of phenol and methylene blue dye present in water stream. Chemosphere 57, 547- 554.
- [43] Huang, Z.; Maness, P.; Blake, D. M.; Wolfrum, E. J.; Smolinski, S. L.; Jacoby, W. A. Bactericidal mode of titanium dioxide photocatalysis. J. Photochem. Photobiol. A. **2000**, 130, 163-170.
- [44] Wei, C.; Lin, W.; Zainal, Z.; Williams, N.; Zhu, K.; Kruzic, A. P. Bactericidal activity of TiO₂ photocatalyst in aqueous media: toward a solar- assisted water disinfection system. Environ. Sci. Technol. **1994**, 28, 934-938.

- [45] Cho, M.; Chung, H.; Wonyong, C.; Yoon, J. Linear correlation between inactivation of E. coli and OH radical concentration in TiO₂ photocatalytic disinfection. *Wat. Res.* **2004**, 38, 1069-1077.
- [46] Maness, P. C.; Smolinski, S.; Blake, D. M.; Huang, Z.; Wolfrum, E. J.; Jacoby, W. A. Bactericidal activity of photocatalytic TiO₂ reaction: toward an understanding of its killing mechanism. *Appl. Environ. Microbiol.* **1999**, 65, 4094 – 4098.
- [47] Mozgawa, W. & Bajda, T. (2005). Spectroscopic study of heavy metals sorption on clinoptilolite. *Physics and Chemistry of Minerals*, Vol. 31, (February 2004), pp. 706–713, ISSN (electronic): 1432-2021.
- [48] Godelitsa, A. (1999). Transition metal complexes supported on natural zeolitic materials: an overview. In: *Natural microporous materials in environmental technology*, P.
- [49] Murray B M, 1994. Environmental chemistry of soils [M]. USA: Oxford University Press.
- [50] Donald L S, 1998. Environmental soil chemistry [M]. San Diego: Academic Press.
- [51] Scott, M., A, Kathleen, A., C., Prabir, K., D. (2003). Handbook of zeolite science and technology, Marcel Dekker Inc., USA.
- [52] Dean, L. A., and Rubins, E. J., 1947, Exchangeable phosphorous and the anion exchange capacity: *Soil Sci.*, v. 63, p. 377.
- [53] Abd-Allah S., El Hussaini O., and Mahdy R., "Towards a more safe environment: characterization of some clay sediments in Egypt for safe environmental applications," *Australian Journal of Basic and Applied Sciences*, vol. 4, **2007**, pp. 813-823.
- [54] Chen, D., Ray, A. K. *Chem. Eng. Sci.* 56 (**2001**) 1561.
- [55] Serpone, N., Pelizzetti, E. *Photocatalysis: Fundamentals and Applications*, Wiley, New York, **1989**, pp. 489–537.
- [56] Sen, T.K., Mahajan, S.P. and Khilar, K.C. (2002) Adsorption of Cu²⁺ and Ni²⁺ on iron oxide and kaolin and its importance on Ni²⁺ transport in porous media, *Colloids Surf. A*, **211**, 91-102.
- [57] Salim R., Al-Subu M.M. and Sahrhage E. (1992) Uptake of cadmium from water by beech leaves, *J. Environ. Sci. Health A*, **27**, (3), 603-627.
- [58] Cheung C.W., Porter J.F. and McKay G. (2000) Elovich equation and modified second-order equation for sorption of cadmium ions onto bone char, *J. Chem. Technol. Biotechnol.*, **75**, 963-970.
- [59] Sen, T.K. and Khilar, K.C. (2006) Review on subsurface colloids and colloid-associated contaminant transport in saturated porous media, *Adv. Colloid Interf. Sci.*, **119**, 71-96.

- [60] Gurses A., Dogar C., Yalcin M., Acikyildiz M., Bayrak R. and Karaca S. (2006). The adsorption kinetics of the cationic dye, methylene blue, onto clay, *J. Hazard. Mater.*, **131**, 217-228.
- [61] Bahnemann, D.W., Cunningham, J., Fox, M. A., Pelizzetti, E., Pichat, P., Serpone, N., in: Heltz, G. R., Zepp, R.G., D.G. Crosby, D. G. (Eds.). *Aquatic and Surface Photochemistry*, Lewis Publishers, Boca Raton, FL, **1994**, p. 261.
- [62] Maurino, V., Minero, C., Pelizzetti, E., Vincenti, M. *Coll. Surf. A* 151 (1999) 329.
- [63] Mills, A., LeHunte, S., (1997). An overview of semiconductor photocatalysis. *Journal of Photochemistry and Photobiology. A* 108:1-35.