Using Compost and TiO_2 Nano-Particles as Retention Media for Treatment of MSW Leachate

By

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ABSTRACT

Solid waste is a major challenge to developing countries. Urban areas of Pakistan are estimated to produce 40,000 tons /day and are projected as 75,000 tons /day by 2025. Almost 60 % of generated waste is collected and dumped in open area as a common practice. Till date there is no operational sanitary land fill site in the country expect one in Lahore. Thus, waste dumping poses serious threat to community health, groundwater, surface water resources, soil and reduced plant diversity. More than 1000 chemicals have been identified in groundwater contaminated by landfills leachate that can pollute the environment. The objective of this study was to develop a bio retention media that can filter pollutants from the leachate. For the said purpose, vermi compost was chosen as a bio-retention media, but the problem is compost itself leach organics and phosphorus along with copper and other heavy metals. To deal with the leaching, TiO_2 nano-particles immobilize on silica sand were used as an additional layer that has excellent sorbtion capacity along with photo catalytic capability. A leaching experiment was designed in a leaching column and was irrigated with original leachate collected from dumpsite of Islamabad. Result of this study concluded that TiO_2 nano particles (NP) were successfully immobilized on the silica sand and addition of a layer of NP significantly improved leachate quality. Immobilized NP reduced the contaminant flow from the compost itself. Moreover, UV application on TiO_2 NP decreased the nitrite leaching from the compost. Also significantly reduced organic carbon and ortho-phosphorus in addition to the leaching of metals like lead and chromium.

Chapter 1

1 INTRODUCTION

1.1 Back Ground

Developing countries like Pakistan is facing a major challenge in term of solid waste ; Urban areas of Pakistan alone is estimated to produce almost 50,438 tons of solid waste daily and is projected to produce 109,244 tons/day by 2025. (Hoornweg & Bhada-Tata, 2012) Increasing population in addition to economic accomplishments and absence of training in modern municipal solid waste (MSW) management have become prominent factor due to which struggles for improving MSW management system have persisted more difficult. With the efficient collection of such a huge quantity of solid waste, its disposal is also a challenge in a country like Pakistan where till now no proper sanitary land fill is operational. Uncontrolled and unmanaged dumping in open area is in practice by the Government and private waste collection agencies. Moreover hazardous and nonhazardous is being dump without considering any protective measures in dumping grounds, rivers or agriculture land. The said condition is not only resulting in health risk to the communities but also resulting in pollution of ground water through leaching from these dumps.

Leachate may contain elements of inorganic and organic nature. Xenobiotic organic compounds (XOCs) and also heavy metals that are generally classified as the hazardous substances present in leachate. XOCs and heavy metals which are Hazardous can be toxic, carcinogenic, corrosive, reactive, flammable, mutagenic, teratogenic, and also eco-toxic, other than theses hazards, leachate is bio accumulative and/or persistent in environment. Municipal landfill leachate have been identified with more than 200 organic compounds, with more than 35 compounds having the probable of causing harm to the environment as well as human health. Land fill contaminate ground water and more than 1000 chemicals have been identified underground water of area having landfill. The major\ part of these compounds are originated from vegetation decomposing and product of degraded natural materials, containing cellulose and hemicellulose up to 60% of the dry weight of total MSW.

In developing country like Pakistan where there is no limitation of land but resources are limited certain cost effective and innovative measures must be needed to integrate it with design and construction of these dumpsites to avoid the spread of pollution from these sites, as the MSW consist of Hazardous and nonhazardous.

1.2 Open Dumping in Pakistan

Open dumpsites are very common in developing countries, this is due to the less budget for waste disposal and lack availability of trained professional. In Pakistan Open dumping of MSW is very common practice. Open dumping poses serious danger to groundwater and also soil resources .(Ali et al., 2014)

Pakistan is facing rapid weakening of environmental conditions due to the bad system of collection and disposal of solid wastes. Therefore, metropolitan waste management is becoming a major concern in cities. Very few efforts have been done to advance the waste collection and disposal system. This has some serious outcomes ranging from worsening of soil quality to vanishing of plant diversity. (Ali et al., 2014)

Figure 1.1 Open municipal solid waste dump in Pakistan

1.3 Leachate Composition

Leachate may contain elements of inorganic and organic nature. Xenobiotic organic compounds (XOCs) and also heavy metals that are generally classified as the hazardous substances present in leachate. XOCs and heavy metals which are Hazardous can be toxic, carcinogenic, corrosive, reactive, flammable, mutagenic, teratogenic, and also eco-toxic, other than theses hazards, leachate is bio accumulative and/or persistent in environment. Municipal landfill leachate have been identified with more than 200 organic compounds, with more than 35 compounds having the probable of causing harm to the environment as well as human health. Land fill contaminate ground water and more than 1000 chemicals have been identified underground water of area having landfill. The major\ part of these compounds are originated from vegetation decomposing and product of degraded natural materials, containing cellulose and hemicellulose up to 60% of the dry weight of total MSW.

1.3.1 Heavy metals in MSW leachate

Leachate coming from municipal solid waste (MSW) has elevated concerns as a possible pathway emission of contaminant (Huang et al. (2009);(Michalzik et al., 2007). Heavy metals are potential pollutants in leachate of MSW, and are usually exist ranging from concentrations of micrograms/liter to milligrams/liter (Christensen et al., 2001). The movement of these species of metals may be increased with time as the waste get more acidic and even oxidizing conditions rules (Kjeldsen et al., 2002)

Heavy metals usually exist in the arrangement of free cations or in labile complexes (which can easily breakdown) and have more harmful outcome on aquatic ecosystem and organisms than non-labile complexes of metals, since the braked downed metal form is both very portable and can absorb easily onto and pass into marine organisms through tissue (Øygard et al., 2007). less than 10% metals in landfill leachate are present as free metal ions according to literature. (Baun & Christensen, 2004).

1.4 Environmental Impacts of Leachate

1.4.1 Soil and leachate

Due to movement of leachate in the soil, It has contaminated soil with heavy metals i.e. lead, manganese, copper, zinc, cadmium and chromium and the presence of these heavy metals within soils leads to solemn harms as biodegraded is not possible.

1.4.2 Ground water and leachate

Due to the fact that ground water pollution is of a main concern because population in the urban areas is totally dependent on groundwater. Keeping in mind this problem of leaching, Huge amounts of wastes from cities, municipalities, and industries are generated worldwide. Currently huge quantities of Slid waste get into the environment with slight or no treatment particularly in countries that are developing. Ground-water and surface water resources are also threthened by uncontrolled and unmanaged landfills (Futta et al., 1997). Infiltration recharge from surface water, direct migration and inter-aquifer exchange also contaminate Ground-water. The first and second processes affects primarily surface aquifers , third and the fourth may affect surface and also deep aquifers. Due to the above mentioned threats great number of studies in recent year on the impact of landfill leachates on the surface and ground-water has been done. (Abu-Rukah & Al-Kofahi, 2001)

1.5 Liner System

A landfill liner is a permeable barrier of low level that is placed under the engineered landfills which is aimed to reduce the migration of leachate to aquifers and nearby water bodies. Geo synthetic clay liners (GCL) are used nowadays for municipal solid waste landfills. This is quite a new technology and is preferred over conventional liners due to its easy installation, low permeability and its ability to self-repair when holes are caused by swelling. Other examples of liners can be Granular activated carbon, natural excavated soils, plastic, etc.

1.5.1 Single-liner systems

Single liners usually made of a clay liner, sometimes a geosynthetic clay liner, or a specialized plastic sheeting geomembrane. sometimes Single liners are used in landfills that are designed to keep construction and demolition debris (C&DD).

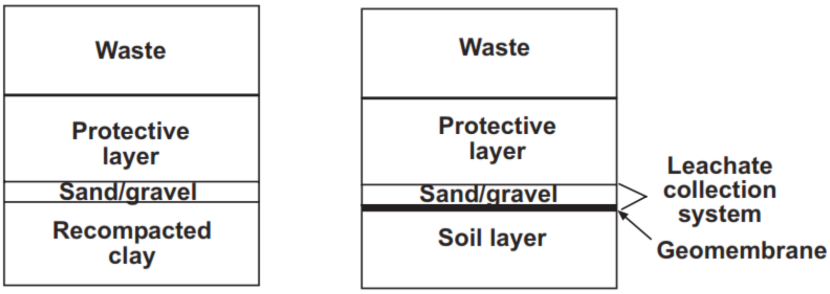


Figure 1.2 Example of single linear system

1.5.2 Composite-liner systems

A composite liner usually consists of a geomembrane in addition to combination with a clay liner (Box 2). Composite-liner systems are extra effective in controlling leachate movement into the subsoil beneath in contrast to a clay liner or a single geomembrane layer. municipal solid waste (MSW) landfills required composite liners system

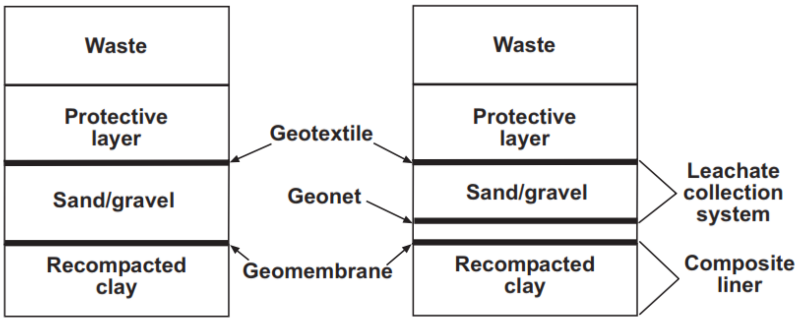


Figure 1.3 Example of composite linear system

1.5.3 Double-liner systems

A double liner usually made of two single liners, may be two composite liners, a single or a composite liner. The top (primary) liner usually purposes to accumulate the leachate, while the inferior (secondary) liner survey as a leak finding system and standby to the primary liner. Double-liner systems in some municipal solid waste landfills are used in all landfills with hazardous waste

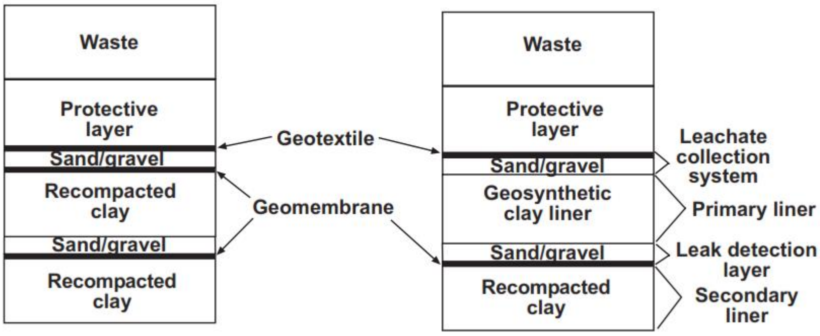


Figure 1.4 Example of double linear system

1.6 Compost as Liner

The organic matter (compost) Structurally contains different functional groups of organic including phenyl hydroxyl, carbonyl, imidazole, amino, sulfonic groups and sulfhydryl. These groups provide sulfonic groups for a wide range of reactive shells that can bond with heavy metals. (Al-Mashaqbeh & McLaughlan, 2014). so compost can also be used a barrier or bio adsorbent layer.

Compost can also be blended with the native soil available in arid areas and then this mixture is used as barrier layer for infiltration in landfill closure covers. gave minimum hydraulic conductivity, optimum moisture content.(Elshorbagy & Mohamed, 2000)

In context of these properties research must be designed to check the efficiency and role of different adsorption material that could act as a barrier layer and minimize the mobility of leachate to ground water.

A similar approach was also adopted in graduate study conduction by institute of environmental science and engineering in which they use compost and sand as retention media.

1.7 TiO_2 Photo Catalyst

The efficiency of such as titanium dioxide (TiO_2), which is a photocatalytic materials, to degrade organic contaminants in water and in air has been under study from more than 35 years.(McCullagh et al., 2007) Titanium dioxide (TiO_2) is widely been used as a photocatalyst for solar energy transformation, construction materials and environmental applications such as paints, concrete tiles, and glasses due to its remarkable properties that may include chemical steadiness, excellent optical transparency, high index of refraction, low budget, and non-toxicity.(Thamir et al., 2016)

1.8 Objectives

- To retain the amount of organic and other contaminants from leachate.
- To Study the contaminant adsorption capacity of
    - Compost
    - Compost + Nanoparticles
- Effect of UV on Photocatalytic Capacity of TiO_2 in the experimental setup

1.9 Scope of the Study

The scope of this study is to identify a cost effective and sustainable solution for leachate treatment from open dumps. Development of bio-adsorbent layer for adsorption of different pollutants. Development of bio adsorbent layer for adsorption of heavy metals comes in leachate from waste stream. Performance evaluation of photocatalytic TiO_2 np + Compost under UV and without UV

Chapter 2

2 Literature Review

2.1 Solid Waste Generation in Pakistan

World bank suggest that urban areas of Pakistan alone is estimated to produce almost 50,438 tons of solid waste daily and is projected to produce 109,244 tons per day by 2025 of which 67 percent is organic waste, 18 percent plastic , 5 % paper waste and 7 % all other types of waste. (Hoornweg & Bhada-Tata, 2012). In a research done at Data Ganj Bakhsh Town (DGBT) using Continual random sampling used, the rate of waste generation was 0.84 kg/cap/day. Organic, paper and plastic are the main components of waste , It account for about 91% of the generated total waste and There was 67.02% organic component in the waste.(Batool & Ch, 2009).

2.2 Leachate

The landfill waste consists usually 20-80% moisture in developing countries**.** This moisture in the waste and rain fall over the landfills generates leachate. In addition to it several type of sewage treatment and industrial process sludge are being disposed with other type of waste in the landfills which have already high water content. It’s obvious that the areas which receive heavy precipitation will generate high quantities of leachate as compared to arid and semi-arid areas. Leachate can be minimized or it can be throwback to the waste quantity in the form of leachate re=showering. It is also in practiced in Italy and is also presently allowed in USA for Slid waste landfills.

Leachate, s a chemical substance, consists of the components of solid waste mass and takes with it along where it flows. Thus there is no general type of leachate and the characteristics of leachate depend on the site specific waste. Leachate quality is an important consideration to avoid groundwater pollution when the liner material has more leakage chances or it is not that efficient to adsorb the contaminants.(Koerner & Soong, 2000)

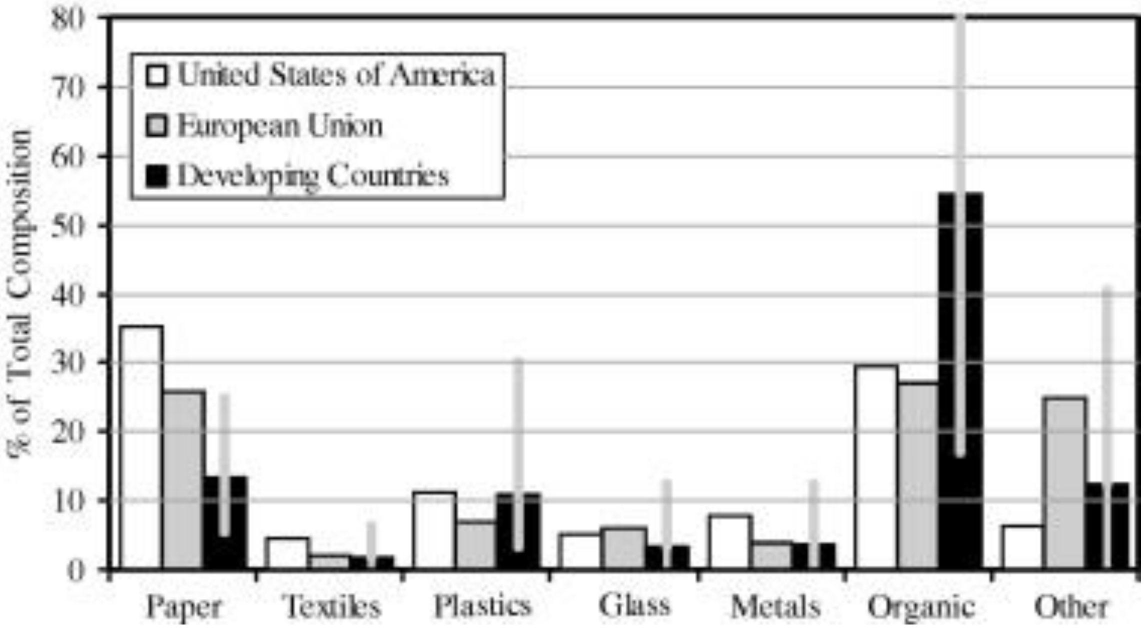


Figure 2.1 Comparison of municipal solid waste composition of developed countries (United States and those in the European Union) against the average of 19 developing countries. Vertical bars provide the range of composition of each material type for the developing countries only (USEPA, 2003; Eurostat, 2003)

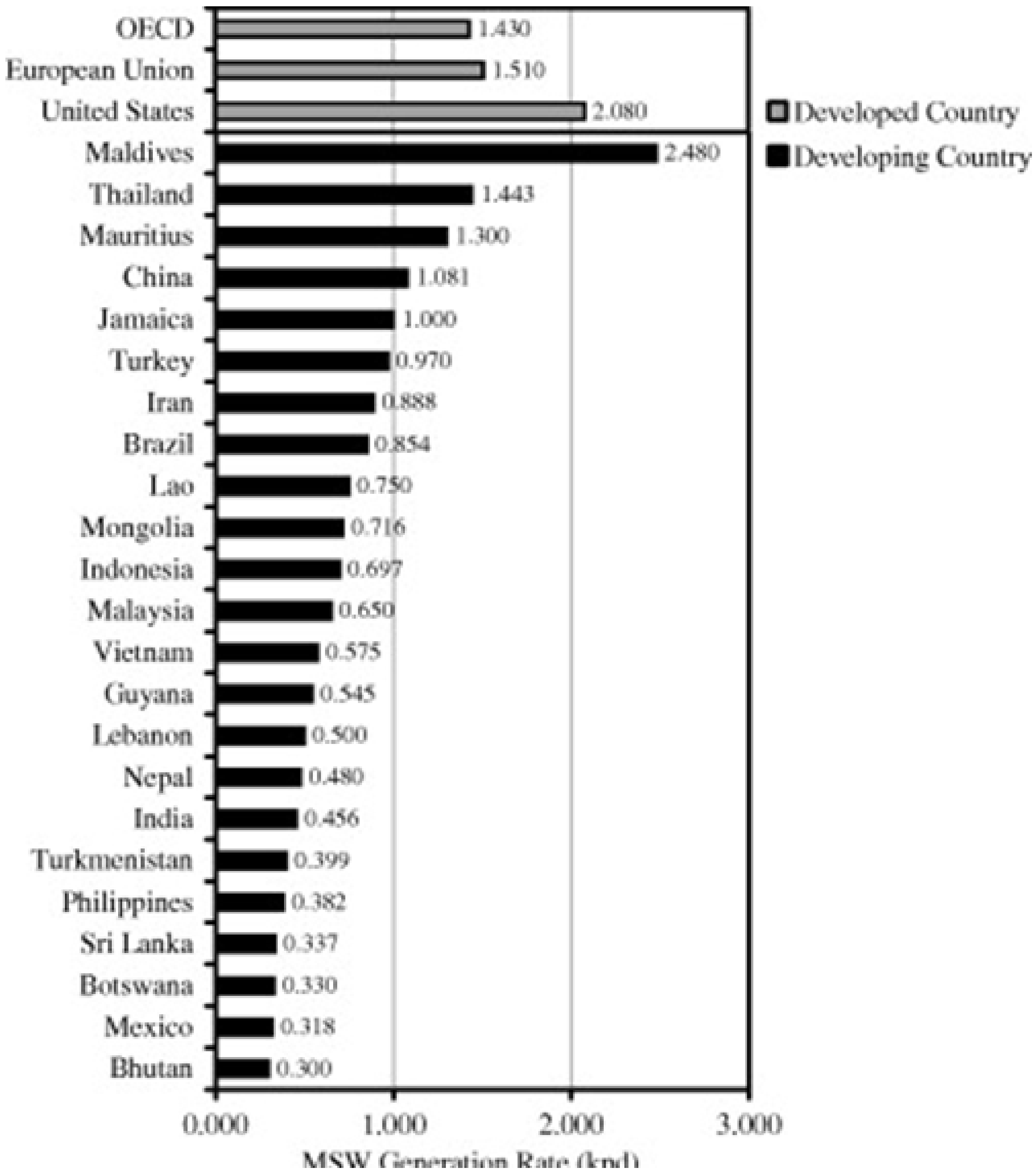


Figure 2.2 Municipal solid waste generation rates (kg/person/day) for 23 developing countries compared to rates of developed countries. (OECD, Organization for Economic Cooperation and Development; European Union – Developed Countries only)

2.3 Generation of Leachate in a Young Landfill

Leachate samples were collected from fourteen landfills in the state of Florida, USA, which contained mainly putrescible waste (municipal solid waste and construction waste), Munciple solid waste incineration ash. or both in combination. To form a mass balance of total dissolved solids (TDS) the percolation assessment included traces of metals, anions and nutrients. As predictable from the old studies, complex matrix of contaminants is leached from MSW in addition ash of percolation MSWI ash leached higher than 98% of metal salts. The MSWI leached samples has higher pH was slightly acidic or neutral, which contradicts the results commonly reported in the literature. It is hypothesized that the cause is a short-circuit of precipitation in the landfill owning to the less hydraulic conductivity reported in ash dumps. The difference in pH probably contributed to the results in the trace metals characteristic of MSWI ash in percolates such as aluminum. The authors concluded that the results of the research in the following study are an symptom of the differences between the studies on the quality of laboratory leachate and the conditions encountered in the field. Furthermore, a characterization of organic matter by qualitative and quantitative analysis has determined that COD is not an accurate indicator of organic matter in leachate from landfills with a significant ash fraction of MSWI.(Moody & Townsend, 2017)

2.4 Leachate Quantity and Quality

20 pollution parameters were examined in the leachate on seasonal basis. The leachate composition varied extensively depending on degree of stabilization, seasonal production, and mainly on influence of different climatic conditions from a landfill in

Thessaloniki, Greece. When the leachate was collected fresh all the parameters showed higher values markedly while the pH lean towards increase from acidic to alkaline with time in the leachate that is mature, therefore it was extra stabilized. Likewise the concentrations of toxic metals were low in fresh samples of leachate and they were observed even lower in the older samples.

The max seasonal mounts production of leachate was observed in spring and in the end of winter. The amount of leachate generated may be proportional to the water that percolates through the waste in landfill and also it depends on the rainwater that the landfill receives. Therefore, there should be less water entering in the landfill in order to reduce the quantity of leachate generation. It was also found that leachate production is greater whenever the disposed waste is fewer compressed, compaction was found to decrease the rate of filtration .(Tatsi & Zouboulis, 2002)

2.5 Landfill Leachate in Arid Areas

Since the leachate generation in arid areas has been ignored on the supposition that they receive less precipitation so less leachate could be generated. A study was conducted in Kuwait on two unlined landfills one of the two was active and the other was old (closed). The temperature in Kuwait ranges from of 20-50 degree centigrade usually and the annual average rainfall is 110 mm. The examination of data collected confirmed that both landfills leached were heavily polluted with organics, salts and heavy metals. After assessing the water balance at these sites a model was presented which showed that the reason of leachate generation in arid areas could be capillary water, content of moisture in the waste and rising of water table. Surface conditions such as sand humps and impact of dry wind situations and humidity in summertime can affect leachate generation. In arid areas ever-increasing water table can alone be a major aspect for generating large amounts of leachate. In arid areas the chemical composition of leachate is difficult to recognize because the properties of leachate do not demonstrate any tendency with the type of waste dumped, waste layer thickness and also with age.(Al-Yaqout & Hamoda, 2003)

2.6 Liner Materials

2.6.1 Clay

Clay barriers can be used in public landfills for groundwater protection. It has showed the best retention capacity to be used as adsorbent to retain metallic cations such as copper. Also the elimination of heavy metals by adsorption dependents on pH [5, 6].(Bellir et al., 2005)

2.6.2 Crushed shales

The shales that are crushed satisfy the main properties of clay liners i.e. they have low hydraulic conductivity in order to control leachate generated from the waste. And also the hydraulic conductivity stables by the reaction of species from the waste when the leachate comes in contact with the liner. The compacted shales show low compressibility for compactions of level. It has also adequate shear strength to withstand the bearing capacity and failures of slope. These requirements are satisfied by usually the natural clay materials but the vastly plastic clays that dehydrate are not preferred because the crashes due to desiccation result in the increase in amount of leachate. (Mohamedzein et al., 2005)

2.6.3 Silty soil

Silty soil excavated in construction projects can also be used as liner material for landfill. It has also been found that leachate infusion does not show variation in the hydraulic conductivity of the excavated soil. Also hydraulic conductivities in laboratory are on 10^{-9} m/s. thus it meets the $1.x10^{08}$ m/s criterion which is also in the Turkish regulations to be used it as liner.(Bozbey & Guler, 2006)

2.6.4 Mudstone

Materials such as mudstone can also be used as landfill liner. The liner must limit the adding of water carefully because addition of more or less water may increase the water conductivity of the liner. It is also concluded that the mudstone liner contains greater than 2.43 cm gravel and 1.78 cm sandy soil in width then the water conductivity of the liner will be lesser than 10^{-7} cm per s. (Sheu et al., 1998)

2.7 Compost as Linear

2.7.1 Clay and Organic Matter

The interactions of chemicals with soil is often studied in discontinuous systems. The clay and the organic material can also be immobilized on a support that is inert, the feasibility investigation of producing porous media with hydrodynamic properties that are similar, but with different surface features. The coating of different materials on silica sand grains helps to study the relations of chemical products and colloids with vigorous flow experiments in a medium that is porous with a structure that is defined (Jerez & Flury, 2006)

2.7.2 Compost, Sand and Biochar

Compost can also be used as bio retention systems in order to improve soil quality, water penetration and holding of pollutants. Compost is comprising of dissolved organic compounds, phosphorus and nitrate, which can dehydrate and potentially contaminate surface and ground water. To reduce the nutrients leaching and organic substances dissolved that are released by compost, the biochar can be mixed in bioretention systems. Biochar and co-composted biochar mixed in matured compost can lessen the leaching of organic carbon, nitrogen and phosphorus. The compost sand mixture was most active in reducing the leaching of nitrates and phosphorus among the media.

Biological conservation systems are based on vegetation and mixtures of soil, sand and compost to filter out the rainwater. The study quantifies the composition of the compost leachate after simulated intermittent storm events. Urban compost crews were watered to simulate 6-hour and 24-hour rainstorms in the Seattle-Tacoma region. The flux was analyzed by pH, electrical conductivity (EC) Concentration of particulates, surface tension, dissolved organic carbon (DOC), phosphorus, nitrogen and copper. The results show a decrease in chemical concentrations during individual storms and after repeated storms. The decrease in phosphorus, copper and DOC concentrations in repeated storms was slower than in nitrate and EC.(Mullane et al., 2015)

2.7.2.1 Removal of nitrates, phosphorus, copper, and dissolved organic matter by compost

Bioretention systems are designed to remove contaminants from stormwater; the following study was to evaluate elimination of nitrates, phosphorus, copper, and dissolved organic matter (DOM) from compost- modified bioretention systems, and to examine the part of DOM on leaching down of copper. Counterfeit bioretention systems were drained with rainstorm water for seven storms with in interval of two-weeks. Copper and DOM complexes are much low toxic than labile copper ions, therefore aquatic organisms have reduced damaging effects of copper with compost modified. (Chahal et al., 2016)

2.7.2.2 Zinc uptake by compost

In another study Zinc adsorbtion on different grain size compost was determined in sets and column studies with a synthetic storm water to evaluate adsorption ability and kinetics. The outcomes showed pseudo equilibrium for acceptance and raised from 2 hours to more than 120 hour as the grain size of compost raised from 75 micrometer to 6.75 mm. .(Al-Mashaqbeh & McLaughlan, 2012)

2.7.2.3 Nitrate removal by compost

In a study by Alcala, Jones et al. 2009 Compost-based materials have been proposed as a biofilter to overcome the environment pollution in many areas to overcome contaminated water and soil. The objective the project is to develop methods to produce products of compost to remove nitrates in rainwater biological filtration applications, from solid waste materials. Compost products were produced with different raw materials and evaluated for efficiency of nitrate removal. Compost products of three different are produced with different amount of wood chips and grass, along with dry compost materials from the town of Brownsville City Landfill , which are evaluated by the column study. All compost products are produced and some nitrates have removed BMLF materials. The project has demonstrated that compost materials can be effectively used to remove nitrates, to improve surface water quality and raw materials and mixtures can affect the ability to remove nitrate materials.(Alcala et al., 2009)

2.8 TiO_2 for Treatment of Leachate

In the recent of years, photo-assisted titanium dioxide (TiO_2) oxidation has demonstrated great possibility for landfill leachate treatment. In the study Heterogeneous TiO_2 photocatalysis along with pretreatment and post treatment was used for MSW landfill leachate. As a final point, proportional evaluation of this method with other innovative oxidation processes (AOPs) and returns and disadvantages of the technologies are underlined together with future research opportunities.(Hassan et al., 2016)

2.8.1 Removal of aromatic compounds by TiO_2

In this study by Rocha, Vilar et al. 2011 different varied (TiO_2/UV, TiO_2/H_2O_2/UV) and similar (H_2O_2/UV, Fe_2+/H_2O_2/UV) photocatalytic methods were evaluated as an alternate for the treatment of a matured landfill leachate. The adding of H_2O_2 to TiO_2/UV system enhanced the decrease of the aromatic compounds from 15 percent to 61 percent, while mineralization is nearly the same. The DOC and aromatic part removal was also similar for the H_2O_2 to UV and TiO_2/H_2O_2/UV methods (Rocha et al., 2011)

2.8.2 Photo catalytic nitrate degradation by TiO_2

In another study, nitrate luminescence in a water environment at 292 K was studied in an intermittent system that opened up to the ambient. Humic acid was added as a promoter ans Titania was tested as a photocatalyst. A 28% conversion was achieved after 80 hours when 44 mg / l nitrate solution was exposed with a high-pressure Xe light; The main product is nitrite. The addition of humic acid (20 mg / l) has accelerated the reduction of nitrate to nitrite, but the promotion mechanism cannot be determined explicitly. The degradation of catalyst nitrate comes with a uniform reduction of more toxic nitrite; It requires any efficient catalytic system to reduce nitrite levels.(Bems et al., 1999)

The photo degradation of nitrate in an aqueous solution was examined in this study by using dissimilar Au/TiO_2 photocatalysts and oxalic acid as hole catcher. Though complete removal of oxalic acid is possible under conditions provided, complete nitrate reduction was also not achieved and the level of alteration showed a dependence on hole catcher concentration. (Anderson, 2012)

Different Samples of iron-doped titania was prepared, and was examined as photocatalysts in two different reactions: nitrite oxidation and Cr(VI) drop at pH 6.5. For Cr(VI) reduction, all the doped samples were less in activity than TiO_2 with no reasonably differential activity. (Navío et al., 1998)

2.8.3 Reduction of phosphorus by TiO_2

The effects of nano-TiO_2 is very little known about that how the conversion and movement of phosphorus (P) in sediments resumed in a study by Luo, Wang et al. 2010 Chemical sequential extracts were used to study P fractions and their release in sediments was resumed under the influence of nano-TiO_2 and UV irradiation. The results showed that the sediment content of P in all the fractions decreased when increasing the concentration of nano-TiO2 in UV irradiation. Obviously nano-TiO2 in UV irradiation does not dissolve P immobilizer and release the reducing P. from the resold sediments, probably because (1) some of the P released by the fractions was re-refined by P released by OM; (2) Nano-TiO2 photocatalyst reduces the bonding ability of recombined sediments. Results showed that the nano-TiO2 photocatalyst process can bring potential to adjust and transport P sediments in water environment. (Luo et al., 2010)

The porous ceramic filter medium (PCFM) has been applied to reduce P release in lake sediments and we wonder whether nano-TiO2 coating can improve PCFM's P absorption in lake sediments. The results showed that sediment only release of TP is in small amount within 8 hours. The effect of P sediment removal in all fractions can reach a maximum of 8 hours and 22 days in stirring and static experiments respectively. Remaining concentrations of Ca-P, Fe / Al-P, IP, OP and TP in sediments were 85 mg / kg, 255 mg / kg, 310 mg / kg, 95 mg / kg and 431 mg / kg, respectively. , and the removal rates are 19.04%, 44.81%, 43.04%, 45.09% and 44.10%, respectively, the results show the adsorption of sediment P on the nano-film PCFM -TiO2 membrane coating has great potential to reduce internal phosphorus pollution and regulate sediment transport P in water environment.(Zhang et al., 2014a)

Chapter 3

3 MATTERIAL AND METHODOLOGY

3.1 General

General scheme of the experiment work includes Selection of the leachate collection site and sample collection. Selection of compost, silica sand and TiO_2. Designing of experimental setup. Preparation of TiO_2. Pre-analysis of leachate and compost. Execution of leaching experiment and post analysis of the treated leachate.

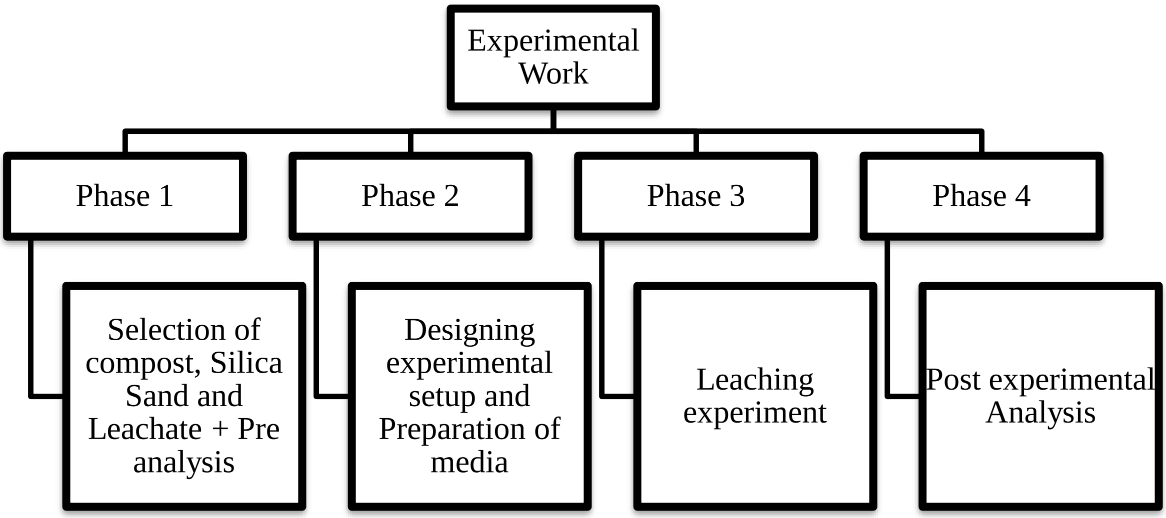


Figure. 3.1 Showing Various Phases of experiments conducted during the research

3.2 Selection of Material and Leachate Collection Site

Silica Sand was obtained from Rawal Treatment Plant. The sand was sieved using Sieve # 10 and Sieve # 16 to obtain a particle size between 1.18mm & 2.00mm Inert Sand was obtained from a construction site near School of Mechanical and Manufacturing Engineering (SMME), NUST. Sieved sand was washed and air dried. Vermi-compost was obtained from (National Agricultural and Research Centre (NARC), Islamabad. Vermi-compost was mixed with distilled water, and was kept on a mechanical shaker for 24 hours, after which it was removed and then air dried. Leachate was obtained from open dumpsite of 1-12 Islamabad in HDPE container. the container was rinsed two or three times and transported to laboratory where it is stored in a refrigerator. All sampling and preservation method carried out for the quality analysis.

3.2.1 Selection of Laboratory Material

Titanium tetra-iso-propoxide TTIP (Daejung Korea) were used as precursor for synthesis of TiO_2 nanoparticles. Silica Sand (from Rawal Treatment plant, Rawalpindi) was used as immobilization substrate. Phenol (Merck Germany) was used as organic pollutant model. All chemicals that were used are of analytical grade except silica sand and glassware (Pyrex, Germany) was used after rinsing with distilled water.

3.3 Designing of Leaching column

A round acrylic column was made with diameter of 3 inches and was enclosed from both ends with nozzles at each end for inward and outward flow of leachate. Plastic Tubes of 10 mm were used to irrigate leaching column. Leachate is forced upward and collected from the top side of the leaching column. the height of the column is 3 inches.

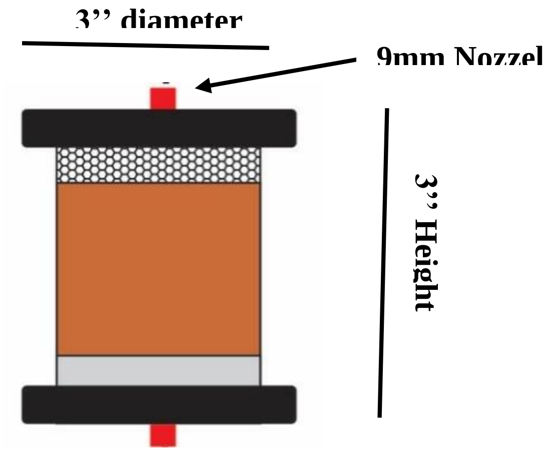


Figure 3.2 : Details of leaching column used in the experiment

3.4 Media Preparation

3.4.1 Synthesis of Titania nanoparticles

Titanium tetra-iso-propoxide (TTIP) was used as precursor for preparating TiO_2 nanoparticles via sol-gel method (Bahadur et al., 2016). 50 ml of 98% ethanol (AnalaR) was took in a conical flask and 5 ml of TTIP was added drop wise with continuous stirring. 1-2 drops of nitric acid (Merck Germany) was added into the solution to keep its pH acidic and the solution was kept for stirring for 4 h. The solution was then allowed to settle overnight. The settled particles were then rinsed with distilled water and was centrifuged at 5000 round per minutes for 10 min. This procedure was repeated for 5 times before the particles were kept in oven for 24 h. Finally, the particles were then calcined at 450 °C with in a muffle furnace whose model is NEY M-525 Series II for 6 hours to remove impurities if any and convert the catalyst into active anatase phase.

3.4.2 Preparation of Catalyst

Silica Sand of 0.7 to 0.8 mm were used as supporting material for the immobilization of nanoparticles using heat attachment method (Neppolian et al., 2002). The TiO_2 nanoparticles were coated onto Silica sand, Oven dried at 105^0C for 24 hours, initially the Silica Sand were dipped in dilute nitric acid for overnight and washed with distilled water. Three grams of each nanoparticle were dispersed in 100 ml of distilled water in respective beakers and sonicated for 10 min. Silica Sand (30 g each) were added to the prepared suspension and magnetically stirred at 300 rpm for 20 min. The mixtures were then dried overnight in an oven at 120 °C. After drying the mixture, it was calcined in muffle furnace at 400 °C for about 2 hours in to remove impurities and enhance the adhesion onto silica sand support.

3.4.3 Pretreatment of Adsorbents

Before applying catalyst to Silica Sand it was treated with dilute nitric acid. The silica sand were dipped in dilute nitric acid solution overnight and then washed with distilled water, and dried in an oven for an hour as shown in Fig 3.3. This pretreatments were carried out to remove impurities from the silica sand further to make its surface rough for better catalyst attachment/adhesion. Vermi-compost was mixed with distilled water, and was kept on a mechanical shaker for 24 hours, after which it was removed and then air dried.

3.5 Characterization Parameters

Initial parameter testing was done on the leachate after diluting it 40 times. The following parameter was selected for leachate before and after the leaching experiment.

.The leachate was tested for following parameters

3.5.1 pH

The pH was measured using an inoLab WTW series pH/cond 720 EC/TDS meter, Germany. The meter was calibrated using suitable buffer whose pH was known. The pH of the water is the sample bottle was measured by dipping the pH glass electrode. Equilibrium between electrode and sample was established by stirring the sample to ensure homogeneity. Using the same temperature was also recorded in degree centigrade.

3.5.2 Electrical Conductivity

Electrical conductivity was measured using inoLab WTW series ph/cond 720 EC/TDS meter, Germany. Measuring conductively is done by calculating the resistance occurring in an area of the solution under test defined by the probe's physical design. A voltage is provided between the two electrodes that are immersed in the solution, and the drop in voltage by the resistance of the solution is used to calculate conductively per centimeter .

3.5.3 Total Dissolved Solids

Total dissolve solids of the leachate was measured by gravimetric method. China dish was pre-weighted and 50 ml water sample was filtered and poured in a china dish. Leachate sample was evaporated in water bath then china dish was dried in oven at 180 ^{O}C. After drying china dish was weighted.

So mg TDS/L = (A-B) x 1000 / sample volume

Where A= weight of the residue (dried) + dish in mg, B = weight of the dish in mg

Given formula was used to calculate total dissolve solids from waster sample

3.5.4 Total kjeldahl Nitrogen

The ammonia nitrogen and organic nitrogen collectively gives total kjeldalh nitrogen. the total Nitrogen is determined right by digesting the whole sample and distillation of both, the ammonia nitrogen present in the sample , as well as that is released by digested organic nitrogen, then proceeding with the ammonia nitrogen test.

$$\text{Organic-Nitrogen} + H_2SO_4 \longrightarrow (NH_4)_2SO_4 + CO_2 + H_2O$$

When acid is first added to the leachate sample, the organics turn black. A clearing of the liquid indicates complete destruction and conversion after 1 to 2 hours of boiling. on cooling, a sodium hydroxide reagent is added to raise the pH and to convert the ammonium to ammonia as:

$$(NH_4)_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2NH_3^- + 2H_2O$$

The released ammonia is distilled into an indicated boric acid solution

$$NH_3 + H_3BO_3 \longrightarrow NH_4^+ + H_3BO_3^+$$

The color of the mixed indicator change, which indicates adsorption of ammonia. the the distillated (borate ions) in titrated against a standardized acid that in turn quantifies the amount of ammonia evolved from the sample

$$\text{H2BO3-} + H^+ \longrightarrow H_3BO_3$$

3.5.5 Nitrite

Nitrite is measured using colorimetric method. Nitrite reacts with sulfanilamide and also N-(1-naphthyl)-ethylene-diamine dihydrochloride to give a red-violet diazo dye.

The red diazo dye is then measured on the base of its absorbance at visible range on 540 nm using an Oasis Scientific UV/Vis Spectrophotometer model T-60 UV PG, UK. The intensity of this color is relative to the nitrite concentration.

Nitrite + sulfanilamide + N-(1-naphthyl)- ethylenediamine → diazo dye

3.5.6 Ortho-Phosphate

Orthophosphates were measured using an Oasis Scientific UV/Vis Spectrophotometer T-60 UV PG, UK. The absorbance was measured against a wavelength of 470nm. In an orthophosphate solution, ammonium molybdate reacts and form molybdophosphoric acid. In presence of vanadium, vanadomolybdophosphoricacid $[PO_4.VO_3.16MoO_3]4-$ (yellow in color) is produced. The intensity of this yellow color is relative to the phosphate concentration. Added 1 ml of molybdovendate reagent in 25mL of distilled water (as blank, for zeroing) as well as in 25mL of sample to be tested, left them for 3 minutes. Placed blank in holder, adjusted zero, placed sample cell in holder, pressed read and noted down the results in P (which will be orthophosphorus) in sample

3.5.7 Total Phosphate

All form phosphorus compound in sample is converted to orthophosphate using strong acid digestion $HClO_4$ or H_2SO_4-HNO_3. The sample is measured using an Oasis Scientific UV/Vis Spectrophotometer T-60 UV PG, UK. The absorbance is measured against a wavelength of 470nm. Spectrophotometer T-60 UV PG, UK. The absorbance was measured on a wavelength of 470nm. In an orthophosphate solution, ammonium molybdate reacts and form molybdophosphoric acid. In presence of vanadium, vanadomolybdophosphoricacid $[PO_4.VO_3.16MoO_3]^{4-}$ (yellow in color) is produced. The intensity of the yellow color is relative to the phosphate concentration. Added 1 ml of molybdovendate reagent in 25mL of distilled water (as blank, for zeroing) as well as in 25mL of sample to be tested, left them for 3 minutes. Placed blank in holder, adjusted zero, placed sample cell in holder, pressed read and noted down the results in P (which will be orthophosphorus) in sample.

$$\text{All form of Phosphorus-compound in sample} \xrightarrow{\text{Strong Acid digestion HClO4 or H2SO4-HNO3}} \text{Orthophosphate}$$

$$PO_4^{-3} + MO_7O_{24}^{6-} + VO_{3-} \xrightarrow{\text{Acid}} [PO_4.VO_3.16MoO_3]^{4-}$$

3.5.8 Dissolved Organic Carbon

Combustion / NDIR Method is used for TC and is measured by injecting a portion, 10 or 100 microliter, of the sample in a preheated combustion tube that is packed with an oxidation catalyst. The water get vaporized and TC with both the organic carbon and inorganic carbon, is converted to carbon dioxide (CO_2). Then the carbon dioxide is passed with the carrier gas stream from combustion tube to a NDIR (non-dispersive infrared gas analyzer Oxygen) and concentration of this carbon dioxide is measured. The TC concentration in the sample is gained by the calibration curve prepared with standard solutions. IC is evaluated by injecting some portion of the same sample in an IC reaction chamber that is filled with phosphoric acid solution. All IC converted into carbon dioxide is measured with a NDIR. TOC is obtained from the difference of TC and IC.

3.5.9 X-Ray Diffraction (XRD)

XRD analysis of pure TiO_2 np immobilized on Silica Sand was carried out using JEOL JDX-II, X-ray diffractometer. The analysis was done by using Cu Kα radiation at a voltage of 40 kV and 30 mA of current. The scanning was also done between 10^o to 80^o at the rate of 2^o per minute.

The size of crystal is determined by XRD analysis using Scherer equation

$$L = \frac{k\lambda}{\beta \cos\theta}$$

Where,

K = 0.9, shape factor of spherical particles

$\lambda = 0.15405$ nm, $CuK\alpha_1$ wavelength

β = Full width of a diffraction line at one half of maximum intensity (FWHM) radian

θ = The diffraction angle of crystal phase

3.5.10 Scanning Electron Microscope (SEM)

Scanning Electron Microscope provides images of high resolution. The focused beam of electrons generates images that provide information like appearance, form, size, elemental composition of specimen. The Nova NanoSEM 450 scanning electron microscope (SEM) is used to observe the morphology of prepared grains and catalyst powders. Qualitative and quantitative compositional analysis of the samples was carried with microscope that was equipped with highly precise Oxford Energy Dispersive X-ray (EDX) detector.

3.6 Experiment setup

Leachate was forced from the bottom to the media in the columns using . The leachate used was obtained from IJP Road, Islamabad. The original leachate was diluted 40 times. The columns were irrigated with a flow rate of 1 ml/min. The total duration of the Control Run was 24 hours and the total duration of the Main Run (with UV and without UV) was also 24 hours. The samples were collected in DI washed polyethylene terephthalate (PET), and then stored in a cool place until further testing.

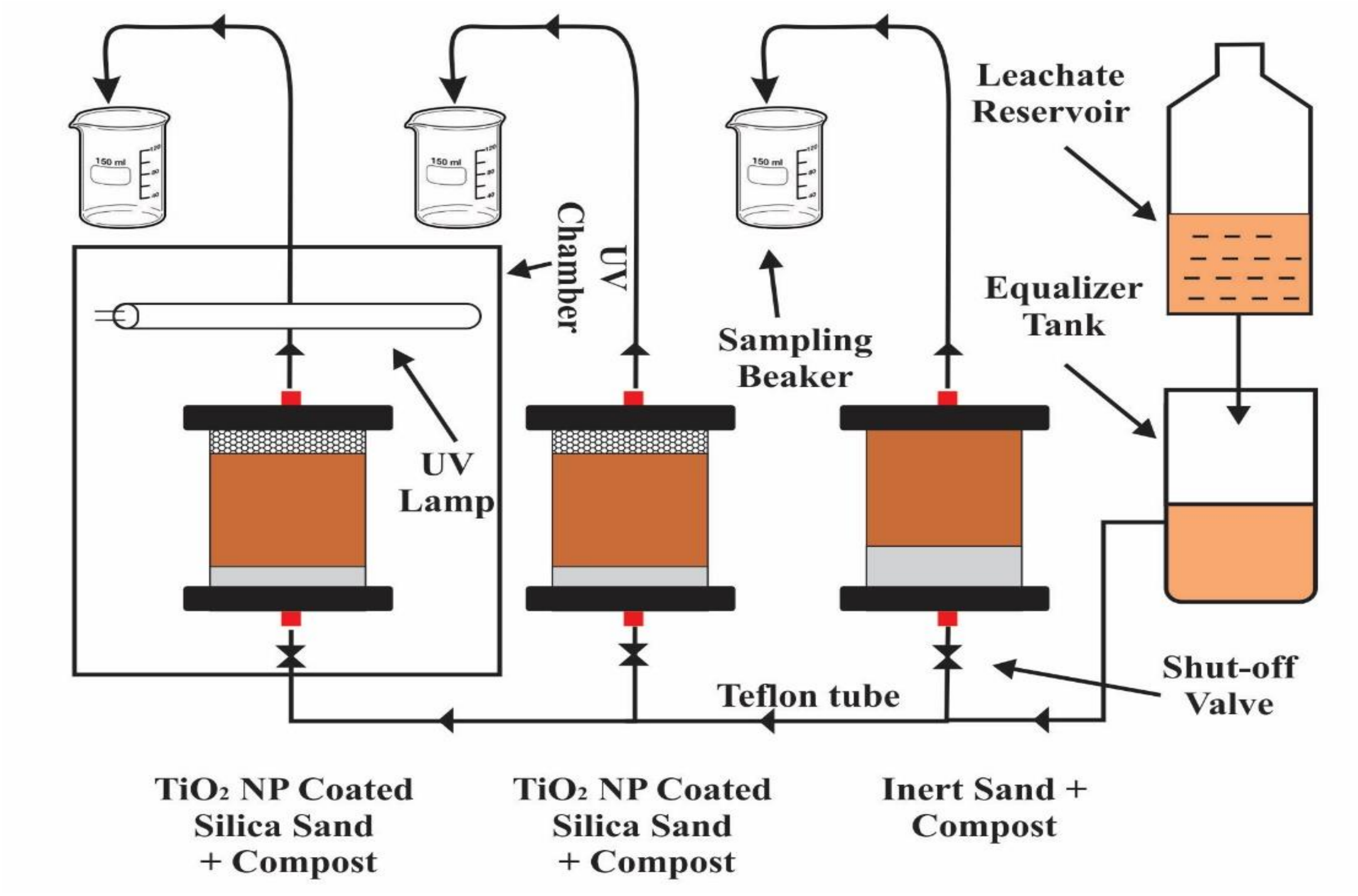


Figure 3.3 Details of leaching column used in the experiment

Chapter 4

4 RESULTS AND DISCUSSION

4.1 Media Characterization

Sand was obtained from a construction site near School of Mechanical and Manufacturing Engineering (SMME), NUST. The sand was sieved using Sieve # 10 and Sieve # 16 to obtain a particle size between 1.18mm & 2.00mm. Sieved sand was washed and air dried. Vermi-compost was obtained from (National Agricultural and Research Centre (NARC), Islamabad. Vermi-compost was mixed with distilled water, and was kept on a mechanical shaker for 24 hours, after which it was removed and then air dried.

Table 4.1 Characteristic of raw compost used in the study

Parameters	**Values**
pH	6.5 – 7.5
Moisture Content (%)	20 – 30
N (%)	1 – 2
P (%)	0.2 – 0.3
K (%)	0.8 – 2
TOC (%)	>20
C:N	13 – 20
Cu (mg/g)	>0.02
Zn (mg/g)	>0.1
Fe (mg/g)	1 – 1.5
Mn (mg/g)	0.3 – 0.5

4.2 Leachate Characterization

The leachate was filtered by using regular filter paper to remove large debris like leaves and soil particles.

Initial parameter testing was done on the leachate after diluting it 40 times. The leachate was tested for pH, Electrical Conductivity, Total Dissolved Solids, total kjeldahl Nitrogen Nitrates/Nitrite, Orthophosphate, Total Phosphate and Dissolved Organic Carbon.

DOC was measured using an Oasis Scientific UV/Vis Spectrophotometer T-60 UV PG, UK .The absorbance was measured against a wavelength of 465nm. The result obtained for DOC was 27.155 mg/L. Orthophosphates were measured using an Oasis Scientific UV/Vis Spectrophotometer T-60 UV PG, UK. The absorbance was measured against a wavelength of 470nm. The result obtained for Orthophosphates was 4.241 mg/L and for Total Phosphate 30.132 mg/L

Nitrates were measured using an Oasis Scientific UV/Vis Spectrophotometer T-60 UV PG, UK. The result obtained for Nitrates was 2.182 mg/L.

pH was measured using an EU-Tech Cyber Scan pH 510 pH meter, USA .The result for pH was 7.8. Electrical conductivity was measured using inoLab WTW series ph/cond 720 EC/TDS meter, Germany. The result for EC was 277 µS/cm. Total Dissolved Solids were measured using an inoLab WTW series ph/cond 720 EC/TDS meter, Germany. The result for TDS was 137 mg/L.

Table 4.2 Characteristic of Leachate used in the Study as Leachate

Parameters	Results
Ph	7.8
Electric Conductivity µS/cm	277
Total dissolve solid (mg/L)	137
Total kjeldahl Nitrogen (mg/L)	5.2
DOC (mg/L)	27.15
Orthophosphate (mg/L)	4.24
Total Phosphate (mg/L)	30.13
Nitrite (mg/L)	2.182
Cu (mg/L)	>0.02
Ld (mg/L)	>0.1
Cr (mg/L)	1 – 1.5

4.3 X-ray Diffraction (XRD)

The identification of all phases were done by matching experimental patterns to the JCPDS powder diffraction file. The pure TiO_2 phase anatase was only identified with JCPDS card no 21-1272. Rutile phase were not identified in diffraction peaks.

XRD pattern of pure TiO_2 is shown in Fig.4.1 along with its characteristics peaks. The XRD

pattern displayed a major peak at 2 theta value of 25.24° also with successive peaks at 36.90°, 37.72°, 38.53°, 47.99°, 53.82°, 54.97°, 62.04°, 62.60°, 68.75°, 70.27°, and 74.96° this confirms the existence of pure anatase structure of TiO_2. Further Average particle size of pure TiO_2 is calculated as per Scherrer equation is found out to be 48 nm.

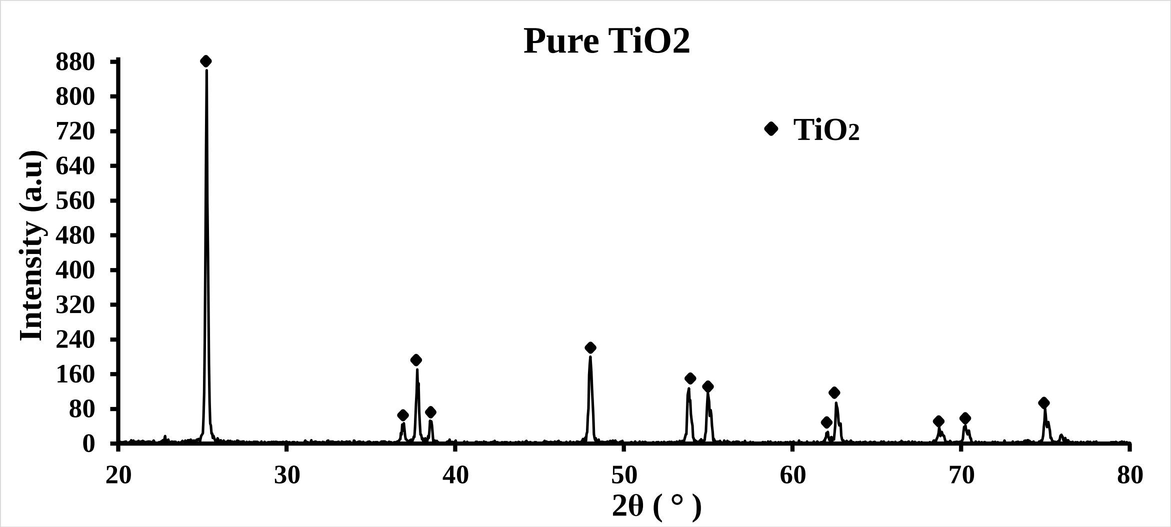


Figure 4.1 XRD patterns of Pure TiO_2 used in the Experiment

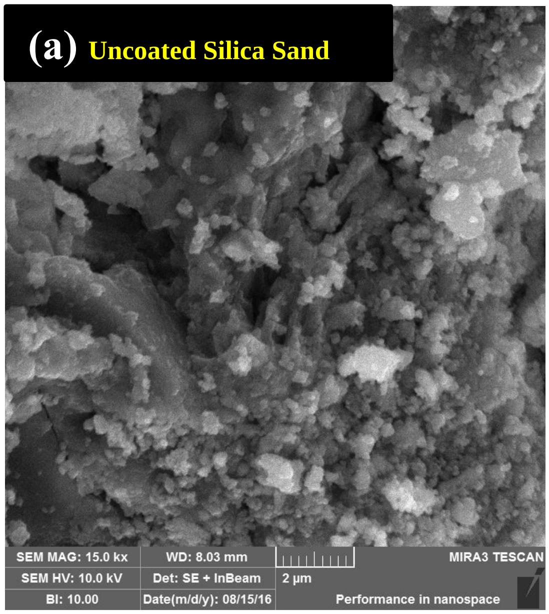
Table 4.3 X-ray Diffractometer Results of Pure TiO_2

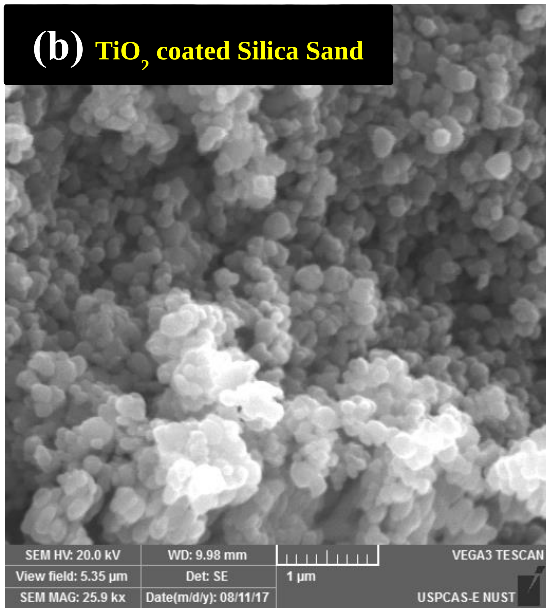
Sr. No.	Peak Angle	d-spacing	FWHM
1	25.23	3.52	0.15
2	37.73	2.38	0.19
3	47.99	1.89	0.23
4	53.82	1.70	0.19

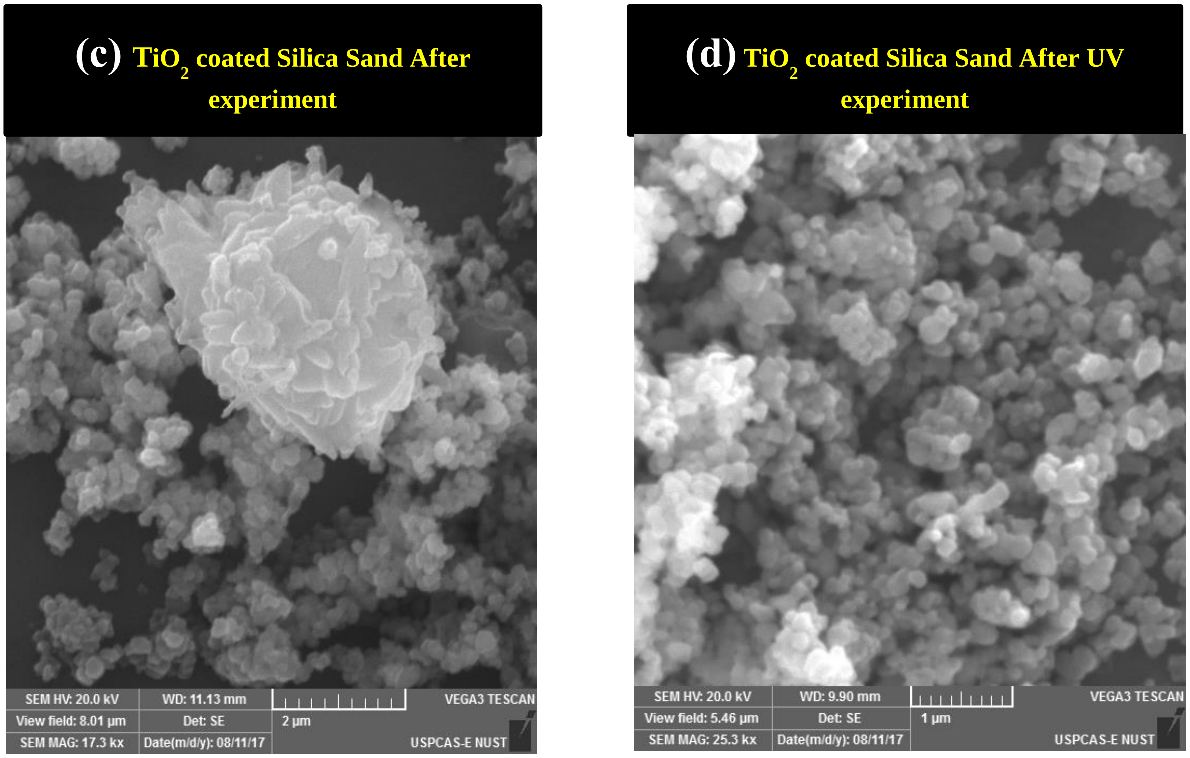
4.4 Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) of the samples is also done from IST. Figure (a) shows the Scanning Electron Microscopy image of Uncoated Silica Sand. The figure show a course structure Fig (b) Show SEM image of TiO_2 coated Silica Sand at 1 micro meter and it shows the successful coating of titania nanoparticles on sand Illustrative images of catalyst after calcination at 550°C

Figure (c) shows the image of TiO_2 coated Silica Sand After the experiment without UV and Figure (d) shows the image of TiO_2 coated Silica Sand After the experiment with UV. Both figures shows that the titania is still present on the sand and can be reused.







(c) TiO_2 coated Silica Sand After experiment

(d) TiO_2 coated Silica Sand After UV experiment

Figure 4.2 SEM images of catalyst (a) shows the SEM image of Uncoated Silica Sand Fig (b) Show SEM image of TiO_2 coated Silica Sand Figure (c) and (d) shows the image of TiO_2 coated Silica Sand After the experiment and under UV respectively.

The micrograph images showed the formation of compactly packed catalyst nanoparticles with even distribution of Titania on the Silica support. The partical size distribution from these images can be judged visually in a range of about 40-80 nm . SEM images of samples appears to be consist of of agglomorated nanoparticles. Therefore well dispersed TiO_2 particles can easily be accessed by pollutants in leachate.

4.5 pH and EC

The figure above includes pH, electrical conductivity, as a function of cumulative flux. Generally, the pH of the leachate coming from all three treatments increased during the start of the leaching experiment, but get even as the leaching tend to continue (Fig. 4.3). The initial pH of the inoculated leachate samples of all treatments was 7.8. In the succeeding samples until 0.42 L cumulative flux, the pH raised and plateaued at a pH between 7.5 and 8. The increase of pH is due to leaching of cations from bases and because of the buffering capacity of the compost.

The pH of the first two samples in control and treatment without UV is higher and then reduce eventually, but the pH of the treatment under UV is showing a constant behavior, this is possibly due to the photo catalytic actively of the TiO_2 nano particles that break down certain cations.

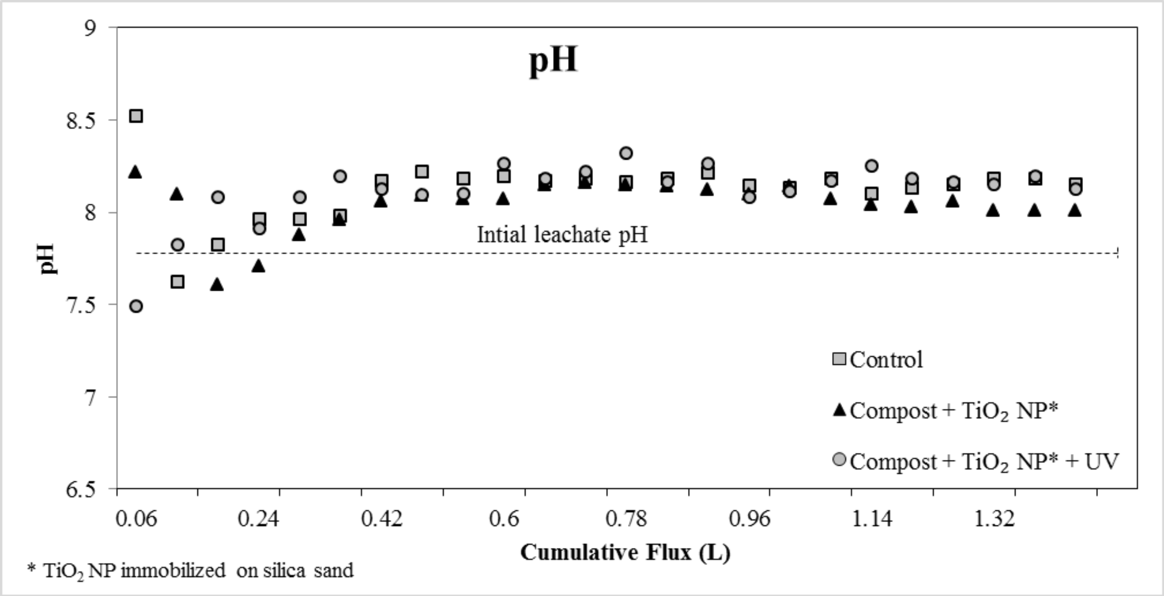


Figure 4.3 pH during leaching experiment conducted using TiO_2 NP immobilized on silica sand in the presence and absence of UV

4.6 Electrical Conductivity

The electrical conductivity of the treated leachates from all treatments showed a decreasing trend as leaching advanced (Fig. 4.4). The initial electrical conductivities were higher in the treatment performed under UV than in treatment performed without UV and Control respectively. Electrical conductivities were higher for the first 2 to 3 hours, equivalent to about 200 ml cumulative flux, and it get dropped below 1 dS/m. Each of treatments was considered by a distinct peak in electrical conductivity monitored by a continuous decreasing in electrical conductivity as the leaching advanced. The mounts of successive leaching reduced continuously; though, peak concentrations stayed above 0.4 dS/m even after leaching of 24 hours. The fast decline in electrical conductivity of the Leachate in reference to increased irrigation was also detected n study by (Xia et al., 2007), which irrigated a compost containing biosolids and yard waste with deionized water for cumulative 330 mm of water flux. Our study also showed that electrical conductivities never get below 1 dS/m in treatment under UV which is contrary to study of (Xia et al., 2007).

The Electric Conductivity of the treatment under UV is higher than all other treatments and never come down to the initial concentration of leachate. Similar trend is also observed by treatment with UV and control also show similar trend. The high electric conductively in treatment under UV is due to the photo catalysis of complex molecules present in compost to simpler components.

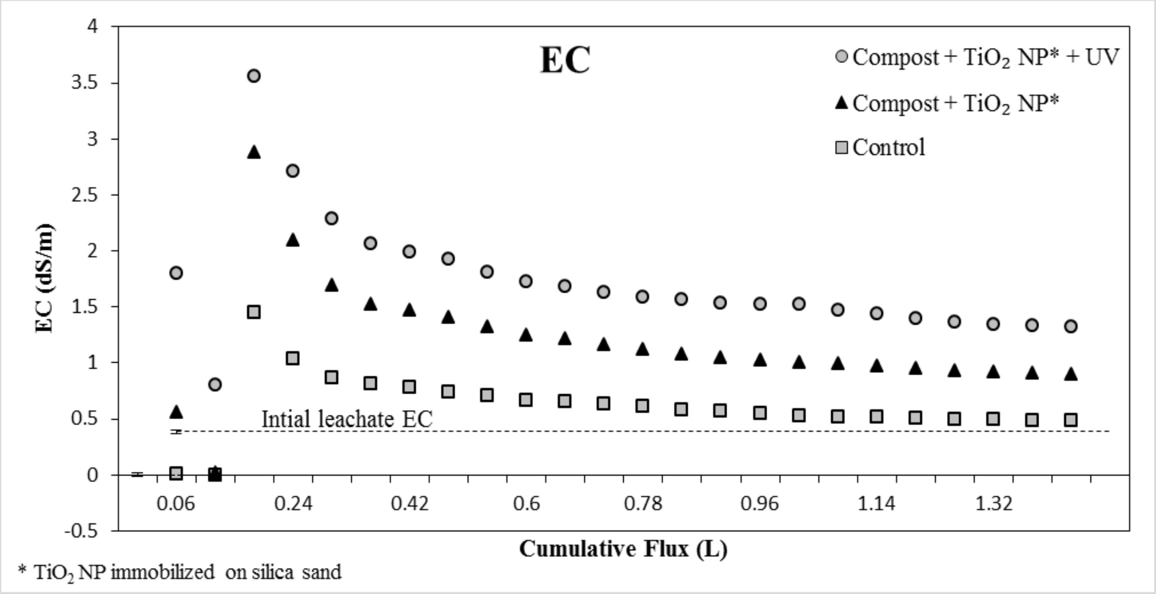


Figure 4.4 Electric Conductivity reduction during leaching experiment conducted using TiO_2 NP immobilized on silica sand in the presence and absence of UV

4.7 Ortho-Phosphorus

The leaching pattern of total phosphorus and ortho-phosphorus was found to be similar treatments with the applications of nano particles under UV and without UV. This was also noticed by (Kong et al., 2007) and (Abu-Rukah & Al-Kofahi, 2001) where concentrations of phosphorus in the leachate get increased after the next leaching event, and it get never lower below 10 mg/L, and differed from that observed by (Iqbal et al., 2015),. Higher concentrations of phosphorus in leachate was also observed by (Kong et al., 2007; Xia et al., 2007) and is because due to the difference in feedstock (biosolids and yard waste mix) and may be due to the higher phosphorus content present in the compost similar to our study.

More phosphorus leached from the control and less phosphorus leached from treatment under UV. has been explained by (Zhang et al., 2014b) who showed that the sediment released just a minor amount of TP in 8 h treatment with TiO_2. It also suggested that the removal efficiency of P in sediment in all forms can reach maximum.

The phosphorus that is leached was almost solely in the form of ortho-phosphorus. This I sduw to composting procedure, in which organic phosphorus get mineralized and soluble when it comes in interaction with the water (Sharpley and Moyer, 2000).

Contrary to the study by Phosphorus do not adsorb to the exterior of the major portion of biochars (Yao et al., 2012; Hale et al., 2013) n tis study TiO_2 sorb certain amount of Phosphorus as shown by the results of the treatment without UV

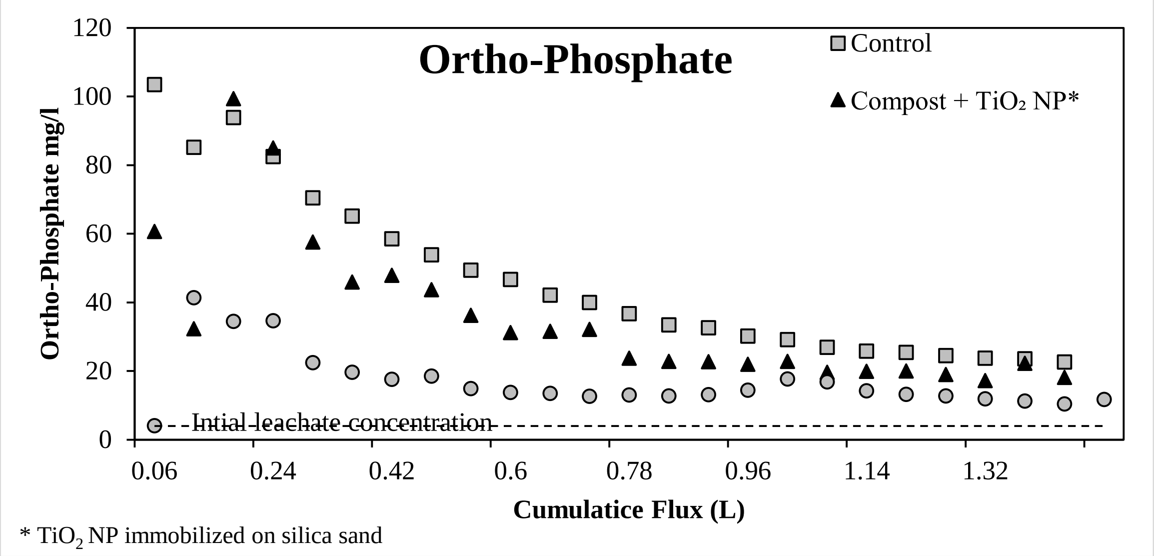


Figure 4.5 Ortho-phosphorus reduction during leaching experiment conducted using TiO_2 NP immobilized on silica sand in the presence and absence of UV

4.8 Total Phosphorus

The X axis of the figure below represents cumulative flux in litres and Y axis represents total phosphate in mg per liter The leaching pattern of total phosphorus and ortho-phosphorus was found to be similar to treatments with the applications of nano particles under UV and without UV. In the treatment under UV the after leahing of almost 200 ml total reach the level of intial concentration of total phosphorus and never goes beyond this level till the end of the experiment which shows that Titania Nano particles can significantly reduce phosphorus leaching. This was also noticed by (Kong and his coworkers and and Abu-Rukah and his coworkers where phosphorus concentrations in the leachate increased after the second leaching event, and never declined below 10 mg/L, and differed from that observed by the study of Iqbal and it coworker.

More phosphorus leached from the control and less phosphorus leached from treatment under UV. has been explained by the study of Zhang and its coworkers who showed that the sediment released only a small amount of TP within 8 h treatment with TiO_2

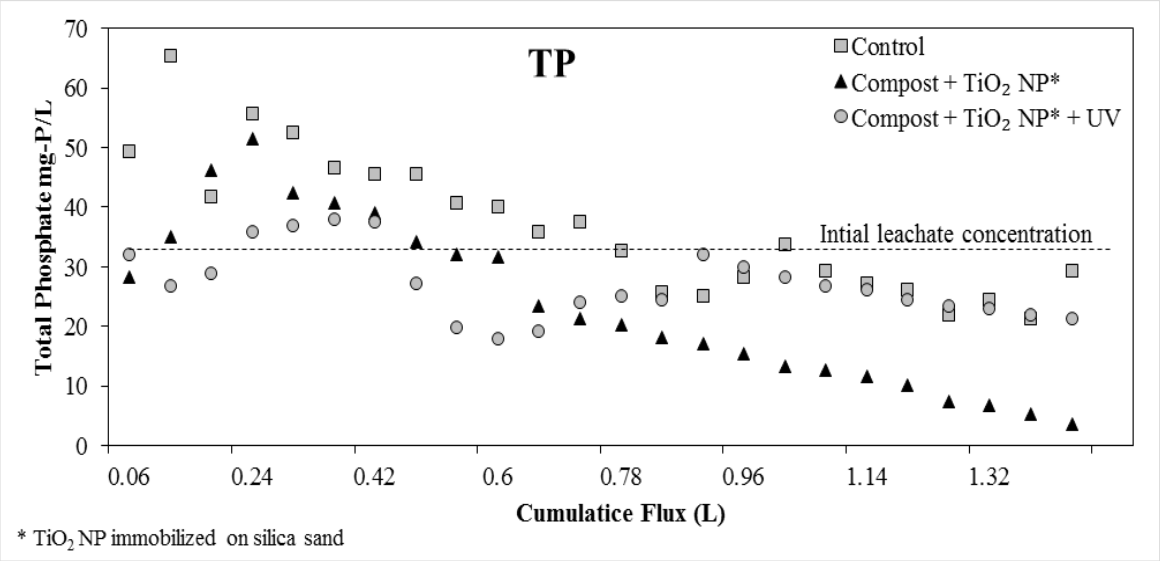


Figure 4.6 Total-phosphorus reduction during leaching experiment conducted using TiO_2 NP immobilized on silica sand in the presence and absence of UV

4.9 Total Dissolved Solids

TDS was high in the initial flux of 0.6 L in the range of 0.2-0.8 g/l but decreased sharply and stabilized in the range of 0.2-0.4 g/l respectively. The initial high TDS may also have been due to the presence of salts that leached in the initial flux. The treatment under UV light shows a slight difference from the control. which may be due to the mineralization of certain compounds. The trend is similar to that of EC.

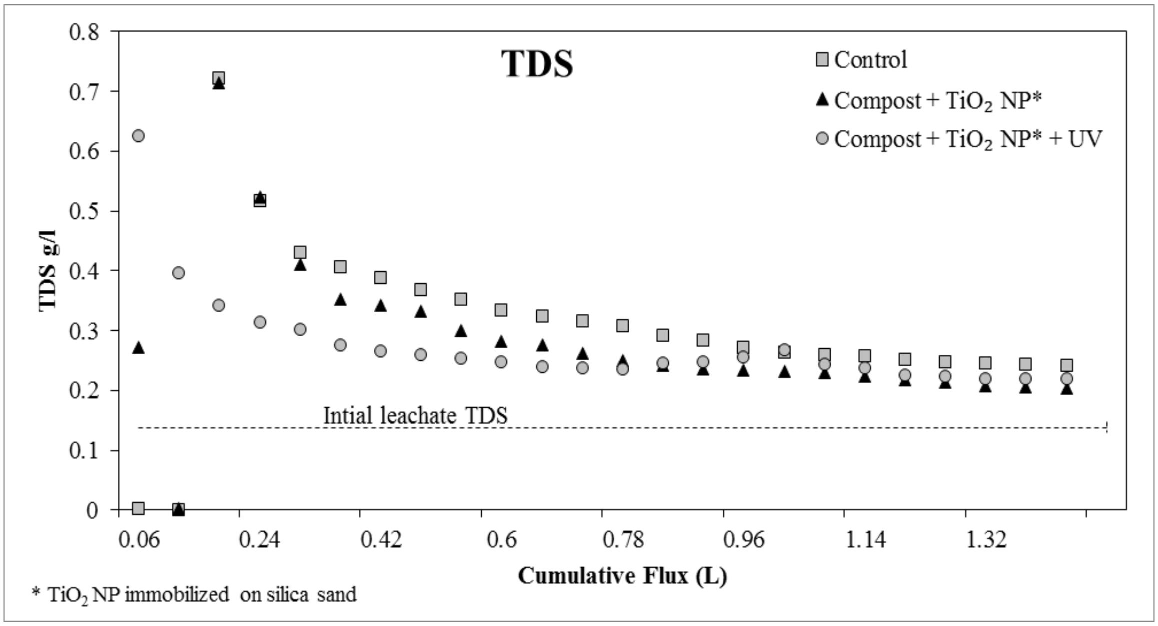


Figure 4.7 reduction during leaching experiment conducted using TiO_2 NP immobilized on silica sand in the presence and absence of UV

4.10 DOC

Although the amount of DOC filtered from each treatment in comparison to the amount of C contained in the columns is very low, significant amounts of DOC have been filtered during all three treatments. Significant differences can be seen between DOC filtering between different treatments, suggesting that TiO2 NP absorbs / catalyzes a significant amount of DOC. In contrast to (Beesley et al., 2014) our treatments added with NP TiO2 observed a slight reduction in the water soluble organic carbon concentration of water in pores when the mixture was mixed copost and biochar, but similar (Dias et al., 2010; Prost et al., 2013) found that modified organic fertilizers can absorb organic matter.

Due to the very low absorbance compared to the study (Mayer, 1999), we can assume that the flow in the unsaturated porous medium provides less contact between liquid and absorbent than the batch reaction, so the adsorption determined by batch adsorption testing can overestimate absorption in unsaturated conditions

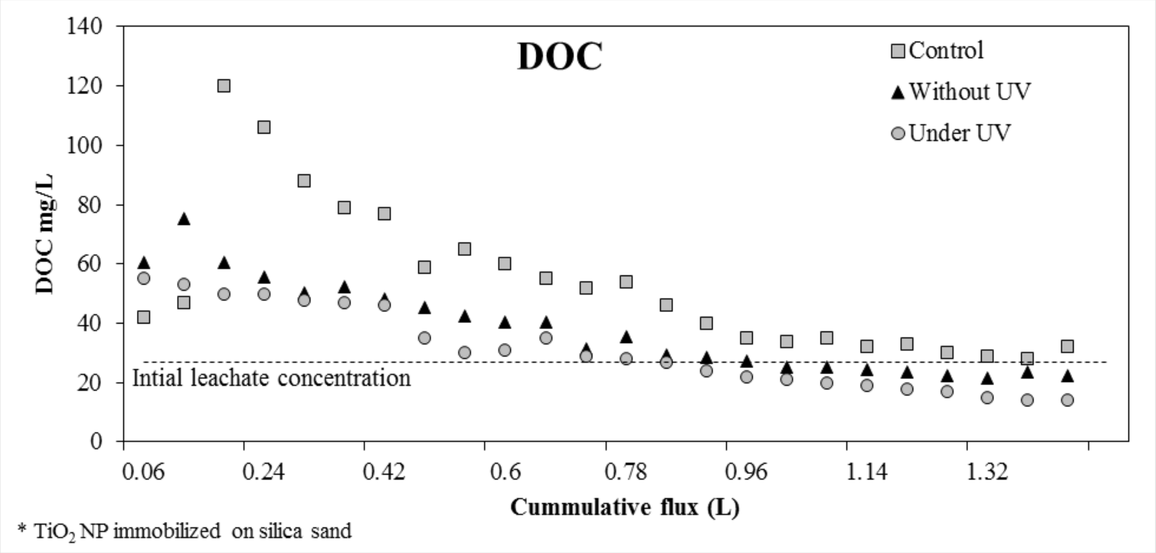


Figure 4.8 reduction during leaching experiment conducted using TiO_2 NP immobilized on silica sand in the presence and absence of UV

4.11 Total Kjeldal Nitrogen

TKN in fig below also shows the same behavior the reduction in concentration is due to the adsorption at TiO_2 NP surface and with treatment under UV show less concentration due to mineralization of some of the simple species of nitrogen in the leachate.

TKN shows similar leaching trend in all the three treatment but the concentration of TKN in control run containing only compost is high because of the leaching of the available nitrogen in compost. for the treatment performed under UV and without UV shows the same behavior the reduction in concentration this is due to the adsorption at TiO_2 NP surface and with treatment under UV show less concentration due to mineralization of some of the simple species of nitrogen in the leachate

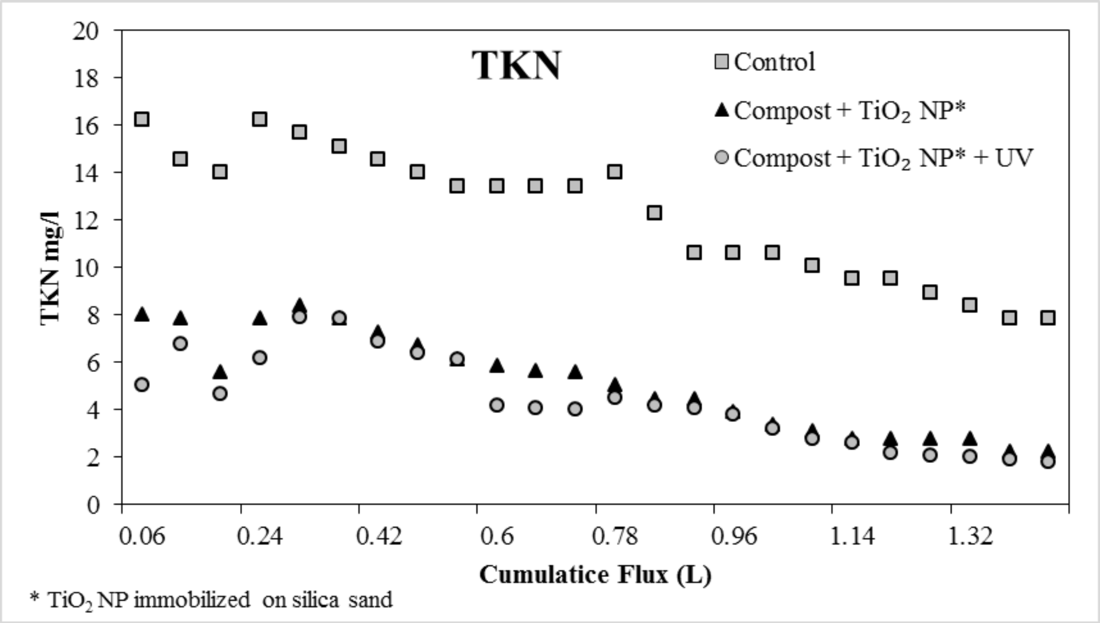


Figure 4.9 Total Kjeldal nitrogen trend during leaching experiment conducted using TiO2 NP immobilized on silica sand in the presence and absence of UV

4.12 Nitrite

Contrary to the study by (Knowles et al., 2011); (Iqbal et al., 2015) which say that because of the negative charge of biochar surface, nitrate and nitrite do not get sorbed, TiO_2 np being positively charge particles sorbs nitrate. Observed reduced nitrite leaching from in the figure above is due to the photo degradation of nitrite to nitrate.

The nitrite is reducing according to the study in which photocatalytic degradation of nitrate in aqueous solution has been determined in this study by using different Au/TiO_2 photo catalysts. (Anderson, 2012)

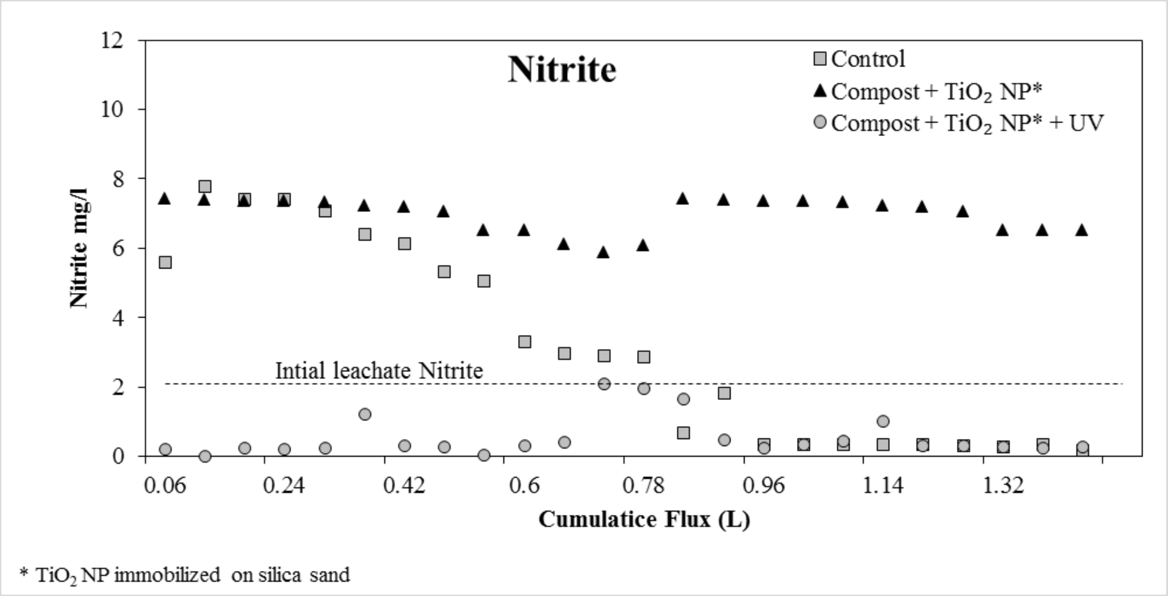


Figure 4.10 Nitrite reduction during leaching experiment conducted using TiO_2 NP immobilized on silica sand in the presence and absence of UV

4.13 Heavy Metals

Metals like copper and heavy metals like lead and chromium show significant reduction in all the three experiments.

4.13.1 Copper

The X axis of the graph below represents cumulative flux in liters and Y axis represents copper concentration in mg per liter. At the start of the experiment the concentration of copper was high due to the leaching of the copper form the compost and copper available in leachate. But later its shows decreasing treand n all the three treatments. The treatment with UV reach the level of initial concentration of copper in leachate after leaching of 0.45 L contrary to treatment with UV and control which reach that level after 0.72 liter more leaching. This is because of the photo degradation of copper and it significantly improves leachate quality

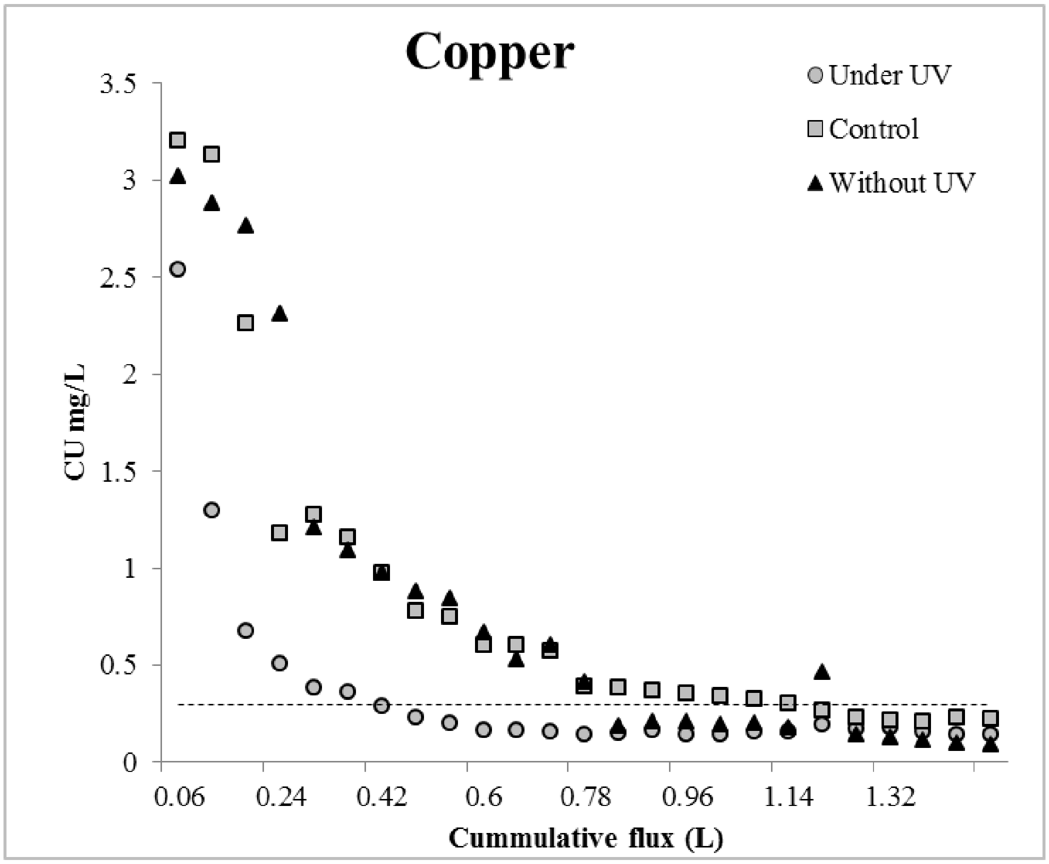


Figure 4.11 Copper trend during leaching experiment conducted using TiO_2 NP immobilized on silica sand in the presence and absence of UV

4.13.2 Lead

The concentration of the lead is only observed in the control experiment and maximum concentration was observed to be 0.016. In all the other experiments Lead was not detectable.

Lead concentration was only observed in control while lead is detectable in other two treatments under UV and without UV. Which shows that Titania Nano particles adsorb the lead from the leachate. Since there is very minute quantity of lead in the leachate so the observed lead is coming from compost.

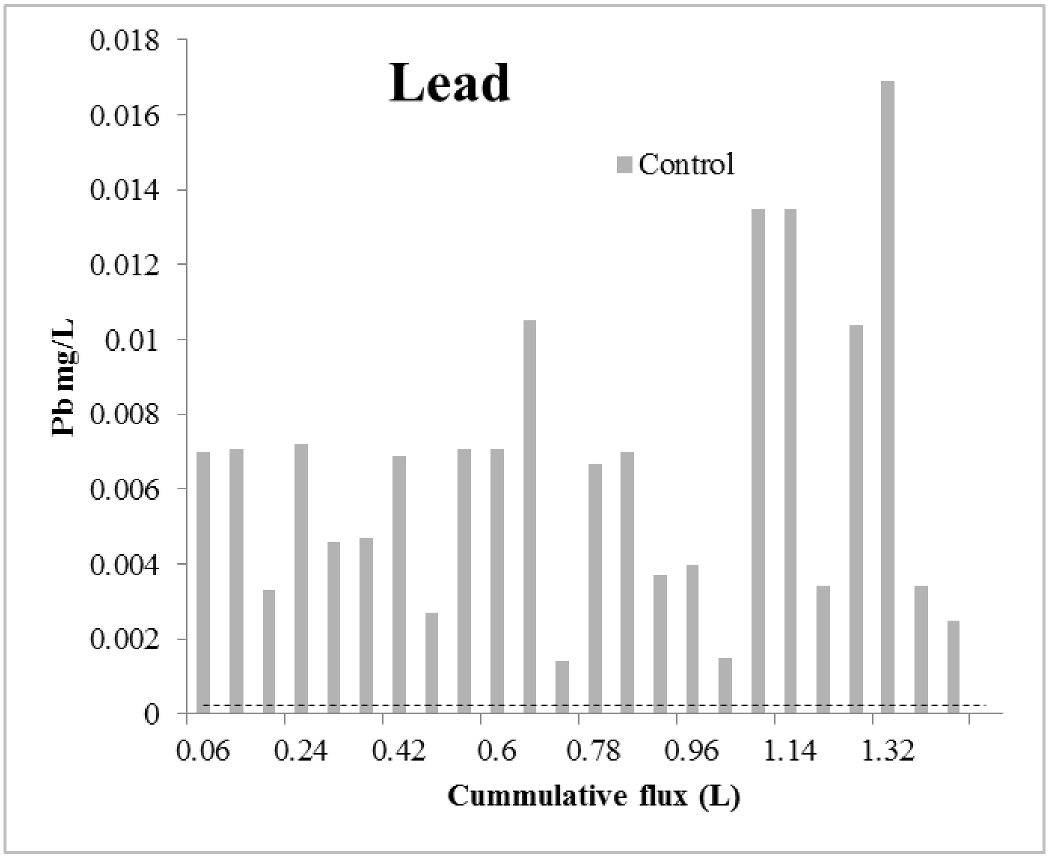


Figure 4.12 Trend of lead during leaching experiment conducted using TiO_2 NP immobilized on silica sand in the presence and absence of UV

4.13.3 Chromium

At the start of the experiment the concentration of chromium was high due to the leaching of the copper form the compost and leachate.

The trend of the chromium is quiet dispersed. At the start of the experiment the concentration of chromium was high in control and treatment without UV then treatment under UV this is due to the leaching of the chromium form the compost and leachate. Later after leaching of about 0.8 Liter chromium level in treatment under UV reached very close to the initial concentration of chromium present in leachate.

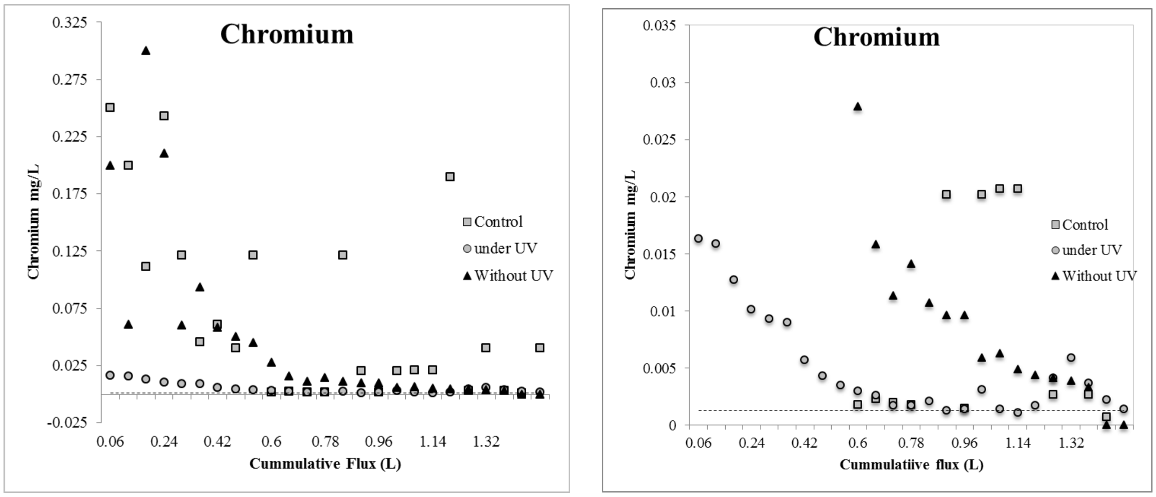


Figure 4.13 Trend of Chromium metal during leaching experiment conducted using TiO_2 NP immobilized on silica sand in the presence and absence of UV

5 CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

The 6olumn adsorption experiment was successfully operated for cumulative leaching 1.4 x 10^5 mm which is equivalent 5 years of rain in semi-arid area to of for both control and main run (under UV and without UV). A reliable, technical and meaningful data was collected during the column adsorption study. Some Important conclusions that can be drawn from this study are,

- TiO_2 nano particles were successfully immobilized on the silica sand and the result of SEM confirmed it.
- Compost keeps on leaching contaminants even after being washed by the de-ionized water addition layer of TiO_2 significantly improve leachate quality.
- Titania Nano-Particles immobilize on silica sand reduces the contamination flow from the compost itself but does not completely eliminate
- Titania Nano-Particles immobilize on silica under UV decreases the Nitrate leaching from the compost it also reduces organic carbon and ortho-phosphorus leaching and reduce metals as well .

5.2 RECOMMENDATIONS

Although this study clarifies about the compost effects as a bio retention media but still there are still some areas that can be a very good research options.

Some of the important recommendations from this study are,

- Pure compost may not be used as a bio-retention media as it leaches contaminants. It can be used in combination with Titania Nano-Particles imoobilize on silica. Doing so, will reduce the contaminant leaching from compost and the mixture will serve as a better bio-retention media.
- Other Catalyst than, Titania Nano-Particles must also be studied for better efficiency. Further such setup must be designed which is practically applicable to the present local condition.
- Other adsorbants must also be evaluated in different layer for removing specific pollutants from leachate. Comparison of results with doped Titania Nano-Particles imoobilize on silica may also be done.

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