LEACHING AND ECO-TOXICITY STUDIES OF METALS IN SEWAGE SLUDGE AND FLY ASH MIXTURE

A

Thesis submitted

in fulfillment of the requirement for

For the award of degree of

DOCTOR OF PHILOSOPHY

By

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SARVA SHAKTIMATE PARMAATMANE SRI RAMAAYA NAMAHA

I bow before Sri Ram, who is vested with all powers!

I bow before the source and reservoir of all powers!

I bow and seek shelter with the Supreme Soul, Sri Ram!

I dedicate and surrender myself unto Him!

'Parmaatmaa': The Supreme soul.

All that happens, and all that will happen, is by His Will. If we could do something by ourselves, we would. By ourselves, we cannot do anything at all. As it pleases the Lord, He preserves us. || 1 || O my Dear Lord, everything is in Your power. I have no power to do anything at all. As it pleases You, You forgive us. || 1 || You Yourself bless us with soul, body and everything. You Yourself cause us to act. As You issue Your Commands, so do we act, according to our pre-ordained destiny. || 2 || You created the entire Universe out of the five elements; if anyone can create a sixth, let him. You unite some with the True Guru, and cause them to understand, while others, the self-willed manmukhs, do their deeds and cry out in pain. || 3 || I cannot describe the glorious greatness of the Lord; I am foolish, thoughtless, idiotic and lowly. Please, forgive servant Nanak, O my Lord and Master; I am ignorant, but I have entered Your Sanctuary. || 4 || 4 || 15 || 24 ||

Shri Guru Granth Sahib, Page 736

This thesis is dedicated to my mom, dad, husband, brother,

bhabhi, nephews and my in-laws

who always had been my inspiration and support

throughout this working period

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CERTIFICATE

This is to certify that the research work entitled "Leaching and eco-toxicity studies of metals in sewage sludge and fly ash mixture" which is submitted by Ms. Monika, in fulfillment of the requirement for the award of the degree of Doctor of Philosophy in the Department of Biotechnology and Environmental Sciences, Thapar University, Patiala is a record of candidate's own independent and original work carried out by her under our joint supervision and guidance. The material embodied in this thesis has not been submitted in part or full to any other university or Institute for the award of any degree.

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I hereby declare that the thesis entitled **"Leaching and Eco-toxicity studies of metals in sewage sludge and fly ash mixture"** which is being submitted to the Department of Biotechnology and Environmental Sciences, Thapar University, Patiala, in partial fulfillment of the requirement for the degree of **Doctor of Philosophy**, has previously not formed the basis for the award of any other thesis of degree, diploma, or any other similar title or recognition.

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ABSTRACT

Leaching is the process of release of certain materials from a carrier into a liquid. Leaching and eco-toxic studies in different sewage sludge and fly ash mixtures were carried out. The 5 g mixture of FA/SS of three different ratios (1:1, 1:4 and 4:1) were taken and mixed with 100 mL of deionised water. The samples were then place on the rotatroy shaker at 120 rpm for 10 h at controlled temperature conditions of 26° ± 1C. The samples were then allowed to settle down and the supernantant was vaccum filtered with the help of 0.45 µm. The leachate was tested for Pb, Cd, Ni, Cu and Co using atomic absorption spectrophotometer (ECIL, India, Model AAS 4129). The leachate was also tested for different water quality parameters such as electrical conductivity, sulphate, chloride, total hardness, permanent hardness, chemical oxygen demand, total kjeldahl nitrogen (TKN), total solids, total dissolved solids, turbidity etc. It was observed that the leachate from the mixture with higher amounts of sewage sludge showed more metal contents and higher contaminants of different water quality parameters, whereas the leachate samples from the mixtures with lesser content of sewage sludge and higher content of fly ash (samples with FA/SS 4:1 ratio) showed very less or no leaching.

Experiments were performed with different fly ash and sewage sludge mixtures (1:1, 4:1 and 1:4) to achieve the optimised conditions for leaching of metals. It was observed that with the fly ash-sewage sludge mixture (1:4) leaching of metal ions was the maximum for copper metal (1.5 ppm), and minimum for the Pb (0.2 ppm). For other metals it was 0.0 ppm for Cd and 1.0 ppm for Ni. A decrease in leaching of metals was observed with increase in fly ash content in FA/SS mixture (1:1) which was 0.1 ppm for Pb, 0.0 ppm for Cd, 0.1 ppm for Ni, and 0.3 ppm for Cu, respectively. A decreasing trend in leaching of metal ions was observed with increased fly ash content in the fly ash-sewage sludge mixture. In FA/SS 4:1 ratio the decreased leaching of metal ions (0.0 ppm for Pb, 0.0 ppm for Cd, 0.1 ppm Ni, 0.2 ppm Cu) was observed in comparison to 1:4 and 1:1 FA/SS mixtures.

It was confirmed from the experimental data that FA/SS mixture (4:1) was the optimum dose (the selected dose of FA:SS mixture for lesser leaching from the aqueous solution) for the minimum leaching of heavy metal ions into the aqueous medium. Optimum number of washings for the maximum removal of the metals was checked with different samples of fly ash and sewage sludge mixtures. The samples were tested for leaching of metal ions at acidic pH conditions followed by different number of washings with distilled water. Different washing were given with distilled water to FA/SS mixture in order to analyse leaching from the mixture. It was observed that leaching of metal ions decreased up to three washings only. No further decrease was observed in the fourth wash. So, three washings were considered as the optimum number of washings. Selection of optimum time of shaking was done by analyzing the leaching of metals with optimized FA/SS ratio (4:1) at different hours of shaking time. It was observed that the initial metal contents of 0.3 ppm for Pb, 0.1 ppm for Cd, 0.5 ppm for Ni and 0.9 ppm for Cu-metal decreased after shaking time of 30 minutes to 0.3 ppm (Pb), 0.1 ppm (Cd), 0.4 ppm (Ni), 0.7 ppm (Cu), respectively. No substantial change in leaching of metal ions was observed after a shaking time of 60 and 90 minutes. After shaking the FA/SS (4:1, optimized) mixture for 120 minutes, it was observed that no metal ion leached into the aqueous solution which confirmed that all the metals were leached up to 120 minutes. So, 120 minutes was considered as the optimum shaking time. Experiments were conducted with optimized FA/SS ratio (4:1), varying the pH from 2-8. It has been observed from the experimental results that minimum leaching of heavy metal ion takes place at pH 8 conditions.

So, after conducting several experiments with different fly ash and sewage sludge mixtures the effect of fly ash as adsorbent of heavy metal was analyzed from sewage sludge leaching in various FA/SS mixture, it was observed that FA/SS 4:1 dose, three liquid wash, 2 hours shaking time and pH 8 conditions were the optimized conditions to arrest the leaching of metal ions from sewage sludge.

Different experiments were carried out with the optimised dose of FA/SS 4:1 ratio shaken with synthetic solutions of metals at different concentrations of 5, 10, 15 and

20 ppm and it was observed that maximum removal was achieved with the optimised dose of FA/SS mixture in 5 ppm concentration with 100% removal efficiency.

Experiments carried out with different doses of FA/SS mixture revealed that the leachate with higher dose of fly ash contained lesser microbial count. These results were supported by the eco-toxicity studies carried out separately.

Eco-toxicity studies were carried out on 2 fish species zebra and guppy fish with three different age groups 60, 90 and 120 day old fish. The eco-toxicity studies of fish was analyzed by checking their survival rate after 96 h time period in optimised FA/SS mixture, different sewage sludge samples, and control sample. Ten fish per chamber of 5 L capacity were added in control sample (no FA/SS mixture), optimised FA/SS (4:1) mixture, and in four different concentrations (5, 10, 15 and 20%) of sewage sludge. The survival rate was checked after 96 hour time period. It was observed that no death of fish was observed in the control sample and the optimised fly ash-sewage sludge (4:1) mixture. As the sewage sludge concentration increased from 5% to 20%, the metal content found in the fish sample (on acid digestion of the dried fish sample) also increased and death of all the fish was observed in samples with 20% weight by volume of sewage sludge. So, it is clear from the experimental data that FA/SS 4:1 ratio is the best dose for arresting the leaching of heavy metal ions in to the aqueous medium.

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LIST OF ABBREVIATIONS

AAS	Atomic absorption spectrophotometer
CAC	Chemically activated carbon
BOD	Biochemical oxygen demand
ASTM	American society of testing materials
APHA	American Public Health Association
EDTA	Ethylene di-amine tetra-acetic acid
NRCC	National Research Council of Canada
PCDD	Polychlorinated dibenzo-*p*-dioxins
ODW	Oven dry weight of sample
NTU	Nephlometric turbidity unit
PAHs	Poly aromatic hydrocarbons
COD	Chemical oxygen demand
MSW	Municipal solid waste
TDS	Total dissolved solids
TSS	Total suspended solids
EC	Electrical conductivity
TKN	Total Kjeldahl Nitrogen
MPN	Most probable number
CFB	Circulated fluidized bed
PH	Permanent hardness
ANOVA	Analysis of variance
EBT	Erichrome black tea
AC	Activated carbon
DO	Dissolved oxygen
DS	Double strength
SS	Sewage sludge

TH	Total hardness
DF	Dilution factor
TS	Total solids
Cd	Cadmium
Co	Cobalt
Cu	Copper
Fs	Furans
FA	Fly ash
Ni	Nickel
Pb	Lead
Zn	Zinc

Introduction

CHAPTER 1

INTRODUCTION

1.0 Sewage sludge

Due to increasing urbanization and industrialization there is a dramatic increase in the volume of municipal wastewater produced worldwide. This wastewater contains all the substances that enter in human metabolism, such as food, beverages, pharmaceuticals, a great variety of household chemicals and the substances discharged from trade and industry to the sewer system (Kroiss, 2003).Sewage sludge refers to the residual, semi-solid material left from industrial wastewater, or sewage treatment processes – also referred as settled suspension obtained from conventional drinking water treatment, and numerous other industrial processes. The term is also sometimes used as a generic term for solids separated from suspension in a liquid; this 'soupy' material usually contains significant quantities of 'interstitial' water (between the solid particles).The disposal of sewage sludge in the environment and its management has now become a major problem worldwide. Due to the production of sewage sludge in large quantity, the considerable scarcity of landfill spaces, land filling process is considered as an unsuitable and costly option as a long-term substitute. The treatment and disposal of sewage sludge is an expensive and environmentally sensitive problem. It is also a growing problem worldwide since sludge production will continue to increase as new sewage treatment works are built and environmental quality standards become more stringent. With some traditional disposal routes coming under pressure, and others such as sea disposal having been phased out, the challenge facing sludge managers is to find cost-effective and innovative solutions while responding to environmental, regulatory and public pressures. Recycling and use of wastes are the preferred options for sustainable development, rather than incineration or landfilling, but with sewage sludge this is not straight forward because of perceptions over contaminants, pathogens and its faecal origin, particularly by the food retailers.A large number of problems are associated with sewage sludge as it is composed of substances which are responsible for the unpleasant character of untreated wastewater. Besides the presence of toxic substances or materials, sewage sludge also contains many of the valuable materials also. To sustainably treat sewage sludge it is important to estimate the composition of sewage sludge. (Rulkens, 2003b) characterized the composition of sludge in different groups of components, which are present in the sludge:

- Non-toxic organic carbon compounds, Kjeldahl-N, phosphorus containing components; Toxic pollutants
- Heavy metals, such as Zn, Pb, Cu, Cr, Ni, Cd, Hg, As (varying from more than 1000 mg/L to less than 1 mg/L)
- Inorganic compounds such as silicates, aluminates, calcium and magnesium containing compounds
- Dioxins, pesticides, endocrine disrupters, linearalkyl-sulfonates, nonyl-phenols, etc.
- Pathogens and other microbiological pollutants

1.1 Leaching of metals

Heavy metals are found in the wastewater streams of industrial processes, including textiles, paper, paint manufacture, leather tanning, battery manufacture, dyeing, and others; their removal has attracted much practical and academic interest owing to increased concern with their environmental impact. Methods for removing metals from a water stream include adsorption, which is a highly effective and economical process provided the correct adsorbents are applied in an environment that favours adsorption. Activated carbon is the conventionally adopted adsorbent for removing metals from water. However, the high cost of activated carbon limits its use as an adsorbent in developing countries. Coal fly ash was used to study adsorption of several cations (Cu^{2+}, Ni^{2+}, Zn^{2+}, Pb^{2+}) within various experimental conditions: dry/wet fly ash, pH, metallic ion/fly ash ratio. A number of different processes like ion exchange, adsorption, surface precipitation, bulk solution precipitation could be responsible for the removal of heavy metals in aqueous solution by fly ash. Precipitation lead to complete removal of heavy metals by formation of hydroxide ions. The removal of hexavalent chromium using fly ash involved a chemisorption mechanism associated with the bonding between active alumna sites and the chromate anion. Adsorption studies carried out to estimate heavy metal removal using fly ash on wastewater at Varanasi, India showed that removal was in the following order: Pb>Zn>Cu>Cr>Cd>Co>Ni>Mn. Adsorption of Cd, Ni, Cd, Pb, Zn and Ag on fly ash and they found that the process was spontaneous and endothermic. Also fly ash could be a useful agent in conditioning sludge prior to vacuum filtration. Fly ash, agricultural ashes and lime exhibited increased metal retention percentages through adsorption and precipitation, as it was expected due to their structure, while sawdust acted as sorbent. Lignite fly ash, agricultural ashes, lime and sawdust were chosen for the experimental study of their metal uptake capacity, according to the proposed stages, during the treatment of an acidic liquid waste loaded with metals (Cu, Zn, Fe, Ni, Cd, and Cr). A number of heavy metals present in the sewage sludge and in the fly ash needs removal because of the presence of a number of harmful effects on the environment as well as on the human body listed as follows:

- Lead influences the nervous system, slowing down nerval response. This influences learning abilities and behaviour.
- In humans methyl mercury affects among other organs also the brain, and it is documented that (as for lead) children in the embryonic stage receive mercury via the placenta causing persistent effects on children mental development.
- Cadmium accumulates especially in the kidneys leading to dysfunction of the kidney with increased secretion of e.g. proteins in urine (proteinuric) and other effects.

Leaching of heavy metals from sewage sludge is a potential concern during ash disposal and beneficial use. The leaching (or extraction) of heavy metals from sewage sludge is mostly governed by adsorption/desorption and/or dissolution. Our previous leaching studies for raw ash indicated that the equilibrium concentrations of heavy metals including Cd(II), Cr(III), Cu(II), Ni(II), and Pb(II) in solution are far below the saturation concentration. Therefore, the leaching of these metal ions is mostly governed by the adsorption-desorption mechanism. Heavy metals and other toxic pollutants are considered extremely pernicious because they are toxic, nondegradable, and environmentally persistent. Heavy metals when introduced into water are either remains in dissolved form or are leached down with excess water, or else partially fixed temporarily or permanently in sediments contaminating further to ground water. Adsorption is one of the methods commonly used to remove heavy metal ions from various aqueous solutions with relatively low metal ion concentrations. The efficiency of adsorption relies on the capability of the adsorbent to adsorb metal ions from the solutions onto its surfaces.

The term heavy metal refers to any metallic chemical element that has a relatively high density and is toxic or poisonous at low concentrations. Examples of heavy metals include mercury (Hg), cadmium (Cd), arsenic (As), chromium (Cr), thallium (Tl), zinc (Zn), nickel (Ni) and lead (Pb). Heavy metals are natural components of the Earth's crust. They cannot be degraded or destroyed. To a small extent they enter our bodies via food, drinking water and air. As trace elements, some heavy metals (e.g. copper, selenium, zinc) are essential to maintain the metabolism of the human body. However, at higher concentrations they can lead to poisoning. Heavy metal poisoning could result, for instance, from drinking-water contamination (e.g. lead pipes), high ambient air concentrations near emission sources, or intake via the food chain. Heavy metals are dangerous because they tend to bioaccumulate. Bioaccumulation means an increase in the concentration of a chemical in a biological organism over time, compared to the chemical's concentration in the environment. Compounds accumulate in living things any time they are taken up and stored faster than they are broken down (metabolized) or excreted. Heavy metals can enter a water supply by industrial and consumer waste, or even from acidic rain breaking down soils and releasing heavy metals into streams, lakes, rivers, and groundwater. Unlike organic pollutants, heavy metals do not decay and thus pose a different kind of challenge for remediation. A well-documented environmental disaster associated with heavy metals is the Minamata disease cause by mercury pollution.

Due to anthropogenic activities, the soil organic matter is often depleted in Mediterranean dry and semiarid areas. In order to revert the desertification process use of sewage sludge as a land reclamation technique is done. Different soil were supplied with metal-enriched sewage sludge and the leachates were collected and analysed for pH, EC, organic carbon Cu, Ni and Zn concentrations. The result showed that soils supplied with sewage sludge showed higher leaching for the nickel metal in basic soils. It was also observed that organic matter However, overall the total amount of Cu, Zn, and Ni leached through the 30 cm columns of the metal-enriched sewage sludge increased in comparison to the control soils. Continuous supply of sewage sludge to soil can cause major groundwater pollution and reduce the soil quality thereby leading to serious health effects also.

Studies were carried out by (Ozturk et al., 2004) on the leaching of boron after application of soil-sewage sludge mixture. Clinoptilolite type natural zeolite, was used for filling of the columns after mixing with sewage sludge at a rate of 30 tons ha^{-1} and with two different particle sizes (0.1–0.25 and 1.0–2.0 mm) of clinoptilolite each at the concentrations of 1%

and 2%. The result showed that boron leaching was affected both by the particle size and the application rate of clinoptilolite affected both boron leaching from soil compared to the control treatment (soil and sewage sludge mixture). The total soluble boron leaching was varied from 66–92% reached 96% for the control treatment, following application of 80 cm depth of water in all treatments. In the cases of the 1% application rate of 0.1–0.25 and 1–2 mm sized clinoptilolite 78% and 92% of the total boron leached, respectively. While it was 66% and 87% of total soluble boron leached on the application of 2% application rate of 0.1–0.25 and 1–2 mm. Boron concentrations in the soil layers increased as application rate increased and particle size of clinoptilolite decreased because of its high adsorption capacity. Adsorption isotherms indicated that clinoptilolite had a high adsorption capacity for boron compared to the sewage sludge and soil.

Studies were conducted by (Fumagalli et al., 2013) to study the effect of nitrogen leaching after the application of different sewage sludges to the arable land in the Lombardy region (northern Italy). The effects of fertilisation using four different sludge types on N leaching were simulated at five sites under cultivation with maize and rice crops. The result showed that the mean annual leaching was 22 to 154 kg N ha^{-1}. The higher the ammonium N content in the sludge was, the greater the potential for N leaching was found to be. Therefore, the studies concluded that sewage sludge application to arable land in the northern Italy did not always appear to be advantageous for protecting the environment from leaching.

It was investigated by (Muchuweti et al., 2006) the vegetables irrigated with mixtures of wastewater and sewage sludge not only caused excessive accumulation of heavy metals in soil but also affect food quality and had implications on human health. The study showed that crops irrigated with sewage sludge admixture heavily contaminated the crops with the four regulated elements: Cd, Cu, Pb and Zn. This contamination is at its highest in two of the staple dietary crops maize and *tsunga*. *Tsunga* leaves contained 3.68 mg kg^{-1} Cd, over 18 times the permissible level by the EU standards (0.2 mg kg^{-1}); Cu concentrations were 111 mg kg^{-1}, 5 times the EU Standard (20 mg kg^{-1}); concentrations of Pb were 6.77 mg kg^{-1}, over 22 times the permissible levels allowed by both EU standards and UK guidelines (0.3 mg kg^{-1}); Zn concentrations were 221 mg kg^{-1}, over 4 times the guideline value (50 mg kg^{-1}). The study shows that consumption of such contaminated vegetables irrigated with sewage sludge can pose serious health risks.

1.2 Fly ash

Fly ash is the finely powdered residue that results from the combustion of pulverized coal and is carried away from the combustion chamber by exhaust gases (Jala and Goyal, 2006). It was estimated in 2001 that 61 million metric tons (68 million tons) of fly ash was produced annually in India; however, constructive use of fly ash is very low. Fly ash is finer in comparison to Portland cement and lime consisting mainly of spherical particles in the size ranges between 10 and 100 micron. Fly ash primarily contains the oxides of silicon, magnesium, iron and calcium. Aluminium, potassium, titanium, sodium and sulphur are also present to a lesser degree. Fly ash helps in improving the physical, chemical and biological properties of the soil. It was reported that fly ash may improve the physical, chemical and biological properties of problem soils and helps in enhancing the plants macro and micronutrients (Sharma and Kalra 2006; Lee et al., 2006), (Pandey and Singh 2010; Garg et al., 2003). The high concentration of K, Na, Zn, Ca, Mg and Fe in fly ash increases yield of agricultural crops.

1.3 State of fly ash in India

Out of the total 75% of the total installed power generation units which are coal-based, only 230 - 250 million MT coal is being utilized every year in India. The total generation of ash is more than 110 million metric tonnes. It is expected that total ash generation shall cross 180 million metric tonnes by the end of 2013. Not only this, presently it has been observed that 65,000 acres of land is occupied by ash pond30% of the ash is being used for the construction purposes such as in fillings, embankments, blocks and tiles, cement making etc.

1.4 Scope and Outline of this thesis

Although numerous studies have appeared in the field of heavy metals removal from sewage sludges, less attention has been paid to the implementation of fly ash for this purpose. The main objective of this thesis is to gain more scientific and practical insights to study the leaching and eco-toxicological studies of sewage sludge-fly ash mixture and the heavy metals removal from anaerobically digested sludge by mixing it with fly ash. The leaching and eco-toxicological studies of fly ash-sewage sludge mixture were carried out after optimizing certain conditions with various FA/SS mixtures such as:

1. Optimised adsorbent dose
2. Optimised acid dose

3. Optimised shaking time
4. Optimised number of washings
5. Optimised pH

Chapter one gives brief introduction about sewage sludge and fly ash. It also discusses about toxic effects from sewage waste and how leaching of metals takes place from sewage sludge. Chapter two describes review literature and debates on sewage sludge management. It discusses about the use of various low cost adsorbents such as palm oil fuel ash, maize cob, waste tea, coconut husk etc. for heavy metals removal. It also discusses about the need for the novel techniques using fly ash as an adsorbent in fly ash – sewage sludge mixture. Why there is need for research on leaching and eco-toxicological properties of fly ash–sewage sludge mixture and its significance in the research area. What are the gaps in the research area and objectives of the proposed work. Chapter three outlines various material and methods used in the leachate analysis. Chapter four provides standard methods are used for the analysis of fly ash and sewage sludge. In chapter five, experimental studies were conducted on optimisation of various parameters of FA/SS mixture namely optimised dose (FA/SS) mixture, optimised pH, optimised acid, optimised washings and optimised time. In chapter six, leaching studies were carried out on optimised dose (4:1) FA/SS mixture with different synthetically prepared metal solutions. Leaching studies were also carried out on sewage sludge at varying pH conditions (2-8) in various FA/SS mixture. In chapter seven, several experiments were carried out on microbiological and eco-toxic studies in leachate of FA/SS mixture. Chapter eight discusses the overall research and provides conclusions and recommendations.

Review of literature

CHAPTER 2

REVIEW OF LITERATURE

2.0 Sewage sludge

Sewage sludge is defined as the insoluble residue produced from the municipal wastewater treatment after aerobic and anaerobic digestion processes. Disposal of sewage sludge and its management is a major problem throughout the world and currently land application as soil amendment is normally practised in a small amount in agriculture. Marchioretto (2003) reported that different metal ions in sewage sludge present in different forms such as sulfied, oxides, hydroxides and silicates (in bound form with organic matter of sludge). The mobility of metals from sewage sludge depends on their specific chemical forms and bindings (Fuentes et al., 2004).

2.1 Sewage sludge problems and its management

Sewage sludge is toxic in nature and contains a number of toxic pollutants such as PAH's (polyaromatic hydrocarbons) which are very harmful to the environment if sewage sludge is disposed off directly to the environment. Maria (2005) collected different wastewater samples and sewage sludge samples. The measurements were obtained to investigate the effect of different treatment stages on PAH content in wastewater and sewage sludge. Ultrasonic method with cyclohexane, dichloromethane was used to extract PAHs from sewage sludge and wastewater samples. For the qualitative and quantitative measurement of PAH's gas chromatography and mass spectroscopy was used. The results showed average removal efficiency of PAH in sewage sludge were about 83–85%, it was 46–70 g/d of PAHs (carcinogenic PAHs content 4–12%). Whereas PAH load drained off to the environment constituted approximately 37% of inflow to the wastewater treatment plant (15–17% with treated wastewater, 19–22% with stabilized sludges and less than 0.2% with mineral sewage sludges). A number of ecotoxicity and leaching experiments were conducted by (Shoji et al., 2005) to evaluate the toxicity of sludge. The leachability and toxicity of various chemicals in several industrial waste sludge such as dewatered sludge were examined by using the standard leaching test. The results revealed that Daphnia sp. acute immobilization test was one of the most effective bioassays to detect toxicity of sludge eluates. It was observed that sludge leachate inhibited Daphnia mobilization, plant and alga growth. It was also recommended to check the relative ecotoxicity potential of sludge leachate before its disposal to the environment or use for landfill. It has been reported that the leaching of metal ions follows the following order Cd > Zn >Pb> Fe >Mnin municipal sewage sludge collected from the wastewater treatment plant of Thessaloniki (Fytianos et al., 1998). Also, it was observed that the maximum leaching of heavy metal ions from the sewage sludge takes place at the lower pH. Berkun and Aras (2007) has reported that increasing amount of solid waste and wastewaters from municipalities and their resultant disposal has been one of the major environmental problems in Turkey. It has been investigated that most of the unsegregated municipal and industrial solid wastes mixed along-with with hospital and hazardous wastes are directly dumped to the nearest lowlands and river valleys and into the sea. The direct dumping of the waste in to the valleys, rivers and sea can be hazardous both to the aquatic life and can cause serious problems.

The presence of different toxic contaminants such as PAHs, PCDD/Fs and pathogenic bacteria present in the sewage sludge are also a cause of serious environmental concern (Pepper et al., 2006; Dai et al., 2007). Melo et al. (2002) studied that the chemical and biological compositions of sewage sludge depend on the wastewater composition. Tys and Frac (2008) studied the characteristics of sewage sludge and also reported that the protease, urease, dehydrogenase and phosphatases affect the soil on its application. Authors also discussed about the impact of sewage sludge on ammonification, nitrification as well as population number of a number of micro-organisms responsible for those processes. Zhang et al. (2008) showed that leachate pH was the predominant factor influencing heavy metal leachability.

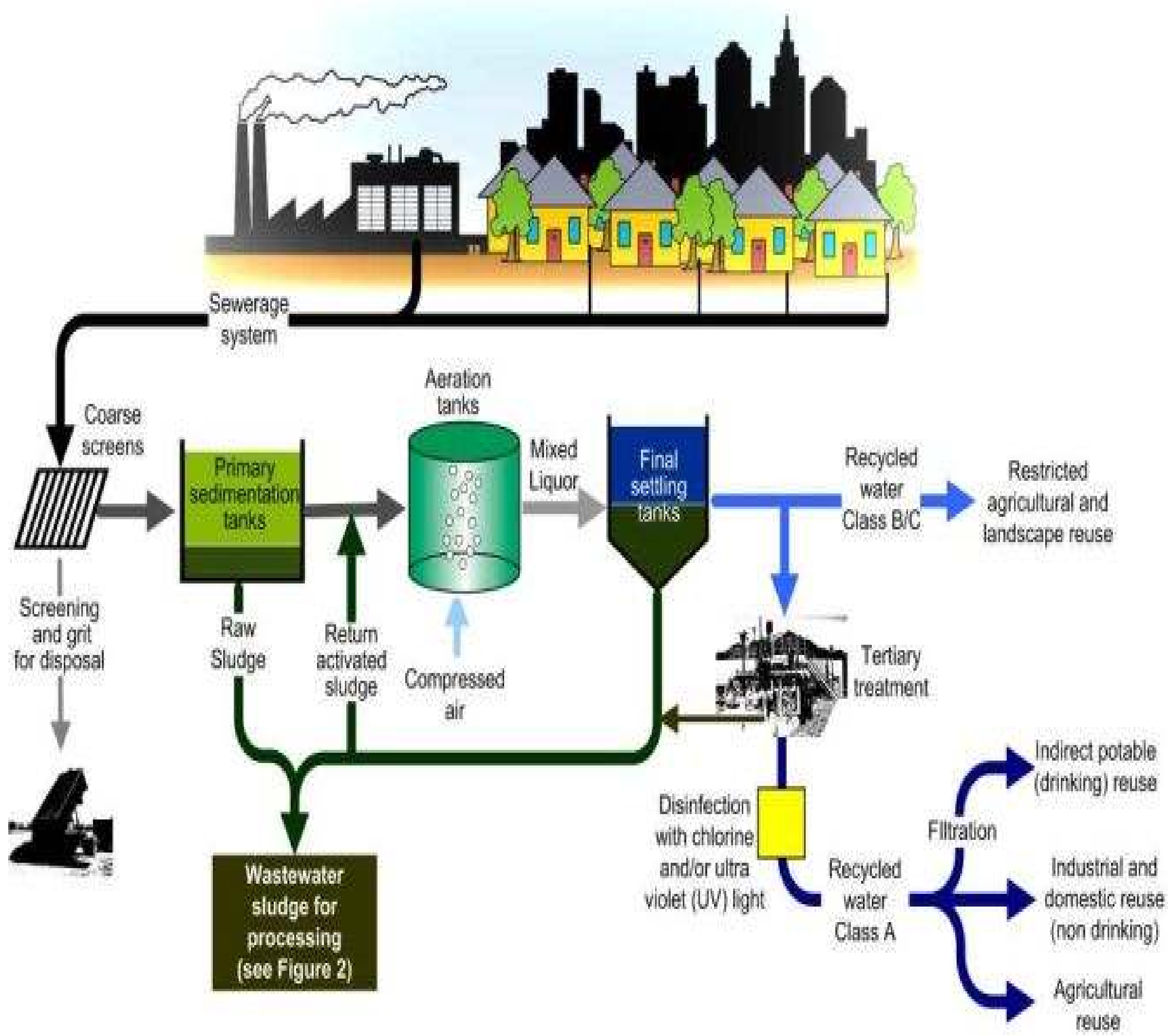

Figure 2.1[1]: Processes in a typical wastewater (sewage) treatment plant which produce wastewater sludge for processing into biosolids

[1] Australian & New Zealand Biosolids Partnership <http://www.biosolids.com.au/what-are-biosolids.php>

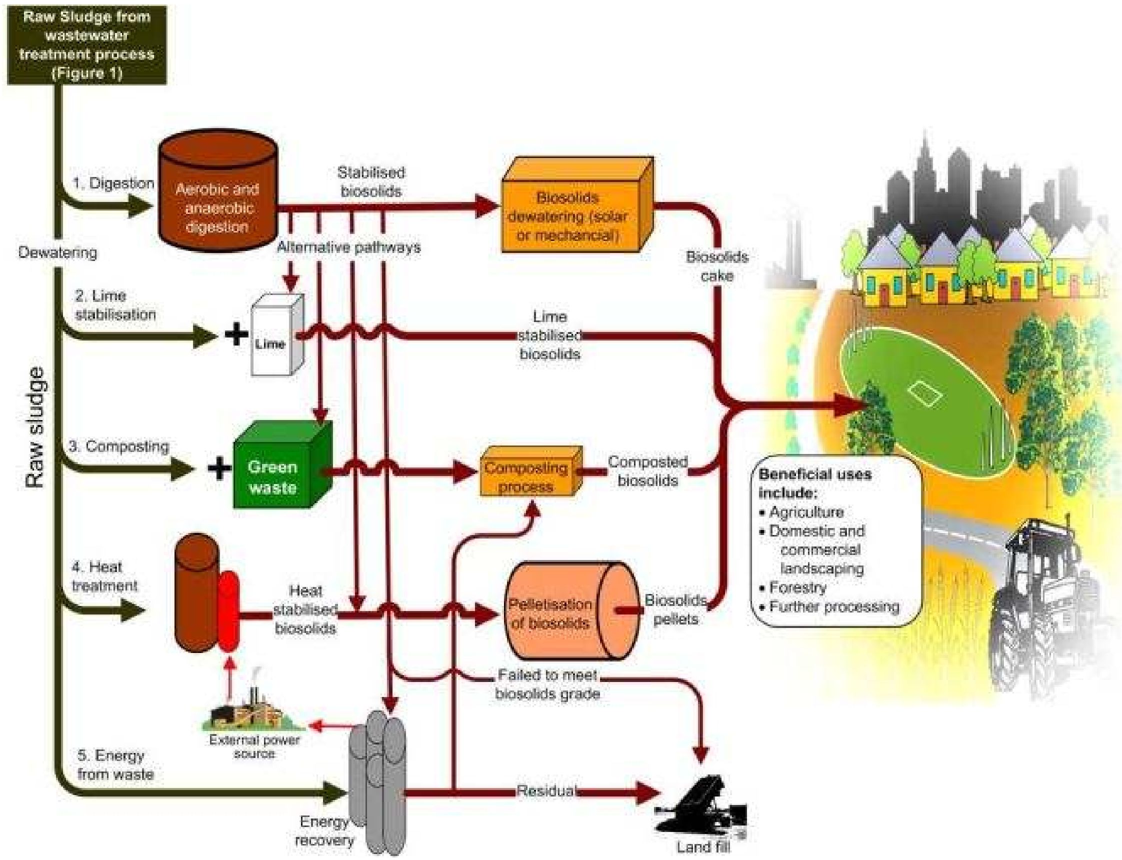

Figure 2.2[2]: Five typical production systems for biosolids with possible alterative productions pathways

The leaching of Cu, Pb and Zn was mainly controlled by precipitation and dissolution reaction, whereas surface complexation had some effect on the leaching of Cr, Cd and Ni for certain pH ranges. Xue et al. (2003) reported that long-term manure-borne copper and zinc supply to the grassland soils resulted in increased surface water quality criteria. It was concluded that more leaching from organic soil in comparison to mineral soil contribute significantly to the observed elevated Cu and Zn concentrations of the river.

2.1.1 Landfill disposal

- From management and materials handling perspective, land filling is the simplest solution
- From an economic standpoint, land filling presently compares favourably with other options

[2]*Ibid*

- From an environmental standpoint, landfilling prevents release of sludge borne pollutants or pathogens, concentrating the sludge

A new treatment technology named ad converter slag solidification (CSS) has been developed by Eung and Yim (2005). This treatment technology was considered for recycling of the sludge in landfill cover. It was also observed that negligible leaching of heavy metals takes place after treating the sludge from this technology. It was reported by (Song and Lee, 2010) that sewage sludge composting is also one of the best suitable solution for the proper management and recycling of sludge. It was observed that sewage sludge compost application improved soil characteristics such as moisture, organic matter, N content, respiration, soil porosity and bulk density.

2.1.2 Incineration disposal

- Sewage sludge incineration reduces volume of material to be disposed off
- Completely destroys pathogens
- Decomposes organic chemicals
- Recovers heat value contained in sewage sludge

Lin and Ma (2012) reported that incineration of sewage sludge is one of the most important method in the resource recovery disposal of sewage sludge. It was investigated by (Chen and Yan, 2012) that heavy metals fixation in the slag produced during sewage sludge incineration will reduce emission of the metals to the atmosphere and making the incineration process environmentally friendly. Also, it was reported by (Sangar et al., 2001) that incineration is one of the major methods for the disposal of sewage sludge.

2.1.3 Land application

- Land application seeks to reuse the organic matter and plant nutrients in biosolids
- Land application of biosolids returns materials to soil to produce another crop

(Wang, 1997) reported that sewage sludge production in the coming years will increasewith the dramatic increase of municipal wastewater treatment ratio (treated/produced).This problem of sewage sludge disposal can be solved by proper land utilization of sewage sludge. Land utilization of stabilized sewage sludge can make a positive contribution to agriculture, forestry, horticulture and city development. Several field experiments were conducted by (Wang et al., 2008) to study the effect of sewage sludge application on the heavy metal content in soils and grasses. It was observed from the experimental results that sewage sludge application increased the nutrient content of the soil, especially organic matter. Sewage sludge application is also found to be good where food chain contamination with cadmium is not a concern.

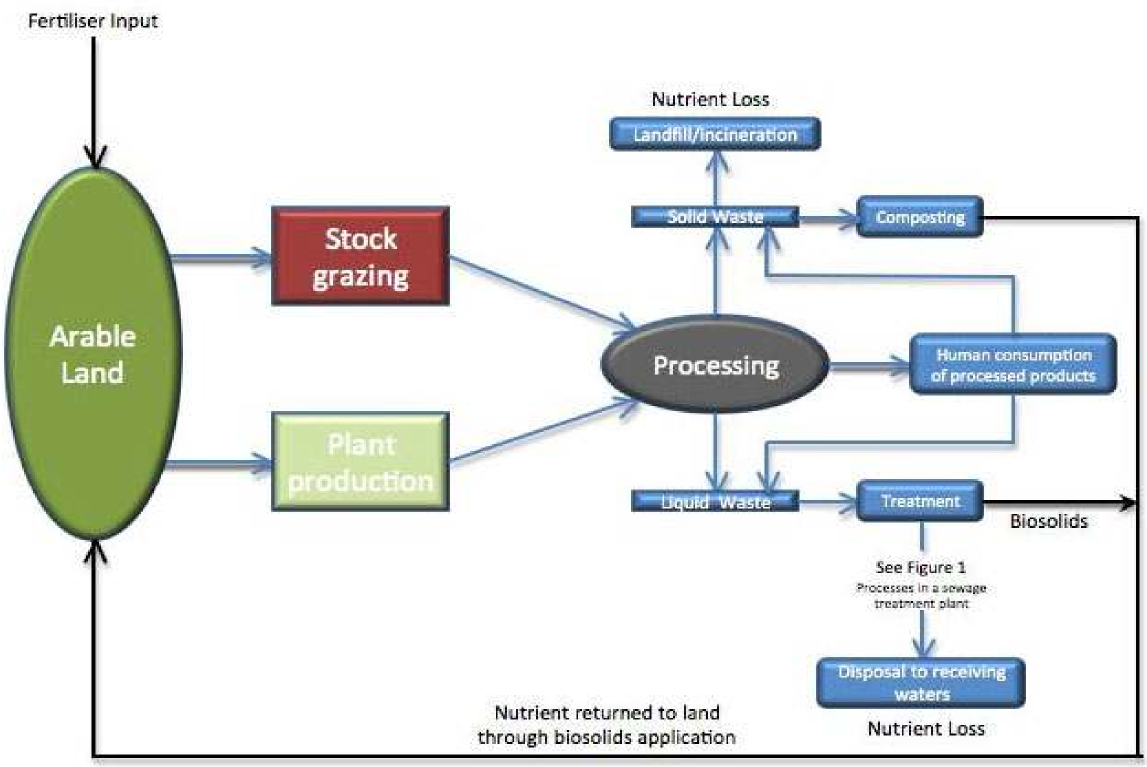

Figure 2.3[3]: Nutrient flows through urban environment

2.2 Use of various low cost adsorbents for heavy metals removal

Cost is one of the important parameter for comparing different adsorbent materials. However, cost information is seldom reported, and the expense of adsorbents varies depending upon their availability. These days, because of the increased cost of adsorbents various low cost-adsorbents are gaining importance. Some of the low-cost adsorbents reported are: Bark/tannin-rich materials; lignin; chitin/chitosan; seaweed/algae/alginate; xanthate; zeolite; clay; fly ash; peat moss; modified wool and modified cotton; tea waste; maize cob etc.

2.2.1. Palm oil fuel ash

[3] *Ibid*

It is the ash derived from palm oil wastes. It is used as an adsorbent for heavy metal ions such as Cr(III) and Zn(II). The batch equilibrium studies demonstrated that ash exhibited Langmuir maximum adsorption capacities for Cr (III) and Zn(II) of 251.6 and 126.7 μ mol/g dry weight of ash. Palm oil fuel ash showed maximum adsorption capacity for (95.2 mg/g) at pH 5 condition (Gulnaziya et al., 2006).

2.2.2. Pine saw dust

It was investigated (Moodely et al., 2011) that pine saw dust can be used as one of the promising solution for the removal of nickel ions from multi-component aqueous media. Different experiments were carried out and effects of variables such as (dose, pH and initial concentration) were studied. It was observed that (2 g) adsorbent dose, (2.625 mg/L) high initial concentration and (3.9) pH conditions resulted good adsorption capacity of 65.9 x 10^{-3} mg/g. Moreover the experimental results were better fitted in Frendulich isotherm than the Langmuir model. Pine sawdust, is a natural abundant and low-cost adsorbent. So it can be used to remove nickel (II) ions from wastewater.

2.2.3 Maize cob

It is used as an adsorbent for removal of lead from aqueous solutions and effluents from battery and paint industries. Pb^{2+} removal by maize cob from battery effluent was 99.99%. Pb^{2+} removal by maize cob from paint effluents were 66.16%. It has been reported by (Opeolu et al., 2009) that maize cob has great removal capacity for Pb^{2+} from industrial effluents.

Caliphs et al. (2009) studied the removal of Pb(II) from aqueous solutions by using tassel powder adsorbent by studying the effects of contact time, pH and concentration etc. It was investigated that the removal of different metals was in the following percentage: Pb (ND-100%), Se (100%), Sr (5.41–59.0%), U (100%) and V (46.1–100%) was attained using tassel. The uptake of the metals from environmental samples was dependent on pH, ionic strength and levels of other competing species.

2.2.4 Waste tea, coconut husk, coconut shell

It was reported (Orhan and Buyukgungor, 1993) that a number of scientists used waste tea, coconut shell, and coconut husk as low cost adsorbents. The removals of different heavy metals Cr, Zn, Ni from three different electroplating plant effluents were carried out. The metal binding capacity differed for the different adsorbents. The Coconut shell was more effective for Ni ((97.36% removal). It was reported by (Tan et al., 1993; Babarinde, 2002) that all the three adsorbents showed high rate of adsorption Zn (Coconut shell, 99.74%, coconut husk 99.76% and waste tea 90.74% removal).

2.2.5 Biosorption

Biosorption is a physiochemical process that occurs naturally in certain biomass which allows it to passively concentrate and bind contaminants onto its cellular structure and (Volesky and Bohumil, 1990). After conducting a controlled experiment on living and dead strains of *bacillus sphaericus* Velasquez and Dussan (2009) found that the biosorption of chromium ions was 13–20% higher in dead cells than living cells. Sharma et al. (2011) investigated that utilization of waste cyanobacterial biomass of Nostoclinckia was helpful for the biosorption of Cr(VI) from aqueous solution. It was found that maximum Cr(VI) biosorption was achieved at the acidic pH conditions (2-4) with different initial concentrations of metal in aqueous media.

2.2.6 Bioleaching

Bioleaching is the process of extraction of metals from their ores by using living organisms. Hung et al. (2006) reported that bioleaching may be an alternative or adjunct to conventional physico-chemical treatment processes of municipal solid waste (MSW) fly ash to remove hazardous heavy metals.

2.7 The need for novel techniques

2.7.1 Fly ash as an adsorbent in fly ash-sewage sludge mixture

Jusoh et al. (2007) and, Kang et al. (2008) showed that activated carbon (AC) adsorbents are widely used in the removal of heavy metal contaminants from the wastewater. It is mainly used because of its large micropore and mesopore volumes and thus resulting in the high surface area and better adsorption capacity. A large number of researchers are studying the use of AC for removing heavy metals from wastewater. Reynolds et al. (2002) reported that the utilization of fly ash for sewage sludge grooming and maintenance may substitute lime and has minimized the costs of lime purchase, land filling and proved as a feasible and best management option for both fly ash and sewage sludge waste and solved disposal problem of the two wastes produced in large amounts. However, lime application in the sewage sludge stabilization depends upon a number of factors including the time of stabilization, dose of the lime supplied and its associated costs etc.

It was reported by (Gandhimathi et al., 2013) that landfill leachate is one of the major pollution factor resulting from municipal landfill sites. Physical and chemical processes are the better option for pre-treatment or full treatment of landfill leachate. He used combined coagulation-adsorption process as pre-treatment of landfill leachate collected from municipal solid waste open dumping site. First of all, the physico-chemical characteristics of stabilized and fresh leachate were examined. The coagulation process was carried out by using alum and ferric chloride and adsorption studies were carried out on fly ash a low cost adsorbent. The effect of different parameters was studied such as coagulant dose, adsorbent dose, pH and contact time. After conducting various experiments it was observed that the effective optimum coagulant dosages were 0.6 g/L and 0.7 g/L for alum and ferric chloride respectively for stabilized leachate and in case of fresh leachate it was 0.8 g/L and 0.6 g/L for alum and ferric chloride respectively. The result revealed that the COD removal efficiency was 28% with alum treated stabililzed leachate whereas it was 82%by coagulation using alum and adsorption using fly ash for stabilized leachate. The results obtained showed that combined coagulation and adsorption process can be used effectively for stabilized leachate treatment.

Studied were carried out by (Ching et al., 2008) to study the effects of the lime treatment on fractionation and extractabilities of heavy metals (Cu, Pb, Cr, and Zn) in sewage sludge by using various extraction tests. The results of the study revealed that the higher affinity for organics the heavy metals was in unlimed sludge, the more unstable the heavy metals were in lime-stabilized sludge. As a consequence, the amounts of organically-bound metals in unlimed sewage sludge and the percentage of heavy metals extracted from lime stabilized sludge were in the same order of Cu >Pb> Cr > Zn. Single extraction conducted at various pHs revealed that this effect was due to the irreversible dissolution of organics and some metals having a higher affinity for organics (e.g., Cu) at very high pH during processing and air drying of lime-stabilized sludge. Since heavy metal stabilities depended on the amounts of the metals existing as the organically-bound form in unlimed sludge, it is valuable to examine the forms of heavy metals in sewage sludge prior to the treatment of sewage sludge with lime.

Various studies were carried out by (Cheng et al., 2010) on sewage sludge conditioning by using fly ash modified with the help of sulfuric acid to improve the sludge mechanical dewatering properties. The optimised modification conditions considered for the experiment were: acid concentration, 4 mol l^{-1}; ratio of acid to coal fly ash, 5:1 ml g^{-1} with soaking time of 3 h. The result revealed that acid concentration and soaking time played a crucial role in coal fly ash modification. The results showed that SRF of the sludge significantly decreased with coal fly ash addition, and the MCFA showed much stronger conditioning capacity than the raw coal fly ash (RCFA). Under a MCFA (Modified coal fly ash) dosage of273%, the SRF (Specific resistance to filtration) of the sludge decreased from 1.86×1013 to 4.23×1011 mkg^{-1}, and the filter cake moisture decreased from 86.90% to 56.52%. The sludge conditioning mechanisms with MCFA mainly included improving floc formation through charge neutralization and adsorption bridging and providing the water transmitting passages by skeleton builder.

Studies were carried out by (Gonzalez et al., 2010) on Chilean petroleum coke fludized bed combustion fly ash and its application for the removal of copper, lead and hexavalent chromium removal. The Chilean petroleum coke fluidized ash was chosen because of presence of high Ca and SO_4^{2-} content, being anhydritethe major crystalline mineral phase, with minor proportions of calcite, portlandite and lime. Not only this also to environmental characterization of this fly ash, leaching tests allowed concluding that fly ash (FA) is a non-hazardous residue. The removal kinetics and isotherms tests result reveals that fly ash show high removal efficiencies for Cu^{2+}, Pb^{2+} and Cr(VI), being the possible main mechanisms precipitation (in the case of Cu^{2+} and Pb^{2+})and a possible reduction (in the case of Cr(VI)). Moreover, according to European and Chilean leaching tests, FA should be considered as a non-hazardous material, despite its high Ni and V contents. Chemical sequential extraction shows that Pb^{2+} precipitate could be of an environment concern, whereas Cu^{2+} precipitate could be safely disposed in landfills or recovered. A possible disadvantage of the proposed fly ash (FA) use may be the spontaneous carbonation process observed in long term fly ash storage, diminishing fly ash reactivity.

Meunier et al., (2008) explored electrochemical technique in laboratory pilot scale for the removal of heavy metals (Zn and Cu) from sewage sludge. Three electrolytic cell arrangements using different electrodes materials were tested: mild steel or aluminium bipolar electrode (EC cell), Graphite/stainless steel monopolar electrodes (ER cell) and iron-monopolar electrodes (EC-ER cell).The result reveals that the best metal removal efficiency were obtained with EC and EC-ER cells operated respectively at current intensities of 0.8 and 2.0A for 30 and 60 min of treatment. Under these conditions, the yields of Cu and Zn removal from leachate varied respectively from 92.4 to 98.9%and from 69.8 to 76.6%.

It has been investigated by (Badriya et al., 2011) that a number of techniques such as nano-filtration technique and absorption process has proved beneficial for the removal of certain heavy metals such as Cu(II), Cd(II), Mn(II), Pb(II) As(III), and As(V) from aqueous medium. It was reviewed by (Jamali et al., 2009) that the ash prepared from the hazelnut shell was successful in the removal of cadmium ions from the water solution at different conditions of appropriate equilibrium time, amount of adsorbent used, concentration of adsorbate, pH of the solution and particle size of the sorbent using a batch system. Kersch et al. (2004) observed that residues of fly ash and sewage sludge contain large amounts of heavy metals which are toxic in nature. These toxic heavy metals pollute the groundwater after coming in contact with water. Zeid et al. (2009) observed that whatever precipitating agent is used, vacuum filtration is more efficient in water elimination than in centrifugation from sludge and in the removal of heavy metal ions from the mixture of fly ash, sewage sludge and soil by the precipitation process from the aqueous medium. It has been observed by (Kuncoro and Fahmi, 2013) that fly ash was used as an adsorbent for removal of Hg and Pb from aqueous solution. Several other researchers (Daci et al., 2011; Wang et al., 2007; Visa 2012; Shyam et al., 2013), (Wang and Tade 2008; Salam et al., 2011; Koukouzas et al., 2010) used fly ash as low cost adsorbent for treating wastewater and removing heavy metal ions from aqueous solution. Fu and Wang (2011) reported that the combination of both NaOH and Na_2S showed better removal efficiency of heavy metals such as for Pb^{2+}, Zn^{2+}, Cu^{2+} and Mn^{2+} ions. Studies were conducted to study the effect of (Sahoo et al., 2013) alkali modified coal fly ash was used as a potential adsorbent in comparison to untreated fly ash for the removal of metals from acid mine soil. Different parameters were considered such as the effect of dose, competing cations and contact time were investigated to study the adsorption of metals. The result revealed that the sorption of metals was rapid in the initial stages and slowed with time. The optimum time and dose observed for metal removal was 180 min and 120 g/L. The adsorption kinetics of different metals (Al, Fe, Ni, Pb, and Zn) onto MFA followed a pseudo second-order reaction, which implies that chemisorption is the adsorption. It was observed from the desorption data that most of the metals desorbed in the acidic media, implying that the adsorbent can be regenerated and reused efficiently. Also the results showed that modified fly ash (MFA) can be an effective and low-cost adsorbent for the treatment of AMD.

It has been reviewed from the literature survey that a number of techniques such as ion-exchange, adsorption and membrane filtration are widely used for the treatment of wastewater contaminated with heavy metals. It has been reported that pyrite and synthetic iron sulphide also proved helpful in the removal of Cu^{2+}, Cd^{2+} and Pb^{2+} from the aqueous medium. Ozverdi and Erdem (2006) reported that pH below three was observed to be the best for the removal of heavy metals using the chemical precipitation. It was reported by (Sharma and Kalra, 2006) that fly ash may improve the physical, chemical and biological properties of problem soils and helps in enhancing the plants macro and micronutrients. The high concentration of elements like K, Na, Zn, Ca, Mg and Fe in fly ash increases yield of agricultural crops. Fly ash as an adsorbent has been proved beneficial in the removal of heavy metal ions like cadmium and copper from waste water. It was noticed that the adsorption capacity increases as heavy metal ion concentration decreases.

Kadirvelu and Namasivayam (2003) have reviewed that fly ash was used in a number of beneficial applications to minimize the waste and decrease the cost of disposal. It has been observed by (Kadirvelu et al., 2003) that activated carbon prepared from coconut coir-pith was helpful in the removal of heavy metal ions from the aqueous solution. Coal fly ash is a cheap adsorbent because of its easy availability. As a matter of fact, although fly ash is considered as a waste, several studies have indicated their efficiency in the removal of heavy metallic ions in aqueous phase. It has been reported that mixing fly ash with either poultry litter or sewage sludge could increase soil solution Ca and Mg concentrations and lead to a less dispersive system (Jackson and Miller, 2000).It is possible that alkaline fly ash is a ferro–alumin–silicate mineral containing substantial quantities of magnesium oxides (MgO), and calcium oxides (CaO) (Carlson and Adriano 1993; Ben and An, 2004). Soluble Cd in sewage sludge may be strongly adsorbed by these oxides under alkaline condition when SS was mixed with fly ash. Mixing fly ash with sewage sludge increased the solution Ca and Mg concentrations. Total Cd, Pb, and Zn contents in artificial soils were significantly lower than the Control standards for pollutants in sludges from agricultural use (GB 4284-84, 1985). The results obtained from incubation experiment suggested that alkaline fly ash stabilized soluble

Cd and Pb from sewage sludge. The heavy metals present on the cell surface of the micro-organisms in the sludge can be easily removed by treating with acid as acid helps in dissolving them (Shiro Yoshizaki and Tahei Tomida, 2000).The addition of fly ash to sewage sludge not only reduced the total coliform population present in the sewage sludge and but also proved helpful in minimizing the leaching of metal from the sewage sludge(Zhang et al., 2008; Wong and Selvam, 2009). Incorporation of these two beneficial mixtures (Fly ash and sewage sludge) as reported by (Jianmin et al., 2008) increased the efficient environmental friendly management process of both widely produced wastes. When pH was less than 3 or above 7, increasing amounts of arsenic were leached or desorbed from the fly ash. The leaching and adsorption behaviour of arsenic was explicated with the speciation of surface sites and arsenic. It was investigated by (Papadimitriou et al., 2008) that leachate pH was the major factor in influencing heavy metal leachability. The leaching of Cu, Pb and Zn was mainly controlled by precipitation/dissolution reactions, whereas surface complexation had some effect on the leaching of Cr, Cd and Ni for certain pH ranges.

Wang et al. (2006) developed a mathematical model to quantify effects of pH and ammonia on metal adsorption on the leaching of Copper (II) and Cadmium (II) from coal fly ash. Metal speciation calculations indicated that the formation of less absorbable metal ammonia complexes (which decreased metal adsorption) enhanced metal leaching. A number of equilibrium studies were conducted by (Weng and Huang, 2004) to determine the removal capacity of fly ash for the zinc metal ions(Zn^{2+}) and from the experimental results it was observed that the absorption capacity for the removal of zinc metal increases with increase in pH and fly ash content in the solution. A total 99% removal efficiency for Zn was observed.

It has been reported by (Ahlberg et al., 2006) that the basic soils (soils with pH above 7) with higher content of organic matter showed more leaching for Ni whereas there is no increase for Cu in all soils and Zn in basic soils amended with metal-enriched sewage sludge. The total amount of leaching was observed up to a depth of 30 cm columns in comparison to control soils (without sewage sludge) in a study carried out by (Toribio and Romanya, 2006). The sewage sludge stabilization was done by the addition of fly ash to the sewage sludge (Zhang et al., 2008; Xuet al., 2012; Samaras et al., 2008; Wang et al., 2013). It was observed that the sewage sludge mixture amended with fly ash in different ratios showed decrease in leaching of heavy metal ions when tested in all the cases (Papadimitriou et al., 2008).

It was reported by (Sajwan et al., 2003) that stabilization potential of sewage sludge was achieved by the addition of fly ash and/or lime. It was observed by (Page et al., 1979) that the application of fly ash to the sewage sludge not only reduced the leaching of metal ions into the aqueous medium but can also be applied as soil amendment. Historically, the use of FA in agriculture has been based on its liming potential and supply of essential elements such as Ca, B, S and Mo (Martens, 1971; Page et al., 1979). However, the use of FA as an agricultural amendment can be enhanced by blending it with potentially acid-forming organic by-products such as SS, poultry and cattle manure which are significantly rich in N and P (Adriano et al., 1980). This is one of the best applicable methods for the proper utilization of the two widely produced waste materials in an efficient manner (Papadimitriou et al., 2008).

Weng and Huang (2004) conducted the adsorption equilibrium studies to determine the removal characteristics of Zn^{2+}onto fly ash and the results showed that the amount of Zn^{2+} adsorbed increases as the concentration and pH of the solution increase with a final total removal efficiency of 99%. The application of fly ash for removing heavy metals date back as early as 1975, when its effectiveness as a low cost adsorbent was evaluated for removing chromium ions such as Cr6+and Cr3+. Bioleaching by A. Niger may be an alternative or adjunct to conventional physico-chemical treatment processes of MSW fly ash to remove hazardous heavy metals (Hung et al., 2006; Pathak and Sreekrishnan, 2009). Feng et al. (2007) observed heavy metal concentration and geno-toxicity in a study conducted on MSW and bottom ash. Sajwan et al. (2007) reported that the leaching of cation increased rapidly in the soils amended with a mixture of 1:1 sewage sludge and fly ash.

Papadimitriou et al. (2008) observed that addition of fly ash to sewage sludge significantly reduced the total coliform population of the sludge and minimized metal leaching from the sludge. These two mixture enhance the efficient environmental friendly management process of both widely produced wastes.

Sajwan et al. (2003) reported that land disposal of fly ash (FA) and sewage sludge (SS) is a major problem due largely to their potentially harmful constituents. It has been investigated that combined use of FA and SS however may help in reducing the environmental pollution problem. It has been reported that with higher doses of FA/SS mixture more leaching and downward migration of heavy metal ions likely to occur. It is confirmed from the experimental results that combined use of FA and SS, lesser leaching will take place. So, low to moderate rates of FA and SS mixture can be used as soil amendments and will be beneficial for the plant growth.

Fly ash as an adsorbent proved beneficial in the removal of heavy metal ions such as cadmium copper, nickel, zinc etc. and other non-metal contaminants as well. The adsorption capacity increases as heavy metal ion concentration decreases. Not only this, fly ash has been used in a number of beneficial applications to minimize waste and decrease the cost of disposal (Kadirvelu and Namasivayam, 2003). It has been reported by (Tofan et al., 2008) that the monolayer adsorption capacity of energy pit coal fly ash are observed on the basis of Langmuir constant and Lagergren pseudo-first order equation. The result shows that fly ash may prove a low cost and better adsorption material for the environmental technologies.

Although fly ash is considered as a waste, several studies have pointed out their efficiency in the removal of heavy metallic ions in aqueous phase from sewage sludge (Mohan and Gandhimathi, 2009; Wang et al., 2009). (Kersch et al., 2004) reported that remanants of sewage sludge or fly ash are usually contaminated with toxic heavy metals, which shows their leaching potential. Metals leach out from the remanants of fly ash and sewage sludge after contact with water, thus polluting the ground water. If aqueous concentrations of metals are exceeded, these remanants require expensive disposal.

The heavy metals present on the cell surface of the micro-organisms in the sludge can be easily removed by treating with acid as acid helps in dissolving them. The addition of fly ash to sewage sludge not only reduced the total coliform population present in the sewage sludge but it also proved helpful in minimizing the leaching of metal from the sewage sludge (Zhang et al., 2008). Incorporation of these two mixture (Fly ash and Sewage sludge) as reported by (Jianmin et al., 2008) increased the efficient environmental friendly management process of both widely produced wastes. It was observed that when pH was less than 3 or above 7, increasing amounts of arsenic were leached or desorbed from the fly ash.

2.4 Significance in research area

As we have discussed above, what is sewage sludge waste and how toxic it is if disposed as it in the environment as it is, how the largely produced waste fly ash can be better utilized in its treatment for its safe disposal. Why there is emerging need to study the leaching and ecotoxicological properties of fly ash – sewage sludge mixture.

- To study the physico-chemical properties of produced materials (from fly ash-sewage sludge mixture), their leachates and assessment of their environmental impact
- Use of fly ash as a barrier for arresting leaching of metals from sewage sludge
- To evaluate adsorbing capacity of fly ash from fly ash-sewage sludge mixture. The safe recycling of fly ash (FA) and sewage sludge (SS) in the agricultural processes comprises an important environmental technology on waste management. Soils amended with FA and SS may change their ability to adsorb heavy metals due to either increase of soil pH or decomposition of sludge-borne organic matter.
- Disposal of sewage sludge after mixing with alkaline fly ash can prove beneficial from environmental point of view. The use of sewage sludge mixed with fly ash (particularly alkaline fly ash) however has the potential of its use in restoration of degraded land, as alkaline fly ash due to its liming effect can stabilise/immobilise the contaminants while supplying organic carbon and other essential nutrients.

2.5 Gap in the proposed research area

As we have seen the significance of this research area as discussed in the above section but still there are some gaps in the research area. I noted the following gaps in the research area.

1. Fly ash and sewage sludge is the conventionally adopted adsorbent for removing metals from aqueous medium as it is low cost adsorbent.
2. Disposal of growing amount of fly ash and sewage sludge creates environment problems as their management and disposal is a major problem worldwide.
3. In case of an environmental application the possible leaching of metals into the ground water should be avoided.

2.6 Objectives of the proposed work

Keeping in mind the gap in the research area, it is proposed to study the effect of leachate released from fly ash and sewage sludge mixture and retention of metal ions in the mixture. Following are the objectives of the proposed research work ---

- Optimization of fly ash and sewage sludge mixture for leaching characteristics
- Investigate the effectiveness of fly ash and sewage sludge to adsorb selected heavy metals using different synthetic metal solutions for leachability test
- Eco-toxicity studies

Materials &Methods

CHAPTER 3

MATERIALS AND METHODS

Different samples of fly ash and sewage sludge were collected from various locations. Experiments were conducted to determine the efficiency of fly ash in removing heavy metals from sewage sludge using variant fly ash –sewage sludge mixtures and to determine the capacity to act fly ash as a stabilizer for minimizing leaching from sewage sludge. The control sample used was the leachate obtained from soil (without fly ash and sewage sludge mixture).Batch leaching studies were carried out to evaluate the leaching and toxic potentials of different metals in sewage sludge waste samples. Effects of different variables, namely contact time, acid dose, adsorbent dose, number of washings, pH on various fly ash- sewage sludge mixtures were investigated. Experiments were carried out in batches with 1:20 solid to liquid ratio. This chapter describes different research approaches and techniques used. Physical and chemical analysis of fly ash and sewage sludge samples were analysed as per ASTMC618. Three ratios of fly ash - sewage sludge mixtures were prepared and the leachate analysis was done. All the leachate samples were taken in duplicates. Statistical analysis of the data was done by calculating their mean, relative standard deviation, standard error and represented in figures with the help of error bars. Various statistical parameters were analysed as per the methods provided by Rao, 1996 using Graph pad Prism Software 2.01, SPSS software and Microsoft Excel

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In order to evaluate the leaching and eco-toxicity of metal ions in sewage sludge (SS) and fly ash (FA) mixtures, a systematic study was planned. The present study was divided into various parts:

1. Sampling of sewage sludge and fly ash samples.
2. Optimization of ratios of fly ash and sewage sludge.
3. Using cadmium and lead metal solutions for the leachability test.
4. Investigating the effectiveness of fly ash and sewage sludge mixture to adsorb selected heavy metals.
5. Monitoring of the collected samples for physical and chemical analysis as per American Society of Testing Materials (ASTM) C618 method for the analysis of

various water quality parameters of the leachate prepared from different ratios of fly ash-sewage sludge mixtures as per APHA (American Public Health Association) standard method of water and wastewater.

6. Evaluation of microbiological eco-toxicity studies from several ratios of fly ash- sewage sludge mixtures.

3.0 EXPERIMENTAL

Samples of fly ash were collected from Panipat thermal power plant, situated about 100 Km from the national capital New Delhi, from the different silos and the sewage sludge was collected from the Okhla sewage treatment plant, New Delhi. Typical chemical and physical properties of the fly ash used for adsorption experiments are presented in table 3.1and table 3.2, respective. In all the experiments distilled water was used.

3.1 Waste samples

Various samples of fly ash and sewage sludge were mixed in different proportions (w/w) of 1:1, 1:4, 4:1, suspended in desired amount of distilled water (50% W/V) under varying pH conditions.. The leachates were analysed for variant parameters such as total hardness, Ec, TKN etc. in respect to different FA/SS mixture.

3.2 Physical and chemical characterization of fly ash and sewage sludge

The physical and chemical characterisation of fly ash and sewage sludge samples was done as per the standard methods of ASTM C618 (American Society of Testing materials).

3.2.1 Fly ash reaction (pH)

Fly ash and sewage sludge were mixed in three different ratios (w/w) of 1:1, 1:4 and 4:1. 5g each of fly ash/ sewage sludge mixture was mixed with 25 mL of distilled water, stirred thoroughly to mix properly the solid sample in the liquid for at least half an hour and then kept in stationary conditions for another half an hour. The pH of the supernatant liquid was measured as per the method given by (Jackson, 1967) using a Thermo Orion Model 290 pH meter after calibration with buffer solution of three different pH 4.0, 7.0 and 9.2.

3.2.2 Electrical conductivity

The electrical conductivity was determined in μScm^{-1} as per the method given by (Jackson, 1967) as detailed below: The sample solution was prepared by the same method as for pH measurement.

1. Ten g of soil /fly ash was placed in a 100 ml beaker and 20 ml distilled water was added.
2. The soil-water mixture was allowed to stand undisturbed until the soil settled completely.
3. Before taking reading, the conductivity meter (Orion Model 125) was calibrated with 0.01 M potassium chloride solution.

3.2.3 Total nitrogen

Total nitrogen in the supernatant liquid was estimated by the Kjeldahl method given by (Jackson, 1967) as detailed below:

1. 5g of each sample of fly ash/sewage sludge was mixed thoroughly with 3 mL sulphuric-salicylic acid followed by the addition of 5g of sodium thiosulphate. Samples were heated for 5 minutes followed by cooling up to room temperature and then 10g of the digestion mixture (98g K_2SO_4 + 2g $CuSO_4$ + 1g salicylic acid) was added. The contents were mixed well in a Kjeldahl flask.

2. Samples were then kept in a digestion assembly at a controlled temperature of 100±2°C for atleast two hours.

3. A change in colour from dark brown to greenish white was observed and then contents of the samples were cooled and diluted with 300mL distilled water.

4. 300mL of the digested sample, 50mL NaOH solution and glass beads were added to the distillation flasks. Contents of the flask were distilled at 100±1°C.

5. The distillate was collected until the boric acid volume reached 200mL with the help of a receiver tube in a conical flask containing 50mL boric acid.

6. After adding two drops of the mixed indicator the distillate (200mL) was titrated against H_2SO_4(0.02 N) until the endpoint colour changed from green to pink.

Calculation

$$\text{Total N (mg/L)} = \frac{\text{(T-B) x Normality of } H_2SO_4 \text{ x14 x 1000}}{\text{Volume of sample (mL)}}$$

Where, T is the titre value for the sample and B is volume of sulphuric acid used for the blank.

3.2.4 Chloride (Cl^-)

Chloride content of the samples was determined by argentometric titration method. Chlorine in the form of chloride ion is one of the major inorganic anions in water and waste water.

Reagents required

Standard $AgNO_3$ solution (0.0141 N) – 3.4g of dried $AgNO_3$ was dissolved in distilled water to make 1 litre solution and was stored in a dark bottle.

Potassium chromate indicator solution – 5g of K_2CrO_4 was dissolved in 100mL of distilled water.

Procedure

50mL of the sample was taken in a titration flask and 3-4 drops of K_2CrO_4 indicator were added. The solution was titrated against standard $AgNO_3$ solution till yellow colour changed to light brick red. The titration was repeated five times and a mean of the readings was used for further calculations.

Calculation

$$Cl^- \text{ (mg/L)} = = \frac{N_2 \times V_2 \times 35.5 \times 1000}{V_1(mL)}$$

Where: N_2 = Normality of std. $AgNO_3$ solution (0.0141N)

V_2 = Volume of $AgNO_3$ solution (mL)

V_1 = Volume of sample taken (50mL)

3.2.5 Biochemical oxygen demand (BOD)

It is used as a measure of the quantity of oxygen required for the oxidation of biodegradable organic matter present in water sample by aerobic biological action. The BOD of 50% (W/V) leachate of sewage sludge was estimated.

Reagents required

Phosphate buffer

Dissolved KH_2PO_4(8.50g), K_2HPO_4(21.75g), $Na_2HPO_4.7H_2O$ (33.4g) and NH_4Cl (1.7g)separately in about 500mL distilled water and diluted to one litre each. The pH was 7.2 without further adjustment.

Magnesium sulphate solution

Dissolved 22.5g $MgSO_4 .7H_2O$ in distilled water and diluted it to make one litre solution.

Calcium chloride solution

Dissolved 27.15g $CaCl_2$ in distilled water and diluted it to make one litre solution.

Ferric chloride

Dissolved 0.25g $FeCl_3.6H_2O$ in distilled water and diluted it to make one litre solution.

Procedure

1. Dilution water was prepared, by adding 1mL/L of each of the four nutrients; namely, phosphate buffer, magnesium sulphate, calcium chloride and ferric chloride to distilled water in the same serial and the solution was diluted to make 1L dilution water.
2. Seed water was prepared by acclimatizing the 'seed' (1-5 mL/L) at 20ºC.
3. Prepared dilutions according to the requirement 5L and keep it to 20°C. Thoroughly aerated the dilution water either by diffused aeration or mixing to increase its DO concentration as near as possible to the saturation concentration. Collected the representative sample for which BOD_t has to be measured, find out dilution factor through the procedure described in dilution factor.
4. Transfer the water into BOD bottles through siphoning from aspirator bottles (outlet of the aspirator bottle may be provided with rubber tubing). Other end of the rubber tubing is inserted to the bottom of the BOD bottle, which is placed in a one litre capacity beaker, and sample may be allowed to overflow the BOD bottle. After that remove the tubing from the bottle and stopper it.
5. Filled at least five bottles for each sample three bottles kept at 20°C after numbering them for 5 days.
6. The bottle which incubated at 20°C, ensured that each bottle had the water in the funnel portion for acting as a water seal and covered the bottle mouth and neck with aluminium foil in order to avoid drying out of the water seal during incubation. After the desired period of incubation (5 day) at 20°C test the bottle for DO concentration considered this DO as the final DO.

Calculation

$BOD(mg/L) = DF [(DO_{is} - DO_{fs})] – (DO_{ib}-DO_{fb}) (1-1/DF)]$

Where:

X °C = 20°C

DO_{is} = initial DO of the diluted sample.

DO_{fs}= final DO of the diluted sample.

DO_{ib} = inital DO of the blank sample.

DO_{bf} = final DO of the blank sample.

DF = Dilution factor.

X = Temperature.

3.2.6 Chemical oxygen demand (COD)

Chemicals required

a) Standard dichromate for closed reflux colorimetric method (0.0347 M).

b) Ferrous ammonium sulphate solution (0.01M).

c) COD reagent (25g of Ag_2SO_4 + 2.5 L of conc. H_2SO_4).

d) Ferroin indicator.

Procedure

1. Added 1.5 mL standard dichromate solution in COD vials and 3.5 mL of sulphuric acid reagent along the side wall of the tube. Took accurately measured /diluted quantity of homogenized 2.5 mL sample and added in the COD vials. Closed the tube lightly and mixed the contents carefully by shaking tubes up and down.
2. Digested the samples in HACH COD reactor for 2 hours at 150 ±2ºC.
3. After 2 hours the samples were cooled and titrated with FAS (0.01 M) solution in the presence of Ferroin indicator.

Calculation

$$\text{COD (mg/L as } O_2\text{)} = \frac{(A - B) \times M \times 8000}{SampleVolume(mL)}$$

A = mL of FAS consumed for blank

B = mL of FAS consumed for sample

M = molarity of FAS

3.2.7 Organic carbon

Total organic carbon was estimated by Walkley and Black method (1934).

Reagents

1. Potassium dichromate (1 N) solution: 49.04g of potassium dichromate was dissolved in distilled water to prepare one litre of solution.
2. Ferrous ammonium sulphate (0.5 N) solution: 198g of ferrous ammonium sulphate was dissolved in water to prepare one litre of solution.
3. Diphenylamine indicator: 0.5g of diphenylamine was dissolved in a mixture of 20mL water and100mLof concentrated sulphuric acid.
4. Concentrated sulphuric acid.
5. Orthophosphoric acid (85%) and 0.5g of sodium fluoride (NaF).

Procedure

1. 1g of fly ash/sewage sludge was taken in a 500 mL conical flask and 10mL of $K_2Cr_2O_7$ (1N) solution was added. The flasks were then swirled for proper mixing of the solid sample.
2. Further, addition of 20mL of H_2SO_4 was done and the flask was kept undisturbed for atleast 30 minutes.
3. After 30 minutes time period 200mL of distilled water was added to the mixture, 10mL of orthophosphoric acid, 0.5g of NaF and 1mL diphenylamine indicator were also added to the flask.
4. The contents were then titrated with freshly prepared ferrous ammonium sulphate solution (0.5 N) till the end point from (blue-violet to green) was achieved. A blank was also run without the solid sample.

Calculation

$$\text{Organic carbon (\%)} = \frac{10(B-T)\times 0.003\times 100}{B\times ODW(g)}$$

Where:

B denotes the volume of ferrous ammonium sulphate solution required for blank titration (mL).

T denotes the volume of ferrous ammonium sulphate solution needed for fly ash/sewage sludge sample titration (mL).

ODW denotes the weight of oven dry sample (grams).

3.2.8 Sulphate

Sulphate was estimated by gravimetric method. Sulphate ion is one of the major anions in natural waters. It is of importance in public water supplies because of its cathartic effect upon when it is present in excessive amounts. For this reason 250mg/L is recommended for human consumption.

Reagents required

1. Hydrochloric acid + water (50% HCl).
2. Barium chloride solution – Dissolved (100gm) barium chloride in distilled water and diluted it to make one litre solution.
3. Silver nitrate nitric acid reagent – Dissolved (8.5g) of $AgNO_3$ and added 0.5mL conc. HNO_3 in 500mL distilled water.

Procedure

1. Took 100mL FA/SS extract filtered with Whatmann filter paper No. 42and added 1mL dilute HCl solution to it.
2. Placed it on heater and heated to boiling than gently and slowly added 10mL of $BaCl_2$ solution until precipitates appeared to be complete, then added 2mL excess.
3. Digested the precipitates at 80 to 90 ºC overnight or not less than 2 hour.
4. Take pre-dried weight of Whatman filter paper 41 or 44. Filtered the sample slowly and then washed the filtrate with warm water. Continued washings until washings are free of Cl^- as indicated by testing with $AgNO_3^-$ HNO_3 reagent.
5. Placed the filter with precipitate in pre-weighed China or platinum crucible and dried at 104ºC for constant weight.
6. In gravimetric method with ignition simply dried the filter paper and transferred in muffle furnance at 500-800 ºC for one hour. Do not let filter paper in the flame.
7. Cooled in desiccator and weight calculations were same in both the methods.

Calculation

$$\text{Sulphate (mg /L)} = \; = \frac{\text{mg BaSO}_4 \times 411.6}{\text{Sample volume (mL)}}$$

3.2.9 Nitrate (Nitrate Electrode Method)

Principle

The nitrate ion electrode was a selective sensor that develops a potential across a thin, porous, inert membrane that held in place a water-immiscible liquid ion exchanger. The electrode responds to nitrate activity about 10^{-5} and 10^{-1} M (0.14 to 1400mg nitrate-nitrogen per litre). The lower limit of detection is determined by the small but finite solubility of the liquid ion exchanger.

Reagents used

a) **Nitrate-free water**

Redistilled or distilled water was used to prepare all solutions and dilutions.

b) **Stock nitrate solution**

Dried potassium nitrate (KNO_3) in an oven at 105ºC for 24 h. Dissolved 0.7218g in water and diluted it to 1000mL; 1.00mL = 100 µg nitrate-nitrogen. Preserved with 2mL $CHCl_3$/L. This solution was stable for at least 6 months.

c) **Standard nitrate solutions**

Diluted 1.0, 10 and 50mL stock nitrate solution to 100mL with water to obtain standard solutions of 1.0, 10 and 50 mg NO_3^--N/L, respectively.

d) **Buffer solution**

Dissolved 17.32g of $Al_2(SO_4)_3$. $18H_2O$, 3.43g Ag_2SO_4, 1.28g H_3BO_3, and 2.52g sulfamic acid (H_2NSO_3H), in about 800mL water. Adjusted to pH 3.0 by slowly adding 0.1N NaOH. Diluted it to 1000mL and stored in a dark glass bottle.

e) **Sodium Hydroxide**

NaOH(0.1N)

f) **Reference electrode filling solution**

Dissolve 0.53g $(NH_4)_2SO_4$ in water and dilute to 100mL.

Procedure

Preparation of calibration curve

1. Transfered10mL of 1mg NO_3^--N/L standard to a 50mL beaker, add 10mL buffer, and stirred with a magnetic stirrer.
2. Immersed tips of electrodes and recorded millivolt reading when stable (after about 1 minute).
3. Removed electrodes, rinsed and blot dried. Repeated for 10-mg NO_3^--N/L and 50mg NO_3^--N/L standards.

4. Plotted potential measurements against NO_3^--N concentration on semi-logarithmic graph paper, with NO_3^--N concentration on the logarithmic axis (abscissa) and potential (in millivolts) on the linear axis (ordinate).
5. A straight line with a slope of + 57 ± 3mV/decade at 25ºC resulted. Recalibrated electrodes several times daily by checking potential reading ofthe10 mg NO_3^--N standard and adjusted the calibration control until the reading plotted on the calibration curve was displayed again.

Measurement of sample

1. Transfered10mL sample to a 50mL beaker, add 10mL buffer solution, and stirred (for about 1 min) with a magnetic stirrer.
2. Measured standards and samples say about the same temperature. Immersed electrode tips in sample and recorded potential reading when stable (after about 1 minute).Read concentration from calibration curve.

3.2.10 Turbidity (Nephelometric Turbidimeter)

Reagents Preparation

a) Dissolved hydrazine sulphate (1.0gm) in distilled water and diluted it to make 100mL in a volumetric flask.

b) Dissolved Hexamethylene Tetramine (10gm) in distilled water and diluted it to make 100mL in a volumetric flask.

c) Mixed 5mL of each of the above solution (a) and (b) in a 100mL volumetric flask and allow to stand for 24 hours at 25 ± 30ºC and dilute to 1000mL.The solution had a turbidity of 40 NTU.

d) The solution can be kept for about a month.

Calibration of the Apparatus

a) Switched on the instrument and kept it on for some time.

b) Selected appropriate range depending upon expected turbidity of the given sample of water.

c) Set zero of the instrument with turbidity free water using a blank solution and adjusted zero with set zero knob.

d) Took standard suspension into another test-tube and prepared as in selection for 0 to 200 NTU range, use 100 NTU solution.

e) Took its measurement and set displayed to the value of standard suspension with calibrating knob.

f) Now the instrument was ready to took measurement of any solution of unknown turbidity.

Operation of Instrument

a) Switched on Nephelometric turbidity meter and waited for few minutes till it warmed.

b) Set the instrument at 100 on the scale with a 40 NTU standard suspension. In this case, every division on the scale equal to0.4 NTU Turbidity.

c) Shaked thoroughly the sample and kept for some time to eliminate the air bubbles.

d) Took sample in Nephelometer sample tube and put the sample in sample chamber and find out the value on the scale.

e) Diluted the sample with turbidity free water and again read the turbidity.

3.2.11 Total solids (TS)

Total solids referred to the material residue left in the vessel after evaporation of a sample and was subsequently dried in an oven at 100°C temperature which included total suspended solids (TSS), the portion of total solids (TS) retained by a filter and total dissolved solids (TDS) the portion that passed through the filter.

Procedure

1. A clean evaporating beaker kept at 103-105°C for 1 h was cooled in a dessicator and weighed. The process was repeated until a constant weight was obtained.
2. 100mL of well mixed sample was transferred to preweighed evaporating beaker and placed in an oven at a temperature slightly lower than boiling point to avoid splattering of sample.
3. After the complete evaporation of sample the evaporating beaker was transferred to a dried oven at 103-105°C for 24 h.
4. Beaker was cooled in a desiccator and weighed. The process of drying and cooling, dessication and weighing was repeated until a constant weight was obtained.

Calculation

TS (mg/L) $= \frac{(A - B)\times 1000}{SampleVolume(mL)}$

Where

A= Final weight (mg) of the evaporating beaker + residue

B= Initial weight (mg) of the evaporating beaker

3.2.12 Total dissolved solids (TDS)

Procedure

1. 100mL of sample was well mixed and filtered through Whatman filter paper no. 42. The samples were transferred to preweighed beaker or evaporating dish and placed in oven at 103°C-105°C.
2. The samples were then placed in dessicator to remove traces of water from an almost dry sample. The samples were then cooled and weighed. The procedure was repeated until a constant weight of the sample was obtained.
3. Duplicates were also maintained at the same set of conditions. The total dissolved solid in the sample was calculated with the following formula.

Calculation

Total dissolved solids (TDS) mg/L $= \frac{(A - B) \times 1000}{SampleVolume(mL)}$

Where

A = Final weight (mg) of the evaporating beaker + residue

B = Initial weight (mg) of the evaporating beaker

3.2.13Total Suspended Solids (TSS)

Apparatus

Glass-microfibre filter, filtration apparatus with suction flask, desiccators, analytical balance, drying oven for evaporation at 103°C-105°C and vacuum pump were used.

Procedure

1. The Whatman filter paper No. 42 kept in an oven was cooled in a dessicator and weighed to note the initial weight. The above step was repeated until a constant weight of Whatman filter paper No. 42 was obtained.

2. 100mL of well mixed sample was filtered through Whatman filter paper using filtration assembly.
3. Filter paper was carefully removed from filtration apparatus and transferred to oven for drying.
4. The filter paper was dried for at least 24 h at 103 to 105°C in an oven, cooled in a dedicator and weighed. The cycle of drying, cooling in desiccator and weighing was repeated until a constant weight was obtained.

Calculations

Suspended solids (mg/L) = Total residue - Dissolved residue

Total suspended solids (TSS) mg /L $= \frac{(A-B)\times 1000}{Sample Volume(mL)}$

Where

A = Final weight (mg) of Whatman filter paper and dried residue

B = Initial weight (mg) of Whatman filter paper

3.2.14 Hardness

Reagents required

N/100 (0.01M) EDTA solution

Dissolved sodium salt (4.0gm), di-sodium dihydrogen ethylene diamine tetra acetate in water added $MgCl_2$(0.1g)and diluted it to make one litre solution.

Ammonia buffer

Dissolved ammonium chloride (6.75g) in 75mL of liquid ammonia and diluted it to make 100mL with distilled water.

Erichrome Black-T indicator

Dissolved pure solid dye stuff (0.2g) in 15mL tri-ethanol amine. Added 5mL of absolute ethanol to reduce the viscosity or 0.4% of solution of the dye stuff in methanol or kept as such dye stuff after crushing it into powder form.

Standard hard water (1ml = 1mg $CaCO_3$)

Dissolved $CaCO_3$(1g) in little diluted HCl. Boiled it to remove CO_2 for sometime and heated to dryness on water bath. Now again dissolved dry precipitate and diluted it to make one litre solution.

Standardization of EDTA solution

EDTA was standardized by using standard hard water ($CaCO_3$ solution) to find the actual molarity of EDTA solution. Procedure of standardization was same as given for water samples.

Procedure

1. Pipette out 50mL of the hard water sample into a 250mL conical flask. Added 2mL of the buffer solution and added 3 drops of Erichrome Black-T (or a pinch if solid) indicator.
2. Titrated the solution with standard EDTA solution from the burette until the colour changes from wine red to clear blue at the end point. Experiment was repeated to get three concordant readings.
3. Took 250mL of the hard water sample into 500mL beaker; boiled it gently when the volume left 50mL cooled it and diluted to make it 250mL.
4. Took 50mL of above solution in 250mL conical flask and added 2mL of the buffer solution and Erichrome black-T as in step 1. Noted down the EDTA value.

Calculation

There are two types of water hardness. Temporary and permanent hardness. Total permanent water hardness was calculated with the following formula:

Total hardness (as $CaCO_3$) $= M2 \times V2 \times M.W. \times 100 \div V1$

Where:

M2 = Molarity of standarized EDTA solution

V2 = Volume of EDTA solution used (ml)

V1 = Volume of sample taken (ml)

M.W. = Molecular weight of $CaCO_3$ (100)

Calcium estimation (Ca^{2+})

Calcium content of the water samples was estimated by using the complexometric titration method (EDTA).

Requirements

EDTA solution (0.01 M)

Dissolved EDTA (3.723g) in double distilled water and diluted to make the volume one litre solution. EDTA solution was standardized with $CaCO_3$ solution to know the actual molarity of the EDTA solution.

Standard NaOH solution (1 N)

Dissolved NaOH (8gm)in double distilled water and diluted to make the final volume 200mL solution.

Murexide indicator (solid)

Procedure

25mL of extract was taken in titration flask. 1mL NaOH (1N) solution was added to raise the pH (11.3). To this, a pinch of solid murexide was added. Pink colour appeared. Sample was titrated against standard EDTA solution till the colour changes from pink to purple. The experiment was repeated to get three concordant readings.

Calculation

Ca^{2+}(mg/litre) = $M2 \times V2 \times M.W. \times 1000 \div V1$

Where

M2 = Molarity of standardized EDTA solution

V2 = Volume of EDTA solution

M.W. = Molecular weight of calcium (mL)

Magnesium determination (Mg^{2+})

Magnesium content of the water samples was calculated indirectly using Ca^{2+} and total hardness content of water samples by using the following formula:

Mg^{2+} (mg/L) = [Total Hardness – (Ca^{2+} × 2.5)] × 0.243

Total Permanent Hardness = Calcium Hardness + Magnesium Hardness

Temporary hardness = Total hardness – Permanent Hardness

3.2.15 Percent Absorption test

Procedure

1. First of all, weighed 1000g of saturated surface dry fly ash/sewage sludge sample in the tray of known weight.
2. After this, the sample was dried in an oven at temperature 100-110ºC for atleast 24 hours time-period.
3. Weighed the dried sample with tray.
4. Calculated the absorption capacity as the percentage of oven dried mass.

Calculation

Percent absorption = $\frac{W1 - W2}{W2} \times 100$

3.2.16 Fineness of Fly ash / Sewage Sludge

Procedure

1. Weighed 100g of fly ash/sewage sludge sample. After weighing transferred the sample to a clean dried test sieve.
2. The sample was then sieved to pass a 2-mm sieve and the sieve and pan were held in both hands, sieved with gentle wrist motion until most of the fine material had passed through and the residue looked fairly clean. The whole process took 5 minutes.
3. After 5 minutes sieve was covered and the pan removed. The pan emptied and wiped with a clean cloth.
4. All the coarse material particles were collected during taping of the sieve.
5. Again the sieving process was continued as described above for the next 15 minutes.
6. After 15 minutes finishing with the sieving process the residue were weighed.

Calculation

Fineness = $\frac{mass\ of\ residue\ in\ g \pm C}{100}, percent$

Where

C = Correction factor

3.2.17 Bulk Density

Procedure

1. First of all empty specific gravity bottle was weighed and the weight was noted down as W1.
2. After this the weight of bottle filled with the sample to be analysed was noted down as W2.
3. Note down the volume of water in (mL) needed to fill the bottle as in 2 up to the brim.
4. The bottle was filled with powdered sewage sludge/fly ash mixture and weighed.

Calculation

Weight of empty bottle = W1

Weight of bottle and FA/SS mixture = W2

Weight of FA/SS mixture = W2-W1

Volume of the soil or volume of water needed to fill the bottle = V mL

Bulk density of the sewage sludge/fly ash = $W2 - W1 \div V$ g cm^{-3}

3.2.18 Specific Gravity

Specific gravity of the sewage sludge/fly ash was directly related to bulk density. It was used as an index to analyse the soil quality as in case of bulk density.

Procedure

1. Took 500g of oven dried fly ash or sewage sludge sample at 105ºC.
2. Took the weight of empty glass bottle (W1). The bottle was filled with oven dried fly ash/sewage sludge sample and again noted down the weight as W2.
3. In the third step, the bottle was filled up to brim with water and noted down its weight as W3.

Calculation

Specific gravity = $W2 - W1 \div W3 - W1$

Where,

W1 = weight of the empty glass bottle

W2 = weight of bottle + soil

W3 = weight of bottle + water

3.2.19 Percent Removal Efficiency

The removal efficiency of different heavy metal ions was also calculated at the different pH conditions which were as follows:

The percent removal efficiency was calculated by using the formula:

$$\frac{C_i - C_f}{C_i} \times 100$$

Where

C_i = initial concentration, C_f = final concentration

3.3 Leaching assay

The solid samples of fly ash and sewage sludge mixtures (FA/SS mixtures) were assessed for their leaching properties. In general, when solid waste comes in contact with water, the water gets contaminated with solutes (heavy metals) and stream out of the solid waste, which is termed as leachate. At the laboratory, a similar procedure was adopted to identify the leachability characteristics of FA/SS mixture. The 5g mixture of FA/SS in the ratio of 1:4, 1:1 and 4:1 were taken and were allowed to mix with 100mL of deionized water (Solid to liquid ratio 1:20). The samples were placed on rotatory shaker at 120rpm for 10hour. The process was carried out at controlled temperature conditions of 26±1ºC. Afterwards, the samples were allowed to settle down and the supernatant liquid was vacuum filtered with the help of 0.45µm membrane. Metal contents in the supernatant liquid were analysed with the help of atomic absorption spectrophotometer (ECIL, India, Model AAS 4129). The effect of pH of various leachate was studied using different pH conditions.

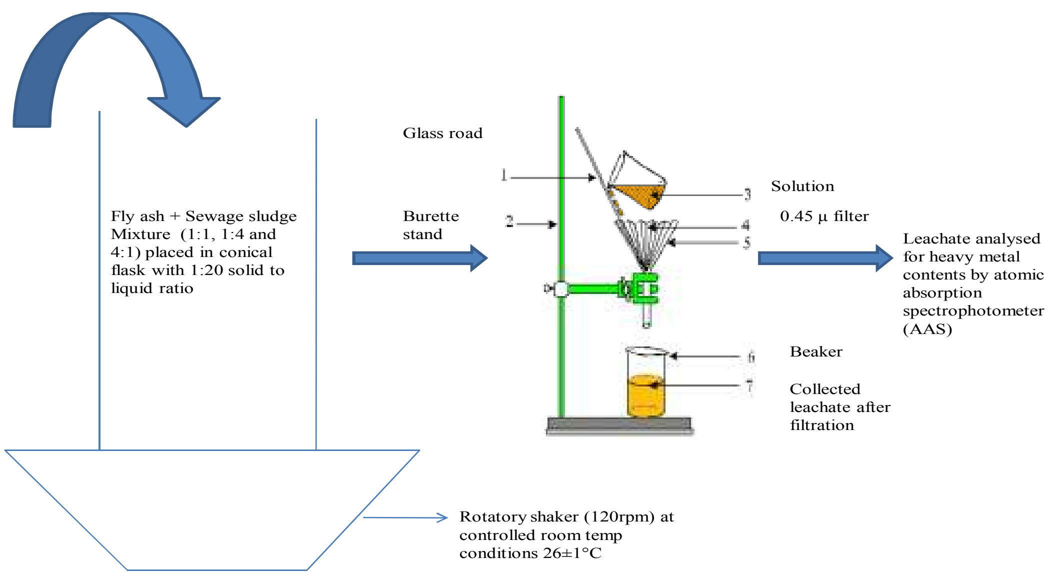

Fig 3.1 Experimental methodology for analyzing leaching of metals from fly ash – sewage sludge mixture

3.4 Heavy metal analysis

The fly ash sample collected from the thermal power plant, Panipat was brought to the laboratory of Thapar University, Patiala. The samples were oven dried at 120ºC and after that checked for the soluble heavy metal ions in to the aqueous solution. The 5g solid sample of fly ash was taken and suspended in 100mL distilled water (1:20 solid to liquid ratio) and placed on the rotatory shaker at 120rpm for a time period of 10 hour. The supernatant liquid was then vacuum filtered through 0.45µm membrane. The filtrate liquid were then analysed for the leaching of soluble metal ions in the aqueous solution. Different standard solutions for the different metal ions were prepared from the analytical grade salts in the laboratory. The leaching of heavy metals was studied for the five heavy metals; Pb, Cd, Ni, Cu and Co. The metals were studied with the help of atomic absorption spectrophotometer (ECIL, India, Model 4129). Samples were read two times and a mean value and relative standard deviation, standard error were computed.The effect of pH also studied on the leaching of heavy metal ions. The pH adjustment was done with the help of HNO_3(1N) and NaOH(1N) solutions.

1. To ensure accuracy in preparation, great care must be taken at all stages, with careful, accurate weighing, careful transfer of solid and clean glassware.
2. Solids that are to be used to make standard solutions must fulfill some criteria, i.e. they must be pure, dissolve in water easily, should not decompose and have a relatively high molar mass.

Preparation of AAS Standard Solutions

Standards for the establishment of calibration curves for AAS were prepared. Make up of different standard solutions were done by the analytical grade salts. Five standard solutions in different concentrations were prepared. To make up five standard solutions on stock solution is prepared and diluted aliquots of it.

Lead

Dissolved 1.5980g of lead nitrate ($Pb(NO_3)_2$) in 100ml. of deionised water. Diluted to 1 litre in a volumetric flask with deionised water.

Cadmium

Dissolved 2.0360g of cadmium chloride in 250 ml deionised water. Diluted to 1 litre in a volumetric flask.

Nickel

Dissolved 4.9530g of nickel nitrate ($Ni(NO_3)_2.6H_2O$) in 1 litre volumetric flask with deionised water.

Copper

Dissolved 3.7980g of ($Cu(NO3)_2$ $3H_2O$) in 250ml of deionised water. Diluted to 1 litre in a volumetric flask with deionised water.

Zinc

Dissolved 1.2450 g of zinc oxide (ZnO) in 5ml of deionised water followed by 25ml of 5M hydrochloric acid. Diluted to 1 litre in a volumetric flask with deionised water.

Iron

Dissolved 4.8400 g of iron (111) chloride ($FeCl_3.6H_2O$) in 200 ml of deionised water. Diluted to 1 litre in a volumetric flask with deionised water.

Procedure for AAS operation

1. Took the proper (the relevant) hollow cathode lamp.
2. Aligned the instrument, position the monochromator at the correct wavelength, selected the proper monochromator slit width (set prescribed monochromator slit width), and adjusted the hollow cathode current (set prescribed lamp current) according to the manufacturer's recommendation. Subsequently, lighted the flame and regulated the flow of fuel and oxidant.
3. Adjusted the burner and nebulizer flow rate for maximum percent absorption and stability, and balance the photometer (optimize the lamp orientation for maximum).
4. Aspirated with distilled water (when not running a standard or sample). The absorbance should be zero; this number (0 mg/L, 0abs) is a data point for the subsequent calibration curve.
5. Run a series of standards of the element under analysis and construct a calibration curve by plotting the concentrations of the standards against the absorbance.
6. Aspirated the samples and determine the concentrations from the calibration curve.
7. Read the metal concentration value in mg/L from the calibration curve.

The analysis on the AAS of each sample was carried out in duplicates and for accuracy of the results the mean and relative standard deviation was computed for each set of values.

Parameters for the AAS

AAS Parameters

a) Lamp: hollow cathode lamp

b) Fuel: Acetylene

c) Oxidant: Air

3.5 Microbiological Analysis

3.5.1 MPN test for total coliforms

The microbiological analysis of the samples was carried out according to the standard method of the American Public Health Association (MPN test 9221-B, APHA 2005) without any pH adjustment.

3.5.1.1 Presumptive test

Principle

The presumptive test is specific for detection of coliform bacteria. Measured volumes of water extracts to be tested are added to lactose fermentation broth containing an inverted gas vial. Because these bacteria are capable of using lactose as carbon source (the other enteric organism are not), their detection is facilitated by use of this medium. In addition, to lactose, the medium also contains surface tension depressant, bile salts used to suppress the growth of organisms other than coliform bacteria.

Tubes of lactose medium are inoculated with 10mL, 1mL and 0.1mL aliquots of the water extracts. The series consists of atleast three groups each composed of the three tubes of the specified medium. The tubes in each group are then inoculated with the designated volume of the water extract. The greater the number of tubes per group, the greater the sensitivity of the test. Development of the gas in any of the tubes is presumptive evidence of the presence of coliform bacteria in the sample.

Media used: Maconkey broth (double strength and single strength)

Procedure

1. The whole process involved preparation of three series, of solution.
2. For the first series, three tubes (which include three different ratios of SS/FA) marked as double strength (DS) and filled with 10ml of double strength Maconkey broth.
3. Rest six tubes of the remaining two series (three tubes of each series contained three different ratios of SS/FA), were marked as single strength and added 10ml of single strength Maconkey broth to each tube.
4. Upon preparation of three series, media is sterilized at 120ºC for 15 minutes. After sterilization it was cooled and then inoculated with 10mL aliquot of water sample in the three tubes labelled as DS (first series); 1mL aliquot was added in three single strength tubes (second series) and lastly, 0.1mL aliquot was added in the remaining three single strength tubes (third series).

5. In the last step, all tubes were incubated for 24 to 48 hours at 37±0.1º C.
6. The whole process involved preparation of three series, of solution.
7. For the first series, three tubes (which include three different ratios of SS/FA) marked as double strength (DS) and filled with 10ml of double strength Maconkey broth.
8. Rest six tubes of the remaining two series (three tubes of each series contained three different ratios of SS/FA), were marked as single strength and added 10 ml of single strength Maconkey broth to each tube.
9. Upon preparation of three series, media is sterilized at 120ºC for 15 minutes. After sterilization it was cooled and then inoculated with 10 mL aliquot of water sample in the three tubes labelled as DS (first series); 1 mL aliquot was added in three single strength tubes (second series) and lastly, 0.1 mL aliquot was added in the remaining three single strength tubes (third series).
10. In the last step, all tubes were incubated for 24 to 48 hours at 37±0.1º C.

3.6 Eco- toxicity Studies

The eco-toxic studies were carried out on two fish species viz. Danio rerio (Zebra fish), Poecilia reticulate (guppy fish) with leachate of Sewage sludge, and optimised (FA/SS) mixture 4:1 ratio obtained by leaching assay and accumulation of different heavy metals ions studied by two fish species. However, the fish were not fed during the last 48 h of adaptations and throughout the toxicity test duration of 96 h for each metal. All the experiments were conducted in the glass aquaria with 5 L water capacity. The toxicity tests with three age groups of fish viz., 60, 90 and 120 day old fish were conducted in glass aquaria with four distinct concentrations of sewage sludge leachates 5%, 10%, 15% 20% weight by volume. Ten fish were introduced for each sample leachate solution.

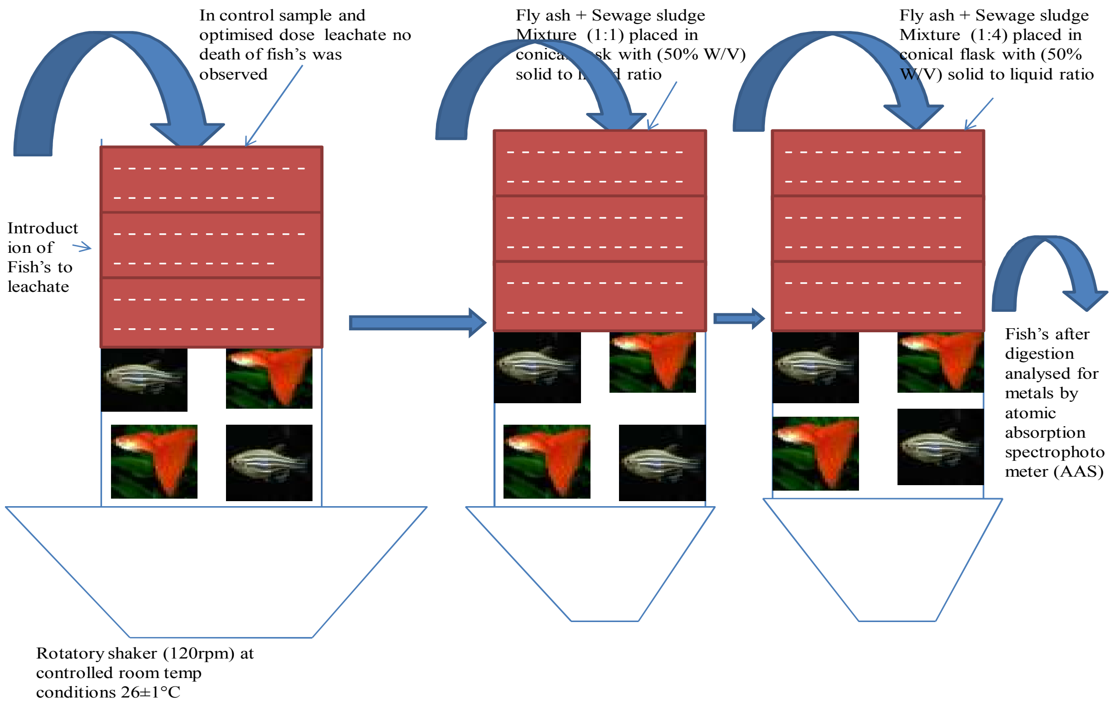

Fig 3.2 Experimental methodology followed for eco-toxicological studies

3.7 Statistical Analysis

The different fly ash-sewage sludge mixtures were taken in duplicated and mean, standard deviation, standard error and variation was calculated and represented in figures with the help of error bars. The various statistical parameters were analysed as per the methods given by Rao, 1996 using Graph pad Prism Software 2.01, Statistical Package for Social Science (SPSS) and Microsoft Excel.

3.7.1 Variance

The variance is measured as the square of the units in which the variable X is measured. For example, if X is the height in centimeters (cm), the variance will be measured in cm2 (square centimeters). The formula for variance is:

$$\text{Variance} = \frac{\sum \left(Xi - \overline{X}\right)2}{n} = \frac{\sum Xi2 - n\overline{X}2}{n}$$

= Sum of the squares of the deviations of individual values from the mean x ÷ sample size where n is the number of observations; x is the arithmetic mean of the observations ofX_2s are the individual observations – $x_1, x_2 \ldots\ldots\ldots\ldots x_i \ldots\ldots\ldots\ldots x_n$.

3.7.2 Standard Deviation

It is convenient to have a measure of variation expressed in the original units of X and this can be done by taking the square root of the variance. This quantity is known as the standard deviation and is,

SD = √Variance.

3.7.3 Standard Error

The standard error (SE) is a measure of the variation or dispersion of the means of a set of measurements. It is therefore, smaller than the standard deviation of a single series of measurements form the same of population. It is used to compare means with one another.

Formula for S^2= variance = $\sum(X - X)^2{}_i/(n-1)$

= $(\sum X i^2 - nX^2/(n-1)$= (SS-CF) ÷(n-1)

Standard deviation = square root of variance = $\sqrt{S2}$

Standard error = √ (variance/sample size) = $\sqrt{(S^2/n)}$

Standard error is the standard deviation of the means of measurements. It is an indication of the magnitude of variation between sample mean values. Standard error is also called the standard deviation of the mean.

Results & Discussion

CHAPTER 4

RESULTS AND DISCUSSION

Physical and chemical analysis of fly ash samples is defined which was done as per ASTMC618. The sewage sludge and fly ash samples were analyzed for heavy metals using atomic absorption spectrophotometer (ECIL, India, Model AAS 4129). Experiments were conducted in batches. Replicates of all the samples were taken for analysis and evaluation of results was carried out by calculating the mean, standard deviation and standard error values. Different experiments were conducted to find out the optimum conditions with regard to pH, number of wash offs, adsorbent dose, acid dose, contact time where the leaching of metals was the minimum. As the wastes are likely to be washed off with rain water so dose of fly ash was optimised to know which ratio prevents leaching the most.

4.0 Optimization of variable parameters

Fly ash bulk sample was collected from the Thermal Power Plant, Panipat (India) and dried in oven at 120ºC for five hours. A large number of samples were collected from different locations of the stock, mixed and replicas of the composite sample were taken for analysis. Physical and chemical analysis of the fly ash sample was carried out in accordance with ASTM Standard C618 (widely used methods for physical and chemical analysis of fly ash). Results of the analysis are given in Tables 4.1 and 4.2. The sewage sludge sample was collected from the Wastewater Sewage Treatment Plant Okhla, New Delhi, (India). Sewage waste water from the territory of Delhi, the national capital of India with a population of more than one million people, is collected and treated at the waste water treatment plant of Okhla, New Delhi situated on the outskirts of the city. At the treatment plant, the sewage sludge goes through different treatment processes including primary and secondary treatment and at the end, the sewage sludge is placed on the sludge drying beds. Samples from five different locations of the sewage sludge were taken from the drying beds and were tested for the heavy metal contents in laboratory, replicas of sewage sludge composite, mixed and a composite sample was crushed, homogenized by a high speed blender, sieved with 2 mm sieve and dried in an oven at 120ºC for five hours.

Different standard solutions for metals including Pb, Cd, Co, Ni and Cu were prepared by using their analytical grade salts. Analysis of the composite sample was done for heavy metal contents using atomic absorption spectrophotometer (ECIL, India, Model AAS 4129). The complete description of heavy metal concentrations in the digested sample of sewage sludge are shown in Table – 4.3.

Table 4.1–Physical Analysis of Fly Ash Samples as per ASTM C 618

Parameter	Value
Specific gravity (OD)	1.705±0.021 g/cc
Specific gravity	1.785 ±0.011g/cc
Density	1.701±0.002g/cc
Percent Absorption	4.712 ±0.054%
Fineness modulus (Fly ash)	7.522±0.23%
pH (Raw fly ash sample)	7.5±0.02
Organic Carbon	0.23±0.01%

Table 4.2–Chemical Composition of Fly Ash as oxides as per ASTMC618

Constituent	wt. (%)
SiO_2	55.78
Al_2O_3	26.22
Fe_2O_3	9.65
CaO	3.25
MgO	1.25
SO_3	0.15
Na_2O	0.39

Table 4.3 –Metal concentration in composite sewage sludge samples by atomic absorption spectrophotometer

S. No	Metals	Mean ±(mg/kg))SE Values
1	Fe	14284±0.025
2	Mn	200 ±0.04
3	Cu	132 ±0.03
4	Zn	1909 ±0.02
5	Cd	2.75 ±0.015
6	Co	ND
7	Ni	35.1 ±0.025

Sewage sludge samples were analyzed for some heavy metals. Iron was present in maximum concentration (14.3g/kg) while Cd was present in the minimum concentration (2.75mg/kg). Fly ash samples were also analysed for the heavy metal contents. Results of the analysis are given in Table 4.4

Table 4.4- Soluble concentration of different metals in fly ash samples

S. No	Parameters	Mean (mg/L)
1	Pb	0.005
2	Cd	0.006
3	Ni	BDL
4	Cu	0.009
5	Zn	0.010
6	Mn	0.0145
7	Fe	BDL
8	Al	0.405

BDL: Below detection limit (Detection limit of AAS for Ni =0.009 mg/L)

Table 4.5 - Physico-chemical properties of in (50% W/V) leachate of sewage sludge sample collected from Okhla sewage treatment plant, New Delhi

S. No	Parameters	Values	Permissible Limit
1.	pH	6.5	5.5-9.0
2.	Temperature (ºC)	25.8	45ºC
3.	Electric conductivity (mS)	31,500	-
4.	Salinity (%)	80	-
5.	Total solids (TS) (mg/L)	80,000	-
6.	Total dissolved solids (TDS) (mg/L)	20,300	2100
7.	Total suspended solids (TSS) (mg/L)	18,000	50
8.	Biochemical oxygen demand (BOD) (mg/L)	2500	350
9.	Organic matter (Raw sewage sludge) (g/L)	40.81	
10.	Chemical oxygen demand (COD) (mg/L)	4500	250
11.	Chlorides (mg/L)	11,500	1000
12.	Turbidity (NTU)	2000	
13.	Sulphate (mg/L)	1500	-
14.	Ammonical-nitrogen (mg/L)	15	50
15.	Organic-nitrogen (mg/L)	200	-
16.	Cu (mg/L)	65.5	3.0
17.	Cd (mg/L)	0.825	1.0
18.	Co (mg/L)	ND	-
19.	Ni (mg/L)	21	3.0
20.	Pb (mg/L)	65.5	1.0
21.	Zn (mg/L)	189.6	15

A number of parameters were optimised before studying the leaching and eco-toxicological characteristics of several FA/SS mixtures. After optimising different parameters leaching characteristics were studied and effectiveness of optimised parameters in terms of leaching from sewage using fly ash as adsorbent were analysed from FA/SS mixtures. The various optimised parameters are listed as follows:

- Optimised absorbent dose
- Optimised acid dose
- Optimised number of washings
- Optimised shaking time
- Optimised pH

4.0.1 Optimum adsorbent dose

Selection of optimum adsorbent dose was done in order to analyse the effect of maximum adsorption capacity of various FA/SS mixture. Fly ash and sewage were mixed in three ratios (1:4, 1:1, 4:1) to identify the most effective ratio as an adsorbent. 5g of FA/SS mixture of each ratio was added in a conical flask of 250mL capacity containing 100mL distilled water (1:20 solid/liquid ratio). Each sample was shaken on a rotatory shaker for one hour duration. The shaker was set at 120rpm. The mixture was vacuum filtered over membrane filter having pore size of 0.45um. The filtrate was analyzed for the heavy metals Pb, Cd, Ni and Cu using atomic absorption spectrophotometer (ECIL, India, Model AAS 4129).

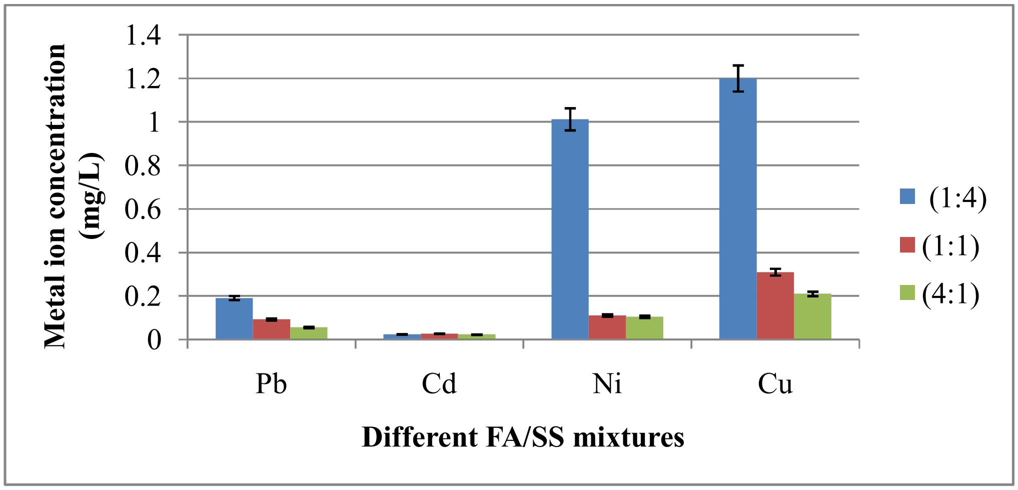

Figure 4.1 - Effect of adsorbent doses on the removal of heavy metals in different FA/SS mixtures in aqueous medium

Several experiments were performed with various fly ash and sewage sludge mixtures (1:1, 4:1 and 1:4).4:1FA/SS mixture was found to be the optimum dose for the minimum leaching of heavy metals into the aqueous medium. It is clear from Figure 4.1 shown above that in the 1:4 FA/SS mixture the leaching of metals was the maximum for copper metal (1.5mg/L), and minimum for the Pb-metal (0.19mg/L).For other metals it was 0.02 mg/L for Cd, 1.01 mg/L for Ni. A decrease in leaching of metals was observed with increase in fly ash content in FA/SS mixture (1:1) which was 0.09 mg/L for Pb, 0.02 mg/L for Cd, 0.11 mg/L for Ni, and 0.31mg/L for Cu, respectively. A decreasing trend in leaching of metal was observed with increased fly ash content in the fly ash-sewage sludge mixture. In the (4:1) FA/SS mixture the decreased leaching of metals was observed in comparison to 1:4 and 1:1 FA/SS mixture. It was 0.05 mg/L for Pb, 0.02 mg/L for Cd, 0.10 mg/L Ni, 0.21 mg/L Cu, respectively. The experimental result reveals that the 4:1 FA/SS mixture is the optimum dose for the minimum leaching of metal ions into the aqueous medium. It was observed by (Lin and Yang, 2002) that the metal retention capacity increased with increase in the mass of fly ash which could be attributed to the increase in the available surface area per unit volume of solution for adsorption. Adsorption at solid–solution interfaces is an important means due to its less cost, the use of fly ash as conventional adsorbents may be an economical way of treating wastewater compared to the use of zeolite products and residues converted from coal fly ash. Furthermore, use of coal fly ash as an adsorbent for heavy metal ions adsorption from wastewater could relieve or eliminate the problems regarding the disposal of huge quantities of coal fly ash generated by thermal power plants every year.

4.0.2 Selection of optimum acid dose

Selection of optimum acid dose was done to achieve the stable pH of FA/SS mixture in the range of 2-3. Different doses of (1 N HN O_3) acid were tested to attain a stable pH in the range of 2-3 to achieve maximum leaching of the heavy metal ions. Out of two doses of acid taken (1.5 mL HNO_3, 2.5mL HNO_3) it was observed that maximum solubilization of the metals was achieved with 2.5 mL (1 N HNO_3) acid dose. So, 2.5 mL acid dose was selected as the optimum dose of acid to achieve a stable pH in the range of 2-3.

Table 4.6 - pH values of supernatant liquid of FA / SS mixtures (5g) of different compositions shaken with 1.5 mL nitric acid (1N) at 120 rpm

Time of Shaking (hours)	pH		
	FA (20%)	FA (50%)	FA (80%)
0	6.6	7.0	7.0
1	5.0	3.4	3.3
2	5.2	4.2	4.0
3	5.3	4.5	4.3
4	5.8	5.5	5.5
24	6.1	6.12	6.0
72	6.1	6.0	6.0

Table 4.7 - pH values of supernatant liquid of FA/ SS mixtures (5g) of different ratios shaken with 2.5 mL nitric acid (1N) at 120 rpm

Time of Shaking (hours)	pH		
	FA (20%)	FA (50%)	FA (80%)
0	3.1	2.7	2.4
1	4.8	4.2	2.8
2	2.7	2.5	2.2
3	5.2	4.7	3.7
4	5.3	4.9	4.0
24	5.4	5.1	4.5
72	5.5	5.3	4.6

4.0.3 Selection of optimum number of washings

Selection of optimum number of washings was carried out to study the release of different metals from several FA/SS mixtures. Various samples of fly ash and sewage sludge mixture were taken in three ratios (1:1, 4:1 and 1:4). The samples were tested for leaching of metal ions at acidic pH conditions followed by different number of washes with distilled water. It was observed that in the 1:4 FA/SS mixture the Pb content was 42 mg/L initially which decreased to 7.9 mg/L and then to 2.6 mg/L in second and third wash, respectively. No further decrease was observed in the fourth wash. So, three washes were considered as the optimum number of washes. A similar decreasing trend was observed for other heavy metal ions Cd, Ni, Cu and Zn.

4.0.4 Selection of optimum time of shaking

Selection of optimum time was done by analyzing the leaching of metal ions with optimised4:1 FA/SS mixture at variant hours of shaking time. The samples of fly ash-sewage sludge mixtures were placed on the rotatory shaker at 120rpm under controlled temperature conditions of 26ºC. It has been observed from the experimental results that the leaching of different metal ion varies with different shaking time condition at the optimised

4:1 FA/SS mixture as shown in Figure 4.2. It was observed that in 30 minutes shaking time the release of metal was 0.3 mg/L for Pb, 0.1 mg/L for Cd, 0.5 mg/L for Ni and 0.9mg/L for Cu-metal which decreased finally to 0.3 mg/L (Pb), 0.1 mg/L (Cd), 0.4 mg/L (Ni), 0.7mg/L (Cu) and no so much change in leaching of metal ions was observed in 60 and 90 minutes shaking time. After shaking time of 120 minutes, as shown in Figure 4.2 it was observed that no metal ion leached from solid (4:1, optimised) FA/SS mixture into the aqueous solution which confirm that all the metals were leached up to 120 minutes. So it is confirmed from the experimental data that complete adsorption of the heavy metal ions leached from sewage sludge takes place at 120 minutes beyond this time there is no further adsorption takes place. So 120 minutes was considered as the optimum shaking time.

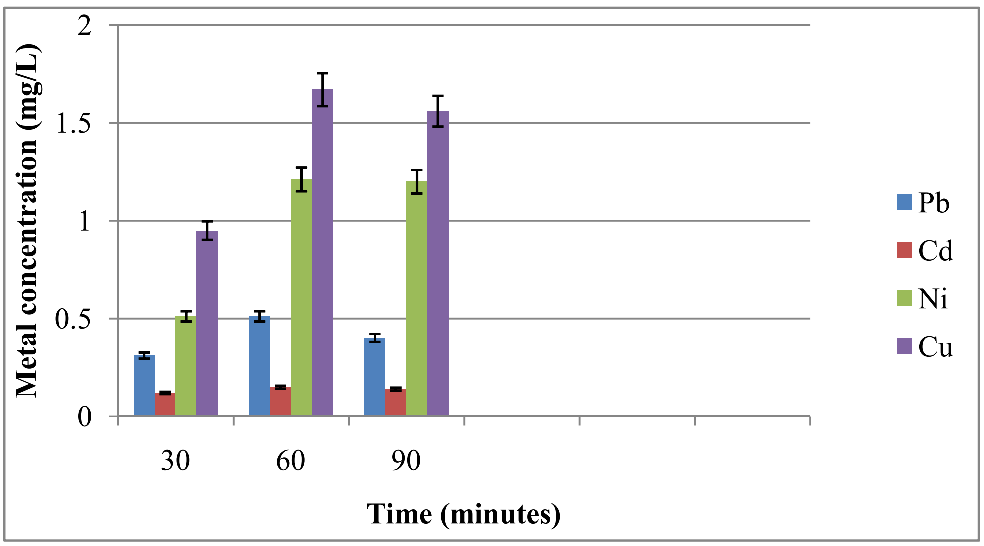

Figure 4.2 - Effect of shaking time on leaching of metals with optimized dose (FA/SS), 4:1and pH 8 conditions in aqueous medium

4.0.5 Selection of optimum pH

Experiments were conducted with optimised (4:1) FA/SS mixture, and the pH was varied from 2-8. It was observed from the experimental results that maximum leaching of heavy metals takes place at the acidic pH conditions. The leaching of heavy metals was maximum for Pb (10.61 mg/L), and minimum for Cu (0.09 mg/L) at pH 2 condition. But with increase in pH above 5 a major decrease in leaching of metal ions was noticed as shown in Figure 3. It was observed that Pb which was 10.61 mg/L at pH 2 decreased to 0.51 mg/L at pH 7 conditions; Ni initially was 5.3 mg/Lat pH 2 which decreased to 1.21 mg/L at pH 7. A similar decreasing trend was observed for cadmium metal into the solution. As it is clear from the Figure 4.3 a different leaching trend for Cu, was observed, the maximum leaching observed was 1.67 mg/L at neutral pH 7 condition. No leaching of heavy metals was observed at pH 8 condition. Hence, pH 8 was considered to be the optimum pH. Since the basic pH conditions with optimised (4:1) FA/SS mixture are helpful in the minimum release of heavy metals in to the environment.

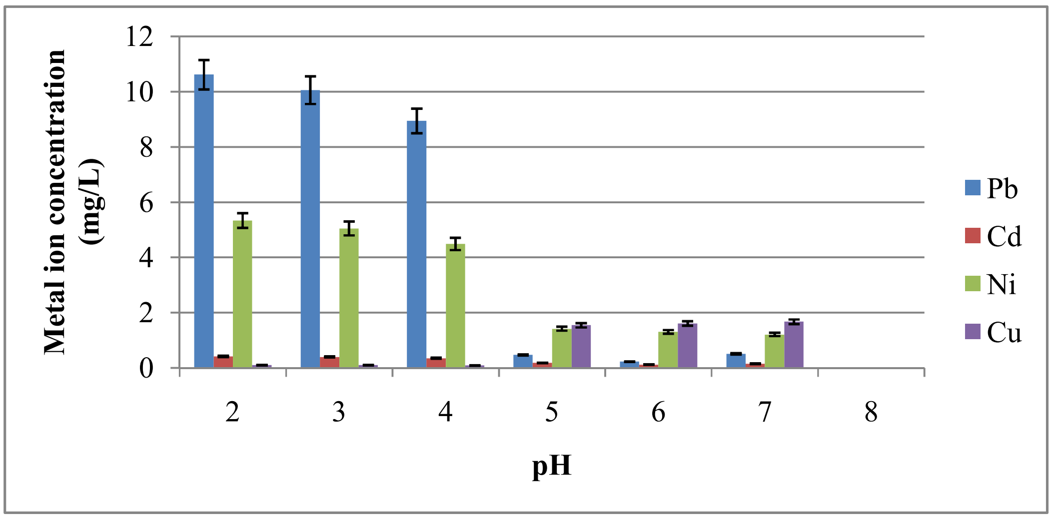

Figure 4.3 - Effect of pH on leaching of metals with optimized (FA/SS) 4:1 mixture in aqueous medium

Not only this, the experimental result revealed that basic pH 8 condition with optimum shaking time of 2 hours and optimised adsorbent dose of 4:1 FA/SS mixture, 100% removal efficiency for the four heavy metals (Pb, Cd, Ni and Cu) was achieved. It has been reported by (Jain and Tyagi, 1993) that more solubilisation of heavy metal ions was observed at the pH values lower than 5.9. On the other hand it has been reported by (Tyagi et al., 1998) that not much difference was observed in final metal solubilisation in working with aerobic sludge at initial pH varying from 3.0 to 7.0.

Leaching of heavy metals

CHAPTER 5

LEACHING OF HEAVY METALS

Leaching of heavy metals was studied for optimised and unoptimised fly ash -sewage sludge mixtures. Three (1:1, 1:4 and 4:1) FA/SS mixtures were taken to study the leaching of various metals (Pb, Cd, Ni and Cu) under varying pH conditions (2-8). Solid water ratio 1:20 was studied assuming this ratio simulates each rain episode. The leachate analysis for different FA/SS mixtures was carried out for various parameters such as electrical conductivity, sulphate, chloride, hardness, chemical oxygen demand, turbidity, nitrate etc. The objective of the study was to analyse the effect of optimised dose (4:1) FA/SS mixture with unoptimised doses (1:1, 1:4) of FA/SS mixtures. Replicates of all the samples were taken for analysis. The heavy metal analysis was carried out using standard method of atomic absorption spectrophotometer(ECIL, India, Model AAS 4129).Precision of results, statistical analysis of the data is carried out in terms of relative standard error, standard deviation and variance.

5.0 Studies on leaching of heavy metals

5.1 Leaching of Pb

Studies were carried out on the leaching of heavy metal ions from fly ash- sewage sludge mixtures at different pH followed by different washings for various heavy metal ions. 5g FA/SS mixture was mixed in 100mL distilled water (1:20 solid to liquid ratio) with 10 hour shaking time at 120rpm under controlled temperature conditions of 26°C. In case of 1:4

FA/SS mixture the maximum leaching at pH 2 for Pb was 42.4mg/L during (leach-1) which finally reduced to 2.6mg/Lin (leach-3). With increase in concentration of fly ash content decreased leaching of metal ions was observed into the aqueous solution. It was observed that with 4:1 FA/SS mixture it was 10.6mg/L during (leach-1), which decreased to 0.6 mg/L in (leach-3) respectively. A similar decreasing trend for Pb was observed for 1:1 FA/SS mixture. The leaching was almost similar for three ratios at pH 3 and 4 conditions. At higher pH condition (pH 5) minimum leaching of metals into aqueous solution was observed. In case of 1:4 FA/SS mixture, with pH 5 the Pb leached was observed as 2.5 mg/L during (leach-1), 2.0mg/L during (leach-2) and 1.4mg/L in the (leach-3) respectively. A more decreased leaching was observed in 1:1 FA/SS mixture which was 0.8mg/L metal (leach-1), which finally reduced to 0.2 mg/L (leach-3) respectively. While in the 4:1 FA/SS mixture least leaching was observed this was 0.5 mg/L (leach-1) and finally reduced to 0.4mg/L (leach-3). The results indicated that in pH above neutral pH conditions, lesser leaching was observed in the 1:4, 1:1 FA/SS mixtures, whereas in the 4:1 FA/SS mixture no leaching was observed at basic pH (8) condition as shown in Figure 5.1 which reveals that complete adsorption for the Pb from the aqueous solution takes place at this pH condition also provides additional binding sites and thus Pb was retained in greater amounts. It was investigated by (Gaber et al., 2011) maximum solubilization of Pb from sewage sludge was observed and hence achieved maximum extraction efficiency (Cr-88%, Cu-82%, Ni-86%, Pb-94%, Zn-89%) at pH value lower than 2 and acid contact with 1hour contact time.

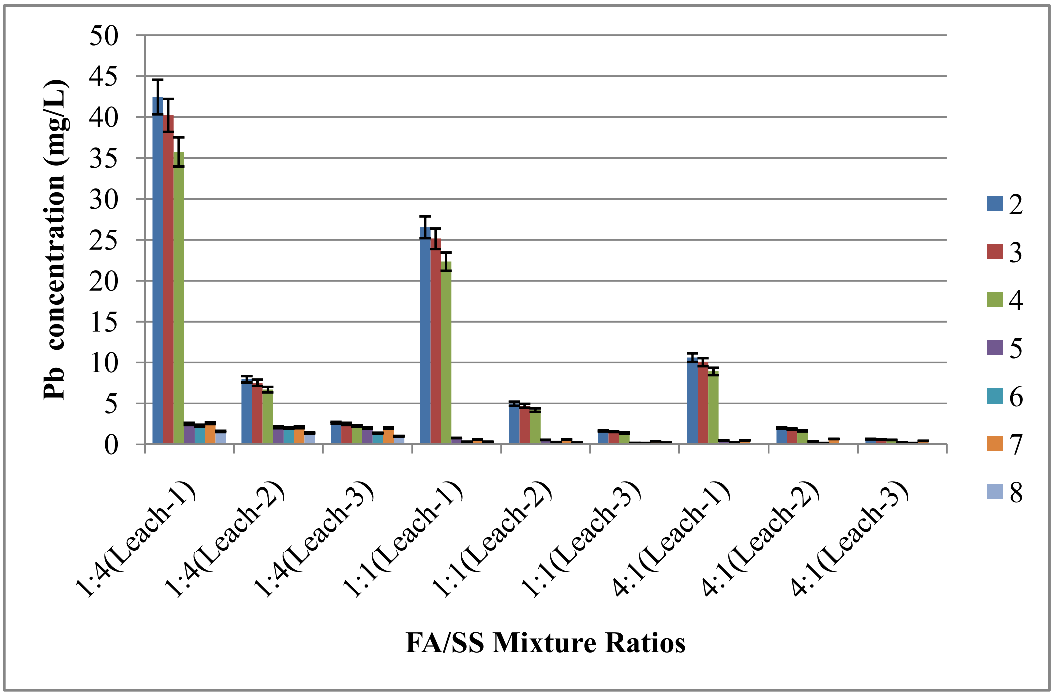

Figure 5.1–Concentration of lead in the leachates at different pH values for the different FA/SS mixtures at different washings after shaking for 10 hours

It has been reported by (Visa and Duta, 2007) that heavy metals removal on fly ash (FA) are pH dependent. (Chaiyasith et al., 2006) reported that the lowest $Cd^{2+,}$ Ni^{2+} and Cu^{2+}adsorption efficiency occurred when fly ash (FA) was treated with HCl 2N; this effect is caused by a positive surface charge leading to repulsions between the surface ($SiOH^{2+}$)and metal ions. Moreover, silica and alumina form alumino-silicates with the pH dependent structures.

5.2 Leaching of Cd

The analysis for leaching of Cd was carried out with different ratios of FA/SS mixtures i.e. (1:4 FA/SS), (1:1 FA/SS), (4:1 FA/SS). It can be seen from the experimental results that maximum leaching of Cd was observed is 1.7 mg/L (leach-1) at pH 2 in the 1:4 FA/SS mixture which was reduced to 0.10 mg/L in (leach-3). In case of 1:1 FA/SS mixture, it was 1.0mg/L in (leach-1) which decreased to 0.2mg/L in (leach-2) and 0.1mg/L in (leach-3) respectively. Whereas in the 4:1 FA/SS mixture it was 0.4mg/L in (leach-1), which decreased to 0.07 mg/L in (leach-2), 0.02 mg/L in (leach-3) respectively. The leaching trend was almost similar for the three ratios of FA/SS mixture i.e. (1:4, 1:1, 4:1) at pH 3 and 4 conditions. At basic pH condition that is at pH 5 lesser leaching of metal ions was observed as shown in (Figure 5.2) in the aqueous solution. At pH 5 condition in the 1:4 FA/SS mixture, with pH 5 the maximum Cd leached is 0.35 mg/L in (leach-1), 0.2mg/L in (leach-2) and 0.2mg/L in (leach-3). A more decreased trend in leaching was observed with 1:1 FA/SS mixture which was 0.2 mg/L, 0.1mg/L, 0.07 mg/L in leach-1, 2 and 3 respectively. While in the 4:1 FA/SS mixture least leaching was observed which 0.18 mg/L was in leach-1 and which finally reduced to 0.13 mg/L in leach-3. It can be seen from the experimental results that lesser leaching was observed at basic pH (8) condition. At pH 8 condition the leaching of Cd in the 1:4 FA/SS mixture was 0.10 mg/L (leach-1) which decreased to 0.9 mg/L in (leach-3), in case of 1:1 FA/SS mixture, it was 0.19 mg/L in (leach-1) and decreased to 0.17 mg/L in (leach-3) whereas in the 4:1 FA/SS mixture no leaching was observed that is complete adsorption took place at this optimised ratio.

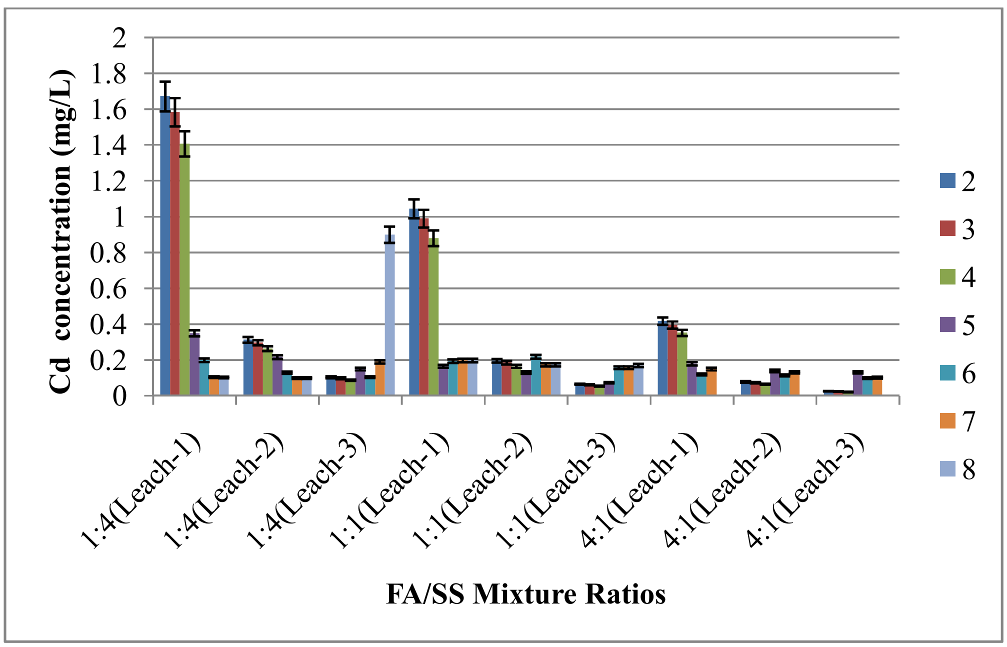

Figure 5.2- Concentration of cadmium in the leachates at different pH values for the different FA/SS mixture at different washings after shaking for 10 hours

5.3 Leaching of Ni

As it can be seen from the experimental results shown in (Figure 5.3). The maximum leaching of Ni was 21.32 mg/L at pH 2 in the 1:4 FA/SS mixture in (leach-1), 3.99 mg/L in (leach-2) and 1.33 mg/L in (leach-3) respectively. In case of 1:1 FA/SS mixture it was 13.32 mg/L, 2.49 mg/L, and 0.83 mg/L, in leach-1, 2 and 3 respectively. Whereas in case of 4:1 FA/SS mixture, it was 5.33 mg/L in (leach-1), which finally reduced to 0.33 mg/L in (leach-3). Almost similar results for leaching of Ni were observed at pH 3 and 4 conditions for various ratios of FA/SS mixtures. Also it can be seen from the experimental results as shown in (Figure 5.3) that with increase in pH lesser leaching of metal was observed. At pH 5 condition, in the 1:4 FA/SS mixture Ni leached is 4.00mg/L, 2.01 mg/L, and 2.19 mg/L in leach-1, 2 and 3 respectively. A similar decreasing trend for leaching was observed with 1:1 FA/SS mixture which was 3.10 mg/L, 3.05 mg/L, and 3.00 mg/L, in the leach-1, 2 and 3 respectively. While in the 4:1 FA/SS mixture least leaching was observed which was 1.41 mg/L was in (leach-1) and finally reduced to 1.20 mg/L in (leach-3). At pH 8 condition in case of 1:4 FA/SS mixture the leaching of Ni was 1.48 mg/L for (leach-1) which decreased to 1.15 mg/L in (leach-3), in the 1:1 FA/SS mixture it was 3.10 mg/L in (leach-1) and further decreased to 1.5 mg/L in (leach-3) whereas in the 4:1 FA/SS mixture no leaching was observed that is complete adsorption took place at this optimised ratio.

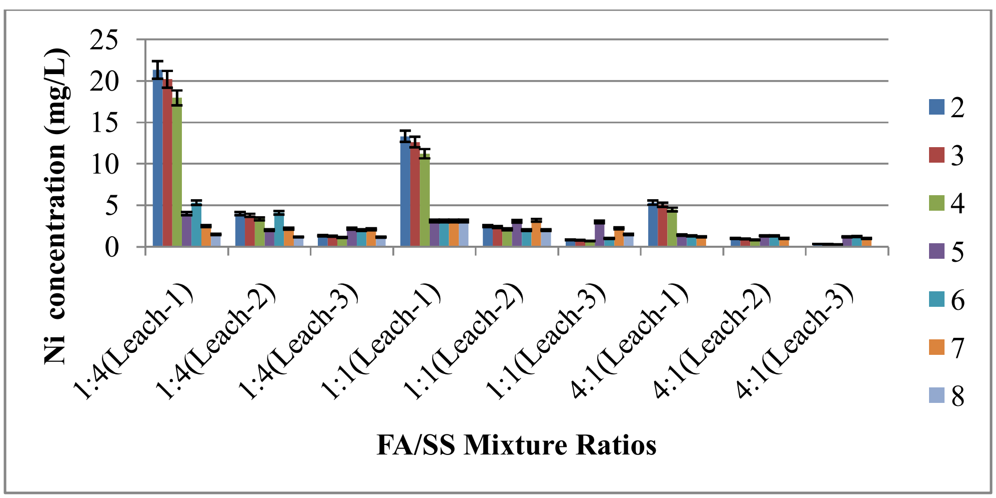

Figure 5.3- Concentration of nickel in the leachates at different pH values for different FA/SS mixture at different washings after shaking for 10 hours

5.4 Leaching of Cu

It has been reported by (Covarrubias *et al.,* 2005) that the exposure of the zeolite surface to water causes the ionization of surface hydroxyl groups (Si OH and Al OH). The degree of ionization depends on pH, and the acid/base reaction occurring at the hydroxyl groups may results in surface charge development. As it can be made clear from the experimental results as shown in (Figure 5.4) that the maximum leaching for Cu in the 1:4 FA/SS mixture at pH 2 conditions was 0.399 mg/L, 0.07 mg/L and 0.02 mg/L in leach-1, 2 and 3 respectively. While in case of 1:1 FA/SS mixture, it was 0.24 mg/L, 0.04 mg/L and 0.01 mg/L in leach-1, 2 and 3 respectively. Whereas in the 4:1 FA/SS mixture it was 0.09 mg/L in (leach-1), which finally reduced to 0.006 mg/L in (leach-3) respectively. Almost similar leaching trend for variant FA/SS mixtures was observed at pH 3 and 4 conditions. Whereas, at pH 5 condition in the 1:4 FA/SS mixture Cu leached is 2.45 mg/L in (leach-1), 2.10 mg/L in (leach-2) and 2.00 mg/L in (leach-3) respectively. A more increased trend for leaching of Cu was observed with 1:1 FA/SS mixture which was 2.89 mg/L, 1.86 mg/L and 1.82 mg/L in leach-1, 2 and 3 respectively. In case of 4:1 FA/SS mixture, leaching 1.54 mg/L was observed in the (leach-1) which further decreased to 1.21 mg/L in the leach-3. Lesser leaching was observed at basic pH (8) condition. In case of 1:4 FA/SS mixture, at pH 8 leaching of Cu in the leach-1(1.40 mg/L) decreased to (1.02 mg/L) in the (leach-3).In the 1:1 FA/SS mixture, it was 1.89 mg/L in the leach-1which decreased to 1.69 mg/L in leach-3 whereas in 4:1 FA/SS mixture no leaching was observed, as complete adsorption took place at this optimised ratio. Solubilisation of the metals depends on pH of the solution.

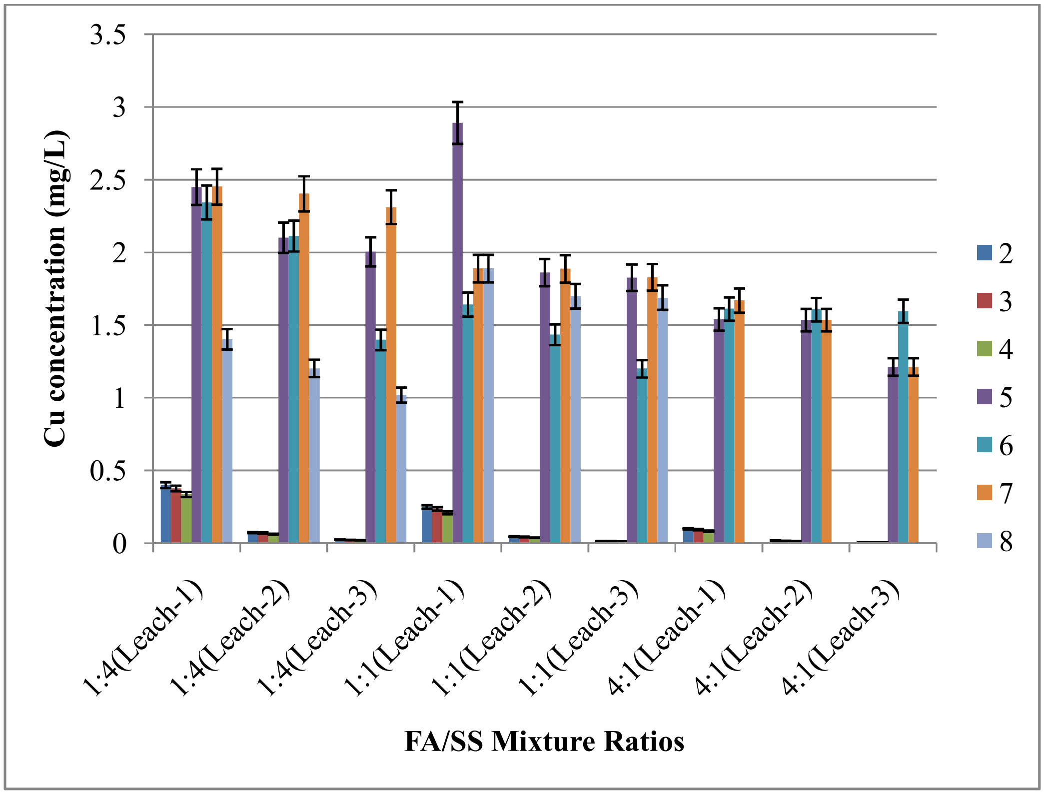

Figure 5.4–Concentration of copper in the leachate at different pH values for different FA/SS mixtures for different washings after shaking for 10 hours

5.5.0 Analysis of Leachate

The analysis of different water quality parameters such as electrical conductivity, sulphate, chloride, total hardness (hardness due to presence of Ca^{2+}, Mg^{2+}, and HCO^{3-}ions present in the water), permanent hardness, COD, TDS, nitrate, ammonical-nitrogen, organic-nitrogen was done for all the three ratios of fly ash and sewage sludge mixtures (1:4, 1:1, 4:1) at three different pH conditions 5, 6 and 7. The effect of different pH conditions was studied by (kharub et al., 2012) on different leachate of various fly ash-sewage sludge mixture. The results shows that (>pH 4) with higher doses of fly ash are more favourable for the lesser leaching and showed better adsorption capacity.

The results with optimised 4:1 FA/SS mixture for different water quality parameters at pH 5 are: Electrical conductivity observed initially was 500mmhos/cm in leachate of FA/SS mixture mixed with distilled water (50%W/V), which decreased to 298mmhos/cm in the leach-3, sulphate contents decreased from 300mg/Lin the leach-1 to 80mg/L in the leach-3, chloride decreased from 100mg/L to 40 and 36mg/L in the leach-2 and 3, respectively. A similar decreasing trend was observed for hardness, turbidity, total dissolved solids, total khjehldal nitrogen and nitrate. After studying results of the leachate analysis it was observed that the values for all the parameters decreased in various leachates. The values achieved were observed within the permissible limits.

5.5.1 Electrical conductivity

It was reported by (Trivedy and Goyal, 1986)that the presence of total soluble mineral salts in water make the water salty and sour in taste and hence makes it unsuitable for drinking purpose. In the present study, the electrical conductivity varies in three ratios of FA/SS mixtures and at various pH conditions. It was observed that at pH 5 condition in 1:4 FA/SS mixture it was 10,000 mmhos/cm (leach-1), it was 4000mmhos/cm in (1:1) and 500mmhos/cm in the 4:1 FA/SS mixture (leach-1)which further decreased to 7500mmhos/cm, 1000 m mhos/cm and 298mmhos/cm in leach-3 of (1:4), (1:1) and (4:1) FA/SS mixture, respectively. A similar decreasing trend was observed for various FA/SS mixtures at pH 5 and 6 conditions shown in Figure 5.5. It can be revealed from the experimental results shown in Figure 5.5 that EC decreased with increase in pH. Also, more electrical conductivity was observed in samples with lower pH conditions and with higher content of sewage sludge whereas lesser electrical conductivity was observed in samples with higher content of fly ash at higher pH 7 condition. Specific conductivity measurements are frequently used in water analysis to obtain a rapid estimate of dissolved solid content of a water sample. The dissolved solid content can be approximated by multiplying the specific conductance by an empirical factor varying from about 0.56 to 0.90 (Eskilstuna et al, 2002).

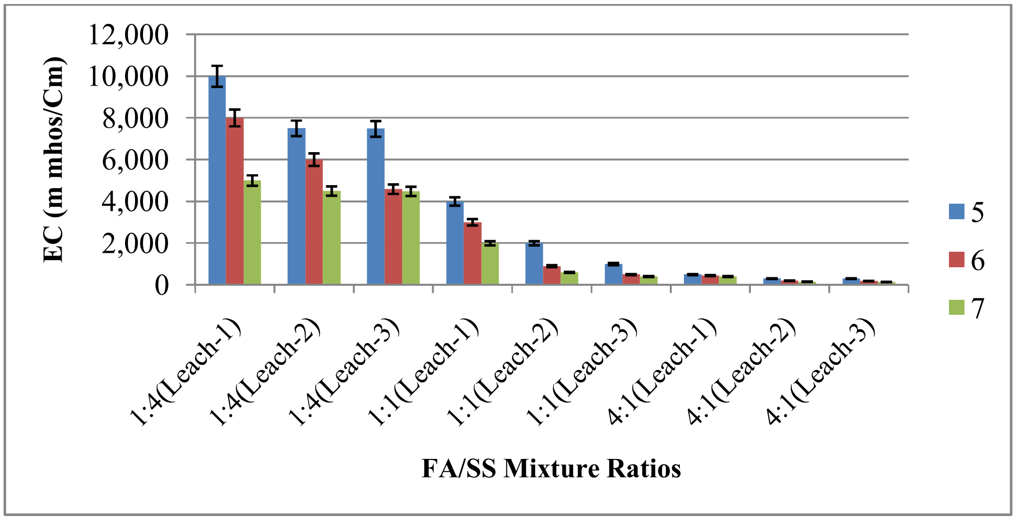

Figure 5.5 – Electrical conductivity of FA/SS leachate at different pH conditions

5.5.2 Sulphate

Sulphates are indirectly responsible for two serious problems when associated with the handling and treatment of wastewaters. These are odour and severe corrosion resulting from the reduction of sulphate to hydrogen sulphide (H_2S) under anaerobic conditions. In sewage sulphides formed initially, ultimately oxidation of sulfides to form sulphate, which is a stable product. In the present study, the sulphate varies with several ratios of 1:4, 1:1 and 4:1 FA/SS mixtures under various pH conditions. The estimated sulphate content in FA/SS mixtures at pH 5 ranged from 1020-790 (mg/L), 700-463(mg/L), 300-80 (mg/L) in different leachate as shown in Figure 5.6. Higher amount of sulphate was observed in FA/SS mixture (1:4), which was due to the presence of more content of sewage sludge which is the source of sulphate. At low pH, sulphur is present as sulphides of Ca, Mg, K, NH_4, metal sulphides-first these compounds are oxidised as sulphate which unlike sulphides are soluble and a rise in sulphate see. A similar decreasing trend was observed for the different FA/SS ratios with increased pH and fly ash contents. More sulphate content was observed in samples at lower pH conditions, and with higher content of sewage sludge whereas lesser sulphate was found in samples with lesser content of sewage sludge and at higher pH conditions which confirms that sewage sludge is the source of sulphate. Sulphate is a naturally occurring ion in almost all kinds of water bodies and is a major contributor to total hardness. Sulphate content more than 200mg/L is not good for domestic purposes; beyond this limit, sulphate causes gastro-intestinal irritation.

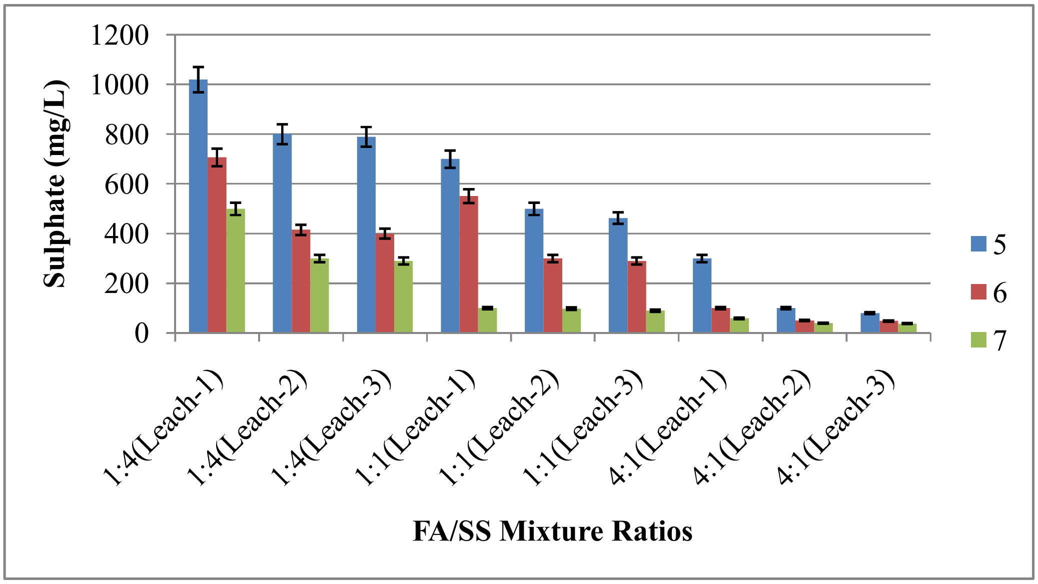

Figure 5.6 – Sulphate content in different FA/SS mixture leachate at different pH conditions

5.5.3 Chloride

It was investigated by a number of researchers that the presence of chloride in drinking water sources can be accredited to the suspension of salt deposits (National Academy of Sciences, 1977), effluents from chemical industries (Little, 1971), oil well operations (Pettyjohn, 1971), sewage (Pettyjohn, 1972), irrigation drainage (Bond and Straub, 1973), refuse leachate (Schneider, 1970), sea spray and seawater intrusion in coastal areas (NRCC, 1977). Presence of these suspensions of salt deposits in water may lead to contamination of both surface and groundwater. It has been reported that chloride ion is highly movable and is finally transported into closed basins or to the oceans (NRCC, 1977). It is present extensively in nature in the form of salts of sodium chloride (NaCl), potassium chloride

(KCl) and calcium chloride ($CaCl_2$). Also leaching of chlorides from different rocks in soil and water takes place through the process of weathering. It was also reported by (Gray, 1994) that the chloride ions are mobile in nature and hence can easily be transported to basins and oceans.

In case of 1:4 FA/SS mixture at pH 5 condition, the chloride content of 244 (mg/L) in (leach-1), decreased to 90 (mg/L) in the leach-3, while in the 1:1 FA/SS mixture it was 180 (mg/L) in the leach-1 which reduced to 102 mg/L in the leach-3. In the 4:1 FA/SS mixture it was 100 (mg/L) in the leach-1 and finally reduced to, 36 mg/L in the leach-3. A similar decreasing trend with increased pH condition was observed for different FA/SS mixture as shown in Figure 5.7. Chlorides are generally present in municipal sewage and are derived from the kitchen wastes, human faeces and urinary discharge etc., thus increasing the concentration in the sludge. Higher amount of chloride content was found in 1:4 FA/SS mixture may be due to one of the above reasons. It was observed from the experimental data that lesser sulphate was observed in the samples with increased pH conditions. More sulphate was observed in samples with higher dose of sewage sludge, and at lower pH conditions while samples with higher content of fly ash showed lesser sulphate contents at higher pH conditions. A high concentration of chloride was observed at low pH due to the greater solubilisation of organic waste.

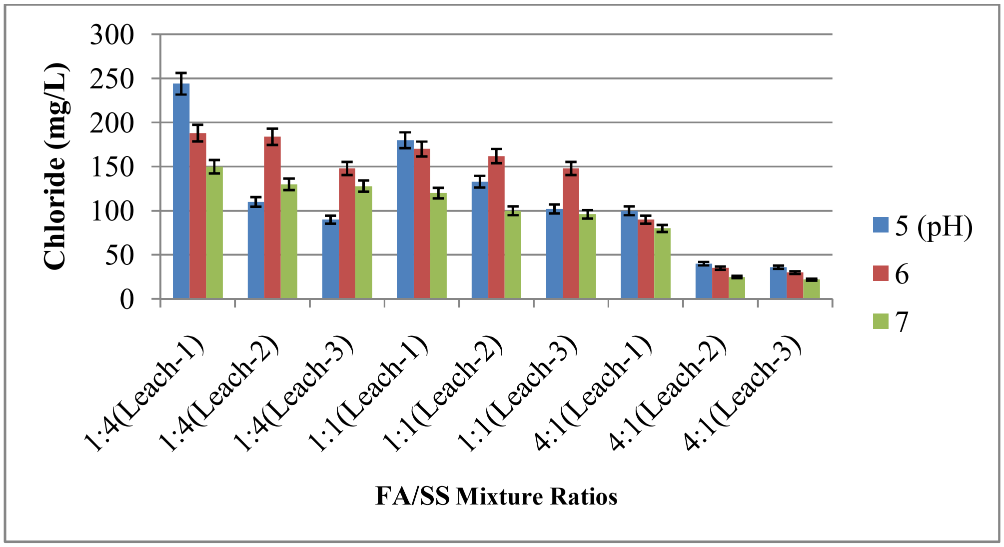

Figure 5.7 – Chloride content in different FA/SS mixture leachate at different pH conditions

5.5.4 Hardness

Hardness of water is caused by presence of multivalent metallic cations which are due to Ca, Mg and associated CO_3 and HCO_3. It has been reported by (Hujare, 2008) that total hardness value was high during summer than in monsoon. High values of hardness during summer can be due to decrease in water volume and increase in rate of evaporation of water. In the present study, the total hardness fluctuates with different ratios of FA/SS mixtures under different pH conditions as shown in Figure 5.8. Its maximum value was observed at pH 5 condition. In the 1:4 FA/SS mixture it was 316 mg/L while in the 1:1 it was 200 mg/L and 90 mg/L in the 4:1 FA/SS mixture after the leach-1 which further decreased to 276 mg/L, 110 mg/L and 83 mg/L in the leach-3 of 1:4, 1:1 and 4:1 FA/SS mixtures, respectively.

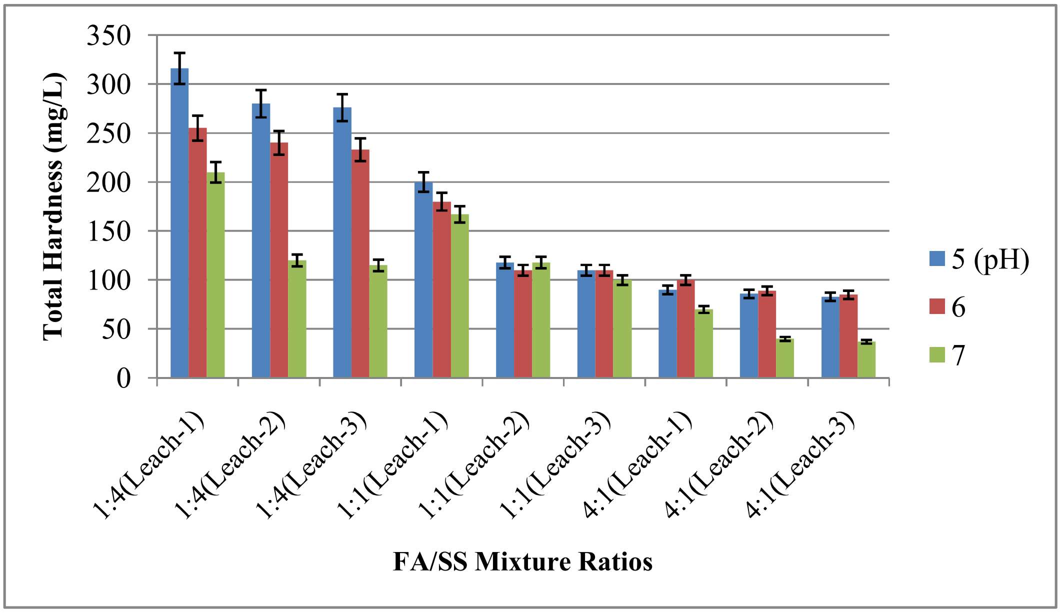

Figure 5.8 – Total hardness in different FA/SS mixture leachate at different pH conditions

Hardness is mainly due to the presence of HCO_3^-, CO_3^{2-}, and Cl^- of Ca^{2+} and Mg^{2+} in water. A higher incidence rate of gallbladder disease, urinary stones, arthritis and arthropathies has been reported in areas supplied with drinking water harder than 500 mg/L of $CaCO_3$ if leachate mixed with ground water. Depending on the interaction with other factors, such as pH and alkalinity, water with hardness above 200 mg/L may cause scale deposition in the distribution systems. On the other hand, soft water with hardness less than 100 mg/L has a greater tendency to cause corrosion of pipes as a result of the presence of heavy metals, such as Pb, Zn, Cu and Cd in drinking water. A similar decreasing trend was observed for different ratios with increasing fly ash content in the mixtures.

5.5.5 Chemical oxygen demand (COD)

It has been reported by (Deb et al., 1996) that in batch tests 19% to 56% of COD removal was achieved with the help of unseived fly ash having 6% carbon in 24 hours time-period from secondary effluent. The experimental result shows that COD removal efficiency depends on the dose of fly ash content supplied. It was observed that the COD removal increased with increased dose of fly ash. He also found that the removal of COD is logarithmically related to three parameters

1) Time of mixing, 2) initial COD and 3) concentration of fly ash. The investigations by (Eye and Basu,1970) showed that fly ash was capable of reducing COD of a secondary effluent by about 30 percent at a fly ash concentration of about 1600 mg/L when the initial COD was around 60 mg/L and removal of sewage sludge containing fly ash by coagulation with lime was very efficient**.**

It was observed from the experimental results that in various ratios of fly ash- sewage sludge mixtures, maximum COD were observed in samples with higher content of sewage sludge. It was 980 (mg/L) in leach-1 with 1:4 FA/SS mixture which reduced to 770 (mg/L), 760 (mg/L) in leach-2 and 3, respectively. The COD goes on decreasing with decrease in organic matter content that is, it was 400 mg/L in (1:1), 200 mg/L in (4:1) during leach-1 which reduced to 398 mg/L and 140 mg/L with subsequent washings in 1:1 and 4:1 FA/SS mixture, respectively at pH 5 conditions. But a decrease in COD was observed with increase in pH conditions of 6 and 7 and showed similar decreasing trend with decreased sewage sludge in different ratios of FA/SS mixture. So, the chemical oxygen demand (COD) of all water samples is considerably high and it confirmed the presence of organic pollutants in the underground water. It clearly indicated that sewage water released from the treatment plant containing high organic load interfered with the underground water through percolation or through direct contact.

The lesser decrease of COD at pH 6 and 7 may be due to dissolution/precipitaton of some of the materials. At lower pH conditions the dissolution rate increases and hence more release of pollutants take place. In case of 1:4 FA/SS mixture the organic waste released by sewage sludge was more due to high amount of sewage sludge and comparatively lesser was observed in 1:1 and 4:1 FA/SS mixture due to less content of sewage sludge and higher content of fly ash. In case of 1:1 FA/SS mixture the maximum COD observed was approximately 500 mg/L which reduced to 200 mg/L in the 4:1 FA/SS mixture at pH 5.0 conditions. The solids present in FA/SS mixture are not very high. Fly ash contains fewer solids in aqueous form whereas in sewage it was normally 500-1000mg/L of total solids. The suspended solids are those which remain undissolved in sample just as salt. It can be seen in Figure 5.9 that a similar declining trend was observed at pH 6 and 7 conditions in various FA/SS mixtures followed by subsequent washings.

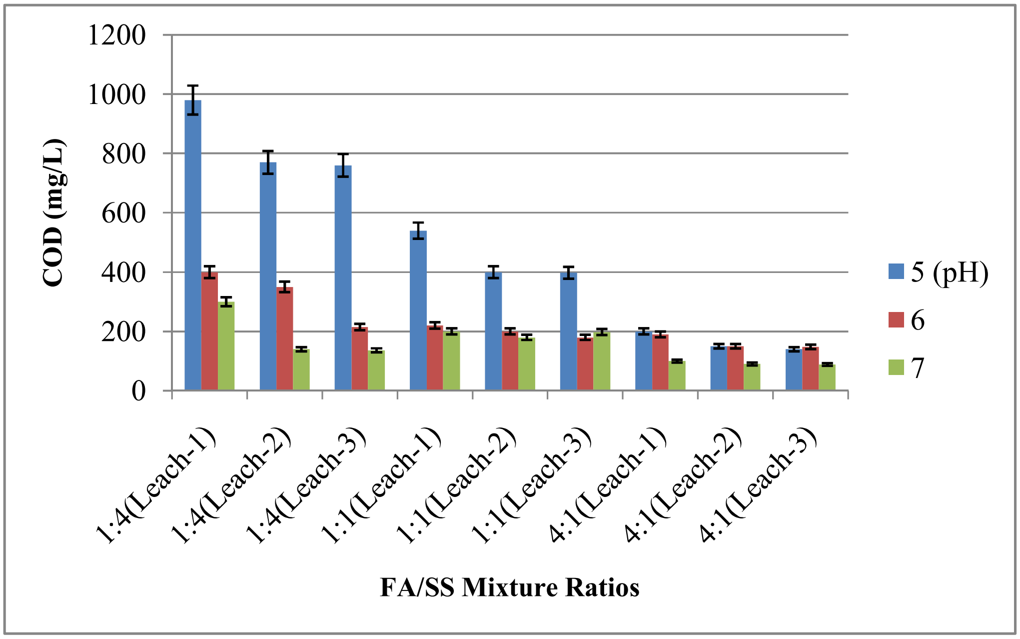

Figure 5.9 –Chemical Oxygen demand in different FA/SS mixture leachate at different pH conditions

5.5.6 Total dissolved solids (TDS)

The TDS indicates the inorganic pollution load of the water sample. It is clear from the experimental results (Figure 5.11) that the maximum concentration of total dissolved solids was observed in the 1:4 FA/SS mixture (2000 mg/L) during the leach-1 which decreased to 1590 mg/L in the leach-3.It ranged from 1400 to 690 mg/Lin the 1:1 FA/SS mixture and 800 to 380 mg/L in the 4:1 FA/SS mixture with subsequent washings at pH 5 condition. The solids further comprise of organic and inorganic minerals and salts. Organic salts consist of carbohydrates, fats and nitrogenous compounds. The higher amount of TDS

(2000 mg/L) was observed in the 1:4 FA/SS mixture which was due to the presence of both organic and inorganic solids which are present as supplementary amount in sewage sludge. The experimental data as shown in Figure 5.10 reveals the variation in total dissolved solids values with increased pH. It was observed that at neutral pH condition the TDS in the 1:4, 4:1 FA/SS mixture reduced from 1700 to 1270 mg/L and 550 to 260 (mg/L) in leachate with different washings.

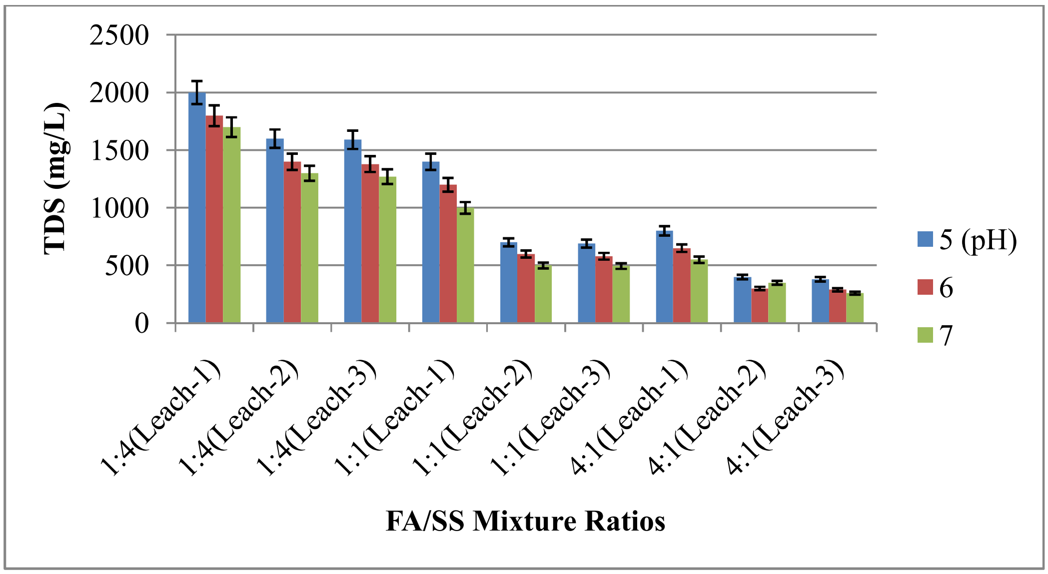

Figure 5.10- Total dissolved solids (TDS) in different FA/SS mixture leachate at different pH conditions FA/SS mixture

5.5.7 Turbidity

Sewage sludge normally becomes turbid if dissolved in water due to the presence of fecal matter, degraded pieces of paper, greases, vegetable debris, fruit skin etc. whereas fly ash after settling is less turbid as compared to sewage sludge (NPCS Board of Consultants & Engineers). Turbidity varied in the different samples of FA/SS mixtures, as shown in Figure 5.11. It was noticed that among the samples with 80% sewage sludge content i.e., in the 1:4 FA/SS mixture the turbidity of 1500 NTU during first wash reduced to 1000 NTU in third wash. Lower values were observed at neutral pH 7 condition which was 1200 NTU during first wash which further reduced to 850 NTU in the third wash. Low pH helps to destroy some materials which increase the solubility and thereby increasing the turbidity. Whereas, in case of 1:1 FA/SS mixture, initially a lesser turbidity was observed in comparison to 1:4 FA/SS mixture. Initially, it was 800 NTU, 700 NTU, 600 NTU at pH 5, 6 and 7 conditions which further reduced to 550 NTU, 450 NTU, 350 NTU in different leachate with subsequent washings. A least, turbidity was observed in the 4:1FA/SS mixture, that is, in samples with more fly ash content, initially it was 200 NTU, 100 NTU, 90 NTU which decreased to 100 NTU, 60 NTU and 50 NTU followed by subsequent different washings in different leachate. It is clear from the experimental results (Figure 5.11) that maximum turbidity was present in samples with higher doses of sewage sludge; the turbidity level reduced with decreased sewage sludge content and increased fly ash content. The larger turbidity might be due to the presence of human excreta, waste materials, suspended particulate matter and other dissolved salts in the sewage sludge.

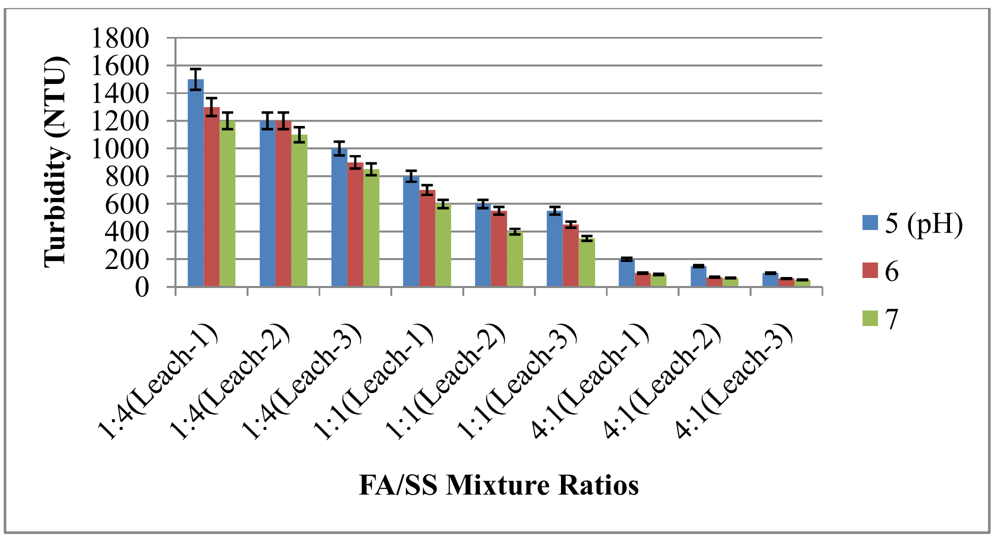

Figure 5.11 - Turbidity of different FA/SS mixture leachate at different pH conditions

5.5.8 Nitrate

It was observed from the experimental results as shown in Figure 5.12 that the maximum nitrate content (500 mg/L) in the 1:4 FA/SS mixture reduced to (300 mg/L) in the 1:1

FA/SS mixture, 40 mg/L in the 4:1 FA/SS mixture which finally reduced to298 mg/L, 90 mg/L, 28.3 mg/L, respectively in the 1:4, 1:1 and 4:1 FA/SS mixture in different leachate at pH 5 condition. A similar decreasing trend was observed at the pH 6 and 7 conditions. It was reported by (Lundberg et al., 2008) that nitrate plays important role in the host protection mechanism. Nitrogen radicals are also effective against tumour cells (Ying and Hofesth, 2007). All nitrogen species, lead to increased concentrations of nitrate in the plasma (Schopfer et al., 2003; Lundberg et al., 2004, 2008; Cui et al., 2006). It has been reported by a number of researchers that the leaching of highly contaminated wastewater loaded with organic and inorganic pollutants into the ground for a longer period of time affects both the underground water quality and the water table.

Nitrate is a naturally occurring compound and is one of the important components of vegetables. It is reported by (Lundberg et al., 2008; Camargo and Alonso, 2006) that nitrate is formed from the dead decaying plants and animals into the environment. It was also investigated by (Lundberg et al., 2004, 2008) that nitrate bio-transformation is complex in nature. The presence of nitrogen in sewage sludge indicates the presence of organic matter. The maximum concentration of nitrate in the 1:4 FA/SS ratio is due to the availability of high concentration of sewage sludge in the sample as the transformation of ammonical nitrogen to nitrite and nitrite to nitrate is the phenomena taking place. So, the nitrate content is higher, if sewage sludge is not used anaerobically. Hence nitrate is high in 1:4 FA/SS mixture. Whereas, in the 4:1 FA/SS mixture the concentration of nitrate is the minimum. Fly ash is not having high amount of nitrogen. So, the overall the concentration of nitrate is lesser as compared to 1:1 and 1:4 FA/SS mixture.

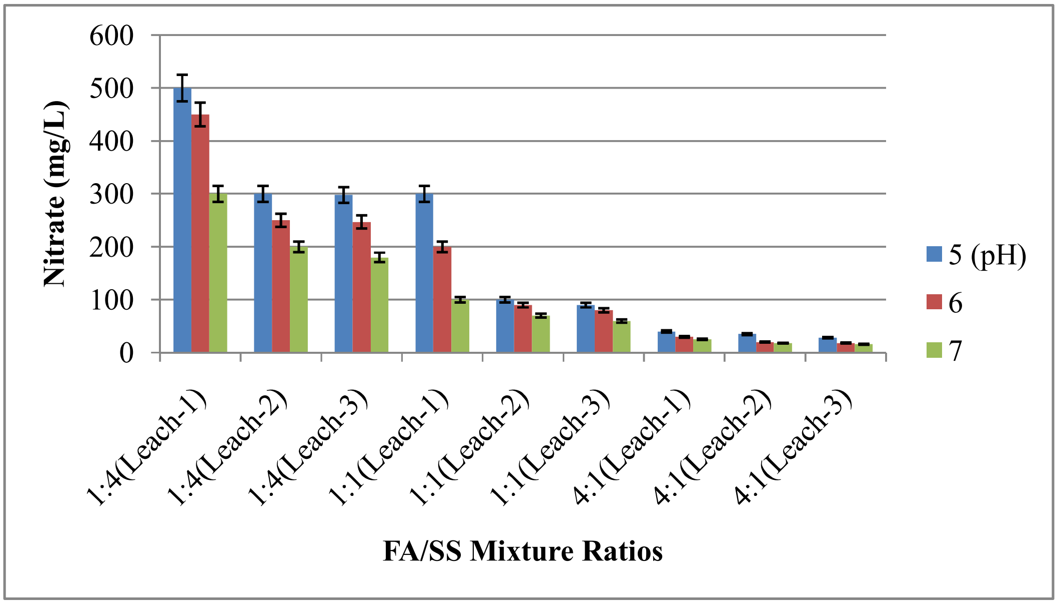

Figure 5.12 - Nitrate in different FA/SS mixture leachate at different pH conditions

5.5.9 Total Kjeldahl Nitrogen (NH_3N + Organic N)

It was observed from the experimental results that maximum ammonical-nitrogen content was present (25 mg/L) in the 1:4FA/SS mixture, 10 mg/L in the 1:1 FA/SS mixture, 2 mg/L in the 4:1 FA/SS mixture which further decreased in different leachate to 13 mg/L, 4.8 mg/L, 1.2 mg/L at pH 5 condition. While at neutral pH conditions, a lesser amount of ammonical-nitrogen was observed. Initially, it was 16 mg/L in the 1:4 FA/SS mixture, 4 mg/L in the 1:1 FA/SS mixture and 0.5 mg/L in the 4:1FA/SS mixture, respectively. The concentration further reduced to 8 mg/L, 0.98 mg/L and 0.001 mg/L with subsequent washings in different leachate. The values of ammonical-nitrogen showed that sample was collected after complete decomposition as the transformation of total kjeldhal nitrogen into nitrate has taken place as shown in Figure 5.13. Ammonia exists in equilibrium with the aqueous form. Further oxidation occurs as follows:

$NH_3 + H_2O \Leftrightarrow NH_4^+ + OH^-$

$NH_4^+ + 2O_2^- \rightarrow NO_3^- + 2H^+ + H_2O$

During the oxidation process ammonia in the presence of oxygen converts to nitrate. So in the sludge nitrate remains in higher concentration than the ammonia as shown in Figures 5.13 and 5.14.

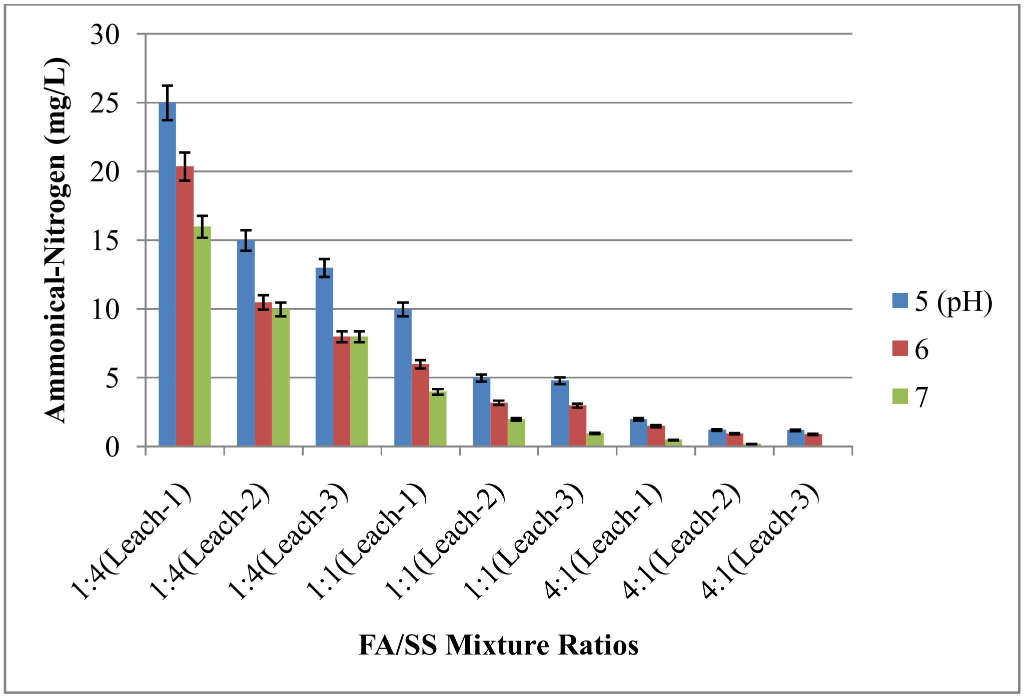

Figure 5.13– Ammonical- nitrogen in different FA/SS mixture leachate at different pH conditions

A higher concentration of ammonical nitrogen was observed as shown in Figure 5.14. At pH 5 conditions the maximum organic-nitrogen observed was 180 mg/L in case of 1:4 FA/SS mixture during leach-1 which reduced to 168 mg/L, while in the 1:1 FA/SS mixture where 50% of sewage sludge is present, it was observed as 40 mg/L which further reduced to 20 mg/L in various leachate obtained with different washings. In the 4:1 FA/SS mixture initially it was 17 mg/L and then reduced to 8 mg/L in various leachate obtained with different washings with water. A similar decreasing trend was observed at pH 6 and 7 conditions. The experimental results show that in samples with higher percentage of sewage sludge with fly ash, there is more organic-nitrogen in the samples. It was observed that at the lower pH conditions due to more dissolution of organic matter and more organic-nitrogen was observed in the samples (Figure 5.14). Also the experimental data, reveals that where more content of fly ash was present there is lesser concentration of all the water quality parameters were observed which confirms that fly ash is able to decrease different impurities from the waste water and can also prove as beneficial adsorbent for the lesser leaching of both metals ions and different water quality parameters to make the water acceptable for further use different agricultural and industrial purposes.

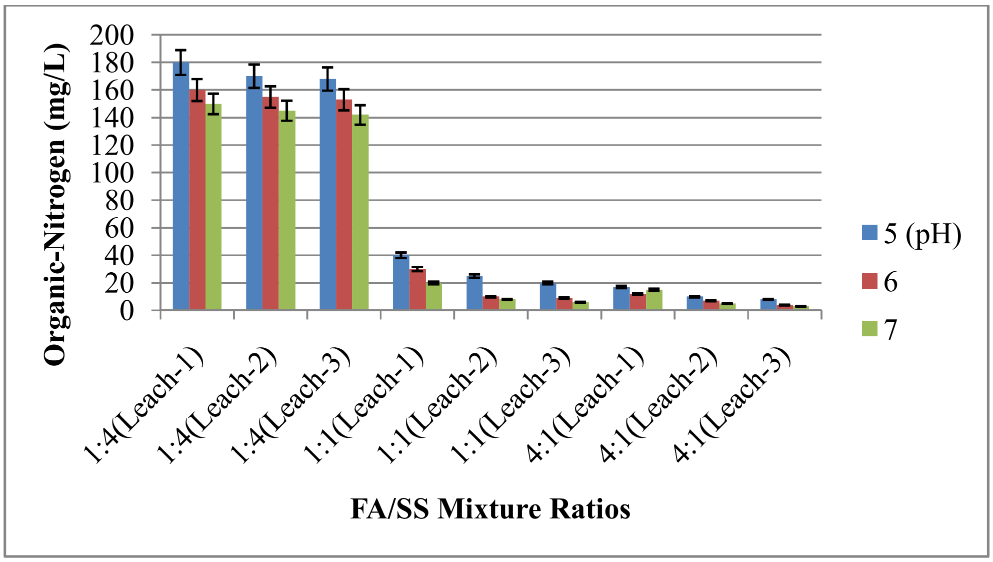

Figure 5.14 –Organic- nitrogen in different FA/SS mixture leachate at different pH conditions

Use of Synthetic metal solutions for leachability test

CHAPTER 6

USE OF SYNTHETIC METAL SOLUTIONS FOR LEACHABILITY TEST

Synthetic solutions of different metals were prepared to study the effect of optimised FA/SS 4:1 mixture. Solid to liquid ratio taken was (1:20).Four concentrations of synthetic metal solutions 5mg/L, 10mg/L, 15mg/L and 20 mg/L prepared from analytical grade salts. Shaking time varied 0-3 hours at 120 rpm on shaker under controlled temperature conditions of 26±1ºC.Leaching of metals from sewage sludge was studied at varying pH conditions (2-8) in several FA/SS mixtures to study the effect of pH on the leaching of metals from sewage sludge. Replicates of all the samples were taken and the heavy metal content in the leachate was tested with the help of atomic absorption spectrophotometer (ECIL, India, Model AAS 4129).The precision of results were carried out in terms of mean, standard deviation and standard error values. A comparison of the results was made with the optimised FA/SS (4:1) mixture. Leachability tests were performed with optimised fly ash-sewage sludge mixture using various synthetic metal solutions.

6.0 Leachability test of optimised FA/SS mixture using synthetic samples of metal salts

6.1 Lead concentration after uptake by optimised dose

Leaching of heavy metals from sewage sludge was tested at different pH conditions. Besides this, leaching characteristics of the sewage sludge were tested using synthetically prepared metal solutions. Lead and cadmium were selected for the leachability test and the leaching was tested with optimised dose of (4:1) FA/SS mixture. Four different concentrations 5mg/L, 10mg/L, 15 mg/L and 20 mg/L were selected for both the metal solutions with different hours of shaking time ranging from 0-3 hours. The experimental results revealed that optimised dose of FA/SS (4:1) mixture showed better removal efficiency of Pb and Cd metals while the FA/SS mixture sewage sludge showed increased leaching on shaking time of 10 hours and after that it became constant. The metal removal efficiency can be put in the following order:

Metal removal efficiency with optimised dose of FA/SS (4:1) mixture

Cd(5 mg/L) 100% > Cd(10 mg/L) 84% > 41.3% Cd(15 mg/L) > 37.5% Cd(20 mg/L)

Pb(5 mg/L) 100% >Pb(10 mg/L) 77% > 72% Pb(15 mg/L) > 50% Pb(20 mg/L)

Two synthetically prepared metal salt solutions of lead and cadmium were taken in different concentrations for the leachability test. The time of shaking was varied using the optimised dose FA/SS (4:1) mixture. The four different synthetically prepared metal ion concentrations 5 mg/L, 10 mg/L, 15 mg/L and 20 mg/L were chosen for the study in different sets. The experimental results (Figure 6.1) confirm that the metal concentration, after shaking it for one hour, reduced in a specific pattern. The metal which was initially 5 mg/L reduced to 1.8 mg/L, 10 mg/L to 5.5 mg/L, 15 mg/L to 7.5 mg/L, 20 mg/L to 13.7 mg/L, respectively. It was observed that after shaking the FA/SS (4:1) mixture with metal salt solution of 5 mg/L for two hours resulted in the removal of whole of the metal content in the synthetic sample. Whereas out of 10 mg/L metal solution the concentration reduced to 2.3 mg/L, 15 mg/L to 4.2 mg/L and 20 mg/L to 10 mg/L respectively. Similar results were observed after shaking for three hours time period.

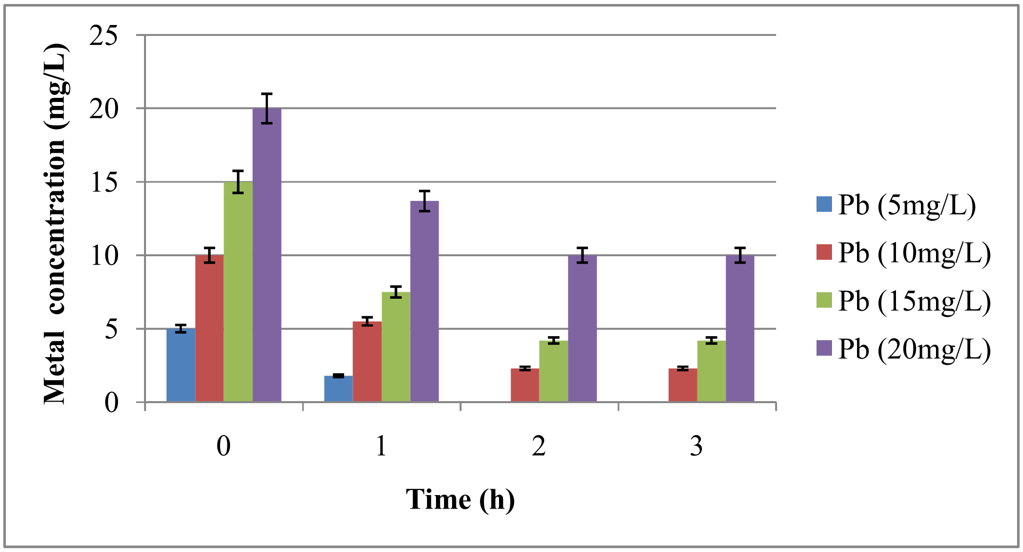

Figure 6.1 - Metal concentration after uptake by optimised fly ash-sewage sludge mixture (4:1) at different shaking times

6.2 Cd-concentration after uptake by optimised dose

Different concentrations of 5, 10, 15 and 20 mg/L of cadmium metal ion were chosen for the study. The experimental results (Figure 6.2) confirm that the metal concentration, after shaking for one hour, reduced in a pattern similar to that of lead metal. The different metal concentrations similar to that of lead metal reduced as follows: 5 mg/L reduced to 0.8 mg/L, 10 mg/L to 2.5 mg/L, 15 mg/L to 11.5 mg/L, 20 mg/L to 14.5 mg/L respectively. The metal concentration was then checked after shaking for two hours also and it was observed that in 5 mg/L concentration no metal was present in the aqueous solution which confirmed that all the metal was taken up by the optimised FA/SS (4:1) ratio, whereas out of 10 mg/L, concentration reduced to 1.6 mg/L, 15 mg/L to 8.8 mg/L and 20 mg/L to 12.5 mg/L, respectively. Similar trends were observed after shaking for three hours time period.

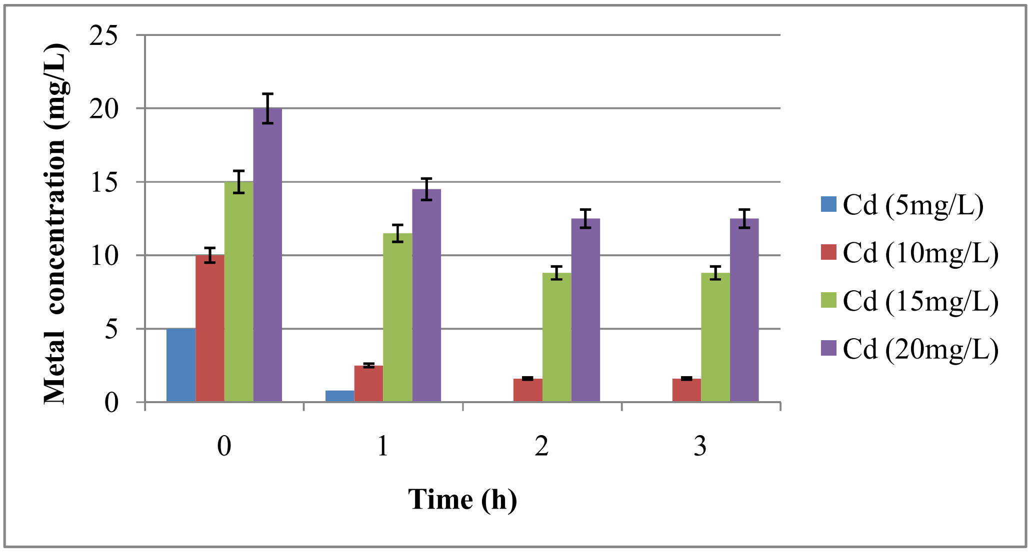

Figure 6.2 - Metal concentration after uptake by optimised fly ash-sewage sludge mixture (4:1) at different shaking times

It was observed from the experimental results (Figure 6.3) that 100 % removal was observed in 5 mg/L metal ion concentration, 77 % in 10 mg/L, 72 % in 15 mg/L and 50 % in 20 mg/L.

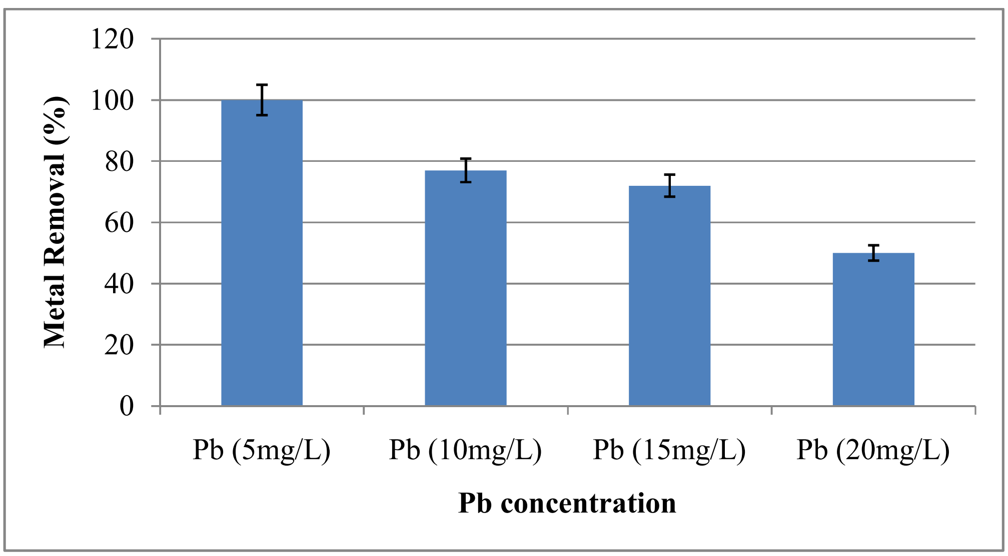

Figure 6.3 – Lead removal efficiency by optimised Fly ash/Sewage sludge ratio (4:1) for different metal concentrations

So it is clear from the results that the optimised FA/SS mixture (4:1) is the best dose for the maximum adsorption capacity for the metal solution and to reduce the leaching further into the aqueous media. Similarly, it was observed that for the cadmium metal ion, the results show (Figure 6.4) that 100% removal was achieved for 5 mg/L, 84% for 10 mg/L, 41.3 %, 37.5% for 15 and 20 mg/L, respectively at the optimised (4:1) FA/SS ratio.

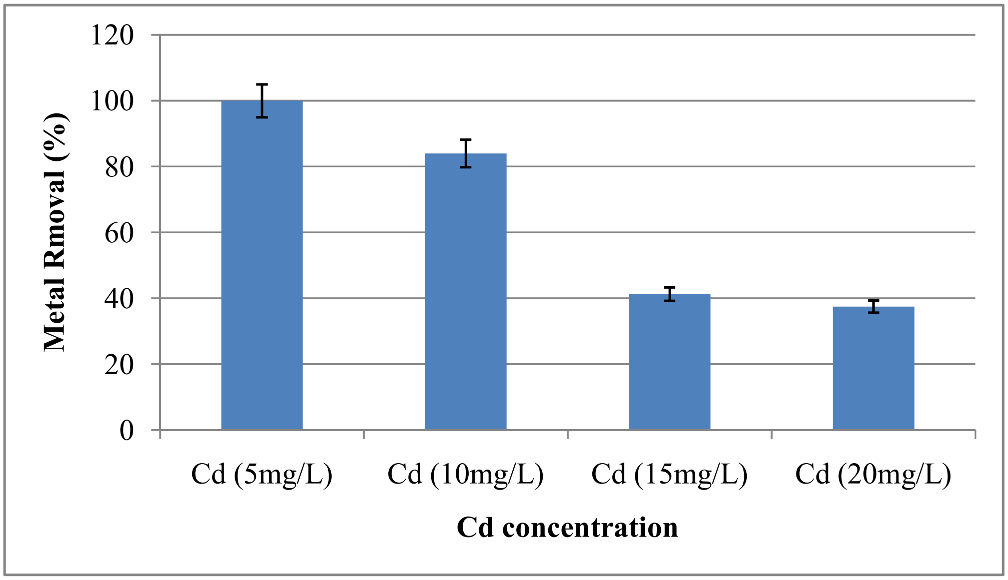

Figure 6.4 –Cadmium metal removal efficiency by optimised Fly ash/Sewage sludge ratio (4:1) for different metal concentrations

After studying the results obtained with optimised 4:1 FA/SS mixture a comparison was done for the leachability test with four different concentrations of FA/SS mixture at different hours of shaking from (0-12 hours). It was observed from the experimental data Figure 6.5 that leaching was 0.6% for 5 mg/L concentration after 2 hours shaking which increased to 3 % after 10 hours of shaking and then became constant as no further increase was observed. It was 0% for 10 mg/L at 0 hour of shaking but increased to 1.3% up to 10 hours shaking time. For 15 mg/L, the leaching increased from zero at 1.2 mg/L and for 20 mg/L, it increased to 0.8%. A similar increasing trend in leaching up to 10 hours shaking time was observed for Pb with different concentrations Figure 6.6.

Leaching from sewage sludge at pH 8 conditions

The trend in leaching of different concentrations of lead using the optimised FA/SS ratio (4:1) with optimised shaking time of hours is shown below:

Pb(20 mg/L) 22 mg/L>Pb(15 mg/L) 16 mg/L>Pb(10 mg/L) 12 mg/L>Pb(5 mg/L) 7 mg/L

Cd(20 mg/L) 20 mg/L> Cd(15 mg/L) 15 mg/L> Cd(10 mg/L) 10 mg/L> Cd(5 mg/L)5 mg/L

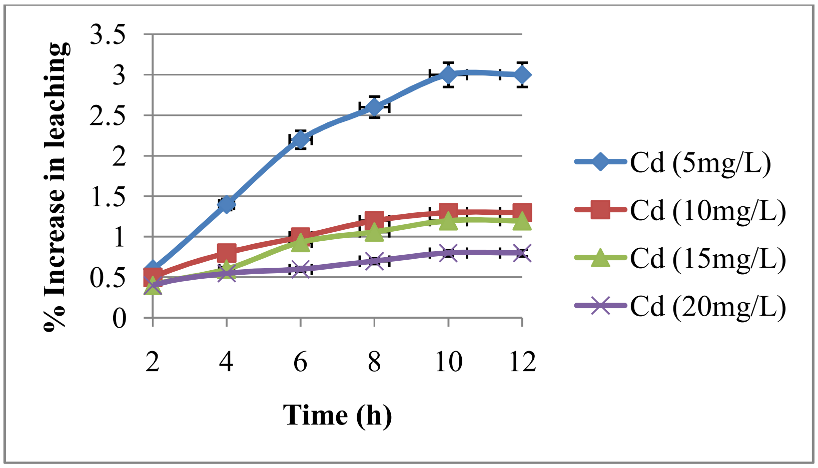

Figure 6.5 -Leaching of Cd from sewage sludge sample at different hours of shaking time

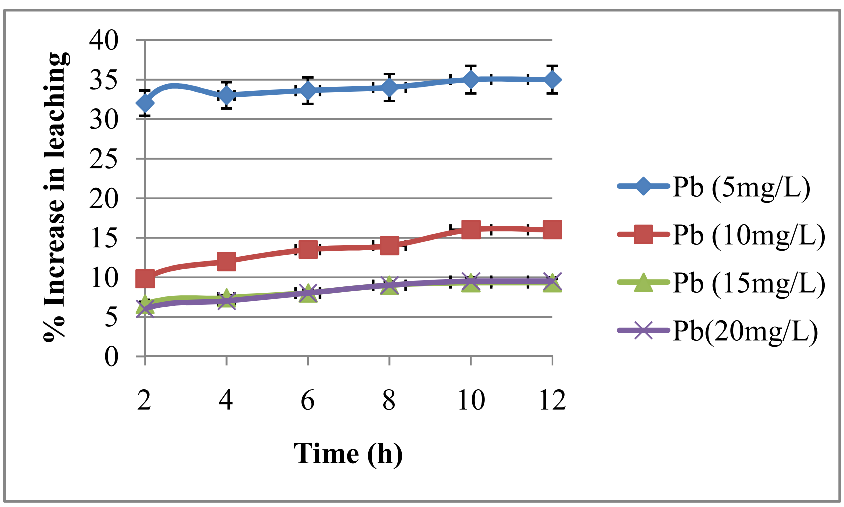

Figure 6.6 -Leaching of Pb from sewage sludge sample at different hours of shaking time

The findings of present study are supported by many other researchers. Kharub et al. (2012) investigated that removal efficiency for heavy metal ions increases with mixture of FA/SS containing higher dose of fly ash. The results show that the maximum removal trend was observed with FA/SS (4:1) mixture.

6.3 Leaching of metals at different pH conditions from sewage sludge

6.3.0 Leaching of Fe from sewage sludge

Figure 6.7 shows the evolution of heavy metals concentrations in the extract as a function of pH in the ANC test. A lag period was found prior to heavy metals release. However, when pH was less than 6.0, the concentration of dissolved heavy metals rapidly increased. This observation is in agreement with the results obtained by (Coz et al., 2004. Transformation from hydroxides precipitate to more soluble ions is the main reason for such a big increase in heavy metals concentrations. It has been reported by (Butcheret al., 1996) that Zn and Cd exist as mixed hydroxides, $CaZn_2(OH)_6$ and $CaCd(OH)_4$ phase in S/S matrix, respectively. Therefore, with decrease in the extract pH, the dissolution of metal hydroxides and the release of the heavy metals ions into solution can be expected. Moreover, the dissolution of calcium silicate hydrate (C-S-H) is also responsible for the release of heavy metals from S/S matrix. The dissolution of organic material initially presented in S/S matrix tend to increase the potential leaching of heavy metals (Lim et al., 2006).

The leaching of heavy metal ions from sewage sludge was studied at different pH conditions. The pH was varied from 2-8 conditions. The leachate was checked for the release of metal ions from sewage sludge under different pH conditions with the help of atomic absorption spectrophotometer. It was observed that the acidic pH conditions are more favourable for the maximum release of heavy metal ions from sewage sludge. The leaching of Fe varied from pH 2 to 8 as shown in Figure 6.7.The maximum leaching of Fe was observed at pH 2 it was (54.27 mg/L) after leach-1 which decreased to 10.17 mg/L in the leach-2 and 3.39 mg/L in leach-3. While at pH 3 and 4 conditions, almost similar results were observed. At pH 5 condition the leaching after leach-1(42.8mg/L) decreased 8.0 mg/L after leach-2and 2.6 mg/L in the leach-3, respectively. A lesser release for leached Fe was observed at 8 it was 31.4 mg/L in leach-1, which reduced and decreased to 1.96 mg/L in leach-3.

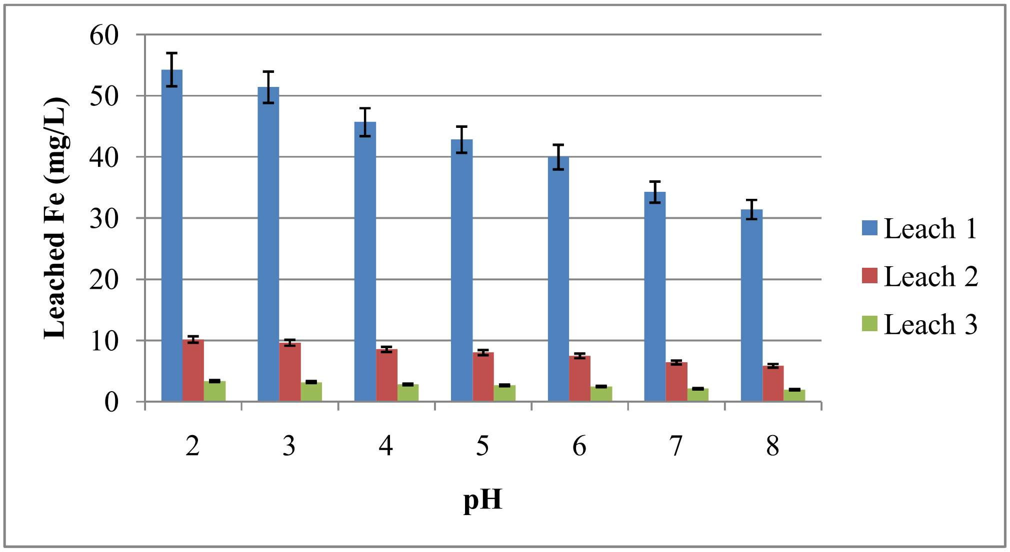

Figure 6.7 - Leached metal (Fe) concentration at different pH conditions

6.3.1 *Leaching of Cu from sewage sludge*

The experimental results (Figure 6.8) show that the maximum leaching of Cu was observed at pH 2 condition. It was 5 mg/L after the first wash in leach-1 which decreased to 0.5 mg/L after the second wash in leach-2 and 0.15 mg/L after the third wash in leach-3. While at pH 3 and 4 conditions, almost similar results were observed. At pH 5 condition the leaching after first wash in leach-1 was 2.0 mg/L which further decreased with washing to 0.4 mg/Lin second wash in leach-2 and 0.1 mg/L after the third wash in leach-3, respectively.

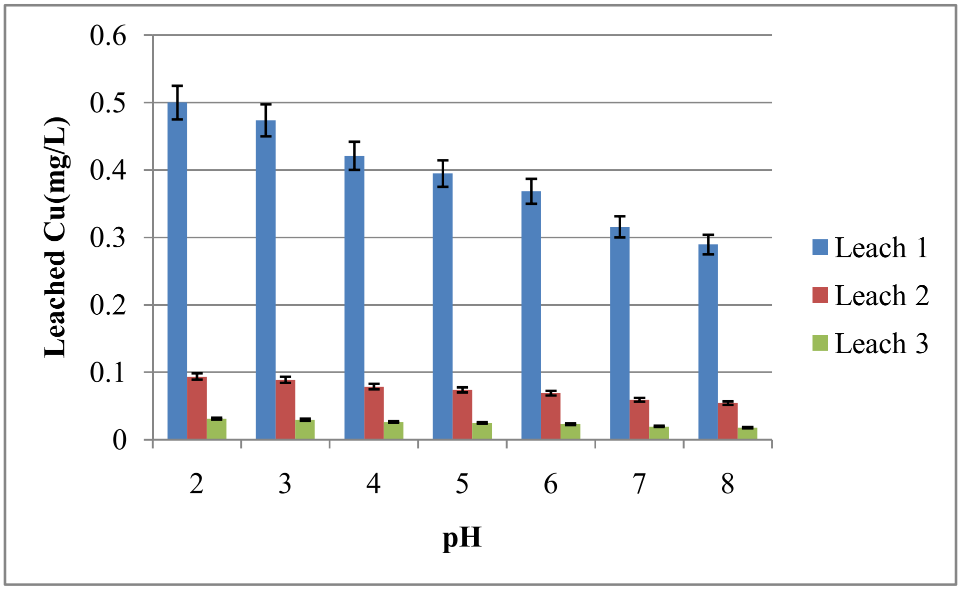

Figure 6.8 - Leached metal (Cu) concentration at different pH conditions

It was observed that with increase in pH the leaching of metal ion decreased. With increase the percentage adsorption was decreased; because OH^- ions increased the hindrance of diffusion as well as some of the trivalent cations may react with OH^- ion and precipitated and there by decreased the free metal ions available in the solution (Mohan and Pittman Jr, 2006; Blazquez et al., 2009).At neutral pH condition the leaching of Cu was 1.6 mg/L after first wash in leach-1 which decreased to 0.3 mg/L after second wash in leach-2 and 0.1 mg/L after third wash in leach-3, respectively. A lesser release of the leached Fe was observed at the alkaline (pH 8) condition which was 1.4 mg/L in the first wash in leach-1 which further decreased to 0.1 mg/L after third wash in leach-3 followed by different washings of the sewage sludge.

6.3.2 Leaching of Zn from sewage sludge

The experimental data (Figure 6.9) shows that the maximum leaching of Zn was observed at pH 2 condition. It was 1450 mg/L after the first wash (leach-1) which decreased to 272 mg/L after the second wash (leach-2) and 91 mg/L after third wash (leach-3), respectively. At pH 3 and 4 conditions almost similar results were observed. At pH 5 condition the leaching after first wash in leach-1 was 1146 which decreased to 215 mg/L after second wash in leach -2 and 72 mg/L after third wash in leach-3, respectively.

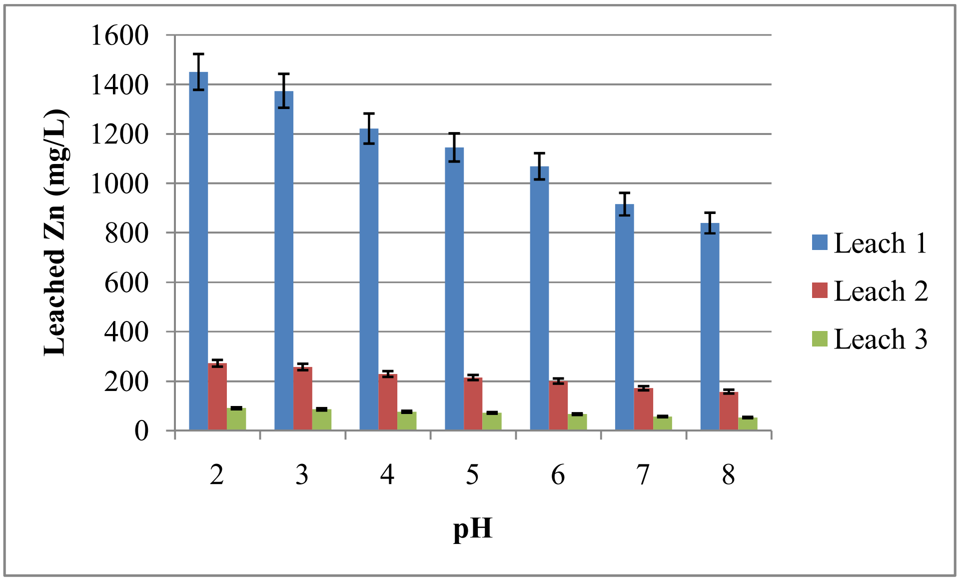

Figure 6.9 – Leached metal (Zn) concentration at different pH conditions

It was observed that the low pH conditions allow maximum leaching as compared to the higher pH conditions. At the neutral pH condition the leached Zn content was 916 mg/L during first wash (leach-1) which decreased to 172 mg/L after second wash (leach-2) and 57 mg/L after the third wash (leach-3). A lesser release for leached Zn was observed at the higher pH 8 condition which was 840 mg/L after first wash in leach-1 and decreased to 52 mg/L in the third wash in leach-3.

6.3.3 Leaching of Cd from sewage sludge

The experimental result (Figure 6.10) shows that the cadmium (Cd) leached at pH 2 condition. It was 2.1 mg/L after first wash (leach-1) which decreased to 0.4 mg/L after the second wash (leach-2) and 0.1 mg/L after the third wash (leach-3). While at pH 3 and 4 conditions almost similar results were observed. At pH 5 conditions the leaching after the first wash in leach-1 was 1.6 mg/L which further decreased with washing to 0.3 mg/L and 0.1 mg/L after the second in leach-2 and third wash in leach-3 respectively.

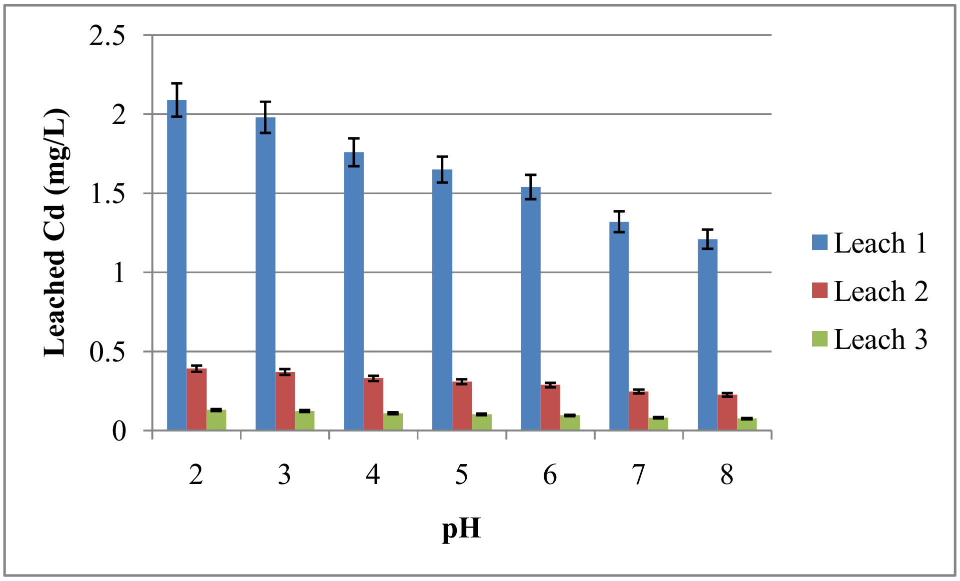

Figure 6.10 – Leached metal (Cd) concentration at different pH conditions

It was observed the lower pH conditions are more favourable maximum leaching as compared to the higher pH conditions. At the neutral pH condition the leached Cd content was 1.32 mg/L after first wash (leach-1) which decreased to 0.24 mg/L after the second wash (leach-2) and 0.08 mg/L after the third wash (leach-3). A lesser release for leached Cd was observed at the alkaline pH 8 condition which was 1.21 mg/L after the first wash (leach-1) and decreased to 0.07 mg/L in the third wash (leach-3) respectively.

6.3.4 Leaching of Ni from sewage sludge

The leaching of Ni varied from pH 2 to 8 and it was noted that the lower pH conditions allow maximum leaching as compared to higher pH conditions. As it can be seen from the experimental results shown in Figure 6.11that Ni leached at pH 2 condition was found to be 26.6 mg/L during the first wash in leach-1 which decreased to 4.5 mg/L during the second wash in leach-2 and 1.6 mg/L during the third wash in leach-3. The leaching reduced with increase in pH conditions. At pH 5 condition the leaching during the first wash in leach-1 was 21.0 mg/L which decreased with washing to 3.9 mg/L and 1.3 mg/L in the second leach-2 and third wash leach-3 respectively.

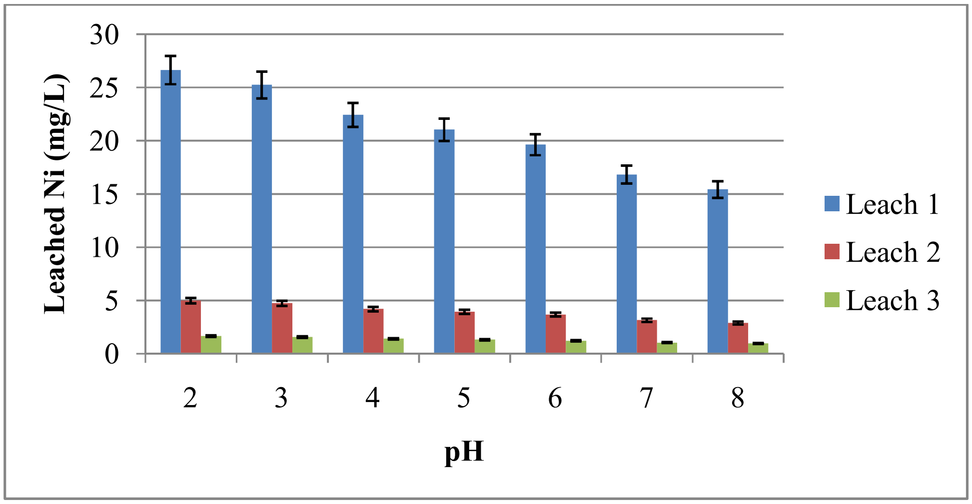

Figure 6.11 – Leached metal (Ni) concentration at different pH conditions

Whereas, at pH 7 condition the neutral pH conditions the leached Ni content was 16.8 mg/L during the first wash (leach-1) which decreased to 3.1 mg/L during the second wash (leach-2) and 1.0 mg/L during the third wash (leach-3). A lesser release for leached Ni was observed at the higher pH conditions which was 15.4 mg/L during the first wash (leach-1) and decreased to 0.9 mg/L during the third wash (leach-3), respectively.

6.3.5 Leaching of Pb from sewage sludge

The maximum leaching of Pb was observed at pH 2 condition. It was 53.0 mg/L during the first wash in leach-1 which decreased to 9.9 mg/L during the second wash in leach-2 and 3.3 mg/L during the third wash in leach-3. At pH 3 and 4 conditions almost similar results were observed. At pH 5 condition the leaching during the first wash in leach-1 was 41.9 which decreased with washing to 7.8 mg/L and 2.6 mg/L in the second leach-2 and third wash leach-3, respectively.

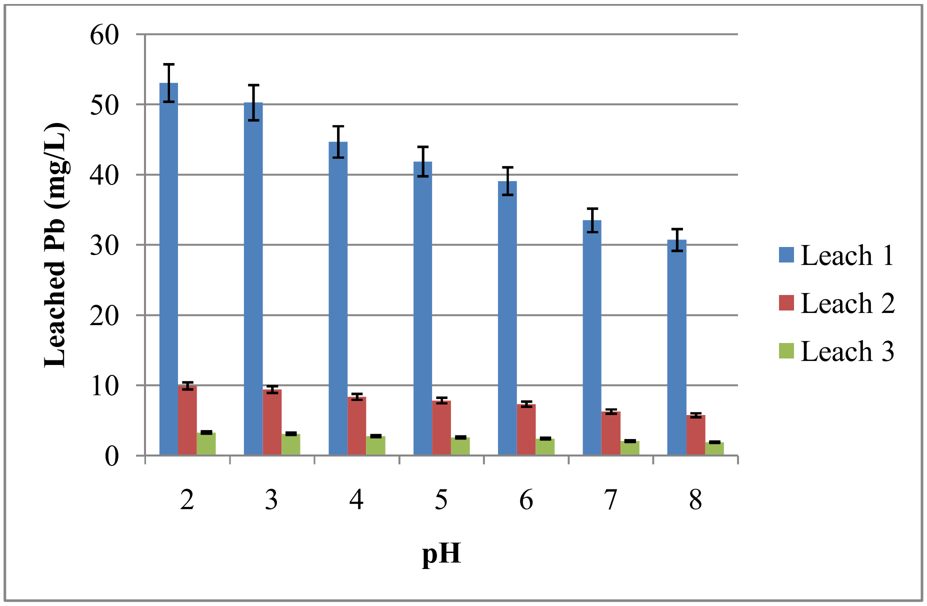

Figure 6.12 – Leached metal (Pb) concentration at different pH conditions

At pH 6 condition the leached Pb content was 39.1 mg/L during the first wash in leach-1 which finally reduced to 2.4 mg/L followed by three subsequent washings. Whereas at the alkaline pH conditions a lesser release for lead metal was observed. It was 30.7 mg/L and was reduced to 1.9 mg/Lin leach-3 followed by different washings of the sludge. It was noted that the low pH conditions allow maximum leaching as compared to higher pH as shown in (Figure 6.12).

6.4 Effectiveness of the optimised fly ash and sewage sludge mixture for leachability test

6.4.0 Cr concentration after optimised dose (4:1) FA/SS mixture

The effectiveness of FA/SS optimised ratio was studied by taking different metal solutions at different hours of shaking time. It has been observed from the experimental data shown in (Figure 6.13) that the 100% percent removal efficiency was achieved with 5 mg/L concentration for different heavy metal ions at the shaking time of two hours with the optimised FA/SS ratio (4:1).

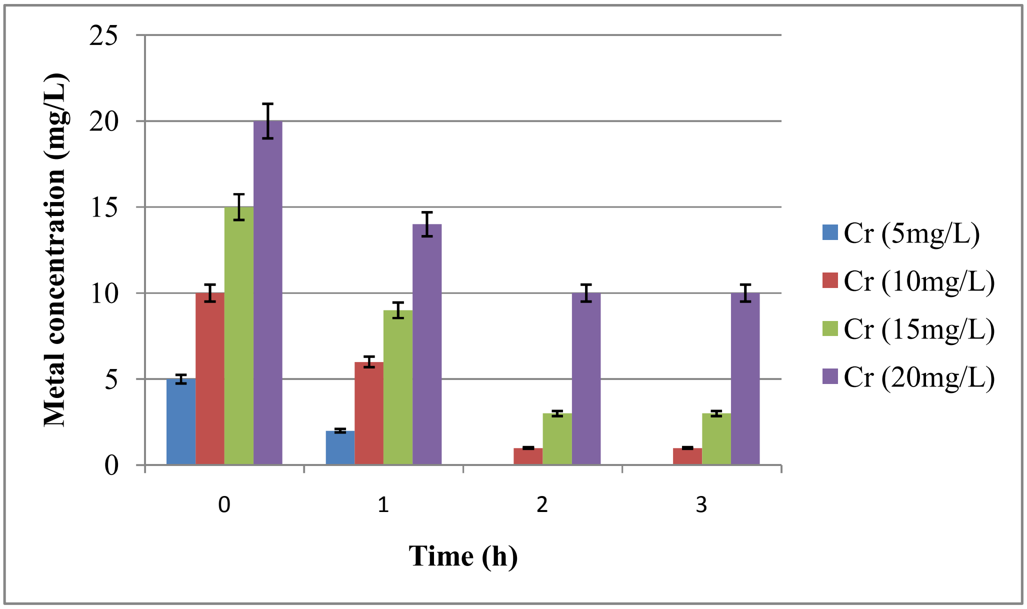

Figure 6.13 -Metal concentration in leachate after uptake by optimised fly ash-sewage sludge mixture (4:1) at different concentrations of chromium

It was observed from the experimental results that at 0 hour of shaking there is no adsorption for Cr-metal ion was observed. After shaking for one hour it was observed that the metal which was initially 5 mg/L reduced to 2 mg/L, 10 mg/L to 6 mg/L, 15 mg/L to 9 mg/L, 20 mg/L to 14 mg/L, respectively. The metal concentration was then checked after shaking for two hours. It was observed that in 5 mg/L concentration no metal was present in the aqueous solution which confirmed that all the metal was observed by the optimised FA/SS (4:1) ratio. Whereas, the metal concentration was reduced to 1 mg/L, 15 mg/L to 3 mg/L and 20 mg/L to 10 mg/L, respectively. Similar results were observed after shaking for three hours time period.

6.4.1 Cu concentration using the optimised dose FA/SS (4:1) mixture

It was observed from the experimental results that at 0 hour of shaking there was no adsorption of Cu-metal solution. After shaking for one hour, it was observed that the metal which was initially 5 mg/L reduced to 2 mg/L, 10 mg/L to 6 mg/L, 15 mg/L to 9 mg/L, 20 mg/L to 14 mg/L, respectively.

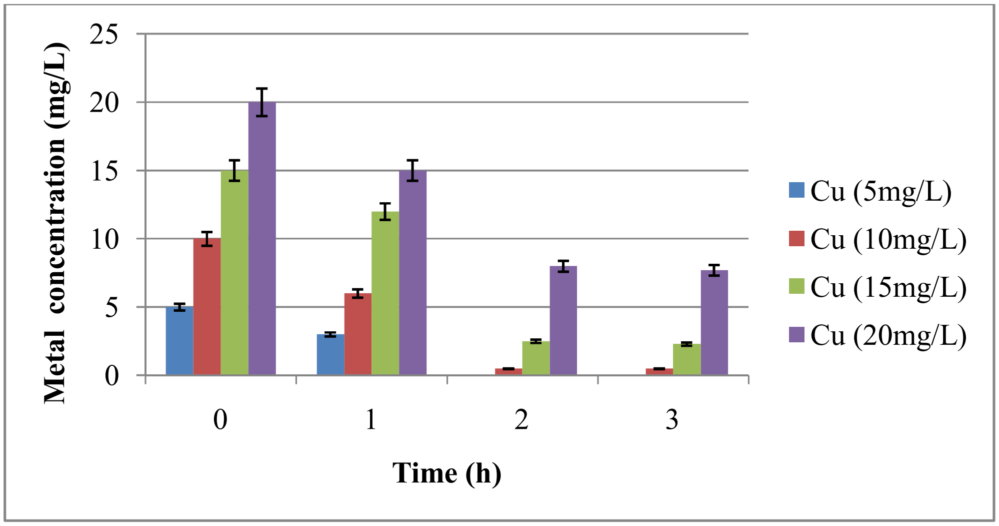

Figure 6.14 -Metal concentration in leachate after uptake by optimised fly ash-sewage sludge mixture (4:1) at different concentrations of copper

The metal concentration was then checked after shaking for two hours and it was observed that from the copper solution of 5 mg/L all the metal retained was absorbed by the optimised (4:1) FA/SS ratio and no metal was found in the supernatant solution. Whereas, in 10 mg/L the concentration reduced to 1 mg/L, 15 mg/L to 3 mg/L and 20 mg/L to 10 mg/L, respectively. Similar results were observed after shaking for three hours time period as shown in (Figure 6.14).

6.4.2 Ni concentration after shaking with optimised dose of FA/SS (4:1) mixture

The metal concentration was then checked after shaking for two hours and it was observed that from the Nickel solution of 5 mg/L all the metal retained was absorbed by the optimised (4:1) FA/SS ratio and no metal was found in the supernatant solution. Whereas, in 10 mg/L the concentration reduced to 1.5mg/L, 15 mg/L to 3.5 mg/L and 20 mg/L to 8mg/L, respectively. Similar results were observed after shaking for three hours time period (Figure 6.15).

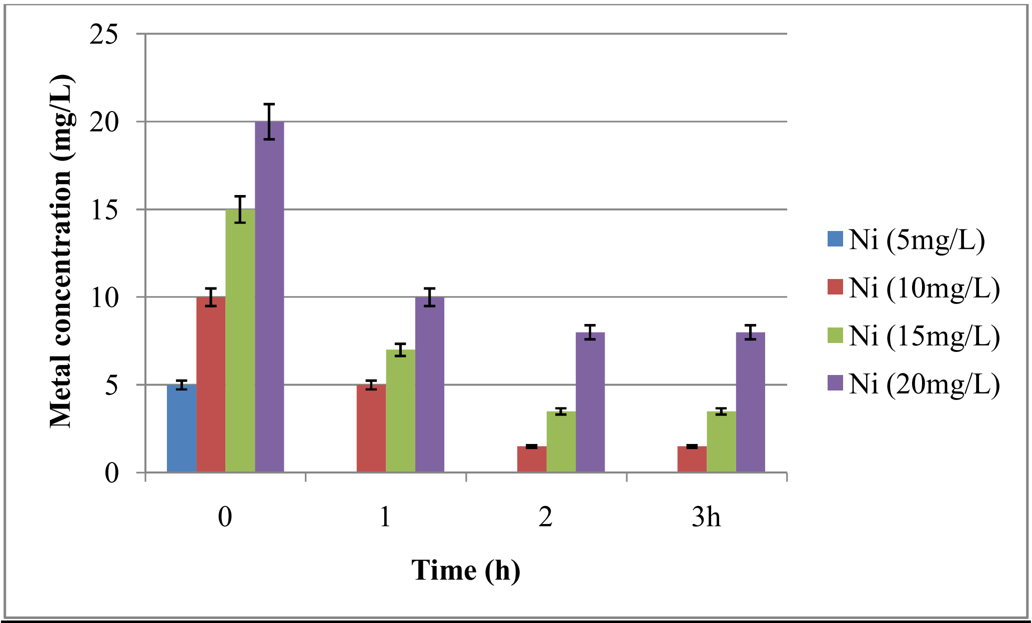

Figure 6.15 -Metal concentration in leachate after uptake by optimised fly ash-sewage sludge mixture (4:1) at different concentrations of nickel

6.4.3Zn concentration after shaking with optimised dose of FA/SS (4:1) mixture

The metal concentration was then checked after shaking for two hours and it was observed that from the Zinc solution of 5mg/L all the metal retained was absorbed by the optimised (4:1) FA/SS ratio and no metal was found in the supernatant solution. Whereas, in 10 mg/L the concentration reduced to 3mg/L, 15 mg/L to 2 mg/L and 20 mg/L to 5mg/L, respectively. Similar results were observed after shaking for three hours time period (Figure 6.16).

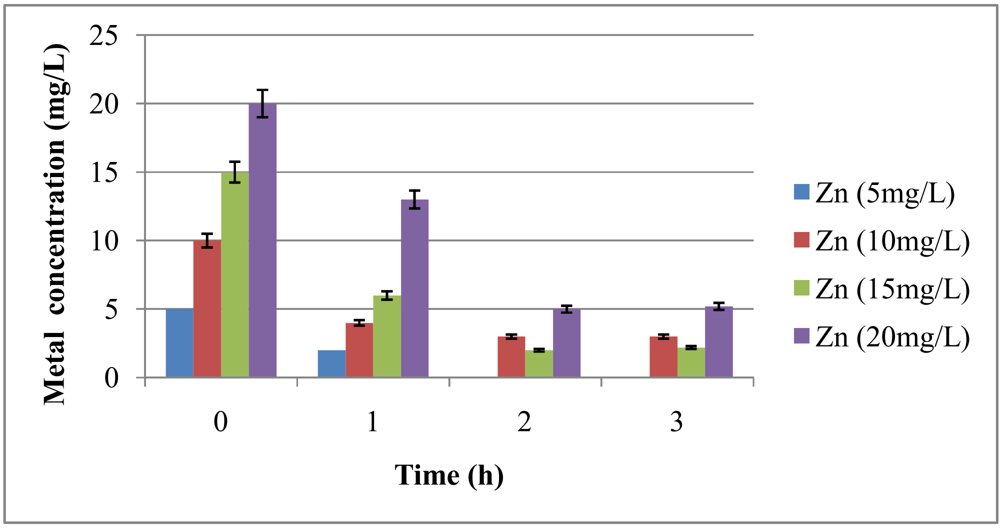

Figure 6.16 -Metal concentration in leachate after uptake by optimised fly ash-sewage sludge mixture (4:1) at different concentrations of zinc

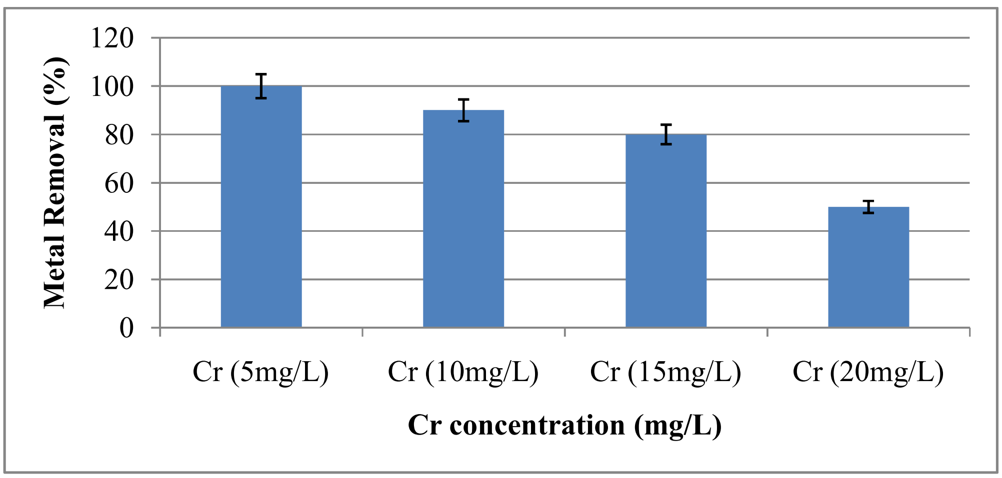

Figure 6.17 -Metal removal efficiency by optimised fly ash/Sewage sludge ratio (4:1) for different concentrations of chromium

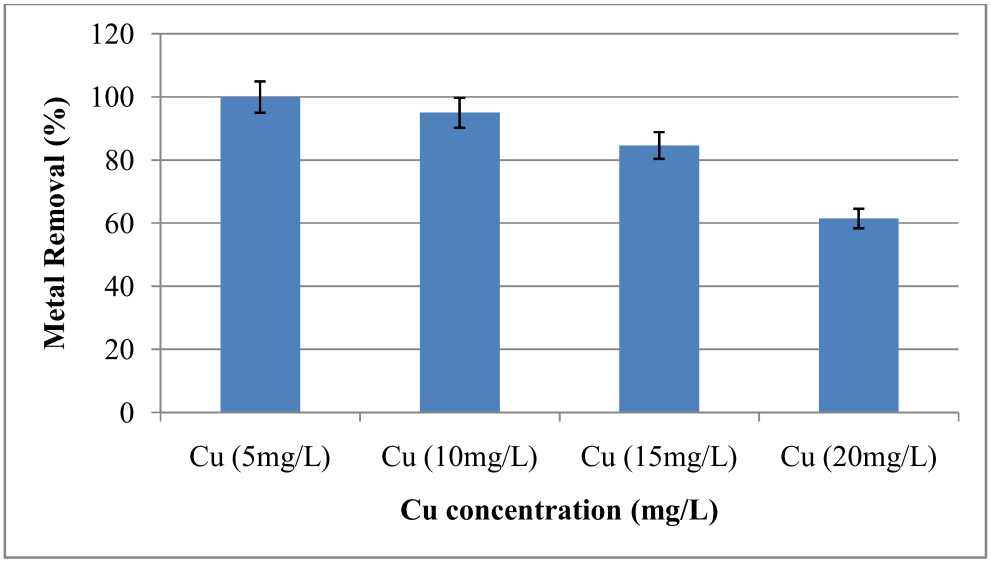

Figure 6.18 -Metal removal efficiency by optimised fly ash/Sewage sludge ratio (4:1) for different concentrations of copper

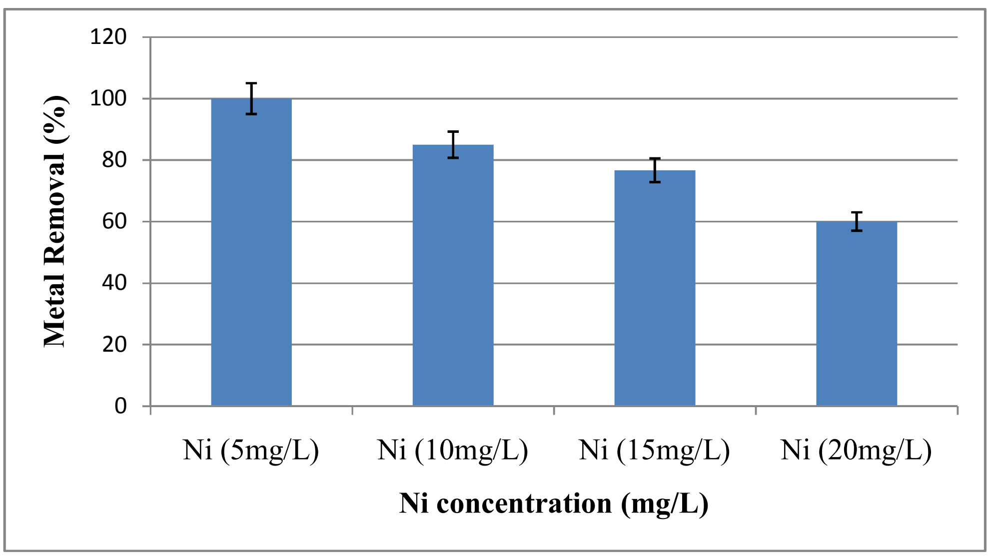

Figure 6.19 -Metal removal efficiency by optimised fly ash/Sewage sludge ratio (4:1) for different concentrations of nickel

Percent removal efficiency by optimised FA/SS (4:1) at different hours of shaking

It was observed from the experimental results that 2 hours shaking time was sufficient to achieve the maximum uptake of heavy metal ions from the synthetically prepared metal solutions by the optimised FA/SS (4:1). The best metal removal efficiency (%) was achieved at 2 hours shaking time by FA/SS (4:1) mixture at pH 8 condition for Cr-metal ion (Figure 6.17).

Chromium metal removal efficiency using the optimised FA/SS (4:1) mixture for different concentrations of metal solutions can be written as:

Cr(5 mg/L) 100% > Cr(10 mg/L) 90% > 80% Cr(15 mg/L) > 50% Cr(20 mg/L)

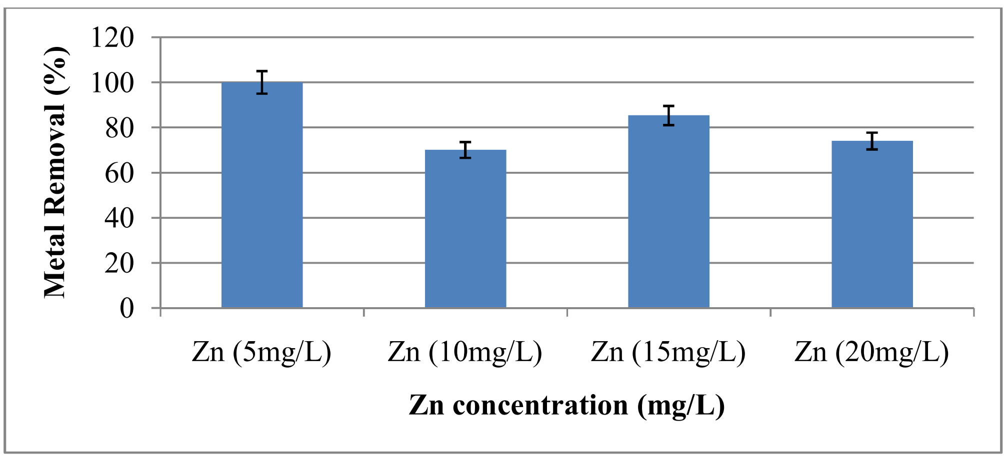

Figure 6.20 -Metal removal efficiency (%) by optimised fly ash/Sewage sludge ratio (4:1) for different concentrations of zinc

Experimental results have shown a similar pattern in respect of Cu, Ni and Zn metals (Figure 6.18, 6.19, 6.20) in different concentrations, so it can be concluded that 2 hours of shaking at 120 rpm and pH 8 are the optimum parameters for the metal uptake with optimised FA/SS (4:1) mixture and after that the metal removal efficiency becomes constant.

Microbiological &Eco-toxic studies

CHAPTER 7

MICROBIOLOGICAL AND ECO-TOXIC STUDIES

Several experiments were conducted to study microbiological and eco-toxic studies in different leachate of FA/SS mixture. The objective of the study was to see the toxic effect of different FA/SS mixture on fish's species and to study the microbial count in different FA/SS mixture leachate. The microbiological analysis was carried out using the most probable number (MPN) – method and total coliform removal was studied. The eco-toxic properties were carried out on two fish species Guppy and Zebra. The fish's were dissected in to smaller pieces, oven-dried at 120ºC for 24 hours time period until a constant weight is achieved. The digestions of fish's were done with ultrapure HNO_3 and H_2O_2 in (1:1 v/v) samples were digested until complete dissolution. The samples were analysed for different heavy metal ions (Pb, Cd, Ni, Cu and Zn) with AAS (ECIL, India, Model AAS 4129).

7.0 Evaluation of microbiological and Eco-toxic studies from different Fly ash-Sewage Sludge mixtures

The microbiological analysis was carried out in the supernatant liquid of sewage sludge – fly ash mixtures of three different ratios. The test was conducted using the experiment and most probable number (MPN) – method. The leachate of various FA/SS mixture was analyzed after incubation in microbial cultures. The results shown in Table 7.1 indicated that the initial concentration of total coliforms in supernatant liquid was 2.4×10^4MPN/100mL, 150MPN/100mL and 120MPN/100mL of 1:1, 4:1, 1:4 SS/FA ratios, respectively which were reduced to 28MPN/100mL, 4MPN/100mL and 3MPN/100mLafter shaking for 10 hours. This decrease in total coliforms counts was observed after the third wash. The addition of fly ash to sewage sludge in different ratios not only reduced the leaching of heavy metal ions but has also proved helpful in reduction of total coliforms population present in the sewage sludge.

Table 7.1 - Total coliform removal of the microbial community at different sewage sludge/fly ash ratios

SS/FA (with different washings)	Mixing/Shaking time (hrs)	Total coliform Removed
1:1(1)	10	2.4×10^4
1:1(2)	10	1200
1:1(3)	10	28
4:1(1)	10	150/100ml
4:1(2)	10	11
4:1(3)	10	4
1:4(1)	10	120Cells/100ml
1:4(2)	10	21
1:4(3)	10	3

7.1 Eco-toxicity Studies

The eco-toxic effect of heavy metals ions in marine environments and their accumulations in fish has been reported during topical years (Canli and Atli, 2003; Ayenimo et al., 2005; Dural et al., 2006; Davies et al., 2006; Yalcin et al., 2008; Burger and Gochfeld, 2005; Chindah et al., 2009). Two fish species Poecilia reticulate (Guppy fish) and Danio rerio (Zebra fish) species were used for the eco-toxicity test. The fish species were purchased from fish aquarium Sheravali gate, Patiala and were acclimated to the laboratory conditions for 7 days. However, the fish were not fed during the last 48 h of adaptations and throughout the toxicity test duration of 96 h for each metal. The toxicity tests with three age groups of fish's viz. 60, 90 and 120 day old fish were conducted in glass aquaria at room temperature conditions (26± 1°C). Ten fish per glass chamber of 5 L water capacity were added in control sample (no FA/SS mixture), optimised 4:1 FA/SS mixture, and in four different concentrations (5, 10, 15 and 20%) of sewage sludge. The total mean values in terms of weight and total length of different age group of fishes are shown in Table 7.2. The bio-available concentrations of different heavy metal ions in different percentages of sewage sludge 5, 10, 15 and 20% (W/V) used are shown in Table-7.3.

Four different concentrations of the sewage sludge leachate 5, 10, 15 and 20% (W/V) and the optimised 4:1 FA/SS mixture were used to check the eco-toxicity among three age groups (60, 90 and 120 days) of fish species. The survival rate was checked after 96 hour time period. The different metal concentration was checked after the digestion. The fish's were dissected in to smaller pieces, put in petri-dishes oven-dried at 120ºC for 24 hours time period until a constant weight is achieved. When the samples were confirmed completely dry, they were then ground to fine powder with the help of Pestle and mortar and stored in air tight plastic containers. After this the dissected pieces of fish's were put in to digestion flasks. The digestions of fish's were done with ultrapure HNO_3 and H_2O_2 in (1:1 v/v). The digestion flasks were heated to 130ºC on hot plate until complete dissolution and further diluted with the help of distilled water. After this, the samples were analysed for different heavy metal ions (Pb, Cd, Ni, Cu and Zn) with the help of atomic absorption spectrophotometer (ECIL, India, Model AAS 4129). The experimental results shown in Table-7.4 and 7.5.

The Poecilia reticulate (guppy fish) of 60 days was kept in the leachate of the optimised dose FA/SS mixture for 96 hours and the metal concentration in the fish was observed for different concentrations of the leachate 5% to 10%, 15 % and 20%. The accumulation for Pb-metal observed was 2.36µg/g with 5% leachate, 5.13 µg/g with 10%, 6.72 µg/g with 15% and 13.14µg/g with 20% leachate which increased in 120 day old fish to 26.10 µg/g with 5% leachate, 38.23 µg/g with 10% leachate, 54.14 µg/g with 15% and 79.65 µg/g with 20% leachate, respectively. The development of metal toxicity involves the initial binding of metals, followed by the internal partitioning of metal between detoxified and metabolically active forms (Luoma and Rainbow, 2005). This process of modified uptake is the first indication of metal's interaction within the organisms. A lesser accumulation for Cd-metal was observed which was 0.4 µg/g with 5% leachate, 0.98 µg/g with 10% leachate, 1.05 µg/g with 15% leachate, 2.3 µg/g with 20% leachate among 60 day old guppy fish.

In 90 day old fish it was 2.90 µg/g with 5% leachate, 4.24 µg/g with 10% leachate, 7.14 µg/g with 5% leachate, 9.81µg/g with 20% leachate which increased to 9.68 µg/g with 5% leachate, 16.2 µg/g with 10% leachate, 22.24 µg/g with 15% leachate, 39.18 µg/g with 20% leachate in 120 day old fish. Cd is biologically non-essential, non-biodegradable and its compounds have the potential to cause toxicity to the fish. The continuous exposure of Cd at low level may cause significant impacts on biological processes in fish (Karlsson-Norrgran and Runn, 1985). The sensitivity of fish to particular toxicant depends on the exposed species, its developmental stage, genetics and age (Stoskus et al., 1999).

The 60 day old fish were significantly more sensitive to the toxicity of water-borne Cd and Co followed by that of 90 and 120 day age groups. Therefore, the sensitivity of fish towards various metals decreased with age due to their ability to concentrate heavy metals that exerted significant impact on the tolerance limits of fish (Giguere et al., 2004). It has been observed from the experimental results that out of the five selected heavy metal ions (Pb, Cd, Ni, Cu and Zn) the maximum accumulation of the Zn metal was observed which was 0.98 µg/g initially in the control sample which increased with increased percentage of the leachate solution that is 92 µg/g with 5% leachate, 159 µg/g with 10% leachate, 197 µg/g with 15% leachate , 270 µg/g with 5% leachate in 90 day old fish which was increased to 160 µg/g with 5% leachate,236 µg/g with 10% leachate, 342 µg/g with 15% leachate, 378 µg/g with 20% leachate solution. Bioaccumulation of metals indicates the quantity taken up by an organism and the mechanism of metal distribution in various organs/tissues and the ability of fish for metals retension (Murugan et al., 2008). Nussey et al. (2000) reported variable bioaccumulation of Cr, Ni and Mn in different tissues of cyprinid fish (*L. ambratus*) depending on their size, sex and season. Fish gills are important site for the entry of heavy metals that provokes lesions and gill damage (Bols et al., 2001), while liver and kidney play a major role in metal detoxication (Vinodhini and Narayanan, 2008).

A similar increasing trend was observed for Ni, Cu and Zn heavy metal ions in both Poecilia reticulate (guppy fish) and Danio rerio (Zebra fish). (Gul et al., 2009) observed imbalanced swimming patterns and lazy movements in *Poecilia reticulate* during chronic exposure of Zn. Among the three age groups, 60days all the three fish species showed higher sensitivity against Cr, while 240 day fish appeared least sensitive.(Abdullah et al., 2007) reported higher tolerance by 90 day fish to Fe, Pb, Mn, Ni and Zn than that of 60 and 30 day *C.catla*, *L. rohita*and *C. mrigala*.

Javed and Abdullah (2006) reported acute toxicity of Fe and Ni to *C. catla*, *L. Rohita* and *C. Mrigala* that varied significantly with age as well. It was observed from the experimental results that 7 fish died in sewage sludge leachate 5%, 9 in 10%, 10 in 10% and 10 in 15%. It is concluded that from the results that sewage sludge contains a large concentration of toxic heavy metal ions, whereas, no death was observed in the control experiment and in leachate of 4:1 (FA/SS) samples which further confirmed that the optimised 4:1 FA/SS mixture is the best dose and leachate obtained from this ratio is non-hazardous in aquatic environment also.

Table 7.2–Total weight and length values of Guppy and Zebra fish species (with three age groups 60 day, 90 day, 120 day) used for the eco-toxicity test

Age group	Fish Species	Total weight of oven dried Fish Sample(mg)	Total length of Fish (mm)
60 day	Guppy	40	19
	Zebra	50	26
90 day	Guppy	60	22
	Zebra	72	31
120 day	Guppy	120	25
	Zebra	130	40

Table 7.3 - Bio-available [4]concentrations of metals present in the sewage sludge samples

Sewage Sludge concentrations (W/V)[5]	Metal Concentration in mg/L				
	Pb (mg/L)	Cd (mg/L)	Ni (mg/L)	Cu (mg/L)	Zn (mg/L)
5%	1.75	0.15	1.21	3.27	47.7
10%	3.89	0.45	2.42	6.54	95.4
15%	5.25	0.52	3.63	9.84	143.1
20%	7	0.69	4.84	13.08	190.8

[4]The fish's were dissected in to smaller pieces, oven-dried at 120ºC for 24 hours time period until a constant weight is achieved. The digestions of fish's were done with ultrapure HNO_3 and H_2O_2 in (1:1 v/v) samples were digested until complete dissolution. The samples were analysed for different heavy metal ions (Pb, Cd, Ni, Cu and Zn) with AAS (ECIL, India, Model AAS 4129).

[5]These are the weight by volume concentrations of different volumes of sewage sludge used in different percentages mixed with distilled water and the leachate have the above listed metal concentration in them.

Table 7.4 – Accumulation of different metal ions in guppy fish with different age groups during 96 h exposures

Guppy fish Age (days)	Leachate Source W/V	No. of fish exposed	Pb(µg/g) Dry Fish weight	Cd(µg/g) Dry Fish weight	Ni(µg/g) Dry Fish weight	Cu(µg/g) Dry Fish weight	Zn(µg/g) Dry Fish weight	No of fish died
60 days	Control[6]	10	0.56	0.001	0.64	0.95	0.98	0
	4:1 FA/SS	10	0.53	0.003	0.67	0.92	1.02	0
	5%	10	2.36	0.4	4.06	8.02	92	7
	10%	10	5.13	0.98	9.10	20.38	159	9
	15%	10	6.72	1.05	24.04	30	197	10
	20%	10	13.14	2.3	40.44	50.42	270	10
90 days	Control	10	0.76	0.004	0.94	1.90	2.08	0
	4:1 FA/SS	10	0.78	0.006	0.99	1.89	2.01	0
	5%	10	6.56	2.90	14.06	18.06	128	8
	10%	10	11.14	4.24	26.05	36.68	198	9
120 days	Control	10	0.94	0.009	1.52	2.01	1.95	0
	4:1 FA/SS	10	0.96	0.011	1.45	2.05	1.99	0
	5%	10	26.10	9.68	23.04	35.01	160	7
	10%	10	38.23	16.2	29.23	46.24	236	9

[6] Control (without fly ash-sewage sludge mixture)

Table 7.5 – Accumulation of different metals in Zebra fish with different age groups during 96 h exposures

Zebra fish Age (days)	Leachate Source W/V	Sewage Sludge W/V	No. of fish exposed	Pb(µg/g) Dry Fish weight	Cd(µg/g) Dry Fish weight	Ni(µg/g) Dry Fish weight	Cu(µg/g) Dry Fish weight	Zn(µg/g) Dry Fish weight	No of fish died
60 days	Control[7]	0	10	0.66	0.001	0.74	0.83	1.32	0
	4:1 FA/SS	4:1 FA/SS	10	0.644	0.003	0.76	0.82	1.30	0
	5%	5	10	2.56	0.9	6.06	10.02	94	6
	10%	10	10	6.144	1.2	12.12	23.38	154	9
	15%	15	10	12.68	2.25	29.08	35	271	10
	20%	20	10	21.24	3	48.48	53.44	324	10
90 days	Control	0	10	0.98	0.006	0.90	1.90	1.88	0
	4:1 FA/SS	4:1 FA/SS	10	0.94	0.003	0.88	1.94	1.90	0
	5%	5	10	10.56	6.9	15.06	21.02	143	7
	10%	10	10	14.14	7.2	21.12	34.38	198	8
120 days	Control	0	10	1.01	0.008	1.21	1.99	1.90	0
	4:1 FA/SS	4:1 FA/SS	10	1.04	0.010	1.24	1.96	1.87	0
	5%	5	10	26.56	18.9	33.06	43.02	202	7
	10%	10	10	30.14	29.2	39.12	56.38	296	8

[7]Control sample (without fly ash-sewage sludge mixture)

Conclusions

&

Recommendations

CHAPTER 8

CONCLUSIONS

Fly ash and sewage sludge samples were collected from different locations. The samples of fly ash and sewage sludge were characterized for their physical and chemical analysis using the ASTCM C618. Several standard solutions were prepared from the analytical grade salts in the laboratory for the analysis of different metal contents in the fly ash and sewage sludge samples. Heavy metal contents of the digested samples were studied with the standard protocol of atomic absorption spectrophotometer. All the samples were taken in duplicates in order to get the accuracy of the results. Prior to analysis of the metal contents, the samples were mixed in three different ratios and FA/SS (1:4, 1:1 and 4:1) mixture were prepared. Solid to liquid ratio taken was 1:20. The mixture were shaken on rotatory shaker at 120 rpm under controlled temperature conditions of 26±1°C. The leachate obtained after filtration with 0.45µ membrane filter were analysed for heavy metal contents with the help of atomic absorption spectrophotometer (ECIL, India, Model AAS 4129). The aim of the above experiments was to find out the optimum conditions with regard to pH, number of wash offs, adsorbent dose, acid dose, contact time where the leaching of metals was the minimum. Dose of fly ash was optimised to know the ratio that prevents leaching the most. After conducting different experiments and considering their results, the following can be concluded as the optimised conditions:

- Optimised dose (4:1) FA/SS mixture
- Optimised shaking time 2h
- Optimised acid dose 2.5mL (N) HNo_3
- Optimised pH 8
- Optimised washs 3 (leachate-3)

It was observed that out of the three 1:4, 1:1 and 4:1FA/SS mixture, the 4:1 FA/SS mixture was proved best for arresting the leaching of metals from sewage sludge and was concluded as the optimised dose.

After optimizing the different operating conditions, the leaching of metals and leachate analysis for optimised (4:1) FA/SS mixture and unoptimised FA/SS (1:1, 1:4) mixture was analyzed at different pH conditions. The aim of the study was to analyse how effective fly ash as an adsorbent is playing its role after mixing it with sewage sludge or will it prove successful in eradicating the problem of leaching from sewage sludge and thereby, protecting the ground water table? A comparison of unoptimised (1:1, 1:4) FA/SS mixture was made with optimised (4:1) FA/SS mixture. The results reveal that the optimised FA/SS mixture is the best and the sewage sludge can be disposed of safely to the environment after mixing sewage sludge with fly ash in (4:1) FA/SS mixture.

As discussed in chapter 6, synthetic solutions of different metals were prepared to study the effect of optimised FA/SS 4:1 mixture. Solid to liquid ratio of FA/SS mixture and distilled water taken was 1:20. Four concentrations of synthetic metal solutions 5 mg/L, 10 mg/L, 15 mg/L and 20 mg/L prepared from analytical grade salts. Shaking time varied between 0-3 hours at 120 rpm on shaker under controlled temperature conditions of 26±1ºC. Replicates of all the samples were taken and the heavy metal content in the leachate was tested with the help of atomic absorption spectrophotometer (ECIL, India, Model AAS 4129). The precision of results were carried out in terms of mean, standard deviation and standard error values.

Samples of sewage sludge alone were experimented for their leaching behavior under varying pH conditions (2-8). The maximum leachable concentration of different metals from sewage sludge samples at acidic, neutral and alkaline conditions were studied up to three leachate. The objective of the study was to analyse the leaching of metals from sewage sludge. The results reveal that sewage sludge contains higher amount of toxic heavy metals which leach out more under acidic conditions. So it is not safe to dispose of sewage sludge directly in to the environment.

It was concluded from the experimental results that in the absence of fly ash, leaching from sewage sludge continues up to 10 hours shaking in the aqueous medium and in the presence of optimised dose of FA/SS mixture, the leaching is arrested within 2 hours, under optimised conditions.

As discussed in chapter 7, the microbiological analysis to determine total coliform removal, was carried out using the most probable number (MPN) – method. The objective of the study was to analyse the microbial count in leachate of FA/SS mixture used. The results obtained from the microbiological analysis of 1:1, 4:1, 1:4 sewage sludge and fly ash ratios showed that the initial concentration of total coliforms was 2.4 × 104 MPN/100ml, 150 MPN/100ml and 120 MPN/100ml which were finally reduced to 28, 4 and 3 in different leachates.

The eco-toxicity studies of leachate samples were carried out for Zebra and Guppy fish species with different age groups (60, 90, 120 days). The fish's were dissected in to smaller pieces, oven-dried at 120ºC for 24 hours time period until a constant weight is achieved. The digestion of fish's was carried out with ultrapure HNO_3 and H_2O_2 in (1:1 v/v) samples until complete dissolution. The samples were analysed for different heavy metals (Pb, Cd, Ni, Cu and Zn) with AAS (ECIL, India, Model AAS 4129). No death was observed in any of fish's species with leachate of control (without FA/SS) mixture and optimised 4:1 FA/SS (5% w/v) which proved that fly ash has not only arrested the leaching of metal from sewage sludge, but is also helpful in reducing the toxicity level.

The experimental results proved that fly ash a good adsorbent for the heavy metals released from sewage sludge. Therefore, the sewage sludge can be disposed off while mixing it with fly ash and such disposal may only have very low toxic effects than the toxic effects of the sewage sludge disposal without fly ash.

RECOMENDATIONS

It is noted that not much work has been carried out in the field of leaching and eco-toxicological studies of metals in sewage sludge- fly ash mixture. Advanced processes need to be developed to study the leaching and eco-toxicological studies from sewage sludge using fly-ash sewage sludge mixture. In the coming years, fly ash can prove as one of the best treatment process due to its cost-effectiveness and can reduce the solid waste management problem of both the widely produced wastes (fly ash and sewage sludge). There is a need of the future research in this area that will lead to reduction of the solid waste management problem and fly ash as a low cost adsorbent for heavy metals from sewage sludge using optimised dose of fly ash-sewage sludge mixture (4:1) can prove as an asset.

Future research must also investigate the effectiveness of optimized (4:1 FA/SS) fly ash-sewage sludge mixture as an adsorbent in combination with other adsorbents. More eco-toxicity studies need to be carried out on various sewage sludge concentrations with different fish's species to analyse the toxic effects of the sewage sludge. It is advisable that sewage sludge should be properly treated and characterized depending on its source of origin prior to mixing it with fly ash. Further, without characterization and treatment, sewage sludge should not allow to be disposed off alone in the environment.

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List of Research Publications

1. **Monika Kharub**, Anita Rajor and Susheel K Mittal "Assessment of total coliform removal and leaching of metal ions from sewage sludge-fly ash mixture at different pH and washing conditions" have been published in African journal of Biotechnology Vol. 11(40), pp. 9612-9618, 17 May, 2012 Available online at http://www.academicjournals.org/AJB DOI: 10.5897/AJB11.4057. ISSN 1684–5315 © 2012 Academic Journals **(IF :0.57)**
2. **Monika Kharub**, Anita Rajor and Susheel K Mittal "Fly ash-Sewage Sludge Mixture as a barrier of heavy metal leaching" have been published in Research Journal of Chemistry and Environment **(IF: 0.379)**
3. **Monika Kharub**, Anita Rajor and Susheel K Mittal "Sewage Sludge as a green manure supplement in agriculture" Journal of Applied Ecology and Environmental Research (Communicated).

Papers Presented in National/ International Conferences

1. **Monika Kharub**, Anita Rajor, Susheel K Mittal "Fly Ash –Sewage Sludge Mixtures for Abatement of Leaching of Heavy Metal ions into the Aqueous System," has been published in National Symposium on chemistry in 21st century, held at GND University, Amritsar from Dec 23-24, 2011.
2. **Monika Kharub**, Anita Rajor, Susheel K Mittal "Role of pH, adsorbent dose and number of washing in leaching of metal ions from fly ash-sewage sludge mixtures," has been published in International conference on Hydrology and Ground water expo, held in Hilton San Antonio Airport, USA, on September 10-12, 2012.http://dx.doi.org/10.4172/2157-7587.S1.005.
3. **Monika Kharub**, Anita Rajor, Susheel K Mittal "Leaching of Heavy Metals from Fly Ash- Sewage Sludge Mixture at different pH and washings," in International Conference on Energy-Water-Waste Nexus for Environment Management at Department of Energy and Environmental Sciences, held in Choudhary Devi Lal University, Sirsa (Haryana), on 28-30 January, 2012.
4. **Monika Kharub**, Anita Rajor, Susheel K Mittal "Leaching of heavy metals from fly ash-sewage sludge mixture at optimised conditions," International Conference On Global Trends In Pure And Applied Chemical Sciences, held at Hotel Inder Residency, Goverdhan Vilas, Ekling Nagar, Shikharbadi Road, Udaipur (Rajasthan) 313001 India, from 3-4 March, 2012.