MATERIALS & METHODS
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Fly ash generated from the different industrial activities and from the thermal power plants which produces the environmental problems. The severity of different environmental problems increases along with the increasing quantity of fly ash therefore there was a need to find out an alternative techniques which can convert the waste fly ash in to resource and it can be used for the various purposes. The present work was design to study the certain problem of fly ash in vicinity of thermal power plant and simultaneously identify the reuse potential of fly ash with the designed objectives, which were worked out during the present investigation at the identified study area Parli thermal power station.

Study visits:

The selected study area Parli thermal power station was visited frequently to identify the different environmental problems due to the fly ash. The nearby areas were served for the different environmental problems. The thermal power station was visited to get an idea about the quantity of generation of fly ash and to get an idea about the types of ash, the disposal of fly ash and to identify their uses in nearby areas. The direct observation method was employed to get an idea about the gravity of environmental problems associated with the fly ash.

Collection of fly ash samples:

The different types of fly ash were observed at Parli thermal power station depending upon their collection and disposal method. The fly ash collected below the boiler called bottom ash. The ash collected at electrostatic precipitator (hopper) called fly ash or ESP fly ash. The collected excess fly ash mixed with the water and slurry has been prepared. The slurry of fly ash was pumped out by using powerful electric pumps to fly ash disposal site i.e. shallow pits or constructed
pond near the thermal power station. The disposed fly ash in such pond called pond ash.

In the present study the three types of fly ash samples were collected from Parli thermal power station for the laboratory exercise viz. bottom ash, ESP fly ash and pond ash.

The fly ash was collected in different categories from the thermal power plant.

- **Dry fly ash (ESP):** The dry fly ash was collected from electrostatic precipitators. After combustion of coal the ash particles are separated in electrostatic precipitators. The charged particles are attracting towards the opposite charged field. By discharging the current the fly ash particles was collected in hoppers.

- **Bottom ash:** The bottom ash mainly contain unburned coal particles with some amount of coal. The bottom ash is collected from the bottom of boilers.

- **Pond ash:** In the electrostatic precipitator the two types of fly ash has been generated i.e. fine quality ash and the rough particle size fly ash. These types of ash are being mixed with water to make slurry and this slurry is directly pumped in fly ash dumping pond, which is constructed near thermal power plant.

These types of ash were collected from Parli thermal power station and used for characterization study reuse and recycle potential study. The samples were collected during the period December 2006 to January 2010.

**3.1 Characterization of fly ash:**

The characterization of fly ash has been carried out in the laboratory. The physical characteristics of the fly ash such as pH, electrical conductivity, moisture content, settling time and water holding capacity were studied in the laboratory. The chemical characteristics such
as oxide of elements present in the fly ash such as silicates, aluminates, iron oxide, calcium oxide, magnesium oxide, titanium oxide etc. were studied.

3.1.1 Physical characteristics of fly ash:

In the physical characteristics of fly ash the shape and size of fly ash particles were studied by using the scanning electron microscope. The particular size was magnified and their size was determined in µmeter. The scanning electron microscopic image indicating the different shape, size and indicating porosity were studied to the fly ash. The morphological features of fly ash nanostructures were studied by using SEM, JEOL JSM 6360 secondary electron imaging.

The physical parameters such as the pH, electrical conductivity, moisture content, settling time and water holding capacity of the different fly ash types were determined by following widely used methods (Trivedi and Goel, 1986, APHA, 1998, Kaul and Gautam. 2000)

3.1.1. a. pH:

The pH of the fly ash leachate was measured by using digital pH meter (Model LI 120, Elico Ltd, India). The sample has been prepared by mixing 10 gram of oven dried fly ash sample in 100 ml distilled water. This solution was stirred, continuously, for half an hour and to determine its pH by using pH meter (Page et al.,1979)

3.1.1. b. Electrical Conductivity:

The electrical conductivity of the fly ash leachate was measured in µS (Siemens)/cm by using digital conductivity meter (Model EI 611, Elico Ltd, India). The sample has been prepared by mixing 10 gram of oven dried fly ash sample with 100 ml distilled water. This solution was stirred, continuously, for half an hour and after settling its electrical conductivity was measured.
3.1.1. c. Moisture Content:

The moisture content of collected fly ash was determined as the weight of water content present in fly ash samples. It is expressed in the unit of percentage.

To determine the moisture content, 50 gm of collected fly ash has been taken. This sample was stored at the room temperature. The initial weights \( W_w \) of fly ash samples were taken. Then the samples were oven dried at 90°C for overnight and the weight \( W_d \) was taken. The loss of water/moisture by evaporation was determined by taking the difference between \( W_w \) and \( W_d \). The moisture content was expressed in percentage unit. The calculation of moisture content of fly ash samples was carried out by using following formula.

\[
\text{Moisture Content (\%) } = \frac{W_w - W_d}{W_w} \times 100
\]

3.1.1. d. Settling time of particles:

Size of the particle is one important factor in determining the rate of settling at which particles settle in the aqueous medium. Layers of sediment can result from different sized particles settling out of the water.

The 5 to 50 gm of fly ash sample at eh interval 5 gm were taken in the measuring cylinder of 100 ml capacity containing distilled water. Mix the distilled water and fly ash thoroughly and make up the volume up to 100 ml. After the mixing allow the particles to settle down. Determine the settling time of particle by using stop watch for the complete settlement of fly ash particle (Vuthaluru, 2010).

3.1.1. e. Water Holding Capacity:

The water holding capacity of fly ash was determined by following method given by Trivedi and Goel, (1986).
3.1.2 Chemical characteristics of fly ash:

The chemical characteristics of fly ash such as its metal oxide components were determined by using XRD technique and their XRD spectrum has been taken. From the XRD spectra the elemental oxides were identified with their quantities.

The X-ray diffraction and atomic absorption spectroscopic techniques were used for the analysis of different metal oxides and metals present in the fly ash samples. The calibration of the equipments has been done by using the 1000 ppm metal standard i.e. “Accu Trace Reference Standards” provided by the Accu Standard, USA which is imported by RECL limited, New Delhi.

The 100 g of fly ash was weighed and mix with 1 liter of distilled water. With the help of magnetic starred the samples was mixed thoroughly for 24 hrs at room temperature. By evaporating some amount of distilled water by boiling the leachate sample was prepared. These samples were analyzed for the metal content by using AAS (Modle SL 163, Elico Limited).

The presences of different metal oxides in the fly ash were studied by X-ray diffractometer (XRD, PhilipsPW-3710CrK _ line). The XRD study has been carried out by using activated dry mass of fly ash. The samples were analyzed in central facility center of Shivaji University, Kolhapur.

3.1.3 Metallic constituents of fly ash:

The metallic constituents of the fly ash collected from thermal power plant were subjected to the study of metallic constituents present in fly ash samples.

Sample preparation:

The samples of fly ash were analyzed by AAS for metallic constituents present in it. The samples were prepared by using acid
digestion technique. The 1 gm of dry weight of each sample of fly ash has been taken for the study. The amount was dissolved in 10 ml 3:1 percent solution of conc. HNO₃ and H₂SO₄ for overnight. Then these samples were shacked thoroughly and digested on hot plate for 30 minutes. If the brown fumes are coming, it indicates the presence of sulphur content present in the sample. Boil the sample till the brown fumes was stopped with continuous addition of conc. HNO₃. (Trivedi and Goel, 1986).

After the completion of digestion cool the flask and add 40 ml double distilled water in to maintain the final volume of the sample to 50 ml. this sample is used for the AAS analysis by diluting it as per the requirement.

**Preparation of standard curve:**

The concentration metals are easily determined by atomic absorption spectrophotometer (AAS). The atomic absorption uses essentially monochromatic radiation to excite vaporized atoms in their ground state the instrument consists of a light source. The light source usually a hallow cathode tube emits essentially line radiation of the same wavelength as that of emitted by the element and easily absorbed and detected in AAS.

The AR grade chemicals were used to prepare the stock solution of each metal which is analyzed in AAS. The series of standard i.e. 10, 20, 30 to 100 ppm was prepared and analyzed in AAS. The standard curve was plot against concentration vs. absorbance.

**Sample analysis:**

The acid digested samples were analyzed in atomic absorption spectrophotometer by using reference metal lamb (Hallow Cathode Lamp). When the samples were aspirated in to the flame the metal ions looses their ground state and emits the radiation at exited state. These radiations are absorbed by the reference source of light produced by a
reference light. The display shows the absorbance of the metal. These readings when plotted on the standard curve from which one can get the amount of metal ion present in the sample from the absorbance value.

The bottom ash, ESP fly ash and disposed pond ash collected from Parli thermal power station were subjected to the analysis of the metals such as arsenic, cadmium, chromium, cobalt, nickel, copper, lead manganese, mercury and zinc. The results were expressed in mg/100gm dry weight of fly ash.

3.2 Potential study of fly ash:

In the present study the adsorption properties of fly ash was used for the removal of metals from the wastewater / contaminated water prepared in laboratory. As a low cost technology fly ash can be potentially used for the removal of selected heavy metals from the aqueous solution effectively. The fly ash may be effectively used for the removal of different pollutants from wastewater.

The adsorption phenomenon of the fly ash can be used for the removal of nickel and zinc from the wastewater or from the aqueous solution of nickel and zinc

Preparation of adsorption material:

The fly ash samples were used successfully for the adsorption phenomenon. The fly ash samples were firstly activated heating in muffle furnace at 400 to 500°C for about 2 to 3 hours. The fly ash samples were treated with excess of ortho-phosphoric acid with constant stirring for the removal of remains of the organic matter in it. The treated fly ash samples then rinse by using distilled water for the removal of excess amount of acid. The acid treatment can increase the adsorption property of fly ash. The fly ash sample was further dried in hot air oven for an hour and used for the removal of selected metals.
The nickel and zinc were selected as a selected metallic ingredients whose aqueous solution of know concentration were prepared in the laboratory by using nickel and zinc water soluble compound such as nickel chloride and zinc sulphate. The laboratory prepared solutions were used for the experimentation of removal of nickel and zinc.

3.2.1 Removal of nickel and zinc at different concentrations:

The concentration of nickel and zinc were prepared from 10 to 100 ppm at the interval of 10 ppm and were subjected to the removal by using the 5 gm treated fly ash.

Experimental procedure:

The nickel and zinc solution were prepared by diluting 100 ppm stock metal ion solution obtained by dissolving 2.744 gm of ZnSO₄·H₂O and 4.049 gm of NiCl₂·6H₂O in 1 liter distilled water provided by Molychem. The different concentration of metals was prepared by diluting the stock solution by using distilled water. This concentration was used for the adsorption study.

The adsorption study was carried out in the 250 Borosil conical flasks. The 5gm amount of fly ash samples were added in the solution. The solution was constantly stirred by using magnetic stirrer / mechanical stirring. After completion of time the sample is allow settling down and supernatant was taken for the analysis of nickel and zinc. By the addition of different dose of fly ash samples and different interval of time the adsorption study was carried out.

Analysis of samples:

The analysis of the samples has been carried out for the determination of nickel and zinc content by using AAS technique (APHA, 1998)
3.2.2 Removal of nickel and zinc at different doses of fly ash:

The nickel and zinc known concentrations of aqueous solutions were prepared in the laboratory and subjected to the removal by using treated fly ash in varying quantities to determine the optimum range of removal of nickel and zinc. From this study one can identify the optimum quantity of treatment fly ash required for the optimum rate of removal therefore the various concentration of nickel and zinc viz. 20, 40, 60 and 80 ppm solution were prepared and subjected to the various quantities of the treated fly ash.

3.2.2.a Removal of nickel and zinc at 20 ppm:

The 20 ppm concentration of nickel and zinc were prepared and were exposed to the various quantities of fly ash ranging from 0.5 gm to 5.0 gm at the interval of 0.5 gm. The solution was exposed up to 30 to 60 minutes and supernatant samples were subjected to analysis of nickel and zinc by using AAS method (APHA, 1998).

3.2.2.b Removal of nickel and zinc at 40 ppm:

The 40 ppm concentration of nickel and zinc were prepared and were exposed to the various quantities of fly ash ranging from 0.5 gm to 5.0 gm at the interval of 0.5 gm. The solution was exposed up to 30 to 60 minutes and supernatant samples were subjected to analysis of nickel and zinc by using AAS method (APHA, 1998).

3.2.2.c Removal of nickel and zinc at 60 ppm:

The 60 ppm concentration of nickel and zinc were prepared and were exposed to the various quantities of fly ash ranging from 0.5 gm to 5.0 gm at the interval of 0.5 gm. The solutions were exposed up to 30 to 60 minutes and supernatant samples were subjected to analysis of nickel and zinc by using AAS method (APHA, 1998).

3.2.2.d Removal of nickel and zinc at 80 ppm:
The 80 ppm concentration of nickel and zinc were prepared and were exposed to the various quantities of fly ash ranging from 0.5 gm to 5.0 gm at the interval of 0.5 gm. The solutions were exposed up to 30 to 60 minutes and supernatant samples were subjected to analysis of nickel and zinc by using AAS method (APHA, 1998).

### 3.2.3 Effect of pH on removal of nickel and zinc at different concentrations:

The pH is one of the important parameters affecting the rate of adsorption of adsorbent. In the present investigation to study the effect of pH on the rate of adsorption of the selected metallic ions i.e. nickel and zinc at the various concentrations were undertaken. The concentrations such as 5 ppm, 10 ppm, 20 ppm and 50 ppm of nickel and zinc were prepared. The pH value of prepared concentrations of nickel and zinc were made in acid and basic medium with the pH values 4, 5, 7.2, 8 and 10. These variables pH range solutions of nickel and zinc exposed to the 5 gm of treated fly ash in each 100 ml aqueous sample. The fly ash was exposed up to 30 to 60 minute and after settlements the supernatant solution were subjected to the nickel and the zinc content analysis by using atomic absorption spectrophotometric method. The percent removal was calculated from the observations by taking the difference between initial concentration of metals and concentration after fly ash treatment and converting it to the percent removal.

### 3.2.4 Effect of exposure period on removal of nickel at different concentrations:

In the removal of metal exposure period may play the role. To identify the relationship of exposure period with the rate of adsorption the present experiment was design.

The 20, 50, 70 and 100 ppm concentration of nickel were prepared and exposed to the 5 gm treated fly ash for the removal. The exposure
time of fly ash was varied from 5 to 30 minute at the interval of 5 minute and after completion of the desired exposure period samples supernatant solutions were subjected to the nickel analysis by AAS method (APHA, 1998). The percentage removals of nickel were determined by using the conversion factor and the difference between initial and final concentration of nickel.

3.3 Use of fly for plant growth:

Fly ash is combustion by product from the thermal power plants containing micronutrients and metallic ingredients. The fly ash contains all natural occurring essential elements as occurs in the soil. Due to which the fly ash also plays the important role in soil reclamation and helps in plant growth.

The fly ash has been used as a source of nutrient for the growth of plants. Therefore the experiment has been design to study the fly ash potential as a source of nutrient necessary for the growth of plants. For this first the physico-chemical properties of the soil were studied along with nutrient status. The nutrient content present in the composting raw material along with the important parameters was studied. The compost was prepared by using composting material and prepared by using pit method (Set –I). The organic composting matter was subjected to prepare the vermicompost by using the earthworm *Esinia foiteda* in vermin box in the laboratory (Set – II). The partial decomposed organic material mixed with the bacterial culture (*Azatobacter sp.*) used for the composting (Set – III) (Menon *et al.*, 1989).

3.3.1 Physical parameters and nutrient content of soil and raw material:

The soil where the effects of fly ash and compost on the growth of plants were studied, the soil and raw material used for the preparation of
compost, their initial parameter were determined in the laboratory. The parameters such as pH, electrical conductivity, organic carbon, nitrogen, phosphorus, potassium, calcium and magnesium content of the soil and raw material were determined in the laboratory by following standard method given by (Trivedi and Goel, 1986, APHA, 1998).

3.3.2 Physical parameters and nutrient content of composts after 15, 30 and 45 days

The compost was prepared from the raw domestic material (garden, household, kitchen waste, street swiping waste etc.) by using different composting technique such as pit composting, vermin-composting and bacterial culture mixed compost. (Maiti and Nandani, 2006)

The prepared compost was subjected to the physical and chemical parameters analysis such as pH, electrical conductivity, organic carbon, nitrogen, phosphorus, potassium, calcium and magnesium. The physico-chemical parameters were determined at the interval of 15 days and the parameters were determined up to 15 to 45 days. From the three observations taken at the interval of 15 days, the mean values of physical and chemical parameters were determined.


3.3.3 Chlorophyll and polyphenol content study in cultivated plant:

To study the effect of fly ash with the prepared compost on the growth of selected plant Pisum sativum and Trigonella foenumgraecum, the mixture of prepared compost along with soil and fly ash was prepared in equal proportion (1:1:1 soil: compost: fly ash). The selected plants were grown on the mixture of fly ash and compost with soil in the laboratory along with controlled containing soil and organic compost.
After 20 to 25 days the plant leaves were taken and their chlorophyll and polyphenol content were determined by following the method described by Adoni et al. (1985), Trivedi et al., 1998.

3.3.3.a Chlorophyll and polyphenol content *Pisum sativum*:

The crop plant *Pisum sativum* was cultivated as control plant in the soil and compost in equal proportion. The experimental *Pisum sativum* were cultivated in the soil, compost and fly ash in equal proportion and used for the cultivation of plant in the laboratory. The three sets were prepared by using three types of compost and the chlorophyll and polyphenol content were determined in them after 20 to 25 days. The chlorophyll and polyphenol content in the controlled and fly ash exposed plant were determined by following the method described by Adoni et al. (1985), Trivedi et al., (1998). The results of chlorophyll and polyphenol were expressed in mg/gm of dry weight of plant tissue.

3.3.3.b Chlorophyll and polyphenol content *Trigonella foenumgraecum*

The crop plant *Trigonella foenumgraecum* was cultivated as control plant in the soil and compost in equal proportion. The experimental *Trigonella foenumgraecum* were cultivated in the soil, compost and fly ash in equal proportion and used for the cultivation of plant in the laboratory. The three sets were prepared by using three types of compost and the chlorophyll and polyphenol content were determined in them after 20 to 25 days. The chlorophyll and polyphenol content in the controlled and fly ash exposed plant were determined by following the method described by Adoni et al., 1985; Trivedi et al., 1998. The results of chlorophyll and polyphenol were expressed in mg/gm of dry weight of plant tissue.

3.4 Occurrence of metals:
The different metallic elements present in earth crust in different forms in different quantities. The smaller quantities of leached metallic ions from the complex or from the earth crust acts as a micronutrient to the living components present in the environment. Therefore it is necessary to assess the occurrence of different micro metallic elements in the environmental components.

In the present study the selected metallic ions occurrence or availability in the soil and different leaving components of study area were undertaken. The metallic components present in soil in vicinity of thermal power station were determined to get an idea about the normal quantities present in the soil.

The bottom ash and fly ash collected from thermal power station were disposed in the fly ash disposal site in the selected nearby areas of thermal power station. To identify the role of fly ash for increasing metallic ions quantity in the surrounding environmental component, the metallic ions present in fly ash were determined. The ash disposal sites samples were collected and analyzed for metallic ions along with surface water, ground water, plant materials.

The sampling was carried out in the year 2009 during rainy season. The polythene bags were used for the collection of plant material and soil samples, whereas the groundwater and leachate were collected in plastic bottles. About 17 different samples containing 5 soil samples, 5 different plant species, 4 ground water samples and 3 leachate samples from the ash pond for the study of occurrence of metals and heavy metal content in vicinity of fly ash dumping sites preset near the thermal power plant.

3.4.1 Heavy metals in disposed pond ash:

The metals present in disposed ash (the slurry in of ash in pond) were determined in the laboratory. The selected metals such as arsenic,
copper, cadmium, lead, mercury and zinc were determined in the pond ash. The ash samples were collected from the fly ash dumping pond. It was digested in acid and subjected to the AAS analysis for the determination of heavy metals (Trivedi and Goel, 1984; APHA, 1998).

3.4.2 Heavy metals in soil samples near fly ash dumping site:

The soil samples were collected from nearby area of thermal power stations where fly ash has been dumped. The collected samples were subjected to the analysis of selected heavy metals contents such as As, Cu, Cd, Pb, Hg and Zn by following the method of AAS as described by Trivedi and Goel, (1984) and APHA, (1998). The results were expressed in mg/100gm soil samples. The 5 soil samples were collected and analyzed in laboratory for the detection of heavy metals.

3.4.3 Heavy metals in ground water samples near fly ash dumping site:

Four groundwater samples in vicinity of the fly ash dumping sites were collected for the analysis of heavy metals. The atomic absorption spectrophotometric method was used to determine the metal content present the ground water samples (APHA, 1998; Kaul and Gautam, 2000).

3.4.4 Heavy metals in the leachate:

During the rainy season the water accumulated in the fly ash dumping pond was sampled for the determination of leached metallic content in the leachate. Total 3 samples were collected from three sites of fly ash dumping pond and were subjected to the analysis of heavy metals viz. As, Cu, Cd, Pb, Hg and Zn by following AAS technique (Maithi, 2004)

3.4.5 Heavy metals content in Plant samples:

The selected plants species viz. Cynodon dactylon Pers., Parthenium hysterophorus Linn., Cassia auriculata. Linn., Lantana
camara Linn., Catharanthus roseus Linn which are growing on the dumped fly ash were studied for the occurrence of heavy metals. The plant may have absorbed the heavy metal content from the fly ash, therefore the plants materials (leaves) were collected from sampling sites. All the samples were subjected for the heavy metal analysis.

The plant materials of collected plant species were washed with tap water thoroughly and the samples were sun dried and oven dried at 80°C for overnight. The dried samples were ground with mortar and pestle. The digestion was carried out in the ratio of 1 g samples powder 10 ml con. HNO₃ and H₂SO₄ in 3:1 proportion and analysis were carried out for As, Cu, Cd, Pb, Hg and Zn by using AAS (Model: Elico SL – 168) (APHA, 1998).

3.5 Heavy metal Pollution Index:

The water quality indices are a useful and relatively easy way to assess the composite influence of overall heavy metal pollution. Quality indices make use of a reproducible series of judgments to compile the effects of all of the heavy metal pollution parameters. For the heavy metal pollution index the method developed by Mohan et al., (1996) was used. The average means concentration of the six heavy metal viz., As, Cu, Cd, Pb, Hg and Zn was used for the heavy metal pollution index. The critical pollution index considered unacceptable is 100.

3.5.1 Metallic constituents present in surface and ground water samples:

The water samples were collected from both surface and ground water (bore well) resources in surrounding areas of Parli thermal power station near fly ash dumping sites by using plastic cans. All the samples are labeled properly for the indication of source of that sample. The
groundwater and surface water samples were collected during monsoon season.

The collected samples were analyzed for different heavy metal content like As, Cu, Pb, Cd, Hg and Zn by using Atomic absorption spectrophotometer (Elico SL – 163). The digestion and concentration of different metals were carried out by using concentrated acids in 1:3 proportions H\(_2\)SO\(_4\) and HNO\(_3\) (Zeng Yei Hseu et al., 2002)

3.5.2 Heavy metal pollution index calculation method:

The quality of water with respect to heavy metal is represented by using heavy metal pollution indices. The HPI is developed in two basic steps and totally based on the weighted arithmetic quality mean method. Establishing a rating scale for each selected parameter giving weightage to selected parameter and by selecting the pollution parameter on which the index is to be based on.

For the calculation of HPI, the different parameters (metals) have great importance and they might extend the pollution index. The other parameters are also importance as various parameters depends on the intended use of the water. The metal such as Arsenic, Copper, Cadmium, Lead, Mercury and Zinc was used for the calculation of HPI.

The HPI is calculated form the following equation

\[
\text{HPI} = \frac{\sum_{i=1}^{n} W_i Q_i}{\sum_{i=1}^{n} W_i}
\]

Where \(W_i\) = Unit Weightage of \(i^{th}\) parameters, \(Q_i\) = Sub index of the \(i^{th}\) parameter, \(n\) = is the number of parameters considered. Weighted arithmetic index method has been used for calculation of HPI. The unit weight \((W_i)\) has been found out by using formula
\[ Wi = \frac{K}{Si} \]

Where \( K \) = proportionality constant, \( Si \) = standard permissible value of \( i^{th} \) parameter. The sub-index of \((Qi)\) of the parameter is calculated by

\[ Qi = \sum_{n=1}^{n} \frac{|Mi - Ii|}{Si - Ii} \]

Where \( Mi = \) is the monitored value of heavy metal of \( i^{th} \) parameter, \( Ii = \) is the ideal value of \( i^{th} \) parameter which is taken from the Indian drinking water specification (Indian Standard, 1991, IS 10500), \( Si = \) is the standard value of the \( i^{th} \) parameter, in ppb.

### 3.6 Recovery of Metals:

The gravimetric techniques were used for the recovery of metals from the fly ash. In this the specified reagents and experimental protocol were used for the recovery of the metals in the compound form. The recovery of nickel and zinc were selected as fly ash has shown comparatively higher quantity of nickel and zinc in certain samples of fly ash.

#### Recovery of Nickel:

An ethanolic solution of DMG quantitatively precipitate Ni++ ions as Nickel dimethyl glyoxime from the neutral or slightly acidic nickel salt followed by addition of excess of NH4, a scarlet red precipitate is obtained. It is washed by hot distilled water dried at 120\(^{0}\)C and weighed as Nickel dimethly glyoxime \([\text{Ni(DMG)}_2]\)
The fly ash leachate sample is taken for the gravimetric estimation of Nickel. The diluted sample was then treated with hot distilled water with addition of dilute H$_2$SO$_4$ and Conc. HNO$_3$. The solution is boiled till the color changes to yellow; this yellow color is due to Iron ions. Then the Ammonium Chloride is added to this solution with content stirring and adds ammonia to precipitate the iron ions from the sample.

Boil the solution; allow the precipitate to settle down. Filter the solution by filter paper. What the precipitate and add few drops of methyl red indicator and acetic acid. When the DMG solution is added with ammonia solution the precipitate of the Nickel is formed. After drying of that precipitate we get the Nickel as Ni(DMG)$_2$. (Gurudeep Raj, 2009)

\[
\text{Wt. of Ni present in Ni(DMG)$_2$} \times 58.69 \times 1000 \times 1000 \\
\text{Nickel} = \frac{288.9112}{\text{Mg/100gm}} \times 25
\]

**Recovery of Zinc:**

Zinc is precipitated as the white double salt, zinc ammonium phosphate. ZnNH$_4$PO$_4$ from finely acidic solution using a solution of diammonium hydrogen phosphate as precipitant. The precipitate is dried at 105°C and weighed.

**Precipitation of zinc:**

The 25 ml of sample is taken in 100 ml distilled water. the conc. HCL was added with few drop of methyl red indicator. The dilute ammonia solution is added to this solution drop wise. The color of solution turns reddish to yellow. Now add solid ammonium acetate, ammonium chloride to this solution and heat the content till boiling, after that the freshly prepared 10% diammonium hydrogen phosphate is added
to this solution. After half an hour the precipitate is form in granular and crystalline form.

**Filtration and washing:**

The precipitate is filter through Gougch crucible and washing of precipitate is done by using 3-4 times with 1% diammonium hydrogen phosphate solution to remove entire chloride content. Finally wash the ppt. with 50% alcohol to remove excess of diammonium hydrogen phosphate from the precipitate (Gurudeep Raj, 2009).

\[
\text{Wt. of Ni present in } \text{ZnNH}_4\text{PO}_4 \times 65.38 \quad \frac{1000 \times 1000}{178.3992} \times 25
\]

**3.7 Zeolites:**

The zeolites are the oxides of silicates and aluminates and present in the nature and having a potential for the diverse use in the chemical reaction and in other applications. The pure form of zeolites has a specified use. The mixture of the different oxides of silicates, aluminates and other oxides of metals also display the similar kind of properties and can be used as catalyst in chemical reaction and can be used specifically for the certain uses such as removal of specified ingredients from the wastewater etc.
3.7.1 Synthesis of Zeolites:

The coal fly ash, the main raw material was collected from the Parli thermal power station (PTPS), Parli (Vaijnath), district Beed of Maharashtra State. The fly ash samples mainly contain amorphous and crystalline content of various metal oxides.

![Flow diagram of hydrothermal synthesis of zeolite](image)

Figure 3.1. Showing flow diagram of hydrothermal synthesis of zeolite

By following the flow chart and mentioned steps below, the zeolites were synthesized in the laboratory from fly ash.

The fly ash samples were passed through different mesh size sieve to avoid the larger particles during the synthesis process. The sieved fly ash was further treated with HCl acid to increase the activity in zeolite formation, because of this the formation of highly active Na-aluminates and silicates, which are readily soluble in water and enhance zeolite formation. The acid also remove the amount of iron present in fly ash to some extent, this will also increases the activity, thermal stability and acidity of zeolite which was aiming for better catalytic applications.
The synthesis of the zeolites is done in following steps.

1. Mixing – The Sodium Hydroxide (NaOH) was mixed in fly ash by maintaining the ratio of 1:2 approximately. The mixture of NaOH and fly ash is mixed thoroughly by using mortar and pestle for half an hour and send for the fusion reaction.

2. Fusion - The well mixed martial of NaOH and fly ash was fused by using steel tray at different temperature ranging from 450 -500°C approximately for 1 hour.

3. Grinding – The fused material mixture was cooled at room temperature. This mixture was grind well in mortar and pestle after that the water is added in this material for further hydrothermal reaction. The water used for this reaction is approximately 1 litre for 100 gm of fly ash used. The slurry was agitated and kept in hot air oven at 90°C for 5 to 6 hours without disturbing it.

4. Agitation – The precipitate generated after the curing stirred at room temperature from several time.

5. Curing – it is remedial step, for treating the slurry the mixture is further heated at 90°C for certain time.

6. Filtration – The filtration of this mixture was carried out by using Whatman filter paper.

7. Washing – The filtrate was washed with hot distilled water to remove excess amount of sodium hydroxide.

8. Drying – The filtrate was dried at room temperature overnight to remove all moisture content.

The dried powder formed after synthesis is zeolite which was ready to use in different applications. The sodium hydroxide added to the fly ash not only works as an activator, but also adjusts the sodium content in the starting material. Mullite and a- quartz present in the fly ash are the sources of aluminum and silicon, respectively, for zeolite formation.
Experimental Setup:

The wastewater collected from the municipal sewers system was subject to the treatment by using the zeolites synthesized from the fly ash. The 100 ml of wastewater samples was taken in 250 ml beaker for the treatment. The 50 mg of synthesized zeolite was added to the sample for the treatment with constant stirring. The zeolite particles provide surface for the adsorption of different organic and inorganic content present in the wastewater samples. After interval of 10 minute interval the sample is analyzed for the different parameter such as COD and BOD and some metallic ions to check the percent removal.

3.7.2 Applications of zeolites:

The synthesized zeolites were used for giving the treatment to the municipal waste water for the reduction of BOD, COD and for the removal of micronutrients.

3.7.2.a Physico-chemical analysis of domestic wastewater

Before the application of the zeolites for giving treatment to wastewater it was necessary to assess the physico-chemical analysis of wastewater. The wastewater was collected from the sewer system and its physico-chemical parameters viz. pH, EC, temperature, turbidity, total alkalinity, total acidity, total hardness, chloride, sodium, potassium, TS, TSS, TDS, COD and BOD etc. were analyzed by using the widely accepted methods (Adoni, 1985, Trivedi and Goel 1986, APHA, 1998, Kaul and Gautam, 2000) , The determined parameters will be considered as reference for the assessment of percent reduction of BOD and COD.

3.7.2.b Use of Zeolites for reduction of BOD:

The collected wastewater was subjected to treatment by using synthesized zeolites. The 100 ml wastewater samples was taken and mixed with 50 mg of synthesized zeolites. The content was mixed for desired time period. The wastewater samples were exposed for various
times period 10 to 100 minutes at the interval of 10 minutes. After the completion of desired time period the supernatant samples was subjected to BOD analysis. The results were compared with the initial BOD values of wastewater and from this observation the percent reduction of BOD was calculated. (Reference)

3.7.2.c Use of Zeolites for reduction of COD:

The collected wastewater was subjected to treatment by using synthesized zeolites. The 100 ml wastewater samples was taken and mixed with 50 mg of synthesized zeolites. The content was mixed for desired time period. The wastewater samples were exposed for various times period 10 to 100 minutes at the interval of 10 minutes. After the completion of desired time period the supernatant samples was subjected to COD analysis. The results were compared with the initial COD values of wastewater and from this observation the percent reduction of COD was calculated. (Reference)

3.7.2.d. Use of zeolites for reduction of BOD and COD at various pH and quantity of zeolites:

The prepared zeolites from collected fly ash samples were used to study the reduction efficiency of BOD and COD at different quantity of zeolites and various pH values. The quantities (dose) of zeolites used were 10, 20, 30 and 40 mg/100ml waste water. Whereas the pH values used in domestic wastewater treatment and after 60 minutes time interval for the reduction of BOD and COD in percentage were recorded at pH 5, 6, 7 and 8.

3.7.2.e Use of zeolites for reduction of micronutrient:

The synthesized zeolites were used in waste water treatment to study the micronutrient reduction efficiency. The synthesized zeolites were used in the quantity of 50 mg zeolites per 100 ml waste water for
the treatment 60 minutes time period. In present investigation the percent reduction in Ca, Mg, Na, K, P and Fe were analyzed (Kumar et al., 2006)