3.1. Study area

Ghaziabad is one of the fastest growing industrial cities of U.P. state (India), situated in the middle of the Ganga-Yamuna doab alluvial plain, lies on the Grand Trunk road and a mile east of the Hindon river between 28° 40’ to 28° 67’ N latitude and 77° 25’ to 77° 42’ E longitude. Ghaziabad District is heavily populated with a total population of 27, 55,000. Out of which 46% population resides in the urban areas, where density is as high as 8630.0person/km² (Census, 2001). A growing Industrial city, also known as Industrial Hub of Uttar Pradesh with 14,160 small-scale and 145 medium/heavy industries, has an important place in industrial development in the state (http://ghaziabad.nic.in/Default.htm).

3.2 Physiography and Climate:

Ghaziabad district is a monotonous flat plain dissected by rivers Hindon and Kali and their tributaries. Ravenous tract is developed along the drainage ways and land resource stand degraded close rivers to Ganga, Yamuna and Hindon. The fertile plain is dotted with barren patches of flat lands which are bare lands having kankar pan at shallow depth and alkaline soil on the surface spread as white sheet. Elevation of the land surface is 220-222m (mean-sea level) in North to 204m in the South and central part. The overall physiography is plain along with slight slap in North-South (Waheed, 2008). The district is endowed with typical tropical climate with extremes in summer as well as winter season. The temperature rises to 40°C or more during May every year, and drops to 5°C during January. The Monsoon goes up to September starting in the middle of June month of the year (http://ghaziabad.nic.in/Default.htm).

3.3 Geological setup:

Geologically territory starts at Southern part, ending with the western edge of Yamuna river ≈35 km., the alluvial deposits of Quaternary age mainly composed of unconsolidated clay, silt, sand with varying proportion of gravel and kankar. Lithological studies suggested that the alluvial deposit in this region belong to older alluvium and comprises of the silt formed as a result of sedimentation during the age of Pleistocene era (Waheed, 2008).

3.4 Sampling and Analytical procedure:
Geographical coordinates (N-latitude and E-longitude) were measured using a calibrated GPS locator model GPS 72H. Collection of different ground water samples carried out from different sites of Ghaziabad in pre-post monsoon season (Table 3.1)

3.4.1 Sampling Methods

A selection criterion was established to get the pin-pointing of appropriate ground water location sites for quality assessment. Hand-pumps which are active, functional and continuously in use for drinking and domestic purposes were selected to collect water samples. Furthermore, sampling network was designed in such a way that selected Hand-pumps represent the whole study area.

A total number of 250 ground-water samples (deep-shallow bore Hand pump, India Mark-II) were collected from the study area. Hundred and twenty five (125) in May-2011, and the same number in November-2011 ground-water samples were collected for representation of pre-post monsoon season respectively. To get the exact scenario of the ground-water aquifer, flushing of water was carried out (for duration of 10 to 15 minutes) to avoid the inactive water. Double distilled water was used to rinse the water container. For heavy metal analysis, water samples were collected in acid pre washed 500ml bottles of polyethylene. Nitric acid was used to preserve the heavy metal samples. At laboratory all the samples were stored at $4^0C$.

3.4.2. Physico-chemical Analysis

A number of physico-chemical parameters were analyzed in the collected ground-water samples as: Conductivity, Resistivity, Salinity, Total Alkalinity( as CaCO₃), Bicarbonate(HCO₃ as CaCO₃), Carbonate, Total Dissolved solid(TDS), Calcium and Magnesium-hardness (as CaCO₃), Total-hardness(CaCO₃), Ammonical nitrogen, Nitrate, Nitrite, Sulfate, Phosphate, Fluoride, Chloride Bromide, Silica, Pottasium, Sodium, Calcium. Among the heavy metals Aluminium (Al), Boron (B), Beryllium (Be), Molybednum (Mo), Nickle (Ni), Tin (Sn), Vanidium (V), Zink (Zn), Magnesium (Mg²⁺), Chromium (Cr-VI, Cr⁷⁺), Iron(Fe-II), Copper(Cu-II), Manganese(Mn) and Lead(Pb-II).

All parameters were determined in the Environmental Chemistry Division laboratory of CSIR-Indian Institute of Toxicology Research Center-Lucknow, following the standard methods (APHA, 2002).
Analytical methods used to analyze various physic-chemical parameters and metal ions in the water samples are as follows:

**3.4.2.1 pH**

pH is expression of hydrogen ion activity in an aqueous solution. pH for the ground water samples were measured at room temperature (25°C) using pH meter (model 744, Metrohm, Switzerland). pH electrode was conditioned using 1M KCl solution and calibrated with buffer solution of pH 4.01, 7.0 and 10.01 respectively.

**3.4.2.2 EC (Electrical-conductivity):**

Electric current passing capability of a sample represents the electrical-conductivity measured either in mili-siemen per centimeter or in micro-siemen per centimeter. Total amount of ions present in a ground-water sample is the measurement of the electrical-conductivity. The measurement was carried out by using the Thermo-Orion (USA, model no. 162A)-conductivity meter at room temperature. Conductivity electrode was calibrated with Orion standard stored at room temperature (1413 µS/cm and 12900µS/cm).

**3.4.2.3 Salinity:**

Electrical-conductivity and total dissolved solid present in a given ground-water sample denote the salinity, measured in parts per thousand (ppt). Salinity of ground water samples were measured at room temperature using multi parameter ion meter (Model Thermo Orion-USA).

**3.4.2.4 Alkalinity:**

Generally denotes the capacity of ground-water sample to neutralize of an acid.

\[
\text{Alkalinity} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+] 
\]

Where [ ] refers to the concentration in moles/L. By convention the alkalinity is not expressed in unit but rather in unit of milligrams as CaCO₃ per liter or normality (eq/L).

The alkalinity determination of ground-water samples were carried out by following the Titration method (Method No. 2320B, APHA, 2002). The method involves the titration of ground-water sample with 0.1 N H₂SO₄ acid by adding Phenolphthalein indicator (end point at pH 8.3 shows the Phenolphthalein-alkalinity) and methyl-orange (end point at pH 4.5 shows total alkalinity) indicator respectively.
3.4.2.5 Total dissolved solid (TDS):

The well shaked ground-water samples were passed through the filter paper (No.42). Filtered sample was subjected to heating in a pre-weighed evaporation-dish till the complete dryness at 180°C temperatures. Total dissolved solid is represented by the weight increased in the evaporation dish.

\[
\text{TDS (mg L}^{-1}) = \frac{(X - Y).1000}{\text{Volume of sample (ml)}}
\]

Where,

\(X=\) weight of the evaporation dish with residue; \(Y=\) weight of empty evaporation dish

3.4.2.6 Total Hardness (mg/L as CaCO₃)

Total hardness was estimated by EDTA Titrimetric method (Method No. 2340C, APHA 2002). Following chemicals were used

**EDTA solution (0.01M)**

3.723g of disodium salt of EDTA was dissolved in 1L of the doubly distilled water.

**Buffer solution:**

(a) 16.9g NH₄Cl was dissolved in 143.0 ml of Conc. NH₄OH

(b) 1.179g EDTA and 0.780g of MgSO₄.7H₂O were dissolved in 50 ml doubly distilled water.

**Eriochrome Black T indicator**

0.5g indicator and 100g NaCl were mixed well.

**Murexide indicator**

0.2g Ammonium purpurate and 100g NaCl were mixed well.

**NaOH (1N)**

40g NaOH was dissolved in 1L of double distilled water.

50 ml of samples were mixed well with 1ml of buffer solution+100-200 mg of Eriochrome Black T-indicator. The solution changed to wine red color. This solution is titrated with EDTA solution till the end point(blue color formation) obtained and note the volume used of EDTA solution.

\[
\text{Total Hardness (mg L}^{-1}) = \frac{(X - Y).1000}{\text{Volume of sample (ml)}}
\]
Where:

\[ X = \text{volume of sample used for titration}; \ Y = \text{mg of CaCO}_3 \text{ which is equivalent to the 1.0 ml of titrant EDTA} \]

**Calcium hardness (mg/L as CaCO}_3\)**

50 ml of sample mixed with 2ml of NaOH solution and 100-200 mg of Erichrome Black t indicator, color of solution changed to pink. Titration of this solution was carried out by the EDTA solution getting the end point color become purple. Calculation was done by using the formula:

\[
\text{Ca Hardness (mg/L)} = \frac{(X - Y) \cdot 1000}{\text{Volume of sample (ml)}}
\]

\[ \text{Mg-Hardness} = \text{Total hardness} - \text{Ca-Hardness} \]

**3.4.2.7 Chloride:**

Chlorides occur in all natural waters in varying concentrations. Concentration is usually greater in ground water than surface water. Chloride was estimated using Argentometric titration-method (Method No. 4500-Cl\', APHA 2002).

50ml of water sample was taken along with blank (distilled water) and 1.0 ml of K\textsubscript{2}CrO\textsubscript{4} indicator was added and titrated by using the Silver nitrate standard solution showing the end point by color changes to pinkish-yellow.

\[
\text{Cl (mg/L)} = \frac{(S - B) \cdot 35450}{\text{Volume of sample (ml)}}
\]

Where:

\[ S = \text{volume of sample in ml}; \ B = \text{Volume of blank sample}; \ N = \text{normality of Silver nitrate solution}. \]

**3.4.2.8 Fluoride:**

The fluoride was estimated by SPADNS method (Method No.4500-F\textsuperscript{-} D, APHA 2002)
Fluoride stock solution

221.0 mg anhydrous NaF was dissolved in 1L doubly distilled water.

Zirconyl acid reagent

0.133 of ZrOCl₂8 H₂O was dissolved in 25 mL double distilled water. 350mL conc. HCl was added and the whole mixture was diluted to 500mL.

SPADNS

0.958g SPADNS was dissolved in 500mL of distilled water.

50mL of water sample was taken in 100mL beaker; 5mL of each SPADNS solution and zirconyl acid reagent were added. The whole content was mixed well and the optical density was measured at 570nm by setting the zero absorbance with reference solution.

3.4.2.9 Nitrate:

Nitrate for the ground water samples were determined by Ultraviolet spectro-photometric screening method (Method No. 4500-NO₃⁻ B,APHA 2002).

Reagents: HCl (1N)

Stock nitrate solution

0.7218g KNO₃ was dissolved in 1000 ml distilled water. 1mL=100µg N. It was preserved with 2ml CHCl₃/L.

50mL water sample was taken. 1mL HCl was added mixed thoroughly. Blank was also prepared is the same way using distilled water. Absorbance was measured at 220 nm using Spectro-photometer against blank. Absorbance at 275nm was also measured to determine the interference of dissolved organic matter. Calibration curve using suitable aliquot of standard nitrate in range 0-7 mg NO₃⁻ nitrogen/L by diluting to 50mL was prepared following the above procedure. Nitrate concentration in water samples were estimated using linear standard calibration plot.

3.4.2.10 Phosphate:

Phosphate was determined using stannous chloride method (Method No. 4500-PD, APHA 2002).

Ammonium Molybdate reagent

12.5g (NH₄)₆Mo₇O₂₄.H₂O was dissolved in 87.5mL double distilled water. 140 mL conc. H₂SO₄ was added to 200 mL double distilled water and cooled. Molybdate solution was added in the cooled mixture and diluted to 1L.
Stannous Chloride reagent

2.5g fresh SnCl₂·2H₂O was dissolved in 100 mL glycerol, heated continuously on a water bath and stirred with a glass rod. 100 mL ground water sample was taken in a conical flask (250 mL). 4 mL Molybdate reagent and 0.5 mL stannous chloride reagent were added. Blue color appeared. Absorbance was recorded by Spectro-photometer at 690nm using double distilled water. Standard calibration curve was prepared by measuring the absorbance of standard phosphate solutions. Phosphate concentration in the water samples were estimated using this linear standard calibration plot.

3.4.2.11 Sulfate:

Sulphate was determined using Turbidimetric method (Method No. 4500-SO₄⁻²-E, APHA (2002).

Reagents

Standard Sulfate solution

0.111g anhydrous Na₂SO₄ was dissolved in doubly DW and diluted to 1L.

Barium Chloride: BaCl₂ crystals.

Buffer solution A

30g MgCl₂·6H₂O, 5g CH₃COONa·3H₂O, 1g KNO₃, 0.111g Na₂SO₄ and 20 mL CH₃COOH were dissolved in 500mL double distilled water and diluted to 1L.

50 ml of ground-water sample diluted to 100 mL. 20 mL of buffer solution and 5g BaCl₂ crystals were added and stirred for 1 minute. Turbidity at 420 nm was recorded on spectro-photometer. Standard curve was prepared by measuring standard sulfate solution absorbance. Sulfate concentration present in water samples were calculated using the linear standard calibration curve.

3.4.2.12 Dissolved Silica:

The dissolved silica content was determined spectrophotometrically at a wavelength of 410 nm by Molybdosilicate method (Method No. 4500-SiO₂ C, APHA 2002). Silica standard were prepared in the range of 5-20mg/L using sodium metasilicate. In 50 mL of each water sample in rapid succession water and HCl added in 1:1 ratio and 2.0mL ammonium molybdate reagent (prepared by dissolving 10gm ammonium molybdate in 100 mL distilled water) was mixed thoroughly and kept for 5-10 minutes.
2mL Oxalic acid solution was mixed properly. Absorbance was taken after 2 minutes but before 15 minutes, measuring time from addition of oxalic acid.

3.4.2.13 Bicarbonate:

The Bicarbonate content was determined titrimetrically. Methyl-orange indicator was added (2 drops) in 20 ml water sample and titrated against 0.02NH$_2$SO$_4$. End point appeared as light pink color. Bi-carbonate concentration was estimated using following expression:

$$\text{Bicarbonate (mg/L)} = \frac{X \times 61 \times 0.02}{\text{Volume of sample (ml)}}$$

Where, x = Volume of titrant used.

3.4.2.14 Major Cations (Na$^+$, Mg$^{++}$, K$^+$, Ca$^{++}$):

The concentration of the alkali metals Na$^+$, K$^+$, Ca$^{++}$ determined on Flame-photometer (ELECO CL 378). Six point calibrations was made by preparing multi-elemental standards of Na$^+$, K$^+$, Ca$^{++}$ varying the concentration 10-100ppm, using 1000mg/L stock solution. Ground water samples were analyzed after successful calibration of Flame photometer.

3.4.2.15 Heavy metals:

Reagents and required chemicals were purchased from Merk (India Ltd). Stock standard solutions of metals were prepared by dissolving ultrapure metals/compounds (99.99 % pure) obtained from Merck, India Ltd.

For the ‘total metal’ estimation water samples were acidified in the field with concentrated HNO$_3$ (5 ml/l of water sample, to reduce the $p^H$ of the sample, $p^H > 2.0$). The total metal content was determined by digesting 200 ml of sample with a mixture of concentrated HNO$_3$ and HClO$_4$ acid (10 ml + 2 ml). Whatman filter paper (no. 42) were used to filter the digested sample, finally volume were made 10 ml with 0.1 N HNO$_3$ and analyzed for heavy metals using ICP-AES (Model Labtam- 8440).

Quality assurance

Analytical methods were assured by using the RSD-relative standard deviation (5 to 10%). All the measurements were taken in triplicate and the average value were
recorded for each measurement. For quantification standard-metals-solution curve were used of desired concentrations.

3.5 Adsorbent-synthesis (Zeolite) for removal of heavy metals:

Panki-thermal power plant-Kanpur (India) was selected for the collection of coal fly ash sample. Analytical grade reagents were used for the synthesis of absorbent. 0.1N H$_2$SO$_4$ and 0.1N NaOH solutions were applied to maintain the pH of the solutions. The amount of the metals in water sample was detected by AAS-atomic absorption spectrophotometer. In the present investigation, fly ash zeolite (FAZ) was synthesized by using the fly-ash, NaOH pellets.

3.5.1 Fusion Methodology

The collected coal flyash sample was subjected to the calcinations (heated at temperature 800$^\circ$C) to remove the volatile and un-burnt carbon. Larger particles were removed by sieving the flyash sample in the 100 mesh size BSS Tyler. Fly-ash and NaOH pellets were taken in 1:1.2(by weight) ration and mixed well to get the homogenous mixture; obtained mixture was heated at 600$^\circ$C for duration of 1 to 2 hours. The fused mass cooled, grind to get powdered form, mixed with distilled water, and then slurry was left for 12 hours (for aging). Crystallization of the obtained aluminosilicate was carried out at 110$^\circ$C for 24 hours. Synthesized material was washed with distilled water by using the vacuum-filtration unit to remove the un-reacted NaOH and dried at 60$^\circ$C for the application (Mishra and Tiwari, 2006).

3.5.2 Characterization of developed zeolite

The formed zeolites were characterized for their surface area, composition and size. The following characterization techniques were used to confirm the formation of zeolite synthesis.

3.5.2.1 Characterization by XRD-analysis:

Different crystalline phase developed in the synthesized zeolite (FAZ) was examined through the X-ray diffraction pattern obtained by the analysis of the material by X-Ray-Diffractometer(Panalytical X-pert pro USA). For integration JCPDS were applied.

3.5.2.2 Characterization by Surface areas:
Surface area of the developed zeolite particles were measured by Surface Area Analyzer (1C-Quantachrome USA) which work on the nitrogen-adsorption-desorption isotherm (Braunauer et al., 1938) by using the BET equation.

### 3.5.2.3 Characterization by SEM:

Surface topography was examined by SEM-micro graph (SEM model LEO 430, Cambridge, England).

### 3.5.2.4 Chemical Characterization (XRF):

For the chemical composition X-Ray Fluorescence Spectrometer was applied.

### 3.6 Batch Adsorption experiment for removal of heavy metals by developed zeolite:

Batch adsorption mode was selected for the equilibrium isothermal studied of heavy metal removal in aqueous solution. Cr-III, Cu-II, Zn-II, Ni-II and Co-II were selected for the mixed metal removal studies. Nitrate salts of the respective metals were purchased from Merk India Pvt. Ltd. In this study 50, 100, 150, 200, 250 and 300ppm concentration were selected for preparation of mixed heavy metal solution, pH 3,4 was adjusted by using the 0.1 to 10M- solution of HNO₃ and -NaOH. It was considered that there were no significant changes in the chemistry of the solution during the adjustment of pH value.

### 3.6.1 Adsorption-kinetics:

100ml of mixed metal solution containing 50,100ppm concentration subjected to adsorption by adding the 0.120g of synthesized zeolite (FAZ) at 3, 4 pH values. Time duration was fixed 10-240minutes for studies. At regular time interval 0.5ml of solution were taken out for metal concentration studies. For filtration Whatman filter paper of 0.45 μm was applied. To get the exact concentration of metals HNO₃ 2% solution were added in the samples to be analyzed by AAS.

### 3.6.3. Adsorption Efficiency/capacity:

It is the measurement of the adsorbed metal per gram of adsorbent (FAZ) and calculated by using the equation:

\[
\text{Removal Efficiency } q_e(\%) = \frac{C_0-C_e}{C_0} \times \frac{V}{m} 
\]

Where;

\( C_0 \) = initial concentration of metal ; \( C_e \) = the equilibrium concentration of metal, \( V \) = volume of solution, \( m \) = zeolite amount in gram. In our study 0.120g of the zeolite were mixed in 100ml metal solution (50 to300ppm) at pH 3.0 for a period of 240 minutes.
Software used

The different software’s (Surfer, Design Expert 6.0) were used in this study is mainly for simplify the environmental problems more accurately.