

## **2.1 INTRODUCTION**

This chapter summarizes the detailed experimental procedure of batch as well as column systems. In addition to it, an overview of the various characterization techniques i.e. Scanning Electron Microscopy analysis, Fourier Transform-Infrared (FT-IR) spectroscopy, X-Ray Photoelectron Spectroscopy, Energy-Dispersive X-Ray Spectroscopy, X-ray diffraction analysis, Brunauer-Emmett-Teller, and Raman spectroscopy which are utilized to characterize the prepared adsorbents have been described. The various models of isotherm such as Langmuir, Freundlich, and Dubinin-Radushkevich isotherm models and their important parameters were discussed in detail. In addition to it several widely used kinetic models were also applied to the experimental data which are also described in this section of the thesis. The experimental procedure of fixed-bed up-flow continuous column experiments along with various kinetic models of the breakthrough curve are explained in this chapter

## **2.2 MATERIALS**

All the chemicals used in the synthesis process and adsorption experiments are of analytical grade and used without further purification. All the reagents and Chemicals used in all the experimental procedure are summarized in Table 2.1. In the present work, the deionized double distilled water (DW) was utilized throughout the experiments. The stock solution of fluoride ion i.e. 1000 mg/L was prepared by dissolving 221 mg of NaF into the 1000 mL of water, and the other test solutions of desired concentration were prepared from stock solution by subsequent dilution. The standard stock solution of lead ion of strength 1000 mg/L was prepared by dissolving 159.8 mg of lead nitrate into 1000 mL of DW water. Further, for the adsorption experiments, different concentration of the solution was prepared from the subsequent

dilution of the stock solution. Table 2.1 represents the list of chemical used throughout this work.

**Table 2.1 List of chemicals used in this work**

S.No	Chemical name	Chemical formula	Molecular weight (g/mol)	Physical appearance	Manufacturer
1	Graphite powder	C	12.0	Dark Grey/solid	Sigma-Aldrich
2	Zirconyl chloride octahydrate	ZrOCl <sub>2</sub> .8H <sub>2</sub> O	322.25	White /solid	Sigma-Aldrich
3	Phosphoric acid	H <sub>3</sub> PO <sub>4</sub>	98.0	Colourless/Liquid	Sigma-Aldrich
4	Sulphuric acid	H <sub>2</sub> SO <sub>4</sub>	98.08	Colourless/Liquid	Sigma-Aldrich
5	Potassium permanganate	KMnO <sub>4</sub>	158.03	solid	Sigma-Aldrich
6	Sodium Fluoride ion	NaF	41.99	White /solid	Sigma-Aldrich
7	Hydrochloric acid	HCl	36.46	Colourless/Liquid	SD Fine
8	Sodium hydroxide	NaOH	40	White/ Pellets	Qualigens
9	Magnesium nitrate hexahydrate	MgNO <sub>3</sub> .6H <sub>2</sub> O	256.41	White /solid	SD Fine
10	Hydrogen peroxide	H <sub>2</sub> O <sub>2</sub>	34.01	Colourless/Liquid	Sigma-Aldrich
11	Lead nitrate	PbNO <sub>3</sub>	331.21	White /solid	Sigma-Aldrich

## 2.3 SYNTHESIS OF GRAPHENE OXIDE

GO was synthesized by a typical process by oxidizing the graphite powder [Zhang *et al.* (2012)]. In the typical process of GO synthesis, Graphite powder (3g) and  $\text{KMnO}_4$  (15g) were mixed in the solution containing concentrated  $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$  (360:40 mL) in 9:1 ratio. The resulting mixture was stirred at  $50^\circ\text{C}$  for 12 h then, it was cooled to room temperature. The cooled reaction mixture was then decanted into a beaker containing ice. Further, 30%  $\text{H}_2\text{O}_2$  (3 mL) solution was added to it and subjected to stirring for another two h. The solid black compound thus obtained was washed with HCl (5%) for 3-4 times and with DW repeatedly till the pH become neutral. For each wash, the material was suspended through ultrasonication and recollected through centrifugation at 10000 rpm for 15 min. In the last obtained product was vacuum dried for 24 h.

## 2.4 CHARACTERIZATION OF THE ADSORBENT

### 2.4.1 Determination of Zero point charge (pHzpc) of the adsorbent

The term zero point charge pH of the adsorbent can be defined as the pH value at which adsorbent acquires zero net charges. It is a unique property of the adsorbent in which surface of the adsorbent is negatively charged above this pH value whereas adsorbent surface bear positive charge below this pH [Mohan *et al.* (2016)]. The pHzpc in this investigation was determined by solid addition method as described by Lataye *et al.* (2006). Initial pH of 0.1 mol/L NaCl solutions ( $\text{pH}_i$ ) was adjusted from pH 2 to 11 by adding either 0.1M HCl or 0.1 M NaOH solutions. In the typical process the specific amount of adsorbent (40 mg) was added to 50 mL of 0.1 mol/L NaCl solution in 150 mL conical flasks and stirred for 300 min, and thereafter the final pH ( $\text{pH}_f$ ) of the

solution was measured. The difference in the initial and final values of pH ( $\text{pH}_f - \text{pH}_i$ ) was plotted against the initial pH ( $\text{pH}_i$ ) and the point at which  $\text{pH}_f - \text{pH}_i = 0$  was taken as the  $\text{pH}_{\text{zpc}}$ .

#### **2.4.2 Scanning Electron Microscopy (SEM) Analysis**

The size and surface morphology of the prepared adsorbent was characterized by scanning electron microscopy (SEM). The SEM analysis is one of the most versatile characterization tool used for the examination and analysis of microstructural analysis of the materials by scanning the surface of materials. The image obtained from the SEM analysis is the three-dimensional appearance of the specimen which is the important feature of the SEM images. SEM analysis utilizes the high energy beam of the electron to generate the signals from the specimen. The microstructure and elemental composition of the prepared adsorbents were examined by Field Emission-Scanning Electron microscopy (FE-SEM, Quanta 200 F EG of FEI, USA)

#### **2.4.3 Energy Dispersive X-ray Analysis (EDX)**

The chemical composition of the adsorbent can be analyzed with Energy Dispersive X-Ray Spectroscopy which is a micro analytical technique that is commonly attached with Scanning Electron Microscopy (SEM). EDX analysis provides the elemental analysis of the small area i.e. in the nanometer range. The electron beam from the equipment when interacting with the specimen produces X-rays that are characteristic of the element present in the specimen. The high energy beam fall on the sample then the electrons are ejected from the atoms of the specimen. The vacant space of the electron are then filled by the higher state electrons, and in this process, X-ray is emitted in order to balance the energy difference between the two

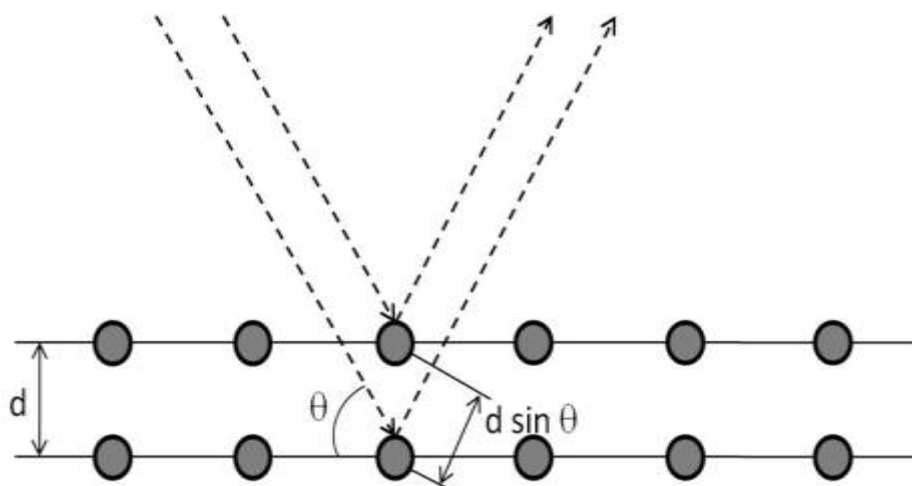
states of electrons. The X-ray energy beam emitted is characteristic of the element from which it was originated. Chemical compositions and purity of the adsorbents were determined by FE-SEM, Quanta 200 F EG of FEI, USA equipped with Energy-Dispersive X-ray Spectroscopy (EDXs).

#### **2.4.4 X-ray Diffraction (XRD) analysis**

X-ray diffraction (XRD) is a rapid, reproducible and non-destructive analytical technique utilized for identification and characterization of crystalline materials [Lu *et al.* (2001)]. It also gives valuable structural information i.e. crystal structure, phase, preferred crystal orientation (texture), crystallinity, average grain size, and crystal defects. This technique is based on the principle that the reflection angle of X-rays from the sample is associated with the crystal structure and composition of the sample. The peaks of the X-ray diffraction pattern are produced by constructive interference of a monochromatic X-rays at specific angles of each set of lattice planes in a sample. Miller indices are very useful for characterizing the unknown materials. Incident X-ray of fixed wavelength is focused on the material at an angle of  $\theta$  to the atomic plane of the crystal. The interaction among X-rays and the electrons of the sample is anticipated by the process of X-ray reflections by the atomic planes. The constructive interference (and a diffracted ray) is produced when incident X-ray interact with the sample when it satisfies Bragg's law, and the generated diffracted X-rays are then diagnosed and counted. This law establish the linear correlation between wavelength, and interplaner spacing of solid sample material can be calculated by Braggs equation written as:

$$n\lambda = 2d\sin\theta \quad 2.1$$

Where  $n$  is an order of reflection i.e 1, 2, 3,  $\lambda$  represents the wavelength of incident radiation,  $d$  is the interplaner spacing and  $\theta$  is the Bragg angle. Bragg's law of diffraction is shown in Figure 2.1.



**Figure 2.1** Bragg's law of diffraction

Where  $D$  is the crystallite size (in nm),  $k$  represents dimensionless constant ( $\approx 0.9$ ),  $\lambda$  is wavelength,  $\beta$  indicates FWHM in radian and  $\theta$  is diffraction angle. International Centre for Diffraction Data (ICDD) is the database of the vast variety of the crystalline materials which enables us the phase recognition of prepared samples. The intensities of the peaks are related to the distribution of the atom in the lattice. Thus, the X-ray diffraction pattern gives the correct conception about the atomic arrangement in a given material. X-ray diffraction spectra in this work were recorded using a MiniFlex2 Goniometer (Rigaku, Tokyo, Japan under 30kV/15mA -X-Ray,  $2\theta/\theta$  –continuous scanning mode within the scanning range  $20-90^\circ$ ) instrument employing

Cu-K $\alpha$  radiation ( $\lambda=1.54059 \text{ \AA}$ ) using Ni-filter. The sample was scanned at the rate of  $4^\circ$ / minute. XRD data were indexed by comparing with standard data reported earlier on the parent compound. Lattice parameters and lattice volume were determined by least square fitting of XRD data using a software program 'Cel'.

#### **2.4.5 Fourier Transform Infrared Spectroscopy (FTIR)**

Fourier Transform Infrared Spectroscopy (FTIR) provides primary specific information about chemical bonding and molecular structure of the materials. FT-IR spectroscopy is a fast and non-destructive technique with minimum sample requirement. When molecules are subjected to infrared radiation chemical bond vibrate at characteristic frequencies as they absorb the radiation of specific frequencies which matches to the frequencies of vibrations between the bonds of the atoms. The increase in the absorption of infrared radiation occur due to alteration in the dipole moment of the molecule and the larger the change in dipole moment more intense will be absorption band observed. In this investigation Spectrum 100, Perkin Elmer spectrometer was utilized to record the IR spectra of the sample in the range of 400 to 4000  $\text{cm}^{-1}$  using KBr pellet method. The absorption in FTIR spectroscopy is expressed in terms of wavelength or wave number. The absorption spectra of the infrared spectroscopy are mostly plotted as transmittance against wave number.

#### **2.4.6 X-ray photoelectron spectroscopy (XPS)**

X-Ray photoelectron spectroscopy is a surface sensitive analytical technique used for the determination of the elemental composition of the parts per million range, empirical formula, chemical state and electronic state of the elements that exist within a material [Yamashita & Hayes (2008)]. This technique based on the

principle of photoelectric effect which involves the binding energy ( $E$ ) of a core level electron is overcome by the energy of radiant X-ray photon. The electron of the core level is excited and ejected from the sample. The kinetic energies of the ejected photoelectron are measured by electron spectrometer and the work function associated with it  $\phi$ . According to the conservation of energy the binding energy of an emitted electron is essentially given by the following equation:

$$E_B = h\nu - E_k - \phi \quad 2.2$$

The binding energy associated with the electron ejected is the characteristic of the orbital from which it is ejected. Furthermore, the binding energy of the photoelectron also depends on the final electronic configuration of orbital after emission of the electron thus it gives important information about the material. It is used for the qualitative elemental identification of the element [Vij (2007)]. In different chemical compounds, the binding energy of inner shell electrons may vary due to differences in chemical or structural configuration [Gresch *et al.* (1979)]. In our work, X-ray photoemission spectra of the sample was executed on a KRATOS (Amicus model) high-performance analytical instrument using Mg K source ( $h\nu = 1253.6$  eV) under  $1.0 \times 10^{-6}$  Pa pressure.

#### 2.4.7 Surface area measurement (BET)

The surface area of the solid material experimentally determined by most common and popular Brunauer-Emmett Teller (BET) method. This technique involves the method which evaluate the surface area of solid materials and is based on physical adsorption of gas molecules [Vanhecke *et al.* (2017)]. BET method involves the cooling of the sample to liquid nitrogen temperatures and exposed to  $N_2$  gas as an



adsorbent. For this study, the specific surface area of the samples was measured using Brunauer–Emmett–Teller (BET) method by Micrometrics, USA, FAP 2020 Model.

#### **2.4.8 Raman Spectroscopy**

Raman spectroscopy is an important tool for the measurement of the wavelength and intensity of inelastically scattered light from molecules. Raman spectroscopy was invented by Sir C.V. Raman and he published the first paper on this sensitive tool with K.S. Krishnan. Raman spectroscopy (RS) is a widely used method for analysis of a broad range of forensic samples. It is based on Raman Effect, i.e. a small fraction of scattered photon having different frequency than that of monochromatic incident radiation.

Raman spectroscopy involves inelastic scattering of incident light through its interaction with vibrating molecules. It act as a probes for the molecular vibrations. Raman spectroscopy has historically played a significant role in the structural characterization of graphitic materials. Raman spectroscopy has been an important tool in such investigations because the Raman spectrum is particularly sensitive to the microstructure of the carbon [Wang *et al.* (1990)]. Raman spectroscopy has been used to analyze the structural and electronic characteristics of graphitic materials, and provide essential information on the defects (D band), the stacking order (2D band, and in-plane vibration of  $sp^2$  hybridized carbon atoms (G band) [Ni *et al.* (2008)].

## 2.5 EXPERIMENTAL PROCEDURE

### 2.5.1 Batch adsorption studies

The literature survey showed that the large extent of the adsorption studies for the removal of lead and fluoride ion are performed in batch mode due to its simplicity. Batch adsorption experiments also provide the introductory information of kinetic and equilibrium adsorption data [Lim & Aris (2014), Nawaz *et al.* (2014) Qaiser *et al.* (2009)]. Batch adsorption studies are generally carried out in the laboratory to obtain maximum adsorption capacity of the adsorbents and to explore important parameters for large scale application [Auta & Hameed (2014), Song *et al.* (2011)]. Batch mode experiments are widely used for the adsorption of metal ions from solution phase for the treatment of small amount of water.

In the batch adsorption experiments the solution of pollutant species was mixed with known amount of the adsorbent, and the mixture was kept under shaking condition. The adsorption process continued until equilibrium between metal concentration in solution and adsorbed concentration of metal is achieved. Equilibrium condition can also be defined as the rate of adsorption become equals to the rate of desorption. Batch adsorption experiment involves the static equilibrium because it does not alter with time [Goel *et al.* (2005), Nguyen *et al.* (2015)]. Once the equilibrium is attained the adsorbent is removed by centrifugation or filtration in order to regenerate it for further utilization. The amount of pollutant ion adsorbed by the adsorbent can be calculated by following equation [Singh *et al.* (2016)]:

$$q_t = \frac{(c_i - c_t) \times V}{w} \quad (2.3)$$

where  $q_t$  (mg/g) is the adsorption capacity of the adsorbent at time  $t$ ,  $C_0$  (mg/L) represents the initial concentration of the adsorbate,  $C_t$  is the residual concentration of the adsorbate after time  $t$ ,  $V$  represent the volume of the solution (L), and  $W$  is the mass of the adsorbent (g).

In this work batch experiments were performed in Erlenmeyer flask containing the specific amount of adsorbent dispersed in 25 ml of aqueous solution of pollutant ions. The pH, metal ion solution, and temperature set at required point. The pH of the solution was adjusted with 0.1 M HCl and 0.1 M NaOH solution. The flask containing reaction mixture was then kept for shaking in the electrically thermostated reciprocating shaker ( Hindco Scientific Ind. Mumbai) at 200 rpm. The progress of the adsorption process was examined at every 10 minutes for a time period of 120 minutes. After that, the adsorbent was removed from the adsorbate and filtrate was analyzed for the residual amount of pollutant ions. All the adsorption experiments were conducted for three times and the mean values of result used in the analysis.

### **2.5.2 Adsorption Isotherms**

At the equilibrium condition of any adsorption system at a particulate temperature there is a definite distribution of adsorbate species at the interface of solid-liquid and in bulk occurs. An adsorption isotherm predicts the relationship in between amount of adsorbate adsorbed and the amount of adsorbate remain in the solution at equilibrium [Hameed & Daud (2008)]. Isotherm study is an important investigation which anticipates the information about the adsorbents surface properties, the behavior of the adsorption, maximum adsorption capacity of the adsorbent and gives parameters to design large scale adsorption systems [Fu *et al.* (2015)]. Therefore, it is necessary to

predict the applicability of correct isotherm for the given adsorption system. For the evaluation of maximum adsorption capacity of the given adsorbent derivation of isotherm modeling is the most suitable and reliable method. Moreover, isotherm studies also help to predict the extent up to which performance of adsorption system can be enhanced but also gives an idea about the operating condition at which system will be more effective.

In the present work Langmuir, Freundlich, and Dubinin–Radushkevich isotherm models were applied to the adsorption equilibrium data to investigate the mechanism properties as well as the distribution of the adsorbate in adsorbent and solution phase.

### 2.5.2.1 Langmuir adsorption isotherm

It is the most widely used isotherm model for the adsorption of pollutant species from aqueous solution. This model assumes that the adsorption surface is entirely homogenous in nature and correspond to the monolayered coverage of the adsorbate molecules. Furthermore, this model also postulates that adsorption energy is constant and once an adsorbate molecule occupies the adsorption site, no further adsorption takes place at that active site. Therefore after saturation point, no further adsorption takes place [Hameed & Daud (2008), Khan *et al.* (2015)]. The Langmuir model in its non-linear form can be written as:

$$q_e = \frac{Q^0 b C_e}{1 + b C_e} \quad (2.4)$$

The linear form of the above equation is:

$$\frac{C_e}{q_e} = \frac{1}{Q^0 b} + \frac{C_e}{Q^0} \quad (2.5)$$

where  $q_e$  (mg/g) and  $C_e$  (mg/L) are the adsorbent pollutant species and equilibrium concentration of pollutant species respectively,  $b$  (L/mg) is the Langmuir constants related to the free adsorption energy whereas  $Q^0$  (mg/g) is also a Langmuir constant which represents monolayer adsorption capacity of the adsorbent. The values of  $Q^0$  will be helpful for the comparison of the adsorption performance of different adsorbent.

Furthermore, another essential characteristic of Langmuir isotherm can be expressed in terms of separation factor ( $R_L$ ) which is the dimensionless quantity and used to estimate the suitability of particular adsorbent. The separation factor is defined by the following equation:

$$R_L = \frac{1}{1+bC_0} \quad (2.6)$$

where  $C_0$  (mg/L) is initial adsorbate concentration, and  $b$  (L/mg) represents the Langmuir constant. The value of  $R_L$  indicate the type of the isotherm: favorable ( $0 < R_L < 1$ ), linear ( $R_L = 1$ ), irreversible ( $R_L = 0$ ), unfavourable ( $R_L > 1$ ) [Fu *et al.* (2015)].

### 2.5.2.2 Freundlich sorption isotherm

Another widely used isotherm model is the Freundlich isotherm model which is derived by assuming the heterogeneous nature of the adsorbent surface with the interaction between the adsorbed molecules. It is appropriate for the highly heterogeneous system. This isotherm proposes that the adsorption energy decreases exponentially at the saturation point of adsorptional centers of an adsorbent [Rangabhashiyam *et al.* (2014)].

The non-linear for of the Freundlich isotherm can be expressed as:

$$q_e = K_F C_e^{1/n} \quad (2.7)$$

Above equation can be linearized to obtain the following equation:

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \quad (2.8)$$

where  $n$  and  $K_F$  represent the Freundlich constant and are the characteristic of the adsorption system. The value of  $k_F$  suggests the relative adsorption capacity and  $1/n$  shows the intensity of the adsorption as an empirical parameter. The value of  $n$  depends upon heterogeneity of the adsorbent, and its value for beneficial adsorption should lie in the range 1–10 [Khan *et al.* (2015)].

### 2.5.2.3 Dubinin–Radushkevich isotherm model

The Dubinin–Radushkevich isotherm is utilized for the estimation of apparent free energy of the adsorption which is the characteristics of the adsorption systems [Rangabhashiyam *et al.* (2014)]. This model is an empirical model applicable for adsorption of subcritical vapors onto porous solids following a pore filling mechanism. It is widely applied to explore the adsorption mechanism of the heterogeneous surface with the Gaussian energy distribution. The isotherm is generally applied to distinguish between the physical and chemical nature of the adsorption of pollutant species with the help of its mean free energy. The linear form of this model can be expressed as:

$$\ln q_e = \ln X_m - \beta F^2 \quad (2.9)$$

where  $X_m$  stands for the maximum adsorption capacity of the adsorbent ( $\text{mmol g}^{-1}$ ) and  $q_e$  is the amount of pollutant species adsorbed ( $\text{mmol g}^{-1}$ ).  $\beta$  is a constant of this model which can be calculated from the slope of the plot of  $\ln q_e$  versus  $F^2$ .  $F$  is the Polanyi potential which is determined by the following equation:

$$F = RT \ln \left( 1 + \frac{1}{C_e} \right) \quad (2.10)$$

where R and T represent the gas constant and temperature respectively. The free energy of adsorption (E) is related with  $\beta$  by the following equation:

$$E = \frac{1}{\sqrt{-2\beta}} \quad (2.11)$$

The value of E is utilized for predicting the type of adsorption, and if its value is less than 8 kJ mol<sup>-1</sup> then the adsorption is physisorption whereas, if the value of E lies in between 8 kJ mol<sup>-1</sup> to 16 kJ mol<sup>-1</sup> then the adsorption show chemisorption behavior and reported to involve ion exchange process [Ghasemi *et al.* (2014), Matouq *et al.* (2015), Hanafiah *et al.* (2014), Pezoti *et al.* (2016), Dissanayake *et al.* (2016), Chathuranga *et al.* (2014)].

### 2.5.3 Adsorption Kinetics

In order to design the treatment plant for the removal of pollutant species from water, it is important to predict the rate at which pollutant is eliminated from the aqueous solutions. Kinetics studies are necessary because it also influences the mechanism of the adsorption. Adsorption kinetics greatly influenced by chemical and physical properties of the adsorbent. Parameters of the adsorption kinetics control the residences time of the uptake of the pollutant species at the solution–solid interface and also give valuable information for the design of water treatment plant [Wang *et al.* (2013)]. Therefore, the experimental data were applied to several kinetic models in order to explore the adsorption mechanism and rate of the adsorption. In this work, the adsorption process was investigated by different kinetic models which include pseudo-first-order, pseudo-second-order, mass transfer, Weber-Morris model, and Richenberg model. These models are most commonly used to describe the adsorption of dyes as

well as other pollutants (heavy metals) on solid adsorbent surface [Zhang *et al.* (2012), Demirbas *et al.* (2009), Doğan *et al.* (2007), Kaur *et al.* (2015), Ranjan *et al.* (2009)].

### 2.5.3.1 Pseudo-First-Order kinetic model

The equation for first-order kinetics model is termed as Lagergren equation [Lagergren (1898)] used for adsorption which is based on the solid capacity of liquid/solid adsorption system. The equation can be expressed as:

$$\frac{dq_t}{dt} = k_s (q_e - q_t) \quad (2.12)$$

Eq. (2.12) can be integrated for the following boundary conditions to obtain Eq. (2.15):

$$t=0, q_t=0 \quad (2.13)$$

$$t=t, q_t=q_t \quad (2.14)$$

$$\log(q_e - q_t) = \log(q_e) - \frac{k_s}{2.303} t \quad (2.15)$$

where  $q_e$  and  $q_t$  (mg/g) is the amount of adsorbate adsorbed on the adsorbent surface at equilibrium and at a time 't' respectively. The rate constant of pseudo first order is represented by  $k_s$  ( $\text{min}^{-1}$ ) which can be calculated from the slope of  $\log(q_e - q_t)$  versus  $t$  plots.

### 2.5.3.2 Pseudo-Second-Order kinetic model

This model postulates that the rate of the adsorption is directly proportional to the square of the active sites of the adsorbent.

This model is expressed as follows [Singh *et al.* (2005)]:

$$\frac{dq}{dt} = k'_2 (q_e - q_t)^2 \quad (2.16)$$



Eq. 2.17 integrated for the following conditions and rearranging to obtain the following equation:

$$t = 0, q_t = 0 \quad (2.17)$$

$$t = t, q_t = q_t \quad (2.18)$$

$$\frac{t}{q_t} = \frac{1}{k'_2 q_e} + \frac{1}{q_e} t \quad (2.19)$$

$$h = k'_2 q_e \quad (2.20)$$

where  $q_e$ ,  $q_t$ , and  $t$  have the same meaning as explained for pseudo-first-order kinetics.  $k'_2$  is the equilibrium rate constant, and  $h$  represents the initial adsorption rate. The parameters involved in this equation can be determined from the plot of  $t/q$  against  $t$ .

### 2.5.3.3 External mass Transfer

The transfer of pollutant species from adsorbate to the adsorbent surface is generally characterized by four process i.e. external mass transfer (boundary layer diffusion), or intraparticle diffusion, or both the process occurred one by one. There are following four steps which contribute in the solid-liquid adsorption process [Mohan *et al.* (2017), Sahmoune & Ouazene (2012)]:

1. Transfer of the pollutant species from the bulk to the periphery of the adsorbent.
2. External diffusion: this is the second step in which diffusion of the solute occurs from the boundary film to the adsorbent surface.
3. Intraparticle diffusion: it is the third step which involves the diffusion of the adsorbate within the intraparticles spaces and pores of the adsorbent.
4. Adsorption and desorption of the pollutant species at the active sites on the adsorbent.

In general, step one assumed to be very fast because this step designed to performed under rapid shaking condition which discriminates the effect of transport of the pollutant species, therefore, this step cannot be rate limiting step. Furthermore, the third step involves the adsorption which is assumed to be a very fast process and cannot be taken into account for the determining rate [Singh & Pant (2006), Hamayun *et al.* (2014)]. Hence; overall rate of the adsorption reaction will be governed by external diffusion or intraparticles diffusion process.

Taking in to account mass transfer process, McKay *et al.* model has been used for this investigation:

$$\ln\left(\frac{C_t}{C_i} - \frac{1}{1+mk}\right) = \ln\left(\frac{mk}{1+mk}\right) - \left(\frac{1+mk}{mk}\right)\beta_t S_s t \quad (2.21)$$

where,  $C_i$  and  $C_t$  (mg/L) represents the initial pollutant concentration and concentration after time  $t$  (min). The  $m$  is the mass of the adsorbent per unit of volume (g/L),  $k$  is the Langmuir constant and  $S_s$  represent the specific surface area of the adsorbent per unit volume of the reaction mixture ( $\text{cm}^{-1}$ ).  $\beta_t$  stands for the coefficient of external mass transfer ( $\text{cm}^2/\text{s}$ ).

#### 2.5.3.4 Intraparticle diffusion

The intraparticle diffusion model also termed as Weber-Morris model and is of great importance as it plays an essential role in the rate determining step. In the batch mode of adsorption, it is possible that adsorbate species transfer into the pores and intraparticles spaces of the adsorbent. Therefore, adsorption kinetic data is also applied to Weber-Morris model in order to ascertain the possibility of intraparticle diffusion to be the rate controlling step. Intraparticle diffusion rate constant ( $k_{id}$ ) at different

temperature can be determined by Weber-Morris model which can be expressed as follows [Sheela *et al.* (2012), Zhang *et al.* (2010), Naiya *et al.* (2009), Wu *et al.* (2011)]:

$$q_t = k_{id}t^{0.5} + C \quad (2.22)$$

Where  $k_{id}$  (mg/gh<sup>0.5</sup>) can be determined by the slope of the plot of  $q_t$  versus  $t^{0.5}$ .

### 2.5.3.5 Richenberg model

The Richenberg model [Richenberg (1953)] is also applied to investigate the possibility of external diffusion and intraparticle diffusion involved in the mechanism and is represented as an equation given below:

$$G = 1 - \frac{6}{\pi^2} \exp(-B_t) \quad (2.23)$$

where  $G = q_t/q_e$  and  $B_t$  is the mathematical function of  $G$ .  $B_t$  can be calculated from respective value of  $G$  given by the following equation:

$$B_t = -0.4977 \ln(1 - G) \quad (2.24)$$

The plot of  $B_t$  vs.  $t$  gives the idea about actual rate determining step of the adsorption.

If the plot does not pass through the origin, then intraparticle diffusion is not the individual rate controlling step.

### 2.5.4 Thermodynamic studies

The thermodynamic evaluation of the adsorption process is necessary because it provides the idea about Gibbs free energy change ( $\Delta G^\circ$ ) which is used to predict the feasibility of the adsorption process. Additionally, other parameters such as enthalpy

change ( $\Delta H^\circ$ ), and entropy change ( $\Delta S^\circ$ ) can also be determined by this study which is used to describe whether the adsorption process is endothermic or exothermic in nature.

Thermodynamic parameters were calculated from the following equation given below

[(Tanhaei *et al.* (2015), Yoon *et al.* (2014), Yagub *et al.* (2014) Kumar *et al.* (2010)].

$$\Delta G = -RT \ln K_c \quad (2.25)$$

where R is the universal gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ), T is the temperature (K).

The equilibrium constant ( $K_c$ ) of the adsorption can be defined as:

$$K_c = \frac{C_{Ae}}{C_e} \quad (2.26)$$

The enthalpy change ( $\Delta H^\circ$ ) and entropy change ( $\Delta S^\circ$ ) is related with free energy change ( $\Delta G^\circ$ ) as given follows:

$$\ln K_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (2.27)$$

The values of  $\Delta H^\circ$  and  $\Delta S^\circ$  can be calculated by the slope and the intercept of the plots of  $\log K_c$  versus  $1/T$  whereas, the value of  $\Delta G^\circ$  values were calculated using Eq. (2.26).

### 2.5.5 COLUMN ADSORPTION STUDY

Batch adsorption studies are commonly employed for adsorptive remediation of lead and fluoride ion. Literature review reveals that generally batch experimentation are employed for the studies of the adsorption of fluoride ion [Cheng *et al.* (2014), Xiang *et al.* (2014), Azari *et al.* (2015), Sun *et al.* (2016), Pandi and Viswanathan (2016), Kanrar *et al.* (2016), Kuang *et al.* ,(2017)] and lead ion [Wang *et al.* (2016), Sui *et al.* (2012), Ren *et al.* (2012), Fan *et al.* (2013) Sun *et al.* (2016)]. Furthermore, batch study

is more convenient and easy to perform at the laboratory scale but is less suitable for large-scale or field application. The batch equilibrium studies provide the fundamental information about the efficiencies of the pollutant adsorption system but these facts are not enough for being applied for the various practical applications (such as continuous mode) [Zulfadhly *et al.* (2001)] where contact time is not sufficient for the establishment of equilibrium. Thus, in order to assess the feasibility of adsorbent for practical application detailed continuous column study is necessary. Various types of continuous systems i.e. continuous stirred tank reactors, moving bed, fluidized bed, and fixed bed are used for adsorption systems. The packed bed column system in comparison to other systems is more convenient and frequently used system as it works like ion exchange column [Aksu (2005)]. The fixed bed column operation explores the way for the treatment of large volumes of polluted water in a very short period of time [Auta & Hameed (2013), Tan *et al.* (2008), Mohammed *et al.* (2016)]. Application of continuous column system found to be a very effective process for the cyclic adsorption-desorption system because it is primarily affected by concentration gradient which acts as a driving force for the adsorption. Therefore, this technique allows the effective and efficient utilization of adsorbent uptake capacity and in turn better quality of treated water is obtained [Charumathi & Das (2012)]. Additionally, the large volume of contaminated water can be continuously treated by employing a definite amount of adsorbent in the column.

The fixed bed column experimentation can be operated in single, series or parallel mode. Furthermore, influent can be subjected to the column in up flow or down flow manner in which down flow mode is the theoretically inexpensive system because

its operating procedure depends upon gravitational force. Whereas up flow systems required a peristaltic pump to pump the influent upward through the packed adsorbent bed and this system involves power consumption. However, down flow system poses many shortcomings which include the little control over retention time of the effluent which is affected by intraparticle spaces, volume of the bed, bed depth of the reactor. So in order to achieve the desired metal concentration the waste water may be subjected to various treatment cycles. An additional disadvantage of this system includes the potential for compaction of the bed with conventional backflow of the waste stream due primarily to increased retention times [Atkinson *et al.* (1998)].

Another very crucial step of the column study is the reuse and regeneration of the exhausted column which is necessary to make the adsorption technology more efficient and economical. Thus, the experiments for the desorption of pollutant ion from the column is essential for the repeated use of adsorbent. Adsorbent captures the contaminant ions either by physical bonding, chemical bonding, ion exchange process or by combination of these bonding. If the adsorption process accompanied by physical bonding then the desorption is generally and easily achieved by the treatment with distilled water. However, acid or alkali solution is used for desorption process in case of chemisorption process. As a consequence, the regeneration study gives clear information about the mechanism of adsorption.

A few literature are available on the fixed bed adsorption of fluoride ion [Paudyal *et al.* (2013), Ghosh *et al.* (2015), Tovar-Gómez *et al.* (2013), Nguyen *et al.* (2015)] and particularly by graphene [Marin *et al.* (2016)]. Similarly, fixed bed column studies of lead ion removal is also very uncommon and very few number of literature is

found to reported the fixed bed investigation [Lim and Aris (2014), Cruz-Olivares *et al.* (2013), Oguz and Ersoy (2014), Nguyen *et al.* (2015a), Nguyen *et al.* (2015b)] specially by graphene-based adsorbent [Islam *et al.* (2014), Zhou *et al.* (2015), Zhou *et al.* (2016)].

Thus keeping all the above facts in mind the adsorptive remediation of fluoride ion and lead ion using rGO/ZrO<sub>2</sub> and GO/MgO nanocomposite respectively in continuous up-flow fixed-bed column system has been conducted and important parameters were evaluated. Additionally, regeneration and reuse studies were also carried out to make it cost effective for repeated utilization.

#### **2.5.6 Fixed bed column adsorption experiments**

The typical set up for the Continuous up-flow fixed-bed column experiment is shown in Figure 2.2. Fixed bed column adsorption experiments were performed in the column made up of borosilicate column with 30 cm height and an internal diameter of 1 cm. The column was packed with known quantity of the adsorbent to achieved the required bed height of the adsorbent. The adsorbent bed was packed in between glass wool layers which were supported by glass beads. The peristaltic pump (Miclins PP-10) was used to pump the pollutant ion solution upward into the column at ( $\pm 30^{\circ}\text{C}$ ). The samples were collected at regular time interval of 10 min and analyzed for the residual amount of pollutant ion. The column operation was stopped when the effluent pollutant ion concentration exceeded a value of 99% of the initial metal ion concentration.

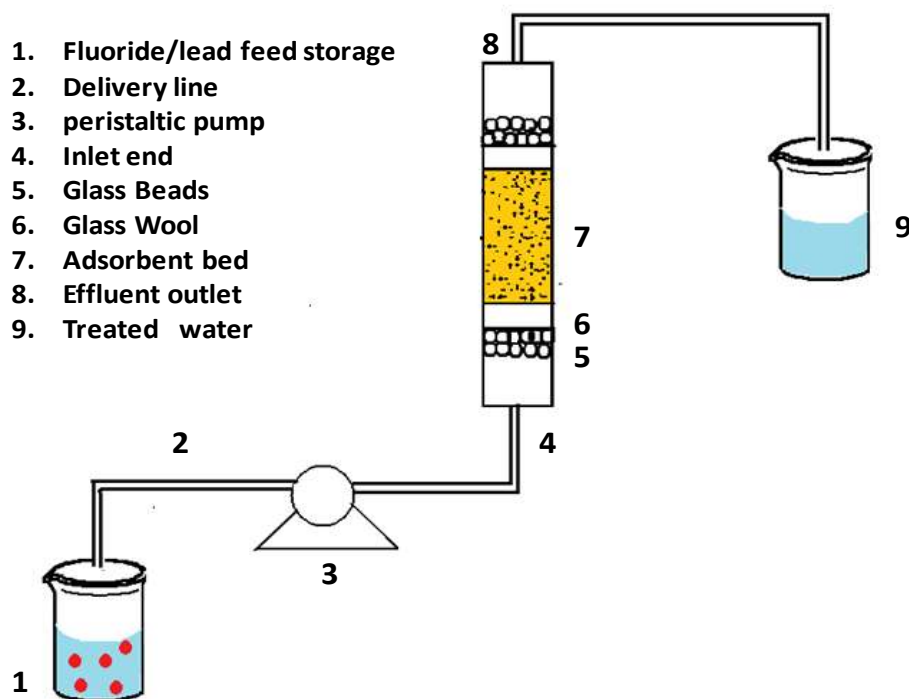


Figure 2.2 Continuous up-flow fixed-bed column experimental setup

### 2.5.7 Desorption and column regeneration studies

The column should be regenerate for the multiple usages. The desorption experiments were also performed on the same column. In the typical procedure of desorption the column bed was washed by deionized double distilled water by the up-flow manner with the same speed as used for adsorption experiments. Furthermore, the 10% NaOH and 0.1 M HCl solutions were used for desorption of fluoride and lead respectively. The reagent for desorption was introduced in upward flow way at a flow rate of 1.66 mL/min. Thereafter, the concentration of pollutant ions was measured at the specific time interval in the effluent. Then the adsorbent bed of the column rinsed with the distilled water until the pH of the effluent become neutral. The regenerated



column was utilized for the another adsorption cycle followed by desorption up to the three consecutive adsorption-desorption cycle to analyze the reusability of the prepared adsorbent.

## **2.5.8 MODELLING AND ANALYSIS OF COLUMN DATA**

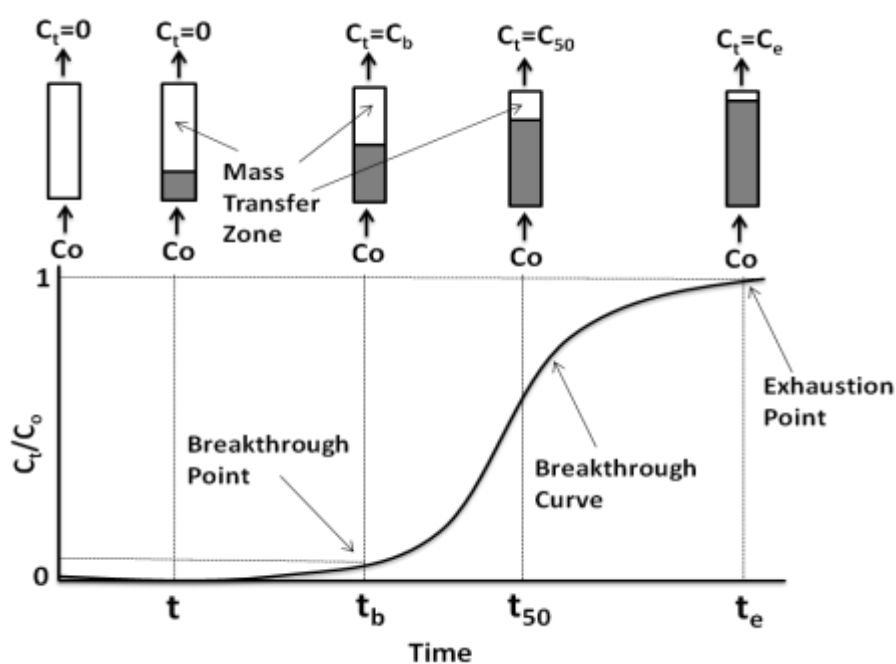
### **2.5.8.1 BREAKTHROUGH CURVE**

The batch adsorption results are of great importance, but the practical utility of the adsorbent for the removal the pollutants from the water is mainly evaluated by the column experiments. In fixed bed column experiments, the adsorbent always remains in contact with the fresh aqueous solution of pollutant ion. The upward flow is more beneficial than down flow because in this system pollutant species stay for a longer time which would result in high uptake of the adsorbent. In the typical setup of fixed-bed up-flow operations, the metal ion solution is added from the lower part of the column, and the spent adsorbate is collected from the top of the column bed. The lower portion of the column bed experiences the highest concentration  $C_0$  of the pollutant ion. With the progress of time, the bottom part of the adsorbent bed becomes saturated with ions and become ineffective for further adsorption. In this system, the equilibrium between ions in the solution and ions adsorbed has never been established at any point of the adsorption because it is dynamic adsorption system and the metal ion solution continuously enter and leaves the column.

In the fixed bed column adsorption system, the breakthrough curve is a very important matter because it provides the clear indication of the breakthrough point. Breakthrough point provides elemental and major information for the design of a large-scale column adsorption system. Without the information of the breakthrough curve

one cannot determine a rational scale of a column adsorption for practical application. Breakthrough time and the shape of the curve are the critical parameters for explaining the behaviour of adsorption column. Breakthrough curve can be defined as the plot of relative concentration of given pollutant ions versus time where the relative concentration can be given as the ratio of concentration at time  $t$  to the initial concentration ( $C_t/C_0$ ). The breakthrough point can be defined as a point with respect to the time where the effluent concentration exceeds the maximum allowable discharge concentration of a specific water pollutant. Whereas another important parameter known as exhaustion point is the exhaustion time or saturation time ( $t_e$ ) which can be stated as the time at which metal concentration in the effluent reached up to 99% of the initial metal ion concentration [Nguyen *et al.* (2015b)]. Fixed bed column study can be operated in single column operation or multiple column operations. The single column system used if the breakthrough curve found to be sharp and steep i.e. breakthrough occurs near the point of column saturation [McKay (1995)] whereas, multiple column is utilized when the breakthrough occurs early than the saturation point [Kundu *et al.* (2004)]. Figure 2.3 represents the typical schematic diagram of breakthrough curve [Calero *et al.* (2009)]. The various characteristic parameters related to the remediation of fluoride ion and lead from water by fixed bed column experiments by rGO/ZrO<sub>2</sub> and GO/MgO nanocomposite respectively were evaluated by different breakthrough models [Hasan *et al.* (2010), Ranjan *et al.* (2009), Wang *et al.* (2015), Sadaf and Bhatti (2014)]. The breakthrough time for this work set to be the time at which pollutant ion concentration reaches 1.5 mg/L and 0.01 mg/L for fluoride ion and lead respectively. These concentration corresponds to the maximum permissible limits of the fluoride ion

and lead. When the effluent concentration exceeded to the 99% of the effluent concentration which is the point of exhaustion and this time is known as exhaustion time.



**Figure 2.3** A typical schematic diagram of breakthrough curve

Effluent volume ( $V_{\text{eff}}$ ) was calculated from the equation given below:

$$V_{\text{eff}} = Q \cdot t_e \quad (2.28)$$

In this equation,  $Q$  represented the flow rate (mL/min), and  $t_e$  is the total time of flow (min). The breakthrough curves can be obtained by plotting the dimensionless concentration  $C_t / C_0$  versus time ( $t$ ) or volume ( $V_{\text{eff}}$ ) of the effluent. The total metal ion adsorbed  $q_t$  (mg/g), by the column at constant flow rate and concentration can be

calculated by integrating the plot of adsorbed concentration ( $C_{ad}$ ) versus the flow time (min) which is given as follows:

$$q_{total} = \frac{QA}{1000} = \frac{Q}{1000} \int_0^{t_{total}} C_{ad} dt = \frac{Q}{1000} \int_0^{t_{total}} (C_0 - C_t) dt \quad (2.29)$$

where  $Q$  is the volumetric flow rate (mL/min),  $q_{total}$  (q mg/g) is the total metal ion adsorbed by the column for a given initial concentration ( $C_0$ ) and flow rate ( $Q$ ) can be found by calculating the area ( $A$ ) under the breakthrough curve which is obtained by integrating the adsorbed  $F$  concentration ( $(C_{ad} \text{ (mg/L)} = \text{inlet } F \text{ concentration } (C_0) - \text{effluent } F\text{-concentration } (C_t))$  versus time  $t$  (min) plot.

The optimization experiments of fixed bed adsorption studies usually carried out at the small scale in the laboratory. The experimental results obtained from experiments can be well interpreted with the help of various mathematical models in order to predict the column performance. [Cruz-Olivares *et al.* (2013), Salman *et al.* (2011)]

#### 2.5.8.2 Bed Depth Service Time (BDST) model

The BDST is one of the widely used models which is used for investigating the adsorption process in fixed bed column studies [Foroughi-dahr *et al.* (2016), Dotto *et al.* (2015), Simate & Ndlovu (2015)]. This model was firstly described and proposed by Bohart and Adams [Bohart & Adams, 1920] and modified by Hutchins [Hutchins (1973)].

This model used to predict the uptake capacity of the column at different breakthrough values and it assumes that the adsorbate is directly adsorbed on the adsorbent surface by ignoring the possibility of the intraparticle mass transfer and external film

resistance. This model predicts the efficiency of the column under constant operating conditions in order to achieve the desired breakthrough point. It gives the simple relationship between the bed depth and service time in terms of process concentration and adsorption parameters. The service time can be defined as the total time period up to which adsorbent is able to adsorb the specific amount of impurity from aqueous solution before regeneration is needed. The service time is the most important parameter to decide the efficiency of the column. First of all the BDST model is given by Bohart and Adams which is given below:

$$\ln \left[ \frac{C_0}{C_b} - 1 \right] = \ln \left[ \exp \left[ \frac{k_a N_0 Z}{u} \right] - 1 \right] - k_a C_0 t \quad (2.30)$$

The original Bohart and Adams model is more complicated because it requires at least nine individual column test for the calculation of the different data which is very lengthy, expensive and tedious process.

Therefore, nowadays the modified version of BDST model is being used because it is more simple and only three column experiments are needed to gather the valuable information. Adams and Bohart equation was modified by Hutchins [Hutchins (1973)] into a linear equation which is given as follows:

$$t = \frac{N_0 Z}{C_0 u} - \frac{1}{K_a C_0} \ln \left[ \frac{C_0}{C_b} - 1 \right] \quad (2.31)$$

In this equation,  $C_0$  and  $C_b$  (mg/L) are the initial and breakthrough concentration of the metal ion.  $u$  represent the linear flow velocity (cm/min) of the adsorbate,  $N_0$  is the capacity of the adsorbent bed,  $K_a$  (L/mg/min) represent the rat constant of the BDST

model,  $Z$  is the bed height (cm) of the column and  $t$  is the time (min). Equation 2.31 can be written as the equation of straight line as:

$$t = aZ - b \quad (2.32)$$

in which

$$a = \text{slope} = \frac{N_0 Z}{C_0 u} \quad (2.33)$$

and

$$b = \text{intercept} = \frac{1}{K_a C_0} \ln \left[ \frac{C_0}{C_b} - 1 \right] \quad (2.34)$$

The chief advantage of the BDST model is that it can be used to calculate the slope of any other flow rate with the known slope of given flow rate which helps in designing of new column for different flow rates without experimentation. Equation (2.33) rearranges by inserting the new slope but intercept remains unchanged as it depends upon the inlet solute concentration. The eq. 5 modified as follows [(Ranjan *et al.* (2009), Mohan *et al.* (2017))]:

$$a' = a \frac{u}{u'} = a \frac{F}{F'} \quad (2.35)$$

Critical bed depth is another important characteristic parameters which is used to predict the column efficiency. It is defined as the theoretical value of bed depth of the adsorbent which is enough to avoid the breakthrough at  $t=0$  and is calculate by the equation given as follows :

$$Z_0 = \frac{u}{K_0 N_0} \ln \left[ \frac{C_0}{C_b} - 1 \right] \quad (2.36)$$

### 2.5.8.3 Thomas model

This model is the most common and widely used model which predict the relationship between time and concentration [Cavas *et al.* (2011)]. This model is one of the most common and widely used to describe the performance theory of the adsorption process in fixed-bed columns. Thomas model assumes the Langmuir kinetics of adsorption–desorption without axial dispersion, and is derived for the adsorption system which obeys second-order reversible reaction kinetics [Muhamad *et al.* (2010), Chu (2010), Gokhale *et al.* (2009)]. Other assumptions of this model involves fixed bed column experience negligible axial and radial dispersion, constant column void fraction, constant physical properties of the adsorbent (solid-phase) and the adsorbate solution, isothermal and isobaric process conditions, intraparticle diffusion and external resistance during the mass transfer processes are considered to be insignificant phase [Kalavathy *et al.* (2010)]. The linearized form of this model can be described by Eq. (2.38):

$$\ln \left[ \frac{C_0}{C_b} - 1 \right] = \frac{K_{th} q_0 m}{Q} - K_{th} C_0 t \quad (2.37)$$

where  $K_{Th}$  is the Thomas model constant,  $q_0$  is the adsorption capacity of the bed (mg/g), and  $t$  is the total flow time (min). The values of  $K_{th}$  and  $q_0$  can be calculated by the linear plot of  $\ln (C_0/C_t - 1)$  Vs.  $t$ .

### 2.5.8.4 Yoon-Nelson Model

The Yoon Nelson Model is a relatively simple model than Thomas model because it does not require comprehensive data about the of adsorbate [Lin *et al.* (2009), Xiang *et al.* (2010), Barron-Zambrano *et al.* (2010)]. This model is based on

the assumption that the rate of decrease in the probability of adsorption for each adsorbate molecule is proportional to the probability of adsorbate adsorption and the probability of adsorbate breakthrough on the adsorbent. It is a model for a single component system, the linearized equation of model expressed as Eq:

$$\ln \left[ \frac{C_t}{C_0 - C_t} \right] = k_{YN}t - \tau k_{YN} \quad (2.38)$$

where  $K_{YN}$  ( $\text{min}^{-1}$ ) is the rate constant and  $\tau$  (min) is the time required 50% adsorbate breakthrough. The parameters i.e.  $k_{YN}$  and  $\tau$  can be calculated from the intercept and slope of the linear plot of  $\ln [C_t/C_0 - C_t]$  vs.  $t$  graph.

## 2.6 Regeneration and reuse of the adsorbent

The regeneration and consequential reuse of the adsorbent is a very important aspect for the industrial applications of the adsorbent in order to reduce the operational cost of the treatment plant. Therefore, for utilization of the maximum efficiency of the adsorbent and for repeated use of adsorbent, the desorption studies should be carried out on the adsorbent. In the process of desorption the adsorb metal ions isolated from the adsorbent surface. However, the process of desorption should not cause any damage to the adsorbent because it will lead the reduction in its adsorption capacity (Volesky (2001)]. For the desorption study of fluoride the column was packed with specific amount of rGO/ZrO<sub>2</sub> to achieve the bed height of 7.5 cm and the flow rate was maintained at 1.66 mL/min and fluoride concentration at 25 mg/L. The NaOH solution (10%) solution was used for desorption fluoride from the rGO/ZrO<sub>2</sub> loaded column bed in up flow way. In the case of lead desorption the loaded adsorbent was eluted with the 0.1 M HCl as a regenerating agent. For this purpose, the column was packed with



sufficient amount of GO/MgO nanocomposite to achieved the bed depth of 7.5 cm while the flow rate and lead concentration kept constant at 1.66 mL/min and 80 mg/L respectively.

## **2.7 Analysis of fluoride and lead in aqueous solution**

The concentration of fluoride in the solution was measured using Thermo Orion expandable ion analyzer EA 940 connected with fluoride ion selective electrode. During the measurement of fluoride ion concentration, the buffer TISAB III was used to maintain optimum pH. For a calibration, purpose solution of different concentration was prepared i.e. 1000, 100, 10, 1, and 0.1ppm. The samples for fluoride ion measurement were prepared by adding 1.0 mL of total Ionic Strength Adjustment Buffer (TISAB) into the 10 mL fluoride ion solution.

The analysis of lead was performed with Atomic Absorption Spectrophotometer, AAS (Shimadzu AA-6300, Japan). The hollow cathode lamp was utilized as the light source and was set at 283.3 nm wavelength for lead ion using 10 mA lamp current, 0.7 nm slit width, and deuterium lamp was used for background correction. In order to generate flame the 98% acetylene delivered at 4.0 L/min at a pressure of 0.9kg.cm<sup>2</sup> together with compressed air supplied at flow rate of 17.5 L/min and 3.5 kg.cm<sup>2</sup> gas pressure. The instrument was calibrated from 0.5 to 5 mg/L which were prepared by successive dilution of the standard stock solution.