

3.1 Introduction

This chapter embodies information regarding various materials used for experimentation, adsorbates and adsorbents, analytical instruments used for characterization of adsorbents, and methods involved all through the research work.

3.2 Materials

Reagent bottles (125 mL), beakers, conical flasks, measuring cylinders, pipettes, burettes, volumetric flasks, test-tubes, mortar-pestle, double distilled water, micropipette have been used during the experiments.

3.3 Reagents

Aluminium sulfate ($\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$), copper sulphate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$), hydrochloric acid (HCl), sulphuric acid (H_2SO_4), nitric acid (HNO_3), sodium perchlorate (NaClO_4), sodium hydroxide (NaOH), potassium hydroxide (KOH) and ammonium hydroxide (NH_4OH) were procured from Merck, Mumbai, India. Cetyl trimethylammonium bromide (CTAB) was purchased from Himedia India. Milky latex of *Calotropis* plant was obtained from fresh leaves of the plants.

3.4 Instruments

For synthesis and characterization of adsorbents various sophisticated analytical instruments were used. X-ray diffractometer (MINIFLEX, RIGAKU), Scanning electron microscope (Quanta 200, FEI), Transmission electron microscope (Technai G2 20 S-TWIN and FEI, Morgagni 268D), Fourier Transform Infra-Red Spectrophotometer (PerkinElmer Spectrum Version 10.03.05), Atomic Absorption Spectrophotometer (Shimadzu AA7000), Centrifuge (REMI PR-24), water bath shaker (Narang Scientific Works, Pvt. Ltd. Delhi), Analytical balance (0.1 mg) (VIBRA), pH meter (IKON) and Tubular Furnace (IKON) were used in present study.

3.5 Adsorbates

An adsorbate is a substance that gets adsorbed on the surface during the process of adsorption. For present study the two adsorbates namely chromium and nickel were selected. The purpose of their selection lies behind the fact that these two metallic species have pervasive applications in different industries and their adverse effects are well known.

3.5.1 Chromium

Chromium (Cr) is the earth's 21st most abundant element and the sixth most abundant transition metal having density of 7.19 g cm^{-3} enlisting it into category of heavy metals. Chromium is one of the most commonly used metals in various industries such as leather tanning, electroplating, mining, paint and pigment formulation, textile dyes, wood preservation, cement, metal finishing, stainless steel, alloys, photographic materials etc.

[Othman et al. 2012; Anirudhan et al. 2013], metallurgical processes [Bansal et al., 2009]. Chromium is used in metallurgy to impart corrosion resistance and a shiny finish; its salts imparts emerald green colour to glass and thus it is used in production of synthetic rubies. Chromium can exist in several chemical forms in nature exhibiting variable oxidation states ranging from 0 to +6 [Sharma et al., 2007]. However, only two of them viz., trivalent and hexavalent chromium are stable enough to exist in the environment. The distribution pattern of chromium species as a function of pH of the aqueous medium is depicted in Figure 3.1.

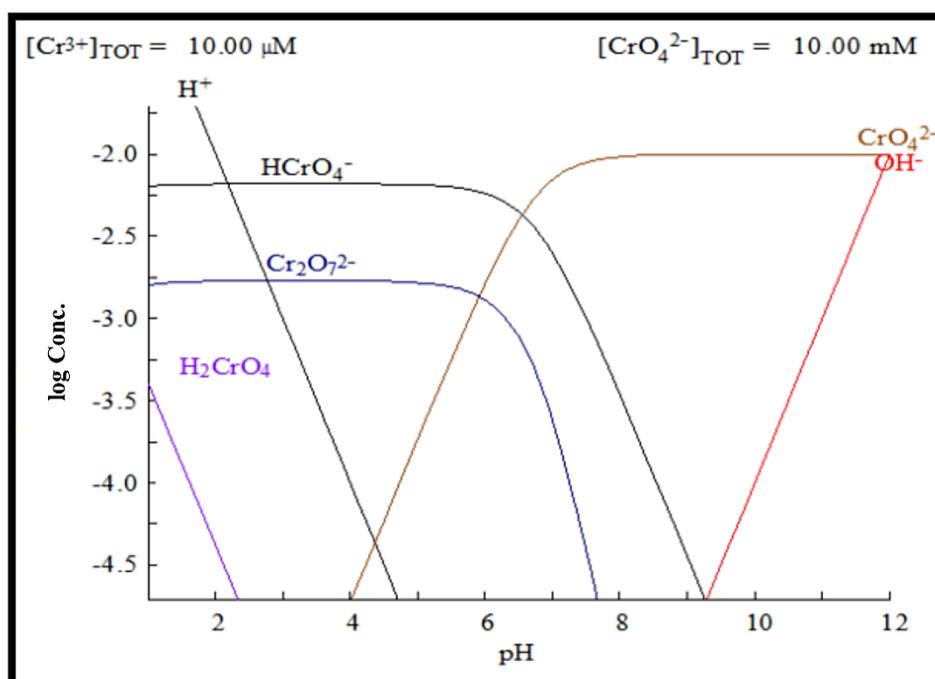


Figure 3.1 Speciation diagram of Chromium

Chromium is regarded as both beneficial and detrimental for living beings. Trivalent chromium (Cr^{3+}) exists in natural waters in various hydrolyzed forms such as

mononuclear species like $\text{Cr}(\text{OH})^{2+}$, $\text{Cr}(\text{OH})_2^+$, $\text{Cr}(\text{OH})_4^-$; neutral species namely $\text{Cr}(\text{OH})_3^0$; and poly-nuclear species such as $\text{Cr}_2(\text{OH})_2$ and $\text{Cr}_3(\text{OH})_4^{5+}$ [Mohan et al., 2005; Mohan et al., 2006]. Cr(III) is insoluble and is recognized as an essential micronutrient for living beings that combine with various enzymes necessary for transformation of sugar, protein and fat in the body. It is also used in a number of commercial products, including dyes, paint and pigments formulation, salts used in tanneries, etc.

Hexavalent chromium (Cr^{6+}) on hydrolysis produces only neutral and anionic species, predominantly CrO_4^{2-} , HCrO_4^{2-} , and $\text{Cr}_2\text{O}_7^{2-}$ depending upon the pH of the medium. It is reported to be 500 times more toxic than Cr(III) and known to be carcinogenic and mutagenic [Sharma et al., 2007; Bhattacharya et al., 2008]. The health hazards associated with it has been tabulated in Table 1.3. Besides, it may also cause a number of health troubles including perforation of nasal septum, renal tubular necrosis, bronchitis, dermatitis, vomiting, liver and kidney disorders, etc. Skin contact may result in systematic poisoning damage or even severe burns and interference with the healing of cuts or scrapes. Eye exposure may cause its permanent damage [Mohan et al., 2006].

The maximum permissible limit of chromium in wastewater is 5 mg/L for trivalent chromium [Acar and Malkoc, 2004]. And the tolerance limit of hexavalent chromium is 0.1 mg/L for discharge in to surface inland water and 0.05 mg/L for potable water [USEPA, 1990].

3.5.2 Nickel

Nickel (Ni) is the 24th most abundant element in order of natural abundance in the Earth's crust [Krishnamurti, 1991; Kanan, 1990] comprising about 3% of the composition of earth. Nickel is 5th most abundant element by weight and is a member of transition series having density of 8.908 g cm⁻³. Nickel is a silvery-white metal with a slight golden tinge that takes a high polish. The chief ores of nickel are arsenides and sulphides. It is one of only four elements that are magnetic at or near room temperature. Although it can exist in several different oxidation states but Ni²⁺ is the only prevalent and important oxidation state in aqueous chemistry of nickel as shown in its speciation diagram (Figure 3.2).

Nickel and its compounds have many commercial and industrial applications. It is extensively used in different industries such as electroplating, steel industries for making stainless steel and high temperature and corrosion resistant other nickel alloys, storage battery, porcelain enameling, metallurgical and chemical operations, food processing, pigment [Padmavathy et al., 2003; Malkoc, 2005]. Additionally, some nickel salts such as nickel chloride, sulphate, nitrate, carbonate, hydroxide, acetate and oxides are of great commercial importance [Grandjean, 1984; Clarkson, 1988]. Nickel is also present in petroleum residue. It is frequently used as a catalyst in hydrogenation reactions. In spite of being an essential micronutrient for animals and involved in the synthesis of vitamin B₁₂, it exhibits toxic effects at high concentrations [Cempel and Nickel, 2006]. Higher concentration of nickel is reported to cause several health hazards. The primary target organs for nickel-induced systemic toxicity are the lungs, kidney, cardiovascular system, the immune system and blood [Young, 1995; Coogan et al., 1989; Nielsen et al., 1999].

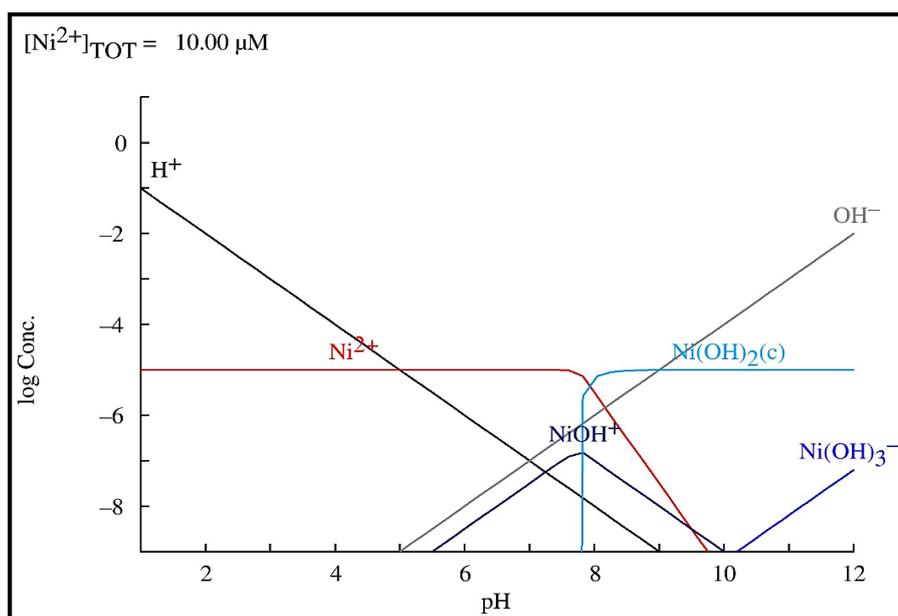


Figure 3.2 Speciation diagram of Nickel

It exhibits pathological effects such as skin allergies, lung fibrosis, cancer of the respiratory tract and iatrogenic nickel poisoning [Clarkson, 1988; Kasprzak et al., 2003], hepatic toxicity, nephrotoxicity, produce haematological effects in both animals and humans. Many harmful effects of nickel are due to the interference with the metabolism of essential metals, such as Fe(II), Mn(II), Ca(II), Zn(II), Cu(II) or Mg(II), which can suppress or modify the toxic and carcinogenic effects of nickel. The toxic functions of nickel probably result primarily from its ability to supplant other metal ions in enzymes and proteins or to bind to cellular compounds containing O-, S-, and N-atoms, such as enzymes and nucleic acids, which are then hindered [Scott-fordsmand, 1997, Clarkson, 1988]. Nickel has been shown to be immune-toxic, causing contact dermatitis or asthma [Clarkson, 1988]. Even though nickel is insoluble, many nickel salts are readily soluble in water and hence water contamination by nickel is common. The permissible limit of

Ni(II) in drinking water is 0.01 mg/L and for industrial wastewater is 2.0 mg/L [Sharma et al.,1992].

3.6 Adsorbents

Adsorbents are the materials that have the ability to extract certain substances from gases, liquids, or solids by causing them to adhere to its surface without getting any change in their physical properties. For the current study two materials were selected as adsorbent namely nano-alumina and nano-cupric oxide for removal of selected adsorbates based on the perusal of the literature.

3.6.1 Nano-alumina (n-Al₂O₃)

Alumina has been considered as one of the most promising advanced materials for a variety of applications due to its distinctive chemical, mechanical and thermal properties. It is isostructural with gamma-Fe₂O₃ and perhaps the most important nanomaterial used as a support for metal catalysts [Shirai et al., 2009]. Alumina and nano alumina powder both have variety of applications in electronics, medicines and industries. Alumina has unique properties such as resistance to aggressive media and hardness. It can be used at high pressure and at high temperature conditions without changing its function. It has many applications in fire retard [Laachachi et al., 2009], catalyst [Lukić et al., 2009], insulator [Touzini et al., 2007], surface protective coating [Keyvani et al., 2010], and composite materials [Lach et al., 2011], polymer science; and in research [Dorre and Hubner 1984; Munro, 1987; Valente et al., 2004; Watchman and Hubner, 1990; Park et al., 2005; Ksapabutr et al., 2004].

3.6.2 Nano-cupric oxide (n-CuO)

Cupric oxide (CuO) nanoparticles are of particular interest because of their interesting properties and promising applications in many important areas. Copper oxide nano powder is a black and incombustible material which is insoluble in water, but soluble in acids. This material has been used in various applications such as microelectronic, microcircuits, nanowires, microbacteria and nanofluids. Copper oxides, especially, which are p-type semiconductor have been widely used as heterogeneous catalysts in oxidizing processes of organic synthesis [Ebbesen and Ajayan, 1992; Bordiga et al., 2001]. It is also used in polymers to increase their electrical conductivity, as well as in car industries to reduce pollution, batteries, super-capacitors, solar cells, gas sensors, bio sensors, nanofluid, catalysis, photodetectors, energetic materials, field emissions, super-hydrophobic surfaces. One of the most important applications of this powder is replacement of expensive catalysts such as platinum and palladium. The application of CuO as an adsorbent has been explored by various research groups for removal of arsenic and organic pollutants from waste water and findings suggested that properties such as high surface area, high point of zero charge, unhindered performance in presence of competing ions, and no requirement of pH adjustment enable it to be used as affective adsorbent material [Abdizadeh et al., 2011].

3.7 Analytical procedures

3.7.1 Batch adsorption experiments

Batch mode of experimentation was conducted for determination of selected metallic species viz. chromium and nickel as adsorbates from aqueous solutions. Stock

solutions of both the metals ions were prepared by dissolving requisite amount of their respective salts in 1000 ml of distilled water. Thereafter, working solutions required for experiments were prepared by dilution of respective stock solutions. The requisite pH of the solutions was maintained with the help of 0.1 N HCl/NaOH. The ionic strength of the aqueous solutions of metallic ions was maintained at 1.0×10^{-2} M by NaClO₄. For batch adsorption, 50 ml of metal ion solution of different concentrations were taken in different reagent bottles of 150 ml capacity and then appropriate amount of adsorbent was added in each bottle containing solution and the resulting suspension was equilibrated by shaking at 90 rpm at a fixed temperature in a temperature controlled water bath shaker for desired period of time. After equilibration, adsorbent was separated from solution by centrifugation at 10000 rpm for 10 min. The supernatant was decanted and residual concentration of chromium/nickel was analyzed with AAS.

The adsorption capacity (q_e) and removal (%) were calculated by using following equations [Sharma et al., 2008]:

$$q_e = (C_i - C_e) / W * V \quad (3.1)$$

$$\text{Percent removal of Metal ion (\%)} = (C_i - C_e) / C_i * 100 \quad (3.2)$$

where, W is the mass of adsorbent used (g), V is the volume of the metal ion solution (L), C_i and C_e are liquid phase concentrations of metallic ions (mg/L) initially and at equilibrium, respectively.

Each experiment was carried out in triplicate and average values were used for modelling and optimization.

3.7.2 Design of experiment (DOE) for optimization of experimental parameters

Conventional and classical methods of studying a process by maintaining other factors involved at an unspecified constant level does not depict the combined effect of all the factors involved. This method is also time consuming, protracted, labour-intensive and requires a number of experiments to determine optimum levels, which are unreliable. These limitations of a classical method can be eliminated by optimizing all the affecting parameters collectively by statistical experimental design such as response surface methodology (RSM). The application of statistical experimental design techniques in sorption processes could result in improved product yields, reduced process variability, closer confirmation of the output response to nominal and targeted requirements, as well as reduced development time and overall costs.

3.7.2.1 Response surface methodology (RSM)

Response surface methodology is a statistical approach that combines various statistical and mathematical techniques for optimization of any process in which the response of interest is governed by several independent variables [Ravikumar et al., 2005]. The objective of this approach is the modelling of experimental data acquired from pre-defined experimental design and optimization of the response controlled by various process parameters [Ghorbani et al. 2008]. It is able to optimize all of the pertinent parameters and omitting restrictions of a single-factor optimization process [Ferreira et al., 2009]. This methodology of optimization includes following three considerable steps viz., performing the statistically designed experiments and investigating the response of

such combinations, estimating the coefficients in a mathematical model that best fits the experimental conditions and predicting the responses and examining the sufficiency of the fitted model [Montgomery 2012]. Furthermore, RSM helps to specify the relationships between output variables called responses (Y) and input variables called factors (X_i s) [Reddy et al. 2008].

$$Y=f(X_1, X_2, X_3, \dots, X_n) \quad (3.3)$$

3.7.2.2 Box-Behnken design (BBD)

Box-Behnken design (BBD) of RSM which was employed to optimize the removal process of adsorbate molecules on the surface of adsorbent particles is a spherical and revolving design which requires experiment number according to $N = k^2 + k + cp$ where k is the factor number and cp is the replicate number of central point [Souza et al. 2005]. On account of its reasonable design and excellent outcomes it has led researchers to adopt it frequently for process optimization. This design emphasizes cubic points which leads to only 3 degrees of freedom (-1, 0, +1), where -1, 0 and +1 are the minimum, central and maximum coded cubic values, respectively [Kumar et al. 2009]. According to the prediction of BBD model of RSM in a MINITAB16 software, a total of 15 experiments are required to be performed to calculate 10 coefficients of second-order polynomial equation and to optimize the levels of selected variables under study such as, initial metal concentration, pH of the solution and adsorbent dose. It minimizes the number of factorial combinations required to evaluate the effects of factors on a response. Furthermore, RSM is advantageous due to its appropriate possibility in making various

projections, providing graphical illustrations. Thereby, this method provides visual interpretation of the functional relations between the response and experimental variables [Zinatizadeh et al., 2010; Yang et al., 2009].

For the purpose of statistical computations, the three selected independent variables were typified as concentration of solution (x_1), pH of solution (x_2) and adsorbent dose (x_3) respectively. The level and range of the experiments are selected on the basis of preliminary experiments and are listed in Table 3.1, and the percent removal of Cr (VI) was selected as dependent variable.

In the optimization process, the responses can be simply related to chosen factors by linear or quadratic models. A quadratic model, which also includes the linear model, is given as:

$$Y = a_0 + \sum a_i X_i + \sum a_{ii} X_{ii}^2 + \sum a_{ij} X_i X_j + e \quad (3.4)$$

where, Y is the predicted response, X_i and X_j are the coded independent variables related to the factors, a_0 is the constant coefficient, a_i is the i th linear coefficient, a_{ii} is the i th quadratic coefficient and a_{ij} is the different interaction coefficients of the model, and e is the error of model.

Table 3.1 Experimental ranges and levels of independent factors

Factors		Ranges and levels		
		-1	0	+1
Concentration (ppm)	x_1	5	15	25
pH	x_2	2	6	10
Dose (g/L)	x_3	2	6	10

3.7.2.3 Analysis of variance (ANOVA)

The data resulted from the regression equation are then verified by analysis of variance (ANOVA) by fitting the data of all independent observations in response surface quadratic model. The analysis of variance (ANOVA) study is extensively used for evaluation of the significant main and interaction effects of various factors affecting the removal efficiency of the process as well as for statistical validation of the adequacy of response surface models. It consists of comparison between the variation due to the treatment (change in the combination of variable levels) and the variation due to random errors inherent to the measurements of the generated responses [Bezzer et al. 2008]. This comparison assists in the evaluation of the significance of the regression used to anticipate responses considering the sources of experimental variance. The significance of each coefficient term is determined by the values of F and P, and the larger the value of F and the smaller the value of P, the more significant is the coefficient [Jain et al. 2011].

3.7.2.4 Surface plots, Contour graphs and Optimization plot

The graphical explication of the interactions of the result of experimentation was generated and presented in the form of contour and surface plots by Minitab Software. Surface plots and contour plots provide assistance in understanding the relationship between the response and experimental levels of each variable under investigation. Surface plots are graphs that can be used to explore the potential relationship between three variables. The predictor variables are displayed on the x- and y-scales, and the response (z) variable is represented by a smooth surface (3D surface plot). A 3D surface plot displays a 3-dimensional view of the surface useful for establishing desired response values and operating conditions. 3D surface plots can provide a clearer concept of the response surface than contour plots. Contour plots exhibit the 3-dimensional relationship in two dimensions, with x- and y-factors (predictors) plotted on the x- and y-scales and response values represented by contours. A contour plot is like a topographical map which provides a 2-dimensional view of the surface where points that have the same response are connected to produce contour lines of constant responses. Contour plots are useful for establishing the desired response values and operating conditions.

An optimization plot is an optimal solution plot that shows how different experimental settings affect the predicted responses. The optimization plot shows the affect of each factor (columns) on the responses or composite desirability (rows). The vertical red lines on the graph represent the current factor settings. The numbers displayed at the top of a column show the current factor level settings (in red). The horizontal blue lines and numbers represent the responses for the current factor level.

3.8 Adsorption isotherm experiment

The analysis of adsorption isotherms is indispensable in understanding the sorption mechanism, surface properties and the affinity of the adsorbent in addition to designing the adsorption process model [Gusain et al., 2014]. By means of batch mode of equilibrium analysis relating to quantity of adsorbate adsorbed on the surface per unit weight to the concentration of adsorbate remaining in the solution can be calculated. For isotherm studies, prefixed amount of different adsorbents were added into reagent bottles containing 50 mL of different concentration of adsorbate solutions. All the reagent bottles were then shaken in a water-bath thermostatic shaker at certain defined temperature (303, 313, 323 and 333 K) for adsorption to reach equilibrium. Different isotherm models have been developed for describing the sorption equilibrium among which two most frequently used isotherms namely Langmuir and Freundlich are used to analyze the behaviour of adsorbate-adsorbent couple at equilibrium.

3.8.1 Langmuir isotherm model

The Langmuir isotherm is probably the best known and most widely used isotherm model which is based on the assumptions of monolayer coverage of adsorbate at specific homogeneous sites on the adsorbent's surface without having any interaction. Under specified conditions, once the surface sites get fully occupied with adsorbate molecules, no further adsorption occurs on the sites and eventually the surface sites acquire saturation.

The non-linear equation for Langmuir isotherm is represented as follows [Langmuir, 1916]:

$$q_e = b Q^0 C_e / (1 + b C_e) \quad (3.5)$$

where, C_e (mg/l) is the equilibrium concentration of the solute, q_e (mg/g) is amount adsorbed at equilibrium, Q^0 (mg/g) is the adsorption capacity related to monolayer coverage and b (L/mg) is the Langmuir constant related to the affinity of the binding sites and energy of adsorption, the higher the value of b , the higher the affinity of the binding sites. The linear form of the model is given as [Srivastava et al., 2008].

$$C_e/q_e = 1/Q^0 b + C_e/Q^0 \quad (3.6)$$

The value of Q^0 and b can be determined from the slope and intercept of the plots of C_e/q_e against C_e , respectively.

3.8.2 Freundlich isotherm model

The Freundlich isotherm is applicable for non-ideal multi-layer adsorption with a uniform energy distribution and reversible adsorption on heterogeneous surfaces where the possibility of adsorption onto adsorbate saturated sites still exists. It can be expressed as follows [Allen and McKay, 1980]

$$q_e = K_F C_e^{1/n} \quad (3.7)$$

The logarithmic form of the above equation is as shown as:

$$\log q_e = \log K_F + 1/n \log C_e \quad (3.8)$$

where, q_e is the equilibrium concentration of solute on adsorbent (mgg^{-1}), C_e is the equilibrium solute concentration (mgL^{-1}), K_F (mgg^{-1}) (Lg^{-1}) $^{1/n}$ is the Freundlich constant

related to sorption capacity and $1/n$ is the surface heterogeneity factor that takes the value closer to zero in heterogeneous surface ($1/n < 1$ indicates normal Langmuir isotherm while $1/n$ above 1 indicates bi-mechanism and cooperative adsorption) [Pandey et al., 2010].

The value of K_F and $1/n$ can be calculated by the slope and intercept of the plot of $\log C_e$ vs $\log q_e$. After finding the value of $\log K_F$, its antilog is found out to determine K_F . Low n value indicates high adsorption at strong solute concentration.

3.9 Adsorption kinetic experiments

The prediction of adsorption kinetics is imperative in designing and modelling of industrial adsorption processes. The kinetic parameters derived from kinetic study which delineate the rate of adsorbate uptake on the adsorbent by following an appropriate pathway with the passage of time provide useful information regarding the adsorption processes. Adsorption process, in general is supposed to be administered by one or more steps such as any possible chemical reaction, diffusion and mass transfer processes, etc. and in order to examine its mechanism and kinetics as well as potential rate-controlling steps, pseudo-first order model, pseudo-second order model, Weber-Morris intra-particle diffusion model are most frequently employed [Uma et al. 2013]. Kinetic experiments were identical to the equilibrium tests. 50 mL adsorbate solutions were shaken with requisite amount of adsorbent and were taken out of the water bath at preset time intervals and the concentrations were analyzed.

3.9.1 Pseudo first order model

This was the first equation for explaining the sorption of liquid/solid system based on adsorbent capacity. The Lagergren's pseudo-first-order equation can be expressed as [Lagergren, 1898]:

$$dq/dt = k_1 (q_e - q_t) \quad (3.9)$$

The integrated form of above equation is expressed as follows [Gusain et al., 2014]:

$$\ln (q_e - q_t) = \ln q_e - k_1 t \quad (3.10)$$

Non-linear form of the equation can be written as [Gusain et al., 2014]:

$$q_t = q_e (1 - \exp(-k_1 t)) \quad (3.11)$$

where, $k_1(\text{min}^{-1})$ is the first order rate constant, q_e and q_t are the amount of adsorbate species adsorbed on adsorbent at equilibrium and at any time, t , respectively. The values of k_1 are evaluated from the slope of the graph between $\log (q_e - q_t)$ vs t at different temperatures.

3.9.2 Pseudo-second-order model

Pseudo-second order model is most widely used and is based on the assumption that the rate limiting step is chemi-sorption in nature. The model is mathematically represented as follows [Ho and McKay, 1998]

$$dq/dt = k_2 (q_e - q_t)^2 \quad (3.12)$$

The linear form can be represented in integrated form as follows [Ho and McKay, 1998]

$$t/q_t = 1/k_2q_e^2 + t/q_t \quad (3.13)$$

Equation 3.13 can be expressed non-linearly as follows:

$$q_t = k_2q_e^2t / 1 + k_2q_et \quad (3.14)$$

$$h = k_2q_e^2 \quad (3.15)$$

where, k_2 ($\text{g mg}^{-1} \text{ min}^{-1}$) is the rate constant for pseudo-second-order model equation, q_e and q_t are the amount of adsorbate species adsorbed on adsorbent at equilibrium and at any time, t , respectively, and h ($\text{mg g}^{-1} \text{ min}^{-1}$) is the initial sorption rate.

The values of k_2 and q_e are acquired from the slope and intercept of the plot between t/q_t vs t .

3.9.3 Intra-particle diffusion model

The intra-particle diffusion model proposed by Weber and Morris is examined for the possible diffusion of adsorbate into pores of adsorbent. The intra-particle equation can be represented as [Weber and Morris, 1963]:

$$q_t = k_{id} t^{0.5} + C \quad (3.20)$$

where, k_{id} is the intra-particle diffusion rate constant ($\text{mg g}^{-1} \text{ min}^{-1}$), q_t is the adsorption capacity at any time t (min) and C (mg/g) is the film thickness i.e., intraparticle accumulation at the boundary layer. Value of C gives an idea about the boundary layer thickness. Larger the value of C , greater will be the boundary layer effect on the adsorption process.

The values of intra-particle diffusion rate constant k_{id} and C are evaluated from the slope and intercept of the plot of q_t against $t^{0.5}$ respectively. The probability of intra-

particle diffusion to be the rate-controlling step in the process is ascertained by the plot that must pass through the origin ($C=0$).

3.9.4 Boyd model

Boyd model distinguishes the film diffusion (boundary layer) and pore diffusion (diffusion inside adsorbent pores). It can be expressed in the following form [Hu, et al., 2011]:

$$F = (1 - 6/\pi^2) \exp(-B_t) \quad (3.21)$$

$$B_t = -0.4977 - \ln(1 - F) \quad (3.22)$$

$$F = q_t/q_e \quad (3.23)$$

where, F is the fraction of adsorbed adsorbate at any time t (min); q_t (mg/g) and q_e (mg/g) represent the amount of adsorbate adsorbed at any time t (min) and at equilibrium, respectively, and B_t is a mathematical function of F . B_t calculated by the above equation should be plotted against t . If the line did not pass through the origin, then it indicates that film diffusion is the rate controlling step for the process and governs the overall process.

3.10 Linear and non-linear analyses of isotherm and kinetic parameters

In order to assess the best process for determination of kinetic and isotherm parameters, isotherm and kinetic data were analysed by linear and non-linear methods. In recent years, linear regression for the best fitting of isotherm and kinetic data has been one of the most feasible tools for the mathematical analysis of adsorption systems. But due to inherent biasness associated with it, and also its inappropriateness for isotherms

with more than two parameters, alternative isotherm parameter sets were determined by non-linear regression. Linear methods include the fitting of the data in the linear isotherm and kinetic equations whereas, non-linear methods include the use of curve fitting using Origin along with fitting to the non-linear isotherm and kinetic equations. Non-linear curve fitting for isotherm and kinetic parameter determination using Microcal origin was done by customizing a non-linear function for isotherm and kinetic model. The customized equations were same as non-linear equations of isotherm and kinetic models (Equations 3.5, 3.7, 3.11, 3.13 and 3.15). Curve fitting using Microcal origin is done with parameter initialization taken as 1.

3.11 Adsorption thermodynamic study

For the feasibility and spontaneity of any process, energy and entropy functions must be taken into consideration. The thermodynamic parameters namely change in free energy (ΔG°), changes in enthalpy (ΔH°), and changes in entropy (ΔS°) of adsorption provide information regarding practical aspects of the adsorption process. Furthermore, the thermodynamic parameter succours to deduce adsorption mechanism too [Liu, 2009]. For their evaluation, experiments were performed at four different temperatures viz., 303, 313, 323 and 333 K.

In the study of adsorption thermodynamics, equilibrium constant derived from various adsorption isotherm models namely Langmuir, Freundlich, Frumkin, Flory-Huggins, etc. coupled with certain specially defined formulas is indispensable for the precise determination of thermodynamic parameters. In the present study attempts have

been made to fit the experimental data to the well known model viz. Langmuir isotherm model for elucidating the adsorption process.

3.11.1 Langmuir adsorption model

The most commonly used model for description of sorption process is Langmuir sorption model largely because of its simplicity and elucidation at microscopic level regarding sorption energy and monolayer coverage. For describing the adsorption process at equilibrium through Langmuir isotherm, the following equation has been employed [Salvestrini et al., 2014; Brown et al., 2009; Elkady et al., 2011];

$$q_e = q_{max} \cdot (C_e K_L / C_e K_L + 1) \quad (3.24)$$

where, q_e and q_{max} correspond to adsorption capacity of adsorbent at equilibrium and its maximum value (milligram per gram); C_e refers to the equilibrium concentration of adsorbate in solution (moles per liter), K_L is the Langmuir equilibrium constant of adsorption (Liters per moles). The Langmuir constant, K_L is most frequently used for the determination of ΔG° on the basis of the given thermodynamic equation [Liu, 2009]:

$$\Delta G^\circ = -RT \ln K_a \quad (3.25)$$

where, ΔG° is the Gibbs free energy change, K_a is the thermodynamic equilibrium constant (without unit), R is universal gas constant ($8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$), and T is the absolute temperature in Kelvin.

In the above equation it can be observed that equilibrium constant is a unit-less quantity whereas, Langmuir constant possess units of liter per moles, so to incorporate it into Equation (3.25) for determination of changes in free energy of adsorption, a modified equation has been given as follows [Brown et al., 2009]:

$$\Delta G^\circ = -RT \ln [K_L/\gamma_e \cdot (1 \text{ mol} \cdot \text{L}^{-1})] \quad (3.26)$$

Here, γ_e correspond to activity coefficient at adsorption equilibrium. The experimental data is fitted to the Eq. (3.26) accordingly and the value of ΔG° has been calculated. Subsequently, the values of ΔH° and ΔS° were also determined from the slope and intercept of the plot of $\ln K_L$ vs. $1/T$, respectively.

3.12 Desorption experiments

Regeneration of exhausted adsorbents in water treatment is one of the crucial aspects as it controls the economy of water treatment technology. In order to ascertain the possibility of reuse of exhausted adsorbent, desorption experiments were conducted. For desorption of metal ions as adsorbate different solvents such as H_2SO_4 , HCl , HNO_3 , NaCl , NaOH , KOH and NH_4OH of 0.1 M concentration were tested. The requisite amount of exhausted adsorbents was added into different solvents and then stirred at certain 350 on a magnetic stirrer for 2 h. Later on, adsorbent was filtered and dried in hot air oven. Metal concentration was analyzed in each solvent to select the better desorbing medium. The regenerated adsorbents were used again for adsorption of particular adsorbate to investigate their reuse efficiency.