Chapter 3

MATERIALS AND METHODS

3. MATERIALS AND METHODS

3.1.   Materials

Reagent bottles (125mL), beaker, conical flasks, measuring cylinders, pipettes, burettes, volumetric flasks, pestles, mortar, distilled water, micropipettes, etc. have been used during the experiments.

3.2.   Reagents

Ferric Chloride ($FeCl_3$), ferrous sulphate heptahydrate ($FeSO_4 .7H_2O$), cadmium chloride($CdCl_2$), potassium dichromate ($K_2Cr_2O_7$), hydrochloric acid (HCl), sulphuric acid (H_2SO_4), nitric acid(HNO_3), sodium sulphite (Na_2SO_3), silver nitrate ($AgNO_3$) sodium hydroxide (NaOH), potassium hydroxide (KOH) and ammonium hydroxide (NH_4OH) were procured from Merck, Mumbai, India and $ZrOCl_2.8H_2O$ was purchased from Himedia India.

3.3.   Instruments

Instruments were used to prepare and characterize the adsorbent materials. X-ray diffractometer (MINIFLEX, RIGAKU), DTA/TGA (Labsys™ TG–DTA 16, SETARAM Instrumentation), scanning electron microscope (Quanta 200 f, FEI), transmission electron microscope (Technai G2 20 S-TWIN and FEI, Morgagni 268D), Fourier transform infra red spectrometer (PerkinElmer Spectrum Version 10.03.05), raman spectrometer (Renishaw inVia Raman spectrometer), magnetic property measurement system (MPMS® 3, Quantum Design. Inc., MPMS-XL,USA), X- ray photoelectron spectroscope (Kratos Analytical Instrument, Shimadzu group company, Amicus XPS UK), surface area analyzer (Smart instruments, SMART SORB 92/93), water bath shaker (Narang scientific works), analytical balance (VIBRA) and pH meter (IKON, India) and tubular furnace (IKON) were used in the present study. Chromium and cadmium concentration in aqueous solutions were determined by atomic absorption spectrophotometer (AAS, Szhimadzu AA7000).

3.4.   General experimentation

3.4.1. Development of nano iron oxide/hydroxide

Nano crystalline iron oxide/hydroxide was synthesized by co precipitation method with slight modification to the method reported by Puvvada et al. (2012). $FeCl_3$ solution was heated up to 353 K with regular stirring, it was followed by addition of 5 ml of sodium sulphite. Afterwards 1 ml of concentrated HCl was added to it. $FeSO_4.7H_2O$ with half molar strength as of $FeCl_3$ was added to it after 5 min. Afterwards, NaOH solution (6.41M) was added to it drop wise. The NaOH solution was added till pH of the solution attained pH between pH 10 - 10.5.The solution was then stirred for 1h. After 1 h, the precipitate was centrifuged and separated. The centrifuged precipitate was then washed with distilled water, ethyl acetate and diethyl ether. The material after washing was dried in a desiccator for 12 h, which was evacuated by vacuum pump.

Three samples of nano crystalline iron oxide/hydroxide were synthesized with varying initial molar concentration of precursor. The sample with initial iron precursor concentration is given in Table 3.1. The chromium and cadmium removal (%) did not show any significant difference in preliminary experiments using all three samples. Hence, sample 1 is used due to high yield of adsorbent synthesized in same time.

Table 3.1 Quantity of iron precursor for synthesis of nano crystalline iron oxide/ hydroxide

Sample no.	$FeCl_3$ (M)	$FeSO_4.7H_2O$ (M)	Total iron concentration (M)
1	0.132	0.066	0.2
2	0.066	0.033	ca. 0.1
3	0.033	0.0165	0.05

3.4.2. Development of nano crystalline zirconia

Nano crystalline zirconia was synthesized by precipitation method. $ZrOCl_2.8H_2O$ solution was prepared (0.025 to 0.075 M) in 1000 ml of water. Afterwards,

ammonia solution (25%) was used to precipitate the $ZrOCl_2.8H_2O$ solution along with uninterrupted stirring on a magnetic stirrer at controlled agitation speed for 1 h. While stirring, the pH of the solution was maintained in the range of 10-10.5 and it led to creation of precipitate of zirconium hydroxide. Afterwards, the precipitate was filtered and subsequently washed with distilled water many times. The washing of the precipitate continued till the complete removal of chloride from solution. The test for complete chloride removal was conducted with the help of silver nitrate ($AgNO_3$) solution. The precipitate after washing dried at 353-363 K for 24 h. The dried material was crushed by pestle and mortar and sieved through 65 µm sieve. Afterwards, the material with three initial molar concentrations 0.025, 0.05 and 0.075 M was calcined for 3 h at 773 K and 873 K with a heating rate of 10K/min.

All samples showed insignificant difference in preliminary experiments for removal of chromium and cadmium from aqueous solutions. Hence, sample 1A is used due to high yield of adsorbent available at same time.

Table 3.2 Initial molar concentrations of precursor with different calcination temperatures for synthesis of nano crystalline zirconia

S.No.	Sample code	Initial molar concentration (M)	Temperature (K)
1	1A	0.075	773
2	1B	0.075	873
3	2A	0.05	773
4	2B	0.05	873
5	3A	0.025	773
6	3B	0.025	873

3.4.3. Determination of pH_{zpc} of nano crystalline zirconia and iron oxide/hydroxide

The pH_{zpc} of the synthesized material was determined with titrimetric method (Mishra and Kumar 2014;Sahoo *et al.* 2014). A 0.01 M NaCl solution was prepared and its pH was adjusted in the range of 2 to 12 by using NaOH and HCl.

Then 50 ml of 0.01 M solution was taken in reagent bottles, afterwards 0.20 g of the adsorbent was added in reagent bottles containing 0.01 M NaCl solution of different pH. The reagent bottles were then kept for 48 h, afterwards final pH of the solution was measured. The graph is plotted between the $pH_{initial}$ and 'pH_{final} vs. $pH_{initial}$'. The point where lines of $pH_{initial}$ and pH_{final} intersect is the pH_{zpc} of the materials. In present studies, the pH_{zpc} of nanocrystalline zirconia and nanocrystalline iron oxide/hydroxide were determined to be 6.78 and 7.65 respectively.

3.4.4. Batch adsorption experiments

Batch experiments for the removal of chromium and cadmium from their aqueous solutions with both the adsorbent materials were conducted. Working solutions of chromium and cadmium required for experiments were prepared by dilution of stock solutions. The requisite pH was maintained with 0.1 M HCl or NaOH. Reagent bottles of 100 ml were used; 50 ml of desired chromium solution along with required amount of adsorbent dose were taken in 100 ml reagent bottles. Afterwards, the bottles were agitated at 120 rpm in a thermostat water bath shaker for a period of equilibrium time. The equilibrium time of each study is given in Table 3.2. Afterwards, the solutions were centrifuged at 10000 rpm for 10 min. The supernatant was decanted and residual concentrations of chromium and cadmium were analyzed with AAS.

The chromium or cadmium amount adsorbed on per unit mass of the adsorbent (mg/g) were determined by the following expression (Dubey *et al.* 2013):

$$q_e = \frac{(C_i - C_e) V}{W} \tag{3.1}$$

Table 3.3 Equilibrium time of chromium and cadmium by nano crystalline iron oxide/hydroxide

S.No.	Adsorbate-adsorbent systems	Equilibrium time (min)
1	Chromium - nano crystalline zirconia	45
2	Chromium - nano crystalline iron oxide/hydroxide	60
3	Cadmium - nano crystalline zirconia	20
4	Cadmium - nano crystalline iron oxide/hydroxide	20

Here, q_e is the amount adsorbed on per unit mass of the adsorbent (mg/g) at equilibrium, C_i and C_e (both in mg L^{-1}) are the initial and the equilibrium concentration of chromium/cadmium respectively, W is the weight of adsorbent (g), and V is the volume of solution (L).

The removal (%) of chromium and cadmium is calculated by using the following equation (Sharma *et al.* 2010;Srivastava *et al.* 2015):

$$\text{Removal (\%)} = \frac{(C_i - C_e) \times 100}{C_e} \tag{3.2}$$

3.4.5. Regeneration experiments

Regeneration studies of the used adsorbents were conducted at room temperature. Initially chromium/cadmium was adsorbed on the adsorbent. The adsorbent was added in chromium/cadmium solution (50 mg L^{-1}, pH = 2, adsorbent dose = 5 g L^{-1} for chromium removal with zirconia; 50 mg L^{-1}, pH = 2, adsorbent dose = 8 g L^{-1} for chromium removal with nano crystalline iron oxide/hydroxide; 50 mg L^{-1}, pH = 7, adsorbent dose = 5 g L^{-1} for cadmium removal with iron oxide/hydroxide and initial concentration 5 mg L^{-1}, pH = 7, adsorbent dose = 8 g L^{-1} for cadmium removal with nano crystalline zirconia). The solution was stirred at 350 rpm on magnetic stirrer for a period of 2 h. Chromium/cadmium loaded on adsorbent afterwards was isolated by filtration and subsequently dried in oven at 323 K. Afterwards, adsorbent was regenerated by taking regenerating agent (HCl, HNO$_3$, H$_2$SO$_4$ for chromium and NaOH, KOH and NH$_4$OH for cadmium) in a beaker with adsorbent loaded with adsorbate. The solution was stirred at 350 rpm on magnetic stirrer for 2h. Afterwards, adsorbent was filtered and dried in oven. Subsequently chromium/cadmium removal (%) efficiency was checked by putting regenerated adsorbent in chromium/cadmium solution (20 mg L^{-1}, pH = 2, adsorbent dose = 5 g L^{-1} for chromium removal with zirconia; 50 mg L^{-1}, pH = 2, adsorbent dose = 8 g L^{-1} for chromium removal with nano crystalline iron oxide/hydroxide; pH = 2, adsorbent dose = 4 g L^{-1}, 50 mg L^{-1}, pH = 7, adsorbent dose = 5 g L^{-1} for cadmium removal with iron oxide/hydroxide and initial concentration 5 mg L^{-1}, pH = 7, adsorbent dose = 8 g L^{-1} for cadmium removal with nano crystalline zirconia).

3.5.   Response Surface Methodology

Adsorption experiments were designed via response surface methodology (RSM). The parameter range and other conditions in adsorption study are discussed in following pages.

3.5.1. Chromium removal with nano crystalline zirconia

Four parameters were studied for their influence on removal (%) of chromium. The parameters were initial concentration, pH, adsorbent dose and temperature. The numbers of experimental runs were 31 and were generated by Minitab 16 software. The parameters along with their range are given in Table 3.4.

Table 3.4 Level of variables chosen for CCD in adsorptive removal of chromium utilizing nano crystalline zirconia

Factors	Parameter values				
	- (-2)*	-1*	0*	+1*	+ (+2)*
Initial concentration (X1) (mg L^{-1})	5	20	35	50	65
pH (X2)	0.5	3	5.5	8	10.5
Adsorbent dose (X3) (g L^{-1})	2	4	6	8	10
Temperature (X4) (K)	298	303	308	313	318

* coded values

3.5.2. Chromium removal with nano crystalline iron oxide/hydroxide

Four parameters were studied for their influence on removal (%) of chromium. The parameters were initial concentration, pH, adsorbent dose and temperature. The numbers of experimental runs were 31 and were generated by Minitab 16 software. The parameters along with their range is given in Table 3.5

In the current experiments, central composite face-centered (CCF) design is used. The CCF has 3 degrees of freedom (-1, 0, +1). Four parameters were studied in the CCF design i.e. initial concentration, pH, adsorbent dose and temperature, respectively.

The relationship between coded and non coded parameters was obtained from the following equation (Montgomery 2012):

$$\text{Coded value} = X_i - X_n / X \tag{3.3}$$

Here, X_i is the value of uncoded value of i_{th} factor X_n is the midway average value of low high, X is the step change. The total number of experiments was obtained by operating CCF design of RSM in Minitab 16 software were 31. In this, there were 16 factorial points, 8 face centred points and 7 replicates (Anupam *et al.* 2011).

$$N = 2^k + 2k + n_o = 2^4 + 2 \text{ x } 4 + 7 = 31 \tag{3.4}$$

n_o is the number of central runs, N is total number of experiments and k is the number of factors.

Table 3.5 Level of variables chosen for RSM design in adsorptive removal of chromium utilizing nano iron oxide/ hydroxide

Factors	Parameter values		
	-1*	0*	+1*
Initial concentration (X1) (mg L^{-1})	20	35	50
pH (X2)	2	6	8
Adsorbent dose (X3) (g L^{-1})	4	6	8
Temperature (X4) (K)	303	308	313

* coded values

3.5.3. Cadmium removal with nano crystalline zirconia

Three parameters namely initial concentration, pH and adsorbent dose were studied for their influence on removal (%) of cadmium. The numbers of experimental runs were 20 and were generated by Minitab 16 software. The parameters along with their range are given in Table 3.6.

Table 3.6 Level of variables chosen for BBD in adsorptive removal of cadmium utilizing nano crystalline zirconia

Factors	Parameter values		
	-1*	0*	+1*
Initial Concentration (X1) (mg L^{-1})	1	5.5	10
pH (X2)	4	5.5	7
Adsorbent dose (X3) (g L^{-1})	4	6	8

* coded values

3.5.4. Cadmium removal with nano crystalline iron oxide/hydroxide

Three parameters, viz. initial concentration, pH and adsorbent dose were studied for their influence on removal (%) of cadmium. The number of experimental runs was 20 and was generated by Minitab 16 software. The parameters along with their range are given in Table 3.7

Table 3.7 Level of variables chosen for BBD in adsorptive removal of cadmium utilizing nano iron oxide/ hydroxide

Factors	Parameter values		
	-1*	0*	+1*
Initial Concentration (X1) (mg L^{-1})	20	35	50
pH (X2)	4	5.5	7
Adsorbent dose (X3) (g L^{-1})	2	3	4

* coded values

3.5.5. Regression and ANOVA table

A second order polynomial is used to explain the relationship between the response and input variables in all four adsorbent – adsorbate systems (Montgomery 2012):

$$Y = {}_0 + \sum {}_i x_i^2 + \sum {}_{ii} x_i^2 + \sum\sum {}_{ij} x_i x_j + \text{€}_r \qquad (3.5)$$

Y denotes the predicted response, i and j vary from 1 to the number of independent process variables. ${}_{0,}$ ${}_{i,}$ ${}_{ii,}$ ${}_{ij}$ were the offset term, linear effect, square effect and interaction effect calculated by the least squares method, €_r is the error of prediction and X_i and X_j are coded independent process variables (Aydın and Aksoy 2009;Montgomery 2012). ANOVA table lists the total sum of squares, source of variation and their degree freedom. ANOVA table also lists F statistics and p value. The p value is used to determine the significant factor.

3.5.6. Surface plots and Contour graphs and optimization plot

The surface plot and contour plot are generated by Minitab 16 software. A three dimensional view is generated from the surface plot. It may provide a clearer picture of the response surface. Contour plot is the two dimensional plot generated

by the Software. In contour plot, all the same responses are connected to produce contour lines. The optimal solution is provided by optimization plot. It graphically represents the interaction of parameters with responses. The vertical red lines and numbers at top in red represent the current parameter value.

3.6.   Adsorption isotherm and kinetic experiments

Isotherm and kinetic parameter determination were executed by nonlinear and linear methods. Linear methods include the fitting of the data in the linear isotherm and kinetic equations.

3.6.1. Langmuir isotherm

The Langmuir isotherm model is based on the assumptions that adsorption occurs on a homogenous surface and in the plane of the surface there is no interaction between adsorbate and adsorbent (Liu *et al.* 2012).

The nonlinear form of Langmuir isotherm model is represented as follows (Langmuir 1916;Ngah 2011):

$$q_e = \frac{bQ_o C_e}{1 + bC_e} \tag{3.6}$$

The linear form of Langmuir isotherm model is as follows (Dastkhoon *et al.* 2015;Yadav *et al.* 2013):

$$\frac{C_e}{q_e} = \frac{1}{bQ_o} + \frac{C_e}{Q_o} \tag{3.7}$$

Here C_e (mg L^{-1}) is the equilibrium concentration of the solute, q_e (mg/g) is amount adsorbed at equilibrium and Q_o (mg/g) and b (L/mg) are constants related to the adsorption capacity and energy of adsorption, respectively.

3.6.2. Freundlich isotherm

Freundlich isotherm is based on the assumptions that adsorption occurs on a heterogeneous surface and at diversity of adsorption sites. The nonlinear form of Freundlich isotherm model is written in expressed as follows (Freundlich 1906;Mazaheri *et al.* 2015):

$$q_e = K_F C_e^{1/n} \tag{3.8}$$

The linear form of Freundlich isotherm model is as follows (Gimbert *et al.* 2008):

$$\log q_e = \log K_F + \frac{\log C_e}{n} \tag{3.9}$$

K_F and n are the Freundlich constants. Here, n giving a sign of how congruent the adsorption process is, and K_F {(mg/g) (L/mg)$^{1/n}$} represents the quantity of chromium adsorbed on the adsorbent for a unit equilibrium concentration.

3.6.3. Adsorption kinetic studies

Parameters obtained by kinetic modelling were helpful in design of adsorption processes. In present study, pseudo-first order and pseudo-second order kinetic models were used to analyze the kinetics of adsorption of chromium and cadmium.

The nonlinear form of the pseudo-first order kinetic model is as follows (Kumar 2006):

$$q_t = q_e \left(1 - \exp(-k_1 t) \right) \tag{3.10}$$

The linearized form of the pseudo-first kinetic model can be expressed by the following equation (Kumar 2006):

$$\log(q_e - q) = \log q_e - \frac{k_1 t}{2.303} \tag{3.11}$$

Where k_1(min^{-1}) is the pseudo-first order rate constant, q_e and q are the amount of adsorbate species adsorbed on adsorbent at equilibrium and at any time (t), respectively. The values of k_1 calculated from the slope of the graph between 'log (q_e - q) *vs.* t' at different temperatures.

The nonlinear form of pseudo-second order kinetic model can be expressed nonlinearly as follows (Ho 2006):

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \tag{3.12}$$

The linearized form of pseudo-second order model can be expressed as follows (Ho 2006):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (3.13)$$

Where k_2 (g.mg^{-1} min^{-1}) is the rate constant for pseudo-second order model equation. The values of k_2 and q_e are acquired from the slope and intercept of the plot between 't/q_t *vs.* t' .The isotherm and kinetic data fitted non-linearly by using Error function analysis and customized function in Microcal origin. The error function analysis method uses following error function. A brief discussion on error function used and their determination are given following pages (Chan *et al.* 2012;Ho *et al.* 2002).

3.7.   Nonlinear fitting of isotherm and kinetic data

The nonlinear curve fitting of isotherm (Langmuir and Freundlich models) and kinetic (pseudo-first and pseudo-second order models) models were done by using error function analysis of Solver add-in of Microsoft excel and curve fitting.

3.7.1. The sum of the square of the errors (ERRSQ)

The sum of the squares of the errors method equation can be written as follows: (Gimbert *et al.* 2008):

$$\sum_{i=1}^{n} (q_{e,i,calc} - q_{e,i,meas})^2 \qquad (3.14)$$

Here, $q_{e,i,calc}$ represent the theoretically adsorbed concentrations of adsorbate on adsorbent and $q_{e,i,meas}$ represent the experimentally determined adsorbed adsorbate concentration. In spite of its extensive use, the function is biased for better fit towards higher concentration range. It is due to increased magnitude of error with increase in concentration, which leads to increased square of errors.

3.7.2. Hybrid fractional error function (HYBRID)

HYBRID method resolves the drawback of ERRSQ. HYBRID method includes division of square of errors by measured values. In addition to measured values, it

also includes degrees of freedom of the system and number of parameters of the
isotherm or kinetic equation as a divisor in the equation (Chan *et al.* 2012):

$$\frac{100}{n-p} \sum_{i=1}^{n} \frac{(q_{e,i,meas} - q_{e,i,calc})^2}{q_{e,i,meas}} \tag{3.15}$$

Here, n is the degree of freedom and p is the number of parameters.

3.7.3. Marquardt's percent standard deviation (MPSD)

MPSD error function is quite alike to geometric mean error distribution to a
certain extent. MPSD error function is tailored according to number of degrees of
freedom of the system (Sarici-Özdemir and Önal 2014):

$$100 \sqrt{\frac{1}{n-p} \sum_{i=1}^{n} \frac{(q_{e,i,meas} - q_{e,i,calc})^2}{q_{e,i,meas}}} \tag{3.16}$$

3.7.4. The average relative error (ARE)

This error function minimizes the fractional error distribution across the whole
concentration domain (Chan *et al.* 2012):

$$\frac{100}{n} \sum_{i=1}^{n} \left| \frac{q_{e,i,calc} - q_{e,i,meas}}{q_{e,i,meas}} \right| \tag{3.17}$$

3.7.5. The sum of the absolute errors (EABS)

EABS is analogous to the ERRSQ. Isotherm or kinetic parameters acquired by
utilizing this error function furnish a finer fit. As amount of the error enhances, it
biases the fit towards the elevated concentration data (Gimbert *et al.* 2008).

$$\sum_{i=1}^{n} |q_{e,i,calc} - q_{e,i,meas}| \tag{3.18}$$

Each error function produces different set of isotherm parameters; an overall
optimum parameter set is difficult to be identified. To make meaningful

comparisons between different isotherm parameters, error functions are normalised and combined to produce a so called sum of normalised errors for each parameter set for each isotherm. The calculation for each isotherm parameter is as follows (Ho *et al.* 2002):

1) One isotherm is selected along with one error function. Afterwards error function is minimized and isotherm parameters for that error function are determined.

2) Rest of the error functions determined for that isotherm parameter set.

3) All other isotherm or kinetic parameter sets and associated error functions values determined for that isotherm.

4) Select each error function and take ratio the value of the error function for a given parameter set to the maximum value of the error function from all parameter set for the isotherm or kinetic data.

5) All normalised errors added for each parameter set.

The parameter set with least normalised error can be selected as optimum for the isotherm model, provided there is no bias in the data. The parameter set providing the smallest normalised error can be selected as optimum for that isotherm model provided that there is no bias in the data. The coefficient of determination is also used in addition to aforementioned error function analysis for it's eligibility to predict best fit isotherm and kinetic models. Coefficient of determination is calculated for each parameter determined.

3.7.6. Microcal origin

Curve fitting function of Microcal origin is also used for fitting nonlinear equations. Non-linear curve fitting for isotherm and kinetic parameter determination using Microcal origin was done by customizing a nonlinear function for isotherm and kinetic model. The customized equations were same as nonlinear equations of isotherm and kinetic models (Equation number 3.6, 3.8, 3.10 and 3.12). Curve fitting using Microcal origin is done with parameter initialization

taken as 1. There are no bounds selected on the determination of parameters. The function form was originC.

3.8.   Intraparticle diffusion model.

The kinetics data was also fitted in intraparticle diffusion model (Weber and Morris 1963). Weber and Morris model is represented by following equation (Asfaram *et al.* 2015;Weber and Morris 1963):

$$q_t = k_{diff} t^{1/2} + C_b \tag{3.19}$$

Where q_t (mg/g) is the amount of adsorbate adsorbed on the surface of the sorbent, at time t, k_{diff} (mg/g min$^{1/2}$) is intraparticle diffusion rate constant. The k_{diff} is calculated from the slope of plot between 'q_t *vs.* $t^{1/2}$' and C_b is intercept. In addition to intraparticle diffusion model, Boyd model is also used to fit the kinetic data. Boyd model is depicted by the following equation (Boyd *et al.* 1947):

$$F(t) = 1 - \left(\frac{6}{\pi^2}\right) \sum_{n=1}^{\infty} \left(\frac{1}{n^2}\right) \exp(-n^2 Bt) \tag{3.20}$$

Where,
$$B = \frac{\pi^2 D^i}{r^2} \tag{3.21}$$

Where D^i is the effective diffusion constant,   is mathematical constant, r is radius of particle, Bt is calculable mathematical function of F(t), F(t) is the fractional attainment at time t:

$$F(t) = \frac{q_t}{q_e} \tag{3.22}$$

Where, q_t and q_e are the uptake of adsorbate (mg/g) at any time t and at equilibrium, respectively. The above equation is simplified as follows (Reichenberg 1953):

$$Bt = -0.04977 - \ln(1 - F(t)) \tag{3.23}$$

A graph was plotted between 'Bt *vs.* t' representing the Boyd plot.