CHAPTER III

3. MATERILS AND METHODS

3.1 MATERIALS

3.1.1 Chemicals

All the chemicals employed in the present study were commercially available high purity Analar grade (Merck India or SRL India) and were used as received. Double distilled water was used throughout the work and the second distillation was made over alkaline permanganate.

3.1.2 Cleaning of Glassware's

All glassware's used in the present study Borosil grade were cleaned well by soaking them in a detergent solution first and then in nitric acid (10%) for a period (48 h). These were then rinsed with doubly distilled water prior to use.

3.1.3 Preparation of metal ion solutions

The metal ions chosen for the adsorption studies in the present work are Iron (II), Copper (II), Nickel (II) and Chromium (VI). Stock solutions (1000 mg/L) of Fe(II), Cu(II), Ni(II) and Cr(VI) were prepared by dissolving required amount of metal salt in one litre of distilled water. The weights of the respective salts taken are listed in table.3.1

Table 3.1   Weight of the salts taken for the preparation of stock solutions

Metal ions	Metal salt	Weight to be dissolved for one liter (g)
Fe(II)	$FeSO_4.7H2O$	4.9786
Cu(II)	$CuSO_4.5H_2O$	3.9301
Ni(II)	$NiSO_4. 6H_2O$	4.4784
Cr(VI)	$K_2Cr_2O_7.5H_2O$	5.6583

3.1.4 Preparations of dye solutions

The dyes employed for the adsorption studies in the present work are Malachite green, Rhodamine B, Methylene Blue and Safranin. All the dyes for the study were commercially available high purity Analar grade (Merck India) and used without further purification. Stock solution (1g/L) of the dyes was prepared by dissolving required amount of the respective dye in one liter of distilled water. The weights of the respective dyes taken are listed in table.3.2

Table 3.2 Weight of the dyes taken for the preparation of stock solutions

Dyes	Weight to be dissolved for one litre (g)
Malachite Green	1.0
Rhodamine B	1.0
Methylene Blue	1.0
Safranin	1.0

3.1.5 Preparation of Adsorbent

The natural plant material *Gloriosa superba stem* was collected from nearby Thiruvarur district the leaves were washed with distilled water several times to remove the dirt and dust and was Carbonized with concentrated Sulphuric acid (w/v) and washed with water. Afterward, the primary carbon was activated at 1100 ^{o}C for 8 hrs in a muffle furnace to obtain activated nano carbon. The activated nano carbon was there after kept at room temperature in an inert atmosphere of nitrogen and washed with hot distilled water and 0.5 N Hydrochloric and until the pH of the material reached 7.0 the activated nano carbon was also dried in a hot air oven at 110 ^{0}C, ground well and sieved to obtain the desired particular size and stored in desiccators for further use.

3.2 Characterization of AGSNC adsorbent

The wide usefulness of AGSNC is a result of its specific surface area, high chemical and mechanical stability. The chemical nature and pore structure usually determine the sorption activity [189, 190]. The AGSNC utilized in the present research work was characterized [191- 193] as follows:

3.2.1 Determination of Particle size

The particle size of the adsorbent AGSNC was measured using the Carl Zeiss Light microscope (Axiostar plus). The ocular micrometer with a dimension of 10x was attached in order to determine the particle sizes of adsorbent. Each division on the scale of the ocular meter is 0.01mm. The length and breadth of each particle were measured. By the application of multiplication factors, the size of the particle was calculated.

3.2.2 Density

The sieved adsorbent was closely packed in a dry graduated glass tube and weighed. This procedure was repeated for ten times. The difference in mass with the initial mass of the graduated glass tube before close packing was noted. The mean mass of the adsorbent/volume gives the density of the AGSNC adsorbent.

3.2.3 Moisture content

The moisture content of the adsorbent was analysed using the moisture balance. One gram of the adsorbent placed in a petriplate and it was heated in a ventilated drying oven at 120 ^{0}C for 2 hours. After heating, the plate was quickly covered, cooled in a desiccator and weighed. The loss in weight of the adsorbent represented the mechanical or hydroscopic moisture.

3.2.4 Loss on ignition

One gram of adsorbent was placed in pre weighed silica crucible and it was ignited at 1000 ^{0}C for 4 hours in an electric muffle furnace. Then it was cooled in desiccators and weighed. The weight loss was calculated as loss on ignition.

3.2.5 Water soluble matter

Five gram of the adsorbent was weighed and transferred into a 500 ml beaker. About 100 ml of distilled water was added and heated to boiling with continuous stirring. Stirring was continued for 5 minutes after the flame was removed. The adsorbent material was allowed to settle and the supernatant liquid was filtered through a crucible fitted with an asbestos mat. The procedure was repeated thrice with the residue in the beaker using 100 ml of water each time. The combined filtrate was concentrated to less than 100 ml over a water bath, cooled and made up to 100 ml mark in a standard flask. Exactly 50 ml of the concentrate was transferred in to a china dish and evaporated to almost dryness and finally dried in an electric oven, maintained at 105 +/- 5 ^{0}C, cooled in a desiccator and weighed. The procedure of drying and weighing was repeated at 30 minutes intervals, until the difference between two consecutive weighing was less than 5 mg. The percentage of water soluble matter was then calculated by the following formula

Water soluble matter (%) = M×100×2 / (M_1/100) (100 – X)

Where, M = mass of the residue in grams

M_1 = mass of the adsorbent taken for test in grams (5g)

X   = percent of moisture present in the material

3.2.6 pH of aqueous solutions

About 100 mg of adsorbent was mixed with 50 ml of distilled water and equilibrated for 1 hour by agitating in a thermostated shaker at 120 rpm. The pH of the supernatant was measured using pH meter.

3.2.7 Zero point charge (pH$_{zpc}$)

The pH at the potential of zero charge (pH$_{zpc}$) of the carbon was measured using the drift method. The pH of a solution of 0.01M NaCl was adjusted between 2 and 12 by adding diluted solutions of hydrochloric acid or sodium hydroxide. Nitrogen was bubbled through the solution at 25 ^{0}C to remove dissolved carbon dioxide until the initial pH stabilized. 50 mg of adsorbent was added to 50 ml of the solution. After the pH had stabilized (typically after 24 hours), the final pH was recorded. The graphs of final pH versus initial pH were used to determine the points at which initial pH and final pH values were equal. This was taken as the pH$_{zpc}$ of the carbon. The results obtained from the above characterization studies are given in table 3.3.

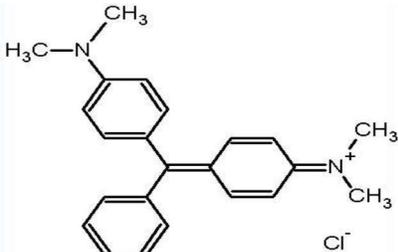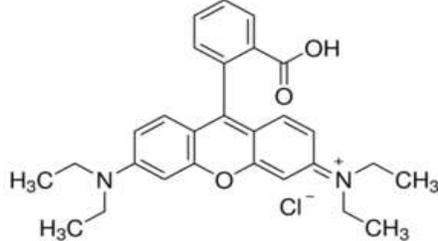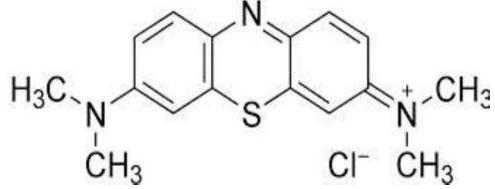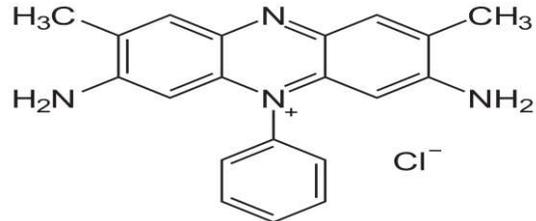**Table 3.3 Characterization of the adsorbent**

Analysis	Value
pH$_{zpc}$	6.200
Specific gravity	0.105
Moisture content, %	0.089
Bulk density, g cm^{-3}	0.010
Particle density, g cm^{-3}	0.010
Conductivity, μS/cm	30.16

3.3 METHODOLOGY

Concentration of the metal ions/dyes before and after adsorption was measured using a UV-Visible double beam spectrophotometer (Systronics 2203). Standards for the establishment of calibration cure for UV-Visible spectrophotometer analysis was prepared by diluting the stock solutions so as to have 10 to 250 mg/L of the metal ions/dyes and the absorbance of the solution at the respective wave length was recorded. The wave length of maximum absorbance for Iron (II), Copper (II), Chromium (VI), Nickel (II), Malachite Green, Rhodamine B, Methylene Blue and Safranin are given in table 3.4.

TABLE: 3.4 WAVE LENGTH FOR THE ESTIMATION OF METAL IONS/DYES

Metal ions and Dyes	Wave length (nm)
Iron (II)	530
Copper (II)	620
Chromium (VI)	590
Nickel (II)	480
Malachite Green	630
Rhodamine B	550
Methylene Blue	660
Safranin	544

Name	Chemical Formula	Molar Mass	C.I.Nr.
Malachite Green		364.90	42000
Rhodamine B		479.02	45170
Methylene Blue		373.90	52015
Safranin		350.85	50240

ADSORPTION STUDIES

3.3.1 Batch equilibration method

All experiments were carried out at 30, 40, 50 and 60 $^\circ$C temperature in batch mode. Batch mode was selected because of its simplicity and reliability. The batch experiments were done in different Erlenmeyer glass flasks of 250 ml capacity. Prior to each experiment, a predetermined amount of absorbent was added to each flask. The stirring was kept constant (120 rpm) for each run throughout the experiment to ensure

equal mixing. Each flask was filled with a known volume of sample before commencing of stirring such as metal ion/dye solution with an initial concentration of 10 mg/L to 250 mg/L, the flask containing the sample was withdrawn from the shaker at the predetermined time interval, filtered and the residual concentration of the metal ions/dyes was measured by UV-Visible Spectrometer [194].

3.3.2 EFFECT OF VARIABLE PARAMETERS

3.3.2.1 Dosage of adsorbents

Different doses consisting of 10 to 250 mg/50 ml of the adsorbent mixed with the fixed concentration of metal ions/dyes solutions and the mixture was agitated in a mechanical shaker. The percentage of adsorption for different doses was determined by keeping all other factors constant.

3.3.2.2 Initial concentration

In order to determine the rate of adsorption, experiments were conducted with different initial concentrations of dyes ranging from 50 to 250 mg/L and metal ions ranging from 10 to 125 mg/L. All other factors were kept constant.

3.3.2.3 Contact time

The effect of period of contact between the adsorbent and adsorbate on the removal of the metal ions/dyes and in a single cycle was determined by keeping particle size, initial concentration, dosage, pH and temperature constant.

3.3.2.4 Initial pH

Adsorption experiments were carried out at a wide range of pH of the solution i.e. 3-9. The acidic and alkaline pH of the medium was maintained by adding the required amounts of dil. hydrochloric acid and sodium hydroxide solution. The parameters like

particle size of the adsorbent, metal ion or dye concentration, dosage of the adsorbent and temperature were kept constant while carrying out the experiments.

3.3.2.5 Other ions

Adsorption studies of a specific metal ion or dye in the presence of chloride ions were experimentally verified using the adsorbent. This one involved in the determination of the percentage of metal ion or dye adsorbed from particular initial concentration of the dye or metal ion solution with the varying concentration of the added ion keeping all other factors constant.

3.3.2.6 Temperature

The adsorption experiments were performed at four different temperature viz. 30, 40, 50, and 60 ^{o}C in a thermo-stated shaker machine (Remi India). The constancy of the temperature was maintained with an accuracy of ± 0.5 ^{o}C.

3.4 Adsorption isotherms

The sorption isotherm is highly significant in the removal of metal ions and dyes by the adsorption technique, as it provides an approximate estimation of the sorption capacity of the adsorbent [195]. The equilibrium data for the removal of metal ions and dyes by the sorption on the adsorbent at different temperature have been used in Langmuir and Freundlich isotherms.

$$\text{Langmuir isotherm:} \quad C_e/Q_e = 1/Q_m b + Ce/Q_m \qquad \text{..... (3.1)}$$
$$\text{Freundlich isotherm:} \quad \log Q_e = \log K + 1/n \log C_e \qquad \text{..... (3.2)}$$

Where, C_e is the equilibrium concentration of the adsorbate adsorbed per unit mass of adsorbent at equilibrium (mg/g); Q_m and 'b' are Langmuir constants related to the adsorption capacity and energy of adsorption, respectively. The values of Q_m and 'b' have

been obtained from the linear correlation of C_e/Q_e against C_e. The Freundlich constants K_f and 'n' are the measures of adsorption capacity and intensity of adsorption respectively and these values have been calculated from the linear correlations of log Q_e Vs log C_e. The essential characteristics of the Langmuir isotherm can be described by a separation factor R_L, which is defined as $R_L = 1/(1+bC_o)$ where, 'b' is the Langmuir constant and C_o is the initial concentration of the metal ions or dyes. The values of R_L indicate the shape of the isotherm as follows [196].

R_L value	Types of isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

3.5 Adsorption kinetics

The study of the adsorption dynamics describes the solute uptake rate and evidently this rate controls the residence time of adsorbate uptake at the solid-solution interface [197]. The kinetics of adsorption on the adsorbent was analyzed using pseudo second-order [198], Elovich [199] and Intra-particle diffusion [200] kinetic models.

The conformity between experimental data and the model predicted values was expressed by the correlation coefficient (γ), (γ, values close or equal to 1). The relatively high correlation coefficient (γ) value indicates that the model which successfully describes the kinetics of adsorption on the adsorbent.

3.5.1 The pseudo-second- order equation

The pseudo-second-order adsorption kinetic rate equation is expressed as

$$dq_t / d_t = k_2(q_e - q_t)^2 \qquad\qquad ….. (3.3)$$

Where, k_2 is the rate constant of pseudo-second order adsorption (g mg^{-1}min^{-1}). For the boundary conditions t = 0 to t = t and q_t = 0 to q_t = q_t the integrated form of Eq. (3.3) becomes

$$1/(q_e - q_t) = 1/q_e + k_2t \qquad \text{….. (3.4)}$$

This is the integrated rate law for a pseudo-second-order reaction. Eq. (3.4) can be rearranged to obtain Eq. (3.5),which has a linear form:

$$t/q_t = (1/k_2q_e^2) + ((1/q_e)t \qquad \text{….. (3.5)}$$

If the initial adsorption rate (h) (mg g^{-1}min^{-1}) is:

$$h = k_2q_e^2 \qquad \text{….. (3.6)}$$

Equation (3.5) and (3.6) becomes

$$t / q_t = 1 / h + 1 / q_e\, t \qquad \text{….. (3.7)}$$

The plot of (t/q_t) and t of Eq. (3.7) should give a linear relationship from which q_e and k_2 can be determined from the slope and intercept of the plot, respectively. The pseudo-second-order rate constants k_2, the calculated 'h' values, and the correlation coefficients (γ) are summarized

3.5.2 The Elovich equation

The Elovich model equation is generally expressed as

$$dq_t / d_t = \alpha \exp (-\beta q_t) \qquad \text{…..(3.8)}$$

Where, α is the initial adsorption rate (mg g^{-1} min^{-1}) and β is the desorption constant (g mg^{-1}) during any one experiment. In order to simplify the Elovich equation. Chien and Clayton assumed $\alpha\beta t >> t$ and by applying boundary conditions q_t = 0 at t = 0 and q_t = q_t at t = t Eq.(3.8) becomes:

$$q_t = 1/\beta \ln (\alpha\beta) + 1/\beta \ln (t) \qquad\qquad .....(3.9)$$

If the adsorption fits the Elovich model, a plot of q_t Vs ln(t) should yield a linear relationship with a slope of $(1/\beta)$ and an intercept of $(1/\beta) \ln (\alpha\beta)$. The obtained Elovich model parameters α, β, and correlation coefficient (γ) are summarized.

3.5.3 Intraparticle diffusion model

The intra-particle diffusion model used here refers to the theory proposed by Weber and Morris [200] based on the following equation for the rate constant:

$$q_t = k_{id} \, t^{(1/2)} + C \qquad\qquad .....(3.10)$$

Where, k_{id} is the intra-particle diffusion rate constant (mg g^{-1}min$^{-1/2}$) and C is the constant. If the rate limiting step is the intra-particle diffusion, the graphical representation of (q_t) absorbent ions (mg g^{-1}) depending on the square root of the contact time ($t^{1/2}$) should yield a straight line passing through the origin. The slope of the plot of q_t Vs $t^{1/2}$ will give the value of the intra-particle diffusion coefficient (k_{id}) and correlation coefficient (γ) indicates the fitness of this model. The intercept value indicates that the curve is not passing through the origin. So, the intra-particle diffusion is not only a rate controlling step. The values of intra-particle parameters were summarized.

3.6 Thermodynamic parameters

The standard free energy change (ΔG^0) enthalpy change (ΔH^0) and entropy change (ΔS^0) were calculated from the variation of the thermodynamic equilibrium constant K_0. The values of K_0 for the adsorption process were determined by the reported method [201, 224]. The thermodynamic parameters were calculated using the following equations.

$$K_0 = C_{solid}/C_{liquid} \qquad \qquad ….. (3.11)$$

$$\Delta G^0 = -RT \ lnK_O \qquad \qquad ….. (3.12)$$

$$\Delta G° = \Delta H°-T\Delta S° \qquad \qquad ….. (3.13)$$

$$lnKo = \Delta G°/(RT)=\Delta S°/ (R) - \Delta H°/(RT) \qquad \qquad ….. (3.14)$$

$$logK_0 = \Delta S°/ (2.303R) - \Delta H°/(2.303RT) \qquad \qquad ….. (3.15)$$

$\Delta H°$ and $\Delta S°$ were determined from the slope and intercept of the plot of In K_0 versus 1/T and these were tabulated.

3.7 Desorption studies

Desorption studies help to elucidate the nature of adsorption and recycling of the spent adsorbent loaded with metal ions and dyes. If the adsorbed metal ions or dyes can be desorbed using water, then the attachment of the metal ions or dyes on the adsorbent by weak bonds. If sulphuric acid or alkaline water desorp the metal ions or dyes, then the adsorption is by ion exchange. If organic acids, like acetic acid can desorp the metal ions or dyes, then the metal ions or dyes is held by the adsorbent through chemisorptions [202]. The effect of various regents used for desorption studies are carried out by using 0.1 M hydrochloric acid, sulphuric acid, nitric acid, sodium chloride and water.

3.8 Data Analysis

The experimental data were analyzed using microcal origin (version 6 and 8) Computer Software. The goodness of fit was discussed using correlation coefficient r and standard deviation (SD).