CHAPTER II

EXPERIMENTAL SECTION
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2.1 Adsorbent materials

Commercially available chitin (Otto Kemi, C1904) and chitosan (Otto Kemi, C0181) were obtained from M/S B.R. Corporation, Mumbai, India. Chitin was supplied in the form of flakes and chitosan as coarse grains with sieve sizes below 22 BSS. The adsorbents were pulverized with mortar and pestle and sieved into different sizes using scientific test molecular sieves manufactured by ELITE Scientific Instruments Co., Mumbai. Chitin was categorized into three mesh sizes viz., 72 BSS, 30 BSS and 22 BSS. Only two mesh sizes viz., 72 BSS and 30 BSS could be sieved from the coarse grains of chitosan and hence the experiments were carried out using these two dimensions.

2.2 Binding sites

The amino sugars of chitin and chitosan are the major effective binding sites for metal ions, forming stable complexes by coordination. The electrons present in the nitrogen atom of amino and N- acetylamino groups establish dative bonds with transition metal ions. Some hydroxyl groups in these bio-polymers may also function as donors. Hence, deprotonated hydroxyl groups can be involved in the coordination with metal ions.

2.3 Treatment of the adsorbents

The adsorbent materials of different sizes were treated first by boiling in 0.1 N HCl for three hours. The solution was decanted and the residue was
treated further by boiling in 0.1N NaOH again for three hours. The treated adsorbents were washed several times with double distilled water. The materials were soaked in double distilled water for sufficient amount of time (till it registered neutral pH), as swelling would make more sites available. Later the adsorbents were dried in an oven. Only the chemically treated adsorbents were used for the experiments.

2.4 Characteristics

2.4.1 Chitin

Chitin is a high molecular weight linear polymer of N-acetyl D-glucosamine (N-acetyl-2-amino-2-deoxy-D-glucopyranose) units linked by (3-D bonds. In its natural state, it occurs in intimate association with many other substances including protein and in crustacean with calcium carbonate and colouring matters. Its separation usually requires rather lengthy treatments with aqueous solutions of acid and alkali. It is a highly water insoluble material resembling cellulose in its solubility and low chemical reactivity. It may be regarded as cellulose with hydroxyl at position C-2 replaced by an acetamido group\textsuperscript{116}. Its poor solubility is a result of the close packing of chains and its strong inter and intramolecular bonds of four different types among the hydroxyl and acetamido groups. The extremely low solubility of chitin excludes it from the formation of fibres\textsuperscript{75}. Few attempts to produce fibres from chitin were commenced by Kunike\textsuperscript{117} and later on by Tokura\textsuperscript{118}. Chitin is a white, hard, highly crystalline, inelastic, nitrogenous polysaccharide. It is
soluble in hexafluoroisopropanol, hexafluoroacetone, chloroalcohols in conjunction with aqueous solutions of mineral acids and dimethyl acetamide containing 5% lithium chloride. Hydrolysis of chitin with concentrated acids under drastic conditions produces relatively pure amino sugars, D-glucosamine. The nitrogen content in it varies from 5 - 8% depending on the extent of deacetylation, Acetic anhydride affords fully acetylated chitins. Linear aliphatic N-acyl groups above propionyl, permit rapid acetylation of hydroxyl groups of chitin. High benzoylated chitin is soluble in benzyl alcohol, dimethyl sulfoxide, formic acid and dichloroacetic acid.

2.4.2 Chitosan

Chitosan is the N-deacetylated derivative of chitin. It is soluble in aqueous solutions of some acids\textsuperscript{119}. Some selective N-alkyldenations and N-acylations have also been attempted to make it soluble. Though several water-soluble or highly swelling derivatives were obtained, development of solubility of it in common organic solvents was found to be difficult by these methods. The nitrogen in chitosan is mostly in the form of primary aliphatic amino groups, Chitosan derivatives are easily obtained under mild conditions and can be considered as substituted glucans. N-acylation with acid anhydrides or acyl halides introduces amiclo groups at the chitosan nitrogen. At room temperature, it forms aldimines and ketimines with aldehydes and ketones, respectively. Chitosan is relatively inert to alkali metals and alkaline earth
metals and this makes it superior to the other polymers tested for transition metal recovery in alkaline or saline waters\textsuperscript{110}.

2.5 Adsorption mechanism

The operative mechanism is determined by the polarity of the solvent, nature of the solute and crystalline nature of chitin\textsuperscript{110}. In chitin, the active centres for hydrogen bond are the acetamido and amino groups\textsuperscript{21}, van der Waals attraction appears to arise due to the attraction between the chitin chain and the electron system of the solute molecule.

Chitosan forms chelates with the metal ions by releasing hydrogen ions. Hence the adsorption of the metal ions on chitosan depends strongly on the pH of the solution. Chitosan membranes are applied successfully to remove metal ions. Various studies of chitosan revealed varying mechanisms of sorption, mainly as a function of metal ion; coordination index and hydrolysis constants are predominant criteria. The metal sorption occurs by precipitation or deposition of metal aggregate mechanisms\textsuperscript{122}, by complexation\textsuperscript{123} or by simple sorption\textsuperscript{124}.

2.6 Particle size determination

The particle sizes of the adsorbents with different mesh sizes were measured using the Carl Zeiss Light microscope (Axiostar Plus). In order to determine the particle sizes of the adsorbents, the ocular micrometer with a dimension of 10x was attached. Each division in the scale of the ocular micrometer is 0.01mm. The length and breadth of each particle was measured.
using the ocular micrometer scale. As no two single particles are alike in length and breadth, about twelve different particles were chosen for the measurements of length and breadth. By application of multiplication factors, the sizes of the particles were calculated. Also, statistical tool application was necessary, as twelve different particles were under measurements. The calculated standard deviations added or subtracted to the sieve sizes give the sizes of the particle of the respective samples. The plates of the microscopic structures of chitin and chitosan viewed under Carl Zeiss Light Microscope are provided in figures 2.4 and 2.5. These figures depict the five chosen particle sizes: three of chitin and two of chitosan.

2.7 Density

Densities of the adsorbents were found by mass/volume of the adsorbents. The adsorbents with different particle sizes were closely packed in a dry graduated glass tube and weighed. The mean value was obtained by repeating the procedure for ten times. The difference in mass with the initial mass of the graduated tube before close packing was noted. The mean mass/volume determined gave the density of the adsorbent.

2.8 Moisture content

The moisture content of the two adsorbents was determined using the moisture balance. Table 2.1 provides the data of the particle size, density and moisture content of the five samples used for the adsorption studies.
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Particle size - 0.21 mm

Particle size - 0.50 mm

Particle size - 0.71 mm

Figure 2.1 Microscopic structure of chitin
Particle size - 0.21 mm

Particle size - 0.50 mm

Figure 2.2 Microscopic structure of chitosan
Table 2.1 Physical characteristics of the adsorbents

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Mesh size (BSS)</th>
<th>Particle size (mm)</th>
<th>Density (g/cc)</th>
<th>Moisture content (%)</th>
<th>Particle size (mm)</th>
<th>Density (g/cc)</th>
<th>Moisture content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>72</td>
<td>0.21</td>
<td>0.4815</td>
<td>2.6</td>
<td>0.21</td>
<td>0.2783</td>
<td>6.5</td>
</tr>
<tr>
<td>2.</td>
<td>30</td>
<td>0.50</td>
<td>0.4797</td>
<td>2.5</td>
<td>0.50</td>
<td>0.2724</td>
<td>7.7</td>
</tr>
<tr>
<td>3.</td>
<td>22</td>
<td>0.71</td>
<td>0.4625</td>
<td>2.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

2.9 Metal ions employed

The metal ions chosen for the adsorption studies using chitin and chitosan in the present work are iron(III), copper(II), zinc(II) and chromium(VI). All the chemicals employed for the analysis were either AnalaR, GR or other high purity grade and were used without further purification. Ammonium ferric sulphate, cupric chloride, zinc sulphate, potassium dichromate, sodium chloride, sodium nitrate, sodium sulphate, hydrochloric acid, sodium hydroxide and sodium perchlorate were purchased from Ranbaxy, Qualigens, S.d.Fine Chem. and CDH.

Water was deionised and doubly distilled, the second distillation was made from alkaline KMnO₄ using an all glass distillation still. All weighings were taken using analytical balance, AE 240, Mettler make.
2.10 Adsorption dynamic experiments

2.10.1 Batch equilibration method

The adsorption experiments were carried out in a batch process at room temperature except where stated otherwise. In a typical case, 10 mg of the adsorbent material was added to 50 nil of the metal solutions with an initial concentration of 10 mg/L. The contents were shaken thoroughly using a mechanical shaker rotating at a speed of 120 rpm. The solution was then filtered at preset time intervals and the residual metal ion concentrations were measured.

2.10.2 Analysis of the samples using Atomic Absorption Spectrometer

The residual concentrations of the metal ions of each adsorption unit were measured from the filtrate of the treated samples, using Atomic Absorption Spectrometer, Perkin Elmer model AAnalyst 100. Duplicate measurements were made such that the residual concentration values were reproducible within ± 2%. High quality acetylene gas of 99.9% purity supplied by Shivaji and Co., Madurai, South India was used for the sample analysis.

The concentrations of the metal ions left over were measured at respective wavelengths and slit widths as indicated in table 2.2.
Table 2.2 Wavelengths and slit; widths employed for the estimation of metal ions*

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Metal ion</th>
<th>Wavelength (nm)</th>
<th>Slit width (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Iron</td>
<td>248.3</td>
<td>0.7</td>
</tr>
<tr>
<td>2.</td>
<td>Copper</td>
<td>324.8</td>
<td>0.7</td>
</tr>
<tr>
<td>3.</td>
<td>Zinc</td>
<td>213.9</td>
<td>0.7</td>
</tr>
<tr>
<td>4.</td>
<td>Chromium</td>
<td>357.9</td>
<td>0.7</td>
</tr>
</tbody>
</table>

* A Analyst 100 Instruction Manual, 2000

2.11 Adsorption kinetics

The kinetics of the adsorption of metal ions onto the adsorbents is linked with the forces between the reactive surface sites of the adsorbent molecules, atoms, ions etc. The effective rate of adsorption is determined by one or more of several steps. Individual steps in the transport mechanism involves (i) the degree of mixing produced by the agitation in the mechanical shaker, (ii) mass transfer from the bulk liquid phase to the external surfaces of the adsorbent, (iii) reaction at the phase boundaries, (although this process is usually considered as very fast and neglected in the resistance steps), (iv) pore diffusion in the fluid phase within the particles and (v) diffusion in the adsorbed state, usually designated as particle phase diffusion, intraparticle diffusion or homogeneous solid phase diffusion125.

Adsorption experiments were carried out by varying particle size of the adsorbents, contact time, initial concentration of metal ions, dosage of the
adsorbents and pH of the medium. The influence of other ions like chloride, nitrate, sulphate and also of the ionic strength on the rates of adsorption was determined. The fraction of adsorption, $Y_t$ and the intraparticle diffusion rate constants, $k_i$ were also calculated. The effect of temperature on the adsorption was determined in the range of 293-323 K. The thermodynamic constants for the adsorption processes of each system were calculated. The results of all experiments conducted at 303 K are presented in detail in the following chapters and are used in the discussion part of this thesis.

2.12 Effect of variable parameters

2.12.1 Particle size

The adsorption capacities of three samples of chitin and two samples of chitosan having different dimensions were determined. Merc, the contact time, initial concentration of metal ions, dosage of the adsorbents, pH of the medium and concentration of other anions were kept constant.

2.12.2 Contact Time

The effect of period of contact on the removal of the metal ions by the adsorbents in a single cycle was determined by keeping particle size, initial concentration, dosage, pH and concentration of other ions constant.

2.12.3 Initial concentration of metal ions

In order to determine the role of adsorption, experiments were conducted with different initial concentrations of metal ions ranging from 2-14 mg/L. All other factors were kept constant.
2.12.4 Dosage of adsorbents

Three different doses consisting of 10, 20 and 30 mg of both the adsorbents respectively were mixed with die metal ion solutions and the mixture was agitated in a mechanical shaker. The adsorption capacities for different doses were determined at definite time intervals by keeping all other factors constant.

2.12.5 pH

Adsorption experiments were carried out at pH 3, 5, 6, 7 and 8. The acidic and alkaline pH of the media was maintained by adding the required amounts of dilute hydrochloric acid and sodium hydroxide solution. Addition of sodium hydroxide solution increased the pH of iron(III) in aqueous solution and led to its complexation as the solution itself was acidic. Therefore, the studies related to iron(III) were limited to all experiments except the effect of pH. The parameters like particle size of the adsorbents, metal ion concentration, dosage of the adsorbents and concentration of other ions were kept constant while carrying out the experiments. The pH of the samples was determined using a portable pH meter, Systronics make. The pH meter was calibrated with 4.0 and 9.2 buffers.

2.12.6 Chloride

The experiments were done in the presence of varying chloride environments ranging from 10 to 1000 mg/L of chloride solution. While doing the experiments, the absence of other anions was ensured.
2.12.7 Nitrate

The sorption experiments were done in the presence of nitrate ions of concentrations ranging from 10 - 1000 mg/L by keeping all other factors constant.

2.12.8 Sulphate

The sorption capacity of the adsorbent was evaluated in the presence of sulphate ions whose concentrations varied from 10-1000 mg/L. The absence of other ions was ensured in this case also.

2.12.9 Ionic strength

Perchlorate solutions ranging from 10 - 1000 mg/L were prepared and mixed with the metal solutions. Experiments using these solutions were carried out in order to evaluate the effect of ionic strength on the sorptive characteristics of the adsorbents.

2.12.10 Temperature

The adsorption experiments were performed at four temperatures, viz., 293, 303, 313 and 323 K in a thermostat attached with a shaker, TECHNO make. The constancy of the temperature was maintained with an accuracy of ± 0.5 °C.

2.12.11 Time dependence of the fraction of adsorption

The time dependence is determined by plotting the fraction of adsorption, \( Y_t = \frac{C_0 - C_t}{C_0 - C_e} \), against the retention time, \( t^{1/2} \), where, \( Q \), denotes the initial concentration of the metal ions, \( C_t \), the concentration of the
metal ions at the present lime intervals and equilibrium concentration. The rate of the fraction of adsorption, \( Y_t \) as a function of half power of time is calculated from the three - staged curves illustrated for different particle sizes and doses of chitin and chitosan as reported earlier\(^{126}\).

2.12.12 Intraparticle diffusion

The sorption process is an overall conjunction of several mechanisms with a preponderant pari played by intraparticle diffusion\(^{115}\). Hence the sorption performances of the adsorbents are determined by the influence of the diffusion mechanism on metal ions uptake. Pore diffusion in the fluid phase, within the particles represents the diffusion in the adsorbed stale. When pore diffusion limits the adsorption process, the relationship between the initial adsorbate concentration and the rate of the reaction will not be linear. If seems that pore diffusion limits the overall rate adsorption by the adsorbents.

As the metal ions arc vigorously agitated during the adsorption period, it is probably reasonable to assume that the rate is not limited by mass transfer from the bulk solution to the external surface of the adsorbents. Weber and Morris\(^{127}\) pointed out that a functional relationship common to the majority of the intraparticle dillusion treatments is that, the uptake varies almost proportionately with the half power of time. Sorption rates are expressed as the square root of time. So the influence of the intraparticle dillusion is estimated by evaluation of initial sorption rates. The intraparticle diffusion is the rate determining step in the adsorption process of the metal ions by the
adsorbents. The values of the intraparticle diffusion rate constants, \( k_p \) are calculated for the experiments performed at different particle sizes and doses of the adsorbents.

2.13 Adsorption isotherms

Adsorption in a solute-solution interface results in the migration of particles from the solution to the surface of the solid, until a dynamic equilibrium is reached between the concentrations of the adsorbent and adsorbate. The time at which adsorption equilibrium is attained is known as the equilibrium time and the concentration of the adsorbate at that time is known as the equilibrium concentration.

The distribution of the metal ions between the liquid phase and the adsorbent is a measure of the position of the equilibrium in the adsorption process and the distribution ratio can be represented by an isotherm. Adsorption isotherms are important to describe how adsorbates will interact with adsorbents and are critical in optimizing the use of chitin and chitosan as sorbents. Quantification of the adsorption capacity of these materials for the removal of metal ions from the solution was studied using Freundlich and Langmuir adsorption equations. Experimental data corresponding to the mixture containing 50 ml of 10 mg/l metal ions and 10 mg of the adsorbents were used for plotting the adsorption isotherms. The parameters of Freundlich and Langmuir isotherms confirm the hierarchy of the adsorbent efficiency.
2.13.1 Freundlich isotherm

The Freundlich equation is applicable to heterogeneous surface energies, where the energy term varies as a function of surface coverage, strictly due to variation in the heat of adsorption. Freundlich isotherm is widely used in the environmental engineering practice to model the adsorption of pollutants from an aqueous medium empirically. Batch isothermal data fitted to the lineal form of the Freundlich isotherm is represented by the equation:

\[ \log q_e = \log K + \frac{1}{n} \log C_e \]

where \( q_e \) = amount of metal ions sorbed per unit weight of the sorbent (mg/g) and \( C_e \) = equilibrium concentration (mg/L) of metal ions in the solution. The fit of the data indicates the intercept, \( K \) which is roughly an indicator of the sorption capacity and the slope, \( 1/n \), of the sorption intensity, the constants incorporating all the factors affecting the adsorption process. The values of \( K \) and \( 1/n \) are calculated from the graph.

2.13.2 Langmuir isotherm

The Langmuir isotherm is based upon the assumption of monolayer adsorption onto a surface containing finite number of adsorption sites of uniform energy with transmigration of adsorbate in the plane of the surface. The linear equation of Langmuir adsorption isotherm is applied in the form

\[ \frac{C_e}{q_e} = \frac{1}{Qb} + \frac{C_e}{Q} \]
where Q and b are the Langmuir constants, indicating the adsorption capacity and energy of adsorption respectively. C and q have their usual significance.

2.13.3 Equilibrium parameter

The essential characteristics of Langmuir equation can be expressed in terms of a dimensionless separation factor or equilibrium parameter \( R_L \) which is defined as \( R_L = 1/ (1 + b C_0) \) where b is the Langmuir constant and \( C_0 \) is the initial concentration of the metal ions. The values of \( R_L \) indicate the shape of the isotherm as follows:

<table>
<thead>
<tr>
<th>( R_L ) value</th>
<th>Type of isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_L = 1 )</td>
<td>linear</td>
</tr>
<tr>
<td>( 0 &lt; R_L &lt; 1 )</td>
<td>favourable</td>
</tr>
<tr>
<td>( R_L = 0 )</td>
<td>irreversible</td>
</tr>
</tbody>
</table>

2.13.4 Activation parameters

The thermodynamic equilibrium constants, \( K_o \) for the sorption reactions were determined by the method suggested by Khan and Singh. Thermodynamic parameters were calculated from the variation of the thermodynamic equilibrium constants, \( K_o \) with temperature. The standard free energy change (\( \Delta G^\circ \)), enthalpy change (\( \Delta H^\circ \)) and entropy change (\( \Delta S^\circ \)) were calculated using the following relationships.

\[
\Delta G^\circ = -RT \ln K_o
\]

\[
\ln K_o = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}
\]

From the slopes and intercepts of the plots of \( \ln K_o \) Vs \( 1/T \), \( \Delta H^\circ \) and \( \Delta S^\circ \) were determined.
2.14 Study of co-ions

Adsorption studies of a specific metal ion in the presence of other metal ions were experimentally verified using both the adsorbents. This involved the determination of the residual iron(III) in the mixture containing equal amounts of copper(II), zinc(II) and chmmim(VI) ions. Similarly, estimation of copper(II), zinc(II) and cliroimium(VI) from the solutions containing equal amounts of the other metal ions also were carried out.