CHAPTER 2

ANALYTICAL TECHNIQUES UTILIZED IN THE PRESENT WORK

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2.1 Introduction

The thesis contains the work related to 1) Synthesis of adsorbents using the Smectite clay, Montmorillonite, MMT 2) Exploration of the applications of synthesized adsorbents for arsenic (III), antimony (III) and vanadium (V) extraction from aqueous solution and their detection.

At various stages of the research performed, the fabricated adsorbents have been characterized using various techniques such as X-ray Diffraction (XRD), Fourier Transform Infrared Attenuated Total Reflectance (FT-IR-ATR) Spectrometry, Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), TGA (Thermogravimetric analysis), DTA (Differential Thermal Analysis), DSC (Differential scanning calorimetry), and UV-Visible (UV-Vis) spectroscopy.

2.2 X-Ray Diffractometry (XRD)

X-ray diffractometry is an effective tool in studying the nature of crystalline substances. This technique is used to characterize the crystallographic structure, crystallite size (grain size) and preferred orientation in polycrystalline or powder solid samples. XRD can be applied to characterize the heterogeneous solid mixture to determine relative abundance of a crystalline compound.
X-ray diffraction is recognized as one of the most powerful, non-destructive, analytical tools used for the fingerprint characterization of crystalline materials and determination of their structure. The basic principle underlying the identification of a material by X-ray is that each crystalline substance has its own characteristic atomic structure which diffracts X-ray in a characteristic pattern. The recognition of the pattern establishes uniquely the diffracting substance.

When a beam of X-ray falls onto a crystal, lattice, its atoms, owing to the forced vibration induced in the electrons, act as secondary source of X-rays [Figure 2.1]. The frequency and wavelength of these emitted rays are identical with those of incident beam. In general, a crystal is said to scatter X-rays, but by analogy with optical diffraction, one may expect that in certain directions the individual scattered wavelets may recombine, in phase, to produce a strong reinforced but deviated beam. For a single row of atoms, the necessary condition for reinforcement is that the primary and secondary rays make equal angles with line row of atoms, which appears to be reflecting the beam. The reflection analogy was first pointed out by Bragg (1937) and it is quite customary for X-ray crystallographers to talk of the reflections of the X-rays by crystals [001, 002].

The beam of X-rays, however, penetrates in such a manner that atoms in many successive rows (successive planes in three dimensional crystals) also become secondary sources. Thus, a final condition must be fulfilled to produce a final comprehensive reinforced reflection, the path difference must be equal to ‘n’ where n is an integer and \( \lambda \) is the wavelength of incident beam. We thus reach the conclusion that a strong reflected beam is produced when the Braggs equation is satisfied (Equation 2.1).

\[ n\lambda = 2d\sin\theta \]

\( \lambda = \) the wavelength of incident radiation
\( d = \) the distance between the lattice planes
\( \theta = \) the diffraction angle
\( 2\theta = \) Scattering angle
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The value of n determines the order of reflection, by analogy with optical diffraction. Characterization of crystalline materials by this method is accompanied by using X-rays of known wavelength and knowing the value of θ at which diffraction occurs. The interplanar distance ‘d’ can be calculated by making use of the above equation. The diffraction pattern is thus a fingerprint of a crystalline compound. The crystalline component of a mixture can be identified individually [003].

The XRD technique has been used in the present research work for structural analysis of the adsorbents for the intercalation feasibility of MMT after modification with CTAB, CPC, LCV and Chitosan [Chapter 3] and the adsorbents after metal treatment [Chapter 4, 5, 6]. XRD measurements have been carried out using XRD D8 Discover Bruker with Cu Kα radiation (λ = 1.54 Å). The voltage and the current of X-ray tube were 40 KV and 40mA, respectively. The scanning was done by step scanning with a step sized of 0.02 step and the integration time of 1s per step to get noise free X-ray diffractograms.

Precautions

(i) The powdered samples should be properly and uniformly grounded to eliminate substrate interference.

(ii) An adequate quantity of sample should be available so that perfect diffraction is achieved [004, 005].
2.3 Thermal Method of Analysis

Thermal method of analysis involves thermo gravimetric analysis (TGA), differential thermal analysis (DTA), differential scanning calorimetric (DSC), thermometric titration etc. Data are obtained with continuously recorded pattern as a function of time. It can be considered as thermal spectra.

Thermogravimetric Analysis (TGA), is an analytical technique, measures the amount and rate of change in the weight of a material as a function of temperature in a controlled air/oxygen or in an inert/nitrogen atmosphere [Figure 2.2]. This method is useful for determining sample purity, thermal stability and for studying decomposition reactions. Thermogravimetric Analysis, TGA, is an analytical technique used for the determination of the changes in weight of a substance as a function of temperature. In TGA, mass loss is observed if a thermal event involves loss of a volatile component. Chemical reactions, such as combustion, involve mass losses. The physical changes, such as melting, do not involve the loss of mass. The measurement can be carried out in air/oxygen or in an inert/nitrogen atmosphere and the weight is recorded as a function of increasing temperature. This method is useful for determining sample purity, thermal stability as well as for studying decomposition reactions.

In the present work TGA-DTA thermograms were recorded on Perkin Elmer Diamond TGA-DTA at a heating rate of 10°C/min. and a flow rate of 100ml min⁻¹. The technique has been used for analysing the thermal stability of the adsorbents synthesized using clay for the assertion of the modification of MMT [Chapter 3, section 3.1] and after
interaction with arsenic (III) [Chapter 4], antimony (III) [Chapter 5] and vanadium (V) [Chapter 6] respectively.

2.4 Fourier Transform Infra-Red (FT-IR)-ATR Spectrometry

Fourier Transform Infrared spectroscopic technique is one of the preferred methods of infrared spectroscopy. It is an analytical technique that is used to identify materials. In this technique, infrared radiation is passed through a sample. Some of the infrared radiation gets absorbed by the sample while some of it gets transmitted. The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. Like a fingerprint no two unique molecular structures produce the same infrared spectrum.

There are several major advantages to the use of Fourier transform instrument.

The first is the throughput, or jaquinot, advantage, due to which the power of the radiation that reaches the detector is much greater than that in dispersive instrument, and much greater signal to noise ratios are observed. A second advantage is their extremely high resolving power and wavelength reproducibility that make possible the analysis of complex spectra in which the sheer number of lines and spectral overlap make the determination of individual spectral features difficult. A third advantage arises because all elements of the source reach the detector simultaneously. This characteristic makes it possible to obtain data for an entire spectrum in one second or less.

Fourier transform spectroscopy differs from conventional spectroscopy in that all of the resolution elements for a spectrum are measured simultaneously, thus reducing enormously the time required to obtain a spectrum at any chosen signal-to-noise ratio. An entire spectrum of 1500 resolution elements can then be recorded in about the time required to observe just one element by conventional spectroscopy. This large decrease in observation time is often used to markedly enhance the signal-to-noise ratio of the Fourier transform experiments. This inherent advantage is termed as the Fellgett, or multiplex advantage [006].
The working of a Fourier Transformed Infrared spectrometer is discussed below:

The heart of the instrument is a Michelson interferometer which consists of a beam splitter and a fixed and movable mirror. Radiation from a continuum source collimated by an off-axis spherical mirror enters the interferometer. The beam splitter reflects about half of the beam to the fixed mirror and transmits the other half to the movable mirror. These two split beams are then reflected back to the beam splitter and the combined beam is then split again with about half going back to the source and the other passing through the sample compartment to the detector. When the distance from the beam splitter to the fixed and movable mirrors are equal, that is, the optical retardation (x) between the two arms of the interferometer is zero, constructive interference occurs and the beam leaving the beam splitter has maximum intensity. When the optical retardation is not zero, the beams from the two arms of the interferometer interact destructively depending on the phase change for each wavelength. Since all the wavelengths enter the interferometer, the interferogram consists of polychromatic radiation and for an ideal Michelson interferometer the mathematical expression for the intensity (I) at each displacement (x), is given by

\[ I(x) = \int_{0}^{\infty} 2I(\nu) R(\nu) T(\nu) \{1 + \cos(2\pi \nu x)\} \, d\nu \]

where \( \nu \) is the frequency of radiation in nitrogen (for \( N_2 \) purged instruments), \( I(\nu) \) is the intensity of radiation for frequency (\( \nu \)) and \( R(\nu) \) and \( T(\nu) \) are the reflectance and transmittance of the beam splitter at frequency (\( \nu \)). For a 100 % efficient beam splitter \( R(\nu) = T(\nu) = 0.5 \), so that

\[ I(x) = \frac{1}{2} \int_{0}^{\infty} I(\nu) \{1 + \cos(2\pi \nu x)\} \, d\nu \]

The AC component of the interferogram contains all valuable information and is called the interferogram function \( F(x) \). This quantity is measured by the instrument.

\[ F(x) = I(x) - I(\infty) = I(x) = \int_{0}^{\infty} A(\nu) \cos(2\pi \nu x) \, d\nu \]

where \( A(\nu) = 2I(\nu) R(\nu) T(\nu) = I(\infty) \)

since at \( x= \infty \) the \( \cos(2\pi \nu x) \) term averages to zero.
A single beam spectrum is obtained from the interferogram by performing a Fourier transformation on $F(x)$ to give

$$A(\nu) = \int_{-\infty}^{\infty} F(x) \cos(2\pi \nu x) \, dx$$

And since $F(x)$ is an even function, symmetric about $x = 0$, we can express it as

$$A(\nu) = 2 \int_{0}^{\infty} F(x) \cos(2\pi \nu x) \, dx$$

Thus a transmittance spectrum is obtained by ratioing the sample spectrum to the instrument background.

In practice, the interferogram cannot be measured to a retardation of 0 to $\infty$ and the effect of using a finite retardation causes the spectrum to have a finite resolution [007-009].

The FT-IR spectra were recorded in transmission mode using KBr pellet at room temperature using Perkin-Elmer FTIR spectrometer. The spectra were recorded in the region 4000cm$^{-1}$ to 400cm$^{-1}$ the co-addition of 64 scans with a resolution of 4cm$^{-1}$.

Figure 3.3.6: Schematic representation of a Fourier Transformed Infrared spectrometer
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ATR uses a property of total internal reflection resulting in an evanescent wave. A beam of infrared light is passed through the ATR crystal in such a way that it reflects at least once off the internal surface in contact with the sample. This reflection forms the evanescent wave which extends into the sample. The penetration depth into the sample is between 0.5 and 2.0 micrometres, with the exact value being determined by the wavelength of light, the angle of incidence, the indices of refraction for the ATR crystal and the medium being probed. The number of reflections may be varied by varying the angle of incidence. The beam is then collected by a detector as it exits the crystal.

![Figure 2.4: Schematic representation of multiple reflection ATR system](image)

In the present work, FT-IR-ATR technique has been utilized to study the functional groups present on the surface of adsorbent [Chapter 3], that may be helpful for preparation of modified adsorbents, to study the structural changes in the back-bone of adsorbents in the presence of arsenic (III), antimony (III) and vanadium (V) to reveal the various interactions of the metal/s to adsorbent surface [Chapter 4, 5, 6].

**Precautions**

(i) Care is taken at the time of pellet fabrication. It is not too thick to obstruct the light to pass through it.

(ii) To avoid interference of CO$_2$ and water, IR chamber is flushed with nitrogen.

(iii) The sample is properly dried so that water interference could be minimized.

(iv) The sample spectra is taken after recording the fresh background.
2.5 Ultraviolet-Visible (UV-Vis) Spectrometry

UV-Vis spectroscopy involves the spectroscopy of photons in the UV-Visible region of the electromagnetic spectrum [010].

Organic compounds, especially those with a high degree of conjugation absorb light in UV or visible regions of the electromagnetic spectrum depending upon their electronic structure.

UV-Vis spectrum is essentially a graph of light absorbed versus wavelength in a range of UV or visible regions. Such a spectrum can often be produced directly by using a UV-Vis spectrophotometer. It measures the intensity of light passing through a sample (I) and compares it to the intensity of light before it passes through the sample (I₀). The ratio I/I₀ is called the transmittance and is usually expressed as a percentage (%T). The relation between absorbance, A, and % transmittance is given below (Equation 2.3).

\[ A = -\log \left( \frac{\%T}{100\%} \right) \]  
(2.3)

Absorption of energy leads to transition of an electron from ground state to excited state. Thus, the position of absorption maxima for a molecule depends on the difference in the energy of ground state level to that of excited state; larger the difference between the energies, higher is the frequency of absorption and thus smaller will be the wavelength. Absorption band shows two important characteristics: (i) The position of the band which depends on the energy difference between electronic levels and (ii) second is the intensity that depends on both the interaction between the radiation with the electronic system and the energy difference between the ground and excited states.

A spectrophotometer consists of a light source, a sample holder, a diffraction grating or monochromator to separate different wavelengths of light, and a detector. The radiation source is often a tungsten filament, a deuterium arc lamp and more recently light-emitting diodes and xenon arc lamps [011].

Detector is typically a photodiode or a charged coupled device (CCD). A spectrophotometer can either the single beam or double beam. In a single beam instrument, a fixed wavelength light source or a continuous source is utilized. In either type, the instrument is calibrated with a reference cell containing only solvent to determine the I₀ value necessary for an absorbance instrument. The dual beam design
greatly simplifies this process by simultaneously measuring I and I₀ of the sample reference cells, respectively as shown in Figure 2.5.

Figure 2.5: Schematic diagram of dual beam spectrophotometer

In Chapter 3, UV-Vis studies have been conducted to investigate the amount of LCV adsorbed from its solution [Chapter 4].

The adsorption of metal upon the adsorbents and their respective concentrations adsorbed/unadsorbed has also been revealed using UV-Vis studies [Chapter 4, 5, 6].

Precautions

(i) To eliminate the solvent interference, the background spectrum is taken prior to the sample investigation.
(ii) Cuvette is cleaned properly before taking the UV-Vis spectrum.
(iii) In case of films, the samples is dried before taking spectra.

2.6 Scanning Electron Microscopy (SEM)

The combination of high magnification, larger depth of focus, greater resolution and ease of sample observation makes the SEM one of most powerful tools for studying the surface morphology of the samples. The instrument produces a largely magnified image by using electrons to form an image [011].

Figure 2.6 shows the schematic revealing the components of scanning electron microscope. Here a beam of electrons is produced at the top of the microscope by an electron gun. Normally tungsten is used in thermionic electron guns owing to its highest melting point and lowest vapour pressure of all metals; however lanthanum hexabromide can also be used if the vacuum system is upgraded.

The electron beam is scanned over the specimen in a series of lines and frames called a raster. Once the beam hits the sample, electrons and X-rays are ejected from the sample.
Detectors collect these X-rays, backscattered electrons and secondary electrons which convert them into a signal that is sent to a screen similar to a television screen producing final image [012, 013]. In the present work, SEM instrument, having model LEO 440 PC with magnification in the range 5 X to 300,000 X and resolution of 2·5-55 nm, has been utilized to investigate the surface morphology of adsorbent after metal interaction [Chapter 4, 5, 6] and before interaction [Chapter 3].

**Precautions**

(i) If the sample conductance is not suffice then a few Å thick conductive gold coating is done by sputtering before analysis to have better resolution.

(ii) The dimension of the sample should be ~ 0·5 cm × 0·5 cm.

**2.7 Transmission Electron Microscopy (TEM)**

Transmission electron microscopy is a powerful technique for characterization of materials, pertaining to shape, size and distribution at nano scale [014, 015]. Much smaller wavelength of electrons ($\lambda = 0·03$ Å) provides much higher resolution. In TEM, the electron gun acts as the source of the stream of monochromatic electrons which is
focused to a small, thin, coherent beam by the use of two condenser lenses. The beam of electrons is transmitted through an ultra thin specimen on interaction which is focused by the objective lens into an image. The image is passed down the column through the intermediate and projector lenses, being enlarged all the way. The image strikes the phosphor image screen and light is generated, allowing the user to see the image. The darker areas with higher contrast are those from where fewer electrons are transmitted due to high density or thickness of the sample while the areas of lower contrast show the areas having less density or thickness. SEM has also been employed to reveal modified Montmorillonite formation [Chapter 3] and the immobilization of metal on these adsorbents after treatment [Chapter 4, 5 and 6].

TEM can be used as electron diffraction camera by suitable combination of the microscopic lenses. This is done by inserting a suitable diffraction aperture instead of objective lenses aperture. Here the orientation of the crystal, the size and shape of crystallite are estimated from the shape and structure of the pattern.

Figure 2.7: Photographic image and schematic representation of High Resolution Transmission Electron Microscope

For the analysis of the samples prepared, a small drop of well-dispersed solution of the material to be analysed has been put onto a carbon-coated copper grid of 2·05 mm in diameter, followed by the solvent evaporation using a dessicator at room temperature.
The instrument used for this analysis is TEM, JEOL JEM 200CX operated at an electron accelerating voltage of 50 - 300 kV and for high resolution images, HRTEM Tecnai G2 F30 STWIN has been used [Figure 2.7]. The HRTEM had TEM Resolution as 0·19 nm and camera length of 80 – 5600mm.

**Precautions**

(i) Selection of the solvent for TEM analysis is in such a way that it would neither interfere with the sample nor damage the grid.

(ii) The energy of the electron beam is optimized as per the need of the sample.

### 2.8 Specific surface area by BET method

The Langmuir isotherm provides a simple picture for looking at surface adsorption, it is not an accurate representation of how nitrogen actually adsorbs to the surface. This is because more than one nitrogen molecule can adsorb to each site on the alumina. A better approximation for this process is to use the BET Isotherm (named for its inventors, Brunauer, Emmett, and Teller). The BET isotherm allows for multiple nitrogen molecules to adsorb to each alumina site.

The assumptions used to derive BET isotherm are

- Gaseous molecules behave ideally
- Multiple nitrogen molecules can be adsorbed to each site
- Each adsorbed molecule provides site for adsorption of molecule in the above layer
- All sites on the surface are equivalent
- No adsorbate - adsorbate interactions occur
- An adsorbed molecule is immobile
- Nitrogen in the second and higher layers are assumed to be liquid like

The BET isotherm is accurate when $P/P_0$ is between ~0.05 and ~0.3, pressures at which only a few complete layers have formed. At low pressures the BET isotherm does not do a good job at describing adsorption because in deriving the isotherm it was assumed that all the sites on the alumina surface are equivalent. This is not the case and when only a few molecules have been adsorbed, effects from
inhomogeneities in the surface become more important. As more molecules adsorb these inhomogeneities average out [016].

At high pressures, the cracks and roughness of the surface cause the BET isotherm to fail. This is especially true for very porous materials where the indents have a width of only a few monolayers. This is because the cracks can only hold a few monolayers and as the cracks fill up, the effective surface area of the solid where the nitrogen adsorbs can change [017].

The specific surface area of the sample is estimated from the amount of nitrogen adsorbed in relationship with its pressure, at the boiling temperature of liquid nitrogen under normal atmospheric pressure. The observations are interpreted following the model of Brunauer, Emmett and Teller (BET Method).

The empty test tubes (with lids) are inserted in flowing nitrogen for 1 hour or until constant weight. The test tubes are then removed from the oven and left for cooling for 5 minutes. One test tube is to be used for the analysis and the other two for calibration. A sufficient amount of sample is added to the test tube and weighed.

The test tube and lid are then placed in the flowing-gas degassing unit for the time necessary based on the nature of the sample and then left for cooling for 5 minutes. Place the test tube (with lid) on its rack and weigh. The BET-N\textsubscript{2} method of analysis has been conducted in the present research work for the analysis of surface area of the adsorbents synthesized [Chapter 3] and the adsorbents after metal treatment [Chapter 4, 5 and 6].

2.9 Zetametry

The particles in a colloidal suspension or emulsion usually carry an electrical charge that may arise due to:

- ionization of surface chemical groups to produce a charged surface;
- adsorption of ions of opposite sign;
- deliberately added chemical compounds that preferentially adsorb on the particle surface to generate the charge.
However, the amount of charge on the particle surface is an important particle characteristic as it determines many of the properties of the suspension or emulsion.

The charge on the surface of each particle is counter balanced by ions of opposite sign in the surrounding solution. The charge on the particle surface is normally considered to be attached rather firmly to it and to remain there more or less indefinitely (though they may get exchanged with charges of similar type in the solution).

The surrounding (balancing) charge, by contrast, is much more loosely associated with the particle.

Figure 2.8: Schematic representation of zeta potential

The thermal motion of the solvent molecules and ions causes the counter charge to spread in a diffuse layer that stretches out for some distance (of the order of nanometres) from the particle surface as shown in Figure 2.8. The counter-ions tend to congregate around the particle and very few co-ions can get close to the surface because of the repulsion from the charges on the particle. Farther away from the particle the co-ions suffer less repulsion and eventually, at distances of almost a few tens of nanometres, the numbers of cationic and anionic charges are evenly balanced.

To measure the charge on a particle electric field is applied to the suspension to measure how fast the particles move due to the applied field. This process is called electrophoresis. The bigger the charge on the particles, the faster they move. The electric field pulls the
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Particle in one direction but it also pulls the counter ions in the opposite direction. Some of the counter ions will move with the particle, hence the measured charge will be a net charge taking that effect into account. The electrostatic potential near the particle surface changes very quickly (and linearly) from its value at the surface through the first layer of counter ions and then changes more or less exponentially through the diffuse layer. The junction between the bound charges and the diffuse layer is marked by the broken line. The surface that separates the bound charge from the diffuse charge around the particle, marks where the solution and the particle move in opposite directions when an external field is applied. It is called the surface of shear or the slip surface.

The microfluidic substrate in contact with an aqueous solution gives rise to an electrical double layer. In general, protonation, deprotonation, adsorption and other reaction equilibria define a net charge density, \( q_0 \) (Ccm\(^{-2}\)), on the surface. This charge density creates an electric field, drawing oppositely charged ions (counter ions) towards it and driving like-charged ions (co-ions) away from it. This shielding layer is commonly known as a Debye layer or electrical double layer (EDL) [018-019]. The Stern layer of counter ions lies at the distance of closest approach from the surface, dictated by the size of the ion. The electrostatic potential on the surface that is measured when one measures the velocity of the particles in a d.c. electric field. The velocity (in metre second\(^{-1}\)) for a unit field strength (1Voltmetre\(^{-1}\)) is called the electrophoretic mobility (µE). The zeta potential (ZP) is thus a function of the surface charge which develops when any material is placed in a liquid. It is a very good index of the magnitude of the electrostatic repulsive interaction between particles.

The zeta potential is commonly used to predict and control dispersion stability. The characteristics of the solid-liquid interface may also influence, adhesion, flotation. If the repulsion between approaching particles is large enough they will bounce away from one another that keeps the particles in a state of dispersion. If the repulsive force is not strong enough, the particles will come together and may stick in a permanent doublet. Then other particles may come along and also be caught in the growing aggregate. The suspension is then unstable and the aggregates will quickly settle out from the surrounding medium.

In the present work, zeta potential analysis has been utilized to investigate the surface charge of adsorbent after synthesis [Chapter 3].
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References


[65]
