11.1 X ray power diffraction fluorescence (XRD) spectrometry

X-ray radiography is used for creating images of light-opaque materials. It relies on the relationship between density of materials and absorption of X-rays. Applications include a variety of medical and industrial applications. X-ray crystallography relies on the dual wave/particle nature of X-rays to discover information about the structure of crystalline materials. X-ray fluorescence spectrometry depends on characteristic secondary radiation emitted by materials when excited by a high-energy X-ray source and is used primarily to determine amounts of particular elements in materials.

X-ray diffraction is a versatile analytical technique for examining crystalline solids, which include ceramics, metals, electronic materials, geological materials, organics and polymers. These materials may be powders, single crystals, multilayer thin films, sheets, fibers, or irregular shapes, depending on the desired measurement. X Ray diffractometers fall broadly into two classes: single-crystal and powder. Single crystal diffractometers are most often used to determine the molecular structure of new materials. Powder diffractometers are routinely used for phase identification and quantitative phase analysis but can be configured for many applications, including variable-temperature studies, texture and stress analysis, grazing incidence diffraction and reflectometry.

The theoretical basis of X-Ray diffraction stands on Bragg’s equation given by where \( n \) is the order of reflection \( n = (1, 2, 3, \ldots) \), the wavelength, \( d \) the distance between parallel lattice planes, and the angle the incident beam and a lattice plane, known as the Bragg angle. When the path length in the crystal (2dsin) is a multiple of the wavelength, constructive interference occurs and diffracted intensity is obtained. In general, the d-spacing is a function of the lattice parameters (a,b,c) and angles defining the unit cell, and the Miller indices (h, k, l) denoting a particular reflection. As such, it is the geometry of the crystal lattice that determines the position of the peaks in an X-ray diffraction pattern. In general, the more symmetrical the material, the fewer the peaks in its diffraction pattern. The diffracted intensities associated with those peaks are determined and arrangement of atoms within the crystal lattice. The radiation used in a typical diffraction measurement contains
several wavelengths, which are characteristics of the material producing the X rays.

Diffraction effects are observed when electromagnetic radiation impinges on periodic structures with geometrical variations on the length scale of the wavelength of the radiation. The interatomic distances in crystals and molecules amount to 0.15–0.4 nm which corresponds in the electromagnetic spectrum. Accordingly, phenomena like constructive and destructive interference should become observable when crystalline and molecular structures are exposed to X-rays. X-rays have photon energies between 3 and 8 keV. There are three different types of interaction in the relevant energy range. In the first, electrons may be liberated from their bound atomic states in the process of photo ionization. Since energy and momentum are transferred from the incoming radiation to the excited electron, photo ionization falls into the group of inelastic scattering processes. In addition, there exists a second kind of inelastic scattering that the incoming X-ray beams may undergo, which is termed Compton scattering.

Also in this process energy is transferred to an electron, which proceeds, however, without releasing the electron from the atom. Finally, X-rays may be scattered elastically by electrons, which is named Thomson scattering. In this latter process the electron oscillates like a Hertz dipole at the frequency of the incoming beam and becomes a source of dipole radiation. The wavelength of X-rays is conserved for Thomson scattering in contrast to the two inelastic scattering processes mentioned above. It is the Thomson component in the scattering of X-rays that is made use of in structural investigations by X-ray diffraction.

X-ray diffraction (XRD) patterns of blank and metal loaded biosorbents are shown in Figs. 11.1 to 11.15. Many compounds were identified from the d-spacing values provided by the XRD pattern. These are given in Table 11.1. Silica (SiO$_2$) and calcite (CaCO$_3$) were observed in all samples, hematite (Fe$_2$O$_3$) was identified in the blanks and metal loaded aerobic, anaerobic and sewage sludge samples. XRD of copper loaded biosorbents showed the presence of bornite (Cu$_5$FeS$_4$) whereas chromium loaded samples showed the presence of green cinnabar (Cr$_2$O$_3$).
Table 11.1: Major compounds identified by XRD in blank and metal loaded biosorbents

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Biosorbent</th>
<th>Major compounds identified by XRD</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Industrial Aerobic sludge (Unused)</td>
<td>Silica (SiO$_2$), calcite (CaCO$_3$), hematite (Fe$_2$O$_3$).</td>
</tr>
<tr>
<td>2.</td>
<td>Industrial Aerobic sludge-Cu(II)</td>
<td>Silica (SiO$_2$), calcite (CaCO$_3$), hematite (Fe$_2$O$_3$), bornite (Cu$_5$FeS$_4$)</td>
</tr>
<tr>
<td>3.</td>
<td>Industrial Aerobic sludge-Cd(II)</td>
<td>Silica (SiO$_2$), calcite (CaCO$_3$), hematite (Fe$_2$O$_3$).</td>
</tr>
<tr>
<td>4.</td>
<td>Industrial Aerobic sludge-Cr(III)</td>
<td>Silica (SiO$_2$), calcite (CaCO$_3$), hematite (Fe$_2$O$_3$), green cinnabar (Cr$_2$O$_3$)</td>
</tr>
<tr>
<td>5.</td>
<td>Industrial Aerobic sludge-Ni(II)</td>
<td>Silica (SiO$_2$), calcite (CaCO$_3$), hematite (Fe$_2$O$_3$).</td>
</tr>
<tr>
<td>6.</td>
<td>Industrial Anaerobic sludge (Unused)</td>
<td>Silica (SiO$_2$), calcite (CaCO$_3$).</td>
</tr>
<tr>
<td>7.</td>
<td>Industrial Anaerobic sludge-Cu(II)</td>
<td>Silica (SiO$_2$), calcite (CaCO$_3$), bornite (Cu$_5$FeS$_4$).</td>
</tr>
<tr>
<td>8.</td>
<td>Industrial Anaerobic sludge-Cd(II)</td>
<td>Silica (SiO$_2$), calcite (CaCO$_3$),</td>
</tr>
<tr>
<td>9.</td>
<td>Industrial Anaerobic sludge-Cr(III)</td>
<td>Silica (SiO$_2$), calcite (CaCO$_3$), green cinnabar (Cr$_2$O$_3$)</td>
</tr>
<tr>
<td>10.</td>
<td>Industrial Anaerobic sludge-Ni(II)</td>
<td>Silica (SiO$_2$), calcite (CaCO$_3$),</td>
</tr>
<tr>
<td>11.</td>
<td>Municipal Sewage sludge (Unused)</td>
<td>Silica (SiO$_2$), calcite (CaCO$_3$), fluorite (CaF$_2$), hematite (Fe$_2$O$_3$).</td>
</tr>
<tr>
<td>12.</td>
<td>Municipal Sewage sludge-Cu(II)</td>
<td>Silica (SiO$_2$), calcite (CaCO$_3$), fluorite (CaF$_2$), hematite (Fe$_2$O$_3$), bornite (Cu$_5$FeS$_4$).</td>
</tr>
<tr>
<td>13.</td>
<td>Municipal Sewage sludge-Cd(II)</td>
<td>Silica (SiO$_2$), calcite (CaCO$_3$), fluorite (CaF$_2$), hematite (Fe$_2$O$_3$),</td>
</tr>
<tr>
<td>14.</td>
<td>Municipal Sewage sludge-Cr(III)</td>
<td>Silica (SiO$_2$), calcite (CaCO$_3$), fluorite (CaF$_2$), hematite (Fe$_2$O$_3$), green cinnabar (Cr$_2$O$_3$),</td>
</tr>
<tr>
<td>15.</td>
<td>Municipal Sewage sludge-Ni(II)</td>
<td>Silica (SiO$_2$), calcite (CaCO$_3$), fluorite (CaF$_2$), hematite (Fe$_2$O$_3$),</td>
</tr>
</tbody>
</table>
11.2 Fourier transform Infra-red/spectrum (FT-IR) spectroscopy for Industrial Aerobic sludge

The technique of IR is used both to gather information about the structure of a compound and as an analytical tool to assess the purity of a compound. Infrared refers to that part of the electromagnetic spectrum between the visible and microwave regions. Electromagnetic spectrum refers to the seemingly diverse collection of radiant energy, from cosmic rays to X-rays to visible light to microwaves, each of which can be considered as a wave or particle traveling at the speed of light. Infrared radiation is absorbed by organic molecules and converted into energy of molecular vibration. In IR spectroscopy, an organic molecule is exposed to infrared radiation. When the radiant energy matches the energy of a specific molecular vibration, absorption occurs. The wavenumber, plotted on the X-axis, is proportional to energy; therefore, the highest energy vibrations are on the left. The percent transmittance (%T) is plotted on the Y-axis. Absorption of radiant energy is therefore represented by a “trough” in the curve: zero transmittance corresponds to 100% absorption of light at that wavelength. FTIR studies of raw and metal loaded dried aerobic sludge was carried out and the results were shown in Fig 11.16 to 11.20.

According to the analysis of the complicated IR spectra, some characteristic peaks can be assigned to the involvement of the main functional groups present in sludge. Spectra of the blank and metal-loaded biosorbent samples before and after the biosorption process were recorded in the range (4000 to 400) cm$^{-1}$. The band located at 3452.76 cm$^{-1}$ in raw biosorbent, assigned to -OH and -NH (amides) stretching, showed shifting at 3420.3 and 3349.82 cm$^{-1}$ in metal loaded biomass. In raw sludge, the peak at 2920.24 cm$^{-1}$, which was attributed to -CH stretching and -OH stretching of the carboxylic group, was shifted to 2911.51 and 2925.62 cm$^{-1}$ in blank and metal loaded biosorbent, respectively. The sorption peak present at 1655.03 cm$^{-1}$ was representing the -CdO stretching of hydroxyl, aldehyde, or ketones with hydrogen bonding, -CdC stretching, and -CdN stretching and this peak showed a shift in blank and metal loaded biomass and was found at 1649.64 and 1645.08 cm$^{-1}$, respectively. The peak at 1458.84 cm$^{-1}$ was shifted to
and 1319.98 cm\(^{-1}\) in blank and metal loaded biosorbent respectively, while the peak at 1130.8 cm\(^{-1}\) was shifted to 1163.0 cm\(^{-1}\) in raw sludge and was missing in metal-loaded biosorbent. The band located at 1050.45 cm\(^{-1}\) in raw wheat bran also showed a change and was shifted to 1056.25 and 1038.50 cm\(^{-1}\) in blank and metal loaded biosorbent respectively. The consistency of the results indicated that the biosorption of metal ions by dried aerobic sludge was mainly depended on ionic interaction and complexion. Amino and carboxyl groups were considered as the main functional groups involved in the biosorption process. It was expected that FT-IR spectra of the biosorbent after metal ion biosorption should change since the coordination sites of functional groups were coordinated to metal ions. In this case, the FT-IR technique plays an important role in the confirmation of metal ions by distinguishing the peak position and peak intensity by comparison of the FT-IR spectra before and after metal ion biosorption. So, from the FT-IR technique, it was confirmed that carboxyl and hydroxyl functional groups were involved in coordination to metal ions.

**Fourier Transform Infrared (FTIR) Analysis of Industrial Anaerobic Sludge**

It is the absorption measurement of different IR frequencies by a sample positioned in the path of an IR beam. The main goal of IR spectroscopic analysis is to determine the chemical functional groups in the sample. Different functional groups absorb characteristic frequencies of IR radiation. Thus, it is an important and popular tool for structural elucidation and compound identification. Infrared radiation spans a section of the electromagnetic spectrum having wavenumbers from roughly 13,000 to 10 cm\(^{-1}\), or wavelengths from 0.78 to 1000 \(\mu\)m. It is bound by the red end of the visible region at high frequencies and the microwave region at low frequencies. IR absorption positions are generally presented as either wavenumbers or wavelengths (I). Wavenumber defines the number of waves per unit length. Thus, wavenumbers are directly proportional to frequency, as well as the energy of the IR absorption. IR absorption information is generally presented in the form of a spectrum with wavelength or wavenumber as the X-axis and absorption intensity or percent transmittance as the Y-axis.
Transmittance (T) is the ratio of radiant power transmitted by the sample (I) to the radiant power incident on the sample (I₀). The transmittance spectra provide better contrast between intensities of strong and weak bands because transmittance ranges from 0% to 100%, whereas absorbance ranges from infinity to zero.

Fourier transform infrared (FTIR) spectrum of the potential biosorbent before and after reaction with metal ions were taken to determine the various functional groups present on the surface of the biosorbent, which may help in the binding of metal ions to the surface of the sorbent. This can be determined by observing the changes in the spectra of the raw and metal-loaded biosorbent. The spectroscopic analysis of the biosorbent was done using FTIR analysis (Nicolet 5700, Nicolet, Inc., USA) in the wavenumber range of 400-4000 cm\(^{-1}\). The biosorbent samples before and after reaction with metal ion were dried in an oven at 80°C for 3.0 h before the analysis.

To understand the possible interactions between the function groups on the surface, the dried anaerobic sludge was examined using FT-IR spectroscopy both before and after its application and the results are shown from fig 11.21 to 11.25. The broad peak at 3448.95 to 3361.71 cm\(^{-1}\) is likely to be due to the overlap of O–H and N–H stretching vibrations (primary and secondary), indicating the presence of both surface free hydroxyl groups and chemisorbed water. The peaks at 2921.8 cm\(^{-1}\) and 2368.42 cm\(^{-1}\) correspond to the C–H symmetric stretch of the methylene groups (−CH\(_2\)) and deformation vibration of methyl groups (−CH\(_3\)). The peak at 1649.10 cm\(^{-1}\) can be attributed to C-O stretching vibration. The peaks at 1324.26 and 1228.42 cm\(^{-1}\) are due to the C–O stretching vibration of ketones, aldehydes and lactones or carboxyl groups. Some shifts in wave numbers from 1046.5 cm\(^{-1}\) to 1038.5 cm\(^{-1}\) were however noticed in the spectra of dried anaerobic sludge before and after use. This suggests that amide, hydroxy, carboxylate and C–O groups could participate in biosorption on the surface of biosorbent used because of the shifts in wave numbers, which results from change in bonding energy in these corresponding functional groups.
**Characterization of surface by FT-IR for municipal sewage sludge**

Infrared (IR) spectroscopy measures the absorption of IR radiation by materials as the atoms vibrate about their bonds. It is primarily used to identify bond types, structures and functional groups in organic and inorganic compounds. IR sensitive vibrations are associated with changes in dipole moments. IR spectroscopy measures vibrational energy levels in molecules. It can be used for both qualitative and quantitative analysis, to identify molecules and compounds, and to determine the presence or absence of certain types of bonds and functional groups. The double and single bonds associated with carbon-hydrogen and carbon-oxygen bonding (=C-H, -C-H, C-O and C=O) can be distinguished by IR absorption. When functional groups can be bonded at different locations on molecules, IR spectroscopy can frequently identify the positions at which the functional groups are attached. The reason is that vibrational frequencies differ when functional groups are attached at different sides in molecules. When illuminated by IR radiation of the appropriate frequencies, atoms, ions, and functional groups in molecules will vibrate about their bonds and energy will be absorbed. Each bending and stretching vibrational mode of a molecule or functional group will absorb at a particular frequency. When exposed to appropriate IR frequencies, energy will be absorbed from the incident radiation as vibrational intensities increase. Many IR frequencies have no effect at all and will not be absorbed.

In the present work, the FT-IR technique has been successfully applied to characterize the functional groups of raw municipal sewage sludge as biosorbent. The variations in the spectral change before and after the biosorption of metal ions were noticed. An attempt was also made to compare the FT-IR spectra of various metal-loaded biosorbent was compared to derive a conclusion. FT-IR spectroscopy was used to obtain information on the nature of possible interaction between the functional groups of blank and metal-loaded dried sewage sludge. The FT-IR spectra of dried unloaded sorbent and metals loaded [Cu(II), Cd(II), Cr(III) and Ni(II)] sorbent are shown from fig 11.26 to 11.30. It can be observed that these spectra changes in intensity and shift in wavenumbers. The change in position, appearance or disappearance of related peaks is related to their involvement in the
biosorption process. The FTIR spectra is a useful tool to identify functional groups in a molecule, as each specific chemical bond often has a unique energy sorption band, this technique also gives structural and bond information on a complex. Spectra of the blank and metal-loaded biosorbent samples before and after the biosorption process were recorded in the range (4000 to 400) cm\(^{-1}\).

These peaks showed a shift in blank and metal-loaded biosorbent and were present at 3352.49 and 3323.11 cm\(^{-1}\), respectively. The band located at 3409.24 cm\(^{-1}\) can be attributed to \(-\text{NH}\) stretching (amides), \(-\text{OH}\) (hydrogen bonding, intramolecular). In raw sludge, the peak at 2925.2 cm\(^{-1}\), which was attributed to \(-\text{CH}\) stretching and \(-\text{OH}\) stretching of the carboxylic group, was shifted to 2923.46 and 2923.53 cm\(^{-1}\) in blank and metal loaded biosorbent, respectively. The sorption peak present at 1649.04 cm\(^{-1}\) was representing the \(-\text{CdO}\) stretching of hydroxyl, aldehyde, or ketones with hydrogen bonding, \(-\text{CdC}\) stretching, and \(-\text{CdN}\) stretching and this peak showed a shift in blank and metal loaded biomass and was found at 1648.3 and 1649.64 cm\(^{-1}\), respectively. The sorption peaks at 1240.69, 1130.8 and 1034.54 cm\(^{-1}\) showed the existence of \(-\text{C-N}\) stretching (amines) and \(-\text{CO}\) stretching of \(-\text{COOH}\) in raw sludge. Thus, the FTIR studies have revealed the complex nature of raw sewage sludge. The functional groups that were mainly present on raw biosorbent were bonded \(-\text{OH}\), \(-\text{NH}\) stretching, \(-\text{CdO}\) stretching, \(-\text{C-O}\) stretching, \(-\text{CdC}\) stretching and the \(-\text{CdN}\) stretching. In metal-loaded biomass, these peaks were either shifted or reduced, which suggests the vital role played by these functional groups in the sorption of metal ions.

11.3 Thermo-gravimetric analysis (TGA-DTG-TG)

Thermal oxidation of industrial aerobic sludge

Thermal analysis was used to ascertain the thermal stability of the industrial aerobic sludge. Although many different thermal techniques are commonly used, thermo gravimetric analysis (TGA), differential thermal analysis (DTA) and derivative thermogravity (dTG) is referred exclusively. The thermal analysis (TGA, DTA and dTG) of Cu(II), Cd(II), Cr(III) and Ni(II) was performed using a Perkin Elmer Pyris Diamond TG/TGA instrument at a fixed heating rate of 10 Kmin\(^{-1}\) over a temperature range of 25 to 1000°C.
Biosorbent sample was uniformly spread over the balance pan. The degradation runs were taken under an inert atmosphere (flowing nitrogen) for pyrolysis and an oxidizing atmosphere (flowing dry air) for gasification at a flow rate of 100 ml min\(^{-1}\).

It is necessary to properly dispose the spent dried aerobic sludge and/or utilize it for some beneficial purpose. Cd(II), Cr(III), Cu(II) and Ni(II) loaded biosorbents were studied for their thermal degradation characteristics by thermo gravimetric instrument (Thermo nicolet, Model Magna 760). The differential thermal analysis (DTA), differential thermal gravimetry (DTG) and thermo gravimetric (TG) curves of the blank and metals loaded biosorbent under oxidizing atmosphere at the heating rate of 10 K min\(^{-1}\) are shown from Fig. 11.31 to 11.35. TGA and DTA curves could be used to deduce drying and thermal degradation characteristics. The TG traces show the loss of moisture and the evolution of some light weight molecules including water up to 250 °C. The weight loss was 11.3% for blank dried aerobic sludge, 9.2% for Cd(II), 8.67% for Cr(III), 8.01% for Cu(II) and 9.8% for Ni(II) respectively. Higher temperature drying (>100 °C) occurs due to loss of the surface tension bound water of the particles. Blank and metal loaded biosorbent do not show any endothermic transition between room temperature and 550 °C, indicating the lack of any crystalline or other phase change during the heating process. The rate of weight loss was found to increase between ~250 °C to ~510 °C (54.23% for blank 70.2%, for Cd(II), 63.20% for Cr(III) 58% for Cu(II) and 67.86% for Ni(II), respectively. In these temperature ranges, the metals loaded biosorbent oxidized and completely lose their weight. The strong exothermic peak centered between ~250-510°C is due to the oxidative degradation of the samples industrial aerobic sludge these two peaks merge in the metal loaded biosorbent samples, indicating early degradation of carbon in dried aerobic sludge samples. The broad peak as that observed from the first derivative loss curve (DTG) may be due to the combustion of carbon species to CO and CO\(_2\).

The sludge has a heating value of about 3.61 MJ kg\(^{-1}\) before biosorption. Thus, the biosorbent along-with the biosorbed Cd(II), Cr(III), Cu(II) and Ni(II) can be dried and used as a fuel in the boilers/incinerators, or can be
used for the production of fuel-briquettes. The bottom ash may be blended
with clay to make fire bricks, or with cement-concrete mixture to make
coloured building blocks thus disposing of loaded metal biosorbent through
chemical and physical fixation.

**Thermal oxidation of industrial anaerobic sludge**

Thermal Gravimetric Analysis (TGA) measures the masses of samples
as they are heated and cooled through standard firing programs. In the case
of TGA analyses, the increase, decreases or constancy of mass of samples at
each temperature in the firing program indicates the presence or absence of
reactions and the nature of each reaction that takes place. For example,
phase changes occur without change of mass; some decomposition reactions
are accompanied by weight loses; and oxidation reactions are accompanied
by weight gains. TGA analyses require small samples (several grams) of dry
powders or particulate suspensions. All such samples must be thoroughly
dried before performing before performing the analyses. Similar to the DTA
analysis technique, TGA analyses are also routinely used to identify during
body development. Some modern instruments simultaneously perform DTA
and TGA analyses.

The differential thermal analysis (DTA), differential thermal gravimetry
(DTG) and thermo gravimetric (TG) curves of the blank, and metals loaded
biosorbent under oxidizing atmosphere at the heating rate of 10 K/min are
shown from Fig. 11.36 to 11.40 TGA and DTA curves could be used to
deduce drying and thermal degradation characteristics. The TG traces
showed the loss of moisture and the evolution of some light weight molecules
including water upto 500°C. The weight loss was 9.79% for blank dried
anaerobic sludge, 10.2% for Cu(II), 13.0% for Cd(II), 12.73% for Cr(III) and
11.16% for Ni(II) respectively. Higher temperature drying (>100°C) occurs due
to loss of the surface tension bound water of the particles. Blank and metals
loaded biosorbent do not show any endothermic transition between room
temperature and 500 °C, indicating the lack of any crystalline or other phase
change during the heating process. The rate of weight loss was found to
increase between ~205 °C to ~525 °C (56.27%, for blank). In these
temperature ranges, the metals loaded biosorbent oxidized and completely
lose their weight. The strong exothermic peak centered between -250-510 °C is due to the oxidative degradation of the samples industrial anaerobic sludge; these two peaks merge in the metal loaded samples, indicating early degradation of carbon in samples. This broad peak as that observed from the first derivative loss curve (DTG) may be due to the combustion of carbon species to CO and CO₂.

The biosorbent before biosorption has a heating value of about 5.63MJ kg⁻¹. Thus, it can be dried along-with the biosorbed Cu(II), Cd(II), Cr(III) and Ni(II) can be dried and used as a fuel in the boilers/incinerators, or can be used for the production of fuel-briquettes. The bottom ash may be blended with clay to make fire bricks, or with cement-concrete mixture to make colored building blocks thus disposing of loaded metal biosorbent through chemical and physical fixation. Thus, spent energy value of the anaerobic sludge could also be recovered.

**Thermal oxidation of Municipal sewage sludge**

Thermogravimetric analysis or thermal gravimetric analysis (TGA) is a type of testing performed on samples that determines changes in weight in relation to change in temperature. Such analysis relies on a high degree of precision in three measurements: weight, temperature and temperature change. As many weight loss curves look similar, the weight loss curve may require transformation before results may be interpreted. A derivative weight loss curve can identify the point where weight loss is most apparent. Again, interpretation is limited without further modifications and deconvolution of the overlapping peaks may be required. To determine composition and purity one must take the mass of the substance in the mixture by using thermal gravimetric analysis.

Thermal gravimetric analysis is the act of heating a mixture to a high enough temperature so that one of the components decomposes into a gas, which dissociates into the air. It is a process that utilizes heat and stoichiometry ratios to determine the percent by mass ration of a solute. If the compounds in the mixture that remain are known, then the percentage by mass can be determined by taking the weight of what is left in the mixture and dividing it by the initial mass. Knowing the mass of the original mixture and the total mass of impurities liberating upon heating, the stoichiometric ratio can be
used to calculate the percent mass of the substance in a sample. TGA is commonly employed in research and testing to determine characteristics of materials such as polymers, to determine degradation temperatures, absorbed moisture content of materials, the level of inorganic and organic components in materials, decomposition points of explosives and solvent residues. It is also often used to estimate the corrosion kinetics in high temperature oxidation.

The differential thermal analysis (DTA), differential thermal gravimetry (DTG) and thermo gravimetric (TG) curves of the blank and metals loaded biosorbent under oxidizing atmosphere at the heating rate of 10 K min⁻¹ are shown in Fig.11.41 to 11.45. The TG traces show the loss of moisture and the evolution of some light weight molecules including water upto 500 °C. The weight loss was 7.88% for blank dried sewage sludge 8.69% for Cr(III), 9.09 % for Cu(III), 8.81% for Cd(II) and 8.06% for Ni(II) respectively. Higher temperature drying (>100 °C) occurs due to loss of the surface tension bound water of the particles. Blank and metal loaded biosorbent do not show any endothermic transition between room temperature and 500 °C, indicating the lack of any crystalline or other phase change during the heating process. The rate of weight loss was found to increase between ~210 °C to ~500 °C 73.4%, for blank, 56.24% for Cr(III), 54.77% for Cu(II), 55.85% for Cd(II) and 57.07% for Ni(II) respectively. In these temperature ranges, the metals loaded biosorbent oxidized and completely lose their weight. The strong exothermic peak centered between ~250-510°C is due to the oxidative degradation of the samples sewage sludge these tow peaks merge in the metal loaded samples including early degradation of carbon in metal loaded municipal sewage sludge samples. This broad peak as that observed from the first derivative loss curve (DTG) may be due to the combustion of carbon species to CO and CO₂.

The dried sewage sludge before biosorption has a heating value of about 5.86 MJ kg⁻¹. Thus, the biosorbent along-with the biosorbed metals can be dried and used as a fuel in the boilers/incinerators, or can be used for the production of fuel-briquettes. The bottom ash may be blended with clay to make fire bricks, or with cement-concrete mixture to make coloured building blocks thus disposing of loaded metal biosorbent through chemical and physical fixation.
Figure 11.2: XRD diffractogram of used aerobic sludge for Cd(II)
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Fig 11.44: TGA-DTG-TG analysis of used dried sewage sludge for Cd(II)
Fig 11.45: TGA-DTG-TG analysis of used dried sewage sludge for Ni(II)