FT-IR and ATR-FTIR Studies of Sludge (CETP) Before and After Adsorption of Dyes from Aqueous Solution

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Abstract. FTIR and ATR-FTIR techniques have been used for the determination of different functional groups present in the sludge from common effluent treatment plant (CETP) before and after adsorption. Sludge is activated at 200°C for 1 hour and used as an adsorbent for the removal of Brilliant Green, Malachite Green and Crystal Violet dyes from aqueous solution. FTIR spectra of the sludge (CETP) before and after adsorption have been compared in the wave number range 400-4000 cm⁻¹. FTIR studies show the presence of major functional groups OH, NH, COOH, C=C which may act as a possible active site for adsorption and structural changes which occur after activation and adsorption of dyes. Our studies show that the sludge contains monosaccharides, peptides, proteins and fats.

Keyword: FTIR, ATR-FTIR, adsorbent, sludge, Dyes.

INTRODUCTION

The degradation of the environment due to the discharge of polluting wastewater from industrial sources poses a real problem in several countries. Textile industries discharge large volume of wastewater into the environment. The wastewater contains a variety of chemicals from various stages of process operations, including bleaching and dyeing. Most of the dyes present in wastewater are toxic and cause allergic dermatitis, skin irritation, cancer and mutation in humans [1-3]. Brilliant green, malachite green and crystal violet dyes are soluble in water and mainly used in textile industries for dyeing cotton, wool, silk, jute, leather, paper, nylon, in manufacture of printing inks and also the biological stain, a dermatological agent in veterinary medicine [4-5]. Therefore, removal of these dyes from water and wastewater is of great importance.

So many efficient methods like physical, chemical and biological are employed for decolorization of textile wastewater. Biodegradation of reactive dyes have been reported using biological methods by treatment with algae, fungi and bacteria. Sewage sludge is a slurry or semi solid waste generated as by-product in sewage treatment. Further treatments of sewage sludge are performed before disposal or application to land [6-7].

In this paper, we have activated sewage sludge into suitable adsorbent and used it for the removal of Brilliant Green, Malachite Green and Crystal Violet dyes from aqueous solution. FTIR Transmittance and Attenuated total reflectance (ATR-FTIR) techniques have been employed to determine the functional groups present in sewage sludge samples before and after adsorption of dyes from aqueous solution [8-15].
FIGURE 1. Image of (a) sludge (b) BG dye water, after centrifuge water and treated dye water (c) MG dye water, after centrifuge water and treated dye water (d) CV dye water, after centrifuge water and treated dye water.
MATERIAL AND METHODS

Sludge sample was collected from CETP, New Delhi, India. The sludge was in the form of small, spherical greyish black particles. The collected sample was sieved to a desired particle size range (100 μm). Sample was heated on muffle furnace at 200 °C for 1 hour and finally stored in vacuum desiccator. The method of converting the waste material into suitable adsorbent was optimized by observing the surface properties of the finished product.

FTIR MEASUREMENTS

The infrared spectra were recorded using Bruker Vertex 80V FTIR spectrometer, coupled with the infrared beamline (BL-06) at Indus-1 synchrotron radiation source at Raja Ramanna Centre for Advanced Technology (RRCAT) Indore, in the wavenumber range 400 - 4000 cm\(^{-1}\) by employing KBr beam splitter and liquid nitrogen cooled MCT detector. A total of 200 scans were coadded at a resolution of 4 cm\(^{-1}\). For powder samples (un-activated sludge, activated sludge and dye loaded activated sludge), the specimens were dispersed in KBr matrix and pelletized in the form of discs. Reference spectra were recorded using bare KBr pellets. Similar process was adopted for sample preparation and measurements for specimens before and after the adsorption of dyes. For liquid samples (dye loaded water and treated water), the IR data were collected using ATR-FTIR method using Bruker IFS125 HR spectrometer. ZnSe ATR in single reflection mode was used for this purpose.

RESULT AND DISCUSSION

Infrared spectroscopic analysis

The adsorption ability of sewage sludge depends upon porosity and chemical reactivity of functional groups at its surface. This reactivity creates an imbalance between forces at the surface when compared to those within the body, thus leading to adsorption by the Vander Waal forces. Knowledge on surface functional groups would give insight to the adsorption capability of the sludge. The FT-IR spectra of un-activated and activated are shown in Figures 2a and2b. The spectra of dyes loaded activated sludge are presented in Figures 3a to 4c. Presence of –OH, COOH, C=C, NH groups may act as a possible active sites for adsorption. OH and NH stretching vibrational modes can be observed between 3100 and 3500 cm\(^{-1}\), C–H stretching - aromatic can be observed between 3000 and 3100 cm\(^{-1}\) and C–H stretching - aliphatic can be observed between 2800 and 3000 cm\(^{-1}\). As shown in the Figure 2, the measured spectra shows a broad band near 3403 cm\(^{-1}\) which indicates the presence of hydroxyl groups on the sludge surface. The presence of these groups is attributed to the absorbed water on the surface of sludge. This band shifts to 3421 cm\(^{-1}\) in activated sludge. The peak at 2858 cm\(^{-1}\) is due to C–H stretching of CH2 groups of monosaccharide moiety. The bands near 1630 cm\(^{-1}\) indicates fingerprint region of C–O, C–O and O–H groups that exist as functional groups of sludge. The peaks at 1457 cm\(^{-1}\) and 1438 cm\(^{-1}\) (\(\nu\) C–O) indicate the presence of carboxylic groups in un-activated and activated sludge respectively. The peak at 1020 cm\(^{-1}\) indicates the presence of C–O (CH2OH) bending [9] which may be due to presence of monosaccharide moiety in both sludge samples. The region between 600 and 900 cm\(^{-1}\) contains various bands related to aromatic, out of plane C–H bending with different degrees of substitution. After adsorption of dyes, peaks of 1020 cm\(^{-1}\) disappeared in dyes loaded sludge. The values obtained are summarized in Table 1.

ATR- FTIR SPECTRA ANALYSIS FOR DYE WATER

For the analysis of the liquid samples, ATR technique was used. The ATR-FTIR measurements of dye water and treated dye water show almost similar pattern. It shows that leaching did not occur during the adsorption on dye on activated sewage sludge. The presence of peaks in the range 3700-3100 cm\(^{-1}\) are due to O–H stretching vibration. Peaks in the range 2150-2100cm\(^{-1}\) and 1638- 2641 cm\(^{-1}\)are due to –CH stretching vibration and C=C of alkynyl group respectively. Peaks at 647 cm\(^{-1}\) and 606 cm\(^{-1}\) may be due to -CH out of plane bending vibration and ring deformation respectively. The values obtained are summarized in Table 2.
FIGURE 2. FTIR spectrum of (a) Sludge and (b) Activated Sludge
(a) 

(b)
FIGURE 3. FTIR spectrum of (a) BG dye loaded activated sludge (b) MG dye loaded activated sludge and (c) CV dye loaded activated sludge.
FIGURE 4. ATR-FTIR comparison between (a) BG dye water and BG dye treated water, (b) MG dye water and MG dye treated water and (c) CV dye water and CV dye treated water.
<table>
<thead>
<tr>
<th>Wavenumber Range (cm⁻¹)</th>
<th>Sludge</th>
<th>Activated Sludge</th>
<th>BG dye loaded Activated sludge</th>
<th>MG dye loaded Activated sludge</th>
<th>CV dye loaded Activated sludge</th>
<th>Functional Group and Vibration</th>
<th>Reference</th>
</tr>
</thead>
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<tr>
<td>4000-3400</td>
<td>3403, 3450</td>
<td>3619, 3421</td>
<td>3694, 3676, 3617</td>
<td>3694, 3676, 3619</td>
<td>3694, 3676, 3619</td>
<td>-OH group, −C≡C−H stretching vibration</td>
<td>Saccharide [9]</td>
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<td>3320-2700</td>
<td>2918</td>
<td>2910</td>
<td>2960, 2951, 2919, 2877, 2867, 2849, 2839</td>
<td>2951, 2919, 2877, 2867, 2850, 2840</td>
<td>2960, 2951, 2919, 2877, 2867, 2849, 2840</td>
<td>CH₂ Asymmetrical stretching vibration</td>
<td>Saccharide [8-9]</td>
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<tr>
<td>2560-2100</td>
<td>-</td>
<td>-</td>
<td>2552, 2520, 2343</td>
<td>2520, 2520, 2343, 2221</td>
<td>2543, 2273, 2077</td>
<td>N≡C≡O stretching vibration</td>
<td>[9]</td>
</tr>
<tr>
<td>1796</td>
<td>1793</td>
<td>1793</td>
<td>1796</td>
<td>1793</td>
<td>1793</td>
<td>−COOH</td>
<td>[9]</td>
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<tr>
<td>1660-1500</td>
<td>1654</td>
<td>1637</td>
<td>1621</td>
<td>-</td>
<td>-</td>
<td>C≡C Stretching vibration</td>
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<td>1450-1380</td>
<td>1457, 1373</td>
<td>1438</td>
<td>1447</td>
<td>1339</td>
<td>1425</td>
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<td>Monosachharide [9]</td>
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<td>1020</td>
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<td>−C−O stretching vibration</td>
<td>[9]</td>
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<td>873</td>
<td>873</td>
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<td>874</td>
<td>874</td>
<td>−C−H out of plane bending vibration</td>
<td>[8]</td>
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</table>
### Tables 2. Comparison between dye water and treated dye water

<table>
<thead>
<tr>
<th>Wavenumber Range (cm$^{-1}$)</th>
<th>BG dye water</th>
<th>Treated BG dye water</th>
<th>MG dye water</th>
<th>Treated MG dye water</th>
<th>CV dye water</th>
<th>Treated CV dye water</th>
<th>Functional Group</th>
<th>Reference</th>
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<tr>
<td>3700-3100</td>
<td>3311</td>
<td>3323</td>
<td>3323</td>
<td>3314</td>
<td>3319</td>
<td>3316</td>
<td>O–H stretching</td>
<td>Polyalcohol and saccharides [9,14]</td>
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<td>2150-2100</td>
<td>2126</td>
<td>2116</td>
<td>2133</td>
<td>2115</td>
<td>2124</td>
<td>2108</td>
<td>–CH and H2O bending vibration (v$_2$+v$_1$)</td>
<td>Saccharide, H2O [9,14]</td>
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<td>1638</td>
<td>H–O–H bending vibration (v$_2$)</td>
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<td>606</td>
<td>606</td>
<td>606</td>
<td>Ring deformation</td>
<td>[8]</td>
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</tbody>
</table>
CONCLUSION

The analysis of FTIR spectra recorded on different sewage sludge samples led to the identification of important peaks in the spectrum, which can reflect structural changes during activation and adsorption of dyes on sewage sludge. From the specific frequency bands, it is possible to follow steps during activation and adsorption of different dyes on activated sewage sludge.

Thus, the FTIR method being fast, non-destructive and very useful for even small quantities and can be used for monitoring the sewage sludge and dyes in the environment.

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REFERENCES

15. IR Spectrum Table & Chart | Sigma-Aldrich. www.sigmaaldrich.com