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USAGE OF FTIR-ATR AS NON-DESTRUCTIVE ANALYSIS OF SELECTED TOXIC DYES

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Abstract

The degradation of the environment which is due to the discharge of polluting wastewater from industrial sources poses a real problem in several countries. Textile industries use large volumes of water in their operations, discharging thus large volume of wastewater into the environment, most of which is untreated. The wastewater contains a variety of chemicals from various stages of process operations, including desizing, scouring, bleaching and dyeing. The main purpose of this paper is to introduce Infrared Spectrometry with Fourier transformation as a non-destructive method for study, identifation and rapid determination of selected representatives of cationic (Methylene Blue), azo (Congo Red, Eriochrome Black T) and nitroso (Naphthol Green B) dyes. In conjunction with the ATR technique, FTIR offers a reliable detection method of dyes without extraction by other dangerous substances.

Spectral interpretation of dye spectra revealed valuable information about the identification and characterization of each group of dyes.

Key words

FTIR-ATR, azo dye, nitroso dye, basic dye, spectrum

INTRODUCTION

During the last century, a huge amount of industrial wastewater, especially from developing countries, was discharged into rivers, lakes and coastal areas. In fact, the flush-and-discharge systems make the crisis and problems of sanitation and wastewater getting worse. In addition, the disposal of toxic dye effluents containing azo dyes has raised public concern and attention to their environmental damage on aquatic life owing to their carcinogenic nature, as well as inhibition of sunlight into the water stream, which impeds the photosynthesis process of aquatic plants and eventually causes an imbalance in our ecosystem (1).

The presence of dyes in effluents is a major concern due to their adverse effects to many forms of life. The discharge of dyes in the environment is a matter of concern for both toxicological and aesthetic reasons. Industries such as dye synthesis, printing, paper, textile, leather, electroplating, pulp mill, plastics, food and cosmetics, all use dyes in order to colour their products and simultaneously consume substantial volumes of water (2, 3, 4).

Dyes are of complex aromatic molecular structures and are stable towards heat and oxidizing agent. It has been reported that most industrial dyes are non-biodegradable, chemically stable, carcinogenic and mutagenic, hence, harmful to human health. Several dyes are toxic to flora and fauna, and therefore pose health hazard. Moreover, presence of industrial dyes in water bodies also decreases light penetration which affects the photochemical activities of marine systems. Therefore, effective treatment of wastewater effluents from these industries via removing the dyes in order to meet regulatory requirement for reuse or discharge is highly desirable (5, 2). Many methods have been developed in the decoloration process, such as adsorption, reverse osmosis, precipitation and ion exchange.

Identification of pigments and dyes is one of the most important targets aimed at the scientific examination of paintings, textiles, illuminated manuscripts and other historical and archaeological materials. Several analytical techniques have been used for this purpose, for example gas chromatography/mass spectrometry, UV–visible spectrophotometry, thin-layer chromatography, high-performance liquid chromatography, reversed phase liquid chromatography and capillary electrophoresis with electrospray mass spectrometric detection, FT–IR spectroscopy and Raman spectroscopy (6). Differences between IR and Raman spectroskopy are listed in Table 1.

Table 1 Differences between Raman and IR spectoscopy

Raman spectroskopy	IR spectroscopy
It is due to the scattering of light by the vibrating molecules	It is the result of absorption of light by vibrating molecules.
The vibration is Raman active if it causes a change in polarisability.	Vibration is IR active if there is change in dipole moment
The molecule need not possess a permanent dipole moment.	The vibration concerned should have a change in dipole moment owing to that vibration.
Water can be used as a solven	Water cannot be used qwing to its intense absorption of IR.
Sample preparation is not very elaborate, it can be in any state	Sample preparation is elaborate; gaseous samples can rarely be used.
Gives an indication of covalent character in the molecule	Gives an indication of ionic character in the molecule.
Cost of instrumentation could be very high.	Comparatively inexpensive.

FT–IR spectroscopy spectroscopy is a non-destructive, fast and sensitive physical technique for the analysis of organic compounds with minimum sample preparation. Some studies have reported earlier on the characterization and comparison of dyes. There are vast applications of infra-red spectroscopy for successful analysis of ancient textile dyes, forensic analysis of dyestuffs and inks. This scheme could even be exploited in the analysis of dyes within the matrix without extraction (7). It can serve as a fingerprint technique for the classification of unknown compounds, nd therefore it is very helpful in classifying raw materials and ingredients that are used in dyes and pigments, polymers, plastics, coatings, laminates, pharmaceuticals, foods and other consumer products.

Characterization of selected samples of dyes

There are several ways for classification of dyes. It should be noted that each class of dyes has a very unique chemistry, structure and particular way of bonding. While some dyes can react chemically with the substrates forming strong bonds in the process, others can be held by physical forces. Some of the prominent ways of classification are given hereunder:

- classification based on the source of materials – natural, synthetic,
- chemical classification of the dyes – based on the nature of their respective chromophores,
- dyes classification according to the molecular structure – cationic, anionic
- industrial classification of the dyes.

Dyes contain chromophores (delocalized electron systems with conjugated double bonds) and auxochromes (electron-withdrawing or electron-donating substituents that intensify the color of the chromophore by altering the overall energy of the electron system). Usual chromophores are -C=C-, -C=N-, -C=O, -N=N-, $-NO_2$ and quinoid rings, usual auxochromes are $-NH_3$, -COOH, $-SO_3H$ and –OH (8).

Based on chemical structure of chromophores, 20-30 different groups of dyes can be discerned. Azo (monoazo, diazo, triazo, polyazo), anthraquinone, phthalocyanine, and triarylmethane dyes are quantitatively the most important groups.

Majority of industrial important azo dyes belong to the following classes: Acid dyes, Basic dyes, Direct dyes, Disperse dyes, Mordant dyes, Reactive dyes and Solvent dyes. The Acid, Basic, Direct and Reactive azo dyes are ionic dyes. Classification of dyes according to their practical use is shown in Table 2 (8).

Table 2 Classification of dyes

Class	Chemical types
Acid	azo(including premetallized), anthraquinone, triphenylmethane, azine, xanthene, nitro and nitroso
Basic (cationic)	cyanine, hemicyanine, diazahemicyanine, diphenylmethane, triaryl-methane, azo, azine, xanthene,acridine, oxazine, and anthraqui-none
Direct	azo, phthalocyanine, stilbene, andoxazine
Disperse	azo, anthraquinone, styryl, nitro, and benzodifuranone
Mordant	azo and anthraquinone
Reactive	azo, anthraquinone, phthalocya-nine, formazan, oxazine, and basic

For the purposes of this article, we selected representatives of azo (Congo red, Eriochrome black T), cationic (Methylene blue), and nitroso (Naphthol Green B) dyes.

Azo dyes

Azo dyes consist of a diazotized amine coupled to an amine or a phenol and contain one or more azo linkages. The criterion of harmfulness of benzidine based dyes is the possibility of cleavage into carcinogenic amines.

Congo red (CR), molecular formula $C_{32}H_{22}N_6Na_2O_6S_2$, is a benzidine-based, direct, anionic diazo dye prepared by coupling tetrazotised benzidine with two molecules of napthionic acid. Congo red is the first synthetic azo dye produced that is capable of dyeing cotton directly. Exposure to the dye has been known to cause allergic reactions. The substance is considered as toxic exhibiting acute, algal, bacterial, protozoan, cutaneous, environmental, microbial, yeast toxicity; cytotoxicity; genotoxicity; hematotoxicity; neurotoxicity, as well as carcinogenicity and mutagenicity. The capability of CR to form carcinogenic amines such as benzidine through cleavage of one or more azo groups is the reason why it falls under the category of banned azo dyes. Thus, the treatment of CR contaminated wastewater can be complicated due to its complex aromatic structure, providing the dye physicochemical, thermal and optical stability, and resistance to biodegradation and photodegradation.Congo red contains an azo (-N=N-) chromophore and an acidic auxochrome ($-SO_3H$) associated with the benzene structure. CR is also called acidic diazo dye (9).

Among the azo-based dyes, Eriochrome Black T (EBT), with molecular formula $C_{20}H_{12}N_3NaO_7S$, which contains the hydroxy naphthalene moiety, has been widely used in the textile industry (10). However, EBT is very much difficult to be decolorized because of its complex structure. Thus, EBT has been classified as a hazardous dye due to its large molecular structure and chemical stability (11). EBT causes skin irritation and serious eye irritation, may cause respiratory irritation and is toxic and harmful to aquatic life with long lasting effects (12).

Cationic (basic) dyes

Cationic dyes carry a positive charge in their molecule. The salt-forming counter-ion is in most cases the colorless anion of a low molecular mass inorganic or organic acid. Many of these dyes can be converted into water-insoluble dye bases by addition of alkali. For this reason, they were formerly called basic dyes; although still in use today, the term should be abandoned.

Some prominent examples of basic dyes are the following: methylene blue, crystal violet, basic fuchsin, safranin, etc. An example of a basic dye having amino groups as their auxochrome is pararosanilin or basic red 9 (according to the strict colour index system of classification) example of alkylamino groups is methylene blue or basic blue 9. Basic Blue 9 is a very popular dye that has vast use.

Methylene blue (MB), with molecular formula $C_{16}H_{18}ClN_3S$, has wide applications including the cottons or wools dyeing, paper coloring, temporarily coloring hair, and coating for paper stock. Due to its known strong adsorption onto solids, MB often serves as a model compound for removing dyes and organic contaminants from aqueous solutions. Although MB is not considered to be a very toxic dye, it can have some harmful effects on human beings. The dye can cause eye burns in humans and animals. It may stimulate the gastrointestinal tract and cause nausea, vomiting, and diarrhea if ingested. It may also cause dyspnea, tachycardia, cyanosis, methemoglobinemia and convulsions if inhaled (13, 14, 15).

Nitroso dyes

These dyes contain nitro or nitroso groups as the chromophores and –OH as auxochrome. Nitroso dyes are metal-complex derivatives of *o*-nitrosophenols or -naphthols.

Naphthol Green B (NGB), with molecular formula $C_{30}H_{15}FeN_3Na_3O_{15}S_3$, is an important commercial green nitroso dye, a complexometric indicator with three SO_3^- groups and a naphthalene structure leading to excellent water solubility and good stability (16, 17, 18). This dye is not bio-degradable and its presence in water is highly undesirable (19). NGB is mainly used for staining wool, nylon, silk, polyamide, paper, and soap (20, 21). As an anion, it acts as acid dye and possesses excellent redox characteristics. Such dye is able to undergo electropolymerization from aqueous solution, producing stable redox active layer (18). NGB causes skin irritation and serious eye irritation, can cause respiratory irritation and is harmful to aquatic life with long lasting effects (22).

MATERIALS AND METHOD

Sample: As samples of each dye group were selected Eriochrome black T (CAS Number 1787-61-7) as mono-azo dye (Sigma Aldrich, DE), Congo red (CAS Number 573-58-0) (Sigma Aldrich, DE) as a diazo dye, Methylene blue (CAS Number 122965-43-9) (Sigma Aldrich, DE) as cationic (basic) dye, and from nitroso group Naphthol Green B (Sigma Aldrich, DE) was chosen.

Method: For FTIR (Varian FT-IR Spectrometer 660) analysis sample of each dye was directly applied to a diamante crystal of ATR (Pike, GladiATR) and the resulting spectra of them were corrected for background air absorbance. The spectra were recorded using a Varian Resolutions Pro and samples were measured in the region 4000 – 400 cm^{-1}; each spectrum was measured 80 times, at resolution 4. To minimize differences which were due to the baseline shifts, the spectra were baseline corrected and ATR-corrected. In IR spectrum of Congo red and Eriochrome Black T in the region between 2300 and 2390 cm^{-1} is presented carbon dioxide located in the ambient air.

RESULTS AND DISCUSSION

It was decided to concentrate on the strongest, best defined and most frequently occurring peaks, as these occurred consistently and were the ones which had been seen in casework spectra. Other small peaks were so small that they may be masked by background noise in the spectra. The infrared spectroscopy is one of the efficient techniques used in the characterization of organic compounds.

IR spectrophotometers as FTIR which was used in the present study to confirm the presence of functional groups as following distinguish stretching vibration band of azo group (-N=N-) from 1504 to 1555 cm^{-1} (7) as shown in Figure 1 in infrared spectrum of diazo Congo red (1531 cm^{-1}), and in spectrum (Figure 2) of monoazo ETB at 1504 cm^{-1}. The peaks at 1612 cm^{-1} and 1531 cm^{-1} are typical for the red azo dyes (23, 24). The asymmetry stretching vibration of S-O(SO_3-H) group appearance at 1196 cm^{-1} and 1336 cm^{-1} to NO_2. Wavelengths around wavelengths 3200 and 3300 belong to O-H.

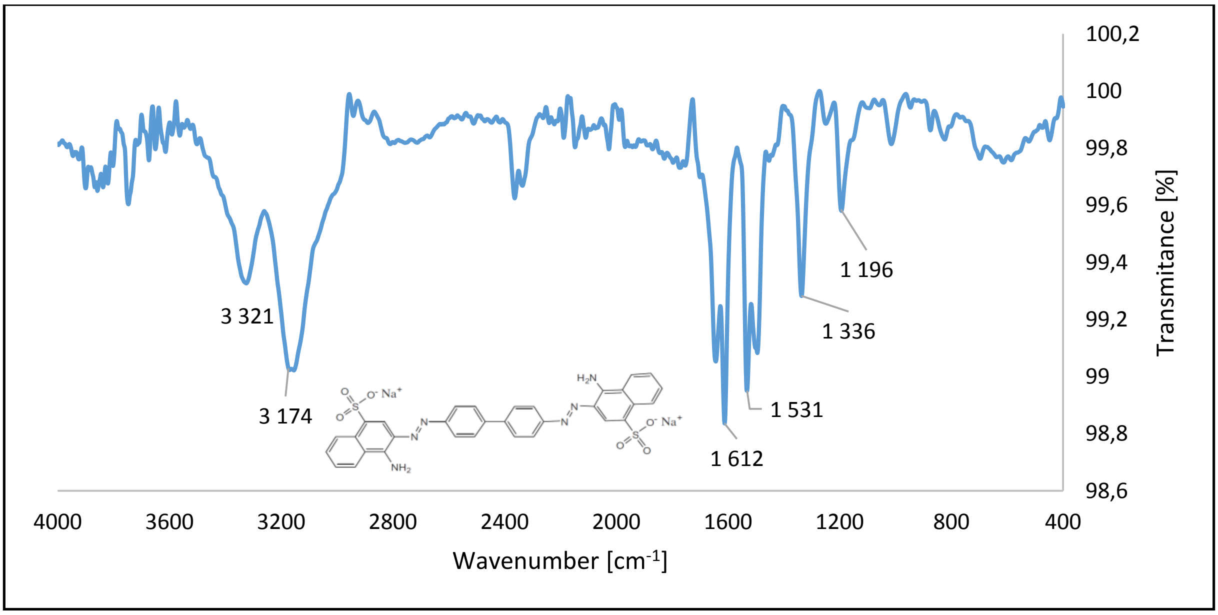

***Fig. 1** Infrared spectrum of Congo red*

In the Figure 2, the aromatic -C-H stretching of monoazo dye Eriochrome black T was found at 2995 and 2902 cm^{-1}. The asymmetry stretching vibration of S-O (SO_3-H) group appearance at 1192 cm^{-1} position, while symmetry at 1043 cm^{-1}. The IR spectrum of EBT exhibited band at 1504 cm^{-1} which is assigned to N=N stretching vibration. The stretching vibrations owing to -NO_2 group were obbserved at 1334 cm^{-1} (8).

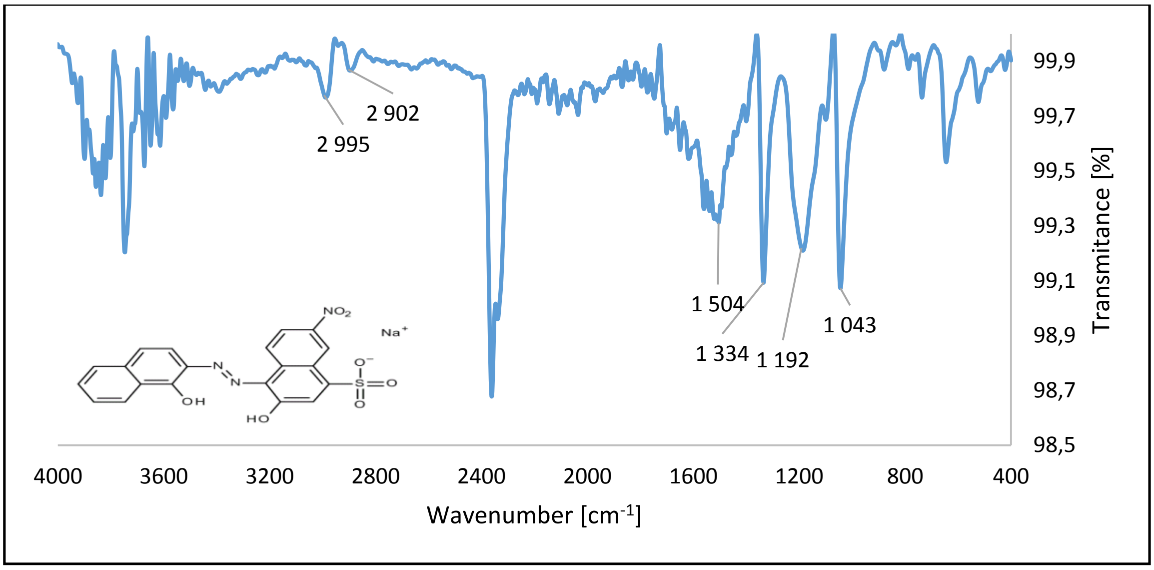

***Fig. 2** Infrared spectrum of Eriochrome black T*

According to (25), the region of 1540 – 1700 cm^{-1} became the most important for FTIR spectra of Methylene blue molecul (Figure 3). The weak band at 1660 – 1714 cm^{-1} corresponds to the C_{het} = $N^+(CH_3)_2$ stretching vibrations. The intense band with the peak at 1593 cm^{-1} corresponds to the C=N and C=C vibrations of MB. In the lower-frequency region the FTIR spectrum becomes complicated due to the noticeable rotational structure. The absorption in the region at 1390 cm^{-1} is attributed to the symmetrical and asymmetrical bending vibrations of the CH_3 functional groups of MB. Peak at 1334 cm^{-1} corresponds to the stretching vibrations of the C-N terminal saturated dimethylamino groups (25, 26).

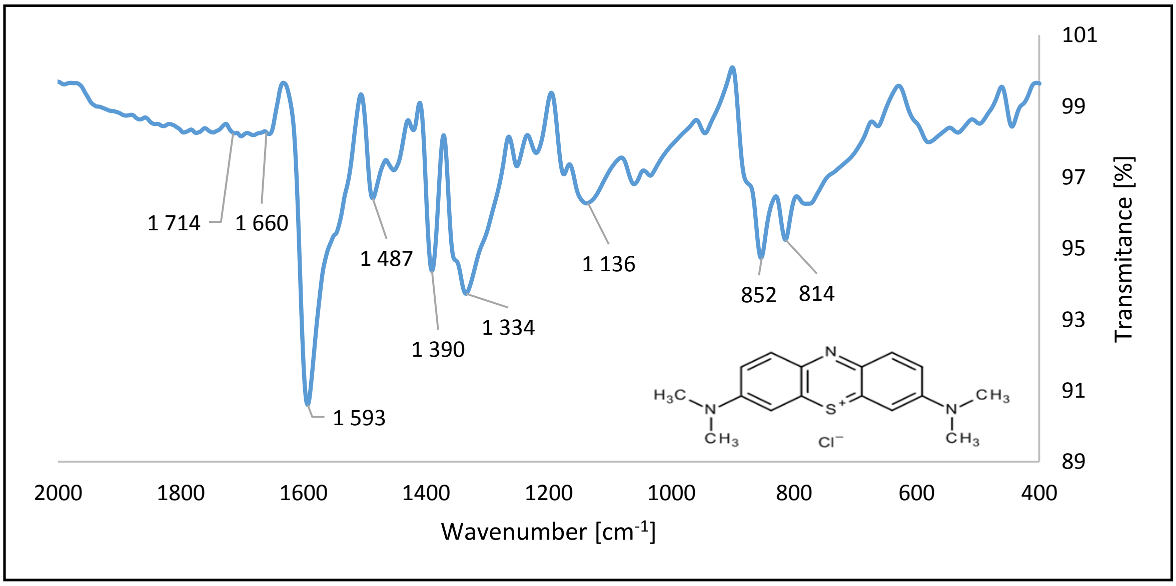

***Fig. 3** Infrared spectrum of Methylene blue*

The FTIR spectrum for the dye Naphtol green B (Figure 4) presents the characteristic bands of the sulfonate groups between 1352 and 798 cm^{-1}, in addition to the bands referring to the aromatic rings between 1603 and 1495 cm^{-1}, owing to the vibrations of naphthalene. Wavenumbers from 1500 to 1600cm^{-1} can be assigned to –C-N=O stretching vibration. The stretching vibrations of S-O (SO_3-H) group appearance at 1034 cm^{-1} and 1119 cm^{-1} (27).

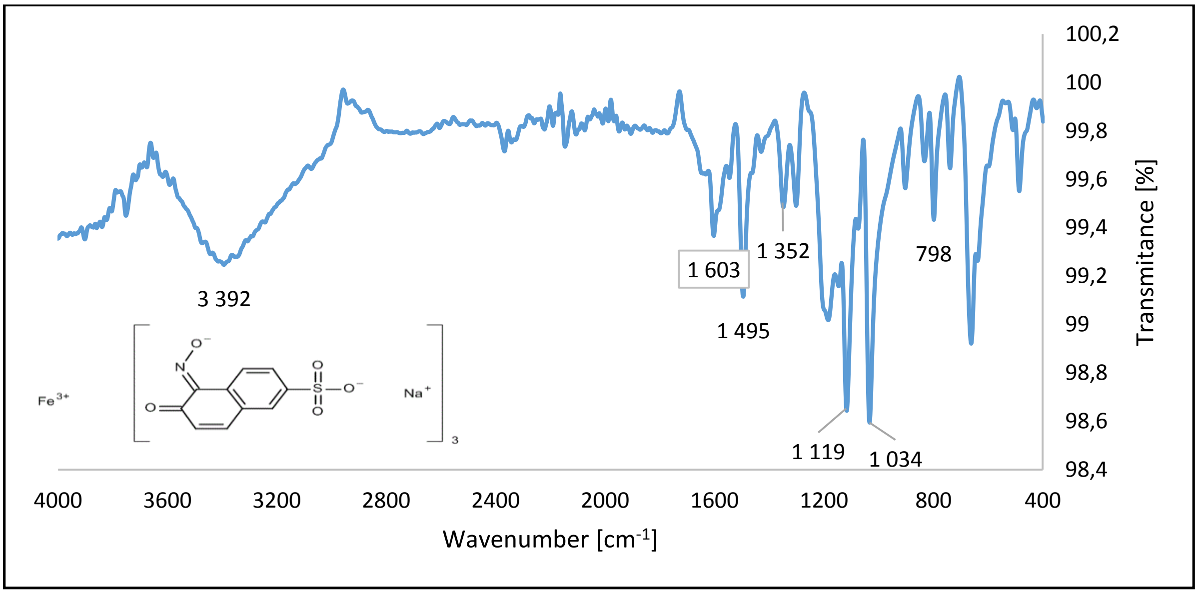

Fig. 4 *Infrared spectrum of Naphtol green B*

CONCLUSION

The spectral interpretation of dye spectra revealed valuable information about the identification and characterization of differend types of dyes without any reductive cleavage of bond present in the dyes. In Table 3, selected typical dyes bands are shown.

Table 3 Typical dyes vibration bands

Wavenumber [cm^{-1}]	**Vibration bands of dyes**
3300 – 3500	O-H stretching
1500 – 1600	N=N stretching
1600 – 1800	COOH stretching
1400 – 1560	N=O stretching
1334	NO_2 stretching
1043 – 1304	SO_3-H stretching
2900 – 2995	O-CH_3 stretching

The methods FTIR is non-destructive, fast and very useful even for small sample quantities and can be used for monitoring the dyes in environment as well as in consumer products.

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