

Spectroscopic Study For The Pollutants Gelbstoff In Diyala River And Its Effect On Raman Spectrum

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Abstract

The aim of this project is to limit the pollutants Gelbstoff in Diyala River and its effect on Raman spectrum by using fluorescence and Raman technique. Many samples of river water were taken from different areas starting from Abu- Seda, Al-Akheder, Swamrah region, Bohrez and mouth of river region in Tigris in south of Baghdad in Al-Rustamiah region where there was an increase in the pollutants as the river runs towards the south. Besides, by taking some samples from the estuary of Diyala River, it was proved that the proportion of the pollutants in this region was higher than in Tigris.

The peak of Raman spectrum ranges between [399-401] nm, and that Raman spectrum shift $\Delta\bar{\nu}$ ranges also between [3508.7-363307] cm^{-1} and oscillator strength of O-H for H_2O molecule is between [687-737.4] N/m. These differences are due to the variation of the saltiness in different regions. All that results are correspondent according to literature.

دراسة طيفية للملوثات (Gelbstoff) في نهر ديالى وتأثيرها على طيف رامان
الخلاصة

إن الهدف من هذا البحث هو لتحديد الملوثات Gelbstoff الموجودة في نهر ديالى وتأثيرها على طيف رامان باستخدام تقنية رامان والفلورة حيث تم أخذ عينة نماذج للنهر من منطقة أبو صيدة و الاخضر ومنطقة السوامرة و بهرز ومنطقة مصب النهر في نهر دجلة في منطقة الرستمية جنوب بغداد حيث كانت هناك زيادة في الملوثات كلما اتحركنا جنوب النهر كذلك كانت نسبة هذه الملوثات أعلى مما موجودة في نهر دجلة من خلال عينة لنهر دجلة أخذت قبل مصب نهر ديالى بدجلة . وكانت قمة طيف رامان تتراوح ما بين [399-401] nm حيث إن إزاحة طيف رامان $\Delta\bar{\nu}$ كانت أيضاً تتراوح ما بين [3508.7-3633.7] cm^{-1} وكانت كذلك قيم ثابت القوة Oscillator Strength تتراوح ما بين [687-737.4] N/m.

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حيث إن هذه الاختلافات كانت بسبب الملوحة المتغيرة من منطقة لآخرى. كانت كافة النتائج متوافقة مع ما جاء من الأدبيات.

1-Introduction

Pollution is considered as one of the serious problems, which man and countries suffer from because of its bad effect on the environment, health, and all the beings because it changes the rate of growth their. It falls into different kinds: air pollution, water pollution and the chemical pollution, which is the result of salts and sulfates.^[1]

The studies on Diyala River are multiple,^[1,2,3,4] and that is because of the importance of this river and its effect on the lives and people. Its area is 32600 km² and it springs from the mountains in west of Iran, and having crossed to Iraq - Iran borders. Its Abu -Tangro branch falls into it, then it runs towards west south crossing Hemreen series to the south and falls into Tigris south of Baghdad.

Gelbstoff which is the mixture of Fulvic Acid and Humic substance.^[8]

These substances have double bonds, which participate in the changes that take place in the resultant spectrum of these substances. Therefore, when the light falls on the dissolving substance, the absorbing part

The most dangerous pollutants in the river are called yellow substance or Gelbstoff where many researchers were concerned with this substance.^[5,6]

2-Theoretical

Gelbstoff is caused by some kind of bacteria that causes the disintegration of plants and animals.^[7] The disintegration results participate in forming the Fulvic Acids; some chemical reactions of the resulting material are formed like saccharin and Amino acid which form the main part for these results. These results in return form the Fulvic Acids, which have particular weights 100000 higher than Dalton. The maximum polymerization and numerous of the reaction results of saccharin materials and Amino Acids lead to the formation of Humic substances or yellow substance follows Lambert-Beer law that states the amount of the absorbing light appropriate with the number of the absorbing particles. This law can be expressed as

$$\text{Log}(I_0/I) = \epsilon CL \text{ ----- (1)}$$

Where

I_0, I : incident and transmitted intensity, respectively. C : is the molar concentration (mol.lit^{-1}).
 L : is the cell thickness (cm).
 ϵ : Molar absorptivity ($\text{lit.}(\text{mol.cm})^{-1}$).

So, the reason why it is called yellow substance Gelbstoff is due to the of high absorption of this material in ultra- Violet ray region and the blue region of the spectrum.^[9] Concerning the molecule of water, which didn't absorb in range of dissolving material absorption, is polarized by the electric field action of the incident rays that leads to emission of Raman spectrum that follow the next law

$$\bar{\nu}_R = \bar{\nu}_{ex} \pm \Delta\bar{\nu} \text{----- (2)}$$

Where

$\bar{\nu}_{ex}$: is the wave number of scattered ray.
 $\Delta\bar{\nu}$: is the difference in the vibration level.

The positive and negative sign represents the shift of Raman spectrum towards the short and long wavelength respectively.

3-Experimental

Many samples were taken from different regions of Diyala River starting from Abu- Seda, border Al-Akheder, Swamrah region and Bohrez ending with mouth of the river in Tigirs at Al- Rustamiah region. Also, a sample for Tigris was taken before its meeting with Diyala River. Besides, a standard sample of tap water was taken for comparison and to check how it is good for drinking.

Measurements were made in spectroflourophotometer RF-540 Shimadzu to measure fluorescence spectrum of the contaminated materials and Raman spectrum of water.

4- Results and discussion

As seen in figure (1), the peak of fluorescence spectrum represented by (b) has relative intensity that differs according to the regions where the samples are taken from. This intensity begins to increase starting from Abu- Seda ending with the estuary in Al-Rustamia.

The increasing of the intensity indicates that the proportion of the pollutants increases and this leads to the absorption increase according to Lambert- beer law.

As it is shown in table (1), the fluorescence of Gelbstoff

increases from the north of the river to the south.

The proportion of these materials in the south of the river (Al-Rustamiah) was very high (beyond the limited spectrum range). Figure (2) shows that the proportion of these materials in Tigris is less than it is in Diyala River because of nature of the regions in which these rivers run. The reason behind the high pollutants in Diyala River is the drainage of drain water into the river especially in Al-Rustamiah, which is considered a lifeless region because of draining the water of Al-Rustamiah station to treat the drainage water coming from Baghdad in Tigris which drains thousands of cubic meters of the sewage and industrial waters that are partially treated.

[10]

Therefore, the proportion of these materials was very high in this region (beyond the limited spectrum range). The concerning spectrum (a), it represents Raman spectrum that can be measured by Spectrofluorophotometer in wavelength (399-401) nm. Which represents the inelastic scattering, which is called Raman phenomenon or Stocks lines toward the long wavelengths. This difference in

Raman spectrum peak is because of various high saltiness from region to other,^[9] also there is an increase in Raman spectrum intensity because of suspensional material which increase from the north of the river to the south as shown in table (3).

The spectrum at the wavelength (350)nm that is beyond the limited spectrum range is because of elastic of Raylie scattering and this spectrum has a frequency equal to that of the excited spectrum. After the excitation, the molecule of water returns to the same level that moved in it without any absorption in the spectrum of falling ray.

From the results, Raman's shift $\Delta\bar{\nu}$ can be considered by using relation (3), which can be written as

$$\Delta\bar{\nu} = 10^8 \left(\frac{1}{\lambda_{ex}} - \frac{1}{\lambda_R} \right) cm^{-1} \text{-----} (3)$$

Where

λ_{ex} : represents the wavelength of excited spectrum.

λ_R : represents the wavelength of Raman spectrum.

The results are shown in table (2)

Oscillator strength k of O-H bond has been considered via relation (4)

$$\Delta\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{M}} \dots\dots (4)$$

$$M = \frac{m_H M_O}{m_H + M_O}$$

Where

M : reduced mass

c : Light velocity

5-Conclusions

As it is noticed in the results; proportion of pollutants Gelbstoff in Diyala River is higher than it is in Tigris because of the nature of the regions through which rivers run. Therefore, these rivers, especially Diyala River, are considered not good for drinking by comparing them with a sample of tap water as it is shown in figure (3). Besides, the proportion of salt was high via the change in the value of Raman spectrum peak. And the technical of spectrofluorophotometer and Raman is easy way to measure the pollution according to the chemical analyses.

Because the particular of water has vibrating terminals with small mass (H

atom), Raman spectrum could be measured by spectrofluorophotometer.

The change in polarization is large via the large amplitude of the vibration, where the energy of vibration proportionally reverses with square root of the reducer mass according to relation (3).

The results show the effect of Raman spectrum on the pollutants, where the shift in the spectrum peak is caused by the high saltiness and the overlap between the spectrum of fluorescence and Raman as in Al-Rustamiah sample and it is one of the problems of measuring this spectrum.

The results are correspondent according to literature.^[11,12]

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Table(1): Shows the value of relative intensity of the pollutants Gelbstoff of the samples.

| Samples | R. I. Gelbstoff (a. u.) % |
|--------------|------------------------------|
| Tap water | 21.8 |
| Abu-Seda | 49.2 |
| Al-Akheder | 50.7 |
| Swamrah | 63.9 |
| Bohrez | 64.4 |
| Al-Rustamiah | Out of scale |
| Tigris | 82.62 |

Table(2): Shows the value of relative intensity and the wavelength and Raman shift of the chosen samples.

| Samples | R. I. of Raman (a. u.) % | λ of Raman (nm) | Raman shift (cm^{-1}) |
|--------------|--------------------------------|----------------------------|-------------------------------------|
| Tap water | 55.0 | 399 | 3508.7 |
| Abu-Seda | 72.8 | 399 | 3508.7 |
| Al-Akheder | 73.1 | 400 | 3571.4 |
| Swamrah | 80.0 | 400 | 3571.4 |
| Bohrez | 83.0 | 401 | 3633.7 |
| Al-Rustamiah | Overlap with fluorescence | ————— | ————— |
| Tigris | 80.2 | 399.9 | 3508.7 |

Table(3): Shows the value of oscillator strength of the chosen samples.

| Samples | Oscillator Strength (N/m) |
|--------------|---------------------------|
| Tap water | 687.0 |
| Abu-Seda | 687.0 |
| Al-Akheder | 712.4 |
| Suamra | 712.4 |
| Bohres | 737.4 |
| Al-Rustamiah | ————— |
| Tigris | 687.0 |

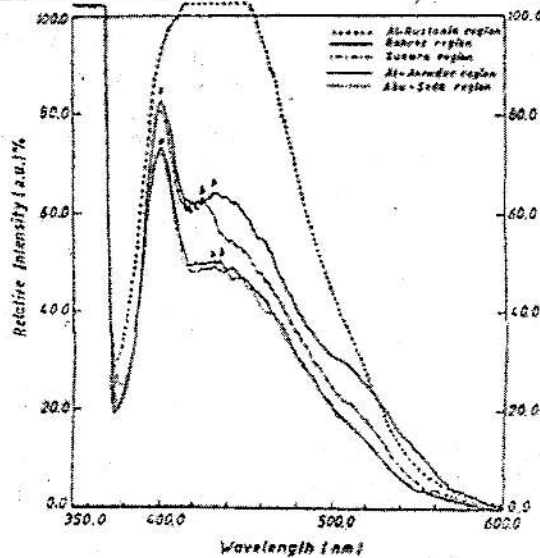


Fig.(1): Shows (a) Raman Spectrum (b) Fluorescence Spectrum of Gelbstoff of difference sample of Diyala River.

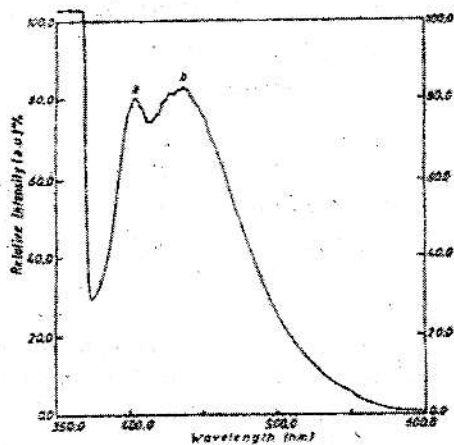


Fig.(2): Shows (a) Raman Spectrum (b) Fluorescence Spectrum of Gelbstoff of Tigris River sample.

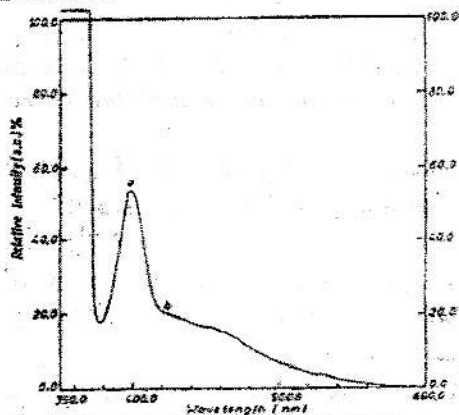


Fig.(3): Shows (a) Raman Spectrum (b) Fluorescence Spectrum of Gelbstoff of Tap water.