Synthesis, Theoretical Treatment and Investigation of Adsorption of 4,4'-(1E,1'E)-(Methylenebis(4,1-phenylene))bis(diazene-2,1-diy1))bis(naphthalen-1-ol) on Olive Peel

Zainab J. Khudair 1*, Khawla K. Jassim 2 and Ameena N. Seewan 3

1,3 Science Dept., College of Basic Education, Al-Muthanna University, Samawah, Iraq
2 Chemistry Dept., College of Science, Al-Muthanna University, Samawah, Iraq
E-mail: chemistry.zainb@mu.edu.iq

Abstract. In this study, the compound 4,4'-(1E,1'E)-(methylenebis(4,1-phenylene))bis (diazene -2,1-diy1)bis (naphthalen-1-ol) synthesized by reaction of 4,4'-Diaminodiphenylmethane with Alpha-naphthol. This compound was identified by using an element C.H.N analyzer, Infra-Red spectrum, Ultraviolet and Visible spectrum, and GC-Mass spectrometry. We used olive peels to adsorb the synthesized dye from an ethanol solution. The results obtained showed that olive peel has a good adsorption on the bis-azo dye. Temperature and pH effect were studied under multiple conditions. The result showed that the adsorption increased with temperature increasing, and adsorption efficiency according to pH as 7<4<9. Theoretical treatment was studied in gas phase for molecular mechanics and semi-empirical computations using the hyper chem8 program. Dipole moment, formation heat and binding energy were done via the methods (PM3 and ZINDO/S) at 25 ºC. Electrostatic potential of active sites were also studied for the newly synthesized bis-azo dye. Vibrational values were evaluate using PM3 method, the theoretical frequencies obtained from the calculations were consistent with the experimental values. HOMO & LUMO (frontier orbitals) were studied by PM3 method, electron ic spectrum was also studied using ZINDO/S method and compared with experimental spectrums. The results obtained were closely related between the theoretical and experimental spectrum.

Keywords: Bis-azo, Olive peel, Adsorption, Theoretical study.

1. Introduction

More than one million tons of dyes are produced annually, 60-70% of them are azo dyes. The use of dyes has increased over the years, and widely used in various industries such as textiles, paint, paper, cosmetics, pharmaceuticals, printing, and foodstuffs [1]. Dyes are one of the main pollutants [2-4]. A literature survey identified adsorption as a potential technique for purifying wastewater from dyes. Adsorption is the most preferred method for treating liquid waste in textile industry compared to other available physical, biological and chemical methods, due to its simple, flexible design and ease of use [5]. Some side products may be produced from the adsorption process, some of which may be beneficial or at least non-toxic. The adsorption process is also considered to involve lower operating costs. Moreover, it has no environmental problems, don’t produce any sludge and produce high quality treated water. Although adsorption is an excellent dye removal technique, it has significant limitations to its application due to the limited availability of low-cost adsorbents [6,7]. One of the most commonly used adsorbent is activated carbon, as it is characterized by its high surface area and great adsorption capacity. Due to the high cost and lack of reusability of activated carbon, the need to explore new adsorbents with low cost, reusable, biodegradable and the possibility of regeneration, as well as the high efficiency of removing dyes, has increased. Many adsorbents have been implemented to adsorb dyes from wastewater with low cost and high efficiency, most of them are natural and
modified clays, modified agricultural by-products, bagasse, chitosan ash, industrial waste, coconut pulp, charcoal, peat and neem leaves [8, 9]. The cost of adsorbents is usually unstable and frequently changing depending on the changes in prices in the markets, and it varies greatly according to the manufacturing companies, even if they contain exactly the same material. The material chosen for a specific application should preferably be less expensive and more suited to specifications to achieve its intended use. The variation and diversity of adsorbents and the expansion in their spread and manufacture make the selection process difficult [10]. In the present work, a new dye was synthesized and its adsorbent effects on olive peels were identified, along with the theoretical study of some properties of the synthesized dye.

2. Experimental

2.1. Chemicals and Instruments
The materials and solvents that were supplied by Sigma Aldrich, Fluka, and BDH. C.H.N elementals were measured by EM - 017. FT-IR spectra were recorded on an FT-IR—8400S plus spectrometer operating from (4000—400 cm⁻¹) in KBr pellets. UV—Visible spectra were recorded by UV—1800 PC Shimadzu, Al-Muthanna University, Semawa, Iraq. The GC-Mass spectra were recorded on at 70 eV using Agilent technologies mass selective detector 5973 watt work in the department of chemistry, Technology Shareef University, Tehran, Iran.

2.2. Preparation of (MBN) compound
The compound of 4,4'¬-((1E,1'E)-(methylenebis(4,1-phenylene))bis (diimide -2,1-diy1))bis (naphthalen-1-ol) (MBN) diazotized by following the method described in literature [11], 4,4'-Diaminodi phenylmethane (0.01mol) was dissolved in conc. HCl (3 mL) and (10 mL) of distilled water, after that the mixture cooled in an ice bath, after the temperature reached less than 5 °C, (10 mL) of cooled solution of (0.01 mole) sodium nitrite was added dropwise to keep the temperature below 5 °C for 15 minutes. After that, the reaction mixture was added to an alkaline solution of (0.02 mole) alpha-naphthol slowly and left for 20 minutes, the reaction mixture irradiated with a microwave at 700 W for 5 minutes, after the reaction was completed, the precipitate was collected by filtration, washed with distilled water and dried.

Physical data of MBN are described in Table 1.

| Color       | melting point (°C) | yield % | m.wt (g/mol) | Found (calc.%) |
|-------------|-------------------|---------|--------------|----------------|
| Dark red    | 232-234           | 90      | 508.57       | 78.51 (77.93)  |
|             |                   |         |              | 4.82 (4.76)    |
|             |                   |         |              | 10.30 (11.02)  |

2.3. Olive peel surface preparation
A surface of olive peel used as an adsorbent was prepared from fresh olives picked and cut into small pieces, washed several times with distilled water to remove dust, dried in the air and grinded into a fine powder, then washed the powder with distilled water and making sure that the impurities were removed and then dried in an oven at a temperature of 60 °C for two hours.

2.4. Preparation of Stock solution
A stock aqueous solution of the synthesized bis-azo dye was prepared at a concentration of 125 ppm by dissolving 125 mg of the dye in 1000 mL of ethanol. Using UV-visible spectrophotometer for determining the maximum absorbance wavelength of MBN at 250-700 nm. To plot the standard curve, several concentrations of MBN dye were prepared from (2-10 ppm), which were used to measure the different dye concentrations in ethanolic solution.

2.5. Study pH effect on Adsorption of MBN
0.1N of hydrochloric HCl and 0.1N of NaOH was added to different concentrations of MBN dye to justify pH, to study the effect of pH changing on adsorption efficiency of MBN dye on 0.05 g of the powdered olive
The mixture stirred at 5 °C for one hour, MBN dye concentrations were determined by measuring the absorbance at wavelength of 488.00 nm of the solution.

2.6. Study the temperature effect on the bis-azo compound adsorption
A volume solutions of 10 mL were used with different concentrations with pH 7 of the MBN dye which was added to 0.05 g of olive peel. The mixture stirred for one hour to be exposed to the same temperature at 298, 308, 318 K, MBN dye concentrations were also determined by measuring the absorbance at wavelength of 488.00 nm of the solution.

3. Results and Discussion
3.1. Synthesis of MBN dye.
MBN was prepared according to the following Scheme:

![Scheme for the synthesis route of MBN compound](image)

The prepared compound was characterized by FT-IR spectroscopy, GC-Mass spectrometry and C.H.N. analysis.

3.2. Spectroscopic Studies:
3.2.1. Infrared Spectral Study:
FT-IR spectrum of MBN showed the disappearance of NH2 stretching bands at 3354 cm⁻¹ and appearance of broad peak for phenolic OH at 3444 cm⁻¹. FT-IR spectrum also showed the appearance of strong peaks at 1618 and 1498 cm⁻¹ for C=C and N=N groups, respectively (Figure 2) [12,13].

![FTIR spectrum of MBN compound](image)

| FTIR Measurement |
|------------------|
| 500 | 1000 | 1500 | 2000 | 3000 | 4000 |
| %T |
| 3444.98 | 3032.20 | 2920.32 | 2848.96 | 1618.33 | 1599.04 |
| 1554.68 | 1498.74 | 1448.59 | 1396.51 | 1300.07 | 1251.84 |
| 1232.55 | 1207.48 | 1176.62 | 1143.83 | 1033.88 | 1012.66 |
| 983.73 | 947.08 | 916.22 | 860.28 | 823.63 | 785.05 |
| 748.41 | 682.82 | 644.25 | 592.17 | 534.30 | 488.01 |

![Table 2. FT-IR spectra of MBN compound.](image)
3.2.2. UV–Vis spectral data for MBN compound:
The azo functional group (-N=N-) usually absorb at the wavelength range from (350 - 370) nm [13]. The electronic spectrum of MBN compound exhibits transitions at (488, 314.5 and 253) nm respectively, these bands probably belong to n-π* and π-π* transition of N=N group [14].

3.2.3. Analysis of mass spectrum:
The mass spectrum of MBN compound showed the molecular ion peak at m/z = 508(R%55), the important fragmentation peaks shown at m/z = 466(R%1), m/z = 367(R%5), m/z = 353(R%20), m/z = 337(R%10), m/z = 171(R%15), m/z = 157(R%5), m/z = 143(R%100), m/z = 129(R%10), m/z = 115(R%50), as shown in ‘Figure 4’.

3.3. Study of Adsorption of MBN compound
The study of adsorption of MBN on the surface olive peel at temperature 298 K was calculated and the amount of absorbent material drawn against equilibrium concentration to give the general form of isotherm adsorption

| 1498 s | 1618 s | 3032 m | 3444 b |

Where: m: medium, s: strong and b: broad

Figure 3. UV-Visible spectrum of MBN compound

Figure 4. Mass spectrum of MBN compound
3.3.1. Effect of Temperature
The effect of temperature on the adsorption of synthesized MBN dye at different temperatures, which are 298, 308 and 318 K was studied at a constant pH. The temperature changes showed an obvious change in the efficiency of dye adsorption on the olive peel, it was found that the adsorption of MBN increases with increasing the temperature, so the reaction is endothermic [15], as it shown in Figure 6.

3.3.2. The Effect of Initial pH
The effect of changing pH on the efficiency of adsorption of the dye on the surface of the olive peels was studied at different pH ranges (4 – 9) by adding acidic or basic solutions, it was found that the adsorption efficiency decreases when the pH is reduced, reaching its highest level at 9 PH value to decrease and reach its lowest levels at 4 pH value and this change can be explained by the fact that at basic medium the efficiency of adsorption increases because positive charges have a tendency to bond with the surface greater than the association with the solvent molecules [16], as shown in Figure 7.
3.4. Theoretical Studies

3.4.1. Energies and Dipole Moment

The study of energetic theoretically could predict the occurrence of molecular processes or not. Low energy systems are the most stable in all computational chemistry techniques, so their molecular structure is compatible with the structure with the minimum energy [17]. Dipole moment was used to measure the charge density of the dye. The accuracy of the overall distribution of electrons in the molecule is difficult to assess because it contains all of the multiple dipole moments. In this study, standard enthalpy of formation ($\Delta H^{f}$), dipole moment ($\mu$) and binding energy ($\Delta E_{b}$) of MBN compound were calculated theoretically by PM3 method and HOMO & LUMO (frontier orbitals) were calculated also by using PM3 method.

Table 3. Formation, binding energies and dipole moment for MBN dye

| $\Delta H^{f}$ (KJ.mol$^{-1}$) | $\Delta E_{b}$ (KJ.mol$^{-1}$) | $\mu$ (debye) | HOMO | LUMO | $\Delta E_{gab}$ (KJ.mol$^{-1}$) |
|-----------------------------|-----------------------------|-------------|------|------|-------------------------------|
| -61922.91                   | -93139.47                   | 4.54        | -8.54| -0.85| 7.69                          |

3.4.2. Theoretical Vibration Frequencies

PM3 method was used to evaluate vibrational frequencies of MBN compound following literature [18]. The theoretical spectra from the semi-empirical computation help explain peaks of the experimental spectrum of MBN. The most characteristic calculated vibrational frequencies were chosen for the bis-azo dye assignment. The theoretical wave number of the synthesized dye showed some differences against experimental values, and these differences are mostly acceptable in computational chemistry.

Table 4. Theoretical and experimental frequencies in cm$^{-1}$ of MBN compound

|            | C=C      | N=N      | C-H     | O-H     |
|------------|----------|----------|---------|---------|
|            | 1684.65* | 1508.60* | 3084.92*| 3144.36*|
|            | 1618.33**| 1498.74**| 3032.20**| 3444.98**|
|            | (3.9)**  | (0.6)**  | (1.7)** | (9.6)** |

Where:
* : Theoretical value
** : Experimental value
***: Error %
3.4.3. Theoretical UV-Spectrum

Theoretical electronic data of MBN dye was evaluated by ZINDO / S method, the results showed that there is high acceptable between the experimental and theoretical data.

| Transitions  | Theoretical | Experimental |
|--------------|-------------|--------------|
| $\pi \rightarrow \pi^*$ | 355.05 nm | 488.00 nm |
| $\pi \rightarrow \pi^*$ | 338.73 nm | 314.50 nm |
| $\pi \rightarrow \pi^*$ | 271.89 nm | 253.00 nm |
4. Conclusion

1- The results showed the ability of olive peels to adsorb the synthesized dye with high efficiency under normal conditions of temperature and pH.
2- Adsorption efficiency of MBN dye on olive peel increases with the increasing of temperature as it follows: 298<308<318 K.
3- Adsorption efficiency of MBN dye on olive peel according to pH values, increases in basic and decreases in acidic mediums as it follows: 4<7<9 pH values.
4- The theoretical results of formation and binding energies showed that the synthesized dye was a stable compound.
5- MBN dye structure was confirmed by the experimental spectra and found that it is almost similar with the theoretical results calculated by PM3 and ZINDO / S methods.
6- Active sites of MBN dye were evaluated theoretically using semi-empirical methods.

Acknowledgement
The authors would like to thank Dept. of Science / College of Basic Education/AL-Muthanna University for the facilities during this work.

References
[1] Dai Q, Zhang S, Liu H, Huang J, and Li L 2020 Bioelectrochemistry, 131 107349.
[2] Sarkheil H, Noormohammadi F, Rezaei A.R. and Borujeni M.K 2014. In International Conference on Agriculture, Environment and Biological Sciences.
[3] El- Haddad M, Regti A, Laamari M.R, Slimani R, Mamouni R, El- Antri S and Lazar S 2014 J. Taiwan. Inst. Chem. Eng, 45 533.
[4] Tsui L S , Roy W R and Cole M A 2003 Color. Technol, 119 14.
[5] Crini G.2006 Bioresour. Technol, 97 1061.
[6] Choy K K , McKay G and Porter J F 1999 Resour. Conserv. Recycl, 27 57.
[7] Reffas A 2010 Étude de adsorption de colorants organics (rouge nylonan et bleu de méthylène) sur des carbons actifs préparés à partir du marc de café, PhD.thesis.
[8] Lora-Wainwright A 2009 Soc. Anthropol. 17 56.
[9] Al-Qodah Z, Yahya M and Al-Shannag M 2017 Desalin Water Treat, 85 339.
[10] Cao X, Huang X, Liang P, Xiao K, Zhou Y, Zhang X and Logan B E 2009 Environ. Sci. Technol, 43 7148.
[11] Wu T Y , Mohammad A W, Lim S L , Lim P N and Hay J X W 2013. Wastewater reuse and management (Springer, Dordrecht) p 47-103.
[12] Purohit D H, Dodiya B L , Ghetiya R M , Vekariya P B and Joshi H S 2011 Acta Chim. Slov, 58 53.
[13] Pavia D L , Lampman G M , Kriz G S and Vyvyan J A 2008, Introduction to spectroscopy. (Cengage Learning).
[14] Jasim K K , Kadhim Z Y , and Khudair Z J 2018 Jour Adv Res. Dyn. Control Syst., 10 159.
[15] Geçgel Ü , Üner O , Gökara G. and Bayrak Y 2016 Adsorp .Sci. .Technol, 34 512.
[16] Vijayakumar G , Tamilarasan R and Dharmendirakumar M 2012 J. Mater. Environ. Sci, 3 157.
[17] Atkins P W 1997 The periodic kingdom: A journey into the land of the chemical elements. Science Masters.
[18] Seewan A N and Alias M F 2013 Baghdad. Sci. J, 10 (Special issue in Chemistry Conference).