Synthesis, Characterization, Theoretical Study and Investigation of Adsorption of 4-(Quinolin-8-yldiazenyl)naphthalen-1-ol on Olive peel

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Abstract. Azo dye {4-(Quinolin-8-yldiazenyl)naphthalen-1-ol} was synthesized by reaction of 8-Aminoquinoline with Alpha-naphthol. The product identified by using (CHN, IR, UV-Visible spectra and melting point. The Olive peel was used to adsorb the azo dye from ethanolic solution; the results showed that the Olive peel is good absorbent. Effect of pH and temperature were studied. It was shown that the efficiency of adsorption decreased at (pH=5 and 7) comparing with the basic medium, and the adsorption decreased with increasing the temperature. A theoretical treatment in gas phase was studied by using hyper chem-8 program for the molecular mechanics and semi-empirical calculations. The heat of formation and binding energy as well as dipole moment was calculated by using ZINDO/1 and PM3 methods at 298 K. The electrostatic potential of t was calculated for the reactive sites of the molecules, PM3 was used to evaluate vibrational spectra of free ligands. The obtained frequencies agreed well with experimental values. The calculation helped to assign unambiguously the most diagnostic bands. The frontier orbital’s (HOMO & LUMO) were calculated by PM3 method. Electronic spectrum was calculated theoretically by using ZINDO/S method and compared it with experimental results. It appeared a closely between the theory and experimental spectrum.

Keywords: Theoretical study, Adsorption, 4-(Quinolin-8-yldiazenyl)naphthalen-1-ol, Olive, azo, quinolone.

Introduction

Dyes are usually present in wastewater in many industries, leather, including textiles, rubber, paper, pharmaceuticals, cosmetics, plastic, printing, and food industries. They contribute to water toxicity and represent a growing threat to the environment and human and animal. Moreover, waste is known to dye things to be toxic¹, cancer-causing², mutagenic³ and cytotoxic⁴. Dyes are usually resistant to light, water, factors oxidizing and a lot of chemicals; hence it is difficult to decompose once released in aquatic systems. Nitrogen dyes are the largest and more versatile class of organic dye-stuffs. These contain one or more azo bonds (−N=N−) as a chromophore group in connection with aromatic structures containing functional groups such as −OH and −SO₂H. The structures aromatic complex azo dyes compounds make them more stable and more difficult to remove from liquid wastes.
that are separate into the water bodies\(^5\). So, the elimination of these dyes from wastewater is an important target from the environmental point of view. The textile industry is an intensive industry with high water consumption and discharge\(^6\). One of the major pollutants found in water resources discharged around textile industries is dye, and more than one million tons of dyes are produced annually worldwide\(^7\). The physical adsorption process at the solid-liquid interface is known to be a powerful method for removing contaminants owing to economical and environment-friendly reasons. The cost of an adsorption process mainly depends on the cost of the adsorbent and its regeneration\(^8\)-\(^21\). Activated carbon is the most widely used adsorbent for this purpose because it has a high capacity for adsorption of organic matter, but its cost is high. In order to decrease the cost of treatment, the attempts have been made to find low-cost alternative adsorbents. Numerous approaches have been made by various researchers to develop cheaper and effective adsorbents to remove dyes from a variety of starting materials from waste\(^23\)-\(^24\). The purpose of this research aims to study the potential of olive peal powder as a low cost adsorbent for dye removal.

The material and methods

All chemicals used in the present work were supplied by BDH, Fluka and Sigma Aldrich and Element C.H.N analyzer were carried out on EM-017. Mth instrument and the FTIR spectra in the range (4000-400) cm\(^{-1}\) were recorded using KBr disc on FT-IR-8000, single beam path laser, Shimadzu Fourier transform infrared spectrophotometer in the laboratory of Chemistry Department, AL-Muthana University. UV-Visible spectra were measured using UV-1800PC Shimadzu in the laboratory of the engineer/College of engineer/AL-Muthana University.

Prepare of the compound 4-(Quinolin-8-yl diazenyl)naphthalen-1-ol\(^25\)

Quinoline-8-amine was diazotized by the following method: quinoline-8-amine (0.01 mol) was dissolved in concentrated HCl (3 ml) and 10 ml of distilled water chilled in an ice bath, and stir well, after reaching 0-5 °C temperature 10 mL coolant solution of sodium nitrite (0.01 mol) added drop of wise so that the temperature should not exceed 0-5 °C during the 15 minute. The resultant solution was added drop wise with stirring to (0.01mol) of alpha-naphthol which dissolves in 10 ml of 2N sodium hydroxide and 10 ml of absolute ethanol. The mixture was stirred for 20 min. Then the dye is precipitated and filtered off, washed with distilled water to be free salts. The dye dried at the room temperature. Table 1 shows the physical data of the new azo compound. The chemical structure of the used dye is given in Scheme 1.

![Scheme 1: Synthesis of 4-(Quinolin-8-yl diazenyl)naphthalen-1-ol](image-url)
Preparation of 4-(Quinolin-8-yl diazenyl)naphthalen-1-ol solutions

The concentration of a stock ethanolic solution of azo dye 100 ppm prepared by dissolving azo dye in absolute ethanol, the maximum absorbance wavelength of azo dye determined by the absorbance spectrum ranged from 200-800 nm by using the UV-Visible spectrophotometer. The standard curve of choosing an azo dye 4-(Quinolin-8-yl diazenyl)naphthalen-1-ol solutions) prepared at concentrations (2-20 ppm.) and detected by using it for measuring azo dye concentration in ethanolic solution.

Preparation of Olive peel surface

The Olive peel used as adsorbent was washed with distal water, dried in the open air and thengoing. The powder was then washed several times with distal water until impurities were removed and then dried in an oven at a temperature of 60 °C during 2 hours.

Study Effect of pH on azo dye adsorption

The pH of 10 ml volumes of solutions containing various concentrations of the dye were adjusted with 0.1N hydrochloric acid and 0.1N sodium hydroxide to various values of pH and mixed with 0.05 g of powdered Olive peel. The mixtures agitated at 25°C for 1 hour and the dye concentration determined by measuring the absorbance of the solution at 467.50 nm.

Study effect of temperature on azo dye adsorption

The 10 ml volumes of solutions containing various concentrations with pH7 of the dye were mixed with 0.05 g of Olive peel. The mixtures were agitated at (298, 308, and 318 °C) for 1 hour, the dye concentration determined as above.

Results and Discussion

A-Spectroscopic Analysis

Azo dye 4-(quinolin-8-yl diazenyl)naphthalen-1-ol was synthesized by the coupling of diazonium salt of 8-aminoquinoline with alphananthol. The azo dye was identified by using FTIR, UV-Visible and C, H, N analysis as well as melting point measurement. Table 1. FT-IR spectrum of 4-(quinolin-8-yl diazenyl)naphthalen-1-ol shown the disappearance of an absorption bands due to stretching vibration of (NH2) of an aromatic amine with appearance of an absorption band due to the stretching vibration of O-H phenolic at (3051.49) cm⁻¹. The spectrum also shown strong absorption bands at (1620.26 and 1454.38) cm⁻¹ due to the stretching vibration of C=C & N=N groups respectively. The UV-Visible spectrum of the azo compound shown three bands at 209.00, 226.00 and 467.50 nm which may be due to π-π* and n-π* respectively of azo group 26, 27.

Table 1: Physical Properties of 4-(Quinolin-8-yl diazenyl)naphthalen-1-ol

| Colour | M. p. °C | Yield % | M.Wt g. Mol⁻¹ | Found (Calc.) % |
|--------|----------|---------|---------------|----------------|
| orange | 186-188  | 85      | 249.27        | C    72.28, 72.89 |
|        |          |         |               | H    4.45, 3.87  |
|        |          |         |               | N    16.86, 17.10 |
Figure 1: FTIR of the azo compound

Figure 2: UV-Visible of the azo compound

B- Study of Adsorption of 4-(Quinolin-8-yldiazeyl)naphthalen-1-ol on Olive peel:

1-Effect of initial PH

The influence of pH on the removal of azo dye onto Olive peel was investigated in the pH range of 5–9 as shown in Fig. 3. The results of this study showed that at pH(9) the removal efficiency of azo dye Olive peel was increased directly with increasing the concentration of azo dye, and the adsorption was decreased with decreasing pH(5), this may be due to that negatively charge on dye structure can be interact electrostatically with the surface groups28, thus we noted that the optimal pH for adsorption is pH(9).
The amount of adsorbed dye (Eq. 1) or the percentages of removal dye (Eq.2) calculated as follows:

\[ q_e = \frac{v}{m} \times (C_0 - C) \]  
\[ E = \frac{C_0 - C}{C_0} \times 100 \]

Where, \( C_0 \) and \( C \) are the concentrations of initial and remaining dye in solution (mg/L). \( Q_E \) is the amount of dye on adsorbent (mg/g). \( v \), the volume of dye solution (L). \( m \), the mass of adsorbent (g) and \( E \), the dye removal percentage (%).

2-Effect of Temperature

The effect of temperature on adsorption of the azo dye solution with pH of solution pH(7) at temperatures 298, 308, and 313°C has been determined. The results for the adsorption of the azo dye has been shown in Figure 4. The study showed that the efficiency of adsorption azo dye on Olive peel was decreased by increasing temperature, and this may be due to the decrease of the physical forces responsible for sorption. Furthermore, the decreased uptake of the cationic dye removal at higher temperatures (above 298°C) may be attributed to the destruction of some active sites on the adsorbent surface due to bonds rupture, as well as the deformation of surfaces at higher temperature⁴⁹. Consequently, the study found that the optimum working temperature was 298°C.

![Figure 3: Effect of pH on the adsorption of azo dye on Olive peel](image-url)
Figure 4: Effect of temperature on the adsorption of azo dye on Olive peel.

C- Theoretical Studies

(HyperChem8.0) is considered as the most important molecular modeling program. Hyper chem is a quantum mechanics program contains all the molecular modeling programs, through this program, it is possible to draw the molecules by selecting the internal coordinates of the molecules and then predicting their spectral properties. In fact, this program presented a big effort in the field of the scientific research. It is a semi-empirical program and provided precise solutions for the experimental difficulties during the study of some hazardous materials, highly sensitive or very active materials.

Energies and Dipole Moment

Energy is one of the most useful concepts in science. The analysis of energetic can predict what molecular processes are likely to occur, or able to occur. All computational chemistry techniques energy such that the system with the lowest energy is the most stable. Thus, the shape of a molecule corresponds to the shape with the lowest energy. The molecular dipole moment is perhaps the simplest experimental measure of charge density in a molecule. The accuracy of the overall distribution of electrons in a molecule is hard to quantify, since it involves all of the multi dipole moments. In this work the heat of formation (H°f), binding energy (E_b) and dipole moment (µ) for (azo compound) were calculated by PM3 method, also, frontier orbital’s (HOMO & LUMO) were calculated using PM3 method. (Table 2).

| ∆Hf | E_b  | µ   | HOMO | LUMO | ∆E_gab |
|------|------|-----|------|------|--------|
| -35695.22 | -53781.79 | 3.57 | -8.35 | -1.34 | 7.01 |
Theoretical Vibration Frequencies of 4-(Quinolin-8-yldiazenyl)naphthalen-1-ol

Vibration frequencies of Azo compound 4-(Quinolin-8-yldiazenyl) naphthalen-1-ol was calculated using PM3 method, because this method is closer agreement with experimental data than others (Table 3). The theoretical spectra from semi-empirical calculation help in the explanation of the experimental spectrum peaks. The most diagnostic calculated vibrational frequencies were chosen for the assignment of azo compound. Figure The theoretical wave number for the prepared compound shows some deviations from the experimental values, these deviations are generally acceptable in theoretical calculations.

(Table 3): Comparison of experimental and theoretical vibrational frequencies for 4-(Quinolin-8-yldiazenyl) naphthalen-1-ol

| Symb | νC=C | νN=N | ν C-H | ν O-H |
|------|------|------|-------|-------|
| 1647.32* | 1478.60* | 3086.73* | 3302.13* |
| 1620.26** | 1454.38** | 2916.47** | 3051.49** |
| (1.6)*** | (1.6)*** | (5.8)*** | (8.2) *** |

Where:

* : Theoretical frequency

** : Experimental frequency

***: Error % due to main different in the experimental measurements and theoretical treatment of vibrational spectrum.

Figure 5: Calculated vibrational frequencies 4-(Quinolin-8-yldiazenyl) naphthalen-1-ol.
Theoretical UV-Spectra of 4-(Quinolin-8-yldiazenyl) naphthalen-1-ol

The theoretical UV-spectrum of azo compound was calculated using ZINDO/S method and showed some deviations from the experimental values, these deviations are generally acceptable in theoretical calculations.

| Transition    | Experimental | Theoretical(ZINDO/S) |
|---------------|--------------|---------------------|
| n→π*          | 467.50       | 401.63              |
| π→π*          | 226.00       | 250.54              |
| π→π*          | 209.00       | 230.00              |

Figure 6: Theoretical electronic spectrum of 4-(Quinolin-8-yldiazenyl) naphthalen-1-ol

Conclusion

1. The value of binding energy and heat of formation show that the azo compound is stable.
2. The values of vibrational frequencies of prepared azo compound which obtained practically approximately are similar to the vibrational frequencies calculated by PM3 method.
3. The electronic transitions of prepared azo compound which obtained, we found that they are similar to the values of electronic transitions calculated by ZINDO/S method.
4. The active sites of prepared azo compound were determined theoretically by using semi-empirical methods.
5. Batch adsorption process is a suitable method for the removal study of organic contaminants in water.
6. The adsorbent is commercially available low cost of adsorbent and less treatments required.
7. Adsorption process is favorable at basic pH for the removal of dye.
8. The adsorption capacity decrease with increase in the adsorbent dose.
9. The increase in temperature cause decreasing in the adsorption process.
10. Adsorption data for wide range of adsorbate concentrations and adsorbent doses were treated by Langmuir and Freundlich isotherms. All the adsorbent and adsorbates followed the Langmuir and Freundlich isotherms.
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