Thermodynamic Studies of Orange G Dye Removal Using Prepared GO/Zno Nanocomposite

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Abstract
The photocatalytic degradation of orange G dye was investigated utilizing a GO/ZnO nanocomposite. Hydrothermal techniques were used to make the nanocomposite. Orange G dye was removed using aqueous suspension solutions with various dye concentrations, as well as 0.15g/100mL of synthesized nanocomposite. To find the ideal condition for completing the dye removal procedure, a range of criteria were explored. Various variables have been investigated such as the influence of the semiconductor mass, dye concentration, light intensity, and temperature. In this research, ΔH＝-0.082 kJ/mol and ΔS＝－0.197 k J/(k·mol), and 61.185 kJ/mol respectively. The irradiation solutions were investigated using a UV-Vis spectrophotometer.
Keywords: Removal, activation energy, orange G dye, Graphene oxide, nanomaterials.

1. Introduction

Large volumes of wastewater containing organic pollutants such as microbial pathogens, heavy metals, toxic organics, phenolic compounds, dyes, insecticides, and pesticides are produced as a result of continued urbanization and industry. Synthetic dyes are widely used in a variety of industries, including medicines, food, leather, paper printing, cosmetics, and textiles , where dyes are mass-produced [1] . Orange G (OG) dye was chosen because it has a wide range of functional groups, including sulfonate, aryl, hydroxyl, and azo groups [2] . The contaminants are frequently removed using membranes, adsorbents, floating foams, and coagulation agents. Pollution oxidation is a cutting-edge technology that is both efficient and non-destructive. The "advanced oxidation process (AOP)" is a method that was developed. As a result of the photocatalytic processes, semiconductor materials have been discovered as promising agents for AOP [3] . Advanced oxidation processes (AOPs) are based on oxidation reactions involving hydroxyl radicals (•OH) to chemically remove organic contaminants. •OH may totally oxidize organic dyes at ambient temperature because of its high oxidation potential (2.8 V) [4] . Because of their toxic-free nature, low-cost component, high stability, and strong oxidizing power, graphene oxide (GO) and zinc oxide (ZnO) have recently become the most widely utilized photocatalysts for dye remediation. ZnO is also recognized for being the most effective photocatalytic degrader of dyes such as TiO2. ZnO has a better electron mobility than TiO2, with a bandgap of 3.37 eV in bulk and an exciton energy of 60 meV, as recently discovered. The conduction band edge is nearly identical to the TiO2 conduction band in terms of state. However, because of the rapid electron–hole pair recombination, the photocatalytic efficiency is still low. As a result, carbon-based materials are known to improve efficiency. Biomaterial-based graphene and its derivatives have attracted a lot of attention because of its unique mechanical, electrical, and thermal capabilities, as well as other standout features like a large surface area and a high transparency factor. Meanwhile, graphene oxide (GO) is gaining popularity as a result of its unique surface patterns containing carboxyl and hydroxyl groups [5] .

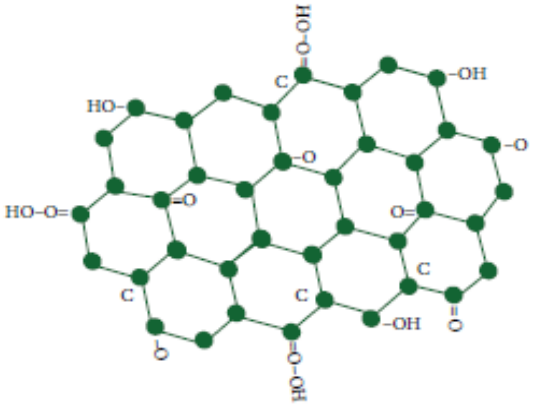

Fig 1. The schematic structure of graphite oxide (GO) .

2. Exprimental Section

Chemicals

Zinc acetate dehydrate, has been supplied by Fluka .
Oxalic acid, supplied by Fluka (Buchs, Switzerland)
Graphene oxide, supplied by Fluka AG.
Orange G dye, supplied by sigma – Aldrich.
All chemicals were employed without any further purification.
2- Photocatalytic degradation processes of Orange G dye using GO/ZnO composites.
Photocatalytic degradation experiments were

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performed for the degradation of Orange G dye in aqueous solution under solar light illumination using GO/ZnO nanocomposite as photo catalyst. A specially designed of photo reactor was used for complete al the experiment which consist of two parts . The first was employed to cool the suspension solution with the help of the cooling water that passed through it. The second part containing the suspension solution with (100 ml) capacity for degraded the dye . The solutions were made with a 100ppm stock solution of Orange G dye in distilled water. A suspension solution mixture for each concentration dye was made possible by stirring. A suspension mixture has been prepared by adding 0.15 g of GO/ZnO nanocomposite to 100 ml of each dye followed by stirring. Respective suspension solution mixture has been irradiated on a bench top Ultraviolet light source . Every 10 minutes, about 2-3 ml of each sample was obtained using a syringe, spun at 3000 rpm for 10 minutes, and the absorption of all samples was evaluated with a UV-Vis spectrophotometer.

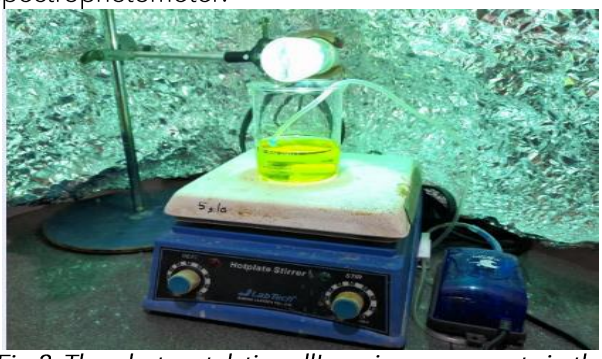

Fig.2: The photocatalytic cell's main components in the photocatalytic degradation of Orange G dye.

3. Result and Discussion

Effect of mass of GO/ZnO nanocomposite on photo catalytic degradation of the Orange G dye

At room temperature, the effect of GO/ZnO nanocomposite mass on the Photo catalysis was used to evaluate the breakdown of Orange G dye using a dye concentration of 10 ppm and an air flow rate of 10 ml/min. The photo catalytic degradation of orange G dye gradually increases, then gradually drops, as the mass of vanadium pentoxide increases till it reaches 0.15g/100ml. When the mass of the GO/ZnO nanocomposite is high, the semiconductor may have the highest light absorption. (0.15g /100ml) is used. The decrease in photo degradation efficiency owing to The first layers of Orange G dye will be the only ones that absorb light. at masses of GO/ZnO nanocomposite more than 0.15 g/100 ml, and the other layers of solution will not receive light photons. In addition, light scattering at Furthermore, at high GO/ZnO nanocomposite loading, light scattering reduces photon intensity, resulting in substantial absorption of light through the first consecutive layers of solution, preventing light from passing through all additional layers in the reaction vessel [6-9] When the loading mass of GO/ZnO nanocomposite is less than the optimum value of 0.15 g/100 ml, the rate of photo degradation of Orange G dye is reduced. This is because the surface area of GO/ZnO nanocomposite decreases, resulting in less light absorption by GO/ZnO nanocomposite, resulting in a lower photo degradation rate of Orange G dye. As shown in Fig.3.

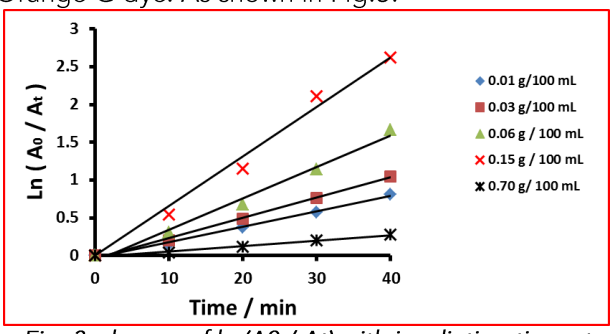

Fig. 3: change of ln (A0 / At) with irradiation time at different temperatures using UV radiation. Initial Orange G dye concentrations 10 ppm, amount of photo catalyst = 0.15 g / 100 ml.

The effect of the initial concentration of Orange G dye on the photocatalytic degradation process

Orange G dye's decomposition period is inversely proportional to its concentration. Different concentrations of 10 ppm, 20 ppm,30ppm,40ppm and 50 ppm of Orange G dye solutions were created to test the effects of starting effects of concentrations on photo degradation rate and efficiency, while other parameters such as temperature and pH remained constant, as shown in Fig. 4. The results showed that increasing the initial concentration of Orange G dye reduces photodecomposition rate substantially. As a result, the Orange G dye breakdown efficiency improves as the initial dye concentration lowers. The reason for this could be that as the photo catalyst's saturation with Orange G dye grows, the active sites of the catalyst decrease and become more filled by Orange G dye molecules, preventing O2 and OH from forming. On the photo catalyst be adsorbed In the end, the creation of OH radicals would be minimized. In simpler terms, photon penetration will be blocked at high concentrations, no photons are adsorbed on the catalyst surface as a result.. As a result, the rate of elimination will be reduced [10-12].

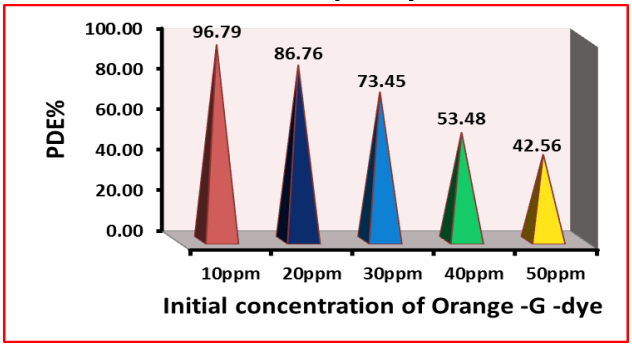

Fig. 4: Photocatalytic degradation efficiency using 0.15g / 100 ml GO/ZnO nanocomposite and 10 ppm of Orange G dye..

Effect of Temperature on photocatalytic degradation of Orange G dye

The effect of Temperature on photocatalytic degradation of Orange G dye was studied in the range of temperature (285 -311) K by keeping other experimental conditions constant at dye concentration of 10 ppm, GO/ZnO nanocomposite catalyst dosage was 0.15 g/100mL.
The results are plotted in Figures. 5. These results indicate that the degradation efficiency not significantly affected with the increase of temperature[13-15].

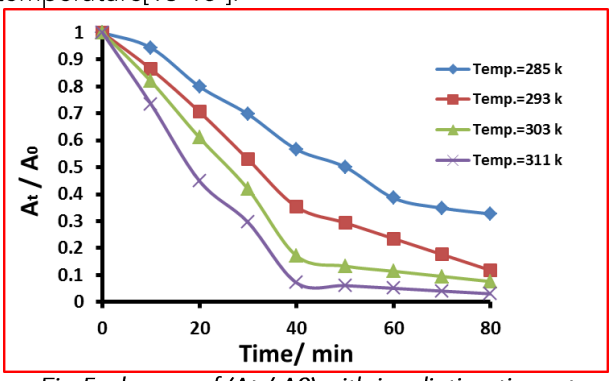

Fig.5. change of (At / A0) with irradiation time at different temperatures using UV radiation. Initial Orange G dye concentrations = 10 ppm, amount of photo catalyst = 0.15 g / 100 ml.

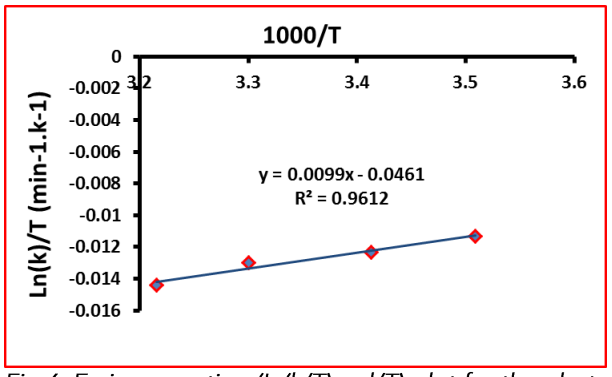

Fig.6: Eyring equation (ln(k/T) vs l/T) plot for the photo degradation of

Orange G dye

Thermodynamic parameters which associated with the photocatalytic degradation of Orange G dye are calculated from the plot of ln k /T versus 1/T According to the Erying equation,as shown in Fig.6.

$$\ln \frac{k}{T} = -\frac{\Delta H^\circ}{R} \cdot \frac{1}{T} + \ln \frac{K_B}{h} + \frac{\Delta S}{R}$$

k is apparent rate constant , KB=Boltzmann's constant [1.381·10−23J/K], T absolute temperature in degrees Kelvin (K), h=Plank constant [6.626×10−34 J·s], R universal gas constant = 8.31441 J mol-1K -1 .
Enthalpy of activation can be determined according to calculated slope from equation (1)

$$\text{Slope} = -\frac{\Delta H^\circ}{R}$$

Entropy of activation can be estimated from the y-intercept of equation (1)

$$\text{Intercept} = \ln\left(\frac{K_B}{h} + \frac{\Delta S^\circ}{R}\right)$$

The Gibbs' free energy can therefore be calculated from the relation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad \ldots\ldots (2)$$

In this research, ΔH=− 0.082 kJ/mol and ΔS=−0.197 k J/(k·mol), and 61.185 kJ/mol respectively.
The negative values of ΔH° show the exothermic nature of the reaction. The negative value of ΔS° suggest the decreased randomness at the liquid/ solid solution. The positive values of ΔG° for the reaction indicate the non-spontaneous nature of photocatalytic degradation of Orange G dye at the temperatures studied [16,17].

4. Conclusion

The hydrothermal technique was used to make a zinc oxide/vanadium pentoxide nanocomposite in this study. The amount of catalyst dosage in the photocatalytic degradation of safranine-T was determined, with the optimum value equaling 0.15 gm / 100 ml of GO/ZnO nanocomposite. The effect of dye concentration was investigated, and the optimum value of Orange G dye 10ppm was discovered. 9mW/cm2 is the light intensity. Because As the concentration of Orange G dye grows, the concentration of OH- adsorbed on the catalyst surface falls, and photocatalytic degradation decreases. Orange G dye breakdown by photocatalysis accelerates as light intensity rises. The photocatalytic degradation of Orange G dye has a percentage efficiency of 95.61 percent. In this research, ΔH=-0.082 kJ/mol and ΔS=−0.197 k J/(k·mol), and 61.185 kJ/mol respectively.

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