# Study ZnO Nano Particles and Activated Carbon Produced from Agricultural Waste Efficiency on Removing Direct Blue 71

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**Abstract**

The Azo group has been one of the chemical structures in classifying dyes which is important due to its cancer causing and negative effects on the environment and interference with the ecology of the water bodies. In this study photo catalytic process was used due to its unique features in decomposition of pollutants to mineral compounds and also the physical process of agricultural waste adsorption to remove DB71 in 3 ways of adsorption/photo catalytic, photo catalytic/adsorption, and simultaneously adsorption and photo catalytic. The results have shown that in all 3 systems in pH=9 with initial dye concentration of 50 mg/L, 100 percent removal efficiency were achieved with optimal ratio of AC/ZnO in the presence of two adsorbent of walnut and almond shells of 0.75/0.096 and 1/0.096 (in adsorption/photo catalytic), 0.024/0.75 and 0.024/1 (in photo catalytic/adsorption) and 0.75/0.288 and 0.75/0.288 (in simultaneous adsorption-photo catalytic), respectively.
In the optimum conditions in all the three systems, COD removal was obtained 47.22, 49.6, 42.21, 39.18, 62.23 and 63.15 percent respectively after 30 hours.

## 2.Materials and Methods

### 2.1. Test Method

At first, maximum wavelength of DB71 determined in the range of 200-800 nm and 586 nm was obtained. The concentration of samples, absorbance were measured by spectrophotometer and by putting them in the standard curve (Abs=0.0243[Dye]), concentration was obtained. Note that all testing was performed according to the standard method book [23]. Schematic of the pilot is shown in figure 1.

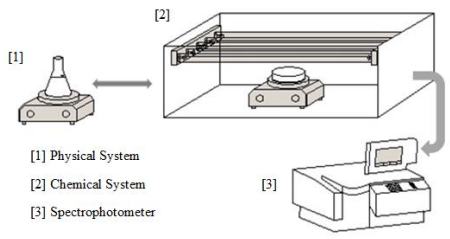
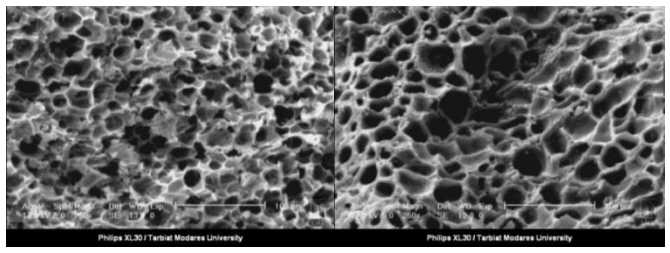



**Table1- Characteristics of Activated Carbon produced from Walnut and almond shells**

| Characteristics | Almond | Walnut | Standars Method |
|---|---|---|---|
| Particle Size (mm) | 0.4-2.38 | 0.4-2.38 | D 2862-97 |
| Bulk density (kg/m$^3$) | 480 | 450 | D 2854-96 |
| Iodine Number | 850 | 900 | D 4607-94 |
| Specific Surface (m$^2$/gr) | 900 | 840 | |
| Ash(%) | 15 | 10 | D2866-94 |
| Moisture(%) | 5 | 5 | D 2867-99 |
| pH | 7.9 | 7.7 | ASTM 3838-80 |
| $pH_{pzc}$ | 8 | 7.8 | |




**(a) (b)**

**Figure 2- Images of Activated Carbon (a)Walnut shell, (b)Almond shell (*250)**

In order to be volume to certain concentration, the mixture was poured into 250 ml flask. To study the removal of Direct Blue 71 according to the results of activated carbon and photo catalysis tests, consolidated experiments have been done in 3 ways: adsorption/photo catalytic, photo catalytic/adsorption and simultaneously adsorption-photo catalytic system after reaching equilibrium time for 2 adsorbents, wastewater was imported to the chemical system to complete the process. In photo catalytic/adsorption system after reaching 50 percent removal efficiency two adsorbents were added to the wastewater to complete the process. In simultaneously adsorption-photo catalytic system use of both adsorption and photo catalytic process was studied. Range of parameters and values of them are given in table 2. Noteworthy that to accuracy of data and determining the error in testing methods all experiments was repeated three times

**Table 2- Studied parameters**

| Parameters | Studied Values |
|---|---|
| pH | 3-11 |
| Catalyst (gr/L) | 0.024-0.384 |
| Adsorbent (gr/L) | 0.5-8 |
| Radiation Intensity (W) | 30-120 |

Direct Blue 71 was purchased from AlvanSabet factory. Also, Nano particles of ZnO were purchased from Nanosany (size=10-30 nm, Real density=5.606 gr/cm$^3$) and $ZnCl_2$from Merck for activating the shells, $K_2Cr_2O_7$, $AgSO_4$ and $HgSO_4$ from Merck for measuring COD, NaOH, $H_2SO_4$ from Merck for adjusting pH and distilled water used for experiments.
The main instruments used in this study include spectrophotometer DR4000, Carry 50 model to measure dye, Ultrasonic cleaner Fungilab UE-6SFD model to separate Nano particles of ZnO, 4 UVC lamp 30W manufactured by Phillips to study their effects on dye removal, stirrer RHB2 for stirring, SEM device manufactured by Philips XL30 model, Cod reactor DRB200 model from Hach company with 16 tube to determine COD, digital pH meter 691 model Metrohm company to measure pH, digital carriage scales, PLS360-3 model from Kern company with accuracy of 0.001 gr to weight the materials.

## 3. Results and Discussions

### 3.1.Photo catalytic/Adsorption system

In this system, after contacting with the least amount of ZnONano particles and 50 percent removal efficiency, soluble was contacted with walnut and almond shells to complete treatment. The results are shown in figure 4. As it can be observed, removal efficiency increased from 0.25 to 0.75 gr/L in the presence of walnut shell but with increase in the amount of adsorbent was not observed in dye removal, also this was seen in the presence of almond shell from 0.25 to 1 gr/L. this was reported by other researchers [3]. According to the results, 0.75 and 1 gr/L walnut and almond shells were chosen as optimum amounts respectively, and also 0.024 gr/L Nano particles of ZnO were chosen as optimum amount of catalyst that removed DB71 completely in 120 min.

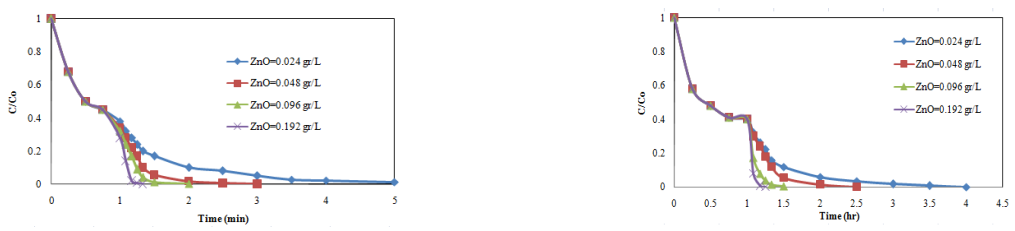



Figure 3- Studying photo catalyst on DB71 removal in consolidated process:
Adsorption (a)Walnut, (b)Almond/Photocatalytic
([Dye]=50 mg/L ،pH=9 ،[$AC_{(Walnut)}$] =0.75 gr/L ،[$AC_{(Almond)}$]=1 gr/L $P_{uvc}$=60 W)

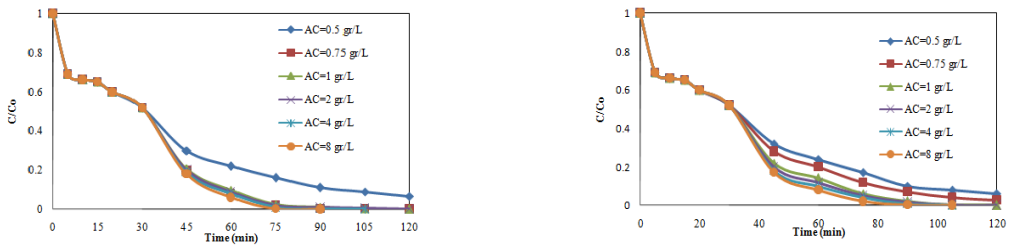



Figure 4- studying Adsorbent on DB71 removal in consolidated process:
Photocatalytic/Adsorption (a)Walnut, (b)Almond
([Dye]=50 mg/L ،pH=9 ،[ZnO] =0.024 gr/L ،$P_{uvc}$=60 W)

### 3.2. Simultaneously Adsorption-Photo catalytic

In this step, the removal efficiency was investigated in the presence of both adsorbent and photo catalyst with different ratios of AC/ZnO. In this system, at first the contaminant particles were absorbed by the adsorbents and then were destroyed by ZnO Nano particles [20]. The results are shown in figure 5. As seen, the removal efficiency increased with the increase in amount of ZnO and decrease of AC due to increase in amount of photo catalyst. In contrast, the removal efficiency decreased with decreasing in amount of ZnO and increasing of AC due to turbidity and lack of proper penetration of UV light by adsorbents. Another reason could be the influence of ZnO Nano particles into the pores of the adsorbent that decreased the removal efficiency. Finally, according to removal efficiency and considering the decrease in photo catalyst mounts AC/ZnO:0.75/0.288 gr/L in consolidated walnut adsorbent-photo catalytic was selected as optimum values and AC/ZnO:0.75/0.288 gr/L was selected in the presence of almond and ZnO respectively.

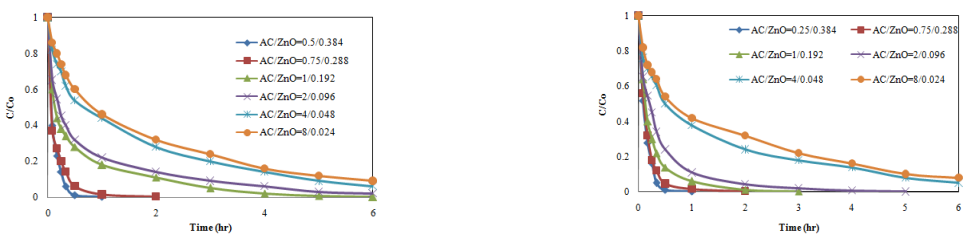



Figure 5- Studying Catalyst on DB71 removal in simultaneously process:
Adsorption (a)Walnut, (b)Almond- Photocatalyts
([Dye]=50 mg/L ،pH=9،$P_{uvc}$=60 W)

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