



## An investigation on Removal Efficiency of Direct Blue 71 by ZnO Nano-Particles and Activated Carbon Produced from Agricultural Wastes

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### ABSTRACT

The present study used the adsorption process of activated carbon produced from agricultural wastes and the photocatalytic process of nano-ZnO to break down complex compounds available in removing Direct Blue 71 (henceforth, DB71). The two processes were done under three varied circumstances-adsorption/photocatalytic, photocatalytic/ adsorption, and simultaneous use of the processes. First, DB71 was exposed to activated carbon produced from walnut and almond shells and the efficiency achieved at equilibrium time (45 and 60 minutes) was 55 and 60 percent, respectively. Then, DB71 was exposed to different dosages of nano-ZnO to remove the dye completely. The result showed that amount of AC/ZnO in an optimum condition for two walnut and almond shell adsorbents were 0.75/0.096 and 1/0.096 g/L. Second, (photocatalytic/ adsorption) the complex compound of DB71 with a dosage of 0.024 g/L was broken down as a result of UV radiation. The experiment proceeded with different dosages of walnut and almond shells after achieving the efficiency of 50% in removing DB71 in the second process. The amounts of AC/ZnO were 0.75/0.024 and 1/0.024 for walnut and almond shells respectively under the optimum condition for the second process. In the third process advantages of the simultaneous use of photocatalytic and adsorption processes were taken in which different dosages of AC/ ZnO were used. Given the smaller dosages of nano-ZnO and less dye removal time, amounts of 0.75/ 0.288 g/L and 0.75/0.288 g/L were measured for walnut and almond shells. The findings show that photocatalytic/adsorption process was the more optimal process because of the less dosages of nano-ZnO, efficiency of removing DB71 and shorter dye removing time. Furthermore, the effect of the intensity of UV radiant on the efficiency and time of removing DB71 was also examined. The experiment revealed that removing COD in the optimum conditions were 47.22 and 49.6 and 62.23 and 63.15 percent using walnut and almond shell respectively both in the first experiment and the simulations use of adsorption and photocatalytic processes after 30 hours. While, in the second experiment (photocatalytic/ adsorption) 42.21 and 39.18 percent of COD were removed using walnut and almond shell respectively after 30 hours. The LC-mass test of photocatalytic/adsorption process also showed the degradation of DB 71 complex compounds.

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### INTRODUCTION

Many industries such as textile, plastic and paper are producing large amounts of wastewater, which contains significant amounts of biodegradable compounds [1]. These aromatic compounds cause mutagenicity, cancer and poisoning of living beings, such as fish, algae and mammals [2]. So far, several methods have been used for removing dye from wastewater including Physical methods (e.g. adsorption [3], membrane filtration [4] and ultrasonic waves [5]), Chemical methods (e.g. electrolysis [6], coagulation [7], ion exchange [8] and conventional and advanced oxidation [9]) and biological methods (e.g. MBBR [10], GSBR [11] and trickling filter

[12]). Among the above methods, photocatalytic processes have been the focus of attention for breaking down the compounds into simple compounds and decomposing pollutants to minerals. Among the most common photocatalysts (e.g. ZnO, ZnS, CdS, Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and WO<sub>3</sub>), ZnO has been widely used for the removal of organic compounds [13]. The electrons of nano-ZnO are excited as a result of exposure to UV radiation, which generates electron (e<sup>-</sup>) hole (h<sup>+</sup>) pair, because of the high energy level of the UV lamp. On the one hand, the hole (h<sup>+</sup>) reacts with H<sub>2</sub>O and creates <sup>o</sup>O<sup>2-</sup> and the electrons react with adsorbed molecules on Photocatalyst surface, which generate <sup>o</sup>OH. The products are strong free radicals breaking Chemical bonds in organic compounds and in organic macro molecules and turn them into CO<sub>2</sub> and H<sub>2</sub>O [14, 15].

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Adsorption process is one of the most common wastewater dye removal methods for its relatively suitable speed and efficiency [16]. This method is based on trapping the contamination particles within the organic and inorganic adsorbent matrices [17]. Many natural materials have so far been used for producing activated carbon such as wood [18], oil residue [19], and sawdust [20] and rice husks wastes [21]. But production of activated carbon from agricultural wastes has recently attracted a great deal of attention because of being economical and availability. In the following, a few researches on adsorption and photocatalytic dye removal processes are presented. Joshi and Shrivastava studied removal of Acid Blue 29 (AB29) and Congo Red (CR) by the simultaneous use of activated carbon and Zinc Oxide. The results showed that the decolorization efficiency for AB29 and CR with pH=4 and pH=7 and initial dye concentration 8 and 10 mg/L, were 89.4 % and 92.4 % respectively [15].

Mikhak and Habibi also studied on the photocatalytic degradation of Direct Blue 71 using Titania/Zinc Oxide nanocomposite coatings on photocatalyst on glass substrate. In an optimum condition (i.e. natural pH=6.8 with initial dye concentration 10 mg/L and under UVA 20W), 100 percent removal efficiency was obtained after 24 hours [22]. Similarly, Tabatabaee and his colleagues studied on the removal of Direct Blue 71 using a homogenous catalyst material ( $K_7 [PMo_2W_9O_{39}] 19H_2O$ ) containing tungsten and molybdenum in a slurry reactor. The study obtained 87 percent removal efficiency in an optimum condition (i.e. pH=6,  $C_0=50$  mg/L,  $H_2O_2=0.08$  mol/L as the catalyst, 0.6 g/mol  $K_7 [PMo_2W_9O_{39}] 19H_2O$ ) in 90 min [23].

With above as background, most related studies applied simultaneous use of photocatalytic and adsorption processes for removing dye. However, the present study attempted to use photocatalytic and adsorption processes in varied orders, namely: adsorption/ photocatalytic, photocatalytic/ adsorption, and simultaneous use of adsorption and photocatalytic processes. The study provided a ground for examining the dye removal efficiency in the above different circumstances. It also enabled the researcher to scrutinize the possibility of achieving an optimum efficiency with consumption of a minimum amount of nano-ZnO and activated carbon produced from walnut and almond shells for degradation of complex compounds.

## MATERIALS AND METHODS

### Materials and Equipment

DB 71 was purchased from Alvan Sabet Factory. Also, ZnO nano-particles were purchased from Nanosany (size=10-30 nm, real density=5.606 g/cm<sup>3</sup>). The needed

ZnCl<sub>2</sub> for activating the shells, and K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, AgSO<sub>4</sub> and HgSO<sub>4</sub> for measuring COD, and NaOH and H<sub>2</sub>SO<sub>4</sub> for adjusting pH were all purchased from Merck. Distilled water was also used in all experiments. The main equipment used in this study are as follows: DR/ 4000 Spectrophotometer, Fungilab UE-6SFD Ultrasonic Cleaner, four Philips UVC 30 W lamps, Stirrer RHB2, Philips XL 30 Scanning Electron Microscope (SEM) Hach DR 200 COD reactor, Metrohm 691 digital pH meter, and Kern PLS 360-3 digital Carriage Scales, with an accuracy of 0.001 g.

### The adsorption process

The walnut and almond shells were crushed and saturated in a zinc chloride solution with impregnation ratio of 1:1 for 2 hours. The combination was dried in room temperature before being added to a reactor with total a volume of 200 ml. The reactor's lid was closed completely to ensure that air flow was prevented so as combustion takes place in the absence of oxygen. Then the reactor was heated in a furnace at 600 °C for 2 hours. Then, the product was cooled at room temperature and washed so as to remove the activation material [24]. Finally, it was crushed and sorted in 0.4-2.38 mm range. SEM images were used to see cavities created as a result of carbon activation. Then, the dye solution was put into a 500 ml Erlenmeyer flask. A stirrer with a specified speed (200 rpm) was used to increase the contact between the activated carbon and the dye solution.

### The photocatalytic process

In the photocatalytic process, all experiments were done in a 500 ml plastic container on a stirrer with a certain speed in the pilot in which four UVC lamps with radiant intensity of 30 W were placed at a distance of 10 cm from the substrate [25]. After mixing 50 ml distilled water with nano-ZnO, the mixture was put in an ultrasonic cleaner (40 KHz) to separate ZnO nano-particles. Finally, the combination was put into a 250 ml flask to reach a desired concentration (50mg/L) and volume (250 ml).

### primary experiments

Prior to the experiment, effect of pH, adsorbent- catalyst dosages and the initial dye concentration were measured separately in the adsorption and the photocatalytic processes. The effect of radiant intensity on removing dye was also examined in the photocatalytic process. The parameters, such as pH, catalyst, adsorbent, and radiant intensity were examined in a specified range of values given in Table 1.

TABLE 1. Pre-specified parameters

Parameters	Range of Values
pH	3-11
Catalyst (g/L)	0.024-0.384
Adsorbent (g/L)	0.5-8
Radiation Intensity (W)	30-120

In fact, all the experiments (primary and main experiments) were done three times to ensure about the data accuracy. The standard deviations measured in the experiments indicate the accuracy of the experiments. Finally, SD in optimum conditions was 1.85% that indicates high reliability of the experiments undertaken.

### The processes in varied orders

To study the removal of DB 71 according to the results of activated carbon and nano-ZnO photocatalyst tests, main experiments were done in 3 ways: adsorption/photocatalytic, photocatalytic/adsorption and simultaneous use of adsorption and photocatalytic. The first process began with contact between the dye solution and activated carbon. The process proceeded until the equilibrium time. Then, the dye solution was exposed to UV radiation with different amounts of nano-ZnO. The second process began with contact between the dye solution and nano-ZnO. The process proceeded until 50 percent dye removal efficiency was achieved. Then, ZnO nano-particles were separated from the solution, and walnut and almond shells were added to the solution so that the dye was removed completely. In the third process the two processes were used simultaneously using different amounts of nano-ZnO and activated carbon produced from walnut and almond shells for dye removal.

### Adsorption/ photocatalytic process

The process begins with contact between the dye solution and activated carbon. The process will proceed until the equilibrium time. Then, the dye solution will be exposed to UV radiation with different amounts of nano-ZnO.

### Photocatalytic/ adsorption process

The process begins with contact between the dye solution and nano-ZnO. The process will proceed until 50 percent dye removal efficiency would be achieved. Then, ZnO nano-particles will be separated from the solution, and walnut and almond shells will be added to the solution so that the dye will be removed completely.

### Simultaneous use of adsorption and photocatalytic processes

The two processes are to be used simultaneously using different amounts of nano-ZnO and activated carbon produced from walnut and almond shells for dye removal.

### Analysis of dye concentration

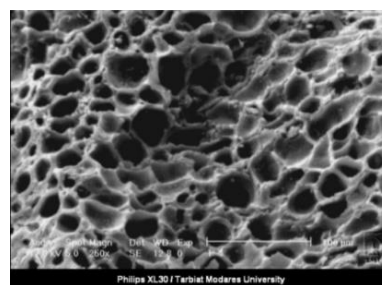
First, wavelength of DB71 was examined within a range of 200-800 nm, and it was found out that the maximum wavelength was 586 nm. The dye absorbance was measured by spectrophotometer and the figures were put into the standard curve ( $Abs=0.0243[Dye]$ ) so as to measure the concentration of the samples. Note that all

testing was performed according to the standard method book [26].

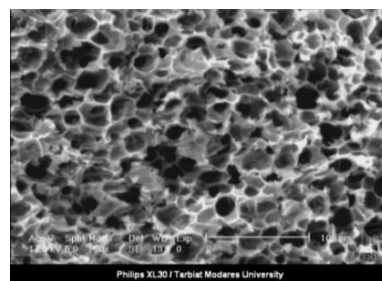
## RESULTS AND DISCUSSION

### Characteristics of Prepared Activated Carbon

Scanning electron microscopy (SEM) showed that carbon texture and development of porosity was strongly affected by characteristics of the starting materials. Figure 1 depicts SEM images of walnut and almond shells after activation the cavities developed on the surface of activated carbon produced from walnut and almond shells indicates that they are well activated. And the characteristics of the prepared activated carbon according to standard method are given in Table 2.



(a)



(b)

**Figure 1.** SEM images of activated carbon a) walnut shell, b) almond shell (magnification of x250)

**TABLE 2.** Characteristics of Prepared Activated Carbon

Characteristics	Walnut	Almond	Standard Method
Particles size(mm)	0.4-2.38	0.4-2.38	D 2862-97
Bulk density (kg/m <sup>3</sup> )	450	480	D 2854-96
Iodine Number	900	850	D 4607-94
Specific Surface (m <sup>2</sup> /g)	840	900	
Ash (%)	10	15	D2866-94
Moisture (%)	5	7	D 2867-99
pH	7.7	7.9	ASTM 3838-80
pH <sub>pzc</sub>	7.8	8	

**Primary experiments**

Prior to the experiment, effect of pH, adsorbent- catalyst dosages and the initial dye concentration were measured separately in the adsorption and the photocatalytic processes. The effect of radiant intensity on removing dye was also examined in the photocatalytic process. The parameters, such as pH, catalyst, adsorbent, and radiant intensity were examined in a specified range of values given in Table 3. In fact, all the experiments (i.e. primary and main experiments) were done three times to ensure about the data accuracy. The standard deviations measured in the experiments indicate the accuracy of the experiments. Finally, SD in optimum conditions was 1.85% that indicates high reliability of the experiments undertaken. The results of the primary experiments are shown in Table 4. The optimum pH and initial dye concentration were determined 9 and 50 mg/L respectively in both processes, therefore pH=9 and  $C_0=50$  mg/L were used as optimum values in the main experiments. The effects of these parameters on removing DB71 were not examined again. The optimal adsorbent, photocatalyst and the radiations were studied in the main experiments.

**TABLE 3.** Pre-specified parameters

Parameters	Range of Values
pH	3-11
Catalyst (g/L)	0.024-0.384
Adsorbent (g/L)	0.5-8
Radiation Intensity (W)	30-120

**TABLE 4.** The results of primary tests

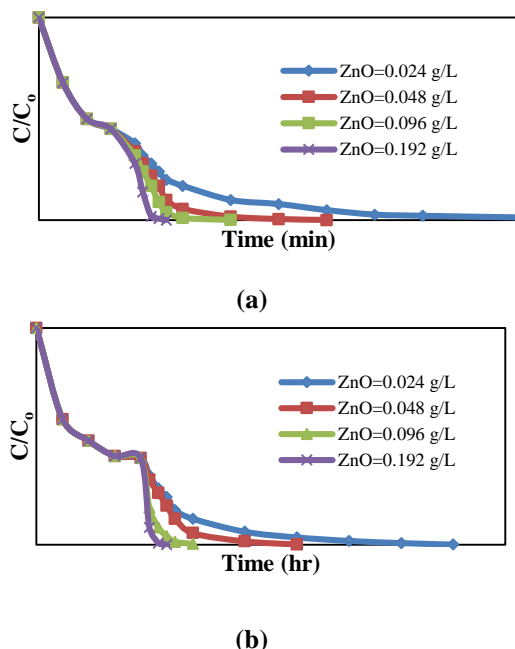
Process Parameters	Adsorption Process	Photocatalytic Process
Dye concentration (mg/L)	50	50
Adsorbent dosage (g/L)	0.75 (Walnut) 1 (Almond)	-
Photocatalyst dosage (g/L)	-	0.288
pH	9	9
Time (min)	45 (Walnut) 60 (Almond)	240
Radiation intensity (W)	-	60
Dye removal (%)	55.31 (Walnut) 60.19 (Almond)	100

**Determining Optimum Dosages of Catalysts**

**Adsorption/ photocatalytic process**

The process was done on two dying solutions with 50 mg/L initial dye concentration. One was in contact with 0.75 g/L walnut shells and the other solution was in contact with 1 g/L almond shells under the optimum conditions measured in the primary experiments. Once the adsorbents reached their equilibrium time, 45 minutes

and 60 minutes respectively, (with removal efficiency of 55.31 and 60.1 percent respectively) different amounts of nano-ZnO were applied for complete dye removal. The results can be seen in Figure 2.



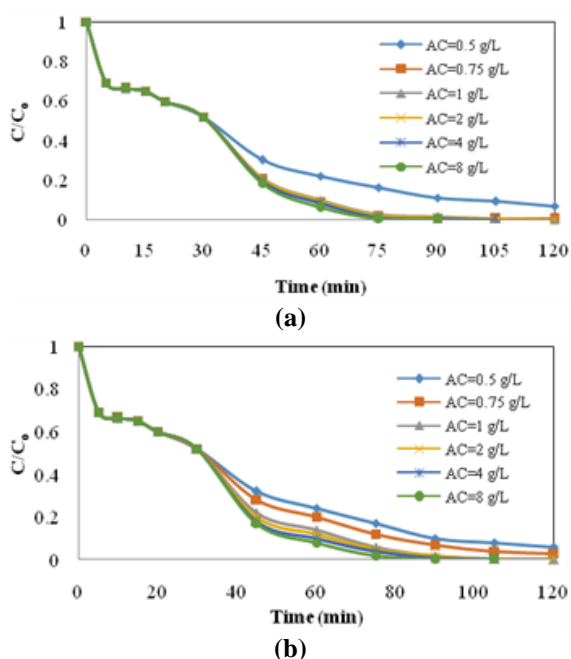
**Figure2:**The effect of different dosages of catalysts on DB71 removal in adsorption/ photocatalytic process (a)Walnut, (b) Almond ([Dye]=50 mg/L, pH=9, [AC<sub>(Walnut)</sub>]=0.75 g/L, [AC<sub>(Almond)</sub>]=1 g/L, P<sub>uvc</sub>=60 W)

Analysis of the data showed that the more dosages of catalyst, the more efficient the dye removal will be, and dye removal time will also decrease. The findings have also been supported by some researchers [27]. In fact, the efficiency was increased to some extent, but it began to reduce by increasing the amount of nano-ZnO and an increase in the turbidity of the nano-ZnO particles, which has also been reported by Considering the measured dye removal efficiencies and the consumed dosages of photocatalyst 0.096 g/L ZnO nano-particles was chosen as the optimum value in both experiments.

**Photocatalytic/adsorption process**

The dye solution (DB71) in which 50% efficiency was obtained using a minimum amount of ZnO nano-particles earlier (Table 3), contacted with varied amounts of walnut and almond shells for removing the dye, completely. The results are shown in Figure 3. As it can be observed, dye removal efficiency increased when we increased the amount of adsorbent (i.e. walnut shells) from 0.25 to 0.75 g/L, but the efficiency did not improve any further when more adsorbent was added to the solution. The same trend was observed when more amounts of almond shells were used (0.25 to 1 g/L). This was also reported by other researchers [28].

The downward trends of efficiency observed after using certain amounts of adsorbents can be explained by the increase of repulsive force between anionic groups on the surface of activated carbon and dye molecules, which in turn, caused interference in adsorption and the cavities remain unsaturated [29], [30]. As the result, 0.75 and 1 g/L walnut and almond shells were chosen as the optimum dosages of adsorbents respectively.



**Figure 3.** The effect of different dosages of adsorbents on DB71 removal in photocatalytic/adsorption process (a)Walnut, (b)Almond ([Dye]=50 mg/L, pH=9,[ZnO]=0.024 g/L, $P_{uv}$ =60 W)

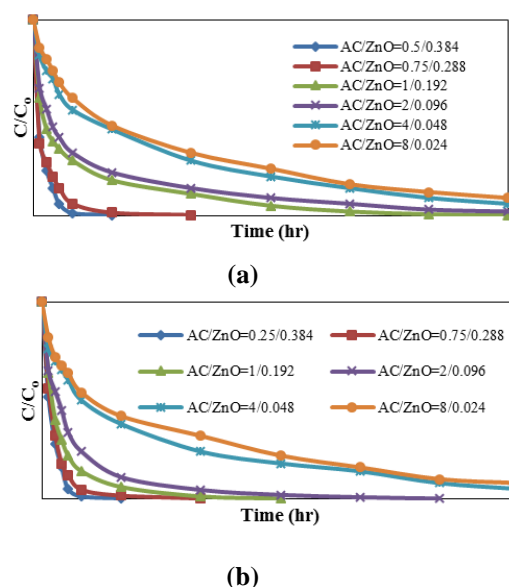
### Simultaneous use of adsorption-photocatalytic processes

The present experiment examines the dye removal efficiency in the simultaneous presence of different amounts of activated carbon and nano-ZnO. Pollutant concentration was adsorbed by the walnut and almond shells and it was degraded by ZnO nano-particles, which are on the adsorbents' surface [31]. The results are shown in Figure 4. Increase in dye removal efficiency resulted from an increase in amount of nano-ZnO and decrease of AC. In contrast, decrease of nano-ZnO and increase in AC resulted in a decrease in the removal efficiency. This was because of turbidity of the solution that did not allow UV light to penetrate into the solution. Moreover, the ZnO nano-particles penetrated in adsorbents cavities. Finally, given the removal efficiency and the decrease of photocatalyst used in the present experiment, AC/ZnO:0.75/0.288 g/L and AC/ZnO:0.75/0.288 g/L were measured as optimum values for walnut and almond shells respectively.

### Determining the optimum UV radiant intensity

The adsorption/photocatalytic process was adopted to study the effect of UV radiant intensity on removing dye. As can be seen in Figure 5, the dye solution was first in contact with walnut shells adsorbent for 45 min (about 50 percent removal efficiency was obtained), then, it was exposed with different UVC radiant intensity with 0.096 g/L nano-ZnO.

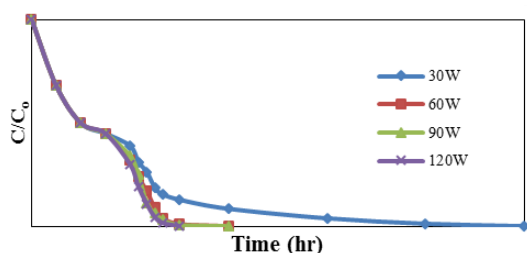
As it was shown, the dye removal efficiency increased with an increase in radiant intensity from 30 to 60W. This can be explained by the increase in UV radiant intensity and emitted photons. However, more increase in UV radiant did not lead to increased efficiency. The reason why the efficiency did not increase any further was that the UV radiant was enough for excitement of ZnO nano-particles and the excess radiant were an energy loss. This finding has also been reported by other researchers [32]. Therefore, 60W radiant intensity was chosen as the optimum radiant intensity. The same optimum radiant intensity (60W) was also measured in primary experiment. Thus, the researcher avoided further examination of the optimum UV radiant intensity in other experiments.



**Figure 4.** Studying the effect of adsorbents and catalyst on DB71 removal in adsorption-photocatalyst process: (a)Walnut, (b)Almond ([Dye]=50 mg/L, pH=9,  $P_{uv}$ =60 W)

### COD removal rates in optimum conditions

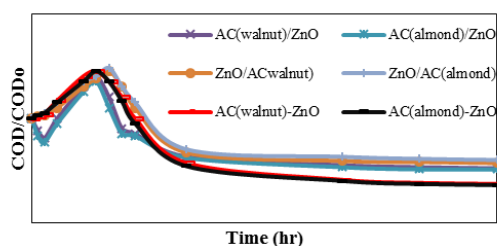
COD tests were done in optimum conditions of all three order of processes, since dye removal did not indicate degradation of pollutants rather only dye factor bonds were broken down in the solution. The COD tests were conducted to measure the pollution brake down. The results are shown in Figure 6.



**Figure 5.** Studying the effect of radiant intensity on DB71 removal in adsorption/photocatalytic process:

(a)Walnut, (b)Almond ([Dye]=50 mg/L,pH=9, [AC<sub>(Walnut)</sub>]=0.75 g/L, [AC<sub>(Almond)</sub>]=1 g/L, [ZnO]=0.096 g/L)

As shown in Figure 6, COD increased in the early hours and then decreased as more time passed by, it started decreasing. Since oxidizing materials in COD test, didn't have the ability to break down hard breaking compounds such as the benzene ring, in other words, the amount of COD was not indicating the actual available amount of organic materials in samples and it showed lower values. As the time went by benzene rings broke down faster and COD amounts decreased. Such an irregular behaviour was because of the difference in the solution's available compounds that was caused by the photocatalytic reaction. Figure 6 shows that the COD removal efficiency in adsorption/ photocatalytic, photocatalytic/ adsorption, and simultaneous use of adsorption-photocatalytic processes after 30 hours were as follows: 47.22%, 49.6%; 42.21%, 39.18%; and 62.23%, 63.15%, for walnut and almond shells respectively. The collated data drawn from the three experiments are illustrated in Table 5.



**Figure 6.** Variation of COD/COD<sub>0</sub> on optimum conditions in 3 supplementary processes

### LC-mass Results

The LC-mass test was used both for a 2-hour sample and a 12-hour sample to determine the products under the chosen optimal conditions. The dye was removed completely in the 2-hour sample while in the 12-hour sample COD changes were consistent. Figures 7 and 8 show the normalization of initial sample with 50 mg/L dye concentration. As can be seen in Figure 8 the largest mass obtained was 914.1 which represented the expected dye. The differences between the mass of the Direct Blue

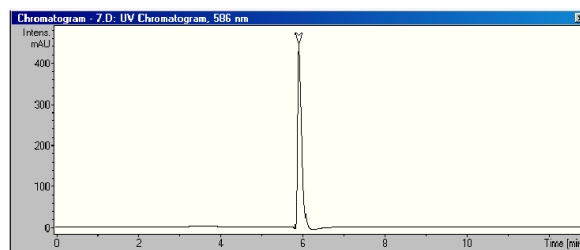
71 with the shown number in the figure could be because of that the dye has lost 4 sodium ions in place of getting 4 protons from the environment.

**TABLE 5.** Comparison of data drawn from supplementary processes on optimum conditions

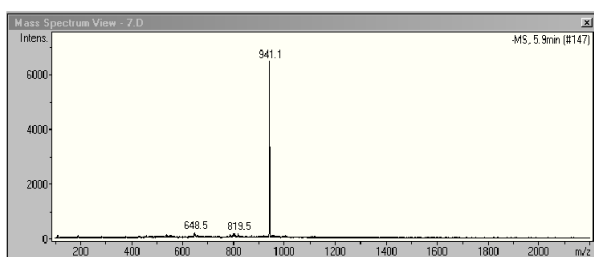
Process	Adsorption/ photocatalytic process	Photocatalytic/ adsorption process	Simultaneous use of adsorption-photocatalytic process
<b>Parameter</b>			
Dye concentration (mg/L)	50	50	50
Adsorbent dosage (g/L)	0.75 (Walnut) 1 (Almond)	0.75 (Walnut) 1 (Almond)	0.75 (Walnut) 0.75 (Almond)
Photocatalyst dosage (g/L)	0.096	0.024	0.288
pH	9	9	9
Time (min)	120 (Walnut) 90 (Almond)	120 (Walnut) 120 (Almond)	120 (Walnut) 120 (Almond)
Dye removal efficiency (%)	100	100	100
COD removal after 30 hr (%)	47.22 (Walnut) 49.6 (Almond)	42.21 (Walnut) 39.18 (Almond)	62.23 (Walnut) 63.15 (Almond)

The results of LC- mass test are shown in Figures 9 and 10. The amount of compounds, produced as a result of breaking DB71, in the 2-hour sample demonstrated that these compounds had complex structures and such wastewater should not enter the environment. The results showed that only the dye factors and the chromospheres were broken down probably after 2 hours and the complete breakdown of the compounds into simple compounds required more time; the 12-hour sample was examined.

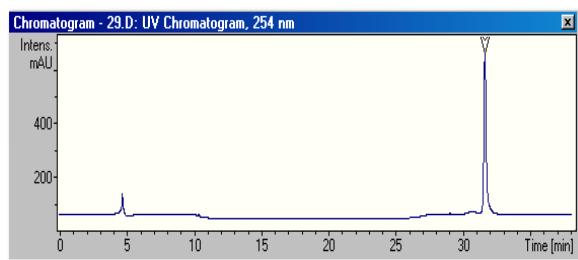
The result of LC-mass test for the 12-hour sample is shown in Figures 11 and 12. As it can be seen in Figure 11, molecular weight of the compounds remained in the environment is not significant. The molecular weight of the compounds is illustrated in further detail in Figure 12.



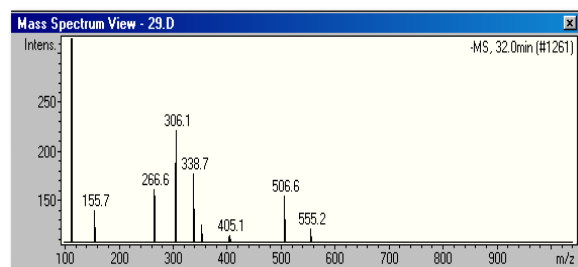
**Figure 7.** Chromatography of initial sample ([Dye]=50 mg/L, pH=9, [AC<sub>(Walnut)</sub>]=0.75 g/L, [ZnO]=0.024 g/L)



**Figure 8.** LC-mass Spectrum of initial sample ([Dye]=50 mg/L, pH=9, [AC<sub>(Walnut)</sub>]=0.75 g/L, [ZnO]=0.024 g/L)

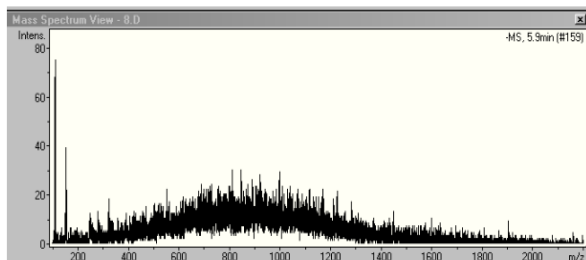


**Figure 9.** Chromatography of 2-hr sample ([Dye]=50 mg/L, pH=9, [AC<sub>(Walnut)</sub>]=0.75 g/L, [ZnO]=0.024 g/L)

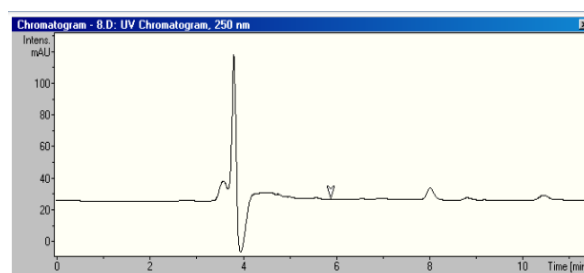


**Figure 10:** LC-mass Spectrum of 2-hr sample ([Dye]=50 mg/L, pH=9, [AC<sub>(Walnut)</sub>]=0.75 g/L, [ZnO]=0.024 g/L)

The peak values in the sample showed simple compounds were remained in the solution. It can be safely said that there was no annular and complex compounds in the solution. In other words, the product complexity gradually decreased, indicating that the process can effectively reduce the effluent's toxicity. Types of the product intermediates formed in reactions depend on many factors, such as experiment's conditions, initial concentration and the time that the intended reaction takes.



**Figure 11.** Chromatography of 12-hr sample ([Dye]=50 mg/L, pH=9, [AC<sub>(Walnut)</sub>]=0.75 g/L, [ZnO]=0.024 g/L)



**Figure 12.** LC-mass Spectrum of the 12-hr sample ([Dye]=50 mg/L, pH=9, AC<sub>(Walnut)</sub>]=0.75 g/L, [ZnO]=0.024 g/L)

## CONCLUSION

This present study demonstrated that nano-ZnO and activated carbon produced from walnut and almond shells were highly efficient in degradation and dye removal of DB71. In short, the results shown that photocatalytic/ adsorption process was more efficient than the two other processes because dye solution degrades in contact with nano-ZnO particles through a photocatalytic process. In continuation, complete dye removal happened after adding activated carbon, which was an efficient dye adsorbent. Thus, less nano-ZnO was consumed in this process. It took 120 minutes to reach complete dye removal efficiency (100%) under the optimum condition (pH= 9, ZnO 0.024 g/L). The efficiency was attained by adding 0.75 g/L walnut shell and 1g/L almond shell in the solution. The results revealed that removing COD in the optimum conditions were 42.21 and 39.18 percent using walnut and almond shell respectively after 30 hours.

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## Persian Abstract

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## چکیده

پژوهش پیش رو برای شکستن ترکیبات پیچیده موجود در Direct Blue71 توسط فرآیند جذب به وسیله ی کربن فعال حاصل از ضایعات کشاورزی و فرآیند فوتوکاتالیستی نانو-اکسید روی انجام شد. این دو فرآیند در سه شرایط متفاوت جذب/فوتوکاتالیستی، فوتوکاتالیستی/جذب و استفاده همزمان از دو فرآیند انجام شد. نخست، DB71 در معرض کربن فعال تولید شده از پوست گردو و بادام قرار گرفت و بازده حاصل در زمان تعادلی ۴۵ و ۶۰ دقیقه به ترتیب معادل ۵۵ و ۶۰ درصد بود. سپس DB71 جهت حذف کامل در معرض مقادیر متفاوت از نانو-اکسید روی قرار گرفت. نتایج حاکی از این بود که مقدار  $AC/ZnO$  در شرایط بهینه برای جذب های پوسته گردو و بادام  $۰,۰۹۶/۰,۷۵$  و  $۰,۰۹۶/۱$  گرم بر لیتر حاصل گشت. در فرآیند دوم (فوتوکاتالیستی/جذب) ترکیب پیچیده DB71 با مقدار  $۰,۰۲۴$  گرم بر لیتر در نتیجه اشعه ماورا بنفش شکسته شد. آزمایش با مقدار متفاوت پوسته گردو و بادام تا رسیدن به بازده ۵۰ درصد حذف DB71 ادامه یافت. برای فرآیند دوم در شرایط بهینه مقدار  $AC/ZnO$  معادل  $۰,۰۲۴/۰,۷۵$  و  $۰,۰۲۴/۱$  به ترتیب برای پوسته گردو و بادام حاصل گشت. در فرآیند سوم مزایای استفاده هم زمان دوفرایند مورد استفاده قرار گرفت و مقادیر متفاوت  $AC/ZnO$  مورد استفاده قرار گرفت. با مقدار کمتر نانو-اکسید روی و زمان کوتاه تر حذف رنگ مقادیر  $۰,۲۸۸/۰,۷۵$  و  $۰,۲۸۸/۰,۷۵$  گرم بر لیتر برای پوسته گردو و بادام اندازه گیری شد. نتایج نشان دهنده این است که فرآیند فوتوکاتالیستی/جذب به دلیل کاهش مصرف نانو-اکسید روی بازده بهتر DB71 و زمان کوتاه تر حذف رنگ دارای بهترین شرایط می باشد. هم چنین اثر شدت اشعه فرابنفش بر بازده و زمان حذف DB71 بررسی شد. آزمایش ها نشان میدهد مقدار حذف COD در شرایط بهینه  $۴۷,۲۲$  و  $۴۹,۶$  و  $۶۲,۲۳$  و  $۶۳,۱۵$  درصد به ترتیب برای پوسته گردو و بادام در آزمایش اول و فرآیند همزمان جذب و کاتالیستی در زمان ۳۰ دقیقه حاصل شد. در حالی که در آزمایش دوم (فوتوکاتالیستی/جذب) پس از ۳۰ دقیقه میزان حذف  $42.21$  COD و  $۳۹,۱۸$  درصد به ترتیب برای پوسته گردو و بادام بود. هم چنین تست  $LC-mass$  فوتوکاتالیستی/جذب نشانگر تخریب ترکیبات پیچیده ی DB71 بود.