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Enhanced Photocatalytic Removal of Direct Yellow 50 by ZnO/MWCNTs Nanocomposite under Solar Light Irradiation through Response Surface Methodology (RSM) Optimization

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ABSTRACT

Photocatalytic degradation of direct yellow 50 dye DY from aqueous solution utilizing ZnO/MWCNTs nanocomposite under irradiation of solar light was studied in the proposed study. ZnO/MWCNTs nanocomposite was initially synthesized via hydrothermal method. The integration of MWCNTs into ZnO NPs structure resulted in increased roughness and porosity, thereby improving active sites onto nanocomposite, which can enhance effective surface area and also can be characterized via different techniques, such as FESEM, TEM, and BET. Response surface methodology (RSM) approach was used in this study. Several factors such as nanocatalyst quantity and concentration of DY dye were best the optimal conditions to examine the best degradation capacity for DY dye with solar light source. In this regard, the best degradation capacity was observed at 0.3 g of ZnO/MWCNTs nanocomposite for concentration 30 mg/L at 25 °C with 1 h irradiation time. Photocatalytic degradation was completed after 60 minutes of solar light irradiation, 93.56 % degradation efficiency of DY dye was also obtained. Thus, capability of nanocomposite was appeared to remove DY dye from wastewater. As a result, successfully syntheses a new form of ZnO nanoparticles embedded with MWCNTs. ZnO/MWCNTs, which may be utilized photocatalytic degradable of DY dye. According to the degradation results, DY dye might be effectively degradation from aqueous solutions utilizing ZnO/MWCNTs nanocomposite.



Introduction

In recent years, environmental pollution resulting from the rapid development of industries has become a cause of widespread concern, as pollutants threaten human life and must be declined. One of the most dangerous pollutants is dyes which ranks third among the common toxic and dangerous pollutants found in wastewater, including dye production, leather tanning, printing, pharmaceuticals, textiles, dyeing, and pollution, urgent metal plating, electrical appliances, or electronic equipment, and so on. Meanwhile, among the most toxic organic pollutants, the concentration of dye in safe drinking water is less than 0.05 mg/L. It has a very high ability to dissolve in water and a carcinogenic effect, and easily penetrates the body through digestion, skin, mucous

membranes, and the respiratory system, causing great harm to living organisms [1-3]. Excessive exposure to dyes may cause acute toxicity, genetic mutations, and carcinogenic diseases, pulmonary congestion, and stomach ulcer inflammation. Dye was a precious heavy metal and is considered as a raw material used in many alloys and for hardening steel and also producing stainless steel [4-6]. Dye plating is used to obtain steel with mirror polished quality, hardness and aesthetics and to improve corrosion resistance. Dye is used as industrial catalysts, printing inks and pigments, glass, copper dyeing, and cement [7-10]. Direct yellow DY dye powder is soluble in water and sufficiently soluble in ethanol to lemon yellow, slightly soluble in acetone and strong sulfuric acid, and utilized for dyeing viscose and cotton. Dead cotton has a certain covering strength and it can also be utilized for printing



Figure 1. Chemical structure of direct yellow 50 DY dye.

viscose fabrics or cotton, wool, silk, polyamide fiber, and blended fabric dyeing. Likewise, it can be utilized for leather, biological shading, and paper, and its heavy metal salt can be used in pigment. Chemical structure of direct yellow 50 DY dye is displayed in Figure 1 [11,12]. In this study. ZnO/MWCNTs nanocomposite were fabricated through free-template and one-step synthesis by hydrothermal method introducing ZnO on the MWCNTs. The physical and optical properties of ZnO/MWCNTs nanocomposite were studied via several characterizations. The photo catalytic possessions of ZnO/MWCNTs nanocomposite were utilized for removal of DY dye from aqueous solution.

Materials and Methods

Preparation of nanocomposite

A hydrothermal method was useful to prepared ZnO/MWCNTs nanocomposite as the following method. 8 g in 50 mL of oxalic acid (Sigma-Aldrich), 99.0%, 10 g in 50 mL of zinc acetate (Sigma-Aldrich), 99.0%, was added to stir for obtaining a white homogeneous suspension. The white homogeneous suspension was then added to 0.04 g in 5 mL of MWCNTs which was acquired from the refinery of bakery factories magnetically agitated for 1 h. The suspension was then placed in 250 ml and heated to 150 °C

for 24 h. The bulk powder cooling, collected, and washed by distilled water. The powder was dried at 65 °C for 24 h.

Result and Discussion

Characterization

The pore structure, pore size distribution, and surface area of ZnO/MWCNTs were determined using the BET technique in the presence of nitrogen. The isotherm of ZnO/MWCNTs shows a small hysteresis loop that can be classified as kind IV. The average pore diameter, surface area, and total pore volume were calculated after incorporating carbon nanotubes into grafted zinc oxide. Interfacial interactions between carbon nanotubes and zinc oxide have an important influence on the structure and pore diameter of the material [13], as depicted in Figure 2.

The FE-SEM technique was used as an important and basic method to characterize the surface morphology and basic physical properties of the adsorbent. The zinc oxide nanoparticles were arranged in a spherical pattern in the form of random, disordered white balls. These pores provided a strong opportunity for the zinc oxide nanoparticles to entangle within them (Figure 3a). FESEM image was also used to characterize the surface morphology of MWCNT [14].



Figure 2. BET technique of ZnO/MWCNTs.



Figure 3. FESEM image of a) ZnO NPs, b) MWCNT, c) ZnO/MWCNTs, and TEM image of d) ZnO/MWCNTs.

It is evident from (Figure 3b) that the MWCNTs are cylindrical, curved, and tangled together. Microscopic images of carbon nanotubes show that the rough porous surface showed phase changes due to the presence of new irregular macromolecules on the surface. This leads to an increase in the prominence of the surface texture and its roughness as (Figure 3c) [15,16].

The surface morphology of ZnO/MWCNTs nanocomposites was studied using TEM technology. It was clear from the figure that the surface had a geometric shape resulting from cloud-like clusters with the presence of irregular agglomerations, resulting from the grafting of the surface with zinc oxide. Here the role of carbon on the surface of zinc oxide in explaining the increase in surface area becomes clear surface of the nanocomposite [17,18].

Experimental design via RSM approach

A design expert software version 13 was used. In experimental design via the response surface methodology (RSM) approach, a CCD approach was used to achieve the minimum required experimental runs. A second-order model was obtained in this approach [19]. Fractional factorial design approach studies the main and a minimum number of experiments doing for interaction effects [20]. Some coded and actual values of variables are listed in Table 1. The true regression can be recognized as the value of the adjusted R-squared (R2 adj) and the coefficient of determination (R²). Although the new elements added to the model are meaningful, the high R² values do not make the model valid for predicting new observations. R² adj is introduced for this case and increases as time increases to develop the model. The presence of inappropriate content in the sample reduces R2 adj. Another term is R2pred, which indicates the model's ability to predict new responses and model over-fitting. Correlation coefficients R^2 = 0.9513, adjusted $R^2 = 0.8886$ close to 1, estimated R^2 (pred R^2) = 0.2284 close to zero, confirming that the model is good for testing but too little for prediction.

Table 1. The coded and actual values as well as ANOVA results obtained RSM study of DY photocatalyticdegradation by the prepared ZnO/MWCNT catalyst

Selected Variables									
Factor	Name	Units	Minimum	Maximum	Coded	Low	Coded High	Mean	Std. Dev.
Α	Conc.	mg/L	20.00	40.00	-1 ↔ 20	0.00	+1 ↔ 40.00	30.00	7.07
В	Mass	gm	0.200	0.400	$-1 \leftrightarrow 0$.20	$+1 \leftrightarrow 0.40$	0.300	0.078
С	Time	min.	20.00	40.00	$-1 \leftrightarrow 20$	0.00	+1 ↔ 40.00	30.00	7.07
ANOVA Results									
Source	Sı	um of Square	es df	Mean	Square	F-valu	ie	p-valu	e
Model		2562.38	9	284	4.71	15	5.18	0.000	8
A-Conc		830.08	1	830	0.08	44	4.27	0.000	3
B-Mass		236.31	1	236	5.31	12	2.60	0.009	3
C-Time		540.38	1	540).38	28	3.82	0.001	0
AB		0.3025	1	0.3	025	0.0)161	0.902	5
AC		36.06	1	36	.06	1	.92	0.208	1
BC		210.54	1	210).54	11	1.23	0.012	2
A ²		142.68	1	142	2.68	7	.61	0.028	2
B ²		244.08	1	244	4.08	13	3.02	0.008	6
C^2		248.75	1	248	3.75	13.27		0.008	3
Residual		131.25	7	18	.75				
Lack of Fi	t	129.76	3	43	.25	11	15.96	0.000	2
Pure Erro	r	1.49	4	0.3	730				
Cor Total	l	2693.64	16						



Figure 4. 3D plot surface and 2D contour plot of the photo-degradation of DY on the surface of ZnO/MWCNT surface.

Model graph

The 3D response surface obtained in DY photodegradation is depicted in Figure 4 together with the corresponding 2D contour plot in ZnO/MWCNT. The efficiency of the e/h splitter depends on the ratio of connected electronic components; the maximum photodegradation rate of the dye was determined as 95.45%, threedimensional space surface. The maximum photodegradation efficiency is 99.45%. Figure 4(c) shows a three-dimensional response surface constructed to illustrate the effect of two variables (catalyst and amount dye concentration) on photodegradation efficiency.

The BPA degradation is mainly affected by the catalyst compared to the initial concentration.

Effect of weight of ZnO/MWCNTs

The influence weight of ZnO/MWCNTs on photocatalytic degradation of DY dye was studied using 30 mg/L, flow rate of air 10 mL/min at 25 °C. When the weight of ZnO/MWCNTs increases, the photo catalytic degradation of DY dye increases until it reaches 0.3 g /200 mL, as shown in Figure 5. The ZnO/MWCNTs has the efficiency to absorb the most light. Thus, 0.3 g of ZnO/MWCNTs gives the best photo degradation capacity because increased amount of photon of light cases leads to the degradation of DY dye.

However, at 0.1 g of ZnO/MWCNTs a reduction was experienced in photo degradation capacity [21-23]. The photo catalytic degradation PDE% of DY dye degradation occurred against the multiple quantities of ZnO/MWCNTs. The photo catalytic activity of the modified ZnO/MWCNTs rises with increasing weight of ZnO/MWCNTs from 0.1-0.4 g/200 mL. This indicates that the active site provided for substrate adsorption on the surface is limited to the quantity of 0.3 g/200 mL ZnO/MWCNTs. because the active sites are consumed via ZnO/MWCNTs during reactions that delay further photo catalytic degradation as show in Figure 6.



Figure 5. Photocatalytic activity of DY dye at different weights of ZnO/MWCNTs.



Figure 6. Effect of weight of ZnO/MWCNTs on PDE% by DY dye.



Figure 7. Impact of Photo degradation of ZnO/MWCNTs by DY dye



Figure 8. Effect several concentrations of DY dye onto (PDE%)

Effect concentration of DY dye

The impact of initial DY dye concentration under UV light utilized from 10-100 mg/L in the presence of 0.3 g of ZnO/MWCNTs, pH solution 5, and light intensity (1.27 mW/cm²). The data are demonstrated in Figure 7. The concentration of DY dye is determining factor in most of of DY elimination dye, especially in photocatalytic degradation. As the DY dye concentration raises, it prevents the penetration of light irradiation into the medium. Thus, DY dye PDE% would increase remarkably, it means that with greater concentration, the DY dye of the PDE% decreases [7-8,24-25].

In Figure 8, it is observed that the DY dye photo catalytic degradation (PDE%) rises as the concentration of DY dye decreases and the photo catalytic degradation increased from (93.67%-62.76%), and this occurs either by reducing holes or (OH) because the sites active will complete the coverage with the DY dye, or increase in the concentration caused an increased adsorption of the DY dye on to ZnO/MWCNTs, which leads to reduced (OH) radical generation, because that is low availability of the free active site on the surface [15,26].

Conclusion

ZnO NPs was grafted onto the MWCNTs framework and then utilized for photo reduction of DY dye, and the ZnO NPs introduction heightened the absorption of solar light. Under solar light irradiation, nanocomposite can completely remove DY dye (30 mg/L) solution in 1 h. After that, the degradation study indicated that the effective DY dye removal from aqueous solutions was accomplished via nanocomposite, with the best degradation at concentration of 30 mg/L from adsorbent, and then improved photo catalytic performance of the produced ZnO/MWCNTs. Through the data, it was found that using nanocomposite significantly affect the photo degradation of DY dye leading to 95% photocatalytic degradation at 60 min.

Conflict of interest

The authors declare that they have no conflict of interest

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