



PHOTOCATALYTIC DEGRADATION *n*-UNDECANE USING COUPLED ZnO-CO₂O₃

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ABSTRACT

The composite of ZnO-CO₂O₃, were prepared by thermal wet mixing method. This research consists of two parts, the first preparation of coupled (ZnO-CO₂O₃) by normal wet treatment mixing then calcinating in a furnace (900°C) for 3 hrs. The mixing semiconductor products were studied by using X-ray diffraction, and FTIR analysis.

The second part of this work includes the study of photocatalytic degradation of *n*-undecane using prepared coupled (ZnO-CO₂O₃), which is achieved by the irradiation of suspended solution consists of different concentration of *n*-undecane with coupled (ZnO-CO₂O₃) by using solar source/mercury lamp (125 Watts). In order to study the effect of mixed metal oxide (ZnO-CO₂O₃) in photocatalytic degradation of *n*-undecane, several experiments were carried out in various conditions to attain the best photocatalytic degradation of *n*-undecane. These experiments include the effect of mass catalyst, light intensity, substrate concentrations and the effect of temperature. The products were analysis by using gas chromatography technique.

Key words: *n*-Undecane, Photocatalytic, ZnO-CO₂O₃.

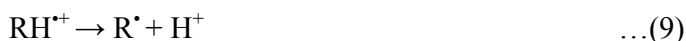
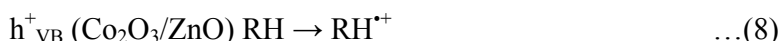
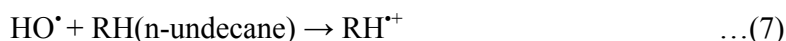
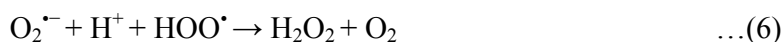
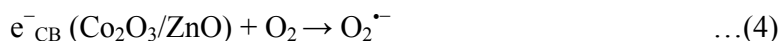
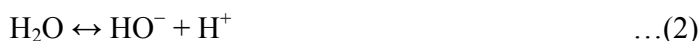
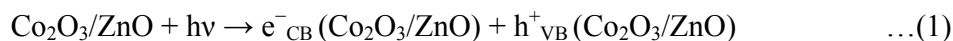
INTRODUCTION

Attention was drawn to *n*-undecane as an environmental pollutant with widespread human exposure. Still, toxicological information is limited. Kjmrgaard et al.¹ reported that the presence of *n*-decane in indoor environments could provoke adverse effects to health such as irritation of the mucous membranes. To prevent health hazards effects of indoor air pollution, urgent and new countermeasures must be implemented, such as using of activated carbon²⁻⁴, also natural sources^{5,6} since the actual purifier systems, employing filters packed

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with adsorbents (activated carbon another natural resources) do not constitute a definite conversion solution, merely transferring the pollutant to a different phase, thus requiring periodic maintenance and producing considerable amounts of waste.

Advanced oxidation processes (AOPs) allow the destruction of organic pollutants mainly through reactions with reactive oxygen species, such as hydroxyl radicals, where complete mineralization to CO₂ and H₂O can be achieved⁷⁻¹⁵. The main reactions that occur on the TiO₂ surface, leading to the formation of electron (conduction band)-hole (valence band) pairs, and consequently leading to the generation of hydroxyl, superoxide and peroxide radicals, are shown in (Eqs. 1 to 6). The reaction of reactive oxygen species or photogenerated holes (high oxidation potential) with the organic pollutant (RH) (Eqs. 7- 9), leads to the structural molecule breakdown until complete mineralization, like the mechanisms suggested by Augugliaro et al.¹⁶



To best of our knowledge, only a very few papers report on the degradation of n-undecane in liquid-phase by Co₂O₃/ZnO.

For instance, Debono et al.¹⁷ investigated the n-decane degradation in a reactor chamber with a bed of TiO₂ immobilized at the bottom of the reactor, achieving 90% of degradation. Monteiro et al.¹⁸ studied the n-undecane degradation in an annular photoreactor under simulated solar irradiation and under different operating conditions (feed concentration, humidity, irradiance, and flow rate), employing a catalytic bed made of cellulose acetate monoliths coated with a photocatalytic paint, achieving more than 90% of n-undecane degradation.

Miranda et al.¹⁹ studied the n-decane degradation by cellulose acetate monoliths coated with P25 or sol-gel TiO₂ films under simulated solar irradiation.

This paper focuses on the photocatalytic degradation of n-undecane by synthesizing (Co₂O₃/ZnO). Firstly, the synthesizing of (Co₂O₃/ZnO) couple. Next, the effect of different operational parameters, and the diversity are presented; a reaction pathway is proposed and detected.

EXPERIMENTAL

Materials and methods

Chemicals

Zinc oxide (ZnO), and cobalte oxide (Co₂O₃) were supplied by Fluka AG, n-undecane was supplied by Sigma-Aldrich. All chemical were using without further purification.

Synthesis of (ZnO-Co₂O₃) couple

The coupled semiconductors (ZnO-Co₂O₃) were prepared by a conventional mixing process. The Co₂O₃ powder, in a range of 0-10 mol%, was mixed with ZnO powder by ball-milling with zirconia balls and deionized water, after dried and calcinated at 900°C for 3 hr.

Photoreactor and procedure

Experiments were carried out in glass photochemical reactor as shown in Fig. 1.

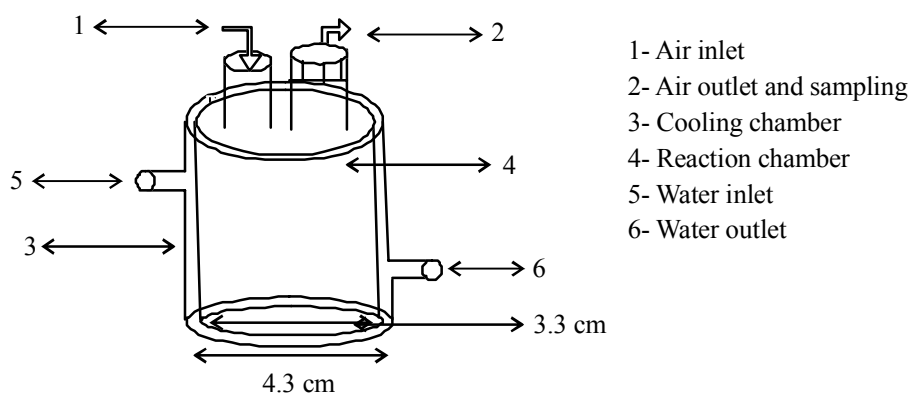


Fig. 1: Main parts of the photocatalytic cell original

RESULTS AND DISCUSSION

Structural characterization

The naked ZnO, Co₂O₃ and prepared coupled semiconductor (ZnO-Co₂O₃) were characterized by following techniques.

XRD Spectrum

Fig. 2 shows the XRD analysis of a) ZnO, b) Co₂O₃, and (c) ZnO/Co₂O₃. From Fig. 2a, different peaks (2θ) appear in spectrum (33.5, 34.5, 36, 47.5, and 56.5) represent naked zinc oxide, all peaks (2θ) appear in spectrum (27.1116, 34.5, 36.8, 30.1, 44.8, 39.8, and 35.3) represent naked cobalt oxide as shown in Fig. 2b.

Many peaks (2θ) appear in spectrum (36.2, 36.8, 31.8, 34.4, 31.3, 31.6, 31.8, 36.5, 36.8, 38.5, 44.8, and 47.5) represent the mixed between zinc oxide and cobalt oxide as shown in Fig. 2c. The mixed semiconductor ZnO-Co₂O₃ give new spectrum which indicates a shift in 2θ and reduce its intensity, also the mixed semiconductor ZnO-Co₂O₃ leads to appear of new peak 2θ in spectrum not exist in the original spectrum, this may due to the distortion for the two crystal lattice of ZnO and Co₂O₃.

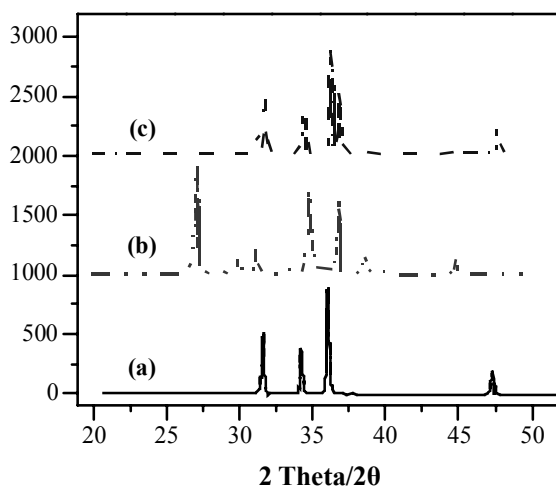


Fig. 2: XRD diffraction spectrum of (a) ZnO, (b) Co₂O₃ and (c) ZnO/Co₂O₃

FTIR Spectrum

Fig. 3a shows FTIR spectra of naked zinc oxide (488.01, and 445.57) cm⁻¹, while Fig. 3b shows FTIR spectra of naked cobalt oxide all peaks appear at (667.39, 578.66, 547.80,

501.51 , 462.93 , 426.28) cm^{-1} . For mixed semiconductors (ZnO – Co_2O_3 , Fig. 3c shows the peaks (675, 598, 475, and 450) cm^{-1} . From the Fig. 3c, it can be seen that the shift in peaks and reduce its intensity, this mean the mixing between two semiconductors occurs.

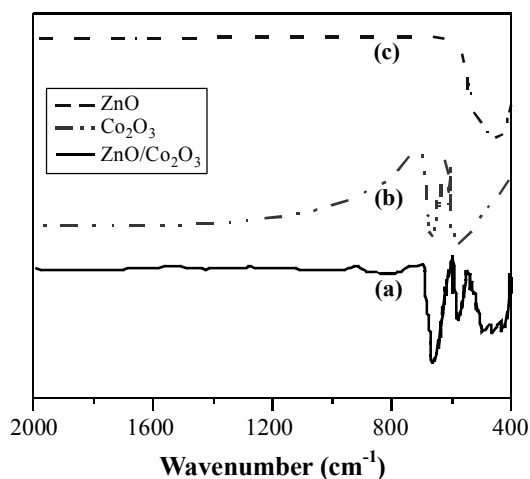


Fig. 3: FTIR Spectrum for (a) ZnO, (b) Co_2O_3 and (c) $\text{ZnO}/\text{Co}_2\text{O}_3$

Photocatalytic degradation of n-undecane

The effect of mass dosage ($\text{ZnO}-\text{Co}_2\text{O}_3$) on photocatalytic degradation of n-undecane

The effect of mass of coupled semiconductors $\text{ZnO}-\text{Co}_2\text{O}_3$ on photocatalytic degradation of n-undecane. The rate of photocatalytic degradation processes of n-undecane, plotted in Fig. 4. Gradually increases as the mass of coupled semiconductors $\text{ZnO}-\text{Co}_2\text{O}_3$ increases until reach to the mass 0.14 g/100 mL then gradually decreases. When the mass of coupled $\text{ZnO}-\text{Co}_2\text{O}_3$ equal (0.14 g/100 mL), the couple can provide the highest absorption of light. The decrease in the efficiency of photodegradation process at the masses of mixed $\text{ZnO}-\text{Co}_2\text{O}_3$ higher than (0.14 g/100 mL) due to the light absorption will be limited only to the first layers of n-undecane and the other layers of solution do not receive light photons. Moreover light scattering at high coupled $\text{ZnO}-\text{Co}_2\text{O}_3$ loading, this lead to decrease the photon intensity, so the strong absorption of light through the first successive layers of solution and prevent light from passing through all other layers in the reaction vessel. Many workers studied this effect^{11,20}. At the loading of coupled $\text{ZnO}-\text{Co}_2\text{O}_3$ below the optimum value (0.14 g/100 mL), the rate of photodegradation of n-undecane also decrease due to the quantity of coupled $\text{ZnO}-\text{Co}_2\text{O}_3$ decrease that mean the surface area decrease, which lead to decrease of light absorption of light by coupled $\text{ZnO}-\text{Co}_2\text{O}_3$, which cause lower photodegradation rate of n-undecane. The kinetic results are plotted in Fig. 5, which shows

that the rate constant of reaction generally increases with increase of photocatalytic concentration.

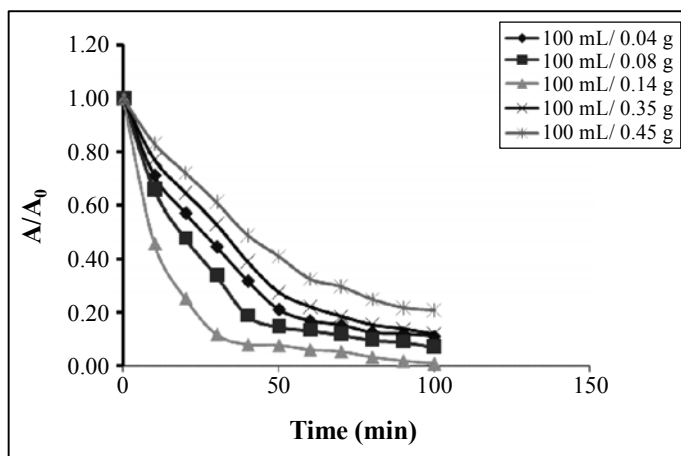


Fig. 4: The effect masses of mixed ZnO-Co₂O₃ on photocatalytic degradation of n-undecane. Experimental conditions: (10 ppm of n-undecane, flow rate of air 10 mL/min, room temperature = 298 K)

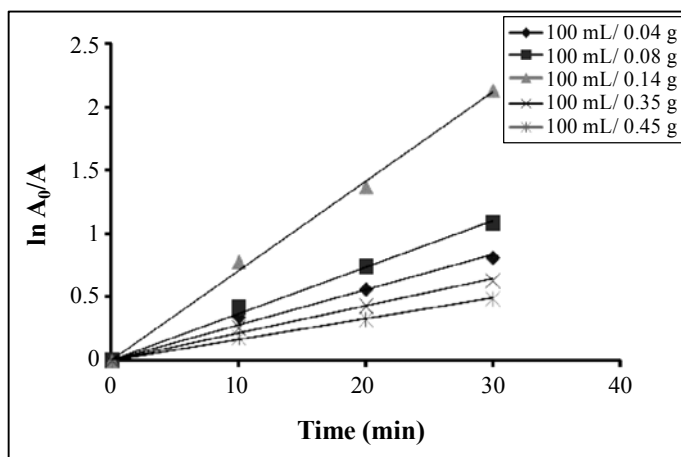


Fig. 5: The change of $\ln(A_0/A)$ with irradiation time at different concentration of n-undecane

Effect of n-undecane concentration on photocatalytic degradation processes

A series of experiments have been done. The effect of change initial n-undecane concentration on photocatalytic degradation of n-undecane was studied in the range (10-100)

ppm. The results are shown in Fig. 6. It has been observed that the rate of photocatalytic degradation gradually decreases with the increasing of initial n-undecane concentration.

This behavior could be explained as the concentration 10 ppm was the optimum concentration to cover the largest area of the coupled ZnO-Co₂O₃ particles, therefore absorbed maximum exciting photons to generate higher concentration of the activated coupled ZnO-Co₂O₃ semiconductor^{21,22}.

Another reason for this behavior is the strong absorption of light by the n-undecane in the sample, which contains high concentration that 100 ppm, n-undecane on (0.14 g/100 mL) of coupled ZnO-Co₂O₃. The excess of n-undecane prevent the penetration of light through the successive layers of n-undecane on the coupled ZnO-Co₂O₃ surface is weak to generate the required excited state of the n-undecane adsorbed on coupled ZnO-Co₂O₃.

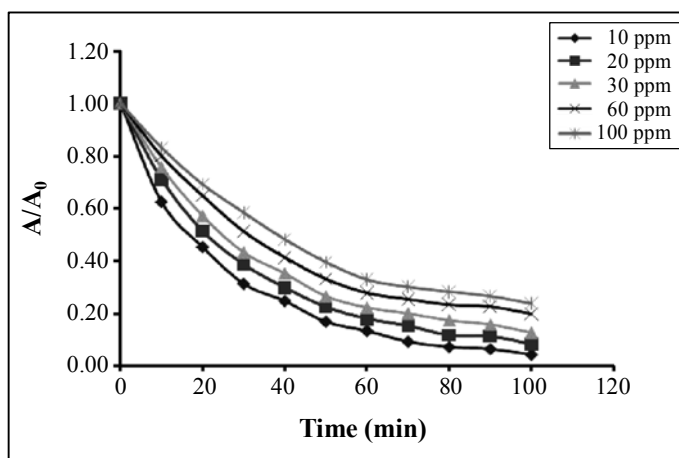


Fig. 6: Effect of irradiation time on photocatalytic degradation of n-undecane at different concentrations. Experimental conditions: (ZnO-Co₂O₃ 0.14 g/100 mL, light intensity 8.22 mW/cm² and temperature 298 K)

Effect of light intensity on photocatalytic degradation

A series of experiment was carrying out to study the effect of light intensity range 2.15-8.22 mW/cm² from high mercury lamp 125 W. Fig. 7, illustrate the effect of light intensity on the photocatalytic degradation of n-undecane. The results indicate that the photocatalytic degradation of n-undecane increases with the increase of light intensity, and the maximum value of light intensity was 8.22 mW/cm². In general the used lamp production photons, this photons increase electrons transfer from valance band to conduction

band in the coupled ZnO-Co₂O₃. This process lead to increase photocatalytic process of n-undecane^{20,22}.

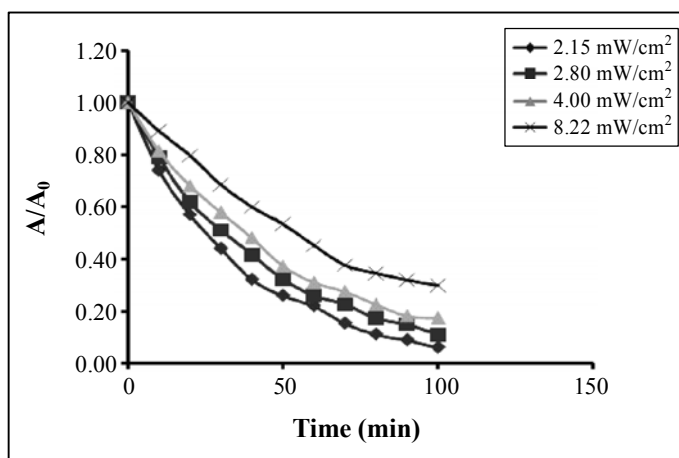


Fig. 7: Effect of irradiation time on photocatalytic degradation of n-undecane at different light intensity. Experimental conditions: (mass of ZnO-Co₂O₃ (0.14 g/100 mL), conc. n- undecane (10 ppm), flow rate 10 mL/min, and temperatur 298 K)

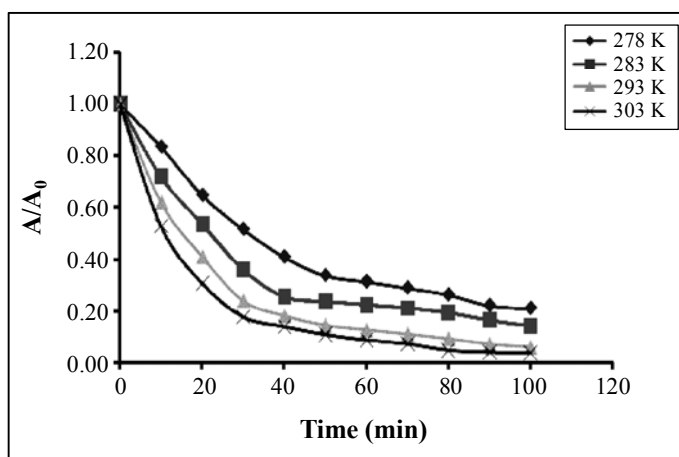


Fig. 8: The change of (A/A_0) with irradiation time at different temperature for photocatalytic degradation rate of n-undecane by using coupled ZnO-Co₂O₃

Effect of temperature on photocatalytic degradation

A series of experiments were carried out to study the effect of temperature on photocatalytic degradation of n-undecane rate using mixed ZnO-Co₂O₃ suspension at different

temperature ranging from 278-303 K. Fig. 8, shows the effect of temperature on the photocatalytic degradation rate of n-undecane at fixed initial concentration 10 ppm and (0.14 g/100 mL) of coupled ZnO-Co₂O₃ as catalyst. Fig. 9 indicates that the photocatalytic degradation rate of n-undecane increases with increase of temperature increase temperature lead to increase photocatalytic degradation of n-undecane because increase temperature cause to increase generate free radicals²³. The amount of activation energy (26.34 J/mole), this value deduced by using Arrhenius equation from Fig. 10.

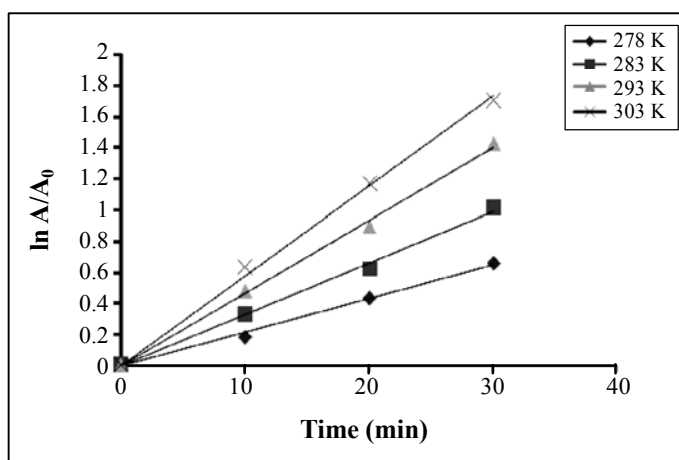


Fig. 9: The change of $\ln(A_0/A)$ with irradiation time at different temperature

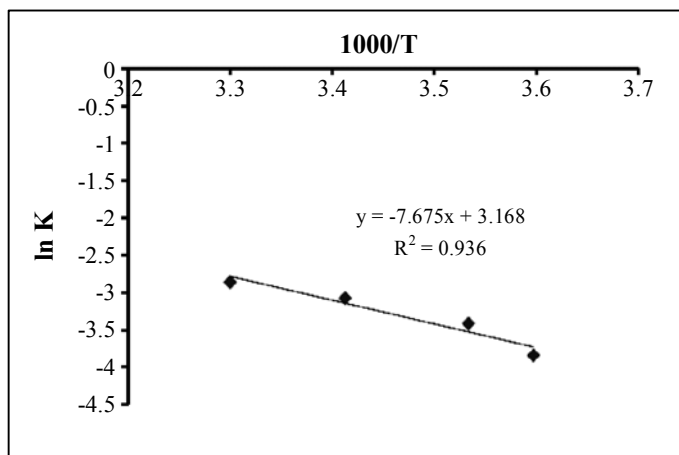


Fig. 10: Arrhenius plots for determination of activation energy for photocatalytic degradation of n-undecane

Gas chromatography analysis

This technique is more useful to determine the fragments of long chain hydrocarbon such as n-undecane. Gas-Chromatography spectrum of n-undecane (PYE UNICAN – 304, FID, PHILIPS) after irradiation for 100 min shows new peaks area percentage of light hydrocarbons are generated that mean the photodegradation of n-undecane occur, results are shown in Fig. 11.

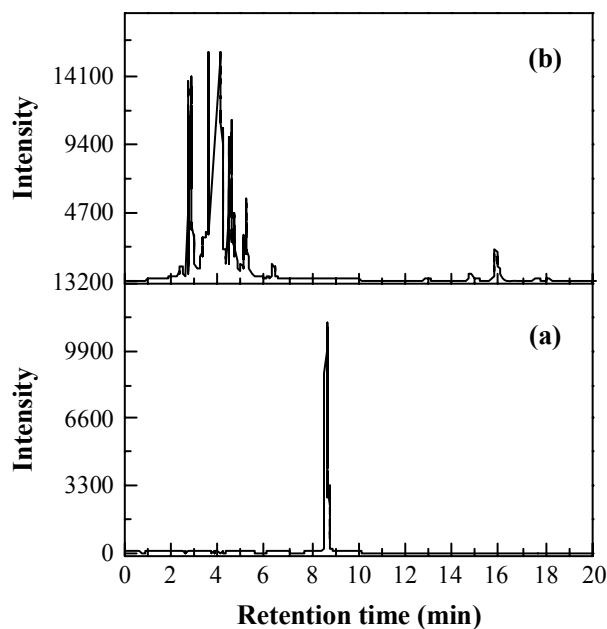


Fig. 11: Gas Chromatography analysis: (a) n-undecane, (b) products of photocatalytic degradation process

CONCLUSION

- (i) The compound has been not degraded in case of absent of catalyst.
- (ii) The compound has been successfully degraded when used the catalyst with the light.
- (iii) The optimum condition for the photocatalytic degradation of n-undecane 0.14 g/100 mL mass of mixed ZnO-Co₂O₃ and 10 ppm concentration of n-undecane.
- (iv) The activation energy about 26.34 J/mole.

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