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Removal of Reactive Yellow 145 Dye from Simulated Industrial Waste Waters over Prepared Supported (Co, Ni) $_3O_4/Al_2O_3$ Spinel Catalyst.

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ABSTRACT

The spinel co- catalyst (Co, Ni)$_3O_4/Al_2O_3$ was prepared using co-precipitation method. The produced material then was calcinated at temperature (600 ^oC) for 4 hour. The resultant catalysts were characterized using powder X-rays diffraction (PXRD), Fourier transform infrared spectroscopy (FTIR). The photocatalytic activity and the adsorption ability of these materials were investigated by following photocatalytic degradation and adsorption of reactive yellow 145 dyes (RY145) from simulated industrial wastewaters. Different reaction parameters and conditions were undertaken, including studying the effect of pH of the solution, the amount of the used catalyst, and effect of the temperature. In addition to that both of Frundlich and Langmuir adsorption isotherms were studied. From the obtained results in this study, it was found that the best efficiency for RY145 removal was around 99.9%. This was achieved at optimal reaction conditions which were pH =3, weight of the catalyst 0.1g and time of reaction was one hour.

Keywords: Spinel oxide, Dyes removal from wastewaters, Reactive yellow dye, Adsorption processes.

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INTRODUCTION

In the last few years it becomes more interesting to discover new methods to remove azo dyes from wastewater, most of the textile industry (clothing), food,and color paper printing industry are using azo dyes [1,2]. These dyes are complex aromatic organic compounds and they have a complex structural of one or more largestazo groups (-N=N-). These groups are responsible for the color,if these groups are broken the color of the desired compound will disappear, besides that, these groups not easily degraded under normal conditions from wastewater. Generally, these dyes create many environmental pollution troubles by formation of carcinogenic materials and releasing a toxic substances [3-5].There are different ways that can be used to remove color textile effluents, including physical and chemical processes such as precipitation, adsorption, air stripping, and photodegradation methods [6-8]. Semiconductor photo-catalysts can be used for degradation of these dyes. photocatalysts is a composite semiconductor that can be used in photocatalytic processes. Alumina (Al_2O_3) is one of the most important supported materials, it has a large surface area, not expensive, inert and easy to prepare so it's used in heterogeneous catalyst preparation, the structure of alumina mainly depends on the calcination temperatures, this can produce different morphologies of alumina such as γ -Al_2O_3 and α-Al_2O_3 in this context, α-Al_2O_3 can be produced by heating to 1100ºC [9,10]

γ-Al_2O_3 can be produced by heating aluminum hydroxide at 400 ºC, gets a soft white powder lover of moisture and dissolves in all acids, due to its large ability towards adsorption, it is widely used in the removal colors from the solution (catalyst) and in chromatography [11]. Also Co_3O_4 cobalt oxide has important properties as a catalyst for environmental application reactions, Co_3O_4 presents with high catalytic activity to oxidation of the volatile organic compounds, the main disadvantages of Co_3O_4 is that its activity will be decreased at high temperatures usually over 500 $^{\circ}$C, cobalt oxides have many applications such as colored glasses, electrochemical capacitors in hydrogenation, and as a very important as a catalyst[12,13].

Nickel oxide can be used in photochemical reactions, especially to dispose of aromatic compounds that are found as pollutant in water, nickel oxide is characterized by distorted structure, due to the presences of excess of oxygen that makes holes between the neighboring ions of Ni^{2+}, and hence oxidize of Ni^{2+} to Ni^{3+} this charge makes the oxide is colored [14].Photodegradation is caused breakdown of the molecule into smaller species, when the particle absorbs photon, electrons in the valence band of the semiconductor are excited to the conduction band from the valence band with leaving positive holes in the valance band. The positive holes react with the adsorbed species on the surface to form radicals while the electrons in the conduction band react with the adsorbed species. The photocatalytic degradation of a dye in the solution involves excitation of the semiconductor particles via absorption photon with a proper energy. Upon this process electron – hole pair on the surface of catalyst would be produced and then these species diffused from the bulk of the catalyst to the surface to participate in redox reactions this surface [15].

Photocatalyst is the semiconductor oxide that is able to increase the efficiency of removal of organic and inorganic pollutants in water and wastewater[16,17]. Reactive yellow 145 its azo disperse dye, it has which has the molecular formula $C_{28}H_{20}ClN_9Na_4O_{16}S_5$ and the molar mass 1026.25 g mol^{-1}.Itssolid material, soluble in water at 25°C [18,19]. The present work aims to study the photocatalytic removal of reactive yellow 145 dye from its aqueous solution using Ni_3O_4-Co_3O_4/Al_2O_3photocatalyst under irradiation with UV light.

MATERIALS AND METHODS

Materials and chemicals

In this study, all the used chemicals were used as they were provided without any further purification. Aluminum nitrate $Al(NO_3)_3.9H_2O$, cobalt nitrate hexahydrate $Co(NO_3)_2.6H_2O$, and nickel nitrate hexahydrate$Ni(NO_3)_2.6H_2O$ were obtained from(BDH company) with Purity of 99.5, 97.9, 99.9% respectively. Sodium carbonate anhydrous Na_2CO_3 obtained from (GmbHcompany**)** with Purity 99.9%. The dye that was used in this study was reactive yellow dye 145, it has a molecular formula ($C_{28}H_{20}ClN_9Na_4O_{16}S_5$) it was obtained from (Al-Hilla textile factory).

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Catalyst synthesis

Supported spinel oxide (Co, Ni)$_3O_4$/Al_2O_3 was prepared with different ratios 40:40:20 % respectively from their starting materials. $Ni(NO_3)_2.6H_2O$, $Co(NO_3).6H_2O$, and Al (NO_3). $9H_2O$. These quantities were weighed accurately and dissolved in 400 mL of deionized water. This mixture was stirred continuously under ambient air condition. The pH of this mixture was monitored by measuring the pH of the solution using a digital pH meter (740 Inolab WTW) and a pH of (5.5-6.2) was recorded for various mixed ratios. Then to this mixture (1M) Na_2CO_3 was added as a precipitating agent and kept the solution at a temperature equal to (70-75) ºC by using the magnetic stirrer (Gallenkamp, England) . The pH was kept approximately around (9), the resultant mixture was left for (2) hours in the same temperature (70-75) ºC with stirring for digestion. Then the resultant mixture was filtered using a Buchner filtration flask and a vacuum pump. The obtained precipitate was dried in an oven (Oven Bs Size Two GallenkampEngland) for overnight at 120 °C. The resultant solid was calcinated at a rate 10 ºC/min for temperature 600 °C [15].

Photocatalytic activity of the prepared catalyst

Irradiation processes in this study, was performed using mercury lamp was Philips- Holland (250 W) without cover glass as a source of UV radiation, hot plate, magnetic stirrer, and photoreaction cell which was made from Pyrex glass with quartz windows figure(2) shows irradiation cell, with a volume of 30 mL. All the experiments were performed by adding the catalyst material into the photoreaction cell, to this aqueous solution of RY145 50 ppm, 30 mL was added. The temperature of the reaction mixture was adjusted at 23 °C.

The radiation process was illuminated from the source and during processing of the reaction temperature was controlled a thermostat. Periodically, 2mL of the reaction samples were withdrawn after every 10 minutes for a total reaction time of one hour. The obtained samples along one hour were centrifuged and separated using centrifuge, this process was repeated for many times to ensure fully separation of the fine particles of the used catalyst of Ni_3O_4-Co_3O_4/Al_2O_3. The absorbance of the supernatant liquid was measured at a wavelength of 418 nm, by using UV-visible spectrophotometer (UV-1650PC Shimadzu, Japan).

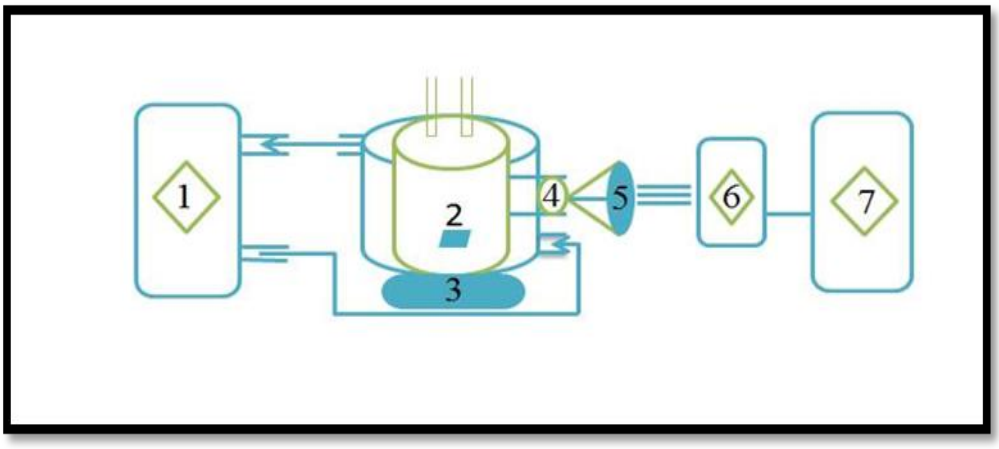

Figure 1: schematic description of the photochemical reactor.

1-Circulating water thermostat , 2- reaction cell , 3- magnetic stirrer , 4- quartz window , 5- lenses, 6- low pressure mercury ,7- power supply unit.

Effect of catalyst weight on the removal of RY145

In order to investigate the effect of the used amount of the catalyst on the efficiency of dye removal a series of experiments were performed to determine the best weight of the catalyst to obtain high effective of dye removal. In each experiment 30 ml dye solution of 50 ppm with a required amount of the catalyst were mixed. The mixture was irradiated with different weights of catalyst (0.05, 0. 1, 0.15, 0.2, and 0.3) g at room temperature for a period of time of one hour.

Effect of temperature on the removal of RY 145 dye

To study the effective of temperature on the rate of photocatalytic reaction of dye removal a solution of 50 ppm, 30 ml was used. Then reaction was performed using different reaction temperatures that were 284, 288, 292 and 296 K. The weight of catalyst was 0.1 g and under irradiation with UV light.

Effect of pH on the removal RY145 dye

The value of pH of the reaction mixture was controlled at the desired values using 0.01 M NaOH or1 M HCl solutions and, then the pH values were measured by a pH meter. For each case0.1 g of catalyst and 30 mL of 50 ppm dye solution were mixed under irradiation with UV light at 296 K for 60 minute.

The efficiency of dye removal was calculated using the following equation:

$$\% \text{ Photo-degradation efficiency} = C_0 - C_t / C_0 \times 100$$

Where the C_0, Ct is the initial and the final concentration of dye.

Adsorption isotherm studies:

In order to investigate adsorption isotherms for adsorption of RY145 over the prepend catalyst. Both of Freundlich and Langmuir isotherms were investigated. To do this a series of experiments were carried out using 30 mL, 50 ppm of dye aqueous solution with 0.1 g of the catalyst at 23^{o}C for one hour.

Catalyst Characterization

X-ray Diffraction (XRD)

The prepared catalyst was characterized by powder X-ray diffraction (XRD), Phillips X-ray diffraction with CuKradiation (1.542 Å, 40 KV, 30 MA), in the 2Θ range, 10-80 degrees(XRD6000, Shimadzu, Japan) .

Fourier Transform Infrared Spectroscopy (FTIR)

Study of the dual and triple prepared catalyst was achieved by using Fourier Transform Infrared (FTIR), FTIR spectra were recorded with (Perkin Elminer Spectrophotometer company).

All spectra were recorded at the wavenumber ranged from 400-4000 cm^{-1}. Samples were made as pellets prior to run by mixing with potassium bromide (KBr).

Surface Area Determination (BET)

The surface area of the prepared catalyst was measured using prep 060 and Gemini BET machine. This was performed using 0.05 g of each sample with flushing N_2 gas to remove pre-adsorbed gases in the sample. BET specific surface area was measured by adsorption of nitrogen at -196 ^{o}C.

Atomic Force Microscopy (AFM)

Atomic force microscopy (AFM) SPM-AA3000 Atomic Force Microscope / Contact Mode Angstrom Advanced INC., 2008, USA.was used in the field of nanotechnology to determine the atomic configuration and topography at the surface of the Nano materials

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RESULTS AND DISCUSSION

Catalyst Characterization

X-ray Diffraction (XRD)

The results of XRD patterns of the prepared materials that were calcinated at 600 ^{o}C are shown in Figure.3. From these patterns, it can be seen that sharper bands of the XRD patterns indicate, large crystallites are present. Also it can be noted that there was a deviation for some peaks for the samples that were synthesized at 600 $^{\circ}$C, also there was variation in the space- d (2..43359, 1..42338, 2..36032), and 2Θ (36.9062 ,65.5276, and 38.0953) for standard values by matching with (JPCDS).This deviation is acquired by influencing between these supported oxides[16,20]. The XRD patterns for these materials are shown in Figure.2.

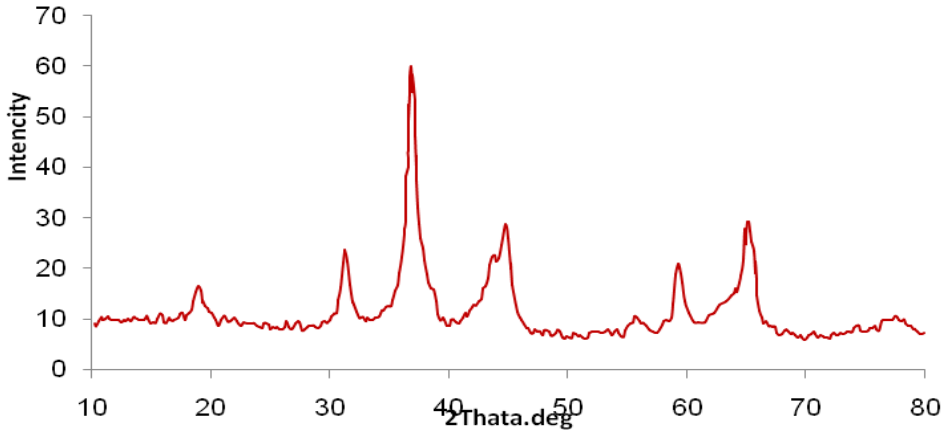

Figure 2: XRD patterns for the Ni_3O_4-Co_3O_4 /Al_2O_3 photocatalyst.

Fourier Transform InfraredSpectroscopy (FTIR)

The functional groups of the synthesized catalysts were investigated using FTIR spectroscopy. FTIR spectra for Ni_3O_4-Co_3O_4/Al_2O_3 showed peaks around 569 to 680 cm^{-1} which can be assigned to characteristic Co-O bond which corresponds to cobalt oxide , also there were peaks around 418.55- 466.77 cm^{-1} corresponds to Ni-O bond in nickel oxide [21,22]. In addition to that, it can be seen that there was a peak appears around 3431.36 cm^{-1} correspond to Al-OH, from dissociative adsorption of H2O on Al2O3[18] as well as to peak around 1629.85 cm^{-1}, this peak correspond to ϒ-Al_2O_3[23]. FTIR spectra for these materials are shown in Figure.3.

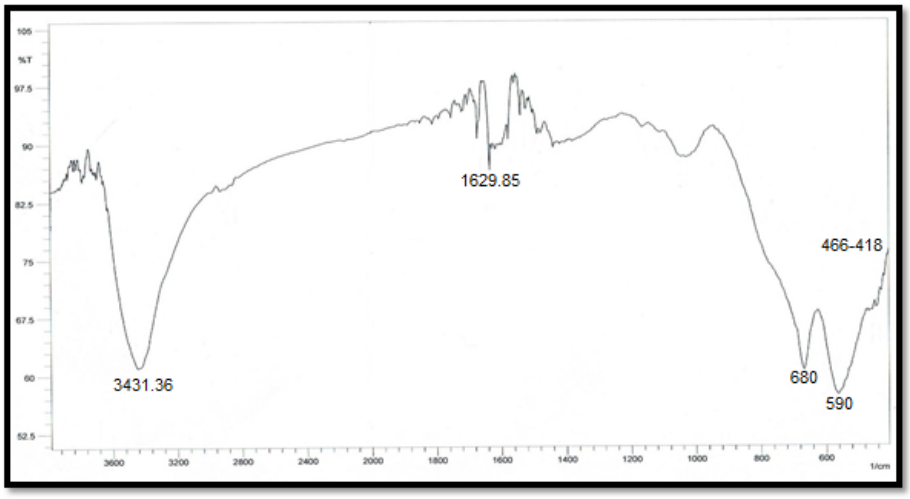

Figure 3: FTIR spectra of the prepared Ni_3O_4-Co_3O_4/Al_2O_3 catalyst.

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Surface Area Determination (BET)

The results of BET surfaces area of the prepared catalyst were123.174 m^2/g and the pore volume was 0.3041 cm^3/g. From these results it can be concluded that these materials have high surface area with relatively large pore volume. This probably arises from porous structure of these materials.

Atomic Force Microscopy (AFM)

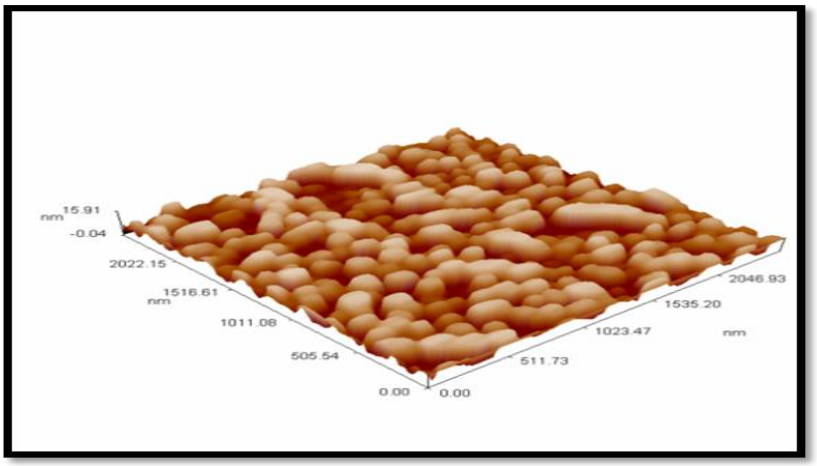

Figure 4: AFM images of Ni_3O_4-Co_3O_4/Al_2O_3 that calcinatedat 600 ºC.

From atomic force microscopy it can be concluded that the average particle diameter decrease with increases of calcination temperature. From these images the average particle at 600 ^oC is 107.29 nm. AFM images of these materials are shown in Figure.4 .

PhotocatalyticActivity of the Prepared Catalyst

The different experimental conditions was evaluated such as catalyst concentration, pH value, illumination time, and temperature by using photo- catalyst to complete degradation of reactive yellow145.

Effect of Catalyst Concentration

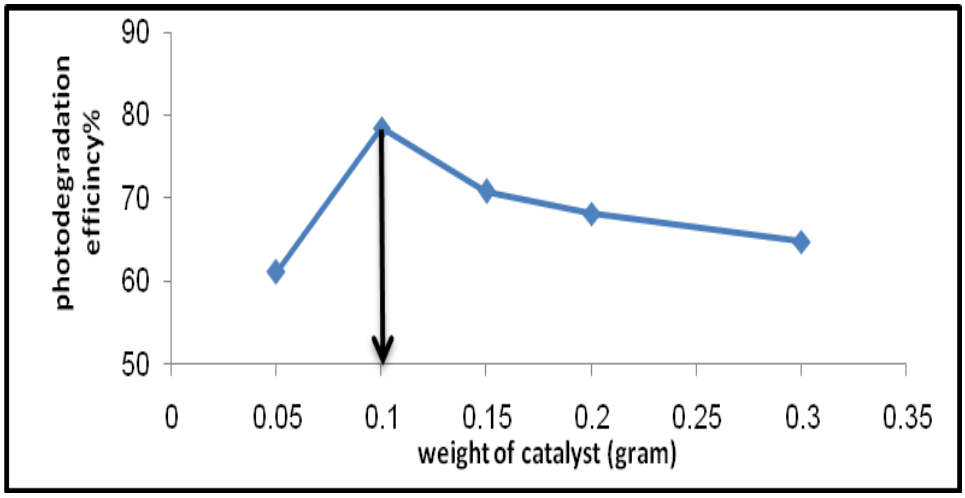

Figure 5: Effect of catalyst loading on efficiency of RY145 dye removal.

The effect of weight of the used catalyst on the photodegradation efficiency of reactive yellow dye was studied by taking different amounts of catalyst ranged from (0.05, 0.1,0.15, 0.2, and 0.3 g) into 30 mL of 50 ppm dye solution under UV light at 23 ^oC for one hour. The obtained results are shown in Figure (5), these

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results showed that there was increased in the activity of dye removal as the amount of the used materials was increased. This probably arises from the increase in the number of active sites available on the catalyst surface for the reaction as the amount of the catalyst was increased. For high concentration of the catalyst more than 0.15 g thephotodegradation efficiency was decreased to 70.8% due to an agglomeration that is caused an increase in the particle size and decrease in specific surface area which leads to decrease in the number of surface active sites [24,25]. Also high amounts of catalyst lead to increase of light scattering (increasing the turbidity). This tends to decrease the passage of irradiation through the sample. Therefore, the most effective photodegradation of reactive yellow145 was observed with 0.1 g of catalyst weight [22,26].

Effect of pH on Photocatalytic Removal of RY145 Dye

The rate of photocatalytic removal of dye is highly influenced by the value of pH of the reaction mixture. An important parameter of photocatalytic reactions on the Ni_3O_4-Co_3O_4/Al_2O_3surfaces is the pH of the solution. The photodegradation efficiencies of dye with different pH values for reaction mixture are shown in Figure (6). Removal efficiency of the dye was decreased with the increase in pH and the highest dye removal efficiency reached to 99.96% at pH= 3. Then the increasing of pH value of reaction mixture to 8 leads todecrease in photodegradation efficiency to around 56.1%. The reduction in the efficiency of dye removal at high pHs values can be attributed to the repulsion forces that are initiated between the negatively charged surface and the anionic groups that are present in dye molecules[27,28]. In addition to that, decrease in the photocatalytic activity of dye removal can be due to increase in the rate of recombination between (e^- /h^+) pairs which commonly increases with increase of pH of the reaction mixture [29,30].

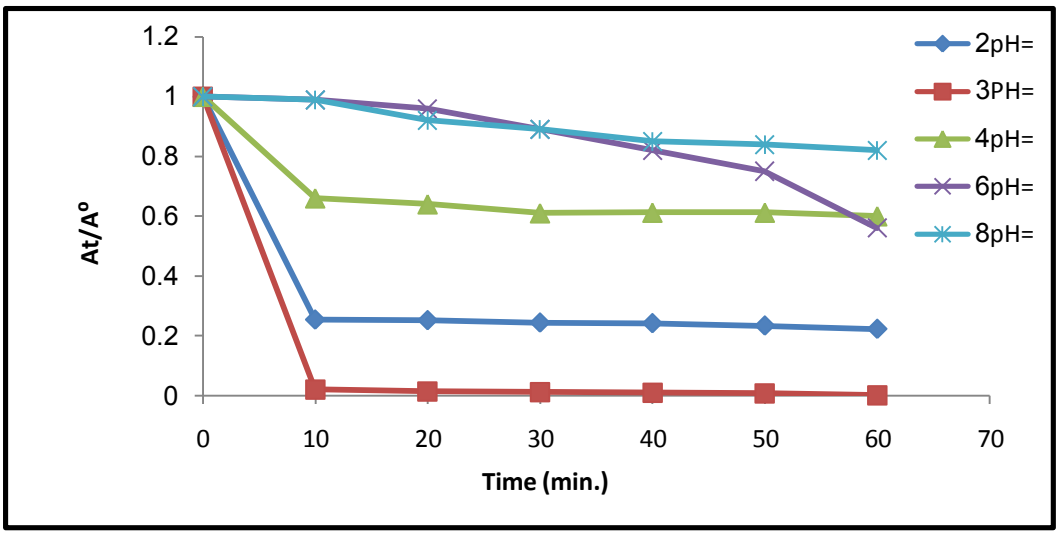

Figure 6: Effect of pH of dye solution on the photocatalytic removal of RY145.

Effect of temperature on the photocatalytic removal of RY dye

The effect of temperature on the photocatalytic removal of dye was studied in the range of temperatures 284-296 K by keeping other experimental conditions constant using dye concentration of 30 ppm and catalyst conc. was 0.1 g/L, pH dye solution equal to (3). The obtained results showed that, the removal efficiency of dye was increased with the increase in reaction temperatures as shown in Figure.7. Generally, these results indicated that the efficiency of dye removal was increased with elevation in temperature. This observation can be attributed to the increase in the production of free radicalsat higher temperatures [28,31,32].

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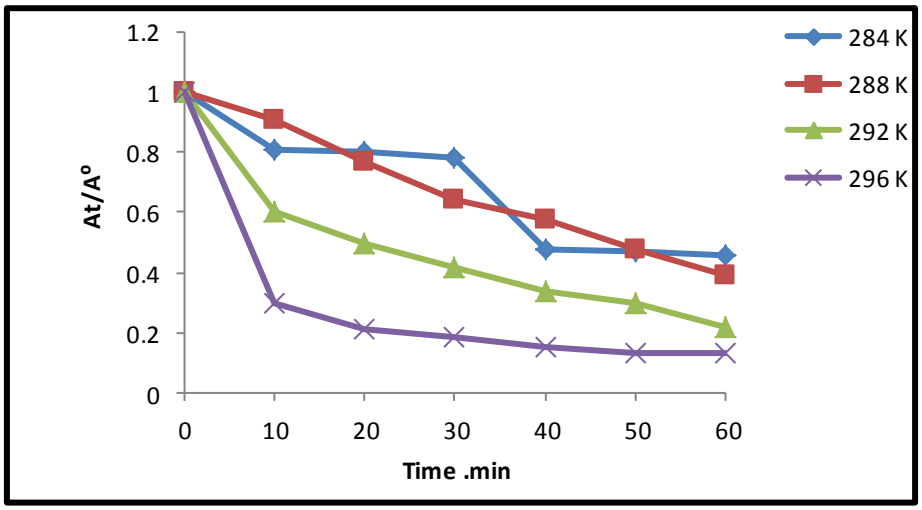

Figure 7: Effect of temperature on photocatalytic removal of RY145.

Effect of Irradiation Time on Removal of Reactive Yellow Dye 145

The effect of illumination time on removal efficiency ofreactive yellow 145 was carried out by measuring the photodegradation efficiency at different periods of time. The obtained results are shown in Figure (7). These results showed that the photocatalytic activity of dye removal was increased with increase of reaction time and reaches to 99.96% after 60 min of illumination time[30,33].

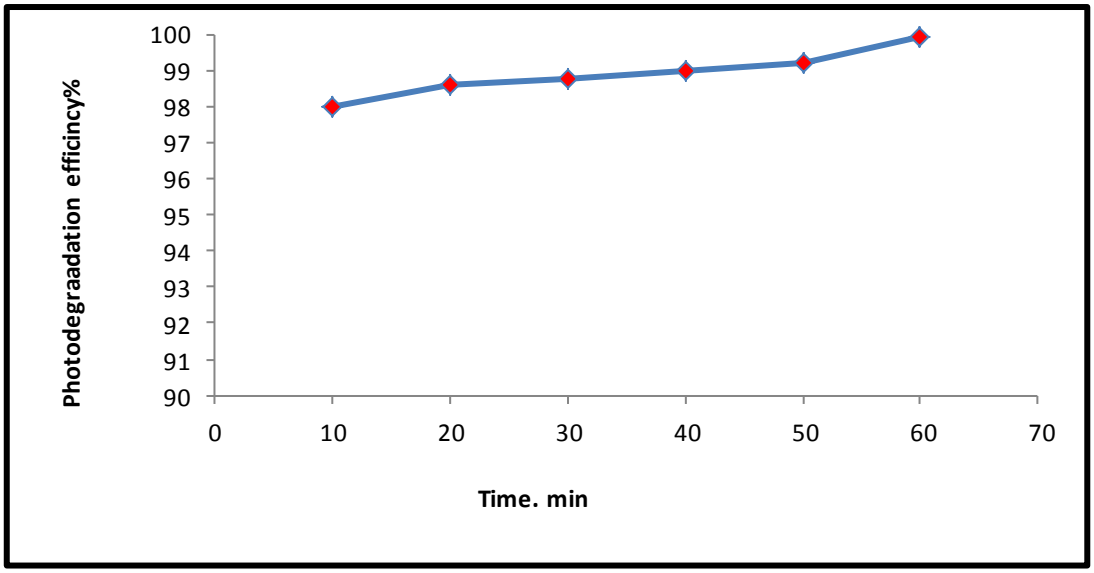

Figure 8: Effect of irradiation time on removal efficiency of reactive yellow145.

Adsorption Isotherms for Dye Adsorption over the Catalyst

The adsorption isotherms were studied using Langmuir, and Freundlich equilibrium models. These isotherms are shown in Figures. 9 and 10 respectively, Table. 1 shows values of Langmuir and Freundlich adsorption isotherms.

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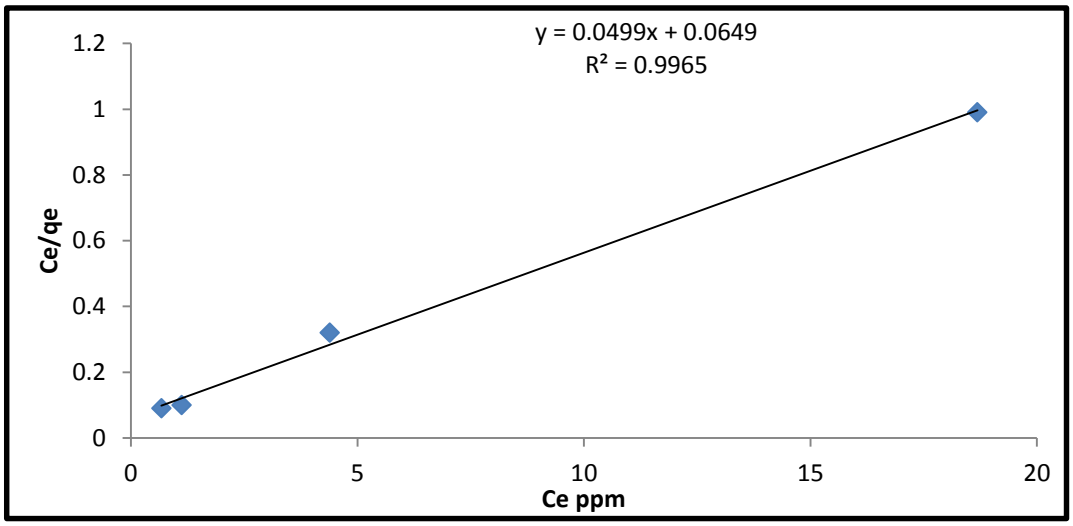

Figure 9: Langmuir adsorption isotherm for adsorption of RY145 on the prepared catalyst.

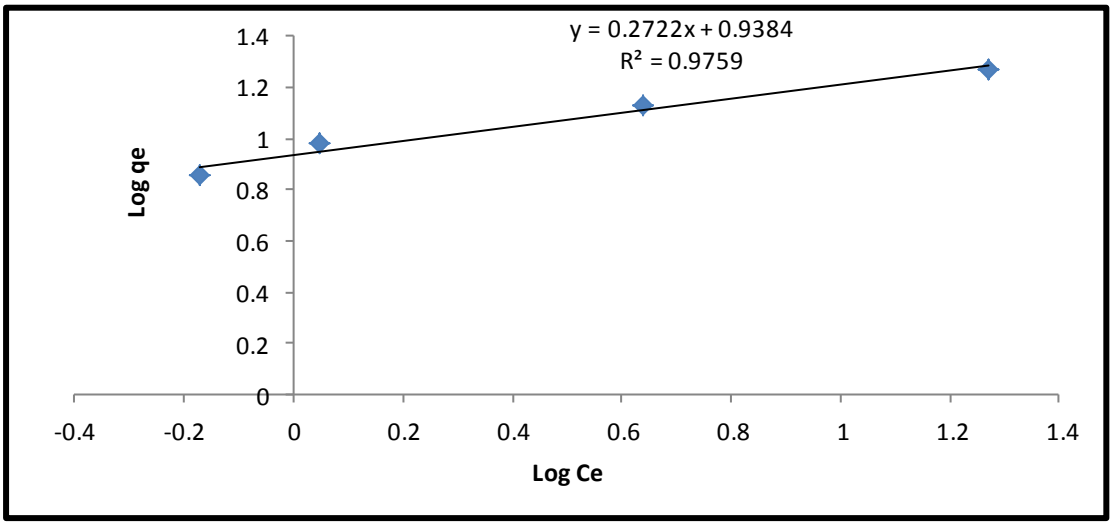

Figure 10: Freundlich adsorption isotherm for adsorption of RY145 over the catalyst

Table 1: Adsorption constants for Langmuir, and Freundlich isotherms

Isotherms	Parameter	value
Langmuir	Qm	20.04
	KL	0.76
	R^2	0.9965
Freundlich	KF	2.55
	N	3.67

From the results that are summarized in Table1, it can be seen that the value of the correction factor ((R^2) that are obtained from Langmuir model is higher than that forFreundlich isotherm. This means that, this process is agree with Langmuir model. The value of (n) that represents the number of adsorbed layers is (3.67) in this case adsorption processes were followed Freundlich adsorption isotherm [34-36].

CONCLUSION

The photocatalytic removal of reactive yellow dye 145 was strongly dependent on the amount of catalyst, pH value, temperature, and illumination time. The complete removal of this dye was achieved using Ni_3O_4-Co_3O_4/Al_2O_3 under UV-visible irradiation. The optimal conditions of dye removal was calculated at pH=3,

catalyst conc. = 0.1gm/L, temperature =23^{o}C, and illumination time of 60 min. The equilibrium adsorption isotherms from the obtained results adsorption isotherms, it was more fitted with Freundlich adsorption model.

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