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Kinetic and Thermodynamic Studies on the Reactivity of Hydroxyl Radicals in Wastewater Treatment by Advanced Oxidation Processes

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ABSTRACT

The removal of dyes from wastewater, is one of the major environmental concerns due to their high color density, and they are toxic at even low concentrations. Adsorption process by advanced oxidation processes (AOPs) has been found to be a more effective method than classical methods for treating dye-containing wastewater. This research, is to investigate the decolorization abilities of azo dye in order to treat organic polluted wastewaters efficiently by AOPs. Various operational parameters such as pH, initial dye concentration and catalyst loading were investigated on the use of ZnO/W in the adsorption of Reactive Red 31 (RR 31) dye. The study also focused on the kinetic and thermodynamic investigation such as activation energy (E_a), standard Gibbs free energy (ΔG^0), standard enthalpy (ΔH^0), and standard entropy (ΔS^0). The kinetics of adsorption of dye followed a pseudo-first order kinetic model. Further, thermodynamic study showed that the photocatalytic decolorization of this dye is an endothermic and spontaneous reaction. This study represents a success of thermodynamic for the application in environmental area. Additionally, cost analysis of the process was discussed. The treatment effectiveness was reported as the electrical energy consumed per unit volume (E_{EO}) of waste-water treated required for 100% decolorization of the investigated compound. Prog. Color Colorants Coat. 13 (2020), 1-10© Institute for Color Science and Technology.

1. Introduction

Due to increasing industrial activities, organic pollutants lead to contamination of the water. These organic compounds such as petrochemical products and dyes that are resistant against biological treatments processes are introduced in to the environment. One of the most dangerous pollutants is Azo dye family that is produced in textile, leather, color and the other industries [1-5]. The introduction of those colored wastewaters into the aqueous environmental resources can originate dangerous sickness. The term degradation is refer to breaking down the bonds in molecule structure in order to convert a toxic one to a nontoxic compound, or breaking down to it is original elements which is called mineralization [6]. Various physical, chemical and biological methods have been widely used to treat these contaminations from wastewaters, but these methods have their own drawbacks [2]. The degradation process usually occurs by chemical, biological, thermal or photochemical processes [7]. In recent years, there has been considerable growth of interest in using environmentally friend semiconductor adsorbent to

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enhance removal of pollutants from wastewater one of which is ZnO which is an inexpensive, non-toxic and highly stable semiconductor [2, 8, 9]. In the field of environmental processes, adsorption plays an important role in many industries, especially in removal pollutants which is more efficient for wastewater [10, 11]. Consequently, adsorption techniques seem to have the most potential use in industrial wastewater treatment [12] because of their proven efficiency in the removal of wide range of organic pollutants [13-15]. Advanced oxidation processes (AOP's) have attracted a great attention as a high performance wastewater treatment technique which based on adsorption process. The removals of dyes from effluents using AOP's provide an alternative treatment, especially if the adsorbent is inexpensive and readily available [16]. The major advantage of AOPs for water pollution control is less investment in terms of initial and operational costs, easy operation, simple design, and nontoxic substances compared to conventional other techniques. It must also be kept in mind there are advantages and disadvantages, their adsorption capacities also vary with varying experimental conditions [17, 18].

In this study, removing of Reactive Red 31 (RR 31) from aqueous solutions has been studied using AOPs. The adsorption of dye has been investigated as a function of contact time, pH, dye concentration, and adsorbent dose. The RR 31 dye has been absorbed by ZnO/W of RR 31-polluted-wastewater. The kinetic and thermodynamic studies have been performed to describe the adsorption process.

2. Experimental

2.1. Materials

Reactive Red 31 (RR31, 95% purity) (chemical formula, $C_{30}H_{15}C_lN_7Na_5O_{15}S_4$), (Monoazo, M.wt = 992.14 g/mol, λ_{max} = 545 nm) was purchased from Alvan Sabet Co. (Iran) Performance Materials and used without further purification. The respective chemical structure is shown in Figure 1. Pure tungsten powder, zinc nitrate, glycine and glucose were purchased from Merck, Co, (Germany) and used without further treatment.

2.2. Preparation of nano-photocatalyst

Pure tungsten powder was added to hydrogen peroxide (37 %) (10 mL) and deionized water (250 mL). Then, the mixture was heated to 80 °C to evaporate the half of the volume of solution. Afterwards, the mixture was mixed with Zinc nitrate (5 g), glucose (2 g), glycine (0.2 g) and deionized water and the resulted solution was dried to 80 °C to evaporate the water and form a yellow gel. Then, the resulting gel was heated for 1 min in 900 W to form a brown foam. Finally, the foam was heated to 500 °C for 1 h.

2.3. Material characterization

The energy dispersive X-ray (EDX) spectra model (JEOL JSM-6400) was used for the analysis to know the elemental composition of the Nano photocatalyst. The same machine was also used to examine the surface of the adsorbent. The Brunauer–Emmett–Teller method (BET) using BELSORP (BELSORP, BEL, Japan) apparatus was used to characterize specific surface area and pore size distributions of the ZnO/W. The pH values were determined with a pH-meter (Thermo Orion 920A). The decolorization of RR31 solution was monitored via measuring absorbance with a UV-Vis spectrophotometer (lambda-950, Perkin-Elmer, USA).

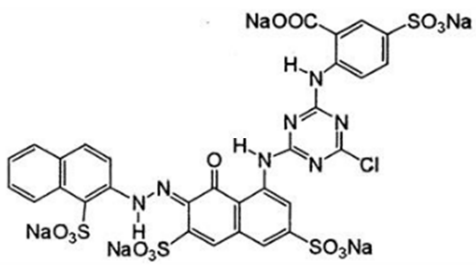

Figure 1: Chemical structure of RR31.

2.4. Photocatalytic procedure

All experiments were performed at laboratory scale. Synthetic wastewater was prepared by dissolving RR31 dye at 20 mg/L concentration. Dye sample solution was pipetted into a 1000 mL homemade photo reactor equipped with a low-pressure mercury lamp (9 W, λ_{max}=254 nm, Philips), and 0.01 g ZnO/W was added as an adsorbent. The suspension was stirred for 30 min in order to reach the adsorption desorption equilibrium. Subsequently, the suspension was exposed to UV light. Then reaction was started. The pH was adjusted to 5 (optimum value) with phosphate buffer (20 mM, pH 7.0). Adsorption was followed by measuring of the absorbance of the solutions at 545 nm with UV-spectrometer. A calibration curve was prepared in the range of 0-100 mg/L of RR31 dye according to the general procedure. At regular intervals; about 3 mL of reaction mixture was sampled and centrifuged for 20 min at 7000 rpm to ensure the total removal of fine photocatalyst particles from the solution. The concentration change during photodegradation have been measured by spectrophotometer at 545 nm is shown in Figure 2. The percentages of the dyes removed from the solution (R in %), were calculated from the equations (Eq. 1):

$$R\ (\%) = (C_0\text{-}C_t)*100/C_0 \qquad (1)$$

where, C_0 and Ce are the initial and equilibrium concentrations of copper in solution (mg/L); C_t is Concentration at t time; V is the volume of solution (L), and m is the mass of adsorbent (g).

3. Results and Discussion

3.1. Characterization study

Scanning Electron Microscopy (SEM) has been a useful tool for characterizing the surface morphology and fundamental physical properties of the adsorbent surface. Figure 3 shows the SEM micrograph of the nanophotocatalyst, which has considerable porous, spongy and almost uniform in size where RR 31 could be adsorbed with a high probability. The presence of a large amount of exhaust gases and high flame temperature applied during irradiation in synthesis process led to the formation of porous structure of nano-photocatalyst [16]. The EDX measurement was recorded for qualitative analysis of the element constitutions of the adsorbents (Figure 4). As the result shows, ZnO/W nano-photocatalyst consists of O, Zn, and W elements (Table 1). The surface areas, total pore volumes and average pore diameters of ZnO/W sample are achieved by BET and are given in Table 2. According to BET results, the radius of pores range less than 2 nm, which confirms the existence of micropores particles of photocatalyst [19].

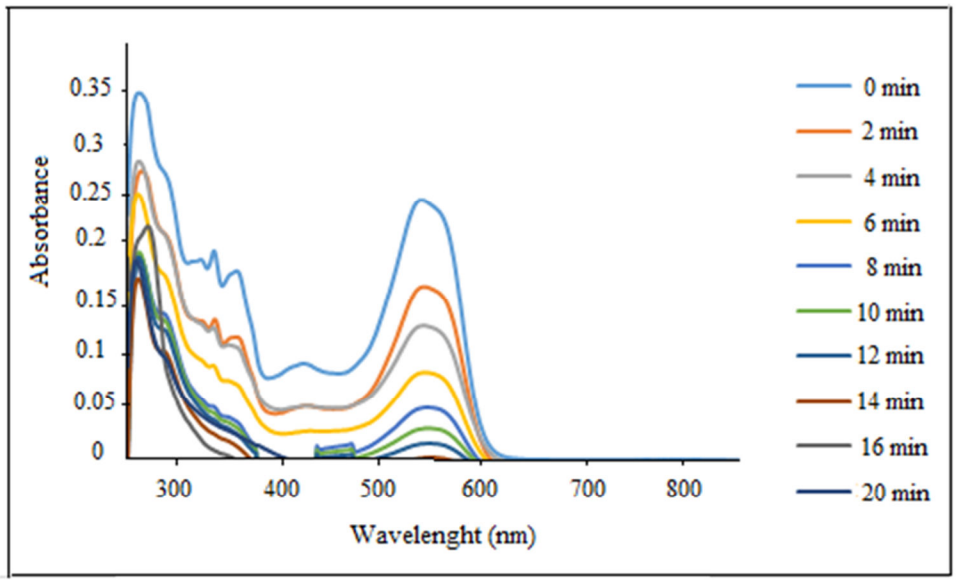

Figure 2: UV-Vis Spectral change for the degradation of 20 mg/L RR31 by ultraviolet light at different time.

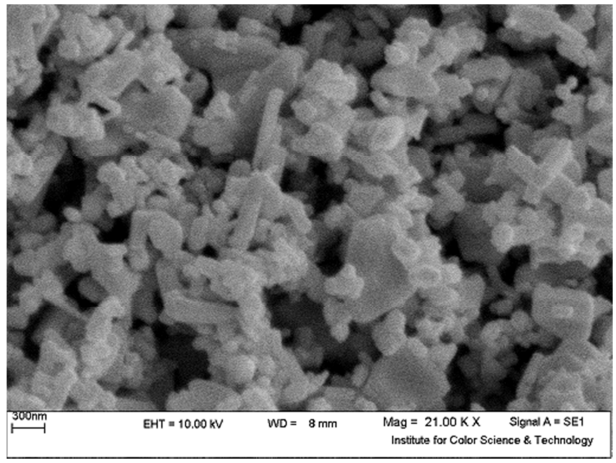

Figure 3: Scanning Electron Microscopy (SEM) of ZnO/W.

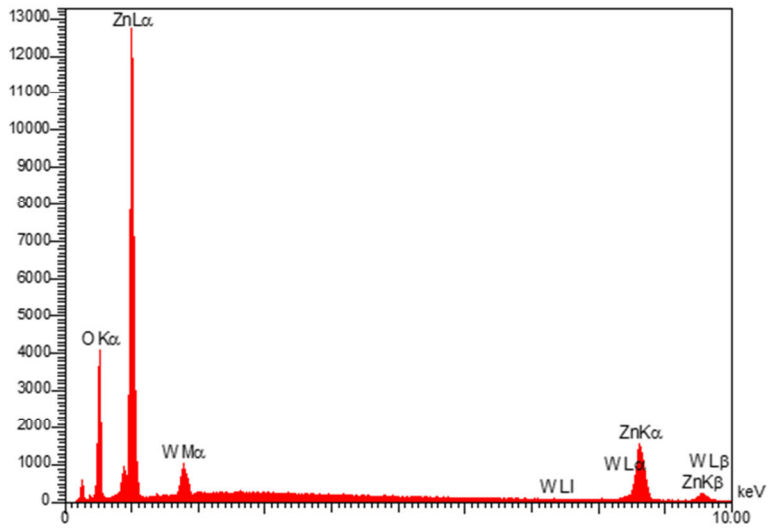

Figure 4: Energy Dispersive X-ray (EDX) spectra of ZnO/W.

Table 1: Results of EDX spectrum.

Elements	Weight (%)	Atom (%)
O	29.06	63.16
Zn	68.33	36.35
W	2.62	0.49

Table 2: Surface areas, total pore volumes and average pore diameters.

Sample	Surface area (m^2/g)	Pore volume (cm^3/g)	Mean pore diameter (nm)
ZnO/W	25.443	0.1799	1.29

3.2. Effect of process parameters on dye removal efficiency

3.2.1. Effect of photocatalyst loading

Photocatalyst loading is an important effective parameter which was evaluated by varying nano-photocatalyst concentrations from 0.005 to 0.015 g/L. The graph plotted (Figure 5) the amount of nano-photocatalyst and decolorization percentage reveals that by increasing catalyst loading up to 0.01 g/L, a complete decolorization was achieved. After an optimum point, a decrease was observed in efficiency which could be explained by an increase in turbidity of the suspension and decreasing the UV light interaction with surface reactive sites [20, 21].

3.2.2. Effect of pH

Dye removal efficiency was affected by pH of the solutions. Decolorization was performed at different pH values. At two extreme acidic and basic conditions, the decolorization rates were high and low, respectively (Figure 6). These results clearly indicated that the maximum ˙OH was generated at pH=5 [16]. Thus, all subsequent experiments were carried out at pH=5. Results revealed that decolorization efficiency of ZnO/W increased with a decrease in pH which reached to the maximum (100%) at pH=5 by increasing oxidation rate.

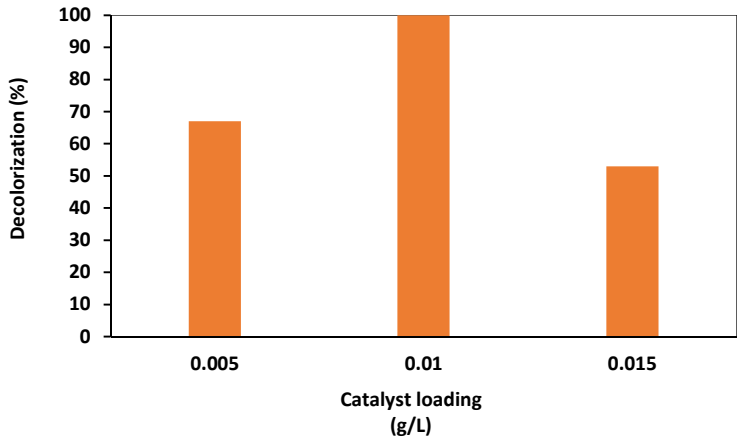

Figure 5: Effect of ZnO/W photocatalyst loading on decolorization efficiency, Reaction conditions: dye concentration 20 mg/L and pH=5.

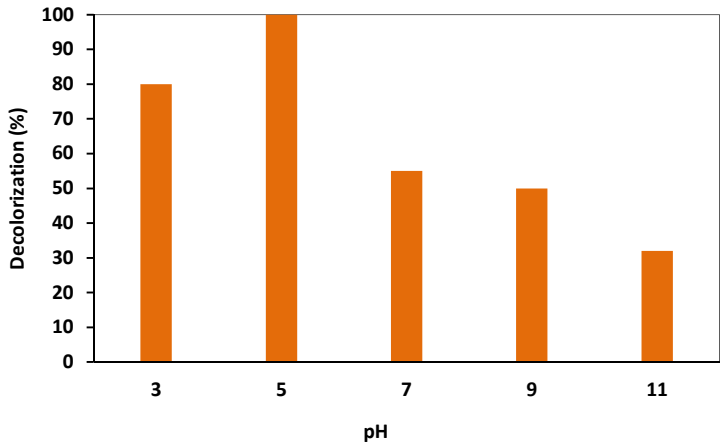

Figure 6: Effect of pH on decolorization of RR 31 by ZnO-W photocatalyst reaction conditions: catalyst loading 0. 01 g/L, dye concentration 20 mg/L.

3.2.3. Effect of initial dye concentrations

After optimizing the experimental conditions (catalyst loading 0.01 g/L, pH=5), the photocatalytic decolorization of RR 31 was carried out with different initial concentrations of dye (10 to 30 mg/L) in order to select the appropriate amount of catalyst loading. Results showed that when the concentration of dye increased, the rate of decolorization decreased from 100 to 81 % (Figure 7). The increasing of dye concentration increases the competitions between ˙OH and dye to adsorb on active site of photocatalyst [22].

3.3. Kinetic studies

The photocatalytic removal of various organic pollutants by means of illuminated photocatalysts can be formally described by the Langmuir–Hinshelwood kinetic model (Eq. 2) [24]:

$$r = dC/dt = \kappa K/1+KC \quad (2)$$

where, r or dC/dt is the rate of dye degradation (mol/(Lmin)),t is the irradiation time (min), C is the concentration of the dye at time t (mol/L), κ is the reaction rate constant (mol/(Lmin)), and K is the adsorption coefficient of the dye onto the photocatalyst surface (L/mol). When the adsorption is relatively weak and/or the reactant concentration is low ($KC \ll 1$) [23], disregarding KC in the denominator and integrating with respect to time t, the equation 2 can be simplified to the pseudo-first order kinetic model equation (Eq. 3):

$$Ln\ (C_0/C) = \kappa\ kt = K_{app}t \quad (3)$$

where, C_0 is the initial concentration of the dye (mol/L), k_{app} is the apparent rate constant calculated from the curves (min^{-1}). If pseudo-first order kinetic model is applicable in this reaction, the plot of ln (C_0/C) against t in Eq. 3 should give a linear relationship, from which k_{app} can be determined from the slope of the plot [25]. Figure 8 shows that, the plot of ln (C_0/C) against time gives a linear relationship. Therefore decolorization of RR31 by ZnO/W photocatalyst obeys a pseudo first order kinetic. Pseudo first order rate constants were 0.1563, 0.1308 and 0.0817 min^{-1} when the RR31 concentrations were 10, 20, and 30 mg/L, respectively. According to Arrhenius law (Eq. 4), to determine activation energy (E_a) for decolorization process, plot ln k vs 1/T, the resulting straight line will have a slope equal to E_a/R (Figure 9). The obtained E_a value was equal to 19.42 kJ/mol. This value is lower than 40 kJ/mol, indicating that the process follows increasing temperature effect on the rate are quite substantial and characteristic of physical adsorption.

$$\ln k = \ln A - E_a/RT \quad (4)$$

where k, A, E_a, and R are rate constant, frequency factor, activation energy and gas constant, respectively.

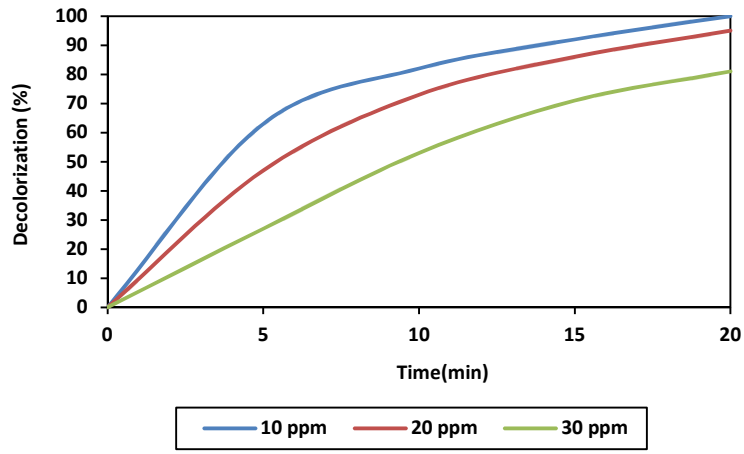

Figure 7: Effect of initial dye concentration on decolorization of RR 31 by ZnO-W photocatalyst reaction conditions: catalyst loading 0.01g/L and pH=5.

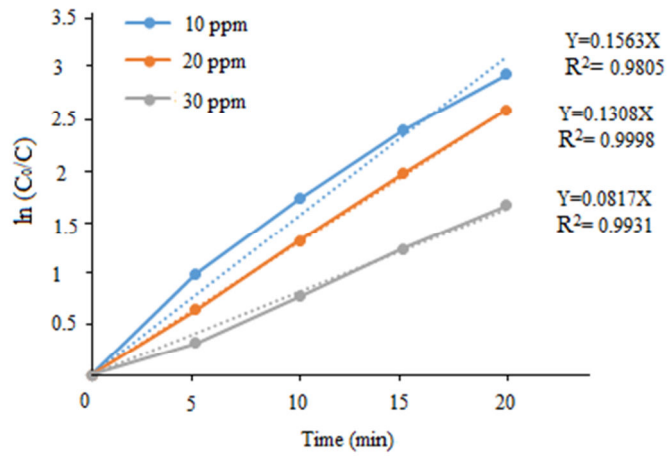

Figure 8: Kinetic study of RR 31 decolorization with different dye concentrations. Reaction conditions: catalyst loading 0.01 g/L, and pH=5

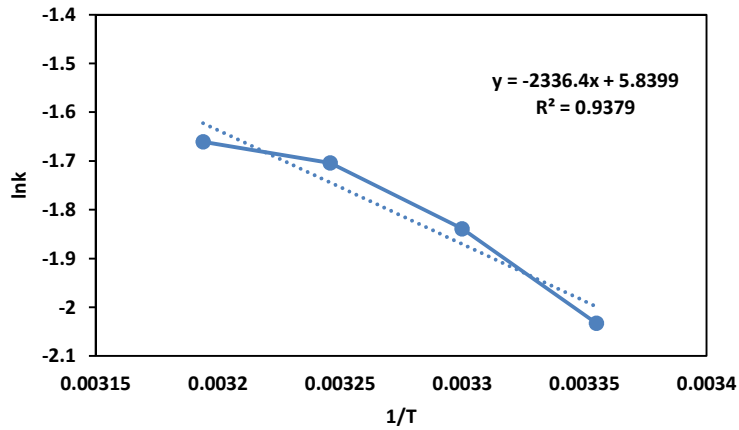

Figure 9: Arrhenius activation energy plot for kinetic study.

3.4. Thermodynamic studies

The thermodynamic parameters are important for a better understanding of the effect of temperature on adsorption process [27, 28, 29]. The effect of temperature on photocatalytic decolorization of dye was studied in the range of temperature 298-313° K by keeping other experimental conditions constant at catalyst dosage 0.01 g/L, pH=5, and initial dye concentration 20 mg/L. According to Van't Hoff equation (Eq. 5), to determine enthalpy (ΔH°), plot ln K_{eq} vs 1/T (where K_{eq} is thermodynamic equilibrium constant), the resulting straight line will have a slope equal to $\Delta H^{\circ}/R$ and intercept equal to $\Delta S^{\circ}/R$ (Figure 10). Other thermodynamic parameters such as Gibbs free energy (ΔG°) and change entropy (ΔS°) are calculated using the following equations (Eq. 6 and 7) [30]. The observed thermodynamic values are summarized in Table 3. These results indicate that the adsorption capacity of photocatalyst increased with increase in temperature of the system from 298-313°K.

$$\text{Ln } K_{eq} = \Delta S^{\circ}/R - \Delta H^{\circ}/RT \quad (5)$$

$$\Delta G^{\circ} = -nRT \ln K_{eq} \quad (6)$$

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \quad (7)$$

The positive value for the enthalpy change, ΔH° (73.6083 kJ/mol), indicates the endothermic nature of the adsorption, which explains the increase of dye adsorption efficiency as the temperature increased. The negative value for ΔG°, implies the decolorization process occur spontaneously, which does not require an external energy source for this process [31, 32]. On the other side, the positive value for the entropy change (ΔS°), indicates that there is an increased disorder at the solid/liquid interface during RR 31 adsorption onto the ZnO/W surface [33, 34].

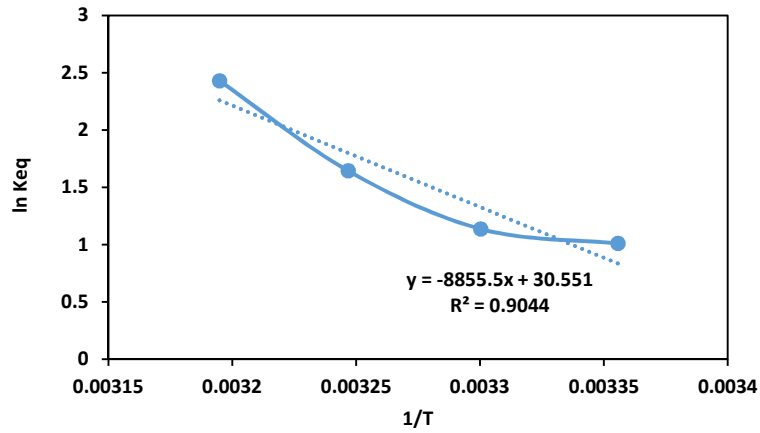

Figure 10: Van't Hoff plot for thermodynamic study.

Table 3: The thermodynamic parameters for the RR31 dye decolorization.

Temperature (˚K)	ΔH˚(kJ/mol)	ΔG˚(kJ/mol)	ΔS˚(J/mol K)
298	73.608	-2.499	252.4
303		-2.863	
308		-4.209	
313		-6.321	

3.5. Economic studies

The effectiveness of treatment process was evaluated based on the electrical energy per order, which is defined as an equation for cost estimation in the case of low pollutant concentrations and first-order reaction rate (which applies in this study) [16]. The electrical energy per order (E_{EO}), is defined as the number of kWh of electrical energy required for 100 % removal of the investigated compound in 1 m^3 of contaminated water [16, 34, 35]. The E_{EO} (kWh m^{-3} per order) can be calculated from the following equation:

$$E_{EO}= \frac{P\times t\times 1000}{V\times 60\times \ln(\frac{C_0}{C})} \quad (8)$$

where, P (kW) is the power rate of AOP system, t (min) is the irradiation time, V (L) is the volume of water in reactor. Also, C_0 and C are the initial and final pollutant concentrations, respectively. Table 4 shows the E_{EO} and the cost of UV/nano-photocatalyst process at different dye concentrations (10, 20 and 30 mg/L). The cost analysis was done based on electricity price of 0.0052 USD/KWh in Iranian market. Comparing E_{EO} values for dye removal of the solutions with 10 and 30 mg/L, it was found that E_{EO} value for 30 mg/L solution is about 2 times more than that for 10 mg/L. It is explained that decreasing in light penetration through dye solution causes less available active site on the photocatalyst surface and lower photocatalytic efficiency [16, 36].

Table 4: Electrical energy per order (E_{EO}) and cost for UV/nanophotocatalyst process.

Dye Concentration (mg/L)	Rate Constant (min^{-1})	E_{EO} (kWh m^{-3} per order)	Cost (USD m^{-3})
10	0.1563	0.6779	0.0153
20	0.1308	0.7692	0.0174
30	0.0817	1.1976	0.0271

4. Conclusions

In this article, the authors have reported a new, efficient, and environmentally friendly adsorbent nano-photocatalyst (ZnO/W) in waste-water treatment which is simple procedure, less investment in terms of initial and operational costs, easy operation, simple design, and nontoxic substances compared to conventional other techniques and applied successfully for decolorization of RR 31 as an azo dye pollutant. The adsorbent element analysis and surface texture were successfully characterized using SEM-EDX. According to the BET results, ZnO/W photocatalyst consists micropores particles. Controlled experimental parameters indicate that the initial rate of photocatalytic decolorization increased with the increase of the catalyst dose up to an optimum loading (0.01 g/L) and acidic solution (pH=5), photocatalytic degradation efficiency was inversely proportional with the dye concentration due to the decrease of the concentration OH° adsorbed on catalyst surface and maximum efficiency was achieved in lowest dye concentration (10 mg/L). The photocatalytic decolorization obeyed pseudo-first order kinetics with an activation energy of +19.42 kJ/mol, consistent with the description of the process as involving physisorption. The thermodynamic parameters of the decolorization of dye solution has been reported. The positive ΔH° refer to endothermic reaction, the negative ΔG° obtained indicate that the reaction is spontaneous. Considering only the energy consumption for the wastewater treatment by AOPs, the cost of energy in Iran is not very expensive, but in regions where the cost of consuming energy is expensive is needed for the development of AOPs, utilizing renewable energy sources such solar energy which is most abundant source of energy.

5. References

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