

Equilibrium, kinetic and thermodynamic study of removal of reactive orange 12 on platinum nanoparticle loaded on activated carbon as novel adsorbent

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Abstract–The proposed research describes the synthesis and characterization of platinum nanoparticles loaded on activated carbon (Pt-NP-AC) and its efficient application as novel adsorbent for efficient removal of reactive orange 12 (RO-12). The influences of effective parameters following the optimization of variables on removal percentages, their value was set as 0.015 g Pt-NP-AC, pH 1, contact time of 13 min. At optimum values of all variables at 25 and 50 mgL⁻¹ of RO-12 enthalpy (ΔH^0) and entropy (ΔS^0) changes was found to be 59.89 and 225.076, respectively, which negative value of ΔG^0 shows a spontaneous nature, and the positive values of ΔH^0 and ΔS^0 indicate the endothermic nature and adsorption organized of dye molecule on the adsorbent surface. Experimental data was fitted to different kinetic models including first-order, pseudo-second-order, Elovich and intra-particle diffusion models, and it was seen that the adsorption process follows pseudo-second-order model in consideration to intra-particle diffusion mechanism. At optimum values of all variables, the adsorption process follows the second-order kinetic and Langmuir isotherm model with adsorption capacity 285.143 mg g⁻¹ at room temperature.

Key words: Adsorption, Reactive Orange 12, Platinum Nanoparticle Loaded on Activated Carbon, Adsorption Isotherm, Thermodynamics and Kinetic of Adsorption

INTRODUCTION

Wastewaters of textile and dyestuff industries lead to pollution of the environment and, therefore, they are toxic and carcinogenic, which causes serious hazards to aquatic living organisms [1-4]. Among various categories of dyes, water-soluble reactive and acid dyes are most problematic because of the inability of conventional methods for their treatment and their high stability during washing is very toxic as main applied dyes for coloring cellulose and cotton [5-9]. Therefore, dye removal from wastewater before disposal to the ecosystem such as the human diet is very important [10,11]. Various physical, chemical, and biological methods, including adsorption, biosorption, coagulation, precipitation, membrane filtration, solvent extraction, chemical oxidation, have been widely applied for the treatment of dye-containing wastewater [12-14]. Among various dye removal processes, adsorption is superior because of its simplicity and low cost in addition of reusability of nontoxic adsorbent; one of the most important properties of the adsorbent which significantly increases the efficiency of the removal process is its surface area and functional atom or group.

In this regard nanoparticles due to their ordered structure, high aspect ratio, ultra-light weight, high mechanical strength and high surface area are very suitable for adsorption [15,16].

Our literature survey did not show any application of metallic nanoparticles loaded on AC for dye removal. Such adsorbents can bind to dye molecules through general mode via AC and soft-soft

or hard-hard interaction via their metallic center. Therefore, in the present work, platinum nanoparticles loaded on activated carbon (Pt-NP-AC) were applied for the removal of reactive orange 12 from aqueous solution in batch method. Influences of temperature, pH of dye solution, effect of adsorbent dose and initial dye concentration were studied under stirred condition. Following optimization of variables, thermodynamic parameters, kinetic and isotherm parameters by fitting experimental data to various possible methods have been calculated to study the nature and mechanism of adsorption.

EXPERIMENTAL

1. Materials and Instruments

All applied reagents such as NaOH, HCl, KCl and reactive Orange 12 (Fig. 1) with the analytical reagent grade were purchased from Merck, Darmstadt, Germany. A stock solution of RO-12 was prepared by accurate weighting and dissolving a suitable amount RO-12 in distilled water, and by its daily dilution, the working solutions with desired concentrations were prepared. The concentration of

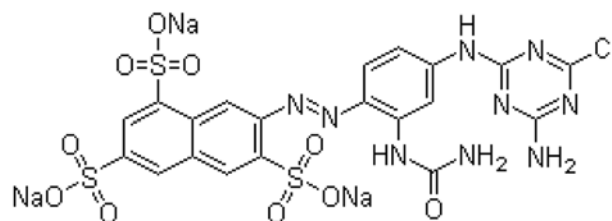


Fig. 1. Chemical structure of reactive orange 12.

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the dye was determined at 412 nm using Jusco UV-Visible spectrophotometer model V-530, pH/Ion meter model-686, thermometer Metrohm, international ASTM sieves and Stirrer model UKA.

2. Methods

The influence of effective variables such as pH, contact time, initial dye concentration and temperature on the removal efficiency of reactive orange 12 using this new adsorbent was studied using one-at-a-time method and batch experiments. In this regard, 50 ml of RO-12 solution with known concentration and pH was mixed completely with 0.015 g Pt-NP-AC and contact time of 13 min and the mixture was agitated at controlled temperature while shaken at constant speed. After each experiment, the mixture was vigorously centrifuged at 4,000 rpm for 10 min and the supernant solution was analyzed for un-adsorbed dye against a reagent blank. Effect of pH on dye removal was studied over a pH range of 1-5, while the initial pH was adjusted by addition 0.1 M HCl or NaOH solution. The amount of RO-12 removal was calculated based on the following equation:

$$\text{Removal (\%)} = ((C_0 - C_t) / C_0) \times 100 \quad (1)$$

where C_0 and C_t (mg L^{-1}) are dye concentration initial and time t , respectively.

Adsorption kinetics was determined by analyzing adsorptive uptake of the dye from aqueous solution at different time intervals. Adsorption isotherm was studied by agitating 50 mL of RO-12 concentrations adsorption isotherm in the range of 25-300 mg L^{-1} with 0.015 g of Pt-NP-AC in batch system until equilibrium was achieved; the adsorption capacity of this new proposed sorbent was calculated from the relationship:

$$q = (C_0 - C_e) V / W \quad (2)$$

Where q (mg g^{-1}) is the equilibrium adsorption capacity, C_e is the dye concentration at equilibrium, V (L) is the volume of solution and W (g) is the weight of adsorbent.

3. Preparation of Pt-NP-AC

The carbon-supported Pt (Pt/C) was prepared according to the literature [17] as follows: 5 ml of platinum solution (0.0555 g of PtCl_4 salt was dissolved in HCl 37% (W/W) solution and diluted to 800 ml of deionized water and stirred vigorously. Then 10 mL 10 mg L^{-1} sodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$) was added and after one minute while stirring, 10 mL solution containing 30 mg NaBH_4 and 100 mg sodium citrate was added quickly. While stirring the mixture for 1 h, 1.2 g activated carbon (mesh 40-50) was added and again was stirred for 48 h and let stand for 24 h until precipitate of the Pt-NP-AC was formed, washed with distilled water and dried at 80°C .

4. Determination of the Zero Point Charge pH (pH_{ZPC})

The point of zero charge pH (pH_{ZPC}) for the Pt-NP-AC was determined by the pH drift method previously reported elsewhere [18]. The point of zero charge (pH_{ZPC}) of this new adsorbent used solid to liquid ratio of 1 : 1,000. For this, the pH of 50 mL water was adjusted to initial values between 1 and 5 by adding HCl or NaOH. Then Pt-NP-AC was added to this solution and stirred for 24 h and following its pH was recorded. Final pH of the solution was plotted against initial pH of the solution. The surface of the material is neutral when $\text{pH} = \text{pH}_{\text{ZPC}}$. The surface is negatively charged at pH values greater than pH_{ZPC} and positively charged at pH values lower than

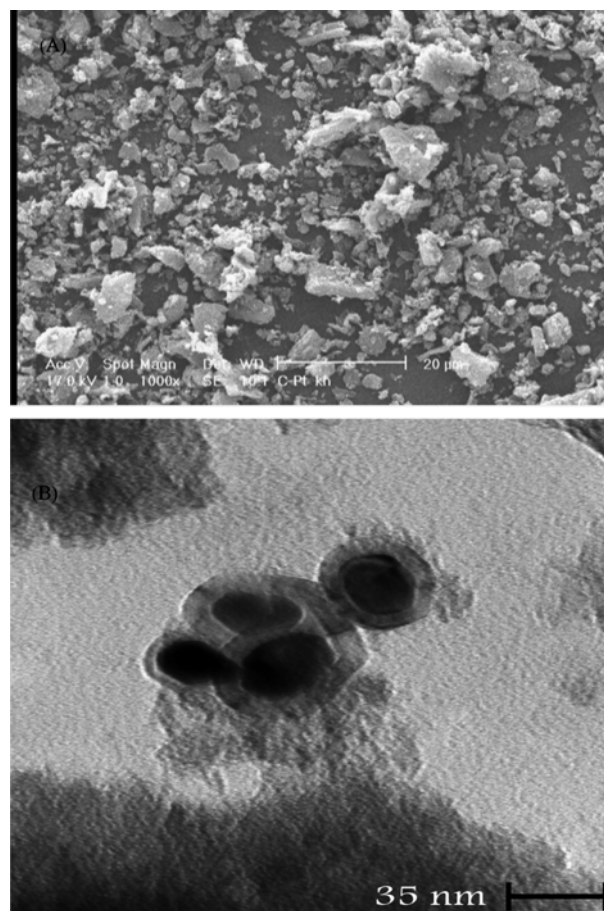


Fig. 2. (A) SEM, (B) TEM of platinum nanoparticle loaded on activated carbon.

pH_{ZPC} [19,20].

RESULTS AND DISCUSSION

1. Characterization of Pt-NP-AC

Fig. 2(A) and 2(B) show SEM and TEM images of the Pt-NP-AC nanoparticles, respectively. The characteristic Pt-NP-AC nanoparticles are observed with a relatively narrow particle size distribution (12-50 nm range).

In preliminary experiments, it was seen that Pt-NP and AC both as sole adsorbent with the same mass have removal efficiency of 78 and 86 %, while the proposed adsorbent has removal percentage of 98%. This synergic effect encourages us to use this new adsorbent for RO 12 removal from wastewater. On the other hand, adsorption was carried out at 10%, 25% and 50% mass ratio of platinum nanoparticle and it was seen that the percentage removal of Re-12 on these percents is 93, 98 and 99%, which for subsequent work it was applied as optimum composition of adsorbent for efficient removal of RO-12. The good advantage of repeated application of this new adsorbent for RO 12 shows that the amount of platinum bladed to solution after 25 times used was lower than 0.01 and after 50-times using was lower than 0.03 mg L^{-1} . This point shows the suitability of this new adsorbent for RO 12 removal without marginal toxicity for ecosystems.

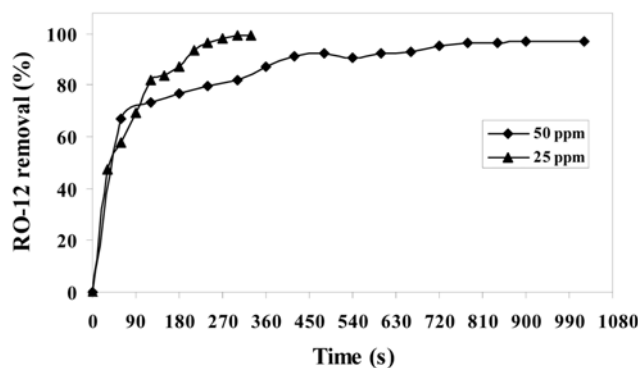


Fig. 3. Effect of contact time on RO-12 removal at 0.015 g of Pt-NP-AC in 50 ml at pH 1, at room temperature and RO-12 concentration 25 and 50 mg L⁻¹.

2. Effect of Contact Time

The adsorption time is one of the most important parameters that significantly affects the performance of RO-12 removal. In this regard, the effect of stirring time in the range of 1-15 min on the efficiency of Pt-NP-AC for removal of RO-12 from 50 mL 25 and 50 mg L⁻¹ of RO-12 solution at pH=1.0 was investigated and respective results are presented in Fig. 3. As it can be seen, raising contact time till 5 and 13 min for 25 and 50 mg L⁻¹ respectively, leads to an increase in RO-12 removal, and further addition of time has not significant influence on removal. At initial contact time due to the availability of the positively charged surface which may be due to electrostatic interaction, the adsorption of anionic RO-12 dye at pH 1 was increased. The later slow rate of RO-12 adsorption probably occurred due to the electrostatic repulsion between the adsorbed negatively charged sorbate species onto the surface of adsorbent and the available anionic RO-12 dye molecule in solution; on the other hand, because of the slow pore diffusion RO-12 the bulk of the adsorbent the rate of adsorption is low [21]. Therefore, for subsequent work the optimum stirring times of 5 and 13 min were selected for initial RO-12 concentrations of 25 and 50 mg L⁻¹, respectively.

3. Effect of pH

The initial pH value of the RO-12 solution is an important par-

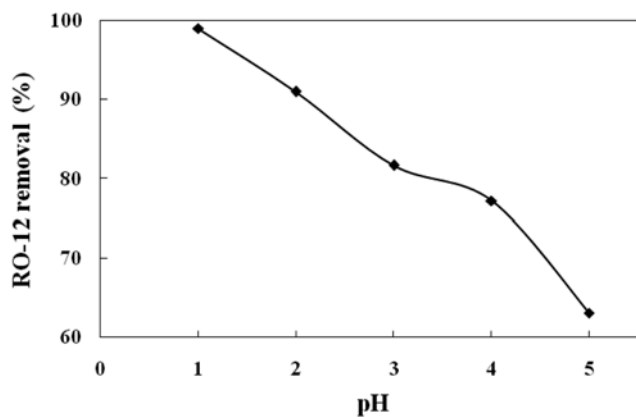


Fig. 4. Effect of pH on the removal of RO-12 by Pt-NP-AC at room temperature, contact time of 15 min, adsorbent dosage of 0.015 g in 50 ml and dye concentration of 50 mg L⁻¹.

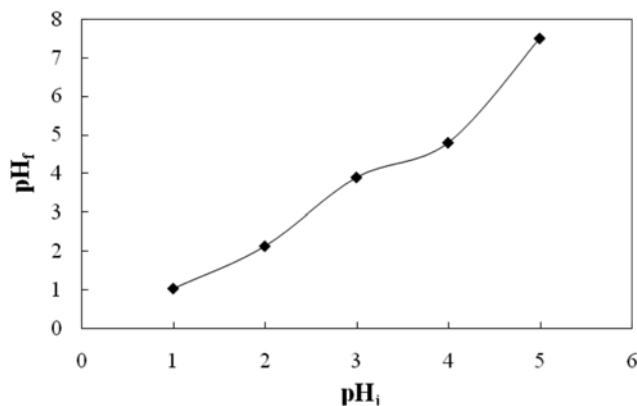


Fig. 5. pH_{zpc} of platinum nanoparticle loaded on activated carbon.

ameter that significantly influences the efficiency. Effect of pH on the removal of RO-12 in 50 mL of 50 mg L⁻¹ solution at contact time of 10 min was investigated and respective results are shown in Fig. 4. Adsorption of each dye on adsorbent may occur via electrostatic and/or chemical reaction between the adsorbent and the dye molecule. Probably at this pH, the proposed adsorbent acts via soft-soft interaction of its platinum atom with nitrogen atom of dye molecule or via hydrogen bonding between RO-12 molecule and activated carbon efficiently adsorbed the dye molecule. At pH 1, because of increasing the H⁺ ion concentration in the system increased and the surface of the Pt-NP-AC absorb H⁺ ions and its charge (Fig. 5) close to neutral. Increasing pH led to dissociation of AC surface functional group (get negative charges) which due to increasing the electrostatic repulsion between RO-12 anions and adsorbent surface the removal efficiency significantly decreased. On the other hand, at alkaline pH the adsorbent surface charge significantly increased which led to a decrease in removal efficiency [22].

The point of zero charge (pH_{ZPC}) of Pt-NP-AC used for the adsorption experiment is determined by using a solid to liquid ratio of 1 : 1,000. For this, 0.015 g of Pt-NP-AC was added to 50 ml of water in the pH range of 1 to 5 and stirred for 1h. Final pH of the solution was plotted against initial pH of the solution and shown in Fig. 5. pH_{ZPC} for Pt-NP-AC was determined as around pH 1. Since adjustment of pH lower than 1 is difficult and maximum recovery was achieved using pH 1, therefore, for subsequent work it was selected as the working pH.

4. Effect of Adsorbent Dosage

The effect of Pt-NP-AC quantity on removal of RO-12 was investigated in batch experiments by addition of various amounts of Pt-NP-AC in the range of 0.005-0.025 g into 50 ml of 50 mg L⁻¹ of RO-12 solution at pH 1 for 15 min. As it can be seen from results presented in Fig. 6, increasing the Pt-NP-AC amount up to 0.015 g led to increasing the RO-12 removal percentage, and further addition did not significantly influence RO-12 removal. This phenomenon can be attributed to greater surface area and the availability of more adsorption sites by further increasing adsorbent surface.

5. Effect of Initial Dye Concentration on Removal of RO-12

The effect of initial concentration of RO-12 on its removal efficiency by Pt-NP-AC adsorbent in the range of 50-300 mg L⁻¹ was studied and respective results are shown in Fig. 7. As is shown, the removal percentage of the RO-12 was found to decrease with the

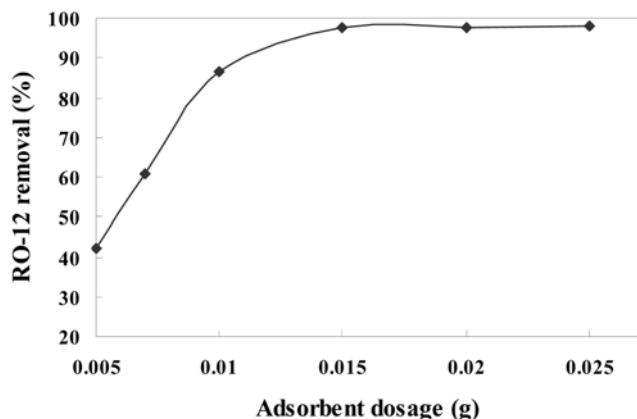


Fig. 6. Effect of Pt-NP-AC dosage on RO-12 removal at dye concentration of 50 mg L⁻¹, at pH 1, and room temperature.

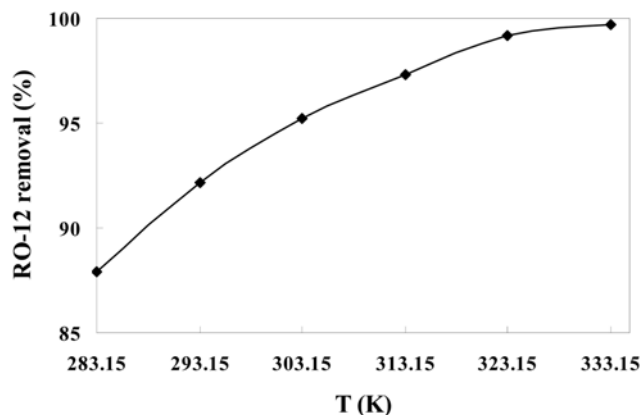


Fig. 8. Effect of temperature on removal of RO-12 at 0.015 g of Pt-NP-AC in 50 ml, pH 1, dye concentration of 50 mg L⁻¹.

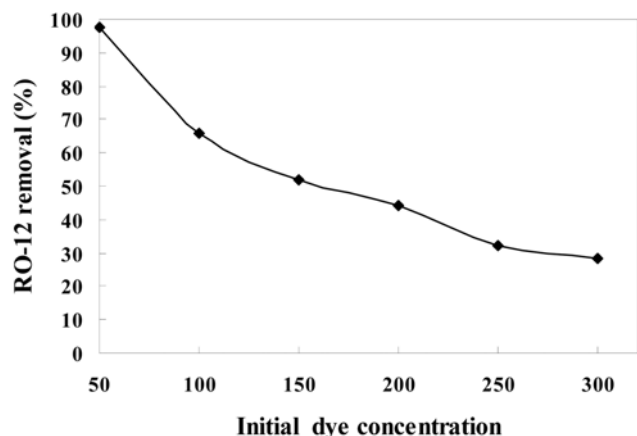


Fig. 7. Effect of initial dye concentration on removal of RO-12 at 0.015 g of Pt-NP-AC in 50 ml, pH 1 and room temperature.

increase in initial dye (RO-12) concentration. This phenomenon can be attributed to the lack of available active sites required for the high initial concentration of RO-12 [23].

6. Effect of Temperature

The effect of temperature on the adsorption RO-12 on Pt-NP-AC as new adsorbent is shown in Fig. 8. The increase in RO-12 removal efficiency by increasing temperature from 283.15 to 333.15 K indicates the endothermic nature of the adsorption process. Tem-

perature significantly influences the viscosity of solution and rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particle. In addition, temperature change leads to influencing equilibrium capacity of the adsorbent for each species [24]. The temperature increase may increase the tendency of de-aggregation and thus the uptake of the monomers of RO-12.

7. Adsorption Equilibrium Study

The adsorption isotherm distribution of analyte between liquid and solid phase at equilibrium state can be investigated by fitting the experimental data to different isotherm models such as Langmuir, Freundlich and Tempkin [25].

The linear form of the Langmuir isotherm model may be written as:

$$C_e/q_e = 1/K_a Q_m + C_e/Q_m \tag{3}$$

The values of Q_m and K_a constants obtained by plotting $(C_e/q_e$ vs. $C_e)$ and the correlation coefficient of this model are presented in Table 1. It was seen that removal of RO-12 on Pt-NP-AC was linear over the whole concentration range studied and were extremely high correlation coefficients ($R^2 > 0.99$).

The Freundlich isotherm is based on an empirical equation applicable for heterogeneous systems and expressed [26] as the following:

$$q_e = K_f C_e^{1/n_f} \tag{4}$$

Where K_f is the Freundlich constant (adsorption or distribution co-

Table 1. Isotherm parameters and correlation coefficients calculated by various adsorption models onto 0.015 g of Pt-NP-AC in 50 ml, pH 1, and room temperature

Langmuir-1: $C_e/q_e = (1/K_a Q_m) + C_e/Q_m$	Q_m K_a R^2	Maximum adsorption capacity reflected a complete monolayer (mgg ⁻¹) Langmuir constant (L mg ⁻¹) Correlation coefficient	285.143 0.213 0.995
Freundlich: $\log q_e = \log K_f + (1/n) \log C_e$	n K_f R^2	Isotherm constant indicate the empirical parameter (g/L) Isotherm constant indicates the capacity parameter (mg g ⁻¹) Correlation coefficient	6.66 6.66 0.954
Tempkin: $q_e = B_1 \ln K_T + B_1 \ln C_e$	B_1 K_T R^2	Related to the heat of adsorption Equilibrium binding constant (L/mg) Correlation coefficient	25.49 340.18 0.964

efficient) (mg g^{-1}) related to the bonding energy, and $1/n_f$ is the heterogeneity factor where n_f shows the deviation from linearity of adsorption. Value of n_f equal to unity shows the linearity of adsorption, while a lower value shows the chemical interaction of the adsorption process. On the other hand, a value higher than unity indicates that favorable adsorption process occurs via physical force. Eq. (4) can be linearized in the logarithmic linear form (Eq. (4)):

$$\log q_e = \log K_f + 1/n_f \log C_e \quad (5)$$

Slope and intercept plot of $\log(q_e)$ versus $\log(C_e)$ indicate the value of K_f and the slope of $1/n_f$ (Table 1). As it can be seen, the Freundlich is an unsuitable model for the whole isotherm interpretation.

Tempkin isotherm model [27] is represented by the following Eq. (6):

$$q_e = B_1 \ln K_T + B_1 \ln C_e \quad (6)$$

Values of B_1 and K_T were calculated from the plot of q_e against $\ln C_e$ (Table 1). Low correlation coefficient of this model show its inapplicability for total isotherm analysis of data.

8. Kinetic Study

The rate of adsorption process is strongly influenced by the state of the solid (generally having very heterogeneous reactive surface) and to the physico-chemical conditions of adsorption process. The kinetics of adsorption processes of RO-12 on the adsorbents was examined by fitting experimental data to pseudo-first-order, pseudo-second-order and Elovich kinetic models according to Eqs. (7)-(9).

The Lagergren pseudo-first-order model [28] described the adsorption kinetic data.

$$\log(q_e - q_t) = \log(q_e) - k_1/2.303t \quad (7)$$

Slope and intercept of plot of $\log(q_e - q_t)$ versus t show the value of k_1 and q_e , respectively. Furthermore, the correlation coefficient R^2 is relatively low for most adsorption data (Table 2), which indicates that the adsorption of RO-12 onto Pt-NP-AC is not a first-

order reaction.

$$(t/q_t) = 1/k_2 q_e^2 + 1/q_e \quad (8)$$

The second-order rate constants were used to calculate the initial sorption rate, given by the following Eq. (9):

$$h = k_2 q_e^2 \quad (9)$$

It was seen that the curve fitting plots of $\log(q_e - q_t)$ versus t do not show good results for the entire sorption period, while the plots of t/q_t versus t give a straight line. Between these two models the criterion for evaluating their applicability is closeness of experimental q_e to theoretical q_e and high value of R^2 . k_2 and equilibrium adsorption capacity (q_e) were obtained from the intercept and slope of the plots of t/q_t versus t , respectively, and respective values for 25 and 50 mg L^{-1} are presented in Table 2. It can be seen that all concentrations R^2 values for pseudo-second-order kinetic model are higher and the calculated q_e values are mainly closer to the experimental data, which shows the applicability of the pseudo-second-order kinetic model for interoperation of adsorption process through the entire sorption period.

The Elovich equation is another rate equation based on the adsorption capacity and is given as follows [29-31]:

$$q_t = 1/\beta \ln(\alpha\beta) + 1/\beta \ln(t) \quad (10)$$

Plot of q_t versus $\ln(t)$ should yield a linear relationship if the Elovich is applicable with a slope of $(1/\beta)$ and an intercept of $(1/\beta) \ln(\alpha\beta)$. The Elovich constants obtained from the slope and the intercept of the straight line, which are reported in Table 2, show that the correlation coefficients R^2 is 0.976 for this model.

Another alternative method for kinetic evaluation of an adsorption process is the intra-particle-diffusion model [32], which is commonly expressed by the following equation:

$$q_t = K_{diff} t^{1/2} + C \quad (11)$$

Table 2. Adsorption kinetic parameters at different initial RO-12 onto 0.015 g of Pt-NP-AC in 50 ml at pH 1, room temperature and RO-12 concentration of 25 and 50 mg L^{-1}

	Model		Initial RO-12 concentration (mg/L)	
			25	50
First-order kinetic $\log(q_e - q_t) = \log(q_e) - k_1/2.303t$	k_1	Rate constant of pseudo-first order adsorption (L min^{-1})	0.0145	0.0048
	q_e (calc)	Equilibrium capacity (mg g^{-1})	92.066	76.81
	R^2	Correlation coefficient	0.944	0.940
Second-order kinetic $(t/q_t) = 1/k_2 q_e^2 + 1/q_e (t)$	$k_2 \times 10^{+3}$	Second-order rate constant of adsorption ($\text{g mg}^{-1} \text{min}^{-1}$)	0.191	0.106
	q_e (calc)	Equilibrium capacity (mg g^{-1})	97.087	169.49
	R^2	Correlation coefficient	0.997	0.999
	h	Second-order rate constants ($\text{mg g}^{-1} \text{min}^{-1}$)	1.804	0.361
Intraparticle diffusion $q_t = K_{diff} t^{1/2} + C$	K_{diff}	Rate constant of intraparticle diffusion ($\text{mg g}^{-1} \text{min}^{1/2}$)	3.327	2.133
	C	Intercept of intraparticle diffusion	26.023	100.68
	R^2	Correlation coefficient	0.9339	0.942
Elovich $q_t = 1/\beta \ln(\alpha\beta) + 1/\beta \ln(t)$	β	De-sorption constant (gmg^{-1})	0.0519	0.0513
	α	Initial adsorption rate ($\text{mg g}^{-1} \text{min}^{-1}$)	79.106	87.98
	R^2	Correlation coefficient	0.979	0.976
q_e (exp)		Experimental data of the equilibrium capacity (mg g^{-1})	82.922	160.485

The values of K_{diff} were calculated from the slopes of q_t versus $t^{1/2}$ while C is the intercept of this plot, which shows the thickness of the boundary layer. The values of these two parameters value are reported in Table 2. The plotting of q_t versus $t^{1/2}$ shows two different lines; rate constant K_{diff} is directly evaluated from the slope of the second regression line. The first line represents surface adsorption at the beginning of the reaction and the second one is the intraparticle diffusion at the end of the reaction.

If the intraparticle diffusion is the sole rate-limiting step [33], the plot of q_t versus $t^{1/2}$ must pass through the origin and the value of C was zero, which shows the intraparticle diffusion model may be the controlling factor in determining the kinetics of the process [34]. The R^2 values, as can be seen from Table 2, are far from unity, showing the unsuitability of this model. These phenomena show that the rate-limiting step is not the intraparticle diffusion process and may be the controlling factor in determining the kinetics of the process.

9. Thermodynamic Study

Thermodynamic parameters were evaluated to confirm the adsorption nature of the present study and can be obtained from the following equation:

$$\Delta G^\circ = -RT \ln K_o \quad (12)$$

where ΔG° is the free energy change (kJ mol^{-1}), R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), K_o the thermodynamic equilibrium constant and T is the absolute temperature (K). Values of K_o may be calculated from the relation $\ln q_t/C_e$ vs. q_t at different temperatures and extrapolating to zero [23]. As can be seen from thermodynamic parameters listed in Table 3, a negative ΔG° value indicates that the removal process is spontaneous and its value decreases with raising the temperature, which shows the feasibility of the adsorption process at higher temperatures. The values of other parameters such as enthalpy change (ΔH°), and entropy change (ΔS°) may be determined from the van't Hoff equation:

$$\ln K_o = \Delta S^\circ/R - \Delta H^\circ/RT \quad (13)$$

ΔH° and ΔG° can be obtained from the slope and intercept of van't Hoff plot of $\ln K_o$ vs. $1/T$ and the data are presented in Table 3. The negative values of ΔH° further confirm the exothermic nature of the adsorption process, while the negative ΔS° values suggest the decrease in adsorbate concentration in the solid-liquid interface, indicating thereby the increase in adsorbate concentration onto the solid phase. This is the normal consequence of the physical adsorption phenomenon, which takes place through electrostatic interactions.

To further support the assertion that physical adsorption is the predominant mechanism, the values of activation energy (E_a) and sticking probability (S^*) were estimated from the experimental data. They were calculated using a modified Arrhenius type equation related to surface coverage (θ) as follows [35]:

$$S^* = (1 - \theta) e^{-(E_a/RT)} \quad (14)$$

The sticking probability, S^* , is a function of the adsorbates/adsorbent system under investigation; its value lies in the range $0 < S^* < 1$ and is dependent on the temperature of the system. The parameter S^* indicates the measure of the potential of an adsorbates to remain on the adsorbent indefinite. The surface coverage (θ) can be calculated from the following equation:

$$\theta = [1 - C_e/C_o] \quad (15)$$

The activation energy and sticking probability were estimated from a plot of $\ln(1 - \theta)$ vs. $1/T$. The activation energy, E_a , calculated from the slope of the plot was found to be 54.60 and 57.92 kJ/mol for 25 and 50 mg L^{-1} respectively for adsorption of RO-12 onto Pt-NP-AC. As can be seen, in continuous to attempt of other researchers, a new sorbent was prepared and characterized and efficiently applied for dye removal from aqueous solutions [36-38].

CONCLUSION

A platinum nanoparticle loaded on activated carbon was synthesized and characterized and tested as adsorbent for the removal of reactive orange 12. The optimum dosage, pH and contact time were obtained as 0.015 g, pH 1 and 13 min, respectively.

Isotherm modeling revealed that the Langmuir equation could better describe the adsorption of dye onto the Pt-NP-AC as compared to other models. Kinetic data were appropriately fitted with the pseudo-second-order adsorption rates. The temperature effect is used to calculate the change in activation enthalpy (ΔH°), free energy of adsorption (ΔG°) and entropy (ΔS°). The analysis of these thermodynamic parameters suggests that adsorption is a spontaneous and endothermic process.

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Table 3. Thermodynamic parameters for adsorption of RO-12 onto 0.015 g Pt-NP-AC in 50 ml at pH 1 at initial dye concentration of 25 and 50 mg L^{-1}

Adsorbent	C_o (mg/L)	Parameter	Temperature (K)					
			283.15	293.15	303.15	313.15	323.15	333.15
Pt-NP-AC	25	k_c	6.781	12.196	27.682	43.987	167.763	202.471
	50		7.274	11.795	20.091	36.616	123.388	348.850
Pt-NP-AC	25	ΔG° (kJ/mol)	-4.506	-6.096	-8.370	-9.851	-13.762	-14.709
	50		-4.671	-6.014	-7.562	-9.374	-12.937	-16.216
	C_o (mg/L)		ΔS° (J/mol K)	ΔH° (kJ/mol)	E_a (kJ/mol)	S^*		
	25		214.792	56.640	54.599	1.278×10^{-11}		
	50		225.076	59.896	57.920	3.611×10^{-12}		

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