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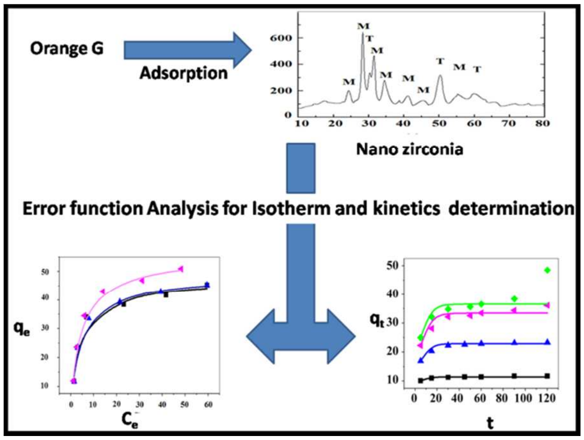
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Nano zirconia
Error function Analysis for Isotherm and kinetics determination
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ARTICLE TYPE

Adsorption of orange G dye on nano-zirconia: error analysis for obtaining the best equilibrium and kinetic modeling

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Abstract: Nano zirconia has been employed for adsorption of Orange G from aqueous solutions. The best-fit equations of linear and non-linear forms of the two adsorption isotherms and kinetic models, namely Langmuir and Freundlich adsorption isotherms, and pseudo-first and pseudo-second-order equations are compared. Sum of the normalized errors and coefficient of determination is used to determine the best fitting model. Results exhibit that non linear forms of isotherms and kinetic equations are more suitable for the fitting the experimental data. The adsorption of Orange G over nano-zirconia follows Langmuir isotherm and pseudo second order kinetic model more closely.

Introduction

Dyes have been widely employed in many industries, such as textile [1], leather [2], printing[3], paper and pulp[4], pharmaceuticals [5], cosmetics [6], wastewater effluents from these industries are of concern to the environment due to large volumes, complex composition and resistance to biodegradation [7]. Orange G is an azo dye. Azo dyes are mountainous group of colorant and make up 70% of all dyes used worldwide [8]. Occupancy of –N=N- chromophore group and aromatic structure make it non-biodegradable, resistant to oxidizing agents and light[9]. Dyes have been removed by multitude of adsorbents. Nano-materials have small size which lead to increased surface area to volume ratio[10], have attracted the attention of researchers for use as adsorbents. Immense reactivity, convenience of parting and extensive number of active sites for interaction with contaminants are certain other attributes that endorsed them to be employed as efficacious adsorbents [11]. Zirconia has chemical inertness [12] and is known to be biocompatible[13]. So, nano-zirconia is used as an adsorbent for removal of Orange G from aqueous solutions.

Adsorption isotherms present an idea about how pollutants interact with the adsorbent, comprehend about surface properties and capacities of adsorbents and are thus essential for the development of adsorption mechanism. The rate of adsorption process and factors affecting the sorption can be explained by the kinetics of the process [14]. Hence, adsorption isotherm and kinetics are significant in designing the sorption systems and assessing their operative performance [15]. Linear regression is frequently used to determine isotherm constants and kinetic parameters. However, the main constraint related to the linearized isotherm expressions is that linearization is marred by metamorphosis of the error structure, defying the error variance and normality assumptions of standard least squares. The change in error distribution pattern bank on the way in which equations are linearized. Aforementioned reasons lead to biasness in the adsorption data. This has led to utilization of non-linearized models along with association of error function analysis. However, each error function yields different isotherm parameters and efforts have been made to make error function analysis free of biasness. Ho et al [16] suggested sum of the normalized errors to make meaningful comparison between the parameter set. In addition to this coefficient of determination is also used with the sum of the normalized error to determine the best adsorption isotherm and kinetic model. In present study, a comparative analysis of linear and non -linear methods was performed for adsorption isotherm and adsorption kinetic model determination via evaluation of their accuracy in parameter prediction.

Materials and methods

Zirconium oxychloride octahydrate was purchased from Himedia, India. Sodium hydroxide (NaOH), Hydrochloric acid (HCl), Ammonium hydroxide (NH_4OH) were purchased from Merck, India. Orange G was purchased from Qualigens, India.

Preparation of adsorbent and batch experiments

Nano zirconia was prepared by precipitation method. Detailed synthesis procedure is given in supplementary information. Removal study of Orange G on nano zirconia was carried out using batch experiments. In each batch experiment, 50 ml of solution of known concentration, pH (pH = 2) with a dose 2 g/l of the nano zirconia were taken in a 100 ml reagent bottle. Afterwards, it was stirred in a water bath shaker at agitation speed of 90 rpm at different temperatures for 2 h. Samples were taken out and supernatant were then centrifuged at 8500 rpm for 10 min. The residual concentrations of dye in aliquot were analyzed with UV-Visible Spectrophotometer (Spectronic 20, Bausch & Lomb, USA) 480 nm [17]. The amount of Orange G adsorbed on per unit mass of the adsorbent (mg g-1) was determined by the following expression[18]:

$$q_e = (C_i - C_e) * V/W \qquad (1)$$

where qe is the amount adsorbed on per unit mass of the adsorbent (mg g-1), C_i and C_e (both in mg L-1) are the initial and the equilibrium concentration respectively, W is the weight of adsorbent (g),V(L) is the volume of solution.

Isotherm and kinetic model determination

In order to select the best equilibrium isotherm and kinetic models, efforts have been made by several workers to use error analysis methods for this purpose[19]. Sum of the square of the errors (ERRSQ), hybrid fractional error function (HYBRID), marquardt's percent standard deviation (MPSD), average relative error (ARE) and sum of the absolute errors (EABS) [20] are the various error function used for removal of orange G .

Optimization of error functions

Each of the error functions is likely to yield a different set of isotherm parameters and an overall optimum parameter set is arduous to be directly distinguished. Hence, to offset this problem and make a meaningful comparison between parameter sets, sum of the normalized errors for each parameter set was adopted [16].The parameter set yielding the minimal normalized error function can be selected as the optimum for that isotherm model provided there is no bias in the data sampling and type of error method selected. In addition to aforementioned error function analysis, coefficient of determination is also investigated for their eligibility to predict best fit isotherm and kinetic model. Parameters for isotherm and kinetic models were determined by linear and non linear regression. Original form of the isotherm equations was applied for determining the isotherm parameters mathematically via non-linear method. The best fit isotherm model is selected on the basis of error functions and coefficient of determination. In this study, five different error functions were investigated. Isotherm parameters were determined in each case by minimizing the respective error functions using the Solver add- in with Microsoft Excel.

Result and discussion

Characterization

Figure 1.

Monoclinic28.1 ($\overline{1}$ 11), 31.4(111) (JCPDS card no. 78- 1807) and tetragonal 30.2 (101), 50.2 (112) and 60.2(211) (JCPDS card no. 79- 1769) phase of nano zirconia was portrayed by X ray diffraction (MINIFLEX II, Desktop XRD, RIGAKU) (Figure 1A in supplementary information). TEM (TECNAI G2, FEI) (Figure 1) analysis have been carried out to evaluate the particle size. Particles were agglomerated and non-homogenous. Average particle size is c.a. 13 nm..Decrease in size of the material in nano dimensions lead to confinment of electronic motion. It leads to less space for charge charge carriers to move. Hence, Band gap energy, electron and hole kinetic energy and density of the charge carriers increases within and at nanopraticle surface. Due to this activity of the substance increases and along with high surface to volume ratio, it act as potential adsorbent for removal of orange G[21, 22]. FTIR (PerkinElmer Version 10.03.05) analysis (Figure 2A in supplementary information) was carried out in the range of 400 to 4000 cm-1 to discern the functional groups present in the adsorbent sample. Stretching vibration [23] and bending [24] vibration of –OH in physioadsorbed water resulted in peaks at c.a. 3400 cm-1 and c.a. 1600 cm-1; c.a. 1380 cm-1, respectively. Peaks at 750 and 500 cm-1 are attributed to the presence of Zr - O2 - Zr asymmetric and stretching mode [25].

Adsorption isotherm

Langmuir isotherm

The Langmuir isotherm is based on the assumption that monolayer adsorption occurs on the surface of adsorbent having constant number of adsorption sites [26] without any departure into the plane of adsorbent surface. Non linear form of Langmuir isotherm is as follows:

$$q_e = b\, Q_o\, C_e/(1+ b\, C_e) \qquad (2)$$

Here Ce (mg/l) is the equilibrium concentration of the solute, qe (mg/g) is amount adsorbed at equilibrium and Q_0 (mg/g) and b (L/mg) are constants related to the adsorption capacity and energy of adsorption, respectively. The linear form of the model is described as [27]:

$$C_e/q_e = 1/Q_o\, b + C_e/ Q_o \qquad (3)$$

Freundlich isotherm

Freundlich equation is based on the assumption of sorption on heterogeneous surfaces supporting sites of variable affinity. It is supposed that stronger binding sites on adsorbent are acquired first by adsorbate and the binding strength reduces with increase of site occupancy. The equation is written in non linear form as follows:

$$q_e = K_F\, C_e 1/n \qquad (4)$$

The linear form of the above equation is as follows:

$$\log q_e = \log K_F + (1/n) \log C_e \qquad (5)$$

K_F and n are the Freundlich constants. Here, n giving a sign of how congruent the adsorption process is, and K_F (mg/g $(L/mg)^{1/n}$) represents the quantity of dye adsorbed on the adsorbent for a unit equilibrium concentration.

Linear approach for isotherm analysis

Adsorption isotherm parameters determined by linear analysis are presented in Table 1. Values of the Langmuir constants, Q^o and b, were calculated from the slopes and intercepts, respectively, of plots C_e/q_e versus C_e . The increase in value of Q^o with increase in temperature depicts the endothermic nature of adsorption process. Similarly in Freundlich isotherm plots, values of K_F and 1/n were calculated from the intercept and slope of plot log q_e vs log C_e respectively. Freundlich isotherm model had a poor correlation value, indicating a poor fit of the model. Comparison of their coefficients of determination deduce that adsorption of Orange G on nano zirconia obey the Langmuir isotherm model. So, on the basis of linear method, adsorption of Orange G on nano zirconia is better explained by Langmuir isotherm.

Non linear approach for isotherm analysis

Figure 3

Figure 4

It has been shown by several workers [15, 28, 29, 30] that linearization of data results into the biasness. So, a non-linear approach for isotherm models using five error functions is conducted. A 'trial and error' approach was used to determine the isotherm parameters by minimizing the error values by employing the solver 'add in' from the spreadsheet software, Microsoft Excel-2007. The estimated isotherm parameters along with coefficient of determination and error function with least normalized sum and are presented in Table 1. However, four out of six systems are better explained by MPSD (Table 1A and 1B in supplementary information). Out of four systems two systems are better jointly explained along with ARE and EABS by MPSD error function. So, MPSD is used as best error functions for determination of isotherm model.

The MPSD error values for Langmuir isotherm system are lower than Freundlich isotherm system. Hence, the system is better explained by Langmuir isotherm than Freundlich isotherm. It is found that the HYBRID function provides better overall results than MPSD (on comparison of coefficient of determination) for Langmuir isotherm. So, HYBRID error function is used to determine the isotherm parameters. Coefficient of determination of error function having least normalized sum is also used to determine the best harmonize isotherm model. On comparing the coefficient of determination, Langmuir isotherm more appropriately accord with experimental data. In addition to this calculated data (i.e. line curve in Figure 2) obtained by minimizing error function (HYBRID) was more proximate to experimental data (i.e. dotted curve points in Figure 2) for Langmuir isotherm (Figure 2). In contrast, calculated data (i.e. line curve in Figure 3) obtained by minimizing MPSD error function was distant from experimental data (i.e. dotted curve points in Figure 3) for freundlich isotherm. The aforementioned discussion further affirmed that the present system is abide by the Langmuir isotherm model. So, coefficient of determination, sum of the normalized errors and Figures (Figure 2 and Figure 3) suggest Langmuir model to be the more appropriate isotherm. Coefficient of determination by non-linear analysis was marginally higher for Langmuir isotherm and Freundlich isotherm than obtained by linear analysis. Aforementioned comparison of coefficient of determination implies non linear analysis is much better analysis tool than linear method.

Figure 4

Figure 5

Adsorption kinetic studies

The kinetics of adsorption depicts the rate of adsorbate uptake on the adsorbent. Kinetic parameters give valuable information about adsorption uptake which is significant in designing and modelling adsorption processes. Several kinetic models have been used to describe the kinetics of adsorption. In the current study, pseudo first order and pseudo second order kinetic models are used to analyze the kinetics of adsorption of Orange G on nano zirconia.

Pseudo first order model

The pseudo first order kinetic model can be expressed by the following equation

$$dq/dt = k_1 (q_e - q_t) \qquad (6)$$

The integrated form of above equation is expressed as follows:

$$\ln (q_e - q) = \ln q_e - k_1 t \qquad (7)$$

Equation can be written in non linear form as follows:

$$q_t = q_e (1 - \exp(-k_1 t)) \qquad (8)$$

Where k_1(min-1) is the first order rate constant, qe and q are the amount of adsorbate species adsorbed on adsorbent at equilibrium and at any time, t, respectively. The values of k_1 from the slope of the graph between 'log (qe - q) vs t at different temperatures.

Pseud-second- order kinetic model

Data were also examined using the pseudo second order kinetic model. Pseudo second order model is based on the assumption that the rate limiting step is chemisorption in nature. The model is mathematically represented as follows [31] :

$$dq/dt = k_2 (q_e - q_t)^2 \qquad (9)$$

where k_2(g.mg-1 min-1) is the rate constant for pseudo second order model equation. The equation can be represented in integrated form as follows [32 33].

$$t/q_t = 1/ k_2 q_e^2 + (1/q_e)\, t \qquad (10)$$

$$h = k_2 q_e^2 \qquad (11)$$

Here h (mgg-1 min-1) is the initial sorption rate. The values of k_2 and q_e are acquired from the slope and intercept of the plot between t/q_t vs t. Equation 11 can be expressed non linearly as follows:

$$q_t = k_2 q_e^2 t / 1 + k_2 q_e t \qquad (12)$$

Linear approach for kinetic model analysis

Kinetic parameters determined by linear and non-linear analyses and corresponding coefficient of determination (r^2) are presented in Table 2. It was seen that kinetic data better pseudo second-order model compared to pseudo-first order model. Further, the theoretical value of q_e obtained from the pseudo-second order more closely with the experimental values. So, on the basis of linear analysis of kinetics of adsorption of Orange G on nano zirconia is better explained by pseudo second order model.

Non-linear approach for kinetic model analysis

Non-linear analysis for kinetic studies is performed as similar to the non-linear analysis in isotherm analysis. The parameter set from error function yielding the minimal normalized error function can be selected as the optimum for that kinetic model. EABS is selected as preferred error function having least normalized sum in five out of eight systems (Table 2 A and 2B in supplementary information). EABS error values for pseudo second order model were lower than those for pseudo-first order than for pseudo second order model at three concentrations i.e. 25, 50, 75 ppm However, EABS error value at 100 ppm is higher for pseudo second order than pseudo first order. Hence the system follows pseudo second order model due to EABS low error values. However, coefficient of determination for EABS error function at 100 ppm was too low. Hence, EERSQ error function was selected to determine kinetic parameters on the basis of higher coefficient of determination values among pseudo second order model. Coefficient of determination of pseudo-second order model was much higher than that of pseudo-first order. So, pseudo-second order function comes out to be more appropriate than pseudo-first order also on the basis of comparison of coefficient of determination. Also, the q_e values calculated for pseudo-second order model were marginally closer than for pseudo-first order model by non-linear regression method. In addition, coefficient of determination for pseudo-first order obtained by non-linear method is higher in comparison to that obtained by linear method. Hence, non-linear method is better approach to obtain kinetic parameters than linear method.

Adsorption thermodynamics

Thermodynamic parameter viz. change in standard free energy (ΔG^o), standard enthalpy (ΔH^o) and standard entropy (ΔS^o) were considered to determine the spontaneity of adsorption process. Thermodynamic parameters were evaluated using following equations [34-36]

$$\Delta G^o = -RT \ln K_L \qquad (13)$$

$$\ln K_L = \Delta S^o/R - \Delta H^o/RT \qquad (14)$$

Here, K_L (L mol-1) is the thermodynamic equilibrium constant and has been calculated from Langmuir constant b[35] and R is the gas constant (8.314J $mol^{-1}K^{-1}$). ΔH^o and ΔS^o calculated from the slope and intercept of plot between $\ln K_L$ and 1/T respectively[36]. The values of ΔG^o, ΔH^o and ΔS^o calculated from Langmuir constant of linear and non linear equations (2 and 3) are given in Table 3. Plot of $\ln K_L$ vs 1/T by non linear parameter (b) is not linear (Figure 4A in supplementary information). However, when only K_L at 308 K and 318 K is used then slope is linear (Figure 5A in supplementary information) and ΔG^o calculated (equation 15) by using ΔH^o and ΔS^o (equation 14) is close to ΔG^o calculated from equation 13[34] :

$$\Delta G^o = \Delta H^o - T\Delta S^o \qquad (15)$$

As, non linear equation is more suitable for fitting isotherm data. Hence, slope and intercept of K_L at 308 K and 318 K vs 1/T at 308 K and 318 K (Figure 5A in supplementary information) are used for thermodynamic parameter (ΔH^o and ΔS^o) determination. The positive values of enthalpy change (ΔH^o = 1.62 KJ mol^{-1}) indicate the endothermic nature of the adsorption process. Negative values of ΔG^o indicate that the process is spontaneous in nature and can occur on its own without requirement of any external source of energy. Further, decrease in values of ΔG^o with rise in temperature indicates that the process becomes more feasible at higher temperatures. The positive values of ΔS^o (0.1030 KJ mol^{-1}) indicate the increase of disorderness at adsorbate-adsorbent interface during adsorption of orange-G on the surface.

Conclusions

Adsorption of Orange G on nano zirconia followed Langmuir isotherm depicted by both linear and non-linear analysis. Error function analysis among the adsorption isotherm found that MPSD error function provided the best overall result. However, HYBRID error function is used on the basis of better coefficient of determination to determine isotherm parameters. Linear and non -linear analysis of kinetic data showed adsorption of Orange G on nano zirconia followed pseudo second order model. Coefficient of determination values was higher for non linear analysis than linear analysis in both isotherm and kinetic studies. Nonlinear analysis is better procedure than linear analysis in both kinetic and isotherm studies. Coefficient of determination helps in determining the better isotherm error function in addition to sum of squares error function. Adsorption of Orange G on nano zirconia is spontaneous and endothermic in nature.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [X ray diffractogram of nano zirconia, FTIR spectra of nano zirconia, Error fuctions, Langmuir isotherm parameters , Freundlich isotherm parameters, Psuedo first order kinetic and Psuedo second order kinetic parameters determined by different error functions for removal of orange G by nano zirconia].

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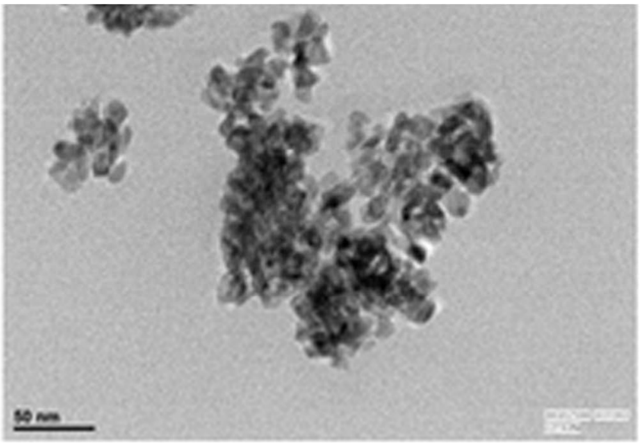

Figure 1 TEM of nano zirconia

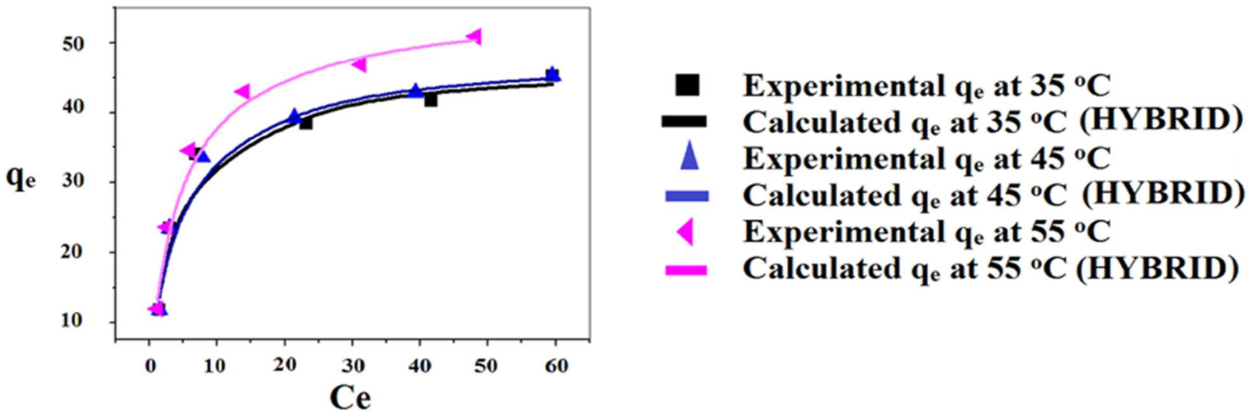

Figure 2 Langmuir isotherm plot for removal of Orange-G using nano crystalline zirconia solution using non linear approach (Initial concentration = 50 ppm, pH = 2, Dose = 2g/l, Stirring speed = 90rpm ; Initials in the parenthesis indicates error function used to determine isotherm parameters)

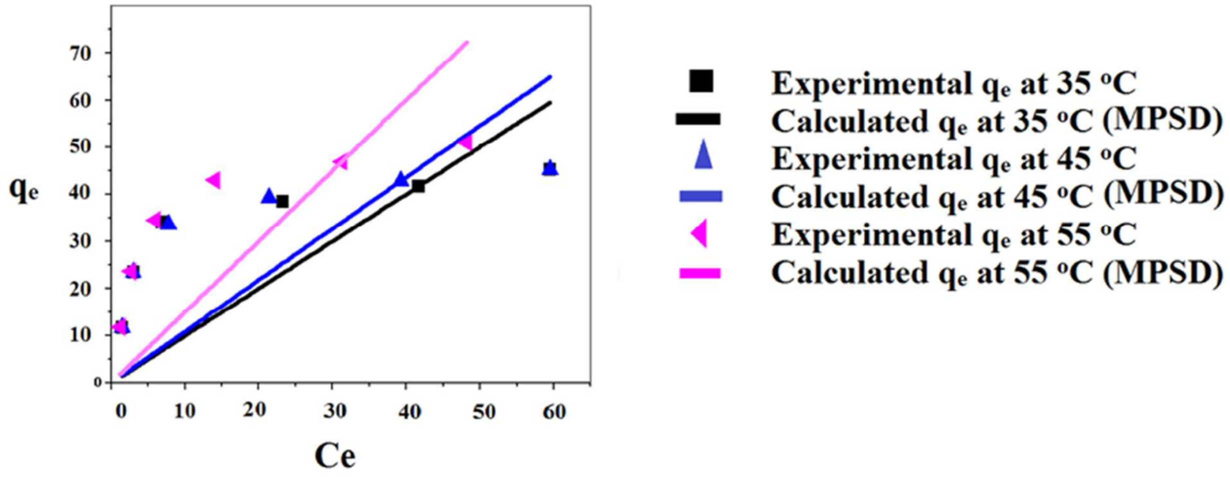

Figure 3 Freundlich isotherm plot for removal of Orange-G using nano crystalline zirconia solution using non linear approach (Initial concentration = 50 ppm, pH = 2, Dose = 2g/l, Stirring speed = 90rpm ; Initials in the parenthesis indicates error function used to determine isotherm parameters)

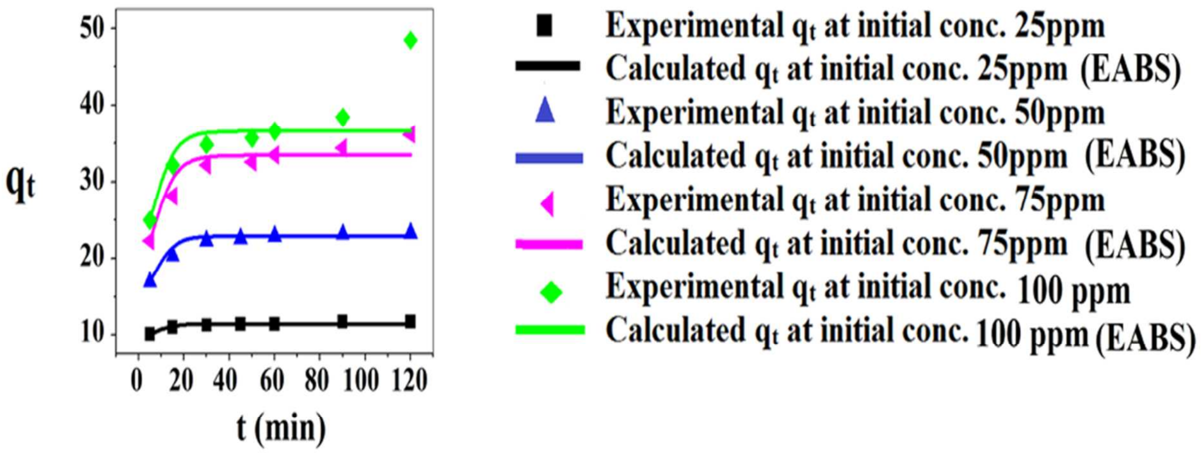

Figure 4. Pseudo first order kinetic model plot for removal of Orange-G using nano crystalline zirconia solution using non linear approach (pH = 2, Dose = 2g/l, Stirring speed = 90rpm; Initials in the parenthesis indicate error function used to determine kinetic parameters)

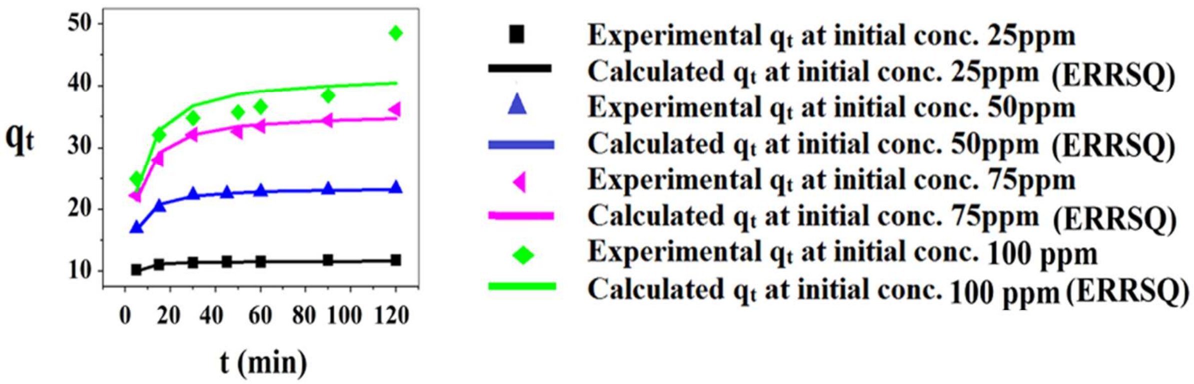

Figure 5. Pseudo second order kinetic model plot for removal of Orange-G using nano crystalline zirconia solution using non linear approach (pH = 2, Dose = 2g/l, Stirring speed = 90rpm; Initials in the parenthesis indicate error function used to determine kinetic parameters)

Table 1 Langmuir, Freundlich isotherm parameters along with coefficient of determination and error function with least normalized sum for adsorption of orange G from aqueous solution on nano zirconia using linear approach and non linear approach (MPSD provide least normalized sum but HYBRID error function has highest coefficient of determination)

				Q^o (mg/g)	**b (L/mg)**		**Coefficient of determination (r^2)**
Langmuir	Linear		35	47.05 ± 1.34	0.2596 ± 0.06152		0.9600
			45	47.76 ± 0.7641	0.2609 ± 0.03274		0.9828
			55	54.25 ± 0.9395	0.2620 ± 0.02931		0.9933
		Error function used					
	Nonlinear	MPSD	35	26.12 ± 19.99	0.5499 ± 0.2722		0.4468
		HYBRID	35	46.65 ± 1.944	0.2836 ± 0.0928		0.9660
		MPSD	45	47.79 ± 2.163	0.2208 ± 0.1128		0.9838
		HYBRID	45	47.09 ±1.685	0.2893 ± 0.0778		0.9660
		MPSD	55	53.85 ± 1.455	0.2832 ± 0.0583		0.9941
		HYBRID	55	54.31 ± 1.573	0.2658 ± 0.036		0.9938
				K_F(mg/g (L/mg)$^{1/n}$)	1/n		Coefficient of determination (r^2)
Freundlich	Linear		35	13.85 ± 2.579	0.3176 ± 0.0674	3.148 ± 0.6757	0.5330
			45	14.31 ± 2.792	0.3111 ± 0.0713	3.214 ± 0.7465	0.5325
			55	14.53 ± 2.417	0.3615 ± 0.0660	2.766 ± 0.5092	0.5262
		Error function used					
	Nonlinear	MPSD	35	1.000 ± 0.2903	1.000 ± 0.2213	1 ± 0.2240	0.6652
		MPSD	45	1.043 ± 0.1978	0.9563 ± 0.3920	1.045 ± 0.4474	0.6712
		MPSD	55	1.200 ± 0.1306	0.8000 ± 0.2626	1.25 ± 0.4216	0.6825

Table 2 Kinetic parameters for removal of Orange-G using nano crystalline zirconia solution via linear and non linear analysis

			Linear analysis				**Non linear analysis**		
Psuedo first order	Conc (ppm)	q_e (experimental)	q_e (mg/g)	K_1 (1/min)	Coefficient of determination (r2)	q_e (mg/g)	K_1 (1/min)	Error function used for parameter determination	Coefficient of determination (r2)
	25	11.75 ± 0.2512	1.388 ± 0.3575	0.0301 ± 0.0069	0.5706	11.45 ± 0.0046	0.4293 ± 0.0028	EABS	0.8000
	50	23.36 ± 1.157	5.581 ± 1.153	0.0421 ± 0.0041	0.7257	22.91 ± 0.3321	0.2688 ± 0.1132	EABS	0.8546
	75	36.16 ± 0.2213	11.19 ± 2.139	0.0226 ± 0.0038	0.7192	33.48 ± 1.087	0.2193 ± 0.0894	EABS	0.7940
	100	48.51 ± 0.7957	20.13 ± 1.947	0.0085 ± 0.0019	0.4934	36.60 ± 0.9890	0.2297 ± 0.0806	EABS	0.4316
	Conc (ppm)	q_e (experimental)	q_e (mg/g)	K_2 (g.mg^{-1} min^{-1})	Coefficient of determination (r2)	q_e (mg/g)	K_2 (g.mg^{-1} min$^{-1)}$	Error function used for parameter determination	Coefficient of determination (r2)
Psuedo Second order	25	11.75 ± 0.2512	11.86 ± 0.0590	0.0632 ± 0.0010	0.8445	11.71 ± 0.0988	0.1040 ± 0.0274	ERRSQ	0.9647
	50	23.36 ± 1.157	23.78 ± 0.0471	0.0191 ± 0.0011	0.9559	23.68 ± 0.1961	0.0205 ±0.0033	ERRSQ	0.9918
	75	36.16 ± 0.2213	37.06 ± 1.218	0.0046 ± 0.0017	0.8507	35.60 ± 0.9533	0.0086 ±0.0024	ERRSQ	0.9641
	100	48.51 ± 0.7957	47.93 ± 4.791	0.0017 ± 0.0010	0.7693	41.80 ± 4.146	0.0058 ± 0.0042	ERRSQ	0.7173

Table 3 Kinetic Values of different thermodynamic parameters

Parameter	**Equation**	**Temperature**	**Parameters using linear equation parameter b**	**Parameters using non linear equation parameter b**	
ΔG° (K J/mol)	$\Delta G^O = -RT\ln K_L$	308 K	-29.89	-30.11	-30.11
		318 K	-30.87	-31.14	-31.14
		328 K	-31.85	-31.89	-31.89
					Non linear using parameter (b at 308 and 318 K)
ΔH° (K J/mol)	$\ln K_L = \Delta S/R - \Delta H/RT$		0.3866	-2.675	1.620
ΔS° (K J/mol.K)			0.0983	0.0892	0.1030
ΔG° (K J/mol)	$\Delta G^O = \Delta H^o - T\,\Delta S^o$	308 K	-29.89	-30.16	-30.11
		318 K	-30.87	-31.05	-31.14
		328 K	-31.85	-31.94	-32.18