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Fractal Adsorption Characteristics and Statistical Analysis Approach of Complex Dye Molecule on Metal Oxide Particles—A Case Study of Reactive Black 5(RB 5) Adsorption onto NiO Nanoparticles

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Abstract - In this study, environmental conditions for high efficient dye adsorption; initial pH, initial dye concentration, temperature, adsorbent concentration were determined as 6.0, 40ºC, 100 mgL-1 and 1 g L^{-1}, respectively. Obtained results from SEM, FT-IR and XRD analyzes were evaluated and compared with founding in literature. It was found that the equilibrium data can be best represented with Langmuir isotherm model, and it was concluded that RB 5-NiO adsorption system behavior was explained the pseudo-second order kinetic model successfully. It was concluded that dye-nanoadsorbent system was exothermic (ΔH <0) and voluntary (ΔG<0). In thermodynamic analysis, RB 5 to NiO system adsorption proved that system has no structural change (S <0) at the adsorbent-solution interface. RSM (Response Surface Method) was used to express the interaction between process variables and responses and to examine the adsorption data. Removal percentages were determined theoretically using Design Expert 9.0.6 software program, and quadratic regression model was developed. It was seen that the adsorption parameters for the highest color removal obtained by the classical method were compared with the parameters found from RSM approach obtained under the same experimental conditions support each other.

Keywords: Adsorption, NiO, nanoparticle, RSM, Reactive Black 5 dye.

1. Introduction

Water has a great importance for living creatures to survive and has also played an important role in the development of civilizations. On a global scale, water limited in terms of availability is a renewable source [1-4]. The numerical expression of the total water in the world is 1.4 billion km^3. The ratios of 97.5% and 2.5% worldwide water are known as salt water in oceans and seas and fresh water in rivers and lakes, respectively. Most water sources are contaminated by liquid organic pollutants caused by the textile, paper, food and cosmetics industries. These liquid pollutants not only cause environmental pollution but also they have toxic and carcinogenic effects. Besides, they can be easily noticed even at very low concentrations. Because of these damaging characteristics, waterborne diseases kill about 12 million people every year, according to the World Health Organization (WHO) report [3]. The pollution of water resources and the attention of environmental problems have resulted in the restructuring of national legislation in the world and in our country.

The main industrial wastewater suppliers produce color pollution are textiles, leather, printing, laundry, tannery, rubber, plastic, paint and etc. The wastewater generated in textile industries vary considerably in terms of quantity and composition. Because of these changes is the composition of wastewater as a result of the renewed business processes and the differences in the process technologies applied. Turkey's textile industry effluents are the largest colored wastewater among the other industries. Paper, leather, rubber and paint are among the sectors that produce colored wastewater after the textile sector.

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In scientific investigations carried out, it was determined that color removal efficiencies at high rates were obtained by choosing the treatment processes based on different principles together. Applications of biological treatment and other treatment technologies are frequently encountered for better quality wastewater discharge to the receiving environment [6]. The main methods used in the treatment of wastewaters containing different types and numbers of pollutants in the world and in Turkey are membrane filtration, ion exchange, oxidation, coagulation-flocculation, adsorption, aerobic and anaerobic biological treatment technologies. Many highly colored wastewater producers having low initial investment cost in Turkey have preferred biological treatment for own wastewater. Biological treatment processes are known as an economical and ecofriendly technologies. While a more efficient dye removal can be achieved by this technology for most pollution removal, it may be insufficient in color removal by self. The reason for this sufficiency is more than one pollutant at high concentrations and the resistance of raw materials such as melanoidin, lignin and their derivatives etc. in wastewater. In this case, more than one treatment technologies can be used together for high pollutant removal efficiency. Therefore, the desired level of color removal can be obtained with one more than combined treatment process.

Adsorption method is often preferred in color removal from wastewater due to the reasons such as simplicity, fast and economical process conditions, high efficiency and harmless end-product from removal process. In this method, zeolite, clay, chitosan, nanoparticles are preferred as an adsorbent. In this experimental study, the adsorption of anionic RB 5 dye with synthesized materials of Ni-based nanomaterials, the interaction between the adsorbent and the solution using classical methods with the help of equilibrium, kinetic and thermodynamic models were investigated and finally the comparison of experimental equilibrium removal percent values with theoretical ones from RSM were evaluated in a batch system.

The primary function of grinding media is to crush and grind ore particles inside rotating mills, such as ball, rod, and semi-autogenous mills, and sometimes in stirred mills such as Vertimill, SVM mills, Sala Agitated Mill, HIGMill, Tower Mill, and ISAMill [2]. In recent years, grinding charges with unconventional shapes have appeared on the market. One example is the cylindrically shaped media called Cylpebs. Cylpebs have greater surface area and higher bulk den-sity than balls of similar mass and size, due to their shape. Cylpebs of the same diameter and length have 50% greater surface area, and 45% greater weight, than balls of the same material. In addition, they have 9% higher bulk density than steel balls, and 12% higher than cast balls. The objective of this paper is to compare Cylpebs and ball grinding media in terms of grinding efficiency for fabrication of nano sized calcite [3-4]. Calcite ($CaCO_3$) was chosen as test material for this study. It is a salt, widely used in the ground nano-form, in paints, food or pharmaceuticals industries and as filler in the paper making process (Garsia et al., 2002).

2. Materials and Methods

2.1. Reagents

$NiSO_4$ and $Ni(OH)_2$ used in nanomaterial synthesis were purchased from Sigma–Aldrich. Also, RB 5 dye was purchased from Sigma–Aldrich. Its Molecular Weight[MW]: 991.82; Molecular Formula [MF]: $C_{26}H_{21}N_5Na_4O_{19}S_6$; λ_{max}: 597 nm. The corresponding chemical structure of RB 5 dye is shown in Figure 1.

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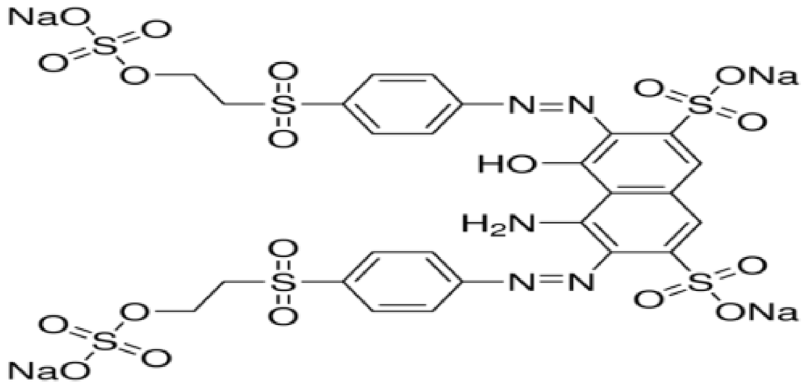

Figure 1. The chemical structure of RB 5.

2.2. Synthesis of nanoparticles

In this method, firstly, 0.5 M $NiSO_4$ solution and 1 M NaOH solution were prepared. Then solutions were mixed and 2.0 grams of agar was added into 25 mL of solution containing this mixture. It was mixed on a shaker for 1 hour at a stirring speed of 200 rpm at room conditions. The solid-liquid mixture formed was separated by filtration and the solid part was taken. Then it was subjected to calcination process at 250^{o}C for 4.5 hours [7- 13].

2.3. Characterization experiments

FTIR (Perkin Elmer, Fourier Transform Infrared Spectrometer), SEM (ZeissSupra 55 Area Emission, Scanned Electron Microscope), and XRD (Philips, X'Pert brand X-Ray Diffractometer) were used for identification of morphological properties and identification of phases and crystal structures of synthesized particles at Advanced Materials Research Center (MEITAM).

2.4. Color removal experiments

Color removal experiments were carried out at 120 rpm constant agitation rate in a batch system. Desired amount of NiO based nanoparticles were weighed and then mixed with 150 mL RB 5dye solutions adjusted to the desired pH values with NaOH and HCl solutions. Samples were taken and centrifuged at specific time intervals (0,5, 15, 30, 60, 120, 180, 240, 300, 360, 420, 1440, 1500, 1600, 1800, 2000) in the shaking water bath. Centrifuged samples were diluted and analyzed by UV-Vis spectrophotometer at 663 nm wavelength. Dye removal % was determined by the following formula;

Dye Removal % = $((C_o\text{-}C_e)/C_o)$ x1 00 [1]

where, C_o and C_e are;

the initial and equilibrium dye concertation in mg L^{-1}, respectively. The amount of dye adsorbed per unit of the adsorbent at equilibrium was calculated in terms of q_e (mg g^{-1}) using equation given below,

The equilibrium amount of dye removal per unit of the nanoparticle was determined in terms of q_e (mg g^{-1}) using equation given below.

Removal capacity $(q_e)=(C_o\text{-}C_e)V/m$ [2]

Where V is the volume of dye solution (L) and m is the mass of the adsorbent(g).

3. Results and Discussions

3.1. Characterization studies for NiO based nanoparticles

SEM analyzes were carried out to investigate the surface properties of the nanoadsorbent used in RB 5-NiO system before and after adsorption. SEM images for NiO based nanoparticles before and after adsorption are presented in Figure 2. It can be seen from the SEM images that the nanoparticles, which have a porous surface before adsorption, are filled with dye molecules after adsorption.

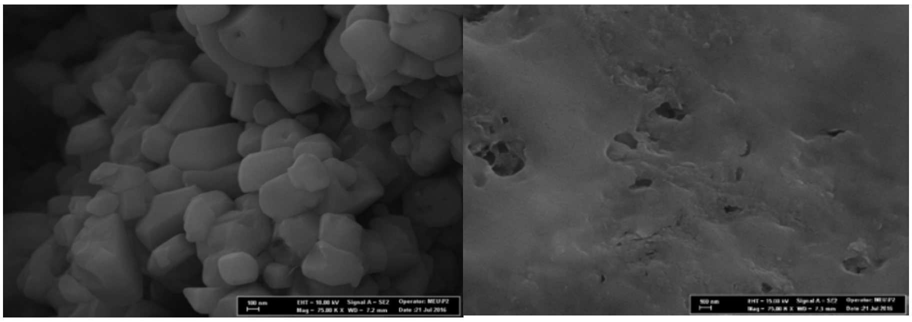

Figure 2. SEM images of RB 5 dye before and after adsorption on NiO-based nanomaterial adsorption.

In order to explain RB 5-NiO adsorption mechanism, FT-IR analyzes of the adsorbent were used before and after the adsorption and presented in Figure 3. In the spectrum of NiO based material; Peaks around 3644 and 3272.34 cm^{-1} correspond to $^{-}$OH group, vibration 1038.43cm-1 corresponds to-Si-O-Si- group, adsorption peaks at 867.91cm-1 correspond to simple hetero-oxy compound frequencies of aromatic phosphates (P-O-C stress) [7, 8, 9]. Tension band at 474.38 cm^{-1} indicates the Ni – O bond [10, 11].

The graph of XRD spectra (X-Ray Diffractometry) analysis for adsorbent phases and crystal properties used in the adsorption of RB 5 dye is given in Figure 4. In XRD analysis, all data were obtained between 10˚ - 80˚ of 2θ value.

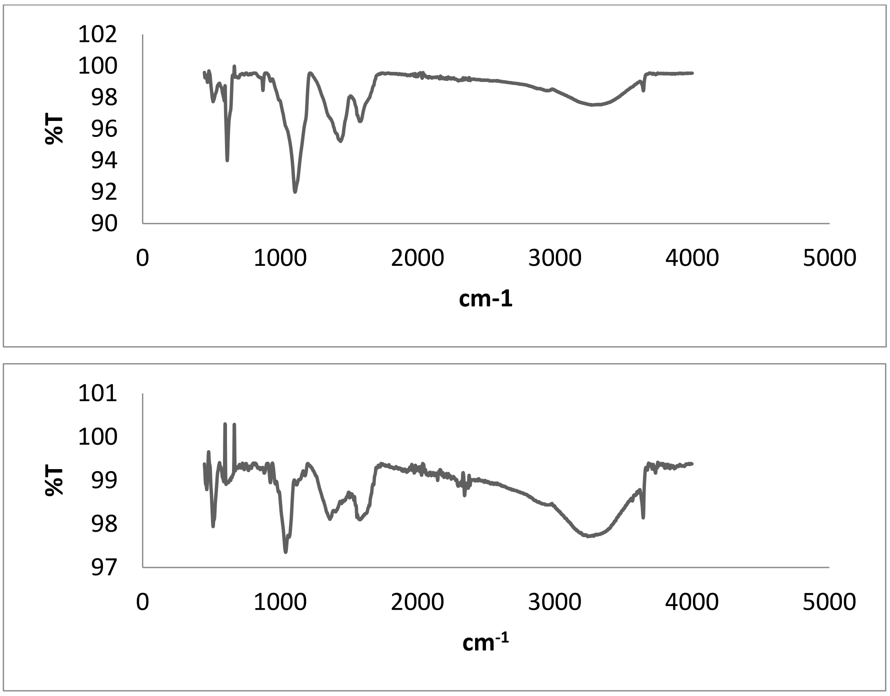

Figure 3. FT-IR spectra of RB 5 dye before and after adsorption.

Figure 4 and 5 show the spectra of XRD (X-ray Diffractometer) analysis spectra to determine the adsorbent phases and crystal properties used in the adsorption of RB 5. The highest characteristic peaks were obtained as 18.6˚ -19.0˚ - 31.6˚ - 37.9˚ - 38.8˚ at 2θ value for the NiO particle, respectively. In XRD analysis, the presence of large-scale peaks in the structure of the NiO-based nanomaterial shows that the crystals are small or structurally irregular, or both are valid, as well as regions of amorphous structure on the material other than the crystal structure.

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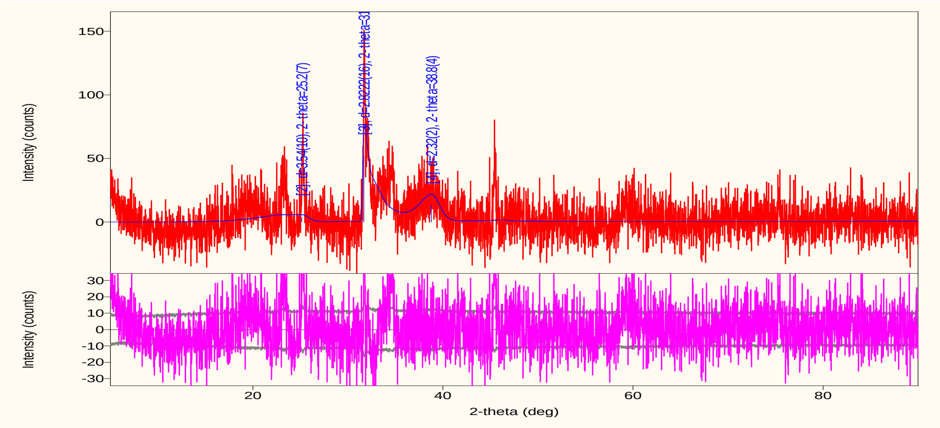

Figure 4. XRD analysis of RB 5 dye before adsorption on NiO based nanomaterials.

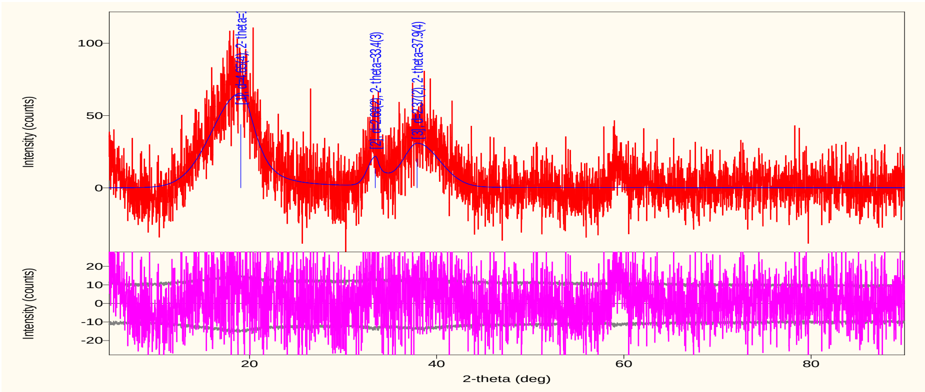

Figure 5. XRD analysis of RB 5 dye after adsorption on NiO based nanomaterials.

3.2. Effects of Environmental Conditions on Adsorption Study

While the effects of parameters such as pH, temperature, initial dye and adsorbent concentration on adsorption were examined by classical method. In this method, the environmental condition parameter value was changed within a determined certain experimental range to investigate its effect, while the other environmental adsorption parameters values were kept constant. pH, temperature, concentration, adsorbent concentration were examined in the range of pH: 2-10, temperature 30^{o}C-60^{o}C, initial concentration 50 mg L^{-1}-500 mg L^{-1}, adsorbent concentration 0.5 g L^{-1}-3 g L^{-1} respectively.

Initial pH is the most important parameter for color removal from wastewater. In this part, pH value was changed between 2.0 and 10. The initial dye solution pH was increased from 2 to 6 the adsorbed dye amount per unit adsorbent mass increased from 21.83 mg g^{-1} to 60.85 mg g^{-1}, respectively. On the other hand, the removal dye percent increased from 22.73 % to 62.19%, respectively. From experimental data, the favorable pH value for the highest removal efficiency is determined as 6.0.

In temperature effect part for adsorption of RB 5 on NiO nanoparticles, when the temperature was increased from 30 ^{o}C to 60 ^{o}C, it was observed that the amount of material adsorbed per unit adsorbent mass decreased from 79.14 to 34.83 at equilibrium. Also the removal dye percent increased from 22.73 % to 62.19%, respectively. In this study, the preferable temperature value for high yield removal was determined as 40 °C (q_d=82.48 mgg^{-1}, 80.19%) and all thermodynamic parameters were evaluated at this temperature value.

In the range of 25–2000mg·L^{-1} dye concentration. When the initial RB 5 concentration was increased from 25 mg L^{-1} to 2000 mgL^{-1} in RB 5 dye adsorption, the adsorbed dye amount per unit adsorbent mass increased from 25 mgg^{-1} to 1489.79 mgg^{-1}, while dye removal percentage decreased from 95.15 to 76.93 respectively.

In the third part of the adsorption effect parameter investigation, the contact time for 50 mgL^{-1} initial dye concentration for equilibrium was found approximately 20 minutes, while this equilibrium time was found to be approximately 100 minutes for higher concentration values. It is due to the presence of empty active areas on the adsorbent surface at low dye concentrations. However, as the initial dye concentration was increased, the driving force was increased too, and the active areas became saturated with dye molecules [12].

In the range of, 0.2 to 3.0g L^{-1} adsorbent dosage range, adsorbent amount was decreased with the increasing adsorbent dose. This was caused that the interaction of the adsorbent particles and agglomeration when the adsorbent was increased. From the same table, it is seen that the increase of adsorbent dosage increases the adsorption yield, and it is observed that the color removal is detected as 98.53% when the amount of adsorbent is 3g in 1L. The adsorbed dye removal percentage value increased from 76.77 % to 91.50%, while dye amount per unit adsorbent mass removal percentage decreased from 95.15 to 76.93 respectively.

In RB 5-NiO adsorption system, the initial pH, the initial dye concentration, temperature and adsorbent concentration 6, 100 mg L^{-1}, 40°C and 0.5 g L^{-1}were determined as desirable removal conditions. Under highest removal conditions for adsorption, the amount of RB 5 adsorbed per unit mass of adsorbent at equilibrium was 75.89 mg g^{-1}and the removal percentage was 74.38%.

3.3. Adsorption Equilibrium

In this part, Langmuir, Freundlich, and Temkin isotherm models [2, 7, 12-18, 20-22, 24-26] have been examined in order to determine the correlation that best represents the experimental equilibrium data obtained at different temperatures in the adsorption of RB 5 dye to NiO-based nanomaterials results are presented below.

Table 1. Isotherm model constants for RB 5 dye on NiO adsorption.

Langmuir Model Constant				
	30°C	40 °C	50 °C	60 °C
Q° (m g^{-1})	126.528	140.845	116.279	136.986
b (L mg^{-1})	0.078	0.039	0.012	0.005
R^2	0.930	0.994	0.997	0.981
R_L	0.113	0.204	0.454	0.666
Freundlich Model Constant				
	30°C	40 °C	50 °C	60 °C
1/n	0.172	0.131	0.260	0.400
n	5.803	7.621	3.840	2.495
Kf [(mg/g)/(L/mg)$^{1/n}$]	45.979	61.775	20.701	8.786
R^2	0.964	0.983	0.991	0.941
Temkin Model Constant				
	30°C	40 °C	50 °C	60 °C
A_t (L g^{-1})	4.187	12.146	0.213	0.055
B (J mol^{-1})	17.224	15.914	22.027	30.843
R^2	94.07	0.987	0.996	0.961

According to Table 1, R^2 values in the Langmuir isotherm model are high and the dimensionless separation factor RL is between zero and one. It is seen that the obtained data fit better Langmuir isotherm model. It can be concluded that NiO-based nanomaterials are suitable adsorbent for the adsorption of RB 5 dye and it is concluded that adsorption is a viable process for RB 5-NiO system.

In literature, Lingamdinne et al. (2017) applied three different isotherm models to describe the adsorption of Pb(II) and Cr(III) by using graphene oxide based inverse spinel nickel ferrite composite. The Langmuir adsorption isotherm data fit well with the experimental adsorption data and Langmuir isotherm regression coefficients was higher than the Freundlich and Temkin isotherm coefficients compared to the other two models. Thus, it was concluded that the Langmuir isotherm is suitable for RB 5-Nio adsorption system [13].

3.4. Adsorption Kinetics

In order to model the adsorption kinetics of RB 5 dye solution onto NiO based nanomaterials, pseudo-first and pseudo-second order kinetic models [9, 10, 12-18, 20-24-26] were applied to the adsorption data obtained at different initial dye concentrations; experimental findings are presented in Table 2 and Table 3.

Table 2. Pseudo-first order rate constant and regression coefficient values of RB 5 dye adsorption onto NiO-based nanomaterial.

C_o (mg L^{-1})	$q_{d,experimental}$	$q_{d,theorotical}$	k_1(dk^{-1})	R^2
50	42.60	28.95	0.035	0.921
100	82.48	97.99	0.052	0.960
200	110.97	99.72	0.039	0.992
300	122.76	88.88	0.028	0.942
400	129.26	103.06	0.033	0.990
500	132.52	104.81	0.028	0.987

Table 3. Pseudo- second order rate constant and regression coefficient values of RB 5 dye adsorption to NiO-based nanomaterial.

C_o (mg L^{-1})	$q_{d,experimental}$	$q_{d,theorotical}$	k_2(g mg^{-1}.min^{-1})	R^2
50	42.60	44.44	0.003	0.999
100	82.48	87.71	0.001	0.999
200	110.97	116.27	0.001	0.999
300	122.76	128.20	0.001	0.999
400	129.26	135.13	0.001	0.999
500	132.52	138.88	0.001	0.999

In the adsorption kinetic model studies, it was seen that the regression coefficients of the pseudo-first-order kinetic model were quite low. At the same time, the difference between the calculated qd values and the experimental qd values indicates that the process does not fit the pseudo-first order kinetic model. RB5-NiO desorption system was determined as more compatible with second-order kinetics in the studies, due to the high R^2 values of the pseudo-second-order kinetic model and the theoretical q_d values calculated from model equation.

3.5. Adsorption Thermodynamics

Thermodynamic parameters such as Gibbs free energy change (ΔG), enthalpy change (ΔH) and entropy change (S) in the adsorption of RB 5 dye onto NiO-based nanoparticle were determined according to Van't Hoff equation [10, 12-18, 20-22, 24-26] Gibbs free energy (G), enthalpy (ΔH) and entropy (ΔS) values calculated from thermodynamic study data are presented in Table 4, respectively.

Table 4. Pseudo- second order rate constant and regression coefficient values of RB 5 dye adsorption to NiO-based nanomaterial.

T(K)	ΔG(J mol^{-1})	ΔH(J mol^{-1})	ΔS(J $mol^{-1}K^{-1}$)	TΔS(J mol^{-1})
298	-2640.95			-42789.8
303	-3359.66			-43507.7
313	-3639.81	-46558.4	-143.59	-44943.6
323	559.15			-46379.5

333	1734.38			-47815.4

According to the adsorption experimental results, all thermodynamic parameters were found to be negative for RB 5-NiO adsorption system. In other words, the adsorption process was determined to be exothermic (ΔH<0), voluntary (ΔG <0) and stable (ΔS <0) systems that run without structural changes at the solid/liquid interface.

4. Adsorption Thermodynamics

Box-Behnken Design Expert 9.0.6 software with four variables was used to optimize parameters such as pH, initial dye concentration, temperature and adsorbent amount in the adsorption of RB 5 dye onto NiO based nanomaterial. The quadratic model was chosen for model calculations [21, 28, 29]. The factors of pH, temperature, initial dye concentration and adsorbent concentration are represented by the letters A, B, C and D, respectively. The % dye removal, which is the response value, is represented by the symbol R_1.

For the adsorption of RB 5 dye to NiO-based nanomaterial, the statistical significance of the model suggested by the program and the results were evaluated and presented with the ANOVA test shown in Table 5.

In this approximation, model equation (suggested by Design Expert 9.0.6 software) as a function of the parameters of pH, temperature, initial dye concentration and adsorbent amount is given in Equation 3 in terms of real values. In these equations A, B, C, D represent pH, temperature, dye concentration and adsorbent amount, respectively.

$$\%\,Removal = -188.91152 + 35.17223 * pH + 5.95074 * T + 0.67653 * C + 23.53433 * X_o - 0.087542 * pH * T - 0.0061625 * pH * C - 0.31750 * pH * X_o - 0.014550 * T * C + 0.008 * T * X_o - 0.0192 * C * X_o - 2.21442 * pH^2 - 0.058392 * T^2 - 0.0002343 * C^2 - 8.963 * X_o^2 \quad (3)$$

Table 5. Box-Behnken ANOVA results for optimization in adsorption of RB 5 dye to NiO-based nanomaterial.

Source	Sum of Squares	Df	Mean Square	F Value	p-value Prob > F
Model	14151.79	14	1010.84	13.98	< 0.0001
A-pH	3328.67	1	3328.67	46.03	< 0.0001
B-T	1296.26	1	1296.26	17.93	0.0008
C-C	2.17	1	2.17	0.030	0.8650
D-X_o	13.27	1	13.27	0.18	0.6749
AB	110.36	1	110.36	1.53	0.2370
AC	6.08	1	6.08	0.084	0.7762
AD	1.61	1	1.61	0.022	0.8834
BC	476.33	1	476.33	6.59	0.0224
BD	0.014	1	0.014	1.991E-004	0.9889
CD	0.92	1	0.92	0.013	0.9117
A^2	8142.73	1	8142.73	112.61	< 0.0001
B^2	1119.66	1	1119.66	15.48	0.0015
C^2	2.23	1	2.23	0.031	0.8632
D^2	32.57	1	32.57	0.45	0.5131
Residual	1012.31	14	72.31		
Lack of Fit	1010.13	10	101.01	184.57	< 0.0001
Pure Error	2.19	4	0.55		
Cor Total	15164.10	28			

It was seen that the model coefficients in the equation suggested by the program were positively signed. While this situation shows the synergistic effect, the negative sign shows the antagonistic effect. According to the program results, all variables in all three equations create a positive effect.

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Error percentage was found at very low levels in the study performed and were found to be 6.01%. With the help of perturbation area, the effects of all factors at a particular point in the design area have been tried to be compared. Accordingly, with the results given by the program, the results obtained under laboratory conditions are pH 6 for NiO-RB5, initial dye concentration 100 mg L-1; temperature 40oC; adsorbent concentration 0.5 g L-1 support each other. By examining the ANOVA tests and the sum of squares values, it was seen that significant results were obtained for the adsorption system.

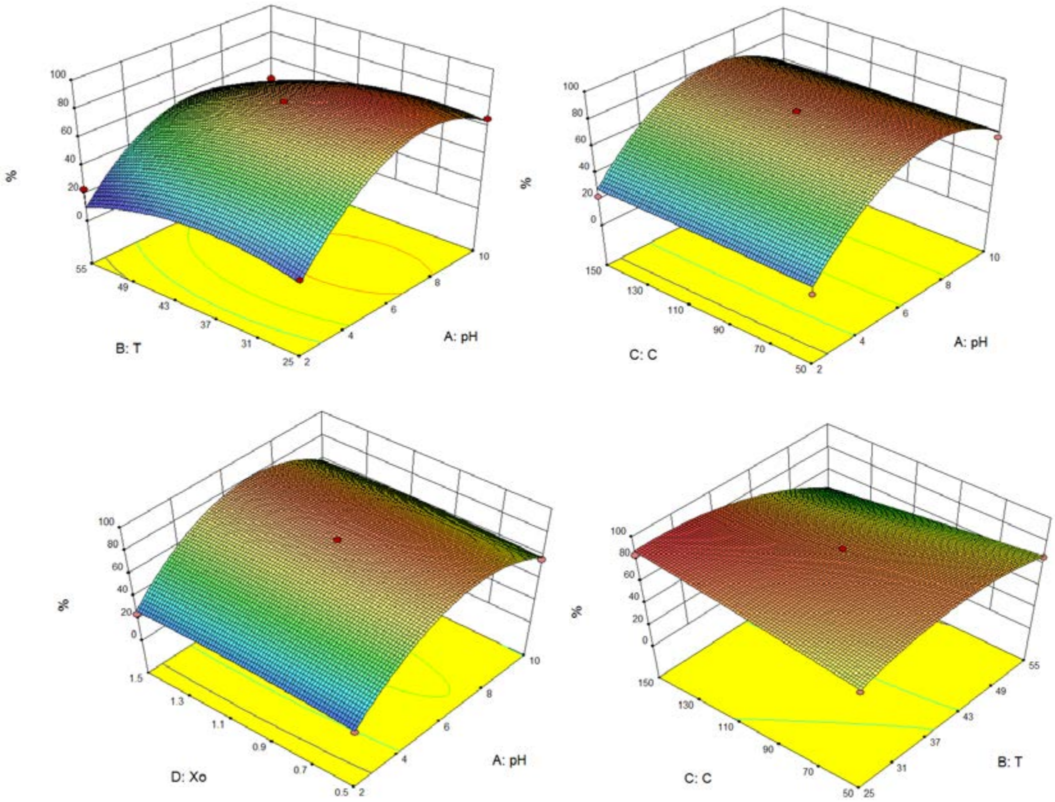

Figure 6. Three-dimensional graphs in the adsorption of RB 5 to NiO.

Perturbation analysis for the system, response surface designs show how the response changes as each factor moves from the selected reference point and other constant factors at the reference value. By using Perturbation chart, the effects of all factors in the design area in optimum operating conditions are compared. The perturbation area helps to compare the effect of all factors at a given point in the design field [21, 28, 29].

According to Figure 6, optimum conditions were found as pH 6, temperature 40 ^{o}C, dye concentration 100 mg L^{-1} and adsorbent amount 1g L^{-1}. When the program results are evaluated, the results of the program and the results obtained in laboratory conditions support each other.

7. Investigation of the Validity of the Model Obtained in the Answer Surface Method Outside the Selected Investigation Range

Optimization of parameters such as pH, initial dye concentration, temperature and adsorbent concentration, which affect the adsorption of RB 5 dye to NiO based nanomaterials, were examined within specified ranges and the results obtained were presented in classical optimization results.

In this section, the probability of the using model equation has been investigated with the proses variables outside the selected experimental range by applying model equation. From RB 5-NiO adsorption data evaluation, it is seen that adsorption system is very sensitive to pH and temperature changes. If adsorption data outside the selected range is used in model equation, some deviations can be occurred in system estimation. The main reason for this deviation is a large number of variables (adsorption parameters effecting sorption yield) in the system. As a result, for highly accurate estimation, number of adsorption variables and experimental range for model equation should be selected carefully. Model equations with a wide range of values can offer the researcher quite a lot of estimation possibilities.

5. Conclusions

In the adsorption of RB 5 dye to NiO based nanoparticles, the initial pH, the initial dye concentration, temperature and adsorbent concentration were determined as 6, 100 mg L^{-1}, 40ºC, 0.5 mg $L^{-1}$for the highest removal yield. At these conditions, the amount of RB 5 adsorbed per unit mass of adsorbent at equilibrium was 75.89 mgg^{-1} and the removal percentage was 74.38%. For equilibrium model description, Langmuir, Freundlich and Temkin isotherm models were applied to the adsorption equilibrium data obtained at different temperatures during the adsorption of RB 5 dye onto NiO-derived nanoparticles; It was observed that equilibrium data fit better with Langmuir isotherm model.

For adsorption kinetic model investigation, the adsorption data results indicated that the conformity of theoretical values with the experimental ones prove that adsorption process cannot be represented by the pseudo-first-order kinetic model. It was concluded that adsorption system was best represented with second-order kinetic model due to the high R^2 values from the model equation and the conformity of theoretical values with the experimental ones.

Thermodynamic parameters such as enthalpy change (ΔH), entropy change (ΔS), free Gibbs energy change (G) were determined with the help of the data obtained at different temperatures in the adsorption of RB 5 dyes to NiO. All thermodynamic parameters were found to be negative in the adsorption of RB 5 to NiO. In other words, the adsorption process was determined to be exothermic ($\Delta H<0$), voluntary ($\Delta G <0$) and stable ($\Delta S <0$) systems that without structural changes at the solid/liquid interface.

In characterization studies; FT–IR was used for the determination of functional groups in the characterization of NiO nanomaterials. It was observed that there were slight shifts from the peaks formed in the FT-IR spectra after the peaks formed in the FT-IR spectra before the adsorbent adsorption. At the second step, in order to determine crystal structure and phase analysis XRD was used. Finally, SEM analyzes were made for surface morphology and it was observed that the pores were filled with dye molecules after dye adsorption.

Finally, parameters affecting RB 5-NiO adsorption system were optimized by using the Response Surface Method (RSM) program. It was observed that the coefficients in the model equations offered by the program were positively signed representing synergistic effect

Accordingly, to the RSM program results, the experimental results carried out in laboratory conditions (conditions for the highest adsorption yield: pH 6, 100 mg L^{-1} initial dye concentration; 40ºC temperature; 0.5 mg L^{-1} adsorbent concentration) confirm classical approach results with great accuracy.

In future studies, it may be aimed to reduce the particle size to even smaller sizes. In this case, a more efficient dye removal can be achieved by increasing the surface area. As a result of the increase in particle size, high dye removal percentages and equilibrium time reduction can be achieved. Also, high technologic processes can be developed for desorption of nanoparticle, to use the sustainable adsorbent repeatedly.

As the future subject related with this investigation under laboratory conditions, batch system results can be adapted to the continuous system and proposed for large-scale applications in order to treat high volume wastewater containing single or/and more than one pollutant with different flow reactors.

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