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Genetic Algorithm Based Nonlinear Optimization of Adsorption Processes

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Abstract: In this study, for different adsorption processes, nonlinear isotherm, kinetic model and thermodynamic parameters were calculated using genetic algorithm-based optimization method. Nonlinear equations were directly used as the model parameters can change to give false results when they are transformed to linear forms. Fifteen isotherms and two kinetic models were considered. All the experimental data was taken from the literature. Methylene green, thiram, and phenol red were used as the adsorbates and silica gel and chemically activated coal mining waste with potassium carbonate (K_2CO_3) or zinc chloride ($ZnCl_2$) were used as the adsorbents. For three different temperatures, the Root Mean Square Error (RMSE) values were obtained between calculated and the experimental data. The biggest RMSE values were obtained as 5.23×10^{-1} for Freundlich isotherm at 45 °C and the smallest RMSE value was obtained as 3.19×10^{-4} for Halsey isotherm at 35°C. For the kinetic study, Lagergren and Particle Internal Diffusion models were applied to the experimental data for three different initial concentrations and it was shown that Lagergren pseudo-first-order Kinetic Model fits better to experimental data. Thermodynamic calculations were made for two different initial pH values and four different temperatures. The Arrhenius factor (A) and Arrhenius activation energies (E_a) (kJ/mol) were also calculated.

Keywords: Adsorption, genetic algorithm, isotherms, kinetics, thermodynamics.

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INTRODUCTION

Separation can be specified as the process that transforms a mixture into two or more products that are compositionally different from each other. Separation is a challenging process; as it is the exact opposite of the common process called mixing, which is a process promoted by the second law of thermodynamics. Therefore, the steps of the separation process are the most costly steps in various industries like chemical, pharmaceutical, and petrochemical industries (1). Adsorption technology has a major share in the separation and purification processes that are the value-adding steps of the process industry. Adsorption is also a crucial element of the removal of unwanted components from wastewater and air streams (2). It has been known for over a century that some solids are able to remove color from solutions that contain dyes. Also, if the air that is contaminated with unwanted odors is passed through charcoal, they can be eliminated. Despite the fact that such processes were not well comprehended until the early twentieth century, they represent the starting of the adsorption technology as a tool for the separation and purification of gases and liquids. Inarguably, adsorption process has been continuously advancing as competition processes like distillation and absorption have been advancing in time (3).

For most of the separation processes, the separation can happen in the presence of a mass separating agent. For adsorption, this mass agent is the adsorbent, or sorbent. Hence, the performance of any separation or purification process by adsorption is directly linked to the quality of the adsorbent, or sorbent (1). In this work, experimental data of studies investigating methylene green (BG5) adsorption with silica gel adsorption (4), thiram adsorption with CMWZn, and adsorption of BG5 or phenol red sodium salt with CMWK adsorbent (5) were used. CMWK and CMWZn are adsorbents that are chemically activated coal mining waste with potassium carbonate (K_2CO_3) or zinc chloride ($ZnCl_2$), respectively. Nonlinear model solutions of the experimental data were used for calculations, and results compared with linear solutions given in the literature (4, 5). There are not many studies in the literature in which many isotherm models, thermodynamic, and kinetic parameters are examined together with experimental data and nonlinear and linear solutions are compared.

EXPERIMENTAL SECTION

Materials

The experimental data obtained using chemicals were listed in Table 1. Thiram in the adsorbates list in Table 1 is the most simple thiuram disulfide and the oxidized dimer of dimethyldithiocarbamate. Thiram is used as an ectoparasiticide to prevent fungal diseases in crops and seeds, as a fungicide and as an animal repellent to protect the fruit trees and ornamentals against rabbits, deer and rodents.

Methylene green is a dye that is a heterocyclic aromatic chemical compound like methylene blue. It is used as a visible light-activated photocatalyst in organic synthesis. Phenol Red sodium salt is widely used as a pH indicator. Silica gel consists of an irregular tridimensional framework of interlacing oxygen and silicon atoms. It has pores and voids of nanometer-scale. It is a porous and amorphous form of silicon dioxide, or silica. The voids mentioned may be containing water or other liquids, or they may be filled with gas or vacuum. Silica gel is an efficient desiccant or drying agent as its high specific surface area which is around 800 m^2/g makes it possible to adsorb the water instantly. The adsorbent used in kinetic studies were prepared from coal mining waste by chemical activation with $ZnCl_2$ and K_2CO_3. In the text, these adsorbents are named as CMWZn and CMWK, respectively. The properties of the chemicals are described in more detail in the original literature (4, 5).

Table 1: The chemicals used for isotherm, kinetic and thermodynamic studies.

Study type	Adsorbents*	Adsorbates**	References
Isotherm	Silica gel	BG5	(4)
Kinetic	CMWZn	Thiram	(5)
Arrhenius equation	CMWK	BG5 or PRNa	(5)
Thermodynamics	CMWK	PRNa	(5)

*CMWK: Chemically activated coal mining waste with K_2CO_3, CMWZn: Chemically activated coal mining waste with $ZnCl_2$.
**BG5: Methylene green, PRNa: Phenol Red sodium salt

Methods

Fifteen different isotherms, two kinetic models, and thermodynamic parameters using experimental adsorption data taken from literature were calculated using genetic algorithm-based optimization with non-linear solutions. All calculations of model parameters and error values were performed using MATLAB®. Since the experimental adsorption data obtained from the literature were calculated by linear optimization, the results with nonlinear solutions in this study are given comparatively.

The amount of molecule adsorbate per unit mass of adsorbent, that is, the equilibrium adsorption capacity of adsorption can be calculated using Eq. 1:

$$q_e=(C_0-C_e)\times V/m \tag{1}$$

where q_e is the amount of adsorbate onto adsorbent (mg/g); C_0 and C_e (ppm) are the concentration of adsorbate at initial and equilibrium, respectively; V is the volume of solution (L) and m is the mass of the adsorbent (g) (4-6).

Adsorption Isotherms

To understand the basics of an adsorption process, one highly depends on the adsorption isotherm of the particular adsorption process. The analytical forms of adsorption isotherm equations depend on the type of the surface phase that can be considered as a monolayer or multilayer, and as localized, mobile. Models mentioned here tend to be complex ones because of the energetic and structural heterogeneity of the adsorbent surfaces that are the main attributes of a many number of adsorbents used in the industry or in the laboratories. If a thermodynamic equilibrium relationship between the quantity of the adsorbed molecule by a unit mass of adsorbent and the amount of adsorbate remaining in the bulk fluid phase at a constant temperature and pH is assumed, various adsorption isotherm models can be derived (6). It is common knowledge that there are over 100 isotherm equations derived based on several mathematical, physical and experimental considerations. One can explain the differences by the fact that the different types of adsorption, solid-gas, solid-liquid and liquid-gas have different properties and hence, these differences should be discussed and explained with different physical pictures and mathematical treatments (7).

In this work, from the 2-parameter adsorption isotherm models, Jovanovich (mono-layer), Halsey (multi-layer), Temkin and Freundlich; from the 3-parameter adsorption isotherm models, Redlich-Peterson, Sips, Koble-Corrigan, Radke- Prausnitz, Fritz-Schlunder(III) (mono-layer) and Brunauer-

Emmett-Teller (BET), Aranovich (multi-layer) models; from the 4-parameter adsorption isotherm models, Fritz-Schlunder(IV), Baudu (mono-layer) and Guggenheim Anderson de-Boer (GAB), Anderson (IV) (multi-layer) models were studied. Root Mean Square Error (RMSE), one of the nonlinear error functions, was used to see the compatibility of nonlinear isotherm models with the experimental equilibrium data.

The error function calculated to justify the suitability of isotherm models to experimental data for understanding the adsorption process, which is defined as Eq. (2) is the RMSE (6):

$$RMSE=\sqrt{\frac{1}{n}\sum_{j=1}^{n}\left(q_{e,\exp}-q_{e,cal}\right)_j^2} \quad (2)$$

where $q_{e,\exp}$ and $q_{e,cal}$ are the amount of adsorption at equilibrium (mg/g) experimentally and calculated with models, respectively. *n* is the number of measurements. Smaller RMSE value indicates better fitness. For different temperatures, isotherm parameters and RMSE values are shown in Table 2.

Table 2: Monolayer or multilayer isotherm parameters and RMSE values calculated with nonlinear optimization for different temperatures.

Isotherm Models*		**Isotherm Parameters**				**RMSE**
2 PARAMETERS	**Freundlich**	k_f	$1/n_f$			
	25°C	5.8482	1.5565	-	-	0.0475
	35°C	0.67	2.44	-	-	0.0327
	45°C	1.06	3.98	-	-	0.5229
	Jovanovich	q_{mJ}	K_j			
	25°C	-1,7891	-1.4511	-	-	0.0559
	35°C	-0.785	-0.759	-	-	0.1434
	45°C	-0.0037	-5.5	-	-	0.1584
	Temkin	B_T	A_T			
	25°C	2.6800	1.578	-	-	0.2646
	35°C	2.1086	1.499	-	-	0.0836
	45°C	1.5391	6.762	-	-	0.0959
	Halsey	K_H	m_H			
	25°C	0.312	-0.704	-	-	0.00046
	35°C	1.159	-0.437	-	-	0.00032
	45°C	0.9867	-0.248	-	-	0.06950
3 PARAMETERS	**Redlich-Peterson**	K_R	a_R	g		
	25°C	3.0066	-10.3	5.38	-	0.0588
	35°C	-3.42	-5.93	-1.08	-	0.0136
	45°C	-2.39	-3.36	-2.27	-	0.243
	Sips	q_{ms}	a_s	B_s		
	25°C	6.75	1.45	1.83	-	0.0303
	35°C	4.44	0.20	2.81	-	0.0488
	45°C	-0.86	-0.50	2.31	-	0.1304
	Koble-Corrigan	A	n_K	B		
	25°C	8.362	1.706	1.0232	-	0.0131

	35°C	4.78	8.94	3.10	-	0.1675
	45°C	-2.73	-9.48	-4.7	-	0.1048
	Radke-Prausnitz	q_{mRPI}	K_{RPI}	m_{RPI}		
	25°C	6.49	3.87	-0.49	-	0.0116
	35°C	1.07	2.42	-1.76	-	0.0288
	45°C	0.80	-4.41	-2.40	-	0.1374
	BET^{b}	q_{mBET}	C_{BET}	C_s		
	25°C	0.88	1.66	-1.55	-	0.0408
	35°C	3.30	-38.50	0.58	-	0.0516
	45°C	0.74	0.95	0.10	-	0.2284
	Aranovich	q_{mAr}	C_{ar}	C_s		
	25°C	-2.86	-7.58	9.47	-	0.0327
	35°C	-0.86	-6.01	13.51	-	0.0408
	45°C	-0.32	48.64	-64.86	-	0.0702
	Fritz-Schlunder(III)	q_{mFS}	K_{FS}	m_{FS}		
	25°C	14.30	5.53	-0.43	-	0.0124
	35°C	9.887	0.76	-1.84	-	0.0700
	45°C	-5.29	0.85	-2.45	-	0.1403
4 PARAMETERS	**Fritz-Schlunder(IV)**	C	a	D	B	
	25°C	7.02	1.63	9.61	65.78	0.1766
	35°C	2.80	2.76	2.77	0.79	0.0306
	45°C	-5.29	-5.20	-6.48	-7.53	0.0710
	Baudu	q_{mB}	b_0	x	y	
	25°C	6.82	0.59	-4.89	1.64	0.0289
	35°C	1.52	0.88	-2.34	3.07	0.0199
	45°C	0.83	-14.25	5.95	5.99	0.0132
	GAB^{c}	q_{mG}	C_{GAB}	K_G	C_s	
	25°C	0.85	-18.89	2.31	-19.7	0.0265
	35°C	0.30	3.92	-16.20	19.42	0.0396
	45°C	0.092	2.30	-20.88	-29.4	0.0909
	Anderson (IV)	$q_{mAn,4}$	$C_{an,4}$	C_s	j	
	25°C	0.53	24.36	7.30	-2.81	0.0016
	35°C	4.21	-0.64	-8.15	-3.54	0.0031
	45°C	-1.25	-2.36	8.49	6.59	0.0522

**Italic* ones are multi-layer isotherm models. ^{b}*BET*: Brunauer-Emmett-Teller, ^{c}*GAB*: The Guggenheim Anderson de-Boer.

Adsorption Thermodynamics

Adsorption is a mass transport marvel that enables the molecules to attach onto the surface of a solid. The thermodynamics behavior of an adsorption process can be examined through three various thermodynamic parameters; standard Gibbs free energy change (ΔG^o), standard enthalpy change (ΔH^o), and standard entropy change (ΔS^o) (8). In order to check the feasibility of the process and the spontaneity, an important tool is the thermodynamic parameters. ΔG^o value provides the information about spontaneity and feasibility of chemical reaction. To determine ΔG^o value, both ΔH^o, and ΔS^o factors are used (9). Valuable information can be obtained once the thermodynamic parameters are correctly estimated; e.g. the negative values of ΔG° show a spontaneous and favorable process. As the ΔG° magnitude gets higher, the adsorption also gets more spontaneous and favorable. When the ΔH° values are negative, this is an exothermic process, whereas when the ΔH° values are positive, the process is endothermic. The magnitude of ΔH° gives an indication on the interactions that happen between the adsorbate and adsorbent. Physisorption, such as Van der Waals interactions, is usually lower than 20 kJ.mol^{-1}, and electrostatic interaction ranges from 20 to 80 kJ/mol. Chemisorption bond strengths can vary from 80 to 450 kJ/mol. When it comes to the ΔS°, negative values indicate that the randomness decreases at the solid solution interface during the adsorption, and positive values indicate the possibility of some readjustments or structural changes in the adsorbate–adsorbent complex. Eventually, if Δ*H*° contributes more than the *T*Δ*S*° to find negative values of Δ*G*°, the adsorption is an enthalpy controlled process; on contrary, if *T*Δ*S*° contributes more than Δ*H*°, the adsorption is an entropy controlled process (10).

The change in free energy (Δ*G*°) of adsorption can be calculated in a way such that

$$\Delta G^0 = -RT\, lnk_{eq} \tag{3}$$

in which *T* is absolute temperature (Kelvin), *R* is the gas constant (8.314 J/mol K) and K_e is the equilibrium thermodynamic constant. The relationship of Δ*G*° with Δ*H*° and Δ*S*° can be written as

$$\Delta G^0 = \Delta H^0 - T\,\Delta S^0 \tag{4}$$

If Eq. (3) is inserted into Eq. (4), it becomes

$$\ln k_{eq} = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{R}\frac{1}{T} \tag{5}$$

Following this, the values of ΔH° and ΔS° can be found by the plot of ln (k_e) versus (1/T). The graph is called the Van’t Hoff plot. Many studies have used this methodology to estimate the adsorption thermodynamic parameters (10, 11).

It is rather easy to use the Van't Hoff plot but it is very important to precisely calculate the k_e which is the equilibrium thermodynamic constant. Actually, if you look at the literature, you can see different ways of calculating the k_e values, and unfortunately some do not make sense. As an example, in most cases, units are used with k_e ; however, from the mathematical viewpoint, a parameter that has a dimension cannot be computed logarithmically. The parameter in transcendental functions must be dimensionless; otherwise, the computation for this parameter is unreasonable (10). Therefore, the parameters were calculated using a nonlinear form of Eq. (5). The thermodynamic parameters (ΔH°, ΔG°, ΔS°) are shown in Table 3.

Table 3: Comparison of Thermodynamic Data Obtained at Different pH (Adsorbates:Phenol Red sodium salt, Adsorbents: CMWK*).

	pH=4.5		pH=8	
	This study	**from Ref. (5)**	**This study**	**from Ref. (5)**
Δ*H*° (J/mol)	-18657	-17709	16212	-15297
Δ*S*° (J/mol.K)	-46.22	-43.10	56.87	53.92
Δ*G*° (J/mol) at 20°C	-5178	-5081	-644	-500
Δ*G*° (J/mol) at 30°C	-4560	-4652	-982	-1040
Δ*G*° (J/mol) at 40°C	-4164	-4219	-1431	-1579
Δ*G*° (J/mol) at 50°C	-3894	-3788	-2202	-2118
RMSE	0.1833	0.1974	0.0623	0.0657

*CMWK: Chemically activated coal mining waste with K_2CO_3

Adsorption Kinetics

To be able to develop sorption kinetics, one needs to know the rate law that describes the sorption system. The rate law is determined by experimentation of the overall chemical reaction equation. There are three main requirements to the rate law:

- Knowing all the molecular details of the reaction, including the energetics and the stereo chemistry.
- Angles and interatomic distances throughout the course of the reaction.
- The individual molecular steps involved in the mechanism (12).

Similar approaches are used to study the adsorption kinetics and thermodynamics. The only difference is the analysis in the adsorbate concentration change over time (11). There are essentially three stages in the adsorption processes:

1. Diffusion across the liquid film surrounding the adsorbent particles, i.e., film diffusion or external diffusion;
2. Diffusion in the liquid contained in the pores and / or along the pore walls, which is called internal diffusion or intra-particle diffusion; and
3. Adsorption and desorption between the adsorbate and active sites, *i.e.,* mass action.

One or more of these stages may have an effect on the adsorption rate. Various models have been proposed to find out which or which of these control the adsorption rate. To test the experimental data for the examination of the controlling mechanisms of the adsorption process, several kinetics models can be used. Some examples of these processes are chemical reaction, diffusion control, and mass transfer (13). Two different kinetic models are studied here: Lagergren Equation (pseudo-first-order kinetic model) and Weber-Morris intra-particle diffusion model.

Lin and Wang (14) prove that the best-fitting nonlinear forms of the kinetic models were better performing than the linear forms. The model parameters may be distorted when the nonlinear equations were transformed to linear forms. Therefore, nonlinear methods have been adopted to obtain the adsorption parameters.

Lagergren pseudo-first-order kinetic model

The first-order kinetics only describes the sorption sites and not the adsorption process as a whole (15). Bhattacharya and Venkobachar (16) presented a simple first order reversible kinetic model that has been applied to several other sorption systems (12, 16). In the pseudo-first-order kinetic model, it is assumed that the rate of occupation of sorption sites is proportional to the number of unoccupied sites (13).

$$q_t = q_e\left(1 - e^{-kt}\right) \tag{6}$$

where q_t and q_e are the amount of adsorption at time t and at equilibrium (mg/g), consequently, and k_1 is the Lagergren rate constant (1/min) (17).

Figure 1 shows pseudo-first-order kinetic model curves in different initial concentrations. In Table 4, kinetic model parameters, k_1, q_e, and RMSE values are given together with linear and non-linear solutions.

Weber-Morris intra-particle diffusion model

Weber and Morris considered only diffusion aspects, but they did not consider how transient adsorption of the adsorbate during the process might be anticipated to change the effective value of the diffusion coefficient *D*. Since sorption is a fast and non-limiting step in the adsorption process, the adsorption rate can be limited by film diffusion or/and intra-particle diffusion. According to intra-particle diffusion, the uptake changes almost proportionally with the half power of time, $t^{0.5}$. The governing equation can be expressed as (18-20);

$$q_t = k_{id} t^{0.5} + C \tag{7}$$

where k_{id} is the intra-particle diffusion rate constant (mg/g. min$^{0.5}$), which can be evaluated from the slope of the linear plot of q_t versus $t^{0.5}$ and the intercept of the plot reveals *C*. The *C* (mg/g) values provide information about the thickness of the boundary layer (17, 19, 21, 22). Figure 2 shows nonlinear Weber-Morris plots in different initial concentrations. Model parameters, k_{id} and *C*, obtained by the linear and nonlinear method, are given in Table 4 together with the RMSE values obtained for the model.

Calculation and analysis of the activation energy

Activation energy is an important parameter that helps illuminate the mechanism formed for the adsorption process (18, 23). The rate constant of the adsorption is expressed as a function of temperature by the Arrhenius type relationship:

$$k = A \cdot e^{(-E_a/RT)} \tag{8}$$

where E_a is the Arrhenius activation energy (kJ/mol), *A* the Arrhenius factor, *R* the gas constant (8.314 J/mol K) and *T* is the solution temperature in Kelvin. The vastitude of activation energy is an indication on the type of adsorption that is mainly chemical or physical. The physisorption processes generally have energies in the range of 5–40 kJ/mol while higher activation energies (40–800 kJ/mol) suggest chemisorption (18, 24). At a certain temperature, the greater the activation energy, the slower the reaction; and the smaller the activation energy, the faster the reaction. In room temperature, if the activation energy calculated is less than 40 kJ/mol the rate of the reaction is quick; if it is greater than 120 kJ/mol, the rate of the reaction is rather slow (23). The data in Table 4 (or Figure 1 and 2) states that the adsorption process is in more accordance with the pseudo-first order kinetic model. So, for this reaction, the apparent activation energy is calculated by the coefficient of k_1 in pseudo-first order kinetic model. Since the calculated E_a values for the systems studied are less than 40 kJ/mol, one can say that the adsorption process is a rapid physical absorption process. The calculated activation energies (E_a), the Arrhenius factors (*A*) and RMSE values are given in Table 5 with comparison with the linear and non-linear solutions.

Genetic algorithm

Genetic algorithm is a heuristic search algorithm. It is evoked by the biological evolution process and is used to find the solution of the optimization problems. The algorithm starts with a set of possible solutions called population and these populations are represented by chromosomes. A well-known application of the genetic algorithm is function optimization. The genetic algorithm contains the basic three operators called mutation, crossover and selection. Mutation randomly changes some of the gene values in a chromosome to create new gene values for better solutions. Crossover operator randomly mixes two distinct solutions' parts to obtain new solutions. Selection operator selects some chromosomes from the population for reproduction. (25).

A simple genetic algorithm steps are as follows (26):

I. Start with candidate solutions to a problem (randomly generate initial population).

II. Create new populations according to the following steps:

Calculate fitness function values for each solution in the population (raw fitness)

a) Select parents based on fitness values.

b) Choose elite members and pass to the next generations.

c) Produce children from the parents using mutation and crossover operators.

d) Replace the current population with the children to create the next generation.

In this study population size was selected 10000 for all calculations. The algorithm was stopped when the number of the iteration reached the value of 1000. While F_M shows the model function, the following Sum Square Error (SSE) fitness function is minimized using the genetic algorithm to find the model parameters.

$$\sum_{i=1}^{n}\left(y_i - F_M(x_i;\theta)\right)^2 \tag{9}$$

where *y* and *x* are experimentally determined values, *n* is the number of the experimental data and **θ** is the model parameter vector.

RESULTS AND DISCUSSION

Table 1 listed the chemicals used for isotherm and kinetic studies the literature from which they were taken. The equilibrium adsorption isotherms are crucial data to understand the adsorption mechanism. In this work, the two, three, and four parameter equilibrium adsorption isotherm models related to monolayer or multilayer adsorption were investigated; while in the original publications where experimental data were taken, only 3 isotherm models were used with their linear forms. In Table 2, isotherm parameters calculated for different temperatures and RMSE values are also given. The smallest error values were 4.6×10^{-4} (Halsey isotherm), 3.19×10^{-4} (Halsey isotherm) and 1.32×10^{-2} (Baudu isotherm) for 25, 35, and 45°C, respectively. The biggest RMSE values are 1.77×10^{-1}; 1.68×10^{-1} and 5.23×10^{-1}. These values are for Fritz- Schlunder (IV) for 25°C, Koble-Corrigan isotherms for 35°C and Freundlich isotherm 45°C, respectively.

Figure 1 and 2 show the Lagergren pseudo-first order kinetic and Weber-Morris Intra-Particle Diffusion plots according to different initial concentrations, respectively. The thermodynamic parameters (ΔH°, ΔG°, ΔS°) were given in Table 3. When the pH value was increased from 4.5 to 8, the thermodynamic parameters also increased. Kinetic model parameters and activation energies calculated in comparison with linear and nonlinear solutions are given in Tables 4 and 5, respectively.

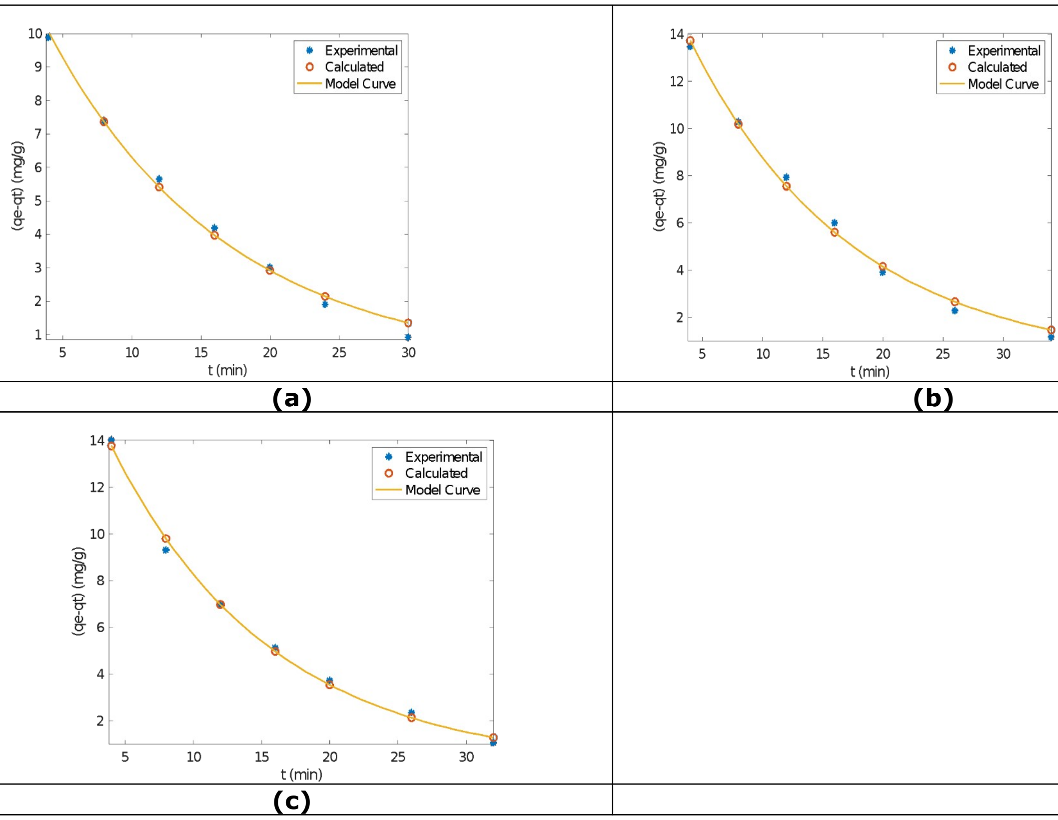
In the literature, in most cases, the pseudo-first order equation of Lagergren is usually applicable over the first 20-30 minutes of the sorption process as it does not work well for the whole range of contact time (27). For thiram adsorption using CMWZn, adsorption time is determined as 36 min (5). Therefore, appropriate results were obtained for the Lagergren pseudo-first order kinetic model. For the non-linear solutions, RMSE values are between 0.2345 and 0.3112, nonlinear RMSE values are between 0.3057 and 0.5334. The RMSE values for the Weber-Morris Intra-Particle Diffusion model are 0.3204 and 0.7429 for C_o = 8 mg/L and C_o = 14 mg/L, respectively. These values are the same for both linear and nonlinear solutions.

CONCLUSION

In this study, codes that are written with genetic algorithm based optimization have been used to calculate 15 isotherm models and 2 kinetic models using experimental adsorption data from the literature. The values calculated with these codes are presented by comparing them with the values in the original publications. While 15 isotherm models are given in this study, since only 2 or 3 isotherm models are used in original publications, only non-linear solutions are given in Table 2. RMSE (Root Mean Square Error) values calculated for non-linear solutions are already quite low values. The error values were calculated using MATLAB®, too. The fact that the RMSE value is close to zero is a sign of the model and its compatibility with the experimental data. Small RMSE values obtained by using the genetic algorithm with nonlinear solutions are a sign that the applied solution is more suitable than linear solutions.

Since the charge intensities and therefore the electrostatic interactions of the adsorbent and adsorbed substances will change depending on the pH value of the environment, the pH of the environment has a great effect on the adsorption. At pH=8, the enthalpy change (ΔH°) was found as positive value (endothermic) with nonlinear equations, but it was found as negative value (exothermic) with linear equations. As it can be understood, the use of nonlinear forms of the equations is important to understand the nature of adsorption processes.

For the kinetic study, Lagergren pseudo-first order kinetic model and Weber-Morris Intra-Particle Diffusion model were applied to the experimental data obtained for three different initial concentrations obtained from the literature. Tables 4 and 5 show that the error values obtained for nonlinear solutions are smaller when compared to linear solutions, except for the Weber-Morris kinetic model.

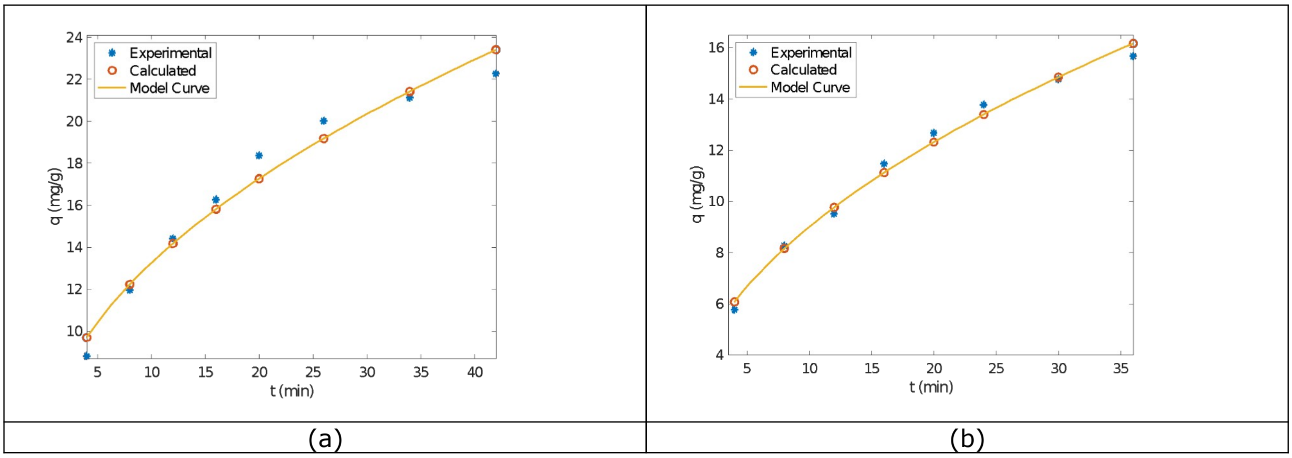


(a)

(b)

(c)

Figure 1: Lagergren pseudo-first-order Kinetic Model curves in different initial concentrations (a) C_o = 8 mg/L (b) C_o = 10 mg/L (c) C_o = 14 mg/L.



(a) (b)

Figure 2: The Weber-Morris Intra-Particle Diffusion kinetic model curves in different initial concentrations (a) C_o = 8 mg/L (b) C_o = 14 mg/L.

Table 4: Comparison of model parameters, linear and nonlinear solutions obtained for Lagergren and Weber-Morris kinetic models.

	C_o= 8 mg/L		**C_o= 10 mg/L**		**C_o= 14 mg/L**	
	nonlinear	**Linear***	**nonlinear**	**Linear***	**nonlinear**	**Linear***
Lagergren pseudo-first-order kinetic model						
k_1 (1/min)	0.077	0.090	0.085	0.088	0.075	0.084
q_e *(mg/g)*	13.66	15.83	19.33	20.11	18.50	20.45
RMSE	0.2345	0.5217	0.2553	0.3057	0.3112	0.5334
Weber-Morris Intra-Particle Diffusion kinetic model						
k_{id} (mg/g.min$^{-1/2}$)	2.5222	2.5252	-	-	3.0583	3.0561
C (mg/g)	1.0219	1.0087	-	-	3.5735	3.5827
RMSE	0.3204	0.3204	-	-	0.7429	0.7429

*from Ref. (5)

Table 5: The Arrhenius factor (*A*) and Arrhenius activation energy (E_a) (kJ/mol) calculated with RMSE values for different systems.

Adsorbates: Methylene Green **Adsorbents: CMWK***	**pH=5**		**pH=8**	
	nonlinear	**linear**	**nonlinear**	**linear**
A	549.6	482.992	0.0091	0.007
E_a (kJ/mol)	13.884	13.552	-17.576	-18.125
RMSE	0.0693	0.0702	0.1661	0.1786
Adsorbates: Phenol Red sodium salt **Adsorbents: CMWK***	**pH= 4.5**		**pH=8**	
A	0.0039	0.006	934.8	655.239
E_a (kJ/mol)	-18.657	-17.709	16.212	15.298
RMSE	0.1833	0.1974	0.0623	0.0657

*CMWK: Chemically activated coal mining waste with K_2CO_3

CONFLICT OF INTEREST

The authors have declared no conflict of interest.

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