EQUILIBRIUM MODELLING OF ADSORPTION OF BASIC DYES ONTO NATURAL CLAY

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Abstract
The adsorption isotherms of basic dyes (Basic Red 22) and (Basic Blue 69) onto natural clay have been studied. The experimental isotherm data have been analyzed using three well - known isotherm models (Langmuir, Freundlich, and Redlich-Peterson). To find out the best fitting isotherm model, the correlation coefficients, and error functions values of SABE, SSE, ARE, HYBRID, and MPSD have been carried out. The results obtained from the adsorption of BR22 and BB69 onto natural clay showed that the Freundlich isotherm model fits the experimental isotherm data significantly better than other models and could be used for design of batch adsorber system.

Keywords: Basic Red 22, Basic Blue 69, Natural Clay, Adsorption Isotherm, Isotherm Models.

1. INTRODUCTION

The adsorption of several organic contaminants in water such as dyes, pesticides, phenols, and chlorophenols has been reported recently in the literatures (Sousa, 2012; Hasan, 2015; Moreira, 2017; Ren et al., 2018 and Mouni et al., 2018). Natural clays are abundantly available low-cost natural resource which is nontoxic to ecosystem. The suitability of natural clay as a natural adsorbent for dyes was recognized previously, where the equilibrium adsorption capacities were determined (Abidi et al., 2015 and 2016).

The natural clay used in the present study was collected from Wadi El- Mohasham Shale, AL- Sheikh Fadl Village, Minia Governorate. The natural clay was crushed and sieved through different standard sieves into various particle size ranges. The clay particle size fractions obtained were vigorously stirred in 6 Vol. % H_2O_2 solution (5 ml/g sample), and then in (2N) CH_3COOH solution (5 ml/g sample) at 90°C to eliminate organic and carbonaceous materials, respectively. The sample was then filtered, washed thoroughly with distilled water and finally dried at 105°C. The dried material was ground to pass through screens and stored in sealed containers to use. Natural clay was prepared for physical, chemical and mineralogical analysis by applying the quartering method on ground clay. The specific surface area of the natural clay was determined using the nitrogen BET surface area method, and the value obtained was 112 m^2 /kg (El-Geundi et al. 2005).

The objective of this paper is to establish a model which both accurately represents the experimental isotherm results of dyes (BR22 and BB69) onto natural clay and could be used for design of batch adsorber system. In this study three well- known isotherm models (Langmuir, Freundlich, and Redlich- Peterson) have been selected to simulate the experimental isotherm data.

2. Experimental:

The adsorbates used in this study were basic dyes (BR22 and BB69).

The concentrations of solutions were measured by a UV- Spectrophotometer (Shimadzu, Inc. Kyoto Japan model UV-1601). All measurements were made at the wavelength corresponding to maximum absorbance, λ_{max} , which are 538 nm for BR22 and 585 nm for BB69.

Adsorption isotherms were determined by the bottle-point method (El-Geundi et al., 2005). The adsorption capacity of the natural clay for basic dyes were determined by contacting a constant mass of adsorbent with a fixed volume of basic dyes solution, the latter having a range of concentrations. The natural clay and basic dyes solution were placed in sealed glass bottles in a Griffin constant temperature shaker bath at constant agitation.

3. Results and Discussion:

The adsorption of a basic dyes (BR22 and BB69) onto natural clay have been studied. The influence of system variable particle size ranges (d_p) on the adsorption capacity have been studied. The results show that the adsorption capacity of clay for BR22 increased from 263.395 to 283.145 mg. g^{-1} with decreasing particle size from 710 -1000µm to 250-355 µm and for BB69 from 300.15 to 315.25 mg. g^{-1} with decreasing particle size from 710 - 1000µm to 250 -355 µm.

Analysis of the experimental isotherm data is important in order to develop a model which both accurately represents the experimental isotherm results and could be used for design purposes. In this study three of models (Langmuir, Freundlich, and Redlich-Peterson) have been selected to simulate the experimental isotherm data.

3.1. Langmuir Model:

The experimental isotherm data for the adsorption of BR22 and BB69 onto natural clay at particle size ranges have been analyzed using the Langmuir model as given by equation (1).

$$q_e = (K_L . C_e)/(1 + a_L . C_e) \qquad (1)$$

Equation (1) may be converted into a linear form convenient for plotting and determining the constants, $\mathbf{K_L}$ and $\mathbf{a_L}$:

$$C_e / q_e = \left(1/K_L\right) + (a_L / K_L)\, C_e \qquad (2)$$

The plot of (**C_e/q_e**) versus **(C_e)** (Figure 1) for different particle size ranges for the adsorption ofBR22 onto natural clay gave linear relationship over a certain concentration ranges.

Values of $\mathbf{K_L}$ and $\mathbf{a_L}$ at different particle size ranges for the adsorption of BR22 and BB69 have been calculated using the least-squares method and are tabulated in Tables (1) and (2) together with correlation coefficients.

3.2. Freundlich Model:

The experimental isotherm data for the adsorption of BR22 and BB69 onto natural clay at particle size ranges have also been analyzed using the Freundlich model as given by equation (3).

$$q_e = K_F . C_e^{1/n} \qquad (3)$$

The equation (3) may be linearized via a logarithmic plot which enables the exponent, **n**, and the constant, $\mathbf{K_F}$, to be determined from equation (4).

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

Inspection of the results derived from the Freundlich analysis of the adsorption of BR22 and BB69 onto natural clay show that a plot of log q_e versus log C_e exhibits some curvature. Indeed, the results can be better represented by more than one straight line. A general equation for the entire concentration range may be expressed as:

$$q_e = K_{F,i} . C_e^{1/ni} \qquad (5)$$

Figure (2) shows the effect of particle size ranges on the Freundlich isotherm for BR22 on the basis of equation (5).

The Freundlich parameters, K_F and **n** have been calculated using the least-squares method applied to the straight lines and are listed in Tables (1) and (2) together with correlation coefficients. In this work the values of **n** are greater than one (**n>1**) which indicates that the BR22 and BB69 show favorable adsorption by natural clay.

Important conclusion can be derived from the data presented in Tables (1) and (2). First, the fact that the Freundlich model successfully describes the experimental isotherm data of BR22 and BB69 over a wide concentration range suggests that the adsorption sites were not saturated at any of the concentration considered in this study.

3.3. Redlich-Peterson Model:

The experimental isotherm data for the adsorption of BR22 and BB69 onto natural clay at particle size ranges have also been analyzed using the Redlich-Peterson model as given by equation (6).

$$q_e = (K_{RP} . C_e) / (1 + a_{RP} . C^{\beta}_e) \qquad (6)$$

Equation (6) may be converted into a linear form convenient for plotting and determining the constants, K_{RP}, a_{RP}, and **β:**

$$\log \{[K_{RP} . C_e / q_e] - 1\} = \log a_{RP} + \beta \log C_e \qquad (7)$$

The plot of ($\log\{[K_{RP}. C_e/q_e] - 1\}$) against ($\log C_e$) for the adsorption of BR22 onto natural clay are shown in Figure (3).

The Redlich-Peterson parameters, K_{RP} , a_{RP} , and β have been calculated using an iterative computer program for data fitting and minimizing the correlation coefficient, and are tabulated in Tables (1) and (2) together with correlation coefficients. However, one starts with a value for K_L from the Langmuir model and this value later modified in order to obtain a better correlation of the three constants.

3.4. Simulation Results and Correlations:

3.4.1 Error Analysis:

Using the appropriate constants of the Langmuir, Freundlich, and Redlich- Peterson models, the theoretical isotherm curves were predicted using known values of Ce. Figures (4) to (9) show a comparison of the experimental points of BR22 and BB69 onto natural clay with the Langmuir, Freundlich, and Redlich-Peterson models, in order to establish which model yields the "best fit". Figures (4) to (9) show the graphical comparison between the experimental and predicted data for BR22 and BB69 onto natural clay using the equilibrium models i.e. Langmuir, Freundlich, and Redlich-Peterson isotherm. In order to confirm the fit model for the adsorption system, it is necessary to analyze the data using error functions combined the values of determination coefficient (R^2) from regressive analysis. These values are a measure of the fitting of the data to an isotherm model, a small of error function would indicate a perfect fit. The calculated expressions of these error functions are as follows (Kundu and Gupta, 2006; Ho et al., 2006):

1-Sum of the Absolute of Error (SABE)

$$SABE = \sum_{I=1}^{n_P} \left| \left(q_{c,cal} - q_{e,\exp} \right) \right|_i \tag{8}$$

2-Sum of the Squares of Error (SSE)

$$SSE = \sum_{I=1}^{n_P} \left(q_{c,cal} - q_{e,\exp} \right)_i^2 \tag{9}$$

3-Average Relative Error (ARE)

$$ARE = \frac{100}{n_P} \left(\sum_{i}^{n_P} \left| \frac{\left(q_{e,cal} - q_{e,\exp} \right)}{q_{e,\exp}} \right|_i \right) \tag{10}$$

4-Hybrid Fractional Error Function (HYBRID)

$$HYBRID = \frac{100}{n_P - p} \sum_{i=1}^{n_P} \left[\frac{\left(q_{e,cal} - q_{e,\exp} \right)^2}{q_{e,\exp}} \right]_i \tag{11}$$

5- Marquardt's Percent Standard Deviation (MPSD)

$$MPSD = 100 \sqrt{\left[\left(\frac{1}{n_P - p} \sum_{i=1}^{n_P} \left(\frac{\left(q_{e,cal} - q_{e,\exp} \right)}{q_{e,\exp}} \right)_I^2 \right) \right]} \tag{12}$$

The values of SABE, SSE, ARE, HYBRID, and MPSD, for the adsorption of BR22 and BB69 onto natural clay at different particle size ranges are shown in Tables (4) and (6). From Table (4) the values of error functions for Freundlich model were the smallest among the three models at the temperature 25ºC and different particle size ranges. Although the highest values of (R^2) for Langmuir isotherm among three models were used, Langmuir model was poorest fit according to error function values of SABE, SSE, ARE, HYBRID, and MPSD. As shown in Table (4) the highest values of error functions were found for Langmuir model at different particle size ranges. On the basis of the error function values, the order of best-fit was Freundlich model greater than Redlich-Peterson model greater than Langmuir. So it could be concluded that the Freundlich model be best to fit for BR22 and the experimental data according to graphical representations and error function values. This showed that the adsorption process might be a heterogeneous adsorption.

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4. Conclusions:

Experimental isotherm data of BR22and BB69 have been compared with theoretical isotherm data and the results obtained showed that the Freundlich model fits the experimental data significantly better than the Redlich-Peterson and the Langmuir models and the Freundlich model fits the experimental data significantly better than the Langmuir and the Redlich Petrson models respectively.

Nomenclature

a_L: parameter of Langmuir model (dm^3/mg)
a_{RP}: parameter of Redlich-Peterson model [$(dm^3/mg)^{1-\beta}$]
C_e: equilibrium liquid-phase concentration (mg/dm^3)
d_P: adsorbent particle size range (μm)
K_F: parameter of Freundlich model (dm^3/g)
K_L: parameter of Langmuir model (dm^3/g)
K_{RP}: parameter of Redlich-Peterson model (dm^3/g)
n: Freundlich exponent (dimensionless)
q_e: equilibrium solid-phase concentration (mg/g)
β: Redlich-Peterson exponent (dimensionless)
n_p: number of experimental points.
P: number of parameters in the isotherm model.
$q_{e,cal}$: calculated equilibrium solid-phase concentration (mg/g)
$q_{e,exp}$: experimental equilibrium solid-phase concentration (mg/g)

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Table (1): Parameters of Isotherm Models of Adsorption of Basic Red 22.

	Langmuir			Freundlich								Redlich-petrson			
				First section of plot				Second section of plot							
dp(μm)	K_L	a_L	C.C.	K_F	n	C.R.	C.C.	K_F	n	C.R.	C.C.	K_{RP}	a_{RP}	β	C.C.
250-355	333.33	1	0.999	133.35	2.48	0.953-4.44	0.989	239.33	28.57	4.44-34.4	0.465	333.33	1.39	0.927	0.993
355-500	200	0.60	0.996	123.87	2.84	1.09-6.63	0.986	204.17	9.90	6.63-16.55	0.718	200	0.716	0.989	0.989
710-1000	76.92	0.231	0.996	85.70	2.59	3.44-15.54	0.951	179.47	8.19	15.54-32.7	0.608	76.92	0.295	0.995	0.995

C.R. Concentration Range

C.C.: Correlation Coefficient

Table (2):Parameters of Isotherm Models of Adsorption of Basic Blue 69.

	Langmuir			Freundlich												Redlich-petrson			
				First section ofplot				Second section of plot				Third Section Plot							
dp(μm)	K_L	a_L	C.C.	K_F	n	C.R.	C.C.	K_F	n	C.R.	C.C.	K_F	n	C.R.	C.C.	K_{RP}	a_{RP}	β	C.C.
250-355	83.33	0.166	0.999	62.52	1.48	2.8-5.2	0.961	127.64	3.7	5.2-29	0.998	287.08	30.3	29-137.5	0.748	83.33	0.284	0.95	0.995
355-500	50	0.1	0.998	34.43	1.28	5.06-9	0.982	108.64	3.51	9-44.5	0.972	264.24	21.74	44.5-148.5	0.653	50	0.197	0.9173	0.988
710-1000	34.48	0.068	0.999	39.81	1.62	6.4-13.1	0.988	94.19	41.322	13.1-61	0.977	245.47	18.52	61-166.5	0.639	34.48	0.119	0.953	0.997

Table (3): Correlation Coeffcients for the Adsorption of BR22.

dp(μm)	Langmuir	Freundlich		Redlich-Petrson
		First plot	Second plot	
250-355	0.999	0.989	0.465	0.993
355-500	0.996	0.986	0.718	0.989
710-1000	0.996	0.951	0.608	0.995

Table (4): Error Function Values for the Adsorption of of Basic Red 22.

Isotherm model	SABE	SSE	ARE	HYBRID	MPSD
dp = 250-355 μm					
Langmuir	305.487	12382.07	19.309	1032.604	23.437
Freundlich	**4.462**	**322.194**	**0.194**	**22.905**	**3.169**
Redlich-Peterson	1.723	1925.001	0.388	155.789	8.109
dp = 355-500μm					
Langmuir	203.364	6043.775	12.151	482.468	15.504
Freundlich	**1.377**	**211.042**	**0.0158**	**17.226**	**3.008**
Redlich-Peterson	14.326	753.567	0.4385	75.305	6.391
dp = 710-1000 μm					
Langmuir	154.384	3393.885	9.5239	266.479	11.562
Freundlich	**10.720**	**638.454**	**0.5855**	**52.520**	**5.243**
Redlich-Peterson	129.445	2990.605	7.0717	251.718	10.405

Table (5): Correlation Coeffcients for the Adsorption of Basic Blue 69.

dp(μm)	Langmuir	Freundlich			Redlich-Petrson
		First plot	Second plot	Third Plot	
250-355	0.999	0.961	0.998	0.748	0.995
355-500	0.998	0.982	0.972	0.653	0.988
710-1000	0.999	0.988	0.977	0.639	0.997

Table (6): Error Function Values for the Adsorption of Basic Blue 69.

Isotherm model	**SABE**	**SSE**	**ARE**	**HYBRID**	**MPSD**
dp = 250-355 µm					
Langmuir	849.810	801226.04	30.494	3152.069	34.551
Freundlich	**1.779**	**149.865**	**0.169**	**7.844**	**2.005**
Redlich-Peterson	2.442	1420.328	0.024	66.187	5.237
dp = 355-500 µm					
Langmuir	800.049	67887.36	30.187	2811.384	34.002
Freundlich	**8.622**	**304.678**	**0.094**	**13.867**	**2.461**
Redlich-Peterson	7.646	3068.48	0.057	144.844	7.797
dp = 710-1000 µm					
Langmuir	741.198	61345.81	27.247	2472.869	30.843
Freundlich	**21.928**	**267.393**	**0.773**	**12.111**	**2.313**
Redlich-Peterson	8.909	710.641	0.311	32.346	3.614

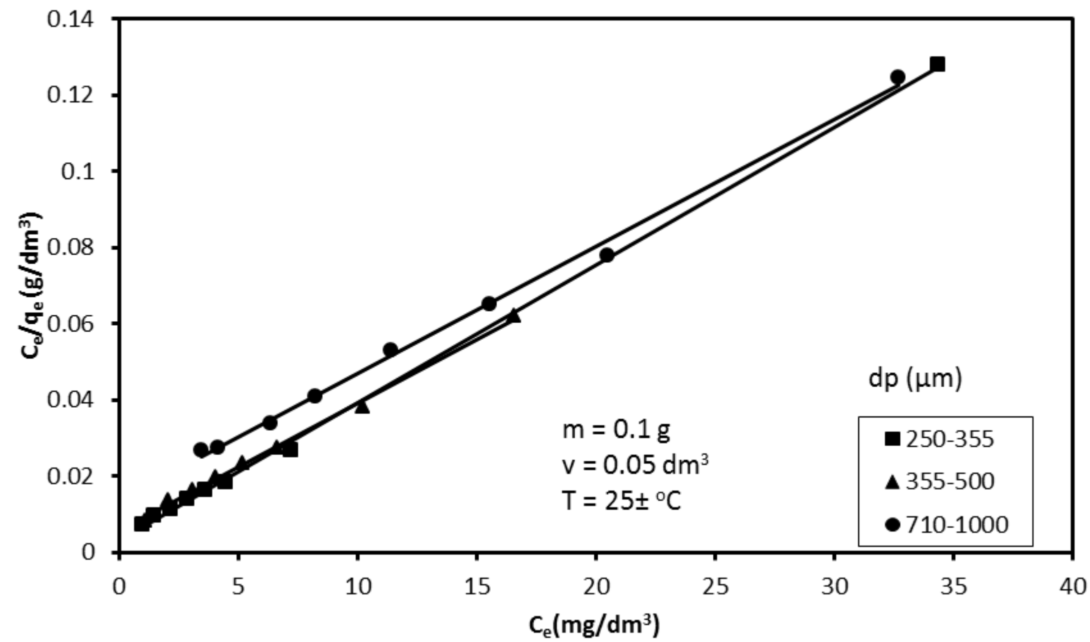

Figure (1): Langmuir Plots for the Adsorption of BR22 onto Natural Clay.

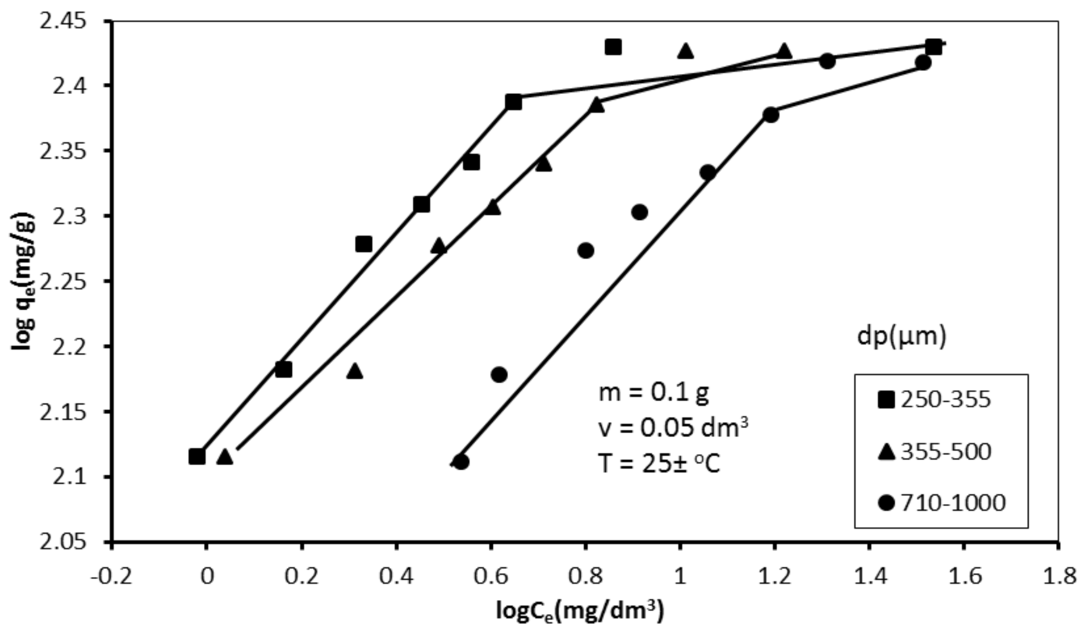

Figure (2): Freundlich Plots for Adsorption of BR22 onto Natural Clay.

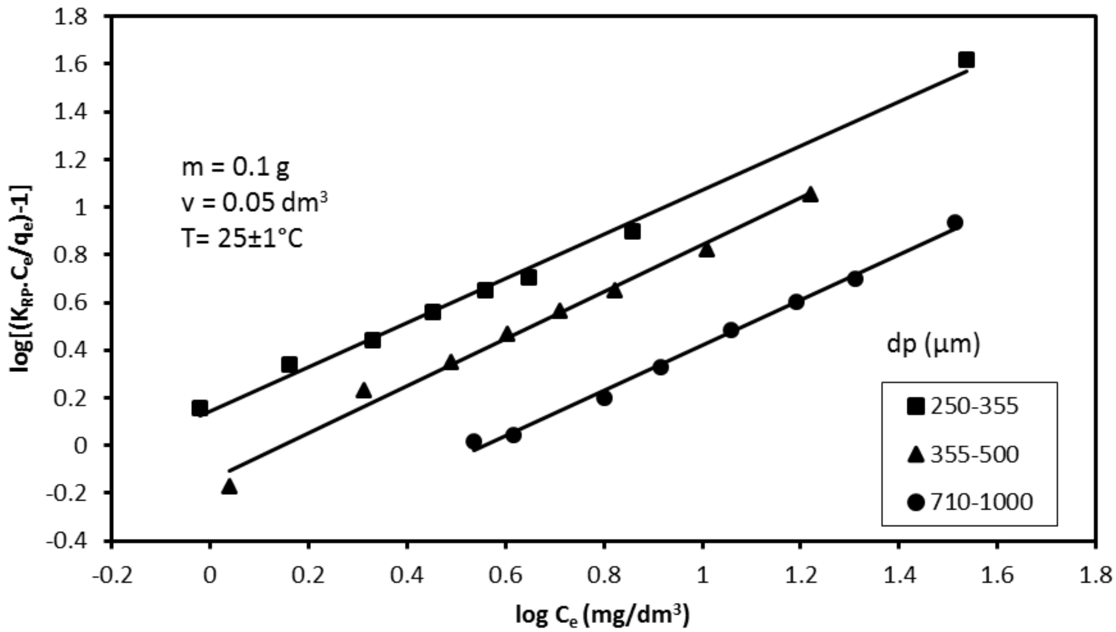

Figure (3): Redlich-Peterson Plots for the Adsorption of BR22 onto Natural Clay .

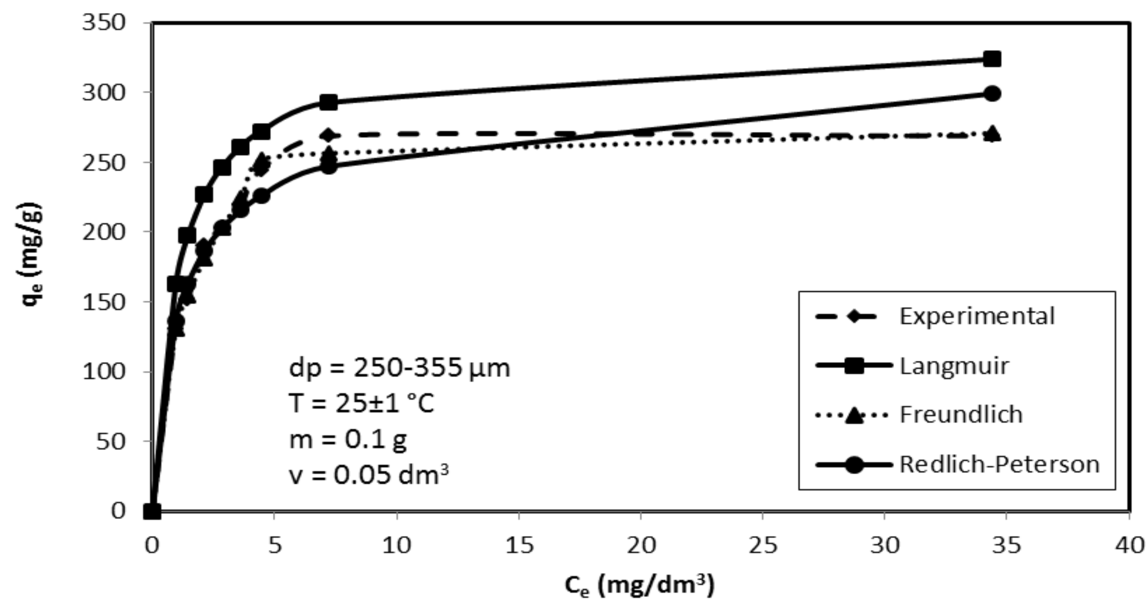

Figure (4): Comparison between Experimental and Theoretical Isotherms for the Adsorption of BR22 onto Natural Clay at dp = 250-355µm.

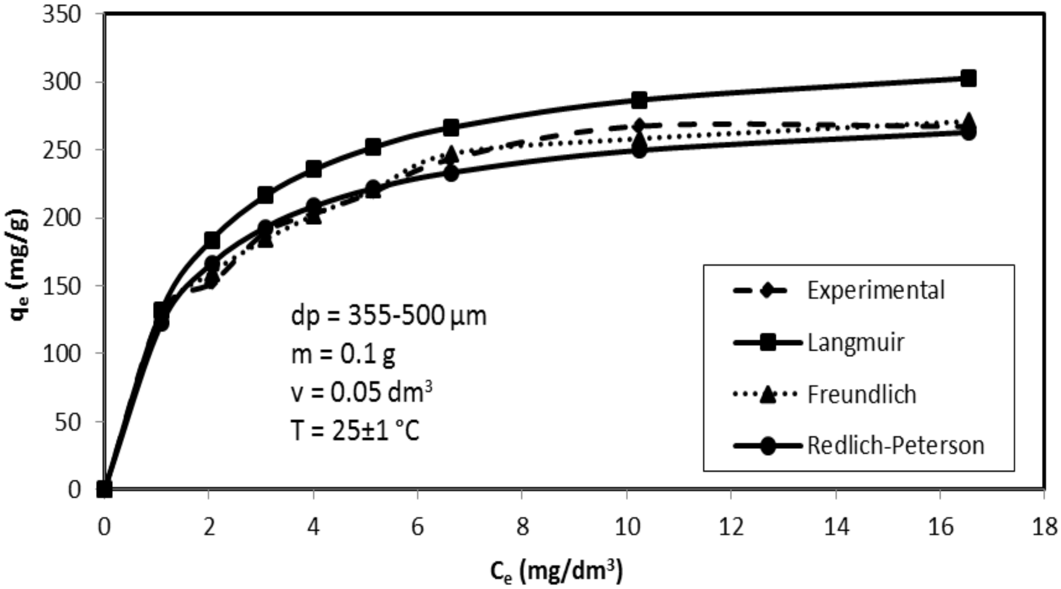

Figure (5): Comparison between Experimental and Theoretical Isotherms for the Adsorption of BR22 onto Natural Clay at dp= 355-500µm.

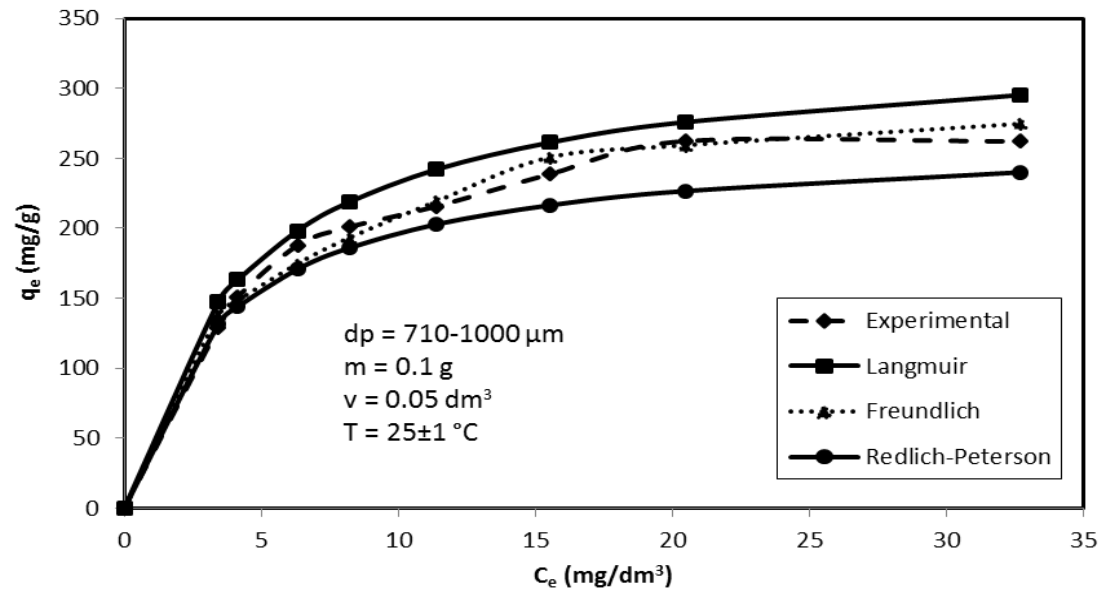

Figure (6): Comparison between Experimental and Theoretical Isotherms for the Adsorption of BR22 onto Natural Clay at dp= 710-1000µm.

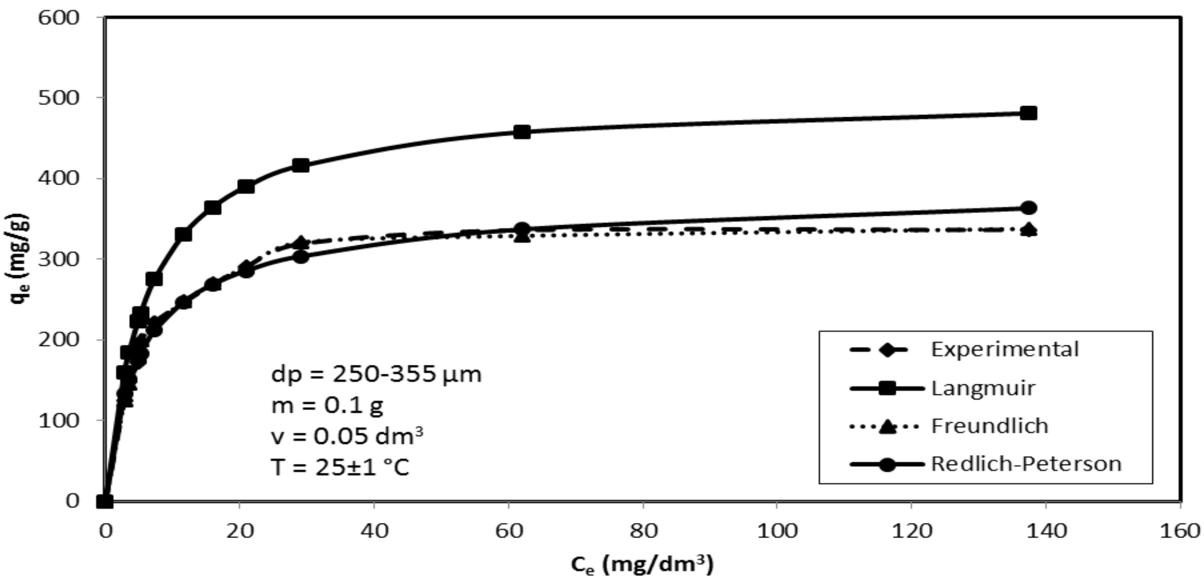

Figure (7): Comparison between Experimental and Theoretical Isotherms for the Adsorption of BB69 onto Natural Clay at dp = 250-355µm.

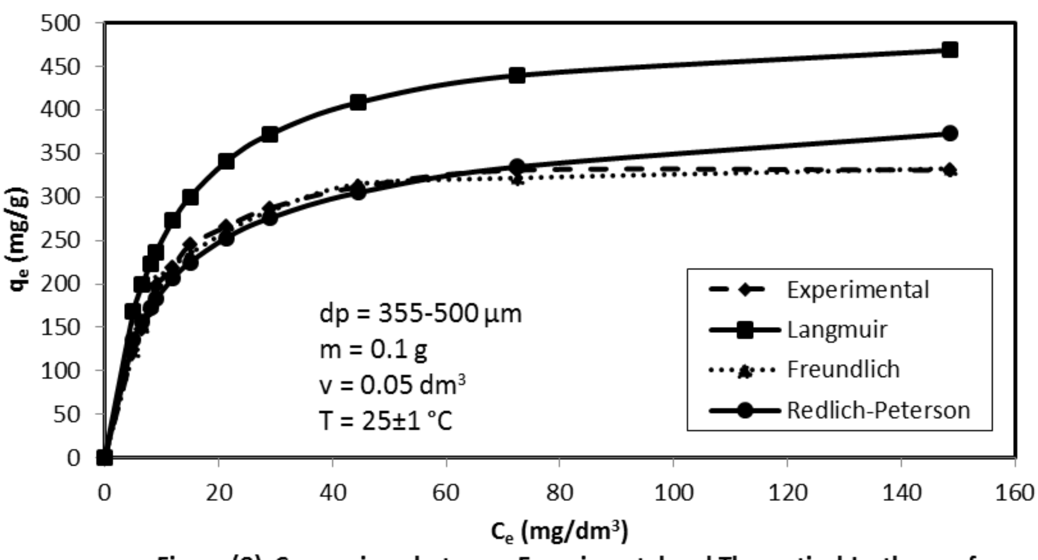

Figure (8): Comparison between Experimental and Theoretical Isotherms for the Adsorption of BB69 onto Natural Clay at dp= 355-500µm.

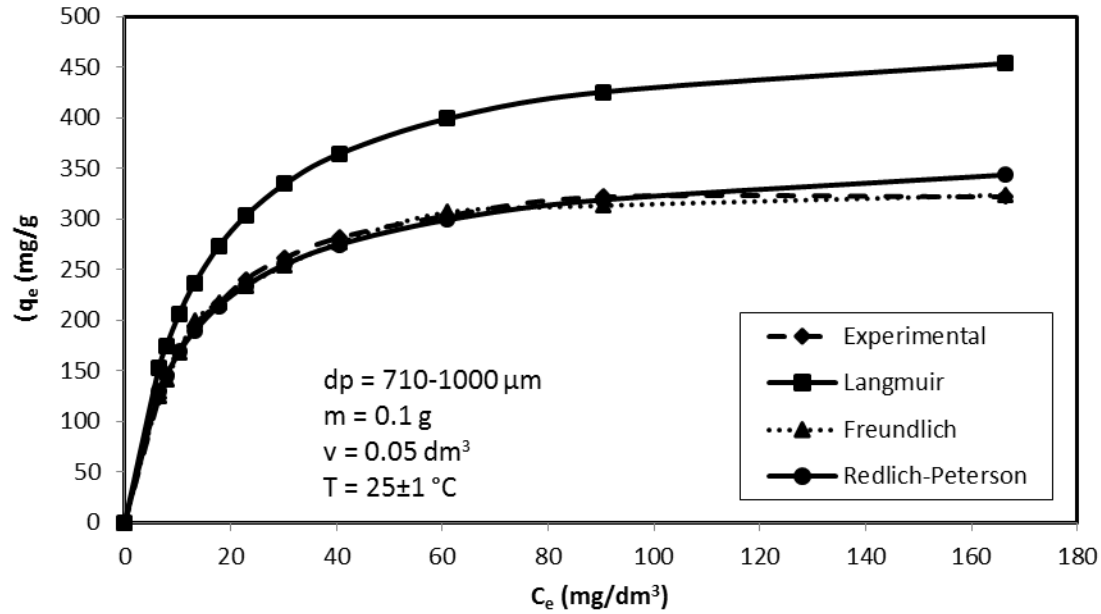

Figure (9): Comparison between Experimental and Theoretical Isotherms for the Adsorption of BB69 onto Natural Clay at dp= 710-1000µm.

الملخص العربي

تم دراسة إمتزاز(ازرق الميثلين٦٩) Basic Blue 69 (والحمراء القاعديه٢٢) Basic Red 22(من المحاليل المائية بواسطة الطفلة الطبيعية . وقد تم دراسة عمليه االتزان والحصول على النتائج المعمليه وتحليلها باستخدام ثالثة نماذج رياضية مشهوره (Langmuir, Freundlich and Redlich-Peterson)

تهدف هذه الدراسه الي تحديد النموذج الرياضي الافضل الذي يمثل النتائج المعملية تمثيلا جيدا وذلك لاستخدامه في تصميم مفاعل لمعالجه المحاليل المائيه. وقد تم تحديد النموذج الرياضي الافضل وذلك بمقارنه النتائج المعملية مع نتائج النموذج الرياضي المقترح و باستحدام معامل الارتباط ومتوسط الانحراف للمنحنيات المستنتجه من النماذج الرياضية.

وقد خلصت الدراسة الي أن نموذج فرندلش(Freundlich)يمثل النتائج المعملية تمثيلا جيدا أكثر من النماذج الاخرى في حاله الصبغتين ، ومن ثم استخدم هذا النموذج في حساب كتلة الطفلة اللازمة لمعالجة كميات مختلفة من المحاليل المائية عند نسب ازالة متعددة.