Bulletin de la Société Royale des Sciences de Liège, Vol 84, 2015, p. 116 - 130

Manuscrit reçu le 5 décembre 2014 et accepté le 7 avril 2015

Application of nonlinear regression analysis to select the optimum absorption isotherm for Methylene Blue adsorption onto Natural Illitic Clay

Otheman AMRHAR[1], Hakima NASSALI, and Mohammed S. ELYOUBI

Laboratory of Materials, electrochemistry and environment, Ibn Tofail University,
B.P:133, Kenitra 14000, MORROCO

Résumé

L'adsorption du Bleu de Méthylène (MB) à partir d'une solution aqueuse sur une argile illitique naturelle (NIC) a été étudiée et les isothermes d'équilibre ont été déterminées. Les données expérimentales obtenues à des différentes concentrations initiales ont été analysées en utilisant six modèles d'isotherme.Afin de déterminer la meilleure isotherme convenable, cinq fonctions d'erreur ont été employées pour évaluer les résultats par la méthode de la régression non linéaire.L'analyse d'erreur a montré que le modèle Redlich – Peterson est le model convenable à décrire les données d'adsorption de MB sur le NIC. En outre, la nature d'adsorption de MB sur NIC a été déterminée à partir des paramètres d'isotherme, et elle est conclue que la physisorption est le mécanisme approprié de l'adsorption de Bleu de Méthylène (MB) sur l'argile illitique naturelle (NIC).
Mots-clés : adsorption, argile illitique naturelle, isotherme d'équilibre, analyse d'erreur.

Abstract

Adsorption of Methylene Blue (MB) from aqueous solution onto Natural Illitic clay (NIC) has been studied and the equilibrium isotherms were determined. The experimental data obtained at different initial concentrations were analyzed using six isotherm models. In order to determine the best fit isotherm, five nonlinear error functions error were used to evaluate the data. The error analysis demonstrated that the Redlich – Peterson model has better described the MB adsorption data onto NIC. Furthermore, the adsorption nature was determined from isotherm parameters, and it was concluded that physic sorption is the appropriate mechanism adsorption to MB onto NIC.

Key Words : adsorption, natural illitic clay, equilibrium isotherm, error analysis.

---

[1] Auteur pour la correspondance: Otheman.amrhar@gmail.com

1. Introduction

Synthetic dyes are aromatic substances that are widely used in many industries such as plastic, paper, textile, etc... The effluents from these industries are contaminated with dyes, which can cause the problems to the environment and to the living beings; hence, it is necessary to treat these effluents by several treatment methods such as coagulation [1], ozonation [2], membrane separation [3], electrochemical technics [4], ultrasonic technics [5], and adsorption [6]. This last method is the most privileged from the different treatment methods of its relatively low cost, high availability, high performance, and its ability to treat dyes in different concentration. Many adsorbents are widely used such as activated carbon [7], chitosan [8], and clay [9-11]. The Modeling of adsorption isotherm data is important as well as to predict the adsorption performance to design the adsorption system. Several isotherm models can explain the solid–liquid adsorption systems, and they can represent the solute uptake process equilibrium conditions. Among these isotherm models we can cited those of two-parameters: Langmuir [12], Frendlich [13], Dubinin–Radushkevich [14], Temkin [15], and those of three-parameters such as: Redlich-Peterson [16], Sips [17] Khan [18] and Toth [19]. The search for the best fit adsorption isotherm using the linear regression method is the widely used technic to evaluate the model parameters, and to determine the best fitting model. However, depending on the way of the isotherm equation linearization, the distribution of error changes either the worst or the best [20]. So, the method of nonlinear regression is used by several researchers to determine the adsorption isotherm parameters [21-23]. It is based on the minimization of error distribution between the experimental data and the predicted isotherm. Several error functions are used to evaluate isotherm data. The most common error functions used are: Nonlinear Chi-square test (X^2), The Sum of the Squares of the Errors (SSE), The Average Relative Error (ARE), The Sum of the Absolute Errors (EABS), The Hybrid Fractional Error Function (HYBRID) [24-29].

In this work, the isotherm models mentioned above were used, to represent the adsorption of methylene blue (MB), onto Natural Illitic clay (NIC). Nonlinear method using error analysis method was adopted to predict the optimum adsorption isotherm, and also, to obtain the isotherm parameters to characterize the adsorption nature of MB onto NIC.

2. Materials and methods

2.1. Adsorbent

The raw clay used in this study was extracted from a quarry that is located in the Khemisset region (Morocco). It was crushed, sieved through a standard ASTM sieve to obtain lower fractions, and then dried in an oven at 110 ° C during 2 hours for the next manipulation. The mineralogical phases constituting the clay have been determined using an XPERT-PRO diffractometer. The significant peaks observed on the XRD patterns of the sample indicated that this clay is composed of illitic, kaolinite and quartz minerals (figure 1).

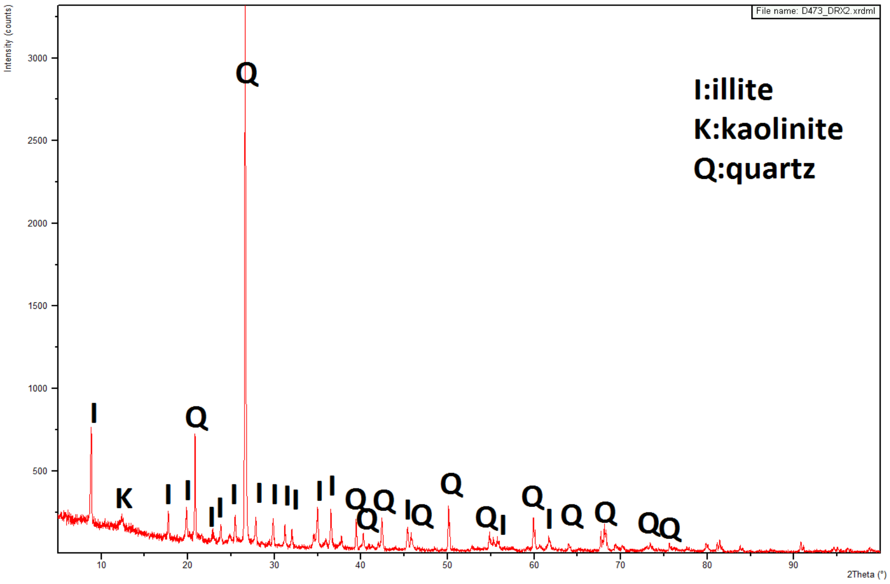

Fig. 1: XRD pattern of natural illitic clay.

2.2. Adsorbate

The dye used in this study is the methylene blue (MB). This is a cationic dye of formula $C_{16}H_{18}ClN_3S$, with 319.852 g/mol as a molecular weight. Its structure is shown in figure 2.

The dye stock solution was prepared by dissolving 0.35g of MB in one liter of distilled water, and the required concentration of the working dye solution was prepared by diluting the stock solution with distilled water.

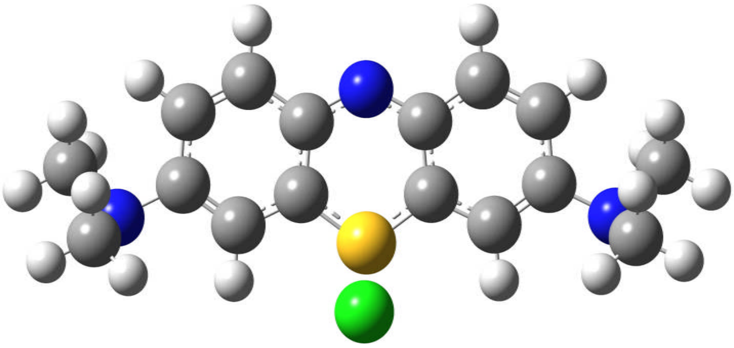

Fig. 2: Chemical structure of methylene blue.

2.3. Process

The adsorption experiments were carried out using the batch technic. A quantity of 20 mg of NIC was mixed with 20 ml of dye solution of knowing initial dye concentration. The mixture obtained was agitated at a speed of 600 RPM with amechanical shaker and in natural pH. The contact was made for 60 min. After the solution and the solid phase were separated by filtration, the remaining concentration of MB in the filtrate was determined by using a SP 2000 UV spectrophotometer.

2.4. Equilibrium isotherms

In order to optimize the design of adsorption system to remove the dye, the appropriate correlations for the equilibrium isotherms were established. Eight different adsorption isotherm models were considered for this study: Langmuir, Freundlich, Dubinin–Radushkevich (D-R), Temkin, Redlich-Peterson, Sips, Khan and Toth since they are the most studied and they are the best understood models.

2.4.1. The Langmuir Isotherm

The Langmuir isotherm theory assumes the monolayer coverage of adsorbate over a homogeneous adsorbent surface where all sorption sites are found to be identical and energetically equivalent [13]. In the equilibrium, the saturation point is reached and the dye occupied the sites, then it was no further adsorption that can be realized at these sites. Therefore, the adsorbent has a finite capacity of adsorption for the dye. The monolayer capacity can be represented by the expression:

$$Q_e = \frac{Q_{\max} K_L C_e}{1 + K_L C_e}$$

Where K_L (l/mg) is the Langmuir isotherm constant, Q_e (mg/g) and Ce (mg/l) are respectively the solid phase concentration and liquid phase concentration of adsorbate at equilibrium, Q_m (mg/g) is the maximum amount of adsorbed dye per an unit weight of adsorbent. More Ce becomes lower, more $K_L C_e$ is less than the unity. $Q_e = Q_{\max} K_L C_e$ is analogous to Henry's law.

2.4.2. The Freundlich Isotherm

The Freundlich isotherm is an empirical equation employed to describe the multilayer adsorption. This model predicts that the dye concentration on the adsorbent will increase with the increase of the adsorbate concentration in the solution [14]. This model is applied in reversible adsorption onto heterogeneous surfaces. It can be expressed by:

$$Q_e = K_f C_e^{1/n}$$

Where K_f (l/mg) is the Frendlich isotherm constant and $1/n$ is the heterogeneity factor which can vary between 0 and 1.

2.4.3. The Dubini–Radushkevich

The Dubini–Radushkevich isotherm is more general than the Langmuir isotherm because it does not assume a homogeneous surface or constant adsorption potential [15]. It is applied to distinguish between the physical and chemical adsorptions. The D-R isotherm equation can be described as follows:

$$Q_e = Q_{max} exp\left(-B_D \left[RT \ ln\left(1 + 1/Ce\right)\right]^2\right)$$

Where Q_{max} (mg/g) is the D-R monolayer capacity, T(K) is the solution temperature. The value of B_D is related to the sorption energy E by means of the following relationship: $E=1/(2B_D)^{0.5.}$. The mean adsorption energy is the free energy change when one mole of the ions is transferred to the solid surface from infinity in the solution. The E value obtained gives information about the adsorption mechanism such that, if the magnitude of E is between 8 and 16 KJ/mol, the adsorption process that has taken place is of chemical type, when $E < 8$KJ/mol, the adsorption process proceeds physically [25].

2.4.4. The Temkin Isotherm

The Temkin isotherm assumes that decrease in the heat of adsorption is linear and the adsorption is characterized by a uniform distribution of binding energies. It is expressed by following equation [16]

$$Q_e = \frac{RT}{b} Ln(K_T C_e)$$

Where $b = RT/B$ is related to heat of adsorption (J/mol), R is the gas constant (8,314 J. $\text{mol}^{-1}.\text{K}^{-1}$), T is the absolute temperature (K) and K_T is the Temkin equilibrium constant *(L/g)* corresponding to the maximum binding energy.

2.4.5. The Redlich-Peterson Isotherm

The Redlich – Peterson [17] is an empirical isotherm which incorporates three parameters. It may be used to represent adsorption equilibrium over a wide concentration range. It combines some elements from both the Langmuir and Frendlich equation, and consequently, it can be employed either in heterogeneous or homogenous systems. It can be described as follow:

$$Q_e = \frac{AC_e}{1 + BC_e{}^g}$$

Where A (L/g) and B (L/mg) are Redlisch–Peterson isotherm constants, g is an exponent which lies between 0 and 1.

2.4.6. The sips Isotherm

The Sips isotherm is a combined form of Langmuir and Freundlich models [18]. At low adsorbate concentrations, this model is reduced effectively to the Freundlich isotherm and did not obey to the Henry’s law. At high adsorbate concentrations, it predicts a monolayer sorption capacity which is characteristic of the Langmuir isotherm. The model can be written as:

$$Qe = \frac{Q_S K_S C_e{}^{1/n}}{\left(1 + \mathrm{K}_S C_e{}^{1/n}\right)}$$

Where Q_S (mg/g) is the sips maximum adsorption capacity, K_S (l/g) is the Sips model isotherm constant, and $1/n$ is the sips model exponent.

2.4.7. The Khan Isotherm

Khan and col [19] have suggested a generalized isotherm for the pure solutions. The khan isotherm model can be expressed as:

$$Qe = \frac{\mathrm{Q}_{\max} b_k C_e}{\left(1 + b_k C_e\right)^{a_k}}$$

With b_k and a_k are the Khan model constant and the Khan model exponent respectively.

2.4.8. The Toth Isotherm

The Toth isotherm [20] is another isotherm that has three parameters Q_t, K_t and $1/t$, and useful in describing heterogeneous adsorption system, which satisfying both low and high-end boundary of the concentration. It is given by:

$$Qe = \frac{\mathrm{Q}_t K_t C_e}{\left(1 + (K_t C_e)^t\right)^{1/t}}$$

With Q_t is the Toth maximum adsorption capacity, K_t is the Toth model isotherm constant, and $1/t$ is the Toth model exponent. If t is close to the unity, this isotherm reduces to the Langmuir sorption isotherm equation.

2.5. Error functions

The nonlinear optimization technic has been applied to determine isotherm parameters. This optimization procedure requires an error function to be defined in order to be able to evaluate the fit of the isotherm to the experimental equilibrium data. In this work, five different error functions were examined by minimizing the respective error function across the concentration range studied, using the *“SOLVER ADD-IN”* with Microsoft’s spread sheet. The error functions studied well detail in the following section.

2.5.1. The Sum of the Squares of the Errors (ERRSQ)

At higher end of the liquid-phase concentration ranges, the magnitude and squares of the errors tend to increase. This illustrates a better fit for the isotherm parameters derivation [26]. This error function can be represented by the equation:

$$\Sigma\left(q_{e\ meas} - q_{e\ cal}\right)_i^2$$

Where $q_{\mathrm{e,calc}}$ is the theoretical adsorbed solid phase concentrations of adsorbate on adsorbent, that have been calculated from one of the isotherm equations, and $q_{\mathrm{e,meas}}$ is the experimental adsorbed solid phase concentrations of adsorbate on sorbent.

2.5.2. The average relative error (ARE)

Developed by Kapoor and Yang [27], this error function attempts to minimize the fractional error distribution across the entire concentration range. It can be expressed by:

$$\frac{100}{n}\sum_{i=1}^{n}\left|\frac{q_{e\ meas}-q_{e\ cal}}{q_{e\ meas}}\right|_{i}$$

2.5.3. The sum of the absolute errors (EABS)

The *“Sum of the Absolute Errors”* approach is similar to the *“ERRSQ”* function. The isotherm parameters which are determined with using this error function will provide a better fit as the magnitude of the errors increase. This biased the fit towards the high concentration data. [28]:

$$\sum_{i=1}^{p}\left|q_{e\ meas}-q_{e\ cal}\right|_{i}$$

2.5.4. Nonlinear chi-square test

This statistical tool is necessary for the best fit of an adsorption system. It is obtained by judging the sum squares difference between the experimental and calculated data, with each squared difference is divided by its corresponding value [29]. The value of chi-square is calculated by using this equation:

$$\sum_{i=1}^{n}\frac{\left(q_{e\ cal}-q_{e\ meas}\right)_{i}^{2}}{q_{e\ meas}}$$

2.5.5. The hybrid fractional error function (HYBRID)

Porter and al [28] have developed this function to improve ERRSQ fit at low concentrations. This function includes the number of degrees of freedom of the system- *the number of data points, n, minus the number of parameters of the isotherm equation, p, - as a divisor*. The expression of this error function is:

$$\frac{100}{n-p}\sum_{i=1}^{n}\left[\frac{(q_{e\ meas}-q_{e\ cal})^{2}}{q_{e\ meas}}\right]_{i}$$

2.5.6. Sum of normalized errors (SNE)

Since each error criteria is likely to produce a different set of parameters of the isotherm, a standard procedure called *“Sum of the Normalized Errors”* is adopted to normalize and to combine the error in order to make a better and meaningful comparison between the parameter sets. It has been used to determine the best fitting isotherm equation by several investigations [30, 31]. The calculation process for the *"Sum of the Normalized Errors"* is made as follows:

1. Selection of an isotherm model and error function, and determination of the adjustable parameters which minimize the error function.
2. Determination of the values for all other error functions for that isotherm parameter set.
3. Computation of the other parameter sets associated with their error function values.
4. Normalization and selection of the maximum parameter sets with respect to the largest error measurement.
5. Summation of all these normalized errors for each parameter set.

3. Results and discussion

3.1. Determination of isotherm model

The nonlinear approach of the two and three parameter isotherm models using the five error functions detailed above was adopted, by using a trial and error procedure to fit the data and to determine the isotherm parameters, through the application of the *SOLVER ADD-IN* with Microsoft's spread sheet. The calculated values of parameters and error analysis are presented in table 1. The values of *"Sum of the Normalized Errors" SNE* were used to evaluate the best error function for selecting the isotherm model and the calculated isotherm parameters (see for instance [31, 32]). Figures in underlined type indicate the minimum values of *SNE* for an appropriate error function. It was found that the *SSE* function provides the best estimation of parameters for all isotherm models that have been examined in this study. The best estimation is due to the low value of *SNE* in 4 out of 8 systems (examining eight isotherms) for all parameter isotherms examined. According to this argument, *SSE* was selected as the like error function for determination and examination of the best fit isotherm models to experimental data. Isotherm models were evaluated using *SSE* function, and the values of parameters for each model are illustrated in table 2-a and table 2-b. The comparison of the isotherm models leads us to suggest that the R-P model has a lowest *SSE* error value and the FREUNDLICH model has a worst fitting degree with experimental data. Figure 2-a and Figure 2-b shows the experimental data and the predicted equilibrium curve using a non-linear method for the two and three parameters isotherm LANGUMIR, FREUNDLICH, D-R TIMKIN and R-P, SIPS, KHAN, TOTH, respectively. It is Clair that the R-P model has the best performance for fitting with experimental data. According to the error values of SSE, we can classify the fitting degree of isotherm models in this order: R-P, SIPS, TOTH, LANGUMIR, D-R, TIMKIN, KHAN and FREUNDLICH.

These results revealed that the equilibrium data were fitted better by the three-parameter model rather than the two-parameter models.

3.2 Isotherm study

In general, the adsorption isotherm indicates how the quantities of molecules are distributed between the liquid and solid phase when the adsorption processes reach balance. It is employed to establish the maximum capacity of adsorption of adsorbate on adsorbents, which is expressed in terms of quantity of colorant adsorbed per unit of mass of adsorbent used. According to R-P model, the exponent "g" value is close to the unity ($g = 0.95887983$). This indicates that the adsorption of MB onto NIC is compatible with the Langmuir form rather than the Freundlich one. The result was also confirmed by the relative errors given in table 2. It can be concluded that surface of NIC is homogenous for MB adsorption i.e. all adsorption sites are equals. This was confirmed by Toth isotherm exponent "t" which is nearly unity ($t = 0.95387316$). It tells us that this is the process occurs a homogeneous surface [33].

Table 1: The calculated value of parameters and error analysis

	X^2	SSE	ARE	EABS	HYBRID
FREUNDLICH					
K_f	9,189853962	9,12683099	8,86060952	8,860609518	9,18985404
1/n	0,152463157	0,15118877	0,15184733	0,15184733	0,15246315
X^2	**1,289836329**	1,29438916	1,38483377	1,384833766	1,289836329
SSE	10,10672566	**10,052797**	10,6407492	10,64074919	10,10672563
ARE	12,67342104	12,5123709	**11,718706**	11,71870601	12,6734214
EABS	6,555671167	6,47432603	6,20101645	**6,201016454**	6,555671165
HYBRID	25,79672659	25,8877832	27,6966753	27,69667532	**25,79672659**
SNE	4,881214883	**4,8578481**	4,94421976	4,944219756	4,881214908
LANGMUIR					
Q_{max}	12,76893845	12,7160234	12,8282724	12,76941605	12,76893845
K_L	5,260734892	5,25793211	4,23489816	6,4204013	5,260734893
X^2	**0,724580769**	0,72582882	0,93602133	0,882874221	0,724580769
SSE	6,19617677	**6,18313048**	7,38434036	7,554633502	6,196176771
ARE	10,17460758	10,191251	**9,99095436**	10,32125175	10,17460758
EABS	5,701749098	5,74538759	5,92170281	**5,448613694**	5,701749096
HYBRID	14,49161538	14,5165763	18,7204267	17,65748442	**14,49161538**
SNE	4,317044887	4,32696646	4,94545677	4,806549658	**4,317044887**
D-R					
Q_{max}	12,33213975	12,2762603	12,5631633	12,56316329	12,33213974
B_D	0,033786625	0,03385573	0,0452793	0,045279302	0,033786625
X^2	**0,731679261**	0,73337111	1,42266765	1,422667646	0,731679261
SSE	6,586613499	**6,56965879**	10,146427	10,14642701	6,586613495
ARE	10,62549054	10,6408452	**10,4172325**	10,41723253	10,62549055
EABS	6,26346637	6,31202581	6,73092256	**6,730922558**	6,263466375
HYBRID	14,63358522	14,6674222	28,4533529	28,45335293	**14,63358522**
SNE	3,60686572	3,61623052	4,97898544	4,978985438	**3,60686572**
TIMKIN					
B	1,588345408	1,55683863	1,50525552	1,505255524	1,588368078
K_t	385,0336768	416,197718	520,187124	520,1871244	385,0075033
X2	**1,059267932**	1,06409828	1,07287571	1,07287571	1,05926793
SSE	8,247805331	**8,18771831**	8,2421045	8,242104502	8,247869817
ARE	11,29506566	10,9777944	**10,8164215**	10,81642146	11,29526131
EABS	6,010934416	5,72471062	5,51976402	**5,519764021**	6,011119561
HYBRID	21,18535863	21,2819656	21,4575142	21,45751419	**21,18535861**
SNE	4,974577137	4,90059186	4,87516691	**4,875166906**	4,974633074

	X^2	SSE	ARE	EABS	HYBRID
R-P					
A	75,79506954	83,1714609	103,829132	103,8291319	75,79506985
B	6,239053799	7,09855239	8,91634673	8,916346734	6,239053807
g	0,974713891	0,95887983	0,95573705	0,955737053	0,974713892
X^2	**0,706201896**	0,71463356	0,81320822	0,813208217	0,706201896 5,767513702
SSE	5,767513684	**5,68081036**	6,46460203	6,464602032	
ARE	9,578569192	9,69142196	**9,3435386**	9,343538597	9,578569216
EABS	5,126954394	5,15560379	4,57919665	**4,579196655**	5,126954395
HYBRID	17,65504739	17,865839	20,3302054	20,33020542	**17,65504739**
SNE	**4,611796076**	4,6363224	4,85230193	4,852301929	4,611796081
SIPS					
K_s	9,32541992	6,32368386	5,04276641	9,746925837	9,325407053
Q_s	12,37648817	12,5603052	12,7231329	12,53016842	12,37646452
1/n	1,328187113	1,10548045	1,22612628	1,218531243	1,328187919
X^2	**0,699721616**	0,71168512	1,5024626	0,916873336	0,699721616
SSE	6,245658467	**6,16321536**	10,3600836	8,033663538	6,24564482
ARE	10,36197438	10,3028665	**10,1388406**	10,44024292	10,36198079
EABS	6,083392985	5,91590087	6,46357534	**5,625145734**	6,083416211
HYBRID	17,49304039	17,7921281	37,561565	22,92183339	**17,4930404**
SNE	3,467974897	**3,44436756**	4,97113072	3,866221877	3,467977788
KHAN					
Q_{max}	1,798265436	1,80977572	1,74670974	1,746722572	1,798307466
b_k	44349,91597	44358,0135	44165,5759	44165,71512	44343,16491
a_k	0,847539701	0,84878564	0,84817005	0,848167395	0,847537117
X^2	**1,289597093**	1,29415512	1,38457185	1,384375195	1,289597119
SSE	10,10483843	**10,0508155**	10,6386687	10,63710243	10,10522858
ARE	12,67111453	12,5084112	**11,7181164**	11,71810585	12,67181558
EABS	6,554892464	6,47347312	6,20070126	**6,20063808**	6,555192657
HYBRID	32,23992732	32,353878	34,6142962	34,60937987	**32,23992798**
SNE	4,812530514	**4,78877619**	4,8706606	4,870218842	4,812668342
TOTH					
Q_t	12,47665411	12,789085	13,0264468	13,04375971	12,44851723
k_t	3,98259214	5,5923917	5,46062402	5,480835197	4,039292727
t	1,292021332	0,95387316	0,88716702	0,883716625	1,292360631
X2	**0,714313585**	0,73032948	0,79290195	0,793420849	0,713569158
SSE	6,321911737	**6,17996277**	6,50084441	6,504632625	6,316446016
ARE	10,43732736	10,1240756	**9,86599021**	9,85640803	10,45100139
EABS	6,074787857	5,66458658	5,57922125	**5,567576341**	6,071671402
HYBRID	17,85783963	18,258237	19,8225486	19,83552123	**17,83922896**
SNE	4,771192642	**4,69224307**	4,86055543	4,859612043	4,76927124

Table 2-a: SSE and values of parameters isotherm models (two-parameters isotherms)

	FREUNDLICH		LANGMUIR		D-R		TIMKIN
K_f(l/mg)	9,12683099	Q_{max}(mg/g)	12,7160234	Q_{max}(mg/g)	12,2762603	B	1,55683863
1/n	0,15118877	K_L(l/mg)	5,25793211	B_D(kJ^2.mol^{-2})	0,03385573	K_t(l/g)	416,197718
SSE	10,052797	SSE	6,18313048	SSE	6,56965879	SSE	8,18771831

Table 2-b: SSE and values of parameters isotherm models (three -parameters isotherms)

	R-P		SIPS		KHAN		TOTH
A(l/g)	83,1714609	Ks(l/mg)	6,32368386	Q_{max}(mg/g)	1,80977572	Q_t(mg/g)	12,789085
B(l/mg)	7,09855239	Qs(mg/g)	12,5603052	b_k	44358,0135	K_t	5,5923917
g	0,95887983	1/n	1,10548045	a_k	0,84878564	t	0,95387316
SSE	5,68081036	SSE	6,16321536	SSE	10,0508155	SSE	6,17996277

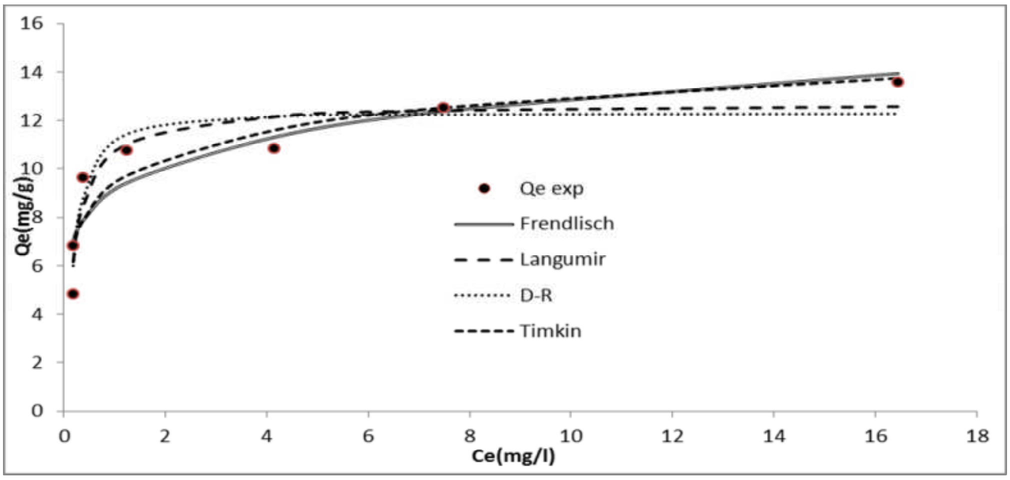

Fig. 3-a: Comparison of isotherm models with experimental data (two-parameter isotherms)

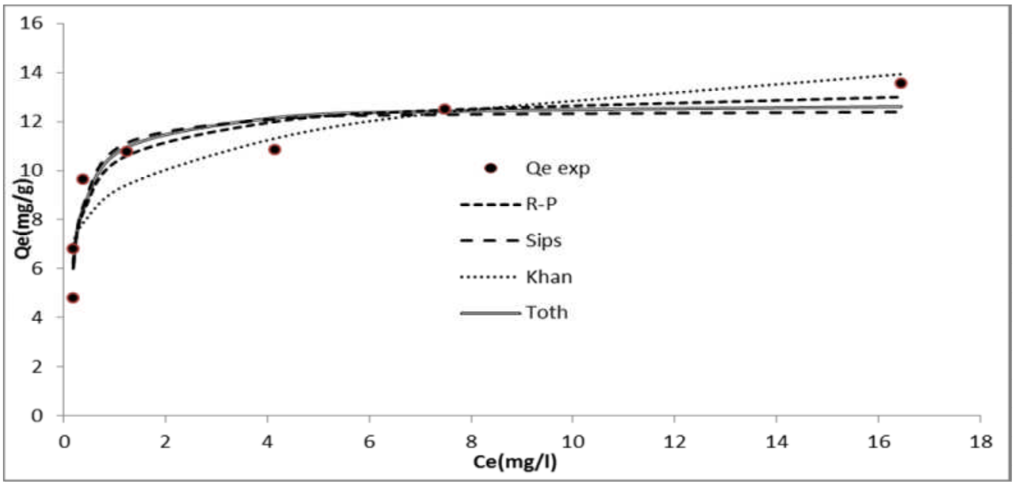

Fig. 3-b: Comparison of isotherm models with experimental data (three-parameter isotherms)

The essential feature of the Langmuir isotherm can be expressed by means of a dimensionless constant "R_L" that is referred to as separation factor or equilibrium parameter. It is defined by the following relationship [34]:

$$R_L = \frac{1}{\left(1 + K_L C_0\right)}$$

Where K_L and C_0 (mg/l) are the Langmuir constant and the highest initial dye concentration respectively. As the "R_L" value lie between 0 and 1, the on-going adsorption process is favorable. The "R_L" value for Methylene Blue onto NIC is 0.00629969, and therefore, its adsorption is favorable. This can also be concluded from the Freundlich model fitting results. The magnitude of the exponent, "$1/n$", gives an indication about the favorability of adsorption such that in favorable adsorption process, the value of $1/n$ should be in the range of 0-1 [34]. In this study, the value of $1/n$ is equal to 0.15118877 values which indicate that this adsorption is favorable. The Freundlich constant "n" is a measure of the deviation from linearity of the adsorption. Since the value of n is above unity (n = 6.6142509), the adsorption being favorable is of physical nature [35].

The constant "b" related to the variation of adsorption energy concluded from Temkin isotherm, is positive. These indicate the adsorption reaction is exothermic [36].The free energy of MB adsorption onto NIC was considered via Dubinine Radushkevich (D-R) model. As can be seen from Table2, this energy that is less than 8 kJ mol^{-1} (E= 3.842987068 kJ.mol^{-1}), confirms that the adsorption process of dye was controlled by physical adsorption process [24].

4. Conclusion

In this work, the equilibrium data of Methylene Blue adsorption onto NIC was fitted using eight different isotherms and five different error function including nonlinear regression method. The standard normalized error procedure SNE was used to select the best error function. Because of the low SNE value, the SSE function was used to obtain isotherm parameters. The R-P model, which is the three-parameter model, was found to provide fit to the equilibrium experimental data. The order of fitting degree of isotherm models was obtained as: R-P, SIPS, TOTH, LANGUMIR, D-R, TIMKIN, KHAN and FREUNDLICH. The isotherm parameters revealed that the adsorption of MB onto NIC is favorable, and confirmed that this adsorption is controlled by physisorption.

References

1. Klimiuk E., Filipkowska U., and Libecki B., *Polish J. Environ. Stud.*, **8** (1999) 81-88.
2. Snider E.H. and Porter J.J., *J. Water. Pollut. Contr. Feder.*, **46** (1974) 886-894.
3. Ahmad A. L., Harris W. A., and Seng S. B., *J. Tekn.*, **36** (2002) 31-44.
4. Sieng H. and Peng L. C. F., *War. Res.*, **28** (1994) 277-282.
5. Zhu H., *Ind. Safety. Envir. Prot.*, **12** (2007 16-18).
6. Mustafa Y. T., Kanti S.T., Sharmeen A., and Ang H.M., *Adv. in Coll. Inter. Sc.*, Review 209 (2014) 172-184.
7. Wang L., Zhang J., Zhao R., Li C., Li Y., and Zhang C., *Desalination*, **254** (2010) 68-74.
8. Annadurai G., Ling L., and Lee J., *J. Hazard. Mater.*, **152** (2008) 337-346.
9. Weng C.H. and Pan Y.F., *J. Hazard. Mater.*, **144** (2007) 355-362.
10. Gürses A., Doğar Ç., Yalçın M., Açıkyıldız M., Bayrak R., and Karaca S., *J. Hazar. Mater.*, **131** (2006) 217-228.
11. Mouzdahir Y. El, Elmchaouri A., Mahboub R., Gil A., and Korili S.A., *Desalination*, **250** (2010) 335-338.
12. Langmuir I., *J. Am. Chem. Soc.*, **40** (1918) 1361-1403.
13. Freundlich H.M. F, *J. Phys. Chem.*, **57** (1906) 385-471.
14. Dubinine M. M., *Chem. Rev.*, **60** (1960) 235-266.
15. Tempkin M.I. and Pyzhev V., *Acta. Phys. Chim. USSR*, **12** (1940) 327-356.
16. Redlich O. and Peterson D.L., *J. Phys. Chem.*, **63** (1959) 1024-1026.
17. Sips R., *J. Chem. Phys.*, **16** (1948) 490-495.
18. Khan A.R., Ataullah R., and Al-Haddad A., *J. Colloid. Interface Sci.*, **194** (1997) 154-165.
19. Toth J., *Acta. Chim. Acad. Sci. Hungar.*, **69** (1971) 311-317.
20. Ho, Y.S., *Carbon*, **42** (2004) 2115-2116
21. Kumar K.V., *Dyes Pigments*, **74** (2007) 595-597.
22. Ho Y.S., *Carbon*, **10** (2004) 2115-2116.
23. Kumar K.V., *J. Hazard. Mater*. **136** (2006) 197-202.
24. Ho Y. S., Porter J. F., and McKay G., *Air. Soil Poll.*, **141** (2002) 1-33.
25. Helfeererich F., Ion exchange, McGraw-Hill ed., New York, NY (1962).
26. Mane V.S., Mall I.D., and Srivastava V.C., *J. Environ. Manage.*, **84** (2007) 390-400.
27. Kapoor A. and Yang R.T., *Gas Sep. Purif.*, **3** (1989) 187-192.
28. Porter, J.F. and McKay, G., *Chem. Eng. Sci.*, **54** (1999) 5863-5885.
29. Boulinguiez B., Le Cloirec P., and Wolbert D., *Langmuir*, **24** (2008) 6420-6424.
30. Kundu S. and Gupta A.K., *Chem. Eng. J.*, **122** (2006) 93-106.

31. Chan L.S, Cheung W.H., Allen S.J., and McKay G., *Ch. J. Chem.*, **20** (2012) 535-542.
32. Gunay A., *J. Hazar. Mater.*, 148 (2007) 708-713.
33. Brdar M., Šćiban M., Takači A., and Došenović T., *Chem. Eng. J.*, **183** (2012) 108-111.
34. Ozdes D., Duran C., Senturk H. B., Avan H., and Bicer B., *Desalin. Water. Treat.*, **52** (2014) 208-218.
35. Özcan A.S, Erdem B., and Özcan A., *Colloids and Surfaces A: Physicochem. Eng. Aspects*, **266** (2005) 73-81.
36. Hadi M., Samarghandi M.R., and McKay G., *Chem. Eng. J.*, **160** (2010) 408-416.