

Modeling of equilibrium data for free cyanide adsorption onto activated carbon by linear and non-linear regression methods

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Abstract. Equilibrium data of free cyanide adsorption onto activated carbon were obtained from a series of batch experiments. Linear and Non-linear regression methods were used to determine the best fit of equilibrium data. The two-parameter models including Freundlich, Dubinin–Radushkevich, Temkin and Langmuir and three-parameter models including Redlich–Peterson and Koble–Corrigan were employed for fitting the equilibrium data. The four Langmuir linear equations are discussed. It was found that the Non-linear regression model is a better way for predicting the isotherm parameters. Among all of the isotherm models, it was revealed that the Koble–Corrigan model fitted the data better than the other.

Keywords: Activated carbon; Cyanide adsorption; Isotherm; Linear and Non-linear regression

1. Introduction

Effluents originated from electroplating and metal finishing plants and various chemical industries contain different amounts of free cyanide and metal cyanide complexes, which are very toxic to humans and aquatic lives [1-4]. There are numerous technologies which can be applied to clean up cyanide contaminated effluents. Among them, the treatment of wastewaters with activated carbon is considered to be an effective method for the removal of free cyanide from waste aqueous solutions [5]. This is due to porous structure, very high surface area, high degree of surface reactivity, and easily availability of activated carbons [5].

In order to determine the adsorption capacity of activated carbons and also to predict the performance of an activated carbon adsorption system, the analysis of the equilibrium data should be performed to find the best fitting equilibrium sorption isotherm [6-8]. The adsorption isotherms describe the relationships between the adsorbent and the adsorbate. Also, the equilibrium parameters predict how the adsorbate interacts with the adsorbent. Freundlich, Langmuir, Temkin, Dubinin-Radushkevich, Redlich-Peterson, Koble-Corrigan are the most widely used isotherms to evaluate the solute uptake process at equilibrium conditions.

The method of least squares with linearly transformed isotherm equations is the most widely used technique for finding the best fit of adsorption isotherm [9-11]. In recent years, the non-linear regression method has been proposed as a better way to find the best fitting of adsorption equilibrium [12]. In the non-linear regression method, the error distribution between the experimental data and the predicted isotherm must be minimized by an iterative procedure [12]. In this investigation, the linear and nonlinear regression methods were used to determine the best fit of equilibrium isotherm for free cyanide adsorption onto activated carbon.

2. Materials and methods

2.1 Reagents

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In this study analytical grade sodium cyanide (NaCN), silver nitrate (AgNO₃), potassium iodide (KI), sodium hydroxide (NaOH) and industrial grade coconut shell activated carbon, produced through a steam activation process by Haycarb company, Sri Lanka, were employed. Before use, a size fraction of -2.36 +2 mm of the activated carbon was separated and dried in air and divided into 1.5g portions. Following acid treatment of carbon with 1% hydrochloric acid solution, the sample was thoroughly rinsed with distilled water and then added to the cyanide aqueous solution of predetermined initial concentration.

2.2 Batch equilibrium experiments and analytical method

Adsorption tests were carried out using a 2.5L capacity glass bottles at ambient temperature (25±2°C). Stock solution of cyanide at the concentration of 2000 mg/L was prepared by dissolving 2.0 g of sodium cyanide in 1 L of distilled water pre-adjusted to pH 10. Experimental solutions at desired concentrations were obtained by dilution of the stock solution with distilled water pre-adjusted to pH 10. The cyanide concentration of each solution was analyzed by titrating against standard silver nitrate solution (0.001M) in the presence of potassium iodide (10 g/L in distilled water) as indicator. Analyses were repeated in triplicate and averaged. The initial cyanide concentrations of the experimental solutions were determined as 102, 202, 306, 396 and 532 mg/L. 500 mL of the experimental solutions were placed in bottles and then 1.5 g prepared activated carbon was added to each bottle. The bottles were rolled at a constant rotation of 100 rpm for 72 h to reach the equilibrium.

Sampling was performed by removing 5 mL aliquots at predetermined time intervals. The samples were then analyzed for cyanide as above mentioned method. The amount of cyanide adsorption at equilibrium, q_e (mg/g), was calculated by:

$$q_e = \frac{(c_0 - c_e)V}{W}$$

where C_0 and C_e (mg/L) are initial ($t=0$) and equilibrium cyanide concentrations, respectively. V is the volume of the solution (L) and W is the mass of dry carbon used (g).

2.3 Validity of adsorption isotherm

Apart from the correlation coefficient (R^2), the Marquardt's percent standard deviation (MPSD) and the hybrid error function (HYBRID) were also used to measure the goodness-of-fit. MPSD and HYBRID can be defined as:

$$MPSD = 100 \sqrt{\frac{1}{N-P} \sum_{i=1}^N \left(\frac{q_{e_i}^{exp} - q_{e_i}^{cal}}{q_{e_i}^{exp}} \right)^2} \quad (3)$$

$$HYBRID = \frac{100}{N-P} \sum_{i=1}^N \left[\frac{(q_{e_i}^{exp} - q_{e_i}^{cal})^2}{q_{e_i}^{exp}} \right] \quad (4)$$

where $q_{e_i}^{exp}$ is the observation from the batch experiment i , $q_{e_i}^{cal}$ is the estimate from the isotherm for corresponding $q_{e_i}^{exp}$, N is the number of observations in the experimental isotherm and P is the number of parameters in the regression model. The smaller MPSD and HYBRID values indicate more accurate estimation of q_e value.

MPSD and HYBRID functions were used in addition to R^2 because the number of parameters in the regression model (i.e., P parameter) is effective in them.

3. Results and discussion

3.1 Linear regression method

In this study, equilibrium data were fitted by four "two-parameter isotherms" including Freundlich, Langmuir, Dubinin-Radushkevich and Temkin and two "three-parameter isotherms" including Redlich-Peterson and Koble-Corrigan. The Langmuir adsorption model describes monolayer adsorption of adsorbate onto a homogeneous adsorbent surface [13]. Moreover, there is negligible interaction between the adsorbed molecules and adsorption sites having uniform energies [14]. The empirical Freundlich model is based upon the assumption of multilayer formation of adsorbate on the heterogeneous solid surface of the adsorbent and assumes that the stronger binding sites are occupied first and that the binding strength decreases with the

increasing degree of site occupation [15]. Values K_F and $1/n$ are Freundlich constants related to adsorption capacity and intensity of adsorption, respectively. The lower fractional value of $1/n$ [$0 < (1/n) < 1$] indicates that weak adsorptive forces are effective on the surface of activated carbon [16]. The Temkin model considered the effects of some indirect adsorbate/adsorbate interactions on adsorption isotherms [17]. The Dubinin-Radushkevich equation assumes that the amount adsorbed corresponding to any adsorbate concentration is a Gaussian function of the Polanyi potential [18]. The three-parameter Redlich–Peterson equation consists of both features of Langmuir and Freundlich isotherm models [19]. Koble–Corrigan model is also three-parameter equation which has an exponential dependence on concentration in the numerator and denominator. This model is a combination of the Langmuir and Freundlich isotherm type models and is usually used with heterogeneous adsorption surfaces [20].

Langmuir isotherm model can be linearized into at least four different types as shown in Table 1. The relative parameters of each type of Langmuir isotherm were obtained from the plots of $[C_e/q_e \text{ vs. } C_e]$, $[1/q_e \text{ vs. } 1/C_e]$, $[q_e \text{ vs. } q_e/C_e]$, and $[q_e/C_e \text{ vs. } q_e]$. Also, the relative parameters of Freundlich, Dubinin-Radushkevich, Temkin, Redlich-Peterson, and Koble-Corrigan isotherms were obtained from the plots of $[\ln(q_e) \text{ vs. } \ln(C_e)]$, $[\ln(q_e) \text{ vs. } \varepsilon^2]$, $[q_e \text{ vs. } \ln(C_e)]$, $[\ln((AC_e/q_e) - 1) \text{ vs. } \ln(C_e)]$ and $[(1/C_e)^p \text{ vs. } (1/q_e)]$, respectively. The linear regression method of least squares is used for drawing the trend lines. In the case of Redlich-Peterson and Koble-Corrigan isotherms, the constants A_{RP} and P were obtained by maximizing the R^2 value using a trial and error method that was optimized by 20 iterations using the solver add-in function, in Microsoft Excel. Linear expression of these isotherm equations and the way to obtain the isotherm parameters are given in Table 1.

The values of the parameters and the correlation coefficients, Marquardt's percent standard deviation (MPSD) and the hybrid error function (HYBRID) obtained are listed in Table 2.

The applicability of the isotherm equation to describe the adsorption process was judged by the correlation coefficients (i.e., R^2). The adsorption isotherm models fitted the data, based on the R^2 values, in the order of: Koble–Corrigan > Redlich-Peterson > Freundlich > Langmuir-type (I) > Temkin > Langmuir-type(II) > Dubinin–Radushkevich > Langmuir-type (III&IV) isotherm.

The above order revealed that the equilibrium data are better fitted by the three-parameter models rather than the two-parameter models. The Koble–Corrigan model was found to best represent the equilibrium data, showing that the surface of activated carbon for adsorption of free cyanide may be heterogeneous with a different energy distribution.

The Freundlich isotherm model fitted the experiment data better than Langmuir isotherm model, also suggested that the surface of activated carbon for adsorption of cyanide is heterogeneous. Furthermore, multilayer adsorption of cyanide has been proposed by Freundlich isotherm model. Value of $n > 1$ represents a favorable adsorption condition. Between different linear types of Langmuir model, type (I) best represent the equilibrium data.

In Fig.1.a the predicted amount of adsorption at equilibrium by various equilibrium isotherm models obtained from the linear regression method was plotted against the experimental values. As shown in Fig.1.a, the difference between experimental data and calculated values by Koble-Corrigan isotherm is very low and it is showing that, this isotherm model is the best isotherm for predicting of the amount of cyanide adsorbed by activated carbon at equilibrium. MPSD and HYBRID values (Table 2), also suggesting that Koble–Corrigan isotherm provides a better model of the sorption system.

Table 1: Isotherms and their linearized expressions

Isotherms	Equations	Linear expression	Plot	Parameters	
Freundlich**	$q_e = K_F(C_e)^{1/n}$	$\ln q_e = \ln K_F + n^{-1} \ln C_e$	$\ln q_e \text{ vs. } \ln C_e$	$K_F = \exp(\text{intercept}), n = (\text{slope})^{-1}$	
Langmuir**	$q_e = (q_m K_L C_e) / (1 + K_L C_e)$	Type(I)	$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m}$	$(C_e/q_e) \text{ vs. } C_e$	$q_m = (\text{slope})^{-1}$, $K_L = \text{slope}/\text{intercept}$
		Type(II)	$\frac{1}{q_e} = \frac{1}{K_L q_m C_e} + \frac{1}{q_m}$	$1/q_e \text{ vs. } 1/C_e$	$q_m = (\text{intercept})^{-1}$, $K_L = \text{intercept}/\text{slope}$
		Type(III)	$q_e = q_m - \left(\frac{1}{K_L}\right) \frac{q_e}{C_e}$	$q_e \text{ vs. } q_e/C_e$	$q_m = \text{intercept}$, $K_L = -(\text{slope})^{-1}$
		Type(IV)	$\frac{q_e}{C_e} = K_L q_m - K_L q_e$	$q_e/C_e \text{ vs. } q_e$	$q_m = -(\text{intercept}/\text{slope})$, $K_L = -\text{slope}$

Temkin**	$q_e=q_m \ln(K_T C_e)$	$q_e=q_m \ln K_T + q_m \ln C_e$	q_e vs. $\ln C_e$	$q_m=\text{slope}, K_T= \exp(\text{intercept}/\text{slope})$
Dubinin–Radushkevich**	$q_e=q_m \exp(-D\varepsilon^2)$ that $\varepsilon=RT \ln(1+C_e^{-1})$	$\ln q_e=\ln q_m - D\varepsilon^2$	$\ln q_e$ vs. ε^2	$q_m=\exp(\text{intercept}), D= -\text{slope}$
Redlich–Peterson***	$q_e=(A_{RP} C_e)/(1+B_{RP} C_e^g)$	$\ln[(A_{RP} C_e/q_e)-1]=g \ln C_e + \ln B_{RP}$	$\ln[(A_{RP} C_e/q_e)-1]$ vs. $\ln C_e$	$g=\text{slope}, B_{RP}=\exp(\text{intercept}), A_{RP}$
Koble–Corrigan***	$q_e=(A_{KC} C_e^P)/(1+B_{KC} C_e^P)$	$(1/q_e)=(1/A_{KC} C_e^P)+(B_{KC}/A_{KC})$	$(1/q_e)$ vs. $(1/C_e^P)$	$A_{KC}=(\text{slope})^{-1}, B_{KC}=\text{intercept}/\text{slope}, P^*$

* optimized using a trial and error method

** two-parameter isotherm

*** three-parameter isotherm

Table 2: Isotherms parameters by linear regression method for the sorption of cyanide by activated carbon.

Isotherms	R ²	MPSD	HYBRID	parameters
Freundlich	0.9902	3.6961	3.4303	$K_F=3.1393 \text{ (mg g}^{-1}\text{)(L mg}^{-1}\text{)}^{1/n}, n=2.4938$
Langmuir	Type(I)	0.9652	12.1201	$q_m=47.62 \text{ (mg g}^{-1}\text{); } K_L=0.007179 \text{ (L mg}^{-1}\text{)}$
	Type(II)	0.9410	10.541	$q_m=37.9 \text{ (mg g}^{-1}\text{); } K_L=0.00129 \text{ (L mg}^{-1}\text{)}$
	Type(III)	0.5902	22.432	$q_m= 31.102 \text{ (mg g}^{-1}\text{); } K_L= 0.01894 \text{ (L mg}^{-1}\text{)}$
	Type(IV)	0.5902	87.725	$q_m= 34.3 \text{ (mg g}^{-1}\text{); } K_L=0.00112 \text{ (L mg}^{-1}\text{)}$
Temkin	0.9515	8.7449	17.0321	$q_m=9.766 \text{ (mg g}^{-1}\text{); } K_T=0.0815 \text{ (L mg}^{-1}\text{)}$
Dubinin–Radushkevich	0.7547	18.9112	96.6844	$q_m=30.08 \text{ (mg g}^{-1}\text{); } D=0.00032 \text{ (mol}^2 \text{ kJ}^{-2}\text{)}$
Redlich–Peterson	0.9946	4.7277	4.2905	$g=0.626; B_{RP}=1.06 \text{ (L mg}^{-1}\text{)}^g; A_{RP}= 4 \text{ (mg g}^{-1}\text{)(L mg}^{-1}\text{)}$
Koble–Corrigan	0.9996	0.9613	0.1522	$A_{KC}=3.52 \text{ (mg g}^{-1}\text{)(L mg}^{-1}\text{)}^P; B_{KC}=-0.45 \text{ (L mg}^{-1}\text{)}^P; P= 0.1$

Table 3: Isotherms parameters by Non-linear regression method for the sorption of cyanide by activated carbon.

Isotherms	R ²	MPSD	HYBRID	parameters
Freundlich	0.9917	4.3973	3.6382	$K_F=2.7149 \text{ (mg g}^{-1}\text{)(L mg}^{-1}\text{)}^{1/n}, n= 2.3368$
Langmuir	0.9455	13.4903	32.4525	$q_m=48.1693 \text{ (mg g}^{-1}\text{); } K_L=0.0065 \text{ (L mg}^{-1}\text{)}$
Temkin	0.9537	9.9992	20.0317	$q_m=10.2647 \text{ (mg g}^{-1}\text{); } K_T=0.0715 \text{ (L mg}^{-1}\text{)}$
Dubinin–Radushkevich	0.7803	34.0710	212.3680	$q_m=33.7236 \text{ (mg g}^{-1}\text{); } D=0.0007 \text{ (mol}^2 \text{ kJ}^{-2}\text{)}$
Redlich–Peterson	0.9917	4.4045	3.6490	$g=0.5723; B_{RP}=112.3118 \text{ (L mg}^{-1}\text{)}^g; A_{RP}= 305.4438 \text{ (mg g}^{-1}\text{)(L mg}^{-1}\text{)}$
Koble–Corrigan	0.9996	0.7899	0.1493	$A_{KC}=3.6145 \text{ (mg g}^{-1}\text{)(L mg}^{-1}\text{)}^P; B_{KC}=-0.42871 \text{ (L mg}^{-1}\text{)}^P; P=0.105963$

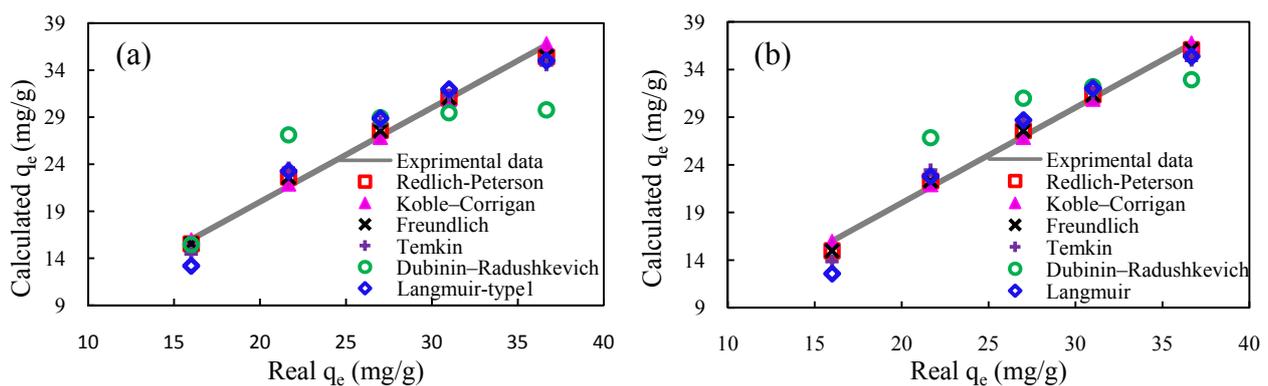


Fig.1. Calculated q_e by different isotherm models obtained from (a) Linear regression method and (b) Non-linear regression method vs. experimental q_e

3.2. Non-linear regression method

In Non-linear regression method, the abilities of the widely used isothermsto model the equilibrium data were examined by a trial-and-error procedure using the *solver* add-in with Microsoft's spreadsheet, Microsoft Excel. The R² value is used to minimize the error distribution between the experimental equilibrium data and the predicted isotherms. Table 3 shows the isotherm parameters obtained using the

Non-linear method. The result of Non-linear regression method also revealed that the Koble-Corrigan isotherm fits the data in the best way. It can be seen that except than the Langmuir isotherm, the Non-linear regression method better fitted the data in comparison with the linear regression method.

The Langmuir constants obtained from the non-linear and linear methods differed even when compared with the results of Langmuir-1, which had the highest coefficient of determination for Langmuir isotherm (Tables 2 and 3). It seems that the best fit was obtained by Langmuir-1 in comparison with other Langmuir linear equations and also the Non-linear regression method due to the highest coefficient of determination and the lowest hybrid error function.

In Fig.1.b. the prediction of the amount of adsorption at equilibrium by various equilibrium isotherm models obtained from Non-linear regression method was plotted against the experimental values. As shown in Fig.1.b., the difference between experimental data and calculated values by Koble-Corrigan isotherm is very lower than the other isotherm models. Comparison between Figs.1.a and b suggests that the Non-linear regression method is a better way to fit the equilibrium data than the linear regression method.

4. Conclusion

Three-parameter isotherm models fitted the cyanide adsorption equilibrium data better than the two-parameter isotherm models and among them the adsorption equilibrium data of cyanide were best represented by Koble–Corrigan isotherm model, showing that the surface of activated carbon for adsorption of free cyanide may be heterogeneous with a different energy distribution.

The Freundlich isotherm model fitted the equilibrium data better than Langmuir isotherm model, revealing that the adsorption of cyanide onto the activated carbon was multilayer adsorption. Also, between four different linear types of Langmuir model, type (I) shows better fitting with experimental data.

It was showed that the Non-linear regression method is a better way to obtain the isotherm parameters.

5. References

- [1] R. Moran, Cyanide Uncertainties: Observations on the Chemistry, Toxicity, and Analysis of Cyanide in Mining-Related Waters, Mineral Policy Center, Protecting Communities and the Environment, Issue Paper No. 1, 1998.
- [2] A. Akcil, T. Mudder, Microbial destruction of cyanide wastes in gold mining: process review, *Biotechnology Letters*, Vol. 25, pp. 445–450, 2003.
- [3] C.A. Papadimitriou, P. Samaras, G.P. Sakellariopoulos, Comparative study of phenol and cyanide containing wastewater in CSTR and SBR activated sludge reactors, *Bioresource Technol.*, Vol. 100, pp. 31–37, 2009.
- [4] H. Deveci, E.Y. Yazıcı, I. Alp, T. Uslu, Removal of cyanide from aqueous solutions by plain and metal-impregnated granular activated carbons, *Int. J. Miner. Process.*, Vol. 79, pp. 198–208, 2006.
- [5] R.R. Dash, C. Balomajumder, A. Kumar, Removal of cyanide from water and wastewater using granular activated carbon, *Chem. Eng. J.*, Vol. 146, pp. 408–413, 2009.
- [6] W. Xing, H.H. Ngo, S.H. Kim, W.S. Guo, P. Hagare, Adsorption and bioadsorption of granular activated carbon (GAC) for dissolved organic carbon (DOC) removal in wastewater, *Bioresource Technol.*, Vol. 99, pp. 8674–8678, 2008.
- [7] K. Li, Z. Zheng, X. Huang, G. Zhao, J. Feng, J. Zhang Equilibrium, kinetic, thermodynamic studies on the adsorption of 2-nitroaniline onto activated carbon prepared from cotton stalk fibre, *J. Hazard. Mater.*, article in press.
- [8] A. Olgun, N. Atar, Equilibrium and kinetic adsorption study of Basic Yellow 28 and Basic Red 46 by a boron industry waste, *J. Hazard. Mater.*, Vol. 161, pp. 148–156, 2009.
- [9] C.A. Basar, Applicability of the various adsorption models of three dyes adsorption onto activated carbon prepared waste apricot, *J. Hazard. Mater.*, Vol. B135, pp. 232–241, (2006).
- [10] A. Olgun, N. Atar, Equilibrium and kinetic adsorption study of Basic Yellow 28 and Basic Red 46 by a boron industry waste, *J. Hazard. Mater.*, Vol. 161, pp. 148–156, 2009.

- [11] K. Vasanth Kumar, K. Porkodi, F. Rocha, Isotherms and thermodynamics by linear and non-linear regression analysis for the sorption of methylene blue onto activated carbon: Comparison of various error functions, *J. Hazard. Mater.*, Vol. 151, pp. 794–804, 2008.
- [12] K. Vasanth Kumar, Optimum sorption isotherm by linear and non-linear methods for malachite green onto lemon peel, *Dyes and Pigments*, Vol. 74, pp. 595-597, 2007.
- [13] T.S. Anirudhan, L. Divya, P.S. Suchithra, Kinetic and equilibrium characterization of uranium(VI) adsorption onto carboxylate functionalized poly (hydroxyethylmethacrylate)-grafted lignocellulosics, *J. Environ. Manage.*, Vol.90, pp. 549-560, 2009.
- [14] K.G. Sreejalekshmi, K. Anoop Krishnan, T.S. Anirudhan, Adsorption of Pb(II) and Pb(II)-citric acid on sawdust activated carbon: Kinetic and equilibrium isotherm studies, *J. Hazard. Mater.*, Vol. 161, pp. 1506–1513, 2009.
- [15] X. Shen, X. Shan, D. Dong, X. Hua, G. Owens, Kinetics and thermodynamics of sorption of nitroaromatic compounds to as-grown and oxidized multiwalled carbon nanotubes, *J. Colloid Interf. Sci.*, Vol.330, pp. 1–8, 2009.
- [16] H.A. Omar, H. Moloukhia, Use of activated carbon in removal of some radioisotopes from their waste solutions, *J. Hazard. Mater.*, Vol. 157, pp.242–246, 2008.
- [17] B.H. Hameed, A.A. Rahman, Removal of phenol from aqueous solutions by adsorption onto activated carbon prepared from biomass material, *J. Hazard. Mater.*, Vol. 160, pp. 576–581, 2008.
- [18] C. Hsieh, H. Teng, Influence of mesopore volume and adsorbate size on adsorption capacities of activated carbons in aqueous solutions, *Carbon*, Vol. 38, pp. 863–869, 2000.
- [19] Y.A. Yahaya, M.M. Don, S. Bhatia, Biosorption of copper (II) onto immobilized cells of *Pycnoporus sanguineus* from aqueous solution: Equilibrium and kinetic studies, *J. Hazard. Mater.*, Vol. 161, pp. 189–195, 2009.
- [20] R. Han, J. Zhang, P. Han, Y. Wang, Z. Zhao, M. Tang, Study of equilibrium, kinetic and thermodynamic parameters about methylene blue adsorption onto natural zeolite, *Chem. Eng. J.*, Vol. 145, pp.496–504, 2009.