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Modeling of Cadmium Removal on Lignite (Thar Coal) from Aqueous System

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Abstract

Complete modeling of cadmium removal on Thar coal which is lignite in its nature has been carried out. A Design of Experiment (DoE) approach has been used for simultaneous optimization of different sorption parameters. DoE showed the positive effect of agitation time on removal of cadmium and negative effect of pH, interaction term pH and amount also showed a negative effect on removal. Values of sorption capacity calculated at optimum parameters for Langmuir, Freundlich and D-R isotherm were 100 mgg^{-1}, 47.86 mgg^{-1} and 8.422 mgg^{-1} respectively. Among all tested kinetic models second order rate equation showed a best fit.

***Keywords*:** Lignite, Design of experiments, Water treatment, Adsorptive removal.

Introduction

Cadmium (Cd) is considered as pollutant of concern because of its adverse effect on endocrine system [1-2]. International Agency for Research in Cancer (IARC) classified cadmium as a group I carcinogen whereas Environmental Protection Agency (EPA) has placed it in group B1 as a probable human carcinogen [3]. FAO–WHO jointly recommend daily intake of cadmium from all sources not more than 1–1.2 µg kg^{-1} body mass [4]. Cadmium salts are soluble in water and can easily be part of our food chain through edible parts of the plant which are grown in polluted soil or irrigated by polluted water [5,6].

Removal of metal ions using solid surface is a good, safe and economical alternate to the commonly available chemical precipitation, nano-filtration and ultra-filtration, reverse osmosis, solvent extraction, and ion exchange [7,8]. Activated carbons is one of the most widely used surface owing to their high removal capabilities for a large number of heavy metal ions, but the high cost of activated carbons limits their usage [9].

However, there are only few investigations reported on the use of raw coal as effective adsorbent and in all few cases studied metal is chromium [10]. To the best of our knowledge there is no report on modeling of removal of any contaminant using Thar coal. The Thar coals are lignite with number of minerals on its surface [11]. We anticipate exploiting the surface groups/minerals of coal for removal of Cd(II) ions. Our aim is to optimize cadmium removal by Design of Experiment (DoE) by taking in account all interaction parameters by multivariate sorption. By DoE different removal parameters can be optimized using lesser number of experimental runs. Advantage of DoE is the possibility to study interaction effects of different parameters on removal which can in turn help to find actual optimum parameters, which is not possible by uni-variant analysis. We herein also report a detailed kinetic and thermodynamic study of cadmium removal by lignite Thar Coal.

Materials and Methods

Sample of Thar coal was collected from Thar Coal reservoirs (Tharparkar, Sindh, Pakistan). Sample was crushed, powdered and sieved to mesh size of 30. Powdered coal was dried in an oven at 100°C.

Standard solutions

Stock solution of cadmium (1000ppm) was prepared by dissolving weighed amount of cadmium acetate. Dilute solutions (10-100ppm) were prepared by successive dilution from stock solution.

Instrumentation

A Perkin Elmer Atomic Absorption Spectrometer (Model-AA800) was used for the determination of cadmium concentration in the solutions before and after adsorption. The instrument was calibrated by standard method and absorbance of the solutions was measured.

pH measurements were carried out using Thermo Scientific Orion 5 Star (ISE. Cond. DO Benchtop, 8102BNUWP; made in USA) pH-meter. For the batch adsorption studies Shaking Incubator Model 1-40000 Irmeco GmbH (Geesthacht/ Germany) was used.

Energy dispersive spectroscopic (EDS) study of coal

Surface of coal was characterized by Energy Dispersive X-ray (EDX) analysis using BRUKER X-FLASH 4010 133ev (Made in Germany). Fig. 1 shows the presence of Carbon (56.99%), Oxygen (38.22 %), sodium (0.74), Mg (0.48), Al (0.94), Silicon (1.54), sulfur (0.33), calcium (0.57) and Iron (0.19).

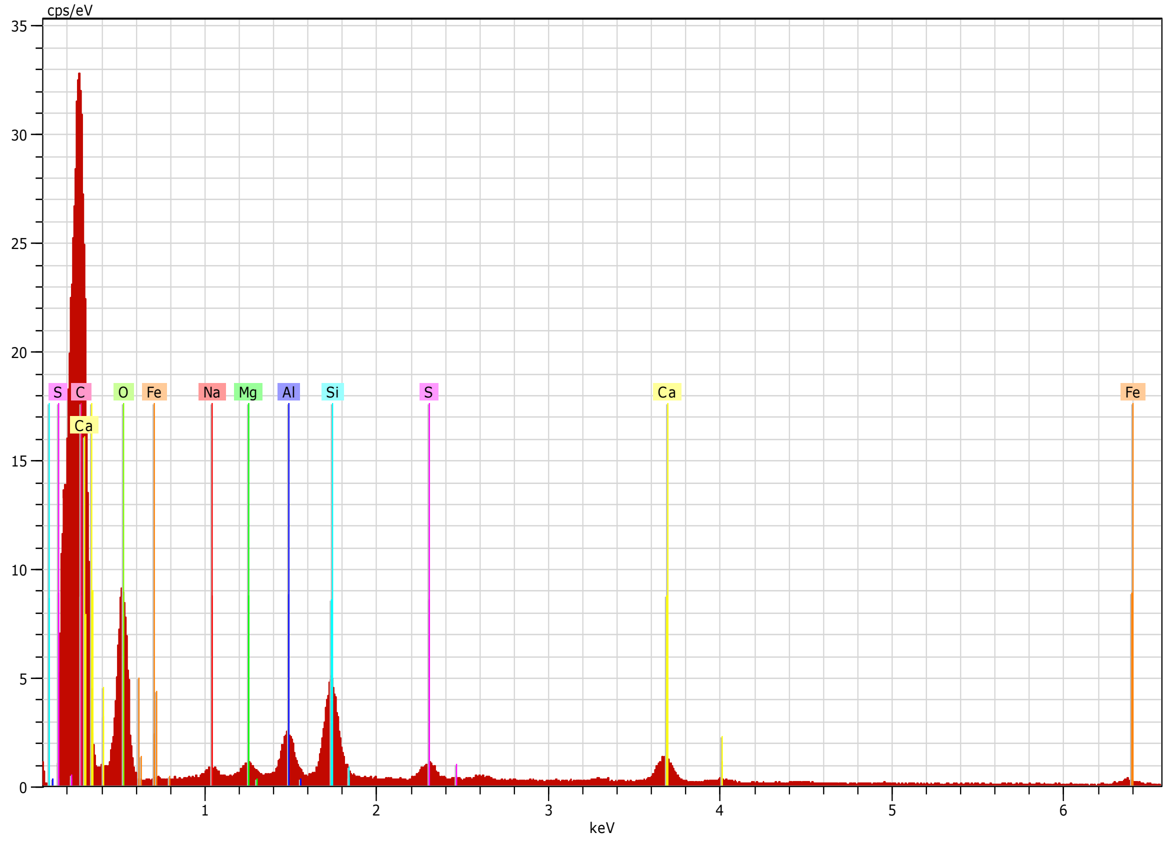

Figure 1. **EDS of the raw Thar coal sample**

Batch sorption experiments

Modeling of cadmium removal on coal surface was first optimized by designing multivariate experiments and conducting them by batch sorption experiments [12]. Weighed amounts (0.01-0.1g) of raw grinded coal were mixed with 20 ml sample solution containing cadmium ions (10-100 ppm). The pH of solution was maintained between 2 to 9 and the mixtures were agitated at 100 rpm for 10-180 min., while temperature was kept constant at 30°C. Removal efficiency of coal was calculated from equation (1):

$$\% \text{removal} = \frac{C_o - C_e}{C_o} \times 100$$

(1)

Where C_o and C_e are the before and after adsorption concentration of cadmium ions.

Experimental design

A design consists of eighteen experimental runs were developed using Draper-Lin composite model to optimize the individual as well as interaction effect of cadmium concentration, pH of cadmium solution, amount of coal and agitation time on the removal of cadmium by coal [13-14]. Table 1 shows the design variables and their ranges used for experimental trials, whereas Table 2 shows the trial levels along with both predicted and experimental values of cadmium removal.

Table 1. **Levels of factors used in experimental design for removal of cadmium ions.**

Independent variable Range	Coded levels		
	-1	0	+1
Amount, A (mg)	10	55	100
Concentration (mgL^{-1}), B pH, C	10	55	100
Time, D (min.)	2	5.5	9

Table 2. **Experimental design and results for the removal of cadmium (II) ions.**

	Coded values				% Removal (Predicted)	% Removal (Experimental)
	A	*B*	*C*	*D*		
1	-1	-1	+1	-1	90.2	90.3
2	-1	-1	-1	-1	92.8	93.2
3	0	+1	0	0	95.0	95.1
4	+1	+1	-1	-1	76.9	76.5
5	+1	+1	+1	-1	99.8	99.9
6	0	0	0	-1	99.9	99.9
7	-1	+1	+1	+1	100.0	100.0
8	+1	0	0	0	77.0	77.1
9	0	0	+1	0	97.4	97.5
10	+1	-1	+1	+1	100.0	100.0
11	0	0	-1	0	49.2	49.3
12	+1	-1	-1	+1	78.5	78.6
13	-1	+1	-1	+1	100	100
14	0	-1	0	0	78.0	78.1
15	-1	0	0	0	88.1	88.1
16	0	0	0	+1	59.1	59.2
17	0	0	0	0	78.7	78.5
18	0	0	0	0	55.0	55.1

Results and Discussion

Interpretation of residual and response plots

To assess the applicability of the model experimental values were plotted against the fitted values. Fig. 2a show that experimental points are reasonably aligned showing the normal distribution indicating the validity of equation used for design. To check the maximized response 3D response graphs were plotted by taking two test variables and other two were fixed at their optimum response. Fig. 2b shows the combined effect of sorbent amount and cadmium ions concentration in solution. Sorption increases with increase in sorbent amount. Fig. 2c shows the intellectual effect of pH and sorbent amount, adsorption of cadmium on coal decreases with increase in pH of the solution. Fig. 2d shows that sorption increases with increases in agitation time. Combined effect of concentration and pH is shown in Fig. 2e. While combined effect of time and concentration is shown in Fig. 2f.

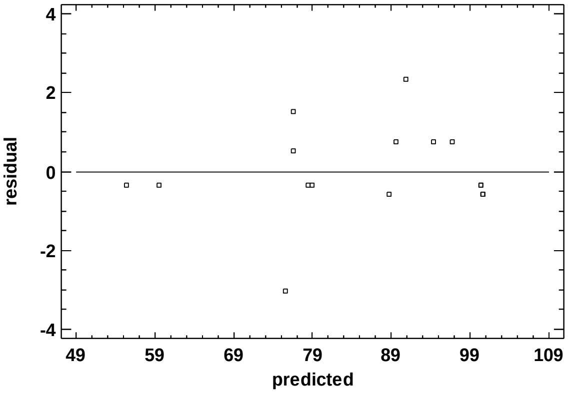

Figure 2a. **Residual plot of model against predicted removal values of cadmium ions**

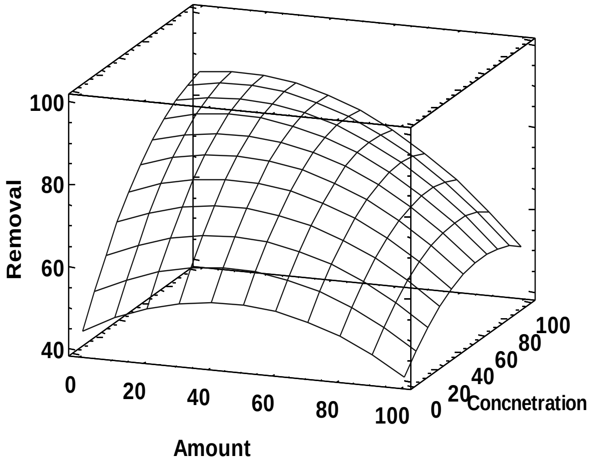

Figure 2b. **Response surface plots for interaction effect of amount and concentration on removal**

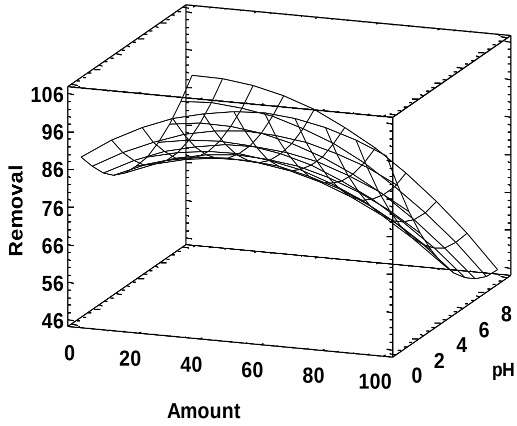

Figure 2c. **Response surface plots for interaction effect of amount and pH on removal**

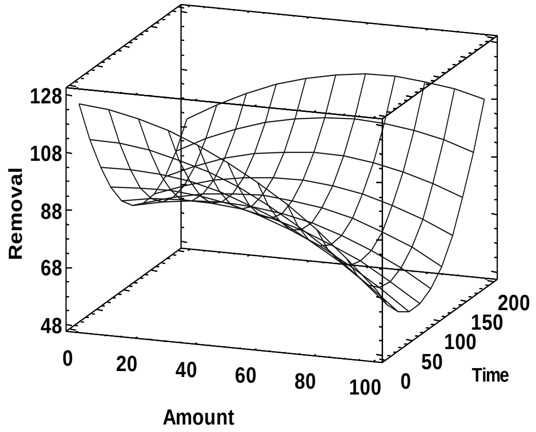

Figure 2d. **Response surface plots for interaction effect of amount and time on removal**

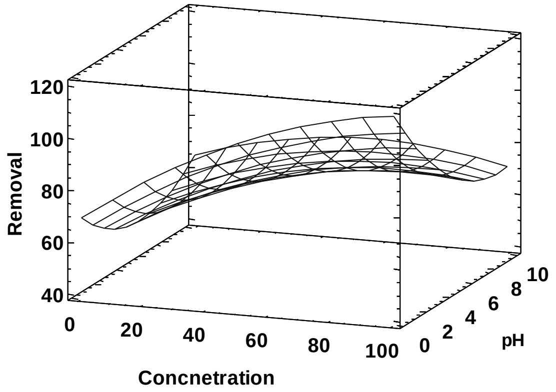

Figure 2e. **Response surface plots for interaction effect of concentration and pH on removal**

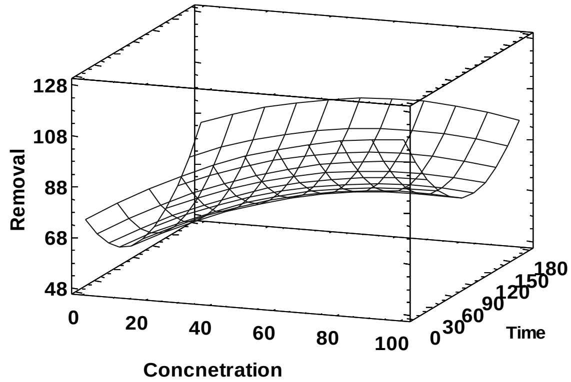

Figure 2f. **Response surface plots for interaction effect of concentration and time on removal**

Pareto chart

Fig. 3 shows the pareto chart of the estimated effects in decreasing order of magnitude. From the pareto chart it is clear that the agitation time has the positive significant effect on the sorption, while the pH and interaction term pH and amount has the negative significant effect on the sorption.

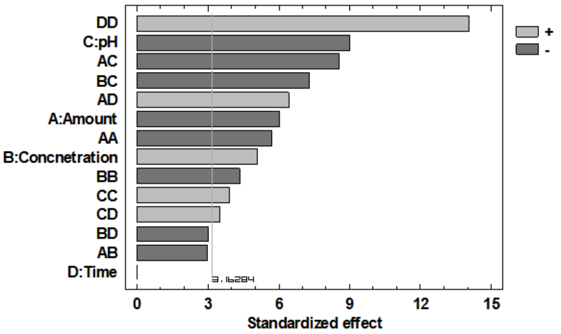

Figure 3. **Pareto chart for the sorption of cadmium ions on coal**

Predicted optimum parameters and method validation

In order to validate the method, experiments were carried out at optimum parameters amount 38 mg, concentration 93 mg L^{-1}, pH 2.0, and time 130 min, predicted by software. Experimental values were very close to predicted values for the removal of cadmium. The closeness of these values proved the validation of CCD model for prediction of optimum parameters for the removal of cadmium.

Kinetics modeling for removal of cadmium of Sorption

In order to get insight of the adsorption mechanism different kinetic models were evaluated using the data obtained at different time intervals keeping pH, concentration and sorbent amount at their optimum values. Data was tested by different kinetic equations [15-16] namely Lagergren (eq. 2), second order (eq. 3) and Moris-Weber (eq. 4).

$\log(q_1 e - q_t)$ Lagergren kinetic model. A basic and widely applied Lagergren model was tested to validate the data using equation (2):

$$\log(q_e - q_t) = \log q_e - \frac{k_t}{2.303} \qquad (2)$$

$$\frac{t}{qt} = \frac{1}{k_2 q_{e^2}} + \frac{1}{qe} t \qquad (3)$$

$$a_t = k_i \sqrt{t} \qquad (4)$$

Where qe is the amount of cadmium ions adsorbed at equilibrium, qt is the amount of cadmium ions adsorbed at time (t).

Cadmium removal data did not follow both Lagergren and Morris-Weber models but the data was very good fit to the pseudo second order model Fig. 4 with the R^2 value of 0.9997 also the q_e value obtained from plot (625 mgg^{-1}) was in good agreement with experimental value (631 mgg^{-1}). These results indicate that the rate limiting step may be chemical adsorption involving valent forces through sharing or the exchange of electrons between the coal and cadmium ions [17].

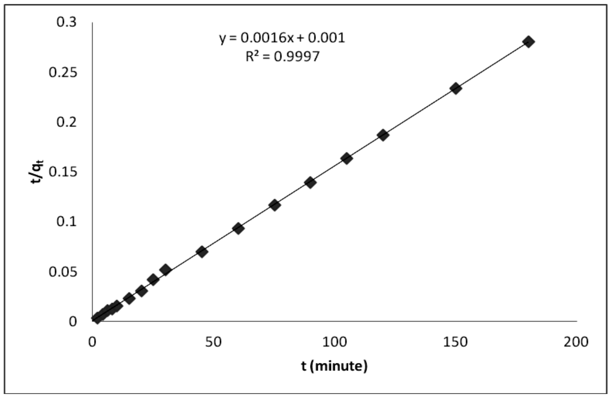

Figure 4. **Pseudo second order plot for adsorption of cadmium ions**

Equilibrium study

Removal % of cadmium ions were recorded by changing the concentration of cadmium solution and keeping all other parameters such as pH, shaking time, adsorbent dose and volume of adsorbate at their optimum value. The data was examined for the applicability of equilibrium adsorption isotherms to check the type of adsorptive removal.

Langmuir isotherm

To check weather removal follows the monolayer adsorption phenomenon linear form of Langmuir isotherm was applied using following equation:

$$\frac{C_e}{C_{ads}} = \frac{1}{Qb} + \frac{C_e}{Q} \qquad (5)$$

Where Q is the maximum sorption capacity (mgg^{-1}) and b is the Langmuir constant. The sorption capacity calculated was 100mgg^{-1}. The graph between Ce and Ce/Cads was linear with the regression coefficient of 0.996 which supports the finding of kinetic model i.e. pseudo second order [17]. Separation factor was calculated by using equation 6.

$$R_L = \frac{1}{1 + bC_i} \qquad (6)$$

RL value describes the type of Langmuir isotherm [12] to be irreversible (R_L= 0), favorable ($0 < R_L < 1$), linear (R_L=1) or unfavorable (R_L>1). R_L factor calculated for the sorption of cadmium on coal was found to be in the range of 0.002-0.28indicating the favorable sorption of cadmium ions onto the surface of coal.

Freundlich isotherm

Freundlich isotherm is an empirical equation employed to describe the heterogeneous system.

$$\log C_{ads} = \log K_F + \frac{1}{n_F}\log C_e \qquad (7)$$

Where 1/n is the heterogeneity factor, if 1/n <1 it is referred that adsorption is chemi-sorption in nature and if 1/n >1 adsorption is co-operative in nature [18]. Sorption capacity and value of 1/n calculated for the Freundlich isotherm was 47.86 mg g^{-1} and 0.4458 respectively.

D-R isotherm

D-R equation is the fundamental equation to quantitatively describe the adsorption by micro porous sorbents. Equation 8 was used to calculate DR isotherm parameters.

$$\ln C_{ads} = K_{D-R} - \beta\varepsilon^2 \qquad (8)$$

where Cads is the amount of cadmium ions adsorbed per unit mass of coal and ε is polanyi potential calculated from Ce which is the amount of cadmium ions in liquid phase at equilibrium while β is D-R constant. D-R capacity calculated from the slope of the plot was 8.422 mg.g^{-1} and the energy for the adsorption of cadmium ions was 16.14 KJ mol^{-1} calculated using following equation.

$$E = \frac{1}{\sqrt{-2\beta}} \qquad (9)$$

Thermodynamic study

Sorption of cadmium ions onto the coal was calculated by varying the temperature from 10-40°C while other conditions were kept at their optimum values.

$$\ln K_C = \frac{F_e}{1-F_e} \qquad (10)$$

where F_e is the fraction sorbed at equilibrium, was plotted against 1/*T*. The values of Δ*H*, Δ*S* and Δ*G* were calculated using the relationships from the slope and intercept of the linear plot,

$$\ln K_c = \frac{-\Delta H}{RT} + \frac{\Delta S}{R}\, and\, \Delta G = -RT\ln Kc \qquad (11)$$

The values of ΔH, ΔS and ΔG were 53.67595 KJ mol^{-1}, 0.163707 J mol^{-1} K and-5.38418 to-2.46306 KJ mol^{-1}respectively. Positive value of ΔH indicates the endothermic nature of sorption which in turn shows the chemical interaction of coal constituents and cadmium ions.

Conclusion

This paper reports a complete equilibrium, kinetic and thermodynamic modeling of cadmium removal on Lignite (Thar Coal). EDS study of coal showed number of minerals onto the surface. A multivariate design was successfully developed for optimization of sorption parameters. Kinetic and thermodynamic values showed chemical interaction between cadmium ions and Thar coal.

References

1. M. K. Daud, S. Ali, M. T. Variath and S. J. Zhu, *Chemosphere.*, 93 (2013) 2593.
2. S. Telisman, P. Cvitkovic and J. Jurasovic, *J. Environ. Health Persp.*, 108 (2000) 45.
3. J. C. Merrill, J. J. P. Morton and S. D. Soileau, Metals: cadmium, in Principles and Methods of Toxicology. (A. W. Hayes, Eds) Taylor and Francis, London, UK, (2001) 665.
4. G. Bortoleto, G. T. Macarovscha and S. Cadore, *J. Braz. Chem. Soc.*, 15 (2004) 313.
5. M. K. Daud, M. T. Variath, S. Ali, U. Najeeb, M. Jamil, Y. Hayat, M. Dawood, M. I. Khan, M. Zaffar, S. A. Cheema, X. H.

Tong and S. Zhu, *J. Hazard. Mater*., 168 (2009) 614.

6. P. N. Williams, M. Lei, G. Sun, Q. Huang, Y. Lu, C. Deacon, A. A. Meharg and Y. G. Zhu, *Environ. Sci. Technol*., 43 (2009) 637.
7. E. Korngold, S. Belfer and C. Urtizberea, *J. Desalination*, 104 (1996)197.
8. C. N. Mulligan, R. N. Yong and B. F. Gibbs, *J. Eng. Geol*., 60 (2001)193.
9. B. M. W. P. K. Amarasinghe and R.A. Williams, *Chem. Eng. J*., 132 (2007) 299.
10. J. Anwar, U. Shafique, M. Salman, Waheed-uz-Zaman, S. Anwar and J. M. Anzanoc, *J. Hazard. Mater.*, 171 (2009) 797.
11. A. Sarwar, M. N. Khan and K. F. Azhar, *Energy Sources, Part A: Recovery, Utilization and Environmental Effects.*, 36 (2014) 525.
12. S. Q. Memon, S. M. Hasany, M. I. Bhanger and M. Y. Khuhawar, *J. Colloid Interf. Sci.*, 291 (2005) 84.
13. J. Li, Y. Shi, Y. Cai, S. Moua and G. Jiang, *Chem. Eng. J*.**,**140 (2008) 214.
14. M. J. Sanchez, H. J. Beltran and M. C. Carmona, *Indust. Crops Prod.*,33 (2011) 409.
15. D. M. Ruthven, Principles of adsorption and adsorption processes, wiley, NY (1985).
16. H. QIU, L. LV, B. Pan, Q. ZHANG, W. ZHANG and Q. ZHANG, *J. Zhejiang University SCI. A.*,10 (2009) 716.
17. Y. S. Ho, *J. Hazard. Mater*., 136 (2006) 103.
18. K. Y. Foo and B. H. Hameed, *Chem, Eng*., J. 156 (2010) 2.