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Adsorption Performance for the Removal of Cu(II) on the Ammonium Acetate Modified Sugarcane Bagasse

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ABSTRACT

Sugarcane bagasse, an agricultural waste biomass was innovatively used to prepare ammonium acetate modified sugarcane bagasse via a simple wet impregnation method. The prepared adsorbent was used for the adsorptive removal of copper from aqueous solution. It was found that an increase in adsorbent dosage significantly increased the removal efficiency for copper. Compared to the raw bagasse, the adsorption capacity of the modified bagasse was dramatically enhanced by 116.2%. At pH 5.0, 7.0 and 9.0, the reaction kinetic data were simulated and compared using pseudo-first-order, pseudo-second-order and Elovich kinetic models. Results indicate that both pseudo-second-order and Elovich kinetic models could better describe the adsorption kinetics. This demonstrates that the adsorption of copper onto the modified bagasse was a chemisorption process in which the rate-determining step is diffusion in nature. Thermodynamic analysis demonstrated the enthalpy and entropy of the adsorption process as 643.6 KJ mol^{-1} and 250.5 J mol^{-1} k^{-1}, respectively. The positive value of the reaction enthalpy implies that the uptake of copper increases with a rise in the reaction temperature. The adsorption of copper was spontaneous and endothermic in nature.

INTRODUCTION

Adsorption technique is regarded as one of the most efficient and practical approaches for water purification on the basis of its simplicity and availability of a wide range of adsorbents (Zhang et al. 2014). Various environmental pollutants, including heavy metal ions and organic pollutants proved to be effectively removed by adsorption process (Crini 2006, Gupta et al. 2009). Besides expensive activated carbon, there are many low-cost adsorbents such as agricultural waste biomass, which can be used directly and indirectly for practical water treatment (Bhatnagar & Sillanpa 2010). Agricultural wastes are generated in a huge amount annually. Many agricultural wastes such as sugarcane bagasse, rice husk and wheat straw were successfully used for the adsorptive removal of organic pollutants from wastewater (Han et al. 2008, Sadaf et al. 2014, Nawaz et al. 2014, Song et al. 2011). Agricultural wastes demonstrate their prosperous future in water treatment.

However, these raw agricultural wastes themselves might be ineffective for the removal of some pollutants such as special dyes and heavy metal ions. As such, agricultural wastes are usually subjected to the pretreatment before application of water treatment. Agricultural wastes usually contain a large amount of floristic fibre and functional groups such as carboxyl, hydroxyl, amidogen, which are expected to be responsible for the biosorption process (Han et al. 2006, Gupta et al. 2009). If other useful functional groups were immobilized on the biomass, then the adsorption performance of the modified adsorbents could be enhanced to some extent. One of the best approaches to utilize these agricultural wastes is to synthesize adsorbents by means of a simple wet impregnation method, which is capable of enhancing the adsorption performance dramatically (Li et al. 2015).

In this research, sugarcane bagasse, one of the typical agricultural waste biomass, is innovatively used to prepare ammonium acetate modified sugarcane bagasse via a simple wet impregnation method. As a comparison, both the raw bagasse and the modified bagasse were used for the adsorptive removal of copper from aqueous solution. The adsorption kinetics under different solution pH conditions were investigated and the experimental data were fitted by typical kinetic models including pseudo-first-order, pseudo-second-order and Elovich kinetic models. By the study of adsorption isotherm and thermodynamic analysis, the adsorption mechanism was also analysed and discussed.

MATERIALS AND METHODS

Chemicals: All chemicals used were of analytical grade and used without further purification. Copper sulphate was used to prepare the stock Cu^{2+} solution. Deionized (DI) water was used throughout the study. Other chemicals used were of analytical grade.

Adsorbent preparation: Sugarcane bagasse (bagasse) was collected from Guangxi province of China. It was washed, dried, crushed and sieved using a 40 mesh sieve. Firstly, desired amount of the pretreated bagasse was soaked in 100 mL of 0.5 M ammonium acetate solution for 60 min under constant stirring. Then the treated bagasse was collected by filtration and dried at 80°C overnight. The prepared ammonium acetate modified bagasse was stored in desiccators before use.

Batch adsorption studies: The stock solutions of Cu(II) (500 mg/L) were prepared in DI water at pH 5.0. All working solutions were prepared by diluting the stock solution with DI water to the desired concentration. Adsorption of Cu(II) onto the ammonium acetate modified bagasse was conducted in a series of cylindrical flasks. A desired amount of ammonium acetate modified bagasse (20 mg) was added to a conical flask containing 50 mL of Cu(II) solution with a concentration of 5 mg/L. For the kinetic study, 400 mg of adsorbent was added to 1000 mL of Cu(II) solution. Constant stirring was maintained by mechanical agitation for 24 h. Finally, samples were collected and filtered through a 0.45 µm pore-size membrane before measurement. The reaction temperature was controlled at a constant of 25°C. All the initial solution pH was maintained at pH 5.0 except for the pH effect study. The solution pH adjustment was conducted by addition of diluted HCl or NaOH solution.

Analysis of copper: The Cu(II) ions in the filtrate were measured using an atomic absorption spectrophotometer (WFX-110A) (Ngah & Hanafiah 2008). The adsorption capacity of Cu(II) (q_e and q_t) was calculated by the following equations:

$$q_e = \frac{V \times (C_0 - C_t)}{m} \quad ...(1)$$

$$q_t = (C_0 - C_t)\, V/W \quad ...(2)$$

Where, q_e and q_t (mg/g) are the adsorption capacity at equilibrium and t min; C_0 is the initial concentration of Cu(II) in solution, while C_e and C_t (mg/L) are the concentrations of Cu(II) at equilibrium and t min, respectively; V (L) is the volume of solution, and W (g) is the mass of adsorbent used.

RESULTS AND DISCUSSION

Effect of adsorbent dosage on copper adsorption: Effect of the dosage of the ammonium acetate modified bagasse on copper adsorption was investigated and the results are illustrated in Fig. 1. The uptake of copper at the adsorbent dosage of 10, 20, 40, 60, 80 and 100 mg achieved were

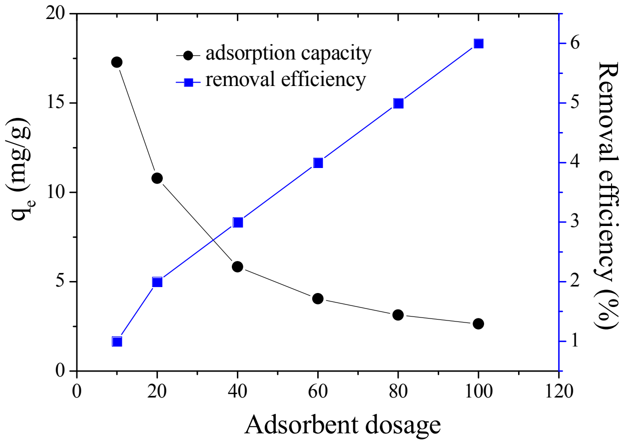

Fig. 1: Effect of adsorbent dosage on the adsorption of copper.

17.28, 10.79, 5.83, 4.04, 3.13 and 2.46 mg/g, respectively. Accordingly, the removal efficiency of copper at the dosage of 10, 20, 40, 60, 80 and 100 mg reached 34.6%, 43.2%, 46.7%, 48.4%, 50.1% and 52.8%, respectively. Considering the uptake and removal efficiency, the dosage of the ammonium acetate modified bagasse was fixed at 20 mg in 50 mL solution in the following tests. On the other hand, compared to the raw bagasse, besides carboxyl and hydroxyl groups, more carboxyl and amino groups are abundant on the surface of the modified sugarcane bagasse. As a result, it is expected that more copper(II) species could be adsorbed on the modified bagasse. It was found that, at the dosage of 20 mg, the uptake of copper using the raw bagasse and the modified bagasse reached 4.99 and 10.79 mg/g, respectively. The adsorption capacity for copper was eventually enhanced by 116.2%. As such, the adsorption capability of bagasse was significantly improved by ammonium acetate treatment.

Adsorption kinetics at different pH conditions: Solution pH could affect the surface properties of ammonium acetate modified bagasse as well as the species distribution of copper(II). Below pH 5, the dominant species of copper was free Cu^{2+} and mainly involved in adsorption process. Above pH 5, copper starts to precipitate as $Cu(OH)_2$ and the effect of adsorption seems to be insignificant. As such, some researchers neglected the influence of higher alkaline conditions. Actually, the uptake of copper at higher pH conditions differed from each other and the kinetic results are presented herein. Effect of solution pH on copper adsorption was investigated at pH 5.0, 7.0 and 9.0, and the adsorption kinetics was simulated by kinetic models.

Pseudo-first-order, pseudo-second-order and Elovich kinetic models were used to fit the experimental data. The mathematical representation of the non-linear models of pseudo-first-order and pseudo-second-order kinetics are

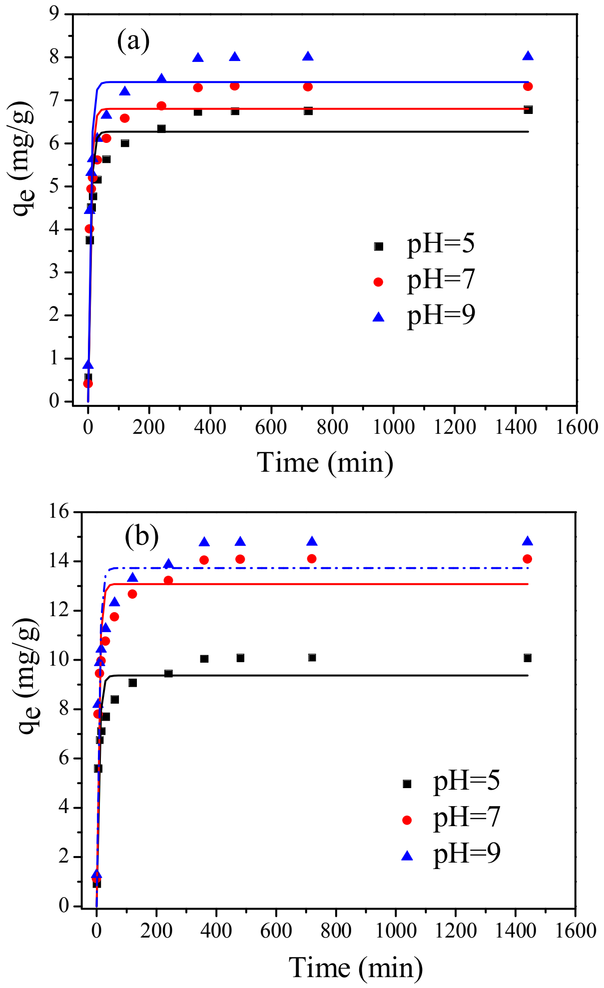

Fig. 2: Pseudo-first-order kinetic simulation for the adsorption of copper using (a) raw bagasse and (b) modified bagasse.

given as (Lagergren 1898, Ho & McKay 1999).

$$q_t = q_e(1 - e^{-k_1 t}) \quad ...(3)$$

$$q_t = \frac{k_2 q_e^{\,2} t}{(1 + k_2 q_e t)} \quad ...(4)$$

Where, q_e and q_t are the adsorption capacities (mg/g) of copper at equilibrium and at time t (min), respectively; and k_1 (min^{-1}) and k_2 (g mg/min) are the related adsorption rate constants for pseudo-first-order and pseudo-second-order models, respectively.

The Elovich kinetic model can be written as (Kithome et al. 1988):

$$q_t = a + b \ln t \quad ...(5)$$

Where a (g mg/min) and b (mg/g) are constants.

As illustrated in Fig. 2, the kinetic data were simulated by pseudo-first-order model at pH 5.0, 7.0 and 9.0. In Table 1, the parameters for the pseudo-first-order kinetic simulation are listed. From Fig. 2, the experimental points have a weak correlation with the curves simulated by pseudo-first-order model. The R^2 values are all not higher than 0.905. Evidently, the adsorption of copper can be divided into three stages, including an initial rapid stage, a slower second stage and a slowest equilibrium uptake stage (Vadivelan & Kumar 2005). At pH 7.0, the removal efficiency reached almost 90.0% at 120 min. The uptake at pH 7.0 for the raw bagasse and the modified bagasse was 6.8 and 13.1 mg/g, respectively. Apparently, the ammonium acetate modified bagasse demonstrated excellent adsorption capability for copper. From Table 1, the calculated q_e values from pseudo-first-order model at pH 5.0, 7.0 and 9.0 are 9.37, 13.1 and 13.7 mg/g, respectively. These calculated q_e values are quite different from the experimental values. From this point of view, pseudo-first-order model failed to describe the adsorption kinetics.

Table 1: Parameters for the pseudo-first-order kinetic simulation for the adsorption of copper using raw bagasse and modified bagasse.

	Raw bagasse			Modified bagasse		
	q_e (mg/g)	k	R^2	q_e (mg/g)	k	R^2
pH=5	6.27	0.129	0.888	9.37	0.129	0.885
pH=7	6.80	0.130	0.905	13.1	0.129	0.892
pH=9	7.42	0.129	0.879	13.7	0.129	0.888

Table 2: Parameters for the pseudo-second-order and Elovich kinetic simulation for the adsorption of copper using the modified bagasse.

	Pseudo-second-order model			Elovich model		
	q_e (mg/g)	k	R^2	a	b	R^2
pH=5	9.79	0.0212	0.958	4.82	0.823	0.971
pH=7	13.7	0.0152	0.962	6.74	1.15	0.975
pH=9	14.3	0.0144	0.960	7.06	1.21	0.973

Pseudo-second-order and Elovich kinetic models were also used to simulate the kinetic data and the results are presented in Fig. 3 and Table 2. Compared to pseudo-first-order kinetic model, the experimental points have a better correlation with the curves simulated by both pseudo-second-order and Elovich models. From Table 2, the calculated q_e values from pseudo-first-order and Elovich model are much closer to the experimental data than those of pseudo-first-order model. All the R^2 values are higher than 0.958 while these R^2 values of Elovich model are slightly higher than those of pseudo-second-order model. This indicates that the uptake of copper by the ammonium acetate modified bagasse was a

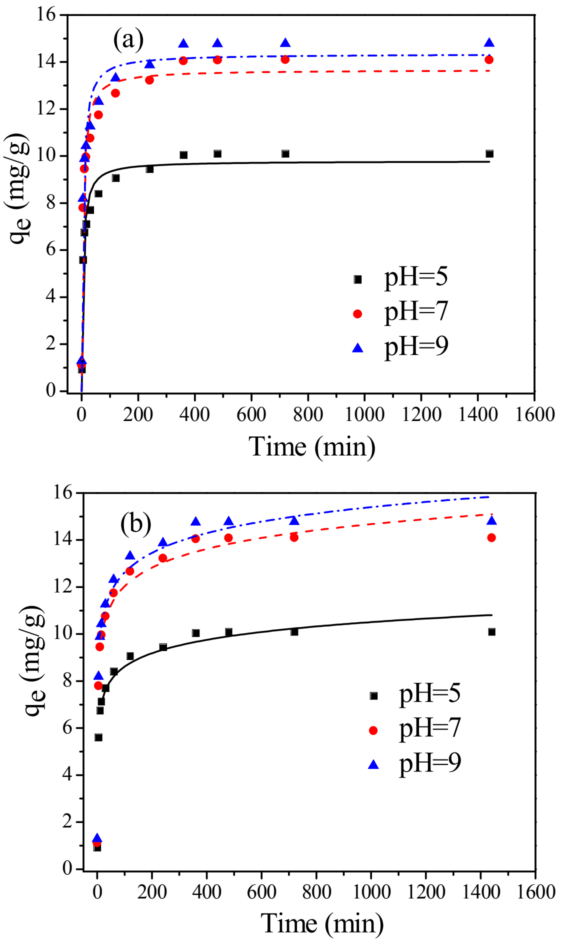

Fig. 3: Pseudo-second-order (a) and Elovich (b) kinetic simulation for adsorptionof copper using the modified bagasse.

chemisorption process and the rate-determining step might be diffusive in nature (Aharoniet al. 1991).

Thermodynamic analysis: Isotherm studies for copper adsorption were carried out at 298, 308 and 318 K by batch experiments, as illustrated in Fig. 4. Both Langmuir and Freundlich models were selected to fit experimental data and the parameters for both models are listed in Table 3.

The saturated monolayer Langmuir isotherm can be represented as (Freundlich 1906):

$$q_e = \frac{q_m k_L C_e}{1 + k_L C_e} \quad ...(6)$$

Where q_e is the amount of copper adsorbed onto the modified bagasse (mg/g), C_e is the equilibrium concentration (mg/L), q_m is the maximal adsorption capacity of the modified bagasse (mg/g) and k_L is the equilibrium adsorption constant related to the affinity of binding sites (L/mg).

Freundlich isotherm is an empirical equation describing adsorption on a heterogeneous surface. It is commonly written as (Yang et al. 2013):

$$q_e = k_F C_e^{\frac{1}{n}} \quad ...(7)$$

Where k_F and n are the Freundlich constants related to the adsorption capacity and adsorption intensity of the sorbent, respectively.

From the fitted curves in Fig. 4, it is observed that copper adsorption increased with a rise in reaction temperatures, indicating that the adsorption process was endothermic in nature. Judging from the experimental data and fitted curves, both Langmuir and Freundlich models could well describe the experimental data. As presented in Table 3, the regression coefficient values of Freundlich model at 308 and 318 K are only slightly higher than those of Langmuir model. In Langmuir model, the calculated maximal adsorption capacities for copper achieved 35.5, 44.4 and 70.7 mg/g at 298, 308 and 318 K, respectively. Therefore, the ammonium acetate modified bagasse shows a great potential for practical water purification.

According to the suggested calculation method, thermodynamic parameters associated with the adsorption processes such as standard free energy change (ΔG^0), standard enthalpy change (ΔH^0) and standard entropy change (ΔS^0) were calculated using the following equations (Yuan et al. 2009):

$$\Delta G^0 = \mathrm{RTlnK_0} \quad ...(8)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad ...(9)$$

$$\ln k_0 = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad ...(10)$$

Table 3: Langmuir and Freundlich isotherm parameters for the adsorption ofcopper at 298, 308 and 318 K.

	Langmuir isotherm			Freundlich isotherm		
	q_m (mg/g)	k_L (L/mg)	R^2	k_F (mg/g)	1/n	R^2
298 K	35.5	0.0573	0.943	5.79	0.348	0.973
308 K	44.4	0.0375	0.981	5.19	0.402	0.966
318 K	70.7	0.0344	0.999	7.38	0.422	0.955

Table 4: Values of thermodynamic parameters for copper adsorption at different temperatures.

T/K	ΔG^0(kJ/mol)	ΔH^0(kJ/mol)	ΔS^0($J\cdot mol^{-1}\cdot K^{-1}$)
298K	-29.4	643.6	2250.5
308K	-44.8	643.6	2250.5
318K	-74.4	643.6	2250.5

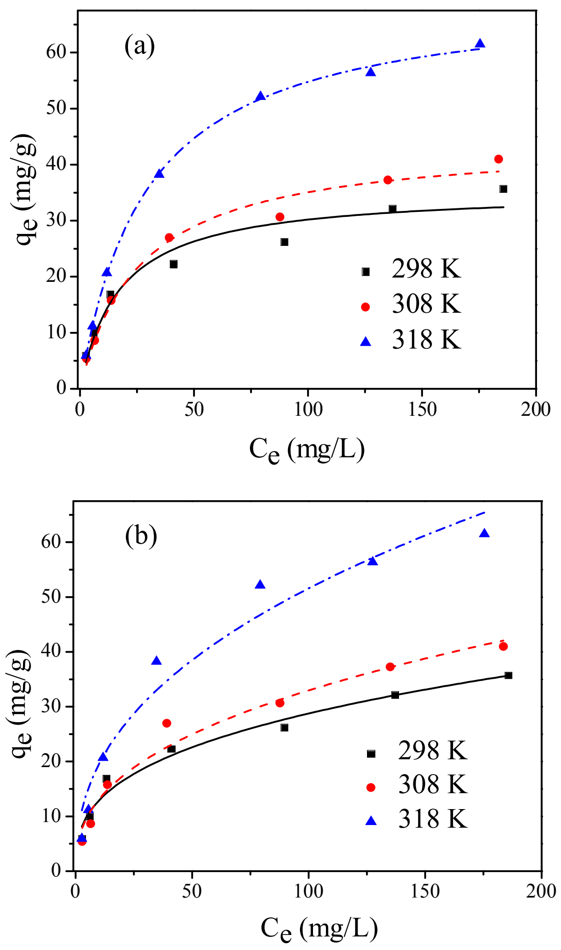

Fig. 4: Experimental points and non-linear fitted isotherm curves by Langmuir (a) and Freudlich (b) models for copper adsorption at 298, 308 and 318 K.

The calculated thermodynamic parameters are presented in Table 4. The enthalpy and entropy of the adsorption process are found to be 643.6 KJ mol^{-1} and 250.5 J mol^{-1} k^{-1}, respectively. The positive value of the reaction enthalpy implies that the uptake of copper increases with a rise in the reaction temperature, which is consistent with the aforementioned results. The negative values of ΔG^0 -29.4, -44.8 and -74.4KJ mol^{-1} at 298, 308 and 318 K, respectively, suggest the spontaneous nature of copper adsorption.

CONCLUSION

The ammonium acetate modified sugarcane bagasse was innovatively prepared by the wet impregnation method. The increased adsorbent dosage significantly increased the removal efficiency of copper. Compared to the raw bagasse, the adsorption capacity of the modified bagasse was dramatically enhanced by 116.2%. By kinetic simulation using pseudo-first-order, pseudo-second-order and Elovich kinetic models, it was proved that the both pseudo-second-order and Elovich kinetic models could better describe the adsorption kinetics at different pH conditions. This indicates that the adsorption of copper onto the modified bagasse was a chemisorption process in which the rate-determining step is diffusion in nature. Thermodynamic analysis indicated that the copper adsorption was spontaneous and endothermic in nature.

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REFERENCES

Aharoni, C., Sparks, D.L. and Levinson, S. 1991. Kinetics of soil chemical reactions: Relationships between empirical equations and diffusion models. Soil. Sci. Soc. Am. J., 55: 1307-1312.

Bhatnagar, A. and Sillanpa, M. 2010. Utilization of agro-industrial and municipal waste materials as potential adsorbents for water treatment-a review. Chem. Eng. J., 157: 277-296.

Crini, G. 2006. Non-conventional low-cost adsorbents for dye removal: a review. Bioresour. Technol., 97: 1061-1085.

Freundlich, H.M.F. 1906. Uber die adsorption in lasungen. J. Phys. Chem., 57: 385-470.

Gupta, V.K. 2009. Application of low-cost adsorbents for dye removal-a review. J. Environ. Manag., 90: 2313-42.

Han, R.P., Ding, D.D., Xu, Y.F., Zou, W.H., Wang, Y.F., Li, Y.F., et al. 2008. Use of rice husk for the adsorption of congo red from aqueous solution in column mode. Bioresour. Technol., 99: 2938-2946.

Han, R.P., Wang, Y.F., Han, P., Shi, J., Yang, J. and Lu, Y.S. 2006. Removal of methylene blue from aqueous solution by chaff in batch mode. J. Hazard. Mater., 137(1): 550-557.

Ho, Y.S. and McKay, G. 1999. Pseudo-second-order model for sorption process. Process Biochem., 34(5): 451-65.

Kithome, M., Paul, J.W., Lavkulich, L.M. and Bomke, A.A. 1988. Kinetics of ammonium adsorption and desorption by the natural zeolite clinoptilolite. Soil Sci. Soc. Am. J., 62: 622-629.

Lagergren, S. 1898. Zur theorie der sogenannten adsorption geloster stoffe. Kungliga svenska vetenskapsakademiens. Handlingar, 24: 1-39.

Li, G.T., Chen, D., Zhao, W.G. and Zhang, X.W. 2015. Efficient adsorption behavior of phosphate on La-modified tourmaline. J. Environ. Chem. Eng., 3(1): 515-522.

Ngah, W. W. and Hanafiah, M.A.K.M. 2008. Adsorption of copper on rubber (*Hevea brasiliensis*) leaf powder: Kinetic, equilibrium and thermodynamic studies. Biochemical Engineering Journal, 39(3): 521-530.

Nawaz, S., Bhatti, H.N., Bokhari, T.H. and Sadaf, S. 2014. Removal of Novacron golden yellow dye from aqueous solutions by low-cost agricultural waste: batch and fixed bed study. Chem. Ecol., 30: 52-65.

Sadaf, S., Bhatti, H.N., Ali, S. and Rehman K. 2014. Removal of Indosol Turquoise FBL dye from aqueous solution by bagasse, a low cost agricultural waste: batch and column study. Desalin. Water Treat., 52: 184-98.

Song J.Y., Zou, W.H., Bian, Y.Y., Su, F.Y. and Han, R.P. 2011.

Adsorption characteristics of methylene blue by peanut husk in batch and column mode. Desali., 265: 119-25.

Vadivelan,V. and Kumar, K.V. 2005. Equilibrium, kinetics, mechanism, and process design for the sorption of methylene blue onto rice husk. J. Colloid Interf. Sci., 286(1): 90-100.

Yang, S.J., Ding, D.H., Zhao, Y.X., Huang, W.L., Zhang, Z.Y., Lei, Z.F. and Yang, Y.N. 2013. Investigation of phosphate adsorption from aqueous solution using Kanuma mud: Behaviors and mechanisms. J. Environ. Chem. Eng., 1: 355-362.

Yuan, X., Xing, W., Zhuo, S.P., Han, Z.H., Wang, G.Q., Gao, X.L. and Yan, Z.F. 2009. Preparation and application of mesoporous Fe/carbon composites as a drug carrier. Micropor. Mesopor. Mat., 117: 678-684.

Zhang, R.D., Zhang, J.H., Zhang, X.N., Dou, C.C. and Han, R.P. 2014. Adsorption of Congo red from aqueous solutions using cationic surfactant modified wheat straw in batch mode: Kinetic and equilibrium study. J. Taiwan. Inst. Chemi. E., 45: 2578-2583.