

Adsorption Behavior of Basic Dye from Aqueous Solution onto Alkali Extracted Lignin

Qinghua Feng, Heli Cheng, Jinling Li, Peng Wang, and Yimin Xie*

Alkali extracted lignin (AEL), isolated from corn stalks with dilute alkali solution under mild condition, was used as a low-cost adsorbent for the removal of methylene blue (MB) from aqueous solutions. Batch adsorption studies were conducted to evaluate various experimental parameters such as pH, contact time, and initial dye concentration for the removal of MB. The kinetic data were analyzed using pseudo-first-order and pseudo-second-order kinetic models, and the adsorption kinetics were found to be well represented by the pseudo-second-order kinetic model. The equilibrium data were perfectly fitted to the Langmuir isotherm equation when compared with Freundlich isotherm equation. Based on the Langmuir adsorption isotherm model, the predicted maximum monolayer adsorption capacity was found to be 121.20 mg g⁻¹ (at 30 °C). The results showed that this adsorbent had a high adsorption capacity, making it a promising alternative for dye removal.

Keywords: Adsorption behavior; Alkali extracted lignin; Methylene blue

Contact information: Hubei Provincial Key Laboratory of Green Materials for Light Industry, Hubei University of Technology, Wuhan 430068, China; *Corresponding author: ppymxie@scut.edu.cn

INTRODUCTION

Dyes, the most visible pollutants, are presented in the effluents discharged from different industries: textile, paper, and dye manufacturing. Besides having possible carcinogenic and genotoxic effects, the dyes in water reduce light penetration and have a negative effect on photosynthesis (Chatterjee *et al.* 2005). The adsorption technique is an effective and attractive process for dye removal (McKay *et al.* 1999). Previously, great efforts have been done to find efficient and low-cost adsorbents (Crini 2006).

Lignin, the second most abundant natural polymer on earth, often appears as a low-valued by-product of pulping. There are many reports in the literature on the adsorption behavior of lignin due to its natural abundance and the availability of functional groups (Dizhbite *et al.* 1999). The dyes are potential adsorbates because of the interactions, *e.g.*, electrostatic and hydrophobic interaction, between lignin and dyes (Hubbe *et al.* 2012). Recently, some adsorbents prepared from lignin have attracted considerable interest. Liu and Huang (2006) prepared a spherical sulfonic lignin adsorbent from sodium lignosulfonate crosslinked by formaldehyde in an aqueous solution suspended in transformer oil. The spherical sulfonic lignin exhibited favorable adsorption of Cationic Red GTL, Cationic Turquoise GB, and Cationic Yellow X-5GL. Fu *et al.* (2013) examined the methylene blue (MB) adsorption by a lignin-based activated carbon, which was prepared from black liquor lignin, as a function of pH and MB concentration. These studies indicate that lignin-based materials can be used as adsorbents for dye removal. However, the adsorption behavior of the precursors of these materials has rarely been reported.

Recently, a new type of technical lignin referred to as alkali extracted lignin (AEL) has been obtained by the extraction of stalks with dilute alkali solution under mild conditions. In our previous study, AEL was found to contain relatively high levels of carboxylic acid groups (Wu *et al.* 2012). Therefore, AEL is thus expected to be effective when used as basic dye adsorbent. In this paper, we studied the adsorption behavior of a basic dye onto AEL. MB was used as the dye to evaluate the adsorption potential of the adsorbent. The impacts of initial solution pH, contact time, and initial dye concentration on the adsorption capacity were investigated.

EXPERIMENTAL

Materials

Alkali extracted lignin (AEL) was produced from the residues of corn stalks used in butanol production by dilute alkali extraction; the residuals were supplied by Songyuan Laihe Chemicals Co., Ltd., China.

Methylene blue (MB) dye is a commercial product of Kermel Reagent Inc, China. The stock solution of 1.0 g L⁻¹ MB was prepared by dissolving appropriate amount of MB in deionized water. The MB stock solution could be diluted to obtain solutions of different concentrations.

Methods

Preparation of the adsorbent

The crude AEL was dissolved in deionized water and centrifuged. Then, the supernatant solution was acidified to pH 2.0 to precipitate the lignin. After being freeze-dried, the lignin was dissolved in an aliquot of 1,4-dioxane. Then, the solution was added dropwise to a stirred diethyl ether-petroleum ether (30 to 60 °C) (1:1 (v/v)) mixture. The precipitated lignin was centrifuged, washed twice with diethyl ether-petroleum ether (30 to 60 °C) (1:1 (v/v)) and then once with petroleum ether. Subsequently, the lignin was vacuum-dried at 40 °C.

Characterization of the adsorbent

The average molecular weight and the molecular weight distribution of lignin were estimated by GPC on an Agilent-1100 apparatus equipped with an Agilent-25 column and a R401 differential refractory detector. THF was used as the eluent. The column was calibrated by narrow-dispersed polystyrene standards.

The hydroxyl group contents of lignin were determined by ³¹P-NMR on a Bruker DRX-400 NMR spectrometer according to the method of Granata and Argyropoulos (1995). The contents of the phenolic and carboxylic group were calculated on the basis of the internal standard (cyclohexanol) and the integrated peak areas.

Equilibrium studies

The impacts of experimental parameters, *e.g.*, initial dye concentration and pH, on the amount of MB removal were studied in a batch mode of operation for 72 h. The pH of MB solution was adjusted with 0.1 M NaOH or 0.1 M HCl solutions. In each adsorption experiment, 25 mL of MB solution with predetermined concentration and pH was stirred (100 rpm) with 0.025 g of the adsorbent at 30 °C, which was more than sufficient to reach equilibrium. The mixtures were then centrifuged and the concentration in the supernatant

solution was measured by monitoring the absorbance changes at a wavelength of maximum absorbance (664 nm) with a Beckman DU-7HS UV spectrophotometer. The adsorption capacity of MB on the adsorbent was calculated by the following equation:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where q_e (mg g^{-1}) is the amount of MB adsorbed on adsorbent, C_0 and C_e (mg L^{-1}) are the initial concentration and the equilibrium concentration of MB solution, respectively, V (L) represents the volume of solution treated, and m (g) represents the amount of the adsorbent added.

Kinetics studies

The adsorption kinetics was investigated by batch experiments. AEL (0.025 g) was transferred into 25 mL of MB solution of different concentrations (50 mg L^{-1} , 75 mg L^{-1} , and 100 mg L^{-1}). The mixtures were stirred (100 rpm) at 30 °C and withdrawn at predetermined time intervals. The samples were then centrifuged and the concentration in the supernatant MB solution was measured as above. All the experiments were carried out at pH 5.0. The amount of adsorption at time t , q_t (mg g^{-1}), was calculated as follows:

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (2)$$

where C_t (mg L^{-1}) represents the concentration of MB solution at the predetermined time t and the other symbols are the same as defined above.

RESULTS AND DISCUSSION

Characterization of the Adsorbent

The molecular weight, and phenolic and carboxylic group contents of AEL are given in Table 1. The $\overline{M_w}$ and $\overline{M_n}$ of AEL was 8870 and 3720 g/mol, respectively. The amounts of aliphatic, phenolic, and carboxyl groups of the AEL were 1.04, 2.97, and 0.68 mmol/g, respectively. The results indicated that AEL with relatively high carboxylic group content was beneficial for cationic dye removal due to their electrostatic interactions. Moreover, AEL cannot be difficultly separated when it was dispersed in water due to its relatively high molecular weight. Quantitative ^{31}P -NMR spectra of the AEL is shown in Figure 1.

Table 1. Molecular Weight and Functional Groups Contents of AEL

Molecular weight			Functional groups contents (mmol g^{-1})		
$\overline{M_w}$	$\overline{M_n}$	$\overline{M_w} / \overline{M_n}$	Aliphatic	Phenolic	Carboxylic
8870	3720	2.38	1.04	2.97	0.68

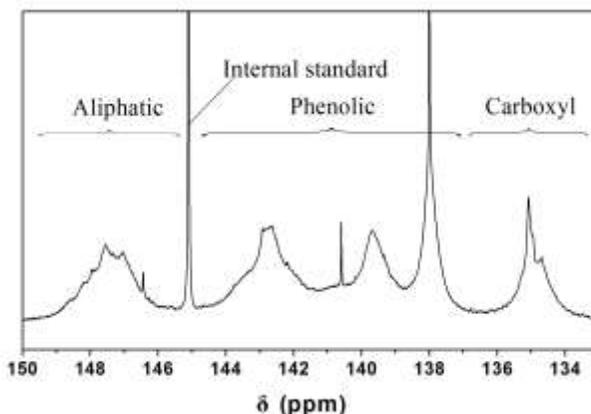


Fig. 1. Quantitative ^{31}P NMR spectra of AEL

Effect of initial pH

The pH of the dye solution was found to have significant impact on the adsorption capacity of dye due to its impact on both the surface binding-sites of the adsorbent and the ionization process of the dye molecule (Vadivelan and Kumar 2005). Figure 2 shows the impact of pH on the adsorption amount of MB onto the AEL. The equilibrium adsorption capacity was low at pH 1.0 (50 mg g^{-1}), then increased and remained nearly constant over the initial pH ranges of 5.0 to 7.0 (*ca.* 82 mg g^{-1}). Lower adsorption at acidic pH was probably due to the presence of excess of H^+ ions competing with the dye cations for adsorption sites. The high adsorption capacity observed at high pH could be explained by the binding of the positively charged dye through electrostatic forces of attraction. A similar trend has been observed by other authors (Pavan *et al.* 2008; Ncibi *et al.* 2007).

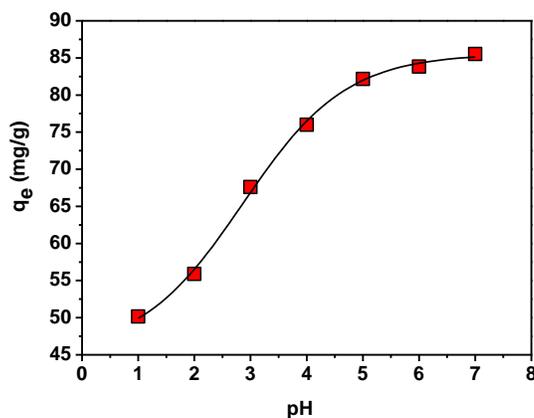


Fig. 2. Effect of initial pH (C_0 , 100 mg L^{-1} ; V , 25 mL; m , 0.025 g; temperature, $30 \text{ }^\circ\text{C}$)

Adsorption Kinetics

Figure 3 plots the amount of dye adsorption versus contact time for different initial MB concentrations. It was found that the amount of dye uptake, q_t , increased with increasing contact time at all initial dye concentrations. Further, the amount of dye adsorbed increased with increasing initial dye concentration. From the figure it was also observed that dye uptake was rapid for the first 10 min, and thereafter it proceeded at a

slower rate, and finally attained saturation. The relatively high adsorption rate in the initial 10 min may be due to the highest levels of vacant sites. As a result, the concentration gradient is the maximum initially. This maximum concentration gradient results in the rapid dye sorption rate in the first 10 min. The concentration gradient is reduced with time due to the accumulation of dye molecules at the vacant sites, leading to a decrease in sorption rate at later stages from 10 to 60 min.

In order to investigate the mechanism involved in the adsorption process, different kinetic models, *e.g.*, pseudo-first-order, pseudo-second-order, and intra-particle diffusion models, have been used in the literature (Crini and Badot 2008). In the present study, pseudo-first-order and pseudo-second-order kinetic models were tested for the adsorption of MB onto the lignin.

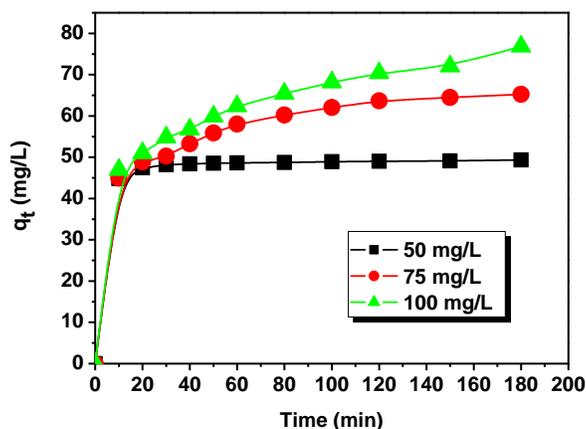


Fig. 3. Adsorption kinetics (V , 25 mL; m , 0.25 g; pH, 5.0; temperature, 30 °C)

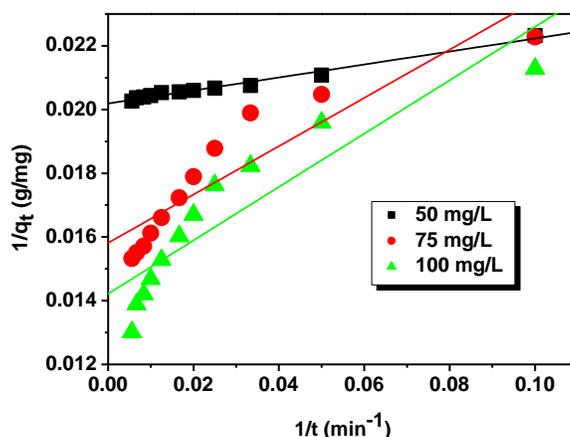


Fig. 4. Pseudo-first-order plots (V , 25 mL; m , 0.25 g; pH, 5.0; temperature, 30 °C)

The pseudo-first-order kinetic model (Deniz and Saygideger 2010) can be expressed as:

$$\frac{1}{q_t} = \frac{k_1}{q_e t} + \frac{1}{q_e} \quad (3)$$

where k_1 (min^{-1}) is the pseudo-first-order rate constant of adsorption, and q_e (mg g^{-1}) is the amount of dye adsorbed at equilibrium. The value of k_1 was obtained from the slopes and the value of q_e was obtained from the intercepts from the plots of $1/q_t$ versus $1/t$ (Fig. 4); their values are listed in Table 2.

The pseudo-second-order kinetic model (Ho and McKay 1998) can be expressed as,

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

where k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) and q_e (mg g^{-1}) represent the equilibrium rate constant and the maximum adsorption capacity for the pseudo-second-order adsorption, respectively. The parameters k_2 and q_e were calculated from the plot of t/q_t against t (Fig. 5). The calculated values are listed in Table 2.

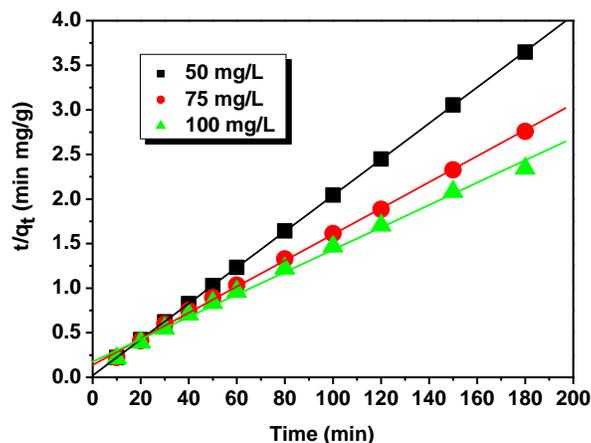


Fig. 5. Pseudo-second-order plots (V , 25 mL; m , 0.25 g; pH, 5.0; temperature, 30 °C)

Table 2. Kinetic Parameters (V , 25 mL; m , 0.25 g; pH, 5.0; temperature, 30 °C)

C_o (mg L^{-1})	50	75	100
$q_{e, \text{exp}}$ (mg g^{-1})	49.05	70.35	81.18
Pseudo-first-order			
$q_{e, \text{cal}}$ (mg g^{-1})	49.53	62.89	70.42
k_1 (min^{-1})	1.011	4.478	5.901
r_1^2	0.9838	0.8092	0.8273
Pseudo-second-order			
$q_{e, \text{cal}}$ (mg g^{-1})	49.51	68.27	79.70
k_2 (min^{-1})	0.01980	0.001571	0.000896
r_2^2	0.9999	0.9958	0.9949

It can be observed clearly from Fig. 4 that the pseudo-first-order model did not fit at concentration of 75 and 100 mg L⁻¹. According to these two models, q_e should represent the sorption saturation for the given condition. In the present study, as shown in Table 2, the values of q_e calculated from the pseudo-second-order model successfully predicted the values of $q_{e, exp}$. Furthermore, the r_2^2 values were found to be higher than those of r_1^2 . The relatively high r_2^2 values, which indicated that the adsorption process of MB onto the adsorbent matched the pseudo-second-order kinetic model. The results suggested that the dye uptake process is attributed to chemisorption. Chemical adsorption could occur by the polar functional groups of the AEL, including carboxyl groups, as chemical bonding agents (Ho 2003).

Adsorption Isotherms

The equilibrium adsorption isotherms help to understand the mechanism of the adsorption phenomenon. The adsorption of MB onto AEL was determined as a function of equilibrium dye concentration. The equilibrium data were analyzed with Langmuir and Freundlich isotherm models, respectively, which are the two most commonly used isotherms. The corresponding adsorption isotherms were plotted and shown in Fig. 6.

The Langmuir model is based on monolayer adsorption. The model assumes that adsorbent has a finite capacity for the adsorbate at equilibrium and that all adsorption sites are identical and energetically equivalent. The linear form of the Langmuir model (Langmuir 1918) could be given by,

$$\frac{C_e}{q_e} = \frac{1}{q_0 K_L} + \frac{C_e}{q_0} \quad (5)$$

where q_0 (mg g⁻¹) and K_L (L mg⁻¹) represent the monolayer adsorption capacity and Langmuir constant, respectively. Values of q_0 and K_L were calculated from the plot of C_e/q_e against C_e . The calculated parameters are listed in Table 3.

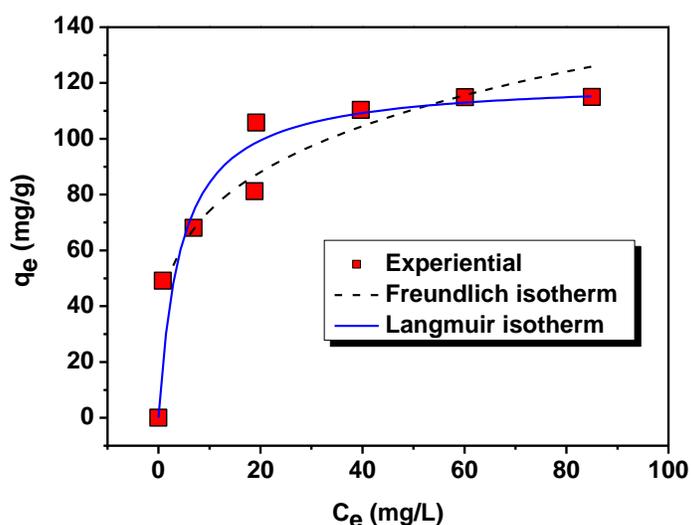


Fig. 6. Equilibrium curves (V , 25 mL; m , 0.25 g; pH, 5.0; temperature, 30 °C)

Table 3. Isotherm Parameters (V , 25 mL; m , 0.25 g; pH, 5.0; temperature, 30 °C)

Isotherm model		
Langmuir	q_0 (mg g ⁻¹)	121.20
	K_L (L mg ⁻¹)	0.2286
	R_L	0.02140
	r_L^2	0.9932
Freundlich	K_F (mg ^{1-1/n} L ^{1/n} g ⁻¹)	49.11
	n	4.8675
	r_F^2	0.9258

The Freundlich equation (Freundlich 1906) can be used to characterize adsorption on heterogeneous surfaces with interaction between adsorbed molecules. Adsorption energy exponentially decreased upon completion of the adsorption centers of an adsorbent. The equation can be expressed as,

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (6)$$

where K_F (mg^{1-1/n} L^{1/n} g⁻¹) and n represent the constants related to sorption capacity and sorption intensity of adsorbents, respectively. The values of K_F and n were determined from the slopes and intercepts of the plots of $\log q_e$ versus $\log C_e$; their values are given in Table 3.

The isotherm constants can be utilized to predict whether an adsorption system is favorable or unfavorable. The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or an equilibrium parameter, R_L , which is expressed by:

$$R_L = \frac{1}{1 + K_L C_0} \quad (7)$$

where C_0 (mg L⁻¹) represents the highest initial dye concentration. As shown in Table 3, the R_L values of all AEL samples were found to be between 0 and 1, indicating that AEL favors the adsorption of MB. The n values in the Freundlich equation can also indicate how favorable an adsorbent is to adsorb the adsorbate. The result showed that the values of n were all in the range of 1 to 10, which implies that dye molecules are favorably adsorbed by the AEL samples. This is in good agreement with other findings regarding the R_L value (Chen *et al.* 2011).

The coefficients of determination (r_L^2 and r_F^2), as listed in Table 3, indicated that the experimental equilibrium data matched the Langmuir model better than the Freundlich model. This suggested the monolayer coverage of MB onto the AEL. The relatively high adsorption capacities of AEL may be due to its high carboxyl content.

As a basis for suggesting the effectiveness of AEL as a potential adsorbent for dyes treatment, it is necessary to compare the value of maximum adsorption capacity

obtained from this study with values from other reported adsorbents. The adsorption capacity for AEL are comparable with of MB adsorption using other adsorbents as shown in Table 4.

Table 4. Comparison of MB Adsorption of this Work and Previous Studies

Adsorbent	Adsorption capacity (mg g ⁻¹)	Reference
Alkali extracted lignin	121.20	This study
Neem (<i>Azadirachta indica</i>) leaf powder	19.61	Bhattacharyya and Sharma 2005
Modified lignin from sugar cane bagasse	34.20	Consolin Filho <i>et al.</i> 2007
Rice husk	40.58	Vadivelan and Kumar 2005
Carbon nanotubes	64.7	Yao <i>et al.</i> 2010
Activated carbon from black liquor lignin	92.51	Fu <i>et al.</i> 2013
Activated carbon from natural lignin	149.25	Kriaa <i>et al.</i> 2011
Activated carbon from apple pulp	283.8	Hesas <i>et al.</i> 2013

CONCLUSIONS

1. Alkali extracted lignin (AEL) exhibited excellent adsorption capacity for methylene blue (MB) from aqueous solutions. The amount of MB uptake increased with an increase in solution concentration and contact time.
2. The adsorption process gave a good fit to the pseudo-second-order kinetic model. The equilibrium data were well fitted to Langmuir sorption isotherms. The monolayer adsorption capacity of AEL was 121 mg g⁻¹.
3. AEL can be used as a promising adsorbent for the removal dyes from aqueous solutions.

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REFERENCES CITED

- Bhattacharyya, K. G., and Sharma, A. (2005). "Kinetics and thermodynamics of methylene blue adsorption on Neem (*Azadirachta indica*) leaf powder," *Dyes Pigm.* 65(1), 51-59
- Chatterjee, S., Chatterjee, S., Chatterjee, B. P., Das, A. R., and Guha, A. K. (2005). "Adsorption of a model anionic dye, eosin Y, from aqueous solution by chitosan hydrobeads," *J. Colloid Interf. Sci.* 288(1), 30-35.
- Chen, H., Zhao, J., Wu, J. Y., and Dai, G. L. (2011). "Isotherm, thermodynamic, kinetics and adsorption mechanism studies of methyl orange by surfactant modified silkworm exuviae," *J. Hazard. Mater.* 192(1), 246-254.
- Consolin Filho, N., Venancio, E. C., Barriquello, M. F., Hechenleitner, A. A. W., and Pineda, E. A. G. (2007). "Methylene blue adsorption onto modified lignin from sugar cane bagasse," *Eclética Química* 32(4), 63-70.
- Crini, G. (2006). "Non-conventional low-cost adsorbents for dye removal: A review," *Bioresour. Technol.* 97(9), 1061-1085.
- Crini, G., and Badot, P. M. (2008). "Application of chitosan, a natural aminopolysaccharide, for dye removal from aqueous solutions by adsorption processes using batch studies: A review of recent literature," *Prog. Polym. Sci.* 33(4), 399-447.
- Deniz, F., and Saygideger, S. D. (2010). "Equilibrium, kinetic and thermodynamic studies of Acid Orange 52 dye biosorption by *Paulownia tomentosa* Steud. leaf powder as a low-cost natural biosorbent," *Bioresour. Technol.* 101(14), 5137-5143.
- Dizhbite, T., Zakis, G., Kizima, A., Lazareva, E., Rossinskaya, G., Jurkjane, V., Telysheva G., and Viesturs, U. (1999). "Lignin – A useful bioresource for the production of sorption-active materials," *Bioresour. Technol.* 67(3), 221-228.
- Freundlich, H. M. F. (1906). "Over the adsorption in solution," *J. Phys. Chem.* 57, 385-470.
- Fu, K. F., Yue, Q. Y., Gao, B., Sun, Y. Y., and Zhu, L. J. (2013). "Preparation, characterization and application of lignin-based activated carbon from black liquor lignin by steam activation," *Chem. Eng. J.* 228(15), 1074-1082.
- Granata, A., and Argyropoulos, D. S. (1995). "2-Chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholite, a reagent for the accurate determination of the uncondensed and condensed phenolic moieties in lignins," *J. Agric. Food Chem.* 43(6), 1538-1544.
- Hesas, R. H., Arami-Niya, A., Daud, W. M. A. W., and Sahu, J. N. (2013). "Preparation and characterization of activated carbon from apple waste by microwave-assisted phosphoric acid activation: Application in methylene blue adsorption," *BioResources* 8(2), 2950-2966.
- Ho, Y. S. (2003). "Removal of copper ions from aqueous solution by tree fern," *Water Res.* 37(10), 2323-2330.
- Ho, Y. S., and McKay, G. (1998). "Kinetic models for the sorption of dye from aqueous solution by wood," *Process Saf. Environ. Prot.* 76 (2), 183-191.
- Hubbe, M. A., Beck, K. R., O'Neal, W. G., and Sharma, Y. C. (2012). "Cellulosic substrates for removal of pollutants from aqueous systems: A review. 2. Dyes," *BioResources* 7(2), 2592-2687.
- Kriaa, A., Hamdi, N., and Srasra, E. (2011). "Adsorption studies of methylene blue dye on tunisian activated lignin," *Russ. J. Phys. Chem. A* 85(2), 279-287.
- Langmuir, I. (1918). "The adsorption of gases on plane surfaces of glass, mica and platinum," *J. Am. Chem. Soc.* 40(9), 1361-1403.

- Liu, M. H., and Huang, J. H. (2006). "Removal and recovery of cationic dyes from aqueous solutions using spherical sulfonic lignin adsorbent," *J. Appl. Polym. Sci.* 101(4), 2284-2291.
- McKay, G., Porter, J. F., and Prasad, G. R. (1999). "The removal of dye colours from aqueous solutions by adsorption on low-cost materials," *Water Air Soil Pollut.* 114(3-4), 423-438.
- Ncibi, M. C., Mahjoub, B., and Seffen, M. (2007). "Kinetic and equilibrium studies of methylene blue biosorption by *Posidonia oceanica* (L.) fibres," *J. Hazard. Mater.* 139(2), 280-285.
- Pavan, F. A., Mazzocato, A. C., and Gushikem, Y. (2008). "Removal of methylene blue dye from aqueous solutions by adsorption using yellow passion fruit peel as adsorbent," *Bioresour. Technol.* 99(8), 3162-3165.
- 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.
- Wu, H. R., Chen, F. G., Feng, Q. H., and Yue, X. P. (2012). "Oxidation and sulfomethylation of alkali-extracted lignin from corn stalk," *BioResources* 7(3), 2742-2751.
- Yao, Y.J., Xu, F.F., Chen, M., Xu, Z.X., and Zhu, Z.W. (2010). "Adsorption behavior of methylene blue on carbon nanotubes," *Bioresour. Technol.* 101(9), 3040-3046.

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