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Study of Isotherm and Kinetics Parameters for Methylene Blue Adsorption onto Wheat Straw

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Abstract

In this work, the wheat straw (WS) was used as an adsorbent. The adsorption of methylene blue (MB) from aqueous solutions onto WS has been studied. Four widely isotherms, Langmuir, Freundlich, Temkin and Sips were examined for MB sorption at different temperatures. The Langmuir isotherm found to be the best to describe sorption of MB on WS. The Langmuir adsorption capacity (Q_{max}) was found to be 172.41 mg g^{-1}. The Sips and Temkin isotherms were also satisfactory but the Freundlich isotherm couldn't describe sorption appropriately in this case. The removal of MB by WS followed pseudo-second order reaction kinetics.

Keywords: Wheat straw, Methylene blue , Isotherm, Kinetic

Introduction:

Nowadays, one of the key environmental problems facing humanity is the increasing worldwide contamination of freshwater systems with thousands of industrial chemical compounds. Out of all contaminants contained in industrial sewage, dyes are the most undesired ones, as human eyes can easily recognize them (W. Zhang, H. Yan, H. Li , Z. Jiang, L. Dong, X. Kan, H. Yang, A. Li, R. Cheng (2011)). People have recently begun to realize the harmful effects of burning straw and thus began considering many ways to use this bioresource(W. Zhang, H. Yan, H. Li , Z. Jiang, L. Dong, X. Kan, H. Yang, A. Li, R. Cheng (2012)). Adsorption by activated carbon is the most common process for dye removal from wastewater. Although, the process is highly effective, the running costs are high with the need for regeneration after each sorption cycle. This has led to the search for other potentially suitable alternative, that is more economical and equally an effective materials for dye removal by adsorption (N. Nasuha, B.H. Hameed (2011)). Using straw as adsorbent is a promising alternative for the removal of dyes in wastewater treatment due to its very low cost (W. Zhang, H. Yan, H. Li , Z. Jiang, L. Dong, X. Kan, H. Yang, A. Li, R. Cheng (2012)).

Experimental:

Materials

The wheat straw(WS) used in this study was obtained from a local wheat field of Ardebil in Iran. The raw material was cleaned and dried at 105˚C for 24 h. The dried WS was then ground and sieved into a size range of 100–500 μm. Finally, the resulting product was stored in an air-tight container for further use. The chemical composition of WS was determined as follows: 43.1% cellulose Kurshchner, 19.31% lignin, 29.02% hemicellulose, 6.8% ash, and 1.64% ethanol/dichloromethane extractable, on an oven-dry weight basis (moisture content 7.8%). The methylene blue(MB) purchased from Merck (No. 115943), was selected as a representative reactive dye for this study.

Results and discussion:

Adsorption equilibrium isotherm

Analysis of the isotherm data is important to develop equations that correctly represent the results and could be used for design purposes(Azadeh Ebrahimian Pirbazari, Elham Saberikhaha & Nima Gholami Ahmad Gorabi (2014)). Table 1 shows the fitting parameters for the measured isotherm data for MB adsorption onto WS on the nonlinear forms of Langmuir, Freundlich, Temkin, and Sips models. The values of nonlinear correlation coefficients (R^2) for the Langmuir, Sips and Temkin isotherm models indicate good fit with the four models. In all the temperatures, the Freundlich isotherm represented the poorest fit of experimental data in comparison with other isotherm equations. The Langmuir equation yielded the best fit to the experimental data in comparison with other isotherm equations in this study. The maximum MB adsorption capacity (mg g^{-1}) belongs to WS which has been shown in Table 1. The monolayer capacity (Q_{max}) is 172.41 mg g^{-1} as calculated from Langmuir model at 303 K.

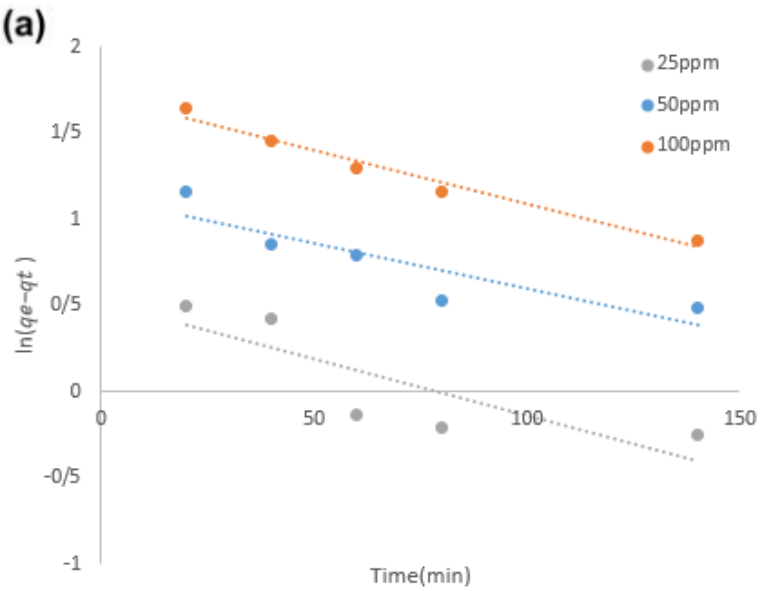
Kinetic models

The dynamics of the adsorption can be studied by the kinetics of adsorption in terms of the order of the rate constant(V. Go ´mez, M.S. Larrechi, M.P. Callao (2007)). The transient behavior of the MB adsorption process was analyzed by using the pseudo-first-order and pseudo-second-order kinetic models. Plotting ln ($q_e - q_t$) against t permits calculation of k_1 (Figure 1(a)). The rate constants, k_1, evaluated from

these plots with the correlation coefficients obtained are listed in Table 2. Plotting t/q against t (Figure 1(b)), gives a straight line where k_2 can be calculated.

Table 1- Isotherm parameters for MB adsorption onto WS

Temperature (K)	**293**	**303**	**323**
Langmuir			
Q_{max} (mg/g)	75.7578	172.4138	106.383
k_L (L/mg)	0.03886	0.01738	0.02779
R^2	0.9898	0.9921	0.9904
Freundlich			
1/n	0.4884	0.6358	0.6052
k_F (mg/g)$(dm^3/mg)^{1/n}$	6.9056	5.4075	5.4438
R^2	0.9197	0.9857	0.9629
Temkin			
b_T (kj)	146.465	104.032	120.747
k_T (L/mg)	0.38446	0.29031	0.28749
R^2	0.9879	0.9831	0.9374
Sips			
Q_{max} (mgg^{-1})	69.44	154.5	147.7
b $((mg^{-1})^{-1/n})$	0.0346	0.02641	0.035
1/n	1.118	0.8491	0.751
R^2	0.9852	0.998	0.9557



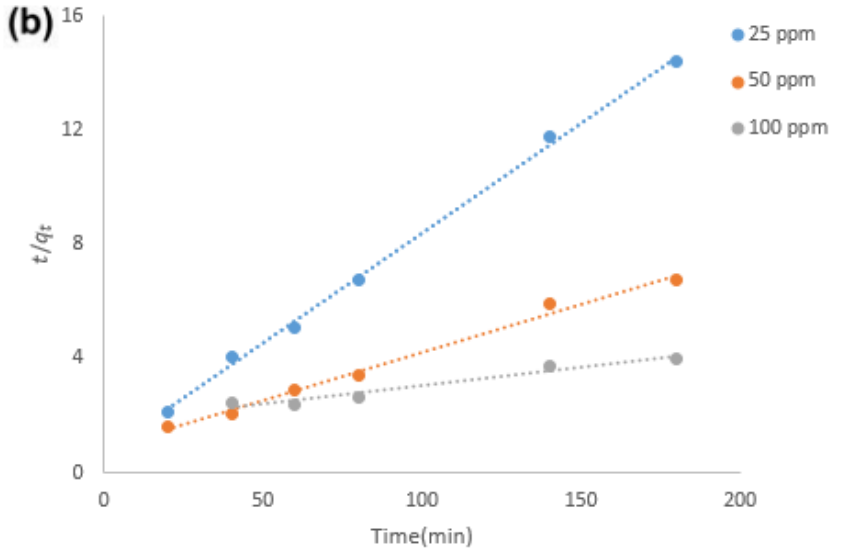


Figure 1. Kinetic models for adsorption of MB onto WS. (a) pseudo-first-order and (b) pseudo-second-order rate equations.

Usually the best-fit model can be selected based on the linear regression correlation coefficient R^2 values. Generally the kinetic adsorption is better represented by pseudo-second-order model for anionic and cationic dye adsorption(Azadeh Ebrahimian Pirbazari, Elham Saberikhaha & Nima Gholami Ahmad Gorabi (2014)). The R^2 listed (in Table 2) for the pseudo-first-order kinetic model was between 0.6813 and 0.9753. The R^2 values for pseudo-second-order model were >0.9535, which is higher than the R^2 values obtained for the pseudo-first-order model. Therefore, the adsorption kinetics could well be satisfactorily more favorably described by pseudo-second-order kinetic model for MB adsorption onto WS.

Table 2 - Kinetic parameters for the adsorption of MB onto WS

C_0 (mg/L)	**25**	**50**	**100**
Pseudo-first-order equation			
$k_1(min^{-1})$	0.0066	0.0053	0.0063
q_e (mg g^{-1})	1.6705	3.0624	5.5356
R^2	0.6813	0.7885	0.9753
Pseudo-second-order equation			
k_2(g mg^{-1} min^{-1})	0.00839	0.0013547	0.000094
q_e (mg g^{-1})	12.987	29.5857	77.51937
R^2	0.9978	0.9909	0.9535

Conclusions:

The Langmuir isotherm found to be the best to describe sorption of MB on WS. The Sips and Temkin isotherms were also satisfactory but the Freundlich isotherm couldn't describe sorption appropriately in this case.
The results revealed that the best kinetic model for MB adsorption with wheat straw, was pseudo-second-order model. Wheat straw showed MB adsorption. The monolayer capacity (Q_{max}) is 172.41 mg g^{-1} as calculated from Langmuir model at 303 K.

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