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Methylene blue adsorption via maize silk powder: Kinetic, equilibrium, thermodynamic studies and residual error analysis

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A B S T R A C T

The potential of maize silk powder (MS) as a natural, widely available and low-cost agricultural waste in order to adsorb methylene blue (MB) from an aqueous solution has been studied. The adsorbent surface morphology has been studied using SEM and FTIR. The effect of operating conditions such as contact time, solution pH and initial MB concentration and the important frequently missed parameters such as salt effect (using NaCl and Na_2HPO_4), temperature effect (for ΔH°, ΔG° and ΔS°), solution pH and detailed error analysis have been determined. A rate study indicated the process followed pseudo-second order kinetics. The adsorption equilibrium was modeled for best fit using ten commonly-used isotherm models and the Jovanovic equation gave the best correlation of the experimental data.

1. Introduction

Today, due to vast sources of pollution, hazardous compounds removal has become one of the crucial issues among industrial companies and nations (Awual et al., 2014; Bayazit and İnci, 2014; Koyuncu and Kul, 2014; Peydayesh and Rahbar-Kelishami, 2015; Yari et al., 2015). Furthermore, much legislation has been enacted by some countries like the USA with regard to wild life and environmental conservation (USEPA, 2015). According to USEPA regulations (USEPA, 2015), there are specific maximum allowable concentrations for each hazardous material such as methylene blue (MB), basic dyes, acidic dyes, congo red, Rhodamine B and others (Namasivayam and Kavitha, 2002). Therefore, several treatment methods have been implemented to remove these compounds from wastewater, including chemical, biological and physical techniques (Borah et al., 2015; Dakiky et al., 2002; EL-Mekkawi et al., 2016; Kannan and Sundaram, 2001; Marković et al., 2015). MB is one significant dye which dissociates into a cation and a chloride anion in aqueous solution and is used as a standard for testing adsorbents; it is widely employed for hair coloring, cotton, paper and silk dyeing (Kazemi et al., 2013; Peydayesh and Rahbar-Kelishami, 2015). MB as a hazardous material with various negative impacts such as heart rate increase, vomiting, shock, jaundice, quadriplegia, and cyanosis for human beings (Ai et al., 2011; Peydayesh and Rahbar-Kelishami, 2015). Different methods have been applied for MB reduction such as magnetic separation (Rizzo et al., 2007), photocatalysis (Zaghbani et al., 2007), ultrafiltration (Malik and Sanyal, 2004), ozonation (Malik and Saha, 2003), oxidation (Yang et al., 2013), flocculation (Cherifi et al., 2013), adsorption (Gong et al., 2005; Jumasiah et al., 2005; Mui et al., 2008; Tan et al., 2007), and so forth.

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Nomenclature

A	Koble–Corrigan parameter
A_1	Redlich–Peterson isotherm constant ($L\,g^{-1}$)
B	Koble–Corrigan parameter
b	Langmuir constant related to the energy of adsorption ($L\,mg^{-1}$)
B_1	Redlich–Peterson isotherm constant ($L/mg^{1-(1/A)}$)
b_T	Temkin constant related to heat of sorption ($kJ\,mol^{-1}$)
C_e	Equilibrium concentration of dye in solution ($mg\,L^{-1}$)
C_0	Initial dye concentration ($mg\,L^{-1}$)
C_t	Final dye concentration ($mg\,L^{-1}$)
D	Koble–Corrigan parameter
h	The initial adsorption rate ($mg\,g^{-1}\,min^{-1}$)
K_D	Hill constant
K_{FS}	The Fritz–Schlunder equilibrium constant ($L\,mg^{-1}$)
K_j	Jovanovic isotherm constant ($L\,g^{-1}$)
K_{LF}	The equilibrium constant for a heterogeneous solid
K_R	The Radke–Prausnitz equilibrium constant
K	Temkin equilibrium isotherm constant ($L\,g^{-1}$)
k_1	Rate constants of the pseudo-first model (min^{-1})
k_2	Rate constants of the pseudo-second order model (min^{-1})
K_f	Freundlich constant indicative of the relative adsorption capacity of the adsorbent ($mg^{1-1/n}\,L^{1/n}\,g^{-1}$)
K_{id}	The intra-particle diffusion rate constant ($mol\,g^{-1}\,min^{-1/2}$)
M	The weight of the used adsorbent (g)
m_{FS}	The Fritz–Schlunder model exponent
m_{LF}	The heterogeneity parameter, lies between 0 and 1
m_R	The Radke–Prausnitz model exponent
N	The number of experimental points
n	Freundlich and Halsey equation exponents
n_H	Hill cooperativity coefficient of the binding interaction
q_e	Amount of dye adsorbed at equilibrium time ($mg\,g^{-1}$)
q_H	Hill isotherm maximum uptake saturation ($mg\,L^{-1}$)
q_m	Maximum adsorption capacity in Langmuir model ($mg\,g^{-1}$)
q_{max}	Maximum adsorption capacity in Jovanovic model ($mg\,g^{-1}$)
q_{mFS}	The Fritz–Schlunder maximum adsorption capacity ($mg\,g^{-1}$)
q_{mLF}	The Langmuir–Freundlich maximum adsorption capacity ($mg\,g^{-1}$)
q_{mR}	The Radke–Prausnitz maximum adsorption capacity ($mg\,g^{-1}$)
q_t	The amount of dye which is adsorbed at time t ($mg\,g^{-1}$)
R	The universal gas constant ($J\,mol^{-1}K^{-1}$)
R_2	The correlation coefficient
T	Temperature (K)
t	Experiment time (min)
V	The used volume of dye solution (L)
ΔH°	Standard enthalpy
ΔG°	Change in standard free energy
ΔS°	Standard entropy
ε	Redlich–Peterson constant

By examining recent research, it can be confirmed that adsorption is one of the most attractive techniques owing to: being simple, flexible, cheap, high performance, and an extensive range of chemical substances separation capabilities (Rozumová et al., 2016).

Several research studies have been conducted to investigate the applications and importance of dyehouse effluent treatment via adsorption on natural and synthesized adsorbents (Abdel-Ghani and Rawash, 2016; Borah et al., 2015; Marković et al., 2015; Namasivayam and Kavitha, 2002; Oladoja et al., 2009; Peydayesh and Rahbar-Kelishami, 2015; Waranusantigul et al., 2003).

Currently, due to the cost, high removal efficiency for large scale applications, engineering convenience and resource sustainability, much attention has been focused on natural adsorbents (Peydayesh and Rahbar-Kelishami, 2015).

MB removal from aqueous solution using dried *Spirodela polyrrhiza* has been studied by Waranusantigul et al. (2003) and a high sorption capacity was reported in the pH range of 3.0–11.0 (Pavan et al., 2008). Furthermore, it has been demonstrated that hazelnut shell is capable of MB elimination from wastewater (Doğan et al., 2009). Sugar beet pulp was reported as a potential source and a well-known natural adsorbent for the removal of cationic dyes such as MB, and the effects of time, initial concentration and pH were studied. It was found that the Langmuir and Freundlich isotherm models were appropriate to describe the adsorption equilibrium. Another natural adsorbent, spent tea leaves, was studied to find the best fit isotherm, and the kinetic data were analyzed for MB removal from aqueous solutions (Hameed, 2009). Very few adsorption studies have been reported based on maize agricultural waste (Foo, 2016; Guyo et al., 2015; Lara-Vásquez et al., 2016). Furthermore, several natural adsorbents such as fish scale, *Platanus orientalis* leaf, pine cone, bentonite clay, roots of *Eichhornia crassipes* and date palm leaves have been used for dye removal (Dawood and Sen, 2012; Hameed and Ahmad, 2009; Kallel et al., 2016; Mohamed, 2015; Petrović et al., 2016; Peydayesh and Rahbar-Kelishami, 2015; Vieira et al., 2009; Wanyonyi et al., 2014).

Maize is recognized as one the top five most cultivated productions of farm crops around the world and is on the top of increasing levels of production for agricultural products with its associated millions of tonnes of husk and powder wastes. Although there is no data available for the adsorption of a cationic dye like MB using maize silk (MS), it can be considered as a prospective natural adsorbent because of its various chemical constituents (i.e. volatile oils, steroids, polyphenols and proteins) and its functional groups such as carboxyl, hydroxyl and carbonyl on the surface.

In the present study, powdered maize silk (PMS), was utilized for removing MB from aqueous solutions. The effects of all operating parameters such as contact time, temperature, pH, and initial MB concentration on MB adsorption have been explored. In addition, to determine the best fit isotherm and isotherm constants for water treatment plant design, nine error functions were determined and tested for the purpose of minimizing the error distribution between experimental data and obtaining the characteristic data from ten dissocial isotherms. Furthermore equilibrium, kinetics and thermodynamic studies were performed.