

# Removal of Methylene Blue from Aqueous Solution by Adsorption onto Crofton Weed Stalk

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Crofton weed stalk (CWS) was used as an adsorbent to remove methylene blue (MB) from aqueous solution. The adsorbent was analyzed by FT-IR and observed by SEM. The porosity and  $\text{pH}_{\text{zpc}}$  were measured. The effects of adsorbent dose, initial dye concentration, solution pH, and solution temperature were investigated. Models of the adsorption kinetics and isotherms were analyzed, and thermodynamic parameters were calculated at different temperatures. The results showed that the adsorption capacity of MB on CWS increased with increasing initial concentration from 10 to 40 mg/L and pH from 2 to 7. The amount of MB removed increased as the adsorbent dosage was increased from 0.2 to 1.2 g/L. The maximum dye adsorption capacity of 28 mg/g was reached at around 120 min in a solution of 40 mg/L. A pseudo-second-order kinetic model described the kinetics well, and the experimental data followed the Freundlich model. The calculated values of standard free energy ( $\Delta G^\circ$ ) and standard enthalpy ( $\Delta H^\circ$ ) were negative, which indicates the adsorption process is spontaneous and exothermic. The values of both free energy and  $\Delta G^\circ$  indicate that the adsorption is a physical process. This work shows CWS could be utilized as an effective adsorbent for treating dye wastewater.

*Keywords:* Adsorption; Crofton weed stalk; Dye removal; Methylene blue

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## INTRODUCTION

Dyes can give various products beautiful colors, and therefore they are widely used in many fields such as textiles, paper, plastic, food, painting, and medicine (Sajab *et al.* 2011; Safa and Bhatti, 2011). Large quantities of dye effluent are produced in the dye manufacturing industries and during the dyeing process. According to incomplete statistics, there are more than 10,000 types of dyes in commercial circulation (Altınışık *et al.* 2010; Senturk *et al.* 2010). About  $7 \times 10^5$  tons of dyes are manufactured worldwide each year, and 10 to 15% may be discharged into bodies of water as effluents that seriously pollute the environment and affect aquatic organisms (Gong *et al.* 2008; Moussavi and Khosravi 2011). Moreover, most of them are toxic and can seriously harm human health (Sun *et al.* 2007). The conventional treatment methods for dye wastewater, such as oxidation (Arslan *et al.* 2000), coagulation (Pattabhi and Yun 2007; Szyguła *et al.* 2009; Verma *et al.* 2012), flocculation (Wang *et al.* 2012), photochemical destruction (Deng *et al.* 1997), ion exchange (Labanda *et al.* 2009), and membrane filtration (Ciardelli *et al.* 2000), are complicated and costly. In addition, some methods require additional chemicals or produce toxic products.

Adsorption can be considered an efficient and relatively low-cost method for the removal of pollutants from wastewater. Activated carbon is an efficient adsorbent. However, its high cost and difficulty of regeneration limit its utilization. Recently, many studies have been carried out to investigate the adsorption capabilities of some low-cost bio-adsorbents such as cork bark and grape stalks (Olivella *et al.* 2012), pine needle (Deniz and Karaman, 2011), sugarcane bagasse (Orlando *et al.* 2003), *Loofa egyptiaca* (El Ashtoukhy 2009), orange peel (Vieira *et al.* 2009), sawdust (Hameed and El-Khaiary 2008), palm kernel fibre (Ofomaja 2007), peanut hull (Gong *et al.* 2005), apple pomace (Robinson *et al.* 2002), and coconut husk (Manju *et al.* 1998). New low-cost adsorbents with high adsorption capacities that are readily available are still needed.

Crofton weed (*Eupatorium adenophorum* Spreng.) is a tufty, semi-shrubby, perennial herbaceous plant native to Central America, mainly Mexico. It easily adapts to different environments and grows fast. It is now distributed widely in many countries. In China, it is an invasive plant and has spread rapidly from southwest to northeast (Lu *et al.* 2005), damaging native ecosystems and causing great economic losses (Yu *et al.* 2005). In recent decades, there have been many attempts to control it, including manual, chemical, and biological methods; however, their effectiveness has been very limited. Compared with ineffective control processes, effective utilization of the weed would provide more benefits. Several studies have reported on the utilization of crofton weed. Extracts of crofton weed were used as pesticides against rats (Kaushal *et al.* 2001), *Aphis gossypii* (Wang *et al.* 2002), tetranychus and panonychus (Liu *et al.* 2004), and *Psoroptes cuniculi* and *Sarcoptes scabiei* (Nong *et al.* 2012) because of their toxicities. The stalk has been used as feedstock for the production of fermentable sugars (Zhao *et al.* 2008) and biogas (Patrabansh and Madan 2000), or as raw material for preparing activated carbon with a large surface area (Xia *et al.* 2008).

Stalk particles have also been used as an adsorbent for removing  $Pb^{2+}$  from aqueous solution (Guo *et al.* 2009). This study reports, for the first time, on the feasibility of utilizing crofton weed stalk (CWS) as a low-cost alternative adsorbent for removing methylene blue (MB) from aqueous solution. The effects of adsorbent dosage, initial dye concentration, pH, contact time, and temperature on MB adsorption onto CWS were investigated. Adsorption kinetics, isotherms, and thermodynamic parameters were analyzed to reveal the mechanism of adsorption of MB molecules onto CWS.

## EXPERIMENTAL

### Adsorbate

MB ( $C_{16}H_{18}N_3OS$ , C.I. 52030,  $\lambda_{max}$  660 nm) was purchased from Alfa Aesar Co. (Tianjin, China). Solutions of MB were prepared by dissolving accurately weighed amounts of the dye in distilled water. Experimental solutions of various concentrations were obtained by further dilutions. Standard curves were developed via measurement of the absorbance of the dye solutions by a UV-visible spectrophotometer (TU-1900).

### Preparation of adsorbents

Crofton weed was collected from Yunnan Province, P.R. China. Its stalk was dried, crushed, and sieved to particles with a size range of 60 to 80 mesh. The particles were extracted with 60% EtOH to obtain flavonoids. The residue was dried and used as an adsorbent. The holocellulose, lignin, alcohol-benzene extracts, and pentosans in the

extracted crofton weed stalk were measured according to Chinese standards GB/T 2677.10-1995, GB/T 2677.8-1994, GB/T 2677.7-1981, and GB/T 2677.9-1994, respectively.

### Characterization of Adsorbent

The nitrogen sorption isotherms were measured by the volumetric method on an automatic adsorption instrument (ASAP2020, USA) at liquid nitrogen temperature (77.2 K). The specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method from the data in a  $P/P_0$  range of 0.06 to 0.2. The point of zero charge ( $\text{pH}_{\text{PZC}}$ ) was determined by the solid addition method (Vieira *et al.* 2009) to determine whether the sorbent surface is negative, neutral, or positive under various pH conditions. To a series of 100-mL conical flasks, 10.0 mL portions of NaCl solution were transferred with pH values ranging between 2 and 11. Then, 0.05 g of adsorbent was added to each flask, which was immediately securely capped and shaken for 10 h. The difference between the final and initial pH values ( $\Delta\text{pH}$ ) was plotted against the initial pH, and the point of intersection on the X-axis corresponds to the point of zero charge ( $\text{pH}_{\text{PZC}}$ ). The chemical structure of crofton weed stalk (CWS) was characterized using an FT-IR spectrometer (Nicolet 560, Nicolet Co., Ltd., USA), and the samples were prepared by the KBr tablet method. The surface morphology of CWS particles was observed using a Quanta 200 scanning electron microscope (SEM). Specimens were observed after spraying with gold.

### Batch Adsorption Studies

Batch adsorption experiments were performed to evaluate the applicability of CWS as an adsorbent for dye waste water treatment. The effects of various process parameters, such as adsorbent dose, initial concentration, and initial pH, were investigated. Solutions were adjusted to various pH values (2 to 10) using 1.0 M HCl and NaOH solutions. Contact times of up to 12 h were employed to find the adsorption equilibrium. Dried samples of CWS were added to 100 mL of MB solution in 250-mL conical flasks. The solutions were shaken on a constant temperature water bath shaker and were separated from the adsorbent by filtration with a 500-mesh nylon screen at the end of the adsorption period. The absorbance of the dye solutions were recorded at  $\lambda_{\text{max}} = 660$  nm. The final concentrations of the dye solutions were calculated from the standard curve obtained from prior adsorption experiments.

The dye removal efficiency ( $R$ ) and the amounts of absorbed dye per unit mass of sorbent at moment  $t$  ( $q_t$ , mg/g) and at equilibrium ( $q_e$ , mg/g) were calculated by using the following equations:

$$R(\%) = (C_0 - C_t) / C_0 \times 100\% \quad (1)$$

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

$$q_e = (C_0 - C_e)V/W \quad (3)$$

where  $C_t$  (mg/L) is the dye concentration at time  $t$ .  $C_0$  and  $C_e$  (mg/L) are the initial and equilibrium concentrations of the dye solution, respectively.  $V$  is the volume of the dye solution (mL), and  $W$  is the amount of the adsorbent (g).

Kinetic studies of MB adsorption on CWS were conducted at a fixed initial MB concentration of 20 mg/L, dose of 0.1 g, and solution pH of 5.76. The temperature was varied to investigate its effects on the adsorption kinetics.

The equilibrium study was performed at three temperatures, 32 °C, 43 °C, and 51 °C. The MB adsorptions from 10 mg/L solutions to which various dosages of CWS (0.02 to 0.12 g) had been added were recorded after 10 h, when they had reached adsorption equilibrium.

## RESULTS AND DISCUSSION

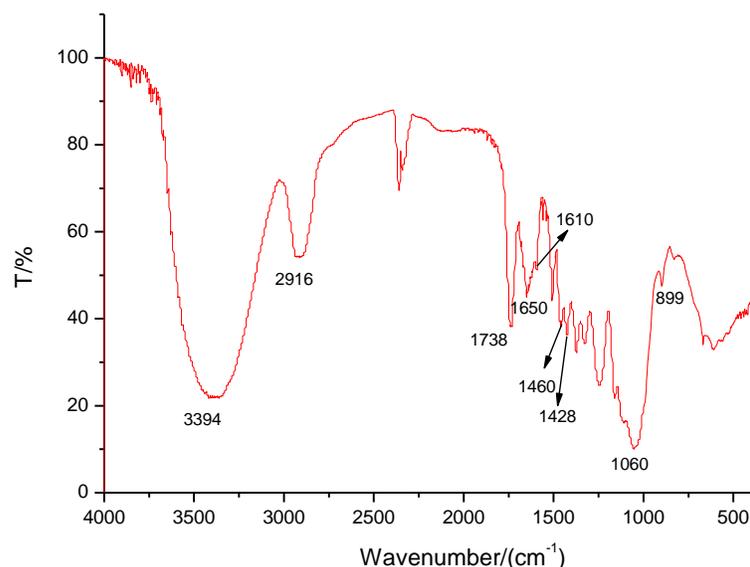
### Characterization of the Adsorbent

After extraction with 60% ethanol, most of the small molecular substrates and soluble oligosaccharides were removed. As shown in Table 1, key compounds in the residue included cellulose, lignin, and pentosans.

**Table 1.** Chemical Composition of Extracted Crofton Weed Stalk (%)

Moisture	Holocellulose	Lignin	Alcohol-benzene extraction	Pentosan
5.85	82.33	13.07	0.43	20.34

The FTIR spectrum of CWS is shown in Fig. 1. The spectrum shows a large number of functional groups, which constitute the biomaterial. The peaks at around 1060  $\text{cm}^{-1}$  and 899  $\text{cm}^{-1}$  are attributed to a pyranoid ring and a  $\beta$ -D-glucoside bond in the cellulose, respectively (Wang and Li 2013). The broad peak at 3382  $\text{cm}^{-1}$  is due to the vibration of an -OH group. The band at 1738  $\text{cm}^{-1}$  ( $\nu_{\text{C=O}}$ ), along with another peak at 1428  $\text{cm}^{-1}$  ( $\nu_{\text{C-O}}$ ), indicates the presence of carboxylic acid groups. The peak at 1650  $\text{cm}^{-1}$  is attributed to the stretching of conjugated carbonyl bonds in the lignin. The other bands around 1610 to 1460  $\text{cm}^{-1}$  are attributed to aromatic rings, aromatic skeletal vibrations, and aromatic ring deformations (Vieira *et al.* 2011).



**Fig. 1.** FT-IR spectrum of CWS

As shown in Fig. 2, CWS exhibited a porous structure. The cell lumens are readily apparent in the SEM images. The pore size was in the range of 25 to 50  $\mu\text{m}$ . There were also many small pores of around 1  $\mu\text{m}$ . Larger pores contribute little to enhance the specific surface area. The BET and Langmuir surface areas were found to be 1.908  $\text{m}^2/\text{g}$  and 2.927  $\text{m}^2/\text{g}$ , respectively, which are far lower than those of activated carbon. The results indicate the absence of significant pore adsorption in the sorption process.

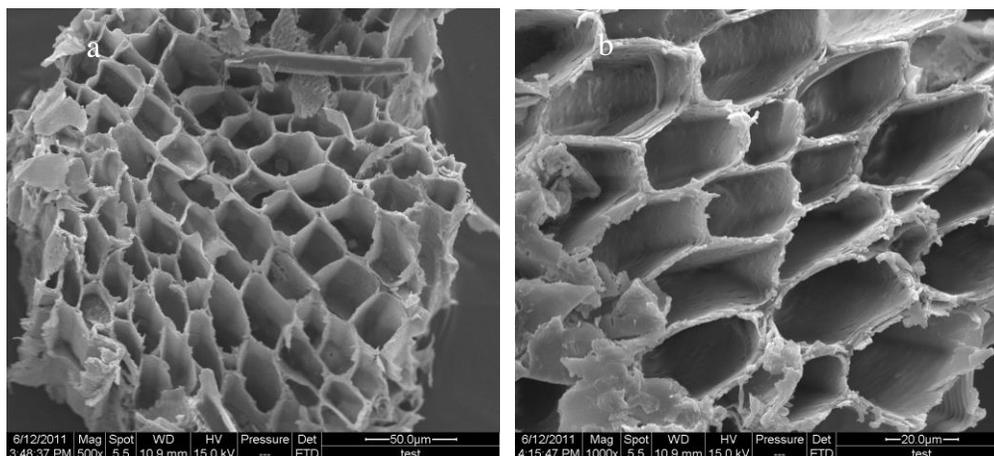


Fig. 2. SEM photos of crofton weed stalk particle (a) 500 $\times$  and (b) 1000 $\times$

### Effect of Contact Time

The effect of contact time on the adsorption of MB onto CWS adsorbent was studied under the conditions given in Fig. 3. The adsorption capacity increased rapidly in the initial stage with an increase in contact time, and then increased gradually as the system approached equilibrium. Equilibrium was reached within 60 min, independently of the temperature.

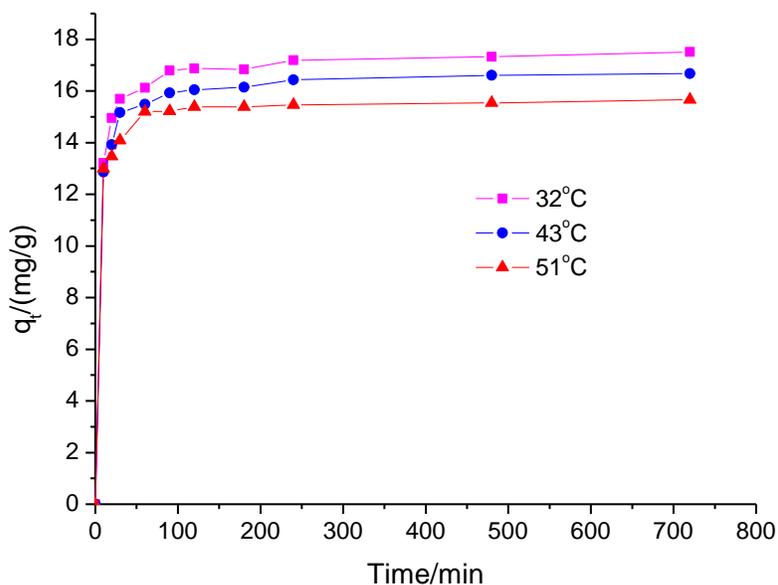
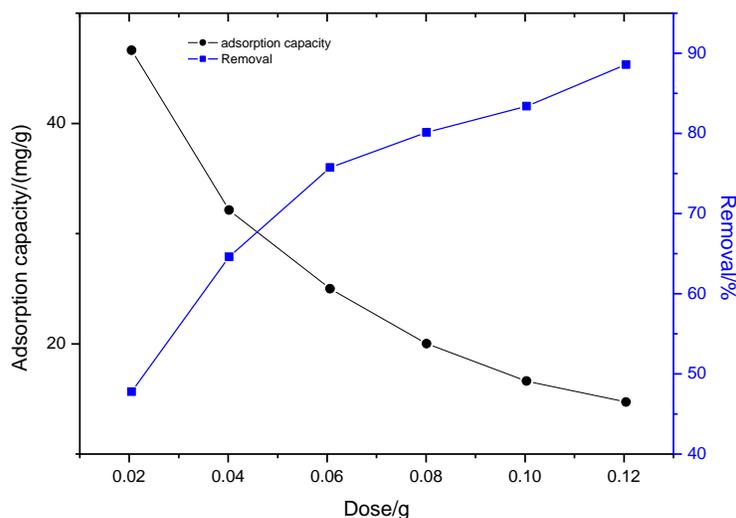


Fig. 3. Effect of contact time on the adsorption capacity of MB (pH 5.63, dosage 1.0 g/L, dye concentration 20 mg/L, volume 100 mL)

### Effect of Adsorbent Dose

The adsorption of MB by CWS was investigated by changing the amounts of adsorbents (20 to 120 mg/100 mL) for an initial MB concentration of 20 mg/L at 32 °C and pH 5.76. As shown in Fig. 4, the adsorption capacity decreased from 46.63 mg/g to 14.71 mg/g; however, MB removal increased from 44.79% to 88.57% with the increase in adsorbent dose from 200 mg/L to 1200 mg/L. The increase in adsorbent dosage favors dye removal. This is due to the greater availability of adsorption sites as well as the larger surface area at higher adsorbent dosage. However, the adsorption capacity decreased because more and more of the active sites were not fully occupied as the dosage was increased.



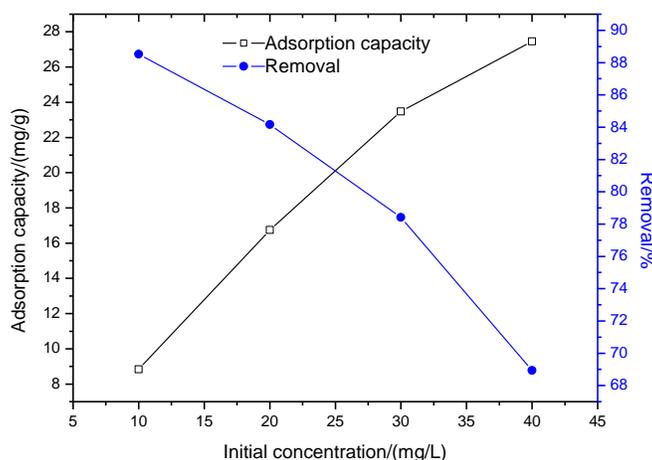
**Fig. 4.** Effect of CWS dose on the biosorption capacity (a) and removal (b) of MB (pH 5.63, dye concentration 20 mg/L, volume 100 mL, temperature 32 °C, and time 10 h)

### Effect of Initial Concentration

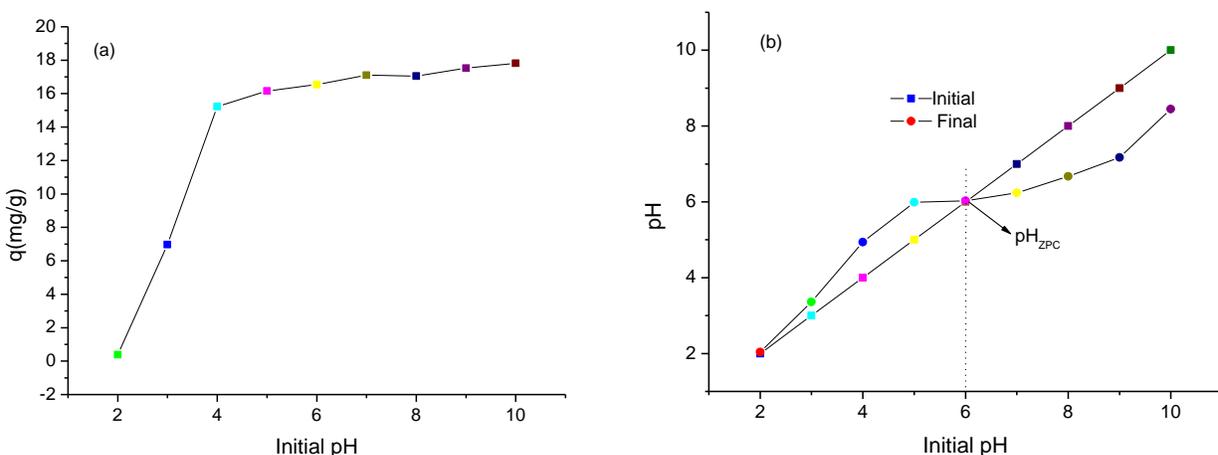
The effect of initial concentration on the adsorption of MB by CWS was also studied, and the results are shown in Fig. 5. The adsorption capacity increased with an increase in initial MB concentration. The opposite trend was observed in the percentage MB removed. When the initial MB concentration increased from 10 to 40 mg/L, the adsorption capacity increased from 8.84 to 27.46 mg/g, whereas the percent removal decreased from 88.52% to 68.93%. This is because the initial dye concentration provides a powerful force to drive mass transfer between the aqueous and solid phases.

### Effect of Initial pH

The effect of initial pH on the adsorption of MB by CWS was examined in the range of 2 to 10 under the conditions given in Fig. 6. The pH obviously affected MB adsorption onto CWS, particularly at lower pH values. As shown in Fig. 6 (a), the adsorption capacity increased from 0.39 mg/g to 17.06 mg/g with an initial pH increase from 2 to 7. The adsorption subsequently changed little as the pH increased beyond 7. Fig. 5 (b) shows that the  $pH_{zpc}$  of CWS particles was around 6.0, which means that the CWS surface was positively charged at pH values below 6.0 and negatively charged at pH values beyond 6.0 because the carboxylic acid groups will be dissociated to form carboxylate ions with the OH<sup>-</sup> increasing (Hubbe *et al.* 2012).



**Fig. 5.** Effect of initial dye concentration on the adsorption capacity (a) and removal (b) of MB (pH 5.63, dosage 1.0 g/L, volume 100 mL, temperature 32 °C, and time 3 h)



**Fig. 6.** Effect of initial pH on the adsorption of MB (a) and final pH (b) (dosage 1.0 g/L, dye concentration 20 mg/L, volume 100 mL, temperature 32 °C, and time 3 h)

The carboxyl groups on the surface of CWS particles play a major role in the adsorption of MB. At lower pH, protons will compete for adsorption sites with MB molecules. Moreover, a positively charged surface causes repulsion of the cationic MB molecules. Those interactions result in the lower adsorption of MB onto CWS. With the rise in pH, the surface of the adsorbent becomes de-protonated, the competition weakens, and positively charged MB cations replace  $H^+$  ions binding to carboxylate ions on the CWS surface, resulting in increased adsorption due to electrostatic attraction.

### Adsorption Kinetics

In order to analyze the controlling mechanism of the adsorption of MB onto CWS, a pseudo-first-order equation, pseudo-second-order equation, and intraparticle model were used to fit the adsorption data. In general, the kinetics have been found to follow a pseudo-first-order model in which adsorption is preceded by diffusion through a boundary. The second-order model is often used to predict the whole adsorption process,

and chemisorption is the rate-limiting step. In addition, the intraparticle diffusion model is often used to determine the diffusion mechanism of the adsorption process.

The pseudo-first-order model (Ahmad *et al.* 2007) can be written as,

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (4)$$

where  $k_1$  (1/min) is the rate constant of the pseudo-first-order adsorption, and  $q_t$  and  $q_e$  (mg/g) are the adsorbed amounts at time  $t$  and at equilibrium. Values of the quantities  $k_1$  and  $q_e$  can be obtained from the slope and the intercepts of the plots of  $\ln(q_e - q_t)$  versus  $t$ . The linear pseudo-first-order plots for the adsorption of MB onto CWS are shown in Fig. 7(a). The related parameters are listed in Table 2. It was observed that the  $R^2$  values were low; moreover, the experimental  $q_e$  values were far from the values obtained from the linear plots. This indicates that the adsorption of MB on CWS does not fit a pseudo-first-order kinetic model.

The pseudo-second-order model can be expressed by the following equation (Dotto *et al.* 2012),

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad (5)$$

where  $k_2$  (g/mg min) is the rate constant of the pseudo-second-order model. The slope and the intercept of the plots of  $t/q_e$  versus  $t$  were obtained to calculate  $k_2$  and  $q_e$ . As shown in Fig. 7 (b) and Table 2, there was an excellent agreement between the experimental and the calculated  $q_e$  values. All  $R^2$  values obtained from the pseudo-second-order model reached 1.000, which indicates that the adsorption of MB on CWS followed the pseudo-second-order model very well.

The initial rate of the adsorption at time approaching zero was estimated from the pseudo-second-order kinetic model from the equation below:

$$h_{0.2} = k_2 q_e^2 \quad (6)$$

The results are listed in Table 2. The highest initial rate of the adsorption was obtained at the lowest temperature in the experimental temperature range.

The half-sorption time,  $t_{1/2}$  is the time required for the sorption to take up half as much as its equilibrium value. It is often used as an evaluation of the adsorption rate.

$$t_{1/2} = 1/k_2 q_e \quad (7)$$

As shown in Table 2, the shortest half-sorption time was obtained at the lowest experimental temperature in this study. Those indicate that lower temperature favors the adsorption of MB onto CWS particles.

The Arrhenius equation (Ahmad and Alrozi 2011) was used to evaluate the activation energy of the adsorption, by application of Eq. 8,

$$\ln k_2 = \ln A - (E_a/RT) \quad (8)$$

where  $k_2$  (g mg<sup>-1</sup> min<sup>-1</sup>) is the rate constant of the pseudo-second-order model. The quantity  $E_a$  (kJ mol<sup>-1</sup>) is the Arrhenius activation energy of adsorption and  $A$  is the Arrhenius factor. When  $\ln k_2$  is plotted against  $1/T$ , the slope of the straight line gives the

result -  $E_a/RT$ . In general, relatively low activation energies (5 to 40 kJ/mol) are characteristic of physical adsorption. As shown in Table 2, the  $E_a$  value was 7.56 kJ/mol for the adsorption of MB onto CWS particles, indicating that the adsorption should be a physically controlled process.

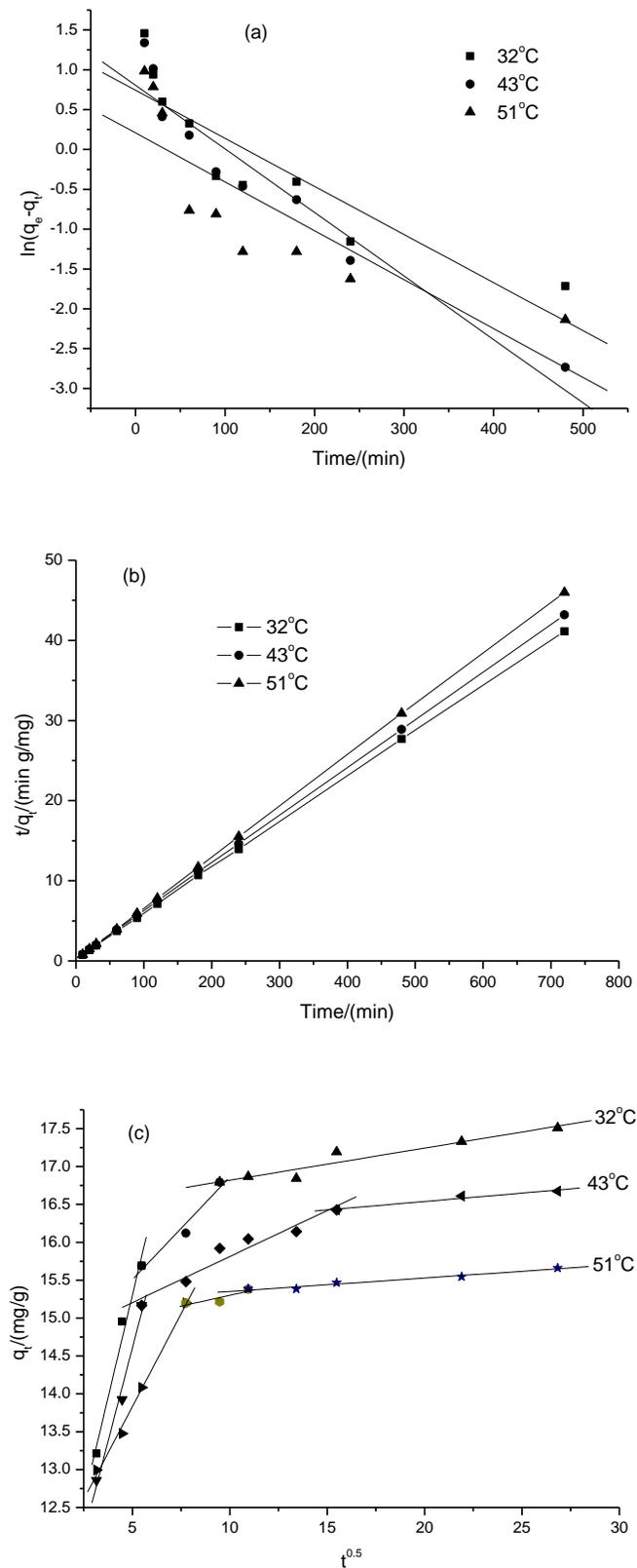
The mechanism of adsorption of the dye on the adsorbent is assumed to involve three steps, one or more of which can control the whole adsorption rate. The steps (Witek-Krowiak 2011) are: (1) mass transfer across the boundary film to the surface of the particle; (2) mass transfer from the exterior surface of the particle to the interior pores via a pore diffusion or intraparticle diffusion mechanism; and (3) diffusion of the adsorbate molecules to active sites either by a pore diffusion process or by a solid surface diffusion mechanism. The intraparticle diffusion model can be represented by Eq. 9 (Huang *et al.* 2011),

$$q_t = K_p t^{0.5} + C_i \quad (9)$$

where  $q_t$  (mg/g) is the absorption capacity at time  $t$ ,  $K_p$  (mg/g min<sup>0.5</sup>) is the intraparticle rate constant, and  $C_i$  is a constant related to the thickness of the boundary layer. As shown in Fig. 7(c), the straight lines did not pass through the origin, and the adsorption of MB onto CWS proceeded in three consecutive processes. This behavior indicates that more than one process affects the adsorption but only one is rate-limiting within a particular time range (Li *et al.* 2007; Zhong *et al.* 2011). The slope of the linear portion reflects the rate of adsorption. As shown in Table 2, the slope decreased from the first portion to the third portion at each temperature, which implies that the intraparticle diffusion of MB molecular species into the micropores was the rate-limiting step in the adsorption process on CWS.

**Table 2.** Kinetic Parameters for MB Adsorption on CWS

Kinetic Models	32 °C	43 °C	51 °C
$q_e$ experimental (mg/g)	17.509	16.675	15.662
Pseudo-first order			
$k_1$ (1/min)	0.006	0.008	0.006
$q_e$ calculated (mg/g)	2.104	2.237	1.231
$R^2$	0.804	0.923	0.682
Pseudo-second order			
$k_2$ (mg/g min)	0.0120	0.0132	0.0143
$q_e$ (mg/g)	17.575	16.750	15.699
$h_{0.2}$ (mg/g min)	3.72	3.69	3.54
$t_{1/2}$ (min)	4.72	4.53	4.45
$R^2$	1.000	1.000	1.000
$E_a$ (kJ/mol)		7.56	
Intraparticle diffusion			
$K_{p1}$ (mg/g min <sup>0.5</sup> )	1.083	0.989	0.490
$C_1$ (mg/g)	9.888	9.663	11.379
$R^2$	0.976	0.985	0.995
$K_{p2}$ (mg/g min <sup>0.5</sup> )	0.271	0.122	0.035
$C_2$ (mg/g)	14.153	14.597	14.927
$R^2$	0.960	0.939	0.864
$K_{p3}$ (mg/g min <sup>0.5</sup> )	0.042	0.022	0.017
$C_3$ (mg/g)	16.396	16.095	15.190
$R^2$	0.919	0.963	0.964



**Fig. 7.** Pseudo-first-order (a), pseudo-second-order (b), and intraparticle (c) kinetic models for MB adsorption by CWS (initial pH, dosage 1.0 g/L, dye concentration 20 mg/L, volume 100 mL)

### Adsorption Isotherms

In this work, two isotherm equations, Langmuir and Freundlich, were fitted to the experimental equilibrium data for MB at various temperatures.

The Langmuir isotherm is based on the hypothesis that uptake occurs on a homogeneous surface by monolayer adsorption without interaction between the adsorbed materials (Li *et al.* 2009). The application of the Langmuir model produces two parameters: the maximum adsorption capacity  $q_m$  and the constant  $b$ . The linear equation (Tang *et al.* 2012) can be expressed as:

$$C_e/q_e = 1/(bq_m) + C_e/q_m \quad (10)$$

As shown in Table 3,  $R^2$  values at different temperatures were determined to be in the range of 0.667 to 0.968. Moreover,  $q_m$  calculated from the Langmuir isotherm was far higher than the experimental value. Therefore, the Langmuir model does not describe the adsorption of MB onto CWS.

The Freundlich isotherm model is an empirical equation for investigating the non-linear adsorption process taking place on heterogeneous surfaces. The linear form of the Freundlich equation (Freundlich 1906) is given as follows,

$$\ln q_e = \ln k_f + (1/n)\ln C_e \quad (11)$$

where  $k_f$  is the coefficient for the adsorbed amount and  $1/n$  is the Freundlich constant.

The parameters of the Freundlich isotherm model for MB adsorption on CWS are shown in Table 3.  $R^2$  values were uniformly higher than 0.979, which indicates a good correlation between the adsorption process and the Freundlich model. In addition, the Freundlich constant ( $1/n$ ) is related to the adsorption intensity of the adsorbent. When  $1/n$  is in the range 0.5 to 1.0, the adsorption occurs readily. As shown in Table 3, the  $1/n$  values were 0.788, 0.810, and 0.544 at 32 °C, 43 °C, and 51 °C, respectively. This indicates that MB molecules were easily adsorbed onto the surface of CWS.

**Table 3.** Isotherm Parameters of the Adsorption of MB onto CWS

Isotherm Models	32 °C	43 °C	51 °C
Langmuir			
$q_m$ (mg/g)	149.24	151.52	49.51
$b$ (L/mg)	0.041	0.039	0.120
$R^2$	0.667	0.755	0.968
Freundlich			
$1/n$	0.788	0.810	0.544
$k_f$ (mg/g)	7.038	6.605	7.613
$R^2$	0.979	0.987	0.983
Dubinin-Radushkevich			
$K_{DR}$ (mol <sup>2</sup> /J <sup>2</sup> )	$-1 \times 10^{-6}$	$-1 \times 10^{-6}$	$-1 \times 10^{-6}$
$q_m$ (mg/g)	34.03	36.88	31.47
$R^2$	0.970	0.979	0.985
$E$ (kJ/mol)	0.71	0.71	0.50

In order to calculate the mean free energy value, the Dubinin-Radushkevich (DR) isotherm was applied for the adsorption of MB onto CWS. The DR equation (Ergene *et al.* 2009) can be expressed as below,

$$\ln q_e = \ln q_m - K_{DR} \varepsilon^2 \quad (12)$$

where  $q_e$  is the equilibrium amount of dye adsorbed on CWS (mg/g),  $q_m$  is the Dubinin-Radushkevich monolayer capacity (mol/g),  $K_{DR}$  is the constant related to sorption energy ( $\text{mol}^2/\text{J}^2$ ), and  $\varepsilon$  is the polanyi potential, which can be calculated as follows:

$$\varepsilon = RT \ln(1 + 1/C_e) \quad (13)$$

where  $C_e$  is the equilibrium concentration of dye (mg/L),  $R$  is the gas constant (8.314 J/mol K), and  $T$  is the temperature (K).

The mean free energy  $E$  (kJ/mol) of sorption can be obtained from  $\beta$  values by use of the following equation:

$$E = (-2K_{DR})^{-1/2} \quad (14)$$

The parameters obtained from DR equations are listed in Table 3. The free energies of MB adsorption onto CWS were 0.71 kJ/mol, 0.71 kJ/mol, and 0.50 kJ/mol under 32 °C, 43 °C, and 51 °C. The fact that the value of  $E$  was below 8 kJ/mol indicates physical adsorption (Safa and Bhatti, 2011).

### Thermodynamic Analysis

Thermodynamic parameters are extremely important for determining the spontaneity of an adsorption process. The standard free energy change ( $\Delta G^\circ$ ), standard enthalpy change ( $\Delta H^\circ$ ), and standard entropy change ( $\Delta S^\circ$ ) are associated with the adsorption process. These parameters can be calculated from the following equations (Baek *et al.* 2010),

$$k_c = C_a / C_e = (C_0 - C_e) / C_e \quad (15)$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ = -RT \ln k_c \quad (16)$$

$$\ln k_c = -(\Delta H^\circ / RT) + \Delta S^\circ / R \quad (17)$$

where  $k_c$  is the equilibrium constant,  $C_a$  (mg/g) is the equilibrium concentration on the adsorbent, and  $C_0$  and  $C_e$  (mg/g) are the initial and equilibrium concentration of dye in the solution, respectively.  $R$  is the universal gas constant (8.314 J/mol K), and  $T$  is the absolute temperature. The values of  $\Delta G^\circ$  and  $\Delta H^\circ$  are obtained from the slope and intercept by plotting  $\ln k_c$  versus  $1/T$ . The thermodynamic parameters are listed in Table 4. The negative value of  $\Delta G^\circ$  for the three tested temperatures indicates the spontaneity and feasibility of the adsorption of MB on CWS under experimental conditions. Moreover, the values of  $\Delta G^\circ$  between -20 and 0 kJ/mol indicate a physical adsorption process (Moussavi and Khosravi 2011). The negative value of  $\Delta H^\circ$  indicates that the sorption is exothermic in nature. The positive value of  $\Delta S^\circ$  shows that an increase in randomness occurs at the interface during the sorption process. The results indicate that the adsorption

capacity decreases with increasing temperature; therefore, lower temperatures favor the adsorption.

**Table 4.** Thermodynamic Parameters of CWS for MB

$\Delta H^\circ$ (kJ/mol)	$\Delta S^\circ$ (J/K mol)	$\Delta G^\circ$ (kJ/mol)		
		32 °C	43 °C	51 °C
-27.70	74.33	-5.04	-4.33	-3.50

## CONCLUSIONS

This study shows that crofton weed stalk (CWS), a biomass derived from a fast-growing invasive wild grass, can be used as an adsorbent for removal of MB from aqueous solutions by an adsorption technique. The adsorption of MB on CWS was dependent on adsorbent dosage, initial dye concentration, solution pH, and temperature. The amount of MB adsorbed on CWS increased as the initial concentration increased and as the pH increased in the range from 2 to 6. Kinetics studies indicated that a pseudo-second-order model described the adsorption process well. MB adsorption onto CWS followed the Freundlich isotherm model. Thermodynamic studies demonstrated that the adsorption processes were spontaneous and exothermic since both  $\Delta G^\circ$  and  $\Delta H^\circ$  values were negative. The adsorption is a physical process. CWS is a promising alternative material to some costly adsorbents for cationic dye removal during wastewater treatment. It is also an effective use of crofton weed straw.

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