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Removal of methylene blue from aqueous solution by wood millet carbon optimization using response surface methodology

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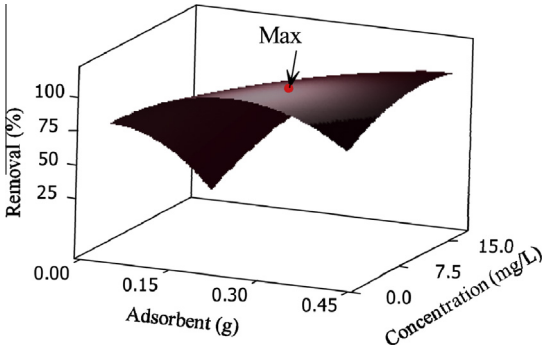
HIGHLIGHTS

- Low-cost and non-toxic walnut carbon (WC) was easily made.
- Walnut carbon was used to remove methylene blue from aqueous solution.
- The dye removal was performed in a very short time (2 min).
- Walnut carbon was re-used after heating.
- Optimization was performed using response surface methodology.

GRAPHICAL ABSTRACT



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ABSTRACT

The use of cheep, non-toxic, safe and easily available adsorbent are efficient and recommended material and alternative to the current expensive substance for pollutant removal from wastewater. The activated carbon prepared from wood waste of local tree (millet) extensively was applied for quantitative removal of methylene blue (MB), while simply. It was used to re-used after heating and washing with alkaline solution of ethanol. This new adsorbent was characterized by using BET surface area measurement, FT-IR, pH determination at zero point of charge (pH_{ZPC}) and Boehm titration method. Response surface methodology (RSM) by at least the number of experiments main and interaction of experimental conditions such as pH of solution, contact time, initial dye concentration and adsorbent dosage was optimized and set as pH 7, contact time 18 min, initial dye concentration 20 ppm and 0.2 g of adsorbent. It was found that variable such as pH and amount of adsorbent as solely or combination effects seriously affect the removal percentage. The fitting experimental data with conventional models reveal the applicability of isotherm models Langmuir model for their well presentation and description and Kinetic real rate of adsorption at most conditions efficiently can be represented pseudo-second order, and intra-particle diffusion. It novel material is good candidate for removal of huge amount of MB (20 ppm) in short time (18 min) by consumption of small amount (0.2 g).

Introduction

Main and significant environmental pollution source are highly color dyes suspended in organic solids or present in bulk solution [1]. Arrival and presence of these pollutants in water significantly damage aquatic life following generation of mutagenic and carcinogenic activity. Textile, paper and printing activities are some source of dye containing wastewater. Versatile (cheep and non toxic material are used for dyes removal present in various media [2–4]. It was found that complex (aromatic) structures dyes due to their high and remarkable stability toward degeneration (phot and

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Nomenclatures

C_t	dye concentration (mg L^{-1}) at time t
Q_e	equilibrium adsorption capacity (mg g^{-1})
C_e	dye concentration (mg L^{-1}) at equilibrium
V	volume of solution (L)
W	weight of adsorbent (g)
k_1	rate constant of pseudofirst order adsorption (min^{-1})
k_2	second-order rate constant of adsorption (mg g^{-1} min^{-1})
H	second-order rate constants (mg g^{-1} min^{-1})
α	initial adsorption rate (mg g^{-1} min^{-1})
β	desorption constant (mg g^{-1})
C	intercept of intraparticle diffusion (related to the thickness of the boundary layer)
K_{dif}	rate constant of intraparticle diffusion (mg g^{-1} $min^{-1/2}$)
F	fraction of solute adsorbed at any time t (mg g^{-1})
Q_m	maximum adsorption capacity reflected a complete monolayer (mg g^{-1}) in Langmuir isotherm model
K_a	Langmuir constant or adsorption equilibrium constant (L mg^{-1}) that is related to the apparent energy of sorption
RL	Dimensionless equilibrium parameter (separation factor)
K_F	isotherm constant indicate the capacity parameter (mg g^{-1}) related to the intensity of the adsorption
N	isotherm constant indicate the empirical parameter (g L^{-1}) related to the intensity of the adsorption
T	absolute temperature in Kelvin
R	universal gas constant (8.314 J K^{-1} mol^{-1})
B_1	related to the heat of adsorption ($B_1 = RT/b$)
K	constant related to the adsorption energy at the D–R isotherm (mol^2 kJ^{-2})
Q_m	theoretical saturation capacity at the D–R isotherm
ε	Polanyi potential at the D–R isotherm
E	mean free energy of adsorption
X^2	chi-squared test statistic
$q_{e,exp}$	experimental data of the equilibrium capacity (mg g^{-1})
$q_{e,calc}$	equilibrium capacity obtained by calculating from the isotherm model (mg g^{-1})
R^2	correlation coefficient

bio degradation), light, heat oxidizing agent and other approach can be considered as more and serious toxic agent for ecosystem. Dyes via direct destruction or inhibition of catalytic capabilities lead to depth in microorganism [5,6].

Among the well known dyes reduction pathways [7–27] more attention was devoted to adsorption that emerged from unique advantages such as highly porous and safe adsorbent. These material due to their unique properties are useful for dyes removal. Carbon simply can be obtained by burning and putting it into a sealed container with very cost effective and non-toxic manner without much energy consumption. All these characteristics of such carbon make it more suitable than commercial activated carbon for diverse application. Methylene Blue (MB) (Fig. 1) manly use for coloring paper, temporary hair colorant, dyeing cottons, wools, while reveal very harmful effects on living things [7–9]. Dyes contaminated ecosystem significantly can perturbed aquatic, plants and human lifes [10–27]. MB due to its chemical resistance to light and oxidizing agent hardly can be removal or eliminated by biological treatment and chemical precipitation [28]. The pestilent and dangerous intermediates/substances created by this dye after undergoing reduction and oxidation in water further increase the need for its removal from wastewater. Therefore, we were motivated to prepare carbon from millet that following subsequent activation is as an ideal MB removal agent. The full characterization of this AC by BET, FT-IR, pH determination at zero point of charge (pH_{ZPC}) and Boehm titration reveal and confirm its applicability to interact with large amount of material through various pathway and mechanism. The experimental runs and optimum conditions were achieved along at least experimental run by central composite design and response surface methodology (RSM). This methodology simply permits to estimate the main effect and interaction of variables through economic and repeatable pathway.

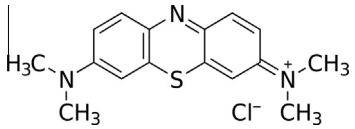

Fig. 1. Chemical structure of methylene blue green.

Subsequent objective of this study was investigation of kinetics and isotherms parameters correspond to MB adsorption onto AC. The whole results confirm the suitability and applicability of the Langmuir model for isothermal study elucidation while the real behavior of adsorption experimental data simply can be represented by combination of pseudo second order and interparticle diffusion model.

Experimental

Materials and instrumentation

The methylene blue with molecular formula $C_{16}H_{18}N_3SCl$ and IUPAC name 3,7-bis(Dimethylamino)-phenothiazin-5-ium chloride, (MW = 319.86 g/mol), with CAS Number of 61-73-4 (United States, Sigma–Aldrich) 100 mg/L as stock solution was supplied by dissolving 10 mg of MB in 100 mL double-distilled water. The effect of solution pH over 2–8 (adjusted via addition of dilute HCl and/or KOH solution) its adsorption removal was studied, while each pH maximum wave length was recorded. All the parameters and experimental data were studied using the software MINITAB (version 16.0).

Preparation of millet carbon

The source material container was heated at 400 °C for 3 h and subsequent production of coal was then slowly cooled to room temperature and rinsed with distilled water. The carbon was grinded to mesh lower than 120 and subsequently was activated by various with mixture of concentrated HCl and HNO_3 with 1:1 valuation. The produced AC was studied by SEM (see Fig. 2), BET and FT-IR. The pH corresponding to the AC point of zero charge (pH_{ZPC}) of was determined by the pH drift method [27,29,30].

Determination of oxygen containing functional groups was carried out as follow (Boehm titration method) [31]: 1.0 g of the AC mixed separately with 15 ml solution of $NaHCO_3$ (0.1 M), Na_2CO_3 (0.05 M) and NaOH (0.1 M) for acidic groups and 0.1 M HCl for basic groups/sites respectively at room temperature for more than