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Malachite green removal using modified sphagnum peat moss as a low-cost biosorbent: Kinetic, equilibrium and thermodynamic studies

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ABSTRACT

Sphagnum peat moss (SPM) as a low-cost biomaterial was treated using hydrochloric acid for the removal of malachite green (MG) from aqueous solution for the first time. In the batch adsorption experiments, the effects of contact time, sorbent dosage, pH, initial dye concentration and temperature on the SPM adsorption capacity were studied. Results indicated that it was favor of adsorption at pH 6.5. Characterization of the adsorbent has been accomplished by SEM, BET, and FTIR analyses. Equilibrium data were accurately fitted onto Langmuir, Freundlich and Temkin isotherms. Investigations showed that the adsorption isotherm data were fitted well to the Langmuir isotherm and the calculated maximum adsorption capacity was about 121.95 mg/g at 20 °C. The adsorption kinetic was better described by pseudo-second order kinetic model. Besides, the thermodynamic parameters, such as ΔG° , ΔH° and ΔS° , were also calculated. Negative value of ΔG° and ΔH° indicated that the adsorption process is spontaneous and exothermic, respectively. It was resulted that the introduced acid modification of SPM is a promising route to prepare a potential biosorbent for MG removal.

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1. Introduction

Synthetic dyes and pigments are one of the major causes of environmental pollution in many industries such as textile, leather tanning, paper production, plastics, cosmetics, and hair colorings. These industries exert highly polluted colored wastewater streams with a large amount of suspended organic solids [1–4]. As a basic dye, MG is a common dye that belongs to triphenylmethane dye class and used extensively for the dyeing of cotton, jute, paper, silk, wool, and leather [1,5]. Despite of widely utilization and consumption, due to the mutagenic, carcinogenic and teratogenic properties, MG may enter into the food chain and could possibly cause injuries to human beings and animals by direct contact, inhalation or ingestion [1,6]. Therefore nowadays, it seems very essential to remove such synthetic dye from industrial effluents before it is discarded into the aquatic environment.

Up to now, the most commonly proposed methods for dye removal from wastewater are adsorption [6–9], membrane process [10], ion exchange [11], precipitation [12], electrochemical oxidation [13] and etc. On the other hand, adsorption has been accepted as a separation technique for the removal of dyes from aqueous solutions, due to

its flexible, simple, efficient and economical nature and it has shown exciting potential in the contamination removal [3,5,14].

Several low cost adsorbents such as sawdust [15], Rice husk [16], treated sawdust [17], Jute fiber [18], treated risk husk [19] and rattan sawdust [20], have been examined on the possibility study to lower dye concentrations and used to water treatment.

Biomaterials such as walnut shell, peat of Brunei Darussalam IV, Tree fern and sphagnum peat moss (SPM) may be used as low cost adsorbents that showing high ability in the treatment of aqueous solutions [3,5,21,22]. Generally, SPM is a light brown to black organic material with large specific surface area which has highly porous structure. Peats are inexpensive widely available plants which can find in many countries such as Brazil, Ireland, Iran and UK. Peat, as an adsorbent, has high cation exchange capacity [21,22]. Beside traditional applications, SPM has been also investigated in the field of wastewater treatment for the removal of heavy metals such as Pb, Cu, Cd [23], mercury [24], and hexavalent chromium [25].

In this paper, adsorption and MG removal capabilities of the modified SPM was tested as a biosorbent. As we know, there is not any report on the application of acid modified peat moss for MG adsorption. Effects of a series of batch experiment parameters such as effects of contact time, pH, initial dyes concentration, adsorbent dosage and temperature on the adsorption capacity were investigated. Moreover, the kinetics, equilibrium (isotherms) and thermodynamic studies were also performed.

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2. Materials and methods

2.1. Reagents

MG ($C_{23}H_{25}ClN_2$, $M_w = 364.92$ g/mol, color index 42000, 99%) dye and other chemical reagents used in this work was supplied from Merck Company (Germany) and used without further purification. The pH was adjusted to a given value by addition of HCl (1 N) or NaOH (1 N) and was measured using a digital pH-Meter (EZODO- PL250, Taiwan). Irish sphagnum peat moss was supplied from Shamrock Company (Kildare, Ireland).

2.2. Adsorbent modification

At first, the collected sorbent was washed several times using distilled water to remove the primary impurities. The washed SPM was dried for 24 h at room temperature. Dried SPMs were ground and sieved with mesh #60 to achieve an average particle size of ~ 300 μ m. Resulted SPM powders were chemically modified by dispersion of 20 g of SPM poured into boiling water and stirred for 90 min. Then, SPMs were put in boiling 1 N HCl solution for 60 min to modify sorbent surface completely. To remove additional HCl at the surface, SPMs were washed with distilled water. At the end, the suspension was filtered with Whatman filter papers (No. 3) and SPMs were dried in ambient temperature for 24 h. The prepared adsorbent was kept in an isolated container at room temperature for future use in the adsorption experiments.

2.3. Adsorption characterization

Fourier Transform Infrared spectroscopy study was carried out at wavelengths in the range 450–4000 cm^{-1} (Perkin Elmer Spectrum, RX1, Germany) to analyze the functional groups, using potassium bromide (KBr) pressed disk technique. The adsorbent morphology was investigated by VEGA\TESCAN scanning electron microscope (SEM) operating at 30 kV accelerated voltage. Besides, the specific surface area was measured by a NOVA[®] Station B Surface Area Analyzer using N_2 sorption method and the Brunauer–Emmett–Teller (BET) model.

2.4. Batch adsorption experiments

A stock solution (500 mg/L) was prepared by dissolving proper amount of MG in deionized water. Batch experiments were carried out to investigate the effect of contact time (0–90 min), pH of the dye solution (2–6.5), adsorbent dosage (0.2–3.2 g/L), initial dye concentration (10–150 mg/L) and temperature (20–45°C). In each experiment except one which was conducted for test of the adsorbent dosage effect, 0.15 mg of SPM was added to 250 mL of MG solution after the pH adjustment. Then, at a constant temperature (20°C), solution was agitated at 160 rpm until reaching the equilibrium condition after 90 min. At the equilibrium state the suspensions were filtered under vacuum condition using filter paper and the residual concentrations of MG in the supernatants were analyzed by measuring the MG concentration at λ_{max} (617 nm) using a double beam UV–visible spectrophotometer (Shimadzu UV-1800, Japan).

The removal efficiency, R , and the amounts of dye adsorbed per unit mass of the adsorbent as well defined by adsorption capacity, q_e (mg/g), were calculated using Eqs. (1) and (2), respectively:

$$R, \% = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

$$q_e = (C_0 - C_e) \frac{V}{M} \quad (2)$$

Where C_0 (mg/L) and C_e (mg/L) are initial and equilibrium concentrations of the MG solutions respectively. V is the volume of the batch solution (L), and M is the amount of the adsorbent (g) used in the experiments.

2.5. Adsorption kinetics

To evaluate the kinetic mechanism of the adsorption process, the pseudo-first-order, pseudo-second-order and intra-particle diffusion models were applied to test the experimental data [26,27].

The linear form of pseudo-first order model is defined as the Eq. (3):

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (3)$$

Where k_1 (min^{-1}) is the Lagergren rate constant of pseudo-first order, q_t (mg/g) and q_e (mg/g) are adsorption capacities at time t (min) and the equilibrium condition, respectively. The values of the constants q_e and k_1 were calculated from the linear plot of $\log(q_e - q_t)$ vs. t .

The pseudo-second-order model is used to evaluate the adsorption kinetic as follows:

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

Where k_2 (g/mg min) is the rate constant of pseudo-second-order model. The value of k_2 and q_e be calculated using the plot of t/q_t vs. t .

The adsorbate species are probably transported from the bulk into the solid phase through intra-particle diffusion. The possibility of intra-particle diffusion which is often the rate-limiting step in many adsorption processes was explored by using the intra-particle diffusion model (Eq. 5):

$$q_t = k_{id} t^{1/2} + C \quad (5)$$

Where C and k_{id} are the constant parameters related to the thickness of the boundary layer (mg/g) and intra-particle diffusion rate constant (mg/g $min^{1/2}$), respectively. C and k_{id} were determined from the intercept and the slope of the q_t versus $t^{1/2}$ plot.

2.6. Adsorption isotherm

The adsorption equilibrium was evaluated using the Langmuir, Freundlich and Temkin isotherm models [11,26,28].

The Langmuir isotherm is based on the assumption of monolayer sorption with a finite number of identical adsorption sites and a homogeneous surface energy distribution is considered. Linear form of the Langmuir isotherm is presented by Eq. (6):

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_L q_m C_e} \quad (6)$$

Where q_e is the equilibrium amount of adsorbate per one gram of the sorbent (mg/g), q_m is maximum adsorption capacity (mg/g), C_e is the equilibrium concentration of adsorbate (mg/L) and K_L is the Langmuir constant (L/mg) related to the affinity of binding sites and the free energy of sorption. When $1/q_e$ was plotted against $1/C_e$, The values of q_m and K_L were obtained from the slope and intercept of the fitted line, respectively. On the other hand, the Freundlich isotherm model for adsorption heterogeneous surface is commonly expressed by following equation:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (7)$$

q_e and C_e were defined in the previous isotherm model. K_F ($((mg/g)/(mg/L)^{1/n})$) and n are the Freundlich constants. K_F and n indicate the sorption capacity and the sorption intensity of the system, respectively. For favorable adsorption, the value of the Freundlich constant should be in the range of 1–10. These parameters can be determined from the plot of $\ln q_e$ vs. $\ln C_e$.

The Temkin isotherm is also available for the heterogeneous adsorption and evaluates the adsorbent–adsorbate interactions on a surface. The linear form of the model is given by Eq. (8):

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