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Microwave-assisted synthesis of tetraethylenepentamine functionalized activated carbon with high adsorption capacity for Malachite green dye

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ABSTRACT

Tetraethylenepentamine-functionalized *Rosa canina*-L fruits activated carbon (TEPFRCA) was synthesized by microwave-assisted method for the fast adsorption and rapid removal of Malachite green (MG) from the solvent phase. The morphological and anatomical characterization of developed adsorbent was carried out using various analytical techniques such as FT-IR and FE-SEM. The impact of various influential parameters such as contact time (1–60 min), initial metal ion concentration (25–65 mg/L), temperature (298–333 K), adsorbent dose (0.001–0.025 g) and initial pH (1–8) of the solution was carried out using a batch adsorption method. The adsorption kinetic and equilibrium data process follows pseudo-second-order reaction kinetics ($R^2 > 0.99$) and the maximum adsorption capacity for TEPFRCA was 333.3 mg/g at 298 K. The whole process of adsorption of MG dye on to the developed adsorbent i.e. TEPFRCA was found to be spontaneous and endothermic under standard conditions.

1. Introduction

Different kinds of dyes are used in various textile industries such as paint, tanneries, pulp, paper, leather, plastics, rubber pharmaceuticals, textiles, food processing, electroplating cosmetics and in wet process such as printing, bleaching, scouring, dyeing, mercerizing and final finishing in coloration of products [1]. Wastewater from those industries contains a great amount of synthetic dyes and the discharge of harmful dyes to rivers without proper treatment causes damage to the environment, including biota, both aquatic and terrestrial [2]. One of the most used basic and cationic dye is Malachite green (MG), that is widely used as biocide, medical disinfectant, and coloring agent on silk, wool, jute, leather, cotton, paper, and acrylic. MG is known to be carcinogenic, mutagenic, and teratogenic to mammalian cell. It has potentially harmful effects on the liver, gills, kidneys, intestines, and gonads in organisms [3].

There are various physical, chemical, and biological methods such as adsorption, biosorption, chemical precipitation, electrochemical treatments, ion-exchange, and membrane filtration which have been used to remove and separate dyes from wastewater [4]. Adsorption process using activated carbon is superior to the other techniques for dye wastewater treatment because of its high efficiency, easy handling and availability of different sorbents [5]. Different industrial, agricultural and forestry types of adsorbents are used to remove MG in the wastewater treatment including lotus leaf [6], waste of rapeseed press cake [7], peanut shell [8], coffee bean [9], spent tea leaves [10] and *Borassus aethiopum* flower biomass [11]. Several other previously developed adsorbents such as carbon nanotubes [12–18], MWCNTs [19,20], nanoparticles and nanocomposites [21–25], rubber tire [26,27], and other low cost adsorbents [28–33] are extensively used for the rapid removal of noxious impurities from the aqueous solution. As regards, the dye removal process has the important difficulty of needing access of the remainder terminating slush [34].

Preparations of activated carbons can be done from various types of materials under different conditions. The activations are obtained by two procedures: physical activation or chemical activation. Physical activation is a two-step process that involves carbonization of a carbonaceous material followed by the activation of the resulting char at elevated temperature. In chemical activation, process is carried out with the precursor being mixed with chemical activating agents such as phosphoric acid, zinc chloride or sulfuric acid. Surface functionalization of activated carbon can change sorption properties such as the reactivity

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and selectivity of activated carbon surface [35]. A number of studies have been conducted on activated carbon surface modification by grafting various organic reagents such as ethylenediamine [36,37], poly(*N*,*N*-dimethylaminoethyl methacrylate) [38], cetyl trimethyl ammonium bromide [39] and 3-aminopropyltriethoxysilane [40]. Microwave radiation has both electrical and magnetic properties [41]. The microwaves supply energy directly to the active carbon bed and this energy was transformed in the form of heat to the intraparticles through dipole rotation and ionic conduction [42].

The aim of this research was to remove Malachite green (MG) dye from aqueous solution using tetrathylenepentamine-functionalized *Rosa Canina*-L fruits activated carbon (TEPFRCA) prepared under microwave treatment. The prepared adsorbent was characterized using FE-SEM and FT-IR. The impact of several influential parameters such as contact time, initial MG dye concentration, temperature, pH and dose adsorbent were well studied and investigated through bath adsorption experiments.

2. Materials and methods

2.1. Materials and instruments

All chemicals used in this study were of analytical reagent grade purchased from Merck, Germany. Malachite green (MG) has formula of $C_{23}H_{26}N_2Cl$, C.I. no: 42,000, FW = 364.92 with λ_{max} of 617 nm. The molecular structure of MG is shown in Fig. 1. To prepare a stock solution containing 100 mg/L of MG, MG hydrochloride was employed. The stock solution was diluted with deionized water to the desired MG concentrations.

The surface textural and morphological structures of the RCAC and TEPFRCA were examined using a field emission scanning electron microscope (FE-SEM) (Hitachi-S4160, Japan) under an acceleration voltage of 20 kV with a high resolution of 3.0 nm. Organic functional groups were determined by FT-IR spectroscopy (Shimadzu-8400S, Japan) in the wavelength of 4000–400 cm^{-1}. BET surface area, total pore volume and pore diameter distribution were measured by Brunauer–Emmett–Teller (BET) method at liquid nitrogen temperature (−196 °C) using conventional gas adsorption apparatus (Belsorp-Mini II, Bel, Japan). The pH measurements were made with a pH meter (Metrohm-827, USA). The samples were dried in program controller (JEIO TECH-CF-02G, Korea). Before and after the adsorptive reaction, samples of solutions were analyzed using UV–vis spectrophotometer (Shimadzu, AA-680, Japan).

2.2. Preparation of tetrathylenepentamine-functionalized Rosa canina-L fruits activated carbon (TEPFRCA)

TEPFRCA was synthesized according to the method described in our previous work [42]. Briefly, 50 g of *Rosa canina*-L fruits was air-dried, crushed and impregnated with concentrated H_2SO_4. Then, the materials were activated in a hot air oven at 150°°C for 24 h. The carbonized material was washed with distilled water and the activated carbon was immersed in a 1% $NaHCO_3$ solution to remove any remaining acids before it was washed again with distilled water until pH of the *R. canina*-L activated carbon (RCA) reached 6.5. Afterwards, it was dried in program controller at 105 °C for 24 h. A uniform particle size of 0.125 mm was obtained using a sieve.

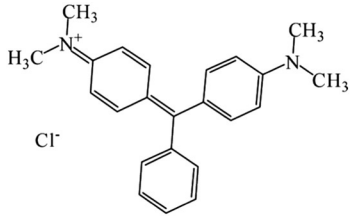

Fig. 1. Chemical structure of Malachite green (MG).

3.5 g of RCA was mixed with a 50 mL of solvent containing deionized water/ethanol (25:25) and stirred for 30 min. 2.5 g of tetraethylenepentamine was then added to the mixture and the mixture was sonicated for 10 min. The mixtures were then heated under microwave irradiation with output power of 500 W for 20 min. The prepared sorbent was washed with Milli-Q water until the pH of the supernatant become neutral. The prepared sorbent was dried for 48 h at 50 °C and used for further study.

2.3. Characterization and analyses

The surface morphological and textural properties of RCA and TEPFRCA were observed by using various analytical techniques such as FE-SEM. The surface anatomical properties of the developed adsorbent i.e. RCA and TEPFRCA were determined using FTIR analysis in the range of 4000–600 cm^{-1}. The KBr powder was used for the sample preparation.

2.4. MG adsorption experiments

The adsorption experiments were carried out in a batch mode in order to optimize and study the impact of different influential parameters such as pH, adsorbent dose, initial dye concentration, contact time and temperature. For various pH tests and investigation of its effect on adsorption of MG, 0.01 g of the TEPFRCA was added to 50 mL of MG solution. The primary concentration of dye was 50 mg/L and the mixtures were shaken for 30 min. The tests were also carried out while the amount of sorbent was from 0.001 to 0.025 g and the pH of solutions was constant at optimum value for investigation of effect of adsorbent dose. For isotherm tests, 0.01 g of the TEPFRCA was added to 50 mL of dye solution. The primary concentrations of ions were 25 to 65 mg/L and the mixtures were shaken at room temperature (298 K) for 120 min to equilibrium. For kinetic experiments, 0.01 g of the TEPFRCA was added to 50 mL of dye solution. The primary concentrations of MG were 50 mg/L and the mixtures were shaken at different times (1–60 min). Thermodynamic parameters were investigated at different temperatures (298, 318 and 333 K) and that primary concentration of dye was 50 mg/L. After ending the contact time, samples were filtered through a Whatman filter paper number 42, and then the residual concentration of MG was determined by UV–Vis spectrophotometer. The amount of dye adsorbed per unit weight of adsorbent or adsorption capacity (q_e) and percentage removal (% Removal) of MG dye by TEPFRCA are expressed by the below equations:

$$q_e = \frac{C_0 - C_e}{m} \times V \quad (1)$$

$$\%\text{Removal} = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

where C_0 (mg/L) and C_e (mg/L) are the dye concentration before and after adsorption tests, respectively, q_e is the adsorption capacity of MG, V (L) is the volume of solution, and m (g) is the amount of TEPFRCA.

2.5. Adsorption of MG

2.5.1. Adsorption isotherms studies

Adsorption equilibrium isotherm was used in order to describe the relationship between amount of adsorbate taken up per gram of adsorbent, qe (mg/g), to the equilibrium solution concentration, Ce (mg/L), at a constant temperature. In this part of study, the adsorption capacity of TEPFRCA was evaluated by isotherm tests, such as Langmuir, Freundlich and Dubinin Radushkevich (D–R) isotherm.

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