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Water remediation using low cost adsorbent walnut shell for removal of malachite green: Equilibrium, kinetics, thermodynamic and regeneration studies

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ABSTRACT

Batch adsorption experiment of malachite green (MG) was studied with walnut shell (WS). Adsorption of MG onto WS was confirmed by FTIR analysis. Particle size, dosage, effect of dye concentration, pH, temperature and ionic strength were investigated. The optimized conditions for adsorption process in this study was carried out using WS of dosage 0.03 g/20 mL dye, at room temperature, ambient pH and agitation rate of 250 rpm for 2 h. The kinetics of the adsorption process was studied using four models: Lagergren 1st order, pseudo 2nd order, Weber–Morris intraparticle diffusion and the Boyd models. Kinetics data is best fitted with pseudo 2nd order. Weber–Morris model showed that intraparticle diffusion may be present, but is not the rate-limiting step while Boyd model suggested that film diffusion may be the controlling mechanism. Four isotherm models namely the Langmuir, Freundlich, Redlich–Peterson and Sips models were used for describing the adsorption process. The inclusion of non-linear isotherm models together with four error functions (ARE, EABS, χ^2 and MSPD) suggested the Langmuir model best described the adsorption process. The Langmuir isotherm predicted the maximum monolayer adsorption capacity of 90.8 mg g^{-1}. Thermodynamic studies showed that adsorption system is spontaneous and endothermic in nature. Regeneration of WS was investigated using three different solvent solutions and the results showed 0.1 M NaOH was able to regenerate and improve the adsorption capability of WS. Based on all the data in this study, WS is a potential low-cost material for the removal of MG.

Introduction

Since ancient time, natural dyes extracted from shells, flowers, roots and certain insects have been used to colour fabric, animal hide and even food. However, most of the use of natural dyes has long been replaced by synthetic dyes, which can be easily produced in large quantities. Today, more than 10,000 dyes have been used in textile, paper, cosmetic and food industries, resulting in a large amount of dye wastewater [1].

Disposal of synthetic dyes into water bodies such as rivers without proper treatment gives rise to severe problems and concerns. Many dyes produce intense colour, even in small concentration, make the receiving water bodies to have unpleasant sight [2] and can hinder light penetration and photosynthesis [3]. In addition, due to their stable and synthetic nature, these dyes resist biodegradation [4]. Many of the dyes and/or their decomposed products are carcinogenic and mutagenic which could harm aquatic fauna, animals and ultimately humans. Therefore, it is imperative to treat the dye wastewaters before their disposal.

Malachite green (MG) is a basic dye that belongs to triphenylmethane dye category and appears as green crystalline powder which when dissolved in water gives bluish–green coloured solution. The molecular structure of the dye is shown in Fig. 1. MG is used for the dyeing of leather, silk, wool and distilleries [5] as well as fungicide and antiseptic in aquaculture industry to control fish parasite and disease. However, according to the reports on animal study, triphenylmethane dyes were found to exhibit mutagenic, carcinogenic, genotoxic and teratogenic properties [6,7].

Many methods have been studied in order to decolourize MG from aqueous solutions. Amongst these methods are biodegradation [8], Fenton [9], ozonation [10] and coagulation [11] where MG was effectively decolourized and/or degraded. However, these methods in general are often costly, require high energy input, large quantity of reagent, ineffective at low concentrations of pollutants and cause formation of toxic secondary sludge [12,13].

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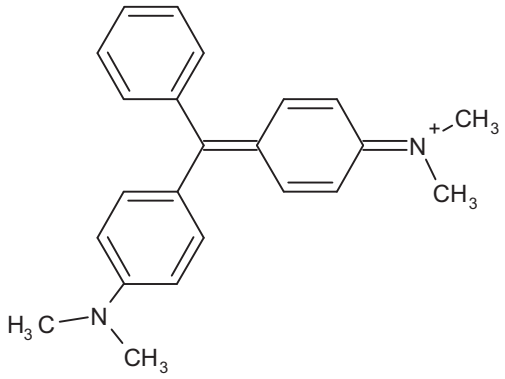

Fig. 1. Molecular structure of malachite green.

Adsorption method has shown exciting potential in removing pollutants such as dyes and heavy metals. Biosorption is a subcategory of adsorption method which usually uses materials that have little or no economical values and often thrown as wastes. Attractive features of this method are abundance of material, cheap, can be reusable, eco-friendly as well as no formation of harmful by-products as the pollutants are simply adsorbed onto the biomass [14]. Also, as the materials especially those which originated from living thing have complex compositions making it possible for many mechanisms such as ion exchange, complexation, coordination and chelation to be operating in an adsorption process [15]. Biosorption has also been studied on the removal of MG using various materials such as rice husk [16], hen feather [17], peat [18], coffee bean [19] and corn cob [20].

Walnut shell (WS) is an agricultural waste material that is generated at high volume as the only edible portion of walnut is the kernel. WS has little economical value and unsuitable to be used as animal feedstock due to the toughness of the shell, unlike cereal straw or sugarcane bagasse which were more commonly used [21]. Moreover, WS has good chemical stability, good mechanical strength and easy to be processed for biosorption [22]. Untreated WS was found to contain tannin which possessed —OH groups that can interact with metals [23], and was reported to be effective at removing heavy metals such as Cr(VI) [24], Pb(II) and Cd(II) [25].

In this study, WS was used to investigate its potential in removing MG from aqueous solution by looking at the equilibrium adsorption isotherm, kinetics, pH, ionic strength, thermodynamic and regeneration ability of WS at optimized conditions.

Materials and methods

Chemical and reagents

Malachite green oxalate ($C_{23}H_{25}N_2{\cdot}C_2HO_4{\cdot}0.5C_2H_2O_4$, Mr 463.50) of 90% dye content was purchased from Sigma–Aldrich Corporation. 1000 mg L^{-1} of MG stock solution was prepared by dissolving the required amount of dye in distilled water. Other concentrations of MG were obtained by dilution of the stock solution. Solution pH was adjusted using NaOH and HNO_3 purchased from Fluka. Spectroscopy grade KBr was used for Fourier transform infrared (FTIR) spectroscopy analysis and was dried in an oven at 110 °C before use. All chemicals were used without further purification.

Walnut shell (WS) was obtained from packaged roasted walnut available at the local departmental store. The WS was soaked and washed with distilled water and oven-dried at 75 °C for 48 h to constant weight. Dried WS was crushed using mortar and pestle before it was blended and sieved to obtain desired particle sizes and stored in desiccators prior to use.

Instrumental

The MG content in solution was measured at λ_{max} 618 nm using Shimadzu UV-1601PC UV–visible spectrophotometer (UV–vis). The elemental CHNS compositions of WS were determined using the Thermo Scientific Flash 2000 Organic Elemental Analyzer CHNS/O. FTIR spectrophotometer (Shimadzu Model IRPrestige-21) was used for the determination of the functional groups present in untreated WS and MG-treated WS. Stuart orbital shaker used for agitation of the solution was set at 250 rpm. Thermo Scientific, Orion 2 Star pH Benchtop was used to measure the pH.

Determination of point of zero charge

The point of zero charge (pH_{pzc}) of WS's surface was determined by the salt addition method using 20 mL of 0.1 M KNO_3 solutions [26]. 0.1 M of HNO_3 and 0.1 M NaOH were used for adjustment of pH of the KNO_3 solutions to the pH range of 2.5–10.0. The pH-adjusted KNO_3 solution was agitated with 0.03 g adsorbent for 24 h, and the final pH was measured. The change in pH (final pH – initial pH) *vs* initial pH was plotted for the determination of the pH_{pzc}.

Batch experiment procedure

Batch experiments were carried out by mixing 0.03 g of adsorbent with 20.0 mL of known concentration of MG in clean conical flasks for all experiment (unless otherwise stated). The mixtures were agitated for 2 h, with exception for contact time experiment. Effect of particle size was investigated by using adsorbent of sieve sizes: >850 mm, 355–850 mm and <355 mm. Effect of adsorbent dosage ranging from 0.02 to 0.06 g/20.0 mL of 100 mg L^{-1} dye solution was studied. Effect of contact time was done by agitating the mixtures and filtered at predetermined time intervals (5–225 min). Parameters such as the effects of initial dye concentration (20–600 mg L^{-1}), pH (3–7), ionic strength and temperature (25, 40, 50, 60 °C) were also investigated. The mixture was filtered and the filtrate was analysed for its dye content using UV–vis spectrophotometer. The Langmuir, Freundlich, Redlich–Peterson (R–P) and Sips isotherm models were used for describing the adsorption process. Lagergren first order, pseudo second order, Weber–Morris intraparticle diffusion and Boyd models were used to give insight into the adsorption kinetic mechanisms. All experiments were carried out in duplicate, and the results were taken as an average.

The amount of dye adsorbed per gram of WS, q_e (mg g^{-1}), was calculated using:

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

where C_i is the initial dye concentration (mg L^{-1}), C_e is the equilibrium dye concentration (mg L^{-1}), V is the volume of MG solution used (L), and m is the mass of WS used (g). The percentage removal of the dye is represented by:

$$\text{Percentage removal} = \frac{(C_i - C_e) \times 100\%}{C_i} \quad (2)$$

Error analysis

The model that best fits the equilibrium data was chosen based on the coefficient of determination (R^2) value, fitting of the non-linear regression and error analyses using the average relative error