Two-stage optimisation for malachite green removal using activated date pits

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Abstract

Water pollution, from industry and agriculture, is a major threat to water security in the light of decreasing global potable water resources. Adsorption is one potential treatment technology for the removal of different contaminants from polluted water. Hard lignocellulose-containing materials with high carbon content, such as date stones, are excellent precursors for the production of activated carbons for adsorption activities. In this study, waste date stone biomass, from the seedless date products industry, was treated and activated chemically for the adsorption of malachite green dye, which is widely used in the plastics and textile industries. Phosphoric acid was used as an activating agent for the date stones, and its adsorption capability was measured and compared to the capacity of natural date stone powder. Experimental equilibrium data were analysed and correlated by four isotherm models: Langmuir, Freundlich, Temkin and Langmuir–Freundlich (also called SIPS). The best fit for the experimental data for both treated and natural date stone was the Langmuir–Freundlich isotherm. The surface areas and maximum malachite green adsorption capacities of the natural date stone and the phosphoric acid-treated date stone were 86 and 909 m²/g, respectively, and maximum malachite green adsorption capacities were 31.5 and 64.7 mg/g, respectively. A two-stage batch adsorber model was developed to optimize the two-step adsorption process to remove malachite green and minimize the amount of adsorbent used for both untreated and treated date stones. The benefits of the two-stage adsorber and chemically activated date stones are discussed in terms of designing for various percentages dye removal, various effluent discharge concentrations and various initial dye concentrations. The two-stage system resulted in a reduction of adsorbent compared with the one-stage system of 36 to 460% to remove the same amount of dye.

Keywords Date stones · Activated carbons · Adsorption capacities · Batch adsorption

1 Introduction

Dyes are a common type of pollutant that are discharged into the aquatic ecosystems by industries such as paper, plastic, leather treatment and printing [1]. Washing, rinsing and dyeing of cloth in the textile industries, in particular, release large quantities of dyes into water bodies [2]. These dyes cause a decrease in light penetration, and some can be very toxic to aquatic life. In addition, their stability to heat and resistance to biodegradation amplifies their environmental threat.

Furthermore, the presence of toxic metal ions and complexes with high quantities of total dissolved solids in dyes results in challenges for various forms of treatment [3, 4].

Malachite green is a widely used commercial dye in several industries, but the dye has a damaging effect on plants and animals in the environment after ingestion or inhalation [5]. In addition, the dye has generated much concern regarding its use due to its reported toxic effects [6]. Many adverse effects from the consumption of the dye due to its carcinogenic, genotoxic, mutagenic and teratogenic properties in animal studies have been reported [7].

There are several treatment technologies for large volumes of contaminated water including various membrane separation techniques, coagulation–flocculation and oxidation activities. However, most of these treatment techniques have several disadvantages such as high capital and operating costs, production of sludge in large amounts, the formation of harmful by-products and disposal problems of the products.

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Among the different techniques of water treatment, adsorption is an attractive method for achieving low pollutant levels, especially if the adsorbent is cheap and does not require pre-treatment [8]. Adsorption is considered superior to the other techniques due to its low capital and operational costs, high efficiency, low energy and sustainability [9, 10]. There are several factors affecting the amount of pollutants removed during adsorption including the type of adsorbent and adsorbate used; the pH and temperature of the system; the initial concentration of the adsorbate; the pore volume, size and distribution; as well as the contact time given for adsorption to take place. Isotherm models indicate the type of adsorption taking place and the amount of pollutant adsorbed after a sufficient time period to reach equilibrium and help to predict the adsorption behaviour on a molecular scale. Thus, the capacity of the pollutant removal can be determined using the most appropriate model.

Waste biomass is now regarded as an effective raw material resource for the production of several products including fuel gas [11–13], fuel oil [14], syngas [15] and biochars [16–19]. Activated carbons are an alternative and are widely used as adsorbent materials [20] for the removal of pollutants from both liquid and gas phases due to their high adsorption capacities. Several studies report the use of biomass wastes to produce activated carbons in a number of applications, for example, apricot [21], bamboo [22], cherry stones [23], coconut shell [24] olive stones [25], peach stones [26], pine cone [27], plum stones [28], sugarcane bagasse [29, 30], rice husk and silk waste [31]. This led to considering activated carbons as a universal adsorbent [32]. Typically, the adsorption capacity of activated carbon is proportional to the pore volume, pore size distribution, internal surface area and surface chemistry [33].

Date stone is a suitable biomass for preparation of sustainable activated carbons due to their high elemental carbon content and consequently high yield after physical or chemical activation. The stones constitute around 10% of the mass of the fruit and are usually discarded after the consumption of the surrounding pericarp. A number of studies reported various optimized preparation conditions [34–36]. Activated date stones are used to remove different types of contaminants including dyes, phenolic compounds, insecticides, herbicides and heavy metals. The physical activation of date stones produced a much lower capacity carbon where the pore volume and surface areas were not reported [37]. However, activated carbon-based date pits have been shown to be effective in removing phenol from petroleum refinery wastewater [38]. The removal efficiency of phenol by activated date pits is higher at 169 mg/g than commercial activated carbons at weak acidic conditions [39]. Date pits are also effective for methylene blue removal, with a capacity of 485 mg/g [40]. This “eco-friendly” adsorbent was also applicable in removing heavy metals [41].

In the present study, date stones/pits were used because of their very low ash content (below 3 wt%) as a precursor for producing activated carbons with a high carbon content [42]. Date stones were treated with phosphoric acid, and their adsorption capacity of malachite green was compared to natural date stones. A two-batch adsorber optimisation model was adopted using the best fit isotherm to minimize the amount of adsorbent used for both natural and phosphoric acid-activated date stones.

2 Experimental systems

In this study, the ability of natural date stone, NDS and phosphoric acid-activated date stone, PAADS, has been compared for the adsorption of malachite green dye. Equilibrium data show the amount of malachite green dye adsorbed after a sufficient time period to reach equilibrium. Adsorption tests were carried out to determine the malachite green dye equilibrium data for the adsorption process. The results were optimized by testing different equilibrium isotherms and different error analysis methods to determine the best fit isotherm and isotherm parameters. In addition, a two-stage batch adsorber optimisation model was developed to further increase the capacity of the produced date stones of malachite green dye.

2.1 Experimental materials—date stones

Natural date stones were acquired from a local company producing seedless date products in Qatar. Only cleaning and washing were applied to remove dust and the remaining flesh on the date stones.

2.1.1 Natural date stone

The first group of date stones was washed and dried without any physical or chemical activation. The washing took place by using distilled water to remove the soluble impurities and dust from the sample. The sample was treated chemically using 0.1 M nitric acid for 1 h. After that, the sample was soaked in methanol for the same time period to clean the sample from any organic and inorganic matter. Finally, the “cleaned” sample was dried for 2 days in an oven at 80 °C, crushed in a mechanical grinder and sieved through a BSS-25 sieve to remove relatively large particles. The remaining material is referred to as “natural date stone,” NDS.

2.1.2 Phosphoric acid-activated date stone

A batch of NDS was treated with 30% concentration *o*-phosphoric acid, H_3PO_4 , using an impregnation ratio of 2:1, as an activating agent. The resulting matter was heated in a closed muffle furnace at 700 °C with nitrogen purge of 100 mL/min.

The high heat increases the surface area of NDS by developing porosity. To neutralize any remaining acid, the charred matter was cooled and washed with dilute ammonia solution. To ensure pH neutralisation, the solution was washed with distilled water until the pH measured was exactly 7. The acid activation process places H^+ ions on the surface of the carbon which will repel the positive basic dyes ions, but in a high pH environment, the surface H^+ ions will diffuse into solution yielding some sites available with a surplus negative charges available to positively charged basic dye ions such as MG. As most textile wastewaters are alkaline, pH 7 is more or less the lower pH one would expect from one of these industrial effluents. Hence, pH 7 is the most conservative pH to target, with the expectation that higher pH would result in improved performance, particularly for the PAADS system. Then, the solution was filtered and dried at 80 °C in an incubator overnight. Finally, the neutral dry sample was sieved through a 1.18-mm sieve after crushing. This batch of modified date stones are referred to as “chemically treated date stone,” PAADS.

2.1.3 Characterisation of the date stones

The suitability of NDS as a precursor for activated carbon was determined through monitoring pyrolysis results. Pyrolysis characteristics were determined using thermo-gravimetric analysis or TGA, TA Instruments (New Castle, DE, USA). During the analysis, the temperature rate was increased by 10 °C/min under nitrogen atmosphere until it reached 600 °C. Biomass pyrolysis can be divided into five components that are removed at different temperature ranges: moisture (< 150 °C), extractives (< 200 °C) hemicellulose (< 250 °C), cellulose (< 300 °C) and lignin (< 400 °C). Pyrolysis of any biomass can be considered as the superposition of more than one component. Thus, the total effect of weight loss during pyrolysis corresponds to the summation of individual contributions of each of the components.

To study the effect of pyrolysis temperature on the char yield, NDS was pyrolysed in a tube furnace at a heating rate of 10 °C/min under nitrogen atmosphere. Target temperatures ranged between 350 and 600 °C with 50 °C intervals. The resultant char was sieved manually in a 125- μ m sieve, and its weight was recorded. The percentage difference between the weights of the charred sample and the original sample determined the char yield.

The total pore volume, mean pore diameter and Brunauer, Emmett and Teller or BET surface area of the two different date stone biomass products were measured and compared to results from the literature.

The effect of treatment of biomass with 30% H_3PO_4 has been shown in several studies to achieve the optimum value of bulk density, ash content, iodine adsorption and pore size diameter for the treatment of dyes in textile effluents [43].

Functional groups for raw date stones have been characterized as mainly acidic comprising hydroxyl (–OH), carboxylic acid (–COOH) and carbonyl (–COO–) [44]. FTIR analysis was not performed, but most organic compounds and functional groups after acid activation and thermal treatment are removed [45]. Several other studies have reported the beneficial effects of properties, especially the surface area of biomass-derived activated carbons using 30% phosphoric acid [46–48].

2.2 Experimental materials—malachite green dye

Malachite green dye was used as the commercial dye supplied by B.D.H Chemical Ltd., Pool, England. The CAS number is 569-64-2, and its chemical formula is $C_{23}H_{25}ClN_2$, its maximum wavelength of absorbance is $\lambda_{max} = 617$ nm, and its molecular weight is 364.9 g/mol. The melting point is 158–160 °C, the boiling point 520.9 °C and density is 1045 kg/m³. It is very soluble in water, methanol, ethanol, amyl alcohol and isopropanol. The solution concentration was altered by diluting the dye stock solution with distilled water. Figure 1 shows the molecular structure of malachite green.

Malachite green has a wide range of industrial applications. The dye is used to colour plastics, silk, leather, paper and other materials. However, the dye has a damaging effect on plants and animals in the environment and also affects humans as it is considered toxic for the human respiratory system and can cause infertility [49, 50]. Malachite green is considered to be one of the most recalcitrant pollutants due to its resistance to light degradation and oxidizing agents [6].

2.3 Adsorption experiments

All the adsorption tests were carried out at 20 °C using a temperature-controlled shaker by mixing 3 g of adsorbent with malachite green solutions of specific concentrations in plastic bottles. The shaker agitation speed was set at 250 rpm. The initial and final concentrations of the sample solution were measured and recorded. The amount of adsorption was calculated using the mass balance equation shown below. The amount of adsorbed malachite green was assumed to be equal to the amount of the dye removed from the solution.

$$\text{Amount of dye adsorbed} = \text{Amount of dye removed} \quad (1)$$

Fig. 1 Malachite green molecular structure

$$m(q_0 - q_e) = -V(C_0 - C_e) \quad (2)$$

Rearranging the equation for q_e :

$$q_e = \frac{V}{m}(C_0 - C_e) \quad (3)$$

where q_e is the amount of dye adsorbed at equilibrium in milligrams per gram; q_0 is the amount adsorbed at time 0, which is equal to 0; V is the volume of the solution in litres; m is the mass of the adsorbent in grams; C_0 is the initial concentration of the dye in milligrams per litre; and C_e is the remaining dye concentration at equilibrium in milligrams per litre. The time for the system to reach equilibrium was measured to be 6 h. However, the isotherm studies were carried for 24 h to ensure the equilibrium has been achieved.

3 Modeling theory and models

3.1 Isotherm models

Isotherms describe the relationship between q_e (mg/g), the amount of contaminant adsorbed, and C_e (mg/L), the equilibrium concentration of the contaminant. It is important to find an efficient and effective model to correlate the equilibrium data. It is important to establish the best fitting isotherm in order to establish the correct design capacity and optimisation of both batch and fixed bed adsorber treatment systems. The data were correlated using four of the most standard isotherm models and have been subjected to an error analysis using the sum of the square of the errors (SSE) method to obtain the best fit isotherm equilibrium constants. The results are shown in Table 2. The models used are represented as follows.

3.1.1 Langmuir isotherm

The Langmuir adsorption model describes adsorption assuming that the adsorbate behaves like an ideal solute and follows Avogadro's law [51]. This model is popular in determining the activated carbon adsorption performance by quantifying the gas–solid and solid–liquid phase adsorption. The Langmuir isotherm is based on several assumptions: the adsorbed molecules do not interact among each other, adsorption occurs through the same mechanism and in a uniform manner along the adsorbent's surface, and that adsorption occurs in a monolayer which means that molecules deposit only at the free surface of the adsorbent and cannot deposit on one another. The Langmuir isotherm is represented by Eq. (4):

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad (4)$$

where q_m (mg/g) and b (L/mg) are Langmuir maximum monolayer adsorption capacity and energy constant of

adsorption, respectively.

To determine the Langmuir adsorption parameters, Eq. (4) was transformed into its linear form represented by Eq. (5):

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \quad (5)$$

Plotting q_e vs C_e for Langmuir form shows a plateau which defines the point of equilibrium saturation where no further adsorption can take place due to the lack of free space.

3.1.2 Freundlich isotherm

The Freundlich adsorption model is similar to the Langmuir model with modification [52]. It describes the non-ideal adsorption and follows a linear fit for a log–log plot of the adsorption data. The Freundlich isotherm is an empirical equation; it is based on observation rather than theory. It can be applied to multilayer adsorption with a non-uniform energy distribution. The adsorbed amount is the sum of adsorption occurring at all sites with individual bond energies. The adsorption energy decreases exponentially until the adsorption process is completed. Thus, the Freundlich isotherm is popular for heterogeneous systems, where the adsorption forces are different along the adsorbent's surface, and the slope determines its heterogeneity level. The Freundlich isotherm is represented by Eqs. (6) and (7):

$$q_e = k_F C_e^{1/n} \quad (6)$$

$$\log q_e = \log k_F + \frac{1}{n} \log C_e \quad (7)$$

where k_F (L/g) and $1/n$ are indications of the adsorption capacity and surface heterogeneity, respectively. $1/n$ ranges between 0, more heterogeneous, and 1, more homogeneous.

3.1.3 Temkin isotherm

The Temkin isotherm originally describes the adsorption of hydrogen atoms onto platinum electrodes in an acidic environment. This makes the Temkin isotherm a preferred model in literature with gas-phase equilibrium but less popular in complex liquid-phase adsorption systems. The Temkin adsorption model assumes that the heat of adsorption decreases linearly with coverage of adsorbate due to adsorbent/adsorbate interactions [53]. This model ignores extreme concentration values at the high and low ends. The binding energies between the adsorbent and adsorbate are uniformly distributed. The Temkin isotherm is represented by Eqs. (8) and (9):

$$q_e = \frac{RT}{b_T} \ln K_T C_e \quad (8)$$

$$q_e = \frac{RT}{b_T} \ln K_t + \frac{RT}{b_T} \ln C_e \quad (9)$$

where K_T (L/g) is the Temkin isotherm equilibrium binding constant, b_T is the Temkin isotherm constant, R is the gas constant (8.314 kJ/mol K) and T is the temperature at 298 K.

3.1.4 Langmuir–Freundlich isotherm

The Langmuir–Freundlich isotherm, also known as the SIPS isotherm [54], is a combined form of the Langmuir and Freundlich expressions to predict heterogeneous adsorption systems less extreme than the Freundlich model. At low concentrations of pollutants, the Langmuir–Freundlich isotherm tends to be closer to the Freundlich heterogeneous isotherm, whereas at high concentrations, it tends to become closer to the Langmuir monolayer isotherm. The Langmuir–Freundlich isotherm is represented by the following Eq. (10):

$$q_e = \frac{K_{LF} C_e^{b_{LF}}}{1 + a_{LF} C_e^{b_{LF}}} \quad (10)$$

where K_{LF} (L/g) and a_{LF} (L/mg) are the Langmuir–Freundlich isotherm constants and b_{LF} is the isotherm exponent.

3.1.5 Sum of squared errors

The sum of the square of the errors is the most widely used error function among researchers to find the best fit isotherm [55] and represents the sum of the square of the residuals. It takes into consideration the variance and its bias. In this case, SSE is the square of the correlation that exists between the calculated and experimental values. SSE is represented the following Eq. (11):

$$SSE = \sum_{i=1}^N \left(q_{e,\text{exp}} - q_{e,\text{iso}} \right)_i^2 \quad (11)$$

where subscripts “exp” and “iso” represent the experimental and isotherm calculated values, respectively. The error analysis results showed that the Langmuir and the Langmuir–Freundlich isotherms describe the experimental equilibrium results very well with the Langmuir–Freundlich isotherm showing the best correlation. Consequently, the Langmuir–Freundlich equation has been selected for use in the optimisation model in Section 3.2.

3.1.6 Akaike information criterion

Akaike information criterion is a measure of the quality of the isotherms compared to other isotherm models, accounting for differences in parameter number. To further compare the isotherm models, AIC was calculated using the AIC function in R-Project. The lower the AIC values, the better is the model fit. AIC is represented in Eq. (12):

$$AIC = 2K - 2\log \left(L(\hat{\theta}|y) \right) \quad (12)$$

where K is the number of estimable parameters and $\log \left(L(\hat{\theta}|y) \right)$ is the log-likelihood at its maximum point of the model estimated.

3.2 Two-stage batch adsorber optimisation model development using the Langmuir–Freundlich correlation

The schematic for the two-stage batch adsorption process is presented in Fig. 2.

In the two-stage batch adsorption schematic shown in Fig. 2, S_{s1} and S_{s2} represent the masses of adsorbent added to adsorber stage 1 and adsorber stage 2, respectively; therefore, the total amount of adsorbent required is $S_{s1} + S_{s2}$. In order to determine the minimum total amount of adsorbent that can be used to achieve the final affluent discharge condition exiting stage 2, it is necessary to minimize this total amount which can be obtained from $d(S_{s1} + S_{s2})/dC_1$ and equating to 0 to find a maximum or minimum value. The solution equation then enables the intermediate concentration, C_1 , to be determined, and using this value, the individual batch masses can be found using Eqs. (14) and (16).

Using the Langmuir–Freundlich isotherm model equation, the material balance for the stage 1 adsorber becomes the following:

$$\frac{S_{s1}}{L_s} = \frac{C_0 - C_1}{q_1 - q_0} \quad (13)$$

$$\frac{S_{s1}}{L_s} = \frac{(C_0 - C_1)(1 + a_{LF} C_1^{b_{LF}})}{K_{LF} C_1^{b_{LF}}} \quad (14)$$

For the stage 2 adsorber unit, it becomes the following:

$$\frac{S_{s2}}{L_s} = \frac{C_1 - C_2}{q_2 - q_0} \quad (15)$$

$$\frac{S_{s2}}{L_s} = \frac{(C_1 - C_2)(1 + a_{LF} C_2^{b_{LF}})}{K_{LF} C_2^{b_{LF}}} \quad (16)$$

The total amount of adsorbent used is as follows:

$$\frac{S_1 + S_2}{L_s} = \frac{1}{K_{LF}} \left(\frac{(C_0 - C_1)(1 + a_{LF} C_1^{b_{LF}})}{C_1^{b_{LF}}} + \frac{(C_1 - C_2)(1 + a_{LF} C_2^{b_{LF}})}{C_2^{b_{LF}}} \right) \quad (17)$$

$\frac{d[(S_{s1} + S_{s2})/L_s]}{dC_1}$ was set equal to 0 in order to determine the minimum total adsorbent required. Thus, Eq. (17) becomes as follows:

$$0 = \frac{1}{K_{LF}} \left[\frac{b_{LF} - 1}{C_1^{b_{LF}}} - \frac{b_{LF} C_0}{C_1^{b_{LF} + 1}} + \frac{1}{C_2^{b_{LF}}} \right] \quad (18)$$

Fig. 2 Schematic figure of a two-stage system

Multiplying by $C_1^{b_{LF}}$ and rearranging

$$0 = \left(\frac{C_1}{C_2}\right)^{b_{LF}} - b_{LF} \left(\frac{C_0}{C_1} - 1\right) - 1 \quad (19)$$

The intermediate concentration, C_1 , was determined by solving Eq. (19) using the Microsoft Excel solver add-in. Thus, the optimal values for the amount of adsorbent of required for each stage could be determined by Eqs. (17) and (19). Different constraints of removal rates and final concentrations of MG in the effluent were set. This allows the comparison of the amount of date stones needed in a single-stage adsorber to that of a two-stage adsorber. The optimisation studies were performed on both natural date stones and the phosphoric acid-activated date stone.

4 Results and discussion

4.1 Characterisation studies

Table 1 shows the measured properties. The PAADS date stone had the highest total pore volume, mean pore diameter and the largest surface area between the two types of date stones.

Both porosity and surface area of the date pits increased significantly after the phosphoric acid treatment. The highest measured surface area for PAADS was around 908 m²/g. The results are in line with data retrieved from literature. Girgis and El-Hendawy [56] reported highest surface area for phosphoric acid-treated date stone as 740 m²/g. The higher

impregnation ratio of 2 adopted in this study resulted in even higher surface area.

According to the data in Fig. 3, the studied date pits have a moisture content of around 8%, soluble extractives of around 7% and residual solids of around 22%. The largest and fastest mass loss was between 250 and 350 °C, indicating a high percentage of hemicellulose and cellulose. In fact, at around 400 °C, almost 70% of the mass was lost. Between 400 and 600 °C, the rate of mass loss slowed down considerably as larger lignin molecules are broken down. As a result, date stones have the potential to be successfully utilized in pyrolysis.

The char yield decreases with higher temperatures (Table 2). The difference between the yields at lower temperatures is high. However, the rate of decrease with temperature is significantly less at higher temperatures as larger lignin molecules are more difficult to break down and the yield is around 25%. This result is consistent with the TGA results.

4.2 Equilibrium studies

Based on the SSE and correlation coefficient (R^2) values in Table 3, the Langmuir–Freundlich or SIPS isotherm provides the best correlation to the experimental equilibrium results. The type of isotherm provides some information about the nature of the adsorption process. In both material cases, NDS and PAADS, the Langmuir and Langmuir–Freundlich are the two best fit isotherms. The Freundlich and Temkin isotherms were discarded for the rest of the study due to their high SSE values. The Langmuir model is indicative of a monolayer adsorption, in which the isotherm will plateau when the maximum saturation capacity is reached, and where

Table 1 Properties of the date stones

Date stone	Total pore volume (cm ³ /g)	Mean pore diameter (nm)	BET surface area (m ² /g)
NDS	0.21	2.31	85.74
PAADS	0.55	2.48	908.6
Literature data* [50]	0.372	–	740

*Data collected at same experimental conditions with lower impregnation ratio = 1.2

Fig. 3 TGA curve for NDS

the adsorption process occurs only at one type of site which all have equal energy. The Langmuir–Freundlich represents a variation on this theme with some heterogeneity but with adsorption at similar energy level sites. Both curves in Fig. 4 show this tendency towards a plateau over the last 4 or 5 points. The plateau indicates that the adsorption process has reached saturation. The results show a significant increase in the capacity of MG adsorption onto date stones after the phosphoric acid treatment. The maximum MG adsorption capacities for NDS and PAADS were 31.5 and 64.7 mg/g, respectively.

The Langmuir–Freundlich isotherm had lower AIC values compared to the two-parameter isotherms. This verifies the SSE results and shows that the number of parameters in the isotherm was not the reason for a better fit resulted by applying this model.

Other studies for the adsorption of malachite green using shells, hulls and derived activated carbons, such as walnut shell [57], wood apple shell [58], oat hulls [59] and apricot stone-derived activated carbon [60], yielded capacities of 90.8, 80.6, 83.0 and 88.1 mg/g, respectively, for malachite green adsorption. The capacity of the phosphoric acid-

treated date stone carbon, 64.7 mg/g, is lower but of a similar order of magnitude.

In Fig. 4, in the equilibrium isotherm for both date stone types, the specific value of the parameter C_e (C_2 in the 2-stage batch adsorber model) is the pollutant concentration in the treated effluent that is being discharged; this value is important as it is the maximum (or must be less than) pollutant concentration value permitted by the legislative discharge limits to be allowed into the receiving waters. It is important to assess what is the adsorbent pollutant adsorption capacity at this value—because this is the capacity in the real treatment plant system and it is very likely that it will not correspond to the maximum capacity of the equilibrium isotherm because of its dependence on C_2 and the slope of the operating line. The equilibrium isotherm will provide this capacity value. Therefore, it is very important to establish this value during design as more adsorbent than the value associated with $q_{e,max}$ will be required.

4.3 Optimisation studies

4.3.1 Natural date stones

The required amount of activated date stone by different treatments to reduce the final effluent concentration of MG to 0.5%, 1%, 5%, 10% and 20% and to reduce the final effluent concentration of MG to fixed values of 0.5, 1, 2, 5 and 10 mg/g was investigated. The parameters of the Langmuir–Freundlich model were used to model the NDS. Figure 5 a–e are the summary of the optimized amount of NDS carbon required when the final effluent concentration of MG is 0.5%, 1%, 5%, 10% and 20% of the initial concentration.

4.3.2 Phosphoric acid-activated date stones

The required amount of activated date stone to reduce the final effluent concentration of MG to 0.5%, 1%, 5%, 10% and 20% and to reduce the final effluent concentration of MG to fixed values of 0.5, 1, 2, 5 and 10 mg/g was investigated. The parameters of Langmuir–Freundlich model were used to model the PAADS. Figure 6 a–e are the summary of the optimized amount of chemically activated date stone carbon required when the final effluent concentration of MG is 0.5%, 1%, 5%, 10% and 20% of the initial concentration.

Figures 5 and 6 are presented to demonstrate how the values of the certain parameters influence the mass of adsorbent required under a set of design constraints. The trends of interest from a design perspective are the percentage of the pollutant, MG, removal and/or the target (design) final treated effluent concentration, which must be achieved in milligrams per litre.

With different percentage MG removal values, from 80 up to 99.5%, the relationship between the intermediate MG

Table 2 Char yield at different temperatures

Temperature (°C)	Yield (%)
350	54.7
400	37.7
450	27.5
500	26.2
550	25.1
600	24.7

Table 3 Isotherm model parameters for adsorption of MG by PAADS and NDS

Isotherms		PAADS	NDS
Langmuir model	b	0.174	0.00583
	q_m	64.7	29.5
	SSE	52.4	3.53
	R^2	0.98	0.98
	AIC	64.2	26.4
Freundlich model	k_F	26.7	1.22
	$1/n$	0.165	0.476
	SSE	404	16.8
	R^2	0.86	0.94
	AIC	92.8	48.2
Temkin model	K_T	8.48	0.0483
	b_T	283	354
	SSE	208	3.89
	R^2	0.93	0.98
	AIC	83.5	27.8
Langmuir–Freundlich model	K_{LF}	14.8	0.203
	a_{LF}	0.221	0.0054
	b_{LF}	0.840	0.96
	SSE	36.2	1.30
	R^2	0.99	0.99
	AIC	61.0	14.4

concentration from stage 1 to stage 2 and initial concentrations is basically linear as demonstrated in Figs. 5a and 6a. The intermediate concentration is much lower with a higher percentage removal of MG or the lower the final required discharge concentration due to the need to run the second batch adsorber at a low equilibrium value to achieve a high final removal percentage. This demonstrates the significance of introducing a second treatment stage in this case. However, in scenarios that require lower percentage removals, a single stage could be sufficient. The minimum required amount of

date stones is expected to be higher as the percentage removal of MG increases. The key design parameter from this study is the minimum total mass of adsorbent, $S_{s1} + S_{s2}$, required and its interrelationship with initial MG concentration and the treated effluent discharge requirement by legislation. Similarly, as the initial concentration, final concentration or percentage removal is increased for a fixed treated effluent discharge concentration, the minimum required amount of date stones increases as shown by the trend of $(S_{s1} + S_{s2})$ with increasing C_0 in Figs. 5b, e and 6b, e. These figures show the total mass of adsorbent required to treat MG containing effluents with increasing initial concentrations, C_0 . This effect is shown to be more significant in the case of PAADS, due to the much lower required minimum amount of date stones. The variation in adsorbent mass is most significant when the removal percentage or target effluent concentration is high, and the influent concentration is low. It is also useful and important to know the extent of treatment in each of the two stages. Consequently, this may be shown by comparing the two stage removal factor parameters— $(C_1 - C_2)/S_{s1}$ vs $(C_0 - C_1)/S_{s1}$ as shown in Figs. 5c and 6c. To compare the effect of each stage, the concentration removal with respect to the minimum required quantity of date stones at each stage was calculated and plotted. As expected, the efficiency (dye removed per mass of adsorbent) of the second stage is lower than that of the first stage due to the lower concentration of MG leaving the first stage and entering the second stage (Figs. 5c and 6c). The NDS showed a much higher loading towards the first stage adsorber (Fig. 5c) than PAADS, particularly at low influent concentrations and high effluent concentrations due to the much higher equilibrium capacity of the latter adsorbent. At a fixed target effluent concentration, the efficiency of adding a second stage is basically constant for the removal rates and influent concentrations tested but increases with a fixed effluent concentration. Therefore, this can be demonstrated by plotting $(C_1 - C_2)/S_{s2}$ vs C_2 as shown in Figs. 5f and 6f. At high target final effluent concentrations and low initial concentrations of MG, the efficiency of the second

Fig. 4 Comparison of experimental results with the Langmuir–Freundlich (SIPS) isotherm

Fig. 5 Intermediate adsorber concentration vs influent concentration (**a**, **d**) and total adsorbent mass vs influent concentration (**b**, **e**) for removal percentage (**a**, **b**) and target effluent concentration (**d**, **e**) as well as

quantity of dye removal in second batch adsorber vs first batch adsorber (**c**) and vs effluent concentration (**f**) for NDS carbon removal of MB using Langmuir–Freundlich model

stage is minimal. Nevertheless, adding a second stage in the cases of low final concentrations is essential as its removal efficiency becomes much higher.

4.3.3 Performance comparison with a single-stage adsorber

Adsorption processes like many chemical reactions may take a long time to reach equilibrium and require a relatively large

mass of adsorbent in a single-stage reactor, and therefore, there is a benefit to be gained by adopting multistage operations in which fresh adsorbent (or new reactant) is added at each new stage. Chemical reactions have gained more prominence for the use of multistage processes, e.g. the six-stage continuous stirred tank reactors used for the production of nylon 6 and in the case of adsorption, the multistage carbon-in-pulp process, CIP, for the recovery of gold from the acidic

Fig. 6 Intermediate adsorber concentration vs influent concentration (**a**, **d**) and total adsorbent mass vs influent concentration (**b**, **e**) for removal percentage (**a**, **b**) and target effluent concentration (**d**, **e**) as well as

quantity of dye removal in second batch adsorber vs first batch adsorber (**c**) and vs effluent concentration (**f**) for PAADS carbon removal of MB using Langmuir–Freundlich model

ore extraction leachate. In the present study, we have compared the amount of adsorbent used in a single-stage batch adsorber reactor with a two-stage batch adsorber.

The minimum total amount required of date stones of both NDS and PAADS was significantly reduced using the optimized two-stage batch adsorber compared with that of a single-stage adsorber. The required amount of activated date stone to reduce the final effluent concentration of MG to 0.5%

and 5% by a single-stage adsorber has been investigated. The parameters of the Langmuir–Freundlich model were used to model the PAADS removal of MG.

Due to the high toxicity and environmental effects of MG, the target operation is to remove the maximum amount of MG dye possible. For this reason, the amount of adsorbent required for the maximum removal percentages for different concentrations of MG was assessed. For

the purposes of economic design, it is important to note the conditions under which the more significant benefits of the two-stage adsorber occur. Table 4 compares the amount of PAADS carbon required in a single-stage adsorber and two-stage adsorber when the final effluent concentration of MG is 0.5% and 5%. The table shows the largest reduction in the amount of date stone needed in lower concentrations and highest percentage removal of MG. These differences were substantial, with the highest removal of 99.50% and lowest initial dye concentration of 50 mg/L requiring 4.6 times more adsorbent for the single-stage system. The results show a rough average of 36% reduction in the amount of date stones required to remove the same amount of MG in a two-stage system compared to a single-stage process. However, for 95% pollutant removal and a high initial pollutant concentration, for example, $C_0 = 500$ mg/L, the difference in the amount of adsorbent required is not so large at 15%: [(9.2–8.0)/8.0].

The economic benefits of the two-stage system over the one-stage system need careful assessment, which we have not covered in detail in this study as we need adsorption rate data. The two-stage process needs two reactors, and although the two adsorbers will each be smaller than the single-stage reactor, there is likely to be some increase in the capital equipment cost and the associated costs. There will be a significant saving in the adsorbent costs and even if the adsorbent can be regenerated, if more adsorbent is required, then the cost of regeneration will be increased. Similarly, if adsorbent disposal is necessary, the costs for larger quantities of hazardous waste adsorbent disposal will be higher. Multistage processes are shorter than single-stage processes; therefore, for the same effluent volume, the adsorber vessel volumes will be smaller.

Table 4 Amount of PAADS adsorbent required for a single-stage adsorption vs two-stage adsorption

Removal %	99.50%		95%	
	S (g)	S1 + S2 (g)	S (g)	S1 + S2 (g)
C_0 (mg/L)				
50	11.5	2.5	2.2	1.3
100	13.5	3.5	3.1	2.1
150	15.1	4.4	3.9	2.9
200	16.4	5.2	4.7	3.6
250	17.6	6.0	5.5	4.3
300	18.8	6.8	6.2	5.0
350	19.9	7.6	7.0	5.8
400	21.0	8.4	7.7	6.5
450	22.0	9.2	8.5	7.3
500	23.0	10.0	9.2	8.0

4.4 Regeneration

Regeneration studies were not undertaken in the time available, but standard regeneration methods could be considered for this type of recalcitrant compound. Since it has nitrogen and a halogen group, thermal regeneration by combustion to burn off the MG would have significant disadvantages, which include the following: energy intensive, carbon dioxide is produced contributing to global warming, a loss of approximately 10–12% of the adsorbent and the loss of the MG itself. But more significantly, the nitrogen would emit NO_x and if the chloride ion is associated with MG in the adsorbed state, then HCl would also be another highly problematic emission. Steam or hot gas stripping has proved popular for recovering volatile organic solvents, but the high melting and boiling points of the recalcitrant MG render this method untenable. The application of using a biological slurry to biodegrade the MG is an option, but MG is biologically quite stable and toxic to most microorganisms, so this process would take a long time and may not be particularly successful. Solvent extraction appears to be a better option using one of the volatile alcohols in which MG is very soluble and, then, possibly using one of the agitated batch reactors to dissolve the MG and then pass the solution to an evaporator or stripping column to recover the solvent for re-use and recover the MG also for re-use. Many toxic laden adsorbents are sent to secure hazardous landfill sites, often after stabilisation by encapsulation or vitrification; this is expensive and results in the consumption of both adsorbent and MG. In the longer term, leaching may become a problem and anaerobic degradation resulting in methane emissions. Consequently, volatile solvent extraction, with recovery of solvent, adsorbent and possibly MG recovery, appears the best option for testing.

5 Conclusion

Activated carbon has been prepared and tested using the waste date stones from the seedless date industry. Equilibrium studies were studied for the adsorption of MG from aqueous solution by untreated date stone and an activated carbon based on phosphoric acid-treated date stone powder. The equilibrium data have been analysed by the Langmuir, Freundlich and Langmuir–Freundlich equilibrium isotherm models, and the characteristic parameters for each isotherm have been determined. The best fit isotherm for both adsorbents was the Langmuir–Freundlich model. Then, the best fit isotherm was used to minimize the amount of adsorbent required in a two-stage batch adsorber design. The optimisation assessment indicates that the total amount of adsorbent increases either with increasing initial concentration of MG dye or with higher removal rate. The efficiency of the second stage was lower than that of the first stage due to the lower equilibrium driving

force. However, the efficiency of the prior was very significant in the case of high initial MG concentrations and/or high percentage MG removal. A comparison of the amount of adsorbent required between a single-stage adsorption process and two-stage adsorption showed that the performance of the latter was significantly better. As a result, the two-stage system resulted in a reduction of adsorbent compared with the one-stage system of 36 to 460% to remove the same amount of MG. For a commercial treatment process, the economic comparison between the adsorbent saving and the increased capital cost of the two-stage adsorber needs to be investigated, but the possible significant cost saving in regeneration and new adsorbent replacement is attractive; it is expected that adsorbent minimisation in a two-stage system could lead to significant cost reductions. This saving needs to offset the increased capital costs of installing two smaller adsorbers vs the installation of one large adsorber. More information of the adsorption rate is required to complete the techno-economic study. The design conditions (initial pollutant concentration) and legislative limit values (C_2 , mg/L) of the pollutant are key factors on deciding to adopt multistage or single-stage operation.

Overall waste date stone-activated carbon has considerable potential for commercial application, but further work is required with respect to adsorption rate, adsorption regeneration, 3-stage adsorber optimized design and performance and a techno-economic study.

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