Sorption of Methylene Blue onto Food Industry Byproducts

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ABSTRACT

Malt spent rootlets (MSR), coffee residues (KES) and their biochars were employed to remove methylene blue from pure aqueous solutions by sorption. Batch experiments were conducted at 25°C and pH 7.5. The effect of pyrolysis temperature of MSR on MB sorption was examined at six temperatures (300, 400, 500, 750, 850 and 900°C). Kinetic and isotherm experiments were conducted for the MSR, MSR pyrolyzed at 850°C, KES and KES pyrolyzed at 850°C. For biochar MSR, BET surface area values ranged from 0.5 to 5.5 m^2/g for pyrolysis temperatures from 300 to 500°C. At pyrolysis temperatures higher than 500°C, high surface areas were observed with a maximum surface area value (300 m^2/g) at 850°C. Based on kinetic experimental data, sorption capacities at 120 min were over 60% of their equilibrium values for all materials used. Based on the isotherm data, the maximum sorption capacities for MSR, biochar MSR, KES, and biochar KES were 73, 127, 112, and 132 mg/g, respectively.

KEYWORDS. Dyes; methylene blue; sorption; biosorbents; biochar.

Introduction

Dyes are categorized into reactive, azo, acid, basic, direct, and dispersing dyes based on their chemical structure and the applied production methods (1). Currently, there are about 10,000 different commercial dyes and pigments and over 7×10^5 tn of synthetic dyes are produced annually world-wide (2).

Water pollution with dyes is becoming a huge environmental problem due to the large variety of dyes used in different human activities. Industries color their products and discharge a large amount of effluents including dyes (3). It is estimated that 10 to 15% of the dyes are lost in the effluent during the dyeing processes. Discharge of colored wastewater without proper treatment can affect the environment in a number of aspects. Even at low concentrations, dyes are visible in effluent, and the high light absorption affects the photosynthesis of aquatic species (2). Most dyes are organic compounds of which the excess increases the chemical oxygen demand (COD) of the water bodies (4). Moreover many dyes are toxic and hazardous to aquatic organisms and their degradation products may be mutagenic and carcinogenic (2, 4).

Methylene blue (MB) is a basic dye with wide applications (5, 6). It is mostly used by industries involved in textile, paper, rubber, plastics, leather, cosmetics, pharmaceutical, and food sectors (2). Basic dyes, like MB, are also considered as cationic dyes because they form a colored cationic salt when dissolved in water (7). Cationic dyes are considered more toxic than the anionic dyes, because they can easily interact with the negatively charged surface of cell membranes, and can enter into the cells. Some of the harmful effects, which MB can cause, are: heart beat increase, vomiting, shock, cyanosis, jaundice, and tissue necrosis in humans (3). Thus, the removal of dyes from wastewater is a significant issue.

There are numerous treatment processes for effluent containing dyes like biodegradation, chemical oxidation, foam flotation, electrolysis, photocatalysis, electro-coagulation, and adsorption (2). Adsorption is one of the most effective processes because of its low cost, ease of operation, and design simplicity (6, 8). Commercially activated carbon is a remarkable sorbent but is expensive due to its high production cost (2). The preparation of low-cost sorbents from waste materials has several advantages, mainly of economic and environmental nature (8). Biochar is a solid material produced by the carbonization of biomass under partial or complete absence of oxygen (9). It is considered as a waste disposal and recycling option solution and at the same time, it is a less expensive material than activated carbon (10, 11). Raw agricultural wastes can also be used as biosorbents (12). Biosorption, may be more desirable due to lower cost and higher efficiency (13). A wide range of low-cost sorbents has been successfully prepared from different waste materials utilizing agricultural as well as industrial and municipal wastes (14).

The scope of the present study was to evaluate the potential use of malt spent rootlets (MSR), coffee residues (KES) and their biochars as low cost sorbents, to remove MB from pure aqueous solutions by sorption. Batch experiments were conducted to obtain the optimum sorption conditions under different MB concentrations and contact times. Furthermore, the effect of MSR pyrolysis temperature on MB sorption capacity was examined.

2. Materials and Methods

2.1. Sorbent materials

MSR were obtained from the Athenian Brewery S.A. (Patras, Greece). They were dried overnight at 50ºC, sieved, and the size fraction of 0.150 to 1.180 mm was selected for the experiments of this study. KES was obtained after espresso coffee was brewed through coffee machines at the University of Patras coffee shops.

MSR and KES were separately weighted and placed into ceramic vessels that were closed with their respective caps. These vessels were custom-made not to allow oxygen to enter the vessels at high temperatures. The vessels with the MSR were placed in a gradient temperature furnace (LH 60/12, Nabertherm GmbH, Germany) at temperatures ranging from 300 to 900°C. KES was pyrolyzed at 850°C. The mass of the MSR and KES was weighted before and after the pyrolysis process and the weight loss due to pyrolysis was calculated. The biochar MSR was powdered before sorption experiments. The surface area, the pore volume, and the average pore size of the biochars were determined using gas (N_2) adsorption - desorption with the Micromeritics TriStar 3000 Analyzer system using the Brunauer, Emmett, and Teller (BET) equation.

2.2. Methylene blue (MB)

High purity MB ($C_{16}H_{18}ClN_3S$ xH_2O) was supplied by Alfa Aesar GmbH & Co. KG, Germany. A stock solution of 1000 mg/L was prepared by dissolving accurately weighed samples of dye in a liter of distilled water. The experimental solutions were prepared by diluting stock solution of MB with distilled water to the desired concentration. The pH of each solution was adjusted by adding drops of a weak NaOH solution and was measured with a pH meter (pH 310 meter, Oakton Instruments, Singapore). The concentration of the MB was determined by measuring the absorbance at 660 nm with a UV-VIS spectrophotometer (U1100, Hitachi).

2.4 Sorption experiments

A small portion (10 mL) of the standard (50 mg/L) MB solution was transferred into 15 mL polypropylene test tubes containing 5 or 10 mg of sorbent. The tubes were hooked on a rotator (J.P. Selecta, Spain) for a specified time in the absence of light. Subsequently, the tubes were placed vertically for the sorbent to settle. The effect of pyrolysis temperature of MSR on MB sorption was examined at six temperatures (300, 400, 500, 750, 850, and 900°C). Kinetic and isotherm experiments were conducted for the MSR, MSR pyrolyzed at 850°C (MSR850), KES, and KES pyrolyzed at 850°C (KES850). For the isotherm experiments, 10 mL solutions with different initial MB concentrations were mixed in 15 mL polypropylene test tubes for 5 h for the MSR and MSR850 and 24 h for KES and KES850. All experiments were performed in duplicates at pH 7.5.

3. Results and Discussion

3.1 Effect of MSR pyrolysis temperature on sorption capacity

The experimental data presented in Figure 1 clearly show that under the experimental conditions studied (C_0=50 mg/L, pH 7.5, and 24 h agitation), the removal of MB increases with increasing MSR pyrolysis temperature. The sorption capacity of MB (q) was very low (9 to 12 mg MB/g biochar) at temperatures ranging from 300 to 500°C, and considerably increased at higher temperatures. The maximum removal of MB was 99 mg/g and was observed at 850°C. Further increase of the temperature to 900°C resulted in lower sorption capacity than that at 850°C. The pyrolysis temperature significantly affected the surface area of the biochar. BET surface values ranged from 0.5 to 5.5 m^2/g for temperatures from 300 to 500°C. At pyrolysis temperatures higher than 500°C, high surface areas were observed with a maximum surface area value (300 m^2/g) at 850°C. The MB uptake was considerably affected by the biochar surface, which increased with the pyrolysis temperature.
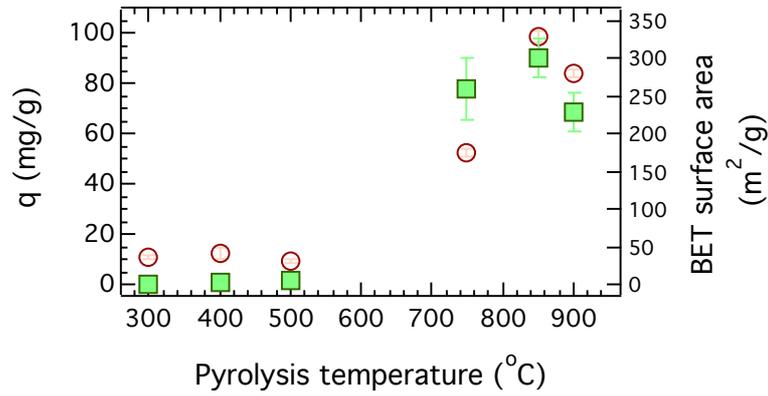
Figure 1. Effect of pyrolysis temperature of MSR on MB removal after 24 h mixing at C_0=50 mg/L and pH 7.5. Circles represent the sorption capacity and squares the BET surface area. Error bars represent standard deviation of duplicates.

3.2 Effect of contact time

The effect of contact time on MB removal for the four materials used is shown in Figure 2. As can be seen from the plots, fast kinetics were observed within the initial 60 min reflecting immediate MB uptake or external surface sorption. A plateau was observed for MSR after 120 min and the sorption capacity was about 40 mg/g. MSR850 exhibited significantly greater sorption capacity that after 120 min it reached a plateau at 94 mg/g. The higher capacity is attributed to the higher surface area of MSR850 than MSR. KES was more effective to remove MB than MSR, and after 120 min a sorption capacity of 64 mg/g was achieved. Although during the first 60 min KES and KES850 exhibited similar sorption efficiencies, the sorption capacity of KES850 increased with time and after 24 h it reached 120 mg/g of MB compared to 85 mg/g of MB for KES. For KES850 a first plateau was observed between 120 and 360 min and a second plateau was observed after 960 min contact time.
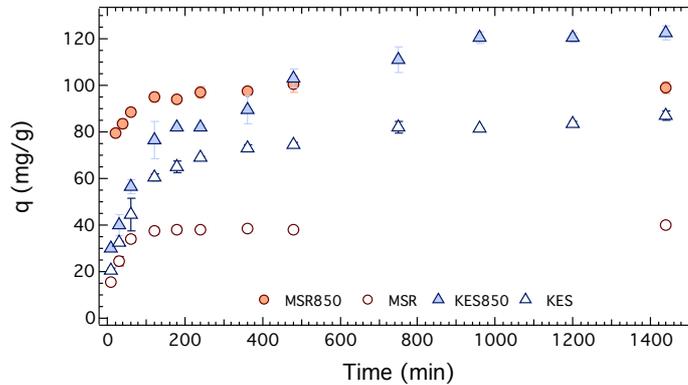
Figure 2. Effect of contact time on MB sorption. Initial MB concentration was 50 and 100 mg/L for MSR and KES based materials, respectively.

3.3 Sorption kinetics

The estimation of kinetic parameters will provide important information for the sorption process. The pseudo-first-order model and the pseudo-second-order model were applied to investigate the kinetics of MB sorption by the four materials studied. The pseudo-first-order equation as suggested from Lagergen (15) is:

$$\frac{dq}{dt} = k_1(q_e - q_t) \tag{1}$$

4

where q_e (mg/g) and q_t (mg/g) are the quantity of MB sorbed per mass unit of biochar at equilibrium and at a given time t, respectively, and k_1 (min^{-1}) is the first-rate constant. Integration and rearrangement of Eq.1 gives the following linear form:

$$LN[q_e - q_t] = LN[q_e] - k_1 t \qquad (2)$$

The values of k_1 and q_e can be determined by the slope of the linear plot of $LN(q_e - q_t)$ versus t (Figure 3).
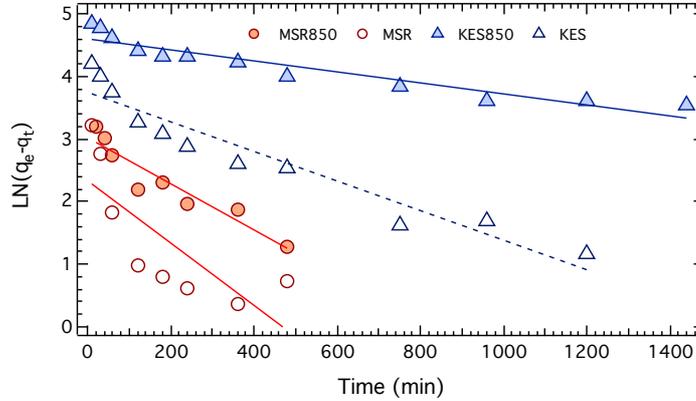
Figure 3. Linear plot of pseudo first-order sorption kinetics of MB.

The expression of the pseudo-second-order rate based on the solid capacity has been presented by Blanchard et al. (16):

$$\frac{dq}{dt} = k_2 (q_e - q_t)^2 \qquad (3)$$

where k_2 is the rate constant (g/mg L). The integration of Eq.3 gives:

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

Where k_2 is the second-order rate constant (g/mg.min). The linear plots of $\dfrac{t}{q_t}$ versus t give $\dfrac{1}{q_e}$ as the slope and

$\dfrac{1}{k_2 q_e^2}$ as the intercept (Figure 4).

The kinetic parameters related to the pseudo first-order and the pseudo second-order kinetic models employed in this study, together with the fitted parameters are given in Table 1. The suitability of the kinetic models can be assessed by both the correlation coefficient (R^2) and the residual sum of squares (RSS):

$$RSS = \sum_{i=1}^{n} \left(q^{exp} - q^{calc} \right)^2 \qquad (5)$$

where q^{exp} and q^{calc} are the experimental and predicted by the model values of q (mg/g), respectively, n is the number of experimental values, and the subscript i=1…n indicates the appropriate sample.
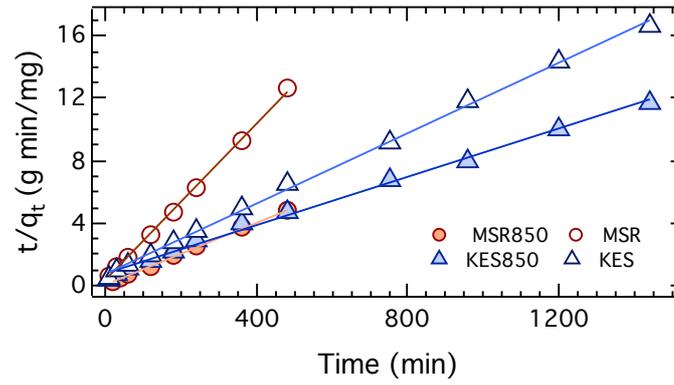
Figure 4. Linear plot of pseudo second-order sorption kinetics of MB.

Table 1. Pseudo first and pseudo second-order kinetic models constants.

Kinetic model	Material			
	MSR850	MSR	KES850	KES
Pseudo first-order				
k_1 (min^{-1})	0.0037	0.005	0.0009	0.0024
q_e (mg g^{-1})	20.4	10.28	99.44	42.06
R^2	0.899	0.601	0.886	0.915
RSS	105	289	1136	22961
Pseudo second-order				
k_2 (g mg^{-1} min^{-1})	1.1×10^{-3}	2.2×10^{-3}	8.15×10^{-5}	1.83×10^{-4}
q_e (mg g^{-1})	101.01	39.37	129.9	42.06
R^2	0.999	0.999	0.995	0.998
RSS	74	29	114	788

As it is seen the pseudo first-order kinetic model does not fit well the experimental data, and the model did not give reasonable values for q_e. The experimental data of the two biochars fitted better than the corresponding raw materials. This finding may suggest that the sorption process, especially for MSR and KES, does not follow the pseudo-first-order sorption rate expression of Lagergren. The experimental data were fitted well by the pseudo second-order kinetic model and the plot of t/q versus t gave a straight line. The R^2 value of the pseudo second-order model exceeded 0.995 and the calculated sorption capacity value determined from pseudo second-order model was closer to the experimental values of sorption capacity. This suggested that the overall rate of MB sorption process appeared to be controlled by chemical processes.

3.3 Sorption Isotherms

The maximum sorption capacity was estimated by fitting the experimental data with the Freundlich and Langmuir models. The two models linear forms are:

$$\frac{C_e}{q_e} = \frac{1}{q_{max}\ K_L} + \frac{C_e}{q_{max}}$$
(Langmuir Model) (6)

$$\ln q_e = \ln k_F + N \ln C_e$$
(Freundlich Model) (7)

where C_e (mg/L) is the equilibrium concentration in the solution, q_{max} (mg/g) is the maximum sorption capacity, K_L is the constant of Langmuir model (L/mg) related to binding energy for sorption, k_F ((mg/g)(L/mg)^N) is the adsorption constant for Freundlich model, and N is the Freundlich exponent related to adsorption nonlinearity. The experimental results and the linearized Langmuir isotherm model are illustrated in Figure 5.
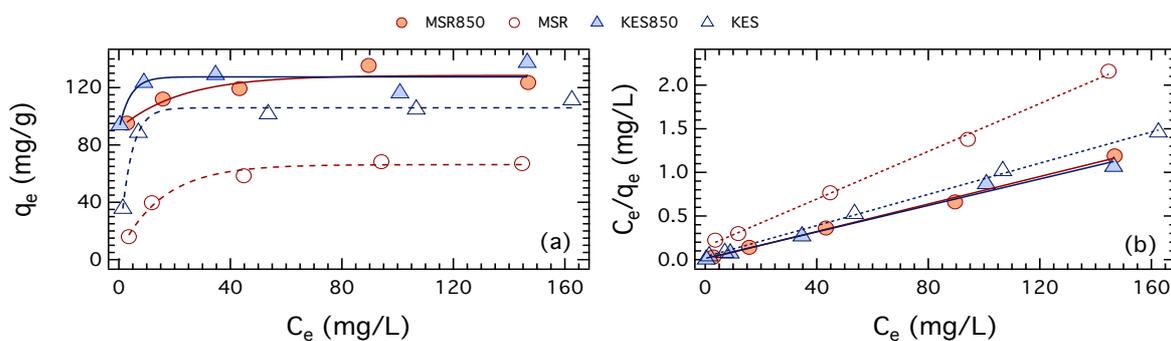
Figure 5. MB uptake by the four materials tested at initial concentration of 50 mg/L solid to liquid ratio of 1 g/L for MSR and 0.5 g/L for the other sorbents, and contact time of 5 h for the MSR based sorbents and of 24 h for the KES based sorbents.

Table 2. Isotherm model parameters for Methylene blue sorption.

Isotherm model	Material			
	MSR850	MSR	KES850	KES
Langmuir model				
q_{max} (mg/g)	127	73	132	112
K_L (L/mg)	1.14	0.093	0.543	0.270
R^2	0.996	0.998	0.987	0.999
Freundlich model				
K_F [(mg/g)(L/mg)^N]	89.0	12.2	102	41.7
N	0.0784	0.3775	0.0518	0.2115
R^2	0.868	0.897	0.732	0.792

The fitting of the experimental results (R^2 from 0.732 to 0.897) indicated that the application of the Freundlich isotherm model did not adequately fit the experimental data (Table 2). The Langmuir isotherm model matched better the experimental results (R^2 from 0.987 to 0.999), in all materials used indicating a limited number of sorption sites. A comparison of the maximum sorption capacity of biosorbents and the derived biochars or activated carbons is presented in Table 3. Some of the q_{max} values for activated carbon are significantly higher than those of biochar and biosorbents. However, for some other activated carbons q_{max} are comparable with those of biochar and biosorbents. Especially q_{max} values for KES, KES850, and MSR850 are comparable with those of most similar materials.

4. Conclusions

MSR and KES were effective for the removal of methylene blue from aqueous solutions. KES was more effective than MSR in dye removal. The pyrolysis of KES at 850ºC resulted in higher maximum sorption capacity by 18%. The pyrolysis temperature of MSR significantly affected the high specific surface area and the optimum temperature was at 850ºC for both the surface area and the sorption capacity. The pyrolysis of MSR at 850ºC resulted in higher sorption capacity by 74%, compared to MSR. MSR and KES and their corresponding biochars seem to be suitable candidates for the removal of methylene blue from aqueous solutions.

Table 3. Maximum sorption capacities of various biosorbents and their corresponding biochars or activated carbon for MB.

Sorbent	q_{max} (mg/g)	Reference
Coconut husk (treated)	99.0	Rafatullah *et al*., 2010 (14)
NaOH-activated carbon from coconut shell	916	Cazetta *et al*., 2011 (17)
Biochar from bamboo	402	Yang *et al*., 2013 (18)
Bamboo based activated carbon	454	Rafatullah *et al*., 2010 (14)
Coffee (untreated)	112	This study
Biochar from coffee	132	This study
Activated carbon from coffee grounds	182	Reffas, 2010 (19)
Rice husk	312	Rafatullah *et al*., 2010 (14)
Rice husk activated carbon	344	Rafatullah *et al*., 2010 (14)
Malt spent rootlets (untreated)	73.0	This study
Biochar from malt spent rootlets	127	This study

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