CSCanada

Advances in Natural Science
Vol. 6, No. 3, 2013, pp. 44-47
DOI:10.3968/j.ans.1715787020130603.2596

ISSN 1715-7862 [PRINT]
ISSN 1715-7870 [ONLINE]
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Bath Adsorption Study of Methylene Blue Dye Onto Sunflower Seeds Husks Activated Carbon

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Received 20 March 2013; accepted 15 June 2013

ABSTRACT

Mesoporous activated carbon prepared from sunflower seeds husks (SSH) using physiochemical activation (potassium hydroxide treatment and carbon dioxide gasification). The optimum conditions for preparing activated carbon from (SSH) were found to be activation temperature of 500 °C, activation time of 1.0 h and chemical impregnation ratio of 1:1. The adsorptions of methylene blue (MB) onto sunflower seed husks activated carbon (SSHAC) were studied with respect to initial MB concentration. The experimental data were analyzed by the Langmuir isotherm, the Freundlich isotherm and the Temkin isotherm. Equilibrium data fitted well with the Langmuir model with maximum adsorption capacity of 410 mg/g at 30 °C for MB concentration range of 50-300 mg/L. Desorption-adsorption studies for the spent SSHAC (saturated with MB) using ethanol as solvent showed that regeneration efficiency around 85%. The results indicated that the SSHAC is very effective for the adsorption of MB from aqueous solutions and can be regenerate to use for more than two adsorption cycles.

Key words: Methylene blue; Adsorption; Sunflower seed husks; Activated carbon

Salman, J. M., & Almutairi, F. D. (2013). Bath adsorption study of methylene blue dye onto sunflower seeds husks activated carbon. *Advances in Natural Science*, *6*(3), 44-47. Available from: http://www.cscanada.net/index.php/ans/article/view/j.ans.1715787020120603.2596
DOI: http://dx.doi.org/10.3968/j.ans.1715787020120603.2596

INTRODUCTION

The presence of dyes in wastewater has become a major issue all over the world. The discharge of dyes in the environment is worrying for both toxicological and esthetical reasons as dyes impede light penetration, damage the quality of the receiving streams and are toxic to food chain organisms (Lee, Choi, Thiruvenkatachari, Shim, & Moon, 2006). Industries such as textile, leather, paper, plastics, etc., are some of the sources for dye effluents (M´etivier-Pignon, Faur-Brasquet, & Cloirec, 2003). Methylene blue (MB), a cationic dye, is the most commonly used substance for coloring among all other dyes of its category. MB can cause eye burns, and if swallowed, it causes irritation to the gastrointestinal tract with symptoms of nausea, vomiting and diarrhea. It may also cause methemoglobinemia, cyanosis, convulsions and dyspnea if inhaled (Ramakrishna & Viraraghavan, 1997). Hence, the treatment of effluents containing such dye is of interest due to its harmful impacts on receiving waters.

Among several methods for pollutants removal from aqueous solution, it was found that adsorption an efficient method for the removal of dyes from wastewater because it has high removal efficiency with simplified in instruments and design. Currently, the activated carbon is the most widely used and effective physical adsorbent to remove the pollutants from aqueous solution (Lee, Choi, Thiruvenkatachari, Shim, & Moon, 2006). However, commercially available activated carbons are still considered expensive (Ghosh & Bhattacharyya, 2002). Activated carbon is prepared from a wide range of starting materials including natural and synthetic resources. Numerous studies have been devoted on the preparation of activated carbon from biomass and agricultural solid wastes (Malik, Ramteke, & Wate, 2007). Therefore, low cost agricultural waste can be selected as raw materials for activated carbons preparation, such as olives pits (Sourja, Sirshendu, Sunando, & Jayanta, 2005), silk cotton hull and maize (Martin, Artola, Balaguer, & Rigola, 2003), jute fiber (Ramakrishna & Viraraghavan, 1997), groundnut shell (Rajeshwarisivaraj, Sivakumar, & Senthilkumar, 2001), corncob (Girgis & El-Hendawy, 2002), bamboo (El-Sheikh & Newman, 2004), rattan sawdust (Wu, Tseng, & Juang, 2005) and sunflower seed husks (Salman, Njoku & Hameed, 2011). Sunflower seed husks are also a low-cost, abundantly available and renewable precursor for production of activated carbon as adsorbent for the removal different pollutants from aqueous solutions.

The purpose of this work was preparing activated carbon from sunflower seeds husks (SSHAC) by physiochemical activation and to evaluate the adsorption potential of (SSHAC) for methylene blue dye.

1. EXPERMENTAL

1.1 Methylene Blue Dye

Methylene blue (MB) supplied by Sigma-Aldrich, was used as an adsorbate in this study. The molecular weight and wave length for MB are 373.9 g/mol and 668nm respectively. Distilled water was used in the preparation of all solutions

1.2 Preparation and Characterization of Activated Carbon

Sunflower seeds husks (SSH) used as starting materials for preparation of activated carbon. The procedure used to prepare the activated carbon was referred to our previous work (Salman, Njoku, & Hameed, 2011). The precursor was first washed to remove dirt from its surface and was then dried overnight at 105 °C. The dried precursors was crushed to particle size of 1-2 mm and carbonized at 350 °C under nitrogen flow for 2 h using stainless steel vertical tubular reactor placed in a tube furnace. The char produced was mixed with KOH pallets with ratio of 1:1; deionized water was then added to dissolve KOH pallets. The dry mixture of char and KOH were placed inside the stainless steel tubular reactor for activation under purified nitrogen (99.995%) flowing at 150 cm^3/min. This flow rate was maintained until the desired activation temperature was reached (which temperature was raised at a heating rate of 10 °C/min). Once the final activation temperature was reach to 500°C, the nitrogen gas flow was switched off, while carbon dioxide gas was switched on, and activation was held for the required period of time (1hr). The activated product was then cooled to room temperature under nitrogen flow (150 cm^3/min) and washed with hot distilled water and 0.1 M hydrochloric acid until the pH of the washed solution reach 6-7.

1.3 Batch Equilibrium Studies

Batch adsorption tests were carried out for adsorption of MB solutions onto prepared activated carbon. The effects of initial MB concentrations and contacting time on the adsorption uptake and percent removal were investigated.

In order to study the effect of initial MB concentration on the adsorption uptake and percent removal, 200 mL of MB solutions with known initial concentrations (50-300 mg /L) were prepared in a series of 250 mL Erlenmeyer flasks. 0.30 g of SSHAC with the particle size of 0.5-1.0 mm was added into each flask covered with glass stopper and the flasks were then placed in an isothermal water bath shaker of 120 rpm at 30°C to reach equilibrium. Aqueous samples were taken from the solution and the concentrations were analyzed. Double beam UV-visible spectrophotometer (Shimadzu-1700, Japan) at wave length of 668 nm was used to determine MB concentrations before, during and after adsorption process. The amount of adsorption at any time, q_t (mg/g), was calculated by:

$$q_t = (C_o - C_t)V / W \tag{1}$$

where C_o and C_t (mg/L) are the liquid phase concentrations of MB dye at the initial and t conditions, respectively. V is the volume of the solution (L) and W is the mass of dry adsorbent used (g).

1.4 Adsorption Isotherms

Three isotherm models were tested for their ability to describe the experimental results, namely the Langmuir isotherm, the Freundlich isotherm and the Temkin isotherm models. The suitability of the isotherm equation to the equilibrium data was compared by the values of the correlation coefficients, R^2. The higher value of R^2 (closer to one), represent the best fit.

1.5 Langmuir Isotherm

Langmuir isotherm assumes monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform strategies of adsorption with no transmigration of adsorbate in the plane of surface (Langmuir, 1918). The linear form of Langmuir isotherm equation is given as:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \tag{2}$$

where C_e (mg/L) is the equilibrium concentration of the adsorbate, q_e (mg /g) is the amount of adsorbate adsorbed per unit mass of adsorbent q_m (mg/g) and b (L/mg) are the rate of adsorption and Langmuir constants related to adsorption capacity, respectively.

1.6 Freundlich Isotherm

Freundlich isotherm in the other hand assumes heterogeneous surface energies, in which he energy term in Langmuir equation varies as a function of the surface coverage (Freundlich, 1906). The well-known logarithmic form of the Freundlich isotherm is given by the following equation:

$$\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e \tag{3}$$

where C_e (mg/L) is the equilibrium concentration of the adsorbate, q_e (mg/g) is the amount of adsorbate adsorbed at equilibrium per unit mass of adsorbent, K_F and n are Freundlich constants.

1.7 Temkin Isotherm

Temkin and Pyzhev considered the effects of indirect adsorbate/adsorbate interactions on adsorption isotherms. The heat of adsorption of all the molecules in the layer would decrease linearly with coverage due to adsorbate/adsorbate interactions (Temkin & Pyzhev, 1940). The Temkin isotherm has been used in the form as follows:

$$q_e = B \ln A_T + B \ln C_e \quad (4)$$

where B is the Temkin constant related to heat of sorption, A_T (L/g) is the Temkin isotherm constant, R is the gas constant (8.314 J/mol K), T (K) is the absolute temperature.

1.8 Activated Carbon Regeneration

The key attribute of activated carbon is its ability to remove a wide variety of toxic organic and inorganic compounds to non-detectable levels in potable water applications. All activated carbon applications end up as exhausted (spent) activated carbon after use. The regeneration of the spent activated carbons saturated with dye was evaluated using ethanol desorption technique (Tanthapanichakoon, et al., 2005).

2. RESULTS AND DISCUSSION

2.1 Effect of Contact Time and Initial Dye Concentration on Adsorption Equilibrium

Adsorption isotherms are usually determined under equilibrium conditions. Figure1 shows the adsorption capacity versus the adsorption time at various initial MB concentrations at 30 °C. It indicated that the contact time needed for MB solutions with initial concentrations of 50–150 mg/L to reach equilibrium ranged between 4 and 6 h. For MB solutions with initial concentrations of 200–300 mg/L, equilibrium time of 8 to 10 h were required. However, the experimental data were measured at 15 h to make sure that full equilibrium was attained.

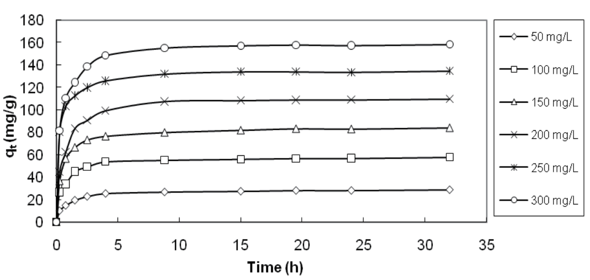

Figure 1
The Adsorption Capacity Variation With Contact Time at Various Initial MB Concentrations at 30 °c.

2.2 Adsorption Isotherms

The isotherm data were analyzed by fitting them to different isotherm models to find the suitable model for design purposes (El-Guendi, 1991). Adsorption isotherm is basically important to describe how solutes interact with adsorbents, and is critical in optimizing the use of adsorbents. Adsorption isotherm study was carried out on three isotherm models: the Langmuir, Freundlich and Temkin isotherm models. The applicability of the isotherm models to the adsorption study done as compared by judging the correlation coefficients, R^2 values. Table 1, listed the results of these three isotherm models, the Langmuir isotherm model yielded the best fit with the highest R^2 value compared to the other two models with maximum monolayer adsorption capacity of MB onto SSHAC 0f 410 mg/g.

Table 1
Isotherm Models Results

Langmuir isotherm model	
q_m (mg/g)	410.0
b (l/mg)	0.014
R^2	0.998
Freundlich isotherm model	
N	1.316
K_F [(mg /g)(l./mg)$^{1/n}$]	7.24
R^2	0.960
Temkin isotherm model	
A (l/g)	4.74
B (J/mol)	57.9
R^2	0.980

Table 2
List The Maximum Monolayer Adsorption Capacity of MB Onto SSHAC Prepared in This Work Compared to Some Data Obtained From the Literature

Adsorbents	Maximum monolayer adsorption capacity (mg/g)	References
SSHAC	410.0	This study
Commercial activated carbon F300	240.0	18
Jute fiber-based activated carbon	225.6	19
Mango seed kernel powder	142.9	20
Bamboo dust-based activated carbon	143.2	21
Coconut shell-based activated carbon	277.9	21
Groundnut shell-based activated carbon	164.9	21
Palm fiber-based activated carbon	277.8	22

2.3 Regeneration of the Spent Activated Carbons

The adsorption-desorption process was done using batch equilibrium test which was performed on the fresh SSHAC where 200 mL of MB solutions of 100 mg/L initial concentration was placed in 250 mL Erlenmeyer flask. The activated carbon (0.30 g) was added into the flask and placed in an isothermal water-bath shaker at 30 ^{o}C, with agitation speed of 120 rpm, and was agitated for 24 h. The concentration was measured using UV–visible spectrophotometer and the concentration of dye adsorbed at equilibrium, C_{ad} (mg/L) was calculated as the difference between the initial and equilibrium concentrations. The spent activated carbon was separated from the solution and washed with distilled water to remove any unsorbed MB. The sample was then dried at 105 ^{o}C in an oven for 12 h and then added into Erlenmeyer flask containing 200 mL of 95 vol% ethanol for the desorption process of dye. The regeneration efficiency was measured by:

$$\%\ Regeneration\ eff = \frac{C_{de}}{C_{ad}} \times 100 \qquad (5)$$

where C_{de} (mg/L) the concentration of MB at equilibrium in desorption process, C_{ad} (mg/L) represent the difference between the initial and equilibrium concentrations of MB in adsorption process. It was found that the percent regeneration efficiency (Eq.5) for the spent SSHAC (saturated with MB) around 85% after two cycles of adsorption-desorption.

CONCLUSION

Methylene blue was found to adsorb strongly onto the surface of the sunflower seed husks-based activated carbon (SSHAC) which prepared by physiochemical activation at 500 ^{o}C, 1hr and 1:1 for activation temperature, activation time and impregnation ratio, respectively. Equilibrium data were fitted to Langmuir, Freundlich and Temkin isotherms and the equilibrium data were best described by Langmuir isotherm model, with maximum monolayer adsorption capacity of 410 mg/g at 30 ^{o}C. In comparison to various activated carbons (adsorbents) used in previous works, it was found that the adsorption potential of the SSHAC was high, in addition to the ability of regenerate the spent SSHAC for more applications.

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