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Comparative Adsorption of Methylene Blue on Different Low Cost Adsorbents by Continuous Column Process

Mohammad Abul Hossain*, Md. Mahbbat Ali and Tajmeri S.A. Islam

Department of Chemistry, University of Dhaka, Dhaka-1000, Bangladesh

*E-mail: hossainabul@yahoo.com

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Abstract. Dyes are commonly found in the effluents of many industries. The effectiveness of adsorption for the removal of dye from wastewaters has been made it an ideal alternative to other expensive treatment methods. Continuous column adsorption is more affective than batch adsorption. A comparative column adsorption study was performed using three different low cost adsorbents for the removal of methylene blue from synthetic wastewater. Sand was collected from Cox's Bazar, and sugarcane bagasse and used black tea leaves were locally prepared in laboratory. Three columns were designed for different adsorbents maintaining all conditions were to be approximately similar. UV-vis spectroscopic method was used for analysis of methylene blue in solution. Column adsorption experiments were performed to investigate the comparison of breakthrough curves and exhaust capacity of three different adsorbents. Column study shows that the adsorption capacity of used black tea leaves is highest. The adsorption capacity of bagasse is lower than tea leaves but higher than sand.

Introduction

There is an ever-increasing demand of fabrics and food in the whole world for the rapid expanding population. The wastewaters discharged from dying and printing processes contain high amounts of dissolved colored materials [1]. The disposal of colored wastes such as dyes and pigments into receiving waters damages the environment, as they are carcinogenic and toxic to humans and aquatic life [2, 3]. Besides the problem of color, some dyes impart non-visibility and can be modified biologically to toxic or carcinogenic compounds. Now a day's concern has increased about the long-term toxic effect of water containing these dissolved pollutants.

Methylene blue is commonly used in textile and printing industries. It is moderately to highly toxic by oral and intravenous routes. Eye contact can cause staining of the eye. Inhalations may cause dryness of mouth, flushed skin, rapid pulse, blurred vision, dizziness, etc. [4]. Therefore, proper treatment of wastewater containing methylene blue is essential before its discharge in aquatic system.

Different methods are available for the removal of dyes like methylene blue from wastewater but most of them are expensive. Adsorption has received considerable attention for color removal from wastewaters as it offers the most economical and effective treatment methods. Due to high cost of activated carbon, adsorption on natural materials such as sand [5-7], saw dust [8-11], rice husk [10-11], used tea leaves [13-14], coconut coir [15], bagasse [16-17], banana pith [11], fly ash [10-11], orange peel [18] and modified biomaterials [19-21] have received considerable interest because of their local availability and their practically low cost. Use of above biomass materials [8-21] in batch adsorption process has been found to be highly effective, cheap and eco-friendly. But their proper process of application is very important.

This study investigates the potential use of some low cost adsorbents for the removal of methylene blue using column method as a model test. The aim of the study was to compare the adsorption capacity of different low cost adsorbents such as sand, sugarcan bagasse and used black tea leaves, in column adsorption process by constructing breakthrough curves for different column materials using ideal operational conditions and determining their column exhaustive capacity.

Materials and Methods

Preparation of adsorbent

Sand. Sand is cheap and easily available in nature. In this study the sand was collected from Cox's Bazar, Bangladesh. Figure 1(a) shows the optical view of the collected sand. It was dried well in an oven (NDO-450, EYELA, Japan) at 105 °C for 4 hours, crushed and sieved through metallic sieve of mesh size 0.140 mm and screened out.

Sugarcane baggase. Sugarcane bagasse (or bagasse) was collected from local market of Dhaka city and washed with boil water to remove the sweet materials. Then it was dried in an oven (NDO-450, EYELA, Japan) at 105 °C for 5 hours, crushed and sieved through metallic sieve of mesh size 0.140 mm and screened out. Figure 1(b) shows the optical view of the collected bagasse.

Used black tea leaves. Fresh black tea leaves were collected from departmental store in Dhaka city, Bangladesh. Figure 1(c) shows the optical view of the collected Fresh black tea leaves. About 50 g of fresh black tea leaves were boiled in 500 mL of distilled water for 2 hours. Boiled tea leaves were washed 3-4 times with hot distilled water followed by cold distilled water in several times until the tea liquor was completely disappeared. After washing, tea leaves were dried in an oven (NDO-450, EYELA, Japan) at 105 °C for 10 hours. Dried used black tea leaves (UBTL) were sieved through the metallic sieve of mesh size 0.140 mm and screened out.

Figure 1. Raw materials of adsorbants: (a) sand, (b) sugarcane bagasse and (c) Fresh black tea leaves.

Methylene blue and its analysis

Methylene blue (MB) is a heterocyclic aromatic compound, also known as methylthioninium chloride. It's IUPAC name is 3,7-bis(Dimethylamino)-phenothiazin-5-ium chloride, CAS number is 61-73-4, molecular formula $C_{16}H_{18}ClN_3S$ and molar mass is 319.85 $g{\cdot}mol^{-1}$. Synonyms of Methylene blue are Basic blue 9, Swiss blue, Chromosmon, Methylthionine chloride and Urolene blue. Methylene blue is a compound consisting of dark green crystals or crystalline powder, having a bronze-like luster. Solutions in water or alcohol have a deep blue color.

Methylene blue is a potent cationic and basic dye with maximum absorption of light around 670 nm. The specificity of absorption depends on a number of factors, including protonation, adsorption to other materials, and metachromasy - the formation of dimers and higher-order aggregates depending on concentration and other interactions [22]. Methylene blue can exist as MB^+, MBH_2^+, $(MB^+)_2$ and $(MB^+)_3$ in aqueous solution. Three different forms of structural formula of methylene blue are presented in Fig. 2 [22].

Analytical grade Methylene blue (MB) was collected from Merck Germany. Required amount of dried methylene blue was taken to prepare 10×10^{-5} M of stock solution by dissolved in distilled water. Further dilution was made whenever necessary. To construct a calibration curve, the absorbance of different concentrated solutions of MB within the range of 1.0×10^{-5} to 4.0×10^{-5} M was measured at pH 6.5 by a double beam UV-vis spectrophotometer (UV-160A, Shimadzu, Japan) using λ_{max} = 665 nm. Measured absorbance was plotted against the respective concentration of MB in different solutions to receive the calibration curve.

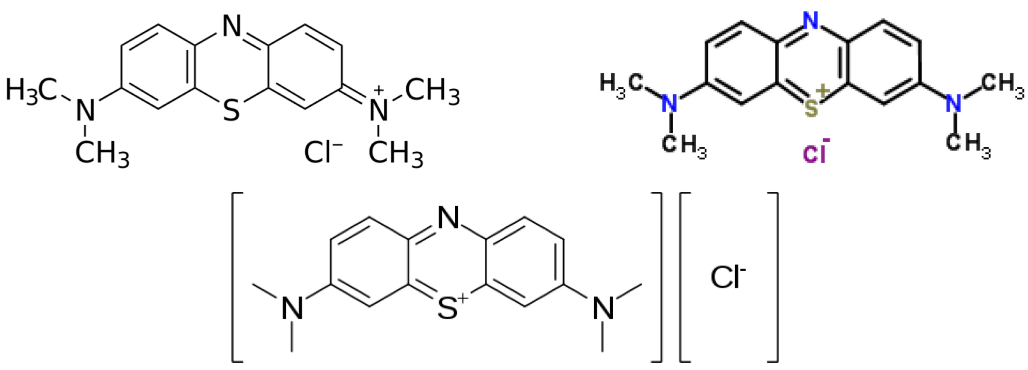

Figure 2. Structural formulas of Methylene blue (MB).

Column adsorption experiments

Column adsorption experiments were carried out using conventional downflow method [23] where three different burettes were packed with three different selected adsorbents of sand, sugarcane bagasse and used black tea leaves, respectively. The particle size of each adsorbent was 0.140 mm in diameter. Glass wool was used in the bottom of each burette. Figure 3 shows an adsorption column used in the study. The characteristic features of different column prepared from different adsorbents are given in Table 1. A fixed concentrated methylene blue solution (4.0×10^{-5} M) was introduced from the top of the column. The flow rate was tried to maintain at 1 $mL\cdot min^{-1}$. The introducing solution is known as eluent and the solution, which is passed through the adsorbent column and is collected after adsorption, is termed as effluent. Samples of effluent from the column were collected at suitable time intervals in different test tubes. In every test tube 20 mL effluent was taken and analyzed by the UV-vis spectrophotometric method as described previously. Breakthrough curves and column exhaust capacity for different adsorbents were determined from the experimental data for each adsorbent.

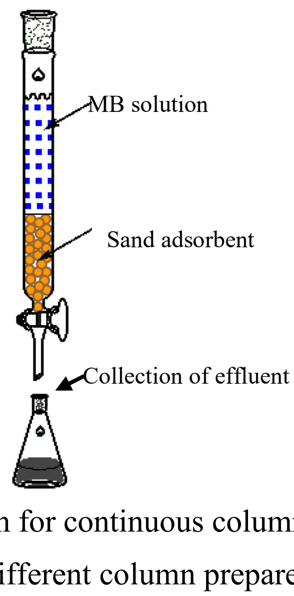

Figure 3. Conventional column for continuous column adsorption study.

Table 1. The characteristic features of different column prepared from different adsorbents.

Name of adsorbent	Amount of adsorbent (g)	Height of the column (cm)	Flow rate of effluent ($mL\cdot min^{-1}$)
Sand	1.0	2.5	1.0
Bagasse	0.2	2.5	1.0
Used black tea leaves	0.2	2.5	1.0

Results and Discussion

Characteristics of adsorbents

Sand, bagasse and used black tea leaves have received considerable interest because of their local availability, cheap and eco-friendly.

Sand. Sand is a naturally occurring granular material composed of finely divided rock and mineral particles. Geological term sand particles range in diameter from 0.0625 to 2 mm. The composition of sand is highly variable, depending on the local rock sources and conditions. The most common constituent of sand is silica (silicon dioxide, or SiO_2), usually in the form of quartz which, because of its chemical inertness and considerable hardness, is resistant to weathering.

Bagasse. Sugarcane is an important agricultural crop in Bangladesh. It is estimated that sugar industries mill over 20 million tons of green cane each year to produce sugar and related products. Concurrently, the sugar industries generate over 2.5 million tons of dry fibrous materials i.e. sugarcane bagasse or bagasse per year as its by-products [16]. Sugarcane bagasse (or bagasse) is the fibrous residual material of the sugarcane stems left after the crushing and extraction process from sugar mills, which normally accounts for 20 – 24% of the cane [16, 24]. As the main sources of sugarcane fibers, bagasse usually consists of rind, vascular bundles, and pith (the parenchyma). In chemical analysis, it was reported [24] that Cellulose (46%), Hemicelluloses (25%) and Lignin (20%) are main composition of bagasse which are very effective for adsorption of dyes like methylene blue. Probable application of bagasse for the treatment of wastewater will reduce sugar mills bi-product to preserve the environmental problems.

Used black tea leaves. Black tea is one of the most widely-consumed beverages in the world, second only to water. As a result, a large amount of bi-product as well as used black tea leaves is produced in tea industry. Like as bagasse, cellulose and lignin are the main compositions of used black tea leaves [14, 25-38] which might be effective for adsorption of methylene blue.

Analysis of adsorbate

Analysis of methylene blue in different solutions, before and after adsorption is very important for the adsorption study. UV-vis spectrophotometric method was used to analyze the methylene blue in different solutions. A calibration curve was constructed by plotting the absorbance as a function of respective concentrations of methylene blue in solution at pH 6.5. The straight line of the absorbance vs. concentration of methylene blue passing through the origin in Figure 4 suggested the validity of Beer-Lambert law. The value of the slope was equivalent to εl. So, the molar absorption coefficient (ε) of methylene blue was found to be 5.175×10^4 L·mol^{-1}·cm^{-1} at 30 °C. Concentration of MB in different solutions was determined from measurement of absorbance divided by the slope of the calibration curve.

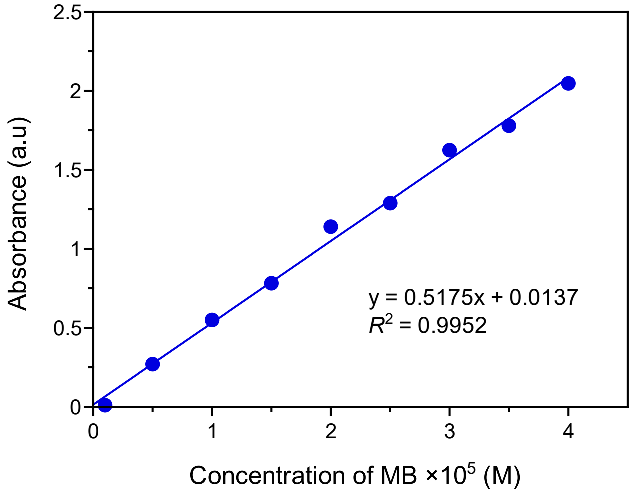

Figure 4. Calibration curve for analysis of Methylene blue.

Column adsorption

Column adsorption study was conducted using down flow technique [23]. In the column, the concentration of the solution in contact with a given layer of adsorbent was practically constant. When the adsorbate solution was introduced at the top of a clean fixed bed column, the adsorption of the most solute occurred in a narrow band at the top of the column termed as adsorption zone. As the process was continuing the upper layer of the column was saturated with solute and the adsorption zone proceed downwards through the bed. As the zone approaches the bottom of the fixed bed, the concentration of the adsorbate in the effluent began to increase. The adsorbate and the adsorbent do not exist in equilibrium in column. Theory of the conventional down flow adsorption column was used to investigate the comparison of nature of breakthrough curves and exhaustion capacity of three different adsorbents for the removal of MB from a synthetic wastewater [23].

Breakthrough curves. Breakthrough curve presents the concentration of effluent as a function of volume of effluent. From the breakthrough curve, the rate of adsorption capability, time required to reach the saturation point, the volume of clear (adsorbate free) effluent can be determined. In all cases of three adsorbent, at first all the MB adsorbed from the solution and allowed to pass only clear water. When the adsorption capacity of adsorbent was over, then MB containing solution was passed through the column. Figures 5 and 6 show the breakthrough curves for the column adsorption of MB on sand, bagasse and used black tea leaves, respectively. Figure 5(a) shows that after collection of 110 mL clear solution from sand column, the effluent start to containing MB which was rapidly increased and became steady (after around 175 mL). Figure 5(b) shows that after collection of 340 mL clear solution from bagasse column, the effluent started to containing MB which was rapidly increased and became steady (after around 550 mL). Figure 6 shows that after collection of 120 mL clear solution from used black tea leaves, the effluent started to containing MB which was slowly increased and became steady (after around 590 mL). Comparing three figures, it is noted that the rate of adsorption of sand and bagasse is very fast compared used black tea leaves given in Table 2. Again, the rate of adsorption of used black tea leaves is slow but adsorption capacity is very high due to the more heterogeneity in UBTL surface [26 and 27]. From the breakthrough curve one can easily determined the maximum volume limit of MB free clear solution for different adsorbents.

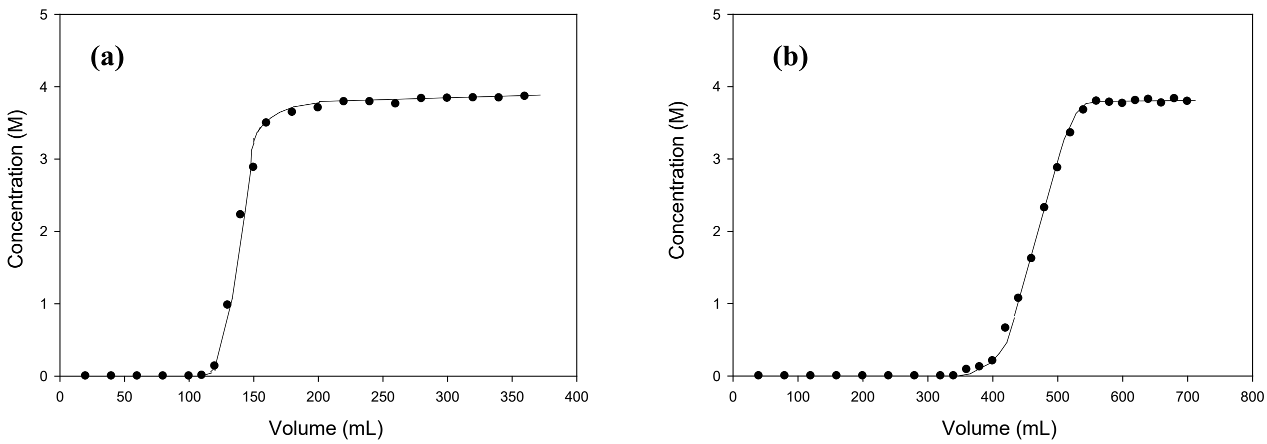

Figure 5. Breakthrough curve of (a) sand and (b) sugarcane bagasse.

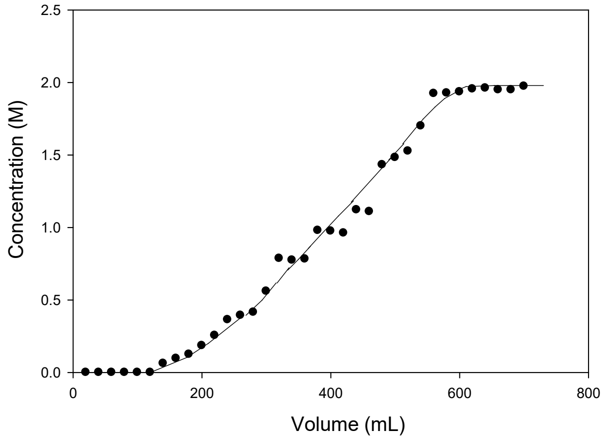

Figure 6. Breakthrough curve of used black tea leaves (UBTL).

Column exhaustion capacity. Column exhaustion capacity of different adsorbents was also determined from the experimental data. This study shows that the amounts of MB removed by different columns are to be inversely proportional to volume of effluents i.e., $(C_o\text{-}C_f) \propto 1/V_f$. This gives a linear equation (1) [14] corresponding to

$$\log(C_o - C_f) = \log B + \log\frac{1}{V_f} \quad (1)$$

where,

C_o = Initial concentration of effluent.
C_f = Concentration of adsorbate in the effluent
V_f = Total volume of effluent
$(C_o\text{-}C_f)$ = Column exhaustion
B = Column exhaustion capacity which depends on the nature column and adsorbent.

Column exhaustion capacity slightly differs from column adsorption capacity. In batch method where adsorption equilibrium exists, adsorption capacity term is used. But in column adsorption process, where adsorption equilibrium never attains, column exhaustion capacity term is used. Figs. 7 and 8 show the $\log(C_o\text{-}C_f)$ vs $1/V_f$ plots for determination of column exhaustion capacity of sand, bagasse and used black tea leaves, respectively to methyleme blue. The calculated values from the slope of the linear plots showed (Table. 2) that the column exhaustion capacity of used black tea leaves is very low compared with sand and bagasse. This higher exhaustion capacity of sand might be due to the more attractive of sand surface with MB.

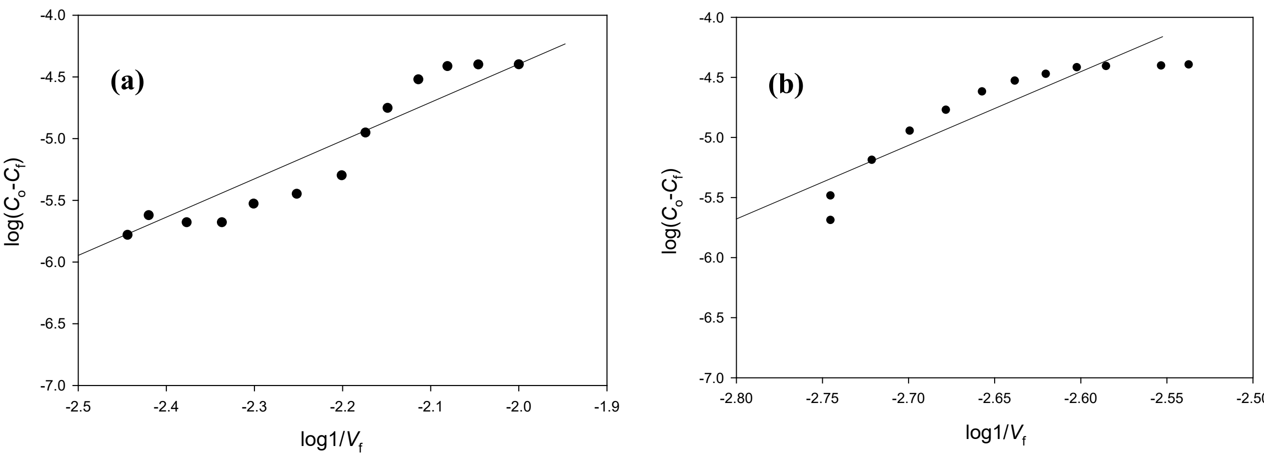

Figure 7. Column exhaustion capacity of (a) sand and (b) sugarcane bagasse.

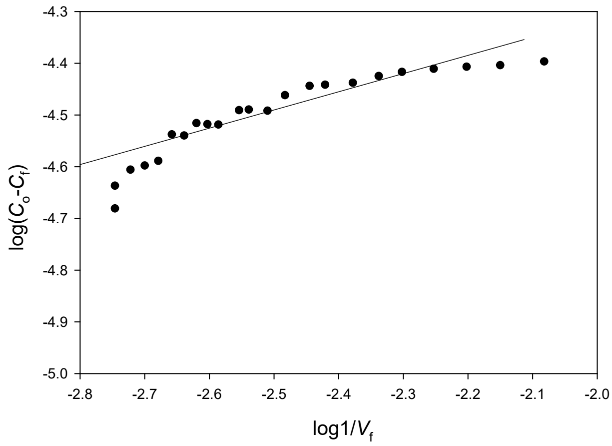

Figure 8. Column exhaustion capacity of used black tea leaves (UBTL).

Table 2. Comparison of column adsorption properties of different adsorbents.

Name of adsorbent	Amount of clear effluent (mL)	Saturation time for column adsorbents (1mL ≈ 1min)	Column exhaustion capacity ×10^5 (mol·g^{-1})	R^2
Sand	110	280	975.66	0.891
Sugarcane bagasse	340	560	29.90	0.823
Used black tea leaves	120	620	0.28	0.841

Conclusions

The conventional down-flow column adsorption studies showed that the column exhaustion capacity of used black tea leaves is higher than that of sand and bagesse for the removal of methylene blue from aqueous solution. Again, the nature of breakthrough curve suggested that the bagasse is more effective to MB due to its high adsorption rate compare with used black tea leaves as well as sand. Another important finding is that the flow rate of effluent can not be controlled by using the conventional downflow column for continuous adsorption process.

Conflict of Interest

The authors declare that there is no conflict of interests concerning the publication of this paper.

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