Chemically modified sugarcane bagasse as a biosorbent for dye removal from aqueous solution

Ho Thi Yeu Ly, Hoang Thi Khanh Dieu, Trinh Minh Tan Sang, Le Nguyen Minh Nha

***Abstract*—The use of adsorbent prepared from sugarcane bagasse, an agro waste from sugar industries has been studied as an alternative substitute for activated carbon for the removal of dyes from aqueous solution. Adsorbents prepared from sugarcane bagasse modified with citric acid was used as a low-cost biosorbent for removal of dyes from the aqueous solution. Adsorption parameters such as initial pH values, dyes concentrations, adsorbent dosages and contact times were investigated by the batch experiments. The Freundlich and Langmuir adsorption isotherm models were used to evaluate the experimental data. The results showed that the adsorption process of dyes onto the modified sugarcane bagasse leaned towards Langmuir model for MSB and Freundlich for SB. Maximum adsorption capacity of MSB was found to be 8.40 mg/g at pH 9. The results showed that the modified sugarcane bagasse with citric acid could be a potential low-priced adsorbent for removal of the color from the aqueous solution.**

***Keywords*—sugarcane bagasse, adsorption, dyes, chemical modified, isotherm models**

1 INTRODUCTION

Dye production industries and many other industries which use dyes and pigments generate wastewater, which is characteristically high in color and organic content [1]. Dyes are widely used in industries such as textile, rubber, paper, plastic, cosmetic etc. Among these various industries, textile ranks first in usage of dyes for coloration of fiber [1, 2].

The textile industry plays an important role in Viet Nam economy. In fact, this industry has been significantly the received investment. But, its fast growth leads to concerns in environmental pollution. It was well known that the textile industry consumes a large volume of water and generates a significant amount of wastewater. In textile industries, about 1000 L of water is used for every 1000 kg clothes processed. It is estimated about 10–15% of the dyes were lost in industrial effluent [3, 4]. Discharge of such coloured effluents impart the colour to the receiving water bodies (rivers, stream and lakes) and causes many significant problems such as increasing the toxicity and chemical oxygen demand. It also reduces light penetration which is a derogatory effect on photosynthesis phenomena [4, 5]. Therefore, wastewater with dyes is very difficult to treat, since the dyes are recalcitrant organic molecules, resistant to aerobic digestion and stable to light, heat and oxidizing agent [1, 6].

Many methods have been studied to remove the color from the textile wastewater and other industries using dyes such as adsorption, coagulation/ flocculation, flotation, oxidation, ozonation, membrane filtration, oxidation and physical methods like membrane filtration, ion exchange and electrochemical techniques. Among them, adsorption has been known as an efficient method to removal the colour [1, 4, 7]. Adsorption techniques were used easily with available low cost adsorbents mainly of biological origin. Therefore, many researches have been conducted to find out alternative low-cost adsorbents. Agricultural waste materials are receiving much more attention as adsorbents for the removal of dyes from wastewater due to its low cost and good availability. Many studies have been undertaken for the removals of pollutants by using a variety of materials used as adsorbents such as apple

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pomace [8], sugarcane bagasse [9], Neem leaf powder [10], banana Pith [11], wheat shell [12], palm tree flower [13], Indian rose wood sawdust [14], rice husk [15], peanut shell [16], coir pith [17], sunflower seed husk [18], orange peel [19] and eucalyptus bark [20] for the removal of different dyes from aqueous solutions at different operating conditions. Sugarcane bagasse, a waste from food, sugar and beverage industries, is a potential adsorbent to remove dyes. Many investigations on bagasse as an effective adsorbent for adsorption of organic pollutants [21, 22] and metals. It is usually modified to enhance its adsorption capacity or used to prepare cheap activated carbon [7, 23].

The objectives of our investigation were to investigate the potential of using modified sugarcane bagasse as a low – cost adsorbent to remove dye from aqueous solutions. Due to their low cost, after these materials have been expended, they can be disposed of without expensive regeneration.

2 MATERIALS AND METHODS

Preparation of adsorbent

The clean bagasse pith selectively collected from the canteen in the University of Technology and Education was washed 2 times with distilled water, then left to dry in the oven at 60 ^oC overnight. After that, the bagasse was ground and sieved. The fraction of 0.20–0.45 mm sizes were collected for experiment then the material was boiled with distilled water at 100 ^oC to removal all the sugar in its structure and was labeled as SB.

Citric acid modified bagasse

The sugarcane bagasse (SB) was treated with NaOH 0.1 M (solid SD/solution = 1/20 w/v) to remove lignin in raw sugarcane bagasse. The mixture was agitated at 250 rpm in 2 hours at room temperature. The mixture was filtered and washed with deionized water to neutral and dried at 55 ^oC in the oven.

In order to enhance the adsorption capacity of sugarcane bagasse, citric acid was used to modify the SB. 20 gram bagasse was mixed with 500 mL of citric acid 0.8 M and then was shaken at 250 rpm for 24 h at room temperature. The bagasse was then separated and put in the oven at 60 ^oC overnight. Again, the bagasse was washed several times with distilled water until neutral. The material was dried in an oven at 60 ^oC. The material which modified by citric acid was labeled as MSB and which was used for this investigation [24]. The products obtained were characterized by FTIR spectra using FTIR system 8400 Model. The surface morphology of the adsorbent was visualised via scanning electron microscopy [SEM] JEOL-5333 (Japan).

Dye solution preparation

In this study the Direct Fast Turquoise Blue (FBL) was used and it was obtained from the chemist supplier. An accurate weighed quantity of the dye was dissolved in double distilled water to prepared the stock solution (500 mg/L). Experimental solution of the desired concentration was obtained by successively dilutions. Dye concentration was determined by using absorbance values measured before and after the treatment, at 610 nm, with Hitachi UV Visible Spectrophotometer (model no.: UH5300).

Experiments were carried out at initial pH values which were controlled by the addition of 1,0 M or 0,1 M of sodium hydroxide, NaOH or hydrochloric acid, HCl

Experimental methods

All the experiments were performed in batch mode at room temperature (30 ^0C ± 1). For the initial pH investigation, a wide ranging from 1 to 11 was used. In each adsorption experiment, 50,0 mL of the dye solution of known concentration and pH was added to 100 mg of adsorbents in 250 mL round bottom flask at room temperature (30 ^0C ± 1) and the mixture was stirred on a rotary orbital shaker at 250 rpm. The sample was withdrawn from the shaker at the predetermined time intervals. The experiment was done by varying the amount of absorbents (0.1 to 1.2 mg/50 mL), concentration of dye solution (40–160 mg/L) and pH (1–11) after the equilibrium time. The effect of the contact time was examined by added 0.4 g adsorbent to 50 mL of adsorbate at a concentration 20 mg/L. For all experiments, the supernatant was used to check the colour removal efficient which was measured by the initial and the final concentration (C_0 and C) of the dye solution. The formula was:

$$\text{Efficiency } \% = \frac{C_0 - C}{C_0} \times 100$$

3 RESULTS AND DISCUSSION

Characteristics of adsorbents

The surface morphology of SB and MSB visualized via scanning electron microscopy, are shown in Fig.1 and Fig. 2.

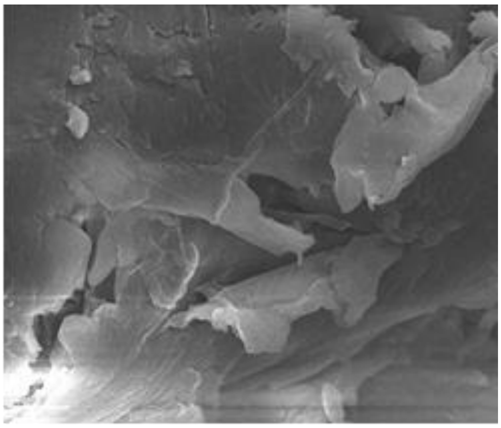

Fig.1. SEM of SB

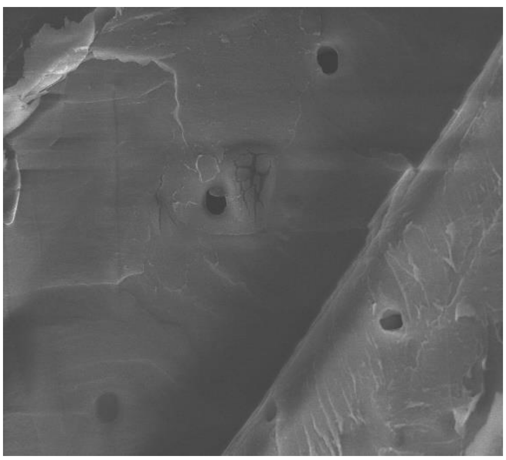

Fig. 2. SEM of MSB

SEM of MSB shown that the surface raw bagasse which was modified with citric acid became flatter than the surface of the raw sugarcane bagasse.

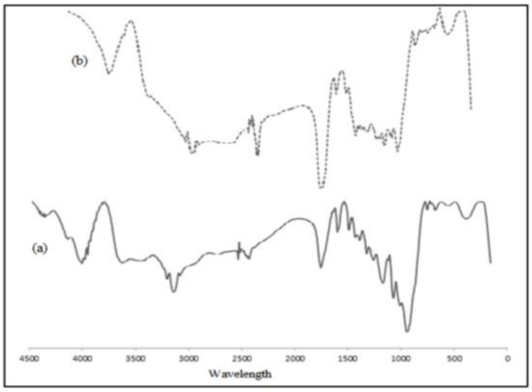

Fig. 3. FITR spectra of (a) raw sugarcane bagasse and (b) modified sugarcane bagasse with citric acid

The spectra of raw bagasse (SB) before (a) and (b) after modification with citric acid (MSB) are shown in Fig. 3. When comparing the FTIR spectrum of MSB to the one of SB, the higher intensity of the peak at 1730 cm^{-1} confirmed by the presence of carboxyl groups in citric acid, leading to the increase the adsorption capacity of MSB for dyes.

Effect of pH

The removal efficiency of the sugarcane bagasse (SB) and the modified sugarcane bagasse (MSB) at different pH is shown in Fig. 4. The results showed that the percentage of dye removal decreased with increasing pH values. At the low pH region, the pH range of 1 to 4, the same adsorption efficiency of SB and MSB became meaningless. When the pH reached to 5, the removal efficiency of two SB and MSB started to be different. The percentage of colour removal of MSB was higher comparing with those of SB. As shown in Fig. 4, at pH 1–2, the dye was removed completely for both SB and MSB. At pH 9, the maximum percentage efficiency of dye removals were observed, 18% for SB and 64% for MSB.

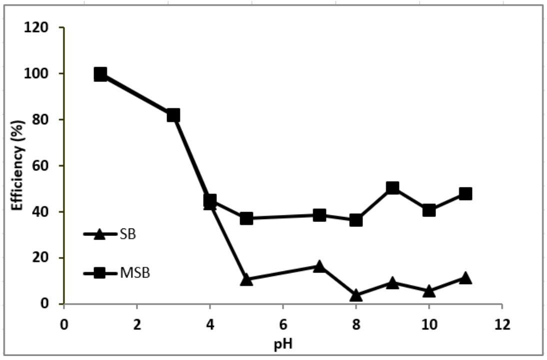

Fig. 4. The dye removal efficiency at different pH, adsorbent mass = 0.1g, C_0 = 20 mg/L

This phenomenon could be explained that at the pH low, the dye became active and it attached to the cellulose structure of the materials. However, the adsorption process at very low pH was not useful due to a large amount of acid must be used to neutralize, leading to high cost of the treatment. Therefore, at pH 9 was used for the investigation of the adsorption process.

Effect of the adsorbent dosage

Fig. 5 illustrated the adsorption efficiency of the modified sugarcane bagasse at different dosages.

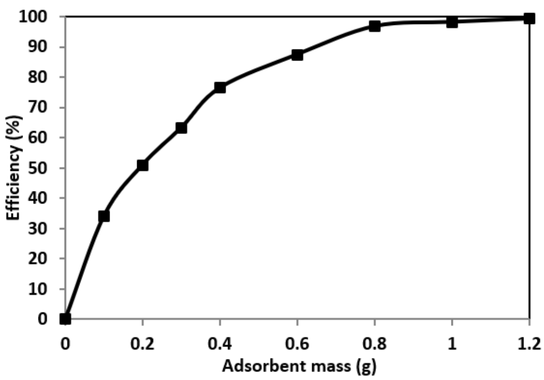

Fig. 5. Dye removal efficiency at different adsorbent dosages pH = 9, C_0 = 50 mg/L

It was observed that the adsorption efficiency increased with increasing the mass of the adsorbent. The percentage adsorption increased from 34.1% at a dose of 0.1 g to 99.3% at a dose of 1.2 g. Obviously, the more material added, the more active site for the dye to attach on. After dose of 0.4 g, the adsorption reached an equilibrium as the increase became stable.

At any given adsorbent dosage, the final pH in the presence of dye was higher compared to those in the absence of dye. This was attributed to the anion-exchange reaction between dye anion and surface-active groups on the adsorbent [1].

Effect of initial dye concentration

Fig. 6 represented the change of adsorption ability at different dye concentration. The higher initial concentration was, the less dye was removed. With the range of initial concentration was 40–160 mg/L, the efficiency dropped from 69% to 35.8%.

Table 1 showed the Freundlich and Langmuir isotherm parameter data. Maximum adsorptive capacity of MSB was nearly twice as SB. This improved the efficiency of the modification of MSB.

Table 1. Freundlich and Langmuir isotherm parameters

	Parameter	SB	MSB
Freundlich	K	20.2675	0.4271
	n	1.4546	2.7273
	R^2	0.9896	0.9582
Langmuir	k_L	0.0137	0.0503
	Q_{max} (mg/g)	4.57	8.40
	R^2	0.9601	0.9848

From R^2, the result showed that the adsorption process of both SB and MSB were followed both isotherm models. But SB seemed to fit Freundlich model while MSB much fitted Langmuir model.

MSB's Q_{max} was compared to other adsorbents in Table 2. Comparing to other materials used to remove dyes from aqueous solution, the results showed that the MSB could be used for removal of dyes from the textile wastewater.

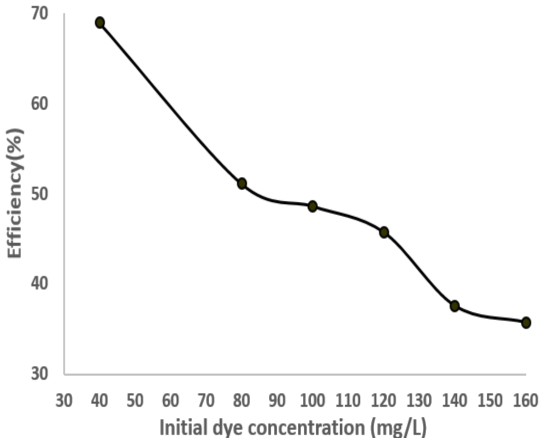

Fig. 6. The dye removal efficiency at different initial dye concentrations, pH = 9, adsorbent dose = 0.4 g

This result from the surface active sites of the adsorbent was limited since the dose was constant. When the color increased, there was not enough the space to the adsorption which led to the decline in the efficiency.

Effect of the contact time

The contact time effect on the adsorption was shown in Fig. 7. As shown in the results, from 15 minutes to 4 hours, the adsorption percentage of removal increased from 72.5% to 91.5%. The longer shaken time was, the more contact between the adsorbent and the adsorbate, which meant the dye had more chances to attach onto the material's cellulose chains. Hence, much dye adsorbed, made the colour removal efficiency higher. After 15 mins, the efficiency still rose, but not much. So, 15 mins could be considered as the optimum contact time.

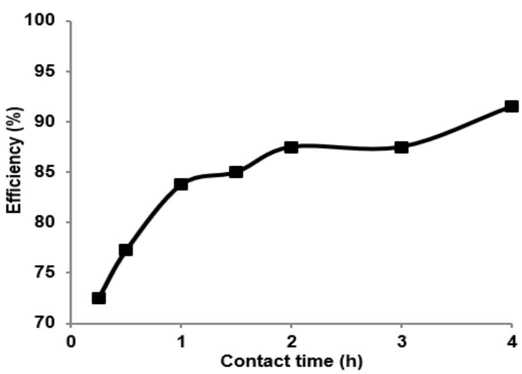

Fig. 7. The dye removal efficiency at different contact times, pH = 9, adsorbent dose = 0.4 g, C_0 = 20 mg/L

Adsorption isotherm

Freundlich and Langmuir adsorption isotherm models were used to evaluate the experimental data.

Table 2. Natural forms of agricultural waste and its dye adsorption capacities

Adsorbent	Q_{max} (mg/g)	Reference
Alunite (Turkey)	2.85	[25]
Glass powder	4.03	[26]
Coir pith	6.72	[27]
Sugarcane bagasse	5.78	[28]
Rice husk	40.59	[29]
Walnut bark	15.1	[30]
Cherry saw dust	39.00	[31]
Banana peel	20.08	[32]
Orange peel	0.07	[33]
Modified sugarcane bagasse	8.40	This work

4 CONCLUSION

Normal sugarcane bagasse pith (SB) and sugarcane bagasse modified with citric acid (MSB) have been studied for the adsorption of textile dye (FBL). The adsorption efficiency of MSB increased with increasing contact time and decreased with increasing initial dye concentration. Optimum condition for adsorption was pH 9, and the adsorbent mass was 0.4 g. The results obtained from the studies showed that the adsorption process of MSB for the Direct Fast Turquoise Blue (FBL) followed the Langmuir and the Freundlich isotherm models in the order of Freundlich < Langmuir. The results showed that the bagasse pith had the potential to be a competitive alternative natural adsorbent.

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Bã mía biến tính hóa học như là một chất hấp phụ sinh học nhằm loại bỏ màu của dung dịch thuốc nhuộm từ dung dịch lỏng

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***Tóm tắt*—Việc sử dụng chất hấp phụ được chuẩn bị từ mía, một chất thải nông nghiệp từ các ngành công nghiệp mía đường đã được nghiên cứu như là một chất thay thế cho than hoạt tính để loại bỏ màu thuốc nhuộm từ dung dịch lỏng. Chất hấp phụ chuẩn bị từ mía được biến tính với citric acid đã được sử dụng như một chất hấp phụ sinh học chi phí thấp để loại bỏ màu thuốc nhuộm từ nước thải dệt. Các thông số hấp phụ như giá trị pH ban đầu, nồng độ thuốc nhuộm, lượng chất hấp phụ và thời gian tiếp xúc được nghiên cứu bằng các thí nghiệm dạng mẻ. Các mô hình đẳng nhiệt hấp phụ Freundlich và Langmuir được sử dụng để đánh giá các dữ liệu thực nghiệm. Kết quả nghiên cứu cho thấy quá trình hấp phụ của thuốc nhuộm tuân theo mô hình Freundlich đối với bã mía chưa biến tính (SB), tuân theo mô hình Langmuir đối với bã mía đã biến tính bằng citric acid (MSB). Khả năng hấp phụ tối đa của MSB là 8,40 mg /g tại pH = 9. Kết quả cho thấy rằng bã mía biến tính sau khi được xử lý, biến tính bằng citric acid có thể là một chất hấp phụ tiềm năng có thể loại bỏ màu của dung dịch thuốc nhuộm.**

***Từ khóa*—bã mía biến tính, hấp phụ, thuốc nhuộm, dung dịch lỏng, các mô hình cân bằng**