Adsorption of Acid Orange 7 by Cetylpyridinium Bromide Modified Sugarcane Bagasse

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Graphical abstract
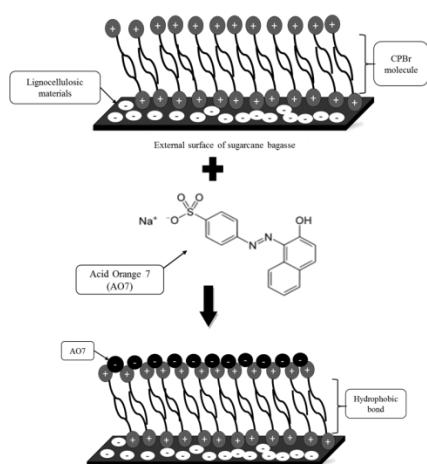
Abstract

In the present study, the adsorption of acid orange 7 (AO7) dye from aqueous solution by sugarcane bagasse (SB) and cetylpyridinium bromide (CPBr) modified sugarcane bagasse (SBC) was examined. SBC was prepared by reacting SB with different concentrations (0.1, 1.0 and 4.0 mM) of cationic surfactant, CPBr. The SB and SBC were characterized using Fourier transform infrared (FTIR) spectroscopy. The adsorption experiments were carried out in a batch mode. The effect of initial AO7 concentrations (5-1000 mg/L), initial CPBr concentrations and pH of AO7 solution (2-9) on the adsorption capacity of SB and SBC were investigated. The experimental adsorption data were analyzed using Langmuir and Freundlich isotherm models. The adsorption of AO7 onto SB and SBC followed Freundlich and Langmuir isotherm models, respectively. The maximum uptake of AO7 was obtained by SBC4.0 (SB treated with 4.0 mMCPBr) with the adsorption capacity of 144.928 mg/g. The highest AO7 removal was found to be at pH 2 and 7 for SB and SBC, respectively. As a conclusion, sugarcane bagasse modified with CPBr can become an alternative adsorbent for the removal of anionic compounds in aqueous solution.

Keywords: Acid orange 7, adsorption, sugarcane bagasse, surfactant

1.0 INTRODUCTION

Textile is the largest industry generates waste effluents that can threat human health and natural environment. Acid orange 7 (AO7) is an anionic dye constitutes more than 15% of the world dye production in the textile industry. AO7 is very stable compound and thus, difficult to be degraded. The presence of azo group as part of AO7 structure [1] is very harmful and can affect human health. Therefore, it is essential to properly treat the wastewater containing AO7.

There are many studies to overcome this problem and various methods of color removal from wastewater i.e. flocculation, coagulation, precipitation, electrochemical destruction and microbial degradation are available. However, all of the conventional treatment methods showed disadvantages i.e. incomplete removal of dyes,

inefficient to treat various classes of dyes, labor intensive and cost consuming. Therefore, extensive studies have been focusing on alternative materials for the removal of dyes from wastewater through adsorption process.

Currently, activated carbon has been employed as an adsorbent for wastewater treatment. However, higher cost, ineffective and non-selective against vat and disperse dyes [2] limit its application. Therefore, the effective and economical adsorbent is highly needed as a potential replacement of activated carbon. Among all of the available materials, adsorption using biomass is the most preferable and currently considered as an effective, efficient and economical method for wastewater treatment [3].

Biomass waste such as sugarcane bagasse (SB) is highly abundant in Malaysia. However, current practices on the disposal of this waste which is

combustion-heat recovery and farmland application lead to serious environmental problems such as air pollution and greenhouse gas emission [4]. Thus, the use of this waste as an adsorbent is of great importance nowadays.

The main structural components of SB are cellulose, hemicelluloses and lignin. The hydroxyl group of cellulose and lignin released hydrogen ions in aqueous solution forming negatively charged surfaces. Since SB possesses negative charge on its structural framework, this biomass exhibits high cation exchange capacity but low or no affinity towards anionic compounds. However, modification of several biomasses such as tea waste [5], coconut coir pith [6], wheat straw [7,8], peanut husk [9] and barley straw [10], with cationic surfactant could enhance their anionic exchange capacity. To the extent of our knowledge, none has been reported on the surfactant modified SB as adsorbent in removing pollutant from wastewater.

By modification with cationic surfactant, the positive charge of ammonium cation on the SB will attract anionic compounds through ion exchange process [5]. Besides, the porous surface texture of SB helps to facilitate the adsorption of the cationic surfactant onto the SB surfaces [11]. Due to positive charge, cationic surfactant has the ability to be adsorbed onto negatively charged support solid surfaces of SB [7]. Therefore, the purpose of this study was to modify the SB with cationic surfactant, cetylpyridinium bromide (CPBr) in order to enhance the adsorption capacity towards AO7 in aqueous solution.

2.0 EXPERIMENTAL

2.1 Preparation of Sugarcane Bagasse

The SB from the species of *Saccharum officinarum L.* was collected from nearby market. The collected SB was crashed and dried at 90°C in an oven for 24 hours. The dried SB was subjected to the pretreatment process [12].

2.2 Preparation of CPBr Modified SB

The pretreated SB was modified with three different concentrations of CPBr i.e. 0.1, 1.0 and 4.0 mM. 500 mg of pretreated SB was placed into 250 mL Erlenmeyer flask containing 50 mL of CPBr solution (Merck, Germany) and stirred under constant stirring for 10 minutes. The suspension was filtered through Whatman filter paper (125 mm) and it was dried at 90°C in an oven for 24 hours. The abbreviations of the samples are listed in Table 1.

2.3 Characterization Technique

The samples of raw and modified SB before and after modification were characterized using Fourier transform infrared (FTIR) spectrophotometer (model Nicolet is5, Thermo Fischer Scientific, USA) using an attenuated total reflectance (ATR) method. The FTIR spectrum was recorded using OMNIC software (version 8.3.103, Thermo Nicolet, USA) at spectral range of 400 to 4000 cm^{-1}.

Table 1 The abbreviations of the samples

Sample Code	Description
SB	Pretreated sugarcane bagasse
SBC0.1	SB modified with 0.1 mM CPBr
SBC1.0	SB modified with 1.0 mM CPBr
SBC4.0	SB modified with 4.0 mM CPBr

2.4 Adsorption Study

The effect of initial AO7 concentrations and pH on the adsorption of AO7 onto SB and SBC were determined at different initial AO7 concentrations and pH ranging from 5 to 100 mg/L and 2 to 9, respectively. The stock solution was prepared by dissolving 1000 mg of AO7 (Sigma-Aldrich, USA) in 1000 mL distilled water.

For the effect of different concentration, 500 mg of samples (SB, SBC0.1, SBC1.0 and SBC4.0) were accurately weighed and placed into 250 mL Erlenmeyer flask containing 50 mL AO7 solution at different concentrations. The suspension was shaken at 200 rpm for 2 hours under room temperature.

For the effect of pH, 500 mg of samples (SB, SBC0.1, SBC1.0 and SBC4.0) were weighed into 250 mL Erlenmeyer flasks containing 50 mL AO7 solution at different pH. The adsorption study was performed as described above.

The AO7 concentration before and after adsorption were determined using visible spectrophotometer (model NANOCOLOR® VIS, Macherey Nagel, Germany) at λ_{487nm}. The amount of AO7 adsorbed at equilibrium, q_e (mg/g) was calculated by the following equation:

$$q_{e=} \frac{(C_i - C_e)v}{w} \qquad (1)$$

Where:

C_i and C_e = AO7 concentration at initial and equilibrium, respectively (mg/L)

v   = volume of AO7 solution (mL)

w   = weight of SB and SBC (g)

3.0 RESULTS AND DISCUSSIONS

3.1 Characterization of Sugarcane Bagasse

FTIR spectra of SB and SBC (SBC0.1, SBC1.0 and SBC4.0) are presented in Figure 1. The distinct peaks in FTIR spectra at 3340 to 3412 cm^{-1} for SB and SBC corresponded to asymmetric and symmetric stretching of –OH group of cellulose and lignin [13]. The peaks at 2900 cm^{-1} were attributed to the –C-H stretch. The bands at 1423 cm^{-1} were assigned to the symmetric CH_2 group of cellulose and the peaks at 1731 cm^{-1} represented C=O group of hemicelluloses. The bands at 1240 cm^{-1} corresponded to C-O-C in cellulose and hemicelluloses. The bands at 1035 cm^{-1} represent C-O stretching and 897 cm^{-1} related to β-glycosidic chains between monosaccharide units [1, 14, 15].

There were slight changes in the FTIR spectra of SBC1.0 and SBC4.0 at 2914 cm^{-1} and 2918 cm^{-1} compared to that of 2897 cm^{-1}. These peaks

demonstrated the overlap of the extra peaks represent C-H bond from the CPBr molecules. The main features of these spectra were attributed to the presence of cellulose, lignin and hemicelluloses which are the natural components of lignocellulosic fibers [16]. It can be observed that the FTIR spectra of SBC were quite similar to that of SB indicating that the modification of SB with CPBr did not promote changes in its chemical structure.
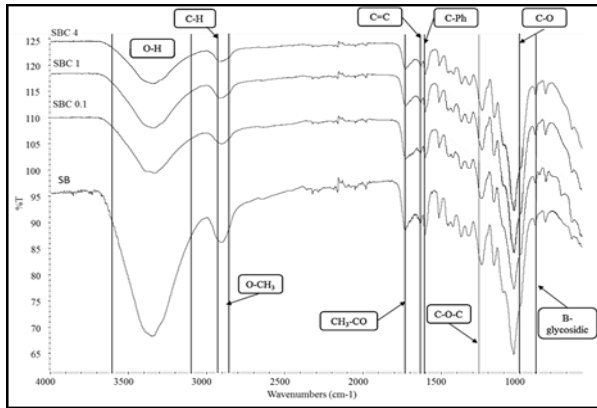

Figure 1 FTIR spectra of SB and SBC.

3.2 Adsorption Isotherm

The adsorption isotherms of AO7 by SB and SBC are presented in Figure 2. More uptake of AO7 by SB and SBC occurred at the initial stage of the adsorption process. The adsorption process gradually becoming slower until the equilibrium point was achieved. At lower AO7 concentrations, there are unoccupied active sites on the SB surfaces. However, as initial AO7 concentrations increased, the sites were gradually occupied by AO7 molecules hence resulted in decreased adsorption sites [1]. Moreover, as initial AO7 concentrations increased, the probability of contact between AO7 and SB increased.

SB and SBC showed different adsorption capacity towards AO7. The adsorption capacity of SBC1.0 and SBC4.0 increased significantly with the increased of AO7 concentrations in comparison to SB and SBC0.1. This was due to the presence of more CPBr molecules on the SB surfaces which can increased the adsorption capacity towards AO7 molecules. The modification of SB with CPBr increased new functional group density on the SB surfaces and facilitated electrostatic interaction between SB and negatively charged AO7.

Due to the negatively charged surface of SB, it can retain and hold cationic molecules on its framework [17]. The modification of SB with CPBr created affinity towards anionic molecules. In the modification process, CPBr molecules are firstly anchored at the interlayer of SB. The CPBr molecules that have a positive charge in the pyridinium group of nitrogen atom, N^+ connected to bromide ion, Br^-. Thus, when SB interacts with CPBr compound, Br^- would be substituted by O^- ion of SB [12]. The Br^- ion could be active site for the adsorption of AO7.

The critical micelle concentration (CMC) of CPBr plays an important role in the adsorption of CPBr onto SB. At concentrations below CMC, the cationic surfactant adsorbed onto the SB surfaces in a monolayer or hemimicelle forms. At concentrations above CMC, the CPBr molecules create organic rich layer and eventually form micelles on the SB surfaces which result in the formation of negatively charged surfaces. The positive charge at the external head group of cationic surfactant is balanced by anions to obtain an electrical double layer [12, 17].
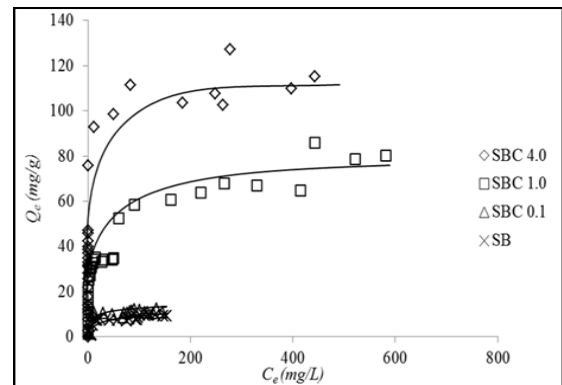

Figure 2 Adsorption isotherm of AO7 by SB and SBC

The schematic diagram on the adsorption of AO7 onto CPBr modified SB is illustrated in Figure 3. The AO7 adsorbed onto CPBr modified SB through anionic exchange with Br^- which was fixed into the interlayer of SB by Van der Waals hydrophobic interaction. As the anionic exchange occurred, the counter ion Br^- desorbed and replaced by AO7. The AO7 was not attached onto raw SB due to the same electrical charge [18].

Similar behavior was obtained for the removal of reactive red 180 by wheat bran [19] and removal of acid orange 7 by unmodified SB [15]. Previous study also reported that the adsorption capacity of treated sawdust increased with an increased in the initial concentrations of dye from 100 to 500 mg/L [20]. As a comparison, SB modified with CPBr showed higher affinity towards AO7 than raw SB. Meanwhile, the presence of CPBr molecules on SB at different concentration resulted in different adsorption capacity on the removal of AO7. The adsorption of AO7 by SBC followed the trend of: SBC0.1<SBC1.0<SBC4.0.

The Langmuir and Freundlich isotherm models were used to predict the adsorption equilibrium of AO7 onto SB and SBC. The Langmuir isotherm is represented by the following equation [21].

$$\frac{C_e}{q_e} = \frac{1}{bQ_o} + \frac{C_e}{Q_o} \qquad (2)$$

Where:
   C_e = concentration of AO7 at equilibrium (mg/L)
   q_e = amount of AO7 adsorbed at equilibrium (mg/L)
   Q_o = maximum adsorption at monolayer coverage (mg/g)

b = Langmuir constant (energy of adsorption) (1/g)

Q_o and b values can be calculated from the slope and intercept y, respectively from the linear plot of C_e/q_e against C_e.

The Freundlich isotherm is represented by the following equation [22]:

$$log_{10}q_e = log_{10}K_f + \frac{1}{n}log_{10}C_e$$

Where:

K_f = adsorption capacity (mg/g)
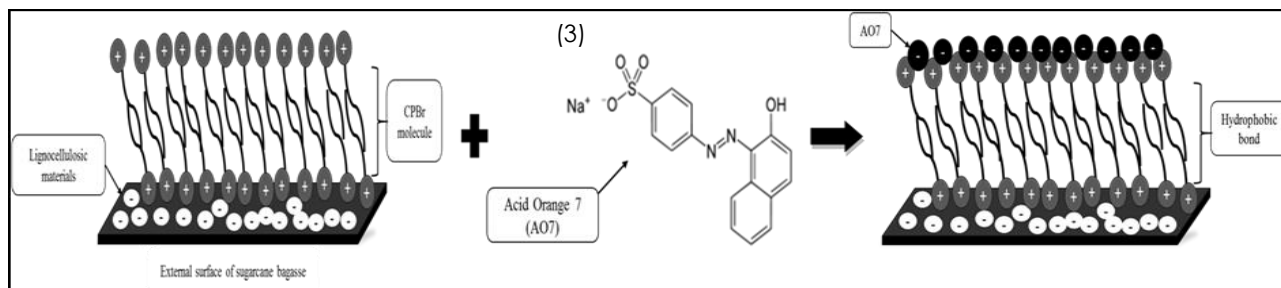
n = intensity of adsorption

(3)

Figure 3 Mechanism of AO7 adsorption onto CPBr modified SB

Table 2 shows the calculated parameters values for both models for all the samples. The applicability of isotherm models was compared based on correlation coefficient (R^2) value. The adsorption of AO7 on SB was better fitted with Freundlich isotherm suggesting multilayer adsorption of AO7 onto heterogeneous SB surfaces. However, Langmuir model provides the best fit for SBC, hence conforming that the monolayer adsorption of AO7 onto SBC with homogenous distribution of active sites. Freundlich adsorption model can also be used for modeling equilibrium data for SBC as their R^2 value is closely to Langmuir adsorption model.

The Q_o reached maximum values of 144.928 mg/g for AO7. It was found that the maximum adsorption capacity of SBC towards AO7 in this study was higher than the value reported in the previous works (Table 3). In addition, the comparison on the adsorption capacity of SBC with other surfactant modified biomasses is listed in Table 4. The maximum adsorption capacity of SBC is slightly lower than hexadecylpyridinium bromide modified peanut husk but relatively higher than other existing surfactant modified biomass.This shows that the modification of SB by CPBr greatly improve its adsorption capacity towards AO7.

Table 2 Langmuir and Freundlich isotherms parameter values for the adsorption of AO7 by SB and SBC

Samples with AO7	Freundlich			Langmuir		
	K_f (mg/g)	n (1/g)	R^2	Q_o(mg/g)	b (1/g)	R^2
SB	3.058	4.314	0.954	9.901	0.162	0.947
SBC 0.1	5.521	6.365	0.913	14.599	0.077	0.912
SBC 1.0	17.446	3.709	0.931	102.041	0.058	0.953
SBC 4.0	49.363	4.847	0.941	144.928	1.078	0.972

Table 3 Comparison of the maximum uptake of various adsorbent for AO7

| Adsorbent	Q_o(mg/g)	References
Cetylpyridinium bromide modified sugarcane bagasse	144.93	Present work
Untreated sugarcane bagasse	28.01	[15]
Spent Brewery grains	30.47	[23]
Azolla rongpong	76.92	[24]
Beech wood sawdust	5.06	[25]
Bottom ash	3.78	[26]

Table 4 Comparison of the maximum adsorption capacity of surfactant modified biomass

Adsorbent	Adsorbate	Maximum adsorption capacity (mg/g)	References
CPBr modified sugarcane bagasse	Acid orange 7	144.9	Present work
HDTMA modified tea waste	Congo red	106.4	[5]
HDTMA modified coconut coir pith	Direct red 12B	76.3	[6]
CPBr modified wheat straw	Light green	70.0	[7]
HDTMA modified wheat straw	Methyl orange	50.4	[8]
CPB modified peanut husk	Light green	146.2	[9]
CPC modified barley straw	Reactive blue 4	31.5	[10]

*HDTMA: Hexadecyltrimethyl ammonium, CPC: Cetylpyridinium chloride, CPBr: cetylpyridiniumbomide

3.3 Effect of Initial pH

The effect of initial solution pH on the adsorption of AO7 onto SB and SBC is presented in Figure 4. The highest AO7 adsorbed on SB and SBC were at pH 2 and 7, respectively. This could be due to the two pK_a values of AO7 (10.61 and 1). AO7 can also exists in three different forms in aqueous solution: H_2L (double protonated, dominant for pH lower than 1), HL^- (mono protonated, dominant in the pH range between 1 and 10.6) and L^{2-} (non-protonated, dominant for pH values greater than 10.6). L^{2-} is the AO7 molecule in the form of $C_{16}H_{11}N_2OSO_3^{2-}$ due to the presence of sulphonic group in the structure of AO7 [27,28]. AO7 speciation is affected by solution pH through the following equilibrium [28]:

$$L^{2-} + H^+ \leftrightarrow HL^- \quad K = 10.6 \tag{4}$$
$$HL^- + H^+ \leftrightarrow H_2L \quad K = 1.00 \tag{5}$$
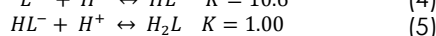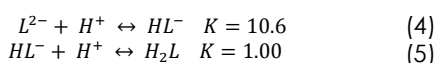
The adsorption of AO7 was the highest at pH 2 for SB and SBC0.1 and the adsorption decreased when the pH increased. It might be due to the dominancy of H_2L and HL^- exists in water and led to the increased of electrostatic attraction of AO7 dye molecules to SB and SBC 0.1. At lower pH, the AO7 molecules are dominant in the form of HL^- and thus require one exchange site for one molecule of AO7 at the respected pH. As H_2L and HL^- coexist at pH 3, this resulted in a partial adsorption of the AO7 (only HL^-) onto the SB surface. This explains the decreased in the adsorption capacity at pH 3 compared to that of at pH 2. However, at high pH (4 to 9), L^{2-} is mostly dominant where two exchange sites for SB and SBC0.1 involved in order for the adsorption to occur, hence resulted in the lower adsorption capacity of SB and SBC 0.1 towards AO7. In addition, the SB surfaces could become negatively charged at pH greater than 4 and the negatively charged surface group of AO7 increased as pH increased. Accordingly, an electrostatic repulsion between the negatively charged dye and the surface group took place and led to a significant decrease in the adsorption capacity of SB [28].

In contrast for SBC1.0 and SBC4.0, the dominancy of AO7 in the aqueous phase is different from AO7 present in SB and SBC0.1. This could be due to the presence of high concentrations of cationic surfactant attached on the surface of SB. For SBC1.0 and SBC4.0, only HL^- is practically present in the solution at pH 7. Meanwhile, H_2L and HL^- coexist with dominancy of HL^- at pH between 3 and 9. At pH between 3 and 9, the increased in positively charged SBC surface as pH increased led to the increased of the electrostatic attraction between the surface positive charges and the negatively charged AO7 molecules (HL^-) and therefore led to the increased in the adsorption capacity of the adsorbent. While at pH 2, only L^{2-} is practically present.

In addition, the present of OH^- in the solution at pH 8 to 9 resulted in the strong competition with the AO7 anions at the exchange sites as more OH^- anion available at high pH. The AO7 dye molecule exists mainly in the anionic form over a wide range of pH, hence proving that the adsorption of AO7 by SBC was due to the anion exchange. In SBC, the reversed charged from negative to positive at the SB surfaces was created by the double layer formation of CPBr. This observation is comparable with the adsorption of SB and SBC 0.1 towards AO7 anions. Due to the distribution of AO7 in water which is in the form of anionic, it is clearly indicated that the SB that has been modified with cationic surfactant are suitable to adsorb AO7 dye molecule in water at suitable pH.
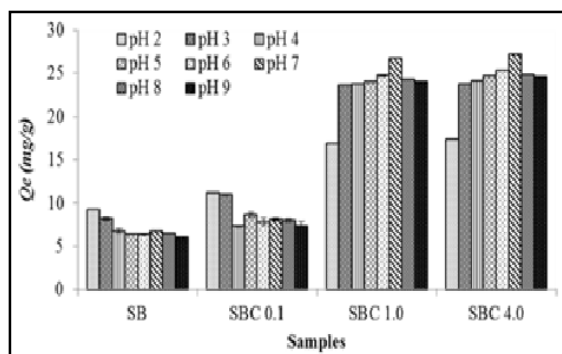
Figure 4 Effect of solution pH on the adsorption of AO7 by SB and SBC

4.0 CONCLUSION

The present study revealed that the CPBr modified SB can be used as suitable adsorbent for the removal of anionic dye from aqueous solution. The modification process did not promote drastic changes in their chemical structure. The adsorption behavior of AO7 on SB and SBC follows Langmuir and Freundlich isotherm model, respectively. The adsorption was found to be higher at pH 2 for SB and pH 7 for SBC. With the availability in abundance and low cost as their advantages, SB modified with cationic surfactant can become a suitable alternative for the treatment of anionic dye from dye polluted wastewater such as textile effluents.

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