

Adsorptive Removal Of Benzene From Aqueous Solution By Surfactant Modified Banana Trunk As Adsorbents

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Abstract. The adsorptive removal of benzene from aqueous solution by four types of surfactant modified banana trunk (BT) adsorbents was investigated through batch adsorption experiments. The surface morphology and functional groups determination were conducted BT adsorbents indicating the significant changes were observed after modifications. The adsorption results indicated that the non-ionic surfactant (i.e. Triton-X 100) modified BT has the highest adsorption capacity (57.52 $\mu\text{mol/g}$) and its adsorption capacity significantly affected by the increase of temperatures, benzene concentrations and contact time.

1.0 Introduction

In recent decades, the phenomena of water pollution have become more severe and frequent problem along with the global development of industrial sectors, especially in developing countries. Benzene represents one of the most common petroleum hydrocarbons that are identified at various contaminated water and wastewater.^[1] It is a volatile, flammable and aromatic hydrocarbon which has been employed as general solvents in many industries. It can enter natural water bodies (rivers and oceans) and even soil from gasoline leakage from underground storage tank, pipelines and transportation due to fault management or accidents.^[2] It is highly toxic and carcinogenic. Due to the low molecular weight, it can be carried easily from industrial areas to residential areas. This may cause extreme danger to human beings when there is long term or acute exposure.

The US environmental protection agency (USEPA) has categorized benzene as a priority pollutant. Furthermore, a regulation has been established where its concentration has to be diminished to the very least quantity in wastewater and water.^[3] Therefore, it is essential to remove its contamination from water and wastewaters. Nowadays, its removal from aqueous solution has been widely studied including volatilization, chemical oxidation, bioremediation, incineration and also adsorption. Among these technologies, adsorption is classified as one of the simplest and efficient operation.^[4] According to recent study, surfactant modified adsorbents such as clays and zeolites are reported to have a promising volatile organic pollutants adsorption performance.^[5,6] In this study, banana trunk was thus selected to be agro-sorbent precursor and was modified with different types of surfactants (i.e. cationic, anionic and non-ionic). The banana trunk was chosen because its contains high percentage of holocellulose where a large number of hydroxyl units present which make it easily to be functionalized.^[7]

2.0 Materials and Methods

2.1 Chemicals

Benzene (99%), isooctane, ethanol, methanol, sodium hydroxide (NaOH pellets), cetyltrimethylammonium bromide (CTAB), sodium dodecyl sulphate (SDS), Pluronic 123 and Triton-X 100 were purchased from Sigma-Aldrich (USA) and Merck (Germany). Freshly prepared double-distilled water was used to prepare solutions used throughout the experiment. Agrowaste biomass of banana trunk used in this study was collected at a nearby residential area located in Taman Universiti, Johor, Malaysia.

2.2 Adsorbents preparation

Banana trunk (BT) was cut into small pieces and dried under sunlight for 3 days. After that, the naturally dried BT was further dried in the oven at 50 °C for another 2 days. The BT was ground and then sieved in order to obtain particles of desired size of 75-150 µm. The BT of desired size was washed by distilled water and ethanol to remove dirt and impurity. The pure BT sample was finally dried in the oven at 50 °C overnight and finally kept in a desiccator for modification. Surface mercerization was conducted onto pure BT to improve the binding sites on the adsorbent surface. A specified amount of the pure BT was immersed into 30% sodium hydroxide (NaOH) solution. The mixture was allowed to stir for 1 hour at room temperature (30±0.5 °C). After that, the reacted BT was filtered and washed by double-distilled water using vacuum filtration. The washed alkaline BT was dried in the oven at 50 °C overnight and finally kept in a desiccator for characterization and further modification. This sample was denoted as M-BT. After surface mercerization by concentrated NaOH solution, four types of surfactants namely *n*-cetyl trimethylammonium bromide (CTAB), sodium dodecyl sulfate (SDS), Pluronic 123 (P123) and Triton-X 100 (TX-100) were used to modify M-BT surface. A desired concentration of surfactant solution was prepared by dissolving an accurate amount respective surfactant with double-distilled water. A certain amount of M-BT (e.g. 500 mg) was immersed into surfactant solutions and was stirred for 24 hours. The reacted samples were then filtered and repeatedly washed with double-distilled water to remove excessive surfactant on the sample surfaces. The sample were then dried in the oven at 50 °C overnight and finally kept in a desiccator. The modified M-BT by *n*-cetyl trimethylammonium bromide (CTAB), sodium dodecyl sulfate (SDS), Pluronic 123 (P123) and Triton-X 100 (TX-100) was denoted as M-CTAB-BT, M-SDS-BT, M-P123-BT, and M-TX100-BT, respectively.

2.3 Adsorbents characterization

The surface morphology of adsorbents was observed by using field emission scanning electron microscope (FESEM) using Hitachi S4800 (Japan). The surface functional groups of adsorbents were analysed by Fourier transform infrared spectroscopy (FTIR) using Perkin Elmer, model Spectrum One (USA) equipped with KBr sampling technique.

2.4 Benzene adsorption

A stock of benzene solution in methanol was prepared using analytical grade benzene (99% purity). A desired concentration benzene solution was then prepared by diluting the stock solution with double-distilled water. Batch benzene adsorption was carried out using a 50 mL glass Erlenmeyer flask with a glass stopper. Solid to liquid ratio of 1:1 was used to conduct batch benzene adsorption. The mixture was allowed to agitate in temperature-controlled shaker at 200 rpm for 24 hours, which is long enough for the mixture to achieved equilibrium conditions. The mixture supernatant was then collected and the residual benzene in it was extracted by isoocane. The concentration of benzene was determined by UV-VIS spectrophotometer (Perkin Elmer, model Lambda 35, USA) at 255 nm. The adsorption capacity of benzene on adsorbate, Q (mg/g) was calculated as:

$$Q \left(\frac{\mu\text{mol}}{\text{g}} \right) = \frac{(C_0 - C)V}{W} \quad (\text{Eq.1})$$

where C_0 is the initial benzene concentration (µmol/L), C is the final benzene concentration (mM), V is the volume of adsorbate solution used for adsorption (L) and W is the mass of adsorbent employed (g).

3.0 Result and Discussion

3.1 Adsorbent characterization

Fig. 1 shows scanning electron microscope (SEM) morphology for BT adsorbents. Based on Fig. 1(a), Raw-BT had hard and smooth surface morphology. However, Fig. 1(b) indicates a rougher and irregular surface. This was attributed by the surface mercerization (NaOH) treatment

onto BT where hard and smooth BT surface had been destroyed. On the other hand, surfactant modified BT displayed more homogeneous and smoother BT surface morphology in comparison to M-BT according to Figs. 1(c), 1(d), 1(e) and 1(f). Fig. 2 displays the FTIR spectra of (a) Raw-BT, (b) M-CTAB-BT, (c) M-SDS-BT, (d) M-P123-BT, and (e) M-TX100-BT. According to Fig. 2(a), obvious peaks can be observed at approximately 3400-3300, 2950-2800, 1600, 1300, 1030 cm^{-1} for Raw-BT. After modification with various surfactants, peaks at 1318.92 cm^{-1} (i.e. acyl C-O), and 77.46 cm^{-1} (i.e. aromatic C-H) were demolished. They were replaced by a sharper peak at approximately 2900 cm^{-1} (i.e. alkane C-H stretch) which represents the surfactant C-H chain. Furthermore, Fig. 2(b) shows a peak at approximately 1385 cm^{-1} which represented N-O stretch for nitro group. On the other hand, Fig. 2(c) displays an unobvious peak at $\sim 1050 \text{ cm}^{-1}$ which indicates the S=O stretch of the sulfoxide group.

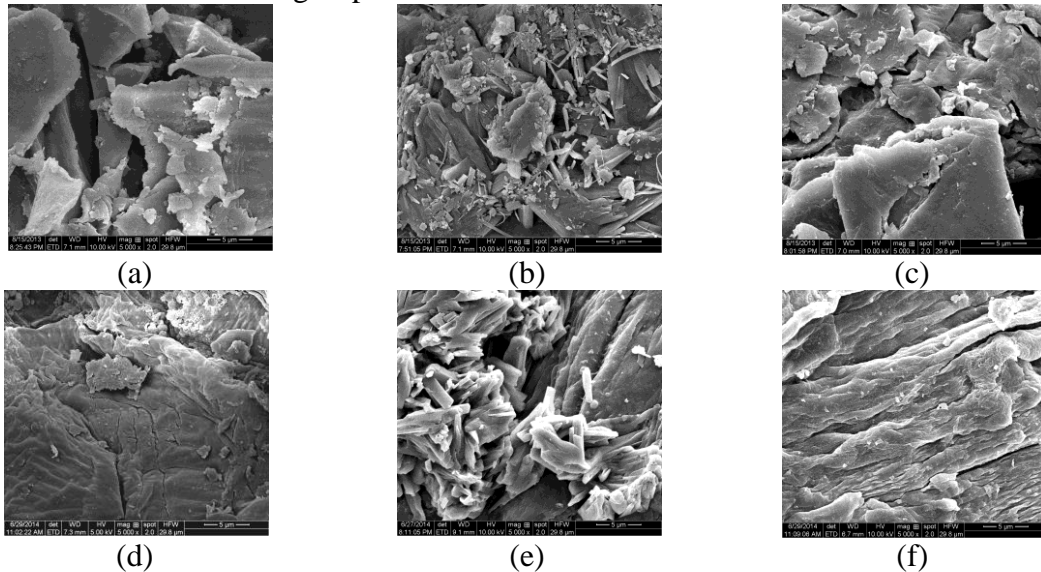


Fig. 1. SEM images of BT adsorbents: (a) Raw-BT; (b) M-BT; (c) M-CTAB-BT; (d) M-SDS-BT; (e) M-P123-BT; and (f) M-TX100-BT.

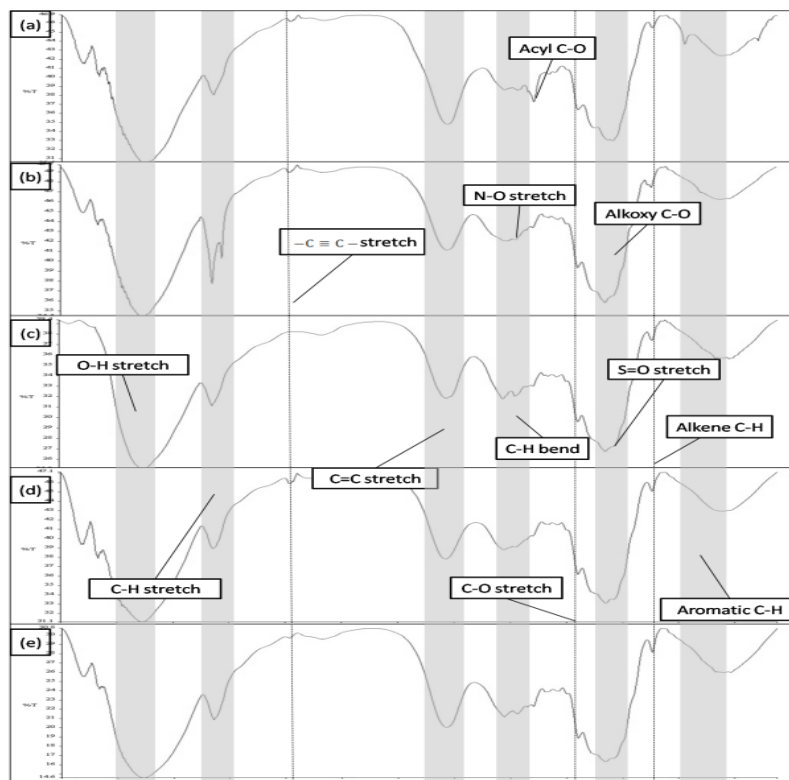


Fig. 2. FTIR spectra of (a) Raw-BT, (b) M-CTAB-BT, (c) M-SDS-BT, (d) M-P123-BT, and (e) M-TX100-BT.

3.2 Effect of adsorbent types

Fig. 3 presents the comparison of benzene adsorption capacity, Q_e ($\mu\text{mol/g}$) onto 4 surfactant modified BT adsorbents. Generally, all the BT adsorbents managed to achieve Q_e more than 30 $\mu\text{mol/g}$. However, M-TX100-BT had obviously achieved the highest Q_e in comparison with the other three BT adsorbents. Thus, the detail study on the effects of benzene initial concentration and contact time were further conducted onto M-TX100-BT.

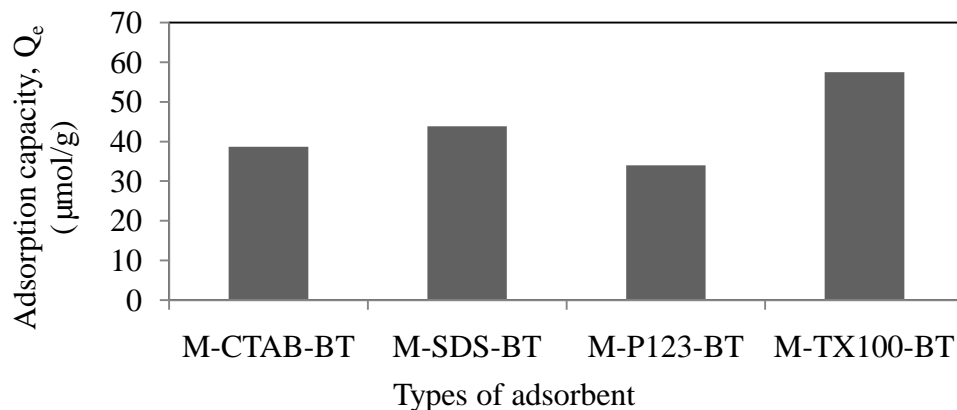


Fig.3. Benzene adsorption capacity, Q_e ($\mu\text{mol/g}$) onto four types of surfactant modified BT. Experimental conditions: contact time = 24 hours; solid to liquid ratio: 1/1; pH = 7; temperature = 30 ± 0.5 °C).

3.3 Effect of contact time

Fig. 5 shows the effect of contact time toward benzene adsorption onto M-TX100-BT. According to Fig. 5, benzene molecules could be adsorbed rapidly at the first 240 minutes. In addition, benzene adsorption rate, Q_t increased gradually in between the time intervals of 240 to 720 minutes. Eventually, Q_e had achieved equilibrium after 720 minutes. The rapid Q_t at the initial moment can be attributed by the availability of large vacant adsorption sites of the M-TX100-BT. Furthermore, the strong electrostatic interaction forces between M-TX100-BT active sites and benzene molecules could be another reason for the fast initial adsorption rate observed. In addition, the increase in temperature led to higher adsorption rate and capacity which may be due to the favorable kinetics and thermodynamics of the adsorption process, respectively.

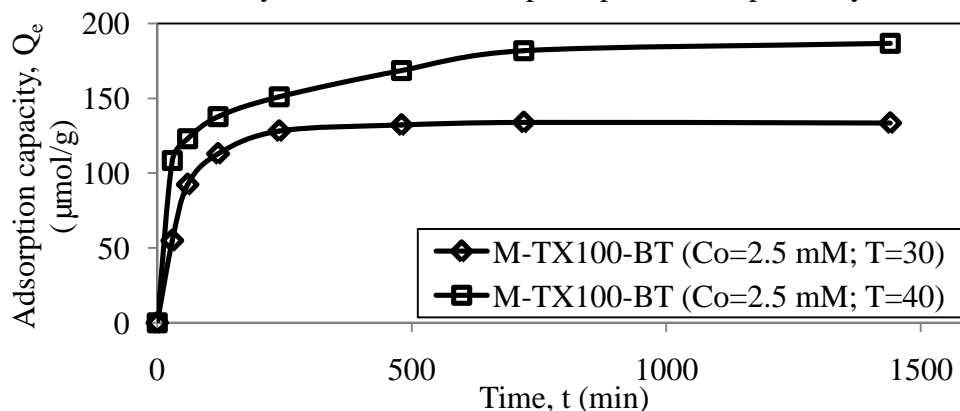


Fig. 5. Effect of contact time on benzene adsorption by M-TX100-BT. Experimental conditions: initial benzene concentration: 2mM; pH = 7; and temperature = 30 ± 0.5 °C.

3.4 Effect of initial benzene concentration

The effect of initial concentration of benzene solution toward adsorption performance onto M-TX100-BT was studied at six different concentrations (i.e. 0.5, 1.0, 2.0, 3.0, 5.0, and 10.0 mM). Fig. 4 presents the relationship between benzene initial concentration, C_o and benzene adsorption capacity, Q_e . It could be observed obviously from Fig. 4 benzene adsorption capacity, Q_e increased when the initial concentration of benzene solution increased gradually from 0.5 to 5.0 mM. This is

due to the increase of benzene molecules as the benzene concentration increased. Hence, the Q_e was also increased and achieved the adsorption equilibrium when the initial benzene concentration of between 5.0 and 10.0 mM. Beyond this concentration, the Q_e remains constant even though the benzene concentration increased. This is because of the active sites on M-TX100-BT surface were fully occupied and the benzene molecules could no longer be adsorbed onto M-TX100-BT. It could also be clearly observed from Fig. 4 that the Q_e was also influenced by solid to liquid ratio (S/L). When S/L decreased to 0.5, the Q_e was relatively $\pm 20\%$ higher. This was due to the fact that higher availability of the benzene molecules that could be adsorbed onto per gram M-TX100-BT as adsorbent dosage decreased.

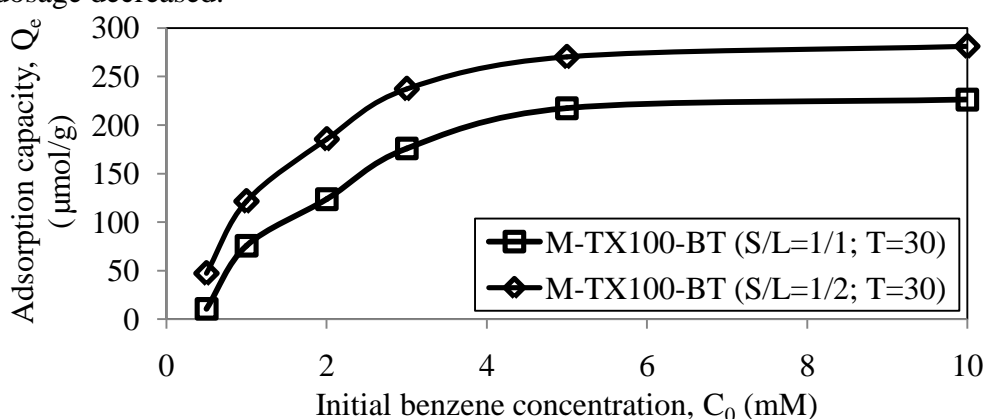


Fig. 4. Effect of adsorbate initial concentration on benzene adsorption by M-TX100-BT. Experimental conditions: contact time = 24 hours; pH = 7; and temperature = 30 ± 0.5 °C.

4.0 Conclusions

Four types of surfactant modification were conducted on BT adsorbents and the results show that the Triton X-100 modified BT (i.e. M-TX100-BT) had the highest benzene adsorption capacity of 57.52 ± 7.3 $\mu\text{mol/g}$. Adsorption parameters studies indicated that and the adsorption was also affected by adsorbent dosages, benzene concentrations, and contact time in which the equilibrium time was obtained of 720 minutes. These results indicate that the low-cost and abundant availability of agrowastes such as banana trunk (BT) could be considered of the possible potential adsorbent precursors and thus the adsorption is an effective alternative process for removal of benzene from aqueous solution.

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