Jurnal
Teknologi

Full Paper

THE REMOVAL OF METHYLENE BLUE AND REMAZOL BRILLIANT BLUE R DYES BY USING ORANGE PEEL AND SPENT TEA LEAVES

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Article history
Received
24 April 2015
Received in revised form
4 May 2015
Accepted
9 May 2015

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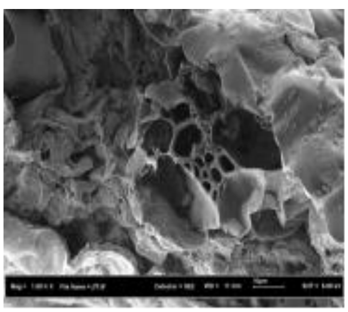
Graphical abstract



Abstract

This study explored the low-cost adsorbent of orange peel and spent tea leave for Methylene Blue (MB) and Remazol Brilliant Blue R (RBBR) dyes removal from aqueous solutions. The removal rate and adsorption capacity on the adsorption of dyes were investigated using the batch adsorption study. The present study indicates that the MB was easier to remove by both orange peel and spent tea leave compared to RBBR with percentage removal of 95.72 % and 99.02 % respectively. The effects of morphology, functional groups, and surface area of adsorbents were investigated by using FESEM, FTIR, and BET. The result proved that orange peel and spent tea leave were promising material as an alternative adsorbent for the removal of MB from aqueous solution.

Keywords: Adsorption, methylene blue, orange peel, remazol brilliant blue r, spent tea leave

Abstrak

Kajian ini menggunakan adsorben kos rendah dari kulit limau dan serbuk teh yang telah digunakan untuk penyingkiran dai Methylene Blue (MB) dan Remazol Brilliant Blue R (RBBR) daripada larutan akueus. Kadar penyingkiran dan kapasiti penjerapan pewarna telah dikaji menggunakan cara 'batch method study'. Kajian ini menunjukkan bahawa MB adalah lebih mudah untuk disingkirkan oleh kedua-dua jenis adsorben kulit limau dan sisa serbuk teh berbanding penyingkiran RBBR di mana masing-masing dengan peratusan penyingkiran adalah 95.72 % dan 99.02 %. Kesan morfologi, kumpulan berfungsi dan kawasan permukaan adsorben dikaji dengan menggunakan FESEM, FTIR dan BET. Hasil kajian membuktikan bahawa kulit limau dan sisa serbuk the adalah bagus sebagai bahan penjerap alternatif untuk penyingkiran MB daripada larutan akueus.

Kata kunci: Penjerapan, methylene biru, kulit oren, remazol brilliant biru R, sisa serbuk teh

1.0 INTRODUCTION

Since dyeing technology has been invented, many color effluents have been produced. Leather, paper and textiles are the various synthetic dyestuff industries that are form after the finding of dying technology [1]. Other industries that are also forms are the tannery and paint industry [2]. The creation of dyes thus leads too many other findings and improvement in the industry involved.

Nowadays, this dyeing process usually uses both organic and inorganic synthetic dye which is present in variety of colors [3]. These dyes are considered as an important aspect as their technology of been produced are developing and are a demand to a lot of different types of industry.

MB is a cationic dye or may also be called basic dyes. These dyes carry positive charged in their molecule. Basic dyes have brilliance intensity of colours and are able to dissolve in water [4]. When dissolve in water, it forms a blue solution but actually at room temperature it appears as solid, odourless, dark green powder. This shows that the dye is soluble in water. MB is been widely used as a model dye to remove basic dye using adsorption studies. If it is recklessly use, vomiting, hard breathing, mental disorder and sweating may occur [5].

MB dye may also causes permanent injury to human and animals eyes. If it is ingested through the mouth, it will produce a burning sensation thus causing painful micturition and methemoglobinemia [6]. This is why this dye should be removed from the wastewater. However, despite its disadvantages, methylene blue is one of the most dyes that is frequently used in the industry [7].

This dye is one of the synthetic dyes with the structure of azo-. It is also an anthraquinone dye [8]. Remazol Brilliant Blue R has the chemical formula of $C_{22}H_{16}N_2Na_2O_{11}S_3$ and the molecular weight of 626.54 g mol^{-1} [9]. Since it is an anthraquinone dye, it is then an anionic dye which has reactive characteristics and is also soluble in water.

Since it is a reactive dye, it may cause unpleasant effect if being released into the environment. The first reason is because of they have low degree of fixation due to the hydrolysis of reactive group in water phase. As an acid dyes, it is also hydrophilic which means they are harmful to the human as they are organic sulphonic acid [4].

They are many method can be done to help in the removal of dyes in wastewater. The method includes physical, chemical and biological. However, each of these methods has its own benefits and drawbacks. As an example, nowadays the methods to remove dyes from wastewater are very expensive and cannot be used to treat wastewater in a wide range. The method such as activated carbon are expensive, Fenton's reagent may produce concentrated sludge and membrane filtration method may not have the ability to treat large volumes of effluent and later may cause clogging [10].

Adsorption is the most common and widely used process in removing dye from wastewaters. Usually, adsorption method uses activated carbon to remove the pollutants from wastewater [10]. However, activated carbon has a high production cost thus the production of it is restricted [11]. This thus leads to researches to find replacement for activated carbon.

Nowadays, adsorption process is considered as low cost, easy to be access and is effective in removing dye because the dye compounds attach themselves to the surface of adsorbents [12]. It is also known in removing either organic or non-organic pollutants in wastewaters [7].

The agricultural sector is one of the biggest and growing sectors in Malaysia, which gives high contribution to the economy of the country. It produces much type of agricultural by-products such as palm, coconut, banana and bamboo [13]. These natural materials are abundant and the waste product from industrial or agricultural process may be considered as inexpensive and easy to be obtained [10]. Agricultural waste has its own characteristic which allows them to act as adsorbents of dye. Other than that, it can also be said as a low-cost adsorbent, as they are abundant in nature and an agricultural waste which requires little or no processing [14].

Orange peels are considered as an agricultural waste. This by-product is also present in the agricultural industries. There are usually residues of orange-juice and soft drink industries. Oranges are largely produced in Brazil and is an important agronomic importance. Based on journals by other researchers, this orange peel have been proven to be able to remove dyes such as methyl orange, methyl violet, Congo red and amido black 10B. Orange peel is said to have amorphous structure and it is because it is an organic materials [8].

Its ability to adsorb dye is mainly because of it is consists of cellulose, pectine, hemicellulose, lignin, low molecular weight hydrocarbons, and hydroxyl group such as carboxyl and hydroxyl. These characteristics help in removing metal ions from aqueous solutions [15].

Spent tea leaves had been considered as an effective adsorbent as it had succeed in removing pollutant in water such as arsenic, and heavy metal ions such as zinc and lead [14]. So its effectiveness in removing methylene blue will be identified. It also is known for having a high adsorptive capacity [16].

2.0 EXPERIMENTAL

2.1 Preparation of Adsorbent

Orange peel and spent tea leave were collected from marketplace and restaurant in Johor Bahru. The sample was washed with tap water and repeated with distilled water to remove any impurities adhering to the surface and then the samples were cut into pieces and oven-dried at 105 °C for overnight. The orange peels were cut into smaller pieces while the spent tea leaves were not since it has already in small pieces. The purpose of washing these materials was to get rid of any stain or dust particles which may be present at the surface of the materials. The spent tea leaves were left for 24 hours in the oven while the orange peels take about three days to be completely dried. The dried samples were ground and sieved through 30-mesh to get a consistent size of adsorbent powder. The fine powders of these agricultural wastes were then preserved in plastic bags for use as adsorbents.

2.2 Preparation of Methylene Blue and Remazol Brilliant Blue R Solution

The stock solution of Methylene Blue and Remazol Briliant Blue R were prepared by dissolve 1.0 g of dye in 1000 ml of distilled water. Distilled water were used to dilute the stock solution of Methylene Blue and Remazol Brilliant Blue R depends to the desired of concentrations.

2.3 Batch Adsorption Studies

The Methylene Blue and Remazol Briliant Blue R adsorption onto orange peel and spent tea leaves were determined by using batch adsorption study for 24 h. The first step was to make a stock solution of the dye that was going to be used. The stock solution must be in the concentration of 1000 mg/L. These solutions were made by mixing 500 ml of distilled water and 0.5 g of dye. The experiments required the use of 5g adsorbents were weighed and put them in conical flasks. After that, the conical flasks containing the adsorbents were filled up with 50 ml of the 1000 mg/L dye solution prepared earlier. The solutions were left on orbital shaker with agitation 120 revolutions per minute (rpm) for 24-hours. After 24-hour, the solutions were then filtrated by using Whatman no. 1 filter paper and determined the BPA concentration by using a UV-Vis spectrophotometer (NANOCOLOR® VIS, Macherey-Nagel, Germany) at 664 nm for Methylene Blue and 593 nm for Remazol Brilliant Blue R.

2.4 Analysis the Adsorption Data

The adsorption data of the orange peel and spent tea leaves obtained from UV-Visible spectrophotometer were calculated to determine the Methylene Blue and Remazol Briliant Blue R removal rate (%) and adsorption capacity (mg/g). The formulas of calculation are as follow:

Removal rate (%) = $$\frac{C_0 - C_x}{C_0} \times 100$$

Adsorption Capacity = $$A = \frac{(C_0 - C_x)V}{M}$$

Where A (mg/g) is the dye adsorption capacity, C_0 (mg/L) and C_x (mg/L) is respectively the initial and equilibrium dye concentrations in the solution, V (L) is the solution volume, and M (g) is the mass of adsorbent.

2.5 Characterization of the Adsorbent Materials

Surface texture and morphology of orange peel and spent tea leaves were analyzed by the field emission scanning electron microscopy (FESEM JEOL 6335F-SEM, Japan) and elementary analyses were performed simultaneously using an EDX spectrometer. The Brunauer–Emmett–Teller (BET) surface areas and monolayer pore volumes of the adsorbents were determined by using provided software, surface analyzer (Quantachrome Instrument, USA). FTIR (Spectrum one, Perkin Elmer, USA) was used to analyzed the functional groups on the surface of sugarcane bagasse and spent tea leaves with the spectral range varied from 4000 to 400 cm^{-1}.

3.0 RESULTS AND DISCUSSION

3.1 Adsorption of Methylene Blue onto Orange Peel and Spent Tea Leave

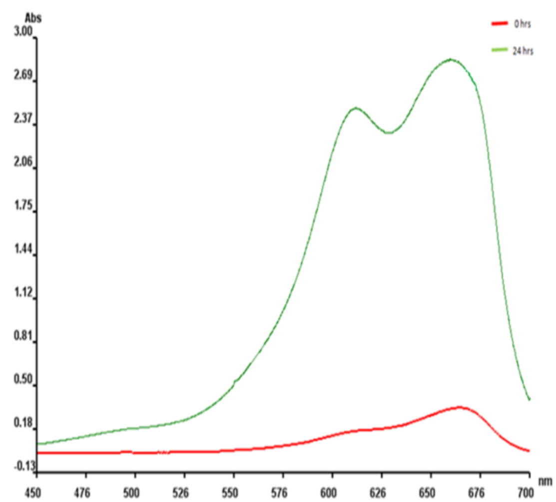


Figure 3.1 Adsorption of Methylene Blue onto orange peel for 24 hours

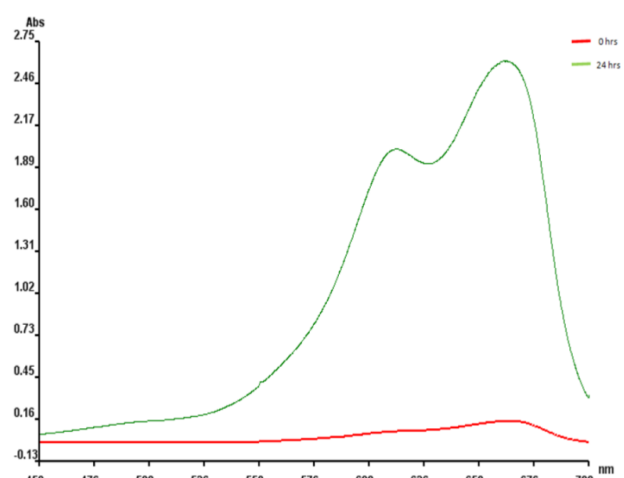


Figure 3.2 Adsorption of Methylene Blue onto spent tea leave for 24 hours

Table 3.1 Removal rate and adsorption capacity of Methylene Blue onto orange peel and spent tea leave for 24 hours

	Orange Peel	Spent Tea Leaves
Percentage of Removal (%)	95.72	99.02

The removal of Methylene Blue illustrated in Figure 3.1 and 3.2 shows that the both types of adsorbents give different percentages. For the removal using orange peel, the percentage is 95.72% while for the spent tea leaves; the percent of removal is 99.02% (Table 3.1). Both of these adsorbents show that they are able to remove methylene blue effectively. These may be due to the characteristic of the surface and the chemical composition of the adsorbents and dye characteristics.

3.2 Adsorption of Remazol Brilliant Blue R onto Orange Peel and Spent Tea Leave

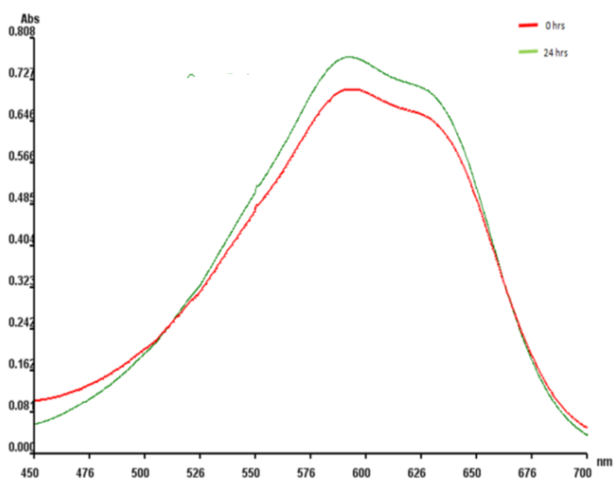


Figure 3.3 Adsorption of Remazol Brilliant Blue R onto orange peel for 24 hours

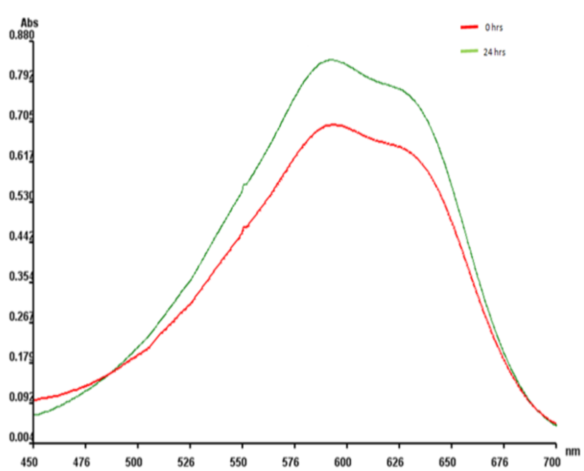


Figure 3.4 Adsorption of Remazol Brilliant Blue R onto spent tea leave for 24 hours

Table 3.2 Removal rate and adsorption capacity of Remazol Brilliant Blue R onto orange peel and spent tea leave for 24 hours

	Orange Peel	Spent Tea Leaves
Percentage of Removal (%)	14.92	11.39

Figure 3.3 and 3.4 show the adsorption of Remazol Brilliant Blue R onto orange peel and spent tea leave. Based on the percentage of removal of Remazol Brilliant Blue R, it can be seen that for both types of adsorbents are low in the percentage removal. For the removal using orange peel, the percentage is 14.92% while for the spent tea leaves; the percent of removal is 11.39% (Table 3.2).

These may be due to the characteristic of the surface and the chemical composition of the adsorbents and dye characteristics. The percentage of removal also depends on the adsorption capacity of the adsorbents.

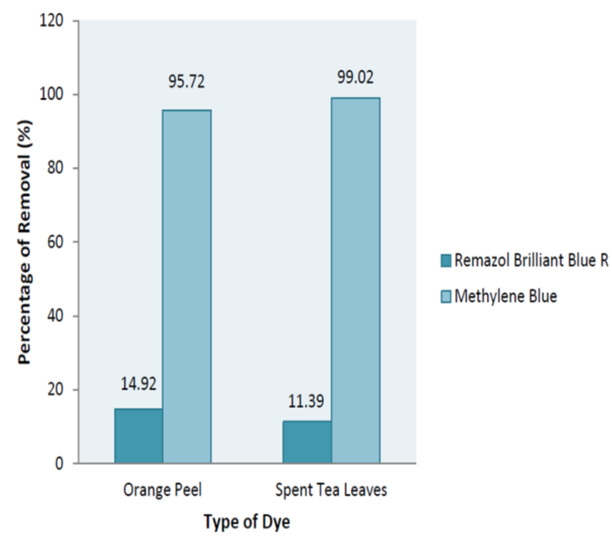


Figure 3.5 Graph of percentage removal of dyes using adsorbents

Figure 3.5 shows the relationship between the percentages of dyes removal by using orange peel and spent tea leaves as adsorbent. It can be seen that both adsorbents shows a positive result in removal of dyes. However both spent tea leaves and orange peel shows highest percentage in removal of Methylene Blue compared to Remazol Brilliant Blue R. The bar chart also shows that methylene blue is much easier to be removed compared to Remazol Brilliant Blue R.

3.3 FESEM Images

Figure 3.6 shows the FESEM images of spent tea leaves. As observed, the surface of the spent tea leaves contain various sizes of pores. The spent tea leave has the structure appears like it has some small cavities on the surface. These pores are clearly visible and are closed to each other. It also shows heterogeneous surface which means that the surfaces are hilly and have valleys like structure. These are perfect for adsorption sites for pollutant. The chance for the adsorbents to trap dye is higher if the surface area of the adsorbent has high heterogenous structure [17]. The lack of porosity indicated a low surface area of the adsorbent [18]. To support the expected relationship between the open area and porosity, the open areas of the spent tea leave were determined by BET (1.76 m^2/g).

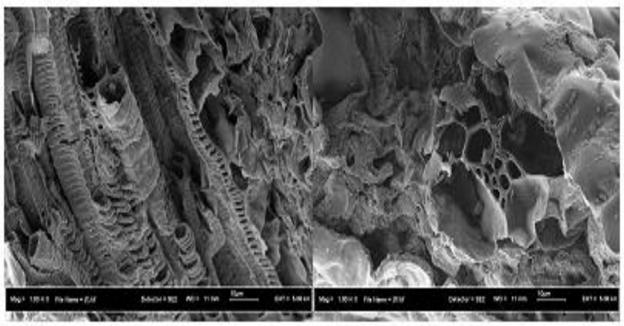


Figure 3.6 Spent tea leaves

Figure 3.7 shows the FESEM images of orange peel. It can be seen that the surface of the orange peel is rough and irregular in shape. The porous surface also indicated that there is an adequate morphology for dye adsorption. The image also indicated that there are present of pores which give the possibility of dyes to be trapped into them [15]. Other than that, heterogenous structures are also observed on the orange peel surface [8]. For raw orange peel, an unsmooth surface with structure of irregular in shape was found in the sample prepared. As shown in the FESEM image of higher magnification the orange peel has a non-porous configuration, in well agreement with previous report [19]. For BET test, durian peel gave the surface area of 1.41 m^2/g.

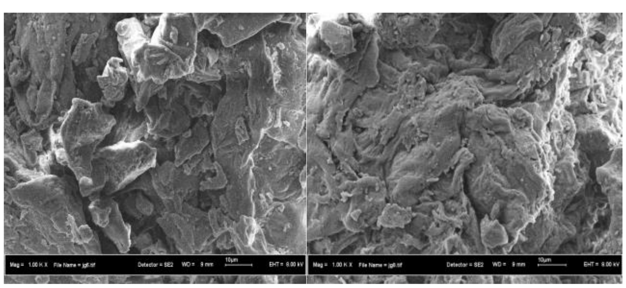


Figure 3.7 Orange Peels

3.4 FTIR Sprectrum

The FTIR is an important method to prepare and identify the functional group that causes adsorption to occur. The infrared spectrum showed a large number of peaks. Each adsorbent may have varies functional group hence causes their adsorption capacity to be different. The functional group may either help or prevent the adsorption process. Figure 3.8 shows the FTIR of orange peels containing many absorption peaks. The exhibition of the peak at the 3390.29cm^{-1} is caused by functional group of alcohols and phenols which have O-H stretch and H-bonded. Peak 2928.76 cm^{-1} and 2133.23 cm^{-1} shows present of alkanes with C-H stretch and alkynes with –C=C- stretch. At 1738.10 cm^{-1} shows the strong functional group of carbonyls. At 1637.91 cm^{-1} and 1519.47 cm^{-1} shows functional groups of 1o anines and aromatics group respectively. Lastly, the peak at 1052.70 cm^{-1} show the presents of C-N stretch of the aliphatic amines. These functional groups help to bind and trap the dye molecules.

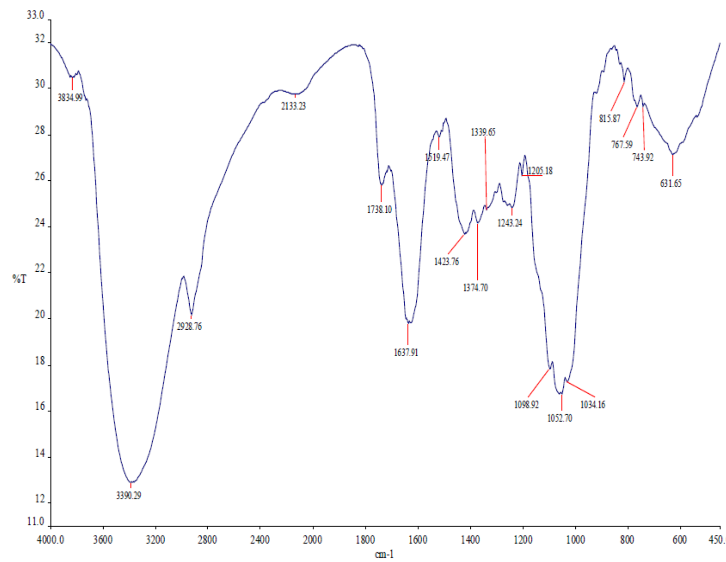


Figure 3.8 FTIR of orange peels

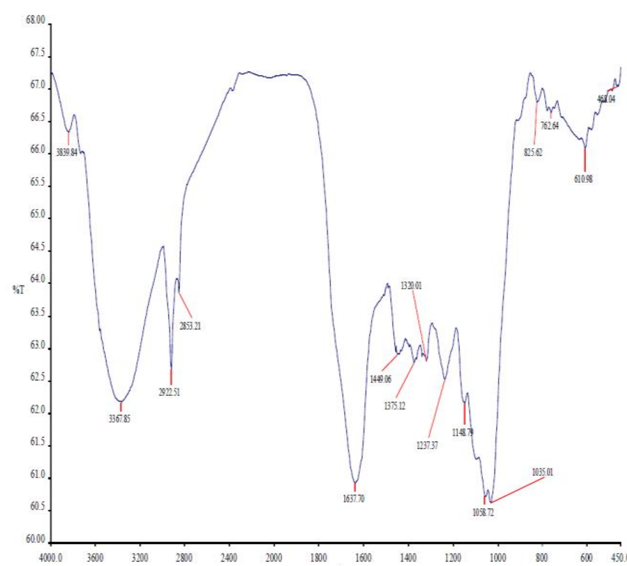


Figure 3.9 FTIR of spent tea leaves

The FTIR in Figure 3.9 shows the infrared spectrum of spent tea leaves. At frequency 3367.85cm^{-1} shows strong and broad properties of alcohols and phenols functional group with O-H stretch and H-bonded. At 2922.51cm-1 and 2853cm^{-1}, both peaks shows alkanes group. Strong carbonyl group is also present at the peak of 1637.7cm^{-1}. At 1449.06cm^{-1} and 1375.12cm^{-1} both shows aromatics functional group and alkanes respectively. Medium aliphatic amines are shown at peak 1237.37 cm^{-1}. Lastly at peak 1320.01 cm^{-1} shows a strong composition of alcohols, carboxylic acids, esters and ethers.

The functional group ether has high electrostatic force of attraction which exists between the charged surface of adsorbents and dye hence enhancing the dye uptake. Both adsorbents show the combination of the functional group carbonyl and hydroxyl group shows presents of carboxyl group. Hydroxyl are alcohols group and have high affinity towards pollutants and also heavy metals. Other than that, both adsorbents shows presence of carbonyl groups. These carbonyl groups can form hydrogen bonds with the dye thus adsorbing them

4.0 CONCLUSION

This research was investigated the agricultural waste as potential adsorbents for BPA removal from aqueous solution. Durian peel had achieved the highest removal of BPA at time 24th hours. Selection of an appropriate adsorbent is one of the key issues regarding the maximum removal of a given type of pollutant, depending upon the characteristic of the adsorbent and adsorbate. The outcomes of this study suggested that the durian peel as a potential adsorbent for BPA removal in aqueous solution. Adsorbent durian peels are economical and easily available resources. Thus, durian peel could be used as low-cost adsorbents which leading to environmental benefits such as reduce the waste material and monetary values of water and effluent handling.

Acknowledgement

The authors would like to acknowledge the Ministry of Education Malaysia for providing LRGS Grant on Water Security entitled Protection of Drinking Water: Source Abstraction and Treatment (203/PKT/6720006) and Universiti Teknologi Malaysia (R.J130000.7809.4L810)) as financial support of this project. This support is greatly appreciated.

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