Decolourization of Textile Effluent by Adsorption on NaOH Treated Textile Venus Clam (Paphia Textile)

M. R. S. Omar and S. S. A. S. Hassan,

Faculty of Chemical Engineering, Universiti Teknologi Mara

***Abstract*—In this work the feasibility of employing Textile Venus Clam (TVC) to remove Basic Red 46 (BR46), an azo dye from its aqueous solutions was investigated. The parameters that influence the adsorption process such as adsorbent dosage, initial dye concentration and contact time were studied in batch experiments. The adsorption of Basic Red 46 was took place at neutral pH of 7 and room temperature. Furthermore, the adsorbent was characterized by using Brunaeur-Emmett Teller (BET) to study the surface area of the adsorbent. The TVC was washed using deionized water and treated with NaOH solution. Then the adsorbent was dried for 24 hours at 100˚C. The adsorbent then crushed and calcined at 400, 500 and 600˚C for 3 hours and stored. For the effect of adsorbent dosage, a range of dosage from 0.3-0.9g of adsorbent in 100mL of 20 ppm of BR46 solution. The process was carried out for 60 minutes in an orbital shaker at 200 rpm. For the effect of initial dye concentration, the optimal dosage was used and a range of initial concentration from 20-60 ppm of BR46 solution. The solution was shake for the same time and speed. The samples were filtered by using filter paper and the dye concentration was measured using UV-Vis Spectrophotometer. The BET analysis showed that the adsorbent has BET surface area of 2.4758 m^2/g and pore volume of 0.003754 cm^3/g. The highest adsorption of BR46 was at 0.9g adsorbent dosage which is 87.48% removal. The highest removal for initial concentration of 20 ppm concentration of dye was 87.6% removal. Thus, it was concluded that TVC can be used effectively as an adsorbent fort the removal of BR46 from aqueous solution.**

Keywords*— *Adsorption, Textile Venus Clam, Basic Red 46, Effluent.

1. INTRODUCTION

The world nowadays is having a big environmental problem such as climate change, pollutions, land degradation, nuclear issues and others. These problems will not only affect our life style but also the future generations. Like colouring agents or dye, they had been polluting the environment because of the increasing demand in industries and had become a serious concern(Rafatullah, Sulaiman, Hashim, & Ahmad, 2010). There are many types of dye that are used by the industries as their colouring agents (Anastopoulos & Kyzas, 2014). Dyes like Methyl Orange, Methyl Red, Malachite Green and Methylene Blue are major pollutants of fresh water reserves because of their toxic and carcinogenic properties (Mane & Babu, 2011; Mane & Vijay Babu, 2013; Yagub, Sen, Afroze, & Ang, 2014).

The discharge of dyes into the receiving water causes a big concern from the environmental point of view. Several industries that are polluting the fresh water with dyes such as textile industry, batik industry, paint industry and printing ink production (Rashidi, Sulaiman, & Hashim, 2012; Wang, Zhu, Jiang, Hu, & Shen, 2016). Damage had done to the environment because of the failure in treating the wastewater whether it is from the industrial and domestic. It is also affecting the human health and cause problems such as organ damage, reduced growth and development, nervous system failure oxidative stress (Dahri, Kooh, & Lim, 2015; Subramaniam & Kumar Ponnusamy, 2015). That is why it is very important to remove or reduce the dyes before it is discharge into the environment.

There are a few technologies that had been developed for removing dye. For regular treatment processes including precipitation, ion exchange, membrane filtration, electroplating and adsorption (Forgacs, Cserháti, & Oros, 2004; Gupta & Suhas, 2009). Many previous researches were already making experiment on removing dye using bio-waste as adsorbent (Ahmaruzzaman, 2008; Bhatnagar, Sillanpää, & Witek-Krowiak, 2015). It had found that treated adsorbent is more effective to adsorb the dye than raw adsorbent as it increases the efficiency of the adsorption. There were several different types of modified bio-waste as absorbent that are used to remove dye such as sea shell, eggshell, banana stream and corncob (Ahmad, Ahmad Puad, & Bello, 2014; Crini, 2006; Sharma, Kaur, Sharma, & Sahore, 2011).

Textile Venus clam can be found abundantly in Malaysia. It is readily available, high efficient and inexpensive to become adsorbents. By utilizing the TVC as adsorbent of dyes, the wastewater which containing dyes can be minimised without using any chemical treatments. As a bio-waste, this could be a great opportunity to produce low cost adsorbents while reducing the pollution (Kazemi, Biparva, & Ashtiani, 2016; Tan, Hameed, & Ahmad, 2007). Basic Red 46 (BR46) is widely used in textile industry as colouring dye. BR46 is a man-made azo dye and large quantity of this dye had been discharged into the environment (Deniz & Karaman, 2011; Deniz & Saygideger, 2011). Due to its toxicity and carcinogenicity, it is required for the BR46 to be treated before discharged into the environment.

2. METHODOLOGY

2.1 Materials

The adsorbent that has been chosen in this research is Textile Venus Clam (TVC). The TVCs are collected from several restaurants and beaches nearby in Kuala Perlis. There are many types of clam such as soft clam, hard clam and many more but for this experiment we are using specifically TVC because it is abundantly available and easy to collect.

The chemicals that will be used in the experiment are sodium hydroxide and Basic Red 46. Sodium hydroxide (NaOH) is a white solid, usually come in pellets or granular form. It is strongly basic and highly soluble in water but insoluble in ether. In this experiment, NaOH is added with water to become NaOH solution and it is used to treat the TVC. BR46 is a mono azo dye used in materials such as wool and silk. It is a dark red coloured powder and has a molecular formula of $C_{18}H_{21}N_6Br$ and molecular weight of 400.9 g/mol.

2.2 Methods

2.2.1Preparation of TVC

The collected TVC will be washed several times using deionized water. The washing process of TVC is to remove all the sand, dirt, and contaminants that is present at the surface of TVC. Half of the TVC will be separated for the untreated TVC adsorbent. Next, the TVC will be treated for 4 hours by using 0.05 M of NaOH solution. The purpose of this process is to increase the surface reaction site of the TVC. The treated and untreated TVC will be dried for 24 hours in an oven at 100 ˚C to extract the water content. After that, the TVC will be crushed using a mortar and pastel to obtain powdered form and calcined at 400, 500 and 600 ˚C for 3 hours. Lastly, the adsorbents will be stored in air-tight container.

2.2.2Characterization of TVC

The characterization of the material used will be made before the experiment is conducted. The equipment that will be used in this study is Brunaeur-Emmett Teller (BET). The purpose of the Brunaeur-Emmett Teller (BET) is used to study the specific surface area of the sample provided including the pore size distribution [bet 1]. It is also useful in evaluation of the material performance and consistency.

2.2.3Experimental procedure

An amount of BR46 dye powder will be dissolved in 1 L of distilled water to prepare 1000 ppm concentration stock solution. A standard solution will be prepared from the stock solution to be used for calibration curve. The calibration curve will be prepared to calculate the amount of dye adsorbed by the TVC. Next, the adsorption studies will be carried out to determine the effect of adsorbent dosage, and the effect of initial dye concentration and contact time. For the effect of adsorbent dosage, a range of dosage amount from 0.3, 0.6 and 0.9 g of TVC powder in 100 mL BR46 solution. The initial concentration of BR46 will be 20 ppm and the process will be carried out for 60 minutes and will be shake on an orbital shaker at 200 rpm. For the effect of initial dye concentration and contact time, the optimal dosage will be used in a range of initial dye concentration 20, 40 and 60 ppm. The solution will be shake for 60 minutes at 200 rpm. The samples are filtered by using filter paper before residual dye concentration is measured by using UV/Vis Spectrophotometer.

3. RESULTS AND DISCUSSION

3.1 Brunaeur-Emmett Teller (BET)

Table 1 shows the BET analysis of untreated TVC samples. The surface area of untreated TVC increase more than 2 times when calcined at 400℃, the pore volume increase 61% and pore size adsorption decrease 103%. At 500℃, the surface area, pore volume and pore size adsorption decrease 1%, 47% and 46%. Lastly, the calcined TVC at 600℃ showed no difference compared to the untreated uncalcined TVC. The surface area, pore volume and pore size adsorption data obtained for the TVC samples showed that the sample can be used for adsorption of BR46 dye at temperature below 400℃. The different result obtained for calcined TVC at 500 and 600℃ may be caused by the damaged TVC due to high and unsuitable temperature of calcination (Asikin-Mijan, Taufiq-Yap, & Lee, 2015; Chowdhury & Saha, 2010).

Table 1: BET Analysis of Untreated TVC

Samples	BET Surface Area (m^2/g)	Pore Volume (cm^3/g)	Pore Size (Å)
Uncalcined TVC	0.6975	0.002326	133.3704
Calcined 400℃ TVC	2.4758	0.003754	65.6354
Calcined 500℃ TVC	0.6901	0.001240	71.8772
Calcined 600℃ TVC	0.6975	0.002326	133.3704

Table 2 shows the BET analysis of treated TVC samples. The surface area of untreated TVC increase 50% when calcined at 400℃, while the pore volume decrease and pore size adsorption decrease 43% and 62%. At 500℃, the surface area, pore volume and pore size adsorption decrease 62%, 72% and 25%. Lastly, the calcined TVC at 600℃ showed decreasing of surface area, pore volume and pore size adsorption by 65%, 73% and 23%. The surface area, pore volume and pore size adsorption data obtained for the TVC samples showed that the sample can be used for adsorption of BR46 dye at temperature below 400℃. The different result obtained for calcined TVC at 500℃ and 600℃ may be also caused by the damaged TVC due to high and unsuitable temperature of calcination (Asikin-Mijan et al., 2015; Chowdhury & Saha, 2010).

Table 2: BET Analysis of Treated TVC

Samples	BET Surface Area (m^2/g)	Pore Volume (cm^3/g)	Pore Size (Å)
Uncalcined TVC	1.5324	0.006002	156.6611
Calcined 400℃ TVC	2.2949	0.003405	59.3461
Calcined 500℃ TVC	0.5805	0.001703	117.3416
Calcined 600℃ TVC	0.5436	0.001646	121.1577

3.2 Effect of adsorbent dosage

The effect of adsorbent dosage on the removal of BR46 dye from aqueous solution onto TVC adsorbent was investigated by contacting 200mL of 20 ppm dye solution at room temperature (20˚C) for a total of 60 minutes at a constant stirring speed of 200 rpm. Different amount of TVC (0.3-0.9g) were tested for this study. **Fig. 1-3** shows the variation of the removal percentage versus contact time for untreated TVC with

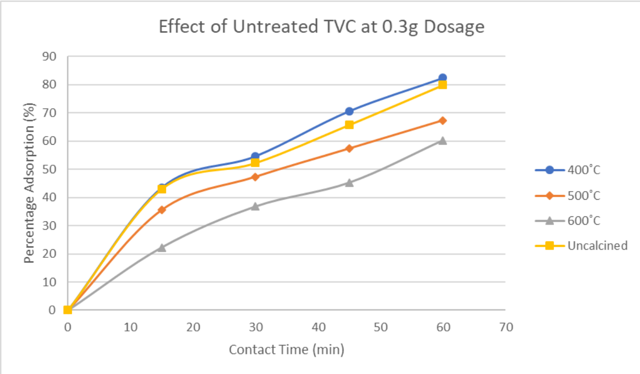

Fig. 1: Percentage adsorption of BR46 for untreated TVC with dosage of 0.3g and concentration of 20 ppm

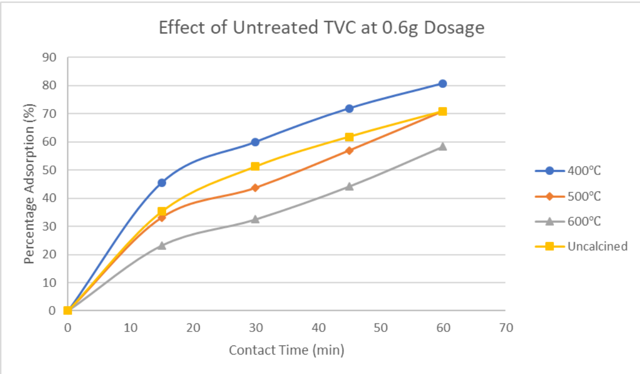

Fig. 2: Percentage adsorption of BR46 for untreated TVC with dosage of 0.6g and concentration of 20 ppm

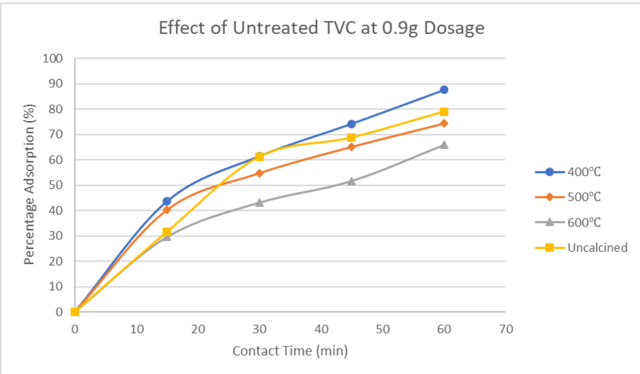

Fig. 3: Percentage adsorption of BR46 untreated TVC with dosage of 0.9g and concentration of 20 ppm

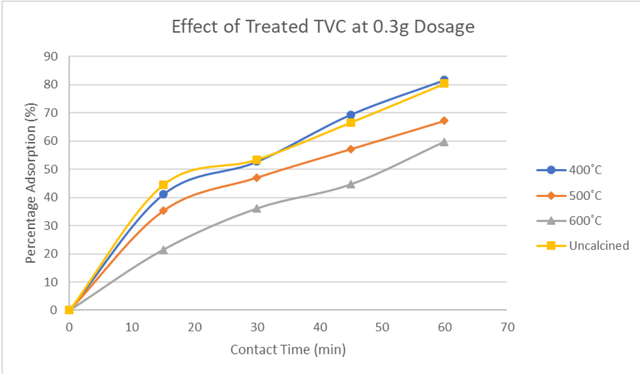

Fig. 4: Percentage adsorption of BR46 for treated TVC with dosage of 0.3g and concentration of 20 ppm

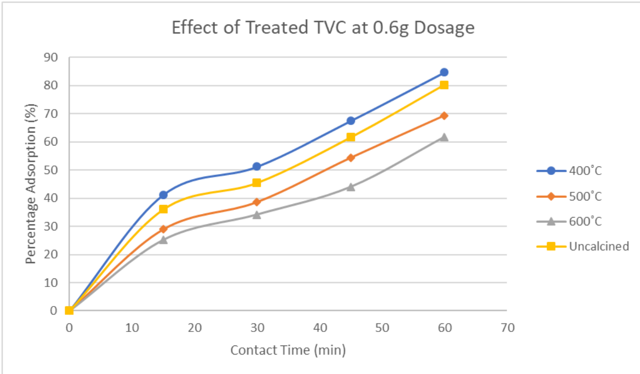

Fig. 5: Percentage adsorption of BR46 for treated TVC with dosage of 0.6g and concentration of 20 ppm

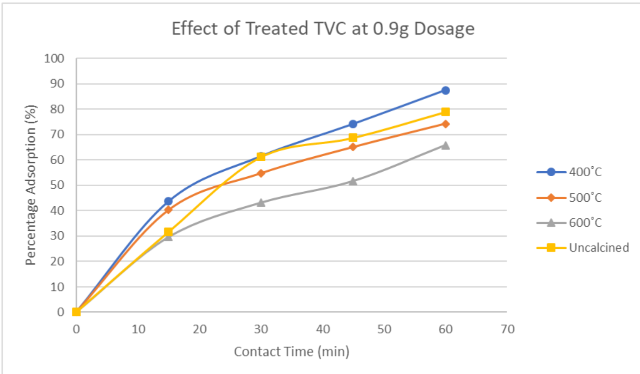

Fig. 6: Percentage adsorption of BR46 for treated TVC with dosage of 0.9g and concentration of 20 ppm

different dosage. Based on the figures, it is shown that the longer the contact time, the higher the percentage adsorption of BR46. It is also shown that the untreated calcined 400˚C TVC has the highest percentage adsorption of BR46 while the untreated calcined 600˚C has the lowest percentage adsorption of BR46. From **Fig.1-3**, the percentage adsorption of dye for untreated calcined 400˚C TVC are 82.41%, 80.80% and 87.48% in 0.3, 0.6 and 0.9g of adsorbent. **Fig.4-6** shows the variation of the removal percentage versus contact time for treated TVC with different dosage. Based on the figures, it is shown that it has the same results as the untreated TVC. It is also shown that for the treated calcined 400˚C TVC has the highest percentage adsorption of BR46 while the treated calcined 600˚C has the lowest percentage adsorption of BR46. From **Fig.4-6**, the percentage adsorption of dye for treated calcined 400˚C TVC are 81.64%, 84.74% and 87.48% in 0.3, 0.6 and 0.9g of adsorbent. From the graphs, it is shown that during the early stage of the experiment, the adsorption of dye is slightly faster during the initial 15 minutes. This is because there are more number of sites available on the TVC adsorbent for the dye to be absorbed (Eletta, Ajayi, Ogunleye, & Akpan, 2016; Ghaedi et al., 2011). Then the slow increase at the later stage is due to less amount of vacant site available for the adsorption process (Saakshy, Singh, Gupta, & Sharma, 2016). There is a study that also shown that by increasing the dosage of the adsorbent, the removal of dye from the aqueous solution will also increases (Haddad, 2015).

3.3 *Effect of initial concentration*

Fig. 7-9 shows the effect of BR46 solution concentration on the adsorption onto the untreated TVC adsorbent. In these experiments, the amount of TVC was constant which are 0.9g of TVC in 200mL of dye solution while the dye concentration was varied from 20 to 60 ppm with different time intervals. By plotting the percentage adsorption versus contact time, it can be seen that the percentage adsorption of

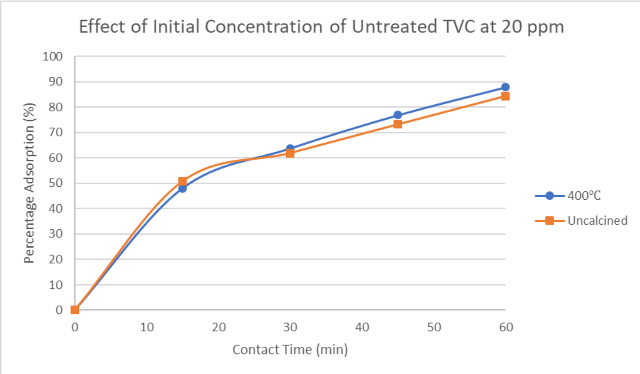

Fig.7: Percentage adsorption of BR46 for untreated TVC with dosage of 0.9g and concentration of 20 ppm

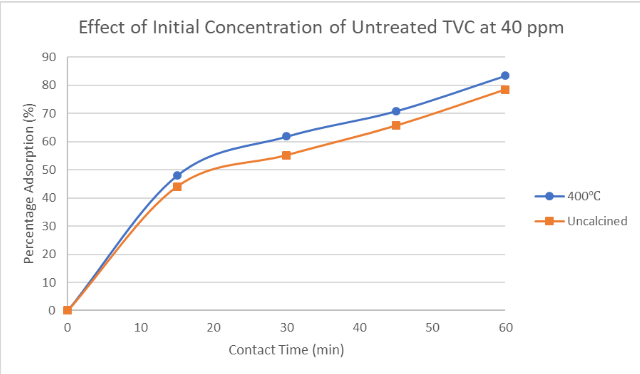

Fig.8: Percentage adsorption of BR46 for untreated TVC with dosage of 0.9g and concentration of 40 ppm

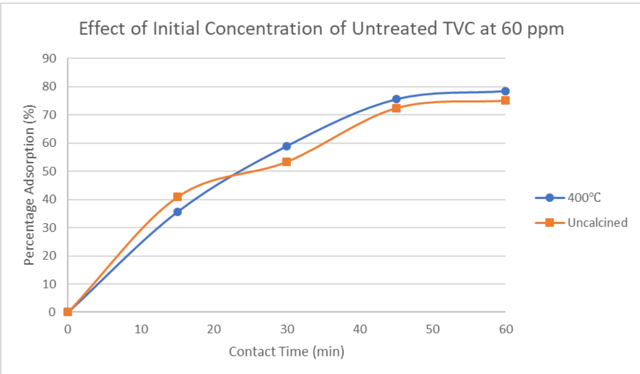

Fig.9: Percentage adsorption of BR46 for untreated TVC with dosage of 0.9g and concentration of 60 ppm

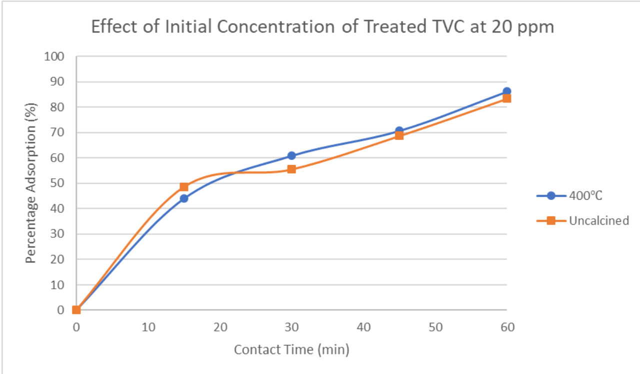

Fig.10: Percentage adsorption of BR46 for treated TVC with dosage of 0.9g and concentration of 20 ppm

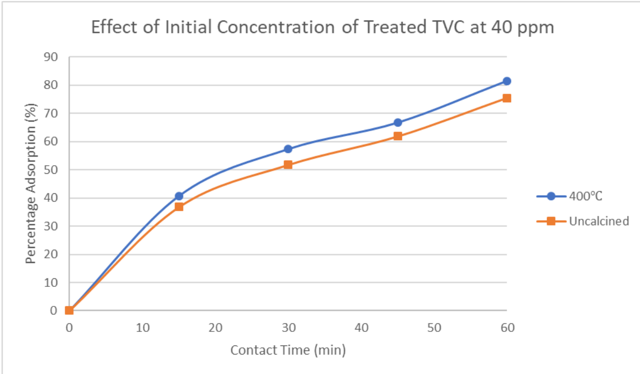

Fig.11: Percentage adsorption of BR46 for treated TVC with dosage of 0.9g and concentration of 40 ppm

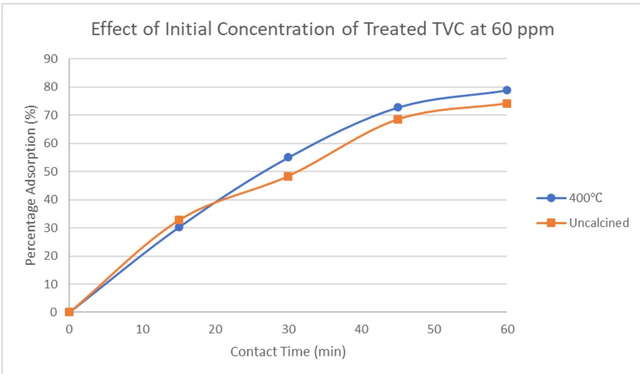

Fig.12: Percentage adsorption of BR46 for treated TVC with dosage of 0.9g and concentration of 60 ppm

the dye increases with increasing of contact time from 0 to 60 minutes for all concentrations. At the time of 60 minute, it is observed that the highest percentage removal using untreated TVC for 20, 40 and 60 ppm are 87.6, 83.47 and 78.48%. Whereas in **Fig. 10-12** shows the effect of BR46 solution concentration on the adsorption onto the treated TVC adsorbent. The experiments are conducted as same as before. By plotting the percentage adsorption versus contact time, it can be seen that the percentage adsorption of the dye increases with increasing of contact time from 0 to 60 minutes for all concentrations. At the time of 60 minute, it is observed that the highest percentage removal using treated TVC for 20, 40 and 60 ppm are 86.19, 81.57 and 78.84%. Based on Fig. 7-12, they shown that the adsorption capacity increases with contact time until 60 minutes. However, the increase is relatively higher during the initial 15 minutes. Rapid increase in adsorption during the initial stage is because due to the availability of vacant sites on the surface of the dye (Pua et al., 2013; Sun, Chen, Wan, & Yu, 2015). The slow increase at the later stage is due to the diffusion of dye into the pores of the adsorbent because the eternal sites are nearly or completely occupied (Ahmad & Alrozi, 2011; Shakoor & Nasar, 2016).

4. CONCLUSION

In the present study, the efficiency of TVC as an adsorbent for the removal of BR46 was investigated. It was found that the adsorption of the dye is affected by various parameter such as adsorbent dosage, initial concentration and contact time. The BET analysis showed that the optimum type of TVC used for this experiment was untreated calcined 400˚C TVC which has BET surface area of 2.4758 m^2/g and pore volume of 0.003754 cm^3/g.

The highest adsorption of BR46 was at 0.9g adsorbent dosage which is 87.48% removal. The highest removal for initial concentration of 20 ppm concentration of dye was 87.6% removal. Thus, it was concluded that TVC can be used effectively as an adsorbent fort the removal of BR46 from aqueous solution. It is recommended that the experiment to be conducted until it achieved the adsorption at equilibrium and conduct more characterization on the adsorbent also. Thus, it is found that the TVC adsorbent is a good and inexpensive adsorbent for dye effluent treatment.

Acknowledgment

I wanted to express my gratitude to several important people which had given strong support all the way from nothing until the research had done. This report cannot be completed without the help and guidance from those important people that do not hesitate in giving me the help when needed. I also wanted to say thank you to Universiti Teknologi Mara for giving me the opportunity to carry out this study.

References

Ahmad, M. A., Ahmad Puad, N. A., & Bello, O. S. (2014). Kinetic, equilibrium and thermodynamic studies of synthetic dye removal using pomegranate peel activated carbon prepared by microwave-induced KOH activation. *Water Resources and Industry*.

Ahmad, M. A., & Alrozi, R. (2011). Removal of malachite green dye from aqueous solution using rambutan peel-based activated carbon: Equilibrium, kinetic and thermodynamic studies. *Chemical Engineering Journal*. Ahmaruzzaman, M. (2008). Adsorption of phenolic compounds on low-cost adsorbents: A review. *Advances in Colloid and Interface Science*.

Anastopoulos, I., & Kyzas, G. Z. (2014). Agricultural peels for dye adsorption: A review of recent literature. *Journal of Molecular Liquids*.

Asikin-Mijan, N., Taufiq-Yap, Y. H., & Lee, H. V. (2015). Synthesis of clamshell derived Ca(OH)2 nano-particles via simple surfactant-hydration treatment. *Chemical Engineering Journal*.

Bhatnagar, A., Sillanpää, M., & Witek-Krowiak, A. (2015). Agricultural waste peels as versatile biomass for water purification - A review. *Chemical Engineering Journal*.

Chowdhury, S., & Saha, P. (2010). Sea shell powder as a new adsorbent to remove Basic Green 4 (Malachite Green) from aqueous solutions: Equilibrium, kinetic and thermodynamic studies. *Chemical Engineering Journal*.

Crini, G. (2006). Non-conventional low-cost adsorbents for dye removal: A review. *Bioresource Technology*.

Dahri, M. K., Kooh, M. R. R., & Lim, L. B. L. (2015). Application of Casuarina equisetifolia needle for the removal of methylene blue and malachite green dyes from aqueous solution. *Alexandria Engineering Journal*.

Deniz, F., & Karaman, S. (2011). Removal of Basic Red 46 dye from aqueous solution by pine tree leaves. *Chemical Engineering Journal*.

Deniz, F., & Saygideger, S. D. (2011). Removal of a hazardous azo dye (Basic Red 46) from aqueous solution by princess tree leaf. *Desalination*.

Eletta, O. A. A., Ajayi, O. A., Ogunleye, O. O., & Akpan, I. C. (2016). Adsorption of cyanide from aqueous solution using calcinated eggshells: Equilibrium and optimisation studies. *Journal of Environmental Chemical Engineering*.

Forgacs, E., Cserháti, T., & Oros, G. (2004). Removal of synthetic dyes from wastewaters: A review. *Environment International*.

Ghaedi, M., Hossainian, H., Montazerozohori, M., Shokrollahi, A., Shojaipour, F., Soylak, M., & Purkait, M. K. (2011). A novel acorn based adsorbent for the removal of brilliant green. *Desalination*.

Gupta, V. K., & Suhas. (2009). Application of low-cost adsorbents for dye removal - A review. *Journal of Environmental Management*.

Haddad, M. El. (2015). Removal of Basic Fuchsin dye from water using mussel shell biomass waste as an adsorbent: Equilibrium, kinetics, and thermodynamics. *Journal of Taibah University for Science*.

Kazemi, S. Y., Biparva, P., & Ashtiani, E. (2016). Cerastoderma lamarcki shell as a natural, low cost and new adsorbent to removal of dye pollutant from aqueous solutions: Equilibrium and kinetic studies. *Ecological Engineering*.

Mane, V. S., & Babu, P. V. V. (2011). Studies on the adsorption of Brilliant Green dye from aqueous solution onto low-cost NaOH treated saw dust. *Desalination*.

Mane, V. S., & Vijay Babu, P. V. (2013). Kinetic and equilibrium studies on the removal of Congo red from aqueous solution using Eucalyptus wood (Eucalyptus globulus) saw dust. *Journal of the Taiwan Institute of Chemical Engineers*.

Pua, F. L., Sajab, M. S., Chia, C. H., Zakaria, S., Rahman, I. A., & Salit, M. S. (2013). Alkaline-treated cocoa pod husk as adsorbent for removing methylene blue from aqueous solutions. *Journal of Environmental Chemical Engineering*.

Rafatullah, M., Sulaiman, O., Hashim, R., & Ahmad, A. (2010). Adsorption of methylene blue on low-cost adsorbents: A review. *Journal of Hazardous Materials*.

Rashidi, H. R., Sulaiman, N. M. N., & Hashim, N. a. (2012). Batik Industry Synthetic Wastewater Treatment Using Nanofiltration Membrane. *Procedia Engineering*.

Saakshy, A., Singh, K., Gupta, A. B., & Sharma, A. K. (2016). Fly ash as low cost adsorbent for treatment of effluent of handmade paper industry-Kinetic and modelling studies for direct black dye. *Journal of Cleaner Production*.

Shakoor, S., & Nasar, A. (2016). Removal of methylene blue dye from artificially contaminated water using citrus limetta peel waste as a very low cost adsorbent. *Journal of the Taiwan Institute of Chemical Engineers*.

Sharma, P., Kaur, H., Sharma, M., & Sahore, V. (2011). A review on applicability of naturally available adsorbents for the removal of hazardous dyes from aqueous waste. *Environmental Monitoring and Assessment*.

Subramaniam, R., & Kumar Ponnusamy, S. (2015). Novel adsorbent from agricultural waste (cashew NUT shell) for methylene blue dye removal: Optimization by response surface methodology. *Water Resources and Industry*.

Sun, L., Chen, D., Wan, S., & Yu, Z. (2015). Performance, kinetics, and equilibrium of methylene blue adsorption on biochar derived from eucalyptus saw dust modified with citric, tartaric, and acetic acids. *Bioresource Technology*.

Tan, I. A. W., Hameed, B. H., & Ahmad, A. L. (2007). Equilibrium and kinetic studies on basic dye adsorption by oil palm fibre activated carbon. *Chemical Engineering Journal*.

Wang, Y., Zhu, L., Jiang, H., Hu, F., & Shen, X. (2016). Application of longan shell as non-conventional low-cost adsorbent for the removal of cationic dye from aqueous solution. *Spectrochimica Acta - Part A: Molecular and Biomolecular Spectroscopy*.

Yagub, M. T., Sen, T. K., Afroze, S., & Ang, H. M. (2014). Dye and its removal from aqueous solution by adsorption: A review. *Advances in Colloid and Interface Science*.