



## RUBBER SEED SHELLS (HEVEA BRASILIENSIS): AN ADSORBENT USED FOR THE REMOVAL OF RHODAMINE B DYE

Rachel Yvonne Nadarajah, Rosmawani Mohammad and Mardawani Mohamad

Faculty of Bioengineering and Technology, Universiti Malaysia Kelantan, Jeli Campus, Locked Bag No., Jeli, Kelantan, Malaysia

E-Mail: [rosmawani@umk.edu.my](mailto:rosmawani@umk.edu.my)

### ABSTRACT

Rubber seed shells (RSS) are seemingly useless and rapidly becoming an agricultural waste. As the industrial world is rapidly developing and becoming technologically advanced in making products, the environment is getting more polluted. The most polluted is the main source of water supply. Waste water treatments are expensive. Rhodamine B (RB) dye is used in all types of industries such as textile, leather, paint, paper, plastics, and etc. Therefore, this project aims to reveal the use of RSS (agricultural waste) as adsorbents for the removal of RB dye. The effect of various parameters such as adsorbent size, adsorbent dosage, initial dye concentration, contact time, and pH were studied. The study showed that up to 99.52% of RB removal can be achieved under optimum conditions (adsorbent size: 0.063 mm, adsorbent dosage: 3.0 g, initial dye concentration: 100 mg/L, contact time: 24 hours and pH 3). The experimental data were analysed with the Langmuir and Freundlich adsorption isotherm models. The equilibrium data were best described in the Langmuir model with a maximum adsorption capacity of 3.185 mg/g. In conclusion, this study indicated that RSS have the potential to become low-cost adsorbents for the removal of RB dye in waste water treatment.

**Keywords:** rubber seed shells, rhodamine B, waste water treatment, langmuir and freundlich.

### INTRODUCTION

In Malaysia, dyes are commonly used in textile, leather, food, paper, plastics, laboratories, and colour industries. Due to the large amount of dyes used in many fields, it can cause waste water pollution. Poor water quality nowadays is due to the increased number of industrial plants and the lack of awareness in treating waste water before discharging into the rivers. Concentrated and carcinogenic dyes can be present in waste water (Low & Lee, 1990). This condition can affect the photosynthesis process due to the reduction of sunlight penetration in aquatic ecosystems. Organisms experience a lack of oxygen intake and aquatic lifecycle is disturbed by the presence of dye.

RB is a red cationic dye which has a positive electrical charge that is used in anionic fabric and negatively charged bearing materials such as wool, silk, nylon and, acrylics. It is often used in fabric, chemical, trace, paint, printing, porcelain, and paper industry. RB is used especially in paper manufacturing as a reagent for antimony, bismuth, cobalt, niobium, gold, manganese, mercury, molybdenum, tantalum, thallium, and tungsten as a biological stain. This dye is known to be toxic and carcinogenic to humans, animals and may cause long term unfavourable effects to the environment.

Therefore, we need to remove dyes from waste water before its release into the environment. Discharge of waste water containing dye is a major problem. Due to this, a lot of technologies are available to treat dyes in waste water but tend to require large capital investment for the treatments. Besides that, various natural and synthetic adsorbents were used to treat waste water. For example, activated carbon is a popular method in industries nowadays due to its high capacity and efficiency in removing dyes in waste water. However, activated carbon has disadvantages such as regeneration difficulties, high cost, which produce chemicals that can

be corrosive in nature and give harmful effects during disposal. Therefore, natural and low-cost adsorbent is the most suitable choice.

In general, there are various types of materials used for adsorbent preparation. It can be in the form of natural materials, agriculture waste materials and industrial waste materials. For industrial materials, they may focus more on low cost adsorbents with a high capacity and efficiency in the removal of dye in waste water treatments. Among the various techniques of dye removal, adsorption is the best technique as it gives excellent results because it can be used to remove different types of dye substances. Recently, a lot of approaches have been taken for the invention of cheaper and effective adsorbents. A number of low cost adsorbents have been used for the removal of dyes. These include sugarcane bagasse (Zhang *et al.*, 2013), hazelnut shells (Carletto *et al.*, 2008), coconut shells (Aljeboree *et al.*, 2014), sunflower seed shells (Suteu *et al.*, 2011), mahogany shells (Sartape *et al.*, 2013), cashew nutshells (Senthil *et al.*, 2010), almond shells (Senturk *et al.*, 2010), durian shells (Kurniawan *et al.*, 2011), periwinkle shells (Bello *et al.*, 2008), pea shells (Gecgel *et al.*, 2013), banana bark (Paper, 2009), orange peels (Namasivayam *et al.*, 1996), jack fruit peels (Inbaraj & Sulochana, 2006), tamarindus indica fruit shells (Vasu, 2008), kapok hulls (Ecjhaio, 2006) and palm shell powder (Sreelatha & Padmaja, 2008).

Malaysia is one of the major producers of rubber responsible for about 47% of the world's total rubber production (Jamal & Yaghoob, 2014). Although the rubber kernel is sent to oil mills, there is still a huge amount of rubber seed shells available as agricultural waste which has become an environmental problem for rubber tree plantations (Hassan *et al.*, 2014). This environmental contamination problem destroys the rubber tree plantation. Therefore, rubber seed shells have been



chosen as a low-cost adsorbent for the removal of RB dye and its use is the first to be reported in this study. The study considered a few parameters such as adsorbent size, adsorbent dosage, initial dye concentration, contact time, and pH. To determine the adsorption favourability, it was analysed using the Langmuir and Freundlich adsorption isotherm models.

## MATERIALS AND METHODS

### Chemicals

Sodium Hydroxide, Hydrochloric Acid (HCl), Sodium Citrate, Citric Acid, Potassium Dihydrogen Phosphate, Sodium Tetraborate-10-Hydrate (Borax), Di-Sodium Hydrogen Phosphate and RB were used in this study. The chemicals used are all analytical reagent grade.

### Material

RSS were collected from Kuala Lipis, Pahang. RB was used as an adsorbate. Distilled water was used to prepare all the reagents and solutions.

### Preparation of adsorbent

RSS were washed with distilled water to remove any attached mud and soluble impurities. Then, it was air-dried. After that, the RSS were grinded and blended into powder form. Then, the powdered RSS were passed through sieves ranging from 0.063 to 0.125 mm. lastly; the sieved samples were kept in a sealed polythene bag for further use in the entire adsorption study (Senthil *et al.*, 2010).

### Preparation of adsorbate (RB stock dye solution)

The solution was prepared by dissolving 500 mg of RB in 500 mL of distilled water in a volumetric flask. The solution was poured into reagent bottle and labelled as 1000 mg/L stock solution.

### Adsorption study and data analysis

Generally, the adsorption study was conducted using 100 mL of dye at certain concentrations and adsorbent amounts. Then, the adsorbent-adsorbate mixture was stirred well for a few minutes, then covered with aluminum foil and left for 24 hours at room temperature. Next, the mixture was filtered using filter paper and the filtrate was analysed using UV-visible spectrophotometer at a maximum wavelength of 540 nm (Dabwan *et al.*, 2015). In this study, a few parameters were optimised such as adsorbent size, adsorbent dosage, initial dye concentration, contact time, and pH.

First, the effect of adsorbent size (raw RSS powder) on the removal of RB was studied at 0.063 mm and 0.125 mm. The adsorption process was conducted using 50 mg/L of RB. Second, the effect of adsorbent dosage was studied at the dosage amounts of 0.5, 1.0, 2.0, 3.0, and 4.0 g. It was conducted using 50 mg/L of RB and the optimum adsorbent size was 0.063 mm. Third, the

effect of the initial dye concentration was studied by varying the dye concentrations. The solution at different initial dye concentrations of 10, 30, 50, 80, 100, 200 mg/L was prepared from a stock solution (1000 mg/L). This experiment was carried out by using an optimum adsorbent dosage (3.0 g). Fourth, the effect of contact was studied within 4 to 28 hours; at intervals of 4h. This experiment was carried out by using an optimum adsorbent dosage (3.0 g) and initial dye concentration (100 mg/L) obtained in the previous steps. Lastly, the effect of pH on the adsorption of RB dye using RSS was studied under the pH range of 2.0 to 10.0. This experiment was carried out using the optimum adsorbent dosage (3.0 g), initial dye concentration (100 mg/L) and contact time (24 hours) obtained in the previous experiments. The pH buffer solution was prepared as stated in our previous work (Rosmawani *et al* 2017).

Data obtained were analysed based on percentage of dye removal using Equation (1). In this study, two types of adsorption isotherm models were used which are Langmuir adsorption isotherm and Freundlich adsorption isotherm. The details regarding the Langmuir and Freundlich equations have been mentioned in a previous research (Hameed *et al.*, 2008).

$$\% \text{ Removal} = \frac{C_o - C_e}{C_o} \times 100 \quad (1)$$

Where,

$C_e$  = Equilibrium dye concentration in the solution (mg/L)

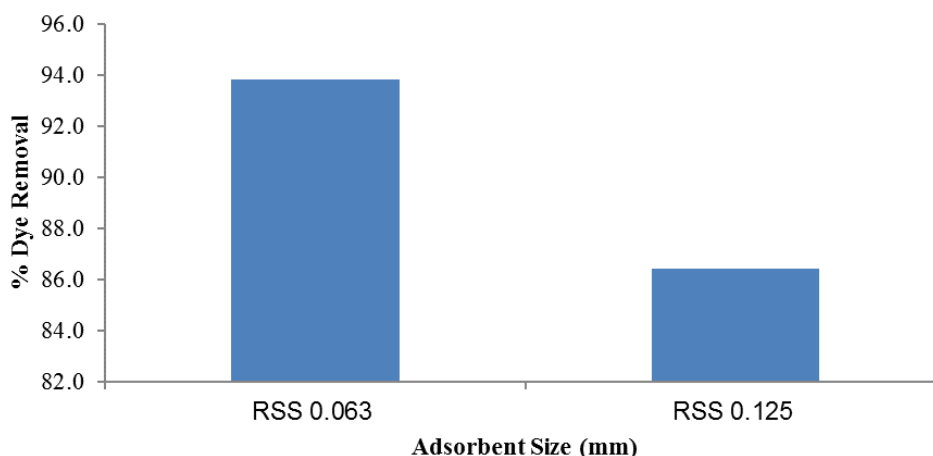
$C_o$  = Initial dye concentrations in the solution (mg/L)

## RESULTS AND DISCUSSIONS

### Effect of adsorbent size

Figure-1 shows the effect of the adsorbent size on the removal of RB using RSS. The effect of adsorbent size was studied at 0.063 mm and 0.125 mm. It can be seen that a smaller adsorbent size (0.063 mm) gave the highest percentage of RB dye removal. The percentage of dye removal at an adsorbent size of 0.063 mm was 93.83% while at the adsorbent size of 0.125 mm was 86.43%. Adsorbent size played a very important role in the adsorption of a dye.

At a fixed adsorbent dosage, the RB uptake increased with smaller adsorbent size due to the greater accessibility to pores and to the greater surface area for bulk adsorption per unit mass of the adsorbent (Namasivayam *et al.*, 1996). Meanwhile, the larger adsorbent size had low efficiency of RB uptake because it was hard to access pores due to less surface area for bulk adsorption per unit of the adsorbent that caused a reduction in adsorption efficiency. Therefore, it can be said that a smaller adsorbent size has a higher capacity in adsorption than the larger adsorbent size (Aljeboree *et al.*, 2014).

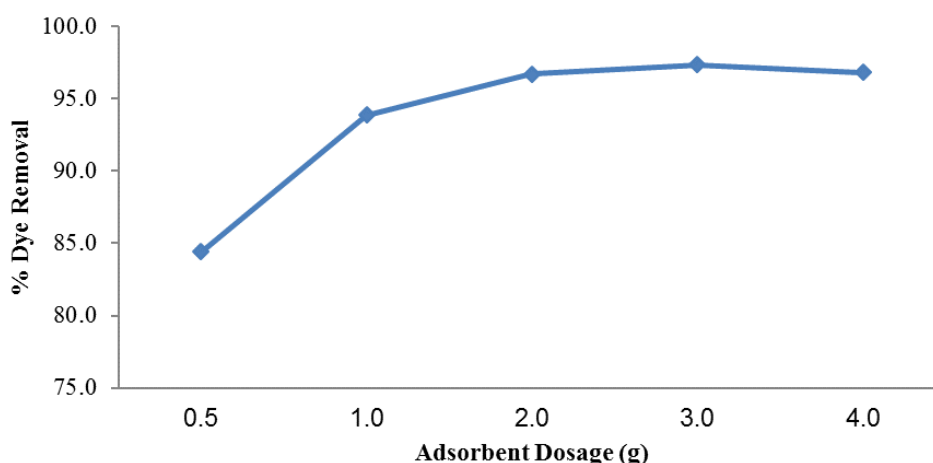


**Figure-1.** Effect of adsorbent size on the removal of RB using RSS.

#### Effect of adsorbent dosage

Based on Figure-2, the highest percentage (97.33%) removal of RB by using RSS was obtained at 3.0 g. Adsorbent dosage is directly proportional to the percentage of dye removal. The percentage of dye removal increased dramatically from 0.5 g (84.43%) to 1.0 g (93.85%) with the adsorbent which continued to increase slowly until it reached the optimum level at 3.0 g and slightly decreased at 4.0 g (96.81%). As the adsorbent dosage increases, the removal efficiency increased. This is due to the increase of the available adsorption surface and adsorption sites (Hameed *et al.*, 2008).

The removal efficiency incidentally started to decrease at 4.0 g when the adsorbent became saturated and gave off significant colour changes to the removal of the adsorbate which lowered the performance of the adsorbent (Gupta *et al.*, 2011). This may be due to higher collision rate between adsorbent particles resulting in less vacant sites of adsorbent available and as a result led to the overlapping of adsorption sites due to collision. Hence, the amount of 3.0 g was chosen as the optimum adsorbent dosage and was used for the subsequent experiment.



**Figure-2.** Effect of adsorbent dosage on the removal of RB using RSS.

#### Effects of initial dye concentration

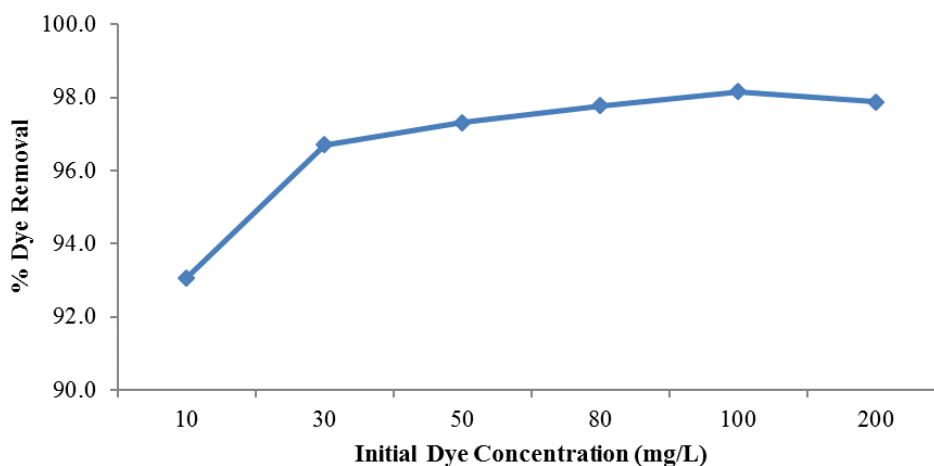
Figure-3 shows that the highest percentage removal of RB using RSS was obtained at 100 mg/L of dye concentration. Based on the data obtained, initial dye concentration of 100 mg/L gave 98.16% of dye removal after 24 hours. Meanwhile initial dye concentration of 10 mg/L showed the lowest percentage of dye removal which is 93.06%. The percentage of dye removal increased when the initial dye concentration was set from 10 mg/L to 200 mg/L. However, the percentage of dye removal slightly decreased after it reached optimum condition at 100

mg/L. The increase in initial dye concentration enhanced the interaction between adsorbate and adsorbent as the initial dye concentration increased. At lower dye concentrations, the number of adsorption sites of the adsorbent was enough to accommodate the number of dye molecules but then it becomes saturated with dye molecules as the concentration increases after 100 mg/L (Singh *et al.*, 2013). The decrease in the percentage of dye removal at 200 mg/L was due to the adsorption sites of the adsorbent becomes fewer and saturated. This condition causes the interaction between the adsorbent



and adsorbate to become weaker and thus does not produce any significant colour changes. Therefore, the initial dye concentration of 100 mg/L was chosen as the

optimum concentration and was used for the subsequent study.

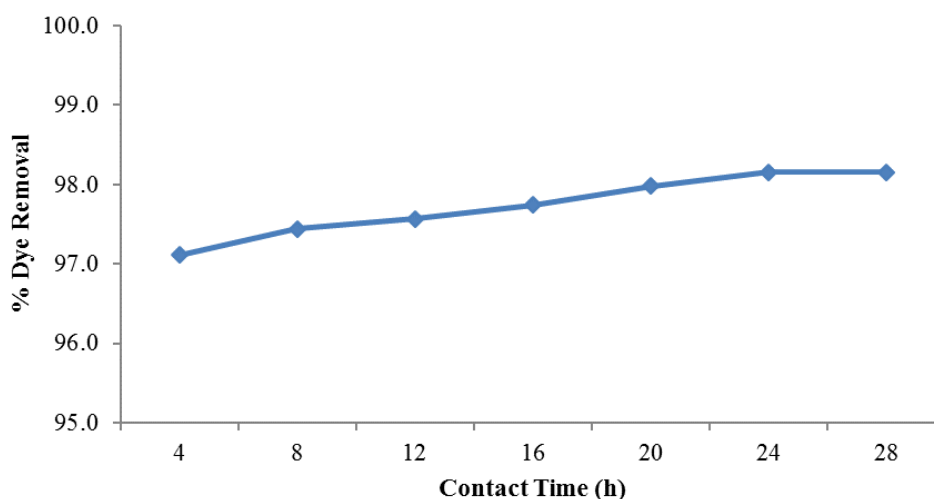


**Figure-3.** Effect of initial dye concentration on the removal of RB using RSS.

#### The effect of contact time

The effect of contact time was carried out from 4 to 28 hours. Figure-4 shows that the adsorption of RB increased with the increase of contact time. The adsorption of RB slightly increased every hour starting from 4 hours (97.11%) until it reached 24 hours (98.16%) of contact time. After 24 hours, the adsorption process showed that the adsorption of RB had reached the

equilibrium state. The slightly increased adsorption rate of RB after 4 hours is due to the RB molecules ability to attach freely into the RSS due to many unoccupied sites available, however the adsorption extent increased with elapsed time until it reached saturation level where the uptake percentage attained a constant value after 24 hours (Etim *et al.*, 2012).

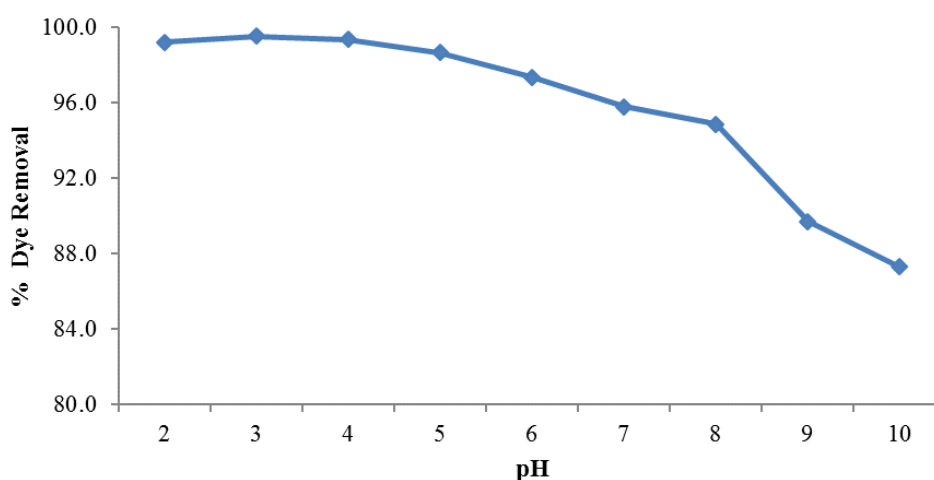


**Figure-4.** Effect of contact time on the removal of RB using RSS.

#### Effect of pH

Based on Figure-5, the highest percentage of RB removal by RSS was obtained at pH 3 with 99.52% and the lowest was at pH 10 with 87.29%. The percentage of dye removal decreased as the pH increased. As the pH

increases from pH 2 to 10, the dye removal efficiency started to decrease dramatically after pH 4. It is well-known that the adsorption characteristics of adsorbents are influenced by the pH of the solution.



**Figure-5.** Effect of pH on the removal of RB using RSS.

Basically, the amount of dye adsorbed on the surface, by the adsorbent, is influenced by the adsorbent surface charge and pH solution. RSS is a negatively charged adsorbent with high content of cellulose, hemicelluloses and lignin (Ismail *et al.*, 2014). In fact, RB exists in two forms, cationic and zwitterionic in polar solvents. At solutions below pH 4, the RB molecules exist in cationic and monomeric forms but in pH above 4.0, RB molecules exist in zwitterionic forms in a solution (Inyinbor *et al.*, 2015). Since pH 3 has higher dye removal efficiency than the rest of the pH range; it shows a change of colour from pink to colourless because RSS contains a lot of negatively charged ions on the surface that are attracted towards the cationic molecules of RB. This causes a strong attraction between negative and positive charges that causes a high percentage of dye removal at pH 3.

At pH 3, the RB dyes are able to enter into the pore structure and obtain a higher adsorption value. After that, as the pH value increases, the electrostatic interaction between the xanthene and the carboxyl groups (COOH) of RB monomers increases aggregation of RB to create a bigger molecular form that are unable to enter into the pore structure of RSS that causes the decrease of dye adsorbed on the RSS. In conclusion, the transformation of the cationic to zwitterionic forms begins when the pH value is greater than pH 3 (Kooh *et al.*, 2016). Furthermore, it was found in previous studies that the pH for RB is mostly found at pH between 3 and 4; removal of RB dye was at pH 3 when using *Casuarina equisetifolia* needles (Kooh *et al.*, 2016), dika nut (Inyinbor *et al.*, 2015) and coffee ground powder (Shen & Gondal, 2013) and reported at pH 4 when using sugarcane bagasse (Zhang *et al.*, 2013) and palm shell powder (Sreelatha & Padmaja 2008). Therefore, pH 3 was the optimum condition for the removal of RB dye using RSS.

#### Adsorption isotherm

The adsorption isotherm used in this study was the Langmuir adsorption isotherm model and Freundlich adsorption isotherm model. Based on the  $R^2$  values shown

in Table-1, the two parameters studied for RB removal using RSS were described better in the Langmuir equation. The adsorption of RB showed better fit for the Langmuir adsorption isotherm model with higher  $R^2$ . Besides that, since the  $n$  value of Freundlich isotherm was negative, therefore it did not fit the Freundlich model (Ho & McKay, 1999; Velmurugan *et al.*, 2011). Hence, the adsorption of RB using RSS is best described in the Langmuir model with a maximum adsorption capacity of 3.185 mg/g. This suggested that the adsorption between RSS and RB dye takes place as monolayer adsorption.

**Table-1.** Adsorption isotherm data for RB adsorption onto RSS at room temperature based on Langmuir Isotherm and Freundlich Isotherm.

Isotherm model	Parameter	Value
Langmuir	$K_L$ (L/mg)	-0.051
	$q_{max}$ (mg/g)	3.185
	$R^2$	1.000
Freundlich	$K_F$ (mg/g)	3.319
	$n$	-43.478
	$R^2$	0.995

#### CONCLUSIONS

This study showed that RSS was able to remove RB dye in an aqueous solution and thus has the capability to become a low cost adsorbent. Smaller adsorbent size has higher capacity in adsorption rather than a larger adsorbent size due to the greater accessibility to pores and to the greater surface area.

#### ACKNOWLEDGEMENTS

The authors are grateful for the financial support from the Ministry of Higher Education via the Research Acculturation Grant Scheme (RAGS), R/RAGS/A07.00/01095A/001/2015/000201.





## REFERENCES

- Aljeboree A. M., Alshirifi A. N. and Alkaim A. F. 2014. Kinetics and equilibrium study for the adsorption of textile dyes on coconut shell activated carbon. *Arabian Journal of Chemistry*. 1(6): 1-13.
- Bello O. S., Adeogun I. A., Ajaelu J. C. and Fehintola E. O. 2008. Adsorption of methylene blue onto activated carbon derived from periwinkle shells: kinetics and equilibrium studies. *Chemistry and Ecology*. 24(4): 285-295.
- Carletto R. A., Chimirri F., Bosco F. and Ferrero F. 2008. Adsorption of congo red dye on hazelnut shells and degradation with (*Phanerochaete chrysosporium*). *BioResources*. 3(4): 1146-1155.
- Dabwan A. H. A., Yuki N., Amni N., Asri M. and Katsumata H. 2015. Removal of methylene blue, rhodamine b and ammonium ion from aqueous solution by adsorption onto sintering porous materials prepared from coconut husk waste. *Open Journal of Inorganic Non-Metallic Materials*. 5(1): 21-30.
- Ecjhaio C. 2006. Preparation and utilization of kapok hull carbon for the removal of rhodamine-b from aqueous solution. *E-Journal of Chemistry*. 3(2): 83-96.
- Etim U. J., Umoren S. A. and Eduok U. M. 2012. Coconut coir dust as a low cost adsorbent for the removal of cationic dye from aqueous solution. *Journal of Saudi Chemical Society*. 1(4): 1-10.
- Gecgel U., Özcan G. and Gürpınar G. C. 2013. Removal of methylene blue from aqueous solution by activated carbon prepared from pea shells (*Pisum sativum*). *Journal of Chemistry*. 2013: 1-9.
- Gupta A., Yadav R. and Devi P. 2011. Removal of hexavalent chromium using activated coconut shell and activated coconut coir as low cost adsorbent. *IIOAB Journal*. 2(10): 8-12.
- Hameed, B. H., Mahmoud, D. K. and Ahmad, A. L. 2008. Equilibrium modeling and kinetic studies on the adsorption of basic dye by a low-cost adsorbent: coconut (*Cocos nucifera*) bunch waste. *Journal of Hazardous Materials* 158(11): 65-72.
- Hassan S. N. A. M., Ishak M. A. M., Ismail K., Ali S. N. and Yusop M. F. 2014. Comparison study of rubber seed shell and kernel (*Hevea brasiliensis*) as raw material for bio-oil production. *Energy Procedia*. 52(7): 610-617.
- Ho Y.S. and McKay G. 1999. Pseudo-second order model for sorption processes. *Process Biochemistry*. 34(5): 451-465.
- Inbaraj B. S. and Sulochana N. 2006. Use of jackfruit peel carbon (JPC) for adsorption of rhodamine-b, a basic dye from aqueous solution. *Indian Journal of Chemical Technology*. 13(4): 17-23.
- Inyinbor A. A., Adekola F. A. and Olatunji G. A. 2015. Adsorption of rhodamine b dye from aqueous solution on *Irvingia Gabonensis* biomass. *Kinetics and Thermodynamics Studies*. 68(9): 115-125.
- Ismail M. D. Mohd S. and Hanafi. 2014. Properties of rubber seed shells flour-filled polypropylene composites: the effect of poly(ethyleneco-acrylic acid). *Bioresources*. 9(4): 7311-7325.
- Jamal O. and Yaghoob J. 2014. Selected research issues in the Malaysian agricultural sector. *Jurnal Ekonomi Malaysia*. 48(2): 127-136.
- Kooh M. R. R., Dahri M. K. and Lim L. B. L. 2016. The removal of rhodamine b dye from aqueous solution using *Casuarina equisetifolia* needles as adsorbent. *Cogent Environmental Science*. 2: 1-14.
- Kurniawan A., Sisnandy V. O. A., Trilestari K., Sunarso J., Indraswati N. and Ismadi S. 2011. Performance of durian shell waste as high capacity biosorbent for Cr(VI) removal from synthetic wastewater. *Ecological Engineering*. 37(10): 940-947.
- Low K. S. and Lee K. 1990. The removal of cationic dyes using coconut husk as an adsorbent. *Pertanika Chemistry Agriculture*. 13(2): 221-228.
- Namasivayam C., Muniasamy N., Gayatri K., Rani M. and Ranganathan, K. 1996. Removal of dyes from aqueous solutions by cellulosic waste orange peel. *Bioresource Technology*. 57(11): 37-43.
- Paper F. 2009. Full Paper Adsorption of rhodamine b by acid activated carbon-kinetic, thermodynamic and equilibrium studies. *Orbital*. 1(2): 138-155.
- Rosmawani Mohammad, Aswinee Tangga Rajoo and Mardawani Mohamad. 2017. Coconut fronds as adsorbent in the removal of malachite green dye. *ARPN Journal of Engineering and Applied Sciences*. 12(4): 996-1001.
- Sartape A. S., Patil S. A., Patil S. K., Salunkhe S. T. and Kolekar S. S. 2013. Mahogany fruit shell: a new low-cost adsorbent for removal of methylene blue dye from aqueous solutions. *Desalination and Water Treatment*. 53(1): 99-108.
- Senthil Kumar P., Ramalingam S., Senthamarai C., Niranjana M., Vijayalakshmi P. and Sivanesan S. 2010. Adsorption of dye from aqueous solution by cashew nut shell: Studies on equilibrium isotherm, kinetics and thermodynamics of interactions. *Desalination*. 261(3): 52-60.



Senturk H. B., Ozdes D. and Duran C. 2010. Biosorption of rhodamine 6G from aqueous solutions onto almond shell (*Prunus dulcis*) as a low cost biosorbent. *Desalination*. 252(7): 81-87.

Shen K. and Gondal M. A. 2013. Removal of hazardous rhodamine dye from water by adsorption onto exhausted coffee ground. *Journal of Saudi Chemical Society*. 1(6): 1-8.

Singh P., Raizada P., Pathania D., Sharma G. and Sharma P. 2013. Microwave induced KOH activation of guava peel carbon as an adsorbent for congo red dye removal from aqueous phase. *Indian Journal of Chemical Technology*. 20(10): 305-311.

Sreelatha G. and Padmaja P. 2008. Study of removal of cationic dyes using palm shell powder as adsorbent. *Journal of Environmental Protection Science*. 2(2): 63-71.

Suteu D., Zaharia C. and Malutan T. 2011. Removal of orange 16 reactive dye from aqueous solutions by waste sunflower seed shells. *Journal of the Serbian Chemical Society*. 76(7): 607-624.

Vasu A. E. 2008. Removal of basic dyes from aqueous solutions by activated carbon prepared from *Tamarindus indica* fruit shells. *Oriental Journal of Chemistry*. 24(7): 947-954.

Velmurugan P., Rathinakumar V. and Dhinakaran G. 2011. Dye removal from aqueous solution using low cost adsorbent. *International Journal of Environmental Sciences*. 1(7): 1492-1503.

Zhang Z., O'Hara I. M., Kent G. A. and Doherty W. O. S. 2013. Comparative study on adsorption of two cationic dyes by milled sugarcane bagasse. *Industrial Crops and Products*. 42(2): 41-49.