Removal of Methylene Blue and Malachite Green Dye Using Different Form of Coconut Fibre as Absorbent

Y.C. Wong*, M.S.R. Senan and N.A. Atiqah

Faculty of Agro Based Industry, Universiti Malaysia Kelantan, Jeli Campus, Locked Bag 100, 17600 Jeli, Kelantan, Malaysia

Abstract: In this study, coconut fibres are grounded and sieved into the size of 150 μm granular form and filament form of uniform size 2.0 cm for absorption test of methylene blue and malachite green dye in single dye solution were studied. As a result, granular form of coconuts have higher percentage removal dye of methyelene blue and malachite green blue which is 98.3% and 99.0%. This study shows a major approach of turning the agricultural waste to an added value product which is absorbent for wastewater treatment especially in textile industries sector.

Keywords: Coconut fibre, absorption, melethylene blue dye, malachite green dye.

1. INTRODUCTION

Water pollution has become a serious problem around the world including Malaysia. Malaysia is one of the country that fall into this negatively impacts on the sustainability of water resources. Many industries sector in Malaysia such as textile, paper, paint, pharmaceuticals, food, leather, cosmetics, tannery, printing and plastics used wide verieties of dye in order to color their product for example such as batik in textile industry. Among those industries sector in Malaysia, textiles industry ranked first in the usage of dyes for coloration of fiber [1]. Considering both volumes discharged and effluent composition, wastewater from the textile industry was declared as one of the major sources of wastewater in ASEAN countries [2].

The wastewaters discharged from dying processes exhibit high biological oxygen demand (BOD), high chemical oxygen demand (COD) are highly colored, hot, alkaline and contain high amounts of dissolved solids [3]. The disposal of colored wastes such as dyes and pigments into receiving waters damages the environment, as they are carcinogenic and toxic to humans and aquatic life [4]. Besides the matters of color, some dye imparts non-visibility and can be modified biologically to toxic or carcinogenic compounds. Nowadays concern has increased about the long-term toxic effect of water bodies containing these dissolved pollutants. The wastewaters discharge from textile industries includes residual dyes; these dyes are not bio-degradable therefore they may cause water pollution and serious threat to the environment [5].

Absorption has been found to be an efficient and economically cheap process to remove pollutants such as colors, dyes and metal impurities [6]. Some of the adsorbent materials that have been used with varying success include rice husk [7, 8] , cornelian cherry, apricot stone, almond shell [9, 10], cotton stalks [11], coir pith [12], wood [13], sunflower stalks [14], charcoal [15, 16] and orange peel [17] were successfully employed for the removal of dyes from aqueous solutions.

Commercially, there are more than 100,000 available dye namely acid, reactive, disperse, vat, metal complex, mordant, direct, basic and sulphur dyes with a production of more than 105 metric tons per year. The prediction is 10-15% of the dye is lost to waste streams as pollutants during dying process in the textile industry and causing the pollution [18]. This study was focused on two basic dye which is methylene blue and malachite green dye.

One of the major problems concerning textile wastewaters is dye effluent [19]. Dyes are chemicals, which is binding with material and give color to the material. Dyes are ionic, aromatic organic compounds with structures including aryl rings which delocalized electron systems. The color of a dye is provided by the presence of chromophore group. Most dyes are non-biodegradable in nature and the dye will be affected the photosynthetic activity in aquatic systems by reducing light penetration [20]. Dyes also impede the solubility of gases in water as well as producing trihalomethanes during chlorination. Due to their chemical structure, dye are resistant to fading when exposed to light, water and many chemicals. It also damages the quality of the

*Address correspondence to this author at the Faculty of Agro Based Industry, Universiti Malaysia Kelantan, Jeli Campus, Locked Bag 100, 17600 Jeli, Kelantan, Malaysia; Tel: +609-9477108; Fax: +609-9477022;
E-mail: yeeching@umk.edu.my

ISSN: 1814-8085 / E-ISSN: 1927-5129/13

receiving streams and is toxic to food chain organisms [21].

Methylene blue dye (MB) is a basic aniline dye, C16H18N3SCl that forms a deep blue solution when dissolved in water. Methylene blue is utilized in coloring paper, temporary hair coloring, dyeing cotton and wools, and coloring of paper stocks [22]. Methylene blue is a dark green powder or crystalline solid. It is widely used as a stain and has a number of biological uses. It dissociates in aqueous solution in the same way that electrolytes dissociate into methylene blue cation and the chloride ion. The removal of methylene blue from any wastewater is of utmost importance due to the serious environmental damage that can occur as a result of contact with it, particularly in the case of people [23]. Malachite green dye (MG) is an N-methylated diaminotriphenylmethane dye. Malachite green dye is a green crystal powder with a metallic lustre. Malachite green, are toxic and must be removed before discharge into receiving streams. MG is one such dye used extensively in textile industry for dyeing silk, leather, cotton, wool and jute. It is also extensively used as a bactericide, fungicide and parasiticide in aquaculture industries worldwide. MG is highly toxic to mammalian cells and causes kidney tumors in mice and reproductive problems in rabbit and fish [24].

Moreover, malachite green has detrimental effects on liver, gill, kidney, intestine and gonads of aquatic organisms [25]. When it was inhaled or ingested by human, it may cause irritation to the gastrointestinal tract and even cancer [26]. Contact of malachite green with skin causes irritation with redness and pain. Intermediate products after degradation of MG are also reported to be carcinogenic [25].

The objectives of this research is to study the comparison and the percentage of dye removal of different forms of coconut fibre (granular and filament form) towards the absorption of methleyene blue and malachite green dye in single dye solution.

2. METHOLODOLGY

2.1. Preparation of Absorbent

Coconut fibers was collected from nearby shop in Jeli, Kelantan and were washed throughly with distilled water and dried at 55°C overnight in oven. Some portion of the fibre were grounded and sieved to the particle size of 150 µm and the rest of the fibre were cutted into the filament form with uniform length at 2.0 cm.

2.2. Preparation of Absorbate

Methylene Blue and Malachite green dye were used in this study as absorbates. The stock solution of MB and MG was prepared by dissolving 1g of dye in 1L of distilled water to give the concentration of 1000 mg/L. Serial dilutions for 50 mg/L were made by diluting dye stock solution in accurate proportions.

2.3. Absorption Process

Dye absorption experiments were performed by taking 50 mL of Methelyne Blue and Malachite Green dye solution with initial concentration 50 mg/L and treated with 0.1 g of dose absorbent in different Falcon tube. The mixture was stirred on rotary orbital shaker at 160 rpm for 2 hours. After that, the dye solution were separated from the absorbent by centrifugation process at 2000 rpm for 5 minutes. The dye removal was determined by spectrophotometer at the wavelength for maximum absorbance (λ max) which is 668 nm and 650 nm for methelyene blue and malachite green, respectively. All experiments were conducted in triplicate and the results stated were the percentage of dye removal. Controls without absorbent were simultaneously carried out to so that the absorption process was due to absorbent and not the wall of the Falcon tube. The percentage removal dye is defined as the ratio of difference in dye concentration before and after absorption (Ci−Ct) to the initial concentration of dye in the aqueous solution (Ci) and was calculated using the equation:

$$\% \text{ Uptake} = (Ci - Ct) \text{ X } 100\% \quad (1)$$

2.4. Effect of Absorbent Dosage and Different Form of Coconut Fibre

The experiments were carried out by taking 50 mL samples of dyes with concentration 50 mg/L in separate Falcon tube and treated with two different form of coconut fibre as absorbent which is granular and filament form with different weight (0.1, 0.2, 0.3, 0.4, 0.5 and 0.6 g).

3. RESULTS AND DISCUSSION

3.1. Effect of Absorbent Dosage (Weight) on the Percentage of Dye Removal for Filament Form of Coconut Fibre in Methylene Blue and Malachite Green Dye

Figure **1** shows the effect of absorbent dosage against percentage dye removal of Methylene Blue

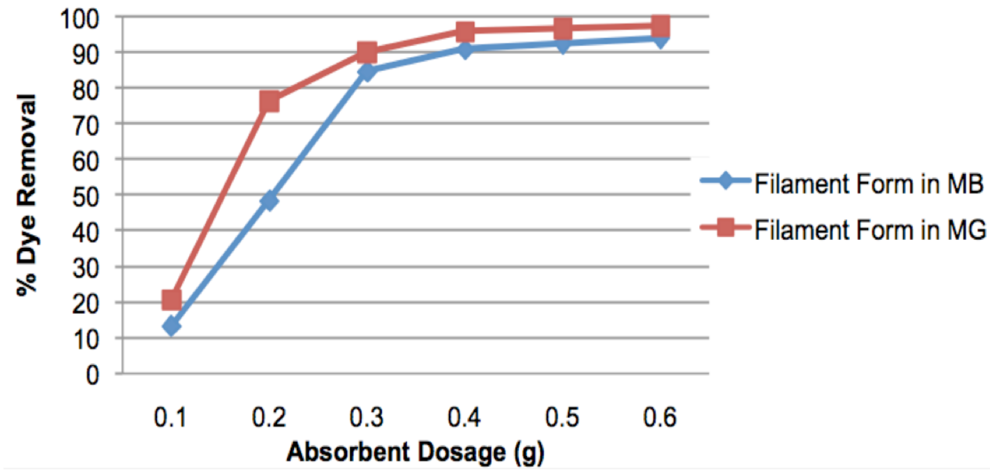

Figure 1: Effect of absorbent dosage on the percentage of dye removal for FFC in MB and MG.

(MB) and Malachite Green (MG) on filament form of coconut fibre (FFC). A series of absorption experiments was carried out with different absorbent dosages (0.1, 0.2, 0.3, 0.4, 0.5 and 0.6 g) at fixed concentration of 50 mg/L at constant the volume of dye solution (50 mL) with constant speed of rotation 160 rpm for 2 hr. Similarly the temperature of the experiment was kept constant at 30°C.

The highest percentage removal of dyes by FFC was at 0.6 g in MB and MG dye. For MB which was 93.9 % and for MG was 97.4 %. The lowest percentage removal of dye by FFC in MB and MG was at 0.1 g which is 13.3 % and 20.7 %. From this comparison, the MG dye was absorbed more effectively by FFC.

The composition of FFC that includes cellulose, hemicelluloses, and lignin contains a large number of hydroxyl groups. Hydroxyl groups play as a important groups in absorbent and adsorbent process [27, 28]. The cationic dye molecules dissociate into positively charged components and absorb on the binding sites of FFC such as hydroxyl groups. In the process of dye absorption, the dye molecules have to first encounter the boundary layer effect, then adsorb from the surface and, finally, they have to diffuse into the porous structure of the adsorbent.

It is clear that the percentage of dye removal is rapid in the initial stages and becomes slow in later stages till saturation is allowed. The final dye removal did not vary significantly after 0.5 g from the start of absorption process. This shows that equilibrium can be assumed to be achieved after 0.5 g absorbent. It is basically due to saturation of the active site which does not allow further absorption to take place. The decrease in absorption capacity with an increase in the absorbent dosage could be ascribed to the fact that some of the absorption sites remained unsaturated during the process [29].

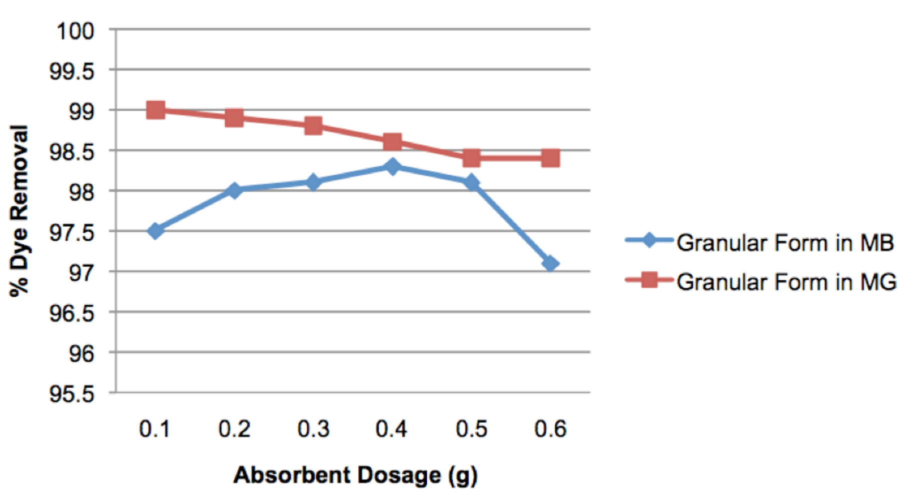

Figure 2: Effect of absorbent dosage on the percentage of dye removal for GFC in MB and MG.

3.2. Effect of Absorbent Dosage on the Percentage of Dye Removal for Granular Form of Coconut Fibre in Methylene Blue and Malachite Green Dye

Figure **2** shows the effect of absorbent dosage against percentage dye removal of Methylene Blue (MB) and Malachite Green (MG) on granular form of coconut fibre (GFC). A series of absorption experiments was carried out with different absorbent dosages (0.1, 0.2, 0.3, 0.4, 0.5 and 0.6 g) at fixed concentration of 50 mg/L at constant the volume of dye solution (50 mL) with constant speed of rotation 160 rpm for 2 hr. Similarly the temperature of the experiment was kept constant at 30°C.

The highest percentage removal of dyes by GFC at 0.4 g in MB and 0.1 in MG dye. For MB which was 98.3 % and for MG was 99.4 %. The lowest percentage removal of dye by GFC in MB and MG was at 0.6 g which was 97.1 % and 98.4 %. The graph shown that the percentage dye removal of GFC in the MB and MG is slightly different. From the comparison, the MG dye was absorbed more effectively by GFC.

The fast uptake of dye at the beginning may be attributed to the rapid attachment of the dye molecules to the surface of the sorbent, followed by slower sorption due to the intraparticle diffusion [30, 31]. The differential uptake of dye also may be influence by their molecular weight of dye. The substances with less molecular weight will diffuse much more faster.

3.3. Effect of Absorbent Dosage on the Percentage of Malachite Green Dye Removal for Granular Form and Filament Form of Coconut Fibre

From Figure **3**, the highest percentage removal of dyes by granular and filament form occurs at 0.1 g and 0.6 g which is 99 % and 97.4 %, respectively. From the comparison, the MG dye was absorbed more effectively by granular form of coconut fibre than the filament form. This may be due to the highest distribution of cellulose in granular form compare to filament form that responsibility in absorption process [29].

From the observation in the granular form, low absorbent dosage show better absorption performance than high absorbent dosage. This increase in absorption with decrease in absorbent dose was due to the availability of more adsorption sites. Another reason may be due to the particle interactive behavior such as aggregation, resulted from high absorbent dosage. Such aggregation would lead to decrease in total surface area of the absorbent and increase in the diffusion path length [32]. The decreasing in the absorption capacity was due to the fact that some of the absorption sites remain unsaturated during the absorption process [33]. When too much absorbent was added into the dye solution, the transportation of dye ions to the active absorption sites will be limited as well, hence reduced the absorption efficiency [34].

3.4. Effect of Absorbent Dosage on the Percentage of Methylene Blue Dye Removal for Granular Form and Filament Form of Coconut Fibre

From Figure **4**, the highest percentage removal of dyes by granular and filament form occurs at 0.4 g and 0.6 g which is 98.3 % and 93.9 %, respectively. The increase in absorption with the increase in absorbent dosage was due to increase in surface area and availability of more absorption site [35]. From the comparison, the MB dye was absorbed more effectively by granular form of coconut fibre than filament form.

For MB dye, granular form of coconut consistently removed almost 100% of the MB dye from the single

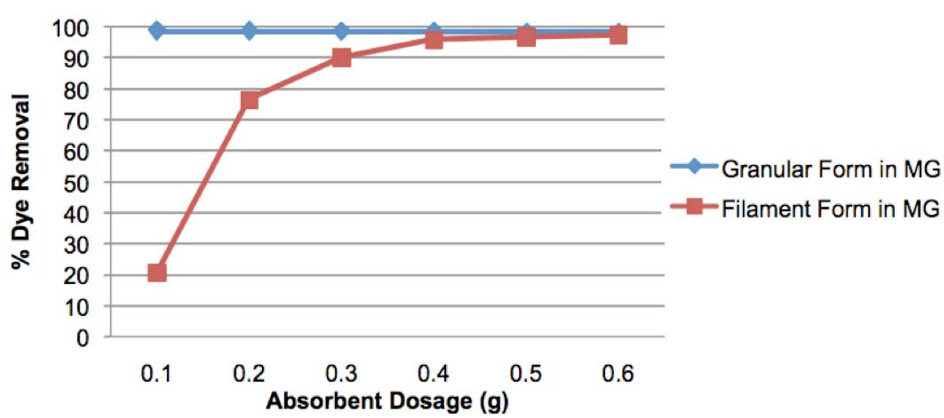

Figure 3: Effect of absorbent dosage on the percentage of MG dye removal for granular form and filament form of coconut husk.

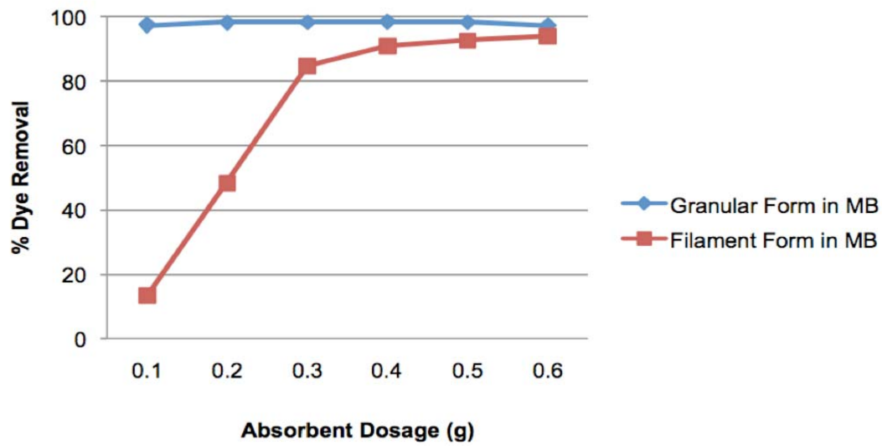

Figure 4: Effect of absorbent dosage on the percentage of MB dye removal for granular form and filament form of coconut husk.

use dye. The percentage of MB removed increased to 98.3 % as the absorbent dosage of the granular form of coconut increased from 0.1 g to 0.4 g while a slightly decrease in absorption was noticed at 0.5 and 0.6 g. This may be due to aggregation of absorption sites resulting indecrease in total absorbent surface area of particles available to MB dye and an increase in diffusion path length [36].

The presence of a higher number of absorption sites on a small mass of the absorbent probably accounts for the reason why small increasing in absorbent dosage had no effect since 0.1 g of absorbent already removed about almost 100%. The higher number of absorption sites on granular form of coconut compared to filament form could probably be as a result of the higher surface area of the granular foam of coconut. The granular form of coconut gave higher percentage absorption when compared to the filament form of coconut husk. This could be as a result of the higher surface area of the granular form of coconut as against the filament form [36].

It was also observed that as absorbent dosage of the filament form of coconut increased, percentage of absorption dye increased. There was found to be a rise in absorption from 13.3 % to 93.3 % as the mass of adsorbent increased from 0.1 to 0.6 g. This may be attributed to increased surface area and availability of more absorption sites [37].

4. CONCLUSION

Coconut fibre husks is a cheap and readily available agricultural byproduct, can be turned into value added product which effectively removed MB and MG dye to nearly 100 %. Furthermore, this study also shown that granular form of coconut fibre husks aborbed MB and MG dye more effectively compared to filament form which may be due to the higher surface area which made readily contacted to the surrounding environment much more better if compared to its filament form.

ACKNOWLEDGEMENT

This research was financially supported by Faculty of Agro Based Industry (FIAT), Universiti Malaysia Kelantan (UMK).

REFERENCES

[1] Saad SA, Daud S, Kasim F, Saleh M. Methylene Blue Removal From Simulated Wastewater By Adsorption Using Treated Oil Palm Empty Fruit Bunch. ICoSM 2007; pp. 293-296.

[2] Setamanit S, Fongsatikul P, Sivadechathep J. ASEAN Achievement and Future Directions in Pollution Control. Ministry of Science, Technology and Environmental, Thailand 2002; p. 33.

[3] Rajeshwari S, Sivakumar S, Senthilkumar P, Subburam V. Carbon from cassava peel, an agricultural waste, as an adsorbent in the removal of dyes and metal ions from the aqueous solution. Bioresource Technol 2001; 80(3): 233-35. http://dx.doi.org/10.1016/S0960-8524(00)00179-6

[4] Lee CK, Low KS, Gan P. Removal of some organic dyes by acid treated spent bleaching earth. Environ Technol 1999; 20: 99-104. http://dx.doi.org/10.1080/09593332008616798

[5] Kumar KV. Optimum sorption isotherm by linear and non-linear methods for malachite green onto lemon peel. Dyes Pigments 2007; 74(3): 595-97. http://dx.doi.org/10.1016/j.dyepig.2006.03.026

[6] Khan AR. Adsorption behavior of citric acid from aqueous solution on activated charcoal. Pak J Sci Ind Res 2002; 45: 82-85.

[7] Malik PK. Use of activated carbons prepared from sawdust and rice husk for adsorption of acid dyes: a case study of Acid Yellow 36. Dyes Pigments 2003; 56: 239-49. http://dx.doi.org/10.1016/S0143-7208(02)00159-6

[8] Mukhtat M, Tahir H. Determination of levels of fluoride and trace metal ions in drinking waters and remedial measures to purify water. Afr J Biotechnol 2008; 6: 2541-49.

[9] Demirbas E, Kobya M, Senturk E, Ozkan T. Adsorption kinetics for the removal of chromium (VI) from aqueous

solutions on the activated carbons prepared from agricultural wastes. Water SA 2004; 30: 535-39. http://dx.doi.org/10.4314/wsa.v30i4.5106

[10] Demirbas E, Kobya M, Oncel S, Sencan S. Removal of Ni (II) from aqueous solution by adsorption onto hazelnut shell activated carbon: equilibrium studies. Bioresour Technol 2002; 84: 291-93. http://dx.doi.org/10.1016/S0960-8524(02)00052-4

[11] Attia AA, El-Hendawy AA, Khedr SA, El-Nabarawy TH. Textural properties and adsorption of dyes onto carbons derived from cotton stalks. Adv Sci Technol 2004; 22: 411-26. http://dx.doi.org/10.1260/0263617042863075

[12] Namasivayam C, Kadirvelu K. Coir pith, an agricultural waste byproduct, for the treatment of dyeing wastewater. Bioresour Technol 1994; 48: 79-81. http://dx.doi.org/10.1016/0960-8524(94)90141-4

[13] Poots VJP, McKay G, Healy JJ. Removal of basic dye from effluent using wood as an adsorbent. J Water Pollution Contr Fed 1978; 50: 926-39.

[14] Sun G, Xie UX. Sunflower stalks as adsorbents for color removal from textile wastewater. Indian Eng Chem Res 1997; 36: 808-12. http://dx.doi.org/10.1021/ie9603833

[15] Khan AR. Adsorption of glycolic and lactic acids from aqueous solutions on charcoal. Pak J Sci Ind Res 1991; 34: 163-66.

[16] Khan AR. Adsorption studies of tartaric acid from aqueous solution on charcoal. Pak J Sci Ind Res 1994; 37: 40-42.

[17] Arami M, Limaee NY, Mahmoodi NM, Tabrizi NS. Removal of dyes from colored textile wastewater by orange peel adsorbent: equilibrium and kinetic studies. J Colloid Interface Sci 2005; 288: 371-76. http://dx.doi.org/10.1016/j.jcis.2005.03.020

[18] Pearce CI, Lloyd JR, Guthrie JT. The removal of colour from textile wastewater using whole bacterial cells: a review. Dyes Pigments 2003; 58(3): 179-96. http://dx.doi.org/10.1016/S0143-7208(03)00064-0

[19] Hamed BH, Din ATM, Ahmed AL. Adsorption of methylene blue onto bamboo-based activated carbon kinetics and equilibrium studies. J Hazardous Mater 2006; 7: 49.

[20] O'Mahony T, Guibal E, Tobin JM. Reactive dye biosorption by Rhizopus arrhizus biomass. Enzyme Microbiol Technol 2002; 31: 456-63. http://dx.doi.org/10.1016/S0141-0229(02)00110-2

[21] Padmesh TVN, Vijayaraghavan K, Sekaran G, Velan M. Biosorption of Acid Blue 15 using fresh water macroalga Azolla filiculoides: batch and column studies. Dyes Pigments 2006; 71(20): 77-82. http://dx.doi.org/10.1016/j.dyepig.2005.06.003

[22] Han R, Zhang L, Song C, Zhang M, Zhu H, Zhang L. Characterization of modified wheat straw, kinetic and equilibrium study about copper ion and methylene blue adsorption in batch mode. Carbohydr Polym 2010; 79(4): 1140-49. http://dx.doi.org/10.1016/j.carbpol.2009.10.054

[23] Altaher H, ElQada E. Investigation of the treatment of colored water using efficient locally available adsorbent. Int J Energy Environ 2011; 2(6): 1113-24.

[24] Anbia M, Ghaffari A. Removal of Malachite Green from Dye Wastewater Using Mesoporous Carbon Adsorbent. J Iran Chem Soc 2011; 8: 67-76. http://dx.doi.org/10.1007/BF03254283

[25] Srivastava S, Sinha R, Roy D. Toxicological effects of Malachite Green. Aquatic Toxicol 2004; 66: 319-29. http://dx.doi.org/10.1016/j.aquatox.2003.09.008

[26] Garg VK, Amita M, Kumar R, Gupta R. Basic dye (methylene blue) removal from simulated wastewater by adsorption using Indian Rosewood sawdust: a timber industry waste. Dyes Pigments 2004; 63(3): 243-50. http://dx.doi.org/10.1016/j.dyepig.2004.03.005

[27] O'Connell DW, Birkinshaw C, O'Dwyer TF. Heavy metal adsorbents prepared from the modification of cellulose: A review. Bioresource Technol 2008; 99: 6709-24. http://dx.doi.org/10.1016/j.biortech.2008.01.036

[28] Jústiz-Smith NG, Virgo GJ, Buchanan VE. Potential of Jamaican banana, coconut coir and bagasse fibres as composite materials. Mater Charact 2008; 59: 1273-78. http://dx.doi.org/10.1016/j.matchar.2007.10.011

[29] Dash B. Competitive Adsorption of dyes (congo red, methylene blue, malachite green) on Activated Carbon. India: Department Of Chemical Engineering National Institute Of Technology, Rourkela 2010.

[30] Hameed BH, Ahmad AL, Latiff KNA. Adsorption of basic dye (methylene blue) onto activated carbon prepared from rattan sawdust. Dyes Pigments 2007; 75: 143-49. http://dx.doi.org/10.1016/j.dyepig.2006.05.039

[31] Banat F, Al-Asheh S, Al-Makhadmeh L. Evaluation of the use of raw and activated date pits as potential adsorbents for dye containing waters. Proc Bioch 2003; 39(2): 193-202. http://dx.doi.org/10.1016/S0032-9592(03)00065-7

[32] Rabia R, Jamil A, Tariq M, Muhammad S, Umer S, Waheed Z. Removal of Murexide (Dye) from Aqueous Media using Rice Husk as an Adsorbent. J Chem Soc Pak 2011; 33(4): 598-603.

[33] Gode F, Pehlivan E. Adsorption of Cr (III) ions by Turkish brown coals. Fuel Proc Technol 2005; 86: 875-84. http://dx.doi.org/10.1016/j.fuproc.2004.10.006

[34] Araujo MM, Teixeira JA. Trivalent chromium sorption on alginate beads. Int Biodeterioration Biodegradation 1997; 40: 63-74. http://dx.doi.org/10.1016/S0964-8305(97)00064-4

[35] Theivarasu C, Mylsamy S, Sivakumar N. Cocoa Shell as Adsorbent for the Removal of Methylene Blue from Aqueous. Univ J Environ Res Technol 2011; 1: 70-78.

[36] Olayinka K, Adetunde O, Oyeyiola A. Comparative analysis of the efficiencies of two low cost adsorbents in the removal of Cr (VI) and Ni (II) from aqueous solution. Afr J Environ Sci Technol 2009; 3(11): 360-69.

[37] Low KS, Lee CK. The removal of cationic dyes using coconut husk as an adsorbent. Pertanika 1990; 13(2): 221-28.

Received on 01-02-2013 Accepted on 07-03-2013 Published on 21-03-2013

http://dx.doi.org/10.6000/1927-5129.2013.09.23