International Journal of Environment 3(2): 126-132, 2014
ISSN: 2077-4508

Adsorption of Methyl Red from Aqueous Solutions Using Activated Carbon Prepared from Coffee Residue

Hossam S. Jahin

Researcher, Chemistry Department, Central Laboratory for Environmental Quality Monitoring (CLEQM), National Water Research Center, Egypt.

ABSTRACT

Coffee residue, which is the waste from coffee agricultures, has been used as a raw material for the preparation of different activated carbons. Activated carbons were prepared from coffee residue by chemical activation with concentrated H_2SO_4 acid; followed by pyrolysis at 400^oC, 500 ^oC and 600 ^oC. Different activated carbons have been prepared for the removal of methyl red dye from aqueous solutions. Batch adsorption experiments were performed as a function of initial dye concentration, contact time, adsorbent dose and pH. Adsorption data were modeled using the Langmuir and Freundlich models. The maximum adsorption of MR dye by coffee residue occurred at an initial pH of 10. Removal efficiency increased with decreasing the dye concentration and increasing dose of adsorbent. The data were in good agreement with both Langmuir and Freundlich isotherms. Since coffee residue, an agriculture solid waste, used in this study, locally available, the adsorption process is expected to be economically for water treatment.

Key words: Reactive dye; Adsorption; Activated carbon; Coffee residue; Wastewater

Introduction

The effluents from textile, leather, food processing, dyeing, cosmetics, paper and dye manufacturing industries are important sources of dye pollution (McKay *et al.,* 1998). Many dyes and their breakdown products may be toxic for living organisms. Therefore, decolorization of dyes becomes an important process in wastewater treatment. However, it is difficult to remove the dyes from the effluent, because dyes are not easily degradable and are generally not removed from wastewater by conventional wastewater systems. Several biological, physical and chemical methods have been used for the treatment of industrial textile wastewater including microbial biodegradation, membrane filtration, oxidation and ozonation (Faur-Brasquet *et al.,* 2003). However, many of these technologies are cost prohibitive, especially when applied for treating large waste streams. Consequently, adsorption techniques seem to have the most potential for future use in industrial wastewater treatment because of their proven efficiency in the removal of organic and mineral pollutants and for economic considerations (Weber, 1978 and Tsai *et al.,* 2001). Activated carbon is perhaps the most widely used adsorbent for the removal of many organic contaminants which are biologically resistant, but activated carbon is prohibitively expensive. The technology to manufacture activated carbon of good quality is not fully developed in developing countries. Moreover, there are many problems connected with the regeneration used activated carbon. Consequently, the high cost of the activated carbon, coupled with the problems associated with regeneration, has necessitated the search for alternate adsorbents. Therefore, there is a need to produce activated carbon from cheaper and readily available materials, which can be used economically on a large scale (Raghuvanshi *et al.,* 2004; McKay *et al.,* 2001; McKay *et al.,* 1997; McKay *et al.,* 1996 and McKay *et al.,* 1987). There is a lack of literature dealing with the possible applications of coffee residues as adsorbents (i.e. for metals (Boonamnuayvitaya *et al.,* 2004 and Azouaou *et al.,* 2010), and in particular as dye adsorbents (Kyzas *et al.,* 2012 and Phatai and Hotthapanid,2014) . Coffee residue from coffee production process is an agricultural solid waste. Normally, coffee residue is disposed by landfill or burnout methods (Boonamnuayvitaya *et al.,* 2005). In this work, activated carbons were prepared from coffee residue by chemical activation with concentrated sulphuric acid at different temperatures. They were used as adsorbents to remove the reactive textile dye: methyl red from aqueous solution. The effect of adsorption parameters such as pH, adsorbent concentration, contact time and initial dye concentration adsorbed by using these carbonaceous materials as low cost adsorbents were also reported.

Corresponding Author: Hossam S. Jahin, Researcher, Chemistry Department, Central Laboratory for Environmental Quality Monitoring (CLEQM), National Water Research Center, Egypt.
E-mail: hossam_gahin@hotmail.com

Int. j. Environ. 3(2): 126-132, 2014

Materials and Methods

2.1. Materials:

Methyle red, an anionic dye is a product of LOBA Company, Egypt. It was used as received without further purification. The structure of the dye is presented in Fig. 1. A stock solution of Methyl red (25 mg/ L) was prepared and suitably diluted to the required initial concentration. A calibration curve of absorbance versa concentration was constructed using a UV spectrophotometer (Shimadzu Model: UV 1601) at maximum wavelength of 525 nm. All chemicals were of analytical reagent grade.

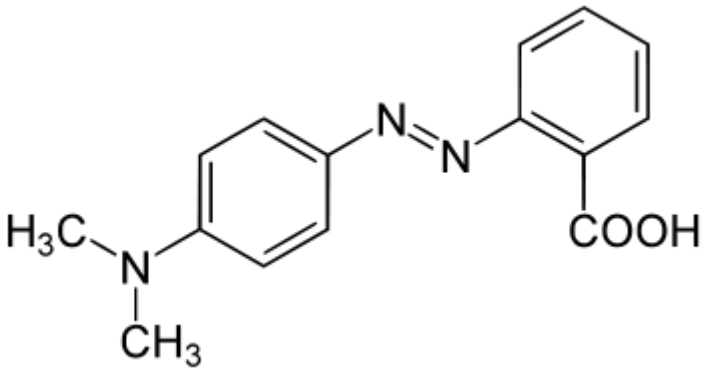

Fig. 1: methyl red structure

2.2. Adsorbent preparation:

The coffee residues were washed several times with distilled water and were left to dry, then they were grained and sieved to an average particle size (0.05 mm). The raw materials were subjected to chemical treatment followed by pyrolysis. The activation was carried out using conc. H_2SO_4 solution, where the sample was heated in H_2SO_4 at hot plate (70 ^{0}C) for 30 minutes, then it was washed with distilled water several times until pH reaches to 4 then the sample was dried at 100 ^{o}C then pyrolysis in a muffle furnace in absence of air at 400 ^{0}C, 500 ^{0}C and 600 ^{0}C for 1 h. After pyrolysis the sample was washed with distilled water to pH 7 if not sodium bicarbonate (0.1M) will be added until required pH, and then the sample washed again with distilled water and dried at 100 ^{0}C, then the activated carbon was obtained.

2.3. Adsorption studies:

Batch adsorption experiments were carried out at room temperature (25 ^{o}C ±2). Exactly 25 ml of dye solution of known initial concentration (25 mg/ l) was stirred at the constant agitation speed with a required dose of adsorbents (0.05 g/ l) for a specific period of contact time (10–100 min) in a mechanical stirrer. The pH of the solutions was adjusted to the required value by adding either 0.5 M HCl or 0.1 M NaOH solution. After equilibrium, the final concentrations (Ce) were measured. The percentage removal of dye was calculated using the following relationship:

$$\% \text{ Removal of dye} = \frac{Ci - Ce}{Ci} \times 100 \quad (1)$$

Where, *C*i and *C*e are the initial and final (equilibrium) concentrations of dye (mg/ l), respectively. Blanks containing no dye were used for each series of experiments as controls.

Results and Discussion

3.1. Investigation of adsorption parameters:

3.1.1. Effect of initial concentration of methyl red (MR) dye:

The effect of initial concentration of MR dye on the percentage of removal of dye on various adsorbents was studied as shown in Fig. 2. The removal percentage of the dye was found to decrease with the increase in initial dye concentration. This indicates that there were reductions in immediate solute adsorption, owing to the lack of available active sites required for the high initial concentration of (MR). Similar results have been reported in literature (Kannan and Sundaram, 2001). The results show that the removal percentage of dye

decreases from 98% to 89%, 93.5% to 74.2% and from 86.3% to 60.5% as the initial dye concentration increases from 5 up to 50 mg/l for activated carbon (AC) dose of 0.05 g of AC1 (at 400 ^{0}C), AC2 (at 500 ^{0}C) and AC3 (at 600 ^{0}C) respectively.

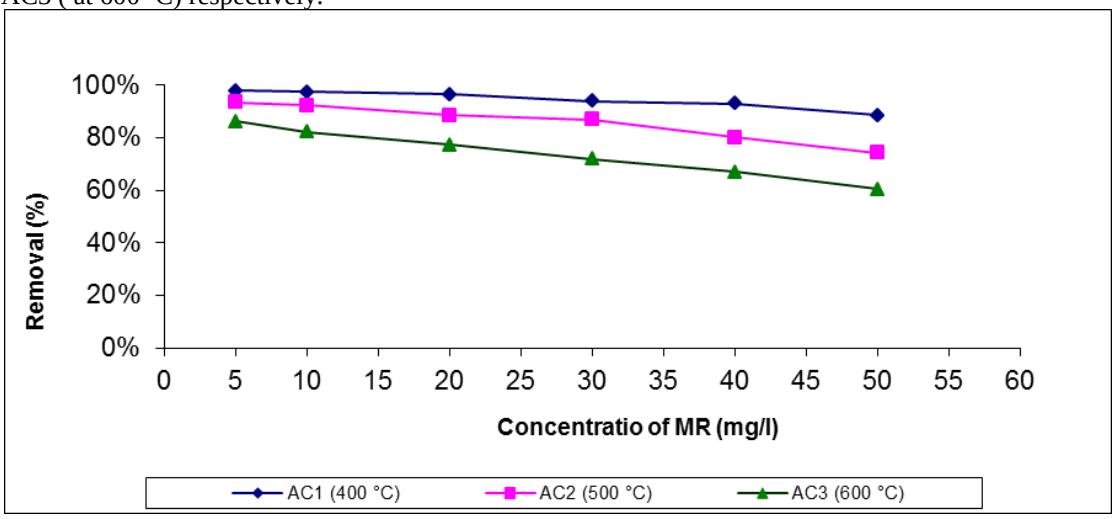

Fig. 2: Effect of initial concentration of methyl red (MR) dye

3.1.2. Effect of dose of activated carbons:

The effect of dose of activated carbons on the removal percentage of MR dye is shown in Fig.3. The percentage removal of MR increased with the increase in dose of adsorbent. This may be due to the increase in availability of surface active sites resulting from the increased dose and conglomeration of the adsorbent (Kannan and Sundaram, 2001 and Garg *et al.,* 2003).

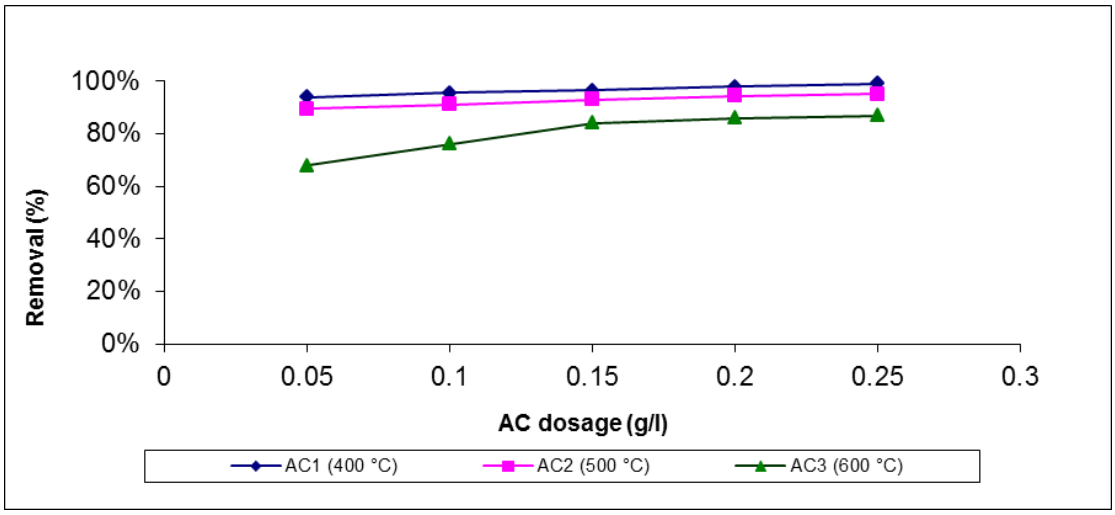

Fig. 3: Effect of dose of adsorbent on dye removal

3.1.3. Effect of contact time:

The effect of contact time on the removal percentage of MR dye was investigated at initial dye concentration (25 mg/l) as shown in Fig. 4. The removal percentage of dye by different activated carbons was slow in the beginning but it gradually increased with time until it reached equilibrium. The rate of removal is lower in the beginning due to smaller surface area available of adsorbent. After adsorption, the rate of dye the uptake is controlled by the rate of dye transported from the exterior to the interior sites of adsorbent particles.

Int. j. Environ. 3(2): 126-132, 2014

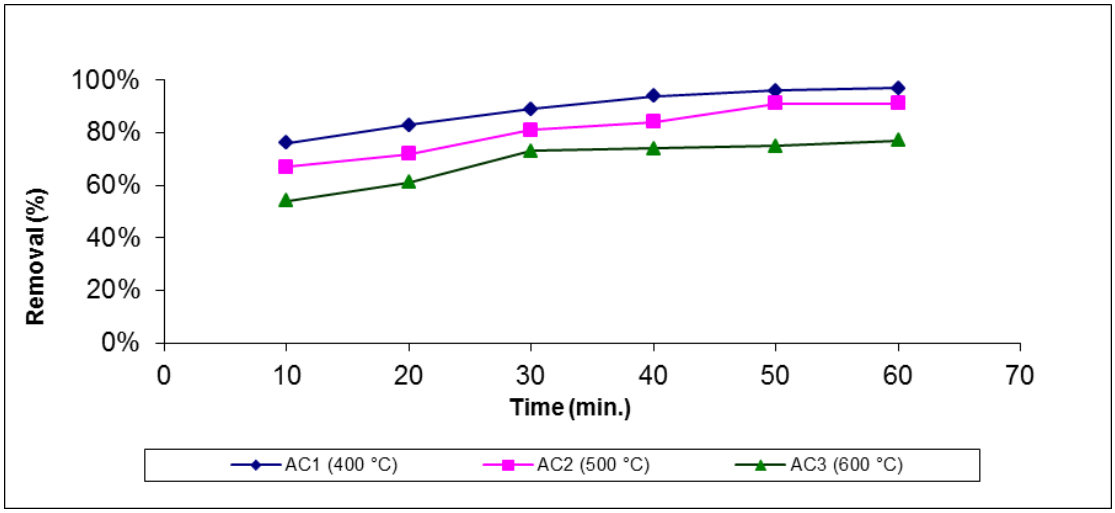

Fig. 4: Effect of time on the removal of dye

3.1.4. Effect of pH:

The effect of initial pH of dye solution on the removal percentage of MR was studied by varying the initial pH under constant process parameters. The results are shown in Fig.5. The dye adsorbed by different types of carbons was higher at higher pH. The optimum pH was attained at pH of ten. As the pH of the solution increase the dye adsorbed increased considerably. The same behavior was observed by many authors (Nigam *et al.*, 2000 and Senthilkumaar *et al.*, 2006).

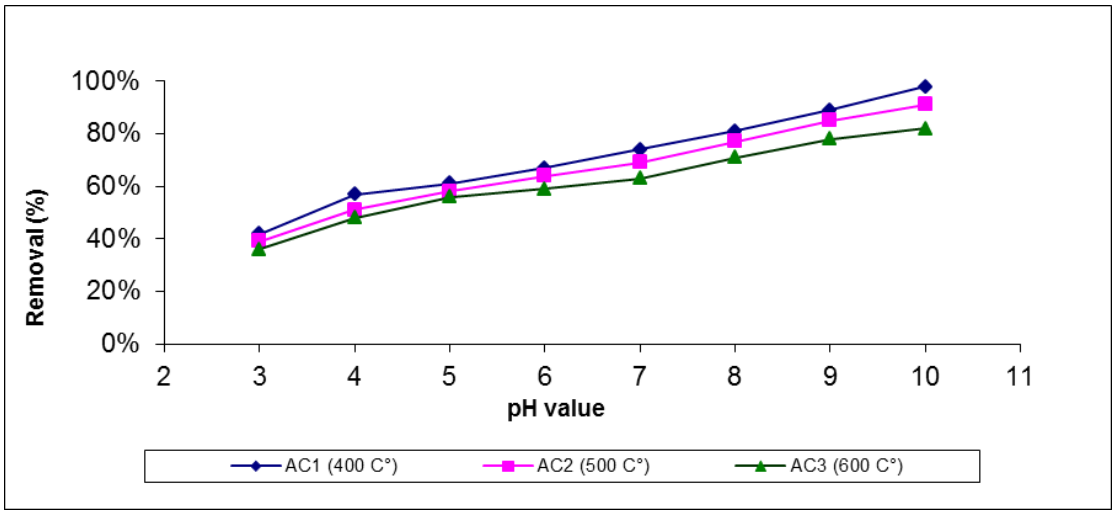

Fig. 5: Effect of the different pH value on the removal of MR dye

3.2. Adsorption isotherms:

In order to optimize the design of an adsorption system to remove the dye, it is important to establish the most appropriate correlations for the equilibrium data for each system. Two isotherm models have been tested in the present study; Langmuir and Freundlich models.

4.2.1. Langmuir model:

Langmuir isotherm model assumes the uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface (Khezami and Capart, 2005). The linearization form of the equation is:

Int. j. Environ. 3(2): 126-132, 2014

$$\frac{Ce}{qe} = \frac{1}{Qob} + \frac{1}{Qo} Ce \quad (2)$$

Where:

C_e: The equilibrium concentration of the adsorbate (mg/l).

q_e: The amount of adsorbate adsorbed per unit mass of adsorbent (mg/g)

Q_o and b: are Langmuir constants related to the adsorption capacity and the rate of adsorption, respectively. The linear plots of *Ce*/*qe* vs. *Ce* show that the adsorption obeys Langmuir isotherm model for all adsorbents (Fig.6).

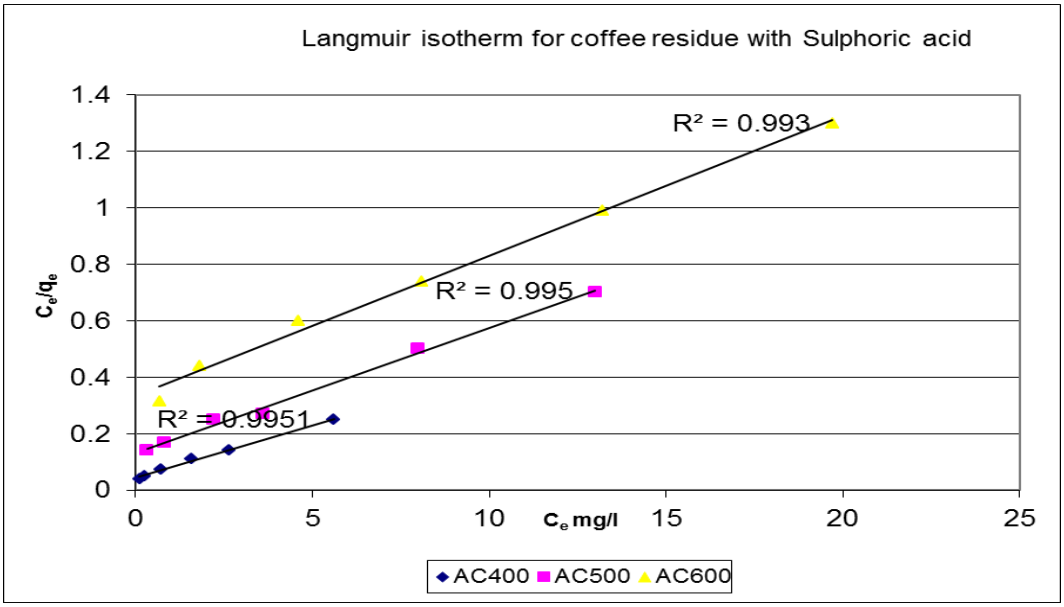

Fig. 6: Langmuir isotherm for adsorption of MR dyes different adsorbents.

3.2.2. Freundlich model:

The Freundlich adsorption model stipulates that the ratio of solute adsorbed to the solute concentration is a function of the solution. The empirical model was shown to be consistent with an exponential distribution of active centers, characteristic of heterogeneous surfaces.

The Freundlich equation has the general form (Casey,1992 and Ludersen,1983).

$$q_e = x/m = kC_e^{1/n} \quad (3)$$

Where:

q_e : The amount of adsorbate adsorbed per unit mass of adsorbent (mg/g)

X : The mass of the adsorbate. (mg)

m: The mass of the adsorbent. (mg)

C_e: equilibrium concentration of the solute remaining in solution. (mg/l)

K and n: are Freundlich constants (Tan *et al.*, 2007).

The equation which is more useful in logarithmic form is:

$$\log(q_e) = \log(x/m) = \log(k) + \frac{1}{n} \log C_e \quad (4)$$

The amount of solute adsorbed, qe, is related to the equilibrium concentration of solute in solution, Ce.

The results in figure 6,7 illustrated that Regression coefficients (R^2) for Langumir and Freundlich models for different conditions were larger than 0.95, indicating that both the models fit reasonably well with the methyl red dyes adsorption.

Int. j. Environ. 3(2): 126-132, 2014

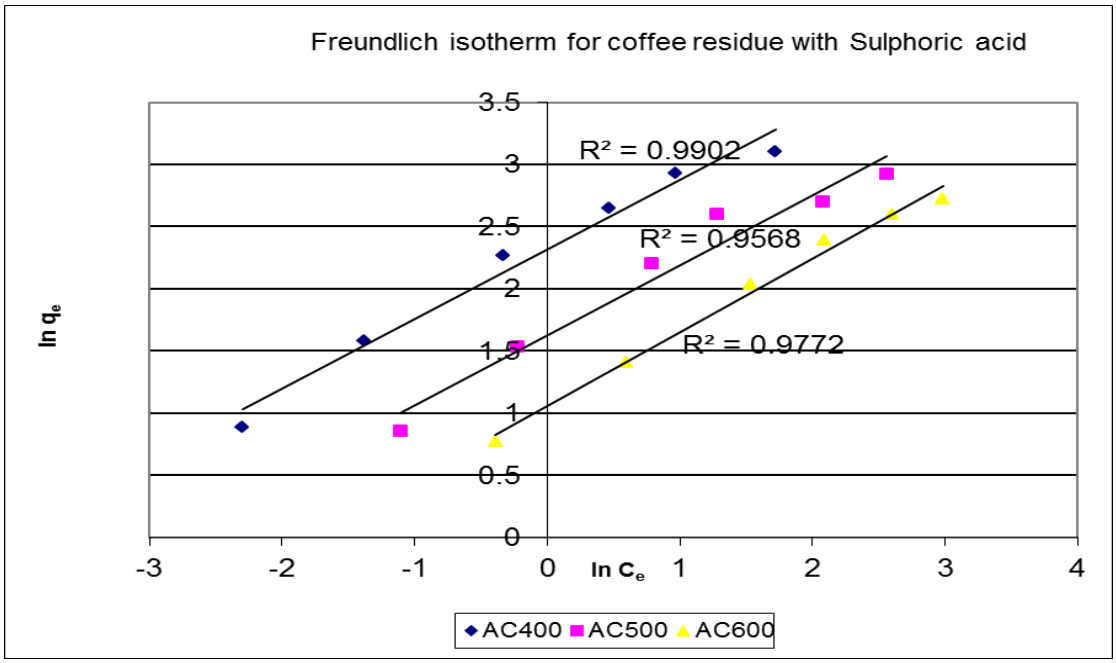

Fig. 7: Freundlich isotherm for adsorption of MR dyes on different adsorbents.

Conclusions:

In this work, three different activated carbons were prepared from coffee residue have been used successfully as an adsorbing agent for the removal of (MR) dye from aqueous solutions. Adsorption was influenced by various parameters such as initial pH, initial dye concentration and dose of adsorbent. The maximum adsorption of MR dye by coffee residue occurred at an initial pH of 10. Removal efficiency increased with decreasing the dye concentration and increasing dose of adsorbent. The Langmuir and Freundlich adsorption isotherm models were used for the description of the adsorption equilibrium of MR dye onto carbon of coffee residue. The data were in good agreement with both Langmuir and Freundlich isotherms. Since coffee residue, an agriculture solid waste, used in this study, locally available, the adsorption process is expected to be economically for water treatment.

References

Azouaou, N., Z. Sodoui, A. Djaafri, H. Mokaddem, 2010. Adsorption of cadmium from aqueous solution onto untreated coffee grounds: equilibrium, kinetics and thermodynamics, journal of Hazaard Materials Matter., 184: 126-134.

Boonamnuayvitaya, V., C. Chaiya, W. Tanthapanichakoon, S. Jarudilokkul, 2004. Removal of heavy metals by adsorbent prepared from pyrolyzed coffee residues and clay, Separation and Purification Technology, 35: 11-22.

Boonamnuayvitaya, V., S. Sae-ung, W. Tanthapanichakoon, 2005. Preparation of activated carbons from coffee residue for the adsorption of formaldehyde, Separation and Purification Technology, 42: 159-168.

Casey, T.J., 1992. Unit Treatment Processes in Water and Wastewater Engineering, Wiley Series, New York, The International Conference on Water and the Environment.

Faur-Brasquet, C., P. Le Cloirec, H. Pignon Metivier, 2003. Adsorption of dyes onto activated carbon: approach of adsorption mechanisms and coupling of AC with ultra filtration to treat coloured wastewaters, Separation Purification Technolology, 31: 3-11.

Garg, V.K., R. Gupta, A.B. Yadav, R. Kumar, 2003. Dye removal from aqueous solution by adsorption on treated saw dust, Bioresource Technology, 89: 121-124.

Kannan, N., M.M. Sundaram, 2001. Kinetics and mechanism of removal of methylene blue by adsorption on various carbons - a comparative study, Dyes Pigments, 51: 25-40.

Khezami, L., R. Capart, 2005. Removal of chromium (VI) from aqueous solution by activated carbons: kinetics and equilibrium studies, Journal of Hazarded Materials B 123: 223-231.

Kyzas, G., N. Lazaridis, A. Mitropoulas, 2012. Removal of dyes from aqueous solutions with untreated coffee residues as potential low-cost adsorbents: equilibrium, reuse and thermodynamics approach, Chemical Engineering Journal, pp: 189-190.

Ludersen, A.L., 1983. Mass Transfer in Engineering Practice, John Wiley and Sons, New York, chapter 7 .

McKay, G., G. Chl Wal Hul, G. Buning Chen, 2001. Film-pore diffusion modeling and contact time optimization for the adsorption of dyestuffs on bagasse pith, Chemical Engineering Journal, 84: 77-94.

McKay, G., J.F. Porter, G.R. Prasad, 1998. The removal of dye colours from aqueous solutions by adsorption on low-cost materials, Water, Air and Soil Pollution, 114: 423-438.

McKay, G., M. El Geundi, M.M. Nassar, 1987. Equilibrium studies during the removal of dyestuffs from aqueous solutions using bagasse pith, Water Research, 21: 1513-1520.

McKay, G., M. El-Geundi, M.M. Nassar, 1997. Adsorption model for the removal of acid dyes from effluent by bagasse pith using a simplified isotherm, Adsorption Science Technology, 15: 737-752.

McKay, G., M. El-Geundi, M.M. Nassar,1996. Pore diffusion during the adsorption of dyes onto bagasse pith, Process Safety Environment Protectection, 74: 277-288.

Nigam, P., G. Armour, I.M. Banat, O. Singh, R. Marchant, 2000. Physical removal of textile dyes from effluents and solid-state fermentation of dye adsorbed agricultural residues, Bioresource Technology, 72: 219-226.

Phatai, P.S. Utara, N. Hotthapanid, 2014. Removal of methyl violet by adsorption onto activated carbon derived from coffee residues, Advanced Materials Research, 864-867: 710-717.

Raghuvanshi, S.P., R. Singh, C.P. Kaushik, 2004. Kinetics study of methylene blue dye bioadsorption on bagasse, Applied Ecology Environment Research, 2: 35-43.

Senthilkumaar, S., P. Kalaamani, K. Porkodi, P.R. Varadarajan, C.V Subburaam, 2006. Adsorption of dissolved reactive red dye from aqueous phase onto activated carbon prepared from agricultural waste, Bioresource Technology, 97: 1618-1625.

Tan, I.A.W., A.L. Ahmad, B.H. Hameed, 2007. Adsorption of Basic Dye using Activated Carbon Prepared from Oil Palm Shell: Batch and Fixed Bed Studies, Desalination, 225: 13-28.

Tsai, W.T., C.Y. Chang, M.C. Lin, S.F. Chien, H.F. Sun, M.F. Hsieh, 2001. Adsorption of acid dye onto activated carbons prepared from agricultural waste bagasse by $ZnCl_2$ activation, Chemosphere., 45: 51-58.

Weber, W.J., 1978. Physico-Chemical Methods of Treatment of Water and Wastewater, John Wiley and Sons Inc.