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FACTORS AFFECTING THE REMOVAL OF A BASIC AND AN AZO DYE FROM ARTIFICIAL SOLUTIONS BY ADSORPTION USING ACTIVATED CARBON

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Abstract

Decolourisation of wastewater, particularly from textile industries, is one of the major environmental concerns these days. Current methods for removing dyes from wastewater are costly and cannot effectively be used to treat wide range of such wastewater. This work describes the use of commercially available granular activated carbon (GAC) as an efficient adsorbent material for dyes' removal. Aqueous solutions of various concentrations of the basic dye Methylene Blue (MB) and the azo-dye Tartrazine at 5-20 $mg.L^{-1}$ and 10-100 $mg.L^{-1}$, respectively, were shaken with certain amount of GAC to determine the adsorption capacity and removal efficiencies. The effects of adsorbent dose, initial pH, initial dye concentration, agitation speed, and contact time on dyes' removal efficiencies have been studied. Maximum dye concentration was removed from the solution within 60-90 min. after the beginning of every experiment. Adsorption parameters were found to fit well into Langmuir and Freundlich adsorption isotherm models with correlation coefficient ($R^2 > 0.99$) in the concentration range of MB and TZ studied.

Keywords: Activated carbon, Adsorption, Methylene Blue, Tartrazine.

1. Introduction

A large number of synthetic dyes have been produced for the purpose of industrial and domestic applications for many years. Most of them have been found to be toxic and carcinogenic. These dyes may enter the aquatic environment from industrial and municipal effluent [1].

The decolourisation of industrial effluents is a challenging and fundamental task related to pollution control, mainly in textile industries. However, the textile industry plays a part in the economy of several countries around the world. The process of dyeing causes the production of more or less coloured wastewater [2]. Effluents discharged from textile and dyeing industries are of low biological oxygen demand (BOD) and high chemical oxygen demand (COD). Disposal of highly coloured waste into receiving water can be toxic to aquatic life. The dyes impede light penetration and upset the biological activity [3]. Dyes also pose a problem because it may be toxic to some organisms and can cause severe damage to human beings, such as dysfunction of kidney, liver, and central nervous system [4, 5]. The treatment of dye bearing effluents is considered to be very complicated process because of its heterogeneous mixtures of many pollutant substances ranging from organic pesticides to heavy metals. In addition, these substances are considered to be non-biodegradable and persistent [6].

Various treatment methods have been applied and investigated by many researchers for treating dye-bearing effluents including, physical, physico-chemical, and chemical processes [7-10]. All these methods have different colour removal capabilities, capital costs, and operating rates. Among these processes, adsorption has been found to be superior compared to other techniques for wastewater treatment in terms of initial cost, simplicity of design, ease of operation, and insensitivity of toxic substances [11]. Activated carbon is the most widely used adsorbent with great success because of its high adsorption capacity comparable to its low cost of production [12].

Activated carbons are multilateral adsorbents and have wide range of applications most of which is dedicated to the removal of pollutant species by adsorption from the liquid and gas phases.

Activated carbons are highly effective in removal of contaminants because of their large surface area, microporous structure, high adsorption capacity, and high degree of surface reactivity. The importance of activated carbons' applications is related to its use in removal of colour, odour, taste, and other undesirable organic impurities from potable water, in the treatment of domestic and industrial wastewater, solvent recovery, air purification in inhabited spaces such as restaurants, food processing and chemical industries, in air pollution control, and in a variety of gas-phase applications [13-16].

The present study was undertaken to evaluate and compare the efficiency of the activated carbon for the removal of the basic dye (Methylene Blue, MB) and the azo-dye (Tartrazine, TZ) from aqueous solution. The removal efficiency was determined to study the effects of contact time, initial concentration of dye solution, pH, adsorbent dosage, and agitation rate.

2. Experimental

2.1. Materials and apparatus

The dyes used in this study were methylene blue dye (molecular formula: $C_{16}H_{18}N_3ClS$, Fig. 1,. left) and Tartrazine (molecular formula: $C_{16}H_9N_4Na_3O_9S_2$, Fig. 1, right) supplied by Morgan Chemical Company and were used without further purification. Other reagents include diluted HCl and NaOH solutions. All reagents were of analytical grade. Distilled water was used throughout the experiments. The dyes' concentrations were determined using Agilent UV-Vis Cary 60 PC scan double beam recording spectrophotometer using 1-cm glass cells. A digital pH meter, type 720 WTW 82362, was used to monitor the pH value during adjusting with either the acidic or basic solution.

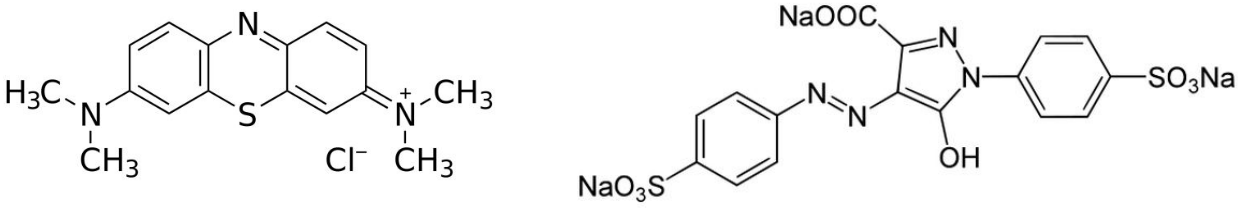

Figure 1. Chemical structures of methylene blue (MB, left) and tartrazine (Tz, right).

2.2. Preparation of the adsorbent

Commercially available activated carbon (500 µm ≤ D ≤ 2mm), supplied by Morgan Chemical Company, was used as the adsorbent without further chemical treatment. A measured quantity of the sample was immersed in hot water for three hours. The washed activated carbon was filtered and oven-dried at 60 °C for 2 hours and then heated to 200 °C for 3 hours under N_2 flow.

2.3. Physical characterisation of activated carbon

The properties of the activated carbon adsorbent including particle size, density, pore volume, and porosity were determined according to the method of American Standard for Testing & Materials (ASTM). The apparent surface area was measured from N_2 adsorption at 77 K in a Quantrachrome Autosorb I-CLP. Total surface areas were calculated using the BET equation [12]. The values for density, total pore volume and BET surface area are 0.447 g cm^{-3}, 0.124 cm^3 g^{-1} and 776 m^2 g^{-1} respectively.

2.4. Preparation of dye solution

A stock solution of the dye was prepared by dissolving 1.0 g of the dye in 1000 mL of distilled water to make a stock solution of 1000 mg L^{-1}. The experimental solution was prepared by diluting definite volume of the stock solution to get the desired concentration. For absorbance measurements, UV-Vis double beam spectrophotometer with PC-scanning facility (Agilent, Inc) was employed;

the activated carbon was filtered before sampling. The maximum wavelength λ_{max} for the methylene blue was measured at 664 nm, while for tartrazine it was at 425 nm. Concentrations were determined from a standard calibration curve.

2.5. Adsorption procedure

The adsorption isotherms have been determined by mixing dyes' solution (100 mL) of known initial concentration of MB (2-20 ppm) and TZ (10-100 ppm) with varied amounts of adsorbents (0.2-1.5 g) using several volumetric flasks. The adsorption behaviours of the samples were studied by evaluating the percentage removal efficiency of methylene blue and tartrazine calculated as the following:

$$\text{Removal efficiency} = [\frac{(C_0 - C)}{(C_0)}] x 100 \tag{1}$$

Where C_0 is the initial concentration of methylene blue, C is the solution concentration after adsorption at any time.

The amount of dye adsorbed per gram of adsorbent (q_e) was calculated as follows:

$$q_e = \frac{V}{m}(C_e - C_0) \tag{2}$$

Where C_o and C_e are initial and equilibrium dye concentrations, respectively (mg L^{-1}), V is dye solution volume (L); m is the mass of adsorbent (g).

The effect of adsorption time on the dye removal at various predetermined intervals from (10-120 min.) using a double beam UV-Vis spectrophotometer with PC scanning facility for measurement of concentration at λ_{max}= 664 nm for methylene blue and λ_{max}= 425 nm for tartrazine was monitored by shaking the reaction mixture and analysing for the dye content at the end of each contact time. The removal efficiency was determined to study the effects of contact time, initial concentration of dye solution and pH, adsorbent dosage, temperature, and agitation rate.

3. Results and Discussion

3.1. Effect of the contact time

The effect of contact time on the adsorption capacity of two dyes by activated carbon was conducted through batch experiments to achieve the equilibrium as shown in Fig. 3. The mechanism of colour removal can be described by the migration of the dye molecule from the solution to the adsorbents particle and diffusion through the surface. The results showed that equilibrium was reached within 90 min. of operation for activated carbon. The adsorption capacity was constant thereafter in the case of both adsorbate observed.

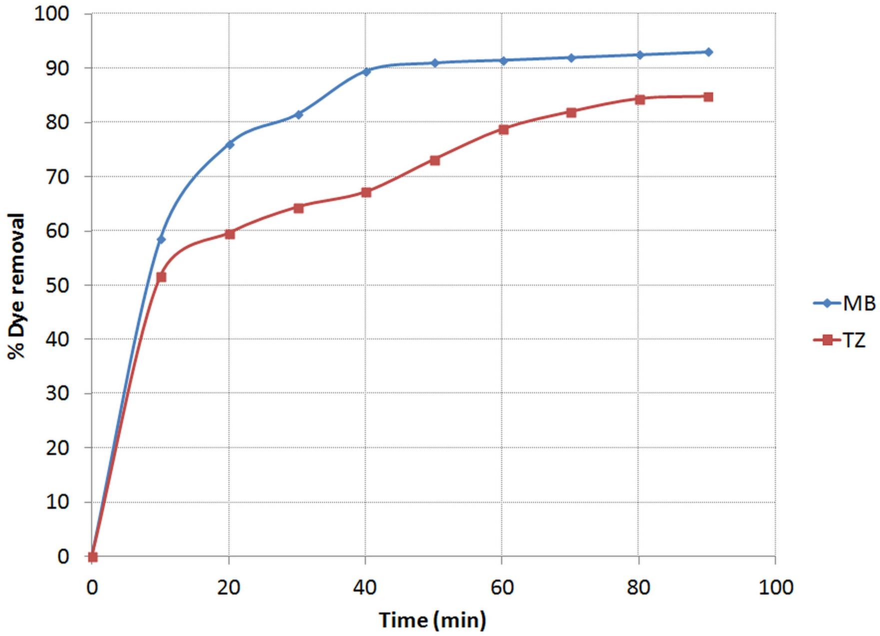

Figure 3. Effect of contact time on the percent removal of MB (20 ppm) and TZ (100 ppm) with activated carbon, 0.5 g of AC, agitation speed, 100 rpm,T= 25 °C and 100 mL solution.

3.2. Effect of initial concentration

The effect of initial concentration of methylene blue (5-20 mg L^{-1}) and tartrazine (25-100 mg L^{-1}) on the removal efficiency using activated carbon are shown in Figs. 4 and 5. The experiments were carried out at fixed adsorbent dose (0.5 g), at room temperature (25 ±1 ºC), neutral pH (7.0), and 100 rpm agitation speed.

The effect of the initial dye concentration depends on the immediate relation between the dye concentration and the available binding sites on an adsorbent surface [17]. Figs. 4 and 5 show the effect of initial dye concentration. Generally the percentage of dye removal decreases with an increase in initial dye concentration, which may be due to the saturation of adsorption sites on the adsorbent surface [11]. At low concentration, there will be unoccupied active sites on the adsorbent surface, and when the initial dye concentration increases, the active sites required for adsorption of the dye molecules will disappear [18]. However, the increase in the initial dye concentration will cause an increase in the loading capacity of the adsorbent and this may be due to the high driving force for mass at a high initial dye concentration [19]. In other words, the residual concentration of dye molecules will be higher for higher initial dye concentrations. In the case of lower concentrations, the ratio of initial number of dye molecules to the available adsorption sites is low and subsequently the fractional adsorption becomes independent of initial concentration.

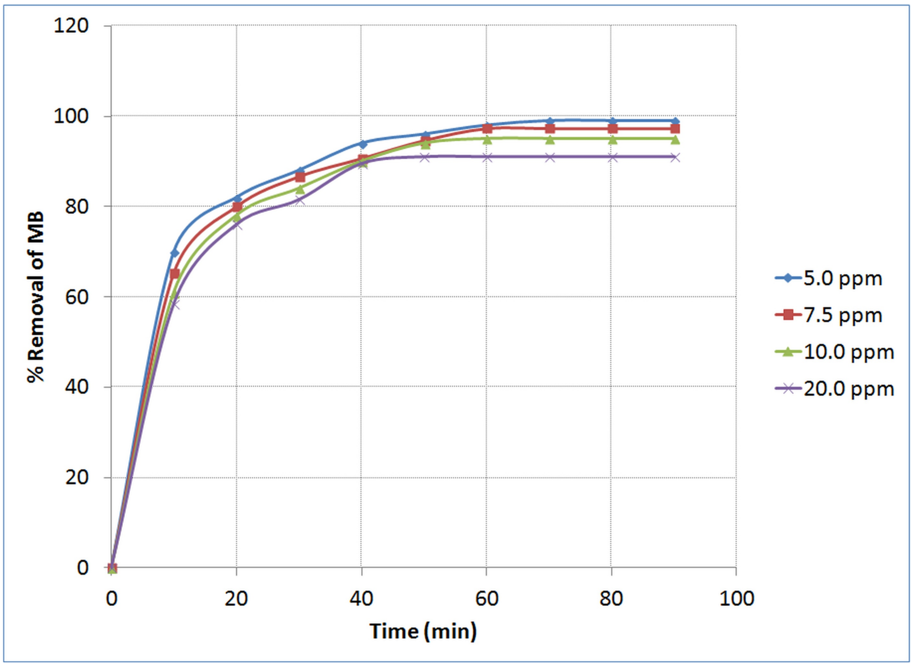

Figure 4. Effect of initial MB concentration on the dye removal efficiency, 0.5 g of AC, agitation speed, 100 rpm,T= 25 °C, and 100 mL solution.

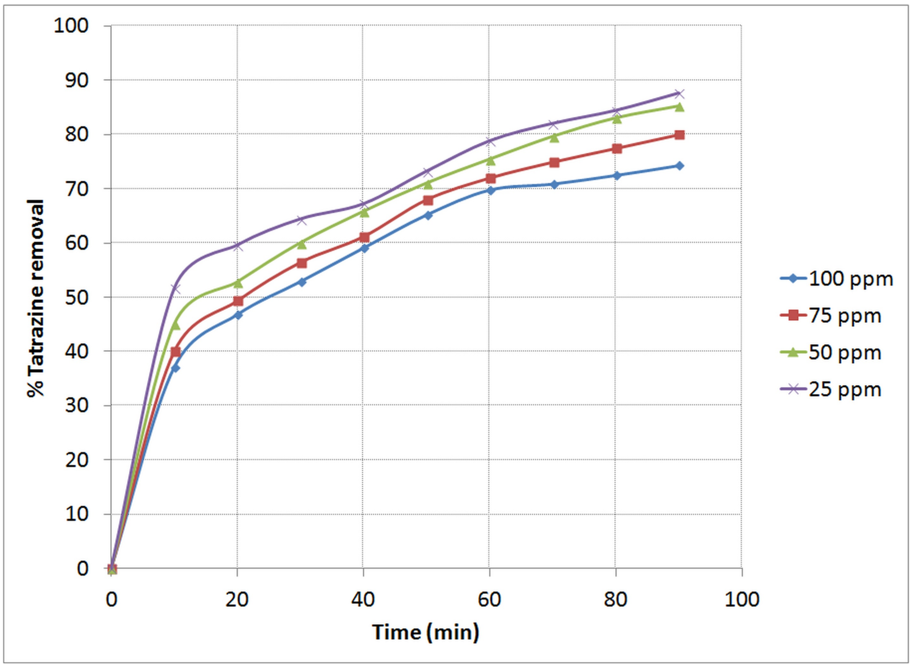

Figure 5. Effect of initial TZ concentration on the dye removal efficiency, 0.5 g of AC, agitation speed, 100 rpm,T= 25 °C, and 100 mL solution.

3.3. Effect of the adsorbent mass

The effect of Activated Carbon (AC) amount on the uptake of the dye was measured for dye concentration 10 mg L^{-1} of MB and 100 mg L^{-1} of TZ, different shaking time (10-120 min), and different quantity of AC (0.2, 0.5, 1.0, and 1.5 g) at pH = 7.0 and at room temperature (25±1 ºC). The results are shown in Figs. 6 and 7. In general, it was found that by increasing the amount of the adsorbent, the adsorption rate increased. This increase was most significant when the amount of adsorbent was increased (0.5-1.5 g). Maximum dye removal was achieved within 60-90 minutes after which a decrease in dye concentration was negligible. Increase in dye removal percentage with adsorbent dose can be attributed to increased adsorbent surface area and availability of more adsorption sites. At the beginning of the process, the rate of dye removal by the AC was fast during the first 30 min and then decreased gradually.

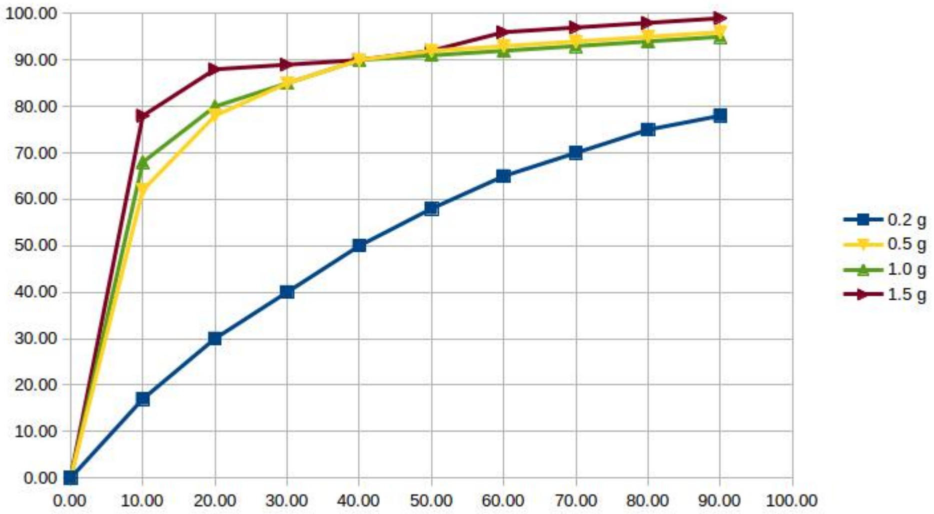

Figure 6. Effect of the amount of AC on the removal efficiency of MB, 10 ppm, 100 rpm, T=25 ^{O}C, and solution volume = 100 mL.

3.4. Effect of pH

The pH value of the solution is an important parametre for the adsorption processes, and the initial pH value of the solution has significant influence compared to the final pH. To study the effect of pH on MB and TZ adsorption, the experiments were carried out at 10 mg L^{-1} initial dye concentration of MB and 100 mg L^{-1} with 0.5 g of adsorbent dosage at (26 ±1 ºC). In this study, a selection among pH values 3.0, 6.8, and 10.0 was suggested based on the fact that most of practical applications are within this range (industries. workshops, etc.). Figs. 8 and 9 show the relationship between the pH value and the removal of MB and TZ.

It can be seen from Fig. 8 that as the solution pH increases, the removal increases as well. Increasing the solution pH increases the number of hydroxy groups, thus increases the number of negatively charged sites and enlarges the attraction between MB dye and adsorbent surface [3, 17].

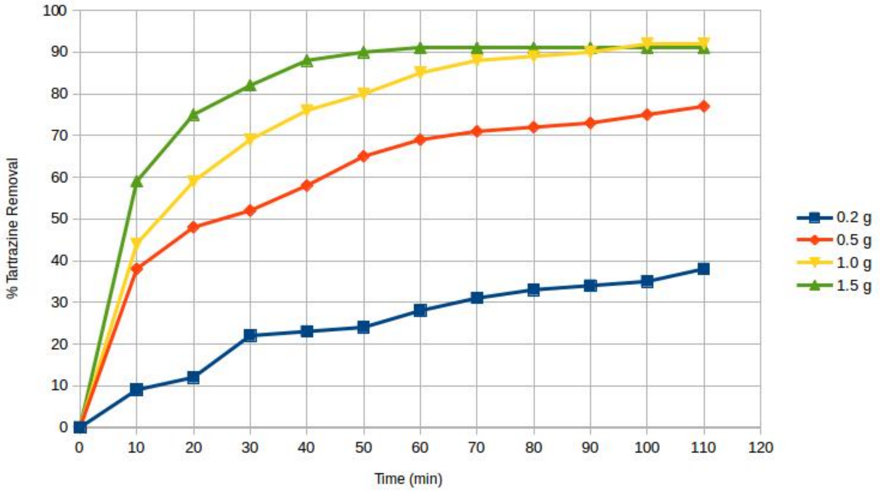

Figure 7. Effect of the amount of AC on the removal efficiency of TZ, 100 ppm, agitation speed, 100 rpm, T=25 °C, and solution volume = 100 mL.

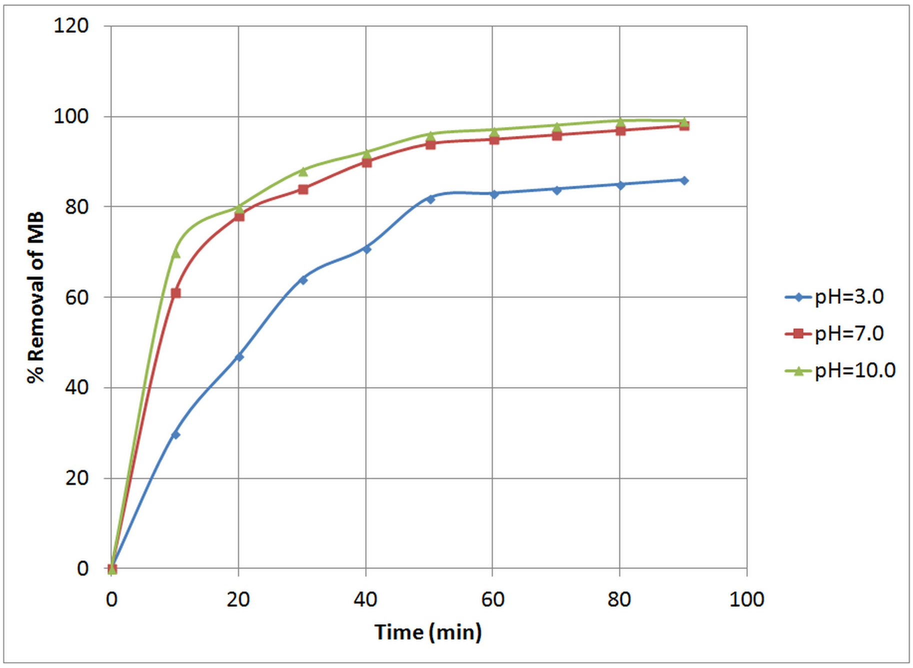

Figure 8. Effect of pH on the removal efficiency of MB,10 ppm, agitation speed, 100 rpm, T=25 °C, and 100 mL solution.

Tabrez *et al*. used fly ash as low-cost adsorbent for the removal of Methylene Blue, Malachite Green, and Rhodamine B dyes from textile wastewater [20]. In their work, they found that the adsorption of dyes increases from 0.426 to 0.467, and 0.232 to 0.394, and 0.286 to 0.367 mg g^{-1} for methylene blue, malachite green, and Rhodamine B, respectively, as the pH was increased from 3.0 to 9.0 [20]. Fig. 7 shows that as the pH increased, the efficiency of the TZ removal decreased. This may be attributed to the fact that the adsorption of TZ dye which contains OH functional group is favoured by the decrease in pH.

Therefore, adsorption may be due to hydrogen bonding, Van der Waals forces, and others. In general, initial pH value may enhance or depress the uptake. This is attributed to the charge of the adsorbent surface with the change in pH value.

The variation of removal efficiency with pH can be explained by considering the difference in the structure of the two dyes. For MB, the acid-base equilibrium can be represented by the following equation:

$$MBH^{2+} \Leftrightarrow MB^{+} + H^{+} \quad (3)$$

In addition, MB has very low pK_a value (less than1.0) and its removal was mainly due to solubilised - unprotonated form MB^+ for all studied pH values. However, Tartrazine [21] has two strong sulphonic acid groups with pK_a = 2.0, one weak acidic acetate group with pK_a = 5.0 and one azo group with pK_a=10.9. Below pH 10.0, TZ should have different chemical forms according to pH, but chromophore (azo group) does not change. Hence, the measured removal concerns all these species. Adsorption experiments were avoided for pH >10.0.

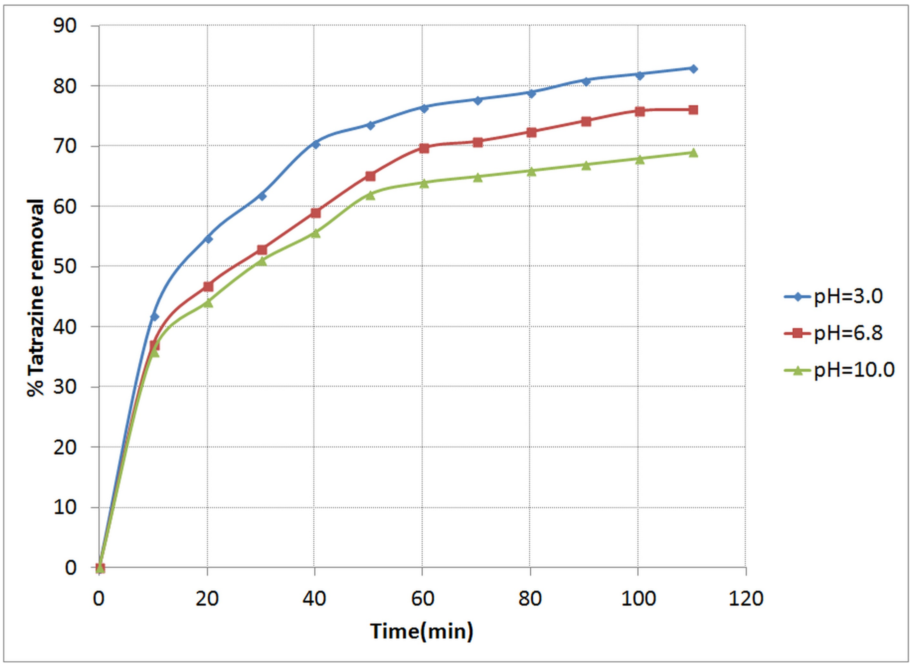

Figure 9. Effect of pH on the removal efficiency of TZ, 100 ppm, agitation speed, 100 rpm, T=25 °C, and 100 mL solution.

3.5. Effect of agitation speed

In a liquid adsorption system, the mass transfer rate of a solute to a particle is affected by liquid film thickness surrounding the particle and the film thickness depends on agitation speed. A series of experiments at different degrees of agitation (from 25 to 125 rpm) were undertaken for the adsorption of MB and TZ on activated carbon as shown in Figs. 10 and 11. The results indicate that the degree of agitation influences the removal efficiency as the agitation rate increases from 25 to 125 rpm. At agitation rates higher than 100 rpm the removal efficiency differs only to a quite small extent for MB adsorption, indicating that the film thickness has insignificant effect when the agitation rate is higher than 100 rpm. Hence, an agitation rate of 100 rpm was selected for all the experiments.

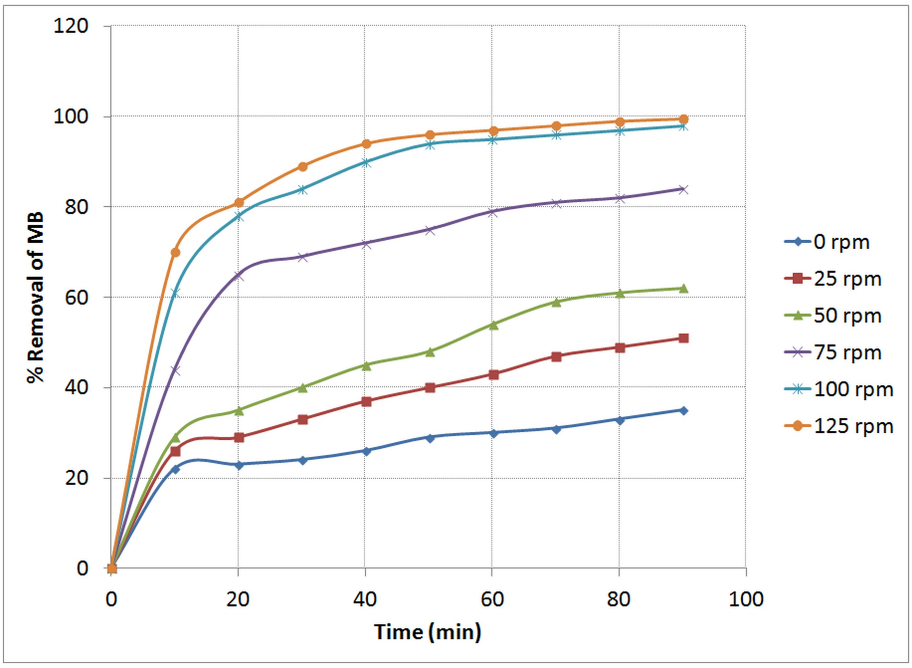

Figure 10. Effect of agitation speed on the removal efficiency of MB, 10 ppm, 0.5 g of AC, T=25 °C, and 100 mL solution.

3.6. Adsorption isotherm

For solid–liquid adsorption systems, adsorption isotherms are important models for the description of adsorption behaviour. When the adsorption reaction reaches equilibrium state, the adsorption isotherm can indicate the distribution of dye molecules between the solid phase and the liquid phase [22]. It is significant for understanding the adsorption behaviour to identify the most appropriate adsorption isotherm model. In this paper, Langmuir and Freundlich isotherms were employed to investigate the adsorption behaviour. Adsorption isotherms were studied at 298 K.

3.7. Langmuir isotherm

Langmuir isotherm is tested on the assumption that adsorption occurs at specific homogenous sites within the adsorbent. Once an adsorbate molecule occupies a site, no further adsorption can take place. Thus, an equilibrium value can be reached and the saturated monolayer curve can be presented in the equation below which has been successful for the explanation of monolayer adsorption. The linear form of Langmuir equation is given below:

$$\frac{C_e}{q_e} = \frac{1}{q_{max} K_L} + \frac{C_e}{q_{max}} \quad (4)$$

where q_{max} is the maximum or monolayer adsorption capacity of the adsorbent (mg g^{-1}) and K_L is the Langmuir adsorption constant (L mg^{-1}), which is related to the free energy of adsorption. Plots of C_e/q_e against C_e at different temperatures are shown in Fig. 12 and 13. The maximum adsorption capacity, q_{max}, and Langmuir constant, K_L were calculated from the slopes and intercepts of the plots respectively. Values obtained for the adsorption of MB and TZ onto the adsorbent are presented in Table 1.

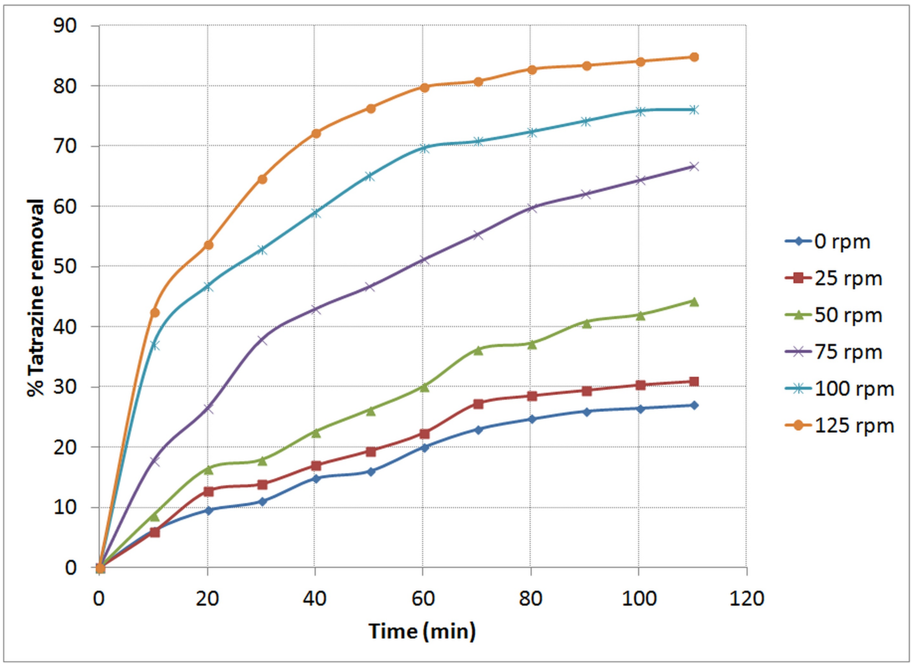

Figure 11. Effect of agitation speed on the removal efficiency of TZ, 100 ppm, 0.5 g of AC, T=25 °C, and 100 mL solution.

Agreement of the experimental data with Langmuir isotherm model indicates the homogeneous nature of activated carbon surface, *i.e.* each dye molecule/activated carbon adsorption has equal adsorption activation energy. The results also demonstrate the formation of monolayer coverage of dye molecule at the outer surface of activated carbon. A similar observation was reported by the adsorption of acid orange 10 dye onto activated carbons prepared from agricultural waste bagasse [23] and by the adsorption of direct dyes on activated carbon prepared from sawdust [24] and adsorption of Congo Red dye on activated carbon from coir pith [25].

It can be predicted whether an adsorption system is favourable or unfavourable using the essential characteristic of the Langmuir isotherm expressed by means of R_L, a dimensionless constant referred to as separation factor or equilibrium parameter defined by (5):

$$R_L = \frac{1}{1 + K_L C_0} \quad (5)$$

where C_o is the highest initial concentration. This parameter suggests the type of isotherm to be irreversible ($R_L = 0$), favourable ($0 < RL < 1$) or unfavourable ($R_L > 1$). It can be seen from Table 1, the value of R_L is less 1 which suggests that the adsorption is favourable.

3.8. Freundlich isotherm

The Freundlich isotherm model is used to describe heterogeneous adsorption process, *i.e.* adsorption which takes place on a heterogeneous surface through a multilayer adsorption mechanism. Freundlich isotherm is expressed by the equation

$$q_e = K_f \, x \, C_e^{1/n} \quad (6)$$

This can be linearised to

$$\log q_e = \log K_f + \left(\frac{1}{n}\right) x \log C_e \tag{7}$$

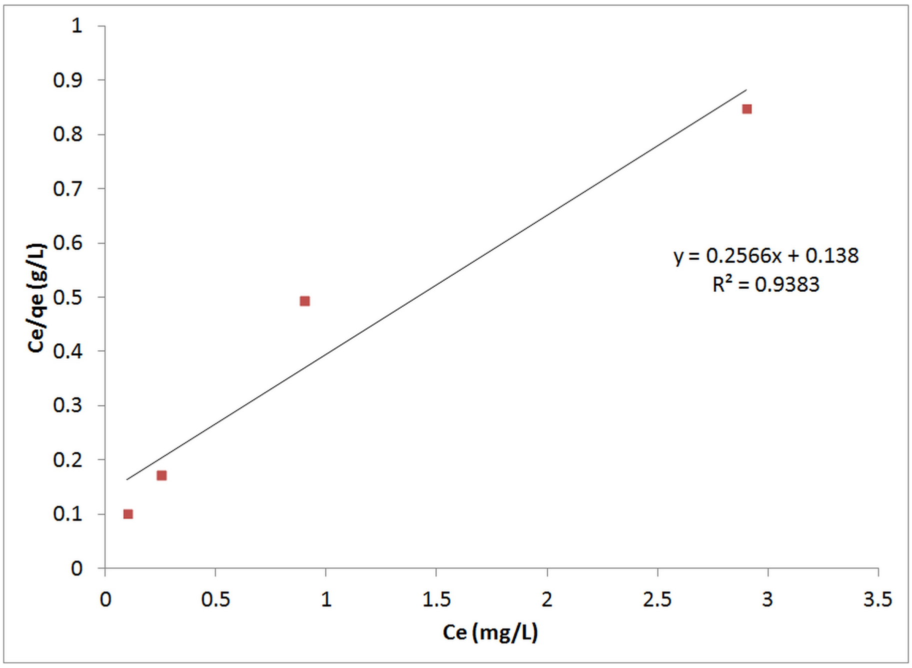

Figure 12. Langmuir adsorption isotherm of MB-activated carbon adsorption at 25°C.

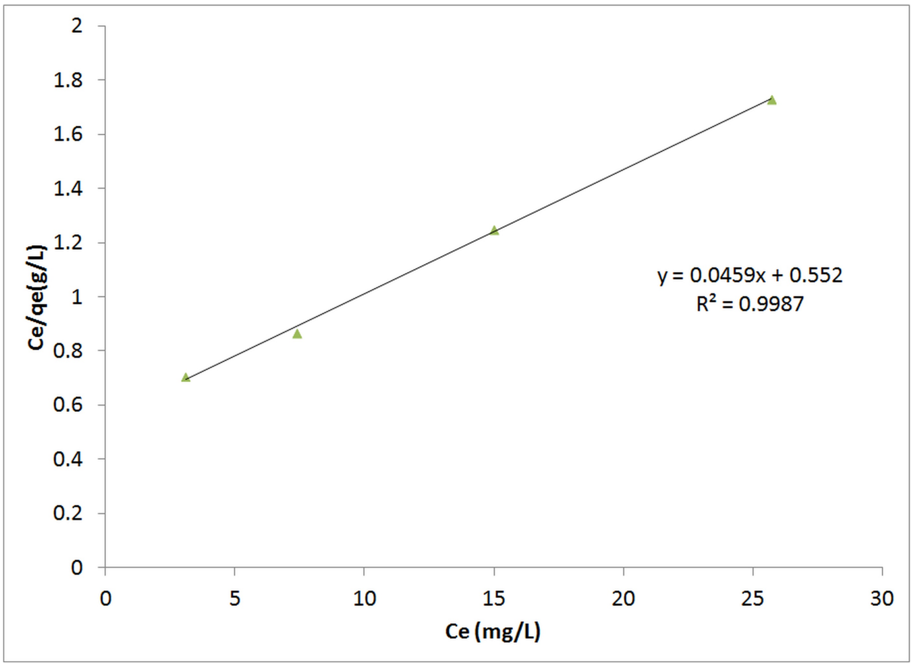

Figure 13. Langmuir adsorption isotherm of TZ-activated carbon adsorption at 25 °C.

where q_e is the amount adsorbed at equilibrium (mg g^{-1}), C_e the equilibrium concentration of the adsorbate (MB and TZ) and K_F and n are Freundlich constants, n giving an indication of how favourable the adsorption process and KF (mg g^{-1} (L mg^{-1}), and n is the adsorption capacity of the adsorbent. K_F can be defined as the adsorption or distribution coefficient and represents the quantity of dye adsorbed onto activated carbon adsorbent for a unit equilibrium concentration. The slope 1/n ranging between 0 and 1, is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero [7, 20]. A value for 1/n below unity indicates a normal Freundlich isotherm while 1/n above one is indicative of cooperative adsorption [23]. The plot of log q_e versus log C_e gives straight lines with slope '1/n' (Figs. 14 and 15), which shows the adsorption. The Freundlich parameters and correlation coefficients (R^2) evaluated from the plots are listed in Table 1. Accordingly, the Freundlich constants (K_F and n) and R^2 presented in Table 1, show that Freundlich model could also be used to explain the adsorption process.

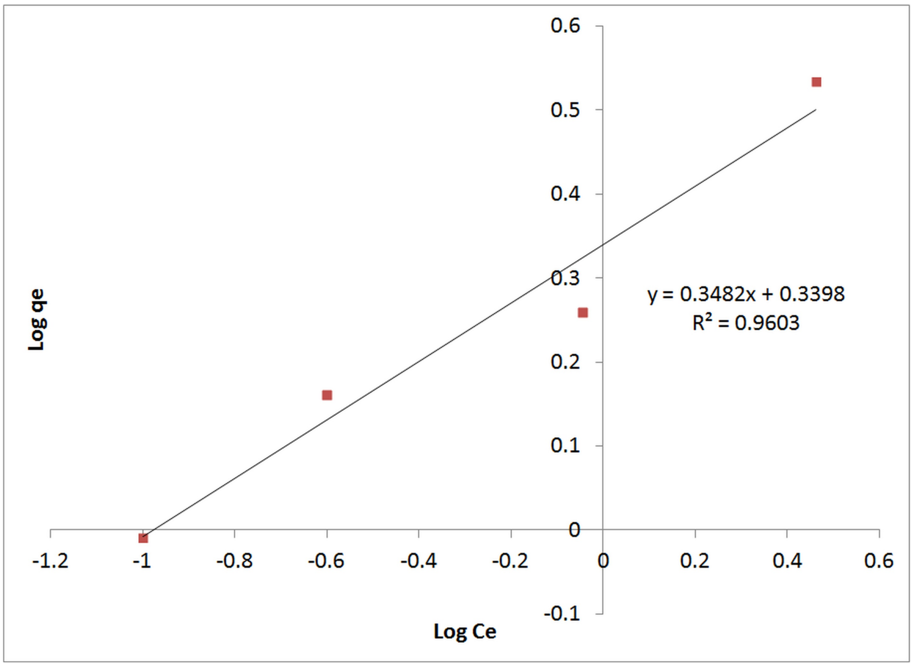

Figure 14. Freundlich adsorption isotherm of MB-activated carbon adsorption at 25 °C.

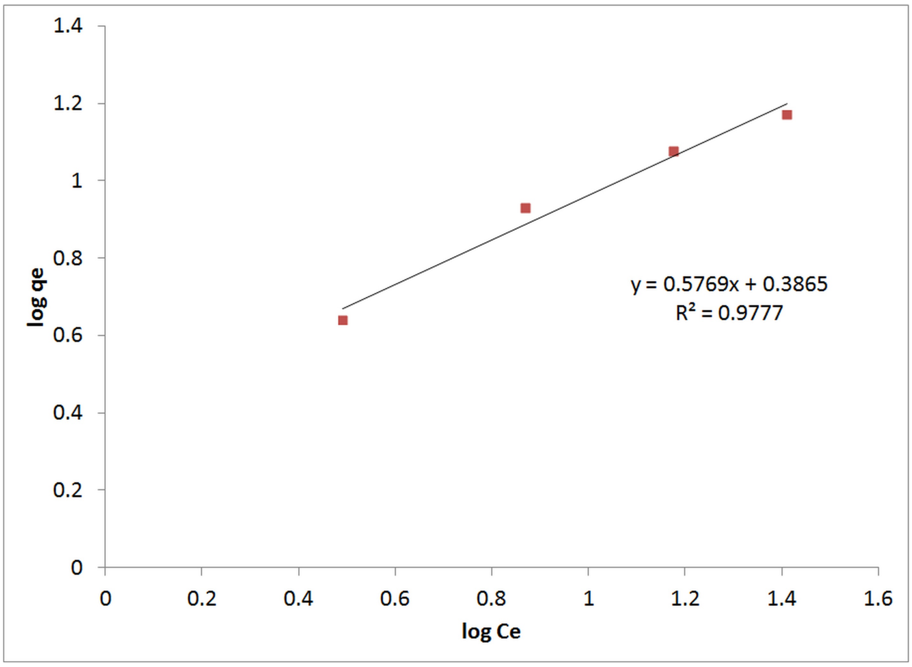

Table 1. Isothermal parameters for the adsorption of Methylene Blue (MB) and Tartrazine [21] on activated carbon.

The correlation coefficient values ($R^2 > 0.93$) (Table 1) show strong positive correlation indicating that the adsorption follows Langmuir isotherm. The maximum adsorption capacity, q_{max}, obtained from the Langmuir plot is 3.78 and 21.8 mg g^{-1} for MB and TZ, respectively. This value is higher than those reported by other researchers working on polymeric materials. For instance, Malana *et al.* [26], reported adsorption capacities of 1.017, 1.875 and 2.610 mg.g^{-1} for Methylene Blue onto three novel polymeric gels.

Figure 15. Freundlich adsorption isotherm of TZ-activated carbon adsorption at 25 °C.

Models	Parameters	Methylene Blue (MB)	Tartrazine [21]
Langmuir Isotherm	q_{max} (mg g^{-1})	3.78	21.8
	K_L (L mg^{-1})	3.3	0.08
	R_L	0.015	0.11
	R^2	0.93	0.99
Freundlich Isotherm	K_F (mg g^{-1} (L mg^{-1})n)	0.39	0.38
	1/n	0.31	0.57
	R^2	0.96	0.97

4. Conclusion

Activated carbon is a promising adsorbent for the removal of the basic and azo-dyes. The removal of Methylene Blue and Tartrazine from artificial solutions using activated carbon has been investigated under different experimental conditions in batch mode. The adsorption of dye was dependent on adsorbent dose, agitation speed, and dyes' concentration in the solution. Initial pH of solution affected the adsorption of this dye. The optimum pH for the removal of Methylene Blue from aqueous solution under the experimental conditions used in this work was 10.0 while for Tartrazine was 3.0. The maximum dye removal was observed within 90 min from the beginning of each experiment. Adsorption data were observed to follow Langmuir and Freundlich isotherm models at the studied temperature.

References

[1] Cheremisinoff P. Handbook of Water and Wastewater Treatment Technology. New York: Marcel Dekker; 1994. ISBN: 0-7506-7498-9.

[2] Ching YS. Adsorption of basic dyes from aqueous solution by various adsorbents. Separation Science and Technology 2004;39(8):1733-1750. DOI : 10.1081/SS-120030779.

[3] Twardowska I, Hea AF, Kettrup WJ. Solid Waste: Assessment, Monitoring and Remediation: Gulf Professional Publishing; 2003. ISBN: 0080443214.

[4] Namasivayam, CRR, Suba S . Uptake of dyes by a promising locally available agricultural solid waste: Coir pith. Journal of Waste Management 2001;2:381-387. DOI: 10.1016/S0956-053X(00)00081-7.

[5] Nemerrov NL. Industrial Water Pollution: Origin, Characteristics, and Treatment. Addison Wesley Publishing Company; 1987. ISBN: 0201052466, 9780201052466.

[6] Ramakrishna KR. Dye removal using low cost adsorbents. Water Science and Technology 1997;36:189-196. DOI : 10.1016/S0273-1223(97)00387-9.

[7] Robinson T, Chandran B, Nigam P. Removal of dyes from an artificial textile dye effluent by two agricultural waste residues, corncob and barley husk. Environment International 2002;28:29-33. DOI: 10.1016/S0160-4120(01)00131-3.

[8] Robinson T, Chandran B, Nigam P. Removal of dyes from a synthetic textile dye effluent by adsorption on apple pomace and wheat straw. Water Research 2002;36:2824-2830. DOI : 10.1016/S0043-1354(01)00521-8.

[9] Robinson TGM, Marchant R, Nigam P. Remediation of dyes in textiles effluent: a critical review on current treatment technologies with a proposed alternative. Bioresource Technology 2001;77:247-255. DOI: 10.1016/S0960-8524(00)00080-8.

[10] Yu LJ, Shukla SS, Dorris KL. Shukla A , Margrave JL. Adsorption of chromium from aqueous solutions by maple sawdust. Journal of Hazardous Materials 2003;B100:53-63. DOI: 10.1016/S0304-3894(03)00008-6.

[11] Marsh H, Heintz EA. Activated carbon: structure, characterization, preparation and applications: In: Marsh, H., Heintz, E.A; 1997. ISBN: 0-8247-5344-5.

[12] Bansal RC, Donnet JB. Active Carbon. New York: Marcel Dekker; 1988. ISBN: 0080455964, 9780080455969.

[13] Deng H, Yang L, Tao G, Dai J. Preparation and characterization of activated carbon from cotton stalk by microwave assisted chemical activation - application in methyene blue adsorption from aqueous solution. Journal of Hazardous Materials 2009;30:1514-1521. DOI: 10.1016/j.jhazmat.2008.12.080.

[14] Chen S, Yue Q, Gao B, Li Q, Xu X, Fu K. Adsorption of hexavalent chromium from aqueous solution by modified corn stalk: A fixed-bed column study. Bioresource Technology 2012;113:114-120. DOI: 10.1016/j.biortech.2011.11.110.

[15] Annadurai G, Jr, Lee DJ . Adsorption of heavy metals from water using banana and orange peels. Water Science Technology 2002;47(1):185-190.

[16] Wang L, Zhanga J, Wang A. Removal of methylene blue from aqueous solution using chitosan-g-poly(acrylic acid)/montmorillonite superadsorbent nanocomposite. Colloids Surfaces A: Physicochemical Engineering Aspects 2008;322:47-53. DOI: 10.1016/j.colsurfa.2008.02.019.

[17] Algidsawi AJK. A study of ability of adsorption of some dyes on activated carbon from date's stones. Australian Journal of Basic and Applied Sciences 2011;5(11):1397-1403.

[18] Annadurai GJRS, Lee DJ, Juang RS, Lee DJ. Use of cellulose-based wastes for adsorption of dyes from aqueous solutions. Journal of Hazardous Materials 2002;B92:263-274. DOI: 10.1016/S0304-3894(02)00017-1.

[19] Tabrez A, Khan IA, Singh V, Sharma S. Utilization of fly ash as low cost adsorbent for the removal of methylene blue, malachite green and rhodamine B dyes from textile wastewater. Journal of Environmental Protection Science 2009;3(11):11-22.

[20] Sidiras D, Batzias F, Schroeder E, Ranjan R, Tsapatsis M. Dye adsorption on autohydrolyzed pine sawdust in batch and fixed-bed systems. Chemical Engineering Journal 2011;171(3):883-896. DOI : 10.1016/j.cej.2011.04.029.

[21] Gurses AKS, Dogar C, Bayrak R, Acikyildiz M, Yalcin M. Determination of adsorptive properties of clay/water system: methylene blue sorption. Journal of Colloid and Interface Science 2004;269(2):310-314. DOI: 10.1016/j.jcis.2003.09.004.

[22] Wtcyc T, Lin MC, Chien SF, Sun HF, Hsieh MF. Adsorption of acid dye onto activated carbons prepared from agricultural waste bagasse by ZnCl2 activation. Chemosphere 2001;45:51-58. DOI: 10.1016/S0045-6535(01)00016-9.

[23] Malik PK. Dye removal from wastewater using activated carbon developed from sawdust: adsorption equilibrium and kinetics. Journal of Hazardous Materials 2004;B113:81-88. DOI: 10.1016/j.jhazmat.2004.05.022.

[24] Namasivayam CDK. Removal of congo red from water by adsorption onto activated carbon prepared from coir pith, an agricultural solid waste. Dyes and Pigments 2002;54:47-58. DOI: 10.1016/S0143-7208(02)00025-6.

[25] Malana MA, Ijaz S, Ashiq N . Removal of various dyes from aqueous media onto polymeric gels by adsorption process: Their kinetics and thermodynamics. Desalination 2010;263:249. DOI : 10.1016/j.desal.2010.06.066.