Journal of Pharmaceutical and Applied Chemistry

ISSN: 2357-0210 VOLUME 4, ISSUES 1, 2018 www.egyptfuture.org/ojs/

A Comparative Study for Adsorption of Methylene Blue Dye from Wastewater on to Three Different Types of Rice Ash

Ibrahim A. Salem, Tarek A. Fayed, Marwa N. El-Nahass, Mohamed Dawood*

Chemistry Department, Faculty of Science, Tanta University, 31527, Egypt.

Received: 11 Feb. 2018, Revised: 18 Apr. 2018, Accepted: 21 Apr. 2018.
Published online: 1 May 2018.

Abstract: High innuendo to organic dyes, such as methylene blue (MB) potentially has retrograde effects and can cause acute health problems leading to a number of particular diseases. Our work aimed at evaluating of three different types of heap fired ash as low-cost adsorbents for the removal of methylene blue (MB) dye from wastewater has been investigated. The effects of pH of solution, dosage adsorbent, contact time and initial concentration were investigated. The results showed that the adsorption of MB is highly influenced by the adsorbent dose, time, initial MB concentration, solution pH and slightly affected by the aqueous medium temperature. Also, the higher percentage of MB removal at lower initial dye concentrations and the equilibrium between MB in the solution and the adsorbent surface was practically achieved in 60 min. The adsorption process was found to obey second-order rate model with endothermic nature. Equilibrium adsorptive data for MB were well represented by Langmuir and Freundlich isotherm models. Additionally, the dye adsorption process was also characterized through the thermodynamic parameters such as Gibbs free energy (ΔG^o), change in heat of adsorption (ΔH^o) and entropy change (ΔS^o). The negative value of ΔG^o indicated spontaneous adsorption of MB onto RHA and ATRH. Finally, RHA show high efficiency in MB removal as low-cost and effective adsorbent.
Keywords: Heap fired ash. Low cost adsorbents. Methylene blue.

1 Introduction

Nowadays, all societies suffer from the problems related with water pollution due to the drainage of industrial effluents to surface water which contaminated with toxic dyes comes from a wide range of industries such as textile, leather, paper, printing, food, cosmetics, paint, rubber, plastic, pesticide, wood preserving chemicals and pharmaceutical industries (Ergene et al. 2009; Kiran et al. 2009). The residual used dyes are discharged into aqueous media without relevant treatment as waste effluents which can color the water even with inappreciable quantities (Ravi et al. 2005). The quality of water is highly affected by this small quantities which causative in diminishing light penetration subsequently, destruction the photosynthesis process. Therefore, the treatment of these harmful dye effluents is urgent emergency due to its negative impacts on water sources. Therefore, the treatment of effluent containing such dye is of great interest due to its harmful impacts on receiving water. Exposure to organic dyes such as methylene blue, leads to a lot of specific diseases and cause severe health problems. Methylene blue, MB, is one of the most synthetic dyes which used for dying cotton, Wood, and silk. Therefore, the treatment of effluent containing such dye is of great interest due to its harmful impacts on receiving water. Several physical, chemical and biological decolonization methods have been investigated. Among of these various techniques of dye removal is the adsorption which gives the best results in the removal of different coloring materials (Jain et al. 2003). Recently, many approaches have been studied for the developing of cheaper and effective adsorbents. Many waste materials including natural, industrial and agricultural have been used as low cost adsorbents in the removal of organic dyes from its aqueous solution. The aim of the work is utilization of different residual ashes from heap firing of physically and chemically treated rice husks as low cost adsorbents for the removal of MB dye as model of adsorbate that widely used in dyeing substances. Our view based on three benefits, firstly, the use of such negligible wastes will solve the disposal problem, secondly, obtainment heat energy from its firing, finally, access to zero cost waste material for adsorption process.

2 Experimental

2.1 Chemicals and Reagents

All chemicals were of analytical quality grade reagents and used without further purification. All solutions were prepared using double distilled water. Methylene blue dye or basic blue 9 is a heterocyclic aromatic compound used as adsorbate without further purification in this study, Fig. 1. Stock solution of MB was prepared by dissolvingan accurately weighed amount of MB in distilled water to obtain a concentration of 100 mg/l, and then diluted to the desired concentrations (5, 10, 15 mg/l).

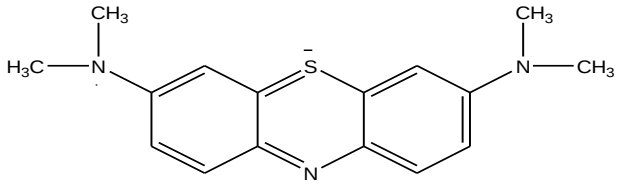

Fig. 1: The chemical structure of methylene blue dye.

2.2 Adsorbent

2.2.1 Preparation of Heap Fired Rice Husk Ash (RHA)

The raw rice husk was washed repeatedly with tap and double distilled water to remove adhering soil, soluble impurities and dust then dried at 120 ºC for 24 h until constant weight. The dried material was heap fired in open air then milled into particles to obtain RHA powder with size ≤ 300 μm then preserved for further use.

2.2.2 Preparation of the Ash of Treated Rice Husk (ATRH)

The dried rice husk was suspended in 1M (HCl or NaOH) solution (1:20, M/V) at 70ºC for 2h with constant stirring. The solution was filtered off, and the rice husk was washed thoroughly with distilled water until the pH of the wash was close to neutral, then dried at 120 ºC for 24 h, heap fired in open air and milled into particles to obtain ATRH powder with size ≤ 300 μm then preserved for further use.

2.2.3 Adsorption Studies

A known weight of powdered RHA and ATRH was added to 100 ml of MB solution in 250 ml conical flask then stirred in a shaker water path under specific variable conditions with pretreating to all flasks used with the respective MB solution for 1 hour before doing the experiment to avoid the adsorption on the flask walls. The effects of shaking time (5-120 min), adsorbent dose (0.1-1.2 g), medium temperature (25-45 ◦C), solution pH (2-11) and initial MB concentration (5, 10, 15 mg/l) were studied through varying one of these parameter while keeping the others constant, all experiments were conducted in duplicate. The absorbance of both elementary MB solution A_o and centrifuged MB solution after adsorption process at equilibrium A_e was estimated spectrophoto metrically at λ_{max} = 664 nm. The removal efficiency of MB was determined according to Eq (1)

$$\text{Removal } \% = \frac{A_o - A_e}{A_o} * 100 \qquad (1)$$

The amount of MB dye adsorbed onto RHA and ATRH was calculated by the subsequent mass balance equation as follows:

$$q_e = \frac{(C_o - C_e)V}{m} \qquad (2)$$

Where qe is the amount of MB adsorbed per unit weight of RHA and ATRH (mg g−1); C_o and C_e are the initial and final concentrations of MB in solution (mg/l) that calculated from beer lambert law; V is the volume of MB solution (l); and m (g) is the mass of the adsorbent used.

2.2.4 Characterization and Instrumentation

The samples were characterized using Jasco FT-IR type 4100 spectrophotometer as KBr pellets in wave number region 4000–400 cm^{-1}. Powder X-ray diffraction (XRD) patterns were recorded at room temperature using GNR, APD 2000 PRO step scans X-ray diffractometer, Cu-K_α radiation (40 kV, 30 mA). The UV/Vis spectra of the dye were recorded on a Shimadzu UV-3101PC scanning spectrophotometer.

3 Results and Discussion

3.1 Characterization of the Investigated Samples

3.1.1 X-Ray Diffraction Analysis

The XRD analysis of the samples are shown in Fig.2, There are two main peaks were observed in the range of 15.2–22.99◦ and this is an indicative of non-crystalline phase existence and confirmed the amorphous nature of the silica present in the various tested materials (Saravanan et al. 2012).

3.2 Degradation of Methylene Blue

3.2.1 Effect of Contact Time

The varying effect of time on the removal of MB by RHA and ATRH was studied in Fig.4 within the range from 5 to 120 min by adding 0.08 g of the adsorbent to 100 ml of MB solutions (C_o= 10 mg/l) and the solutions were shaken at

25ºC. Fig.4 show fast adsorption of MB at the precocious stages of process due to many and more active vacant accessible sites of adsorbents which being occupied as the time increased leading to decreasing the adsorption rate (Marrakchi et al. 2017) till reached equilibrium which observed at 40 min for RHA and ATRH/HCl with similar adsorption capacities 98% and 60 min for ATRH/NaOH with adsorption capacity 91%. Many attempt to increase the shaking time up to 5 hours showed a clear constancy in the adsorption rate.

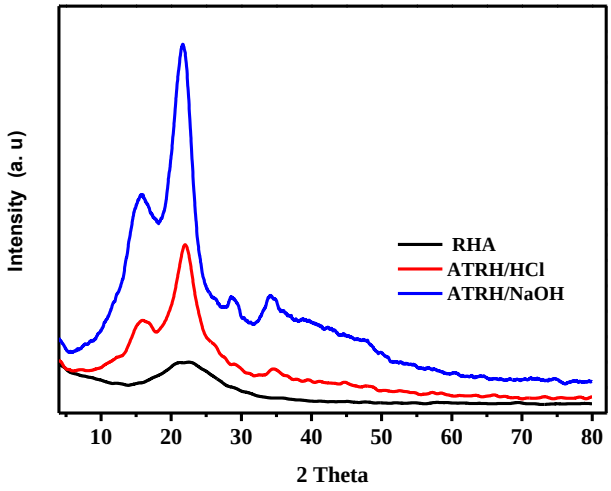

Fig. 2: The XRD pattern of the samples.

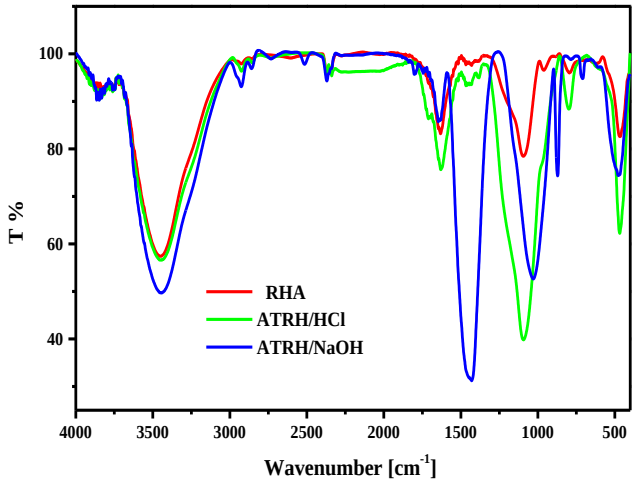

Fig. 3: FT-IR spectra of the samples.

3.2.2 Effect of Adsorbent Dose

Changing the dose of RHA and ATRH within the range from 0.2 to 1.2 g/l was studied and was shown in Fig.5 by shaking MB solution (C_o= 10 mg/l) for 60 min at 25ºC. The

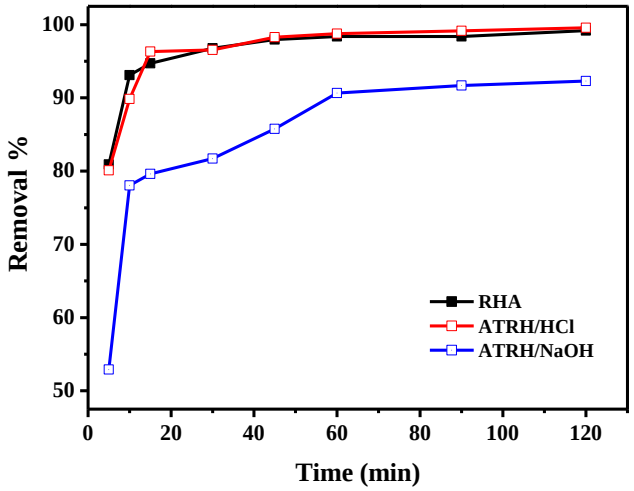

Fig. 4: Effect of contact time on the removal % of MB dye by RHA and ATRH at: Initial dye concentration = 10 mg/l, adsorbent dose = 0.8 g, temperature = 25ºC and unbuffered solution.

dye removal increases up to a certain dose and then it tends to constancy, where the optimum equilibrium dose achieved at 0.8 g/l. With equilibrium, the same trend of 97 % removal was observed for RHA and ATRH/HCl higher than 91 % removal with ATRH/NaOH. The venatic relation between removal efficiency and adsorbent weight can ascribed to increasing the surface area available upon increasing the dose subsequently increasing the active linkage sites participated in the adsorption (Lakshmi et al. 2009).

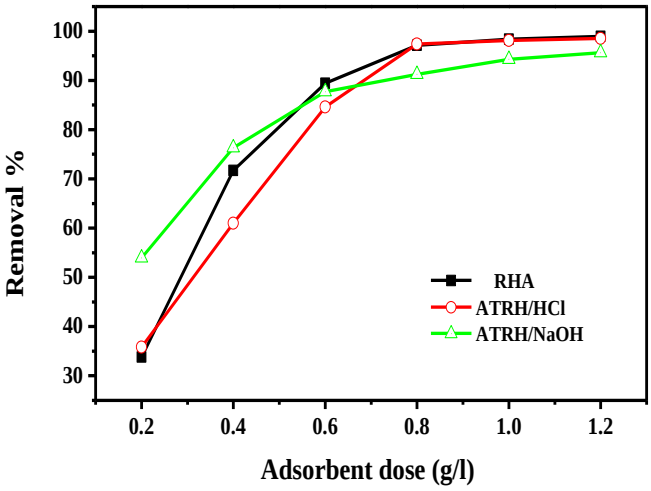

Fig. 5: Effect of adsorbent dose on the removal % of MB dye by RHA and ATRH at: Initial dye concentration = 10 mg/l, time = 60 min, temperature = 25ºC and un buffered solution.

3.2.3 Effect of Temperature

The dye removal percentage dependence upon temperature variation from 25 to 45 ˚C has been studied in Fig. 6 by adding 0.08 g of adsorbent to 100 ml of MB solution with a continuous shaking for 60 min. Removal of MB was slightly affected by changing the medium temperature where the raising of temperature leads to raising the number of allowable energetic sites on the surface results in insignificantly increase in MB removal suggesting that the mechanism of MB adsorption onto RHA and ATRH involved a chemical adsorption process with endothermic nature (Alia et al. 2016).

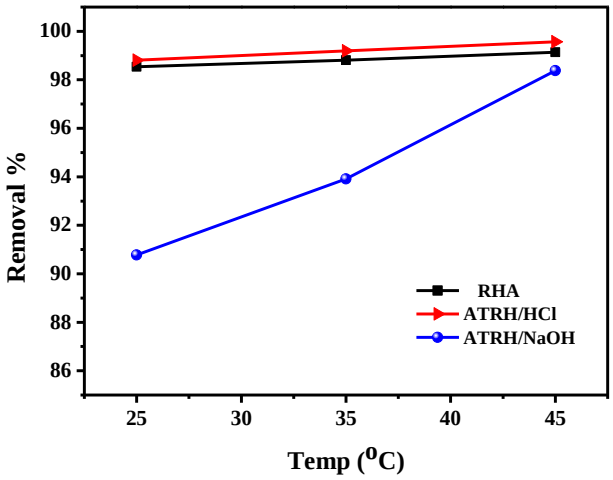

Fig. 6: Effect of temperature on the removal % of MB dye by RHA and ATRH at: Initial dye concentration = 10 mg/l, time = 60 min, adsorbent dose = 0.8 g and un buffered solution.

3.2.4 Effect of Solution PH

Results of pH variation (2, 4, 6, 8, 10 and 11) on MB dye adsorption for 1h at 25ºC are presented in Fig. 7. As the solution pH increases from 2.0 to 11.0 gradually, the MB uptake increases till reached to a maximum value at pH 6.0 with 98, 99 and 93% removal for RHA, ATRH/HCl and ATRH/NaOH, respectively. The hydrogen ions H^+ from the acidic medium (lower pH) compete with MB that protonated in solution forming positively charged $–N^+(CH_3)_2$ in attempt to reach the adsorbent surface, subsequently leads to decreasing the adsorption capacity while, at medium pH values (6-7) hydrogen ion concentration decrease which open the way to the adsorption of MB cations onto the negatively charged adsorbent surface (Nethaji et al. 2015). At basic medium, there is no change in the adsorption capacities for RHA and ATRH/HCl, while with ATRH/NaOH the amount of adsorption has been reduced due to electrostatic repulsion between the negative medium ions and negatively charged surface of the ATRH/NaOH (Njoku et al. 2014).

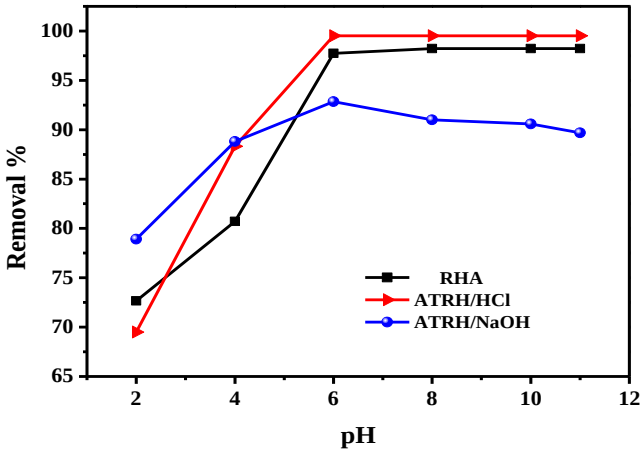

Fig. 7: Effect of pH on the removal % of MB dye by RHA and ATRH at: Initial dye concentration = 10 mg/l, contact time = 60 min, adsorbent dose = 0.8 g/l and temperature = 25ºC.

3.2.5 Effect of Initial Dye Concentration

Three different initial concentrations (5, 10, 15 mg/l) from methylene blue were tested to study the influence of dye concentration on the removal percentage where 0.02 g adsorbent were added in 100 ml dye solution and shaken at 25ºC for 60 min. The inverse relation between the dye removal percentage and its concentration obtained in Fig.8 was due to lower MB cations in solution at light concentrations against available fixed binding sites that saturated at higher concentration sleading to retrogression the percentage removal, which illustrate explicitly the dependence of the dye removal % upon its initial concentration (Njoku et al. 2014).

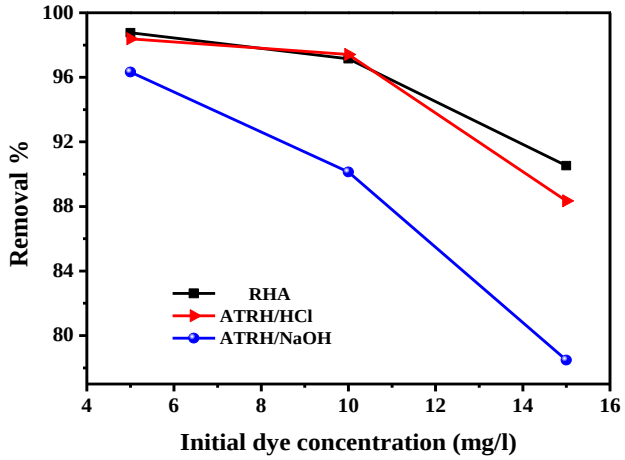

Fig. 8: Effect of initial dye concentration on the removal % of MB dye by RHA and ATRH at: time = 60 min, adsorbent dose = 0.8 g/l, temperature = 25ºC and un buffered solution.

3.3 Adsorption Kinetics

The adsorption mechanism of MB onto RHA and ATRH was studied using both pseudo-first order and pseudo-second order model. The linear forms of pseudo-first and second order model are expressed in Eqs 3 and 4, respectively Safa and Bhatti 2011).

$$\text{Log}\,(q_e - q_t) = \text{Log}(q_e) - \frac{K_1\, t}{2.303} \qquad (3)$$

$$\frac{t}{q_t} = \frac{1}{K_2\, q_e^2} + \frac{t}{q_e} \qquad (4)$$

Where q_e and q_t are the adsorption capacity (mg/g) at equilibrium and time t, respectively, k_1 (min^{-1}) and k_2 (g/mg min) are the first and second order rate constants, respectively. The values of adsorption kinetic parameters are presented in Table 1 and extract from plots inFigs.9 and10. Applying eq (3) results in unequal values between the calculated adsorption capacity (q_e^{cal}) and the experimental adsorption capacity (q_e^{exp}); in addition to the not satisfactory values of the coefficient of correlation R^2< 0.99incontrastto eq (4) where the values of q_e^{cal} and q_e^{exp} for all applied adsorbents are closely the same also the values of the coefficient of correlation R^2 for all tested adsorbents are very high (0.999) which outbalanced that the pseudo-second order model is more applicable to MB adsorption data than pseudo-first order model.

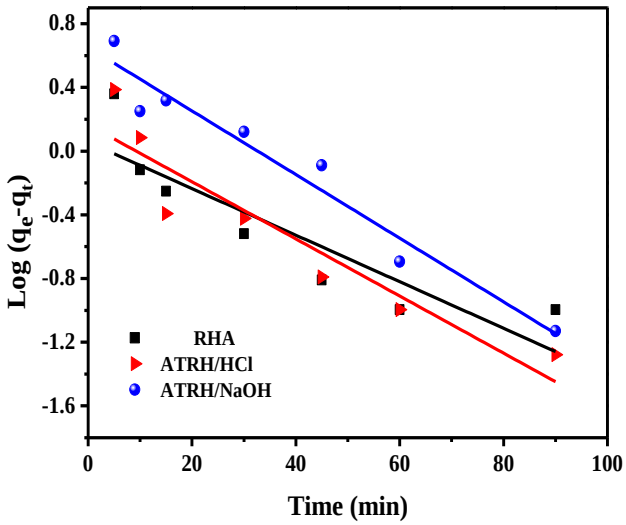

Fig. 9: Pseudo-first-order plot for the adsorption of MB on to RHA and ATRH.

3.4 Adsorption Isotherms

The linear forms of Langmuir and Freundlich isotherms are expressed as shown in Eq (5) and (6) respectively (Sharma et al. 2010)

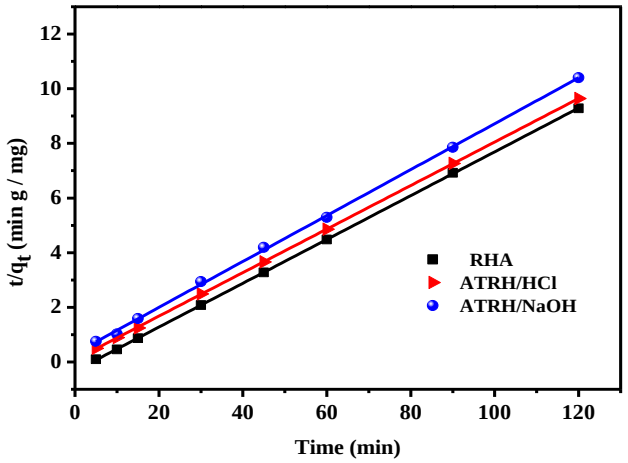

Fig.10: Pseudo-second order plot for the adsorption of MB on to RHA and ATRH

$$\frac{C_e}{q_e} = \frac{1}{q_m\, K_L} + \frac{C_e}{q_m} \qquad (5)$$

$$\text{Log}\, q_e = \text{Log}\, K_f + \frac{1}{n}\, \text{Log}\, C_e \qquad (6)$$

where q_e is the amount of MB adsorbed on the RHA and ATRH surfaces (mg/g) at equilibrium, C_e is the equilibrium MB concentration in solution, q_m is the maximum adsorption capacity (mg/g), while K_L (l/g) and K_F $(mg/g)(l/mg)^{1/n}$ are the equilibrium constants of Langmuir and Freundlich, respectively, all these constants were derived from Figs 11 and 12 and summarized in Table 2. The values of n, q_m and K_L give an indication to the acceptableness of the adsorption process, while the values of correlation coefficients (R^2) give an indication to the fitness of adsorbent to each applied model. If the value of n lying between 2 and 10 this represent good adsorption characteristics but if less than 1 this represent poor adsorption characteristics (Alia et al. 2016). The higher values of n, q_m and K_L in case of RHA give it the preference in binding to MB than ATRH. The experimental R^2 values gives both Freundlich and Langmuir models a better fit to the adsorption data of MB onto RHA and ATRH surface but appears excessively in Langmuir models.

3.5 Thermodynamic Studies

The increase in removal of dye with increasing the temperature reveals an endothermic process which can be explained through thermodynamics parameters by calculating the change in free energy (ΔG°), enthalpy (ΔH°) and entropy changes (ΔS°). These parameters were calculated using equations 7 and8 (Kyzasa et al. 2012):

$$\Delta G^o = -RT\text{Ln}K_c \qquad (7)$$

$$\Delta G^o = \Delta H^o - T\Delta S^o \qquad (8)$$

Table 1: Kinetic parameters for pseudo-first and pseudo-second order kinetic rate models applied to the adsorption process of MB onto RHA and ATRH.

Adsorbent	Pseudo first order			Pseudo second order			$q_{e.}^{exp}$(mg/g)
	$q_{e.}^{Calc}$(mg/g)	K_f (min^{-1})	R^2	$q_{e.}^{Calc}$ (mg/g)	K_s (g mg^{-1} min^{-1})	R^2	
RHA	1.14	0.034	0.892	12.47	0.088	0.999	12.40
ATRH/HCl	1.47	0.041	0.938	12.55	0.075	0.999	12.45
ATRH/ NaOH	4.49	0.046	0.976	11.90	0.022	0.999	11.54

Table 2: Isotherm parameters for adsorption of MB onto RHA and ATRH.

Adsorbent	Langmuir			Freundlich		
	q_m	K_L	R^2	K_F	n	R^2
RHA	17.36	9.62	0.999	13.73	5.56	0.945
ATRH/HCl	15.64	8.54	0.999	12.93	5.88	0.939
ATRH/NaOH	28.42	0.85	0.995	12.47	1.92	0.996

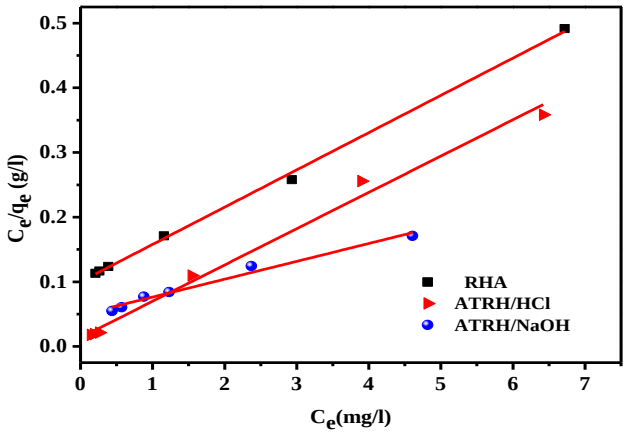

Fig. 11: Langmuir plots of adsorption of MB onto RHA and ATRH.

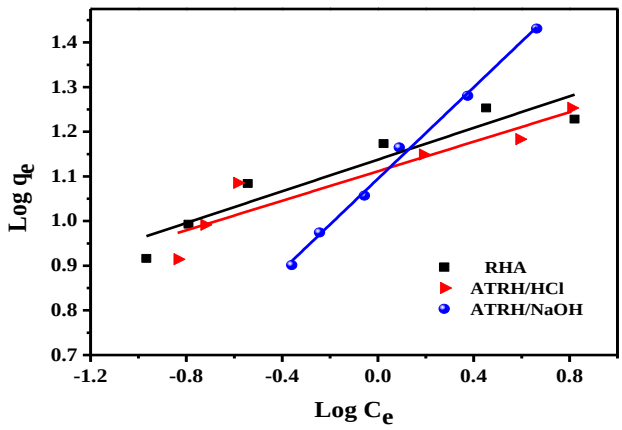

Fig. 12: Freundlichplots of adsorption of MB onto RHA and ATRH.

where K_C is the distribution coefficient for adsorption and is determined as follows (Kyzasa et al. 2012);

$$K_c = \frac{C_a}{C_e} \qquad (9)$$

Where C_a and C_e are the equilibrium MB dye concentration on the adsorbent (mg l^{-1}) and in solution (mg l^{-1}), respectively. The values of ΔH^o and ΔS^o were determined from the slope and intercept of van't Hoff graph Fig 13. The values of ΔG^o for ATRH/HCl > RHA > ATRH/ NaOH indicate that the increase in adsorption capacity which could be related to the increase in specific surface area and to the total pore volume of adsorbent. Based on the obtained values of thermodynamic parameters (Table 3), the negative values of ΔG^o indicate the spontaneous adsorption of MB on adsorbent samples. Adsorption of MB can be considered asphysisorption when the change in free energy for adsorption of MBon samples ranges between −6.22 kJ $mol^{-1}$and −14.98 kJ mol^{-1}. It is known that, the absolute magnitude of the change in free energy for physisorption is between −20 kJ $mol^{-1}$and 0 kJ $mol^{-1}$and that chemisorptions occur between −80 kJ $mol^{-1}$and −400 kJ mol^{-1}. The positive values of entropy change reflect the increased randomness at solid/solution surface. This is a direct consequence of enhancement of the mobility and extent of penetration within the adsorbent pores and enhancing the rate of intra-particle diffusion as well. The positive values of ΔH^o confirm the endothermic nature of the overall adsorption processes (Hassan et al. 2014).

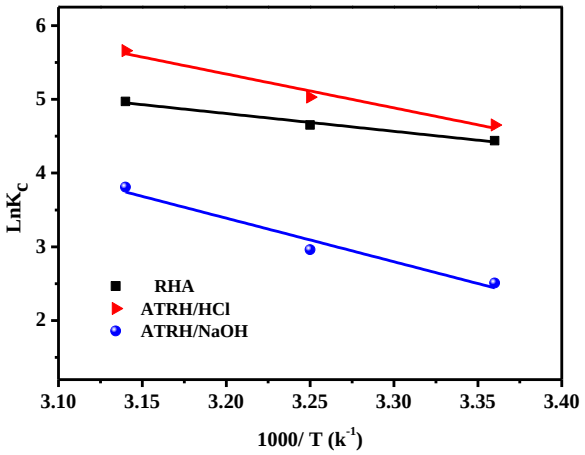

Fig. 13: Plots of (lnK_c) versus (1/T) for the adsorption of MB onto RHA and ATRH.

3.6 Application of the Developed Treatment System.

The utility of powdered heap fired rice husk ash as adsorbent was evaluated for the treatment of two real industrial samples collected from different local fabrics plant in El-Mehala city, Gharbia governorate, Egypt. The decolonization of two real industrial samples was studied by adding 1g of RHA to 50 ml sample solution and stirring the mixture. The absorbance and decolonization efficiency of dyes are shown in Figs 14-16.The results showed the high ability of RHA in degradation of real samples 1 and 2. A significant 96 % dye removal at retention time 15 min for sample 1 while significant 71 and 91 % dye removal for sample 2 at retention time 15 and 30 min, respectively.

Table 3: Thermodynamic parameters for adsorption of MB onto RHA and ATRH

Adsorbent	T (ºK)	ΔGº(kJ mol^{-1})	ΔHº(kJ mol^{-1})Δ	ΔSº (Jmol^{-1}K^{-1})
RHA	298	-10.99	20	103.9
	308	-11.90		
	318	-13.13		
ATRH/HCl	298	-11.51	38.52	167.7
	308	-12.89		
	318	-14.98		
ATRH/NaOH	298	-6.22	49.13	185.4
	308	-7.57		
	318	-10.07		

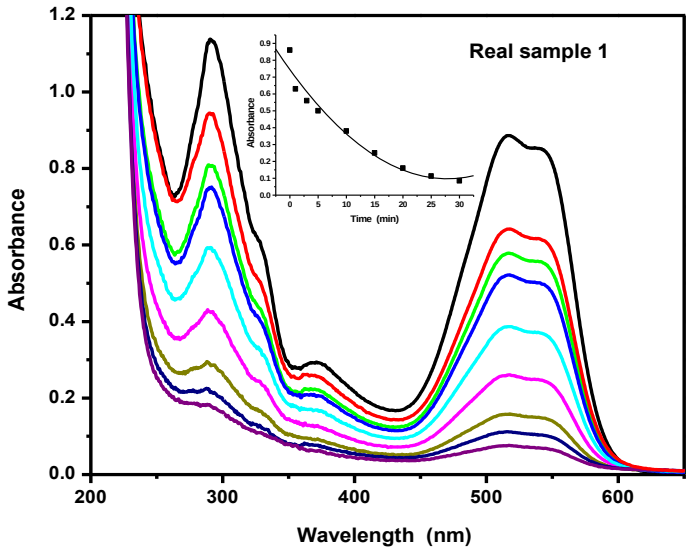

Fig. 14: The absorbance of industrial real sample (1) with RHA.

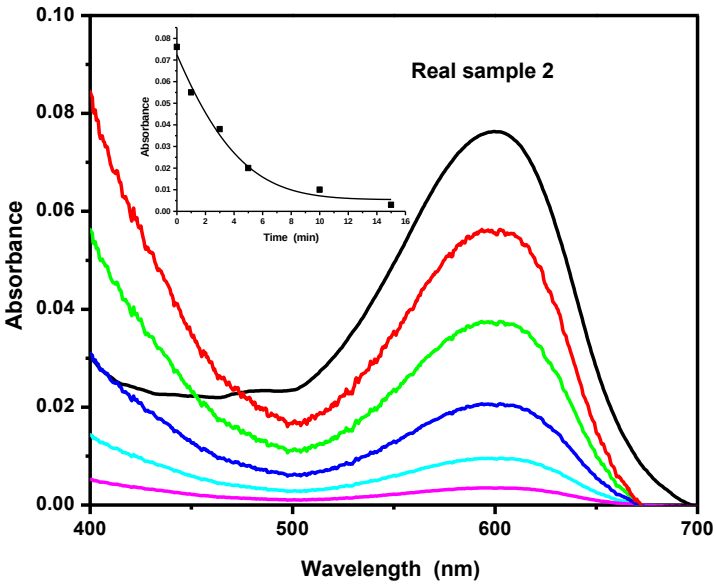

Fig. 15: The absorbance of industrial real sample (2) with RHA.

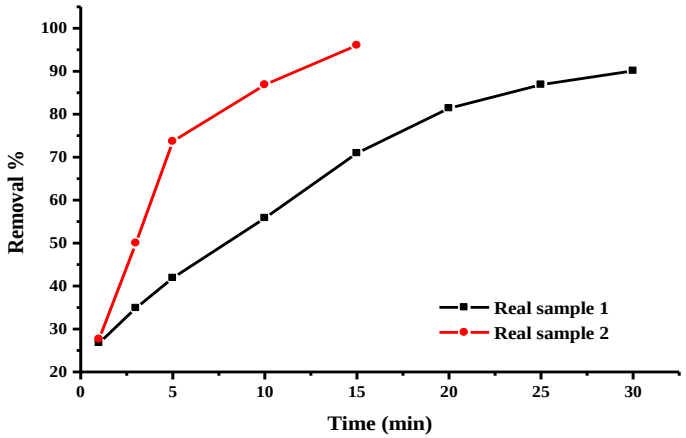

Fig. 16: The removal of two real dye samples solution with time using RHA.

4 Conclusions

The feasibility of heap fired ash from physically treated rice husk (RHA) and heap fired ash from chemically treated rice husk (ATRH) as effective adsorbents for the removal of MB as adsorbate from its aqueous solutions was investigated. The adsorptive study was applied in batch experiments as a function of contact time, adsorbent dose, temperature, solution pH and initial MB concentration, where adsorption of MB is highly influenced by the adsorbent dose, time, initial MB concentration, solution pH and slightly affected by the aqueous medium temperature. The results showed higher percentage of MB removal at lower initial dye concentrations and the equilibrium between MB in the solution and the adsorbent surface was practically achieved in 60 min. The adsorption process was found to obey second-order rate model with endothermic nature. Equilibrium adsorptive data for MB were well represented by Langmuir and Freundlich isotherm models. The negative value of ΔG^{o} indicated spontaneous adsorption of MB onto RHA and ATRH. Finally, RHA show high efficiency in MB removal as low-cost and effective adsorbent.

Acknowledgements

The authors would like to thank Prof. Dr. Alam El-Din Elbastawesy, Dean of Higher Institute of Engineering and Technology, Tanta, Gharbia, Egypt, for the facilities

offered to the student during the preparation of the adsorbents.

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