Araştırma Makalesi / *Research Article*
Çevre Mühendisliği /
Environmental Engineering

Iğdır Üniversitesi Fen Bilimleri Enstitüsü Dergisi, 9(4): 1977-1988, 2019
***Journal of the Institute of Science and Technology,* 9(4): 1977-1988, 2019**

DOI: 10.21597/jist.608915 **ISSN: 2146-0574, eISSN: 2536-4618**

Bazik Yellow 51 Boyar Maddesinin Pirinç Kabuğu ve Yanmış Pirinç Kabuğu Kullanılarak Adsorpsiyonunun Kinetik, İzoterm ve Termodinamik İncelemeleri

Elif BAYRAK TEZCAN[1], Zeynep CEYLAN[2], Filiz NURAN ACAR[2]*

ÖZET: Bu çalışmada; pirinç kabuğu ve yanmış pirinç kabuğu (yakılarak aktif karbon formuna getirilmiş) katyonik bir boyar madde olan Bazik Yellow 51(BY51) boyar maddesinin sulu çözeltiden adsorpsiyonla gideriminde düşük maliyetli bir adsorbent olarak kullanılmıştır. Pirinç kabuğu ve yanmış pirinç kabuğunun karakterizasyonu SEM (Scanning Electron Microscope) ve FTIR (Fourier Transform Infrared Spectroscopy) kullanılarak yapılmıştır. Başlangıç boyar madde konsantrasyonu ve temas süresi, pH, sıcaklık dahil olmak üzere tüm operasyonel parametrelerin boyar madde giderim verimi üzerine etkileri incelenmiştir. Tüm çalışmalar kesikli modda yapılmıştır. Adsorpsiyon verileri Langmuir ve Freundlich izoterm modellerine uyarlanarak analizi yapılmış ve tek tabaka adsorpsiyon kapasitesi hesaplanmıştır. Kinetik veriler yalancı birinci ve yalancı ikinci mertebe kinetik modellerine uyarlanmış ve yalancı ikinci mertebe kinetik modeline uyduğu tespit edilmiştir. Entalpi (ΔH°), entropi (ΔS°) ve serbest enerji değişimleri (ΔG°) gibi termodinamik parametreler de incelenmiştir. Serbest enerji değişimi Bazik Yellow 51 boyar madde adsorpsiyonunun pirinç kabuğu ve yanmış pirinç kabuğu için çalışılan tüm sıcaklıklarda kendiğilinden gerçekleşebileceğini göstermiştir. Bu durum da pirinç kabuğu ve yanmış pirinç kabuğunun, sulu çözeltiden katyonik boyar madde giderimi için uygun bir adsorbent olarak kullanılabileceğini göstermiştir.

Anahtar Kelimeler: Adsorpsiyon, Pirinç kabuğu, Yanmış pirinç kabuğu, Bazik Yellow 51

Kinetics, Isotherm and Thermodynamic Studies of The Adsorption Behavior of Basic Yellow 51 Onto Rice Husk and Burned Rice Husk

ABSTRACT: In this work, rice husk and burned rice husk were used as low cost adsorbents to remove a cationic dye, Basic Yellow 51(BY51) , from aqueous solution by adsorption. Characterization of rice husk and burned rice husk was carried out with Scanning Electron Microscope and Fourier Transform Infrared Spectroscopy. The effects of operational parameters on the efficiency of dye removal including initial dye concentration, contact time, pH, and temperature were investigated. All series experiments were carried out in batch mode. Equilibrium data were analyzed using Langmuir and Freundlich isotherm models and monolayer adsorption capacity was calculated. Kinetic data were studied using pseudo first order and pseudo second order kinetic models and dye removal was found to follow the pseudo second order kinetic model closely. Thermodynamic parameters such as enthalpy change (ΔH°), entropy change (ΔS°) and free energy change (ΔG°) were also investigated. Free energy change showed that adsorption of Basic Yellow 51 was spontaneous at all studied temperatures for rice husk and burned rice husk. It is proposed that rice husk and burned rice husk may be suitable as adsorbents for removal of cationic dyes from aqueous solution.

Keywords: Adsorption; Rice husk; Burned rice husk; Basic Yellow 51

---

[1] Elif BAYRAK TEZCAN (**Orcid ID:** 0000-0003-2033-7551), Istanbul Water and Sewerage Administration, Istanbul, Turkey

[2] Zeynep CEYLAN (**Orcid ID:** 0000-0003-1231-6929), Filiz NURAN ACAR (**Orcid ID:** 0000-0002-8743-4666), Department Of Environmental Engineering, Ataturk University, Erzurum, Turkey

*Sorumlu Yazar / Corresponding Author: Filiz NURAN ACAR, e-mail: facar@atauni.edu.tr

This study is part of Elif Bayrak's master thesis. A part of the study was presented as a poster at the 6th International Symposium on Ecology and Environmental Problems Congress held in Antalya on 17-20 November 2011..

Geliş tarihi / *Received*: 21.08.2019
Kabul tarihi / *Accepted*: 16.09.2019

INTRODUCTION

Many industries produce colored wastewater containing dyes, such as textile, paint, and cosmetic industries. Colored wastewater presents serious problems for receiving environments. Essentiality, this feature of wastewater from industry can severely affect aquatic life due to the reduction in sunlight penetration and toxicity. Besides, many synthetic dyes and color discharges have carcinogenic and mutagenic effects on nature and humans (Haddad et al., 2012). Dyes can be categorized into cationic, anionic and nonionic dyes. Cationic dyes, also called basic dyes, play an important role in the textile industry and are widely used in silk, wool, nylon and acrylic dyeing processes. Water-soluble cationic dyes carry a positive charge on their molecules and release colored cations into the solution. Cyanine, hemicyanine, diazahemicyanine, thiazine, triarylmethane, oxazine and acridine are the main functional chemicals in cationic dyes (Gupta and Suhas, 2009 ; Salleh et al., 2011). The adsorption process is one of the effective methods that has been successfully utilized for color removal from wastewater containing cationic dyes. Many adsorbents have been trialed to reduce cationic dye concentrations in aqueous solutions as an alternative to active carbon, which is an expensive adsorbent. Such alternatives include: sepiolite (Santos and Boaventura, 2016), Moroccan clays (Elmoubarki et al., 2015), wheat straw (Gong et al., 2008 ; Hassanein and Koumanova, 2010), waste carrot leaves and stems (Kuswaha et al., 2011), pineapple stems (Hameed et al., 2009), sugar beet pulp (Vucurovic et al., 2012), rice husk and rice husk ash (Sharma et al., 2010).

Rice husk is abundantly available as a by-product of the rice milling industry and creates potential environmental problems. Every year, millions of tons of rice husk are produced as waste material. Rice husk is an agricultural waste, accounting for about one-fifth of the annual gross rice production in the world. Any possible use of this waste will yield economic as well as environmental dividends (Sharma et al., 2010 ; Chakraborty et al., 2011).

The main aim of this study was to investigate the potential for using rice husk and burned rice husk as adsorbents for the adsorption of Basic Yellow 51 (BY51). The effects of initial dye concentration, contact time, pH and temperature on BY51 adsorption were studied. Adsorption isotherms, kinetic parameters and thermodynamic parameters were also calculated and discussed.

MATERIALS AND METHODS

Cationic dye used in this study was Astrazon Yellow 5GL supplied by Dystar. The color index name of Astrazon Yellow 5GL is Basic Yellow 51 (BY51), C.I. 1480538. The molecular structure of BY51 ($C_{20}H_{25}N_3O_4S$) is shown in Fig. 1. BY51 has molecular weight of 403.49 g/mol. The dye stock solution was prepared by dissolving accurately weighed dye in distilled water to the concentration of 1 g/L. The experimental solutions were obtained by diluting the stock solution of dye in accurate proportions to the desired concentrations.

Rice husk was collected from a rice mill factory in Balıkesir, Turkey. It was washed with distilled water several times to remove all dust-like impurities. The washed material was dried in an air oven at 100 °C for 24 h. Then, the material was ground by a domestic mixer and sieved to constant particle size(<1.00 mm) and the BET Surface Area of RH was measured as $19.82 m^2.g^{-1}$. Dried rice husk was burned in an oven at 500 °C during 1 h. After burning, the material was sieved with a 0.5 mm sieve and the BET Surface Area of BRH was measured as 48.22 $m^2.g^{-1}$. In the experiments, the material remaining under the screen was used. The absorbance of color was read at 425 nm for BY51 solution using a spectrophotometer (Shimadzu -160A). Samples were centrifuged before color analysis and supernatant solution was analyzed for residual color at 425 nm. The primary adsorption test was carried out on both the RH and BRH to compare their adsorption capacity values for BY51 dye removal. Adsorption experiments were conducted in batch mode to investigate the effects of various process parameters such as pH, initial dye concentration and temperature on the adsorption of Basic Yellow 51 with RH and BRH. The selected parameters were solution pH (between 3–8), BY51 concentration (between 25–150 mg L^{-1}), contact time (1–180 min), and solution temperature (between 22 – 40 °C). Conical flasks of 250 mL containing 150 mL of dye solution with known pH, and concentration were shaken in a shaking incubator at 200 rpm, 22 °C for 180 min. After equilibration time, the samples were removed and centrifuged at 4000 rpm for 15 min. Then the centrifuge was analyzed spectrophotometrically for residual adsorbate with the appropriate method (UV–vis spectrophotometer, Shimadzu 160-A). To study the effect of pH, Basic Yellow 51 solutions with varying pH were created using H_2SO_4 (Merck) and NaOH (Merck) solutions.

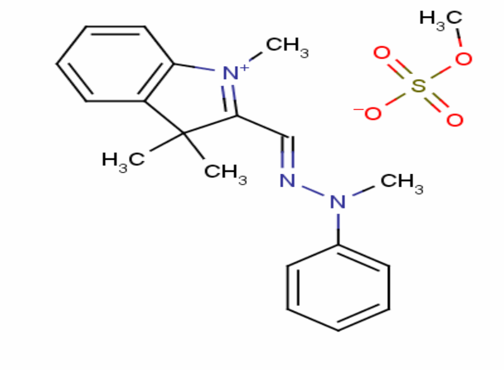

Figure 1. Molecular structure of Basic Yellow 51 dye

Equilibrium and kinetic experiments were carried out by taking a known amount of RH and BRH in 250-mL flasks containing 150 mL of the dye solution with different initial dye amounts (25–150 mg L^{-1}) at original pH of solutions and at 22 °C with 1.25 g L^{-1} adsorbent dosage. Agitation was applied for 180 min, which is enough time to reach equilibrium. Then, the most commonly employed adsorption isotherm models of the Langmuir and Freundlich isotherm models were applied in this present investigation. The kinetic data was analyzed using pseudo-first order and pseudo second order kinetic models. Adsorption of BY51 onto RH and BRH was investigated at 22, 25, 30 and 40 °C under optimized conditions. Various thermodynamic parameters such as enthalpy changes (ΔH°), entropy changes (ΔS°) and Gibbs free energy changes (ΔG°) were used to determine the spontaneity of the adsorption process.

RESULT AND DISCUSSION

Scanning Electron Microscope Analysis (SEM)

The morphological characteristics and surface features of the RH and BRH adsorbents were studied with Scanning Electron Analysis (SEM) (Zeiss Sigma 300). SEM images of RH and BRH before and after dye adsorption are shown in Fig. 2 a, b, c, d. Before adsorption, a hollow and rough structure was determined. After adsorption of dye onto RH and BRH, the surface roughness changed and the pores are packed for both adsorbents.

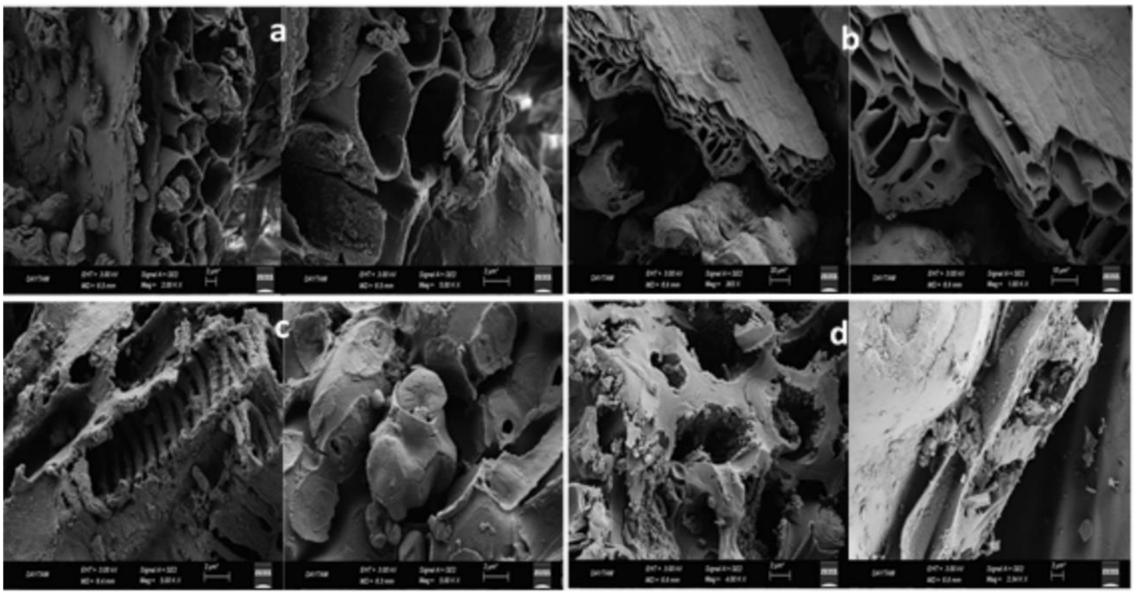

Figure 2. SEM images of RH (**a**) before adsorption, (**c**) after adsorption; SEM images of BRH (**b**) before adsorption, (**d**) after adsorption.

Fourier Transform Infrared Spectroscopy (FTIR)

The functional groups were determined with FTIR spectra (Bruker VERTEX 70v). FTIR analyses were carried out with a scanning range of 4000 – 400 cm^{-1}. The results of FTIR analysis of adsorbents before and after adsorption of BY51 are shown in Fig. 3a and 3b, respectively. RH consists of cellulose, hemicellulose, lignin and wax that presumably occur as alkene, esters, aromatics, ketones and alcohols with oxygen containing different functional groups (Sovattei et al., 2013). The wide peak at 3901.97 to 3566.36 -cm−1 and stretching indicates presence of −OH and −NH groups (Muinde et al., 2017) before adsorption for RH. After adsorption, one peak shifted from 3901.97 to 3903.90 cm−1 on the RH adsorbent. This stretch is due to the silanol group (Si-OH) and to water adsorbed on the surface (Vieira et al., 2014). The peaks at 2929.85 cm^{-1}, 2592.31 cm^{-1}, and 2212.34 cm^{-1} are C-H stretch, -OH from carboxylic acids and CC −≡ from alkynes in the RH, respectively (Muinde et al., 2017). The bands between 1740 cm^{-1} and 1720 cm^{-1} and between 1680 cm^{-1} and 1600 cm^{-1} for RH suggest C=O (ester and carboxylic group from hemicellulose) and C=C (water absorbed) (Ceylan et al., 2018). The stretching of aromatic rings from lignin appeared at 1508.32 cm^{-1} and 1458.17 cm^{-1} for RH adsorbent. Bands at 1080.13 cm^{-1} also defined the presence of O-Si-O vibration attributable to asymmetrical stretching band vibration (Ferraro et al., 2010 ; Hadipramana et al., 2016). The vibration of C-O-H bending (ester) at 1450-1375 cm^{-1}, C-H bending 900-690 cm^{-1} and C-C stretch at 700-400 cm^{-1} (Syafri et al., 2011) were present. For RH, C-C stretch was observed at 607.57 cm^{-1}. The bands between 800 and 468 cm^{-1} for RH suggest the presence of Si-H bonds (Srivastava et al., 2006).

The peaks for BRH are at 3901.97, 3853.75, 3736.36, 3566.36, 2214.27, 1953.88, 1494.82, 1080.13, and 609.50 cm^{-1}. The existence of groups −OH, −NH, Si-OH, C-H, aromatic, C=O stretch, Si-O stretch and C-C stretch were observed. The major shift of the Si-O group band at 1080.13 cm^{-1} is responsible for adsorption (Naiya et al., 2011).

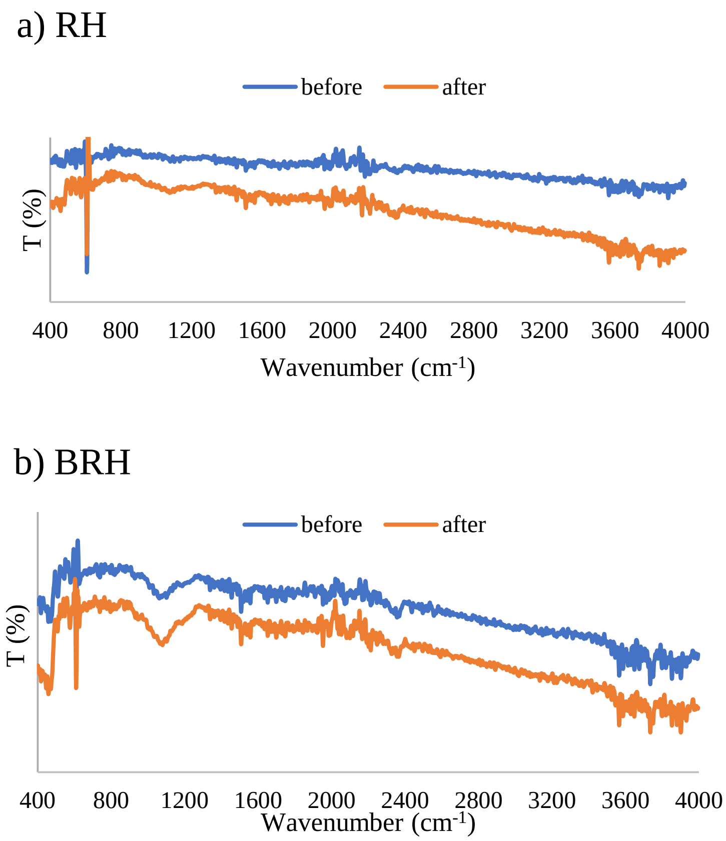

Figure 3. FTIR spectra of (**a**) RH, (**b**) BRH before and after BY51 adsorption.

Effect of pH

The initial pH of the dye solution is one of the most important parameters controlling the adsorption process, particularly the adsorption capacity. The pH of a medium will control the magnitude of electrostatic charges which are imparted by the ionized dye molecules. Therefore, the rate of adsorption will vary with the pH of an aqueous medium (Malekbala et al., 2012). Generally, at low pH solution, the percentage of dye removal will decrease for cationic dye adsorption (Salleh et al., 2011). To study the effect of pH on BY51 adsorption onto RH and BRH, experiments were carried out at 50 mg L^{-1} initial dye concentration with 0.5 g L^{-1} adsorbent dosage at 22 °C for 180 min. Fig. 4 shows the effect of pH on the adsorption capacity at pH ranges of 3–8 for both RH and BRH adsorbents. As can be seen in the figure, an acute increase in dye removal was observed when surrounding pH was increased from 3 to 8. The amount of BY51 adsorbed increased from 9.10 to 31.03 mg g^{-1} and 12.86 to 65.38 mg g^{-1} with the increase in pH from 3 to 8 for RH and BRH adsorbents, respectively. This result indicates that the adsorption was strongly pH dependent. A consistent increase in adsorption capacity of RH and BRH, especially BRH, was noticed as the pH increased from 3 to 4, but further increase in pH from 4 to 8 did not seem to affect the sorption in any way. Similar trends were reported for the adsorption of methylene blue, a cationic dye, onto wheat shells (Bulut and Aydın, 2006), pineapple stem waste, (Hameed and Khairy, 2008) and malachite green (basic green 4), a cationic dye, onto rice straw-derived char (Pavan et al., 2008). The lower adsorption of BY51 at a low pH may be because the adsorbent surface becomes positively charged due to the presence of excess H^+ ions competing with the cation groups on the dye for adsorption sites. At a higher solution pH, the adsorbent surface may become negatively charged, which enhances the attraction for positively charged dye cations through electrostatic forces. Similar observations were reported showing that maximum cationic dye adsorption on agricultural waste occurs at high pH values (Hameed and Khairy, 2008 ; Pavan et al., 2008 ; Wang et al., 2008).

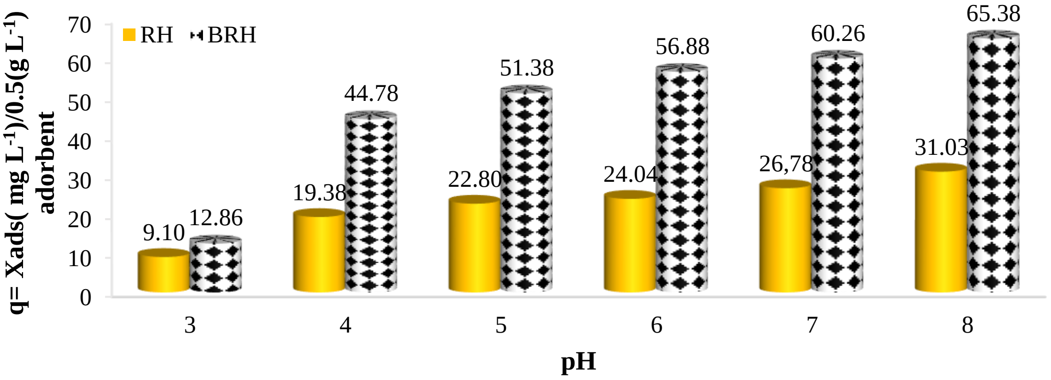

Figure 4. Effect of pH: Comparison of adsorption capacity values for adsorbent (C_o = 50 mg L^{-1}, M= 0.5 g L^{-1}, 22 °C)

Effect of contact time and initial BY51 concentrations

It is essential to evaluate the effect of contact time required to reach equilibrium for designing batch adsorption studies (Hadipramana et al., 2016). The effect of contact time and initial BY51 concentration on the maximum adsorption capacity for the two adsorbents is shown in Figs. 5 and 6. Adsorption capacities were studied using a range of BY51 concentrations between 25-150 mg L^{-1} at fixed adsorbent dosage (1.25 g L^{-1}), natural pH and 22°C temperature for both adsorbents. The effect of initial dye concentration can be determined by preparing an adsorbent – adsorbate solution with fixed adsorbent dose and different initial dye concentration for different time intervals and shaking until equilibrium. The results showed that the adsorption of BY51 increased with an increase in agitation time. However, fast uptake of dye took place in the initial stage of the adsorption process and then the adsorption rate became gradually slower until it reached a constant value for both adsorbent experiments. The uptake of dye was increased from 15.36 to 34.43 mg g^{-1}, and 16.82 to 46.30 mg g^{-1} for RH and BRH adsorbents at 180 min experimental time, respectively, as the initial dye concentration increased from 25 to 150 mg L^{-1}. The increase in 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 transfer at high initial dye concentration (Bulut and Aydın, 2006).

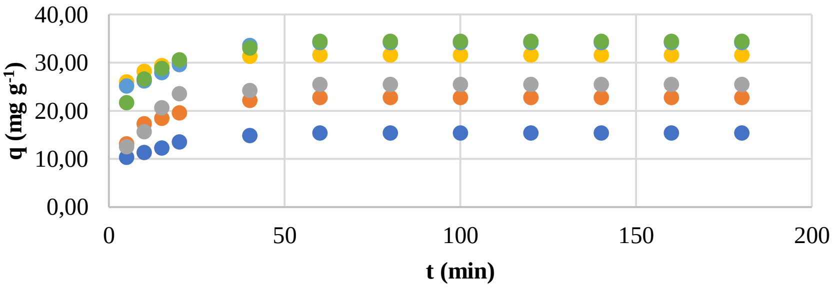

Figure 5. Effect of contact time for various initial BY51 dye concentrations onto RH adsorbent (M= 1.25 g L^{-1}, natural pH, 22 °C, C_0: 25-150 mg L^{-1})

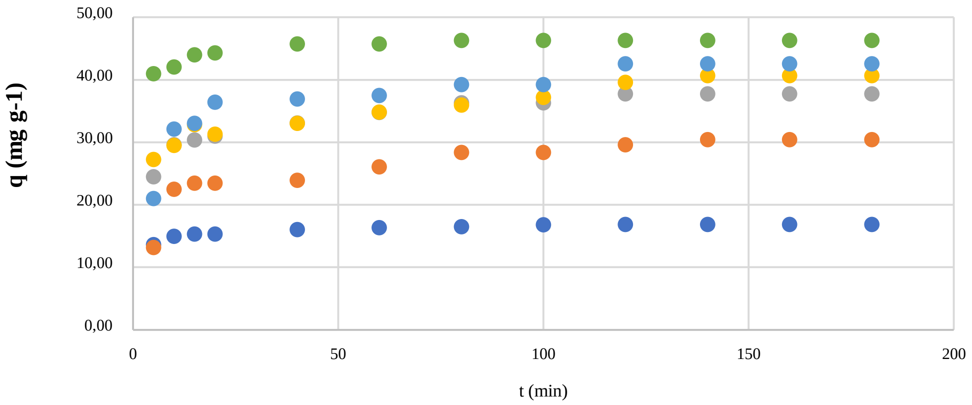

Figure 6. Effect of contact time for various initial BY51 dye concentrations onto BRH adsorbent (M= 1.25 g L^{-1}, natural pH, 22 °C, C_0: 25-150 mg L^{-1})

Equilibrium isotherms

In order to optimize the design of an adsorption system to remove dye, it is important to establish equilibrium data for each system. In the present study, experimental data were tested with the Langmuir and Freundlich isotherm models.

The Langmuir isotherm describes the existence of a monolayer of adsorbate at the outer surface of the adsorbent with a finite number of identical sites and is expressed by (Hameed et al., 2009);

$$q_e = \frac{q_{max}\, b\, C_e}{1+b\, C_e} \text{ or } \frac{ce}{qe} = \left(\frac{1}{Q0b}\right) + \left(\frac{1}{Q0}\right) ce \quad \textbf{(Eq.1)}$$

where q_{max} is the monolayer adsorption capacity of the adsorbent and b represents the constant related to the affinity of the binding sites.

The Freundlich isotherm predicts equilibrium on a heterogeneous surface and hence does not assume formation of a monolayer. The Freundlich equation is given by (Hameed et al., 2009 ; Malekbala et al., 2012 ; Ceylan et al., 2018).

$$q_e = K_F . C_e^{1/n} \quad \text{or} \quad logq_e = \log K_F + \left(\frac{1}{n}\right) logc_e \quad \textbf{(Eq.2)}$$

where K_F and n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively.

The parameters obtained from the Langmuir and Freundlich isotherms and the correlation coefficients are listed in Table 1. The applicability of the isotherm is compared by judging the correlation coefficients (R^2). R^2 values for Langmuir isotherms were found to be higher than those for Freundlich isotherms for both adsorbents. This indicates that the adsorption of BY51 on RH and BRH takes place as monolayer adsorption on a surface that is homogeneous in terms of adsorption affinity and BRH is more effective than RH to remove BY51 dye from aqueous solution.

Table 1. Adsorption isotherm constants for BY51 adsorption onto RH and BRH

Isotherms	RH	BRH
Langmuir isotherm		
q_{max} (mg g^{-1})	38.759	49.020
b (L mg^{-1})	0.071	0.123
R^2	0.985	0.997
Freundlich isotherm		
n	3.47	3.32
K_F	9.25	12.51
R^2	0.979	0.927

Adsorption kinetics

The adsorption kinetics of BY51 onto RH and BRH were calculated with both pseudo first order (Lagergren) and pseudo second order (Ho) kinetic models. The pseudo first order kinetic model is given as (Chowdhury et al., 2011).

$$ln(q_e - q_t) = lnq_e - k_1 t \quad \textbf{(Eq.3)}$$

where q_t (mg g^{-1}) represents the amount of adsorbate adsorbed at a predetermined time t (min), q_e (mg g^{-1}) is the amount of adsorbate adsorbed at equilibrium and k_1
(1 min^{-1}) is the rate constant.

The pseudo second-order kinetic model, known as the Ho equation, is defined as follows (Lagergren, 1898 ; Ho and McKay, 1998):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad \textbf{(Eq.4)}$$

where k_2 (g $mg^{-1}min^{-1}$) is the pseudo second order rate constant and h (mg $g^{-1}min^{-1}$) is the initial adsorption rate.

The rate constants, correlation coefficients and other essential parameters for kinetic rate models were calculated for RH and BRH as seen in Table 2. It can be observed that R^2 values for the pseudo second order were higher than for the pseudo first order model. According to R^2 values, the pseudo first order kinetic model was in the range of 0.7652 - 0.9904 and 0.8993 - 0.9604, whereas the pseudo second order model ranges were 0.9901 - 0.9994 and 0.9889 – 0.9987 for RH and BRH, respectively.

Effect of temperature

Solution temperature is an important parameter for the adsorption mechanism. Any change in the temperature causes a change in adsorption efficiency and adsorption. The effect of temperature on BY51 removal was also investigated using RH and BRH adsorbents at 50 mg/L initial dye concentration and natural pH. The selected temperature values were set at 22, 25, 30, and 40 °C and adsorption capacity results from this study are indicated in Figure 7. Comparing the adsorbents, it is a fact that the adsorption capacity of BRH is higher than RH at all different temperatures. For both adsorbents, a gradual increase in adsorption capacity was detected at an initial dye concentration of 50 mg L^{-1}. The results indicated that the uptake capacity increased with increased temperature, which is attributed to enhanced diffusion of BY51 molecules towards active sites on RH and BRH leading to higher adsorption capacity.

Table 2. Comparison of adsorption kinetic models for different initial BY51 concentrations onto RH and BRH at 22 °C

		Pseudo First Order Kinetic			**Pseudo Second Order Kinetic**			
	C_o	**k_1**	**q_{e1}**	**R^2**	**k_2**	**q_{e2}**	**h**	**R^2**
	(mg L^{-1})	(1 min^{-1})	(mg g^{-1})		(g $mg^{-1}min^{-1}$)	(mg g^{-1})	(mg $g^{-1}min^{-1}$)	
RH	25	0.0099	4.3501	0.9296	0.0089	15.6006	2.1661	0.9901
	50	0.0233	15.0179	0.7652	0.0028	24.9376	1.7413	0.9958
	75	0.0188	13.4245	0.9802	0.0030	26.1780	2.0558	0.9976
	100	0.0108	5.8060	0.9100	0.0071	31.9489	7.2472	0.9976
	125	0.0138	9.1306	0.9904	0.0066	33.7838	7.5329	0.9992
	150	0.0320	17.3420	0.9694	0.0041	35.8423	5.2671	0.9994
BRH	25	0.0127	7.9378	0.8993	0.0042	20.0000	1.6800	0.9889
	50	0.0154	13.7499	0.9243	0.0029	34.7222	3.4963	0.9943
	75	0.0157	15.5200	0.9313	0.0026	43.2900	4.8725	0.9951
	100	0.0209	18.3442	0.9598	0.0022	46.9483	4.8491	0.9963
	125	0.0200	16.0842	0.9604	0.0032	47.3934	7.1876	0.9981
	150	0.0177	11.8905	0.9462	0.0044	48.3092	10.2686	0.9987

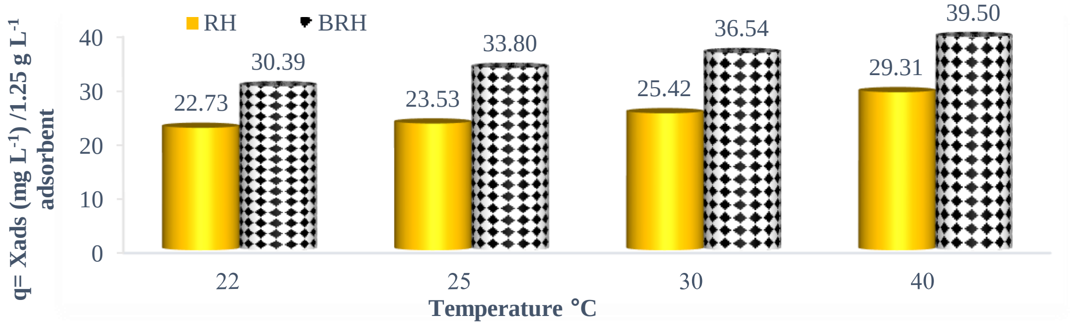

Figure 7. Effect of temperature: Comparison of adsorption capacity values for adsorbents (C_o = 50 mg L^{-1}, M=1.25 g L^{-1}, natural pH)

Thermodynamic parameters

The thermodynamic parameters such as Gibbs free energy change (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were calculated using the following equations (Chowdhury et al., 2011 ; Abbas and Trari, 2015).

$$\Delta G^o = -RTlnK_d \qquad \textbf{(Eq.5)}$$

$$\Delta G^o = \Delta H - T\Delta S^o \qquad \textbf{(Eq.6)}$$

From Eq. 5-6 we get;

$$lnK_d = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R} \qquad \textbf{(Eq.7)}$$

T is the temperature in Kelvin and R is the universal gas constant defined as 8.314 J $mol^{-1}.K^{-1}$. The values of ΔH° and ΔS° were determined from slope intercept of the plot of lnK_d against 1/T (Fig. 8). The values of ΔG° were calculated using Eq 6. The values for the thermodynamic parameters are presented in Table 3. The negative values of ΔG° and the positive values of ΔH° indicate that the adsorption of BY51dye was spontaneous and endothermic. In addition, positive values of ΔS° imply increased randomness of the solid solution interface during adsorption (Chowdhury et al., 2011).

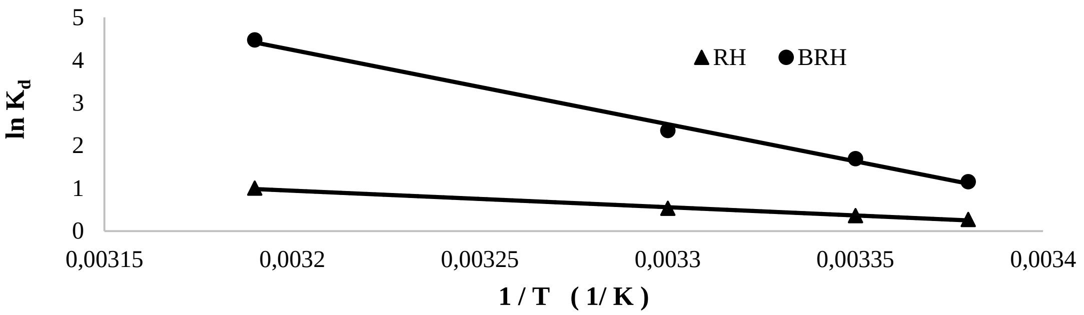

Figure 8. Plots of lnK$_d$ versus 1/T for RH and BRH adsorbents: Continuous lines represent fit of the experimental data (C_o = 50 mg L^{-1}, M=1.25 g L^{-1},natural pH)

Table 3. Thermodynamic parameters (C_o=50 g L^{-1}, M=1.25 g L^{-1}, natural pH)

Ads.	**Temperature** (K)	**ΔG°** (kj mol^{-1})	**ΔH°** (kj mol^{-1})	**ΔS°** (j $mol^{-1}.K^{-1}$)
RH	295	-4.6595	28.1445	111.2
	298	-4.9931		
	303	-5.5491		
	313	-6.6611		
BRH	295	-2.2835	144.5970	497.9
	298	-3.7772		
	303	-6.2667		
	313	-11.2457		

CONCLUSIONS

In this study, the abilities of RH and BRH adsorbents to remove BY51, a cationic dye, from aqueous solution were investigated. At the same time, adsorption performances of RH and BRH were compared under all experimental conditions. Experimental results show that RH was effective for the removal of BY51. However, BRH is an even more effective adsorbent. Equilibrium data obtained had isotherms calculated using two adsorption isotherm equations: Langmuir and Freundlich models. Adsorption isotherms abided well by the Langmuir model for both adsorbents. The maximum adsorption capacity values were found to be 38.76 mg g^{-1} and 49.02 mg g^{-1} for RH and BRH, respectively. The adsorption was dependent on the pH of the aqueous solution, with a high uptake of cationic dye, BY51, at high pH. The kinetic studies of BY51 dye indicated that the adsorption kinetics of dye onto RH and BRH followed pseudo second order kinetics at different dye concentration values. The rise in temperature increases the amount of BY51 dye adsorbed. Thermodynamic data demonstrated that BY51 adsorption onto RH and BRH was spontaneous and an endothermic reaction.

REFERENCES

Abbas M , Trari M, 2015. Kinetic, Equilibrium and Thermodynamic Study on Removal of Congo Red from Aqueous Solutions by Adsorption onto Apricot Stone. Process Safety and Environmental Protection, 98: 424–436.

Bulut Y, Aydın H, 2006. A Kinetics and Thermodynamics Study of Methylene Blue Adsorption on Wheat Shells. Desalination, 194(1-3): 259-267.

Ceylan Z, Mustafaoğlu D, Malkoç E, 2018. Adsorption of Phenol by MMT-CTAB and WPT-CTAB: Equilibrium, Kinetic, and Thermodynamic Study. Particulate Science and Technology, 36(6): 716-726.

Chakraborty S, Chowdhury S, Saha PD, 2011. Adsorption of Crystal Violet from Aqueous Solution onto NaOH- Modified Rice Husk. Carbohydrate Polymers, 86: 1533-1541.

Chowdhury S, Mishra R, Saha P, Kushwaha P, 2011. Adsorption Thermodynamics, Kinetics and Isosteric Heat of Adsorption of Malachite Green onto Chemically Modified Rice Husk. Desalination, 265: 159-168.

Elmoubarki R, Mahjoubi FZ, Tounsadi H, Moustadraf J, Abdennouri M, Zouhri A, Alban AE, Barka N, 2015. Adsorption of Textile Dyes on Raw and Decanted Moroccan Clays: Kinetics, Equilibrium and Thermodynamics. Water Resources and Industry, 9: 16-29.

Ferraro RM, Nanni A, Vempati RK, Matta F, 2010. Carbon Neutral Off – White Rice Husk Ash as a Partial White Cement Replacement. Journal of Materials in Civil Engineering, 22(10): 1078-1083.

Gong R, Zhu S, Zhang D, Chen J, Ni S, Guan R, 2008. Adsorption Behaviour of Cationic Dyes on Citric Acid Esterifying Wheat Straw. Desalination, 230: 220-228.

Gupta VK, Suhas X, 2009. Application of Low-Cost Adsorbents for Dye Removal – A Review. Journal of Environmental Management, 90(8): 2313-2342.

Haddad ME, Mamouni R, Saffaj N, Lazar S, 2012. Removal of a Cationic Dye Basic Red from Aqueous Solution by Adsorption onto Animal Bone Meal. Journal of the Association of Arab Universities for Basic and Applied Science, 12(1): 48-54.

Hadipramana J, Riza FV, Rahman IA, Loon LY, Adnan SH, Zaidi AMA, 2016. Pozzolanic Characterization of Waste Rice Husk Ash (RHA) from Muar. IOP Conferences Series: Materials Science and Engineering, 160: 1-10.

Hameed BH, Khairy MI, 2008. Malachite Green Adsorption by Rattan Sawdust: Isotherm, Kinetic and Mechanism Modeling. Journal of Hazardous Materials, 159: 574- 579.

Hameed BH, Krishni RR, Sata SA, 2009. A Novel Agricultural Waste Adsorbent for the Removal of Cationic Dye from Aqueous Solutions. Journal of Hazardous Materials, 162: 305-311.

Hassanein T, Koumanova B, 2010. Evaluation of Adsorption Potential of the Agricultural Waste Wheat Straw for Basic Yellow 21. Journal of the University of Chemical Technology and Metallurgy, 45: 407-414.

Ho YS, McKay G, 1998. Sorption of Dye from Aqueous Solution by Peat. Chemical Engineering Journal, 70(2): 115-124.

Kuswaha AK, Gupta N, Chattopadhyaya MC, 2014. Removal of Cationic Methylene Blue and Malachete Green Dyes from Aqueous Solution by Waste Materials of Daucus Carota. Journal of Saudi Chemical Society, 18(3): 200-207.

Lagergren S, 1898. Zur Theorie der Sogenannten Adsorption Geloster Stoffe, Kungliga Svenska.Vetenskapsakademiens Handlingar, 24: 1-39.

Malekbala MR, Hosseini S, Yazdi SK, Masoudi S, Malekbala MR, 2012. The Study of the Potential Capability of Sugar Beet Pulp on the Removal Efficiency of Two Cationic Dyes. Chemical Engineering Research and Design, 90(5): 704-712.

Muinde VM, Onyari JM, Wamalwa B, Wabomba J, Nthumbi RM, 2017. Adsorption of Malachite Green from Aqueous Solutions onto Rice Husks: Kinetic and Equilibrium Studies. Journal of Environmental Protection, 8: 215-230.

Naiya TK, Singha B, Das SK, 2011. FTIR Study for the Cr(VI) Removal from Aqueous Solution Using Rice Waste. International Conference on Chemistry and Chemical Process IPCBEE , IACSIT, Singapore 10: 114-119.

Pavan FA, Mazzocato AC, Gushikem Y, 2008. Removal of Methylene Blue Dye from Aqueous Solutions by Adsorption Using Yellow Passion Fruit Peel as Adsorbent. Bioresource Technology, 99(8): 3162-3165.

Salleh MAM, Mahmoud DK, Karim WA, Idris A, 2011. Cationic and Anionic Dye Adsorption by Agricultural Solid Wastes: A Comprehensive Review. Desalination, 280: 1-13.

Santos SCR, Boaventura RAR, 2016. Adsorption of Cationic and Anionic Azo Dyes on Sepiolite Clay: Equilibrium and Kinetic Studies in Batch Mode. Journal of Environmental Chemical Engineering, 4(2): 1473-1483.

Sharma P, Kaur R, Baskar C, Chung WJ, 2010. Removal of Methylene Blue from Aqueous Waste Using Rice Husk and Rice Husk Ash. Desalination, 259(1-3): 249-257.

Sovattei C, Bacani FT, Promentilla MAM, Hinode H, Seinghen H, 2013. Utilization of Untreated and Treated Rice Husk as Adsorbents for Lead Removal from Wastewater. The Research Congress, De La Salle University Manila, March 7-9,2013, pp: 1-7.

Srivastava VC, Mall ID, Mishra IM, 2006. Characterization of Mesoporous Rice Husk Ash (RHA) and Adsorption Kinetics of Metal Ions from Aqueous Solution onto RHA. Journal of Hazardous Materials, 134(1-3): 257-267.

Syafri R, Ahmad I, Abdullah I, 2011. Effect of Rice Husk Surface Modification by LENR the on Mechanical Properties of NR/HDPE Reinforced Rice Husk Composite. Sains Malaysiana, 40(7): 749-756.

Vieira MGA, Neto AFA, Silva GC, Nóbrega CC, Filho AAM, 2014. Adsorption of Lead and Copper Ions from Aqueous Effluents on Rice Husk Ash in a Dynamic System. Brazilian Journal of Chemical Engineering, 31: 519-529.

Vucurovic VC, Razmovski RN, Tekic MN, 2012. Methylene Blue (Cationic Dye) Adsorption onto Sugar Beet Pulp. Journal of Taiwan Institute of Chemical Engineers, 43(1): 108-111.

Wang XS, Zhang Y, Jiang Y, Sun C, 2008. The Removal of Basic Dyes from Aqueous Solutions Using Agricultural By-Products. Journal of Hazardous Materials, 157(2-3): 374-385.