Sigma J Eng & Nat Sci 36 (3), 2018, 803-818

Sigma Journal of Engineering and Natural Sciences
Sigma Mühendislik ve Fen Bilimleri Dergisi

Research Article

EFFICIENT REMOVAL OF BASIC YELLOW 51 DYE VIA CARBONIZED PAPER MILL SLUDGE USING SULFURIC ACID

Ali YARAŞ*[1], Hasan ARSLANOĞLU[2]

[1]*Bartın University, Dep. of Metallurgical and Materials Eng.,BARTIN;* ORCID:0000-0003-1725-7788
[2]*Fırat University, Department of Chemical Engineering,ELAZIĞ;* ORCID:0000-0002-3132-4468

Received: 06.04.2018 Revised: 22.05.2018 Accepted: 25.06.2018

ABSTRACT

In present study, paper mill sludge (PMS) in cellulosic structure carbonized with sulfuric acid was utilized for adsorption of cationic basic yellow 51 (BY 51) dye from synthetic solution. The parameters affecting on removal of BY 51 dye following; initial pH (2-11), amount of carbonized paper mill sludge (CPMS) (0.25-1.5 g/l), initial concentration (0.5-2 mM), time (0-360 min.) and temperature (25-55^{o}C) were studied in the batch adsorption experiments. The physical and chemical properties of prepared CPMS were determined using elemental analyzes, scanning electron microscopy (SEM) and BET techniques. Optimum initial pH was measured to be 7 for the removal of BY 51 dye. The obtained equilibrium data in various initial concentrations of BY 51 dye solution varied from 0.5 to 2.5 mM for three temperatures (25^{o}C, 40^{o}C and 55^{o}C) were applied to Langmuir and Freundlich isotherms. The calculated maximum adsorption capacity (q_{max}) from Langmuir equation was achieved 1089.45 mg/g depending on increasing temperature from 25^{o}C to 55^{o}C. The experimental results for all temperatures were applied to pseudo-first order kinetic model, pseudo-second order kinetic model and intra-particle diffusion model. Consequently, it was good agreement with the second-order kinetic model and the activation energy (E_a) is calculated as 11.642 kJ/mol. Thermodynamic parameters such as enthalpy (ΔH^{o}, +19.32 kJ/mol), free energy (ΔG^{o}, -23.02 kJ/mol) and entropy (ΔS^{o}, 0.142 kJ/molK) were also calculated. The results showed that the adsorption phenomena of cationic BY 51 dye is of endothermic and spontaneous nature. The findings presented that CPMS could be utilized as adsorbent in the treatment of industrial wastewater.

Keywords: Paper mill sludge, basic yellow 51, carbonization, adsorption, isotherm, kinetic.

---

1. INTRODUCTION

Industrial wastewater containing various pollutants in organic and inorganic structures are important causes of environmental pollution. There are also toxic, mutagenic and even carcinogenic influences that remain unchanged for too long, as these pollutants were decomposed in the environment for a certain period of time. Because these pollutants cannot be effectively removed by conventional wastewater treatment methods, they are discharged into the environment again.

A significant amount of waste water generates by textile industries which consume large amounts of water and chemicals [1]. It is known that azo and nitro compounds in these

---

[*] Corresponding Author: e-mail: aliyaras@bartin.edu.tr, tel: (378) 501 16 17

wastewaters are conver ted to amines toxic by microorganisms in nature and carcinogenic amines occur under anaerobic conditions [2–4]. Furthermore, it has been found that the natural degradation of anthraquinone-type dyes in aromatic form is very difficult and that some disperse dyes also accumulate in vivo [1]. At the present time, the American Institute of Paint Manufacturers does not consider other dyes as toxic substances except for benzidine and tri-methane-based dyes [5].

The dyes reduce the light permeability in the water and affect negatively the photosynthesis activity. In addition, the accumulation of these dyes in some microorganisms also increases the risk of transmission of toxic and carcinogenic substances from living organisms. These substances in the organic structure are biodegraded in the aquatic environment and converted into simple and harmless substances and also consuming dissolved oxygen. On the other hand, pigments disturb the aesthetic appearance of natural waters. It is thought that about 1-2 million kg of dyes with an annual production amount of about 10 million kg are released to the environment as dissolved or suspended. From these reasons, removal of textile wastewaters has importance in terms of environment and human health [5].

In recent years, researchers have focused on investigating the removal of organic and inorganic pollutants in wastewaters by adsorption method. A wide variety of agricultural residues and biomass such as clay, fly ash, peat charcoal, activated carbon, orange peel, apple lime, banana peel, corn cob, corn husk, wheat straw, barley crust and water lily plant are utilized as adsorbents in adsorption method [6–9].

There are numerous studies in the literature using active carbon derived from cellulose based organic wastes in the removal of heavy metals, dyes and other contaminants from the wastewaters [10–13]. Due to the high cost of commercial active carbon, different methods are currently being used to obtain activated carbon from organic materials. One of these methods is to decompose the organic materials in the presence of acid by converting the hydrogen and oxygen in their structure into water. In this context, the paper mill sludge (PMS) that is released after processing contains mainly cellulose, hemicellulose and lignin. For this reason, it is possible to obtain activated carbon as a result of reaction of cellulose using sulfuric acid.

The PMS containing cellulosic as well as other organic and inorganic substances in its structure causes significant environmental problems [14, 15]. Despite the fact that adsorbent production from industrial wastes is a continuously developing research field in recent years, there has been no study of the utilization CPMS as adsorbent in the literature. In this study, it has been investigated that PMS carbonized using sulfuric acid can be utilized to remove cationic dye from aqueous solutions after neutralization with sodium carbonate. For this purpose, adsorption experiments were carried out in batch process and the affecting parameters on the removal of BY 51 dye were studied. In addition, kinetic and equilibrium calculations were carried out thermodynamic parameters such as enthalpy (ΔH^o), entropy (ΔS^o) and free energy (ΔG^o) of the adsorption process were determined.

2. EXPERIMENTAL STUDY

Preparation and carbonization of the PMS used in the adsorption experiments is summarized in the following sections.

2.1. Preparation of Material

The PMS was provided from the OYKA paper factory in Çaycuma/Zonguldak in 2016. It was spread on a polyethylene ground as a thin layer and dried by blowing air with a fan. The dried PMS was crushed and sieved. The PMS fractions (*-16 + 30 mesh*) ($0.6 < x < 1.2$ *mm.*) were dried at 50°C for 12 h.

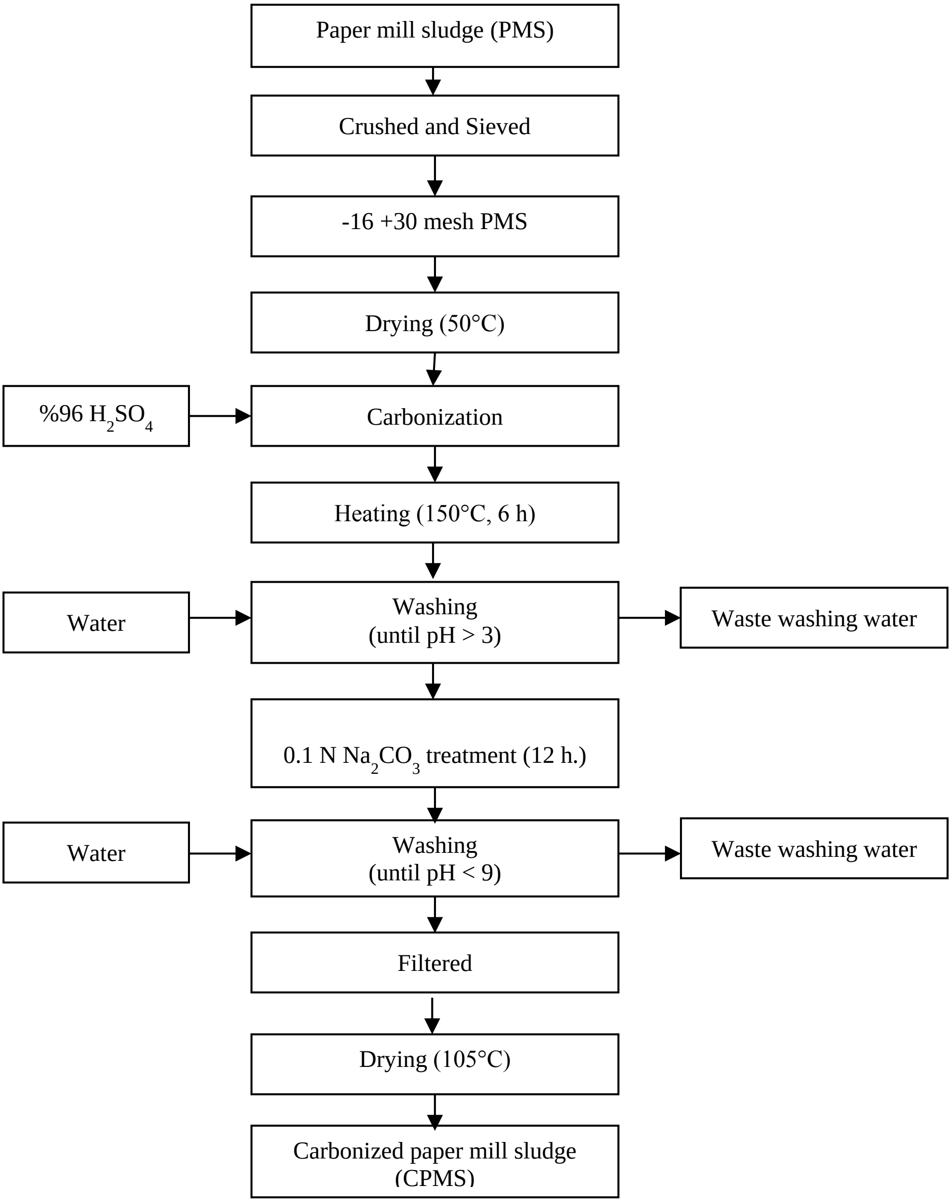

Figure 1. Flow chart of carbonization process

The prepared PMS was carbonized by mixing about 2 times its weight with 96% sulfuric acid. The product was heated at 150°C for 6 hours in order to take place carbonization reaction completely and to remove volatile components. Following that, CPMS was washed with distilled water for about 15 min., about 50 times its weight. The solid residue was washed several more times with distilled water until pH:3 of the wash water reached to remove the remaining sulfuric acid in CPMS. Neutralization was carried out using 0.1 N Na_2CO_3 solution to remove any possible sulfuric acid or other impurities remaining in the pores of CPMS. For this purpose, CPMS was kept in solution for 12 hours, then filtered and washed several times with distilled water until pH of the wash solution was 8-8.5. At the end of the washing process, the solid residue was dried at 105°C and stored in capped containers for utilization in experiments. The flow chart of the CPMS production is shown in Figure 1.

2.2. Preparation of Dye Solutions

Basic Yellow 51 (BY 51) dye ($C_{20}H_{25}N_3O_4S$, molecule weight: 403.5 g/mol) was used in this study. Its chemical formula [1,3,3-trimethyl-2 [(methylphenylhydrazone) methyl] -3H-indolium methylsulfate] is shown in Figure 2. After the stock solution containing 5 mM BY 51 dye was prepared, the working solutions (0.5: 1, 1.5: 2, 2.5 mM) and assay standards were prepared by diluting the stock solution with distilled water at appropriate ratios.

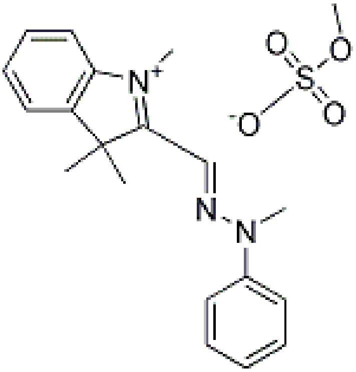

Figure 2. Structural formula of BY 51 dye

2.3. Removal of Dye

All adsorption experiments were carried out in 300 ml erlenmeyer using an adjustable incubator (Zhcheng ZHWY-200D) with a shaking speed and temperature. Initial pH measurements of the dye solutions prepared were carried out using diluted HCl and NaOH solutions with pH meter (Metler Delta 350). After the CPMS was added to the solutions, the mixtures were stirred at the stipulated time and temperature at 200 rpm. After filtered the mixtures, pH was measured of the supernatant and the concentration of the dye was determined.

In preliminary studies, CPMS was added to 200 ml of BY 51 solutions (1 mM) and stirred for 24 h. The necessary measurements were performed on the supernatant and the removal values were calculated. Then, to investigate the effect of initial pH on dye removal, CPMS (1 g/l) was added to dye solutions (1 mM) at different initial pHs, stirred for 24 h. and amount of BY 51 were determined on the supernatant.

Experiments were performed at different concentrations of BY 51 solutions (0,5; 1; 1,5; 2; 2,5 mM) and temperatures 25; 40 and 55°C) using CPMS 1 g/l dosage due to study the effects of temperature and time on removal of BY 51. The experimental results are applied to pseudo-first and pseudo-second order kinetic models and intra-particle diffusion models. The activation energy value of process (E_a) was calculated using the suitable kinetic model. Then, the experimental results were applied to Langmuir and Freundlich isotherms, and some thermodynamic parameters were calculated.

2.4. Analysis of Solutions

Dye concentrations of BY 51 in the solutions were calculated using the visible region spectrophotometer (UV 1201, Shimadzu) according to the absorbance measurements at 425 nm. The removal efficiency of BY 51 dye and its quantity of adsorbed per unit sorbent amount were calculated from following equations;

$$\%Removal = (C_0 - C_s).\frac{100}{C_0} \qquad \text{(Eq.1)}$$

$$q = \frac{(C_0 - C_s).V}{m} \qquad \text{(Eq.2)}$$

C_o and C_s are the initial and final concentration (mM) of BY 51 solution, respectively. q is the volume of BY 51 adsorbed by the unit mass of adsorbent (mM/g), V is the volume of solution (l), m is the mass of sorbent (g). All experiments were performed in two parallel.

2.5. Characterization of Material

SEM image and some properties of the CPMS are shown in Figure 3 and Table 1, respectively (TESCAN MAIA3 XM). As shown Figure 3, it is clearly seen that CPMS has different shapes, sizes and pores.

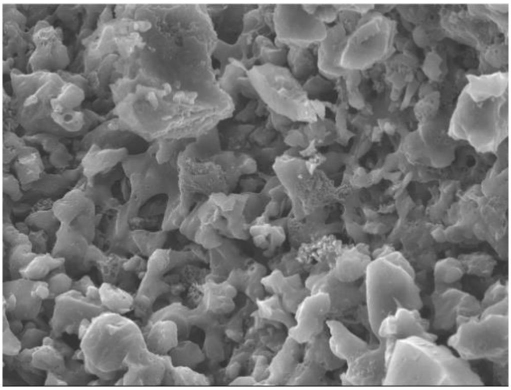

Figure 3. SEM image of carbonized paper mill sludge (CPMS)

Table 1. Some properties of carbonized paper mill sludge (CPMS)

Parameter	Value
Moisture (%)[a]	2.6
Ash (%)[b]	11.4
Bulk density (g/cm^3)	0.65
Conductivity (µs/cm) [c]	45.4
pH[c]	7.80
Surface area (BET-N_2) (m^2/g)	19.5
Particle size (µm)	<150
Iodine index (mg/g)	95.6
COD (mg O_2/L)[c]	69.6
Cation exchange capacity (mg/g)	0.95
Water dissolution (%) [d]	0.45
Copper sorption (mg/g)[e]	0.82

[a] Result of fixed weighing at 105ºC

[b] Ash result at 900ºC.

[c] Measurements in liquid obtained as a result of equilibration of 1 g of the material with 100 ml of water for 24 h.

[d] Measurement of solid material obtained as a result of equilibration of 1 g of the material with 100 ml of water for 24 h.

[e] 1 g of the substance is stirred with 200 ml of 10 mM $CuSO_4.5H_2O$ solution for 24 h. in the pH 4.8 buffer medium and the resultant is analyzed in the solution.

3. RESULTS AND DISCUSSION

At the end of 24 h., the influence of CPMS dosage on removal of the aqueous solution of BY 51 and the results of the final pH of the solutions are demonstrated in Figure 4. Accordingly, it is possible to state that the removal of BY 51 dye from the solution (1 mM) is also increased due to the increase of the sorbent dosage. On the other hand, it is observed that there is not a significant change in the final pH as compared to the initial pH of the solutions, but a slight increase in the pH.

After the adsorbent dosage is selected as 1 g/l, the experiment results on the influence of initial pH of solution on removal of BY 51 dye are given in Figure 5. As seen from Figure 5, there is a noticeable increase in removal of BY 51 dye up to pH 4, while there is no significant raise in subsequent pH values. In addition, when the initial pH of the solution was between 2 and 6, a slight increase was observed in the final pH values of the solution. Similarly, the final pH values are balanced at near neutrality in experiments where initial pH values of solutions ranged from 6 to 10. The final pH was measured as 7.5 in experiments where the initial pH of the solution is 11. Consequently, it can be said that the high amount of dye removal is occurred where the initial pH of is neutral and there is no substantial influence on the removal of the pH change of about 7.1. According to these results, it was decided to carry out the subsequent systematic experiments at pH value of the BY 51 solution without any pH adjustment.

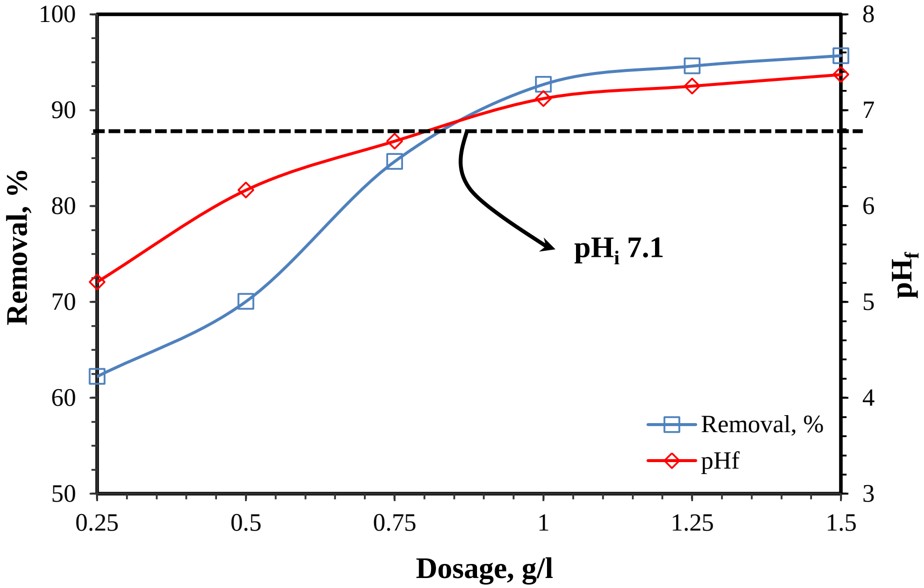

Figure 4. Effect of sorbent dosage on removal of BY 51 dye

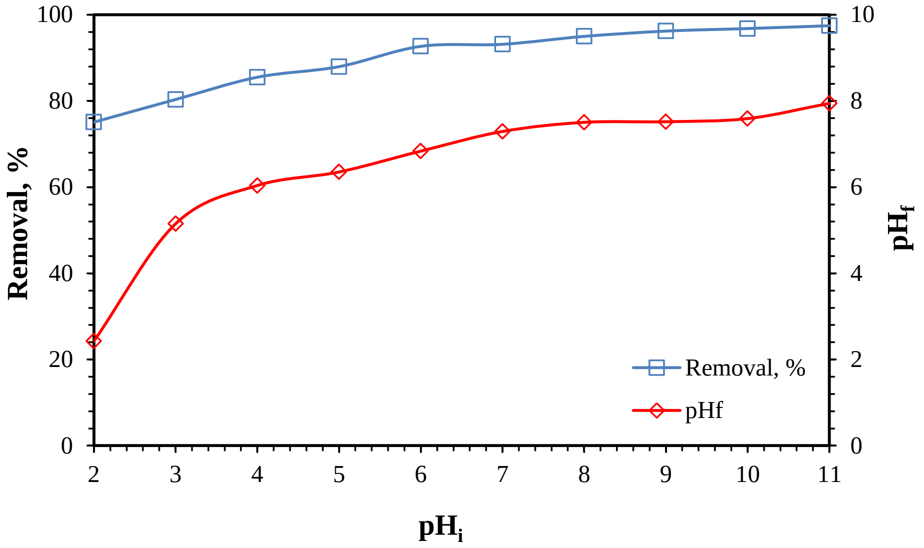

Figure 5. Effect of initial pH on removal of BY 51 dye

Figure 6 shows the sorption capacities of experiments carried out depending on time and initial concentration at various temperatures using 1 g/l dosage of CPMS. As seen from Figure 6, at all temperature values, removal rate of BY 51 increases rapidly up to 60 minutes, while the increase is observed to slow down very slowly. It can be stated practically that the removal of BY 51 is completed at the end of 120 min. However, the application of equilibrium data to isotherms and calculations of kinetic models were performed using the values at 240 min.

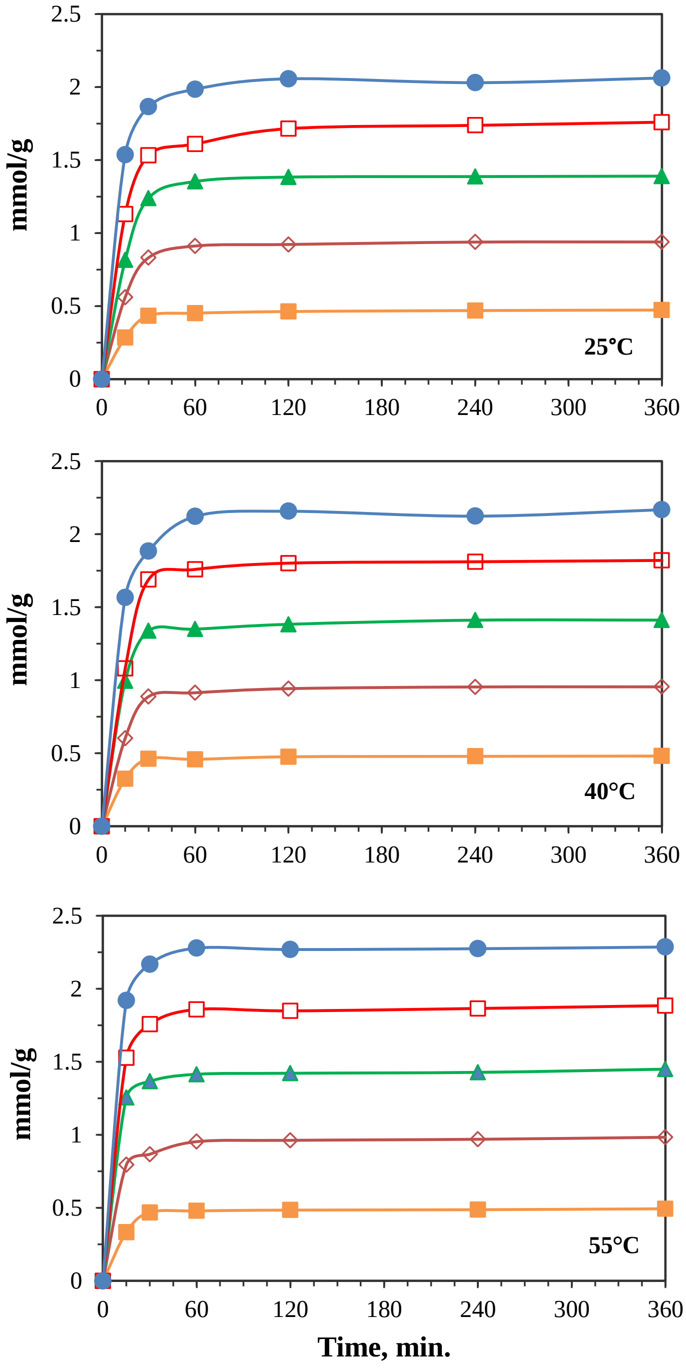

Figure 6. Effect of initial concentration, temperature and contact time on removal of dye (● 2.5 mM; □ 2 mM; ▲ 1.5 mM; ◊ 1 mM; ■ 0.5 mM).

The experimental data were applied to pseudo-first order [16], pseudo-second order [17] and intra-particle diffusion models [18] (Eq. 3, Eq. 4 and Eq. 5 respectively). For that purpose, the reaction rate constants ((k_1(min^{-1}), k_2 (gm^{-1}.min^{-1}) and k (mM.g^{-1}.min$^{-1/2}$)) were calculated from the slope of the linear graphs drawn by the above mentioned equations. The calculated regression coefficients and the calculated reaction rate constants are given in Table 2, respectively.

$$\log(q_e - q_t) = log q_e - \frac{k_1}{2.303} t \qquad \text{(Eq.3)}$$

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

$$q = k . t^{1/2} + I \qquad \text{(Eq.5)}$$

When the kinetic results at different temperatures for different solution concentrations (0.5; 1; 1.5 and 2 mM) were examined, it was found that the most suitable model was pseudo second order kinetic model since the correlation coefficient value (R^2) is the highest, the calculated values and the experimental data are very close to each other (Table 2 and Table 3).

Table 2. Regression coefficients (R^2) and rate constants of pseudo-first order, pseudo-second order and intra-particle diffusion models

Temperature, °C	C_o(mM)	Pseudo I. Order	Pseudo II. Order	Diffusion Model	Pseudo I. Order	Pseudo II. Order	Diffusion Model
		k_1	k_2	k_3	R_1^2	R_2^2	R_3^2
25	0.5	0.024	0.358	0.009	0.7825	0.9997	0.4701
	1	0.027	0.179	0.018	0.7974	0.9996	0.4993
	1.5	0.040	0.127	0.027	0.9488	0.9995	0.4760
	2	0.023	0.083	0.032	0.9338	0.9999	0.6216
40	0.5	0.027	0.502	0.007	0.7614	0.9990	0.4283
	1	0.028	0.209	0.016	0.8466	0.9997	0.4635
	1.5	0.020	0.173	0.019	0.7063	0.9999	0.4752
	2	0.031	0.102	0.032	0.8544	0.9995	0.4352
55	0.5	0.022	0.492	0.007	0.6705	0.9998	0.4197
	1	0.021	0.275	0.010	0.836	0.9999	0.6763
	1.5	0.017	0.294	0.010	0.7622	0.9999	0.6218
	2	0.020	0.198	0.017	0.5938	0.9999	0.5291

Table 3. Calculated constants for pseudo-second order

Temperatue, °C	C_o(mM)	$q_{exp.}$	$q_{cal.}$	k_2	R_2^2
25	0.5	0.471	0.482	0.358	0.9997
	1	0.940	0.959	0.179	0.9996
	1.5	1.388	1.418	0.127	0.9995
	2	1.739	1.793	0.083	0.9999
40	0.5	0.479	0.488	0.502	0.9990
	1	0.954	0.971	0.209	0.9997
	1.5	1.412	1.431	0.173	0.9999
	2	1.812	1.852	0.102	0.9995
55	0.5	0.488	0.499	0.492	0.9998
	1	0.970	0.991	0.275	0.9999
	1.5	1.428	1.454	0.294	0.9999
	2	1.866	1.896	0.198	0.9999

The regression coefficients obtained for temperatures of 25°C, 40°C and 55°C were generally found to be very low. Therefore, activation energy and regression coefficient values for 1 mM dye concentration were found to be 11.642 kJ/mol and 0.9682, respectively. As mentioned earlier, the process is practically reaching the equilibrium after 60 min. Taking into account that the concentrated solutions may reach later equilibrium, the equilibrium time is chosen to be 240 min. and the experimental data applied to the isotherms are presented in Table 4.

Table 4. Equilibrium values for non-linear, Langmuir and Freundlich isotherms

Temperature, °C	C_o(mM)	C_e(mM)	q_e(mM/g)	C_e/q_e	ln C_e	ln q_e	% Removal
25	0.5	0.026	0.471	0.055	-3.660	-0.754	94.82
	1	0.053	0.940	0.056	-2.936	-0.062	94.66
	1.5	0.101	1.388	0.073	-2.296	0.328	93.24
	2	0.246	1.739	0.142	-1.402	0.553	87.60
	2.5	0.450	2.031	0.222	-0.798	0.709	81.86
40	0.5	0.017	0.479	0.036	-4.063	-0.736	96.54
	1	0.038	0.954	0.040	-3.266	-0.047	96.15
	1.5	0.077	1.412	0.054	-2.565	0.345	94.83
	2	0.173	1.812	0.096	-1.753	0.594	91.27
	2.5	0.357	2.124	0.168	-1.209	0.753	85.60
55	0.5	0.009	0.488	0.018	-4.746	-0.718	98.25
	1	0.023	0.970	0.023	-3.791	-0.030	97.73
	1.5	0.061	1.428	0.042	-2.804	0.356	95.93
	2	0.119	1.866	0.064	-2.126	0.624	93.99
	2.5	0.206	2.275	0.091	-1.578	0.822	91.68

Non-linear isotherm graphs demonstrate that the adsorption system has reached saturation (Figure 7 (a)). Accordingly, Figure 7 (b) and Figure 7 (c) show Freundlich (Eq.6) [19] and Langmuir (Eq.7) [20] isotherms plotted at 0.5 and 2.5 mM initial concentrations and at the end of 360 min. The adsorption constants obtained from these isotherm equations are summarized in Table 5. The regression coefficient (R^2) obtained from the Langmuir isotherm is higher than Freundlich isotherm suggests that the adsorption process is a single-layer. Accordingly, it can be stated that the process is in good agreement with Langmuir isotherm because the value of R^2 is closer to 1.

Table 5. Some parameters and regression coefficients from Langmuir and Freundlich isotherms

Temperature, °C	Langmuir			Freundlich		
	b	q_{max}	R^2	1/n	K_f	R^2
25	10.86	2.44	0.9951	0.49	3.42	0.9096
40	15.15	2.52	0.9987	0.58	4.96	0.9290
55	22.19	2.70	0.9908	0.49	5.34	0.9896

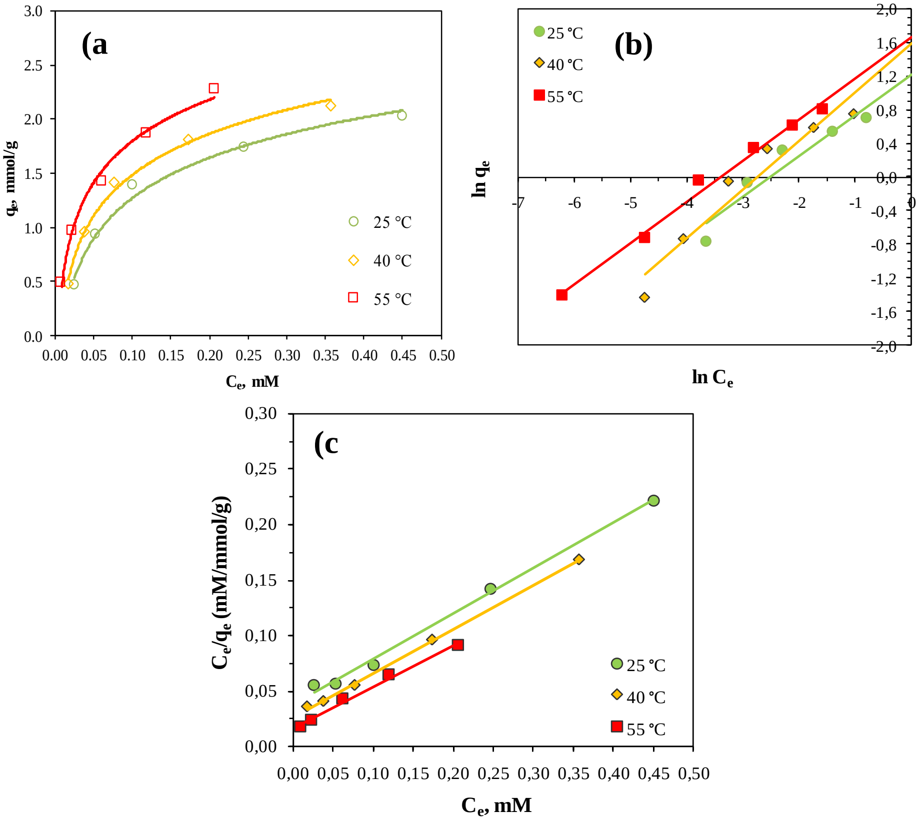

Figure 7. Non-linear (a), Freundlich (b) and Langmuir (c) isotherms

$$ln(x/m) = lnK_f + \frac{1}{n} lnC_e \qquad \text{(Eq.6)}$$

x is the adsorbed amount of dye (mM), m is the adsorbent amount (g), and C_s is the equilibrium concentration of the adsorbed material in the solution (mM). K_f (mM/g) Freundlich constant. n is the dimensionless Freundlich constant.

$$\frac{C_e}{q_e} = \frac{1}{q_{max} \cdot b} + \frac{C_e}{q_{max}} \qquad \text{(Eq.7)}$$

q_{max} is the maximum adsorption capacity (mM/g), and b is constant with respect to adsorption energy (mM^{-1}).

In order to determine whether the adsorption process compatible with the Langmuir isotherm is favourable, the dimensionless values (r) calculated by Eq.8 for various temperatures and initial concentrations are given in Table 6 [21]. Based on Table 6, it is seen that r values change from 0 to 1 for all cases, this situation can be attributed to the fact that the adsorption process is compatible with Langmuir isotherm.

Table 6. Calculated dimensionless r values

Temperature, ºC	R				
	0.5 mM	1 mM	1.5 mM	2 mM	2.5 mM
25	0.156	0.084	0.058	0.044	0.036
40	0.117	0.062	0.042	0.032	0.026
55	0.083	0.043	0.029	0.022	0.018

$$r = 1/(1 + b.C_0) \qquad \text{(Eq.8)}$$

The isotherm characteristic is determined via the r value. In other words, the r magnitude indicates that the adsorption process is irreversible *($r = 0$)*, favourable *($0 < r < 1$)*, linear *($r = 1$)* or unfavorable *($r > 1$)*.

For adsorption systems conforming to Langmuir equations, the theoretical dosage amount that will achieve the particular removal rate can be calculated using Eq.9 [22]. Accordingly, the theoretical dosages calculated in order to be able to remove 99% of BY 51 dye from aqueous solutions at various initial concentrations are presented in Table 7. Based on these results, it can be stated that high amounts of dye removal will be provided at higher temperatures and lower dosages. This situation can be explained by the decrease in the free energy value (ΔG^o) depending on the temperature increase. As shown in Table 8, the fact that ΔG^o for 55ºC is smaller than 25ºC indicates that the sorption process is occurred spontaneously and easier.

Table 7. Calculated dosage values for obtaining 99% removal

Temperature, ºC	m/v				
	0.5 mM	1 mM	1.5 mM	2 mM	2.5 mM
25	3.93	4.14	4.34	4.54	4.75
40	2.79	2.99	3.18	3.38	3.58
55	1.84	2.02	2.20	2.39	2.57

Table 8. Calculated thermodynamic parameters

Temperature ºC	ΔH^o (kJ/mol)	ΔG^o (kJ/mol)	ΔS^o (kJ/mol K)
25	+19.32	-23.02	0.142
40		-25.05	
55		-27.29	

$$\frac{m}{V} = \frac{C_0 - C_e}{\frac{q_{max}.b.C_e}{1+b.C_e}} \qquad \text{(Eq.9)}$$

m/v is the adsorbent dosage (g/l), C_o is the initial concentration of adsorbed material (mM), C_e is the equilibrium value of adsorbed material, q_{max} is the maximum adsorption capacity (mM/g), b is the constant for adsorption energy (mM^{-1}).

The enthalpy (ΔH^o) value of the process is calculated using the Langmuir constant b. The Langmuir constant (b), is a parameter related to the adsorption energy and the relation with the sorption enthalpy is given in Eq.10. ΔH^o was calculated from the slope of the linear line on the 1/T graph plotted against the *lnb* values in terms of Eq.10 (Figure 9). It is possible to say that the adsorption reaction is endothermic since the calculated ΔH^o value is positive (*+19.32 kJ/mol*). On the other hand, a rise in adsorption efficiency due to the increase in temperature confirms this fact. The values of ΔG^o and ΔS^o calculated for different temperatures using Eq.11 and Eq. 12 are given in Table 8 [23]. The positive value of ΔS^o (*0.142 kJ/molK*) also means that the irregularity at the solid-solution interface increases. However, Figure 8 was plotted at the equilibrium time (360 min.) using 1 g/l adsorbent dosage for all temperatures (25°C, 40°C, and 55°C).

$$lnb = lnb^{ι} - \frac{ΔH^{0}}{RT} \tag{Eq.10}$$

$$\ln\left(\frac{1}{b}\right) = \frac{ΔG^{0}}{RT} \tag{Eq.11}$$

$$ΔG^{0} = ΔH^{0} - TΔS^{0} \tag{Eq.12}$$

where $ΔS^o$ change (kJ/mol K), $ΔH^o$ change (kJ/mol), $ΔG^o$ change (kJ/mol); T is the absolute temperature (K), b is the Langmuir constant (mM^{-1}), and R is the gas constant (8.314 J/mol K).

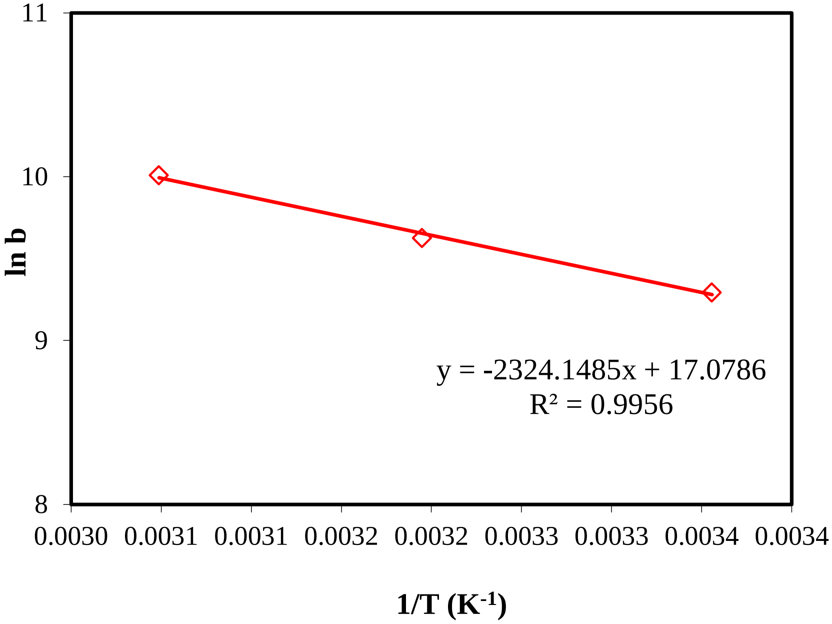

Figure 8. Graph of 1/T - lnb

In literature, it is very important to have adsorption capacities as well as kinetic and equilibrium parameters in the adsorption studies for removal of basic dyes, especially methylene blue (Basic Blue 9). In this context, the adsorption capacity value of our work is compared with the adsorption capacities of the other studies carried out with basic dyes in Table 9.

Table 9. Sorption capacities for removal of basic dyes by various sorbents in literature

Sorbent	Adsorbed	Adsorption capacity (mg/g)	Reference
Activated carbon from textile mill waste	Basic yellow 28	0.44	[24]
Sepiolite	Basic yellow 28	31.54	[25]
Activated carbon from walnut	Basic Blue 9	4.74	[26]
Sulfuric acid-activated rice husk	Basic Blue 9	44.25	[27]
Potato shells	Basic Blue 9	105.26	[28]
Modified Chinese fruit	Basic Blue 9	139	[29]
Sesame crust	Basic Blue 9	359.8	[30]
Palm karnel	Basic Blue 9	43.5	[31]
Coconut shell	Basic Blue 9	212.8	[32]
Modified bentonite	Basic Blue 9	399.74	[33]
Carbonized paper mill sludge	Basic yellow 51	984.54	This study

Since the value of dye removal is very high, it is beneficial to perform chemical oxygen demand (COD) analyzes before and after adsorption. Accordingly, the COD value was found to be 1570 mg O_2/l before adsorption, and 1640 mg O_2/l after adsorption. This situation is likely to be due to the presence of soluble organic substances in the adsorbent, although it is washed well. As a result, in this study, it is not possible to obtain clear results in the analysis based on the color measurement, since the chromophore materials may be removed and the dye structure may be transformed into colorless forms. For this reason, more detailed studies are needed to reach more precise results.

4. CONCLUSIONS

The removal results of the cationic BY 51 dye with carbonized PMS using sulfuric acid are summarized below;

The final pH value of the solution is also increased due to the increase of the initial pH of the solution. In addition, the sorption ratio increases by a certain value by increasing the ambient pH, but is not a significant change after this value.

By increasing the dosage of CPMS to 1 g/l, BY 51 sorption is also increased and there is no significant increase in the higher dosages of CPMS.

Experiments were carried out at 25°C, 40°C and 55°C temperatures in solutions where the initial concentration varied between 0.5 and 2.0 mM;

It was determined that the BY 51 sorption reached the equilibrium at about 240 min. and BY 51 sorption percentage decreased as the initial concentration increased. It was also found that as the temperature increased, the BY 51's sorption on the CPMS also increased. The most suitable model is pseudo second order kinetic model since the correlation coefficient value (R^2) is the highest, the calculated values and the experimental data are very close to each other. Similarly, the magnitude of the calculated regression coefficient values confirms this result. The activation energy (E_a) of the process was calculated to be +11.642 kJ/mol.

In consequence of applying the equilibrium results to the Langmuir and Freundlich adsorption isotherms, it was determined that the Langmuir isotherm represented the sorption process best. On the other hand, the maximum adsorption capacity for temperatures of 25°C, 40°C and 55°C is 2.44; 2.52 and 2.70 mM/g, respectively.

It has been found that the sorption process is favorable because the r value calculated using the Langmuir constant b is in the range $0 < r < 1$. For the removal of 99% BY 51 from the 1 mM solution, a dosage of 4.14 g/l was required at 25ºC, while a dosage of 2.02 g/l at 55ºC was considered sufficient for the removal value.

The positive value of *ΔH°* (*+19.32 kJ/mol*) indicates that the process is endothermic. The fact that the calculated *ΔG°* values are negative indicates that the sorption phenomenon occurs spontaneously and is easier to achieve at high temperatures. The positive value of *ΔS° (0.142 kJ/molK*) also means that the irregularity at the solid-solution interface increases. Consequently, it can be said that the PMS, which is made up of paper production plants, can be utilized to remove the dyes from the wastewater of the textile industry after being carbonized.

REFERENCES

[1] Baughman GL, Perenich TA (1988) Fate of dyes in aquatic systems: I. Solubility and partitioning of some hydrophobic dyes and related compounds. Environ Toxicol Chem 7:183–199.

[2] Weber EJ, Lee Wolfe N (1987) Kinetic studies of the reduction of aromatic azo compounds in anaerobic sediment/water systems. Environ Toxicol Chem 6:911–919.

[3] Chung K-T, Fulk GE, Egan M (1978) Reduction of azo dyes by intestinal anaerobes. Appl Environ Microbiol 35:558–562.

[4] King-Thom C (1993) Degradation of azo dyes by environmental microorganisms and helminthes. Env Toxicol Chem 13:2121–2132.

[5] Allen SJ, Gan Q, Matthews R, Johnson PA (2003) Comparison of optimised isotherm models for basic dye adsorption by kudzu. Bioresour Technol 88:143–152.

[6] Waranusantigul P, Pokethitiyook P, Kruatrachue M, Upatham ES (2003) Kinetics of basic dye (methylene blue) biosorption by giant duckweed (Spirodela polyrrhiza). Environ Pollut 125:385–392.

[7] Robinson T, McMullan G, Marchant R, Nigam P (2001) Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative. Bioresour Technol 77:247–255.

[8] Robinson T, Chandran B, Nigam P (2002) Removal of dyes from an artificial textile dye effluent by two agricultural waste residues, corncob and barley husk. Environ Int 28:29–33.

[9] Robinson T, Chandran B, Nigam P (2002) Removal of dyes from a synthetic textile dye effluent by biosorption on apple pomace and wheat straw. Water Res 36:2824–2830.

[10] Kocaer FO, Alkan U (2002) Boyarmadde Içeren Tekstil Atiksularinin Aritim Alternatifleri. Uludağ Üniversitesi Mühendislik Mimar Fakültesi Derg 7:47–55.

[11] Demirbaş E, Kobya M, Öncel S, Şencan S (2002) Removal of Ni (II) from aqueous solution by adsorption onto hazelnut shell activated carbon: equilibrium studies. Bioresour Technol 84:291–293.

[12] Kadirvelu K, Kavipriya M, Karthika C, et al (2003) Utilization of various agricultural wastes for activated carbon preparation and application for the removal of dyes and metal ions from aqueous solutions. Bioresour Technol 87:129–132.

[13] Kobya M (2004) Removal of Cr (VI) from aqueous solutions by adsorption onto hazelnut shell activated carbon: kinetic and equilibrium studies. Bioresour Technol 91:317–321.

[14] Méndez A, Barriga S, Fidalgo JM, Gascó G (2009) Adsorbent materials from paper industry waste materials and their use in Cu (II) removal from water. J Hazard Mater 165:736–743.

[15] Mohamad S, Bakar NKA, Ishak AR, et al (2014) Removal of phosphate by paper mill sludge: Adsorption isotherm and kinetic study. Asian J Chem 26:3545.

[16] Lagergren S (1898) Zur theorie der sogenannten adsorption geloster stoffe. K Sven vetenskapsakademiens Handl 24:1–39.

[17] Ho Y-S (2006) Review of second-order models for adsorption systems. J Hazard Mater 136:681–689.

[18] Weber WJ, Morris JC (1963) Kinetics of adsorption on carbon from solution. J Sanit Eng

Div 89:31–60.

[19] Freundlich HMF (1906) Over the adsorption in solution. J Phys Chem 57:1100–1107.

[20] Langmuir I (1918) The adsorption of gases on plane surfaces of glass, mica and platinum. J Am Chem Soc 40:1361–1403.

[21] Ho YS, Wang CC (2004) Pseudo-isotherms for the sorption of cadmium ion onto tree fern. Process Biochem 39:761–765.

[22] Unnithan MR, Anirudhan TS (2001) The kinetics and thermodynamics of sorption of chromium (VI) onto the iron (III) complex of a carboxylated polyacrylamide-grafted sawdust. Ind Eng Chem Res 40:2693–2701.

[23] Maddikeri GL, Pandit AB, Gogate PR (2012) Adsorptive removal of saturated and unsaturated fatty acids using ion-exchange resins. Ind Eng Chem Res 51:6869–6876.

[24] Aguiar CRL, Fontana É, Valle JAB, et al (2016) Adsorption of Basic Yellow 28 onto chemically-modified activated carbon: Characterization and adsorption mechanisms. Can J Chem Eng 94:947–955.

[25] Tekin N, Şafaklı A, Bingöl D (2015) Process modeling and thermodynamics and kinetics evaluation of Basic Yellow 28 adsorption onto sepiolite. Desalin Water Treat 54:2023–2035.

[26] Hajati S, Ghaedi M, Mazaheri H (2016) Removal of methylene blue from aqueous solution by walnut carbon: optimization using response surface methodology. Desalin Water Treat 57:3179–3193.

[27] Kaykioğlu G, Güneş E (2016) Kinetic and equilibrium study of methylene blue adsorption using H2SO4− activated rice husk ash. Desalin Water Treat 57:7085–7097.

[28] Guechi E-K, Hamdaoui O (2016) Biosorption of methylene blue from aqueous solution by potato (Solanum tuberosum) peel: equilibrium modelling, kinetic, and thermodynamic studies. Desalin Water Treat 57:10270–10285.

[29] Pan X, Li X, Yang J, et al (2015) Litchi pericarps used as adsorbents for methylene blue removal from solution. Desalin Water Treat 55:1333–1341.

[30] Feng Y, Yang F, Wang Y, et al (2011) Basic dye adsorption onto an agro-based waste material–Sesame hull (Sesamum indicum L.). Bioresour Technol 102:10280–10285.

[31] Belala Z, Jeguirim M, Belhachemi M, et al (2011) Biosorption of basic dye from aqueous solutions by date stones and palm-trees waste: kinetic, equilibrium and thermodynamic studies. Desalination 271:80–87.

[32] Premkumar Y, Vijayaraghavan K (2015) Biosorption potential of coco-peat in the removal of methylene blue from aqueous solutions. Sep Sci Technol 50:1439–1446.

[33] Anirudhan TS, Ramachandran M (2015) Adsorptive removal of basic dyes from aqueous solutions by surfactant modified bentonite clay (organoclay): kinetic and competitive adsorption isotherm. Process Saf Environ Prot 95:215–225**.**