

# Efficient Adsorption of Methylene Blue from Aqueous Solution by Sulfuric Acid Activated Watermelon Rind (*Citrullus lanatus*)

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## Abstract

The lignocellulose-based dried watermelon rind (WR) was modified with sulfuric acid, namely SWR for enhancement of methylene blue (MB) adsorption from the aqueous solution. According to FT-IR analysis, after the modification of WR with sulfuric acid, the functional groups of R-SO<sub>3</sub>H, COOH and -OH groups was formed or enhanced on the surface of the WR. Moreover, the point of zero charge (pHpzc) was changed from 6.3 to 4.1 after modification, which widened the range for adsorbing of cationic dye MB. The adsorption process of MB onto the SWR was suitable for pseudo-2nd-order and Langmuir model and the maximum adsorption capacity of Langmuir was found to be 334.45 mg/g at pH 7. In addition, the adsorption process occurs through the electrostatic interaction, hydrogen bridge formation, electron donor-acceptor relationship, and  $\pi$ - $\pi$  electron dispersing force between functional groups on the carbon surface with MB molecules. Depending on functional groups available on the SWR surface, the MB adsorption mechanism can occur in combination with various interactions.

**Keywords:** Adsorption, Cationic dye, Kinetic, Lignocellulose, Sulfonation, Watermelon rind

## 1. Introduction

As the demand for dyestuffs increases in various industries, the discharge of dye wastewater is also increasing. The amount of dyes produced globally to exceed about 700 million tons as of 2018, and there are more than 100,000 types of commercial dyes used[1]. As dyes use a large amount of water during the dyeing process, the amount of wastewater generated in the dyeing process is enormous[2]. Therefore, since the problem of environmental pollution caused by dyeing wastewater adversely affects aquatic ecosystems and has a potential negative effect on human health, research on various methods to eliminate them is ongoing[3].

In order to remove dye from wastewater, a number of technologies such as aggregation, flotation, precipitation, membrane process, chemical oxidation, biological oxidation and adsorption, etc. have been developed and studied, and each method has advantages and disadvantages. Among them, the adsorption method is the most studied and considered because the removal efficiency is high, and the operation is simple[4]. However, widely used for removing organic pollutants by using an existing adsorbent such as activated carbon is inefficient in terms of cost and is not feasible due to its low economic efficiency[5].

Therefore, bioadsorbents made from inexpensive agricultural waste are becoming the focus on many researchers. In particular, lignocellulose, composed of three major components of cellulose, hemicellulose and lignin, is rapidly emerging as a new eco-friendly adsorbent that can mainly replace the existing adsorbent[1,6]. Lignocellulosic-based watermelon can be an alternative to new adsorbents.

One of the fruits that is loved by many the summer, the flesh of watermelon is used for food. However, watermelon rind (WR), which accounts for 30% of all fruit, is disposed of as garbage without useful recycling[7]. WR is composed of pectin, citrulline, cellulose, protein and carotenoids[7,8]. These polymers are rich in functional groups such as hydroxyl (cellulose), amine (protein) and carboxylic acid (pectin), and have proven to have a great ability to easily bind cationic dyes in aqueous solutions[1,8]. In particular, WR contains the most cellulose, the most abundant organic compound on the earth. Due to these characteristics, WR can be regarded as a potential bioadsorbent, and many researchers conducted dye removal experiments using unmodified natural biomaterials, and reported many positive results[1,6]. However, the application of unmodified biomaterials has significant drawbacks such as low adsorption capacity in aqueous solutions and high release of soluble organic compounds[1,9]. Accordingly, in recent years, there is an increasing tendency to modify biosorbent materials to improve adsorption efficiency and remove soluble organic compounds. Methods of modifying bioadsorbents include physical, chemical, and other methods. Physical modification is generally simple and inexpensive, but due to its low efficiency, it is not widely used. On the other hand, chemical modification has the advantage of being simple and highly

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efficient, and mainly uses acids and bases to modify biomaterials. In particular, several researchers reported that sulfuric acid increases the adsorption efficiency of cationic ions the most among various chemical substances that can modify biomaterials[1,10]. The reason is that the pretreatment of biomaterials using sulfuric acid increases the negative charge and surface area of the adsorbent surface, which leads to an increase in adsorption efficiency[11,12]. Therefore, in this study the surface of lignocellulosic-based WR was modified using sulfuric acid, and the removal efficiency of methylene blue (MB) from aqueous solution was analyzed using modified adsorbent. The experimental results were used to for adsorption isotherms and thermodynamic interpretation, and adsorption mechanism analyzed.

## 2. Materials and Methods

### 2.1. Materials

#### 2.1.1. Preparation of SWR (sulfonated watermelon rind)

Watermelon was purchased at a local market, and the collected watermelon rinds were washed with tap water and then rinsed with distilled water. The washed watermelon rind was cut into small pieces and dried in a drying oven at 85 °C for 24 hours to completely evaporate the moisture. The dried WR was pulverized in a ball mill at 120 rpm for 5 hours, separated into 40–60 mesh (0.25–0.4 mm) using an automatic sieve, and stored in a desiccator for use in the experiment. A 20 g of dried watermelon rind powder was added to ethyl alcohol (60 mL) cooled to -10 °C and mixed completely for 1 hour. After that, it was added to 300 mL of cooled sulfuric acid, and a sulfonating reaction was carried out while stirring at 100 to 150 rpm for 12 hours so as not to exceed 10 °C using a reaction device [Yhana (Model SS-200, 50W)]. Thereafter, it was left at room temperature for 2 to 3 hours to induce the reaction to occur completely, and then washed several times with distilled water until neutral, put in a dryer, and dried for 48 hours at 85 °C. The sulfonated watermelon rinds (SWR) were stored in a desiccator for use in experiments.

#### 2.1.2. Methylene blue (MB)

Methylene blue ( $C_{16}H_{18}N_3S$ ) is a hetero cyclic aromatic compound and is a basic dye. Hydrate is blue and exists in the form of three molecules of water per molecule of methylene blue. MB ( $C_{16}H_{18}ClN_3S \cdot 3H_2O$ , molar mass: 319.85 g/mole, Sigma-Aldrich, USA) was used in powder form. MBs of various concentrations were prepared at a concentration of 1000 mg/L, and then diluted with distilled water to prepare a solution of the required concentration

### 2.2. Experimental design and analytical methods

#### 2.2.1. Batch test

Various parameter experiments to find optimal conditions were performed in the form of batch-test. The SWR was added in 1 L of aqueous solution containing various concentrations of MB according to the experimental plan, and the experiment was conducted while controlling various parameters, such as pH (3–10), amount of adsorbent (0.5–5 g/L), initial concentration of MB (20–500 mg/L), contact time (0–240

minutes), and temperature (25–40 °C). Sampling was performed at a predetermined time while stirring at 120 rpm in a Shaking Incubator. The pH was adjusted using NaOH and HCl, and all experiments were repeated five times, and the average value was used as the experimental result, and the other parameters were fixed in order to experiment with one parameter.

#### 2.2.2. Analytical methods

The chemical composition of SWR and WR was analyzed using an X-ray fluorescence spectrometer (XRF, ZEISS Xradia 520, Germany) spectrometer, and FT-IR was analyzed using Perkins Elmer (FT-IR 1760X, USA). The surface analysis of the adsorbent was performed using Scanning Electron Microscopy (SEM; SEM-EDX, Hitachi, TM3030Plus, Japan), and the  $pH_{pzc}$  was analyzed according to the previous method[13]. The specific surface area, pore size, and distribution analysis of SWR and WR were analyzed from nitrogen adsorption and desorption isotherms using an adsorption analyzer (BELSORP-max, Bel Inc., Japan). The specific surface area was analyzed by Brunauer, Emmett and Teller (BET) analysis, pore distribution by Barrett, Joyner, and Halenda (BJH) analysis, and micropore distribution by t-plot analysis. MB concentration of the collected sample was measured using a spectrometer (HACH DR2800, USA). The amount of SWR was measured using an electronic balance (XP26, Mettler Toledo, Swiss), and the pH was measured using a pH meter (SevenGO pro, Mettler Toledo). Adsorption kinetics were analyzed using Pseudo-1st-order and Pseudo-2nd-order, adsorption isotherms were analyzed using Langmuir, Freundlich and Temkin models, and thermodynamics were analyzed using Gibb's free energy equation.

## 3. Results and Discussion

### 3.1. Characterization of WR and SWR

#### 3.1.1. Physical properties

The results of component analysis of WR and SWR are summarized in Table 1. The major constituents of WR and SWR were carbon and oxygen, and in addition, small amounts of hydrogen and nitrogen were also contained. After sulfonation of WR, the content of oxygen increased and the content of carbon decreased. This may be due to the release of volatile during the sulfonating process, and the relatively high oxygen content is due to the high level of chemical active agent used ( $H_2SO_4$ ; 95–98%). The ratio of H/C and O/C in the bioadsorbent affects the removal of contaminants because it is related to the increase and decrease of the aromatic and carbonyl groups[5,13]. According to previous studies, the aromaticity of the bio-adsorbent increases as the H/C ratio approaches 1, and when the O/C ratio is high, the anionic properties of the bio-adsorbent are strengthened due to the increase of the carboxylate group in the bio-adsorbent, thereby increasing the ability to adsorb cationic substances[2,14]. The H/C ratio improved from 0.045 to 0.13 after sulfonating WR, and the O/C ratio increased from 0.72 to 1.17, and the carboxyl group inside the SWR adsorbent increased after sulfonating WR.

In general, the adsorption capacity is correlated with surface area of

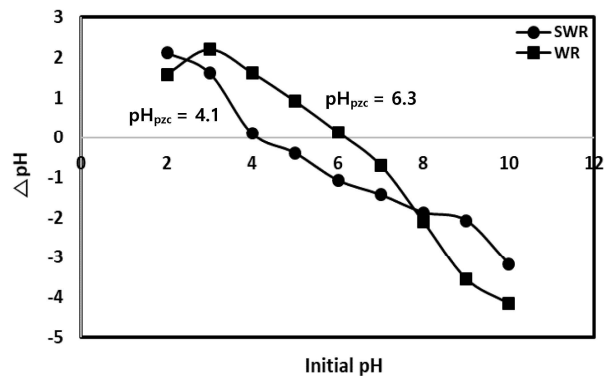
**Table 1. Properties of Dried Watermelon Rind and Sulfonated Watermelon Rind (unit: %)**

Component (mass %)	WR	SWR
O	36.16	49.32
C	50.32	42.16
H	2.26	5.38
N	1.32	1.72
S	-	1.32
Mg	0.08	0.09
Surface property		
Pore volume (cm <sup>3</sup> /g)	0.019	0.153
Pore diameter (nm)	1.056	4.52
BET surface area (m <sup>2</sup> /g)	2.164	163.26

adsorbent[1,15]. However, this characteristic does not apply to all adsorbents, and if the surface area of the adsorbent is too large compared to the material to be adsorbed, the adsorption capacity is rather low[1,4]. Therefore, the increasing in the pore diameter of the adsorbent is not necessarily proportional to the improvement in adsorption capacity. According to previous studies, the pore size of the adsorbent of more 6 nm does not seem to have an advantage in increasing the adsorption efficiency of MB[9,11]. However, the adsorbent with a large surface area but a medium pore diameter showed a high level of MB adsorption capacity exceeding 800 mg/g[1,16]. This is because the size of MB in aqueous solution has dimensions of  $0.400 \times 0.793 \times 1.634$  nm, so the pore size of the adsorbent plays an important role in allowing the diffusion of MB in the pores[11,16]. According to previous studies, MB molecules could not pass through pores of less than 1.0 nm (super-micropores), and adsorbents having a pore structure of at least more 1.33 nm in diameter had higher MB adsorption capacity than activated carbon having a meso-macro (> 30 nm) size[8,11]. The pore size of SWR increased from 1.056 nm of WR to 4.52 nm, which is within the range of micro-meso (2~30 nm) pore structure, and has a size suitable for adsorbing MB in aqueous solution.

### 3.1.2. $pH_{pzc}$

The  $pH_{pzc}$  (point of zero charge) represents the pH value when the zeta potential of the adsorbent reaches zero[2]. If the pH value is lower than the  $pH_{pzc}$  value, more hydrogen ions can be exchanged for heavy metal cations, but the high concentration of hydrogen ions protonates the surface functional groups (e.g. -OH) of the lignocellulose-based adsorbent, increasing the number of surface positive charges[4,17]. Then, the adsorption of cationic ions in the aqueous solution is reduced due to electrostatic repulsion, and the adsorption efficiency of anions is improved[1,18]. Conversely, when the pH value is higher than  $pH_{pzc}$ , deprotonation returns the surface of the functional group to a negative charge, resulting in the opposite effect of cations and anions[19,20]. Therefore, in the adsorption of cationic substances, the  $pH_{pzc}$  of the lignocellulose-based adsorbent should be more acidic for a wider range of pH action, whereas for the adsorption of anionic substances,  $pH_{pzc}$

**Figure 1.  $pH_{pzc}$  of WR and SWR in aqueous solution.**

should be more alkaline. The adsorption efficiency of ionic cationic dyes is linked to the concentration of hydrogen ions in the aqueous solution, and since these various types of ions have different affinity for functional groups on the surface of the adsorbent, it ultimately affects the adsorption capacity.

In order to find the  $pH_{pzc}$  of SWR, the experiment was performed by controlling the pH from 2 to 10, and the results are shown in Figure 1. The  $\Delta pH$  is the value obtained by subtracting the initial pH from the final pH. The  $pH_{pzc}$  of SWR was found to be 4.1, and it was confirmed that there is an acidic functional group on the surface of the SWR. The negative surface charge of SWR can be found in a pH environment above  $pH_{pzc}$ , which favors adsorption of MB. In general, MB adsorption may be due to the presence of OH, COO<sup>-</sup>, and SO<sub>3</sub><sup>-</sup> groups on the SWR surface. According to previous studies, the  $pH_{pzc}$  values of coconut leave and mango peels were 3.2 and 4.6, respectively, after sulfonation[1,21]. When sulfonating a lignocellulose-based biomaterial,  $pH_{pzc}$  decreases by increasing anionic functional groups on the surface of the adsorbent, and low  $pH_{pzc}$  is thought to have a favorable effect on the adsorption efficiency of MB.

### 3.1.3. FT-IR spectra

The FT-IR of WR and SWR provides important information to understand the adsorption mechanism. WR showed very broad cellulose ester peak (1067 cm<sup>-1</sup>), aliphatic CH-stretching characteristic peak (2917 cm<sup>-1</sup>), and bonded OH peak (3392 cm<sup>-1</sup>) (Figure 2). It should be noted that both WR and SWR showed severe vibrations between 1300~1740 cm<sup>-1</sup>, which correspond to C=O carbonyl groups, carboxylic groups and C-O stretches. In addition, at 650 cm<sup>-1</sup>, it is not as strong as the bonded OH peak, but a peak of N-containing ligands also appears. SWR was bonded OH-group (3000~3500 cm<sup>-1</sup>), CH stretching (2900~2800 cm<sup>-1</sup>), C=O carbonyl groups (1740~1680 cm<sup>-1</sup>), carboxylic groups (1670~1640 cm<sup>-1</sup>) and CO stretch (1450~1300 cm<sup>-1</sup>) peak appeared. In addition, it was confirmed that the ether of 1109 cm<sup>-1</sup>, the absorption peak of R-SO<sub>3</sub>H of 1232 cm<sup>-1</sup>, and ketone peaks of 1642 and 1477 cm<sup>-1</sup> were sulfonated. In particular, the peaks of N-containing ligands (650 cm<sup>-1</sup>), R-SO<sub>3</sub>H absorption peak (1232 cm<sup>-1</sup>), carboxylic groups (1642 cm<sup>-1</sup>) and bonded OH-group (3458 cm<sup>-1</sup>) of SWR are appeared larger than that of WR. This indicates that SWR has more functional

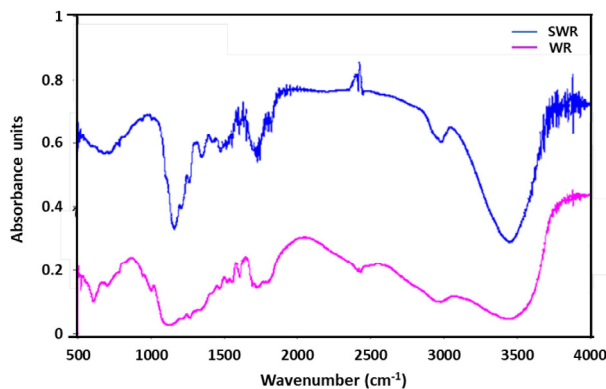


Figure 2. A FT-IR spectra of WR and SWR.

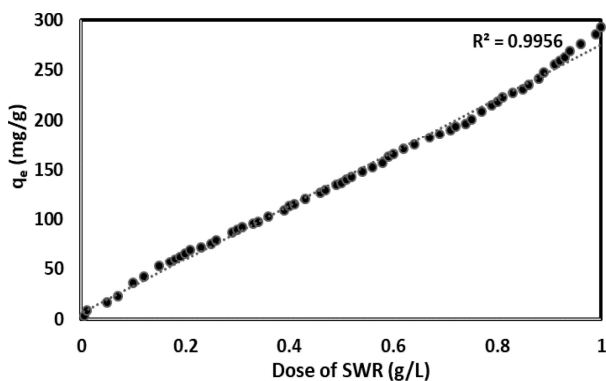


Figure 3. MB removal by different dose of SWR (V: 1 L, pH: 7, T: 298 K).

groups than WR and has a structure that is easier to adsorb MB ions. Osman *et al.*[22] reported that the adsorption capacity is proportional to the number of functional groups in the adsorbent. The formation and enhanced change of  $-R-SO_3H$ ,  $-COOH$ , and  $-OH$  functional groups through sulfonation are thought to have a favorable effect on the adsorption efficiency of MB in aqueous solution.

### 3.2. Effect of various parameters

#### 3.2.1. Amount of adsorbent

Optimizing the amount of adsorbent is one of the major items in the economic evaluation of adsorbents, such as adsorption efficiency. This is because if a large amount of harmful substances can be adsorbed and removed from a small amount of adsorbent, it is possible to be more free from environmental problems and to save materials and energy. In order to find out the effect of the amount of SWR on the adsorption efficiency of MB, experiments were performed with the concentration of MB at 1~300 mg/L, pH 7 and 25 °C and the results of removal efficiency of more than 90% are shown in Figure 3. The correlation between the amount of adsorbent and the amount of adsorption was 0.9956, and as a result of calculating the relationship between the amount of MB adsorption and the amount of SWR adsorbent, about 32.5~36.7 mg of MB per 1 g of SWR could be adsorbed. As the concentration of MB increased, a more amount of SWR was required, which is a phenomenon caused by a decrease in the active point that

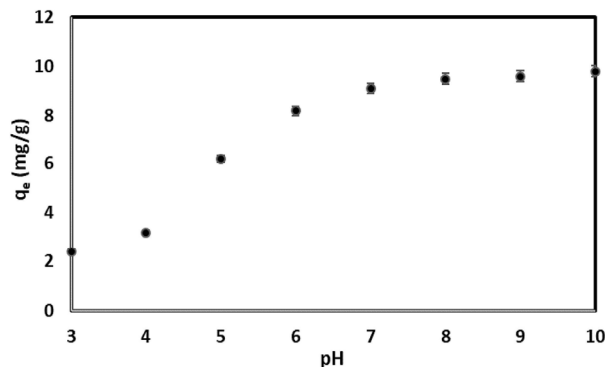


Figure 4. Effect of pH on MB removal (V: 1 L, MB: 10 mg/L, SWR dosage: 1 g/L, T: 298 K).

can be adsorbed on the adsorbent. According to previous studies, 0.8~1.8 g/L was required when MB was removed using SWR, and about 27.96~44.14% MB removal efficiency was improved compared to when using non-sulfonated WR[8]. This is consistent with the research results of many researchers that adsorbed MB and heavy metals in aqueous solutions by sulfonating agricultural waste[1,2,9].

#### 3.2.2. pH

In order to find out the effect of pH change in aqueous solution to the adsorption efficiency of MB onto SWR, the pH was adjusted to 3~10, and the experiment was performed using 1 g/L SWR, and the results are shown in Figure 4. The adsorption efficiency of MB onto SWR increased as the pH increased. In particular, the adsorption efficiency at pH 6 increased by 3.42 times for pH 3. As the pH increases, the sulfuric acid, carboxyl and phenolic hydroxyl groups of the SWR adsorbent are deprotonated to form  $R-SO_3^{2-}$ ,  $R-COO^-$  and  $R-O^-$  groups [11,16]. This is because the electrostatic attraction between the SWR adsorbent and the MB cations in the aqueous solution was improved as the surface of the SWR adsorbent became negatively charged. Note that there was no significant change in the adsorption efficiency up to pH 4, but the adsorption amount increased sharply above pH 5. This is related to the value of  $pH_{pzc}$  mentioned above. The  $pH_{pzc}$  of SWR is 4.1, and if the pH is higher than the  $pH_{pzc}$  value, the surface charge of the adsorbent becomes negative, and cations may be adsorbed. Another reason is that MB exists in aqueous solutions as cationic species and undissociated molecules depending on the pH.

### 3.3. Adsorption kinetics and adsorption isotherm modeling

#### 3.3.1. Adsorption kinetics

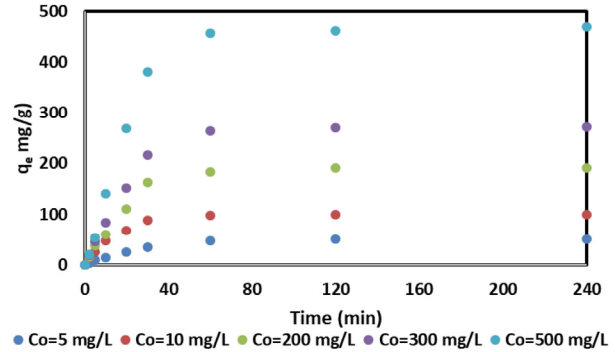
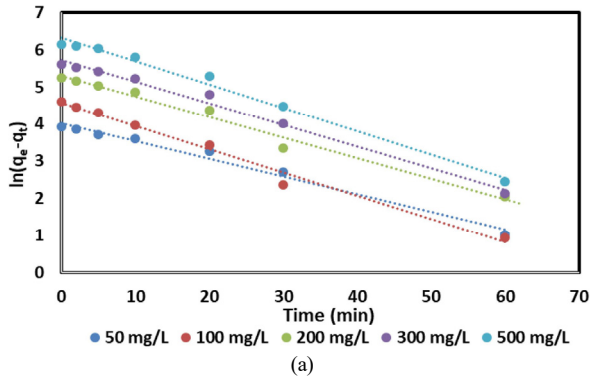
To compare the adsorption rate of MB to SWR, a kinetics experiment was conducted, and the results were analyzed as pseudo-1st-order and pseudo-2nd-order. The main parameters of adsorption kinetics are shown in Table 2 and Figure 5.

As a result of the analysis of the kinetics experiment, the reaction of MB was almost completed within 60 minutes using SWR (Figure S1). The values of  $k_1$  in pseudo-1st-order and  $k_2$  in pseudo-2nd-order decreased as the concentration of MB increased, indicating that the adsorption rate of MB to SWR decreased as the initial concentration of

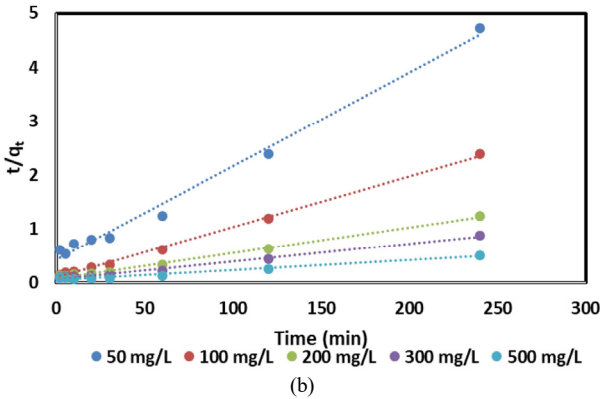
**Table 2. Kinetics Parameters for the Adsorption of MB onto SWR**

	Concentration, C <sub>0</sub> (mg/L)				
	50	100	200	300	500
q <sub>e,exp</sub> (mg/g)	50.83	100.31	191.51	272.17	469.43
Pseudo-first-order [ln(q <sub>e</sub> - q <sub>t</sub> ) = ln q <sub>e</sub> - k <sub>1</sub> t]					
q <sub>e,cal</sub> (mg/g)	56.35	97.38	202.07	309.42	559.59
k <sub>1</sub>	0.0478	0.0624	0.056	0.0582	0.063
R <sup>2</sup>	0.9857	0.9872	0.9834	0.9901	0.9894
Pseudo-second-order $\left[ \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \right]$					
q <sub>e,cal</sub> (mg/g)	51.55	101.01	202.02	285.71	476.19
k <sub>2</sub>	7.30 × 10 <sup>-6</sup>	9.703 × 10 <sup>-7</sup>	1.21 × 10 <sup>-7</sup>	4.287 × 10 <sup>-8</sup>	9.26 × 10 <sup>-9</sup>
h	2.33	10.11	11.64	14.62	18.76
R <sup>2</sup>	0.9911	0.9977	0.9924	0.9906	0.9973

q<sub>e</sub>: amount of MB adsorbed by SWR at equilibrium (mg/g), q<sub>t</sub>: amounts of MB adsorbed by SWR at equilibrium time t (mg/g), k<sub>1</sub>: Pseudo-1st-order constant (1/min), k<sub>2</sub>: Pseudo-2nd-order constant (g/mg·min), t: time (min)



**Figure S1. Influence of initial MB concentration (V: 1L, T: 298 K, pH: 7, SWR dosage: 5 g/L).**



**Figure 5. A plots of (a) pseudo-first-order kinetics and (b) pseudo-second-order kinetics.**

MB increased. The relationship (R<sup>2</sup>) of the kinetic model was measured higher in pseudo-2nd-order (0.9906~0.9977) than that of pseudo-1st-order (0.9834~0.9901). Also, the q<sub>e,cal</sub> calculated in the pseudo-2nd-order model was closer to the measured q<sub>e,exp</sub> compared to the value calculated in the pseudo-1st-order model. Therefore, MB adsorption kinetics by SWR was more suitable for the pseudo-2nd-order model than the pseudo-1st-order model.

### 3.3.2. Adsorption isotherm

The adsorption isotherm is the equilibrium relationship between the concentration of the adsorption layer in the fluid phase and the concentration of the adsorbate in the adsorbent particles of a given temperature[5,9]. An isotherm adsorption experiment was performed to obtain information on the adsorption characteristics of MB onto SWR, and the obtained results were analyzed using models of Langmuir, Freundlich and Temkin, and summarized in Table 3. In the Langmuir isotherm model, one molecule is adsorbed and fixed at each adsorption point, and the adsorption energy at all adsorption points are uniform and there is no mutual attraction between the adsorbed molecules[2,13]. And it is assumed that adsorption is achieved by collisions between each empty adsorption point and molecules[14].

The value of the dimensionless separation constant R<sub>L</sub> [= 1/(1 + K<sub>L</sub>C<sub>0</sub>)] derived from Langmuir was calculated as 0.012, and it was evaluated that the adsorption process of MB using SWR was favorable. In addition, the maximum adsorption capacity of Langmuir was 334.45 mg/g, which was higher than that of coconut (26.14 mg/g) and banana peels (50.51 mg/g) modified with acid, and hazelnut peels (109.90 mg/g) and persimmon leaves (256.0 mg/g) modified with alkali (Table 4).

**Table 3. Adsorption Isotherms for MB onto SWR (500 mg/L, pH: 7)**

Isotherm		Parameters	Values
Langmuir	$\left[ \frac{C_e}{q_e} = \frac{1}{q_{max} K_L} + \frac{1}{q_{max}} C_e \right]$	$q_m$ (mg/g)	334.45
		$K_L$ (L/mg)	0.172
		$R^2$	0.9964
Freundlich	$\left[ \ln q_e = \ln k_F + \frac{1}{n} \ln C_e \right]$	$K_F [(mg/g) (L/mg)^{1/n}]$	3.175
		$1/n$	0.871
		$R^2$	0.9116
Temkin	$[\ln q_e = B \ln k_T + B \ln C_e]$	$B$ (J/mol)	14.40
		$K_T$ (L/mg)	1.152
		$R^2$	0.896

$q_e$ : adsorbed amount of Pb(II) at equilibrium (mg/g),  $C_e$ : Pb(II) concentration at equilibrium (mg/L),  $q_{max}$ : Langmuir maximum adsorption capacity (mg/g),  $K_L$ : Langmuir constant (L/mg),  $K_F$ : adsorption capacity (mg/g)(L/mg)<sup>1/n</sup>,  $1/n$ : adsorption intensity of the system,  $k_T$ : Temkin isotherm constant (L/mg),  $B$ : correlated to adsorption heat.

**Table 4. Comparison of Adsorption Capacities for MB on Various Biomass Materials**

Materials	Adsorbent dose (g/L)	pH	$q_{max}$ (mg/g)	References	
Watermelon rind	0.6	11	131.48	[23]	
Watermelon rind	1	6	334.45	This study	
Pine-fruit shell	3	8.5	529.0	[24]	
$H_2SO_4$ treated biomass	Mango peels	1.4	5-6	277.8	[21]
	Corn cob	1.2	5.6	216.6	[25]
Bagasse		4	9	56.5	[11]
	Hazelnut peels	1.5	9	109.90	[26]
KOH treated biomass	Persimmon leaf	1.5	9	256.0	[26]
Carbonated cellulose/microfibrillated cellulose spheres	0.8	7	303.0	[27]	
APTES-reinforced lignocellulose hydrogel	1.5	6	191.9	[28]	
Acetic acid lignin	1	6	63.3	[20]	
Lignin-derived sulfonated porous carbon	0.8	6	420.40	[29]	
sulfonated lignin-based hydrogel	1	6	495.0	[10]	

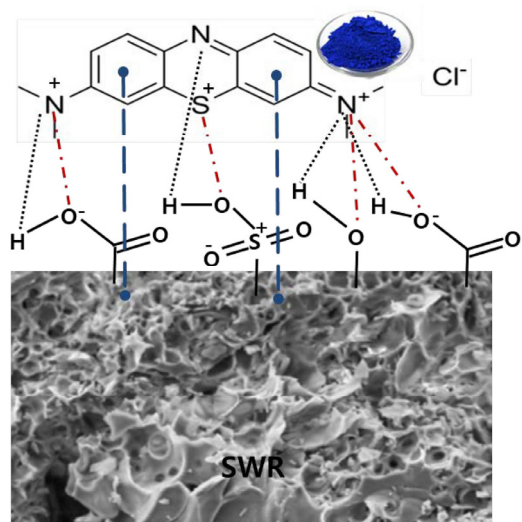
The Temkin isotherm indicates that the heat of adsorption of MB ions decreases linearly rather than logarithmically with coverage[30]. The Temkin constant  $B$  was measured to be 14.40 (J/mol), corresponding to the physical adsorption area ( $B < 20$  J/mol). Therefore, adsorption of MB onto SWR is considered to be closer to physical adsorption caused by the action of Van der Waals force consisting of dispersing force and electrostatic force rather than chemical adsorption of changing chemical form.

The Freundlich isotherm is suitable for adsorption where the Langmuir isotherm does not fit well. In addition, it can be derived theoretically by assuming that the heat of adsorption decreases exponentially according to the degree of covering, assuming that all adsorption points have uniform adsorption strength among the assumptions of obtaining the Langmuir isotherm by statistical method[4,19]. The constant  $c$  represents the number of adsorption points and  $n$  represents the degree of interaction between the adsorbed molecules[13]. If  $n > 1$ , the adsorption isotherm becomes convex due to the small increase in the adsorption amount even when the pressure increases because a repulsive force exists between the adsorbed molecules[15]. The larger the value of  $K_F$ , which represents a measure of the adsorption capacity calculated from the Freundlich equation, indicates that the higher the val-

ue, the better the adsorption capacity, and the  $1/n$  value representing the adsorption strength was generally between 0~1, the adsorption easily occurs[2]. However, if it is larger than 2, it is interpreted that adsorption is difficult[4]. In this experiment,  $1/n$  was analyzed as 0.871, so adsorption of MB onto SWR in aqueous solution was easy and the adsorption strength was appropriate. In addition, it can be seen that the value of  $K_F$  is very high, so the adsorption ability is excellent. The applicability of the adsorption model is that Langmuir's  $R^2$  (0.9964) is higher than Freundlich's  $R^2$  (0.9116) or Temkin's  $R^2$  (0.896), so the adsorption of MB onto SWR is considered to be the most suitable for the Langmuir model.

### 3.4. Adsorption mechanism

The adsorption capacity was affected by the surface area and porosity of the adsorbent, but the aromatic rings and functional groups present on the surface of the adsorbent such as -C=O, -C-O-C-, -OH, -NH<sub>2</sub>, -C=S, -C=N and -S=O etc. plays an important role in increasing the adsorption capacity of MB in aqueous solution[6,10]. The molecular structure of MB that influences the interaction with the adsorbent carbon surface was a 6 carbon aromatic ring, a cation containing nitrogen and sulfur[19]. The process of adsorption of methylene blue to carbon



**Figure 6.** A possible interactions between SWR and MB in aqueous solution: electrostatic attraction (---), hydrogen bonding interaction (.....) and  $\pi$ - $\pi$  stacking interactions (---).

occurs through electrostatic interactions, formation of hydrogen bridges, electron donor acceptor relationships, and the  $\pi$ - $\pi$  electron dispersing force between functional groups on the carbon surface with MB molecules[1,11].

WR are made of carbonaceous substances such as polysaccharides. It consists of low molecular weight compounds such as cellulose, pectin, carotenoids and amino acids, and citrulline and other phytochemicals[8]. The presence of these compounds makes the WR an advantageous platform for the synthesis of activated carbon materials. WR can prove to be a suitable binder for MB adsorption due to the presence of hydroxyl (cellulose) and carboxyl (pectin) groups[8]. According to previous studies, watermelon peels contain a significant amount of phenolic compounds and have a high radical scavenging ability[1,6].

Adsorption of MB in aqueous solution is highly dependent on the various polar functional groups of the surface. According to the results of the FT-IR spectrum, the ratio of peaks of hydroxyl, carboxyl and carbonyl groups on the SWR surface was larger than that of WR, and various polar functional groups were enhanced. In particular, the formation of  $-SO_3$  groups on the surface of the adsorbent through the sulfonation process is expected to play an important role in the adsorption process of MB. Depending on the functional groups available on the SWR surface, the MB adsorption mechanism can occur by various interactions. The various interactions between MB and SWR in aqueous solution can be broadly divided into three categories[8,28]; first, the electrostatic attraction between the positively charged MB cations in the aqueous solution and the negatively charged functional groups of the SWR surface. Second, it is the hydrogen bonding interaction between the surface hydrogen bonds between the functional groups available on the SWR surface and the nitrogen atom of MB, and the third, the  $\pi$ - $\pi$  stacking interaction between the aromatic ring of MB and the graphene framework of SWR (Figure 6).

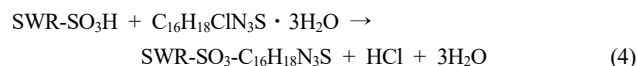
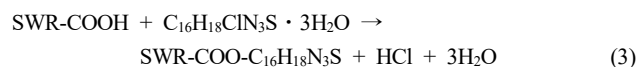
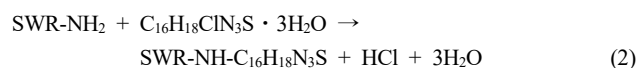
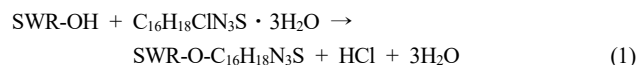
Based on the above-mentioned FT-IR analysis results, it can be con-

**Table 5.** Thermodynamic Parameters for Adsorption of MB onto SWR

Temperature (K)	Thermodynamic [ $\Delta G^0 = \Delta H^0 - T\Delta S^0$ ]		
	$\Delta G^0$ (kJ/mol)	$\Delta H$ (kJ/mol)	$\Delta S$ (J/mol · K)
298	-2.20		
303	-3.02	46.72	164.15
313	-4.63		
323	-6.30		

$q_e$ : amount of MB adsorbed on SWR at equilibrium (mg/g),  $C_e$ : MB concentration at equilibrium (mg/L),  $R$ : universal gas constant (8.314 J/molK),  $T$ : absolute temperature (K),  $\Delta H^0$ : adsorption enthalpy change,  $\Delta S^0$ : adsorption entropy change,  $\Delta G^0$ : Gibbs free energy.

cluded that various types of interactions contribute to the enhancement of MB adsorption on the SWR surface. These views are also consistent with reports by Jawad *et al.*[8] and Surip *et al.*[31]. In addition, similar observations have been reported by other researchers for adsorption to MB on the surface of chemically treated carbon microspheres, multi-walled carbon nanotubes, wrapped carbon nanotubes and graphene-chitosan complexes[1,32]. The mechanism of adsorption of SWR and MB ions in aqueous solution can be explained by the following equation.



In conclusion, sulfonation grafted the  $-SO_3$  group on the surface of the adsorbent, and strengthened the carboxyl group ( $-\text{COOH}$ ) and the hydroxyl group. As a result, the adsorption efficiency of MB onto SWR was improved. However, if the degree of sulfonation is too high, the hydration shell induced by the sulfuric acid group acts as a barrier, preventing the sulfonated adsorbent and the cationic group of accessing each other[10,17]. This can reduce the adsorption efficiency. Therefore, it is necessary to optimize the degree of sulfonation for adsorbent. Adsorption of MB onto SWR is a complex phenomenon due to various interactions.

### 3.5. Thermodynamic interpretation

In the adsorption process, the reaction temperature affects the solubility of MB, which can determine the rate of adsorption as well as all potential ion exchangers[2,11]. The effect of temperature on adsorption efficiency in aqueous solution was investigated, and the results are presented in Table 5.

The values of  $\Delta H$  and  $\Delta S$  were calculated from the slope and in-

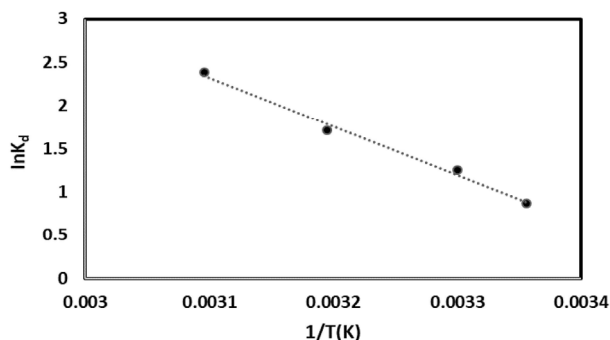


Figure 7. Plot of  $\ln K_d$  vs  $1/T$  for determining of thermodynamic parameters for the adsorption of MB onto SWR.

cept of the van't Hoff plot ( $\ln K_d$  vs  $1/T$ ) as shown in Figure 7. As a result of the experiment, a negative value of  $\Delta G$  indicates that adsorption of MB to SWR is spontaneous. In addition, the positive value of the enthalpy change ( $\Delta H$ ) indicates that the adsorption process is an endothermic reaction, and the positive entropy change ( $\Delta S$ ) indicates that the randomness of the SWR surface increases in the adsorption process. Moreover, the value of  $\Delta G$  falls within the range of 0 to -20, so the MB adsorption process using SWR is a physical process. This is consistent with the analysis of the Temkin constant analyzed above.

Many researchers have reported that the biomaterial-based MB adsorption process is a spontaneous process and an endothermic reaction, and the adsorption efficiency increases with increasing temperature [1,6]. In addition, according to the values of Gibbs free energy and enthalpy change, MB was adsorbed onto the biomaterial-based adsorbent through the physical adsorption process. The cause of this increase in adsorption efficiency was explained by the tendency of the activation of the active adsorption site of the adsorbent or the increase in the number of MB ions discharged from the adsorbent surface to the aqueous solution. On the contrary, there are reports of several researchers that the adsorption efficiency decreased due to the decrease in the thickness of the boundary layer surrounding the adsorbent as the temperature increased. Li *et al.*[27] reported that as a result of removing MB from an aqueous solution by sulfonating a lignin-based material, the removal rate decreased by 18.13% as the temperature increased from 20 to 60 °C. However, many researchers agree that temperatures as high as 50 °C can cause physical damage to bioadsorbents. Therefore, when using a bio-adsorbent to adsorb hazardous substances in an aqueous solution, it is necessary to maintain an appropriate temperature.

#### 4. Conclusions

This study attempted to adsorb MB in aqueous solution by sulfonating a cellulose-based dried watermelon peel bio-adsorbent. The H/C ratio and O/C ratio was increased from 0.045 to 0.13 and from 0.72 to 1.17, respectively, after sulfonating of WR. The  $\text{pH}_{\text{pzc}}$  of SWR was measured to be 4.1, so that the range to adsorb MB was wide, which had a favorable effect on adsorbing the cationic dye MB. The main functional groups of SWR were bonded OH-group, CH stretching, C=O

carbonyl groups, carboxylic groups and C-O stretch peaks, and R-SO<sub>3</sub>H peak. In various parameter experiments, 1 g/L of adsorbent and pH 6 were optimal conditions for adsorption of MB onto SWR. The maximum adsorption capacity of Langmuir was found to be 334.45 mg/g. The adsorption process of MB using SWR was endothermic and corresponds to a physical process according to the thermodynamic analysis. Sulfonating grafted the -SO<sub>3</sub> group on the surface of the adsorbent and strengthened the carboxyl group (-COOH) and hydroxyl group. As a result, the adsorption efficiency of MB onto SWR was improved.

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#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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