

# Removal of basic dye (methylene blue) from wastewaters utilizing beer brewery waste

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## Abstract

In the work, the beer brewery waste has been shown to be a low-cost adsorbent for the removal of basic dye from the aqueous solution as compared to its precursor (i.e., diatomite) based on its physical and chemical characterizations including surface area, pore volume, scanning electron microscopy (SEM), and non-mineral elemental analyses. The pore properties of this waste were significantly larger than those of its raw material, reflecting that the trapped organic matrices contained in the waste probably provided additional adsorption sites and/or adsorption area. The results of preliminary adsorption kinetics showed that the diatomite waste could be directly used as a potential adsorbent for removal of methylene blue on the basis of its adsorption–biosorption mechanisms. The adsorption parameters thus obtained from the pseudo-second-order model were in accordance with their pore properties. From the results of adsorption isotherm at 298 K and the applicability examinations in treating industrial wastewater containing basic dye, it was further found that the adsorption capacities of diatomite waste were superior to those of diatomite, which were also in good agreement with their corresponding physical properties. From the results mentioned above, it is feasible to utilize the food-processing waste for removing dye from the industrial dyeing wastewater.

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**Keywords:** Beer brewery waste; Characterization; Dye adsorption; Industrial dyeing wastewater

## 1. Introduction

Diatomaceous earth (also called diatomite or kieselguhr) originates from sedimentary rocks composed of the fossilized skeletal remains of diatoms. Thus, diatomite consists mainly of about 90 wt% silicon dioxide along with significant quantities of alumina and iron oxide. Due to its specific properties, the porous material has been widely used in industries as filtration medium or filter-aid [1]. It should be noted that the discarded diatomite was mostly from wine brewery, where the high clarity of the polish filtration is required to remove insoluble grain particles and residual yeast from fermented beer before bottling [2]. In the past decades, the food-processing waste was only implanted in soils for the purpose of agricultural application [3], but do not utilize it directly as a value-added resource. Furthermore, this approach has the potential to leach nitrogenous material into

the groundwater, and could also emit a strong odor because the waste contains biodegradable organic matter with a high protein and nitrogen content.

It is well known that the dye effluents, which may be from dyestuff manufacturing and textile industries, may exhibit toxic effects on microbial populations and can be toxic and/or carcinogenic to mammalian animal [4]. Removal of dye from industrial effluents using the adsorption process has been generally considered to be the most efficient method for quickly lowering the concentration of dissolved dyes in an effluent [5]. However, activated carbon, the most widely used adsorbent, remains an expensive adsorbent and has high regeneration cost while being exhausted. For these reasons, there is growing interest in using low-cost inorganic alternatives to carbon adsorbent [6–8]; for example, slag (blast furnace waste) [9–11], bagasse fly ash [12], red mud [13], bottom ash [14], rice husk [15], and wheal husk [16,17]. In this regard, diatomite waste has been studied to obtain the mesoporous silica adsorbent using acid/alkaline activation methods and its application to removal of dye from aqueous solution in the previous works [18,19]. Also, the waste resource

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was tentatively used as an adsorbent for removal of cationic herbicide (i.e., paraquat) from aqueous solution in the previous study [20], suggesting that some functional groups, observed by the Fourier transform infrared (FTIR) spectra, on the surface of clay adsorbent may play an important role in the adsorption of the cationic compound. However, there is no explanation for the difference of adsorption capacity on the basis of physical characterizations and other chemical properties of them.

The main object of this work was to explore the possibility of utilizing diatomite waste (from the beer-finishing process in the wine-brewing plant) directly for the adsorption–biosorption of model dye (i.e., methylene blue) as compared to the adsorption results using diatomite at the same conditions. Thus, the physical and chemical properties of diatomite waste and fresh diatomite were first examined to compare the significant differences between them. The results of the representative experiments of adsorption isotherm and kinetics studies have been also carried out to investigate the adsorption behaviors, and analyze the availability of the pseudo-second-order reaction model. In addition, considering the applicability of diatomite waste and fresh diatomite in the industrial wastewaters containing cationic (basic) dye, this study also examined the batch adsorption tests to evaluate the removal difference between the diatomite waste and fresh diatomite.

## 2. Experimental

### 2.1. Materials

The beer brewery waste was supplied by Shan-Hua Factory of Taiwan Tobacco & Liquor Co. (Tainan, Taiwan). The main components of its precursor (i.e., fresh diatomite) from the manufacturer's brochure (Celite Co., USA) were approximately 91.5% SiO<sub>2</sub>, 4.0% Al<sub>2</sub>O<sub>3</sub> and 1.1% Fe<sub>2</sub>O<sub>3</sub>. In this work, the diatomite waste and fresh diatomite were denoted as SDE and DE, respectively. The cationic dye used as target adsorbate in the adsorption isotherm and kinetic experiments is methylene blue (i.e., Basic Blue 9, or C.I. 52015) with 95+% purity, which was purchased from Katayama Chemical Co. (Japan). Its CAS identification information, chemical formula and molecular weight are 61-73-4, C<sub>16</sub>H<sub>18</sub>N<sub>3</sub>SCl·4H<sub>2</sub>O and 319.89 g/mol, respectively. The molecular structure of the dye was shown in Fig. 1.

### 2.2. Physical characterization

The main physical properties of SDE and DE relating to the Brunauer–Emmett–Teller (BET)/Langmuir surface areas (i.e., S<sub>BET</sub> and S<sub>L</sub>) and total pore volume (i.e., V<sub>t</sub>) were obtained by measuring their nitrogen adsorption isotherm at 77 K in a surface

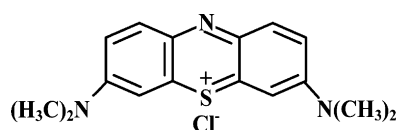


Fig. 1. Molecular structure of methylene blue.

area and porosity analyzer (Model ASAP 2020; Micromeritics Co., USA). The specific surface areas of the samples were obtained by means of the standard methods applied in a relative pressure ranging from 0.05 to 0.3 [21]. The total pore volume was assessed by converting the amount of nitrogen gas adsorbed at a relative pressure (ca. 0.99) to the volume of liquid adsorbate. In order to evaluate the precision of measurement, each sample was repeatedly carried out in triplicate. The surface morphologies of the samples were examined using the scanning electron microscopy (SEM) by an S-3000N (Hitachi Co., Japan) apparatus operated at a 5 or 15 kV accelerating potential. Prior to the observation, the external surfaces of the SDE and DE samples were coated with a thin, electric conductive gold film.

### 2.3. Chemical characterization

The analyses of non-mineral elemental contents (C/H/N/O/S) of SDE and DE were used as a means of examining the organic residues left in the samples. The elemental analyses of the samples (1–3 mg) were performed by using an elemental analyzer (Model CHN-O-RAPID; Heraeus Co., Germany). For each analysis, the standard sample (i.e., acetanilide) was first analyzed for checking the experimental error within  $\pm 1\%$ .

### 2.4. Adsorption kinetics

The apparatus and its experimental methods of adsorption kinetic systems employed in the present work were similar to those reported previously [22]. A representative experiment was designed to obtain the information on the adsorption behaviors of SDE and DE. The experimental conditions were given below: initial methylene blue concentration = 2.5 mg/L, adsorbent dosage = 0.5 g/2 L, temperature = 298 K, initial pH 7.0, and agitation speed = 400 rpm. Prior to the experiment, the adsorption apparatus was immersed in a refrigerated circulating-water bath to maintain isothermal conditions. Each sample of the solution (ca. 15 cm<sup>3</sup>) was withdrawn from the adsorption vessel by using a 20 mL syringe at intervals of 0.5, 1.0, 2.0, 5.0, 10.0, 30.0, 60.0 and 120.0 min. Aqueous samples were taken from the solution and then filtered with fiber membrane (Cat. No.: A045A025A; ADVANTEC MFS Inc., USA). The methylene blue concentration of the filtrate was immediately analyzed with a 1.0 cm light path quartz cells using a spectrophotometer (Hitachi UV-1500A) at  $\lambda_{\max}$  of 661 nm. The amount of methylene blue adsorbed onto the diatomite particles was determined by the difference between initial and liquid-phase concentrations of methylene blue solution. In each experiment, the adsorption was carried out in triplicate.

### 2.5. Adsorption isotherm

The adsorption isotherms of SDE and DE particles were tentatively determined to evaluate its effectiveness in removal of methylene blue from aqueous solution. All the experiments of adsorption capacities of methylene blue were determined by using a batch procedure as described previously [23]. In each experiment, 0.2 g of dry sample was poured into the 125-mL

Erlenmeyer flask. Adsorption was carried out by shaking (at ca. 110 rpm) with fixed value (i.e.,  $0.05 \text{ dm}^3$ ) of methylene blue solutions at different initial concentrations of 0.5, 1.0, 1.5, 2.0 and 2.5 mg/L in a thermostatic shaker bath at  $298 \pm 0.1 \text{ K}$  for all experiments. The methylene blue solutions were contacted for 24 h, and the length of time had been shown previously to approach adsorption equilibrium. All adsorption experiments were carried out in duplicate.

### 2.6. Applicability for treating industrial wastewater

For preliminary comparison, a series of batch adsorption tests were also carried out using diatomite waste and fresh diatomite as adsorbents for treating an industrial wastewater containing cationic dye, which was sampled from a local textile dyeing factory. The main characteristics of the industrial wastewater have been analyzed and given as follows: pH of 7.5, total suspended solid of 102 mg/L, and chemical oxygen demand (COD) of  $535 \pm 41 \text{ mg/L}$ . The stock solution of industrial wastewater was diluted using deionized water to obtain concentrations (denote COD) for batch mode adsorption studies, which were carried out with 500 mg adsorbent and 50 mL of the working solution in 125 mL conical flasks under the temperature of 298 K and the agitation speed of about 150 rpm. At the end of agitation (24 h), the solution was filtered with fiber membrane (Cat. No.: A045A025A; ADVANTEC MFS Inc., USA). The COD concentration of the filtrate was immediately analyzed by using the closed reflux method (Taiwan EPA, NIEM Method W517.50B). All the experiments were investigated in duplicate. All the samples were analyzed in triplicate.

## 3. Results and discussion

### 3.1. Physical characterizations of SDE and DE

The data in Table 1 indicated the BET/Langmuir surface areas and total pore volume of diatomite waste (SDE) and diatomite (DE) adsorbents. The results showed that the pores of these samples should be macroporous and possess fewer adsorption properties, but have great ability to trap suspended solids for separation from liquid solutions. It was also found that the pore properties of SDE were significantly superior to those of DE, indicating that the fibrous residues adsorbed/retained in the pore of SDE could not completely block pore from entering the nitrogen molecule while analyzing its adsorption isotherm for

Table 1  
Main physical properties of diatomite waste (SDE) and diatomite (DE)

Sample	$S_{\text{BET}}^{\text{a}}$ ( $\text{m}^2/\text{g}$ )	$S_{\text{L}}^{\text{b}}$ ( $\text{m}^2/\text{g}$ )	$V_{\text{t}}^{\text{c}}$ ( $\text{cm}^3/\text{g}$ )
Diatomite waste (SDE)	$4.522 \pm 0.445^{\text{d}}$	$7.138 \pm 0.675$	$0.0317 \pm 0.0060$
Diatomite (DE)	$2.133 \pm 0.205$	$3.290 \pm 0.359$	$0.0045 \pm 0.0004$

<sup>a</sup> BET surface area.

<sup>b</sup> Langmuir surface area.

<sup>c</sup> Total pore volume.

<sup>d</sup> Mean  $\pm$  standard deviation for three determinations.

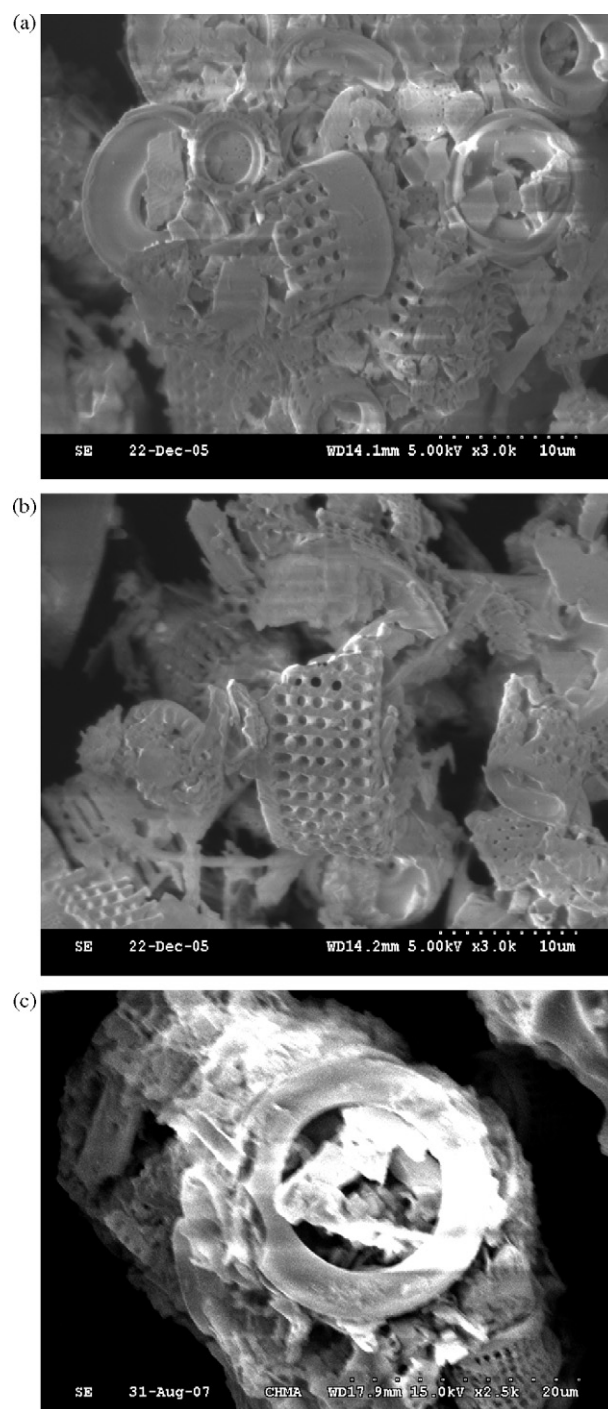


Fig. 2. SEM photographs of (a) diatomite waste (SDE), (b) diatomite (DE), and (c) dye loaded diatomite waste.

determining pore properties and probably provide their organic matrices to enhance the nitrogen adsorption, resulting in the larger surface area as compared to DE.

The examination into the textural structure of diatomite waste (SDE) and diatomite (DE) particles could be observed from the SEM photographs. From Fig. 2, it could be seen that these two samples indicated well-defined pore structures with diameter of about  $1 \mu\text{m}$ . It should be noted that the observation was consistent with the results from the measurements of pore properties in

**Table 1.** In Fig. 2(a), SDE showed the morphology of compact matrix texture, implying that the sample was bound together by the organic residues. Some traps could also be seen in the pores of SDE, resulting in the irregular textures. In contrast with Fig. 2(b), DE appeared as separate particles with clear pore structures. Fig. 2(c) showed that the diatomite structure changed upon adsorbing the dye studied, exhibiting a tendency to form agglomerates.

### 3.2. Chemical characterizations of SDE and DE

The results of organically elemental analyses of diatomite waste (SDE) and diatomite (DE) particles in this study were given in Table 2. The non-mineral elemental contents (including C, N and O) of SDE sample were obviously larger than those of DE sample. It was reasonable that the composition of organic residues trapped in SDE could be regarded as a complex matrix containing cellulose/protein fractions, which should be the origins of yeast and insoluble grain particles. On the other hand, the elemental contents (i.e., C, N, O and S) of DE sample were very close to zero, indicating that the DE particle should be almost composed of minerals (e.g., silica and alumina).

### 3.3. Adsorption kinetics

A simple kinetic analysis of adsorption, pseudo-second-order equation [24], was used to fit the experimental data and also obtain the adsorption capacities of diatomite waste (SDE) and diatomite (DE) adsorbents. The linear form of the equation was described in the following form:

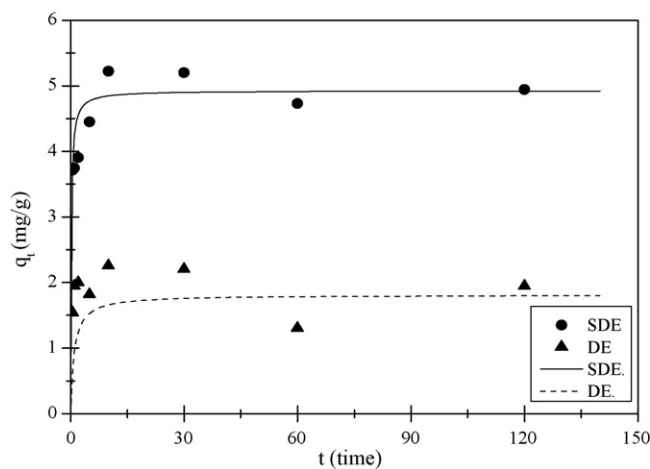
$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \left(\frac{1}{q_e}\right)t \quad (1)$$

where  $k$  is the pseudo-second-order rate constant ( $\text{g}/(\text{mg min})$ ),  $q_e$  the amount of basic dye adsorbed at equilibrium ( $\text{mg}/\text{g}$ ), and  $q_t$  is the amount of basic dye adsorbed at time  $t$  ( $\text{mg}/\text{g}$ ). Rate parameters,  $k$  and  $q_e$ , could be directly obtained from the intercept and slope of the plot of  $q_t$  against  $t$  (Fig. 3).

The values of  $k$ ,  $q_e$ , and correlation coefficient ( $R^2$ ), computed from Eq. (1) and listed in Table 3 revealed the kinetics of dye adsorption onto diatomite waste (SDE) and diatomite (DE) could be described by this model (with the correlation coefficients  $>0.95$ ), which was consistent with the results by Shawabkeh and Tutunji [25]. The value of  $q_e$  of adsorbent SDE was larger than that of adsorbent DE, supporting the fact that adsorbent SDE contained more pore properties as listed in Table 1. It was noted that the ratio (i.e.,  $4.92/1.80 = 2.7$ ) of  $q_e$  values of adsorbents SDE and DE obtained from the kinetic model was approximate to that (i.e.,  $4.522/2.133 = 2.12$ ) of their BET surface areas in

**Table 2**  
Elemental analyses of diatomite waste (SDE) and diatomite (DE)

Sample	C (wt%)	H (wt%)	N (wt%)	O (wt%)	S (wt%)
Diatomite waste (SDE)	0.82	0.29	0.48	1.7	0.00
Diatomite (DE)	0.00	0.30	0.00	0.00	0.00



**Fig. 3.** Plots of  $q_t$  vs.  $t$  for describing the adsorption kinetics of methylene blue onto diatomite waste (SDE) and diatomite (DE) (initial concentration = 2.5 mg/L, adsorbent dosage = 0.5 g/2 L, initial pH 7.0, temperature = 298 K, and agitation speed = 400 rpm; symbols: experimental data, full and dotted lines: calculated from the pseudo-second-order model).

**Table 1.** The rate constants  $k$  also seemed to be proportional to the BET surface areas of adsorbents SDE and DE. According to the results described above, it demonstrated that the beer brewery waste should be considered as an inorganic adsorbent for the direct application to wastewater treatment. By contrast, the adsorption capacity ( $q_e$ ) of chemically activated diatomite (BET surface area =  $98.1 \text{ m}^2/\text{g}$ ) for removal of methylene blue under the “same” conditions is only 9.99 mg/g based on the previous study [18]. In the present work the adsorption capacity of diatomite waste (BET surface area =  $4.5 \text{ m}^2/\text{g}$ ) blue could intake the cationic dye (i.e., methylene blue) of 4.92 mg/g in the aqueous solutions. Therefore, the use of diatomite waste (SDE) should be comparable to the other reported adsorbents such as activated diatomite.

### 3.4. Adsorption isotherm

The adsorption isotherm describes how adsorbed molecules interact with adsorbents when the adsorption process approaches to an equilibrium state. The data is thus critical in optimizing the use of adsorbents. Fig. 4 shows that the residual equilibrium concentrations obtained by the adsorption of methylene blue onto SDE were significantly lower than those onto DE, indicating that the adsorption capacities of the basic dye on SDE were larger than those on DE at the same adsorption con-

**Table 3**  
Kinetic parameters for adsorption of methylene blue onto diatomite waste (SDE) and diatomite (DE)<sup>a</sup>

Sample	$k$ (g/mg min)	$q_e$ (mg/g)	Correlation coefficient
Diatomite waste (SDE)	1.24	4.92	0.999
Diatomite (DE)	0.60	1.80	0.952

<sup>a</sup> Kinetic adsorption conditions: initial methylene blue concentration = 2.5 mg/L, adsorbent dosage = 0.5 g/2 L, agitation speed = 400 rpm, initial pH 7.0, and temperature = 298 K.

Table 4  
Residual COD concentrations of industrial dying wastewaters in the batch adsorption tests<sup>a</sup>

Sample	Residual COD concentration (mg/L) of industrial dying wastewater with dilution ratio									
	1		2		3		4		5	
	I <sup>b</sup>	II <sup>b</sup>	I	II	I	II	I	II	I	II
Diatomite waste (SDE)	161 ± 3	167 ± 4	88 ± 5	97 ± 9	76 ± 9	74 ± 1	68 ± 5	58 ± 3	66 ± 4	60 ± 6
Diatomite (DE)	180 ± 3	188 ± 20	115 ± 2	116 ± 3	94 ± 6	88 ± 2	79 ± 2	80 ± 5	71 ± 2	81 ± 3

<sup>a</sup> Adsorption conditions: dosage = 0.5 g/50 mL, adsorption time of 24 h, and temperature = 298 K.

<sup>b</sup> Indicating that all the experiments were investigated in duplicate.

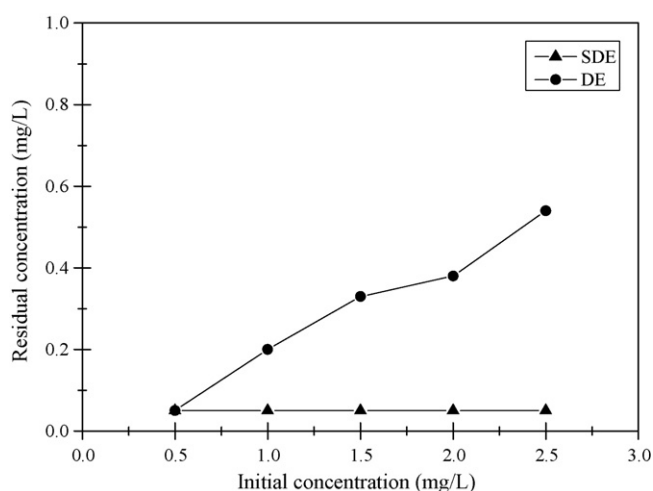


Fig. 4. Plots of residual (equilibrium) concentration vs. initial concentration for describing the adsorption isotherms of methylene blue onto diatomite waste (SDE) and diatomite (DE) (experimental conditions: adsorbent dosage = 0.2 g/50 mL, initial pH 7.0, and temperature = 298 K; the data on the SDE are to be <0.1 mg/L, which is the detection limit of UV–vis spectrophotometer).

ditions. Regarding the adsorption isotherms of methylene blue onto diatomite waste (SDE), the residual concentration at the initial dye concentrations of 0.5–2.5 mg/L is very close to “zero” (i.e., <0.1 mg/L), showing that adsorption equilibrium was not yet approached after the time of 24 h due to the excessive adsorption sites of this adsorbent. This was also consistent with the measured values according to the investigations on pore properties and adsorption kinetics of SDE and DE as described above.

### 3.5. Applicability for treating industrial wastewater

By using the same adsorbents, the almost same COD concentration of industrial dying wastewater and adsorption temperature, the residual COD concentrations in the industrial solutions of using diatomite waste (SDE) were always lower than those of using fresh diatomite (DE) from the results listed in Table 4, showing that the former adsorbent should be superior to the latter adsorbent as applied to the treatment of industrial wastewater containing basic dye. This was in accordance with the results obtained from the measured adsorption capacities of methylene blue in the adsorption kinetics and adsorption isotherm experiments described above.

## 4. Conclusions

This study demonstrated that the beer brewery waste mostly consisting of diatomite could be directly used as a porous adsorbent based on its pore properties, SEM observations, elemental analyses and adsorption properties. The results showed that the pore properties of adsorbent were higher than those of its precursor diatomite, which was also consistent with the measured adsorption capacities of methylene blue (one of basic dyes) at the equilibrium conditions and the results in the applicability for treating industrial wastewater containing basic dye. The ratios of parameters obtained from the fitting of the experimental data with the pseudo-second-order model were in good agreement with the corresponding ratios from their physical properties. It was speculated that the adsorption–biosorption mechanism should play a significant role in the agriculturally inorganic waste mainly due to its retained organic matrix. Further, the results from the applicability examinations in treating industrial wastewater containing basic dye showed that the adsorption capacities of the beer brewery waste were also superior to those of its fresh precursor. It is feasible to utilize beer brewery waste as a low-cost adsorbent for removing dye from the industrial dying wastewater.

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