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Characterization and adsorption properties of diatomaceous earth modified by hydrofluoric acid etching

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Abstract

This work was a study of the chemical modification of diatomaceous earth (DE) using hydrofluoric acid (HF) solution. Under the experimental conditions investigated, it was found that HF under controlled conditions significantly etched inward into the interior of the existing pore structure in the clay mineral due to its high content of silica, leaving a framework possessing a larger BET surface area (ca. 10 $m^2 \, g^{-1}$) in comparison with that (ca. 4 $m^2 \, g^{-1}$) of its precursor (i.e., DE). Further, the results indicated that the HF concentration is a more determining factor in creating more open pores than other process parameters (temperature, holding time, and solid/liquid ratio). This observation was also in close agreement with the examinations by the silicon analysis, scanning electron microscopy, X-ray diffraction, and Fourier transform infrared spectroscopy. The adsorption kinetics and the adsorption isotherm of methylene blue onto the resulting clay adsorbent can be well described by a pseudo-second-order reaction model and the Freundlich model, respectively.

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1. Introduction

Diatomaceous earth (DE), or diatomite, typically consists of 87–91% silicon dioxide (SiO_2), with significant quantities of alumina (Al_2O_3) and ferric oxide (Fe_2O_3) [1]. Due to its specific properties (porous structure, high silica content, low density, low conductivity coefficient, etc.) [1,2], DE has extensively been applied in many ways, such as filter aid [3], adsorbent [4–10], insulating material [11], catalyst support or carrier [12], and natural insecticide or grain protectant [13], etc. It is noted that diatomite only has weak adsorption capacity but excellent absorption power because of its macroporous structure. Thus one of the main end uses of diatomite is used as an absorbent for fluids such as acid, liquid fertilizer, oil, water, and alcohol [1].

Commercial diatomite is generally produced from natural diatomite by calcination processing at about 900 °C [1]. However, in many cases the clay mineral can be chemically treated or activated to modify its pore structure and/or the surface chemistry of the solid. Acid activation of clay minerals (e.g., montmorillonite, bentonite) is a common chemical modification to enhance its adsorption capacity and to give it certain properties for desirable applications [14–22]. It is well known that silica (SiO_2), which is the most abundant component in diatomaceous earth, is quite inert, being attacked only by strong alkali (e.g., NaOH) or hydrofluoric acid (HF) as a consequence of the formation of soluble product (SiO_3^{2-} or SiF_6^{2-}) [23]. Therefore, the wet cleaning and etching of wafers in the semiconductor manufacturing industry is commonly carried out by the use of NaOH or HF [24,25].

Recently, we have described the NaOH activation of spent diatomaceous earth, with a complete characterization and adsorption properties of the resulting solids [22,26]. The pore textures of some resulting solids thus obtained are mesoporous, indicating that they belong to type IV according to the Brunauer, Deming, Deming, and Teller (BDDT) classification [27]. With respect to the activation of clay minerals using HF, the information published is very scarce. This study was further stimulated by the etching reaction between SiO_2 and HF. The main objectives of this work were to study the feasibility of utilizing diatomaceous earth as a precursor in the production of silica-

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like adsorbent by physical and chemical characterization, and further evaluate its adsorption properties for the removal of methylene blue from aqueous solution at 25 °C.

2. Materials and methods

2.1. Materials

The diatomaceous earth was obtained from the Shan-Hua Factory of the Taiwan Tobacco & Liquor Co. (Tainan, Taiwan). The precursor was a calcined product (Grade 577, Celite Co., USA) with a median particle size of 20.8 μm. The typical chemical compositions from the manufacturer's brochure mainly consist of 92.0% SiO_2, 3.3% Al_2O_3, 1.3% of Fe_2O_3. The sample was first dried in the oven (105 °C) at least 2 h and then cooled to room temperature for further characterization and chemical activation. Hydrofluoric acid (HF, 48%), which was purchased from Merck Co. (Germany) in the grade for analysis, was selected as a chemical activator in this study to etch the dried sample for the purpose of creating more finely pores. The adsorbate used in the adsorption experiments was methylene blue (i.e., basic blue 9; C.I. 52015) with purity of min. 99% from the Sigma Chemical Co. (USA).

2.2. Chemical modification

The apparatus and chemical modification with HF employed in the present work are similar to those for chemical activation with NaOH, as reported previously [22,26]. It is noted that HF is actually a very weak acid, and the fluoride ion is highly electronegative. The etching reaction between the glass bottle (mainly composed of SiO_2) and HF will thus occur. Therefore, the solution containing diatomite and HF was first prepared in the polypropylene (PP) plastic bottle because of its good resistance to etching dissolution up to 50% of HF at ambient temperature [28], and then bathed in silicone oil, which was held in Pyrex glass for the purpose of heating on a hot plate. Under various concentrations (0.2–2.5 N of HF), adsorbent dosages (2.5–12.5 grams of 100 ml HF solution), holding times (0.5–8.0 h) and temperatures (25–100 °C), the chemical modification of the dried diatomite by HF was carried out on a laboratory stirrer/hot plate (Model: PC-420; Corning Co., USA) with boiler–reflux condenser. Afterward, the sample solution was filtered in a vacuum filter flask and washed sequentially five times with

deionized water to remove the ions and other residues. The resulting solid was finally dried at 105 °C for 24 h, and stored in the desiccator after drying.

2.3. Physical characterizations

The pore structures of diatomaceous earth and its HF-modified products (denoted as MDE) relating to surface areas, total pore volume, and pore size distribution were obtained by measuring their nitrogen adsorption–desorption isotherms at −196 °C in a surface area and porosity analyzer (Model ASAP 2010; Micromeritics Co., USA). To evaluate its precision, the pore structure of diatomaceous earth used as a reference sample was repeatedly measured at least two times before being measured in the experiments. As shown in Table 1, this automatic instrument has high precision based on the standard deviations. From the data of total pore volume (V_t) and true density (ρ_s), the particle density (ρ_p) and porosity (ε_p) can be further obtained [29,30]. A Siemens D5000 powder diffractometer (Cu$K\alpha$ radiation) was used to obtain powder XRD patterns for the purpose of observing the changes in crystallinity between the samples. The surface textures of the samples were observed using scanning electron microscopy (SEM) with a JEOL JXA-840 (JEOL Co., Japan) apparatus.

2.4. Chemical characterizations

The carbon/hydrogen/nitrogen (C/H/N) contents of diatomaceous earth and its HF-modified products (denoted as MDE) were used to examine the residues of the resulting products in the chemical modification processes. The C/H/N elemental analysis of the samples (1–3 mg) was performed using an elemental analyzer (Model CHN-O-RAPID, Heraeus Co., Germany). For each analysis, the standard sample (i.e., acetanilide) was first analyzed by checking the experimental error within ±1%. To measure the quantity of silicon leached from the modified diatomaceous earths, the silicon content of diatomaceous earth and its HF-modified products was analyzed using an inductively coupled plasma-atomic emission spectrometer (Model ICAP 9000, Jarrell-Ash Co., USA). Prior to analysis, the samples were first digested in concentrated nitric acid/hydrofluoric acid solution to form solution samples. Fourier transform infrared spectroscopy (FTIR) analysis was used for the observation of functional groups on the surface of

Table 1
Surface area and porosity of diatomaceous earth (DE)

S_{BET}[a] (m^2 g^{-1})	S_L[b] (m^2 g^{-1})	V_t[c] (cm^3 g^{-1})	ρ_s[d] (g cm^{-3})	ρ_p[e] (g cm^{-3})	ε_p[f] (−)
3.81 ± 0.01[g]	21.17 ± 0.40	0.0155 ± 0.0009	2.82 ± 0.05	2.70 ± 0.04	0.043 ± 0.004

[a] BET surface area.
[b] Langmuir surface area.
[c] Total pore volume.
[d] True density.
[e] Particle density, calculated by $\rho_p = 1/[V_t + (1/\rho_s)]$, where ρ_s was determined by pycnometer.
[f] Particle porosity, computed by $\varepsilon_p = 1_{(\rho_p/\rho_s)}$.
[g] Mean ± standard deviation for two determinations.

the samples (KBr). The spectrum was measured and recorded (500–2000 cm^{-1}) on a spectrometer (Model DA 8.3, Bomen Co., Canada).

2.5. Adsorption tests

Adsorption behavior of the optimal modified solid (i.e., MDE-2.5 N) was tentatively determined to evaluate its potential for removal of methylene blue from aqueous solution at 25.0 °C. Adsorption experiments were carried out in a ca. 3 dm^3 stirred batch adsorber with four baffles as described in our previous studies [22,26]. In the present study, the adsorption solution was maintained under the same conditions (e.g., solution volume = 2 dm^3, MDE adsorbent dosage = 0.5 g/2.0 dm^3, agitating speed = 400 rpm, pH 7.0) with an outer circulating-water bath for the adsorbability of the basic dye under various initial concentrations (4–12 mg dm^{-3}). For a preliminary comparison, the adsorption behavior of diatomaceous earth under an initial methylene blue concentration of 10 mg dm^{-3} was also carried out under the same solution conditions. The concentration of the dye filtrate was determined immediately through the use of a spectrophotometer (Hitachi UV–2001) at a wavelength UV–maximum (λ_{max}) of 661 nm. The amounts of methylene blue adsorbed onto the two adsorbents were determined as follows,

$$q_t = (C_0 - C_t)(V/W), \tag{1}$$

where C_0 and C_t are the initial and liquid-phase concentrations (mg dm^{-3}) of dye solution at t (min), respectively, V is the volume of dye solution (ca. 2 dm^3), and W is the mass of dry adsorbent used (g).

3. Results and discussion

3.1. Physical characterization

Generally, the Brunauer, Emmett, and Teller (BET) equation has been used for measuring and comparing the specific surface areas of a variety of adsorbents from their nitrogen adsorption–desorption isotherms at 77 K (−196 °C) [27]. In the present study, the BET surface area was regarded as a comparative factor of determining the degree of pore properties of the modified diatomaceous earths.

According to the previous study [22], it was found that the NaOH concentration seems to have the most efficient effect on the development of pores in the base-activated samples. Shown in Fig. 1 is the effect of HF concentration on the BET surface areas of the resulting solids prepared under a fixed holding time of 0.5 h and solid/liquid ratio of 5 g/100 ml. In the HF-modified diatomaceous earth series, the pore property at 60 °C is slightly larger than that at 80 °C. Also, the increase in pore property seems to be proportional to the HF concentration. The observation is consistent with H$_2$SO$_4$-activated solids [22] and NaOH-activated solids [22,26]. The optimal BET surface area (ca. 10 m^2 g^{-1}) can be obtained at a temperature of 60 °C, HF concentration of 2.5 N, holding time of 0.5 h, and solid/liquid ratio of 5 g/100 ml. As compared with the data
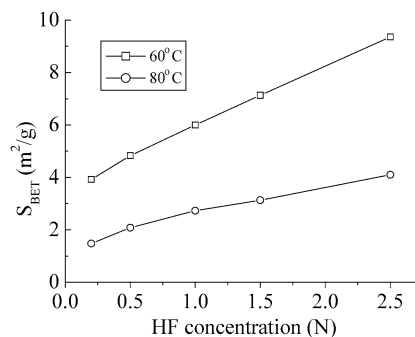

Fig. 1. Effect of HF concentration on BET surface areas of modified diatomaceous earths prepared at the temperatures 60 and 80 °C, holding time 0.5 h, and solid/liquid ratio 5 g/100 ml.
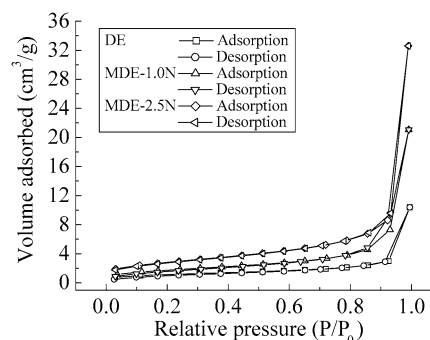

Fig. 2. Nitrogen adsorption/desorption isotherms of diatomaceous earth (DE) and modified diatomaceous earths (i.e., MDE-1.0 N and MDE-2.5 N).

in Table 1, it can be seen that the HF has an etching performance to create more open pores, thus resulting in larger surface areas. The results were further confirmed from the nitrogen adsorption–desorption isotherms and pore size distributions shown in Figs. 2 and 3, respectively. On the basis of the BDDT classification, the patterns of adsorption–desorption isotherms in Fig. 2 belong to a typical type II, indicating that the diatomaceous earth and their modified solids should be still macroporous powders or powers with pore diameters larger than micropores [31]. The foregoing results may be further observed in the pore size distribution curves based on pore areas of the Barrett–Joyner–Halenda (BJH) desorption branch in the measurement of N$_2$ isotherms, as shown in Fig. 3. It is seen that the pores of these clay samples (including DE, MDE-1.0 N, and MDE-2.5 N) have a heterogeneous distribution of pore diameters with major pore ranges below about 100 Å, which may be useful for their possible applications in adsorption of component with large molecular size from liquid phase.

The effects of temperature, holding time, and solid/liquid ratio under specified modification conditions on the BET surface areas of the resulting products are shown in Figs. 4–6, respectively. It seems that these modification parameters play a less important role in the production of porous materials prepared from diatomaceous earth by HF. For example, with increase in the temperature from 25 to 100 °C (boiling) at a HF concentration of 1.0 N, the resulting solids have almost the same BET surface area (seen in Fig. 4). Also shown in Fig. 6, the BET surface areas of the resulting solids tend towards gradual decrease

with increasing adsorbent dosage. The decrease in pore properties is probably due to the lower etching rate of reactions at a higher solid/liquid ratio.

SEM micrographs of diatomaceous earth (DE) and the optimal sample (i.e., MDE-2.5 N) are illustrated in Fig. 7, showing a great difference between the surface textures of these samples. The porous structure examination of the precursor DE can be clearly seen in the SEM photograph (left, Fig. 7), revealing the variety of rigid shapes and macropores/open voids that give the diatomaceous earths a high ability to trap solids or residues for separation from clear liquids. Obviously, the pores can be developed and further enhanced by the chemical modification during the etching reaction by HF, which results in flaws,
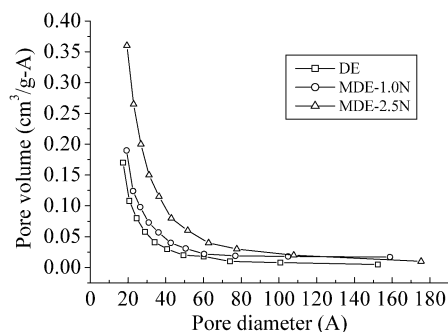
cracks, crevices, and small pores in the small particles shown in Fig. 7 (right).

To observe changes in crystallinity as a result of the HF modification, the powder XRD patterns of some typical samples (including DE, MDE-0.2 N, MDE-0.5 N, MDE-1.0 N, MDE-1.5 N, and MDE-2.5 N) are shown in Fig. 8. It is clear that the XRD patterns having the maximum silica peak at about 22.0° 2θ are not significantly modified by HF etching, showing that the precursor has a high resistance to HF attack, and that its pore property is thus not enhanced under chemical modification conditions. This phenomenon also seems to be in line with the data shown in Fig. 1, in which the increase in BET surface area is only from 3.9 to 9.4 m^2 g^{-1} with increasing HF concentration from 0.2 to 2.5 N.

Fig. 3. Pore size distributions of diatomaceous earth (DE) and modified diatomaceous earths (i.e., MDE-1.0 N and MDE-2.5 N) based on BJH desorption dA/dD pore area.

Fig. 5. Effect of holding time on BET surface areas of modified diatomaceous earths prepared at the HF concentration 1.0 N, temperatures 25–100 °C, and solid/liquid ratio 5 g/100 ml.
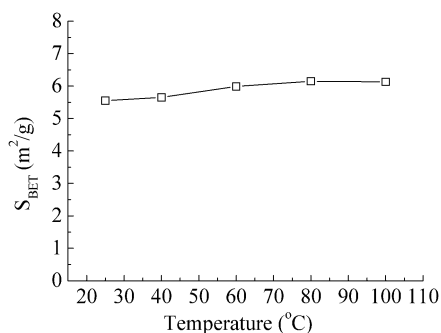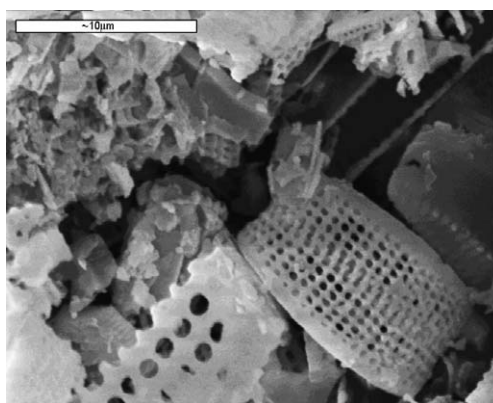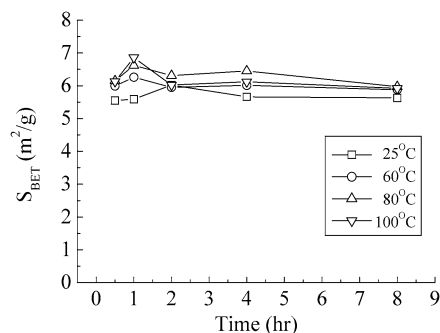

Fig. 4. Effect of temperature on BET surface areas of modified diatomaceous earths prepared at an HF concentration 2.5 N, holding time 0.5 h, and solid/liquid ratio 5 g/100 ml.
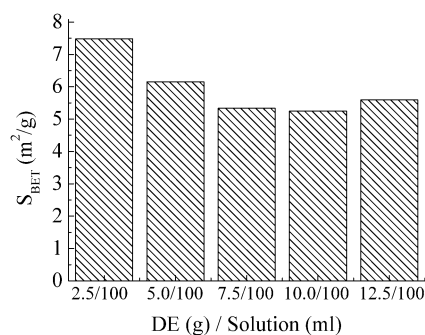

Fig. 6. Effect of solid/liquid ratio on BET surface areas of the resulting solid prepared at HF concentration 1.0 N, temperature 80 °C, and holding time 0.5 h.
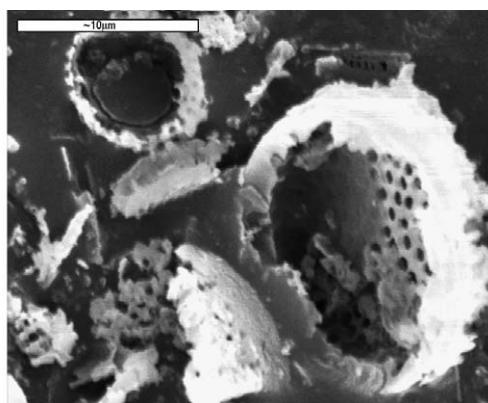

Fig. 7. SEM photographs (×4000) of diatomaceous earth (DE) and modified diatomaceous earth (i.e., MDE-2.5 N).
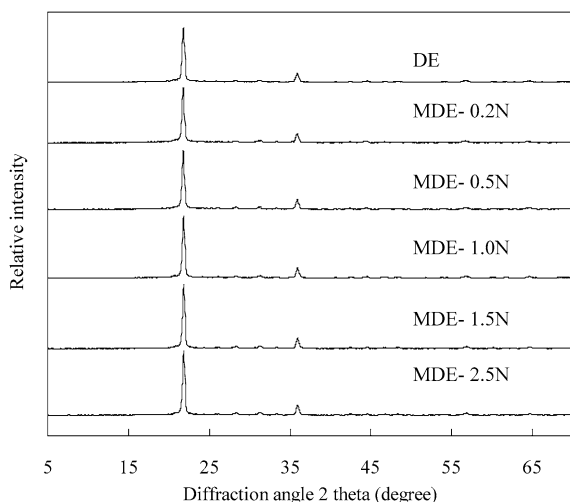
Fig. 8. XRD diffractograms of diatomaceous earth (DE) and modified diatomaceous earths (i.e., MDE-0.2 N, MDE-0.5 N, MDE-1.0 N, MDE-1.5 N, and MDE-2.5 N).

Table 2
Contents of C, H, N, and Si of DE and modified diatomaceous earths (MDEs) (% oven-dried weight)

Sample ID	C (%)	H (%)	N (%)	Si (%)
DE	0.18	0.33	0.10	41.9
MDE-0.2 N[a]	0.05	0.38	0.14	41.8
MDE-0.5 N[a]	0.02	0.34	0.07	41.5
MDE-1.0 N[a]	0.06	0.22	0.09	41.3
MDE-1.5 N[a]	0.07	0.21	0.05	40.9
MDE-2.5 N[a]	0.04	0.13	0.17	38.8

[a] Prepared under conditions of temperature 60 °C, holding time 0.5 h, solid/liquid ratio 5 g/100 g, and various HF concentrations (i.e., 0.2, 0.5, 1.0, 1.5, and 2.5 N).

3.2. Chemical characterization

Table 2 presents the content of carbon (C), hydrogen (H), nitrogen (N), and silicon (Si) of the MDE series. Compared with those of DE (Table 2), the MDE displayed a very distinctive chemical composition. Their carbon contents were significantly lower probably due to the partial dissolution of carbonates. It is particularly interesting that the MDE series possessed a fairly lower silicon contents than that of DE, showing that the etching reaction between silica and HF could occur, and that is also gave rise to their larger pore properties as shown in Figs. 1 and 2. Notably, the etching degree, indicative of silicon content, tends to increase with increasing HF concentration.

The study of the HF-modified solids by FTIR spectroscopy confirms the presence of silica in them. The spectra of the samples DE and MDE series treated with 0.2, 0.5, 1.0, 1.5, and 2.5 N are displayed in Fig. 9. Clearly, there are no significant differences between characteristic bands ranging from 1400 and 400 cm^{-1} (i.e., 1200–1000 and 795 cm^{-1}) due to silicates structure [16,32], which was also seen in the XRD peaks at 2θ of 21°–22° (Fig. 8). This is consistent with the data on BET surface areas shown in Fig. 1. The wide bands centered at ca. 1090 cm^{-1} should be due to Si–O–Si in-plane vibration
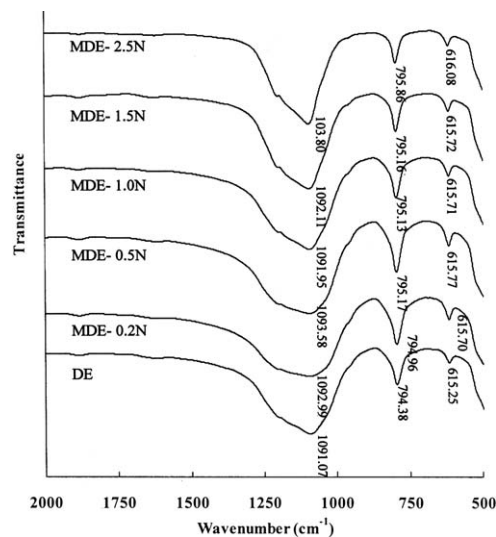

Fig. 9. FTIR spectra of diatomaceous earth (DE) and modified diatomaceous earths (i.e., MDE-0.2 N, MDE-0.5 N, MDE-1.0 N, MDE-1.5 N, and MDE-2.5 N).

(asymmetric stretching). Similar observations can be seen at ca. 795 cm^{-1}, which are also characteristic of silica. Again, the weak absorption peak at 616 cm^{-1} was possibly attributed to Si–O deformation and Al–O stretching [32].

3.3. Adsorption property

In the adsorption experiments, the optimal solid MDE-2.5 N was chosen as a representative adsorbent. The effect of initial dye concentration on the adsorption intake of methylene blue at the adsorbent dosage of 0.5 g/2.0 dm^{-3}, initial pH 7.0, temperature of 25 °C and mixing speed of 400 rpm was carried out and further analyzed using pseudo-second-order kinetic model with its linear form as studied previously [22,26],

$$t/q_t = 1/(kq_e^2) + (1/q_e)t, \tag{2}$$

where k is the pseudo-second-order rate constant (g mg^{-1} min^{-1}), q_e is the amount of methylene blue adsorbed at equilibrium (mg g^{-1}), and q_t is the amount of methylene blue adsorbed at time t (mg g^{-1}). Rate parameters k and q_e, can be directly obtained from the intercept and slope of the plot of (t/q_t) against t. Values of k and q, computed from Eq. (2), are listed in Table 3. As a preliminary evaluation, the starting precursor DE was used as another adsorbent for the adsorption of methylene blue with the initial concentration 10.1 mg l^{-1}. From the data in Table 3, it is clear that the kinetics of methylene blue adsorption on the HF-modified adsorbent follows this model with the regression coefficients of higher than 0.99 in this study. Also, it is consistent with the results based on the data in Fig. 2; namely, the adsorbent MDE-2.5 N has a capacity for the adsorption of methylene blue higher than that of the adsorbent DE because of the larger BET surface area in the former.

Based on the trend in adsorption capacity (i.e., q_e) vs equilibrium concentration (i.e., C_e) in Table 3, the Freundlich model was used to describe the adsorption isotherm because of its su-

Table 3
Kinetic parameters for methylene blue adsorption onto DE and MDE-2.5 N[a]

Adsorbent	C_0 (mg dm^{-3})	k (g mg^{-1} min^{-1})	q_e (mg g^{-1})	Correlation coefficient	C_e (mg dm^{-3})
DE	10.1	0.606	2.68	0.999	9.3
MDE-2.5 N[b]	6.1	0.227	2.36	0.999	5.5
	8.0	0.165	2.64	0.999	7.4
	9.7	0.206	2.85	0.998	9.0
	11.9	0.099	4.27	0.997	10.8

[a] Adsorption conditions: adsorbent dosage 0.5 g/2.0 dm^{-3}, agitation speed 400 rpm, pH 7, and temperature 25 °C.

[b] MDE-2.5 N: produced from HF concentration 2.5 N, temperature 60 °C, solid/liquid ratio 5 g/100 g, and time 30 min.

Table 4
Parameters in the Freundlich isotherm model of MDE-2.5 N at 25 °C

K_F (mg g^{-1} (dm^3 mg^{-1})$^{1/n}$)	$1/n$ (–)	R^2
0.32	1.063	0.927

periority to the Langmuir model from the fitting results:

$$q_e = K_F C_e^{1/n}. \tag{3}$$

Table 4 presents the results of the Freundlich isotherm values using the adsorption capacity data (Table 3) at 25 °C. Obviously, it can be seen that the uptake amount of the modified clay adsorbent is significantly lower than those of the NaOH-activated adsorbents as reported previously at the same C_e [22, 26]. As also illustrated in Table 4, the value of $1/n$ is close to 1.0, which indicated a linear adsorption isotherm.

4. Conclusions

In conclusion, the etching treatment of diatomaceous earth changes the surface properties by using HF solution. It was found that the HF concentration is a determining factor in creating more open pores, thus resulting in larger surface area as compared to other parameters such as temperature, holding time, and solid/liquid ratio. The BET surface area of the optimal resulting solids thus obtained in the study is about 10.0 m^2 g^{-1}, which is significantly larger than that (i.e., 3.8 m^2 g^{-1}) of the starting material. This observation was also in close agreement with the results on the elemental analysis, SEM, XRD, and FTIR. In contrast, the optimal product thus prepared was used as a mineral adsorbent for adsorption of methylene blue (basic dye 9) at 25 °C. The adsorption kinetics and isotherm of methylene blue under various initial dye concentrations can be well described with the pseudo-second-order reaction model and the Freundlich model, respectively.

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