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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.

Keywords: Diatomaceous earth; Chemical modification; Hydrofluoric acid; Characterization; Adsorption

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.