行政院國家科學委員會補助專題研究計畫 ■ 成 果 報 告
□期中進度報告

廢矽藻土資源再生為多孔性材料及其應用於環境荷爾蒙之處理(I)

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中　華　民　國　93　年　10 月　1 日

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嘉南藥理科技大學環境工程與科學系

一、中文摘要

本研究之目的乃利用一套仿旋轉窯爐之水平式旋轉反應爐於不同條件下進行熱再生；並進一步利用硫酸、硝酸、鹽酸、氫氧化鈉等試劑配合不同活化參數(濃度、時間、溫度)進行化學活化。研究結果顯示熱活化對提升廢矽藻土物性效果並不明顯，而化學活化之最佳條件為活化濃度 2.25 M NaOH、活化時間 2 hr、活化溫度為沸騰狀態、樣品重/活化液比為 5/100 的條件下，比表面積由 0.3 m^2/g 提升至約 100 m^2/g，孔洞體積也由 0.0039 cm^3/g 提升至 0.258 cm^3/g。

對活化後之產物做其物理/化學特性分析，包括表面積/孔洞體積、掃描式電子顯微鏡(SEM)、X 光繞射(XRD)、傅利葉紅外線光譜(FTIR)及主要元素，顯示所得之產物從 N_2 之等溫吸脫附分析大致為中孔性結構(Type IV)。進一步以活化後最佳物性產物對環境污染有機物巴拉刈進行吸附實驗，從 Langmuir 及 Freundlich 等溫吸附迴歸，發現此產物為具可觀吸附能力之礦物吸附劑。

關鍵字：矽藻土；化學活化；熱裂解；微孔性

Abstract

The objective of this work is to study thermal regeneration by using horizontally rotary activation furnace under different parameters. Further, chemical activation has been carried out by using acid /alkaline agents such as sulfuric acid, acetic acid, hydrochloric acid and sodium hydroxide, and different activation parameter such as concentration, time and temperature. Under the experimental conditions investigated, the thermal regeneration process is not good for upgrading the physical properties of spent diatomaceous earth, The impregnation conditions at concentration of NaOH 2.25 M, impregnation temperature of boiling, holding time of 2 hr and sample/solution ratio of 5/100 seemed to have the most determining effects on the development of pores. The chemically activated clay have larger surface areas (≈109 vs 0.3 m^2/g) and total pore volumes (≈0.26 vs 0.004 cm^3/g) than those of the spent diatomaceous earth.

The physical and chemical characterization of the resulting products obtained in this study were further examined based on the analyses of surface area/pore volume, scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and main elements. Results showed that these samples are characteristic of type IV from N_2 isotherm, indicating mesoporous structure. Further, the optimal porous material thus obtained was used as mineral adsorbent for paraquat adsorption, showing that it has a good adsorption capacities for removal of this organic contaminant from the fittings of Langmuir and Freundlich isotherms.

Key Words：Spent diatomaceous earth；chemical activation；pyrolysis；porosity

二、緣由與目的

Diatomaceous earth (DE) or diatomite typically consists of 86-94% silicon dioxide (SiO_2), with significant quantity of alumina.[1] Due to its specific properties (i.e., high silica content, high porosity, low density, low conductivity coefficient, *etc*.), DE has been applied as filter aid, adsorbent, filler, packing material for gas chromatography (GC) or high-performance liquid chromatography (HPLC), insulator, catalyst (support), drilling-mud thickener, extender in paints, anticaking agent, natural insecticide, or grain protectant.[2-5] Spent diatomaceous earth (SDE), mainly generated from the food processing and distillery/brewery industries, is an industrial waste. In the past decades, the agro-industrial waste was commonly discarded in the field, or simply disposed of landfill without any pretreatment.[6] Taking into account the sustainable utilization of mineral resource, SDE after activation regeneration as an adsorbent is very scarce in the literature. This study was stimulated by the etching reaction between silica (i.e., SiO_2) and strong base (e.g., NaOH).[7, 8] The main objectives of this work were to study the feasibility of utilizing SDE as precursors in the production of mesoporous silica adsorbent and further evaluate its adsorption properties for the removal of basic dye (i.e., methylene blue) from aqueous solution at 25 ℃..

三、實驗方法與步驟

3.1. Materials

The DE and its waste (i.e., SDE) were obtained from Shan-Hua Factory of Taiwan Tobacco & Liquor Co. (Tainan, Taiwan). The former was a calcined product (Grade No.: 577; Celite Co., USA) with a median pore size of 14.0 μm examined by using LS-230 laser diffraction particle size analyzer (Beckman Coulter, Inc., USA). The chemical compositions from the manufacturer's brochure mainly consist of 91.5% of SiO_2, 4.0% of Al_2O_3 and 1.1 % of Fe_2O_3.. The latter was first dried in the oven for 48 h, and then cooled to room temperature for further characterization and treatment. The carbon/hydrogen/nitrogen (C/H/N) contents of the dried waste sample were analyzed by using an elemental analyzer (model CHN-O-RAPID, Heraeus Co., Germany), showing 0.82% w/w C, 0.29% w/w H and 0.48% w/w N, that were obviously lower than those (i.e., 25.8% w/w C and 2.2% w/w H) reported by Leboda *et al.*.[7] Sodium hydroxide (NaOH), which was purchased from Merck Co. (U.S.A.) with A.C.S. reagent grade, was selected as chemical activator in this study to modify the SDE for the purposes of removing residues left in that and chemically create 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 Sigma Chemical Co. (U.S.A.).

3.2. Chemical modification

Prior to the chemical modification with NaOH, the SDE was preliminarily tested with thermal treatment and common strong acids (incl., sulfuric acid, phosphoric acid, hydrochloric acid, nitric acid and acetic acid) to evaluate the usefulness in increase of pore property (i.e., specific surface area and/or pore volume) because the clay minerals were traditionally achieved by acid activation method that the acid penetration proceeded into the interior of the lattice structure from the edges, leaving a framework possessing a large area.[9-14] However, it was found in the study that the acid activation method had no profound influence on the pore structures compared to those of commercial DE, revealing that silicon dioxide in the frame structure of the SDE was quite unreactive during the thermal and acid treatment. [15,16]

Based on the etching reaction between silica (i.e., SiO_2) and strong base (i.e., NaOH), 5-25 grams of the dried SDE was mixed with 100 ml of the NaOH solutions with various NaOH concentrations. Under the holding times of 0.5 ~ 24.0 h and temperatures of 25 ~ 100 ℃ (boiling condition), the alkaline activation was carried out on a stirrer/hot plate with boiler-reflux condenser . Afterward, the sample solution was filtered in a vacuum filter flask and washed sequentially with deionized water for five times to remove the salt ions and other residues. The resulting solid was finally dried at 105 ℃ for 24 h, and stored in the desiccator after drying.

3.3. Characterizations

The pore structures of DE, SDE and NaOH-activated products relating to surface area and pore volume were obtained by measuring their nitrogen adsorption-desorption isotherms at −196 ℃ in an ASAP 2010 apparatus (Micromeritics Co., U.S.A.).[17] From the data of total pore volume (V_t) and true (helium) density (ρ_s), the particle density (ρ_p) and porosity (ε_p) can be further obtained.[29, 30] The X-ray diffraction (XRD) was employed to observe the changes in crystallinity between the samples by using a Siemens D500 instrument (Cu-Kα radiation). The surface pictures of the samples were made using the scanning electron microscopy (SEM) by a JEOL JXA-840 (JEOL Co., Japan) apparatus. The Zeta potentials of the samples were determined by a Zeta Meter System 3.0 (ZETA -METER Inc., USA) to obtain the charges at the surface of the mineral particles. Each data point was an average of at least five measurements. The Fourier transform infrared spectroscopy (FTIR) analysis has been used for the examination of functional groups on the surface of the samples. The spectrum was measured and recorded (500 ~ 2500 cm^{-1}) on a spectrometer (model DA 8.3, Bomen Co., Canada).

3.4. Adsorption tests

Adsorption behaviors of the samples (incl., DE and optimal activated solid) were tentatively determined to evaluate their potentials for removal of methylene blue from aqueous solution at 25.0 ℃. All the experiments of adsorption dynamics were carried out in a *ca.* 3-L stirred batch adsorber with four baffles as similarly described in our previous studies.[18, 19]

四、結果與討論

4.1. Physical and Chemical Characterizations

The data in Table 1 indicate the BET and Langmuir surface areas, total pore volume, densities and porosity of the starting materials DE and SDE, revealing that these adsorbents possess poor pore properties towards probe molecule (i.e., nitrogen). Based on the Brunauer, Deming, Deming and Teller (BDDT) classification,[17] the adsorption isotherm belongs to a typical Type II, which is most frequently encountered when adsorption occurs on nonporous materials or on materials with macropores or open voids.

It follows from the analysis (seen in Figure 1) of the BET surface area of the resulting solids prepared under the fixed holding time of 2 h and solid/liquid ratio of 5 g/100 m. In the NaOH-activated clay series, the rate of increase in pore property at NaOH concentration of 2.24 M is evidently faster than that at NaOH concentration of 1.12 M. Also, the increase in temperature from 60 ℃ to 100 ℃ tends towards pore development in the clay structure, resulting in a increase in the surface area. On the other hand, the effect of activation time under the activation temperature of 80 ℃ and solid/liquid ratio of 5 g/100 mL on the pore properties of the resulting solids is shown in Figure 2. It seems that the activation time plays a less important role in the production of the porous materials. It is seen that, by increasing activation time from 10 to 24 h at the NaOH concentration of 2.24 M, the BET surface areas of the resulting solids are only increased from 75 m^2/g to 108 m^2/g as a result of the development of porosity. The pore properties were observed to increase gradually at a longer activation time, which should be due to the etching reaction in progress.

According to the data obtained from the preliminary experiments described above, the activation condition at the impregnation temperature of 100 ℃ (boiling) seems to have the most efficient effect on the development of pores. Table 2 lists the pore properties of the resulting products chemically activated from SDE at the activation time of 2 h and solid/liquid ratio of 5 g/100 mL under various NaOH concentrations. In the moderate NaOH concentration range studied (i.e., 0.56-3.36 M), the pore properties (e.g. BET surface area) of the resulting solids basically increase with increasing NaOH concentration; i.e. ASDE-C1 (5.4 m^2/g) ＜ ASDE-C2 (18.3 m^2/g) ＜ ASDE-C3 (98.1 m^2/g). However, the values were observed to decrease gradually at the NaOH concentration of 3.36 M, which was possibly attributed to the rigorous reaction, resulting in that the mesoporous pores produced are blocked by retained mineral and/or NaOH salt residues. In contrast to the data in Figure 2, it is noticeable that the pore property of the sample ASDE-C3 is close to that of the sample (denoted as ASDE-T80) produced at the NaOH concentration of 2.24 M, activation temperature of 80 ℃ and holding time of 24 h, revealing that utilizing boiling condition is an effective approach to decrease in the activation time in the production of mesoporous materials in the study. The nitrogen adsorption/desorption isotherm of the sample ASDE-C3 is shown in Figure 3. Compared with the above-described sample DE, a small hysteresis loop can be seen and closely connected with the interpretation of the Type IV isotherm according to the BDDT classification. It is well known that the Type IV isotherms are characteristics of the mesoporous materials due to the nitrogen condensation.[17] The pore structures can be further deduced from certain shapes of the hysteresis loops. Clearly, the hysteresis loop of the sample ASDE-C3 is corresponding to Type H3 based on the recommendation of the International Union of Pure and Applied Chemistry (IUPAC),[17] which is associated with adsorbents having slit-shaped pores with wide mouth.

The data in Table 3 list the pore properties of the ASDE-series samples chemically activated from SDE at the NaOH concentration of 2.24 M. Generally, the pore properties of the resulting solids were observed to increase at higher activation time. However, it should be noted that the activation time of about 2 h was found to be optimal for higher pore properties presented in the study. As mentioned in the experimental section, after the chemical activation the crude products were subjected to washing with deionized water for five times. It is known that washing with water removes the residues left in the resulting solids.[20] Thus, the final products obtained by washing will yield well-developed porosity in the clay structure. This point had been confirmed in our previous study,[21] which corn-cob was used as a precursor to prepare activated carbon employing the combined activation. The test was performed on the samples ASDE-t3 and ASDE-t3N. The results of pore properties before and after washing of samples are also presented in Table 3. The results clearly show that about 90 % of porosity (reflected by the BET surface area) created in the clay sample was occupied by salts and/or residues in the structure. Small surface area of the unwashed clay sample is because of salts and/or residues left in the products, blocking pore entrances to the nitrogen molecules based on the analysis of adsorption and desorption isotherms of nitrogen for determining BET surface area. The foregoing results may be further observed in the pore size distribution curves based on pore volumes of the Barrett-Joyner-Halenda (BJH) desorption branch in the measurement of N_2 isotherms,[17] as shown in Figure 4. It is seen that the pores of these clay samples (incl., ASDE-t1, ASDE-t2, ASDE-t3 and ASDE-t4), in particular ASDE-t3, have a heterogeneous distribution of pore diameters with major pore ranges below about 15 nm, which may be useful for their possible applications in adsorption from liquid phase.

In order to study the substantial influence of solid/liquid ratio on the porosity development, the chemical activations of SDE impregnated with 2.24 M NaOH solution were carried out at a temperature of 100 ℃ (boiling) and activation time of 2 h under various dosages of SDE. As shown in Figure 5, the BET surface areas of the resulting solids tend towards gradual decrease with increasing dosage ranging from 5 to 25 g/100 mL. The decrease in pore property is clearly due to less etching rate of reaction at higher solid/liquid ratio.

Scanning electron micrographs of the surface structures of some typical samples (incl. DE, SDE, ASDE-T80 and ASDE-t3) are illustrated in Figure 6, showing a great difference between these samples. The porous structure examination of the precursors DE and SDE can be clearly seen in the SEM photographs (Figures 6a and 6b, respectively), revealing the variety of shapes and macropores/open voids that give the diatomaceous earths with high ability to trap solids or residues for separation from clear liquids.

The powder XRD patterns of some typical samples (incl. DE, SDE, ASDE-T80 and ASDE-t3) are shown in Figure 7. Although all the crystalline phases belonging to the main components (e.g. silica) are clearly visible, relative intensity can be served to elucidate the effects of the activation procedure employed on phase crystallinity. It was also found from Figure 8 that the XRD of the samples ASDE-T80 and ASDE-t3 exhibits some lines of reflections at 2θ of 25-30 degree, which are indicative of the probable presence of extraneous impurities such as calcite, quartz and feldspar.[22]

In the series activated with NaOH, the loss of crystallinity and the appearance of amorphous silica were also observed in the FTIR spectra of the samples DE, SDE, ASDE-T80 and ASDE-t3 displayed in Figure 8. Clearly, characteristic bands due to silicates structure are seen between 1400 and 400 cm^{-1}.. Some significant differences between the natural and activated solids can be observed, mainly those corresponding to Si-O bonds in the tetrahedral sheet. The wide bands centered at *ca.* 1090 cm^{-1} should be due to Si-O-Si in-plane vibration (asymmetric stretching).[23, 24]

It is well known that clays are effective natural adsorbents due to their lamellar structures and negatively charged surfaces, which make them good cation adsorbents by ion exchange. The surface charges (denoted as ξ–potential) of the diatomaceous earth may arise from their functional groups at the surface such as –OH.[18] Figure 9 shows the ξ–potential values of the samples SDE and ASDE-t3 as a function of pH. As analytical comparisons, the reference sample silicate was also carried out in this study. As shown in Figure 9, the surface charge decreases as the pH increases. It is noted that as the pH increased the surface hydroxides lose their protons in response to the increasing number of negatively charged sites. Thus, the surface of the activated clay at the experimental conditions (i.e., pH ＞3.0) will exhibit negative charges mainly due to the variable charge from pH dependent surface hydroxyl sites. From the data of zeta potential vs. pH, the isoelectric point or pH of point of zero charge (i.e., pH_{pzc}) of the clay-water system was thus determined to about 2.0, which is very close to the pH_{pzc} values of silicon dioxide at 2.0 and montmorillonite at 2.5.[25]

4.2. Adsorption properties

In the adsorption experiments, the resulting solid ASDE-t3 and the starting material DE were chosen as adsorbents. Table 5 presents the results of Langmuir and Freundlich isotherm fits by using the adsorption capacity data at 25 ℃.. Obviously, it can be seen that the Freundlich model yields a somewhat better fit than the Langmuir mode, as reflected with correlation coefficients (R^2). The adsorption isotherms revealed the activated clay adsorbent can quickly uptake 18.5 mg/g in relatively low concentration of the basic dye in aqueous medium. As also illustrated in Table 5, the value of 1/n is far below 1.0 that indicated a favorable adsorption isotherm. It was further found that the determined parameters of isotherm equations were highly consistent with the pore properties of these two adsorbents as listed in Tables 1 and 3. The maximum adsorption capacity of methylene blue, q_m, was much higher than that of other potential adsorbents such as fly ash and zeolite.[26]

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Table 1. Main physical properties of diatomaceous earth (DE) and spent diatomaceous earth (SDE).

Sample	S_{BET} [a] (m^2/g)	S_L [b] (m^2/g)	V_t [c] (cm^3/g)	ρ_s [d] (g/cm^3)	ρ_p [e] (g/cm^3)	ε_p [f] (-)
DE	3.99	5.54	0.0065	2.256	2.223	0.0146
SDE	0.38	0.56	0.0039	2.413	2.391	0.0091

[a] BET surface area.

[b] Langmuir surface area.

[c] Total pore volume

[d] True density.

[e] Particle density, calculated by: $\rho_p = 1/[V_t+(1/\rho_s)]$.

[f] Particle porosity, computed by: $\varepsilon_p = 1-(\rho_p/\rho_s)$.

Table 2. Main physical properties of the activated spent diatomaceous earths (ASDE series) produced with various NaOH concentrations. [a]

Sample ID	HaOH concentration	S_{BET} (m^2/g)	S_L (m^2/g)	V_t (cm^3/g)	ρ_s (g/cm^3)	ρ_p (g/cm^3)	ε_p (-)
ASDE-C1	0.56 M	5.4	8.9	0.018	2.540	2.429	0.044
ASDE-C2	1.12 M	18.3	31.1	0.060	2.545	2.208	0.132
ASDE-C3	2.24 M	98.1	165.8	0.258	2.731	1.602	0.413
ASDE-C4	3.36 M	72.6	147.4	0.229	2.954	1.762	0.404

[a] Prepared in the conditions of temperature of *ca* .100 ℃ (boiling), holding time of 2 h and solid/liquid ratio of 5 g/100 g.

Table 3. Main physical properties of the activated spent diatomaceous earths (ASDE series) produced with various activation temperatures. [a]

Sample ID	Activation time	S_{BET} (m^2/g)	S_L (m^2/g)	V_t (cm^3/g)	ρ_s (g/cm^3)	ρ_p (g/cm^3)	ε_p (-)
ASDE-t1	0.5 h	21.3	36.7	0.075	2.597	2.174	0.163
ASDE-t2	1.0 h	38.0	65.4	0.150	2.715	1.929	0.290
ASDE-t3 [b]	2.0 h	98.1	165.8	0.258	2.731	1.602	0.413
ASDE-t4	4.0 h	108.9	184.0	0.344	2.829	1.434	0.493
ASDE-t3N [c]	2.0 h	10.8	21.5	0.068	2.729	2.302	0.156

[a] Prepared in the conditions of temperature of *ca* .100 ℃ (boiling), holding time of 2 h and solid/liquid ratio of 5 g/100 g.

[b] The sample ASDE-C3 is identical to the sample ASDE-t3.

[c] Unwashed with deionized water for five times to remove the salt ions and other residues.

Table 4. Parameters in Langmuir and Freundlich isotherm models of methylene blue onto DE and ASDE-t3 at 25 ℃.

Adsorbent	Langmuir			Freundlich		
	q_m (mg/g)	K_L (L/mg)	R^2	K_F $[mg/g\ (L/mg)^{1/n}]$	1/n (-)	R^2
DE	2.24	2.1	0.5577	1.45	0.17	0.7042
ASDE-t3	18.48	270.5	0.9093	15.78	0.09	0.9666

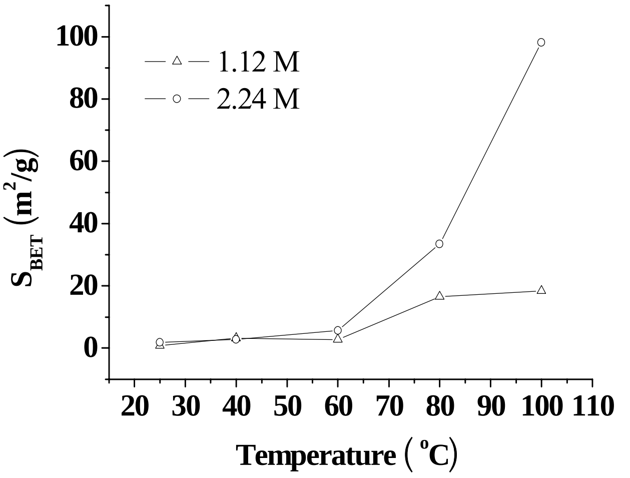

Figure 1. Effect of activation temperature on BET surface areas of the resulting solid prepared at the NaOH concentration of 2.24 M, fixed holding time of 2 h and solid/liquid ratio of 5 g/100 mL

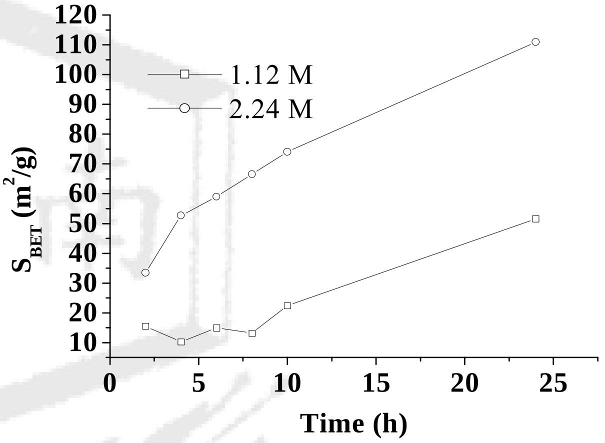

Figure 2. Effect of holding time on BET surface areas of the resulting solid prepared at the NaOH concentration of 2.24 M, activation temperature of 80 ℃ and solid/liquid ratio of 5 g/100 mL

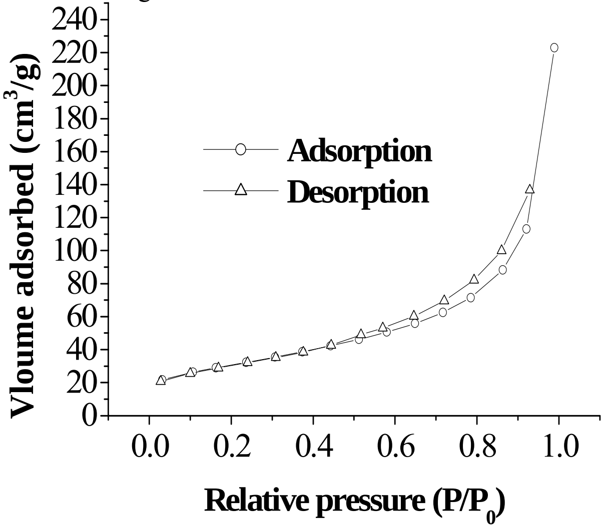

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Figure3. Nitrogen adsorption/desorption isotherms of the resulting solid (ASDE-t3)

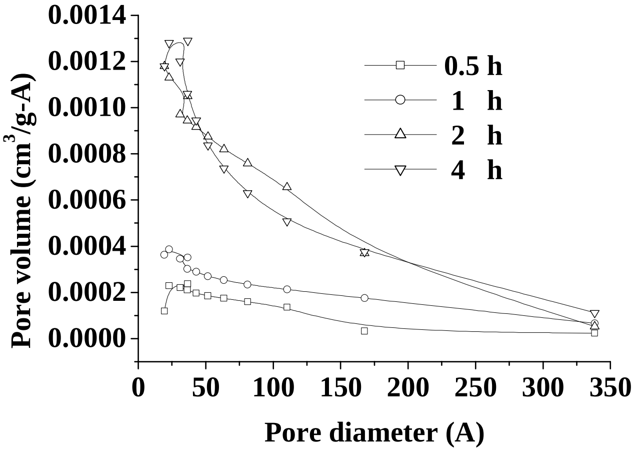

Figure 4. Pore size distributions of the resulting solids.

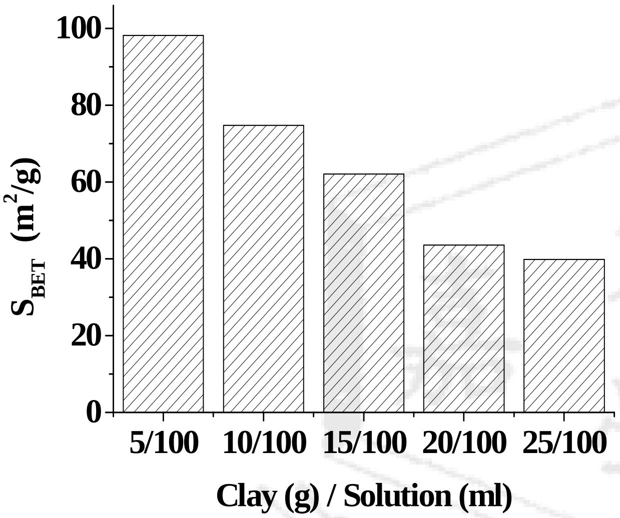

Figure 5. Effect of solid/liquid ratio on BET surface areas of the resulting solid prepared at the NaOH concentration of 2.24 M, activation temperature of 100 ℃ (boiling) and holding time of 2 h.

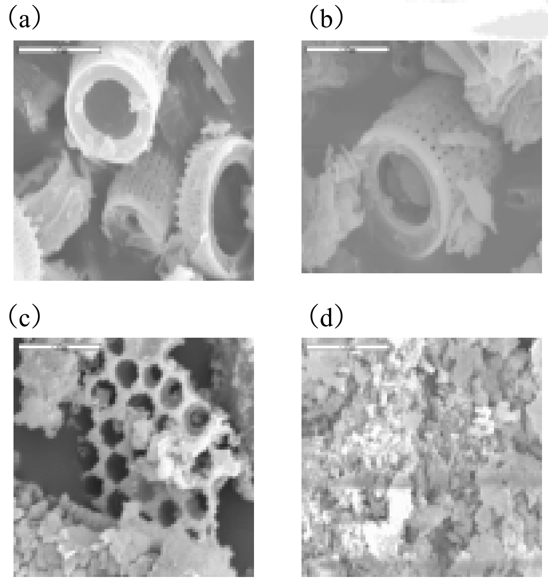

Figure 6. SEM photographs of the starting solids (DE and SDE) and the resulting activated solids (ASDE-T80 and ASDE-t3).

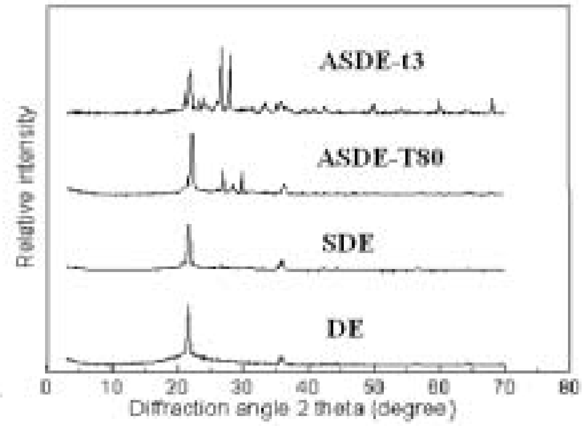

Figure 7. XRD diffractograms of the starting solids (DE and SDE) and the resulting activated solids (ASDE-T80 and ASDE-t3).

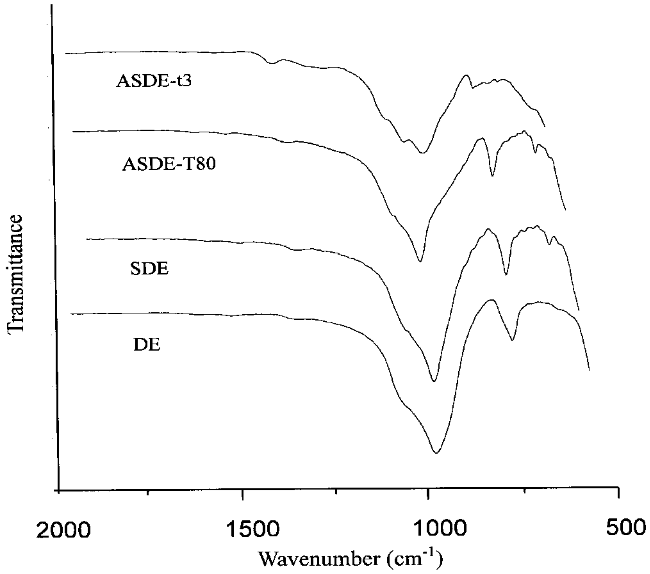

Figure 8. FTIR spectra of the starting solids (DE and SDE) and the resulting activated solids (ASDE-T80 and ASDE-t3).

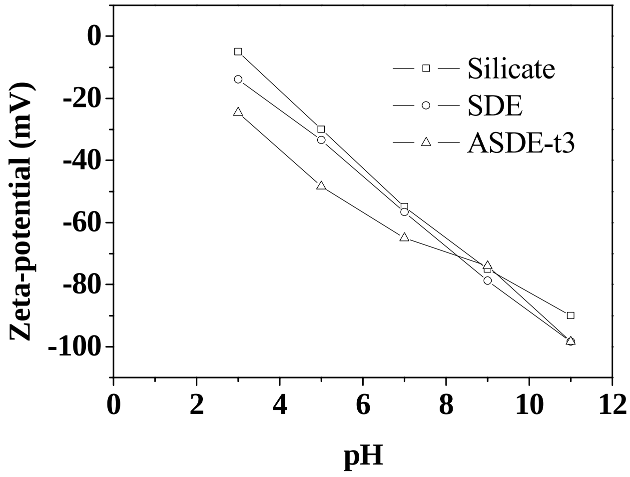

Figure 9. Plots of ξ–potential vs. pH of the starting solid (SDE) and the resulting activated solid (ASDE-t3).

可供推廣之研發成果資料表

□ 可申請專利　■ 可技術移轉　日期：93年10月1日

國科會補助計畫	計畫名稱：廢矽藻土資源再生為多孔性材料及其應用於環境荷爾蒙之處理(I) 計畫主持人：　蔡文田 計畫編號：NSC 92-2211-E-041-00　學門領域：環境工程
技術/創作名稱	中孔性材料製造
發明人/創作人	蔡文田、謝國鎔
技術說明	中文： 將廢矽藻土進行化學活化，可使其比表面積由 0.3 m^2/g 提升至 100 m^2/g 以上，孔洞體積也由 0.0039 cm^3/g 提升至 0.26 cm^3/g 以上。 英文： Using chemical activation, the chemically activated clays have larger surface areas (≈109 vs 0.3 m^2/g) and total pore volumes (≈0.26 vs 0.004 cm^3/g) than those of the spent diatomaceous earth.
可利用之產業及可開發之產品	製酒工業及油脂工業；吸附劑、隔熱材、觸媒載體等。
技術特點	利用廢矽藻土加以化學活化，可製造出高附加價值材料。
推廣及運用的價值	可作為廢水處理劑、公共建材、助濾劑等。

※　1.每項研發成果請填寫一式二份，一份隨成果報告送繳本會，一份送　貴單位研發成果推廣單位（如技術移轉中心）。

※　2.本項研發成果若尚未申請專利，請勿揭露可申請專利之主要內容。