行政院國家科學委員會補助專題研究計畫成果報告

廢活性白土資源再生為黏土-碳吸附劑及其應用於農藥和染料之吸(I)

計畫類別：■個別型計畫　□整合型計畫
計畫編號：NSC 89－2211－E－041－024
執行期間：89 年 08 月 01 日至 90 年 07 月 31 日

計畫主持人：蔡文田
共同主持人：

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執行單位：嘉南藥理科技大學環境工程衛生系

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主持人：蔡文田 嘉南藥理科技大學環境工程衛生系
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一、中文摘要

廢白土為食用油脂工業的最主要固體廢棄物，本研究乃利用一套水平式旋轉反應爐物理活化及化學活化再生此資源性物質。依據孔洞結構分析結果，裂解活化溫度及其停留時間為此再生程序重要操作參數；此外，以不同酸洗及超音波洗淨也是影響因子。由再生產物孔洞結構，顯示部分中孔尚被殘留碳渣封積堵塞。同時由諸多化學性質分析得知，本研究所再生的廢白土與活性白土極為相近，顯示其化學性質並未於再生過程中受到可觀察上的改變。

關鍵詞：廢白土、再生、物理活化、超音波洗淨、特性量測、清淨技術

Abstract

Physical activation and chemical activation in a rotary furnace regenerated a spent bleaching earth (SBE) from an edible oil refinery. Results show that temperature and its holding time are important parameters based on mesoporous structure measurements. In addition, acid-washing and ultrasonic cleaning also play influencing factors on the pore development of crude products. Ultrasonic cleaning as a clean technology was confirmed to be similar to acid-washing with the comparison of physical properties, but the true densities and porosities of the former have larger values than those the later. However, it indicated some mesopores are still closed and/or clogged by carbon residues from the pore properties of regenerated solids. Further, the regeneration methods studied in the present work have negligible effects on the chemical change compared to fresh bleaching earth from the results of XRD, ICP-AES, FTIR and EDX.

Keywords: Spent bleaching earth, Regeneration, Chemical activation, Physical activation, Characterization measurements, Clean technology

二、緣由與目的

在植物油煉製程序中，為了改善油質及油色，需經使用活性白土（Activated bleaching earth，ABE）進行脫色處理，以脫除殘留物及色素物，因而產生所謂的廢白土（Spent bleaching earth，SBE）廢棄物；在 SBE 之特定上因尚留有高達 20～40 wt% 的油份，有引起自燃、臭味等環境安全問題，致使此種事業廢棄物之處理刻不容緩。故行政院環保署特將 SBE 列為再利用之規定對象。根據國外文獻得知[1-10]，SBE 之再生方式可為熱、溶劑萃取、化學等。

本研究先前已嘗試一套自行設計組裝的水平旋轉式再生反應系統[11]，進行 SBE 熱再生及氯鹽化學活化處理之可行性研究，並已證實其可行性。本年度研究重點包括：

1. 以水蒸氣/CO_2 取代 $ZnCl_2$ 等氯鹽常用化學活化劑之可行性，探討物理活化後再生產物之物理性質、吸附性質及化學性質。
2. 評估超音波洗淨方法取代酸洗方法之效能，以避免廢酸液之排放；在此使用含浸 $ZnCl_2$ 所再生的粗產物為對象。

將上述 1.及 2.所再生製得的白土產物進

行特性量測，包括孔洞結構、密度、XRD、元素組成分析、FTIR 分析、SEM-EDX 等。

三、實驗方法與步驟

本研究所使用的實驗裝置系統如圖 1 所示，大致上包括氣體（steam, CO_2, N_2）供應及裂解活化反應兩部分；廢白土取自台灣糖業公司小港副產品加工廠。整個實驗的主要操作參數如表 1 及表 2 所示。

四、結果與討論

1.物理活化

表 3a、4a 及 5a 分別表示為物理活化所再生製得白土之主要物性值、C/H/N 元素值及微量金屬元素值。依這些量測可得到以下論點：

(1)裂解溫度確會影響再生產物特性，但溫度越高，其效應則漸減小。

(2)停留時間在 0 ~ 4 h 間對再生產物之特性影響，以 1 h 之效應最佳，其後則漸減小。

(3)比較兩種物理活化氣體之酸洗產物之效應，蒸氣氣體大致上稍優於 CO_2 氣體。

(4)由 N_2 吸附/脫附等溫曲線得知，依 BDDT 分類為 type IV[12, 13]，表示為一種中孔性物質；同時活性白土之吸附明顯地比再生的產物為高，即表面積及孔洞體積回復率僅達 1/3 ~ 1/2，雖然孔洞結構並未被改變，但表示有部分中孔性孔洞未完全回復，導因於尚有殘留碳渣留於孔洞內部，或堵塞孔洞。此外，由 hysteresis loop 形狀得知，依 IUPAC 分類為 type H3，表示此中孔性物質孔形為 slit-shaped pores，此亦為黏土結構特徵[14]。

2. 超音波洗淨

表 3b、4b 及 5b 分別表示為物理活化所再生製得白土之主要物性值、C/H/N 元素值及微量金屬元素值。依據這些量測可得到以下論點：在 570 ℃及 1 h 停留時間下，含浸 $ZnCl_2$ 化學活化劑，以及使用不同酸洗液和超音波淨洗方法下所製得之再生產物之特性與上述物理活化所得論點頗多相似，主要之相異點如下：

(1)就酸洗而言，結果顯示以 3 N H_2SO_4 酸洗效果較佳，此點有別於傳統上常使用的 3 N HCl 酸洗，但後者於成本及環境衝擊效應較低。

(2)就比較超音波及酸洗方法而言，前者效應稍低於後者，平均 BET 表面積約少 8 %；但就真密度及孔隙度而言，超音波洗淨者明顯高於酸洗者，此可能導因於超音波促使部份粒內孔洞及狹縫崩露，而導致其更緊密的結構及新孔洞生成

五、計畫成果自評

由本計畫成果報告中之圖表得知，與原計畫目標達成率大致吻合，目前已將這些實驗結果據以整理成二篇論文，分別投稿於 Resource Conservation & Recycling 及 Journal of Environmental Science and Health (part B)。

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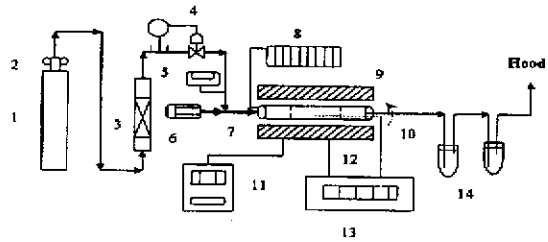

Fig. 1. Schematic diagram of regeneration apparatus: 1. N_2/CO_2 gas cylinder, 2. Regulator, 2. Molecular sieve column, 4. Mass flow controller, 5. Humidity monitor, 6. Syringe pump, 7.Heating belt, 8. Gear pump, 9. Heating furnace, 10. Reactor, 11. Temperature controller, 12. Thermocouples, 13. Temperature recorder, 14. Tar collector.

Table 1. Samples (RBE series) identification and their physical activation conditions [a]

Sample ID	Activating gas	Activation temperature (℃)	Holding time (hr)
RBE-1	CO_2[a]	800	1
RBE-2	CO_2[a]	800	2
RBE-3	CO_2[a]	800	3
RBE-4	CO_2[a]	800	4
RBE-5	H_2O[b]	700	1
RBE-6	H_2O[b]	800	1
RBE-7	H_2O[b]	900	1
RBE-8	H_2O[b]	800	2
RBE-9	H_2O[b]	800	3
RBE-10	H_2O[b]	800	4

[a] Prepared in the activation conditions of constant ramp rate of 10 ℃/min under N_2 flow of 300 cm^3/min and CO_2 flow of 300 cm^3/min at activation temperature.

[b] Prepared in the activation conditions of constant ramp rate of 10 ℃/min and water injection flow of about 0.05 cm^3/min at activation temperature under N_2 flow of 300 cm^3/min

Table 2 Samples identification and their washing conditions in the present study [a]

Sample ID	Washing conditions
RBE-AC1	distilled water [b]
RBE-AC2	0.3 N HCl [b]
RBE-AC3	1.0 N HCl [b]
RBE-AC4	3.0 N HCl [b]
RBE-AC5	3.0 N H_2SO_4[b]
RBE-AC6	3.0 N HNO_3[b]
RBE-AC7	3.0 N H_3PO_4[b]
RBE-US1	0.5 hr ultrasonic cleaning, 60 ℃ distilled water [c]
RBE-US2	1.0 hr ultrasonic cleaning, 60 ℃ distilled water [c]
RBE-US3	2.0 hr ultrasonic cleaning, 60 ℃ distilled water [c]
RBE-US4	1.0 hr ultrasonic cleaning, 30 ℃ distilled water [c]

[a] Thermochemical (impregnated by $ZnCl_2$) regeneration in the conditions with N_2 flow of 250 cm^3/min, the constant ramp rate of 10 ℃/min, temperature of 570 ℃, holding time of 1 hr.

[b] Crude products after thermochemical regeneration were stirred and heated at 60 ℃ with 250 cm^3 of various concentrations of acid solutions for 30 min.

[c] Crude products after thermochemical regeneration were stirred at 250 cm^3 of 30 or 60 ℃ distilled water with different times of ultrasonic cleaning (43 kHz) .

Table 3a. Main physical properties of regenerated solids (RBE series) from physical activation of bleaching earth waste.

Sample ID	S_{BET}[a] (m^2/g)	V_t[b] (cm^3/g)	D_{ave}[c] (nm)	ρ_s[d] (g/cm^3)	ρ_p[e] (g/cm^3)	ρ_p[f] (-)
RBE-1	83.2	0.169	8.11	1.885	1.430	0.241
RBE-2	101.5	0.204	8.04	1.825	1.330	0.271
RBE-3	89.1	0.186	8.36	1.961	1.437	0.267
RBE-4	86.0	0.184	8.52	1.750	1.324	0.243
RBE-5	117.0	0.221	7.55	1.968	1.368	0.305
RBE-6	106.4	0.208	7.83	2.002	1.413	0.294
RBE-7	97.6	0.191	7.84	2.024	1.460	0.279
RBE-8	104.5	0.200	7.66	1.925	1.390	0.278
RBE-9	92.8	0.195	8.39	1.819	1.343	0.262
RBE-10	70.1	0.171	9.76	1.987	1.083	0.254

[a] Denoted as BET surface area.

[b] Denoted as total pore volume.

[c] Denoted as pore diameter, which is estimated by 4 V_t/S_{BET}.

[d] Denoted as true density.

[e] Denoted as particle density, which is calculated below :
$\rho_p = 1/[V_t+(1/\rho_s)]$

[f] Denoted as particle porosity, which is computed below :
$\varepsilon_p = 1-(\rho_p/\rho_s)$

Table 3b. Main physical properties of samples (RBE series) with different washing methods

Sample ID	S_{BET}[a] (m^2/g)	V_t[b] (cm^3/g)	D_{ave}[c] (nm)	ρ_s[d] (g/cm^3)	ρ_p[e] (g/cm^3)	ε_p[f] (−)
RBE-AC1	68.60	0.147	85.83	1.624	1.311	0.193
RBE-AC2	78.70	0.159	80.98	1.484	1.200	0.191
RBE-AC3	81.83	0.161	78.83	1.555	1.243	0.201
RBE-AC4	78.41	0.157	80.15	2.132	1.597	0.251
RBE-AC5	91.74	0.172	75.06	1.526	1.209	0.208
RBE-AC6	75.59	0.1539	81.48	1.433	1.174	0.181
RBE-AC7	84.71	0.1691	79.82	1.543	1.224	0.207
RBE-US1	76.85	0.1685	87.68	2.179	1.594	0.269
RBE-US2	73.70	0.1507	81.80	2.275	1.694	0.255
RBE-US3	77.19	0.1527	79.12	2.278	1.690	0.258
RBE-US4	74.92	0.1528	81.59	2.336	1.721	0.263

[a] Denoted as BET surface area.
[b] Denoted as total pore volume.
[c] Denoted as pore diameter, which is estimated by $4\ V_t/S_{BET}$.
[d] Denoted as true density.
[e] Denoted as particle density, which is calculated from V_t and ρ_s, i.e., $\rho_p=1/[V_t+(1/\rho_s)]$.
[f] Denoted as particle porosity, which is computed from ρ_s and ρ_p, i.e., $\varepsilon_p=1-\rho_p/\rho_s$.

Table 4a. Carbon, hydrogen and nitrogen element analyses of samples (RBE series) from physical activation of bleaching earth waste

Sample ID	C (wt. %)	H (wt. %)	N (wt. %)
SBE [a]	26.22	4.26	0.37
RBE-1	12.94	0.97	0.14
RBE-2	13.54	0.87	0.17
RBE-3	14.18	0.88	0.05
RBE-4	14.28	0.90	0.10
RBE-6	12.96	0.92	0.11
RBE-8	12.92	0.91	0.07
RBE-9	13.78	0.73	0.22
RBE-10	15.45	1.11	0.24

[a] Reference [11].

Table 4b. Carbon, hydrogen and nitrogen element analyses of samples (RBE series) from thermochemical regeneration of bleaching earth waste.

Sample ID	C (wt. %)	H (wt %)	N (wt %)
SBE [a]	26.22	4.26	0.37
RBE-AC1	15.31	1.67	0.38
RBE-AC2	15.54	1.45	0.20
RBE-AC3	15.54	1.36	0.14
RBE-AC4	15.96	1.94	0.37
RBE-AC5	15.46	1.26	0.32
RBE-AC6	15.70	1.39	0.24
RBE-AC7	14.91	1.38	0.41

[a] Reference [11]

Table 5a. Metal composition analyses (unit: weight percent) of samples (RBE series) from physical activation of spent bleaching earth (SBE)

Sample ID	Si (%)	Al (%)	Fe (%)	Mg (%)	Na (%)	K (%)	Ca (%)	Ti (%)
SBE [a]	22.3	2.11	0.617	0.552	0.240	0.423	0.264	0.084
RBE-1	28.6	1.88	0.368	0.881	0.184	0.286	0.163	0.102
RBE-2	27.9	1.84	0.679	0.582	0.339	0.242	0.169	0.097
RBE-3	26.8	1.78	0.707	0.512	0.341	0.195	0.195	0.097
RBE-4	27.1	2.51	0.529	0.875	0.322	0.460	0.276	0.092
RBE-6	27.1	3.15	0.728	0.922	0.388	0.461	0.194	0.097
RBE-8	27.4	2.13	0.687	0.663	0.355	0.308	0.142	0.094
RBE-9	26.3	2.03	0.358	0.765	0.215	0.430	0.143	0.095
RBE-10	26.2	2.37	0.441	0.813	0.279	0.395	0.279	0.093

Reference [18]

Table 5b. Metal composition analyses (unit: weight percent) of samples (RBE series) from thermochemical regeneration of spent bleaching earth (SBE)

Sample ID	Si (%)	Al (%)	Fe (%)	Mg (%)	Na (%)	K (%)	Ca (%)	Ti (%)
RBE-AC1	26.3	2.52	0.462	0.810	0.254	0.555	0.370	0.092
RBE-AC2	26.3	2.41	0.483	0.772	0.289	0.483	0.096	0.096
RBE-AC3	25.0	2.67	0.575	0.725	0.275	0.375	0.100	0.100
RBE-AC4	23.4	1.96	0.344	0.668	0.258	0.452	0.086	0.086
RBE-AC5	22.8	2.31	0.589	0.589	0.306	0.330	0.117	0.094
RBE-AC7	28.6	2.16	0.279	0.744	0.093	0.372	0.209	0.093
RBE-AC7	23.5	1.78	0.379	0.580	0.245	0.357	0.066	0.089