

Innovative technology for controlling VOC emissions

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Abstract

This investigation will show that pyrolysed spent grain obtained from the brewery industry plant can be reclaimed as an adsorbent for removing volatile organic compounds (VOCs). The adsorption capacity of VOCs on the reclaimed adsorbent was approximately equivalent to that of coconut shell activated carbon. The properties of the prepared adsorbent were determined in terms of the Brunauer, Emmett and Teller (BET) surface area, CCl_4 activity and elemental analysis. Further studies using column adsorption tests indicated the column utilization ratio was approximately 86% when 930 ppm (by volume) of methylethyl ketone (MEK) in air was introduced to the column. During the desorption cycle, the percentage of solvent (MEK) recovery was observed to be 94% while a steam consumption rate was at 9 kg steam per 1 kg of recovered solvent and operated at 190°C with a flow rate of 120 ml/min.

1. Introduction

Control of volatile organic compounds (VOCs) emissions can reduce concentrations of ozone and hazardous or toxic chemicals in the atmosphere. Local peak exposures to VOCs may cause genotoxic effects, such as birth defects and miscarriages [1]. Emissions of VOCs occur during various processing steps, but primarily from organic chemical production, petroleum refining, natural gas/gasoline processing and polymer and resin production [2]. Current available control technologies for removal of VOC emissions include coating process modification, the use of low-solvent or solvent-free coatings and the use of control systems, such as carbon adsorption and incineration, either thermal or catalytic [3]. Among the use of control systems, the carbon adsorption process seems to be the most promising technique for removal and recovery of VOCs in low concentration, if high efficiency and low cost activated carbon is made available locally [4]. On the other hand, we hoped that the treated waste can be reclaimed as adsorbent providing low cost and high efficiency function

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to achieve VOC emissions control. This is the rationale for executing this investigation in which the spent grain from the brewery industry plant can be reclaimed as an adsorbent for controlling VOC emissions. The results of the adsorption capacity of VOCs for the reclaimed adsorbent are compared with the findings obtained from commercially activated carbon. In addition, both column adsorption and desorption tests are conducted in order to evaluate the cost effectiveness for removal of VOCs by the reclaimed adsorbent.

2. Materials and methods

2.1 Manufacturing of adsorbents

Spent grain was collected from the Chien-Kuo brewery industry plant in Taipei and put in an oven at 105°C for 24 h. 500 ml of 0.5–5 kmol/m³ ZnCl₂ solution was added to 200 g dry grain and the mixture was put in a water bath for 2 h. After removing the supernatant liquid, the bottom grain was put in an oven for 1 day. 40 g of the above-treated grain were weighed out and put into a quartz tube ($D=50$ mm, $L=1000$ mm) located in the furnace ($D=30$ cm, $L=66$ cm) for carrying out the pyrolysis process. Pyrolysis was conducted in a fixed bed using nitrogen to carry away expelled gases. The temperature was controlled at 500 and 600°C for 1 h. The 10–25 mesh fraction of the reclaimed grain was washed with 3 kmol/m³ HCl, rinsed with deionized water and dried at 105°C for 24 h. The properties of the manufactured adsorbent were characterized by the Brunauer, Emmett and Teller (BET) surface area method (Quantasorb Model-OS-B), carbon tetrachloride activity (ANSI/ASTM D3467-76') and elemental analysis tests.

2.2 Column adsorption/desorption tests

Six typical organic solvents (benzene, toluene, xylene, methylethyl ketone, trichloroethylene and n-hexane) were used to perform the adsorption isotherm tests. The desired organic vapour concentration in the air flowing through the carbon sample was controlled by a regulating valve. The adsorption capacities at equilibrium were measured by a gravimetric method with an adequate apparatus (ANSI/ASTM D 3467-76'). Column breakthrough was evaluated by introducing feed containing 930 ppm (by volume) of MEK at a flow rate of 20 l/min to the column bed ($D=5$ cm, $L=50$ cm) containing 50 g activated carbon (or reclaimed adsorbent) and then continuously recording the effluent concentration of MEK at the exit of the column using the Organic Vapor Meter (AID 580 Model). The exhausted bed was regenerated (or desorbed) by feeding 190°C steam at a flow rate of 120 l/min. Both the breakthrough curves and desorption efficiencies associated with these two adsorbents, i.e. activated carbon and reclaimed adsorbent, were evaluated to determine the possibility of selecting the reclaimed adsorbent for VOCs emission control.

3. Results and discussion

In general, three parameters, i.e. pyrolysis yield, specific surface area and carbon tetrachloride activity, will provide very important information to evaluate both the quality and required quantity of the adsorbent. As cited in the literature [5], it was suggested that the operating condition should focus on adding 0–5 kmol/m³ ZnCl₂ to the treated grain and then heating the mixture at 500°C (or 600°C) for 1 h, to manufacture the adsorbent reclaimed from the spent grain.

In Table 1, it was observed that for all the parameters pyrolysis yields, specific surface area and carbon tetrachloride activity, were increased with increasing ZnCl₂ concentration up to 5 kmol/m³. Both the quality and quantity of the adsorbent reclaimed at a pyrolysis temperature of 500°C was slightly better than that of the adsorbent pyrolysed at 600°C. The more favorable temperature for manufacturing the reclaimed adsorbent was reconfirmed in this investigation by the experimental data observed in the following adsorption/desorption column tests. It is noted that the reclaimed adsorbent, treated with 5 kmol/m³ ZnCl₂ and heated at 500°C for 1 h possesses a higher specific surface area (1060 m²/g) and CCl₄ activity number (94.7), which are superior to the commercially available activated adsorbents.

Table 2 presents the results of analyses of the principal elements for the various adsorbents, in which carbon (60.04–67.35%) in the activated coconut and peat carbons was found to be higher than that (58.51%) in the reclaimed adsorbent (spent grain). In Table 2, it also observed that there was a signifi-

TABLE 1

Results of pyrolysis yield (specific surface area or carbon tetrachloride activity) of the reclaimed adsorbent at various ZnCl₂ concentrations and temperatures

ZnCl ₂ catalyst concentration (kmol/m ³)	Pyrolysis yield ^a (%)		Specific surface area (m ² /g)		Carbon tetrachloride ^b (%)	
	500°C	600°C	500°C	600°C	500°C	600°C
0	33.5	50.5	3	4	8.9	1.8
0.5	46.0	39.0	12	4	10.7	3.9
1.0	53.5	46.0	142	108	13.7	3.2
2.0	56.0	44.0	578	553	35.3	40.2
3.0	54.0	41.0	709	695	59.3	48.2
5.0	59.0	42.0	1060	1033	94.7	92.9

^aPyrolysis yield is defined as:
$$\frac{\text{the solid production weight of pyrolysis}}{\text{the raw material weight of pyrolysis}}$$

^bCarbon tetrachloride activity (Ref ANSI/ASTM D3467-76') is defined as:
$$\frac{\text{the adsorbed weight of carbon tetrachloride adsorbate}}{\text{the weight of adsorbent}}$$

TABLE 2

Results of the principle element concentration in the various adsorbents

Adsorbents	C	H	O	N	S	Al	Ca	Cr	Cu	Fe	Mg	Mn
	(Mass percent, %)											
	(µg/g)											
Activated carbon (peat)	60.04	<0.2	1.85	<0.3	0.85	++ ^b	+ ^a	-	+	++	+	+
Activated carbon (coconut)	67.35	0.37	3.18	0.36	<0.3	- ^c	442.6	47.2	21.1	406.6	212.1	16.
Spent grain	57.10	3.06	20.76	7.12	<0.3	121.6	1491	15.7	40.4	426.3	2414	563
Reclaimed adsorbent (I) ^d	71.99	1.52	4.33	6.90	<0.2	+	++	-	+	+	++	+
Reclaimed adsorbent (II) ^e	56.51	1.18	4.10	3.82	<0.1	118.4	436.1	143	100.6	215.6	573.2	12.

^a + Denotes "Trace"^b ++ Denotes "Low concentration"^c - Denotes "Data not available"^d Reclaimed adsorbent (I) is manufactured from the spent grain pyrolysed at 600°C.^e Reclaimed adsorbent (II) is manufactured from the spent grain by treating with 5 ZnCl₂ kmol/m³ and then pyrolysed at 600°C.

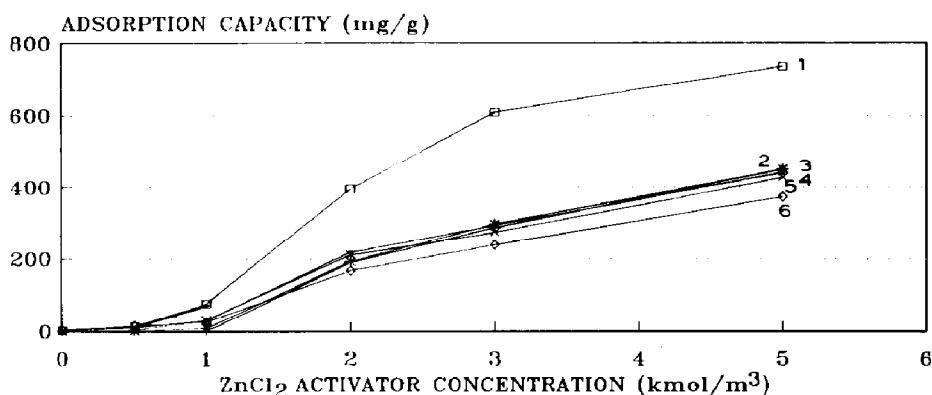


Fig. 1. Effects of activator concentration on the adsorption capacity of VOCs for the adsorbent reclaimed at 500°C pyrolysis temperature for 1 h. 1 - TCE (□), 2 - xylene (*), 3 - TOL (+), 4 - benzene (■), 5 - MEK (×), and 6 - n-hexane (◇).

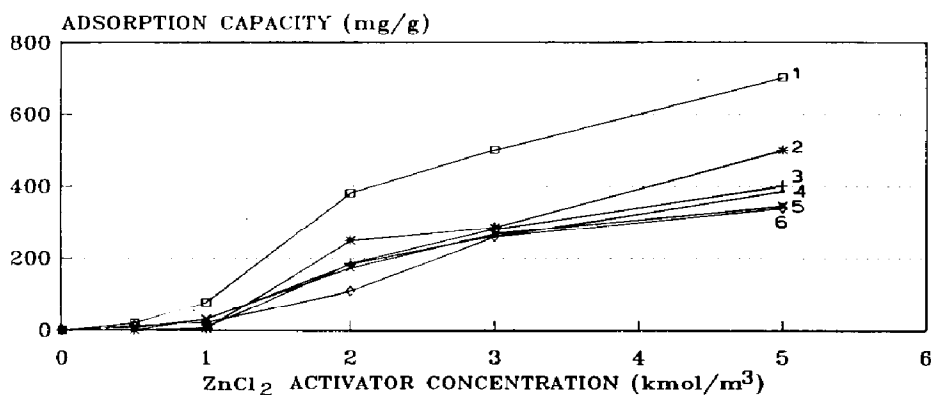


Fig. 2. Effects of activator concentration on the adsorption capacity of VOCs for the adsorbent reclaimed at 600°C pyrolysis temperature for 1 h. 1 - TCE (□), 2 - xylene (*), 3 - TOL (+), 4 - benzene (■), 5 - MEK (×), and 6 - n-hexane (◇).

cant difference in oxygen mass per cent between the raw grain (20.76%) and the reclaimed adsorbent (4.10%). However, the carbon percentage (57.10%) in the spent grain was slightly lower than that (58.5%) in the reclaimed adsorbent after treating with 5 kmol/m³ ZnCl₂ and heating at a pyrolysis temperature of 600°C. The results of the analyses of the inorganic elements, i.e. Al, Ca, Cr, Cu, Fe, Mg, Mn, Zn and Si also are shown in Table 2.

Figures 1 and 2 show the activator (ZnCl₂) concentration has a significant effect on the adsorption capacity of the reclaimed adsorbent for VOCs. However, the pyrolysis temperature (either 500 or 600°C) does not have an appreciable effect on the adsorption capacity of the reclaimed adsorbent. The same conclusion was also made by observation of Figs. 1 and 2, in which a higher adsorption capacity of VOCs was revealed at the 5 kmol/m³ ZnCl₂ level. According to all the findings shown in Table 1, Figs. 1 and 2, it was concluded

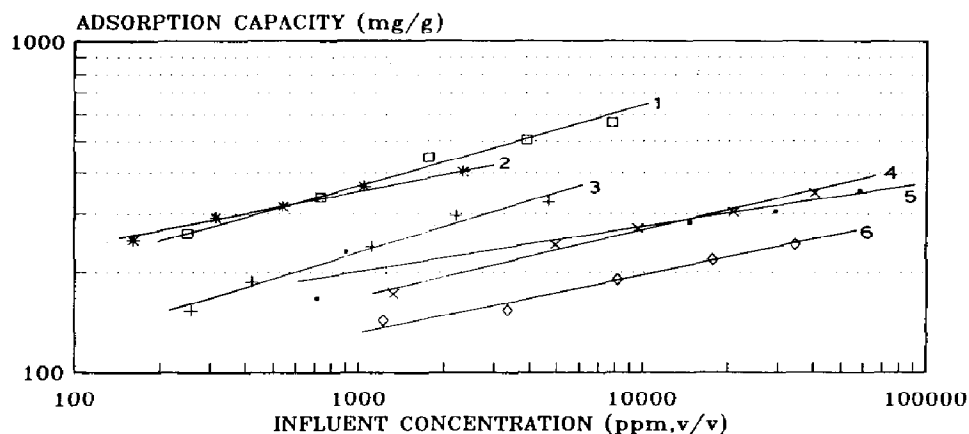


Fig. 3. Freundlich adsorption isotherms for VOCs at 25°C. Numbers as in Fig. 2.

that the optimum condition for manufacturing the reclaimed adsorbent was to add 5 kmol/m³ ZnCl₂ to the treated grain and then heat the mixture at 500°C for 1 h.

The results of adsorption isotherm tests for the reclaimed adsorbent are presented in Fig. 3, which indicates that the adsorption capacity of VOCs on the reclaimed adsorbent decreased in the sequence: TCE > xylene > TOL > benzene > MEK > n-hexane. Table 3 shows the adsorption capacity of the activated carbon (coconut) in the various influent concentrations of VOCs at 25°C. The adsorption capacity of the activated carbon depicted in Table 3 was considered as a reference standard to determine the relative magnitude of adsorption capacity of VOCs on various adsorbents. Table 4 compares the relative magnitude of adsorption capacity of VOCs between the activated carbon (coconut) and the reclaimed adsorbents. In Table 4, it was observed that the adsorption capacity of activated carbon (peat) for the VOCs was 1.02–1.23 times the adsorption capacity of the reclaimed adsorbent and was strongly dependent upon the chemical affinity between the VOCs and adsorbents. For instance, the adsorption capacity of the reclaimed adsorbent (spent grain) for xylene is 0.86–1.39 times that for activated carbon (coconut); while the adsorption capacity of the reclaimed adsorbent (aerobically digested sludge) for xylene is only 0.54–0.74 times that for the activated carbon.

Figure 4 shows the breakthrough curves associated with the reclaimed adsorbent and activated carbon (coconut) when 930 ppm (by volume) of MEK is introduced to the adsorption column. The dotted lines represent the breakthrough curves in which the adsorbent and activated carbon are regenerated by feeding 190°C steam with a flow rate at 120 ml/min. In Fig. 4, it was revealed that the regeneration efficiency of the reclaimed adsorbent is slightly higher than that of the activated carbon because of the relatively closer curves

TABLE 3

The adsorption capacity of the activated carbon (coconut) in the various influent concentrations of VOCs at 25°C

Benzene	Toluene		Xylene		Trichloroethylene		Methylethyl ketone		n-hexane	
	Influent concentration (ppm)	Adsorption capacity (mg/g)	Influent concentration (ppm)	Adsorption capacity (mg/g)	Influent concentration (ppm)	Adsorption capacity (mg/g)	Influent concentration (ppm)	Adsorption capacity (mg/g)	Influent concentration (ppm)	Adsorption capacity (mg/g)
715	209	258	161	289	250	412	229	214	1 229	191
907	224	421	314	299	733	427	261	229	3 352	198
14 671	279	1 120	541	300	1 764	466	283	253	8 190	205
29 436	302	2 207	1 044	306	3 909	503	307	272	17 662	214
58 360	310	4 673	2 318	315	7 835	529	335	273	34 675	222

TABLE 4

Comparison of the relative magnitude^a of adsorption capacity (g/g) of VOCs on various adsorbents

VOCS	Adsorbents				
	Activated carbon (coconut)	Activated carbon (peat)	Reclaimed adsorbent (spent grain)	Reclaimed adsorbent ^b (aerobically digested sludge)	Reclaimed adsorbent ^b (anaerobically digested sludge)
Benzene	1.00 ^c	1.02-1.20	0.80-1.14	0.38-0.85	0.09-0.73
Toluene	1.00 ^c	1.09-1.22	0.68-1.11	0.44-0.63	0.10-0.41
Xylene	1.00 ^c	-	0.86-1.39	0.54-0.74	0.32-0.61
Trichloroethylene	1.00 ^c	-	0.63-1.07	0.34-0.61	0.15-0.41
Methylethyl ketone	1.00 ^c	1.07-1.23	0.80-1.27	0.32-0.61	0.18-0.41
n-Hexane	1.00 ^c	1.06-1.20	0.74-1.09	0.21-0.66	0.08-0.47

^aThe adsorption capacity of the activated carbon depicted in Table 3 was considered as a reference standard to determine the relative magnitude of adsorption capacity of VOCs on various adsorbents.

^bData collected from the previous work done by author Chiang and You (1986) [5].

^cThe relative magnitude of adsorption capacity of VOCs is defined as the ratio between the adsorption capacity of adsorbent and the adsorption capacity of activated carbon (coconut).

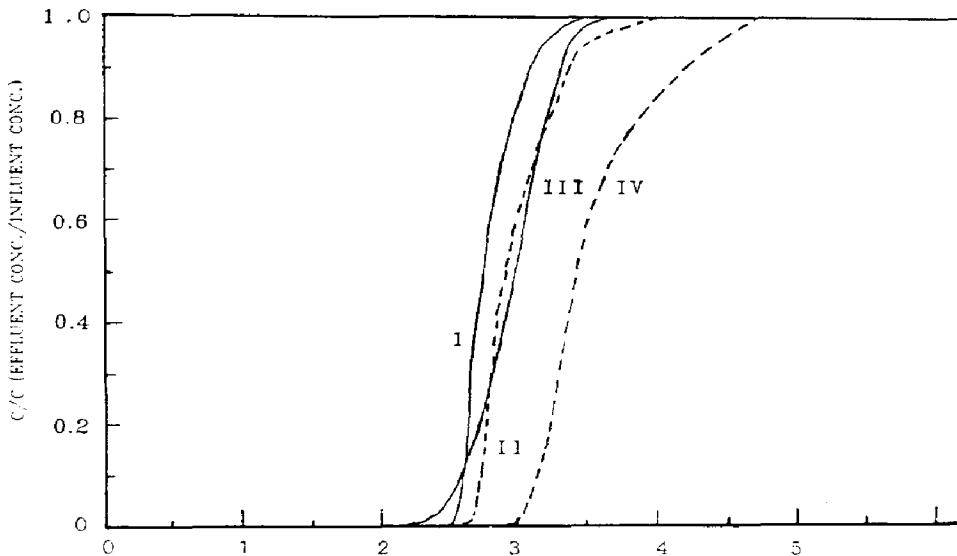


Fig. 4. Results for application 930 ppm (by volume) at 20 l/min flow rate of MEK to the virgin and regenerated adsorbents. I - Reclaimed adsorbent (virgin), II - reclaimed adsorbent (regenerated), III - activated carbon (virgin), and IV - activated carbon (regenerated).

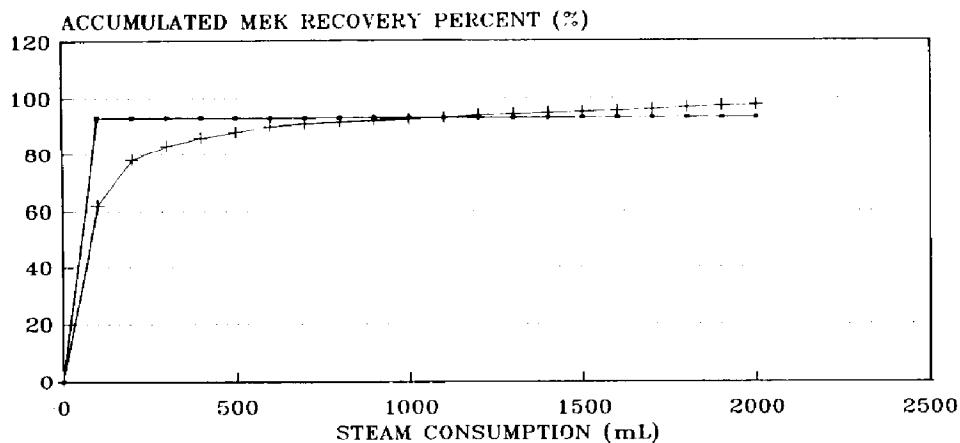


Fig. 5. Regeneration cycle with introducing 190°C steam at 120 l/min consumption rate to the adsorbent columns exhausted with MEK. (■) Reclaimed adsorbent (5 kmol/m³ at 500°C), and (+) activated carbon (coconut).

between the solid (curve I) and dotted lines (curve II) associated with the reclaimed adsorbent were observed.

During the regeneration cycle in Fig. 5, it is observed that as much as 95% of adsorbed MEK on the reclaimed adsorbent can be desorbed when 190°C steam is introduced with a flow rate at 120 ml/min. However, it is noted, that a high and rapid desorption efficiency of MEK on reclaimed adsorbent can be achieved while steam consumption rate is up to 120 ml, i.e. it only takes 1 min to desorb MEK obtaining a 90% efficiency. However, for desorption of activated carbon (coconut) exhausted with MEK, 1200 ml steam needs to be consumed to achieve the same desorption efficiency as with reclaimed adsorbent. Thus, from the view point of desorption efficiency, it was also suggested that the reclaimed adsorbent should serve as a potential adsorbent to remove VOC emissions.

4. Conclusions

Spent grain from the brewery industry plant can be reclaimed as an adsorbent for removing VOCs through use of a pyrolysis technique. The adsorption capacity of VOCs on the reclaimed adsorbent was approximately equivalent to that of coconut shell activated carbon. However, the regeneration efficiency of the reclaimed adsorbent is slightly higher than that of a activated carbon. In addition, since the raw material for manufacturing reclaimed adsorbent is spent grain from the brewery industry plant, it would provide extra economic benefit to allow this newly developed technique to become technically and economically feasible. It thus was concluded that low-cost control technology for VOC emission abatement could be developed through this investigation.

5. Acknowledgement

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