



Adsorbents made from waste ashes and post-consumer PET and their potential utilization in wastewater treatment

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Received 27 January 2003; received in revised form 27 May 2003; accepted 29 May 2003

Abstract

This study was carried out to prepare low-cost adsorbents from different types of waste ashes and post-consumer PET for use in industrial wastewater treatment. PET was melted and blended with ashes. The mixture was then carbonized to form different types of adsorbents. Heavy metal leaching from the adsorbents was greatly reduced compared to leaching from the bulk ashes. The BET surface area of the adsorbents ranged from 115 to 485 m²/g. The acidic sites on the adsorbents varied from 0.84 to 1.56 meq./g, higher than that of the PET carbon. The adsorption of methylene blue (MB) or heavy metals on the adsorbents was not in accordance with their surface areas because acidic sites reaction, affinity adsorption and cation exchange all contribute to the adsorption of the adsorbents. The isotherm for MB adsorption on the adsorbents can be well described by the Langmuir or Freundlich equation but heavy metal adsorption cannot. It is believed that the adsorbents produced in this manner can be used in wastewater treatments for discoloration and heavy metal removal.

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Keywords: Waste ashes; PET; Adsorption; Acidic sites; Heavy metals

1. Introduction

Approximately 1850 municipal solid waste (MSW) incinerators are currently operating in Japan, which represent about 80% of all the incinerators in the world. Japan has 7 times

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the number of incinerators in France which is in second place and 12 times those in US which is in third place. In recent years, diverting waste ash from incinerators away from landfills has become more urgent because of the limited availability of landfill space, rapidly increasing landfill cost, more stringent regulations, frequent public opposition to the siting of new landfills, and environment threats.

Previous studies have shown that waste ash has the potential for agricultural use [1–3]. It may also be used as an additive or starting material for land reclamation, highway construction, water purification, and the production of building materials, such as bricks, blocks, light aggregate and concrete [4,5]. Although the utilization of waste ash is important from an economic and environmental perspective, it is limited by heavy metals contained in the ash. Thus, how to utilize waste ash reasonably and safely without causing environmental problems is a major challenge.

In recent years, many waste materials, such as municipal solid waste, sewage sludge, etc. have been used in Japan to produce carbonaceous materials by some companies to recycle the waste materials and reduce the amount of waste ash. However, the carbonaceous materials are usually consumed within the companies which produce them and are difficult to market commercially, because the quality is rather poor compared to commercial activated carbon.

Plastics are a common waste material in Japan. The annual report on municipal solid waste by the Ministry of Environment (Japan) [6] notes that plastic waste is the second largest component of the waste stream next to paper, accounting for 14% by weight of the waste, compared to 25% for paper.

Polyethylene terephthalate (PET) is the major type of plastic found in MSW. In fiscal 2000, the recycle rate for PET was, however, only 30% compared with 50% for paper. PET is an advanced polymer, with excellent thermal and chemical resistance and mechanical properties. It is exclusively used as film for packing such as beverage bottles, and laminate layers in inner and outer layers of beverage cans.

The current recycling practice is to reprocess the recovered PET bottles to produce recycled PET flake and pellets. The recycled PET is then used to produce fiber, strapping, sheeting, bottles, containers and other compounds [7,8]. Studies have also been conducted using unsaturated polyester made from recycled PET to produce polymer concrete [9]. Nevertheless, PET processing is costly, and a major concern in the process is to remove the contaminants adhered to the inner side of the containers. These contaminations decrease the quality of the recycled PET.

In carbon manufacturing, polymer precursors are used when carbon of low inorganic impurity content is needed. PET consists of different formulations or combinations of hydrocarbon derivatives. Thus, it might be a promising precursor as it has a high percent of carbon (about 63 wt.%) [10]. The carbonization experiment using PET was initially carried out in our laboratory, and heavy metal removal from aqueous solution by the PET carbon was performed. However, we found that the carbonaceous material manufactured from PET was too light and tended to float on the surface of the solution, which made it difficult to measure adsorption.

Previous studies have shown that fly ash is a good candidate material for removing heavy metals from aqueous solution [11,12]. For example, coal fly ash primarily consists of two components—glass beads and microporous material. The latter material has 98% carbon and thus has a positive effect on heavy metal adsorption [13]. However, previous studies

mainly focused only on the adsorption characterization of the ash, and little attention was paid to the leaching of heavy metals from the ash and the adverse effects it may cause to the environment.

The objective of this study was to examine the possibility of producing low-cost adsorbents from waste ashes and post-consumer PET. The study also focused on the stabilization of heavy metals in the waste ashes. Finally, the potential application of the adsorbent in wastewater treatment, such as discoloration and heavy metal removal, were also examined.

2. Experimental

2.1. Sample collection

Four types of waste ashes and one ash slag were collected. The waste ashes were obtained from the city of Nagoya. Coal fly ash (CFA) was obtained from the Hekinan Power Plant, sewage sludge incinerator ash (SSA) was obtained from the Yamazaki Sewage Sludge Disposal Plant, and MSW incinerator fly ash (IFA) and incinerator bottom ash (IBA) were obtained from the Nanyo MSW Disposal Plant. MSW incinerator ash slag (IAS) was obtained from the Resource Recovery Center in the city of Toyohashi.

Among the five types of waste materials, SSA was recovered from an incinerator attached to a fluid bed furnace, and the ash was mainly collected from the cyclone. IAS was from fairly near incinerator, where the waste is primarily carbonated to char at a low air atmosphere. The iron and aluminum contained were removed in this stage, and the residual char was then burned at 1300–1400 °C to form a slag. Finally, the slag was crashed to form small particles for construction use.

After sampling, the ashes were immediately air-dried and coarse contaminants (e.g. wires, nails in IBA) were removed. All the samples were ground to pass a 1 mm sieve. Then, a portion of each sample was dried in an oven at 105–110 °C and stored in desiccators for use. Chemical compositions of the waste ashes are given in Table 1.

PET beverage bottles were obtained from the Resource Recovery Center in the city of Toyohashi. After removing the caps and labels, the bottles were washed with distilled water and dried at room temperature. Then they were shredded to small sizes for use.

2.2. Synthesis procedure

The adsorbents were prepared in three steps: (1) melting of PET; (2) blending of the melted PET and waste ash; and (3) carbonization of the molded mixture. Specifically, 60 g of shredded PET were weighed into a stainless container and heated on a hot plate in a hood. When the PET started to melt (at approximately 280 °C), the power output of the plate was adjusted to control the temperature until the PET melted entirely. Then, 40 g of ash were added into the melted PET and mixed by hand using a stirring rod until they were uniformly and thoroughly mixed; the mixture was then poured into a ceramic boat. The molded mixture was carbonized at 850 °C [14] in a nitrogen atmosphere for 60 min;

Table 1
Chemical compositions of the waste ashes used in this study

	CFA	SSA	IFA	IBA	IAS
Al (g/kg)	160	87.3	30.6	57.2	74.5
Ba (g/kg)	2.3	7.6	1.4	1.5	1.1
Ca (g/kg)	25.8	53.9	191	145	149
Cl (g/kg)	1.5	0.1	283	25.8	0.7
Fe (g/kg)	33.5	63.6	6.5	25.2	24.7
K (g/kg)	22.2	24.9	41.2	20.2	19.3
Mg (g/kg)	9.8	17.5	10.7	11.4	17.6
Na (g/kg)	3.7	12.0	46.7	26.7	15.9
P (g/kg)	7.7	100	2.8	22.2	12.6
S (g/kg)	19.2	44.6	8.4	8.7	3.2
Si (g/kg)	216	112	40.0	76.1	127
Ti (g/kg)	8.5	3.9	4.1	5.1	4.7
Zn (g/kg)	0.1	10.0	14.6	4.5	1.3
Cr (mg/kg)	106	887	76.4	203	571
Co (mg/kg)	60.2	26.6	32.1	46.5	22.3
Cu (mg/kg)	142	1540	772	3596	2771
Cd (mg/kg)	4.8	21.8	175	19.6	4.9
Mn (mg/kg)	222	1192	831	1634	844
Ni (mg/kg)	28.9	1127	27.1	117	12.4
Pb (mg/kg)	106	254	3797	663	69.3
Sr (mg/kg)	1238	539	291	391	381
V (mg/kg)	275	45.9	9.9	19.6	47.0
LOI ^a (%)	3.0	0.7	7.0	1.6	0.0

CFA: coal fly ash; SSA: sewage sludge ash; IFA: MSW incinerator fly ash; IBA: MSW incinerator bottom ash; IAS: MSW incinerator ash slag.

^a LOI: loss on ignition at 800 °C.

the heating rate was 10 °C/min, and the N₂ gas flow rate was 300 ml/min. After cooling to room temperature, the pyrolyzed material was ground and sieved to <2 mm for experiments.

2.3. Total and extractable metal analyses

These experiments were carried out prior to the acidic washing of the adsorbents. Metals in the waste ashes and the adsorbents were digested using the HNO₃–HClO₄–HF method [15] and was analyzed using an inductively coupled plasma atomic emission spectroscope (ICP-AES, Perkin-Elmer). The standard leaching test methods known as Notice No. 13 (for ash) and No. 46 (for slag) of the Ministry of Environment (Japan) was used to examine the metal leaching from the waste ashes and the adsorbents. A solid/liquid ratio of 1:10 was utilized. The pH value of the extracting solvent was adjusted to 5.8–6.3 with 0.01 M HCl and 0.01 M NaOH solutions using a pH meter (Orion 710A). The solution was subsequent vibrated for 6 h at 20 °C and 0.1 kPa. After filtration, metal concentrations in the filtrate were determined by ICP-AES.

2.4. Characterization of the adsorbents

The adsorbents were washed with 50 vol.% HNO₃ solution so as to eliminate the heavy metals and oxidize the surfaces of the adsorbents. Specifically, 40 g of adsorbent and 200 ml of HNO₃ solution were added in a flask and the solution was heated to 50 °C for 2 h and then allowed to cool to room temperature. The acid solution was drained and the adsorbent was rinsed with deionized water until the pH of the rinsing water remained constant. The oxidized adsorbent was then dried at 110 °C for 24 h and stored in a closed container.

The surface morphology of the waste ashes and the adsorbents and their Si, Cl, P and S concentrations were examined using a scanning electron microscope (SEM; JSM-6330F) coupled with an energy-dispersive X-ray spectrometer (EDS; JED-2140). X-ray diffraction (XRD; Rigaku 2500) was also employed at 30 kV and 40 mA using Cu K α radiation to identify crystalline form in the waste ashes and PET during the adsorbent synthesis procedure. The surface areas of the adsorbents were determined from nitrogen adsorption–desorption isotherms at 77 K by a Monosorb (Quantachrome, MS-21, USA) surface analyzer. Samples were out-gassed for 24 h at 200 °C in a vacuum oven before analysis.

Acidic and basic sites on the adsorbents were determined by the acid–base titration method. Briefly, weighed amounts of an adsorbent sample (approximately 0.20 g) were placed in standardized CO₂-free solutions of NaOH or HCl (0.020 M), and the ionic strength was adjusted to 0.100 M by adding NaCl. Then the bottle was sealed and allowed to equilibrate with gentle agitation for at least 48 h at 25 °C. A portion of the ambient solution was then separated, weighed and titrated with either standard 0.05 M HCl or 0.05 M NaOH [16,17].

Cation exchange capacity (CEC; meq./100 g) was determined by the ammonium acetate method. The adsorbents were saturated by rinsing four times with 1.0 M sodium acetate (pH 8.2) and three times with ethanol, and metals were finally extracted with three aliquots of 1.0 M ammonium acetate (pH 7.0). These samples were then diluted and analyzed by ICP-AES.

2.5. Adsorption studies

Adsorption of methylene blue (MB) was carried out in a batch process by varying the adsorbent dose. A weighed sample of the adsorbent was mixed with 50 ml MB solution of known concentration in a series of 100 ml stoppered glass tubes. The mixture was then shaken for 3 h at room temperature. In all case, adsorption equilibrium was reached within 2 h according to our preliminary experiments. The MB concentration in the residue solution was determined using an UV-Vis spectrophotometer (Jasco U-550) at a wavelength of 630 nm.

Cadmium and lead adsorption experiments were conducted in capped 200 ml polyethylene bottles. The stock solutions were prepared from CdCl₂ and PbCl₂ and the pH was adjusted to 5.0 with either 0.1 or 0.01 M HCl and NaOH solutions to avoid precipitation. The ionic strength for both heavy metals was 100 mg/kg. The dosages of adsorbents were selected as 0.05, 0.1, 0.2, 0.3, 0.4 and 0.5 g, respectively. The samples were added to 150 ml solution and shaken at room temperature for 12 h. The samples were then filtered and the residual Cd and Pb concentrations in the solution were determined by ICP-AES.

3. Results and discussion

3.1. Leaching of heavy metals from the adsorbents

Heavy metal leaching from the adsorbents and the bulk ashes was examined using Notice No. 13 (for ash) and No. 46 (for slag) leaching tests issued by the Ministry of Environment (Japan). These experiments were carried out prior to the acidic washing of the adsorbents so as to examine the possibility of applying the adsorbents directly in wastewater treatment in their synthesized forms without further addition treatments.

In order to compare heavy metal leachabilities from the adsorbents and the bulk ashes, metal leaching percentages from the adsorbents and the ashes were calculated by the quotients between the leaching and the total amounts in the adsorbents and ashes. Table 2 shows that heavy metal leaching from the adsorbents is much less than from the bulk ashes. This finding could mainly be attributed to the fact that the particles of the waste ashes were coated by PET during the synthesis process (Fig. 1). Although the leaching percentages for Ba, Ca, Cr, Mg, Pb, Sr and V from some of the waste ashes were approximately 2–16%, they were reduced to <1% for almost all the adsorbents. Higher leaching percentages for Pb from CFA, SSA, IFA, IBA, IAS were found, i.e. 2.84, 0.94, 7.69, 0.82 and 0.16%, respectively. However, the leaching from their synthesized adsorbents was reduced to 0.34, 0.13, 0.06, 0.17 and 0.01%, respectively.

Metal leaching amounts from the five types of adsorbents are listed in Table 3. Relatively higher concentrations of Al, Ba, Ca and K in some of the adsorbents were detected, with the values of around 2–140 mg/l, while the other metals were generally <1 mg/l. Among

Table 2
Comparison of metal leaching percentages from the waste ashes and the synthesized adsorbents

	CFA	SSA	IFA	IBA	IAS	CFAads	SSAads	IFAads	IBAads	IASads
Al	0.06	<0.01	<0.01	1.06	0.06	0.01	<0.01	<0.01	0.19	0.04
Ba	0.40	0.51	3.22	0.19	0.03	0.15	0.27	3.17	0.08	0.03
Ca	9.27	2.30	16.2	0.30	0.14	6.51	0.27	0.33	0.10	0.14
Cr	2.72	<0.01	<0.01	0.81	0.02	<0.01	<0.01	<0.01	<0.01	0.01
Co	<0.01	0.04	0.22	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Cu	0.01	0.01	0.07	0.14	0.03	<0.01	<0.01	0.04	<0.01	0.03
Cd	0.83	0.05	<0.01	0.26	0.01	0.49	<0.01	<0.01	0.17	<0.01
Fe	<0.01	<0.01	0.01	<0.01	0.04	<0.01	<0.01	<0.01	<0.01	0.01
K	1.15	1.12	0.41	1.59	0.59	0.09	0.32	0.23	0.28	0.45
Mg	0.02	2.30	<0.01	0.01	0.10	0.01	0.01	<0.01	<0.01	0.06
Mn	<0.01	0.23	<0.01	<0.01	0.04	<0.01	<0.01	<0.01	<0.01	0.01
Ni	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Pb	2.84	0.94	7.69	0.82	0.16	0.34	0.13	0.06	0.17	0.01
Sr	3.04	1.08	1.86	1.23	0.11	0.69	0.51	0.81	0.55	0.07
Ti	<0.01	<0.01	<0.01	<0.01	0.05	<0.01	<0.01	<0.01	<0.01	0.02
V	0.46	9.49	0.01	0.05	0.40	0.20	<0.01	<0.01	<0.01	0.10
Zn	0.15	0.01	0.27	0.01	0.05	0.16	0.01	<0.01	0.01	0.01

CFA: coal fly ash; SSA: sewage sludge ash; IFA: MSW incinerator fly ash; IBA: MSW incinerator bottom ash; IAS: MSW incinerator ash slag. CFAads, SSAads, IFAads, IBAads, IASads represent adsorbents made from each type of waste ash and PET.

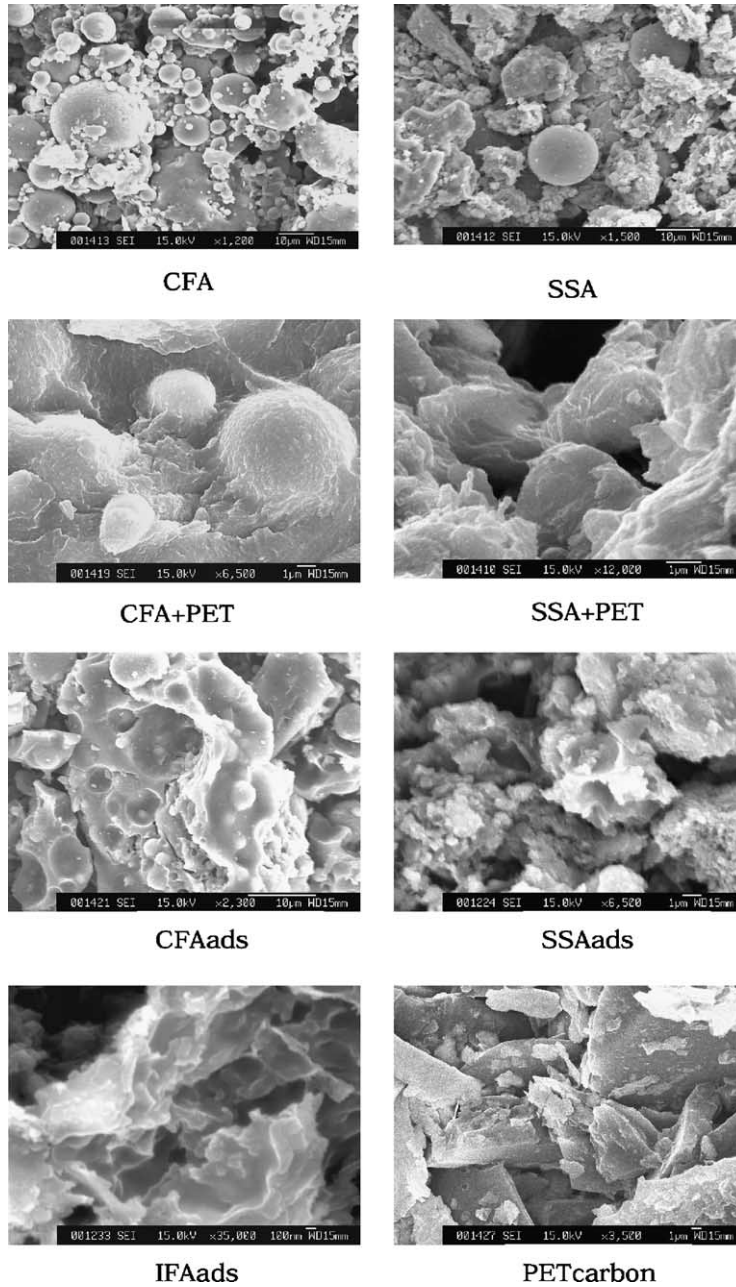


Fig. 1. Selected SEM photographs of the waste ashes and the synthesized adsorbents. CFAads: adsorbent made from CFA and PET.

Table 3
Leaching of selected metals from different adsorbents (mg/l)

	CFAads	SSAads	IFAads	IBAads	IASads
Al	1.04	0.11	<0.01	9.32	0.27
Ba	0.28	1.74	3.97	0.11	0.03
Ca	141	12.2	53.3	12.2	8.13
Cr	<0.01	<0.01	<0.01	<0.01	<0.01
Co	<0.01	<0.01	<0.01	<0.01	<0.01
Cu	<0.01	<0.01	0.03	<0.01	0.06
Cd	<0.01	<0.01	<0.01	0.01	<0.01
Fe	<0.01	<0.01	<0.01	<0.01	0.29
K	1.77	6.75	8.06	4.74	1.89
Mg	0.08	0.08	0.03	0.03	0.90
Mn	<0.01	<0.01	<0.01	<0.01	<0.01
Ni	<0.01	<0.01	<0.01	<0.01	<0.01
Pb	0.03	0.03	0.20	0.09	<0.01
Sr	0.71	0.23	0.20	0.18	0.02
Ti	<0.01	<0.01	<0.01	<0.01	0.06
V	0.05	<0.01	<0.01	<0.01	<0.01
Zn	0.02	0.04	0.03	0.03	0.01

CFAads, SSAads, IFAads, IBAads, IASads represent adsorbents made from each type of waste ash and PET.

the foregoing, the concentrations of environmental concern heavy metals, such as Cr, Co, Cu, Cd, Ni, Pb and Zn were all <0.2 mg/l.

Currently, only a few heavy metals have been listed by the Ministry of Environment (Japan) as industrial wastewater disposal standards, e.g. the standard limits for Cd, Pb and Cr(VI) are 0.1, 0.1 and 0.5 mg/l, respectively [18]. It can be seen in Table 3, the leachate concentrations were <0.01 mg/l for Cd and Cr, and within 0.03–0.20 mg/l for Pb. Thus, although there are no problems with Cd and Cr, the leachate concentration of Pb from IFAads exceeded the standard limits. Hence, it is still necessary to stabilize Pb to a certain degree before synthesizing these adsorbents. To our knowledge, phosphorus acid, dithiocarbamic acid or their soluble salts are good candidates for heavy metal stabilization in waste ashes [19–21]. In this way, the adsorbents may directly be used for wastewater treatment without any further treatment. Alternatively, another option is to wash out Pb and other heavy metals from the adsorbents by acidic solution before they are used for wastewater treatment.

3.2. Surface characteristics of the adsorbents

The adsorbents were washed with 50 vol.% HNO₃ solution. The wash could eliminate heavy metals in the adsorbent as well as oxidize the surface of the adsorbent to form active acidic sites [16,22].

The concentrations of active sites of the adsorbents are shown in Table 4. The acidic site on the adsorbents are within 0.84–1.56 meq./g while it is only 0.56 meq./g on PET carbon. It has been reported that oxidation of carbon with HNO₃ solution caused the increase in acidic and decrease in basic sites [22]. Thus, it is assumed that it is easier to form acidic sites with HNO₃ solution on the adsorbents than on PET carbon.

Table 4
Acidic sites, basic sites and CEC of different adsorbents

Adsorbent	Acidic sites (meq./g)	Basic sites (meq./g)	CEC (meq./100 g)
CFAads	1.56	0.21	23.5
SSAads	0.84	0.32	15.3
IFAads	1.43	0.43	26.8
IBAads	1.22	0.62	24.8
IASads	1.02	0.37	8.62
PET carbon	0.65	0.56	0.64

Selected SEM photographs of the waste ashes and the synthesized adsorbents are shown in Fig. 1. Unlike most thermoplastics which are soft and sticky when melted, PET appears in a fluid state. It can be seen from Fig. 1 that the particles of the waste ashes are coated by the fluid PET after mixing the two types of waste materials at a high temperature, and various porous adsorbents are formed via carbonization treatment.

Fig. 2 demonstrates the BET surface areas of the adsorbents. The surface areas were in a range from 115 to 485 m²/g, highest for CFAads and lowest for SSAads, and followed the sequence CFAads > IFAads > PET carbon > IASads > IBAads > SSAads.

X-ray diffraction patterns for the waste ashes and the adsorbents were examined in order to identify the crystalline phase in the ashes. Representative XRD patterns for IFA and PET are presented in Fig. 3. It can be seen that the XRD diagram for IFA + PET apparently produces a composite diagram without any new peaks. This result may suggest that no chemical reaction occurred between the two types of waste materials when they were mixed at about 280 °C. However, some peaks between 15 and 30° in the XRD diagram for IFAads (adsorbent made from IFA and PET) disappeared, indicating that the crystallinity in PET was destroyed during the carbonization process. The results also suggest that IFA might react chemically with PET to form an amorphous phase during the carbonization process [4].

3.3. Adsorption isotherms

Fig. 4 illustrates the adsorption isotherms of MB onto the adsorbents. The equilibrium data provide information on the capacity of the adsorbent or the adsorbent amount required

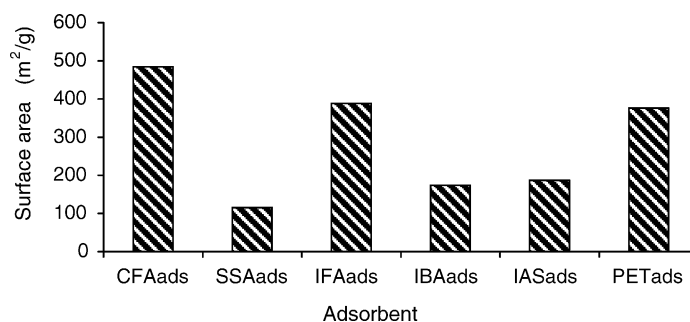


Fig. 2. Surface area of different adsorbents.

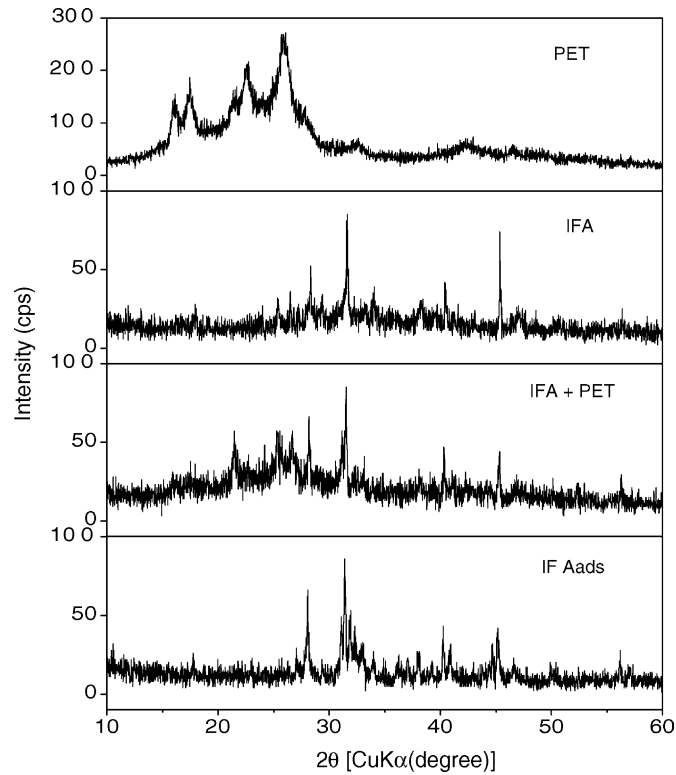


Fig. 3. X-ray diffraction patterns for PET, IFA and IFAads showing the crystalline phase change during the carbonization process. IFA + PET: blended IFA and PET before carbonization; IFAads: adsorbent made from IFA and PET.

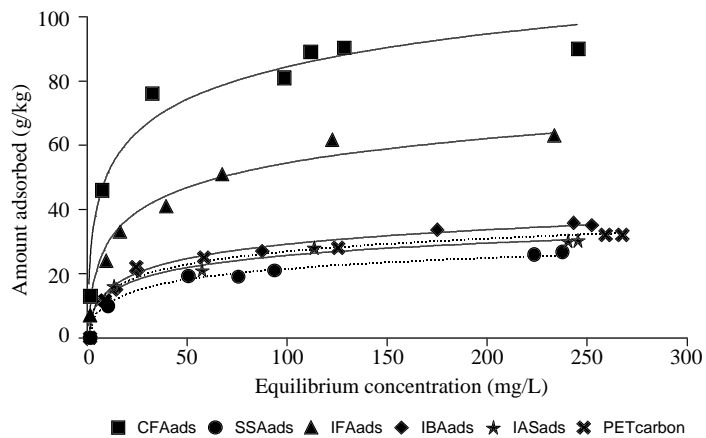


Fig. 4. Adsorption isotherms of methylene blue onto various adsorbents.

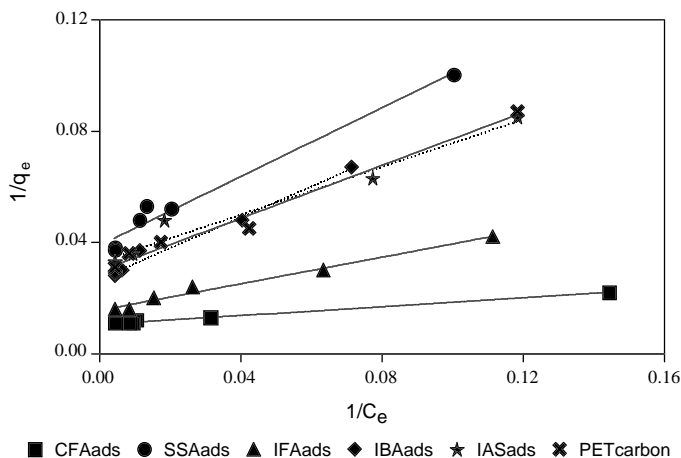


Fig. 5. Langmuir isotherms for the adsorption of methylene blue onto various adsorbents.

to remove a unit mass of MB under the adsorption system conditions. High MB adsorption capacity for CFAads and IFAads was found; their maximum adsorption capacity was generally around two to four times higher than that of the other four types of adsorbents.

In liquid–solid adsorption system, the surface chemistry of adsorbent is more important than the magnitude of surface area. The types and concentrations of adsorption sites that are available on the surface play an extremely important role on the adsorption capacity. This is well demonstrated by the results of this study. For example, although the surface area of PET carbon was around twice that of IBAads and IASads (Fig. 2), the adsorption capacity of PET carbon was not double that of IBAads and IASads (Fig. 4). This is because there are much more acidic sites existing on IBAads and IASads than on PET carbon (Table 4).

The results of MB adsorption onto the adsorbents were fitted to Langmuir and Freundlich isotherms. Langmuir isotherm assumes that maximum adsorption occurs when the surface is covered by adsorbate. The linear form of this isotherm is given by the following equation:

$$\frac{q_e}{q_m} = \frac{K_L C_e}{1 + K_L C_e} \quad (1)$$

where q_e is the amount adsorbed by per unit mass of adsorbent corresponding to complete coverage of the adsorbent sites, C_e the equilibrium concentration of the adsorbate, and q_m and K_L the Langmuir constants related to maximum adsorption capacity and energy of adsorption, respectively.

When $1/q_m$ was plotted against $1/C_e$, straight lines were obtained (Fig. 5), indicating that the adsorption of MB onto the adsorbents follows the Langmuir isotherm. The Langmuir constants K_L and q_m were calculated and presented in Table 5.

High q_m values for CFAads and IFAads were obtained in this study. The removal of MB from aqueous solution by different materials has been studied in recent years and some of these papers provided q_m values. Although these values were obtained at different pH ranges or temperatures, they can be a useful criterion of the adsorbent capacity. The q_m

Table 5
Langmuir and Freundlich constants for MB uptake by different adsorbents

Adsorbent	Langmuir constants			Freundlich constants		
	q_m (mg/g)	K_L (dm ³ /g)	R^2	$1/n$	K_F (dm ³ /g)	R^2
CFAads	92.3	0.143	0.991	0.19	34.4	0.915
SSAads	25.7	0.063	0.976	0.30	5.26	0.972
IFAads	63.5	0.066	0.980	0.31	13.5	0.958
IBAads	36.9	0.049	0.985	0.28	7.78	0.972
IASads	30.1	0.078	0.967	0.26	7.40	0.960
PET carbon	33.4	0.063	0.988	0.27	7.88	0.910

values obtained in this study were 30–103 mg/g, higher than kaolinite (7–20 mg/kg) [23], but lower than carbons prepared from tire char (100–250 mg/g) [24].

The logarithmic form of Freundlich isotherm is given by the following equation:

$$\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e \quad (2)$$

where q_e is the amount adsorbed, C_e the equilibrium concentration of the adsorbate, and K_F and n the Freundlich constants related to adsorption capacity and adsorption intensity, respectively.

Fig. 6 illustrates that the MB adsorption follows the Freundlich isotherm. The Freundlich constants K_F and $1/n$ were calculated and reported in Table 5. The constant $1/n$ between 0.25 and 0.31 indicates favorable adsorption for which $0 < 1/n < 1$. The term $1/n$ also expresses an affinity between the adsorbate and the adsorbents [25]. Therefore, similar values of $1/n$ for different adsorbents indicate that their affinity for MB is similar, and the higher adsorption capacities of IFAads and CFAads could mainly be attributed to the constant K_F .

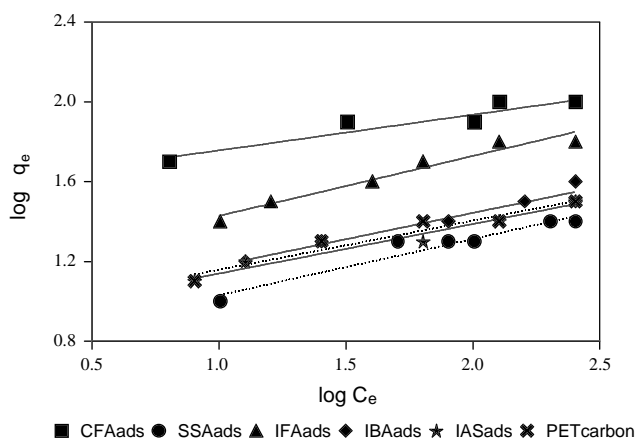


Fig. 6. Freundlich isotherms for the adsorption of methylene blue onto various adsorbents.

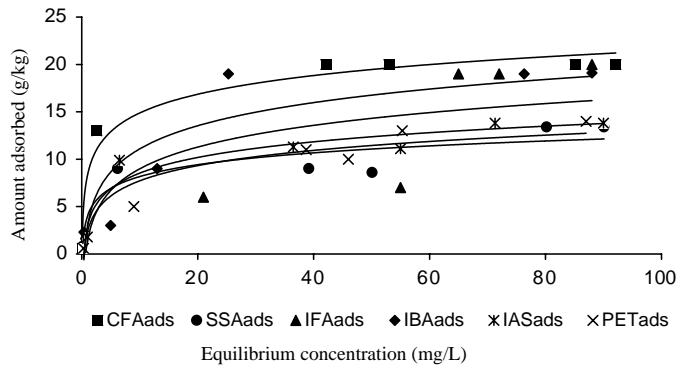


Fig. 7. Adsorption isotherms of Cd onto various adsorbents.

Furthermore, cadmium and lead were selected for heavy metal adsorption experiments in this study and their adsorption isotherms are plotted in Figs. 7 and 8. These experiments were performed with the initial solution pH adjusting to 5.0 and without buffer control of the pH in the adsorption process. The final pH of the equilibrium solutions for the adsorption isotherms varied within 5.0–7.0, lowest for PET carbon and highest for IFAads solutions.

It can be seen from Figs. 2, 7 and 8, the adsorption capacities of the adsorbents are not in accordance with their surface areas, e.g. PET carbon has a higher surface area than that of SSAads, IBAads and IASads, however, its adsorption capacity is not higher in Cd adsorption and lower in Pb adsorption. This could be attributed to the surface properties of the adsorbents. Based on the properties of the adsorbents and their adsorption isotherms, the adsorption mechanisms of the adsorbents for heavy metals are supposed as follows: (1) chemical reactions between the acidic sites on the adsorbents and heavy metals; (2) affinity adsorption which could be attributed to the BET surface area; and (3) cation exchanges between the adsorbents and heavy metals. The CEC of the adsorbents is around 13–42 times higher than that of PET carbon (Table 4); therefore, it plays an important role for heavy metal removals in this study. Moreover, it has been reported that tobermorite

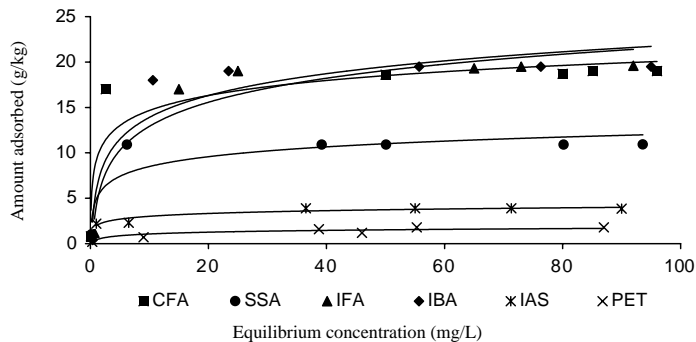


Fig. 8. Adsorption isotherms of Pb onto various adsorbents.

($\text{Ca}_5\text{Si}_6\text{H}_2\text{O}_{18}\cdot 4\text{H}_2\text{O}$), which can be obtained by the hydrothermal treatment of fly ash and lime at a $\text{Ca}/(\text{Si} + \text{Al})$ mole ratio of 1.0, can be used as an ion exchanger and is able to adsorb heavy metals in wastewater [26,27]. It can be seen from Table 1 that the main components of the ashes are CaO , SiO_2 and Al_2O_3 , hence they have the potential capability to form tobermorite.

Additionally, the isotherm data were attempted to fit Langmuir and Freundlich equations. The adsorption of Cd and Pb onto PET carbon could be well described by Langmuir and Freundlich equations with the R^2 values of 0.97–0.99; however, the adsorption of the five types of adsorbents were not in good fits with the two equations with the R^2 values of 0.70–0.85.

4. Conclusions

Although fly ashes have the potential for utilization in wastewater treatment, their adsorption capacities are rather small. Moreover, the heavy metals originally contained in the ashes are of concern because they may leach out and cause environmental problems.

By combining different types of waste ashes with PET, various new types of adsorbents were synthesized in this work. At higher temperature (approximately 280°C), fluid PET could coat the waste ash particles, and various porous adsorbents could be synthesized via a carbonization process. The coating of fluid PET on the particles of waste ashes could also significantly restrict heavy metal leaching from the synthesized adsorbents. Unlike PET carbon, the adsorbents made from waste ashes and PET could settle in aqueous solutions, and make it easier to perform adsorption. Furthermore, some of the adsorbents showed higher removal capabilities for MB and heavy metals from aqueous solutions compared to PET carbon. Consequently, it is believed that the adsorbents produced in this study could be used for treatment of wastewater from dye processes, steel mill, mine factory, electroplating plant, etc. after acidic washing. Moreover, CFAads, SSAads, IBAads and IASads also have the potential to be directly used in wastewater treatment.

Acknowledgements

The authors would like to thank Mr. R. Sasai, K. Sano, Y. Kondo, S. Tsutsumi and M. Yamada for their courtesy assistance in sample collection.

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