

Utilization of Fly Ash from Power Plant for Adsorption of Hydrocarbon Contamination in Water

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Abstract

Adsorption efficiency of polycyclic aromatic hydrocarbons (PAHs) contamination in water with rice husk fly ash from a power plant was investigated in comparison with coal fly ash and silica from rice husk fly ash, with and without surface treatment. Naphthalene was used as a representative for PAHs, and Cethyltrimethylammoniumbromide (CTAB) was used as surface treating agent for the present study. Various factors, such as shaking rate, shaking time, pH of naphthalene aqueous solution, and adsorbent-naphthalene weight ratio, were investigated to identify the optimum condition for each adsorbent. Upon using 0.3 g adsorbent in 100 ml of 10 mg/l naphthalene solution, the optimum condition was observed to be shaking the mixture of an adsorbent and naphthalene solution with pH 2 at 250 rpm for 60 minutes. Similar optimum conditions were also observed for all adsorbents used in the present study, except for the highest efficiency of silica from rice husk fly ash treated with CTAB. In addition, upon varying weight ratios of adsorbent and naphthalene, adsorption efficiency was observed to gradually increase and reach equilibrium at the ratio of 0.7 g adsorbent per mg naphthalene. Therefore, the optimum condition for the present study should be using 0.7 g adsorbent per mg naphthalene in solution with pH 2 and shaking at 250 rpm for 60 minutes. The adsorption behavior of the system was also investigated and found to be in line with Freundlich Isotherm.

Key words : Polycyclic aromatic hydrocarbons, Cethyltrimethylammoniumbromide, Naphthalene, Adsorption, Silica from Rice husk

Introduction

Water polluted with organic compounds has become of increasing worldwide concern. Polycyclic aromatic hydrocarbon (PAHs) are chemical species with 2-6 fused benzene rings and are well-known priority pollutants due to toxic properties, some of which are considered to adversely affect human health. PAHs originate from either natural or anthropogenic sources. Anthropogenic sources include engine exhaust, crude oil, and industrial processes. Natural sources comprise terrestrial coal deposits, volcanic eruptions and forest fires. Main sources of PAHs in water are atmospheric deposition, offshore petroleum activities and deposition from sewage discharge. Most PAHs are hydrophobic compounds with high boiling point, melting points, and electrochemical stability. They can therefore exist, and be accumulated, in soils or water over a long period of time.⁽¹⁾ There are various techniques to

remove these pollutants from soils or water, but the adsorption technique has been observed as one of the most effective techniques for the treatment of organic pollutants.^(3,4) Among various adsorbents, activated carbon is the one most commonly used, but its disadvantages include high cost and difficult regeneration processes.⁽⁵⁾ On the other hand, wastes from power plant such as rice husk ash and coal fly ash have been exploited for the treatment of organic compounds, and they exhibit good properties for being used as adsorbent.

The purpose of this study is to comparatively investigate the possibility of removing PAHs (naphthalene) contaminated in water by using rice husk ash (RA), silica from rice husk ash (SI) and coal fly ash (FA) as adsorbents, with and without CTAB surface treatment. The latter is based on an assumption that the CTAB [CH₃(CH₂)₁₅N(CH₃)₃Br]

adsorbed on the adsorbent surface would increase the hydrophobic property of the adsorbents.⁽⁷⁾ Adsorption Isotherm was also investigated and briefly reported in this paper.

Materials and Experimental Procedures

Materials

Rice husk fly ash was obtained from Patum Rice Mill and Granary PLC, Thailand. Coal fly ash was obtained from the Mae Moh power plant, Electricity Generating Authority of Thailand. CTAB was obtained from Ajax Finechem. All other reagents were of analytical grade.

Equipment

Chemical composition of all adsorbents was characterized by X-ray fluorescence spectrometer, Philips model PW2400. The percentage of carbon was measured by CHN elemental analyzer, Leco CHN-2000. The functional group of the adsorbents was characterized by Fourier transform infrared spectroscopy (FTIR), Perkin Elmer (spectrum one).

CTAB Surface Treatment of Adsorbent

1.4 g of CTAB was mixed with 100 ml of distilled water and 8 g of each adsorbent (RA, SI, FA). The mixture was agitated with a stirrer at 250 rpm for 24 hours. After agitation, the surface-modified adsorbent was collected, washed with distilled water, and then dried in an oven at 60°C for 24 hours.

Adsorption Investigation

An amount of 0.3 g of each adsorbent (RA, CTAB-RA, SI, CTAB-SI, FA, or CTAB-FA) was mixed with 100 ml of 10 mg/l naphthalene aqueous solution. The mixture was shaken at 100-250 rpm for 10-100 minutes. The pH effect was investigated by adjusting the aqueous solution to pH 2-10. Then, the effect of adsorbent-naphthalene ratio was investigated by varying the ratios of 0.1-1.0 g adsorbent per mg naphthalene. To study the adsorption isotherm, experiments were carried out by mixing 0.01-1.0 g of the adsorbent with 100 ml naphthalene solution. The adsorbents were separated by centrifugation at 2000 rpm for 10 minutes and then filtered through Whatman filter paper no. 1. UV-Vis

spectrophotometer was used for the determination of naphthalene concentration at 290 nm.

Results and Discussion

Characterization of Adsorbents

The chemical composition of each adsorbent is shown in Table 1. It was found that SiO₂ is the major component of both RA and SI, where SO₃, Na₂O, K₂O, CaO and P₂O₅ are minor components. In case of FA, both SiO₂ and CaO are major components, where Fe₂O₃, Al₂O₃, SO₃, Na₂O, K₂O and MgO are minor components.

Table 1. Composition of adsorbents

Compound	Weight (%)		
	RA	SI	FA
SiO ₂	82.72	92.71	31.33
SO ₃	0.46	3.62	6.17
Na ₂ O	0.23	2.98	3.11
K ₂ O	3.69	0.27	2.98
Al ₂ O ₃	0.19	0.11	14.75
Fe ₂ O ₃	0.47	0.02	15.35
CaO	1.24	-	22.09
MgO	0.62	-	2.79
P ₂ O ₅	2.12	0.08	0.35
LOI	7.81	-	-

The results of elemental analyzers as shown in Table 2 indicate that percentage of carbon of surface-modified adsorbents increased due to CTAB adsorbed on the surface of the adsorbents. CTAB-SI showed the highest percentage of carbon due to its porous surface and high surface area. These results demonstrate that the modification of adsorbents depended on both the structure and surface area of the adsorbents.⁽⁶⁾

Table 2. Carbon percentage of adsorbents

Adsorbent	%C	Surface Area (m ² /g)
RA	4.24	12.29
CTAB-RA	4.68	10.25
SI	0.00	190.80
CTAB-SI	9.41	106.30
FA	0.06	2.12
CTAB-FA	0.59	5.39

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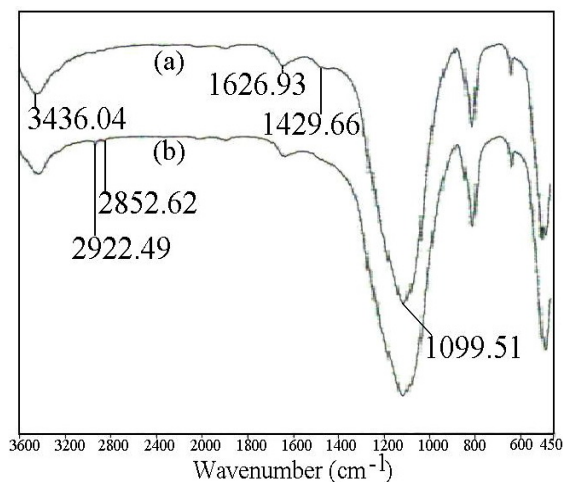


Figure 1. FTIR spectra of (a) RA (b) CTAB-RA

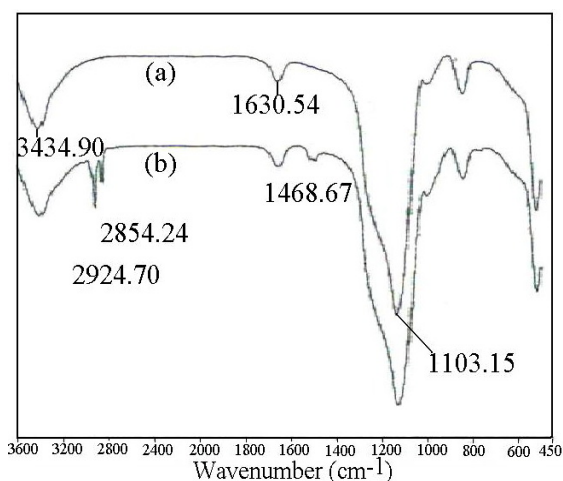


Figure 2. FTIR spectra of (a) SI (b) CTAB-SI

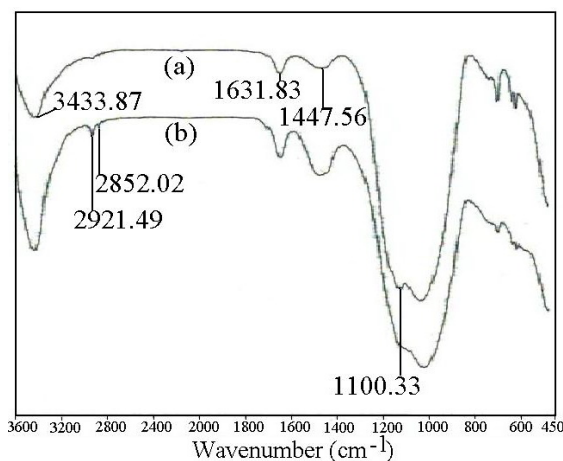


Figure 3. FTIR spectra of (a) FA (b) CTAB-FA

The FTIR spectrum (Figures 1, 2, 3) of RA, SI and FA show peaks at 3436 and 1100-1200 cm^{-1} which could be considered as silanol (Si-OH) and siloxane (Si-O-Si) groups. For RA and FA, the peak at 1630 cm^{-1} indicates the carbonyl group ($-\text{C}=\text{O}$) and the -peak at 1430-1470 cm^{-1} indicates the CH_3 group. For CTAB-RA, CTAB-SI, and CTAB-FA, two new peaks occurred at 2800-2900 cm^{-1} . These indicate C-H stretching vibrations, corresponding to CH_2 and CH_3 groups. This finding provides evidence for the presence of CTAB [$\text{CH}_3(\text{CH}_2)_{15}\text{N}(\text{CH}_3)_3\text{Br}$] on the surface of the adsorbents. The peaks at about 1470 cm^{-1} indicate the presence of CH_3 bending vibration adjacent to $>\text{N}^+<$ of CTAB.

Effect of Shaking Speed

Effect of agitation of the adsorbent/sorbate system in naphthalene adsorption was studied by varying the speed of agitation. An amount of 0.3 g of each adsorbent and 100 ml of 10 mg/l naphthalene concentration were agitated for 60 minutes at 100-250 rpm. The experimental results are shown in Figure 4.

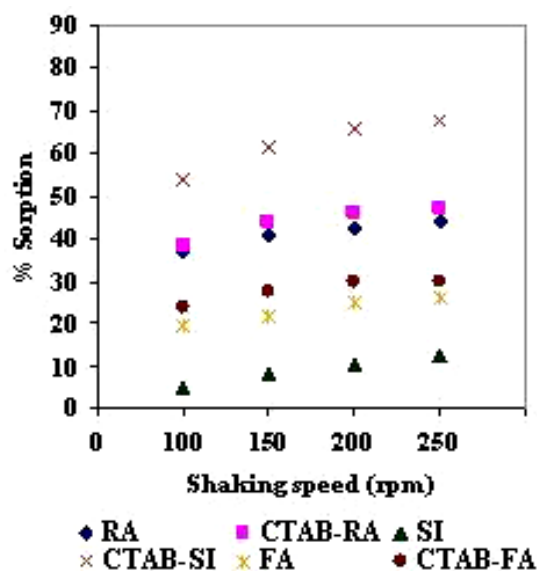


Figure 4. Effect of shaking speed

The naphthalene removal efficiency was noticed to increase with increasing agitation speed from 100 to 250 rpm. This effect can be attributed to the decrease in boundary-layer thickness around the adsorbent particles, resulting in increasing the degree of mixing. The higher uptake of the

naphthalene on CTAB-SI was due to its high porosity and high surface area. It increased the sorption of CTAB on the SI surface, and also the hydrophobicity of CTAB-SI. For convenience, an agitation speed of 250 rpm was selected as the optimum speed for the subsequent adsorption experiment.

Effect of Shaking Time

The effect of shaking time or contact time on percent sorption of naphthalene was studied over a contact time of 10-100 mins. An amount of 0.3 g of adsorbents was shaken at 250 rpm with 100 ml of 10 mg/l naphthalene solution. The percent sorption increased with increasing shaking time, and became constant after 50 minutes (Figure 5). These results can be explained by the fact that an increase of the shaking time would improve the diffusion of naphthalene into the surface of the adsorbents. According to these results, 60 minutes was chosen and used as the optimum shaking time for the subsequent adsorption experiment.

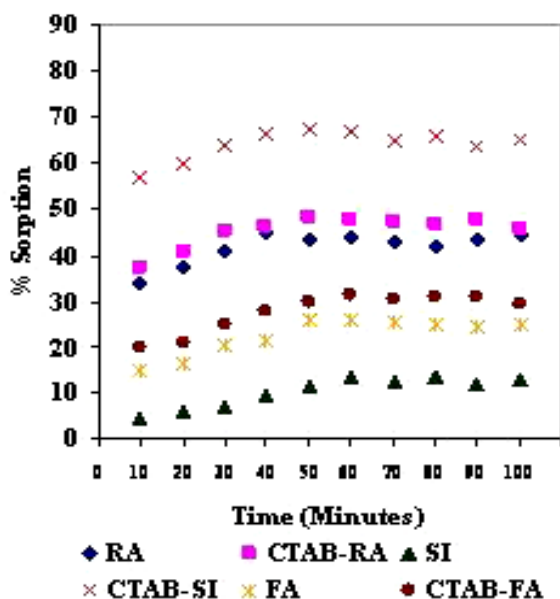


Figure 5. Effect of shaking time

Effect of pH

pH is one of the most important factors that affect the adsorption process. The pH effect was studied in the range of 2-10. Figure 6 illustrates the effect of pH on percent sorption. A quantity of 0.3 g of adsorbents was agitated with 100 ml of 10 mg/l of naphthalene, and agitated at 250 rpm for

60 minutes. With increasing pH from 2 to 10 the sorption decreased for all adsorbents. These observations can be explained in terms of degree of ionization of the adsorbate and the surface charge of the adsorbent. Functional groups on the surface of all adsorbents are silica or aluminosilicate groups, hence showing negative charges on the surface. The lower pH (higher H^+ concentration) would increase sorption due to decreasing negative charges on the adsorbent. Thus, the electrostatic force of attraction between the adsorbent surface and sorbate ion was increased. In the case of CTAB-modified adsorbents, all adsorbents demonstrated a high percent sorption at low pH. CTAB exhibited an amphoteric property due to tertiary amine, showing positive charge at low pH and negative charge at high pH. Consequently, the negative surface would adsorb more CTAB at low pH, hence increasing hydrophobicity. According to these results, pH 2 was chosen and used as the optimum condition for the subsequent adsorption experiment.

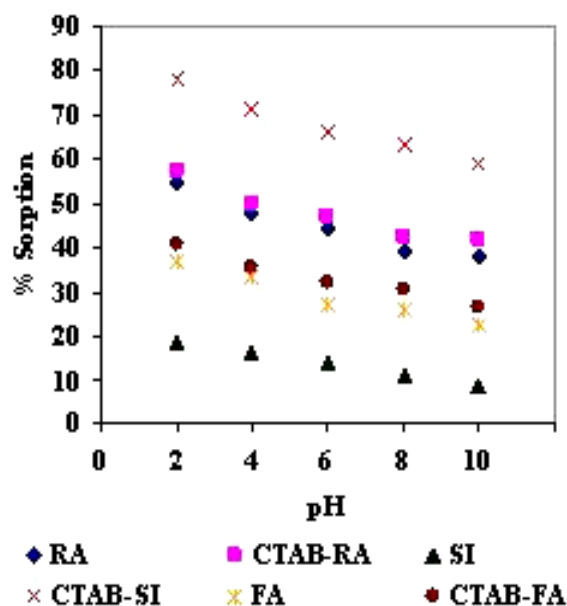


Figure 6. Effect of pH on sorption efficiency

Effect of Adsorbent Dosage

Figure 7 characterizes the effect of adsorbent dosage on percent sorption of naphthalene. For optimizing the adsorbent dosage, 0.1 to 1.0 g of each adsorbent was agitated with 100 ml of 10 mg/l of naphthalene solution, and agitated at 250 rpm for 60 minutes at pH 2. The percent sorption increased with increasing ratios of the adsorbent from 0.1 to

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0.6 g per mg naphthalene and became almost constant between 0.7-0.8 g of adsorbent per mg naphthalene.

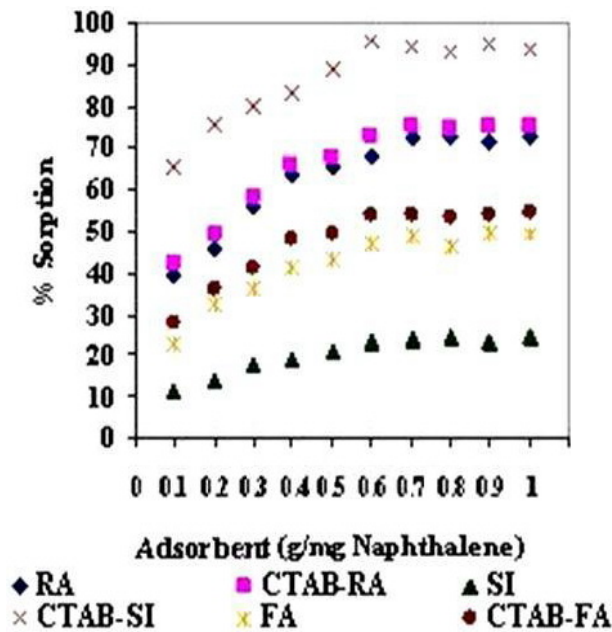


Figure 7. Effect of adsorbent dosage

Adsorption Isotherms

Adsorption isotherms express a specific relation between concentration of sorbate and its degree of accumulation onto adsorbent surface. The adsorption process of naphthalene was tested with Langmuir and Freundlich isotherm models, The Freundlich equation is given as follows:

$$\log X = \log K + (1/n) \log C_2$$

where X is concentration of the adsorbed solute (mg/g), C_e is concentration of the solute in solution (mg/l), K and n are Freundlich isotherm constants related to adsorption capacity. For all experimental sorption data, the correlation coefficient values (R^2) determined for each of the adsorption isotherms indicate that the Freundlich model effectively fit the experimental data.⁽²⁾ These results disclose that the adsorption was physisorption. The values of K and n (Table 3), estimated from the Freundlich equation indicate that the order of sorption capacity of naphthalene are as follows : CTAB-SI > CTAB-RA > RA > CTAB-FA > FA > SI.

Table 3. Freundlich parameters

Adsorbent	K (mg/g)	n
RA	0.11	0.52
CTAB-RA	0.13	0.50
CTAB-SI	1.70	1.01
FA	0.002	0.28
CTAB-FA	0.005	0.32

Comparison of Adsorption Efficiencies

The comparative efficiency of the adsorbents was investigated with the same condition of 0.7 g adsorbents agitated in 100 ml of 10 mg/l of naphthalene solution. The sample was agitated at 250 rpm for 60 minutes at pH 2. Figure 8 presents a comparison of the adsorption efficiencies. Percentage sorption increased when the carbon on the adsorbents increased. Therefore, the adsorption of naphthalene on the adsorbents was due to the interaction of naphthalene with the alkyl group (carbon group) on the adsorbents. The sorption efficiency of naphthalene is as follows : CTAB-SI > CTAB-RA > RA > CTAB-FA > FA > SI. The CTAB-SI showed the highest naphthalene adsorption at 94.1%.

Conclusions

This study showed that adsorption of PAHs (naphthalene) from water can be achieved by using rice husk ash, silica from rice husk ash, coal fly ash as adsorbents, with and without CTAB surface treatment. Adsorption of naphthalene under various conditions such as shaking speed, contact time, pH, and adsorbent dosage were studied. The amount of naphthalene adsorption depended on the amount of carbon on the adsorbent surface. The adsorption order of efficiency is as follows : CTAB-SI > CTAB-RA > RA > CTAB-FA > FA > SI. In other words, CTAB-SI or silica modified with CTAB was validated to be the best adsorbent in this study.

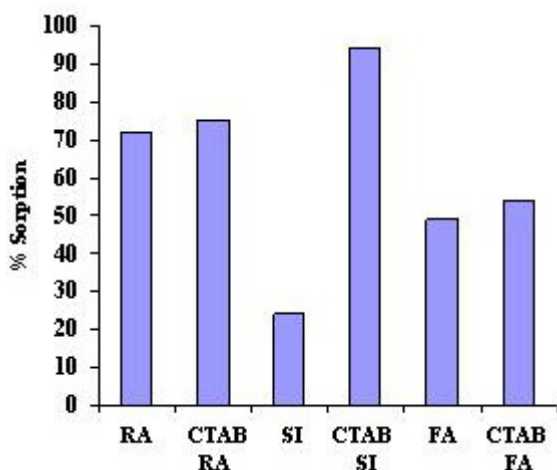


Figure 8. Comparison of adsorption efficiencies

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