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Analysis of polycyclic aromatic hydrocarbons (PAHs) and their adsorption characteristics on activated sludge during biological treatment of coking wastewater

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ABSTRACT

Experiments were conducted to investigate the concentrations of PAHs and their adsorption characteristics by activated sludge in this study. Influence of sorption time, sludge concentration, and pH on PAHs adsorption was evaluated. Furthermore, the isotherms, kinetics of adsorption, and potential risk were also explored. Experimental results show that concentrations of 16 PAHs in coking wastewater sludge were 581.600–2201.633 μg/g, both Linear and Freundlich adsorption models were able to adequately describe the adsorption equilibriums of PAHs onto activated sludge. The adsorption process closely followed the pseudo-second-order kinetic model. The adsorption efficiencies of PAHs depended on the activated sludge concentration and sorption time, while that was not affected by pH. Hydrophobic interaction, distribution, and chemisorption were mainly responsible for the adsorption of PAHs, while the surface area and pore volume of activated sludge had little contribution. Results also indicate that the order of carcinogenic health risk was Benzo[a]pyrene > Dibenzo[a,h]anthracene > Benzo[b]fluoranthene > Indeno [1,2,3-cd]pyrene > Benzo[a]anthracene > Benzo[k]fluoranthene.

Keywords: Coking wastewater; PAHs; Biological sludge; Adsorption mechanism; Influencing factors; Potential risk

1. Introduction

Four hundred and sixty Mt coke in China, important raw material for steelmaking, was yielded in 2012. Coke wastewater, which is generated during high-temperature coal carbonization, coal gas purification, and chemical products refining, was one of the harmful by-products of coke production [1,2]. This wastewater contains high concentrations of inorganic and organic pollutants which include, among others, polycyclic aromatic hydrocarbons (PAHs), heterocyclic compounds, oils, tars, and inorganic substances such as cyanides, sulfides, sulfates, thiosulfates, ammonia, and heavy metal ions [3]. The concentration of each

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component varies as a function of the types of coal used and different modifications of the process employed in the manufacture of the coke. Coking wastewater is notorious for its toxicity and refractoriness, so it is necessary to treat coking wastewater before disposal.

Depending on the type of pollution, treatment methods should be chosen at the lowest cost possible, provided that the highest degree of removal from impurities is maintained [4]. Biological treatment is by far the most widely applied and cost-effective technology in wastewater treatment. PAHs are hazardous organic chemicals, which consist of fused aromatic rings and do not contain substituents or heteroatoms, these compounds are always occurring in a mixture, never separately [5]. The fact of their wide distribution in the environment and a well-documented negative biological activeness, toxicity, mutagenicity, and carcinogenicity makes this compounds one of the most dangerous organic pollutants [6]. PAHs presence in primary, activated, digested, dewatered, and deposed sludge is a consequence of their existence in wastewater and depends on the kind of wastewater (domestic, industrial, rain water). PAHs are successfully adsorbed on the solid particle surface in the process of wastewater purification as a result of their strong affinity to the solid phase [7]. Coking is one of the most important emission sources of PAHs in China, which accounts for 17.9% of the total annual PAHs emission in China, much higher than that in the United States [8,9]. PAHs are extremely harmful to human health and the environment because of their high toxicity, persistence in the environment, and bioaccumulation through the food chain [10]. It has been recognized that adsorption may play the main role in PAHs removal in most wastewater treatment plants due to the high affinity of PAHs for particulate matter [11–13]. Zhang et al. [14] also had reported that PAHs due to adsorption to sludge accounted for 24–76% in the coking wastewater treatment plant. The activated sludge process is indisputably the most frequently employed biological technique in coking wastewater treatment plants [1]. In China, the existing coking wastewater treatment plants mostly use anaerobic/anoxic/aerobic ($A_1/A_2/O$) bio-treatment process, since this combination is easily designed and operated [2]. However, Up to now the information about the adsorption characteristics of PAHs on activated sludge of $A_1/A_2/O$ treatment process is very limited. Adsorption kinetic, isotherm equilibrium, and the influencing factors are essential to improve the removals of PAHs during coking wastewater.

The objective of this present study is to identify and quantify 16 selected PAHs (US-EPA priority PAHs) in the sludge from a coking wastewater treatment plant with $A_1/A_2/O$ system, to character the activated sludge, to investigate the adsorption kinetics and equilibriums of PAHs, to conduct adsorption model determining the adsorption mechanism, to study the effect of mixed liquor suspended solids (MLSS), time and pH on PAHs adsorption by activated sludge, and to evaluate the potential risks of PAHs.

2. Materials and methods

2.1. Chemicals and materials

The standard solution which contained 16 PAHs compounds, each at 2,000 μg/mL and deuterated surrogate (each at 4,000 μg/mL) containing naphthene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12, and perylene-d12 were obtained from Supelco (Bellefonte, PA, USA). Hexamethylbenzene used as an internal standard for gas chromatography analysis was obtained from Aldrich Chemical. All solvents used for sample processing and analysis were HPLC grade. Deionized water was produced by a Milli-Q system (Millipore, Bedford, MA, USA).

For the adsorption experiment, naphthalene, phenanthrene, and pyrene were selected as adsorbates (purity as 99%) based on their typical molecular structures (with 2, 3, and 4 fused rings, respectively).

2.2. Coking wastewater treatment plant description and sampling

A full-scale coking wastewater treatment plant of Ansteel Group Corporation in Anshan, Liaoning province of china, which had been steadily employed for the treatment of actual coking wastewater for several years, was investigated. The scheme of coking wastewater was showed in Fig. 1.

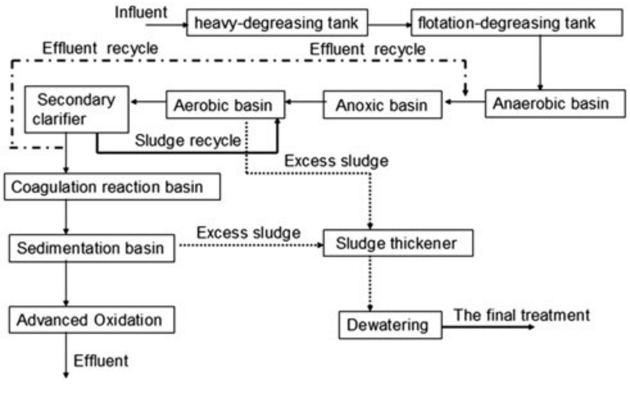

Fig. 1. The flow scheme of the coking wastewater treatment plant.

Sludge samples were gathered from anaerobic tank, anoxic tank, and aerobic tank, respectively. All the samples were taken on five separate days on 18–30 April 2014 and were freeze-dried at −20℃ before identification and quantification of PAHs. The anaerobic/anoxic tank was bio-film sludge, while the aerobic tank was activated sludge. In the aerobic tank, a sludge retention time of 15 d, and an average MLSS level of 5–6 g/L. Inactivated sludge as the adsorbent, which was not freeze-dried, was conducted the adsorption experiments.

2.3. Sample preparation, instrumental analysis, and quality control

The sludge samples were freeze-dried and then ground finely to pass through a 30-mesh sieve, extraction and separation of these samples were conducted according to the procedures described in the previous study [14,15]. PAHs in the coking wastewater sludge were analyzed qualitatively by gas chromatography-mass spectrometry (GC-MS) analysis according to the methods [14,15]. GC-MS analysis was conducted using an Agilent 6890 GC coupled with an Agilent 5973 mass spectrometer detector with a 30 m × 0.25 mm × 0.25 μm film thickness DB-5 MS column. The results were the average of five times.

The R^2 values of the PAH calibration curves were all greater than 0.99. The detection limits of the method ranged from 0.12 to 14.8 μg/g. The average recoveries for sludge samples were 65 ± 8%, 84 ± 9%, 90 ± 7%, 94 ± 7%, and 95 ± 8% for naphthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12, and perylene-d12, respectively.

The fresh activated sludge sample was washed with deionized water and centrifuged at 10,000 rpm for 15 min at 4℃. The pellet was washed and centrifuged twice more. After the last centrifugation, it was diluted to the required MLSS level with aqueous solution and stored at 4℃ before the adsorption experiments started. Deionized water was used for preparing the aqueous solution. 0.01 M $CaCl_2$ was added to the solution for maintaining a constant ionic strength and 200 mg/L NaN_3 was added to minimize biological activity [16]. The volume fraction of methanol in solution of Erlenmeyer flasks was controlled to less than 0.002 to avoid cosolvent effect [17].

2.4. Activated sludge characterization

For the characterization of activated sludge, elemental analysis was performed using a Vario Macro cube elementar analyzer (Elementar Company, Germany).The Brunauer–Emmett–Teller (BET) surface area, pore volume, and pore size distribution were determined using a Micromeritics ASAP 2020 nitrogen adsorption apparatus. The infrared spectra of the samples were analyzed in the range 400–4,000 cm^{-1} on a Bio Rad FTS 175C spectrophotometer using a pellet technique. Sample discs were prepared by mixing 5 mg of the samples with 95 mg of KBr in an agate mortar and scanned. The surface morphology was scanned by environmental scanning electron microscopy (ESEM) (JEOL, JSM 6700F).

2.5. Adsorption kinetic and isotherm experiments

Batch experiments were conducted to evaluate the kinetic and isotherm studies. Hundred and fifty milliliters of Erlenmeyer flasks containing 100 ml aqueous solution at 6 g/L MLSS were agitated on a rotary shaker (150 rpm) at room temperature (25℃). For the kinetic study, samples were collected at various time intervals and were centrifuged at 10,000 rpm for 15 min, and the supernatant was collected for PAHs quantification according to the method [18]. For the adsorption isotherm experiments, five concentrations of PAHs were used in the sorption test, after the equilibrium time, the samples were collected, centrifuged, and analyzed as above. Controls without activated sludge but with different concentrations of PAHs, and controls without different concentrations of PAHs but with activated sludge were prepared at the same time during the sorption test. The PAHs adsorbed by activated sludge were calculated from the mass balance of the PAHs concentrations between the experimental and control samples. All experiments were carried out in triplicate. The results were the average of three times.

Several kinetic models such as pseudo-first-order, pseudo-second-order, as well as the diffusion-based Weber–Morris model [19] are available to understand the behavior of the adsorbent and to examine the controlling mechanism of the adsorption process. In this study, the kinetic data of PAHs were analyzed using pseudo-second-order kinetic model, the linear pseudo-second-order model is given as Eq. (1):

$$\frac{t}{q_t} = \frac{1}{k_1 q_e^2} + \frac{1}{q_e} t \tag{1}$$

where k_1 (g /(μg min)) is the rate constant of pseudo-second-order adsorption, q_e (μg/g) is the PAHs concentration on the sludge. The q_e and k_1 could be determined from the slope and intercept by plotting t/q_t vs. t.

Three classical adsorption models, Linear, Langmuir, and Freundlich isotherms, are employed to describe PAHs adsorption equilibrium. The Langmuir isotherm is valid for monolayer adsorption onto a surface with a finite number of identical sites [20], the linear Langmuir isotherm model is given as Eq. (2):

$$\frac{1}{q_e} = \frac{1}{K_L q_m C_e} + \frac{1}{q_m} \tag{2}$$

where q_m (μg/g) is the maximum adsorption capacity of PAHs on activated sludge, C_e (μg/L) is the PAHs concentration in the aqueous phase at equilibrium, and K_L is the Langmuir constant (L/μg). The values of K_L and q_m could be determined from the intercept and slope by plotting $1/q_e$ vs. $1/C_e$.

The Freundlich model expresses the adsorption process on a heterogeneous surface with different binding energies [21]. The linear form is given as Eq. (3):

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e \tag{3}$$

where k_f and n are Freundlich constants and they could be determined from the intercept and slope by plotting $\ln q_e$ vs. $\ln C_e$.

Specific sorption coefficient K_d (L/g) is a frequently used characteristic value for the evaluation of the sorption behavior. This distribution coefficient is defined as the ratio of equilibrium concentrations of a test substance in a two phase system consisting of an adsorbent and an aqueous phase [22], the form is given as Eq. (4):

$$K_d = \frac{q_e}{C_e} \tag{4}$$

2.6. *Factors affecting the adsorption of PAHs on activated sludge*

The effect of pH was examined at 25℃ at 6 g/L MLSS on a rotary shaker (150 rpm) by assaying the PAH removal efficiency at pH values of 5.0, 6.0, 7.0, 8.0, 9.0, and 10.0, adjusted using NaOH and HCl solutions. To investigate the effect of MLSS concentration on the PAH removal efficiency at 25℃ at pH 7.0, MLSS concentration of 4, 5, 6, 7, and 8 g/L was used, respectively. Controls were prepared at the same time during the sorption test. After the equilibrium time, the samples were collected, centrifuged, and analyzed as above. All experiments were carried out in triplicate. The results were the average of three times.

2.7. *Evaluation the potential risks of PAHs*

A retention time of sludge in the aerobic tank was 15 d and the discharge of excess sludge was an important removal pathway of PAHs. Potential risks of PAHs should be paid attention to avoid secondary pollution. Benzo(a)pyrene equivalent concentration is a useful metric to quantitatively assess the carcinogenic health risk of PAH [23], which is calculated for each sample by multiplying the concentration of each species by its toxic equivalency factor (TEF) [24,25].

3. Results and discussion

3.1. *Quantitative determination of PAHs in coking wastewater sludge*

Table 1 showed that the mean concentrations of total 16 PAHs in the anaerobic sludge, anoxic sludge,

Table 1
Mean PAH concentrations in three sludge samples (unit: μg/g n = 5)

PAH compound	Short name	Anaerobic sludge	Anoxic sludge	Aerobic sludge
Naphthalene	Nap	55.160	48.774	28.741
Acenaphthene	Ace	85.956	126.834	29.636
Acenaphthylene	Acy	142.166	160.512	68.501
Fluorene	Fle	97.7083	102.536	30.043
Phenanthrene	Phe	297.027	164.631	65.304
Anthracene	Ant	159.221	108.600	20.817
Fluoranthene	Flu	188.995	55.625	41.291
Pyrene	Pyr	223.315	79.089	20.329
Benzo[a]anthracene	BaA	187.367	78.278	27.447
Chrysene	Chr	293.487	142.680	55.026
Benzo[b]fluoranthene	BbF	52.825	67.297	43.403
Benzo[k]fluoranthene	BkF	80.229	36.183	18.951
Benzo[a]pyrene	BaP	126.719	54.386	50.847
Indeno[1,2,3-cd]pyrene	Inp	80.450	44.6583	31.069
Dibenzo[a,h]anthracene	DBA	37.724	27.120	19.270
Benzo[g,h,i]perylene	BgP	93.284	40.052	30.925
Total		2,201.633	1,337.255	581.600

and aerobic sludge were 2,201.633, 1,337.255, and 581.600 μg/g, respectively, this was different from the results reported by Zhang et al. [15], the concentration of total PAHs in the coking wastewater sludge was 4,830–6,690 μg/g. Compared with the anaerobic sludge and anoxic sludge, concentration of total PAHs in the aerobic sludge was lower, the discharge of excess sludge could be an important removal pathway of PAHs [14]. Acenaphthylene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, and benzo[a]pyrene were the dominant compounds in the anaerobic sludge. The concentrations of acenaphthene, acenaphthylene, fluorene, phenanthrene, anthracene, and chrysene in the anoxic sludge were all above 100 ug/g, while the concentrations of 16 PAHs in the aerobic sludge were all less than 70 μg/g. The concentration of benzo[a]pyrene, which was usually considered an indicator because of its strong and direct carcinogenicity [26], ranged from 50.847 to 126.719 μg/g in the three sludge samples. 1,602 t of benzo[a]pyrene was discharged to the wastewater in Chinese coking industry [27].

3.2. Time profile of PAHs adsorption on activated sludge

Plots of adsorbed PAHs on the inactivated sludge vs. time at room temperature were showed in Fig. 2. It showed a great tendency to sorb on the sludge in the first 30 min, followed by slow sorption reaction up to the equilibrium time. At all initial concentrations tested, the adsorption reached equilibrium after 1 h. This was consistent with the result which showed that activated sludge sorption equilibrium was achieved within one hour for PAHs [28]. So, 2 h was used as the equilibrium time in the following adsorption isotherm experiments.

Quantitative determination and time profile of PAHs adsorption, adsorption phenomena for PAHs by coking wastewater activated sludge were apparently found. Sorption phenomena play an important role in the fate of organic micropollutants not only in the environment but also in wastewater treatment systems, this is especially the case for hydrophobic micropollutants [28]. In order to reveal the adsorption mechanism, characterization of sludge, the adsorption

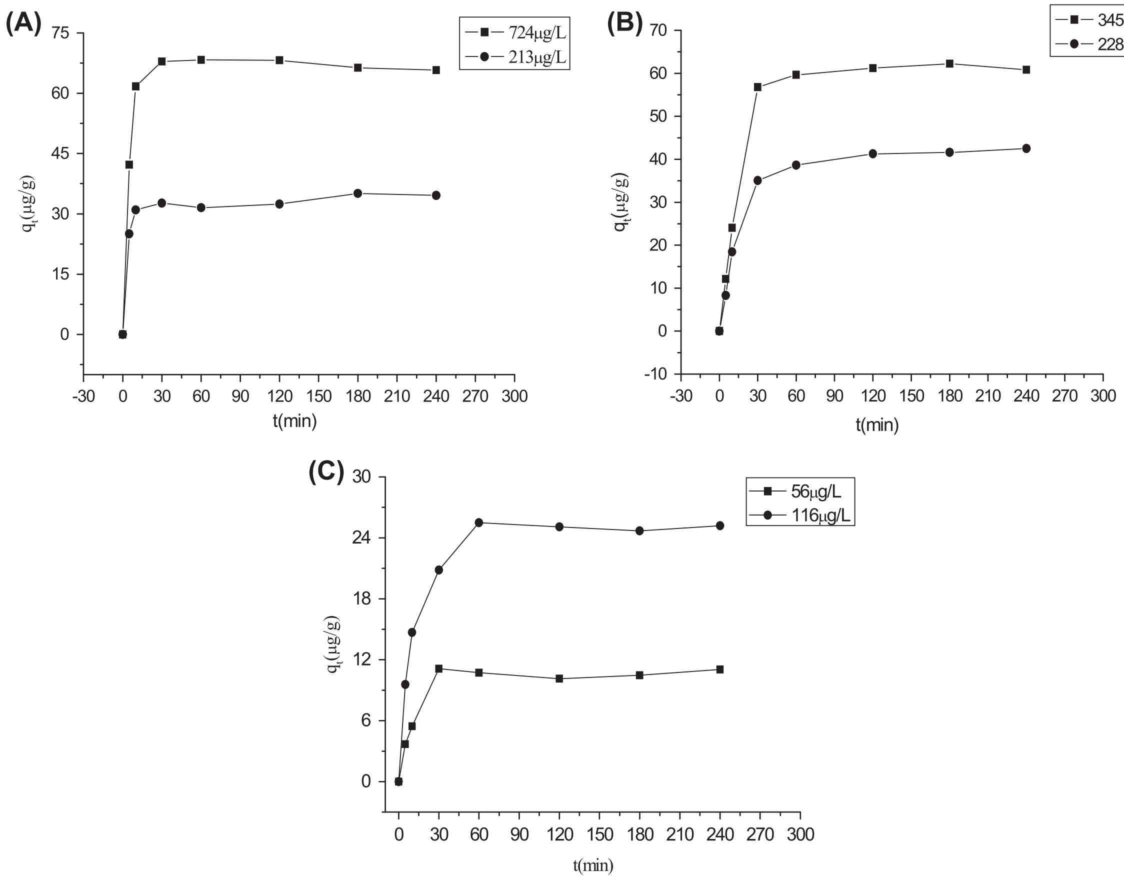

Fig. 2. Time profile of PAHs: (A) naphthalene, (B) phenanthrene, and (C) pyrene adsorption on activated sludge.

kinetics and isotherms of PAHs needed to be investigated.

3.3. Characterization of activated sludge

The N_2 adsorption/desorption isotherms of activated sludge showed that adsorption curve belonged to type III according to the IUPAC classification (Fig. 3(A)). The specific surface area and pore volume of activated sludge were summarized in Table 2 and the pore size distribution was showed in Fig. 3(B). The surface area of sludge was very small, only 1.76 m^2/g, this was consistent with the pore volume, which was 0.01 cm^3/g. This could also be demonstrated by the result of ESEM image, which indicated that activated sludge had a rough and no porous surface (Fig. 3(C)). Elemental analysis was mainly used to determine the total percent values of carbon, hydrogen, oxygen, nitrogen, and sulfur, the results of which were depicted in Table 2. The group frequencies (Fig. 3(D)) for the adsorption bands at 3,000–3,500, 2,920, 2075, 1,650, 1,542, 1,456, 1,240, 1,076, and under 900 cm^{-1} were assigned to stretching/bending vibration of groups as shown in Table 3 [29–33].

3.4. Adsorption kinetics and isotherms

The kinetic constants were presented in Table 4. The model's correlation coefficient was >0.99 and the experimental q_c values were very close to the q_e calculated values. This suggested that the adsorption of PAHs did follow pseudo-second-order kinetic. The kinetic process of naphthalene adsorption onto a high-surface-area carbon was also suitable to be described by pseudo-second-order model [34].

As shown in Fig. 4(A)–(C), linear model of adsorption isotherm fitted well with the experimental data with the correlation coefficients (R^2) greater than 0.95. The specific sorption coefficient K_d for naphthalene, phenanthrene, and pyrene was 0.072, 1.406, and 27.753, respectively. A positive correlation between specific sorption coefficient K_d and octanol-water

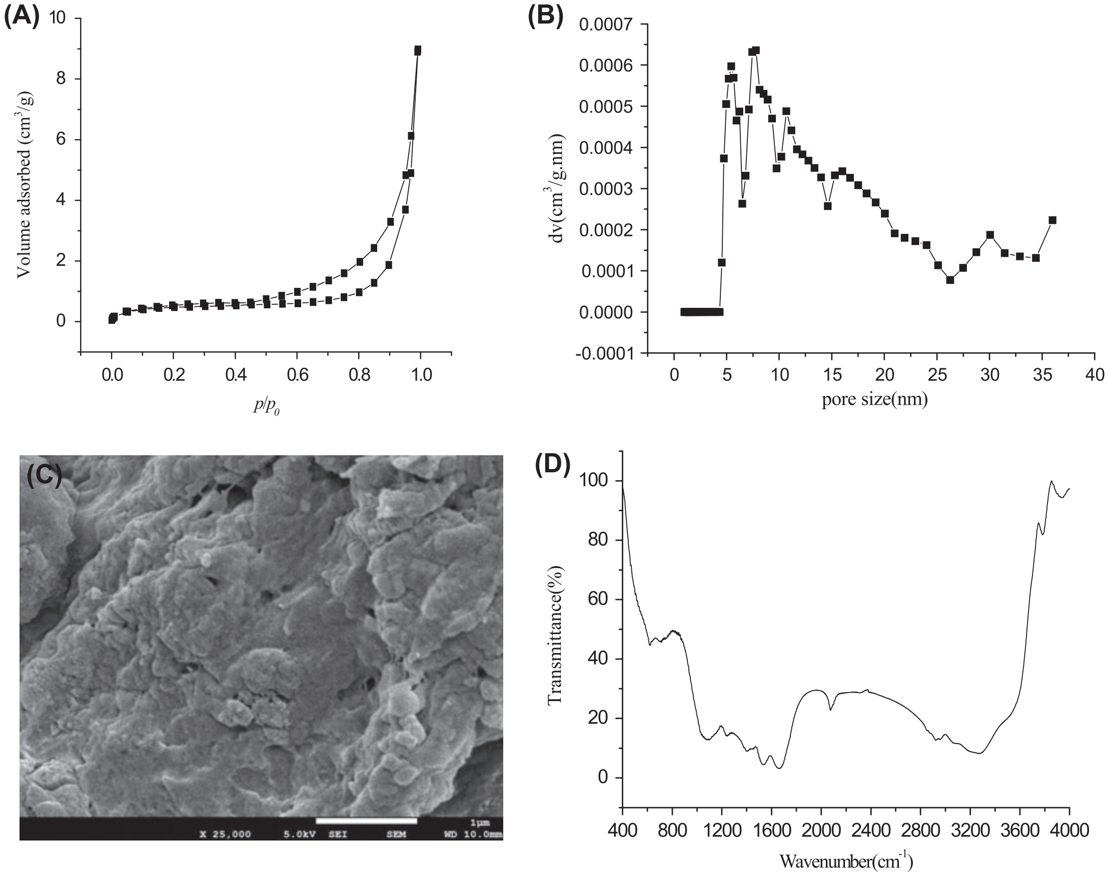

Fig. 3. Characterization of activated sludge: (A) N_2 adsorption–desorption isotherm, (B) pore size distribution, (C) scanning electron microscope, and (D) FTIR spectra.

Table 2
characteristics of activated sludge

Elemental composition (%)					BET	V_t	D_p
Carbon	Hydrogen	Oxygen	Nitrogen	Sulfur	m^2/g	cm^3/g	nm
48.24	5.55	30.03	7.89	3.10	1.76	1.38×10^{-2}	31.52

Note: D_p: average pore diameter.

partition coefficient k_{ow} was found (R^2 = 0.9201) in Fig. 4(D). This can be explained by the order of the PAH hydrophobicity [35], pyrene > phenanthrene > naphthalene, this could also be demonstrated by the results reported by Liu et al. [16].

The results of regression analysis using Freundlich and Langmuir models were showed in Table 5, which indicated that Freundlich model fitted well with the experimental data with the correlation coefficients (R^2) greater than 0.93, this was similar to the results found by Liu et al. [16], who also confirmed that the adsorption of PAHs by activated sludge well followed the Freundlich isotherm. In the Freundlich model, the Freundlich exponent $1/n$ was close to 1 ranging from 0.9179 to 1.038 for naphthalene and phenanthrene, while 2.242 for pyrene. Langmuir model for selected PAHs showed that the assumption of homogenous distribution of sorption energy in the model was not valid, this indicated that no site limitation for monolayer sorption on a surface could be assumed [22].

Adsorption kinetics and isotherms are important physical parameters in the biological process for PAHs removals. According to pseudo-second-order model, both Linear and Freundlich adsorption models, the effective removal of PAH is controlled.

Table 3
Stretching/bending vibration of groups of activated sludge

Wavelength (cm^{-1})	Stretching/bending vibration of groups
Under 900	Benzene ring and fused aromatic rings
1,076	Stretching C–O in the carbohydrate
1,240	Stretching vibration of C–N stretch in protein
1,456	Stretching vibration of C–H in fatty substances
1,542	Bending vibration of N–H in protein
1,650	Stretching of C–C, –COO or C–O in aromatic structure, Bending vibration of N–H in protein
2075	Stretching vibration of –CN and C–C stretch
2,920	Stretching vibration of C–H in fatty substances
3,000–3,500	Stretching vibration of –OH in the carboxylic acid group or phenol, –NH in the amines

Table 4
The adsorption kinetic parameters of PAHs on activated sludge

			Pseudo-second-order model		
PAHs	Concentration (μg/g)	q_c (μg/g)	q_e (μg/g)	k_1	R^2
Naphthalene	724	68.19	66.36	1.13×10^{-2}	0.9995
	213	32.43	34.81	1.21×10^{-2}	0.9984
Phenanthrene	345	61.21	65.66	1.62×10^{-3}	0.9882
	228	42.28	44.96	1.53×10^{-3}	0.9921
Pyrene	116	25.08	26.17	1.47×10^{-2}	0.9986
	56	10.14	11.49	0.76×10^{-2}	0.9958

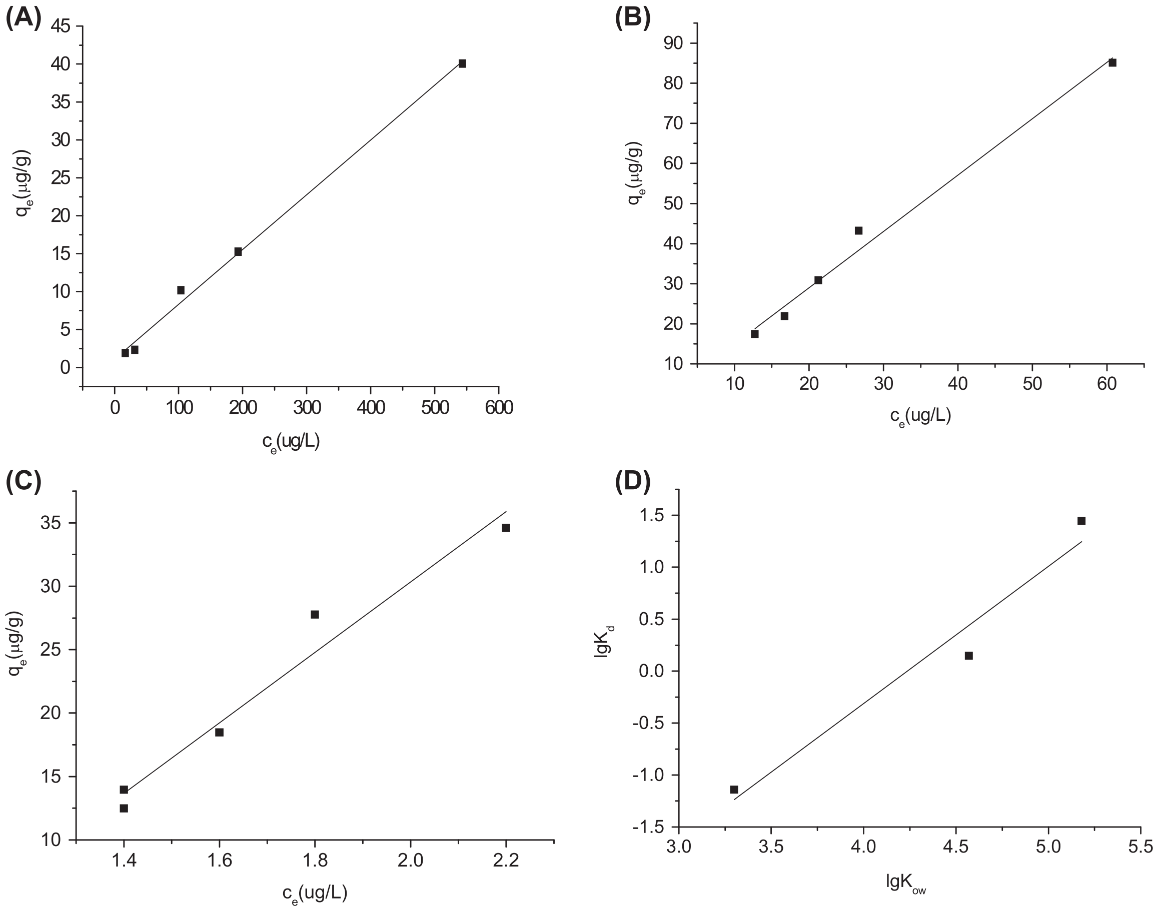

Fig. 4. Adsorption isotherms of PAHs: (A) naphthalene, (B) phenanthrene, (C) pyrene on activated sludge, and (D) the relationship between K_d and k_{ow} of PAHs.

Table 5
The adsorption isotherm parameters of PAHs on activated sludge

	Langmuir model		Freundlich model		
PAHs	K_L	R^2	K_F	$1/n$	R^2
Naphthalene	3.43×10^{-3}	0.8999	0.1249	0.9179	0.9799
Phenanthrene	-2.96×10^{-3}	0.9811	1.2532	1.038	0.9795
Pyrene	−0.331	0.9118	6.4287	2.242	0.9356

3.5. Factors affecting the adsorption behavior of PAHs on activated sludge

The pH value of the solution is an important controlling factor in the adsorption progress, which can influence the solubility of the adsorbate and the electrostatic and dispersive interactions between the adsorbent and adsorbate [34]. The influence of pH on PAHs adsorption was evaluated at a constant temperature of 25℃. Fig. 5(A) showed that the adsorption efficiencies of PAHs were not affected by pH because PAHs were non-polar, non-ionizable aromatic compounds and did not occur in aqueous solution.

In actual coking wastewater treatment system, excess sludge was recycled to aerobic tank in order to keep the concentration of MLSS and the pollutants were removed effectively. Fig. 5(B) showed that the removal efficiency increased with increasing sludge concentration, this can be partially attributed to the

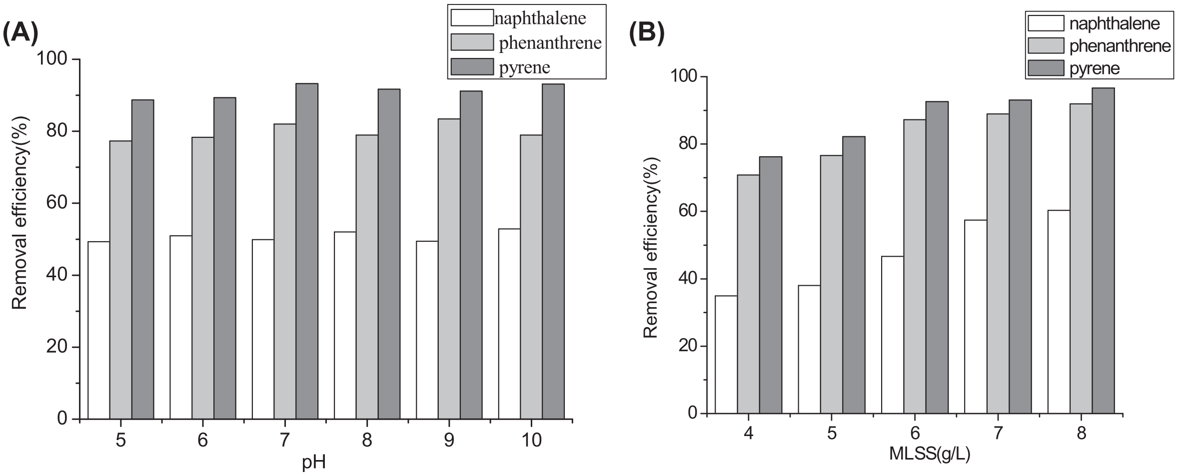

Fig. 5. Adsorption of PAHs on activated sludge as a function of (A) pH and (B) MLSS.

Table 6
Proposed toxicity equivalency factors (TEFs) and evaluation the potential risks for individual PAHs

PAHs	TEF	Concentration (μg/g)	BaP equivalent concentration (μg/g)
DBA	1.1	19.270	21.197
BaP	1	50.847	50.847
BaA	0.1	27.447	2.7447
BbF	0.1	43.403	4.3403
BkF	0.1	18.951	1.8951
Inp	0.1	31.069	3.1069
Ant	0.01	20.817	0.20817
BgP	0.01	30.925	0.30925
Chr	0.01	55.026	0.55026
Ace	0.001	29.636	0.029636
Acy	0.001	68.501	0.068501
Flu	0.001	41.291	0.041291
Fle	0.001	30.043	0.030043
Nap	0.001	28.741	0.028741
Phe	0.001	65.304	0.065304
Pyr	0.001	20.329	0.020329

increased availability of more adsorption sites. However, the removal efficiency changed slightly at sludge concentration larger than 6.0 g/L. In order to improve the removal efficiency of PAHs, the sludge concentration should not be less than 6.0 g/L.

3.6. Adsorption mechanism of PAHs on activated sludge

In a well-stirred solid–liquid system, the PAHs uptake process on porous carbon consisted of three successive steps and three main mechanisms that may be applicable to PAH adsorption had been proposed: the H-bonding formation, the electron donor-acceptor interaction, and the π–π interaction [35]. The sorption equilibriums for naphthalene, phenanthrene, and pyrene had been shown to result within one or two hours at mesophilic temperatures, which were the most common in sludge treatment processes, these kinetics differed completely from those of other environmental systems such as soils and sediments, in which the phenomenon of diffusion limited the transfer of micropollutants to interaction sites, resulting in an equilibrium time of about 24 h [28], also differed from that of porous carbon. Adsorption phenomena for PAHs on coking wastewater activated sludge were apparently found in this study, the adsorption reached equilibrium after 1 h.

The kinetics followed pseudo-second-order model. The pseudo-second-order model indicates that chemisorption dominated in the adsorption process

[36]. By comparing infrared analysis of adsorption of PAHs on activated sludge, it was found that the wavelength at 2,920 cm^{-1} had a blue shift after adsorption of phenanthrene and pyrene. After adsorption of naphthalene, phenanthrene, and pyrene, the wavelength at 900 cm^{-1} shifted to red, the wavelength at 1,076 cm^{-1} had a blue shift (Figures not shown). So, it was speculated that there PAHs could bind to the benzene/fused aromatic ring and C–O in carbohydrate, and at the same phenanthrene and pyrene could bind to C–H in fatty substances. The role of hydrogen bonding could be also inevitable.

Because of the heterogeneous surface with different binding energies and the role of distribution, adsorption equilibriums of PAHs on coking wastewater activated sludge belonged to both Linear and Freundlich adsorption models, this was consistent with the results [37,38]. The order of K_d was pyrene > phenanthrene > naphthalene, and a positive correlation between specific sorption coefficient K_d and octanol-water partition coefficient k_{ow} was found. Elemental analysis showed that the percent values of carbon, hydrogen, oxygen, nitrogen, and sulfur were 48.24, 5.55, 30.03, 7.89, and 3.10%, respectively. Those showed that hydrophobic interaction and distribution role had a great contribution to the PAHs adsorption. While the surface area of activated sludge and the pore volume were very small, they could not be the main contribution.

3.7. Evaluation the potential risks of PAHs

As shown in the Table 6, the equivalent concentrations for Inp, BkF, BbF, BaA, BaP, and DBA were all above 1.0 μg/g, the order of carcinogenic health risk was BaP > DBA > BbF > Inp > BaA > BkF, while that for Ant, BgP and Chr were more than 0.2 μg/g. The equivalent concentrations for Ace, Acy, Flu, Fle, Nap, Phe and Pyr were far less than 0.1 μg/g.

4. Conclusions

This study examined the concentrations of PAHs in the coking wastewater sludge by GC-MS method, the concentrations of 16 PAHs in the sludge were 2,201.633–581.600 μg/g. Adsorption phenomena for PAHs on activated sludge were apparently found, adsorption reached equilibrium after 1 h at an MLSS level of 6 mg/L at 25℃. The process was well fit by the pseudo-second-order kinetic model and the Freundlich isotherm model. At pH 5.0–10.0, there was no significant effect on PAHs adsorption, time and MLSS affected the adsorption process. Hydrophobic interaction, distribution, and chemisorption were mainly responsible for the adsorption of PAHs. Evaluation the potential risks of PAHs showed that benzo (a)pyrene equivalent concentrations for Inp, BkF, BbF, BaA, BaP, and DBA were all above 1.0 μg/g.

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