Pollution characteristics of polycyclic aromatic hydrocarbons in common used mineral oils and their transformation during oil regeneration

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ABSTRACT

The pollution characteristic of polycyclic aromatic hydrocarbons (PAHs) in common used mineral oils, semi-refined oils, refined oils and solid wastes produced during the used mineral oil regeneration process was analyzed. The results showed that total PAHs content in six common used mineral oils was as follows: used engine oil > used quenching oil > used casting oil > used hydraulic oil > used antirust oil > used industrial lubricating oil. Furthermore, this order was dependent on the source of PAHs and oil working temperatures. Additionally, total PAHs content in regenerated oils was as follows: semi-refined oil > refined oil > crude oil, which was related to the catalytic cracking process of crude oil and adsorption refining process of semi-refined oil. The ranking of total PAHs content in regenerated wastes varied depending on the regeneration technology used as follows: waste adsorption sand > acid sludge > waste clay > precipitation sludge > cracked residue. In all types of used mineral oils and regenerated wastes, the maximum and minimum proportions of the total PAHs content were composed of 2–3 ring-PAHs and 5–6 ring-PAHs, respectively. The majority of PAHs in the used mineral oils entered into regenerated wastes during regeneration process, while a small number remained in the regenerated oil.

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Introduction

With the widespread use of coal and petroleum in industrial production and transportation, now mineral oil has become an important fossil fuel worldwide. Mineral oil extracted from oil, coal and oil shale cannot be used continually because external factors alter its original physical and chemical properties, resulting in generation of waste mineral oil (Pratt et al., 1999). There are a variety of toxic materials in mineral oil including heavy metals, benzene series and polycyclic aromatic hydrocarbons (PAHs). This was closely related to the usage and production process of used oils (Magiera et al., 2003). Accordingly, used mineral oil has the potential to cause serious harm to the ecological environment and human health if it is discharged directly into the environment. According to the statistics, a barrel of used mineral oil (200 L) dumped into lake or sea can cause about 3.5 km^2 area of the water pollution (Qiao et al., 2015). If poured into the soil, it can make contaminated site grow nothing even for 3 to 5 years (Qiao et al., 2015). Because of the obvious toxicity and

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flammability, used mineral oil has been listed as a class 8 hazardous waste (HW08) according to the National Hazardous Wastes Catalogue in China (Wang et al., 2013).

However, used mineral oil has high regeneration value through appropriate regeneration technology. Recycled used mineral oil can be used though either energy regeneration or materials regeneration (Zenon et al., 2010). The energy regeneration mainly includes direct combustion and regeneration into fuel oil. Pollutants in the used mineral oil can cause serious secondary pollution to the environment when used mineral oil was burned directly without any treatment. Regeneration into fuel oil is a major renewable way for used mineral oil at present through pyrolysis and catalytic pyrolysis methods. However a lot of secondary pollutants such as oily wastewater, acid slag, waste clay produced in the course of regeneration should be disposed safely. The materials regeneration of used mineral oils refers to the regeneration into the high quality base oil through depth refining process such as short-range distillation, flocculation, hydrofining, and reduced pressure distillation (Bartz, 1998).

Developed countries have formulated a series of strict and detailed laws, rules, regulations and policies for used mineral oil management from collection to disposal, which promotes environmental management and reuse of used mineral oils. In China, there are still many problems associated with used mineral oil management. Compared with the total quantity, the actual amount of used mineral oil brought into hazardous waste management is relatively less (recovery of 6%), and the regeneration utilization is relatively low. What is more, there has been a large amount of environmental pollution events of used mineral oils. Further research into the pollution characteristics of used mineral oil is needed to improve the value of recycled oils and strengthen the environmental management of used mineral oils.

PAHs are considered to be persistent contaminants that may be toxic to living creatures. Because of their mutagenic, carcinogenic and teratogenic properties, 16 PAHs have been classified as priority substances by the United States Environmental Protection Agency (USEPA) and the European Union (EU) (Lindgren et al., 2014). PAHs have been found in crude oil and the recycled oils. In order to further understand the pollution characteristics of PAHs in used mineral oils and regenerated products, this study was conducted to characterize the residual level, composition and transportation of PAHs in used mineral oil, regenerated oil products and regenerated wastes using the City of Chongqing, China as the study area. The results presented herein will be useful for environmental risk assessment and pollution control management of used mineral oil.

1. Materials and methods

1.1. Sample collection

Samples were collected from used mineral oil production and regeneration companies of vehicle maintenance, machining, and chemical synthesis industries in Chongqing, China. Used mineral oil samples in barrels were homogeneously mixed prior to collection. Collected samples included six common types of used mineral oils (engine oil, quenching oil, casting oil, antirust oil, industrial lubricating oil, and hydraulic oil), three kinds of regenerated oils (crude oil, semi-refined oil, refined oil), and five kinds of regenerated wastes (waste adsorption sand, cracked residue, precipitation sludge, acid sludge, and waste clay). Samples were collected into wide brown glass bottles and stored at 8 °C until analysis.

1.2. Sample pre-treatment

The steps used to treat oils were as follows: 2 g of blended samples were placed into 50 mL centrifuge tubes, after which 10 mL of acetone and 2 g of sodium sulfate anhydrous were added. The samples were eddied for 1 min and vibrated for 30 min, then centrifuged at 5000 r/min for 5 min. The supernatant was then filtered through a 0.22-μm membrane and analyzed by gas chromatography–mass spectrometry (GC–MS), as described below. Disposal methods for acid sludge and other samples were identical to those of oil samples, except 10 mL of n-hexane was used instead of acetone.

1.3. Sample testing and quality control

Sixteen types of PAHs, naphthalene (Nap), acenaphthylene (Acy), acenaphthylene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flu), pyrene (Pyr), benzo [a] anthracene (BaA), chrysene (Ch), benzo [b] fluoranthene (BbF), benzo [k] fluoranthene (BkF), benzo [a] pyrene (BaP), indeno [1, 2, 3-cd] pyrene (InP), dibenzo [a, h] anthracene (DBA), and benzo [g, h, i]) perylene (BgP), were measured. The GC–MS instrument (Agilent 7890) was used for sample analysis. Specific chromatographic and mass spectrometry conditions are shown in Tables 1 and 2, respectively.

To further reduce experimental error, parallel experiments, blank experiments and recovery experiments were conducted. The adding standard amount in blank recovery was 5 mg/kg and 10 mg/kg. The recovery was 73.0%–75.3% for Nap, 65.6%–77.8% for Acy, 74.2%–78.0% for Ace, 94.6%–98.7% for Flu, 61.9%–87.9% for Phe, 93.8%–101.6% for Ant, 64.2%–83.27% for Fla, 68.5%–69.3% for Pyr, 80%–89.9% for BaA, 96.6%–97.9% for Chr, 75.4%–83.3% for BbF, 70.1%–71.7% for BkF, 70.5%–85% for BaP, 66.5%–68.7% for InP, 66.3%–79.3% for DBA and 74.8%–83.2% for BgP. The instrument detection limit was

Table 1 – Specific chromatographic conditions during analysis.	
Program	Parameter
Chromatographic column	DB-5MS quartz capillary column, 30 m × 0.25 mm × 0.25 μm
Injection port temperature	260°C
Temperature program	Initial temperature, 60°C; held for 1 min, then increased to 180°C at 20°C/min, where it was held for an additional 1 min. It was then increased to 300°C at 5°C/min, where it was held for 5 min
Carrier gas	Helium with more than 99.999% purity, 1 mL/min flow rate
Sampling method	Un-split sampling
Sample size	1 μL

Table 2 – Specific mass spectrometry conditions for sample testing.

| Program	Parameter
Ion source temperature	230°C
Interface temperature	260°C
Electrospray ionization	Electron impaction source
Ionizing energy	70 Ev
Solvent delay time	5 min

defined as three times the signal-to-noise ratio. Based on 2 g of used mineral oil (capacity of 10 mL), the detection limit of DBA and Bgp were 0.0200 mg/kg and 0.0218 mg/kg, and the detection

limit of 0.0012–0.0115 mg/kg was observed for the other 14 PAHs. Sample testing and blank testing was completed simultaneously. Sixteen kinds of PAHs were not detected in blank testing.

2. Results and discussion

2.1. Analysis of PAHs content in common used mineral oils

Fig. 1 shows the concentration and percentage of PAHs in common used mineral oils. In addition to the used engine oil,
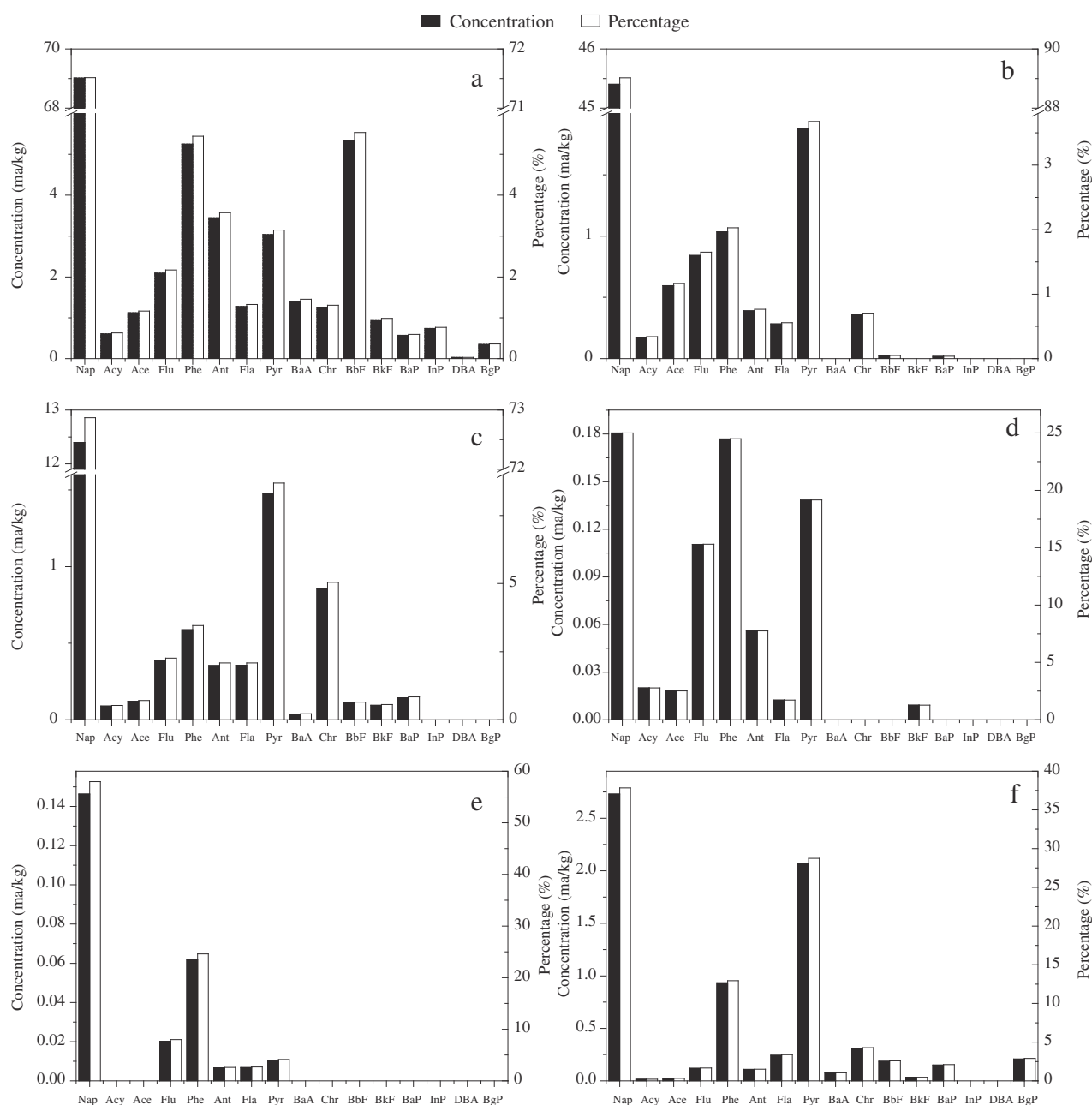
Fig. 1 – Concentration and percentage content of PAHs in six kinds of used mineral oil. (a) used engine oil; (b) used quenching oil; (c) used casting oil; (d) used antirust oil; (e) used industrial lubricating oil; (f) used hydraulic oil. PAHs: polycyclic aromatic hydrocarbons.

not all 16 types of were found in the other five types of used mineral oil. There were great differences in the content of PAHs in different types of used mineral oil. In general, the detection rate increased as the total PAHs content increased. Nap in six common types of used mineral oil was present at the highest levels among PAHs (0.1–69.0 mg/kg), accounting for 25.0%–89.0% of the total.

The total PAHs content of the six kinds of used mineral oil occurred in the following order: used engine oil (96.5 mg/kg) > used quenching oil (51.0 mg/kg) > used casting oil (17.0 mg/kg) > used hydraulic oil (7.2 mg/kg) > used antirust oil (0.7 mg/kg) > used industrial lubricating oil (0.3 mg/kg). These variations were related to the source of the PAHs in used mineral oils. The main sources of PAHs in the used engine oil were base oil, fuel oil and engine oil. The base oil contains a certain amount of PAHs (Wong and Wang, 2001), while the PAHs content in the engine oil would greatly increase with the combustion process of fuel oil. This also explained Wong's findings that total PAHs content in engine oil increased rapidly with increasing mileage (Wong and Wang, 2001). Because of the higher operating temperature (230°C–250°C), engine oil is easily oxidized, which generates new PAHs through mechanism of hydrogen abstraction and carbon addition (HACA) (Zheng et al., 2013). The sources of PAHs in used quenching oil and used casting oil were similar and both came from the oxidation of base oil. The significantly greater total PAHs content in used quenching oil than used casting oil was mainly because of differences in working temperature (>600°C vs. 130°C–180°C, respectively) and working time (Truhan et al., 2005). The sources of PAHs in used hydraulic oil, used antirust oil and used industrial lubricating oil were similar; however, their PAHs contents differed owing to differences in working temperature and working time (Shan-Tan and Isaac, 2008). Specifically, the working temperature of used hydraulic oil was higher (80°C–120°C) than that of used antirust oil and used lubricating oil (generally ambient temperature).

2.2. Analysis of PAHs content in regeneration products

Pollutants in used mineral oils are likely to enter into the regenerated oils or regenerated wastes during the regeneration process. As a result, the PAHs transformation during regeneration process of used oils focuses mainly on the distribution of PAHs in crude oil, regenerated oil products (semi-refined oil and refined oil) and regenerated wastes.

The regeneration of used mineral oil usually combines simple regeneration methods with depth regeneration methods (Lázaro et al., 2002). Simple regeneration of used mineral oil is mainly through heating, centrifugation, sedimentation, adsorption, filtration and other physical methods for regeneration with some additives (Khelifi et al., 2006). During this regeneration process part of PAHs entered into oil residue, acid sludge, waste clay and waste water, while the other part of PAHs remained on the regenerated oils. Depth regeneration can make used mineral oil turn into base oil, fuel oil and diesel oil through the way of sulfuric acid refining, distilling, splitting, hydrogenating, etc. (Khelifi et al., 2006).

2.2.1. Analysis of PAHs content in regenerated oils
The PAHs content in the crude oil, semi-refined oil and refined oil was shown in Table 3. The Nap content in the three kinds of regenerated oils was highest, and its percentage content accounted for more than 50%. The total PAHs content from high to low was as follows: semi-refined oil (273.1 mg/kg) > refined oil (133.8 mg/kg) > crude oil (106.2 mg/kg). This was related to the catalytic cracking process of crude oil and adsorption refining process of semi-refined oil. The composition of crude oil was complex, consisting of a mixture of a variety of used oils. Catalytic cracking is commonly used in refining crude oil into fuel oil. A portion of the PAHs in the cracking process generates low-ring PAHs, and new PAHs are produced from a large number of unsaturated hydrocarbons through HACA mechanism (Böhm and Jander, 1999). This explained why the total PAHs content in crude oil was less than that in semi-refined oil and refined oil.

Table 3 – PAHs concentration in crude oil, semi-refined oil and refined oil (mg/kg).						
PAHs	Crude oil		Semi-refined oil		Refined oil	
	Range	Mean value	Range	Mean value	Range	Mean value
Nap	38.77–76.28	57.93	127.11–154.30	140.71	50.78–109.66	78.67
Acy	0.79–3.18	1.79	2.25–9.63	5.94	0.93–8.05	3.38
Ace	0.66–1.75	1.13	19.97–27.60	23.79	11.96–19.47	15.57
Flu	2.47–27.06	11.06	14.61–27.54	21.08	0.67–12.27	5.83
Phe	6.39–15.78	11.05	n.d.–0.94	0.47	n.d.-0.62	0.39
Ant	2.29–10.88	7.11	26.80–47.74	37.27	13.67–28.77	20.37
Fla	1.38–3.07	1.95	n.d.–0.27	0.13	0.96–1.41	1.16
Pyr	3.00–6.48	4.37	14.52–27.60	21.06	0.23–12.17	6.83
BaA	0.76–4.56	2.18	n.d.	n.d.	n.d.	n.d.
Chr	0.14–4.89	1.92	2.12–6.84	4.48	0.72–0.85	0.80
BbF	n.d.-6.91	2.37	n.d.-0.01	0.01	n.d.-0.02	0.01
BkF	0.01–1.86	0.70	0.12–2.10	1.12	0.10–0.29	0.19
BaP	0.48–1.73	0.97	0.06–9.72	4.89	0.10–0.92	0.50
InP	0.14–2.89	1.07	n.d.–1.72	0.86	n.d.	n.d.
DBA	n.d.–0.11	0.05	n.d.–1.81	0.90	n.d.	n.d.
BgP	0.23–0.86	0.55	n.d.–21.85	10.93	n.d.-0.20	0.08
PAHs	62.33–133.06	106.19	208.79–338.43	273.07	93.74–192.54	133.77

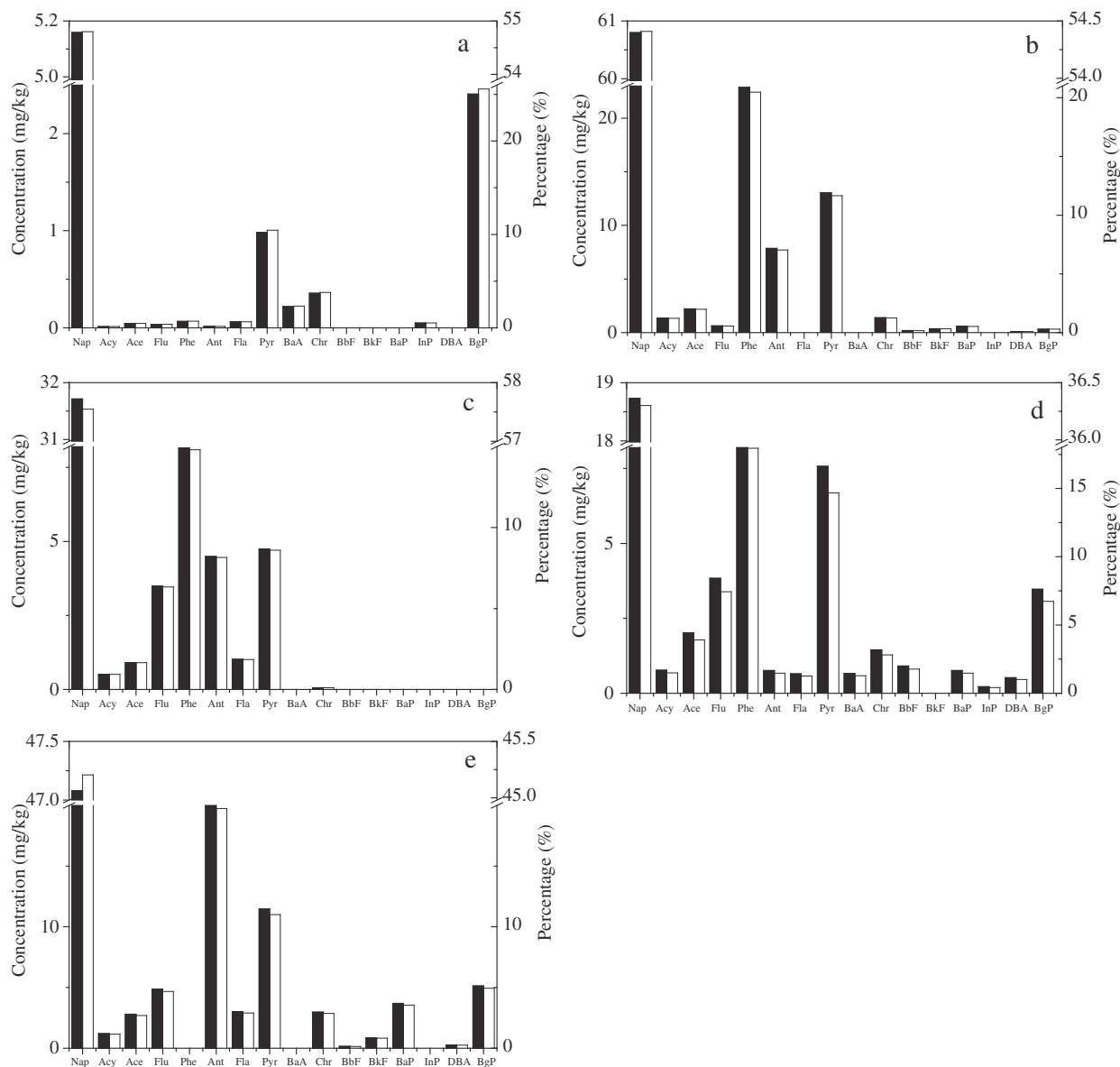PAHs: polycyclic aromatic hydrocarbons; n.d.: not detectable.

Adsorbed materials (such as adsorption sand and clay) were used to conduct the adsorption refining process to improve color and smell of oil products during the transformation from semi-refined oil to refined oil (Khelifi et al., 2006). In that process, a portion of PAHs in the semi-refined oil can be adsorbed onto the adsorption material because of its molecular polarity. Therefore, total PAHs content in refined oil was less than that in semi-refined oil. In summary, the differences in PAHs content in crude oil, semi-refined oil and refined oil were mainly due to catalytic cracking of crude oil and adsorption refining of semi-refined oil.

2.2.2. Analysis of PAHs content in regenerated wastes

The concentration and percentage of PAHs in regenerated wastes are shown in Fig. 2. There were 13 kinds of PAHs in cracked residue at concentrations ranging from 0.0 mg/kg to 5.2 mg/kg. In waste adsorption sand, 12 kinds of PAHs were present at 0.1–60.8 mg/kg, while nine kinds of PAHs at levels of 0.1–31.7 mg/kg were detected in waste clay. There were 15 and 13 kinds of PAHs in precipitation sludge and acid sludge at levels of 0.2–8.7 mg/kg and 0.2–47.1 mg/kg, respectively. Nap was present at the highest levels in five types of regenerated wastes, accounting for more than 35% of the total PAHs. The remaining PAHs were present at relatively low levels in the five regenerated waste oils.

The concentration and compositions of PAHs in the five regenerated wastes showed obvious differences. The total PAHs content from high to low was as follows: waste adsorption sand (111.7 mg/kg) > acid sludge (104.2 mg/kg) > waste clay (55.1 mg/kg) > precipitation sludge (51.6 mg/kg) > cracked residue (9.4 mg/kg). This was mainly caused by different regeneration technologies and methods used in the regeneration process.

Fig. 2 – Concentration and percentage of PAHs in regenerated wastes. (a) cracked residue; (b) waste adsorption sand; (c) waste clay; (d) precipitation sludge; (e) acid sludge. PAHs: polycyclic aromatic hydrocarbons.

Because of the high cracking temperature, a large amount of PAHs that originated from crude oil or generated during the cracking process all entered into the semi-refined oil. Conversely, only a small portion of PAHs from the crude oil remained in the cracked residue. Waste adsorption sand and waste clay were both produced during the adsorption refining process of semi-refined oil. The main differences in PAHs content between waste adsorption sand and waste clay were in their PAHs adsorption ability, and in PAHs content of semi-refined oil and dosage of adsorptive material in the practical process (Teresa et al., 2006). Precipitation sludge was generated during the production of crude oil, indicating that the PAHs in precipitation sludge came directly from the crude oil. Acid sludge was produced during the sulfuric acid refining of crude oil, when a portion of the PAHs in the crude oil was sulfonated or dissolved into sulfuric acid, and eventually into acid sludge.

Thus, it was concluded that most of PAHs in the used mineral oils transferred into the regenerated waste residues in the process of regeneration. According to the derivative principle of hazardous waste, regenerated waste residues with a great amount of PAHs should be conducted safe disposal by qualified enterprises. What's more, it must be strictly forbid irregular or illegal disposal of waste residue such as industrial furnace combustion, civil boiler combustion and discarded, so as to prevent secondary releasing of PAHs into the environment.

2.2.3. Distribution characteristics of PAHs with different numbers of benzene rings

The toxicity of PAHs increased as the number of benzene rings increased (Tsai et al., 2002). Accordingly, it is important to analyze the distribution of PAHs with different numbers of benzene rings. According to the different ring number, PAHs can be divided into those with 2–3 rings PAHs, 4 rings PAHs
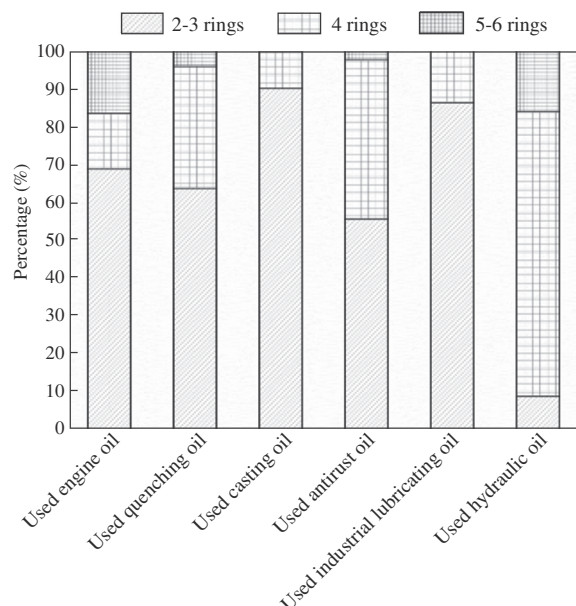
Fig. 3 – Distribution of PAHs with different numbers of rings in waste mineral oil. (a) used engine oil; (b) used quenching oil; (c) used casting oil; (d) used antirust oil; (e) used industrial lubricating oil; (f) used hydraulic oil.
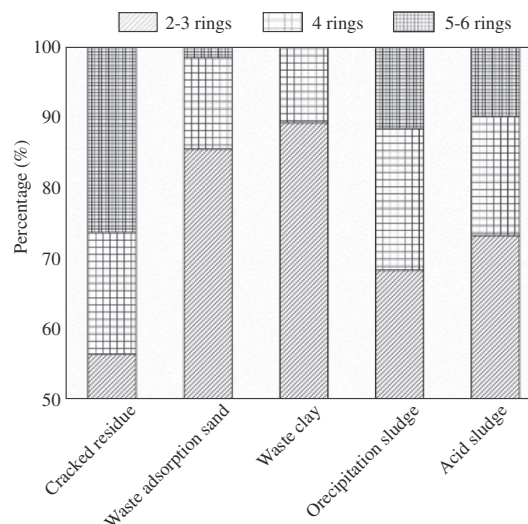
Fig. 4 – Distribution of PAHs with different number rings in regenerated wastes. (a) cracked residue; (b) waste adsorption sand; (c) waste clay; (d) precipitation sludge; (e) acid sludge.

and 5–6 rings PAHs. Fig. 3 shows the percentage content of PAHs with different numbers of benzene rings in the six kinds of used mineral oil. The majority of PAHs had 2–3 rings, comprising 54.5%–95.0% of the total. This was followed by PAHs that had 4 rings (5.0%–37.4%) in six kinds of used mineral oil excluding used engine oil, and then 5–6 rings (0–8.3%). No 5–6 rings PAHs were detected in used lubricating oil. Fig. 4 shows the percentage content of PAHs with different numbers of benzene rings in the five kinds of regenerated wastes. The maximum ratio was 2–3 rings PAHs, which comprised 56.7%–89.4% of the total. This was followed by PAHs with 4 rings (10.6%–20.0%) in five kinds of regenerated wastes excluding cracked residue. The lowest proportion was 5–6 rings PAHs (0–26.1%), and none of these were detected in waste clay.

3. Conclusions

The total PAHs content in six common types of used mineral oils was as follows: used engine oil (96.5 mg/kg) > used quenching oil (51.0 mg/kg) > used casting oil (17.0 mg/kg) > used hydraulic oil (7.2 mg/kg) > used antirust oil (0.7 mg/kg) > used industrial lubricating oil (0.3 mg/kg). These differences were related to the source of PAHs and oil working temperature.

The total PAHs content in regenerated oils was as follows: semi-refined oil (273.1 mg/kg) > refined oil (133.8 mg/kg) > crude oil (106.2 mg/kg), which was related to the catalytic cracking process of crude oil and adsorption refining process of semi-refined oil.

The total PAHs content in regenerated wastes varied according to regeneration technologies and methods were as follows: waste adsorption sand (111.7 mg/kg) > acid sludge (104.2 mg/kg) > waste clay (55.1 mg/kg) > precipitation sludge (51.6 mg/kg) > cracked residue (9.4 mg/kg).

In the six common types of used mineral oils and five regenerated wastes, the majority of total PAHs had 2–3 rings (average 74.7% and 73.1%, respectively), while 5–6-rings PAHs comprised the minority (average 4.4% and 13.1%, respectively).

The migration and transportation of PAHs in the used mineral oils regeneration process varied depending on the specific regeneration technology and method. The majority of PAHs in the used mineral oils during the regeneration process entered into regenerated wastes with, while a small number of PAHs remained in the regenerated oil.

Acknowledgments

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