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

Xiaohui Wu[1], Bo Yue[1,*], Yi Su[1], Qi Wang[1], Qifei Huang[1], Qunhui Wang[2], Hongying Cai[3]

1. State Key Laboratory of Environmental Criteria and Risk Assessment, Chinese Research Academy of Environmental Sciences, Beijing 100012, China
2. Civil and Environmental Engineering Institute, University of Science and Technology Beijing, Beijing 100083, China
3. The Solid Waste Management Center of Chongqing, Chongqing 401147, China

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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.

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

* *Corresponding author*. E-mail: yuebo@craes.org.cn (Bo Yue).

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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

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