The Effective Polycyclic Aromatic Hydrocarbons Removal from Waste Cooking Oils: The Best Evidence Review

Nurul Afwanisa' Ab Razak, Mohd Hafidzal Mohd Hanafi*, Nurul Hanim Razak, Asriana Ibrahim, Anis Ainaa Omar

Centre for Advanced Research on Energy (CARe), Universiti Teknikal Malaysia Melaka, Hang Tuah Jaya, 76100 Durian Tunggal, Melaka, Malaysia.
hafidzal@utem.edu.my

Polycyclic aromatic hydrocarbons (PAHs) are a large group of organic compounds that consist of two or more aromatic rings. PAHs are produced during incomplete combustions of hydrocarbons. Apart from being identified as carcinogenic and mutagenic, PAHs pose a high potential to cause severe health and environmental issues. Oils and lipid matrices, such as Waste Cooking Oils (WCOs), may contain highly concentrated amounts of PAHs that are unsafe. Although vegetable oils are mainly free from PAHs, they are exposed to PAHs contamination from environmental sources. To date, studies on the removal of PAHs in WCOs have been limited despite that many researchers have demonstrated the increasing health risk posed by WCOs. Therefore, this review aims to discuss the best-recommended method to treat WCOs, particularly for removing PAHs. A selected number of the most common biological and physical/chemical treatment methods for PAHs removal were reviewed. In short, this review concluded that the adsorption method using 1 % activated charcoal for 35 min at 110 °C under vacuum bleaching operation at 30 mbar to 35 mbar was considered the most approach to remove PAHs. The method successfully removed 99.7 % of benzo[a]pyrene, signifying the potential application of Activated Carbon (AC) to remove PAHs in WCOs.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are volatile compounds with a high propensity to adsorb onto organic matters and are insoluble in water (Paris et al., 2018). PAHs are produced during incomplete combustions of hydrocarbon due to non-ideal temperature, oxygen capacity, and high moisture. PAHs are started with small and larger hydrocarbons before soot is produced (Hanafi et al., 2018). In 1976, the United States Environmental Protection Agency (US EPA) released a list of 16 PAHs that were evaluated based on the risks towards human health, which later played a significant role as a standardised set of compounds to be analysed, especially in environmental studies (Andersson and Achten, 2015). The list of 16 PAHs include naphthalene, acenaphthene, acenaphthylene, anthracene, phenanthrene, fluorene, fluoranthene, benzo(a)anthracene, chrysene, phyrene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, dibenz(a,h)anthracene, benzo(g,h,i)perylene, and indeno[1,2,3-cd]pyrene.

Oils and lipid matrices such as Waste Cooking Oils (WCOs) contain a highly concentrated PAH level that is harmful because of their lipophilic nature. Vegetable oils are generally PAHs-free, but PAHs could contaminate them through environmental sources, such as raw vegetable material and contamination during seed drying process. They could also be polluted through solvent extraction, soil burning, packaging material, mineral oil residues, and migration of contaminated water or soils (Teng et al., 2019). Edible oils are exposed to a considerable risk of PAHs contamination. The production of edible oils that involve the drying of vegetable seeds before the oil extraction process is susceptible to contamination from PAHs, which are contributed by the release of combustion gases rich in PAHs (Sánchez-Arévalo et al., 2020).

One of the most prevalent reasons that the removal of PAHs should be heavily considered is the direct consumption of fats and oils in food. The volatile and nonvolatile compounds produced during chemical reactions the repeated usage of WCOs cause a carcinogenic effect on humans, such as increased tumor proliferation (Ganesan and Xu, 2020). Besides, several studies have shown that the consumption of WCOs with

saturated fat contents leads to high triglyceride levels in the blood that would subsequently affect the liver function of Wistar rats (Mulyati et al., 2020) and rabbits (Ambreen et al., 2020).

A recent study has claimed that PAHs pose a high potential to cause health and environmental issues due to their carcinogenic and mutagenic effects (Razak et al., 2021a). It is vital to efficiently remove the hazardous emissions of PAHs contaminants (Razak et al., 2021b). Several researchers have focused on the efficient removal of organics pollutants from soil, water (aqueous solution), and atmosphere. The removal of PAHs is divided into biological and physical/chemical treatment methods, as visualized in Figure 1. Few works have attempted to remove PAHs in WCOs, while the available literature has not applied advanced treatment technologies with process parameters. To fill the gap, this review aimed to present the best-recommended method in WCOs treatment to remove PAHs.
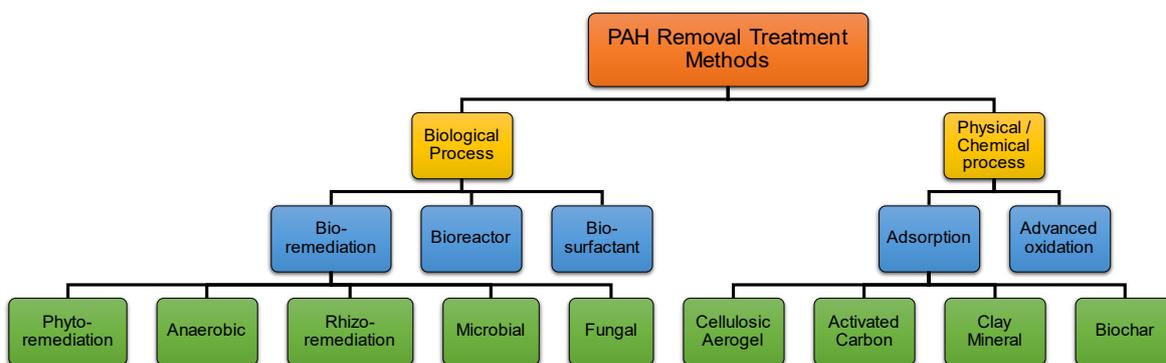

Figure 1: Variety of PAHs removal methods including biological and physical/chemical treatment process

2. PAHs removal treatment

Various methods have been explored to reduce the potentially hazardous properties of PAHs towards the environment and human health. Some of the most common biological and physical/chemical treatment methods for PAHs removal are listed in Table 1. In this study, the literature review was accessed from the Scopus databases, and the data inquiry phrases were set as "Polycyclic Aromatic Hydrocarbons" AND "removal". Based on the search scope, the references were refined to publication years (2012-2021) and type of language (English).

A study conducted by Ma et al. (2017) proved that 99.7 % of benzo[a]pyrene was successfully removed with only 1 % activated charcoal at 110 °C for 35 min under vacuum bleaching operation at 30 mbar to 35 mbar. The advantage of this method was the minimal concentration of activated charcoal applied to yield an extremely high efficiency for benzo[a]pyrene removal. A similar finding was reported to removed 93 % of the total 11 PAHs through the utilisation of powdered SilCarbon TH90 AC with an average particle size of 20 μm (Hale et al., 2012). The high specific surface area of the AC indicates the superior performance of small powdered AC.

In comparison, the main disadvantage of phytoremediation, rhizoremediation, and fungal remediation is the time consumption in which the approach took two years (Chen et al., 2016), 150 d (Liu et al., 2014) and three months (Winquist et al., 2014) to complete the removal process. Mohd-Kamil et al. (2014) reported that the utilisation of microbial treatment was limited to a contaminated site, which would require additional steps to enhance the performance of the bacteria for the ex-situ process. Researchers also concluded that the bioreactor process approach was constrained by complex operating procedures (Qiao et al., 2016), while the application of biosurfactants involves high investment and maintenance costs (Cameotra et al., 2010).

3. Mechanism of adsorption

The adsorption mechanism of PAHs on AC is highlighted in Figure 2. Li et al. (2020) dictate that the mechanism is classified into weak and strong adsorption. The weak adsorption mechanism is mainly through hydrophobic interactions, Van der Waals forces, and hydrogen bonds. Hydrophobic interaction is determined by octane-water distribution coefficient (K_{OW}) or the lipophilicity of a compound. Amino groups (-NH2), hydroxyl groups (-OH), and carboxyl groups (-COOH) in PAHs derivatives are readily adsorbed via hydrogen bond through the AC. The strong adsorption mechanism is due to π-π interaction, π complexation, and electrostatic interaction. The aromatic rings in PAHs consist of a few π electrons that can readily combine with aromatic rings or π bonds on the AC.

Table 1: Details of the process, removal rate, and key performance on the biological and physical/chemical treatment of PAHs

Reference	Treatment methods	Types of Process	Process	Removal rate	Key Performance
Chen et al. (2016)	Biological	Bioremediation	Phytoremediation Ryegrass *Seduce alfredii, Microbacterium sp.* and *Candida tropicalis*, 2 y	96.4 % of the Σ 16 PAHs	High efficiency, low cost and environmentally friendly
Sherafatmand and Ng (2015)			Anaerobic	76.9 % of naphthalene	High level of pollution and limited oxygen flow
Liu et al. (2014)			Rhizoremediation Fire Phoenix, 150 d	99.4 % of the Σ 8 PAHs	Increase the microbial diversity and promote the growth of major bacteria
Mohd-Kamil et al. (2014)			Microbial *Sphingobacterium spiritivorum*, 5 d	95.36 % of phenanthrene	Great efficiency, natural and cost-effective
Winquist et al. (2014)			Fungal *Phanerochaete velutina*, 3 months	94 % of the Σ 16 PAHs	High tolerant concentration of PAHs and extreme conditions
Qiao et al. (2016)		Bioreactor	Aerobic activated sludge treatment, 7 d, 10-35 °C	83-97 % of 4 d PAHs	Manipulate, monitor, and control environmental and operational variables
Cameotra et al. (2010)		Biosurfactants	Fungal *Paenibacillus dendritiformis*, 5 d	96 % of phenanthrene, 83 % of pyrene	Capable of lowering the surface and interfacial tension of the growth medium
Kim et al. (2021)	Physical/ Chemical	Adsorption	Cellulosic aerogel Eulalia, 150-240 °C, 10-30 min, 0.3-5.0 wt%	44.78 % of benzo[a]pyrene	Reduce environmental pollution and enhance the application of by-product
Ma et al. (2017)			Activated carbon 1 % activated charcoal, 110 °C, 35 min, vacuum bleaching at 30-35 mbar	99.7 % of benzo[a]pyrene	Excellent efficiency at very low content of AC addition
Staninska et al. (2015)			Modified mineral clay, humic acid, 24 h	99 % of phenanthrene	Expanded three-dimensional (3D) structure of their molecular sieve properties
Li et al. (2014)			Biochar Wheat straw, 800 °C, 6 h	71.8 %-98.6 % of phenanthrene, fluoranthene, and pyrene	High surface area, porous structure to adsorb contaminants, and high adsorptive capacity
Ates and Argun (2018)		Advanced oxidation processes	Fenton, ozone oxidation, pH 3	>70 % of acenaphthylene, acenaphthene, phenanthrene, fluoranthene, and pyrene	High energy consumption and high maintenance costs, low pH value

An essential interaction between PAHs and AC is found in the π-π electron-donor-acceptance interaction. The π complexation is formed by functional groups or heterocyclic molecules consisting of metal ions that can accept

the delocalized π electrons from the aromatic rings of PAHs. According to Dugyala et al. (2016), electrostatic adsorption is the opposite charge of the functional group of adsorbate and adsorbent.

In this particular adsorption method, the adsorption involves AC with oil containing PAHs, where the mass transfer shifted towards the AC. The proposed adsorption mechanism of PAHs on AC is illustrated in Figure 3. When the PAHs in oil come into contact with a highly porous surface structure of AC, the liquid-solid intermolecular forces cause some of the PAHs molecules from the oil to be concentrated or deposited onto the AC surface. PAHs adsorbed on the AC surface during adsorption are called adsorbate, while the AC adsorbs PAHs are called adsorbent.
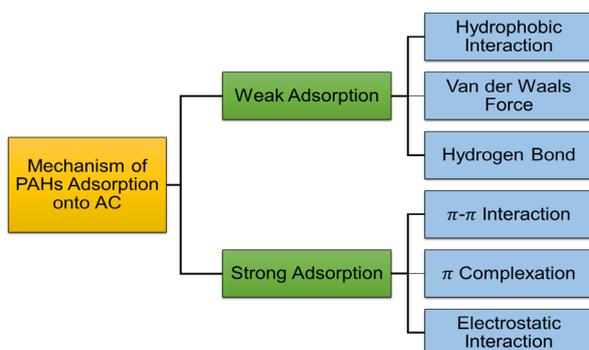

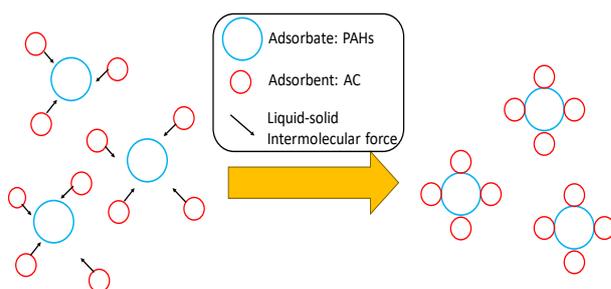*Figure 2: The adsorption mechanism of PAHs onto activated carbon* (Li et al., 2020)

Figure 3: The proposed adsorption mechanism of PAHs on AC in oil

4. Factors affecting the rate of adsorption

Generally, five significant factors affect the adsorption rate of PAHs on AC, including pH level, temperature, particle size and surface area, solubility, and contact time.

4.1 pH level

According to Li et al. (2020), the ionic strength and pH level serve a crucial function in the adsorption and desorption of PAHs onto the AC. The bridging interaction of metal ions and the electron donor-acceptor interaction are the dominant mechanisms by which pH level and ionic strength are associated with the influence on the adsorption and desorption of PAHs. A study by Lamichhane et al. (2016) showed that the pH level of the solution affected the extent of adsorption capacity due to the distribution of surface charge of the adsorbent. The extent of adsorption was varied according to the functional groups of the adsorbate. An elevated positive charge on the adsorbent surface at low pH resulted in higher interaction between the adsorbent and PAHs molecules. The variation of pH level plays an important role in electrostatic adsorption for ionisable organic chemicals, such as PAHs. In brief, a higher PAHs removal rate was achieved using a solution with a lower pH level.

4.2 Temperature

The effect of temperature on PAHs sorption could be described by Van't Hoff. Eq(1), which was derived using the concept of Gibbs free energy.

$$\ln K_{eq} = -\frac{\Delta H}{R}\frac{1}{T} + \frac{\Delta S}{TR} \tag{1}$$

where *ΔH* is change in enthalpy (kJ/mol), *T* is the absolute temperature (K), *ΔS* is change in entropy (kJ/mol/K), *R* is gas constant (8.314×10^{-3} kJ/K/mol), and K_{eq} is equilibrium partition coefficient at a given temperature (cm^3/g) (Lamichhane et al., 2016). In short, higher temperatures led to a greater PAHs removal rate under endothermic reaction.

4.3 Particle size and surface area

Lamichhane et al. (2016) also found that the capacity of adsorbent PAHs adsorption was inversely proportional to the particle size of the media due to adsorption being a surface phenomenon. The extent of adsorption was proportional to the specific surface area, which refers to the portion of the total surface area available for adsorption. According to Li et al. (2020), the pore size distribution and specific surface area of AC significantly influenced PAH adsorption. In brief, a higher PAHs removal rate was obtained using adsorbents with smaller particle sizes and larger surface areas.

4.4 Solubility

The solubility of the adsorbate greatly influences the adsorption capacity of the adsorbents. An inverse relationship was observed between the extent of adsorption of a solute and its solubility in the solvent. It was suggested that the solubility of PAHs exhibited an inverse relationship with molecular weight (Lamichhane et al., 2016).

4.5 Contact time

When hydrophobic organic compound comes into contact with the media, a portion of the compound is rapidly adsorbed by the media components (such as organic matter, clay minerals) through physisorption. However, it takes longer for the remaining fractions to reach sorption equilibrium. The experimental result showed 70 % of PAHs removal was achieved within 2 h of contact time and then gradually reaching equilibrium within 24 h for maximum removal efficiency (Lamichhane et al., 2016). In summary, a longer contact time resulted in higher PAHs removal.

5. Conclusions

In this review, the latest collection of research articles from the Scopus database relating to the highest removal rate of PAHs were presented. The effectiveness of the adsorption process depends on operating variables, including pH level, temperature, particle size and surface area, solubility, and contact time. Based on the recent studies, it was suggested that PAHs removal rate could be enhanced by maintaining a low pH, utilising adsorbents with smaller particle sizes and more significant surface areas, and extending the contact time. Among all the methods discussed, the adsorption using 1 % activated charcoal for 35 min at 110 °C under vacuum bleaching process at 30 mbar to 35 mbar was the most effective approach to remove PAHs. The method successfully removed 99.7 % of benzo[a]pyrene. Due to its excellent efficiency at very low content of AC addition, adsorption by AC is a possible promising method to be applied as WCOs treatment to remove PAHs significantly.

References

Ambreen G., Siddiq A., Hussain K., 2020, Association of long-term consumption of repeatedly heated mix vegetable oils in different doses and hepatic toxicity through fat accumulation, Lipids in Health and Disease, 19(1), 1-9.

Andersson J.T., Achten C., 2015, Time to say goodbye to the 16 EPA PAHs? Toward an up-to-date use of PACs for environmental purposes, Polycyclic Aromatic Compounds, 35(2-4), 330-354.

Ates H., Argun M.E., 2018, Removal of PAHs from leachate using a combination of chemical precipitation and Fenton and ozone oxidation, Water Science and Technology, 78(5), 1064–1070.

Cameotra S.S., Makkar R.S., Kaur J., Mehta S.K., 2010, Synthesis of Biosurfactants and Their Advantages to Microorganisms and Mankind. In: Sen R. (eds) Biosurfactants, Advances in Experimental Medicine and Biology, Springer Science & Business Media, Berlin, Germany, 672, 261-280.

Chen F., Tan M., Ma J., Zhang S., Li G., Qu J., 2016, Efficient remediation of PAH-metal co-contaminated soil using microbial-plant combination: A greenhouse study, Journal of Hazardous Materials, 302, 250–261.

480

Dugyala V.R., Muthukuru J.S., Mani E., Basavaraj M.G., 2016, Role of electrostatic interactions in the adsorption kinetics of nanoparticles at fluid-fluid interfaces, Physical Chemistry Chemical Physics, 18(7), 5499–5508.

Ganesan K., Xu B., 2020, Deep frying cooking oils promote the high risk of metastases in the breast-A critical review, Food and Chemical Toxicology, 144, 111648.

Hale S.E., Elmquist M., Brändli R., Hartnik T., Jakob L., Henriksen T., Werner D., Cornelissen G., 2012, Activated carbon amendment to sequester PAHs in contaminated soil: A lysimeter field trial, Chemosphere, 87(2), 177–184.

Hanafi M.H.M., Nakamura H., Hasegawa S., Tezuka T., Maruta K., 2018, Effects of n-butanol addition on sooting tendency and formation of C1-C2 primary intermediates of n-heptane/air mixture in a micro flow reactor with a controlled temperature profile, Combustion Science and Technology, 190(12), 2066–2081.

Kim D.Y., Kim B., Shin H.S., 2021, Reduction of polycyclic aromatic hydrocarbons (PAHs) in sesame oil using cellulosic aerogel, Foods, 10(3), 644.

Lamichhane S., Krishna K.C.B., Sarukkalige R., 2016, Chemosphere Polycyclic aromatic hydrocarbons (PAHs) removal by sorption: A review, Chemosphere, 148, 336–353.

Li F., Chen J., Hu X., He F., Bean E., Tsang D.C.W., Ok Y.S., Gao B., 2020, Applications of carbonaceous adsorbents in the remediation of polycyclic aromatic hydrocarbon-contaminated sediments: A review, Journal of Cleaner Production, 255, 120263.

Li H., Qu R., Li C., Guo W., Han X., He F., Ma Y., Xing B., 2014, Selective removal of polycyclic aromatic hydrocarbons (PAHs) from soil washing effluents using biochars produced at different pyrolytic temperatures, Bioresource Technology, 163, 193–198.

Liu R., Xiao N., Wei S., Zhao L., An J., 2014, Rhizosphere effects of PAH-contaminated soil phytoremediation using a special plant named Fire Phoenix, Science of the Total Environment, 473–474, 350–358.

Ma Y., Shi L., Liu Y., Lu Q., 2017, Effects of neutralization, decoloration, and deodorization on polycyclic aromatic hydrocarbons during laboratory-scale oil refining process, Journal of Chemistry, 2017, 1–9.

Mohd-Kamil N.A.F., Hussain N.H., Mizad M.B., Abdul-Talib S., 2014, Enhancing Performance of Sphingobacterium spiritivorum in Bioremediation Phenanthrene Contaminated Sand, Remediation, 24(3), 119–128.

Mulyati, Mardhatillah T.D., Widiyanto S., 2020, Liver Function of Hypertriglyceridemia (HTG) Wistar Rats (Rattus norvegicus Berkenhout, 1769) with Treatments of Arthrospira maxima Setchell et Gardner and Chlorella vulgaris Beijerinck, The 6th International Conference on Biological Science ICBS 2019, 10th-11th October, Yogyakarta, Indonesia, 1-12.

Paris A., Ledauphin J., Poinot P., Gaillard J.L., 2018, Polycyclic aromatic hydrocarbons in fruits and vegetables: Origin, analysis, and occurrence, Environmental Pollution, 234, 96–106.

Qiao M., Qi W., Liu H., Bai Y., Qu J., 2016, Formation of oxygenated polycyclic aromatic hydrocarbons from polycyclic aromatic hydrocarbons during aerobic activated sludge treatment and their removal process, Chemical Engineering Journal, 302, 50–57.

Razak N.H., Hashim H., Yunus N.A., Klemeš J.J., 2021a, Integrated GIS-AHP optimization for bioethanol from oil palm biomass supply chain network design, Chemical Engineering Transactions, 83, 571–576.

Razak N.H., Hashim H., Yunus N.A., Klemeš J.J., 2021b, Reducing diesel exhaust emissions by optimisation of alcohol oxygenate blend with diesel/biodiesel, Journal of Cleaner Production, 316, 128090.

Sánchez-Arévalo C.M., Olmo-García L., Fernández-Sánchez J.F., Carrasco-Pancorbo A., 2020, Polycyclic aromatic hydrocarbons in edible oils: An overview on sample preparation, determination strategies, and relative abundance of prevalent compounds, Comprehensive Reviews in Food Science and Food Safety, 19(6), 3528–3573.

Sherafatmand M., Ng H.Y., 2015, Using sediment microbial fuel cells (SMFCs) for bioremediation of polycyclic aromatic hydrocarbons (PAHs), Bioresource Technology, 195, 122–130.

Staninska J., Szczepaniak Z., Cyplik P., Piotrowska-Cyplik A., 2015, The effect of organic and clay fraction on polycyclic aromatic hydrocarbons mobility in soil model systems, Journal of Research and Applications in Agricultural Engineering, 60(1), 98-101.

Teng C., Wu S., Sun Y., Gong G., 2019, Determination of parent and oxygenated Polycyclic Aromatic Hydrocarbons (PAHs) in waste cooking oil and oil deodorizer distillate by GC-QQQ-MS, Journal of AOAC International, 102(6), 1884–1891.

Winquist E., Björklöf K., Schultz E., Räsänen M., Salonen K., Anasonye F., Cajthaml T., Steffen K.T., Jørgensen K.S., Tuomela M., 2014, Bioremediation of PAH-contaminated soil with fungi - From laboratory to field scale, International Biodeterioration and Biodegradation, 86, 238–247.