REVIEW PAPER

Remediation technologies for oil contaminated soil

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Abstract

Crude oil continues to impact many nations as it is among the major sources of fuel. Its role in making life in modern societies comfortable cannot be overemphasized as it is readily available and easy to use. Contamination resulting from its use in industries such as mining, transportation and petroleum especially soil contamination cannot be overlooked. Soil pollution resulting from oil contamination can be seen as being among the twenty-first-century vulnerabilities because if not well taken care of the consequences can be devastating. Soil contamination is of interest in most societies because it affects both the environment and humans. This review highlights common sources of soil pollution and their effects, oil waste disposal methods, soil remediation techniques that are well established and those still in their infancy. Such techniques include bioremediation such as phytoremediation and landfarming, where percent removal of contaminated soils was reported from 68% to 89% in 40 days to 1 year, respectively; physical methods such as excavation and incineration (75-86% removal); chemical methods such as oxidation (48% by Fenton process); and photocatalysis (67% using titanium dioxide). The choice of remediation in mining, transportation and petroleum industries depends on the urgency and hazardous effects of the pollutant. In Zambia, Mopani Copper Mines uses landfarming as a means to mitigate large amounts of soil contaminated with oil wastes, but the process is slow. In the proposed research, photocatalysis coupled with adsorption of oil on clay will be used to assess the effectiveness of this emerging technology to quicken the degradation of oil in soils. Clay will be incorporated with metal ions and with hydrophobic groups to enhance light absorption and oil-clay interaction, respectively. Photochemical remediation techniques for remediation of soils polluted with oil have attracted considerable interest as the processes are reported to enhance the degradation of oils in soil compared to the biological and physical methods. The extent of photo-degradation of oil waste will be evaluated using the Soxhlet technique by determining the percent residual oil. The importance of remediating contaminated soil in any nation cannot be overemphasized as consequences of not remediating this precious resource might be devastating. Since economic development through industrialization will continue, there is need to constantly improve on methods of mitigating the impact of wastes on the environment, especially in developing countries, where engineering of cheap, nontoxic materials for soil remediation is paramount.

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INTRODUCTION

In recent years, worldwide, there has been an adverse impact on the environment due to the increased dependence on anthropogenic activities for economic development. One of the components of the environment that is severely affected by various industrial activities is the soil. Soil pollution is the build-up in the soil of toxic compounds, chemicals, salts or disease-causing agents that adversely affects plant growth and animal health (Ashraf et al., 2014; Yuvaraj and Mahendran, 2020). Soil contamination is of particular interest in most societies since it does not only affect the environment but humans inclusive. When soil is contaminated, in most cases it stops being ideal for purposes of agriculture, recreation and other industrial activities. In the soil, pollutants usually stay for longer periods compared with other media such as air and water. Sources of soil pollution include heavy metals (Su et al., 2014), pesticides, fertilizers, herbicides, solvents, insecticides and petroleum hydrocarbons among others (Havugimana et al., 2015; Sethi and Gupta, 2020). Pollutants often easily go down into the soil and quickly build up but may take a long time to be depleted. Contamination by heavy metals often decrease the productivity of the soil and can make the soil sterile and makes it difficult for plant growth making the place more vulnerable to soil erosion and a possibly unsafe and unstable land (Reicosky, 2018). Fertilizers contain impurities that come from starting materials used in their production (Khan et al., 2017). The agrochemical industry uses tons of pesticides in the control of different types of pests which may be harmful to microorganisms this is because most of these pesticides as well as fertilizers are not always degraded and may end up in water bodies leading to eutrophication and its effects that include foul smell, generation of significant quantities of methane (Morelli et al., 2018; Zhang et al., 2020a).

Soil contamination by agricultural wastes leads to decreased levels of soil fertility, high erodibility, low nitrogen fixation, loss of nutrients, reduction in the crop yield and a disproportion in the soil plant and animal species (Havugimana et al., 2015). Besides, soil pollution also occurs from pharmaceutical companies that carelessly dispose of drugs into water bodies that are swept in underground water that rural people easily access through drinking river water contaminated with various pharmaceutical wastes (Grenni, 2011; Li et al. 2019) and its effects are chronic and sub-lethal as they are deemed persistent (Kapoor, 2015). Pharmaceuticals exist as mixtures in the environment and more often than not these are composed of various chemicals which have different regimes of operations and unspecified adverse drug reactions, more so on untargeted organisms (Pomati et al., 2008). Pharmaceuticals are active biological molecules hence even when the concentrations are low, they may still be toxic and harmful (Allen et al., 2010). Because of this, the health of maritime creatures along with humans must be safeguarded (Pomati et al., 2008, Galus et al., 2013) from chronic exposure (Hernando et al., 2006). Mining industries require the use of oil in huge amounts in their various mining operations and the recent past has witnessed an increase in the use of oil in form of petroleum products due to the advancement of equipment as well as machinery used in the mines. The main components of oil are generally categorized into three classes namely saturated hydrocarbons (alkanes), unsaturated hydrocarbons [unsaturated paraffins and polycyclic aromatic hydrocarbons (PAHs)] and hetero-hydrocarbon compounds as shown in Table 1 (Wang et al., 2017; Srivastava et al., 2019). The authors indicate that saturated components of low boiling points are easily vaporized and do not linger in the soil system. However, PAHs and hetero-hydrocarbons are the most difficult to remove having higher boiling points and the reluctance to dissolve in water. Some of these substances are considered mutagenic, teratogenic and carcinogenic (Ahmad et al., 2020; Gao et al., 2019). An estimated 45% of natural habitats in Europe are contaminated with petroleum hydrocarbons and their products (Borowik and Wyszkowska, 2018). Petroleum hydrocarbons diffuse in the soil, blocking the pores of soil and they tend to be difficult to separate from the soil because they are often firmly sorbed to the organic matter in the soil and squeezed together in the soil (Rajabi and Sharifipour, 2019). Oil discharges by-products that are toxic and persistent to the soil (Devatha, et al., 2019). In addition, crude oil contamination leads to increased soil’s organic carbon content which further causes a consequential reduction in the nitrogen in the soil (Kim et al., 2018). Further, a reduction in the soil moisture because of the hydrophobic layer of oil created around the soil particles triggers a decline in the hydraulic conductivity of the soil by about 10% and the availability of water. Table 1 shows some
components of oil, effect on the soil and the type of remediation process used.

The disposal of large quantities of used oil from mining activities poses a great environmental challenge especially soil contamination. This soil contamination might result from waste oil spillages during storage, transportation, human error or negligence (Jernelöv, 2010). Other industrial activities such as oil extraction and exploration, oil fields, oil drilling as well as production sites can also lead to soil contamination. The petroleum industries also produce billions in tons of natural gas, oil and its by-products. In 2017, a report by International Energy Agency (IEA) estimated daily consumption of at least 97 million barrels of oil per day and a further 100 billion barrels each day by the year 2021 (dos Santos and Maranho, 2018). The mining sector remains a big contributor to soil pollution from the use of large quantities of oil in daily operations of heavy machinery. Oil contaminated soil is among the environmental and ecological challenges resulting from mining activities. Soil pollution resulting from oil contamination can be seen as one of the twenty-first-century vulnerabilities because if not well taken care of the consequences can be devastating. Contamination of soil by waste oil adversely affects land and marine organisms (van der Heul, 2009). Also, the toxicity ensuing from these hydrocarbons causes contamination of land, surface and groundwater adversely affecting biota and prevents agricultural activities from thriving in such soils (Pashkevich, 2017). Other adverse implications of soil pollution resulting from oil contamination include; loss of soil fertility, increased soil toxicity, reduced aesthetic attraction, insufficient nutrient and water availability. According to (Dadrasnia and Agamuthu, 2013) indigenous organisms that live in the soil can also be affected and their food chains altered. As a non-renewable source, the importance of maintaining and remediating contaminated soil cannot be overstated. Soil remediation borders on its bearing on environmental protection, public health including the economy hence the need to expedite the process. In a 2017 perspective analysis, Hansen (2017) affirms that a continued occurrence of environmental contamination from oil spills for as long as there is dependence on petroleum and its products by the mines and society. Mining companies use several methods in their quest to clean and prevent further damage from oil. Skimmers and containment booms, as well as vacuum trailers,

![Table 1: A summary of oil components, effect on the soil and the type of remediation process](image)

<table>
<thead>
<tr>
<th>Oil component</th>
<th>Types</th>
<th>Boiling point</th>
<th>Some effect on soil</th>
<th>Source of contamination</th>
<th>Remediation method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saturated hydrocarbons</td>
<td>Alkanes Isoparaffin cycloparaffins</td>
<td>Low</td>
<td>Changes carbon to nitrogen and phosphorus ratios, pH, and conductivity</td>
<td>i. Petroleum industry –diesel fractions ii. Oil spillage iii. Careless disposal of oil waste iii. Solvents, and pesticides</td>
<td>Natural oxidation Vaporization Biodegradation</td>
<td>Wang et al., 2017; Ali, 2019</td>
</tr>
<tr>
<td>Unsaturated hydrocarbons</td>
<td>Polycyclic aromatic hydrocarbons</td>
<td>High</td>
<td>i. Oil ageing: resistance of soil to any treatment. ii. Covers soil surface prevents carbon dioxide interchange and reduces soil porosity</td>
<td>i. Petroleum industry ii. Oil spillage iii. Careless disposal of oil waste iii. Solvents, and pesticides</td>
<td>Physical and chemical processes</td>
<td>Srivastava et al., 2019; Ahmad et al., 2020</td>
</tr>
<tr>
<td>Hetero-hydrocarbons</td>
<td>Resins Asphaltenes</td>
<td>Higher</td>
<td>i. Oil ageing: resistance of soil to any treatment. ii. Covers soil surface prevents carbon dioxide interchange and reduces soil porosity iv. Increases soil salinity due to trace amounts of salts in the oil</td>
<td>i. Petroleum industry ii. Oil spillage iii. Careless disposal of oil waste iv. Solvents, and pesticides</td>
<td>Physical and chemical process</td>
<td>Srivastava et al., 2019; Ahmad et al., 2020</td>
</tr>
</tbody>
</table>
have been used. Sawdust is another material that mines have made use of in the clean-up of spilt oil though its use is deemed to be hazardous (Godoy-Faúndez et al., 2008). Incineration and excavation are other commonly used methods to clean up soil contaminated with oil. Thus, to prevent on-going destruction to the ecosystem of the contaminated sites, the medium needs to undergo a thorough treatment process. The remediation process may be as simple as the introduction of certain chemicals into the system, to highly complex reactions involving several chemical and biological processes (Agamuthu et al., 2013; Ashraf et al., 2014). The current study was aimed at identifying established commercials as well as newer methods of decontaminating soil contaminated with large quantities of oil from various industrial activities. In addition, the study also looked at the merits and demerits of each mitigation method examined. The main objectives of the review were identifying what method can complement or substitute the bioremediation technique currently used by one of the largest copper mines in Zambia. Specifically, the review sought to find a faster and cheaper way for soil remediation from the mines. The study was performed in 2020 at the Copperbelt University and Mopani copper mines spill-sorb farm in Kitwe, Zambia, respectively.

**MATERIALS AND METHODS**

The study consisted of a review of several published peer-reviewed articles relating to established and emerging technologies on decontamination of oil-contaminated soil. The review used keywords to search for articles discussing remediation of oil-contaminated soils in the last 20 years. To search for these articles, keywords like “biological oil remediation”, “hydrocarbons”, “physical oil remediation”, “chemical oil remediation”, “photochemical oil remediation”, “and oil waste in the mining industry” were used.

**Remediation process for oil-contaminated soil**

Many methods have been advanced to remediate soil polluted with oil during the past thirty years (van der Heul, 2009). To our understanding, these methods focus on ensuring that the hydrocarbons are easily separated and degraded. Nevertheless, a lot of research is still being done to find better techniques to decompose the oil in the soil.

**Biological remediation techniques**

Bioremediation is the defined process through which crude oil compounds are degraded by microorganisms with the aid of enzymatic reactions turning them into carbon dioxide, biomass, and water-soluble compounds (Atlas et al., 2015). Some bacterial species found in the environment such as yeast, fungi, mould and archaea are capable of feeding on compounds of crude oil (Atlas et al., 2015). Bioremediation is an emergent technology which is quite promising in the management of hydrocarbon contaminated soil and when compared either with physical or chemical repair, bioremediation is widely used due to its advantages of being of good effect, rapid degradation rate, and a lack of secondary pollution (Ahmad et al., 2020; Xu et al., 2018). Zhang et al. (2020b) remediated oil-contaminated soil using agricultural wastes through use of a bacterial consortium that was capable of decomposing oil components and the results showed a 68% decomposition of oil after 40 days using swine-water among other additives confirming that certain strains of bacteria can be used in bioremediation. A recent study showed that bacteria such as *Ochrobactrum* sp., *Stenotrophomonas maltophilia* and *Pseudomonas aeruginosa* are good at degrading crude oil (3%v/v) by more than 80% (Varjani et al., 2015), while an 89% degradation of soil contaminated with diesel was reported after 365 days using a different set of bacteria (Szulc et al., 2014). However, since most hydrocarbons are highly hydrophobic and lack bioavailability, bioremediation might not be a suitable remediation approach (Zhu and Aitken, 2010). While there are two main types of bioremediation (in-situ and ex-situ bioremediation), (Azubuike et al., 2016), there are several forms of bioremediation such as biostimulation (Abed et al., 2015; Emami et al., 2014; Ezenne et al., 2014; Hamzah et al., 2014; Huang et al., 2019) bioventing (Amin et al., 2014; Thomé et al., 2014; Mosco and Zytner, 2017) and bioaugmentation (Abdulsalam et al., 2011; Adlane et al., 2020; Roy et al., 2014; Singh et al., 2012) Bioremediation might not be a feasible technique at sites with high concentrations of certain substances that are toxic to most microorganisms such as cadmium, lead and sodium chloride (Speight, 2018). Besides, the process of bioremediation may take several months or even...
Phytoremediation

Phytoremediation, which is also referred to as plant-assisted bioremediation is a soil remediation technique which makes use of plants and their roots. Plant species such as *Centrosema brasilianum*, *Stylosanthes capitata*, *Calopogonium mucunoides*, *Brachiaria brizantha*, *Cyperus aggregatus*, *Eleusine indica* and *Mirabilis jalapa* have been used in phytoremediation of contaminated soils (Merkel et al., 2005; Peng et al., 2009). Peng et al. (2009) utilised *Mirabilis jalapa* to remediate contaminated soil and a percent removal ranging from 41-63% was reported. The root enzymes that are present in plants help in the degradation process as they chemically modify and decompose the noxious waste. Phytoremediation, the practice of using vegetation for remediating the contaminated soil in situ is another cheap approach that is applied to clean up oil-contaminated soil. According to (Nedunuri et al., 2000), it is possible to treat the PAHs and petroleum hydrocarbons among others using this method. The treatment uses the plants’ property of taking up, accumulating, and/or degrading the constituents which are readily available in soil and water environments (Rostami and Azhdarpour, 2019). All the chemical, physical and biological activities that are induced by plants to assist and support the remedy of contaminated substrata all relate to phytoremediation (Yakubu, 2007). Fig. 1 shows some mechanisms involved in phytoremediation as illustrated by (Kamath et al., 2004).

The success of this procedure is attributed to the availability of organic materials as root exudates and mucilage secretion by root caps which are easily degraded and can therefore improve the degradation of oil pollutants (Merkel et al., 2005). Fertilizer can be added for an additional supply of nutrients to the microorganisms and plants. This is among the factors that influence phytoremediation. However, it is not clear how much fertilizer should be added for maximum efficiency (Lim et al., 2016). To that effect, some studies have been performed to ascertain the extent to which the fertilizer must be added (Dadrasnia and Agamuthu, 2014; Merkl et al., 2005) Grasses and roots are reportedly the most common plants used in phytoremediation because their roots cover a bigger area providing more biomass for rhizoremediation (Cook and Hesterberg, 2013; Moreira et al., 2013). Earlier studies on the effect of root coverage on phytoremediation have shown that grass which had extensive root structure and shoot biomass was more effective in soil remediation (Soleiman et al., 2010). When *Festuca arundinacea* and *Festuca pratensis* were used to degrade petroleum hydrocarbons, 80-84% of polyaromatic hydrocarbons were removed with 64-72% being total petroleum hydrocarbons (Soleiman et al., 2010). Though this procedure is very cheap and is used in getting rid of would-be
environmental pollution, it is time-consuming and can take approximately five to seven years (Yakubu, 2007), therefore, suitable for long term results. Other disadvantages of these phytoremediation processes are; certain oil pollutants may be harmful to the plants, some pollutants may need extended periods, the extent of the root system determines the strength of treatment and some plants may not be available throughout the year (Lombi and Hamon, 2005). Besides, nothing seems to be well-known about the bioavailability and the toxicity of the products of biodegradation (Kamath et al., 2004). Despite these pitfalls, phytoremediation procedures are widely accepted and used because they are economical and ecofriendly (Guerra et al., 2018). Ahmad et al. (2020) demonstrated that 63% of hydrocarbons can be decomposed using rye grass in combination with plant growth promoting bacteria in three years. In addition, Devatha et al. (2019), used the topical plant Chromolaena odorata to evaluate its effect on oil-contaminated samples and observed that within 7 days, the total petroleum hydrocarbons (TPH) were reduced up to 50-60% for soils contaminated with 5% and 10% oil, respectively. The reduction in TPH was further evidenced by Fourier transform infrared (FTIR) spectroscopy, where certain functional groups disappeared after the 7-day interval.

Landfarming

Landfarming is a process by which the hydrocarbon polluted soils are widely dispersed in an overlay of nearly half a meter in thickness, some nutrients added, and once in a while, the soils are mixed (Paudyn et al., 2008). Land farms may have different treatment routines due to variations in the locality, climate, soil type and temperature. In much warmer climatic conditions landfarming has been implemented successfully, (McCarthy et al., 2004) while conflicting results have been reported in cold Antarctic and Arctic environments (Paudyn et al., 2008). In this remediation technique which is normally applied to petroleum hydrocarbons, the excavated oil-contaminated soils are firstly dispersed as a shallow layer ground surface where the intervention would be done followed by stimulation activity by microbes within the soil by aeration, the addition of nutrients, water and minerals (Khan et al., 2004). In contrast, when land tillage was used to remediate soil in farmland, the TPHs decreased by 50% after four months. It is important to stress that the core of bioremediation technology is the degradation of pollutants through microbial metabolic activities (Khan et al., 2004). Landfarming is quite slow due to the influences of weather changes that cannot be controlled. With the landfarming technique, only percentages less than 95% can be attained and in most cases some contaminants persist in the soil (Maila and Cloete, 2004). As reported in a review by Khan and colleagues, a concentration of more than 50,000 ppm would be very difficult to remediate (Khan et al., 2004). Landfarming being a class of bioremediation there are high chances of generating and leaving behind (in the soil) even more toxic compounds causing further damage to the soil (Chibwe et al., 2015). Ultraviolet A which falls in the range of 315-387nm comprises almost 95% of the ultraviolet (UV) radiation would be better for landfarming (Yang et al., 2017). Also, contamination of air may result from emissions as a result of volatilization of the compounds from the contaminated soil and may pose health risks to humans (Thomé et al., 2014). Landfarming is often quite slow due to the influences of weather changes that cannot be controlled. Fig. 2 depicts landfarming as a soil remediation technique. The approach’s effectiveness relies on the replication of the microorganisms to undertake the degradation of the pollutants; therefore, the conditions must be suitable for microbial growth (Mosbech, 2002). Being very precise and restricted to biodegradable organic compounds, the method can produce more persistent and even more toxic compounds than the parent pollutant and requires more time to generate the sought results (Sharma, 2012). Table 2 illustrates some commonly used biological remediation methods for processing soil contaminated with oil.

Physical methods

Several physical methods are also used such as soil flushing (Gitipour et al., 2014; Zamudio-pérez et al., 2013), soil washing (Achugasim et al., 2011; de Andrade Lima et al., 2018; Karbassi and Pazoki, 2015; Lim et al., 2016; Moon et al., 2016), soil vapor extraction and thermal desorption (Khan et al., 2004; Park and Zhan, 2003), low-temperature thermal treatment (Falciglia et al., 2011; Jebeli et al., 2019; Ren et al., 2019) and sonication (Effendi and Wulandari, 2019; Collings et al., 2007; Collings, et al, 2007; Shrestha et al., 2009; Li et al., 2013).
Using different concentrations of Triton X-100 and sodium dodecyl sulfate Gitipour et al. (2014) recorded removal percentages of 79.6%, 80.14%, 80.26% and 83.51% respectively. Achugasim et al. (2011) found that a soil washing agent can remove benzene, toluene, ethylbenzene and xylene (BTEX) from oil-contaminated soil with removal percentages being around 95%, 95% and 97% for neutral, basic and acidic pH ranges in that order. Despite the high removal percentages recorded, the procedure was found not to be effective towards polycyclic aromatic hydrocarbons present in the crude oil as was seen from the removal percentages which were less than 3%, 41% and 27%, for the PAHs in neutral, basic and acidic ranges respectively. The conclusion was that persulphate should not be used singly as a washing agent if the removal of hydrocarbons in soil contaminated with crude oil is to be effective. Different washing solutions were used by Moon et al. (2016) to remediate contaminated soil, and they found that tetra acetic acid performed well as a washing solution. Use of this method to treat contaminated soil has attracted debate as the detergents used are said to pollute the soil (van der Heul, 2009). The use of soil vapour extraction and thermal desorption to remove volatile organic compounds and semi-volatile organic compounds was suggested by Khan et al. (2004) but Park and Zhan (2003) were quick to note that contaminants from heavy oils such as diesel and kerosene are not well removed and sometimes, they are not removed at all. Falciglia et al. (2011) demonstrated that the efficacy of thermal desorption and adsorption as remediation techniques in diesel contaminated soil at low temperature was dependent on factors such as temperature, the texture of the soil, composition of soil and how long the treatment lasts. The researchers found that for diesel polluted sandy and silty soils; a temperature of 175 °C was enough to desor the contamination whereas a temperature of 250 °C was needed for clay soils. The use of ultrasonic has shown a considerable effect on desorption of petroleum hydrocarbon in fine soil where the amount of TPHs removed was 61 and 49% from 27.6% silt and 55.3% clay soils, respectively (Li et al., 2013) while increasing the power increased the removal rates (Shrestha et al., 2009). Effendi and Wulandari, 2019 reported a 61 % removal of TPHs in 15 minutes using 160 watts of power, however, it was reported that no further decrease occurred likely due to a steady-state re-adsorption of the TPHs onto the soil. Although studies on ultrasonic remediation are inadequate, Effendi and Wulandari, 2019 anticipate...
## Table 2: Common biological remediation methods for processing soil contaminated with oil

<table>
<thead>
<tr>
<th>Method</th>
<th>Design and area of focus</th>
<th>Key Findings</th>
<th>Gaps/annotations</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bioremediation:</td>
<td>Contaminated soil treated with swine wastewater and wheat bran.</td>
<td>After 40 days a degradation efficiency of 68.27 ± 0.71% was obtained.</td>
<td>i. Use of pig waste to mitigate soil pollution is valuable.</td>
<td>Zhang et al., 2020b; Sivakumar, 2015</td>
</tr>
<tr>
<td>Biological process</td>
<td></td>
<td></td>
<td>ii. Process needs external microbial agents to facilitate the biodegradation process.</td>
<td></td>
</tr>
<tr>
<td>Bioremediation:</td>
<td>Sawdust and the rice straw were used to degrade petroleum in the contaminated soil.</td>
<td>i. The removal percentages for the TPHs after 5 months were 23.9%, 45.2% and 27.5% while for the PAHs rates were 66.3%, 30.3% and 26.9%, for the sawdust, rice straw and control treatments, respectively.</td>
<td>Removal of petroleum was not associated with the variety of the microbes. Not all microbes play a role in petroleum elimination.</td>
<td>Huang et al., 2019</td>
</tr>
<tr>
<td>Biological process</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Bioremediation:</td>
<td>Aged refuse from landfills was used in the treatment of soil contaminated with petroleum.</td>
<td>After 98 days of study, the removal of TPHs to 89.83% from 22.40% was observed.</td>
<td>i) Use of aged refuse increased the biomass of the microbes.</td>
<td>Liu et al., 2018</td>
</tr>
<tr>
<td>Biological process</td>
<td></td>
<td></td>
<td>ii) Safety of the use of aged refuse could not be ascertained.</td>
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<td></td>
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<td></td>
<td>iii) No quantitative percent removal of oil was provided.</td>
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<tr>
<td>Phytoremediation:</td>
<td>Hyparrhenia rufa, Sorghum arundinaceum, Oryza longistaminata and Tithonia diversifolia plant species were used.</td>
<td>i) After 120 days of phytoremediation combined with 5 gkg⁻¹ soil of manure a reduction in the TPHs was observed.</td>
<td>I) Phytoremediation on its own was not ideal for successful bioremediation of the contaminated soil</td>
<td>Ruley et al., 2020</td>
</tr>
<tr>
<td>Biological process</td>
<td></td>
<td></td>
<td>ii) No significant difference between the use of manure 5 gkg⁻¹ soil and 10 gkg⁻¹ soil in treatment of TPHs.</td>
<td></td>
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<tr>
<td>Landfarming:</td>
<td>A combination of landfarming, phytoremediation and chemico-biological methods was used.</td>
<td>i) Landfarming method was the best method among the three remediation techniques employed with the least being phytoremediation.</td>
<td>Landfarming produced better results because of the combination of inorganic and organic fertilizers</td>
<td>Okonofua et al., 2020</td>
</tr>
<tr>
<td>Biological process</td>
<td>Target components were with (PAHs) and (TPHs).</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bioremediation (Natural Process)</td>
<td>The study used three bioremediation methods to remediate petroleum hydrocarbons polluted soil.</td>
<td>After a 90-days trial, about 86% of TPHs were removed by bioaugmentation; 70% by landfarming and bioremediation (57%).</td>
<td>Best results for bioremediation are obtained with a combination of different bioremediation approaches.</td>
<td>Guarino et al., 2017</td>
</tr>
</tbody>
</table>
that ultrasonic remediation can help to sought out the inability of bioremediation to degrade clayey soil when used together or as a pretreatment to bioremediation.

Excavation
The soil that is polluted is removed from the site where contamination occurred to a site or facility where the risk of exposure to potential pollutants may be controlled effectively. This approach can be used for the treatment of both inorganic as well as organic pollutants (Lombi and Hamon, 2005). Likewise, the treatment of excavated soil could also be done on the site, away from the site or the soil may not be treated but dumped in a landfill. However, the fastest and safest way to remedy crude oil-contaminated soil is excavation except that this approach is neither advanced nor cheap (Ahmad et al., 2020). Though this method is simple and efficient, it is very prolonged; can be damaging, time-consuming and also very costly due to the transportation of contaminated soil to the disposal site and the need to take care of the landfill mines created in the process. Because almost 75% of waste created by humanity comes from mining and manufacturing industries, the amount of waste in the mine dumps determines the dangers posed to the environment; as such air pollution from vapours of the contaminants is indiscriminately discharged into the atmosphere (Pashkevich, 2017).

Incineration
During incineration, the polluted soil is burnt in an incinerator at high temperatures under regulated conditions. Once heated the vaporized pollutants are collected or eliminated by pyrolysis. This method is one of the easiest ways to get rid of oil in the soil (Rushton et al., 2007). Using a combustor on a pilot scale, it has been shown that almost all the oil contaminants can be removed from contaminated soil at temperatures of about 800°C (Anthony and Wang, 2006). Onsite incineration is mostly used because it is the cheaper process for remediating contaminated soil, though it must be stressed that this method is not environmentally friendly because the volatile and flammable chemical compounds that are in crude oil may cause environmental pollution (Diphare and Muzenda, 2014). Cost of transportation to access the incinerator may also render the technique expensive (Ball et al., 2012). As can be seen from Fig. 3, incineration produces emissions that lead to secondary pollution (Shen et al., 2016). Table 3 illustrates some commonly used physical remediation methods for processing soil contaminated with oil.

Chemical methods
A number of chemical methods are also used to get rid of oil in contaminated soil. These chemical methods include thermal stripping (Vidonish et al., 2016), chemical oxidation (Ahmad et al., 2020; Ershadi et al., 2011) and photochemical oxidation (Cheng et al., 2016).

Oxidation
Chemical oxidation is another technique employed in removing harmful substances from the soil. Oxidation of the organic contaminants is achieved by the use of oxidants such as hydrogen peroxide, \( \text{H}_2\text{O}_2 \), ozone \( \text{O}_3 \), permanganate \( \text{MnO}_4^- \) and persulphate \( \text{S}_2\text{O}_8^{2-} \) that are reactive and the method is dependent on the soil medium for efficiency (Ahmad et al., 2020; Sutton et al., 2014). A Fenton’s reagent, a combination of hydrogen peroxide and ferric ion \( \text{Fe}^{3+} \) is also often used in chemical oxidation. During Fenton’s reaction, the ferric ion catalyzes the reactions while hydrogen peroxide being an oxidizing agent produces hydroxyl ions (Ahmad et al., 2020). The efficacy of the use of Fenton’s reagent on oil removal from sand at a low pH has been demonstrated in the past (Goi et al., 2006). This technique, when employed under the right conditions, has been found to remove 48% of TPHs in contaminated soils within two hours suggesting that the method might be used to eliminate TPHs from contaminated soils in a short period (Adipah, 2018). Other researchers have made use of ozone as another oxidative method for removing oil from soil because it is easily generated, stored and handled especially, in-situ remediations (Adipah, 2018). Further, soils treated with this technique can be reused as ozone returns back to oxygen in no time (Chen et al., 2019). Some researchers have reported combining ozonation with bioremediation to increase the efficiency of the degradation process (Russo et al., 2012; Javorská et al., 2009; Derudi et al., 2007). Despite the many benefits associated with the use of ozone, it is known to kill indigenous microorganisms in the soil and augmentation is usually required for soil restoration (Jung et al., 2005). The oxidation method is often used in highly contaminated soil because its
application is short term and contaminants can be oxidized within a few weeks. It is yet worth noting that the method might not necessarily be a good choice in low permeability soils (Ogunkeyede, 2016).

**Photochemical oxidation**

Photochemical oxidation involves the transformation of a chemical compound in presence of sunlight (Hnadnadjev-Kostic et al., 2014). In this method, a mixture of the contaminant with a catalyst is irradiated with light (UV or sunlight) which cause oxidation of the organic pollutants leading to the formation of compounds such as water and carbon dioxide. Semiconductor catalysts have a valence band with energetically stable electrons and an unoccupied conduction band of higher energy. Irradiation of these semiconductors activates photocatalytic reactions where an electron (e-) is promoted into the conduction band and a hole (h+) created in the valence band (Liu and Zhang, 2014; Xiang et al., 2011). Consequently, through photocatalytic processes, hydroxyl (OH) radicals along with superoxide (O2-) anion radicals are formed which causes the photochemical oxidation of the organic pollutant at the semiconductor surface. The importance of a high temperature, increased exposure time or the concentration of oxygen is that

### Table 3: Comparison of key findings and disadvantages associated with different physical methods of oil remediation

<table>
<thead>
<tr>
<th>Method</th>
<th>Design and Area of Focus</th>
<th>Key Findings</th>
<th>Gaps/Annotations</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Incineration</td>
<td>Focused on different remediation techniques including their limitations.</td>
<td>Incineration is a cheap remediation method compared to other techniques.</td>
<td>Incineration produces secondary pollutants.</td>
<td>Diphare and Muzenda, 2014</td>
</tr>
<tr>
<td>Excavation</td>
<td>Highlighted some modern remediation techniques.</td>
<td>Excavation is the fastest and safe way to treat contaminated soil.</td>
<td>Excavation is quite time-consuming and damaging at the same time.</td>
<td>Ahmad et al., 2020</td>
</tr>
<tr>
<td>Landfill</td>
<td>Focused on the environmental impact of mine dumps.</td>
<td>Three quarters (75%) of waste originates from mining and manufacturing industries.</td>
<td>Amount of waste in the mine dumps determines the dangers posed to the environment.</td>
<td>Pashkevich, 2017</td>
</tr>
<tr>
<td>Soil washing</td>
<td>Use of organic solvents for hydrophobic organics</td>
<td>Various solvents used were able to remove the organics from 75-86% Removal of contaminants was achieved from 60-86% After seven hours an efficiency of 88.32% was actualized.</td>
<td>The efficiency of oil removal is dependent on oil type, soil type, weather conditions, and penetration depth. Preventive measures are necessary to prevent oil contamination of soils. No single method can completely mitigate oil-contaminated sites. Improvement in the soil quality in terms of physicochemical was reported.</td>
<td>Diphare and Muzenda, 2014 Akpoveta et al., 2012</td>
</tr>
<tr>
<td>Sonication</td>
<td>Removal of persistent organic pollutants.</td>
<td>Rate of removal of pollutants depends on the type of soil, frequency and power of the ultrasound used.</td>
<td>Increasing power increased the removal rates</td>
<td>Shrestha et al., 2009</td>
</tr>
<tr>
<td>Soil washing</td>
<td>Heavy metals and petroleum hydrocarbons</td>
<td>Tartaric acid was suitable for washing away up to 82% TPHs. Hydrochloric acid was found to be a better washing solution for heavy metals.</td>
<td>A suitable washing solution must be determined based on the contaminant, mineralogy of the soil, and the type of the soil.</td>
<td>Moon et al., 2016</td>
</tr>
</tbody>
</table>
it boosts photochemical oxidation in nature (Clark et al., 2007). Fig. 4 shows the generation of hole-electron pairs in an idealized semiconductor.

Photochemical oxidation is a powerful remediation method for decomposition of oil in the soils. Some researchers have used photooxidation with semiconductors as photocatalysts over the years to treat organic pollutants (Liu and Zhang, 2014). Photocatalytic pre-treatment enhanced degradation by improving the solubility of oil and biodegradability (Brame et al., 2013). Progressive combination of the photocatalytic remedy of oil polluted soil with titanium dioxide (TiO₂) and bioremediation can effectively remove TPHs in polluted soil only when sufficient infiltration of light is realized (Yang et al., 2017). Previous reports indicate that photooxidation removed all forms of TPHs suggesting non-selective removal of TPHs while removal increased with increasing moisture content which is in line with the assumption for hydroxyl radical generation water is required (Brame et al., 2013). Photochemical oxidation of oil by use of TiO₂/zeolite composite is a sustainable way of destroying oil deposits minus titanium dioxide diffusing into the environment.

Fig. 3: Incineration of contaminated soil (Koul and Taak, 2018)

Fig. 4: A general scheme for generation of hole-electron pairs in an ideal photocatalyst (Banerjee et al., 2014)
Photochemical oxidation is the most appropriate method in the breaking down of oil (van der Heul, 2009) and organic pollutants (Wang et al., 2014).

Recent reports have concluded that the interactive influence of UV illumination and TiO$_2$ catalysis is responsible for the decomposition of PAHs in contaminated soil (Zhang et al., 2008). However, they also noted that a small number of investigative studies on the photocatalytic oxidation of polyaromatic hydrocarbons on the soil surfaces have been done using TiO$_2$ as the catalyst under UV irradiation. Effendi and Aminati (2019) explored the likelihood of enhancing biodegradation of the TPHs in soil contaminated with crude oil by integrating chemical oxidation using TiO$_2$ under sunlight irradiation as a photocatalyst and bioremediation through the landfarming system. Their study revealed that the amount of TPHs removed increased when a photocatalyst was included as compared to exclusive bioremediation. Despite this positive result, increased degradation rates were not at all times relative to the concentration of titanium dioxide. Natural microbial action and UV light derived energy had an effect on the process of degradation but the effect of UV intensity was not considerable. Addition of a concentration of 2% TiO$_2$ resulted in the greatest TPHs degradation rate up to 67% removal of TPHs within 12 weeks. Because biodegradability and solubility are enhanced during chemical oxidation, Effendi and Aminati (2019) were able to investigate the proficiency of blending photocatalytic oxidation using TiO$_2$ and bioremediation to deal with the constraint of hydrocarbon bioavailability to indigenous microbes and to ensure that the frequency at which TPHs are removed in oil-contaminated soil increased using the landfarming technique. Photochemical oxidation is a non-selective remediation technique which can degrade a variety of contaminants.

**The general problem**

The use of oil in bulk quantities by mining industries leads to soil contamination (New climate economy, 2014) because of the equally large amounts of waste oil generated which often pose a disposal challenge. Spills from oil waste happen due to human negligence and leaking of oil from storage tanks and poorly maintained and serviced machinery. Indiscriminate disposal of waste oil often causes soil contamination leading to land, surface and groundwater contamination. When oil is present in water bodies, aquatic organisms are affected. Waste oil also causes degradation of the environment thereby reducing its capacity to support soil organisms as well as the growth of plants.

**The problem of soil contaminated with oil in mining industries in Zambia**

Mining industries require the use of oil in large amounts in their various mining operations and the recent past has witnessed an increase in the use of oil as petroleum products due to the advancement of equipment as well as machinery used in the mines (New climate economy, 2014). This high oil usage has caused a spike in environmental pollution especially soil contamination resulting from large amounts of oil waste generated from various mining activities. Challenges of waste oil disposal are also being experienced in Zambia, a country that is located in southern Africa. Zambian mining companies such as Mopani copper mines (MCM) also consume large quantities of oil in their daily operations in the process producing equally vast amounts of waste oil. This oil waste often causes soil pollution resulting from indiscriminate disposal as well as other factors related to storage and transportation. In mitigation, MCM uses bioremediation (landfarming) with spill sorb but this method is often slower and takes longer compared to other treatment methods (Maila and Cloete, 2004), thus larger oil spills might remain in the soil for some time, (Zhang et al., 2020b) and may allow even more toxic compounds to linger in the soil. Since the half-lives of some hydrocarbons are as long as 28 years and some may be resistant to degradation, bioremediation is probably not the correct treatment technique (Goi et al., 2006). In response to this problem, the use of photochemical oxidation is an emerging technology that offers the most effective means of treating soil contaminated with oil in addition to providing a sound basis for developing a culturally, socially, economically, and ecologically sustainable remedy for contaminated soils (Yang et al., 2017).

**Spill Sorb Technique at MCM**

Mopani Copper Mines is one of the major players in Zambia’s mining industry and uses vast quantities of oils in its operations. Oil spillage is therefore inevitable and the company has been spending huge...
sums of money on bioremediation of hydrocarbons in soils. The mining firm uses landfarming with spill sorb to treat contaminated soil. Spill sorb is a manufactured organic oil absorbent that has been utilized in adsorbing oil. It is formed from Canadian peat moss once dried after harvesting. Spill sorb has a biological catalyst inside the cell structure. The cells are also a storage for oxygen which is required in the ecosystem and for biodegradation. The catalyst in spill sorb acts together with the microorganisms present to initiate the process of bioremediation. Although the method is biological, it is time-consuming, affected by climatic conditions and usually result in incomplete degradation (Zhang et al., 2020b) because some compounds in the oil are stubborn and not all microorganisms found in the soil can degrade them (Khan et al., 2004). This might lead to increased toxicity levels in the soil (Chibwe et al., 2015), hence cannot be a suitable method.

The proposed method

Photochemical oxidation emerges as a green technology for sustainable oil waste management and soil pollution resulting from hydrocarbons. The on-going study at the Copperbelt University proposes and seeks to promote this method in remedying soils contaminated with hydrocarbons present in the oils. The use of abundant and free sunlight in conjunction with readily available clay inorganic materials in the photochemical oxidation of contaminated soil is not only environmentally friendly but it is also in line with sustainable development methods. Hence, this study will focus on photochemical oxidation and assess its effectiveness in treating oil-contaminated soils with locally engineered clay using sunlight. To increase adsorption capabilities, the clay materials will be chemically modified by incorporating hydrophobic groups within the microstructure of the materials. Chemical modification typically involves the sol-gel process using room temperature reactions. Generally, the material is dispersed in an alcoholic solution followed by addition of hydrophobic groups to increase oil-material interaction and by addition of transition metal solutions in correct amounts to ensure photocatalysis effects are incorporated (Deshmukh et al., 2020). X-ray fluorescence (XRF) and inductively coupled plasma mass spectrometry (ICP-MS) will be used to the percent incorporation of the transition metals. Furthermore, infra-red spectroscopy will be employed to substantiate the added hydrophobic groups onto the clay while UV-visible spectroscopy will determine whether the modified clay will absorb in the visible region of the spectrum. One of the parameters employed to ascertain the degradation process is oil reduction in the soil. This is achieved through Soxhlet extraction and later using Eq.1.

$$\% R = \frac{C_o - C_e}{C_o} \times 100$$  \hspace{1cm} (1)

Where, $C_o$ = initial amount of oil; $C_e$ = amount of oil at time $t$ and $\%$ Residual (R) oil = the percentage of the residual oil after photo-degradation, (Narayan,
Table 4: Summary of chemical remediation methods for processing soil contaminated with oil

<table>
<thead>
<tr>
<th>Method</th>
<th>Design and Area of Focus</th>
<th>Key Findings</th>
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</tr>
</thead>
<tbody>
<tr>
<td>Oxidation: Oxidants such as hydrogen peroxide, ozone was used.</td>
<td>Considered many remediation techniques for soil contaminated with oil.</td>
<td>Chemical methods offer a quick way to remediate contaminated soil.</td>
<td>Some techniques such as incineration must be used with caution as they are generally not acceptable in most societies.</td>
<td>Ahmad et al., 2020</td>
</tr>
<tr>
<td>Oxidation: sulfate radicals</td>
<td>Sulfate radicals were used to remove dissolved ammonia and organic matter from landfill leachates.</td>
<td>Increasing the sulfate dose reduces the efficiency of the sulfate radicals and the pH of the solution.</td>
<td>The method might produce nitrates from ammonia and also a reduction in the pH due to HCl production.</td>
<td>Chen et al., 2019</td>
</tr>
<tr>
<td>Oxidation: Fenton Reagent.</td>
<td>Oxidation using Fenton reagent was used effectively to get rid of contaminants from soil contaminated with the total petroleum hydrocarbon.</td>
<td>A 48% removal rate of the contaminants within 2 hours of treatment was obtained.</td>
<td>Fenton process was hailed as a quick method to remove contaminants from the soil.</td>
<td>Adipah, 2018</td>
</tr>
<tr>
<td>Conventional and microwave pyrolysis.</td>
<td>Conventional carbonization and microwave pyrolysis were compared.</td>
<td>Conventional pyrolysis produced 70% removal of total organic carbon (TOC) while microwave pyrolysis was able to extract up to 77% of TOC. Microwave pyrolysis was suitable for both in situ and ex situ remediation.</td>
<td>Microwave pyrolysis has little adverse impact on animals and the environment hence eco-friendly.</td>
<td>Ogunkeyede, 2016</td>
</tr>
</tbody>
</table>
| Photo-oxidation: using TiO2 under UV irradiation. | Combination of photochemical oxidation using TiO2 as a photocatalyst and the landfarming technique in the remediation of crude oil-contaminated soil. | Addition of 0.5% and 2% of TiO2 to bacteria soaked oil-contaminated soil removed up to 59% and 67% of TPHs in 12 weeks. | i. Photocatalysis enhanced the degradation of the organic pollutants compared to biostimulation alone. 
ii. No correlation between the amount of TiO2 and rates of pollutant decomposition. | Effendi and Aminati, 2019 |
| Photo-oxidation: using TiO2 under UV irradiation followed by bioremediation. | Contaminated soils underwent pretreatment using TiO2 with various concentrations of Ultraviolet radiations (UV A and UV C). | Oil-contaminated soils pretreated with UV radiation removed about 26% of TPHs compared to 15% of non-pretreated soils. | Limited penetration of light into the soil depth hinders the capability of TiO2 to aid bioremediation | Yang et al., 2017 |
| Photo-oxidation: clay-based photocatalysts. | Various advanced technologies involving the use of clay-based photocatalysts were reviewed. | Clay-based photocatalysts can be applied in environmental remediation. | Generation of H2 and CO2 reduction can be done using layered clay | Liu and Zhang, 2014 |
2010) to calculate the percentage reduction. Some common chemical methods including photochemical degradation are illustrated in Table 4.

**Environmental economic evaluation of remediation strategies**

According to Lombi and Hamon (2005), the economic benefits of particular soil mitigation processes largely depend on many factors such as the type of soil contamination, the hazardous effects of the pollutant, and the period of remediation of the chosen method as well as the urgency of the reclamation of the polluted soil. According to a summary provided by the authors, Fig. 5, biological-based approaches are among the most cost-effective methods. Ultimately, the real cost of each method is dependent on the length of remediation procedure involved. Depending on the economic strength of a country and the urgency of land reclamation, different strategies have to be adopted to suit the needs of that particular nation or institution.

**CONCLUSION**

The remediation of the contaminated soil could be viewed as a multi-dimensional crisis resulting from complex factors that influence the efforts to reverse the damage. Also, this crisis could be brought about to choose an appropriate remediation technique for a particular type of contaminants taking into account the cost associated with each particular treatment option. There are several methods of mitigating soils contaminated with oil with each method having its advantages and disadvantages. Bioremediation is particularly attractive as it is a natural process that does not introduce secondary chemicals into the soil and is capable of complete mineralization of oil into benign water and carbon dioxide. However, this process is usually slow as most micro-organisms are incapable of breaking down heavy or long chain components of the oil. Bioremediation is a cheap method, gets rid of wastes without causing disruptions to the environment. However, the method requires a lot of time to get the best results and may therefore prove to be costly in the long run. Phytoremediation as a biological technique may be inefficient as some plants may be sensitive to salinity, pH, water, soil fertility and climate. Also, it might not be appropriate in high concentrations of contaminants. Other plants may be affected by plant diseases and pests. Physical methods such as incineration may be carried out under any weather conditions and are regarded as a fast remediation method. However, this method may not be cheap to set up and operate as it requires a lot of energy. The technique may also cause air pollution. Low temperature technique can remove much as 90% of the pollutants but the method is also quite costly and not environmentally friendly. Soil washing is an easy and effective method though it is prolonged, takes too much time and is expensive. The surfactant used may be harmful because of the likelihood of sticking to the soil particles. Chemical methods such as the use of ozone are often speedy in treating contaminated soil but the use of chemicals may adversely affect the soil and living organisms as a result of leaching and other side effects. Thus, alternative methods that would enhance the breakdown of these fractions are sought to improve the remediation process. Photochemical oxidation processes as chemical remediation techniques are not only economical but also effective as compared to the biological and physical methods in the treatment of oil-contaminated environments. In response to seeking a low cost and accelerated approach to remediating soil-oil contamination, the use of abundant and naturally occurring clay is of considerable interest. In this regard, a combination of adsorption and photocatalysis using various adsorbents has been utilized. Although clay is non-conducting due to the presence of silicon (Si) and aluminium (Al) ions as the backbone of the structural integrity of clay, the materials can be modified by simple sol-gel methodology. The sol-gel process allows for incorporating eco-friendly transition metals such as iron or manganese to increase absorption to 45% of visible light but also allows for the introduction of chelating or hydrophobic groups to increase oil-clay interaction. Additionally, photocatalysis mitigation can help break down long chain hydrocarbon fractions of oil into simple forms that then microorganisms can break down naturally. Thus, reducing the time it takes to reclaim the polluted soil or land. Finally, the remediation of contaminated soil in any nation must be looked at as a crisis requiring immediate attention as consequences of not remediating this precious resource might be devastating.

**AUTHOR CONTRIBUTIONS**

M. Mambwe wrote the manuscript text with input from other authors. K.K. Kalebaila and T. Johnson analyzed and edited the manuscript.
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CONFLICT OF INTEREST

The authors declare no potential conflict of interest regarding the publication of this work. In addition, the ethical issues including plagiarism, informed consent, misconduct, data fabrication and, or falsification, double publication and, or submission, and redundancy have been completely witnessed by the authors.

ABBREVIATIONS

\[
\begin{align*}
\text{\%} & \quad \text{Percentage} \\
\text{Al} & \quad \text{Aluminum} \\
\text{C}_b & \quad \text{Conduction band} \\
\text{C}_0 & \quad \text{Concentration of oil at time zero} \\
\text{C}_t & \quad \text{Concentration of oil at time, } t \\
\text{CO}_2 & \quad \text{Carbon dioxide} \\
\text{Fe}^{3+} & \quad \text{Ferric ion} \\
\text{FTIR} & \quad \text{Fourier transform infrared} \\
\text{H}_2\text{O} & \quad \text{Water} \\
\text{H}_2\text{O}_2 & \quad \text{Hydrogen peroxide} \\
\text{IEA} & \quad \text{International energy agency} \\
\text{ICP-MS} & \quad \text{Inductively coupled plasma mass spectrometry} \\
\text{IR} & \quad \text{Infrared} \\
\text{MCM} & \quad \text{Mopani copper mines} \\
\text{MnO}_4^- & \quad \text{Permanganate} \\
\text{O}_2 & \quad \text{Oxygen} \\
\text{O}_2^- & \quad \text{Superoxide} \\
\text{O}_3 & \quad \text{Ozone} \\
\text{OH} & \quad \text{Hydroxyl radical} \\
\text{PAHs} & \quad \text{Polyaromatic hydrocarbons} \\
\text{R} & \quad \text{Residual} \\
\text{S}_2\text{O}_8^{2-} & \quad \text{Persulphate} \\
\text{Si} & \quad \text{Silicon} \\
\text{t} & \quad \text{Time} \\
\text{TiO}_2 & \quad \text{Titanium dioxide} \\
\text{TPH} & \quad \text{Total petroleum hydrocarbons} \\
\text{UV} & \quad \text{Ultraviolet} \\
\text{V}_b & \quad \text{Valence band} \\
\text{XRF} & \quad \text{X-ray fluorescence}
\end{align*}
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