Remediation of Oil Contaminated Soils using Solvent-Flocculation Extraction

Antonette Malepe, Motshumi Diphare and Edison Muzenda

***Abstract*—**In this work, the recovery of base oil from lubricating oil contaminated soils was investigated using solvent extraction. Lubricating oils are discarded into the ground or landfills and this neither protects the environment nor conserves this important resource. Extraction of used lubricating oil from the contaminated soils can produce more valuable products and reduce environmental contamination. The objective of this work was to recover the base oil from clay, loam and sand oil contaminated soils through solvent extraction using hexane. The influence of particle size distribution, soil moisture and soil characteristics on base oil recovery were studied at a solvent-oil ratio of 1:2. The soils used were collected from an open field, eliminating the need for drying; hence the influence moisture content on the separation efficiency was eliminated. The soil-oil mixture was dissolved in sodium hydroxide (NaOH) solution at 40°C while agitating at 300rpm. During this stage, base oil separated from additives. A solvent was added to extract the base oil from the lubricating oil. Distillation was used to recover the solvent from the solvent-oil mixture. The highest oil recovery (85%) was obtained from sand oil while clay gave the lowest of 40%.

***Keywords*—**Base oil, distillation, lubricating oil, solvent extraction.

I. INTRODUCTION

LUBRICATING oil is a valuable resource and should properly managed [1]. Its functions include lubrication, cooling, cleaning and suspending and as well as protecting metal surfaces against corrosive damage. The main constituent in lubricating oil is the base oil which can be refined from crude oil or synthesized in the laboratory. The base oil, 71.5– 96.2 wt% is blended with chemical additives according to the required grade and specified duty [2].

Lubricating oil undergoes degradation during use altering oil properties due to changes in lubricating oil molecular structure. This is attributed to the cracking, isomerization and polymerization reactions due to high temperatures in the running engines. Therefore oil quality is gradually decreased and should be discarded and replaced [3]. Hence the disposal and recycling of waste oils becomes important [4]. Lubricating oil contaminated soils are environmental challenge and of no economic value. Hence innovative technologies are required for the remediation of oil contaminated soils [5].

Lubricating oil contaminated soils are due to leaking fuel storage tanks, crude oil spills and the disposal of refinery waste and railroad cars. Soils near railroad junctions usually becomes oil contaminated as a result of the use of lubricants and diesel by rail transport as well as the use of waste lubricants on railroads. Contaminated sites often contain contaminants such as benzene, toluene, ethyl-benzene, and petroleum hydrocarbons [6].

Various waste oil treatment techniques exist and these include reprocessing, reclamation and refining. Previously the oil was burnt for energy but it is now re-blended to engine oil after treatment [7]. Reference [8] analyzed and compared various waste lubricating oils regenerative techniques [8]. Some of these techniques are physical in nature capable of separating contaminants only with minimum appreciable colour change. Literature also reports studies focused on the reclamation of used lubricating oils. Hence treatment processes which can improve the colour and enhance the chemical properties of waste lubricants are required. Solvent extraction has received considerable attention in recent years as it overcomes the problems associated with acid sludge produced from chemical treatment.

TABLE I
TYPICAL COMPOSITION OF LUBRICATING GREASE

Ingredient	Wt%
Additives	
Metallic detergent	2.0-10.0
Ash less dispersant	1.0-9.0
Oxidation inhibitor	0.5-3.0
Antioxidation/anti wear	0.1-2.0
Friction modifier	0.1-3.0
Pour point depressant	0.1-1.5
Anti foam	2-15 ppm

Solvent extraction is a clean-up procedure that uses solvents to remove harmful chemicals from contaminated sources. The process involves mixing used oil and solvent in proportions which ensure complete miscibility of the base oil in the solvent.

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The solvent should reject additives and it must have high affinity for base oil. These additives settle and flocculate due to gravitational weight. Distillation is then used to recover the solvent [10]. Solvent extraction is both an efficient and cost effective process for separating hazardous contaminants from non-hazardous materials and concentrating the hazardous materials for further treatment. Some additives can be recycled or reused in oil manufacturing, thus minimizing disposal requirements [10] - [13].

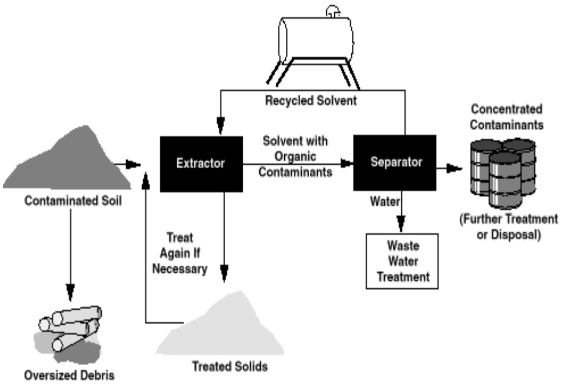

Fig.1 Typical solvent extraction process [20].

Soil characteristics or physical properties are important in the design of solvent extraction processes [14]. Soils are composed of organic material, inorganic/mineral particles, air, and water. A typical mineral soil is 55% solid particles and 45% air and water. The relative constituents of sand, silt, and clay particles influences soil texture. The three broad texture classes are: sands – soils in which sand particles comprise more than 70% of the material by weight; clays – soils in which clay particles comprise at least 35% - 40% of the material; and loams – soils that are a mixture of sand, silt, and clay. A sandy soil has loose, individual grains that can be seen and felt. It readily falls apart when dry. If squeezed when dry, a loamy soil will form a molded shape that will stay together with careful handling. When wet, the molded form is more durable and can be handled without breaking. A clay soil forms hard clumps when dry and is sticky when wet. Wet clay will form a long, flexible ribbon when squeezed [15].

Oil extraction efficiency generally increases with soil moisture [16], [17]. A moisture content less than10 wt. % acts as extraction solvent modifier enhancing its soil penetration ability [6], however in some cases moisture content does not significantly affect the efficiency of oil removal from the soil. For this reason, soils are dried before extraction to eliminate the influence of moisture on the extraction efficiency [18]. The removal of oils from soils is also influenced by soil type and composition. Oil extraction is very challenging for high clay content soils due to the formation of agglomerates and this may require longer contact times [19]. Soils are classified by a distribution of particle sizes and mineral content. Reference [20] reported that an increase in particle sizes allows for diffusion and better accessibility of solvent through the soil matrix, increasing the flow rate of the solvent and rate of extraction. Lubricating oil accumulates preferentially on smaller soil particles [20], as such, the oil is more easily extracted from larger soil fractions such as sand compared to smaller aggregate size fractions, loam and clay [21]. This study focused on the recovery of waste lubricating oils from contaminated soils using solvent extraction.

II. MATERIALS AND METHODS

A. Materials

Clean sand and loam soils were collected from an open field near the University of Johannesburg's Doornfontein campus while clay soil was collected near an open pit in Burgersfort, Limpopo, South Africa. Technical grade n-hexane and analytical grade sodium hydroxide (NaOH) pellets were supplied by Laboratory Equipment Supplies (Pty) Ltd (Germiston, South Africa). Lubricating oil was purchased from Engine Petroleum (Pty) Ltd. In this study, n-hexane was selected as an extraction solvent due to its for base oil.

B. Methods

Particle size distribution analysis was conducted using a stack of sieves from 200-600mm meshes opening size. Contaminated soils were synthesized by mixing lubricating oil with soil at a ratio of 1:8 and allowed to settle and homogenize for 2 month at room temperature.50g NaOH was heated to 60^{o}C to break sodium molecules and then cooled to 40^{o}C to avoid evaporation of the extracting solvent. 100g contaminated soil was added to NaOH solution while agitating at 300rpm for 3 minutes, the mixture was allowed to settle for a further 1 minute. After settling, three layers were formed, soil particles at the bottom, lubricating oil in the middle and sludge at the top, Fig. 2. The sludge is made up of additives, small soil particles and water.

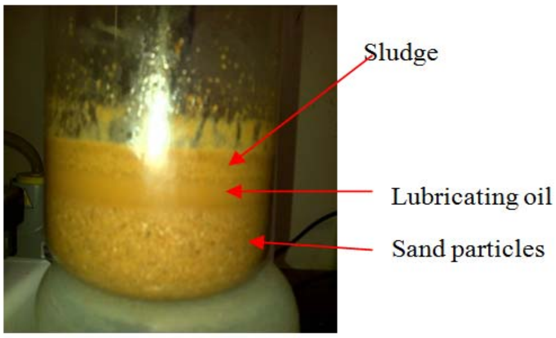

Fig. 2 Separation after addition of Sodium Hydroxide

150g n -hexane was then added and the mixture was agitated for 8 further minutes leading to clear separation of base oil, Fig. 3. The mixture was then filtered using a pressure filter to separate all solids material from the liquid. The filtrate was distilled to separate 3 components which are water, solvent and oil. The experiments were repeated 3 times for each type of soil.

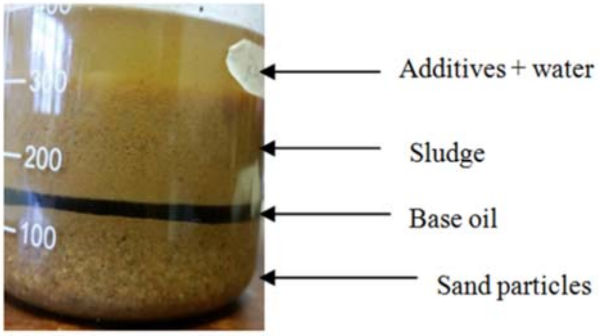

Fig. 3 Separation after addition of n-hexane

III. RESULTS AND DISCUSSION

A. Moisture content

In this study, the soil was collected from an open field eliminating the influence of moisture content and the need for soil drying. Moisture promotes the formation of thin films which reduce the adsorption of polar compounds on the mineral surface. Reference [24] reported the increase in soil recovery with the presence of moisture. This can be attributed to aromatic hydrocarbons with higher polarity compared to saturated hydrocarbons.

B. Particle size distribution

Table II shows the characteristics of the soil samples which were used in this study. Clay soil was found in lowest range of less than 0.002mm of the sieve containers, loam soil in the range of 0.002 to 0.06mm while sand was in the 0.006 to 2mm range. This observation was similar to that reported by [15], [25] Sand particles tend to be rounded or irregular, which creates large pore spaces between particles. Sand particles have a low capacity to hold water and nutrients. Clay particles are the smallest mineral particles and are less than 0.002 mm in size. Clay particles are generally flat, plate-like, and fit closely together hence they have the largest surface area.

C. Soil characteristics

Soil characteristics can influence chemical extraction from soils due to association forces between hydrocarbons and soil organic matter [10], [25]-[27]. The development of good soil structure requires an agent that binds and cements individual mineral particles together. Clay particles with large surface areas can act as binding agents. Organic matter can also be used to cement particles together enhancing water retention capacity.

Fig. 3 shows the effect of soil type on the extraction of base oil from contaminated soils using hexane as a solvent. The highest recovery (85%) and minimum (42%) were obtained from sand and clay respectively. The oil recovery increased with an increase in particle size distribution of the soil. The lowest recovery is clay soils is due to oil retention as a result of entrapments in clay and silt conglomerates. Similar findings were observed by [27]-[29]. References [28], [29] also observed the difficulty of using solvent extraction to recover oil from loam and clay soils fine particles. This is due to the low permeability of packed materials or sediments with high moisture content in loam and clay soils which enhances binding forces between the oil and soil particles as observed in this work. The addition of solvent to the sand mixture resulted in four distinct layers namely water-solvent, sludge, oil and sand. For loam soils, these layers were slightly visible while the separation was not clear at all for clay soil due to the formation of strong agglomerates by clay soils, Figs. 4 a, b, c.

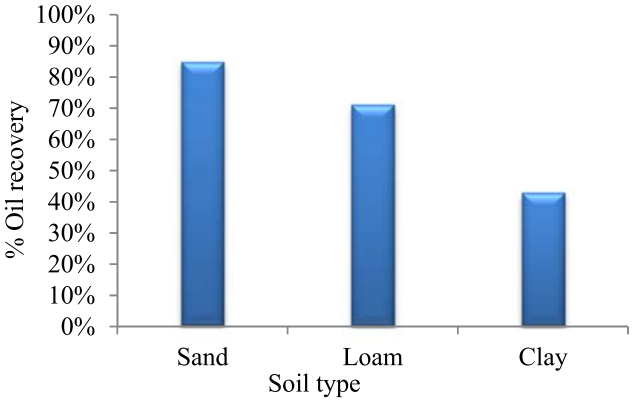

Fig.3 Influence of various soil types on the extraction efficiency of oil

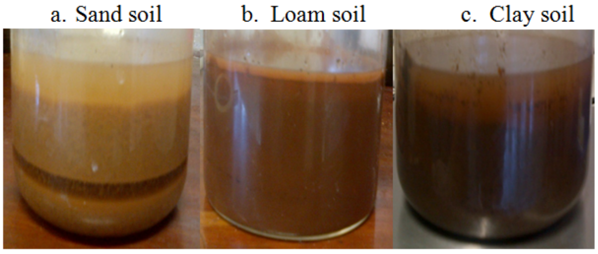

Fig.4 a, b and c Behavior of various soils after extraction

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