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Exploring Neoteric Solvent Extractants:
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and Regeneration of Automotive Catalytic Converters

This work and its defense approved by:

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Exploring Neoteric Solvent Extractants: Applications in the Removal of Sorbates from Solid Surfaces and Regeneration of Automotive Catalytic Converters

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by

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B. Tech., University of Madras, India, 2004

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Abstract

Part A - Removal of Sorbates from Solid Surfaces

Soil washing has been found to be an effective cleaning methodology. This study examines the feasibility and effectiveness of a water-miscible organic solvent – lactic acid as an alternative extraction medium for removing PCP from soils. Pentachlorophenol (PCP) is a chlorinated organic compound that has been found in soils at several contaminated sites.

Mixed solvents containing water and a water miscible solvent have been found to be more effective in extracting organic contaminants than the organic solvents alone. Our aim was to investigate solutions of lactic acid in water as potential alternatives to remove PCP from three model soils: montmorillonite, sediment from Caesar’s Creek, Ohio and this sediment ignited to remove organic matter.

Solutions of different concentrations of lactic acid – water have proven effective in extracting PCP in different spiked soils. PCP extraction was found to be the maximum using a 25% concentration of lactic acid. Richer solutions did not yield a higher removal. The study included optimization of the concentration of lactic acid in water for maximum extraction efficiency and determination and comparison of the extraction of PCP with lactic acid for the three model soils. The effect of organic matter on the extraction was also studied. Initial experiments showed that 24 h was the optimum extraction time. High extraction efficiencies were obtained for montmorillonite (40-80%) and ignited soil (~90%). Caesar’s creek sediment exhibited low PCP extraction due to the presence of soil
organic matter. Specific surface area of soil was also found to be an important factor affecting desorption of PCP. This ex-situ washing of soil with varying concentrations of lactic acid has been tested for maximum removal efficiency.

**Part B – Regeneration of Automotive Catalytic Converters**

In the regeneration of three way catalytic converters (TWCs), various solvents including biodegradable metal chelating agents, ionic liquids and organic acids were tested. The efficiency of novel environmentally friendly solvents in removing various contaminants such as P, Zn, Pb, Cu and S from commercial three way catalysts (TWC) has been investigated. In the first phase, the aim of our work was to investigate the biodegradable chelating agents [S, S]-ethylenediaminedisuccinic acid (EDDS), iminodisuccinic acid (IDSA), nitrilotriacetic acid (NTA) and the ionic liquid 1-butyl-3-methylimidazolium tetrafluoborate, as potential alternatives to organic acids (citric, oxalic and acetic) and compare them with the same for effectiveness. Four samples of catalysts (from front and rear inlets) of two different TWC’s with different mileages and aged under completely different conditions were investigated. In both the samples, zinc removal was found to be dependent on its initial concentration present in the sample. The order of zinc removal was found to be IDSA>EDDS>IL>NTA. The catalysts were also characterized using various techniques – X-Ray diffraction (XRD), SEM (Scanning Electron Microscopy) and BET surface area measurements.

In the second phase, the catalyst monolith was washed with only one solvent, EDDS. EDDS was selected of all those solvents tested because of its environmental benignity and its effectiveness in removing sulfur. SEM-EDS images at low magnification (50 µ)
showed considerable difference in the surface after washing. However, our XRD results indicated that there was no removal of major poison compound phases. Correspondingly, little or no enhancement in Brunauer-Emmett-Teller (BET) surface area was observed between used and the washed samples.
Acknowledgements

I would like to thank my advisor Dr. Dionysios Dionysiou for his guidance throughout the course of my research. I would like to thank Dr. Vasudevan Namboodiri for his valuable comments and ideas. I would like to thank my committee member Dr. George Sorial for his technical feedback and assistance. Thanks are also due to my committee member Dr. Amid Khodadoust for providing soil samples and his input on solvent extraction. Special thanks are due to Prof. Efsthathiou and Dr. Stavroula Christou, principal investigators in the ATKA project, for their collaboration.

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PART A

Removal of Sorbates from Solid Surfaces
Chapter 1. Introduction

During the past few years, there has been an increasing awareness in the removal of organic compounds from soil. Several methods have been employed in sites with soil heavily contaminated with polycyclic aromatic hydrocarbons (PAHs), chlorinated organic compounds, poly chlorinated biphenyls (PCBs), pesticides, herbicides and other toxic chemicals. These methods include soil incineration (1), bioventing (2), biopiling (2), electrochemical treatment, soil vapor extraction and vitrification. Of all the techniques used, soil washing is an effective treatment method to remove organic contaminants and toxic, heavy metals.

Soil washing can be tailored to suit the requirements by modifying the solvent. Soil washing is a very successful soil remediation technique for several groups of organic contaminants. Various solvents have been used in the past. The conventional solvents include methanol, ethanol, acetone, hexane and toluene. Solvent washing is a very viable and cost effective technology depending on the solvent used. Of all techniques available for the remediation of soils, solvent extraction is an efficient process for removing organic contaminants (1). Various groups of organic contaminants like chlorinated organics (3-8), can be removed by this process. Soil extraction or soil washing can be done in-situ or ex-situ. The former process involves washing of soil at its source using a solvent circulation system while the latter requires excavation of soil from the site.
In general soil washing processes require water miscible solvents. This is because soil contains moisture in itself and partially water miscible or immiscible solvents hinder transport in the extraction process and hence reduce effectiveness. \textit{In-situ} processes utilize dilute solutions of solvents. As a result, different solvents have been investigated as mixed solvent systems. Mixed solvents improve the organophilicity of water. Such systems involve varying concentrations of a miscible organic solvent in water. The organic cosolvent added enhances the solubility of the organic contaminants in the aqueous phase exponentially (8, 9). Ethanol (6, 8) and methanol (10) cosolvent mixtures have been investigated for the removal PCP and naphthalene, respectively. The presence of water, especially in \textit{in-situ} flow systems, increases transport of the contaminants.

However, newer classes of solvents which became recently commercially available, including surfactants, were investigated for this application. Surfactants have been used extensively in soil washing to remove organics such as naphthalene, phenanthrene and PCP (11, 12). They have also been investigated for removal of heavy metals (13). They are capable of increasing solubility of the contaminants due to their amphiphilic properties and their formation into micelles. However their fate in surface water and soils has not been researched extensively (14, 15). Another novel class of solvents is ionic liquids (ILs). Considered to be “green” due to properties such as non – flammability and non-volatility, ILs also attracted a lot of interest due to the fact that their properties could be tuned to a particular application by varying the cation and anion (16, 17). Hence ILs such as, butyl imidazolium hexafluorophosphate (bmim [PF$_6$]) and butyl imidazolium

\footnote{References at the end of Part A.}
chloride (bmim [Cl]), in particular, were tested for the removal of organic contaminants including chlorophenols, herbicides and PAHs from aqueous systems (17, 18). Following their success, these ILs were later extended for soil washing (4).

Though ILs are effective in several cases for the extraction of various organic compounds compared to certain conventional solvents (4), there are several questions regarding their sustainability and non-hazardous nature (19). There is little work done on ecotoxicity of ionic liquids. QSAR (Quantitative Structure Activity Relationship) tests have been carried out to investigate ecotoxicity and genotoxicity (20). Studies have also been carried out to investigate sustainability and economic considerations of applications of ionic liquids in research and industry (21). QSAR studies have shown that ionic liquids with the imidazolium group have greater bioaccumulation when compared to common solvents like acetone (4, 20). In addition to this; bmim [PF₆] is only very sparingly soluble in water. For all the above mentioned reasons, the application of ionic liquids in the extraction of environmental samples is only restricted to usage in the laboratory as discussed in Khodadoust et al (4). In the course of this study, the increasing concerns about the possible toxicity of ILs, has lead us to explore alternative extracting solvents.

Cyclodextrins (13), chelating agents like ethylene diamine tetra acetic acid (EDTA) (13) organic acids like citric acid (13), rhamnolipids (22) and polymeric solvents (23) have also been investigated. However, of all these solvents used so far, several possess environmental concerns. The solvents need to be environmentally friendly and biodegradable if they have to be used for soil washing especially for in-situ treatment.
They should not persist in the soil environment. If there are traces of solvent residue in the soil, they should not be toxic. The focus of our recent work is to investigate novel, environmentally friendly, biodegradable solvents which are easily available and comparatively inexpensive.

The solvents used for soil washing need to be water miscible as soil has a certain amount of moisture. Partially miscible or immiscible solvents hinder transport of contaminants and reduce extraction efficiency.

PCP is a highly recalcitrant chlorinated organic compound found extensively in soils, sediments and aquatic systems (6, 24). The main sources of PCP contamination include its use as an antiseptic, herbicide and wood preservative agent. It has also been used as a herbicide and to control molds and slime (25). PCP has been listed as a priority pollutant by the USEPA. PCP has been detected in soils and groundwater in polluted sites. It has also been detected in humans tested in the USA. PCP has a half life of 45 days in the soil environment (26). It is highly hydrophobic ($K_{ow} = 5.0$) and hence tends to persist in soil and sediments (26). PCP exhibits specific organ toxicity towards liver, kidneys and the central nervous system. Since PCP biodegrades very slowly, it is required to apply various remediation techniques for its removal. In order to effectively apply these technologies, PCP interaction with soil and organic matter should be studied. Chiou and co-workers (27-29) have studied extensively the bonding of PCP with soils. The main factor affecting the sorption of organic compounds in soil is the soil organic matter (30). Other factors like pH (31), specific soil surface area (2,7), particle size, CEC (cation
exchange capacity) (32), and moisture (32) also influence PCP adsorption on soil. Hence, the extraction of these hydrophobic organic compounds from soils is mainly influenced by interactions between soils, solvents and the PCP.

1.1 Background

Lactic acid is an aliphatic organic, alpha hydroxyl acid (33). It is the simplest hydroxyl acid. Possessing an asymmetric carbon atom, it exists as two optically active forms (33). It possesses both an acid and an alcohol group and can undergo reactions of both the groups. Lactic acid also undergoes intermolecular esterification forming lactoyllactic acid (33). Lactic acid is a constituent of milk products and a byproduct of metabolism and other bodily functions. Traditionally, it has been produced by fermentation processes of corn steep liquor (34). It is also widely present in soils, produced by the soil microbial population. Laboratory scale studies show that its presence in soil does not affect the natural soil bacteria. The resemblance of its structure to that of the components of soil organic matter has led to studies on its effects on PCP adsorption / desorption into soil (35).

Although the studies of its physical properties have shown that lactic acid is completely miscible with a large number of solvents including water, ethyl ether and ethanol, not much is known about solvents immiscible with lactic acid (33, 36). Hydrocarbon groups are reported to be immiscible with lactic acid (37). For example, benzene and lactic acid have very low mutual solubilities. Solubility of thiophene in lactic acid is greater. Lactic acid is insoluble in chloroform and other halogenated compounds and miscible with
furfural at ambient temperatures (33). Weiser (36), and Leonard et al. (38), reported distribution coefficients between lactic acid and various organic compounds like nitrobenzene, $\alpha$-dichlorobenzene and phenols. The highest distribution coefficients are with alcohols and amines (33). The distribution coefficients were found to be dependant on temperature and the presence of other substances, mostly remaining from the fermentation processes. This investigation was more industrial than environmental; to determine media to extract pure lactic acid from the fermentation broths, since production of pure lactic acid is important for many applications.

The influence of the degree of dissociation on the distribution coefficients has been studied extensively. Weiser (36) found that distribution coefficients increased with increasing concentration of lactic acid in 12 different solvents. Murray (39) studied the effects of pH and dissociation in lactic acid distribution between 1-butanol and water in the presence of alkaline medium. It was reported that the distribution coefficients were considerably higher than values determined with an alkaline medium, leading to an assumption that the sample contained lactoyllactic acid.

Lactic acid has been previously tested for the removal of phenanthrene as well as heavy metals from soil (13). Lactate esters have been found to be good cleaning agents for the removal of oils, greases and paints as well as having excellent solvation properties for pesticides and fertilizers (40). The additional advantages of selection of lactic acid are its biodegradability, non toxicity and environmental benignity. It completely biodegrades in less than 5 days and has been applied extensively in biodegradable polymers (41). Lactic
acid has an extremely low volatility (41) and is completely miscible in water. Due to the property of non-volatility, it has been suggested as a “green solvent” (34). It is almost non-toxic in the aquatic environment producing no effects in goldfish exposed to as high as 430 ppm for > 100 h (42). Having no toxicity issues, it is safe to be introduced into the soil. The resemblance of its structure to that of the components of soil organic matter has lead to studies on its effects on PCP adsorption / desorption into soil (35). USEPA has classified both lactic acid and its ethyl and butyl esters as Class 4A inert compounds. Such a classification is given only to chemicals that have no toxicity and other environmental concerns (34). The presence of lactic acid in soil has been found to affect and enhance biodegradation of highly toxic compounds like toxaphene (5). After the immobilization of PCP in the lactic acid phase, combined biological treatment can be carried out with lactic acid as a primary substrate. The basic criteria of selection of lactic acid are its biodegradability, non toxicity and environmental benignity. Hence, here we explore the solvent properties of lactic acid from an environmental standpoint.

Driven by the need of overcoming the environmental implications of the aforementioned solvents, and searching for a solvent that could be used both in in-situ and ex-situ processes, this work explores an alternate soil washing system using solutions of lactic acid. These lactic acid cosolvents were evaluated for their efficiencies in removing PCP from soils as well as studying the effect of soil organic matter.
Figure 1.1. The chemical structure of lactic acid

Figure 1.2. The chemical structure of pentachlorophenol (PCP)

Table 1.1. Properties of lactic acid (C₃-H₆-O₃)

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular Weight</td>
<td>90.08 AMU</td>
</tr>
<tr>
<td>Melting point</td>
<td>16.8 °C</td>
</tr>
<tr>
<td>Boiling Point</td>
<td>125 – 140 °C</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>1.201</td>
</tr>
<tr>
<td>Log P (octanol water partition coefficient)</td>
<td>0.72</td>
</tr>
<tr>
<td>pKa</td>
<td>3.86</td>
</tr>
<tr>
<td>Vapor Density</td>
<td>N.A</td>
</tr>
<tr>
<td>Vapor Pressure</td>
<td>N.A</td>
</tr>
<tr>
<td>Solubility in water</td>
<td>Completely miscible</td>
</tr>
<tr>
<td>pH</td>
<td>&lt; 1 (concentrated acid), 2.28 (1% solution), 1.75 (10% solution).</td>
</tr>
</tbody>
</table>

Compiled from references: 41, 43, 44, 45
Chapter 2. Materials and Methods

2.1 Soils

Montmorillonite (MT) (Fisher Scientific) is commercially available clay with high surface area. The pH of montmorillonite is 3.9 (4). The material distribution of montmorillonite is 19% sand-50% silt-31% clay (4). The sediment collected from Caesar’s Creek (CC), Ohio is a grayish, brown sandy loam with 3.4 % organic matter, as presented in Table 2.1. CC soil was ignited to remove soil organic matter. Following the procedure suggested by Tam et al., a known weight of soil was ignited in a furnace at 700 °C (35). Then the soil was left to cool in the hood. After this, the PCP was spiked in the soil (see section 2.3). The weight of soil used in extraction was twice that of the other soils. This soil is referred to as ignited soil (IGN) in throughout the thesis.

Table 2.1. Properties of CC sediment

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Method Used For Determination</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inorganic: Sand (%)</td>
<td>ASTM D422</td>
<td>49.2</td>
</tr>
<tr>
<td>Silt (%)</td>
<td>ASTM D422</td>
<td>34.1</td>
</tr>
<tr>
<td>Clay (%)</td>
<td>ASTM D422</td>
<td>16.7</td>
</tr>
<tr>
<td>Organic Matter (%)</td>
<td>ASTM D2974</td>
<td>3.4</td>
</tr>
<tr>
<td>pH</td>
<td>ASTM D4972</td>
<td>7.4</td>
</tr>
</tbody>
</table>
2.2 Extractants

Lactic acid (Aldrich – 95% purity, rest water) in different concentrations was tested as a mixed solvent extractant system. Acetone, dichloromethane (DCM) and methanol were obtained from Aldrich and their purity was HPLC grade or greater. Deionized water (DI) was used to prepare all lactic acid solutions.

2.3 Spiking Procedure

Concentrated stock solutions of PCP were prepared in acetone. A certain amount of the PCP solution was added to water-soil mixtures. Spiking was carried out in 125 mL glass vials with Teflon caps. Each vial was filled up to the top to minimize headspace loss. Each vial was tumbled for 3 weeks at room temperature. Then it was air-dried in the dark in a fume hood for 3-5 days. The final moisture content was maintained at 6% for MT and 8% for CC and IGN. The initial loading was 100 mg/kg PCP for all soils. In order to study the effect of soil organic matter at a higher PCP concentration, a batch of soil with 600 mg/kg concentration was also spiked. This concentration was chosen because heavily contaminated soils have been found to have a concentration ≥ 600 mg/kg (47). Control experiments were performed at each step to quantify for loss due to evaporation and adsorption onto glassware.

2.4 Soil Extraction

All batch shaking experiments were conducted in centrifuge tubes. Soil and solvent were added to the tubes at soil: solvent extraction ratios of 1:5, 1:10 and 1:20 (g: mL). The
samples were vortexed on a lab mixer (vortexer) until they were well mixed. Then they were placed inside a rotating tumbler and tumbled for 24 h at 20 rpm at room temperature. After shaking, the two phases were separated by centrifuging at 5000 rpm for 30 min. The liquid extract was filtered through 0.45 µm filter. The liquid extract was analyzed for PCP using high performance liquid chromatography (HPLC) (see section 2.5). All experiments were performed in triplicates. Each tube was weighed before and after extraction and the weight of the soils was recorded before and after extraction for mass balance calculations. The volume of solvent was also measured for isotherm calculations.

2.5 Analysis of PCP

Quantitative analysis of PCP in lactic acid was conducted using a high performance liquid chromatography (HPLC) (Agilent 1100 series). A reverse phase amide column (RP-16 Discovery Supelco) and a UV-Vis diode array detector were used for HPLC analysis. A mixture of (0.01N sulfuric acid) and acetonitrile in the ratio 30:70 at a flow rate of 1.5 mL/min was used as the mobile phase.

2.6 BET Surface Area of the Soils

The BET surface area of the three soils were measured by Tristar 3000 (Micromeritics Corp, GA), using nitrogen adsorption / desorption analyses.
2.7 Soxhlet Extraction

In order to determine the initial PCP concentration in the soil, a soil sample weighing 2 g was placed into a cellulose extraction thimble (Whatman). The soxhlet apparatus consisted of a 250 mL round bottomed flask, a soxhlet extraction tube, and a bulb type Allihn condenser. The PCP was extracted with a 100 mL of methanol for a period of 24 h, according to USEPA method 3540 C (48). After the extraction cycle was completed, the solvent remaining in the flask and tube was measured. Since the soil was not highly contaminated with PCP, the samples were concentrated to 2 mL using a rotary evaporator before analysis by HPLC.

2.8 Sonication

Sonication has been used as a standard procedure for cleaning of soils (32). Here this procedure was used to determine the initial concentration of PCP in soil and the results were compared with the soxhlet procedure. Sonication is not considered an analytical method for PCP determination. About 2 g of the soil sample was sonicated with 30 ml of methanol for 30 min. The sample was placed in a water bath to dissipate the heat produced by the sonicator tip and minimize loss of solvent by evaporation. The power was adjusted at 60 Hz. As in the other extractions, the sample after extraction was measured and weighed. Table 2.2 gives the initial concentrations obtained from these methods.
### Table 2.2. Initial concentrations of PCP in the soils

<table>
<thead>
<tr>
<th>Sample</th>
<th>Concentration (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MT</td>
<td>100 (soxhlet)</td>
</tr>
<tr>
<td>CC</td>
<td>$137 \pm 33$ (100 mg/kg spike) (soxhlet)</td>
</tr>
<tr>
<td>CC</td>
<td>$602 \pm 25$ (600 mg/kg spike) (sonication)</td>
</tr>
<tr>
<td>IGN</td>
<td>94.9 (sonication)</td>
</tr>
</tbody>
</table>
Chapter 3. Results and Discussion

3.1 Extraction Efficiencies of Lactic Acid

Several solvents have been tested for this purpose. If this application involving the use of lactic acid as an extractant is to be feasible, the solvent has to exhibit several characteristics. Lactate esters have also been found to exhibit good solvation properties towards pesticides (34). Though lactic acid by itself has not been previously used for soil washing, several lactate esters have been found to have cleaning properties (40). We test the soil washing properties of lactic acid in removing PCP from three types of soils. There are various criteria for selection of solvents. The focus here is on the environmental benignity of lactic acid.

3.1.1 Extraction from Montmorillonite.

The extraction results of PCP from Montmorillonite using different concentrations of lactic acid at various soil: solvent ratios are shown in Figure 3.1. The results from Figure 3.1 show that at the soil: solvent ratios of 1:10 and 1:20, the 100% lactic acid produced higher recoveries than the other concentrations evaluated. Lowest PCP recoveries were obtained with water and 1% lactic acid. 10% and 25% lactic acid produced intermediate extraction efficiencies between those obtained with 1% and 100%. The PCP extraction efficiencies of the 25% and the 100% were comparable at higher soil: solvent ratios. Greater efficiencies at higher volumes of solvent (i.e., the higher soil: solvent ratios) indicate increased solvent capability. Since MT has no organic matter, the extraction can be attributed most exclusively to surface interactions.
Figure 3.1. Extraction of PCP from Montmorillonite (MT) (100 mg/kg spike) using 1%, 10%, 25% and 100% lactic acid by volume

3.1.2 Extraction from CC

The comparison of extraction of PCP from this type of soil is shown in Figure 3.2. The 1% lactic acid was as effective as the higher concentrations at higher soil: solvent ratios. At a ratio of 1:5 (g: mL), the extraction efficiency at 1% concentration was considerably higher than those of the other concentrations. At this soil: solvent ratio, the lowest extraction efficiency was obtained from 100% concentration of lactic acid. The highest extraction efficiency was observed in the case of those of 1:20 soil: solvent ratio and 25% lactic acid concentration.
In order to study the effect of soil organic matter alone, the CC soil was burnt off to remove organic matter. The extraction data of this type of soil is represented in Figure 3.3. The process of soil organic matter removal by ignition is a common procedure that has been reported by Tam et al. (35). The extraction efficiencies of 1% and 25% lactic acid are comparable at a soil: solvent ratio of 1:20 g: mL. Extraction with water also exhibits efficiencies of about 40-80%.
Figure 3.3. Extraction of PCP from ignited soil (IGN) using 1%, 10%, 25% and 100% lactic acid by volume

3.2 pH Effects

The pH of the lactic acid mixed solvent was measured before and after the extractions of the 1:5, 1:10 and 1:20 ratios. The pH of the different concentrations of the clean lactic acid ranged from 1.13 to 2.8 for 100% to a 1% respectively. The pH data after extraction show that the soil affected the pH of the solvent. The solution pH for all the soils after extraction was found to be in the range of 4.27 – 4.34 for the three soils at the different soil: solvent ratios.

Discussion. In the partitioning of PCP onto soils, the pH of the soil – solvent systems plays an important role. Solution pH effects have been determined in various systems of mixed solvents (8, 31). The sorption of the ionic form of PCP on soils is mainly due to hydrophobic interactions but pH effects could cause electrostatic forces to dominate (49). In systems of ethanol - water and methanol - water, it was assumed that the pKa values of
PCP increased with increasing fraction of alcohols in the mixtures. In our case, the solution pH of the lactic acid decreased from 2.5 at 1% to 1.13 at 100% concentration. Lower pKa values result in lower dissociation of PCP at the higher lactic acid concentrations (39). The pH of the lactic acid mixed solvents after extraction with ignited soil, montmorillonite, and Caesar’s Creek sediment was 4.27, 4.34 and 4.43, respectively. This indicates that the majority of the desorbed PCP from all the three soils was in the neutral form. A previous study that investigated the effect of amendments like oil and surfactants on PCP adsorption, reported that a 0.2 unit decrease in pH had the same effect as increasing the soil organic content by 1% on the desorption coefficient $K_D$ for a pH range of 3-7 (50).

3.3 Soil Surface Area

One of the physical factors affecting PCP sorption/ removal on soils is the specific soil surface area. BET analysis determined a specific surface area of 6.3 m$^2$/g for the ignited soil as compared to 3.34 m$^2$/g for Caesar’s Creek. The BET surface area for montmorillonite was measured to be 25 m$^2$/g. The burning of the Caesar’s Creek sediment caused some pore size transformations that resulted in an increase in the specific surface area. Though the specific surface area of montmorillonite is much higher than that of the ignited soil, the desorption data indicate greater desorption from ignited soil. The trend is different with the Caesar’s Creek sediment that has organic matter; the desorption at a 10% concentration of lactic acid decreases and then rises again. The desorption data indicate that the extraction of PCP from Caesar’s Creek sediment was due to the solvent interaction with the soil organic matter. In the case of the ignited soil,
the soil surface area was between that of montmorillonite and Caesar’s Creek sediment, but desorption was maximum. In the absence of organic matter, this can be attributed to the soil surface area.

3.4 Solute – solvent – soil interactions

Desorption of PCP increases exponentially with increase in the lactic acid concentration in the solvent. In all the three soils studied, there was a decrease in the desorption at 100% lactic acid. The decrease was very sharp for montmorillonite. This shows that the desorption is not solubility limited. The soil property data show that the surface area of montmorillonite is a magnitude higher than that of ignited soil but desorption from this soil is higher. In the case of the ignited soil, water yields an extraction efficiency of 40 – 80 % indicating that the extraction is mainly a solvent – sorbent mechanism.

Lower extraction efficiencies of PCP from Caesar’s Creek sediment with higher lactic acid concentrations were due to the effect of the organic acid on soil organic matter, which is purely a soil – solvent interaction (51). The natural organic matter present in soil has been compared to a semi-polymeric material that exists as glassy and rubbery states (52). Desorption of organic compounds from such soils involves washing them out of the pores present in the rubbery state. The capacity of the solvent is an important consideration. The soil – solvent interaction is greatly affected by the ability of the solvent to extract from the NOM (natural organic matter) / SOM (soil organic matter).

The desorption of PCP from soil is thus affected by several factors including the type of its bonding with soil. Tam et al. reported that the possible mechanism of PCP adsorption on soil in the presence of organic matter is by electrostatic interactions between the soil
surface and organic acids (35). PCP has also been found to form intermolecular hydrogen bonds with COOH groups found in the soil organic matter (53). The addition of lactic acid in soil with organic matter might have increased the number of COOH groups for PCP bonding hence decreasing desorption in the case of 100% lactic acid.
Chapter 4. Conclusions

Lactic acid used as mixed solvent systems with water was effective in removing PCP from model soil and natural sediment. The desorption increased exponentially with increasing concentrations of lactic acid in the solvent upto 25% and then decreased at higher lactic acid concentrations upto 100%, as observed in other mixed solvent systems with organic solvents. Decrease in desorption at concentrated lactic solutions was observed in the Caesar’s Creek sediment and was attributed to the presence of organic matter. For this sediment, desorption also increased with increase in soil specific surface area.

The designation of “green solvents” has been recently applied to ionic liquids that were considered “green” due to lack of vapor pressure and hence air pollution problems. Lactic acid can be thought to be a “green” solvent from a broader environmental standpoint – non volatility, environmental benignity and non toxic nature. Produced from biological materials, lactic acid can be manufactured in completely “green” processes with no harmful byproducts. This study assessed the effectiveness of lactic acid in a laboratory scale soil washing process. Further site specific and more mechanistic studies are required before field application can be implemented. However, this work can be thought of as the first step towards the development of a soil washing process using lactic acid.
References


(27) Chiou, C. T.; Kile, D. E.; Rutherford, D. W.; Sheng, G.; Boyd, S. A. Sorption of Selected Organic Compounds from Water to A Peat Soil and Its Humic-Acid and


PART B
Regeneration of Automotive Catalytic Converters
Chapter 5: Regeneration of Commercially Aged Three Way Catalytic Converters (TWCs) Using Environmentally Friendly Solvents

5.1 Introduction

Three way catalysts (TWCs) have been in use in automobiles for a few decades now. The installation of these catalytic converters in the exhaust pipes of gasoline powered vehicles helps reduce emissions and hence air pollution. The TWC is able to convert NO\textsubscript{X} to N\textsubscript{2}, CO to CO\textsubscript{2} and the HC\textsubscript{s} to water vapor and CO\textsubscript{2}. Due to this reason, they are referred to as three way converters.

The active metals in the catalytic converters are mostly platinum or palladium – rhodium catalysts. The catalysts undergo deactivation with continued usage. This deactivation can be of various forms including physical blocking of the pores, chemical fouling, mechanical or thermal effects. In all forms of the deactivation, the catalyst fails partially or completely depending on the extent. The causes of deactivation of TWCs are mainly of chemical origin. Poisons like sulfur and phosphorous arising from fuel and fuel additives are the main cause of deactivation [1-5]. Metallic contaminants like lead, iron, nickel, and cadmium arising from the metallic engine parts also contribute to fouling [3]. Physical mechanisms like sintering of catalyst due to thermal and mechanical attrition have also been observed in TWCs. While these poisons can be removed, and the catalysts regenerated, there are other forms of irreversible deactivation. Deactivation mechanisms have been studied extensively. In most cases, the catalyst can be regenerated within its useful life. One of the main reasons for studying deactivation is the possibility of reactivation / regeneration of used TWCs.²

² References at the end of Part B
Reactivation/regeneration of these catalysts has attracted the interest of automobile industries and scientists. The reasons for regeneration are many. Initially the reasons were economic. Later, rising awareness was brought about by environmental reasons. Many methods of regeneration were suggested, namely high temperature heating using hydrogen [4, 6] and thermal chlorine gas treatment [6, 7]. Many of these methods utilize extremely harsh conditions or are invasive. Invasive techniques involve the dismantling of the catalytic converters. This results in generation of waste as all the materials cannot be reused [8]. Such disadvantages with these methods resulted in exploring alternative options such as solvent washing as a regeneration technique. Solvent washing has been carried out with several solvents namely acids such as citric acid [5], oxalic acid [5] and acetic acid [3] and can be implemented in-situ. Metal chelating agents like EDTA have also been tested [9]. These solvents have been effective in removing some poisons present in the TWC and hence have lead to varying levels of regeneration. Some of the solvents such as oxalic acid may cause corrosion of the surface.

The aim of this study was to investigate the solvents given below for catalyst regeneration in a batch washing process as a first step. The extraction efficiencies and the catalytic activity of the washed and the used samples were compared. Extraction was performed on catalyst powders and later on pieces of the monolith.
5.2 Materials and Methods

5.2.1. Sample Selection

The catalytic cartridges were extracted from two gasoline automobiles (Ford model Windstar, 1998) and a Mitsubishi Galant (Cyprus). The Ford catalytic converters were supplied by the catalyst research department, Dearborn, MI, USA. All Ford catalyst samples have the same technical specifications. The information for both the Ford and Mitsubishi TWCs are listed in Table 5.1. The used monolith was removed from an automobile with a mileage of 101,300 miles. A similar catalyst sample with 0 miles (a fresh catalyst) was used as a blank sample. Both catalytic converters contained 0.55 percent by weight palladium. The samples used were from the front inlet of two catalyst bricks. Small pieces of dimensions (2x2x2) cm were used in the extraction experiments. The pieces of the TWC were crushed for XRD and for the BET surface area characterization analyses.

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<tr>
<th>MITSUBISHI (CYPRUS)</th>
<th>FORD (USA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mileage – 161,600 miles</td>
<td>Mileage - 101,359 miles</td>
</tr>
<tr>
<td>Pd and Rh based catalyst</td>
<td>Pd based catalyst</td>
</tr>
<tr>
<td><strong>BASE MATERIAL</strong></td>
<td><strong>BASE MATERIAL</strong></td>
</tr>
<tr>
<td>Cordierite (2MgO-2Al₂O₃-5SiO₂)</td>
<td>Cordierite (2MgO-2Al₂O₃-5SiO₂)</td>
</tr>
<tr>
<td><strong>DIMENSIONS</strong></td>
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</tr>
<tr>
<td>DS / PS Brick 1: 38in³ [3.15in x 4.75in x 2.98in]</td>
<td>DS / PS Brick 2: 46in³ [3.15in x 4.75in x 3.67in]</td>
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<td><strong>CHANNEL SHAPE</strong></td>
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<td>Square</td>
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<tr>
<td><strong>WASHCOAT DETAILS</strong></td>
<td><strong>WASHCOAT DETAILS</strong></td>
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</tr>
</tbody>
</table>
5.2.2. Solvents tested

**Ionic liquid:**
1-butyl-2-methylimidazolium tetrafluoroborate \([(\text{Bmim})^+ (\text{BF}_4^-)]\)

**Biodegradable metal chelating agents:**
- Nitrilotriacetic acid (NTA)
- \([S, S]\)-ethylenediaminedisuccinic acid (EDDS) (Commercial name: E-30)
- Iminodisuccinic acid (IDSA) (Commercial name: Bay pure CX-100)

**Organic acids:**
- Lactic acid
- Acetic acid
- Citric acid
- Oxalic acid

In the above mentioned list, the first two classes are the novel (never tested before for the regeneration of TWC) solvents and the organic acids are for comparison. Though ionic liquids have been used for desulphurization and denitrification of fuels [3], they have not been used for similar applications with solid materials. Another new class of solvents, biodegradable metal chelating agents, was also used in the study- Nitrilotriacetic acid, \([S, S]\) ethylenediaminedisuccinic acid and immunodisuccinic acid. These have been used as solvents to remove heavy metals from soils [4]. To the best of our knowledge, this is the first study that involves such solvents for the removal of contaminants from catalysts.
Figure 5.1. Structure of (a) Bmim[BF₄]; (b) IDSA; and (c) NTA

5.2.3. Catalyst samples

Used TWC samples of known origin were obtained from Mitsubishi (Cyprus) and Ford (USA). Samples were cut from the front and rear of the catalyst cores. This is because the
concentration of the active metals and the contaminants is found to vary in a constant manner between the front and rear of the catalytic cores. On visual inspection the rear portion seems of a lighter color than the front.

These TWC samples were named as follows: FM and RM for front and rear of Mitsubishi catalyst and FF and FR for the Ford catalysts. After extraction, the initials of the solvent were added as a suffix to the existing name. These TWCs were tested in their powder form as the first step in the solvent investigation. In the next step, the best solvent with respect to the extraction efficiencies and the environmental benignity was tested with catalyst pieces and the washed pieces analyzed for catalyst activity. The catalytic activity was compared with the used TWC of the same kind.

5.3. Experimental Methods and Procedures

5.3.1. Materials

Ionic liquid (1-butyl-2-methylimidazolium tetrafluoborate) [(Bmim)\(^{+}\) (BF\(_{4}\))\(^{-}\)] was purchased from Merck & Co. (NJ) with a purity of 97%. Nitrilotriacetic acid (NTA) obtained from Fluka, was used in the form of its soluble sodium salt. EDDS was supplied by Octel Inc., commercially known by the name of octaquest E30. IDSA was supplied by Bayer under the commercial name of bay pure CX-100 and it was synthesized using an environmentally friendly process [4]. Acetic acid, citric acid, oxalic acid and lactic acid were used in the form of 10% solutions. All the solvents used had purity of more than 97%. Acetic, citric and lactic acids had purities of 99%. 

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5.3.2. Extraction procedure

Two ml of solvent and two grams of the TWC sample were placed in a 10 ml extraction vial. Batch shaking extractions were carried out in a temperature controlled laboratory shaker. The extractions with the biodegradable chelating agents were carried out for 24 hours [4]. Extractions were also carried out at 60°C for 2 hours [1] with the organic acids for comparison of the efficiencies of the novel solvents. The extracts were filtered using a 0.45 micron syringe filter before injection into the ICP. All the extracts were 2% acidic solutions for easy detection by the instrument.

5.3.3. Analyses

5.3.3.1. Chemical characterization

Elemental analysis of the liquid extracts was carried out by ICP (inductive coupled plasma) by USEPA method 6010 B for trace metals in solution. Dilutions were performed when necessary before ICP analysis.

5.3.3.2 Catalyst Poisons

Analysis was carried out after dissolution in aqua regia in an open vessel. This procedure is not expected to affect the poison concentration because poisons are found on the substrate. Sulfur and phosphorous were analyzed using the ICP-MS. Platinum, rhodium and palladium were analyzed using ICP-MS. The rest of the elements – zinc, copper, aluminum and lead were analyzed using an ICP-AES (Perkin Elmer 2100). Though the results from the instrument were in mg/l values, they were converted to mg/kg of TWC and expressed as percent removal. The concentrations of the poisons were used as the
basis for removal yield calculations. Though aluminum has been accounted for, it is not counted as a contaminant as it is a major wash coat constituent.

5.3.3.3. Other Analyses

Catalyst characterization was performed by various techniques like X-ray Diffraction (XRD), BET surface area and Scanning Electron Microscopy (SEM).

5.4. Results and Discussion

5.4.1. Initial composition of catalysts

The initial composition of the TWC’s has been determined by the digestion in aquaregia and quantified by methods as described in section 5.3. The results are given in Table 5.2. It can be seen that there is a consistent variation in the concentration of the elements between the front inlet and rear of the TWC [1]. Table 5.2 shows that there is a very similar trend in the composition variation of the two catalysts. In accordance with the published literature [3,19], the concentration of contaminants decrease from the front to the rear inlet and the active metals are more in the front part of the catalyst. Previous
studies showed that this is due to the migration of poisons [1]. However, as seen from both the ICP and SEM results, there is almost no sulfur present in the Ford catalyst.

### Table 5.2. Initial composition (mg/kg) of TWC samples

<table>
<thead>
<tr>
<th></th>
<th>Mitsubishi</th>
<th>Ford</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>FM</td>
<td>RM</td>
</tr>
<tr>
<td>Cu</td>
<td>1229</td>
<td>339</td>
</tr>
<tr>
<td>Zn</td>
<td>24620</td>
<td>5560</td>
</tr>
<tr>
<td>Al</td>
<td>160890</td>
<td>198023</td>
</tr>
<tr>
<td>P</td>
<td>21668</td>
<td>10956</td>
</tr>
<tr>
<td>S</td>
<td>27421</td>
<td>617</td>
</tr>
<tr>
<td>Pb</td>
<td>29267</td>
<td>14298</td>
</tr>
<tr>
<td>Pt</td>
<td>75</td>
<td>2785</td>
</tr>
<tr>
<td>Pd</td>
<td>44</td>
<td>72</td>
</tr>
<tr>
<td>Rh</td>
<td>na</td>
<td>530</td>
</tr>
</tbody>
</table>

FM: Front Mitsubishi; RM: Rear Mitsubishi; FF: Front Ford; RF: Rear Ford.

5.4.2. Extraction efficiencies

The extraction efficiencies of the different solvents were determined for the different contaminants (i.e., S, P, Zn, Cu and lead) for the different samples using the methods described in section 5.3. Consistent trends of contaminant removal between samples were observed. The solvent extractions carried out were effective to an extent with respect to the removal of contaminants.

5.4.2.1 Extraction efficiency of sulfur

Considerable amount of sulfur removal was obtained. The ionic liquid (1-butyl-2-methylimidazolium tetrafluoborate) along with the biodegradable metal chelating agents EDDS and IDSA were effective in removing sulfur. The other organic acids and NTA were not effective in removing sulfur. The sulfur removal can be attributed to the
presence of the secondary NH$_2$ groups in EDDS and IDSA and its absence in NTA. However in the case of the ionic liquid, sulfur removal is probably due to interaction between the extractants and the imidazolium ring system [3].

![Graph of % Removal of Sulfur](image)

Figure 5.2. Removal of Sulfur from “Front Mitsubishi” (FM) sample.

5.4.2.2 Extraction efficiency of zinc

Zinc was also effectively removed by the solvents tested. The maximum removal as seen was obtained by the IDSA. There is a trend observed in the Mitsubishi samples. There is a comparable removal from both the front and rear samples. The initial concentration of zinc is more in the front than in the rear. In all cases except one EDDS (E 30), the removal is more in the front samples than the rear. Zinc removal is concentration dependent – greater % removal with greater amount of zinc present [11].
5.4.2.3 Extraction efficiency of copper

Copper was leached out by both the ionic liquid and the chelating agents. Nearly 80% removal was achieved by IDSA in the “Front Mitsubishi” sample.
Comparison of the trends of copper removal shows that lactic acid was also effective in removing some copper in the Ford sample. But no copper was detected in lactic acid in the case of the Mitsubishi catalyst. The highest extraction in both cases was found to be given by IDSA.
5.4.4 Comparison with previous work

Extraction was also compared with the organic acids as solvents namely acetic acid, citric and oxalic acid. The sample that was considered in these extractions was the Mitsubishi front inlet sample (FM). Batch shaking was carried out at 60°C for 2 hours [11]. The results were compared to the previously published results under the same experimental conditions [11]. Our results are shown in the Figure 5.7. There is a comparable trend with the previously published results. In the removal of copper, the oxalic acid was the most effective followed by acetic acid and then by citric acid. In the case of zinc, citric acid was the most effective, followed by oxalic acid. No zinc was found to be removed by the acetic acid. Phosphorous was not removed by citric acid. Oxalic and acetic acids were found to be effective. In the case of lead, citric acid that was the best, followed by oxalic and acetic acids.

![Figure 5.7. Removal with the organic acids. OA: oxalic, AA: acetic acid, CA: citric acid.](image)

Figure 5.7. Removal with the organic acids. OA: oxalic, AA: acetic acid, CA: citric acid.
5.5. Conclusions and Prospects of Future Work

In this exploratory study we investigated the properties of new environmentally friendly solvents for catalyst regeneration. However, more studies are required to optimize the conditions to make it feasible in a large scale. Studies are also necessary to establish the mechanisms of removal. In the course of this study, it was discovered that NTA has possible carcinogenic properties. It also has the potential to transport cobalt compounds in soil and groundwater systems. Ionic liquids have several issues about their sustainability and stability. Of all these solvents tested, EDDS is the only one that has no reported environmental problem. Considering these reasons and previous extractions of heavy metals with EDDS, which proved as effective as EDTA, the most commonly used metal chelating agent, EDDS is tested on pieces of monolith of the TWC and is discussed in the following chapter.
5.6. Bibliography


(10) Larese, C.; Galisteo, F. C.; Granados, M. L.; Mariscal, R.; Fierro, J. L. G.; Furió, M.;

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Chapter 6. Extraction of TWC Pieces using Biodegradable Metal Chelating Agent – EDDS

6.1 Introduction

Environmental studies have shown that the use and disposal of catalytic converters cause an increase in the low solubility PGM (platinum group metals) in the environment [1]. Specifically, it was found that attrition of TWCs leads to increased incidence of Pd and Pt in the environment. The PGM metals also tend to bioaccumulate in the food chain. Statistics have shown that typical recycling of TWCs is only about 20-30% and in the 80,000 km life of the catalyst, 70% Pd is released into the surroundings along with other trace metals [2]. The recovery from spent catalysts in US was less than 4% in 1999 [2]. There is a lot of waste generated as spent strong acids and metal chelating agents. The disposal of this waste is also of concern. Complexing agents like EDTA increase the solubility of trace metals from the converters in the soil [3], which otherwise have very low solubility in surface waters and soil. In this study we evaluate an environmentally friendly biodegradable metal chelating agent S, S-ethylenediamine disuccinic acid (S, S-EDDS). EDDS has been used as an alternative to EDTA. EDTA is the world’s most widely used metal chelant. However, it is highly persistent in the environment as it cannot degrade biologically. Due to this, there is also a high risk of metal release into groundwater systems. EDDS has been successfully tested for the removal of toxic heavy metals from soils as well as in the enhanced phytoremediation of soils using chelants [4-6]. Apart from being biodegradable and environmentally friendly, EDDS is milder than the acids that are currently being used for this process. As a result of these properties,
there is lesser risk of release of metals into the soil from spent EDDS [4, 5]. Vandevivere et al. studied the biodegradability of metal-EDDS complexes and reported that a 1mM concentration of Ca-, Cr (III)-, Fe (III)-, Pb-, Al-, Cd-, Mg-, Na-, or Zn-EDDS degraded easily [7]. In most soil washing processes, the efficiency of EDDS is comparable to the benchmark EDTA [4, 5]. There is no reported literature of EDDS for TWC regeneration. The majority of the TWC regeneration works published so far concentrate on various aspects of TWC activity parameters like improvements on oxygen storage capacity and the dynamometer tests with previously tested solvents. The parameters like flow rates, temperature etc in the existing regeneration apparatus are varied. This work, however, investigates the efficacy of EDDS, in a batch process.

Based on our initial investigation explained in Chapter 5, EDDS was selected in our next step out of all the solvents tested. The other solvents tested have environmental concerns. NTA, though biodegradable, is reported to cause adverse health effects [5]. The ionic liquid, Bmim[BF₄], is extremely viscous and non volatile. This leads to problems of removal of the ionic liquid from washed samples prior to activity tests. Recent research shows that ionic liquids also pose problems of disposal and toxic product release [11,12]. In comparison to the other solvents tested, EDDS is environmentally benign and has been suggested as an effective substitute to the chelating agent EDTA [5].

The aim of this study was to investigate S, S-EDDS for catalyst regeneration in a batch washing process as a first step. The extraction efficiencies and the catalytic activity of the washed and the used samples were compared. Extraction was performed on catalyst powders and later on pieces of monolith.
6.2 Experimental Methods and Procedures

6.2.1. Sample Selection

The catalytic cartridges were extracted from gasoline automobiles (Ford model Windstar, 1998). The vehicles belonged to the Ford catalyst research department, Dearborn, MI, USA, who graciously supplied the converters. The catalyst samples have the same technical specifications. They are listed in Table 6.1. The used monolith was removed from an automobile with a mileage of 101,300 miles. A similar catalyst sample with 0 miles (a fresh catalyst) was used as a blank sample. Both catalytic converters contained 0.55 percent by weight palladium. The samples used were from the front inlet of two catalyst bricks. Small pieces of dimensions (2x2x2) cm were used in the extraction experiments. The pieces of the TWC were crushed for XRD and the Braunuer Emmett Teller (BET) surface area characterization analyses.

Table 6.1: Technical Specifications of TWC samples

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<tr>
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<td><strong>WASHCOAT DETAILS</strong></td>
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<td>Major oxides are Al₂O₃, CeO₂ and ZrO₂</td>
<td></td>
</tr>
</tbody>
</table>
6.2.2. Chelating agent

EDDS was supplied by Octel Inc., London, UK. The commercial name is Octaquest E30 and is a substitute for EDTA in various applications namely detergents and water treatment. The S, S isomer is used because it is readily biodegraded. The structure of EDDS is given in Figure 6.1.

![](image)

**Figure 6.1. The structure of EDDS [5].**

6.2.3. Regeneration Procedure

The samples (ca. 100 mg) were pretreated by heating (rate 10 K/min) in a 10\% H\(_2\)/Ar flow at 773 K for 1 h [8]. This pretreatment was implemented to guarantee that all the surface palladium would be in metallic form. In this way, acid treatment does not remove active metal (Pd), which would occur if it were partially oxidized. A known weight of the catalyst sample was placed with high solvent ratios (1:50 sample to solvent ratio) in 120 mL Teflon lined vials. The samples were placed in a laboratory shaker for 24 h. This is because higher solvent ratios give higher extraction efficiencies [5] and also help offset the effect of pH as complexing agents like EDDS are highly pH dependant [4,5]. This also helps in extraction of the target metals with the chelating agents in samples that have
many metals present. After extraction, the samples were washed with DI water by shaking in the same manner for 12 h. Then the samples were dried in an oven at 120 °C overnight. The samples were named by adding the suffix EDDS to the name.

6.2.4. Quantitative chemical analysis

The amount of the metals in the liquid extractant was performed using an ICP-MS (Inductively Coupled Plasma – Mass Spectroscopy). The samples were filtered through a 45 µm filter and diluted with water when necessary. The samples were acidified with 2% HNO₃ for enhanced detection by the instrument. Analysis was performed according to EPA method USEPA method 6010 B for trace metals in solution. Though the results from the instrument were in mg/l values, they were converted to mg/kg of TWC and expressed as percent removal. The concentration of the poisons was used as the basis for removal yield calculations. Though aluminum has been accounted for, it is not counted as a contaminant as it is a major wash coat constituent.


SEM-EDS were carried out on a Philips EDAX instrument. In the case of the monolith pieces, they were mounted on the sample holder with the washcoat surface mounted normal to the X-ray electron beam. The elemental analysis was done on channels next to each other so that the values would be representative and there would be less deviation. Analysis of three adjacent channels was performed and the quantitative result in wt% presented here is the average of the three readings. No coating of samples was done prior to analysis to avoid metal contamination from the sputter coater.
6.2.6. X-ray Diffraction analysis (XRD)

XRD patterns of the used and washed samples were recorded using a Siemens diffractometer in the scan mode from 10 to 60 \(2\theta\) (0.02/min).

6.2.7. Surface Area and Pore Size Distribution

BET surface area and pore size distribution analysis were carried out with a Tristar ASAP 3020 (micromeritics corporation) with nitrogen adsorption / desorption experiments. Degassing prior to the measurements was carried out at 200 °C for 2 h.
6.3 Results and Discussion

6.3.1 Extraction efficiencies

**Catalyst powders.** The initial tests were carried out on catalyst powders in order to test the efficiency of the solvent before testing could be done *in-situ* on pieces of monolith. The tests were performed on the powders from the front and rear inlets of both the Ford and the Mitsubishi catalysts. The results of the extraction efficiencies are shown in Table 6.2 for the Ford and the Mitsubishi TWCs.

### Table 6.2. The initial composition of the four TWC samples used

<table>
<thead>
<tr>
<th>Element</th>
<th>FI-M</th>
<th>RI-M</th>
<th>FI-F</th>
<th>RI-F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>1229</td>
<td>339</td>
<td>878</td>
<td>592</td>
</tr>
<tr>
<td>Zn</td>
<td>24620</td>
<td>5560</td>
<td>11984</td>
<td>5520</td>
</tr>
<tr>
<td>Al</td>
<td>160890</td>
<td>198023</td>
<td>188757</td>
<td>165722</td>
</tr>
<tr>
<td>P</td>
<td>21668</td>
<td>10956</td>
<td>14970</td>
<td>0.00</td>
</tr>
<tr>
<td>S</td>
<td>27421</td>
<td>617</td>
<td>712</td>
<td>bdl</td>
</tr>
<tr>
<td>Pb</td>
<td>29267</td>
<td>14298</td>
<td>113</td>
<td>2842</td>
</tr>
<tr>
<td>Pt</td>
<td>75</td>
<td>2785</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>Pd</td>
<td>44</td>
<td>72</td>
<td>1610</td>
<td>nd</td>
</tr>
<tr>
<td>Rh</td>
<td>na</td>
<td>530</td>
<td>na</td>
<td>na</td>
</tr>
</tbody>
</table>

- FI- front inlet ; RI – rear inlet ; M – Mitsubishi ; F- Ford.
- All concentrations in mg/kg of TWC.

Table 6.2 reports the initial amounts in mg/kg of TWC of the basic components and the poisons found in a commercial automobile TWC (Ford) (101,359 miles mileage). As reported, the sample obtained from Ford is a Pd only catalyst. However, our SEM-EDS analysis has found minute quantities of elements like neodymium. The noble metal composition as provided by the manufacturer is about 0.55% Pd washcoat. Cerium and
zirconium have also been found to be present. The washcoat is considered consisting of CeO₂, ZrO₂ and Al₂O₃. Since Al is a component of the TWC, it has been accounted for, but cannot be considered as a contaminant. For the Mitsubishi catalyst, a previous work has reported 27% loading of Al [15, 17]. Table 6.3 also gives the composition of the fresh (0 miles) catalyst. As it can be seen, considerably high compositions of P, S, and Pb are found in the used catalyst, due to prolonged use in an automobile. The contamination of TWCs has been studied extensively and various concentrations of poisons have been reported. Very high concentrations of poisons have been found in a completely aged catalyst of 200,000 km. Figures 6.2 and 6.3 show the removal of Pb, Fe, S, P, Zn and Cu obtained after washing with EDDS in the Mitsubishi catalyst. In the case of the Ford catalyst, the poisoning is almost entirely by P. As seen by both SEM-EDS and ICP, there is only a negligible quantity of S present. The extraction efficiencies of the Ford catalyst are given in Figure 6.4. An important reason for reduced S concentration is the decreasing content of S in fuels due to various EPA standards in the USA since the last decade. It is well known that the source of sulfur contamination in TWCs is the fuel and its additives. The main source of Zn and P is from ZDDP (zinc dialkyl dithio phosphate) which is used as a lubricant and an anti-wear agent in the vehicle systems [9,10].
Figure 6.2. Extraction of metal contaminants from the Mitsubishi TWCs using EDDS

Figure 6.3. Extraction efficiency of EDDS for Front Mitsubishi
6.3.2 Extraction on TWC pieces

The results of the extraction on 2x2x2 cm³ catalyst cubic pieces are given in Table 6.3. As it can be seen from the table, the catalyst was considerably poisoned as seen from the values of the new and the used catalyst. Sulfur was not detected in this catalyst both by ICP – MS and the SEM-EDS analyses. This TWC can be considered to be poisoned almost entirely by phosphorous. The characterization of P-poisoned TWCs has been studied extensively by Rokosz et al. [22]. The P was found to form an overlayer of Zn, Mg phosphates and a layer of aluminum phosphates inside the washcoat. The removal of phosphorous was found to be about 8000 mg/kg from the front inlet where the contamination by P is higher than in the rear inlet.

The removal of P by oxalic acid [17,23] has been investigated before. Oxalic acid is a relatively stronger acid with a pKa of 1.20. Such an acid has been found to have a greater dissolution efficiency towards phosphates, phosphites etc. EDDS, on the other hand, has a pKa value of 6.84 indicating that it is a much weaker acid [5]. Considerably high
concentrations of Fe and Zn are also observed in the liquid extracts. Aluminum leaching from the used samples is significantly higher than the fresh sample. This could be explained by the fact that the poison P was in the form of some Al salt resulting in the removal by the EDDS. A similar case was observed by Galisteo et al. [8] in the washing process of a commercial diesel catalyst by citric acid. The leaching of Al was much greater than that from the new sample. These observations suggest that EDDS is a promising solvent for the removal of the contaminants deposited on a TWC. The leaching of the active metal Pd was much higher in the new sample where it was in an uncombined, elemental form. The extraction of Pd was drastically reduced in the used samples. This can be explained by the fact that at such severe operation conditions, reduction of the PGM (platinum group metals) takes place along with Ce present on the surface [14]. This has been explained in various PGM loaded on the surface of $\text{Al}_2\text{O}_3/\text{Ce-Zr}$ mixed oxides where the hydrogen gas used for reduction is consumed at a rate more than required for the reduction of the active metals and is explained as the “hydrogen – spillover”.

Table 6.3. Regeneration of catalyst pieces (FI – Ford-103,000 miles)

<table>
<thead>
<tr>
<th></th>
<th>mg/Kg</th>
<th>Al</th>
<th>Fe(57)</th>
<th>Fe(66)</th>
<th>Pd</th>
<th>Pb</th>
<th>P</th>
<th>S</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Front inlet</td>
<td>2513</td>
<td>1277</td>
<td>1792</td>
<td>65</td>
<td>553</td>
<td>8658</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Rear inlet</td>
<td>1035</td>
<td>215</td>
<td>48</td>
<td>94</td>
<td>74</td>
<td>339</td>
<td>ND</td>
<td>1800</td>
<td>ND</td>
</tr>
<tr>
<td>NEW</td>
<td>55</td>
<td>ND</td>
<td>ND</td>
<td>118</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
</tbody>
</table>
A main parameter for the extraction of metals by chelating agents is the stability constant K. The stability constant values of the various metals for complexation by EDDS have been determined previously [5]. The log K values are given as 12.7 for Pb [24] and 22 for Fe. CuEDDS (log K = 18.4) and ZnEDDS (log K = 13.4) are stronger complexes than lead [25]. The stability constant (K) is an important parameter which determines the stability of a metal complex in the environment. The conditional log K values of most metal complexes in EDDS have found to be higher than those reported in literature for citric, oxalic and acetic acids which have been reported to be used for the regeneration of TWCs. This also shows that the competition from Ca, Mg and Ba present in the TWC to the complexation of these metals will be lower. Formation of metal – EDDS complexes in soil has been found to be highly influenced by the presence of Ba and Ca present in soils [5]. In our TWC samples, there is a considerable concentration of Ba and Ca. In previous cases, the effect of competition on regeneration of TWCs has not been considered. In the case of EDTA, the extraction of metals could be influenced by competition from Ba and Ca [5].

6.3.3 Characterization results

6.3.3.1 SEM-EDS analysis

Table 6.4 shows the wt% concentration of the elements in the TWC pieces, averaged over two areas on each of the adjacent channels of the washcoat. The SEM-EDS analysis was
carried out on both powders and the monolith pieces of catalyst. In the case of powders, it was not possible to obtain a concentration profile of the components in the TWC. The elemental analysis of the powders was carried out before and after washing. In the case of catalyst monolith pieces, the composition of the channels in the TWC was analyzed. A variation in the elemental composition of the used and washed samples was observed. In the case of the catalyst monolith, the analysis was done on the washcoat directly. As explained in the previous section, the TWC was exposed normally to the electron beam. Al, Si and Pd are clearly detected which are components of the TWC, along with Zn, P, Ni and Mg which are the contaminants in the TWC. Pb, which has been found in our sample in the ICP analyses, is a not major component here. The Pb peak could be present here among the noise as it could be close to the EDS detection limit. Another possibility is that the Pb could be present inside the depth of the washcoat. This configuration doesn’t detect the signals from inside the washcoat. These values are representative of the whole surface.

There is a high probability that the peak marked sulfur is noise, because the major emission lines of S are not present. This is further validated by the fact that the ICP analysis found almost no S present in the samples.

The Figures 6.7 and 6.8 (Appendix 1) show the composition of the same catalyst analyzed as both powder and monolith pieces. One aspect that needs discussion here is that the P emission peak is significant here but the values of wt% show a remarkable decrease in the value when compared to the used catalyst. There is also a reason of possible superimposition by the Zr L peak as the P K and Zr L energy lines are very close to each other at 2 KeV [14, 26]. In the used sample, the peak might correspond to P due
to the high concentration present. In the washed sample, the higher side of the peak must correspond to the Zr emission. This is evident from the SEM analysis of the powders wherein the Zr L peak is visible and in Figure 6.8 has been covered by the P peak. Such characteristics have been observed in previous SEM-EDS analyses of TWCs [14]. The comparison of the SEM-EDS energy lines in Figures 6.7 and 6.8 do not show a significant difference indicating that the composition was very similar in the case of this catalyst, analyzed in both powder and piece forms. The SEM micrographs surfaces (fresh, used and washed) are compared at very low power (Figure 6.9). The surface differences are very clear in the micrographs A, B and C. The surface of the fresh catalyst is very smooth whereas the catalyst after use has some roughness “visible”.

Table 6.4. Wt% concentrations from EDS analysis of Ford catalyst pieces

<table>
<thead>
<tr>
<th>Element (Wt %)</th>
<th>Fresh</th>
<th>Used</th>
<th>Washed</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiL</td>
<td>3.4</td>
<td>1.9</td>
<td>ND</td>
</tr>
<tr>
<td>ZnL</td>
<td>3.6</td>
<td>2.4</td>
<td>ND</td>
</tr>
<tr>
<td>MgK</td>
<td>1.9</td>
<td>1.2</td>
<td>0.83</td>
</tr>
<tr>
<td>AlK</td>
<td>52.4</td>
<td>50.4</td>
<td>34.3</td>
</tr>
<tr>
<td>SiK</td>
<td>5.4</td>
<td>6.5</td>
<td>4.6</td>
</tr>
<tr>
<td>PK</td>
<td>14</td>
<td>14.7</td>
<td>9.08</td>
</tr>
<tr>
<td>SK</td>
<td>0.9</td>
<td>0.7</td>
<td>ND</td>
</tr>
<tr>
<td>PdL</td>
<td>5.8</td>
<td>4.65</td>
<td>4.5</td>
</tr>
<tr>
<td>OK</td>
<td>-</td>
<td>-</td>
<td>46.7</td>
</tr>
<tr>
<td>NdL</td>
<td>12.5</td>
<td>17.3</td>
<td>-</td>
</tr>
</tbody>
</table>
6.3.3.2 XRD analysis

Figure 6.5 shows the 2θ region from 10 – 60 ° of the new, used and the regenerated TWC. The reflections of the cordierite are visible clearly because there are no interferences from other peaks. This is because this sample is uncontaminated. These are marked with (º). The peaks corresponding to 2θ = 29, 33.4 and 48.5 belong the Ce-Zr mixed oxide which is a major washcoat component. At lower values of 2θ, there is considerable interference by the cordierite peaks which are most intense in this region. In the used sample, the peaks corresponding to 28.90, 27.06 and 31.28 were assigned to CePO₄ (Cerium Phosphate – JCPDS file no. 84-0247). These are the three maximum intensity peaks of this compound, which are visible even after superimposition by other peaks. The crystalline structure of cordierite is not altered after use but the mixed oxide peaks become narrower and intense due to sintering. This has also been previously explained by Larese et al. [14]. AlPO₄ (JCPDS file – 84 0854) was also detected at 2θ = 26.4 which was found to be its maximum intensity peak. Calcium zinc phosphate CaZn₂(PO₄)₂ (JCPDS file – 84-1569) was also found at 2θ = 29.70 and 30.23 though the characteristic peak at 21.54 has been masked by cordierite. This compound along with Zn(PO₄)₂, Zn₂P₂O₇ and MgZn₂(PO₄)₂ is responsible for pore closing by forming an impervious glassy layer on the washcoat [22] . The possibility of another cerium phosphate peak (CePO₃)₃ cannot be ruled out completely at 2θ = 25.93 [13]. This phase has been reported to be found previously. There is no distinct difference in the XRD patterns of the used and washed TWC, indicating the removal of some phases. This could also suggest that there was no removal of crystalline phases and hence no improvement in
the surface area was seen. The intensity of some phases containing P is reduced indicating the partial removal of some crystalline phases.

Figure 6.5. XRD patterns obtained in the 10-60 $2\theta$ range over the fresh, used and washed Ford TWC. (*) Cordierite; (%) Alumina sample holder; (@) Ce-Zr oxides; (#) AlPO$_4$; (0) CePO$_4$; (+) CaZn$_2$(PO$_4$)$_2$

6.3.3.3 BET surface area

The BET surface area and the pore size distribution of the new, used and washed samples were compared. The surface area of the fresh TWC (0 miles) was determined to be 22 m$^2$/g. The surface areas of the used and the washed TWC were found to be 10.26 m$^2$/g and 9.53 m$^2$/g respectively. This indicates that washing with EDDS did not cause any marked difference in the BET surface area of the catalyst. In order to confirm that this decrease in the surface area was not due to the solvent, the used TWC was also washed with oxalic acid in the same batch process and no enhancement in the surface area was observed. There are a considerable number of published studies that have compared the BET surface areas of TWCs before and after washing [19, 21, 27]. However, all these
processes are continuous flow systems with recirculation of solvent. The conditions of these systems have been optimized for the catalytic activity. A few of these previous works report their operating conditions and emphasize on their flow rates of the system as an important parameter [9].

The conditions under which the catalyst has been aged also plays an important role in the pore size distribution. With TWC aging, there is a change from the microporous structure of the Ce-Zr oxides to a mesoporous one [28]. Figure 6.6 compares the pore size distributions of the fresh, used and the washed TWC samples. It can be seen that after EDDS washing a similar pore size distribution to that of the used catalyst was obtained. However, the specific volume of the pores decreased after washing. Other published studies report an increase in surface area after washing [21, 27, 29, 30] using acetic, citric and oxalic acids. The increase in the BET surface area after washing is attributed to the uncovering of the pores and was found that oxalic acid was more effective than citric acid [23].

![Pore size distribution curves obtained for the fresh, used and washed Ford TWCs.](image)

Figure 6.6. Pore size distribution curves obtained for the fresh, used and washed Ford TWCs.
6.4. Conclusions

EDDS is found to be an effective solvent for the regeneration of TWCs, with respect to contaminant removal. EDDS can help offset the present environmental limitations imposed by EDTA which can persist in water and soils due to its non-biodegradable nature. On the other hand, EDDS can be easily biodegraded. Metal complexes with EDDS are also easily broken down. This makes the handling of secondary waste very simple.

In our study, EDDS was found to be effective in removal of P, Pb, Cu, Zn and Fe. S was not found in our system. ICP-MS, XRD and SEM results revealed that phosphate compounds are removed by EDDS treatment. However, no significant enhancement was found in the BET surface area. This is thought to be more a result of the process than of the solvent. In order to confirm this and test the solvent in an in-situ process, this solvent will be used in a continuous flow system with recirculation. The effectiveness of this solvent with respect to catalytic activity will also be evaluated with dynamometer tests. These tests will be conducted by our collaborators in Dr. Aggelos Efstathiou’s research group in the Department of Chemistry of the University of Cyprus.
6.5. Bibliography


Appendix 1. SEM analysis

Figure 6.7. EDS energy lines of catalyst pieces (used)

Figure 6.8. EDS energy lines of the same catalyst (powder)
A. SEM micrograph image of the used catalyst

B. SEM micrograph image of the fresh catalyst

Figure 6.9. A, B, C: SEM micrograph images of the Ford catalyst pieces at 50 micron magnification.
C. SEM micrograph image of the washed catalyst (with EDDS)

Figure 6.9 (continued). A, B, C: SEM micrograph images of the Ford catalyst pieces at 50 micron magnification.