

Two-phase solvent extraction of PCBs and heavy metals (Cd, Cu) from contaminated soils

J. A. Gascón, V. Marina, O. Salas and I. Susaeta

Abstract

A bench-scale study was carried out to determine if two-phase solvent extraction technology is an effective treatment to remediate soils heavily contaminated with polychlorinated biphenyls (PCBs) and heavy metals such as Cd and Cu in just one step. The results show that efficiencies of 98% for PCBs and 97% for Cd and Cu are reached in three and four successive extractions, respectively. Optimal operational conditions for this case study were: organic phase/aqueous phase ratio 60/40, minimum acid concentration to obtain the two-phase miscibility, ten minutes extraction time, and four successive extractions. However, these design parameters must be determined for each different case.

Key words: PCBs, cadmium, copper, solvent extraction, treatability study

INTRODUCTION

Solvent extraction is a mass transfer process in which contaminants are transported from the soil to a liquid solvent. Subsequently, contaminants are recovered from this liquid waste and the cleaned solvent is again reused on the process.^{1,2,3}

Soils contaminated with both organic and inorganic compounds are rarely treated using solvent extraction processes because of the negative effect that the immiscibility between organic and inorganic solvents has on the soil-solvent contact when they are used simultaneously. This means that an extraction process should consist of a first extraction step using only the organic solvent to extract the organic compounds, followed by a soil drying process (to avoid the contact between both solvents), and finally, a second extraction step using water to extract the inorganic compounds. This takes a long time, requires large amounts of equipment and, therefore, leads to high costs.^{4,6,7}

However, two-phase solvent extraction technology manages to extract in just one step soils contaminated

with both organic and inorganic compounds. The extraction fluid used is a two-phase mixture of butanone, water, and hydrochloric acid (HCl) in order to concentrate the organic compounds at the upper organic phase and the extracted heavy metals at the aqueous phase.

This mixture has the property of varying its miscibility as a function of the pH, increasing the miscibility when the pH is decreased. This has the advantage that by adding some acid to the mixture, it is possible to have a completely miscible extraction fluid which greatly improves the solvent-soil contact. Afterwards, the mixture can be made immiscible again simply by adjusting the pH to the original conditions with a base, and the organic and inorganic phases can be treated separately.⁹

Treatability studies have been carried out in order to enable better-founded decisions for the implementation of solvent extraction technology and the conditions under which it should be applied. Many factors can affect the success of the selected technology in a soil recovery action, so it is important to develop laboratory scale treatability studies in order to reduce the risk arising from direct implementation of untested technology.⁵

The experience of the implementation of remediation technologies has shown that the direct transfer of the technology performance data from one site to another has many drawbacks. Each site has its own

Received June 2000; accepted September 2000

Authors

J.A. Gascón, V. Marina, O. Salas, I. Susaeta, GAIKER, Parque Tecnológico de Zamudio Edf 202, 48170 Zamudio, Spain. Email susaeta@gaiker.es

unique characteristics that make that transfer risky and thus undesirable.⁸

TREATABILITY STUDIES

The objective of this work is to study at bench-scale the feasibility of using a two-phase solvent extraction technology to remediate in just one step soils contaminated with both organic and inorganic compounds, in addition to the determination of the optimal operational conditions. For this purpose, a soil contaminated with 1471 ppm of PCBs as an organic compound, and 423 ppm of Cd and 888 ppm of Cu as inorganic compounds, was selected. The soil was excavated in a former steel production industrial facility. Soil was contaminated with heavy metals and in the dismantling of the facility, transformer oil was accidentally dropped onto the soil.

A treatability study requires the definition of some parameters to evaluate the feasibility of the technology. Some of these parameters are common to all cases, so they were taken from previous studies. For example, a soil:solvent ratio of 1:5 was fixed as it was observed to be the optimal, and the minimum HCl concentration necessary to obtain the phases miscibility was taken as the 14% of the whole mixture.¹⁰

However, other parameters need to be determined for each specific site because of their dependence on the soil characteristics. In this case, the specific design parameters selected to carry out the treatability study were the following: organic phase/aqueous phase ratio,

acid concentration, extraction time and number of successive extractions necessary to reach the cleaning levels required.

Organic phase/aqueous phase ratio

In order to determine the optimal butanone/water ratio some tests were carried out in which the extraction efficiency of both organic and inorganic contaminants were measured for different mixture ratios.

Tests were carried out for the following organic phase/aqueous phase ratios: 40/60, 50/50, 60/40 and 70/30. The HCl content used in all of them was the minimum necessary to obtain the miscibility of the phases (14%), and the samples were continuously stirred for 24 hours to make sure the equilibrium point was reached. Ratios with a butanone content lower than 40% were not studied because of the impossibility of reaching the immiscibility of the phases after the extraction process.

After the extraction process, the soil was washed twice with clean water in order to eliminate the remaining solvent, and subsequently, was analysed to determine the PCBs, Cd and Cu concentration. PCB content was measured by gas chromatography (HRGC/ECD), and Cd and Cu content by inductively coupled plasma atomic emission spectroscopy (ICP/AES).

Acid concentration

Since heavy metal extraction is higher at low pH, the optimal HCl concentration to obtain the maximum heavy metals recovery was determined, and the effect

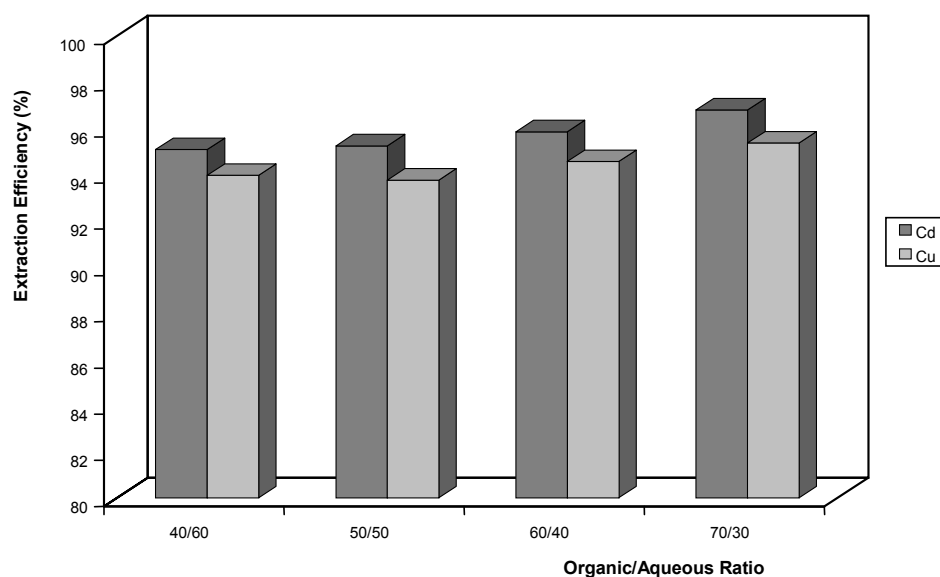


Figure 1. Cd and Cu recovery for different organic phase/aqueous phase ratios

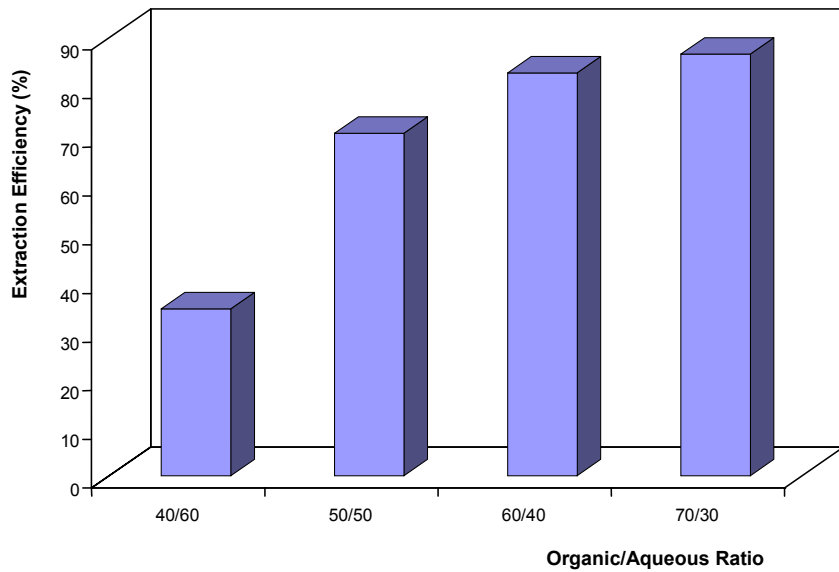


Figure 2. PCB recovery for different organic phase/aqueous phase ratios

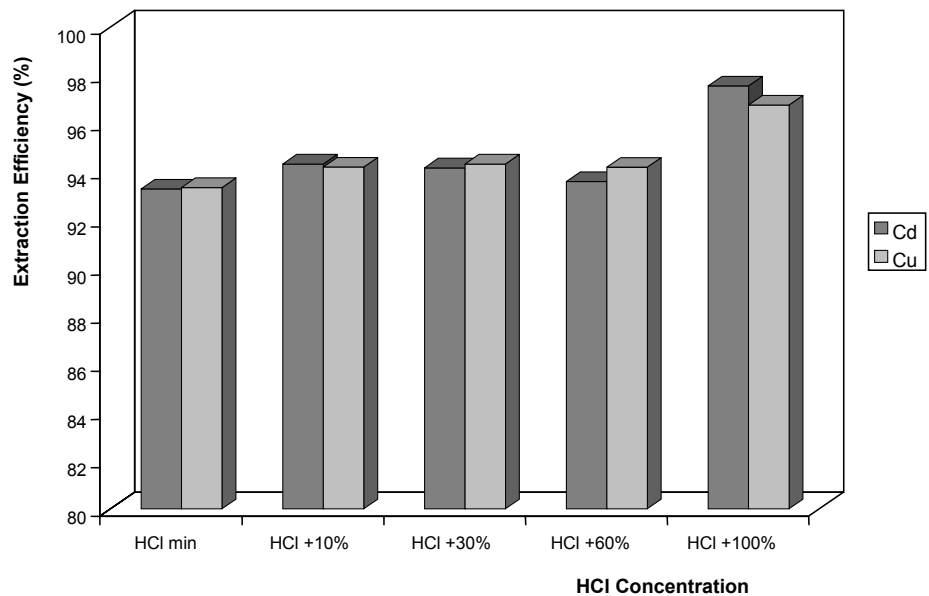


Figure 3. Cd and Cu recovery for different amounts of HCl added

of the HCl addition on the PCB recovery was studied.

Some tests were carried out with a soil:solvent ratio of 1:5, an organic phase/aqueous phase ratio of 60/40, and additions of different amounts of HCl (minimum, +10%, +30%, +60% and +100% by volume).

Extraction time

Optimal contact time is a key parameter in the cost assessment of any decontamination process. In order to determine the minimum time required, the tests described above using the minimum HCl concentration

were carried out, taking samples at different times.

Effect of successive extractions

In order to establish if the two-phase solvent extraction technology is successful or, on the contrary, does not reach the cleaning levels required, the cleaning rate after five successive extractions was determined.

Tests were carried out to undertake five successive extractions on the same soil sample, operating in each stage under the following conditions: soil:solvent ratio

Figure 4. PCB recovery for different amounts of HCl added

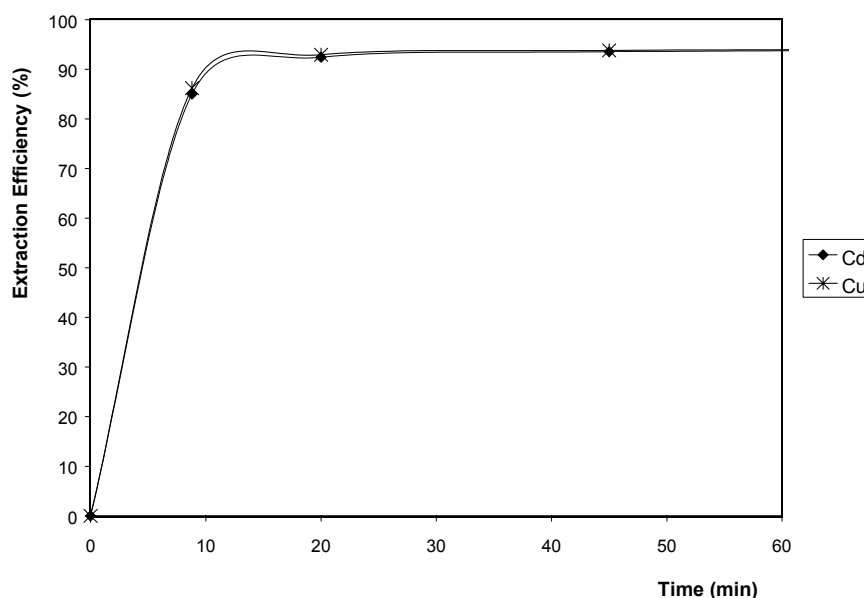
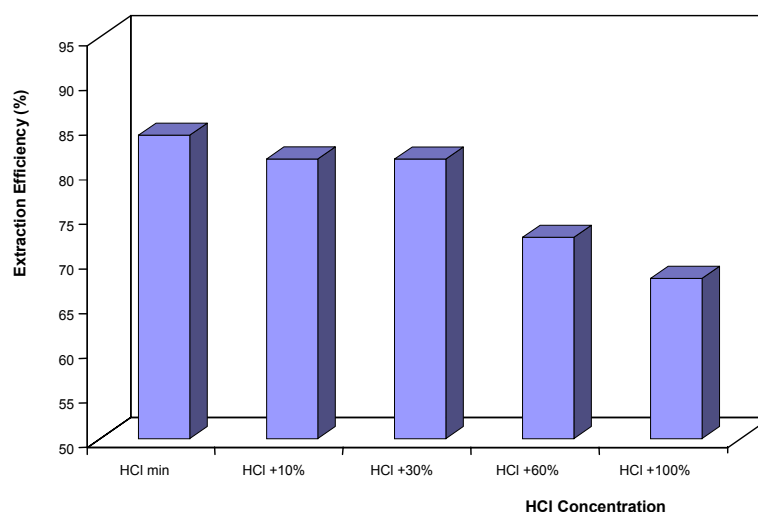


Figure 5. Cd and Cu recovery evolution with time

1:5, organic phase/aqueous phase ratio 60/40, minimum HCl and ten minutes with continuous stirring.

RESULTS

Influence of organic phase/aqueous phase ratio

Figure 1 shows that metal extraction is almost independent of the mixture ratio, obtaining extraction efficiencies for both Cd and Cu of just over 95%. However, Figure 2 shows that the mixture ratio greatly affects the PCB recovery. Since the higher PCB extraction efficiencies are obtained for the mixtures 60/40 and 70/30, and the difference between them is practically negligible, the 60/40 option was selected as it was the cheaper.

Influence of acid concentration

In Figure 3 it can be noticed that HCl concentration hardly affects the Cd and Cu recovery (except for the 100% excess in which case a slight increase of the extraction efficiency is observed). However, Figure 4 shows that HCl concentration presents a significant effect on PCB recovery, decreasing the extraction efficiency as the HCl concentration increases. Thus, the minimum concentration necessary to reach the phases miscibility was selected as the optimal.

Influence of extraction time

The results are shown in Figures 5 and 6. In both figures it can be noticed that contaminant extraction is

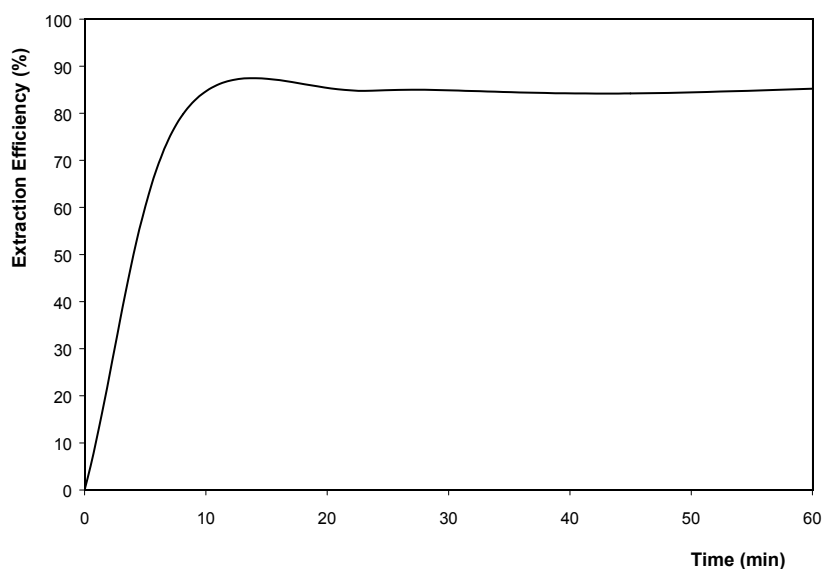


Figure 6. PCB recovery evolution with time

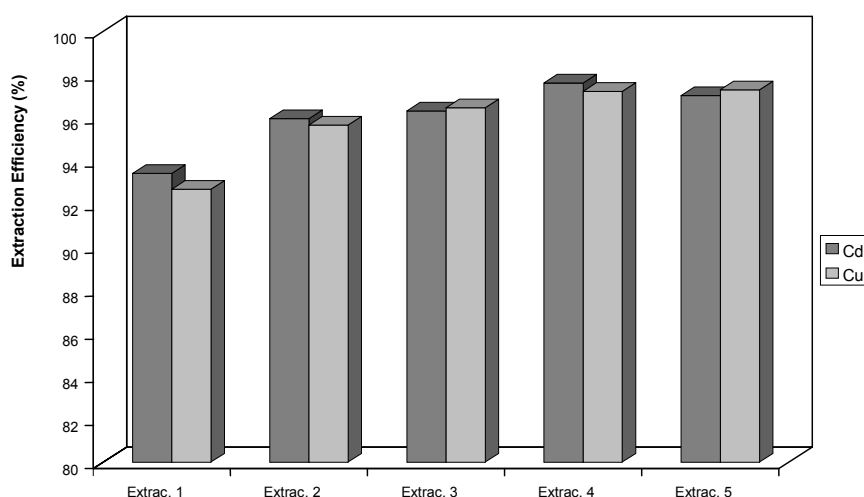


Figure 7. Cd and Cu recovery for five successive extractions

very fast, achieving the maximum recovery in ten minutes. Therefore, ten minutes was considered as the optimal time for each individual extraction.

Influence of successive extractions

Figure 7 shows that the greatest extraction occurs in the first stage, obtaining a recovery of about 94%, and that the extraction continues to a low extent throughout the next three stages to reach a maximum recovery of 97% at extraction 4. In the same way, Figure 8 shows that PCB extraction has a similar behaviour to Cd and Cu, with the greatest extraction in the first stage (84% recovery) and obtaining a maximum recovery of 98% at extraction 3.

CONCLUSIONS

The results of the bench-scale evaluation demonstrate the feasibility of the two-phase solvent extraction technology for the recovery of both organic and inorganic compounds from heavily contaminated soils. For the soil studied, the technology enables us to recover 98% of the organic contamination (PCBs) and 97% of the heavy metals (Cd and Cu).

Design parameters for the two-phase solvent extraction process, such as mixture ratio, acid concentration, extraction time and number of extractions, must be determined for each case. In this case study, the optimal operation conditions were determined as follows: soil:solvent ratio 1:5, organic phase/aqueous phase

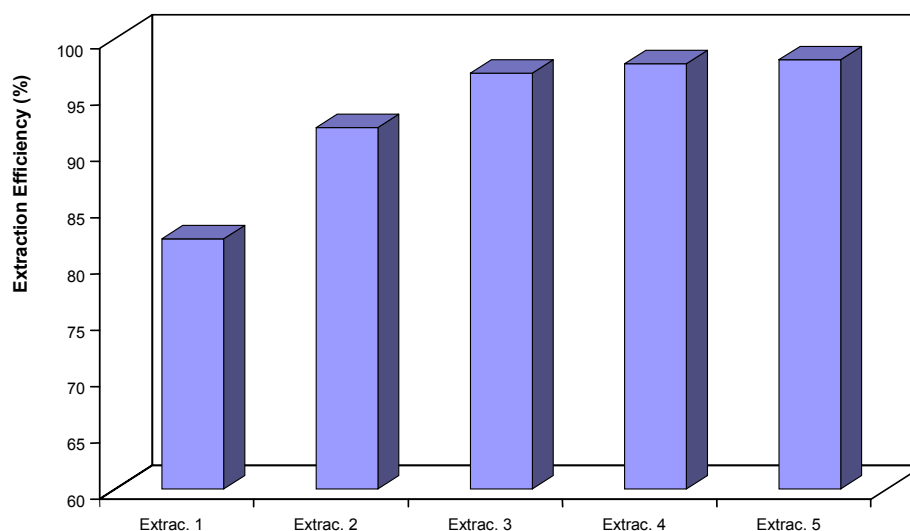


Figure 8. PCB recovery for five successive extractions

ratio 60/40, minimum HCl and four extractions of ten minutes each with continuous stirring.¹⁰

In any case, it is necessary to evaluate the cost and the amount of contaminated soil to be remediated for the selection of the two-phase solvent extraction as a potential remediation technology.¹⁰

REFERENCES

- Hall, D.W., Sandrin, J.A. and McBride, R.E. (1990) *An Overview of Solvent Extraction Treatment Technologies*. Environmental Progress, **9** (2), 98-105.
- Punt, M., Choryhanna, G. and Martin, A. (1992) *Solvent Extraction and Recovery of Petroleum-Derived Hydrocarbons from Soil*. Emergencies Engineering Division, River Road Environmental Technology Centre, Environment Canada.
- Eccles, H. and Holroyd, C.P. (1991) *Solvent Extraction for the Treatment of Contaminated Soil*. Company Research Laboratory, British Nuclear Fuels plc.
- Markiewicz, J. and McGovern, W. (1992) Remediation, recovery and waste minimization, using a solvent extraction process. *Hazardous Material Control*, 48-51, Sept/Oct.
- EPA (1992) *Guide for Conducting Treatability Studies under CERCLA: Solvent Extraction*.
- EPA (1993) Resources Conservation Company B.E.S.T. Solvent Extraction Technology.
- EPA (1990) *Cleaning Excavated Soil Using Extraction Agents: A State of the Art Review*.
- Rulkens, W.H., Grotenhuis, J.T.C. and Soczó, E.R. (1993) Remediation of contaminated soil: state-of-the-art and desirable future developments. In: *Contaminated Soil '93*, Vol. II, pp. 1007-1018. Kluwer Academic Publishers, The Netherlands.
- Brouwers, J. (1994) 'Solvent Stripping Experiments of Packed HCH and Mercury Contaminated Soil'. Presentation at the 3rd HCH and Halogenated Pesticides Forum, Bilbao, September 19-20, 1994.
- Salas, O., Gascon, J.A. and Susaeta, I. (1998) 'Treatability studies on solvent extraction technologies: bench scale evaluation. 5th International HCH and Pesticides Forum. pp. 153-158

Apart from fair dealing for the purposes of research or private study, or criticism or review, this publication may not be reproduced, stored in a retrieval system or transmitted in any form or by any means, electronic, mechanical, photographic or otherwise, without the prior permission in writing of the publisher.

The views expressed in this and in all articles in the journal *Land Contamination & Reclamation* are those of the authors alone and do not necessarily reflect those of the editor, editorial board or publisher, or of the authors' employers or organizations with which they are associated. The information in this article is intended as general guidance only; it is not comprehensive and does not constitute professional advice. Readers are advised to verify any information obtained from this article, and to seek professional advice as appropriate. The publisher does not endorse claims made for processes and products, and does not, to the extent permitted by law, make any warranty, express or implied, in relation to this article, including but not limited to completeness, accuracy, quality and fitness for a particular purpose, or assume any responsibility for damage or loss caused to persons or property as a result of the use of information in this article.