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SCIENTIFIC PAPER

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INVESTIGATION OF OPERATING CONDITIONS FOR SOIL REMEDIATION BY SUBCRITICAL WATER

The aim of the present research is to investigate the application of subcritical water to naphthalene removal from soils. The extraction curves obtained show no clear patterns relating the operating conditions to the extraction time. This is mainly due to anomalies that occurred during some extraction runs. The analysis of the results shows an extraction time rather constant as function of the operating conditions (pressure, temperature, and mass flow). The extraction efficiency, on the other hand, is found to increase at higher hot water flows and lower temperatures, while no dependence is recorded from the pressure or the density. The data interpretation suggests that the film transfer resistance is the extraction rate limiting factor in the flow range considered. Finally, the relationships between the extraction efficiency and the operating conditions, together with the non-achievement of 100% efficiency, seems to confirm some authors' theory on the resistance to desorption due to the presence in the soil of "resistant" and slowly desorbing fractions, constituted by immobile fluid in pores.

Key words: subcritical water; extraction; PAHs; soil remediation; operating conditions.

Many of the contaminants that can be found in soil are inorganic, like heavy metals, as well as organic. Among the organic contaminants, oil and coal refineries are responsible for several cases of soil contamination with polycyclic aromatic hydrocarbons (PAHs). PAHs are a family of compounds formed by at least two carbon atoms linked together. Among the PAHs, naphthalene is the simplest molecule, formed by two rings only. Studies from many authors [1-3] refer to contamination by PAHs at former gas work plant areas with concentration values from tens or hundreds up to 3.0×10^6 ppm at a site near Bedford [3]. In some cases, the concentration of the pollutants in the soil might be so high that they represent potential harm to the vegetation, animals and humans. As a result of growing concern for soil contamination issues, the limits have been set on the concentration of many contaminants, including PAHs, as some of them are known to be carcinogenic [4]. There are many techniques available for soil decontamination, all of them having some advantages and disadvantages

[5]. New methods are therefore being investigated in order to improve the remediation efficiency, lower the "costs" or the remediation time. Soil remediation by subcritical water extraction is one of those methods. There is general agreement in recognizing subcritical water extraction as a rather efficient, fast and low cost treatment for soil remediation. According to some estimates, bioremediation costs for organic toxic chemical contaminations are in the range of one-quarter to one-half of other remediation techniques [6-8]. However, PAHs are hard to biodegrade and persistent in soil, which rules out the applicability of biodegradation for PAH-polluted soils or at best, biodegradation might be used in cases with very light contamination with low-molecular-weight PAHs [9,10]. Earlier Dadkhah and Akgerman [12,13] reviewed other remediation options and advantages of using the subcritical water as a medium for extracting the PAHs from aged soils. PAHs solubility in water at ambient conditions is low and decrease rapidly with insert molecular weight [14,15]. For all of the PAHs there was a little increase in extraction when the temperature was increased from 250 to 300 °C [12,13]. Another advantage of using subcritical water for the extraction was the possibility of the class selective extraction [23]. As the temperature of the water increases its polarity decreases. Hence, less polar con-

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taminants will be extracted first, followed by those of decreasing polarity.

In this study, we investigate the application of subcritical water to naphthalene removal from soils and we study the effect of temperature, pressure and mass flow rates on the extraction efficiency.

EXPERIMENTAL METHOD

The naphthalene used in this study had a purity of 99% provided from Merck Company. The soil type was determined by sieving it by means of sieves with different meshes. The composition of the soil used for the contamination-decontamination process was therefore the following:

- fine sand (0.06-0.25 mm), 55 %;
- medium sand (0.25-0.5 mm), 20%;
- coarse sand (0.5-2 mm), 25%;
- acetone (with purity of 99%, provided from Merck company), the solvent chosen has to dissolve the naphthalene easily and to be far more volatile than the contaminant, in order to evaporate easily and reduce the contemporaneous naphthalene losses;

- toluene (with purity of 99%, provided from Merck company), the solvent chosen for the naphthalene collection has to have good affinity with naphthalene, not be too volatile and not very toxic.

The analyses of the collected samples were carried out by means of a gas chromatograph, operated by helium, as transport medium, air and hydrogen for the flame. The gas chromatograph is calibrated before the experiment by analyzing a sufficiently large number of toluene solutions with known concentrations of naphthalene (10, 50, 100 and 1000 ppm) and octanol (constant). A calibration line is then drawn which allows the calculation of the naphthalene concentration in a solution, giving the ratio of the naphthalene-octanol peak areas and the octanol amount.

The subcritical water extractions were carried out in a laboratory-built apparatus shown in Fig. 1. De-ionized water filled into a 4-L stainless steel feed tank was first purged for 2 h with N₂ to remove dissolved O₂. A high-pressure pump (max. 45 MPa) was used to deliver the water through the system at a constant flow rate of 1.0 and 1.6 g/min. The oven maintained the extractor cell, mass-flow, by-pass stream and was preheated at set operating temperature. The extractor cell was a steel vessel ($V = 32$ ml). About 2 ml of toluene-naphthalene solution were taken from the collection vessels and put into numbered and weighted vials. The solution is weighted. Octanol (ISTD) was added and the solution was weighted again. The vials were closed and agitated. The gas chromatograph was switched on, and the gas fluxes (air, hydrogen and helium) were regulated to the selected values. 1 μ l of the toluene-naphthalene-octanol solution was injected into the gas chromatograph. The naphthalene and octanol peak areas were recorded. From the area ratio, the naphthalene concentration in the toluene-naphthalene solution was calculated, using the calibration line. The by-pass was made with the same pipes as used for the main line. The extractor cell by-pass was used in order to set the operating conditions required, avoiding naphthalene extraction from the soil before the experimental run. During the simulation, the hot water was let flow through the by-pass (thus excluding the extractor vessel already filled with soil from the line) while the regulating valves were adjusted until the approximate operating conditions were reached and kept constant. The by-pass was then closed and the extraction could start, with the required operating conditions set. The collection vessels to be used were numbered and weighted; toluene was then fed into the vessels and weighted. All the vessels were closed and kept refrigerated before and after use in order to minimize solvent losses

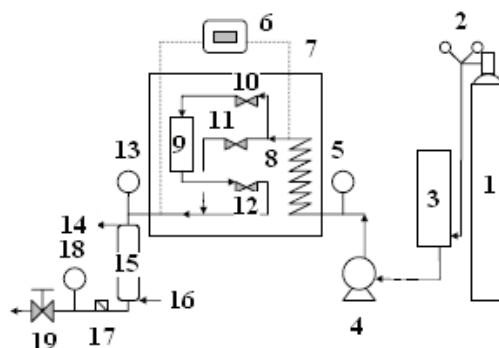


Fig. 1. Subcritical water pilot plant scheme. 1 - N₂ cylinder; 2 - pressure regulator; 3 - pressure indicator; 4 - pump; 5 - pressure indicator; 6 - temperature indicator; 7 - oven; 8 - preheater; 9 - extraction cell; 10 - oven; 11 - bypass stream; 12 - outlet water; 13 - water reservoir; 14 - cooling water out; 15 - heat exchanger; 16 - cooling water in; 17 - microfilter; 18 - temperature indicator; 19 - pressure regulator.

due to evaporation. Collection vessels containing a suitable solvent were changed at chosen intervals to collect the naphthalene extracted. The collection vessels were made out of glass and had an approximate volume of 20 ml.

RESULTS AND DISCUSSION

The extractions were carried out varying the operating conditions pressure, temperature, and mass flow. Two values were assigned to each parameter, for a total number of 10 extractions. The actual total number is 10, in order to take into account extractions with excessive anomalies that had to be repeated. The operating conditions investigated are summarized in the schemes below. Table 1 shows the operating conditions for all of the extractions. Table 2 shows the extraction(s) data for all of the extractions.

Table 1. Operating conditions investigated and corresponding extractions

Extraction number	$Q / \text{g min}^{-1}$	p / MPa	$t / ^\circ\text{C}$
1	1	2.7	260
2	1	3.1	260
3	1	2.7	280
4	1	3.1	280
5	1.6	3.1	260
6	1.6	2.7	260
7	1.6	2.7	280
8	1.6	3.1	280
9	1.6	2.7	280
10	1.6	2.7	280

Comparison of the results

Comparison of the extraction results at constant temperature (1)

At 260 °C the efficiency increases in case of higher mass flow, varying from about 69 to 80% for a

flow varying between 1 and 1.6 g/min (Fig. 2). As the mass flow increases, the time needed to reach the asymptote decreases from 120 to 60–75 min. Small differences in density and no difference in the extraction efficiency were recorded between 2.7 and 3.1 MPa.

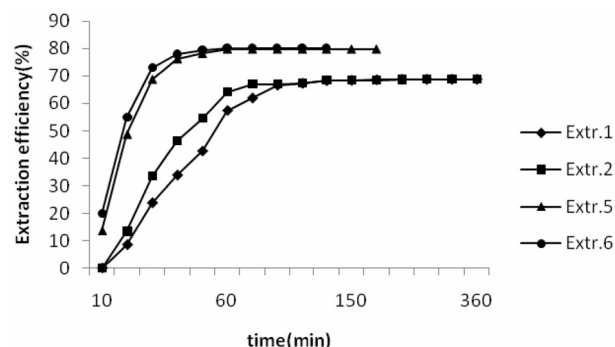


Fig. 2. Comparison of the efficiency curves at 260 °C.

The comparison of the naphthalene extraction curves at 260 °C (Fig. 3) is complicated by major anomalies recorded in the case of the extractions 1 and 2. Difficulties in controlling the operating conditions during the extractions, and probably imperfections in the extraction cell filling and soil compacting, resulted in a time delay of the curves and in double peaks. It is therefore impossible to estimate the peak value of the extractions at 260 °C and 1 g/min without anomalies. It is though likely that the peak position would be the same as for the remaining curves. In case of the mass flow of 1.6 g/min, the curve reaches the peak after 18 min from the beginning of the run.

Comparison of the extraction results at constant temperature (2)

At 280 °C extraction 5 and 11 efficiencies, which values are 95 and 34% respectively, are doubtlessly out of the possible efficiency range. On the other hand, the comparison of the extractions 4, 7, 8, and

Table 2. Extraction data

Extraction efficiency, %	Naphthalene extracted, mg	Naphthalene amount, mg	Naphthalene concentration, ppm	Sample amount, g	Number of sample	Extraction duration, min	Extraction number
68.62	42.71	62.24	999.87	62.25	16	360	1
68.61	44.92	65.47	1011.45	64.73	16	360	2
95.53	60.73	63.57	1000.57	63.53	17	360	3
57.54	36.77	63.90	1000.49	63.87	15	270	4
79.83	60.85	63.68	1000.79	63.63	12	180	5
90.06	55.73	63.20	1000.81	63.14	8	90	6
56.06	40.07	64.92	1000.00	64.92	13	270	7
61.19	51.86	63.59	999.97	63.59	13	270	8
34.39	22.17	64.47	1000.02	64.47	13	270	9
57.28	54.51	63.93	1000.54	63.90	13	270	10

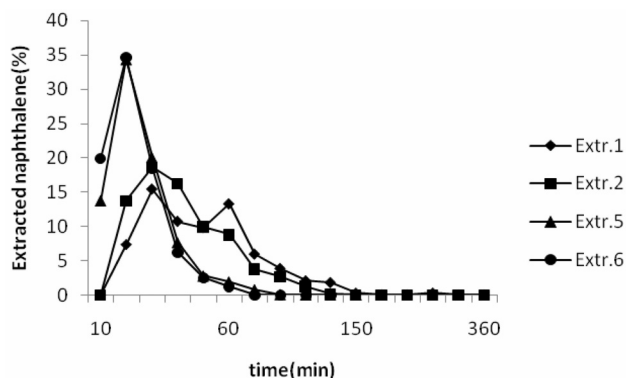


Fig. 3. Comparison of the naphthalene extraction curves at 260 °C.

10 shows similar extraction efficiencies, with the values ranging from about 58 to 60%. Higher mass flows resulted in steeper curves (therefore the asymptote is reached in a shorter time), and in a slight efficiency increase. Higher extraction efficiencies are observed in the case of higher pressure as well, although the variation is rather limited when compared to corresponded density increase.

Because of their major anomalies, extractions 3 and 9 were not included in Fig. 5 since they would not be significant for any further consideration and analysis. The peaks occur after 18 min from the beginning of the run for all extractions. Peaks are higher at higher mass flows, while the pressure seems not to have any relevant effect. The peak height is about 26% of total naphthalene present in the soil at 1.6 g/min, and 23% at 1 g/min. Extraction 6 shows lower peak due to the presence of another peak after 60 min.

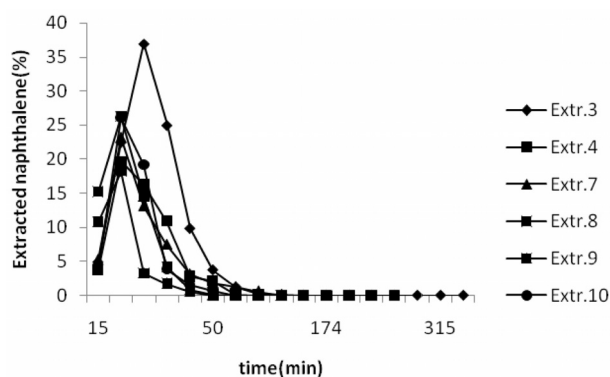


Fig. 5. Comparison of the naphthalene extraction curves at 280 °C.

Comparison of the extraction results at constant mass flow (1)

At 1 g/min the extraction efficiency increases from about 57 to 69% as the temperature decreases from 280 to 260 °C, while the pressure has a modest influence on it, and only at higher temperatures (Fig.

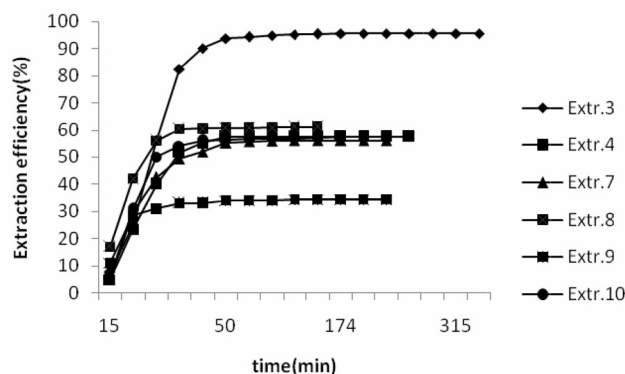


Fig. 4. Comparison of the efficiency curves at 280 °C.

6). On the contrary, the temperature is the only extraction time influencing parameter, causing an extraction time decrease from 120 to 60 min at higher pressures. An apparent pressure effect on the extraction time at lower temperatures is most likely due to the major anomalies affecting extractions 1 and 2, which are better displayed by Fig. 7.

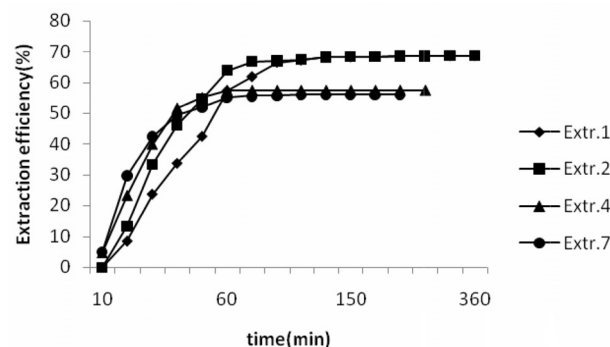


Fig. 6. Comparison of the efficiency curves at 1 g/min.

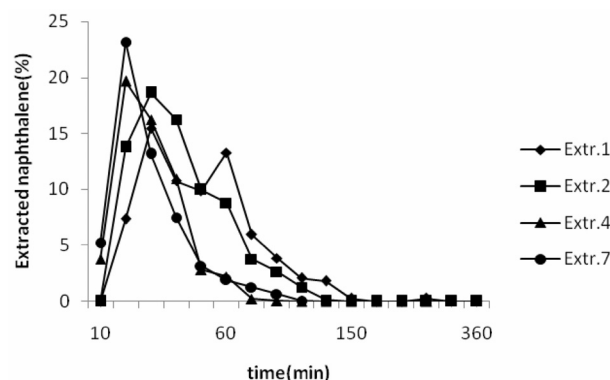


Fig. 7. Comparison of the naphthalene extraction curves at 1 g/min.

Because of the major anomalies in case of extractions 1 and 2, no certain conclusion can be drawn on the curves of Fig. 7.

Comparison of the extraction results at constant mass flow (2)

At 1.6 g/min, as for a mass flow of 1 g/min, the extraction efficiency increases as the temperature decreases, varying between 59 and 80% for 280 and 260 °C, respectively. The pressure effect is rather small and limited to the extractions at 280 °C. The asymptote is reached after 60 min for all the extractions (Fig. 8).

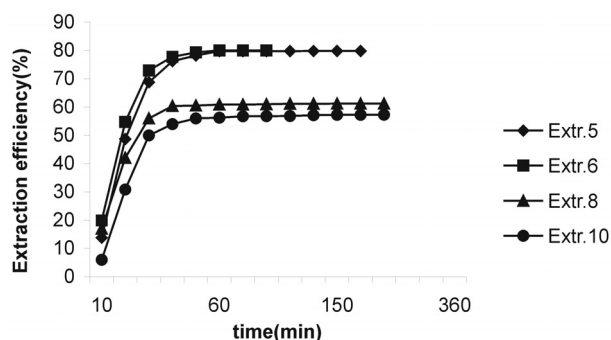


Fig. 8. Comparison of the efficiency curves at 1.6 g/min.

All curves have the same shape and width but different peak height (Fig. 9). The peaks are higher for lower temperatures, reaching 35% of the naphthalene present in the soil at 260 °C against 26% at 280 °C. The peaks occur 18 min after the beginning of the extractions.

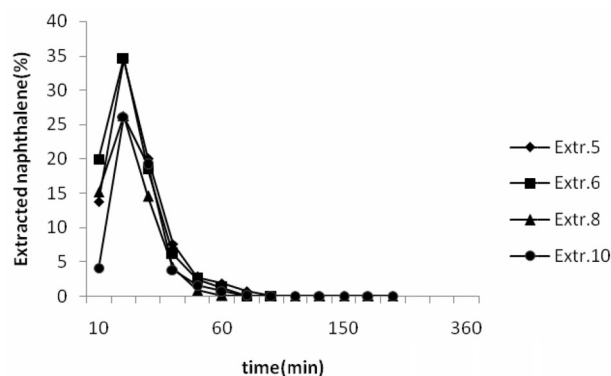


Fig. 9. Comparison of the naphthalene extraction curves at 1.6 g/min.

The extraction curves obtained (Fig. 2, 4, 6 and 8) show no clear patterns relating the operating conditions to the extraction time. This is mainly due to anomalies that occurred during some extraction runs, which limited the meaningfulness of the results. In some cases, though, the data seem to suggest that the extraction time decreases as the mass flow and the temperature increase, while there seems to be no relation with the hot water pressure and density. Any-

how, an extraction time of 90-120 min allows the system to reach the asymptote under all the investigated operating conditions.

CONCLUSION

More certainly, the extraction efficiency increases as the temperature decreases and the mass flow increases. Higher pressures seem to be responsible of a small efficiency increase, but only at higher temperatures (thus lower overall efficiencies). The percentage of naphthalene extracted vs. time follows a curve that has the same shape for all the extractions, besides the cases where a poor control of the operating conditions resulted in anomalies. The extraction percentage peaks always occur after 18 min from the beginning of the extraction run, whenever the operating conditions are sufficiently constant. The peak height increases as the temperature decreases, while the dependence from the flow appears more uncertain. Again, the pressure and density have no influence on the peak height. A systematic study of the effects of excipients was performed by adding a known amount of the excipient to 80 µg/ml NIC or ISRA, filtering off the insoluble excipient, washing the residue, diluting in a volumetric flask and analyzing following the recommended procedure. The results revealed that no significant interference was observed from excipients, such as starch, talc, gelatin, glucose and magnesium stearate.

The present method has the advantages of high sensitivity (detection limit is 1.67 and 1.74 µg/ml for NIC and ISRA, respectively). On the other hand, the proposed method is low cost, selective, accurate and precise (intra-day and inter-day precision) as indicated by the good results of the drugs. Furthermore, the proposed method does not require the elaboration of the procedures which is usually associated with chromatographic methods. The disadvantage of this method is the tediousness of filtration. The proposed method could be applied successfully for the determination of nicedipine and isradipine in pure forms, as well as dosage forms, with no interferences from tablets or capsules excipients.

REFERENCES

- [1] B. E. Andersson, K. Tornberg, T. Henrysson, S. Olsson, *Biores. Technol.* **78** (2001) 37-45
- [2] R. Canet, J. G. Birnstingl, D. G. Malcom, J. M. Lopez-Real, A. J. Beck, *Biores. Technol.* **76** (2001) 113-117
- [3] A. Khodadoust, R. Bagchi, M. T. Suidan, R. C. Brenner, N. G. Sellers, J. Hazard. Mater. **B80** (2000) 159-174
- [4] G. Kilely, *Environmental Engineering*, McGraw Hill International (UK) Limited, (1997)

- [5] T. Castelo-Grande, D. Barbosa, *Electr. J. Environ. Agric. Food Chem.* **2** (2003) 331-336
- [6] G.W. Page, *Contaminated Sites and Environmental Cleanup: International Approaches to Prevention, Remediation, and Reuse*, Academic Press, San Diego, CA, (1997)
- [7] H. De Rore, *Biotechnological processes for cleaning soils and sediments polluted with organics*, presented at the NATO Advanced Research Workshop, for Biotechnologies Radioactive and Toxic Wastes Management and Site Restoration: Scientific, Educational, Business Aspects, Mol, Belgium, (1994)
- [8] J.D. Snyder, *Smithsonian* **24** (1993) 66-77
- [9] S.Y. Yuan, L.C. Shiung, B.V. Chang, *Bull. Environ. Contam. Toxicol.* **69** (2002) 66-73
- [10] M.G. Zemanek, J.T.S. Pollard, S.L. Hrudey, *Environ. Pollut.* **98** (1997) 239-252
- [11] A.R. Clemente, T.A. Anazawa, L.R. Durrant, *Braz. J. Microbiol.* **32** (2001) 255-257
- [12] A.A. Dadkhah, A. Akgerman, *J. Hazard. Mater. B* **93** (2002) 307-320
- [13] A.A. Dadkhah, Ph.D. Dissertation, Texas A&M University, College Station, TX, (2003)
- [14] D. Mackay, W.D. Shiu, *J. Chem. Eng.* **22** (1997) 399-402
- [15] M.D. Erickson, *Analytical Chemistry of PCBs*, Butterworths, London, (1986)
- [16] V.K. Jain, *Environ. Sci. Technol.* **27** (1993) 806-807
- [17] R.W. Shaw, T.B. Bril, A.A. Clifford, C.A. Eckert, E.U. Frank, *Chem. Eng. News* **69** (1991) 26-39
- [18] R.B. Gupta, C.G. Panayiotou, I.C. Sanchez, K.P. Johnston, *AIChE J.* **38** (1992) 1243-1253
- [19] S.B. Hawthorne, Y. Yang, D. Miller, *Anal. Chem.* **66** (1994) 2912-2920
- [20] K. Hartonen, K. Inkala, M. Kangas, M.L. Riekkola, *J. Chromatogr. A* **785** (1997) 219-336
- [21] T. Hyotylainen, T. Andersson, K. Hartonen, K. Kuosmanen, M.L. Riekkola, *Anal. Chem.* **72** (2000) 3070-3076
- [22] Y. Yang, S. Bowdat, S.B. Hawthorne, D. Miller, *Anal. Chem.* **67** (1995) 4571-4576
- [23] B. van Bavel, K. Hartonen, C. Rappe, M.L., *Analyst* **124** (1999) 1351-1354.