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Application of microwave extractions for the assessment of available heavy metals from sewage sludges using the Toxicity Characteristic Leaching Procedure

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Abstract. The Toxicity Characteristic Leaching Procedure (TCLP) is used by the United States Environmental Protection Agency to determine if wastes contain extractable components subject to hazardous waste regulations. However, 18h for extraction are too long to give the information of hazardous characters in time. Therefore, microwave extraction was used to accelerate the TCLP procedure. Parameters influencing microwave extraction such as power, temperature and extraction time were optimized. Several good compromise for metal extraction were as follows: P=300W, T=70°C, t=15min; P=500W, T=50°C, t=15min; P=500W, T=70°C, t=10min. Studies of five sludge samples indicated that As, Pb, Cr and Cu were more suitable for accelerating extraction using microwave than Zn, Cd and Ni, and P=500W, T=70°C, t=10min was the most optimized parameters. The proposed accelerated microwave extraction method could be a valid alternative or supplement to the conventional shaking with a much shorter operating time.

Keywords: microwave; TCLP; extraction; accelerate; sludge; ICP-MS

1. Introduction

With rapid industrialization, the generation of industrial solid and hazardous waste has increased rapidly. In waste water treatment process, a huge quantity of sludge is generated which containing heavy metals. When sewage sludge is used as a soil conditioner, its toxic metal content can limit its application rate. Data from the literature show that more than half of the sludge used are inappropriate for use in agricultural areas due to the leaching property of heavy metals [1].

Leaching protocols used for the analysis of metals in soil, wastes, and other solid materials give an indication of metal release and mobility. A leaching test, the Toxicity Characteristic Leaching Procedure (TCLP), is used by the United States Environmental Protection Agency (EPA) to determine if a waste has the characteristic of toxicity and is therefore hazardous. The TCLP method is a currently recognized international method for evaluation of heavy metal pollution in wastes. It has been widely used to evaluate leachability of heavy metals [2, 3].

Although the TCLP protocol proves to be very useful, it requires 18h time for extraction in the determination of leaching and mobility. Moreover, sludge for TCLP determination need to be dried for 24h at 70°C as recommended elsewhere [4]. Because a lot of sludge are produced in the wastewater treatment plant and need to be carried out in time, waste generators must use knowledge of the TCLP to test if their wastes qualify is suitable for land disposal or is classified as hazardous as soon as possible. Therefore, in this work we propose substituting microwave extraction for the mechanical shaking extraction.

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A technique for accelerating the extraction of metals from sediment is to use microwave ovens. Sequential extraction techniques with application of microwave heating were initially investigated to improve the release of metals in each step of the sequential extraction procedure [5]. Other authors used microwave energy to accelerate extraction procedure of metals. Great reduction of time was attained [6~8]. Up to now, there are no related methods to accelerate the TCLP procedure. In this work microwave extraction is explored as an alternative to traditional shaking in the TCLP protocol to speed up the metal extraction from waste samples. Operational parameters such as power, temperature, and time were optimized to emulate the efficiency obtained by the TCLP protocol. Results obtained by microwave heating methodology were statistically compared to those obtained by the TCLP protocol.

2. Materials and methods

2.1. Sample collection and pretreatment

Samples correspond to sludge from several wastewater treatment plants. The samples were dried for 24h at 70°C and sieved through a nylon mesh to the fraction with particle size less than 150μm and stored in polyethylene bottles. Before extraction 1.00g of sludge was precisely weighed in a weighing bottle. The sludge was placed in an oven (105±2°C) until constant weight. This treatment produced a 1.8% loss of weight. All subsequent measurements were corrected to take account of this loss.

2.2. Chemicals and reagents

The acetic acid was of analytical reagent grade. De-ionised distilled water was used throughout the work. All glassware and polyethylene bottle were cleaned with 10% nitric acid for 48h and rinsed with de-ionised distilled water.

2.3. Conventional TCLP extraction procedures

Two different buffered acidic leaching extraction fluids were used for TCLP depending on the alkalinity and the buffering capacity of the wastes. The samples were analyzed for pH by using glass electrode pH meter, the pH of the sludge we used in this study is more than 5, extraction fluid 2 with a pH of about 2.88 (5.7ml glacial CH_3COOH diluted in 1000ml water) was used. PH values of the solutions were adjusted with 1mol/l HNO_3 and 1mol/l NaOH. An aliquot of 1.00g of each sample and 20ml extraction reagent were transferred into centrifuge tubes and rotated for 18h in a horizontal shaking mixer with a speed of 30±2rpm. At the end of 18h extraction period, the supernatant was separated from the solid phase by centrifugation at 6000rpm for 15min. it was then filtered through Whatman Millipore filtering system with 0.45μm pores to eliminate potential particles resulting from suspended particles. The filtered solution was stored at 4°C before analysis. The concentrations of As, Zn, Pb, Cd, Ni, Cr and Cu in the final solution were determined by inductively coupled plasma spectroscopic analyses (Optima 2100 DV).

2.4. Microwave extraction procedure

All samples were extracted in a microwave sample preparation system [Milestone (Ethos Plus)]. The control software allows setting the microwave power, extraction time, and reaction temperature. A 1.00g aliquot of sample was transferred to the Teflon containers of the microwave oven, and 20ml of acetic acid buffer with a pH of about 2.88 was added. The containers were swirled manually for 30s to wet the entire sample. During this study the effect of microwave power, temperature, and time at that temperature were examined. The aim of the optimization study was to find a set of microwave conditions giving recoveries similar to conventional extraction for metals of interest. All tests used two step digestion programs: the first step was performed with a programmed temperature curve at $\triangle T/\triangle t$=50°C/min up to the fixed temperature; the second step was performed at a constant temperature and power for prefixed time periods. After microwave treatment the samples were treated with the same method as conventional TCLP extraction procedure after 18h extraction period.

Both the conventional TCLP extraction procedures and the extraction with microwave were performed with three replicates. With each batch of extractions, a blank (i.e., a vessel with no sample) was carried out through the complete procedures.

Metal recovery (%) was defined as the ratio: [(metal content using microwave extraction)/ (metal content using the conventional TCLP extraction)] ×100%.

2.5 Quality assurance

In order to guarantee the accuracy of the results, analytical assurance concerning the total contents of metals was achieved by measuring the standard sample (Community Bureau of References (BCR), BCR No.145) and the results were found to be within ±5% of certified values.

3. Results and discussion

3.1 Microwave extraction conditions optimization with the same sludge sample

In order to obtain the desired temperature immediately, the minimum power of the test was set in 300W. Under the condition of 300W power, the effect of extraction temperature and length of exposure on the relative extraction efficiency was evaluated. As illustrated in Fig 1. The relative extraction efficiency increased with an increase of the temperature for As, Cr and Cu, which showed that the dissolved metals of these elements were influenced most by the extraction temperature. For Pb, Cd and Ni, the extraction efficiency increased to a plateau at the temperature of 70°C, and then decreased with extraction temperature increasing, although the extraction time was different. This was probably due to reabsorbtion or precipitation effects. Readsorption processes have also been observed for several metals when conventional sequential extraction schemes were applied to sediments [9].

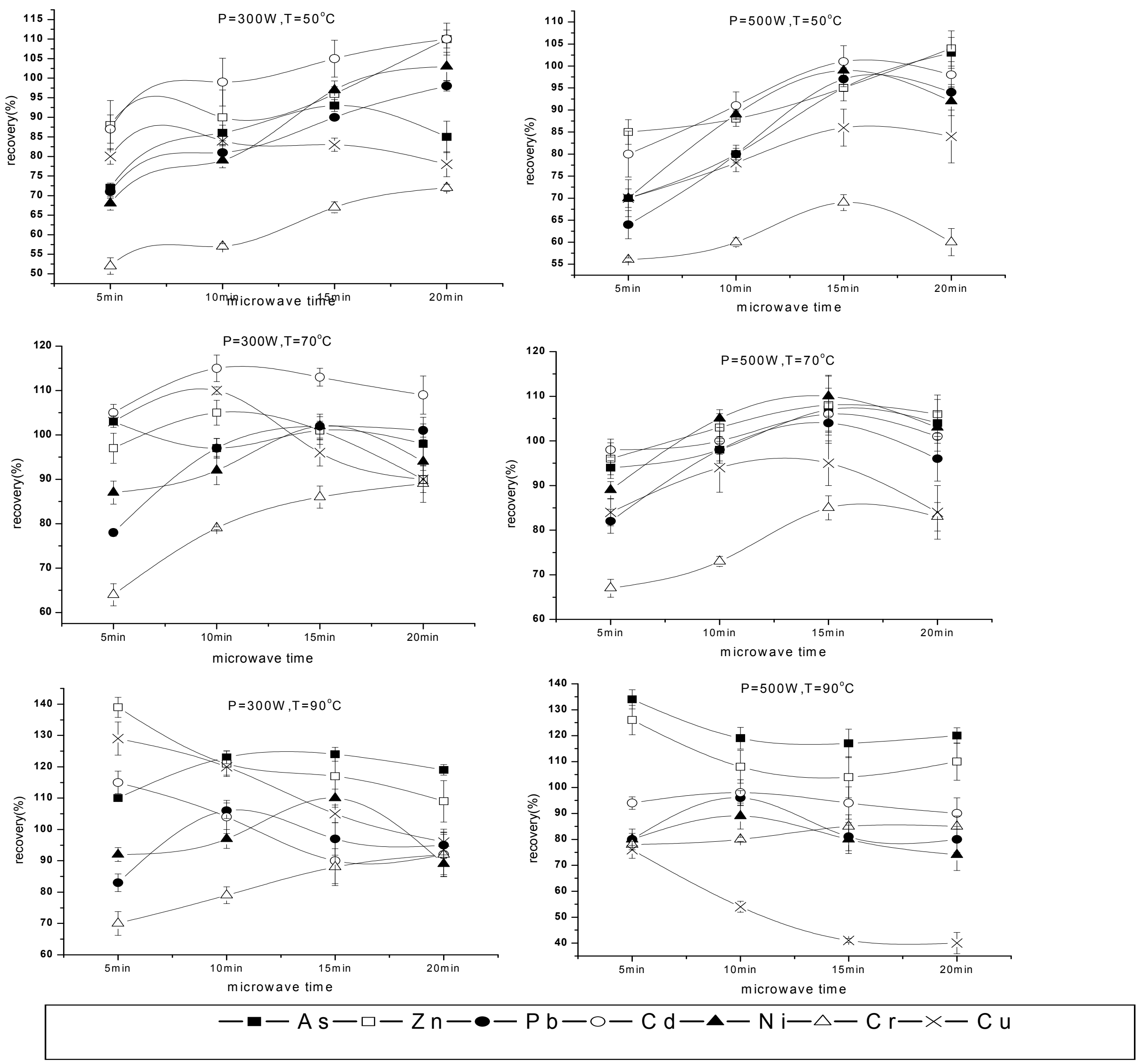


Fig. 1: Effect of microwave power and temperature at different extraction times on recovery percentages (n=3).

As to Zn, the relative active characters made the extraction efficiency reach the plateau under the condition of T=50°C and t=20min. When the temperature increased to 70°C, the phenomenon of readsorption lead to the decrease of dissolved metals. With the temperature increased further to 90°C, enthalpic effect made the solution reach the new equilibrium.

Most measured metals for prolonged periods led to a reduction in the percentage of metal extracted. The only exception was Cr, its extraction efficiency was less than 100% all along.

At 500W power, the readsorption or precipitation phenomenon of dissolved metals caused by changing temperature and extraction time was more evident than at 300W power, especially Cu, other authors [10, 11] have made similar results, noting that with these metals, microwaves produce a reabsorbtion effect. Cr was also readsorbed with increasing the extraction time, even its extraction efficiency was relative low. The reason was that with the increase of power, molecular rotation become more intensive, which lead to the destruction of more crystal structure and organic matter and release of more exchangeable cation. In general, this can be attributed to complicated processes (physico-chemical reaction, ion exchange, adsorption, precipitation, etc.) happened in the solution system.

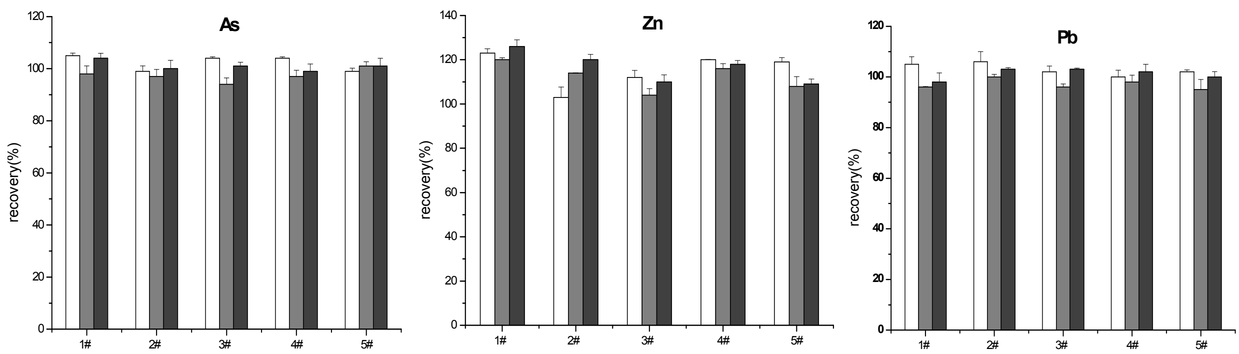
In both cases, all the tests were found that the higher temperature the less time was required to reach the plateau. This behavior is typical of processes with slow kinetics, where reactions become faster. Silvia Canepari has got the same result in studying the effect of microwave temperature on the extraction efficiency [12].

As with the tests, it was not possible to identify a single set of test conditions optimal for all metals. Several good compromise was to use P=300W, T=70°C, t=15min; P=500W, T=50°C, t=15min; P=500W, T=70°C, t=10min. Under these conditions, it was possible to achieve close to 100% extraction and/or plateau extraction values for the majority of metals.

3.2 Further optimization with different sludge samples

The microwave extraction procedure accuracy was evaluated by determining these metals in different sets of samples from different waste treatment plants. Since no certified reference material is available, only values obtained by traditional TCLP procedure in each treatment plant were compared.Five samples were evaluated in duplicates. Three sub-samples of each sample were used for analytical determinations with the optimum extraction procedures.

Fig 2 lists the extraction efficiency of different samples under relative optimized conditions. Comparing this three conditions, P=500W, T=70°C, t=10min was the most optimized parameters. This reduced extraction time from 18h (TCLP procedure) to 10min.



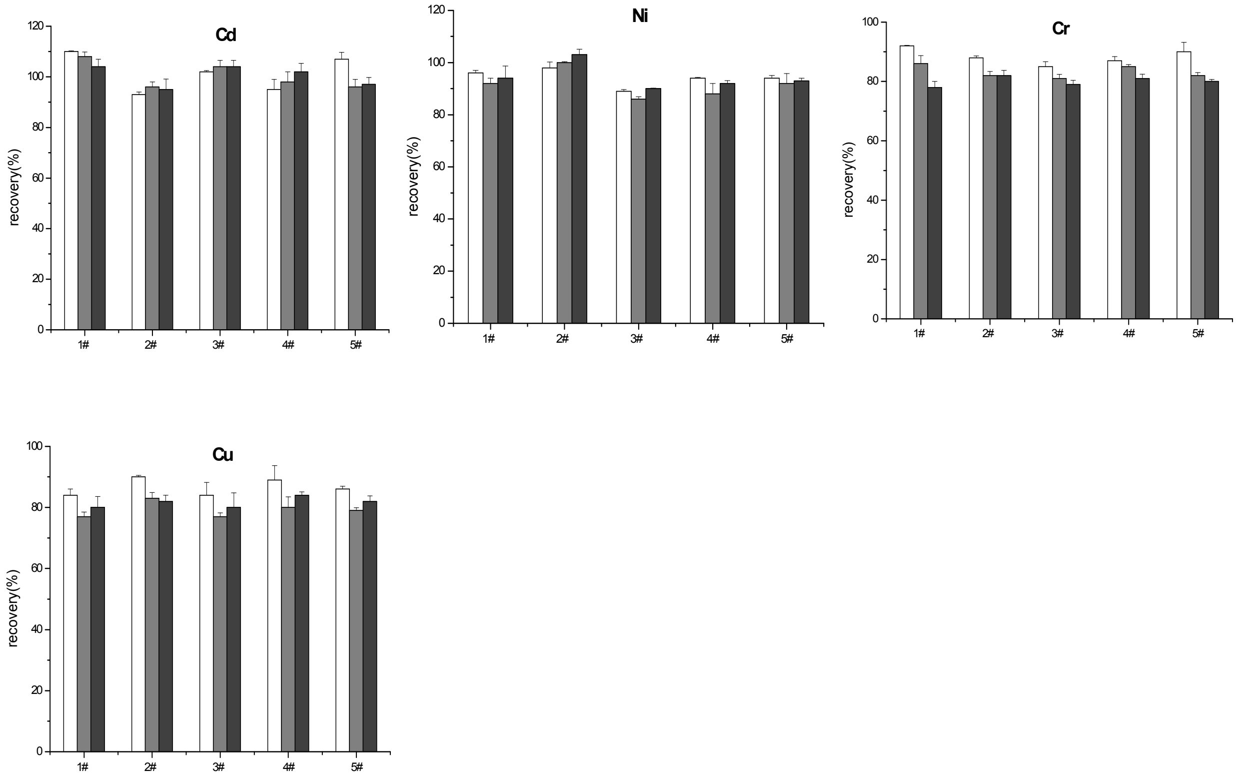


Fig. 2: Comparison of microwave assisted extraction and TCLP protocol in the practical usefulness of three optimum extraction procedures (n=3).

3.3 Comparison of extracion efficiency of different metals

Under the condition of P=500W, T=70°C, t=10min, we compared the extraction efficiency of different metals (Fig.2).The results showed that the extraction efficiency of Zn, Cd and Ni differed greatly in different samples. The biggest difference existed Zn had the biggest 17% difference between samples 1# and 5#. This indicated the dissolved content of these three metals was affected largely by the composition and characteristics of samples. At first, different composition and characteristics of samples lead to leachate pH variation, then resulted in reabsorbtion or precipitation effects of metals in solution. It has been reported that the final leachate pH controls the leachalibility of metals due to its influence on their solubility [13, 14]. In order to testify the impact of pH value on extraction efficiency of different samples, pH of samples 1# to 5# were determined and the values were 8.1, 8.0, 7.8, 7.9, 7.5 respectively. Correlation coefficients of extracion efficiency against sample pH value in these five samples were listed in Tab 1. we can see that the extraction efficiency of Zn, Cd and Ni, especially Zn, is more related to pH value than As, Pb, Cr and Cu. Secondly, the characteristics of these metals were active, and the phenomenon of readsorption and redistribution occurred easily. Gómez-Ariza [9] stated that both readsorption and redistribution occurred and their extent depended on the characteristics of the sediment when conventional sequential extraction schemes were applied to sediments. By contrast, recovery percentage of these metals was affected less by microwave parameters than by samples. heat-effect had a little effect on the physico-chemical process in the solution.

Tab 1: Correlation coefficients of extraction efficiency against sample pH value for different metals (n=5)

metals	As	Zn	Pb	Cd	Ni	Cr	Cu
coefficient	0.29	0.90	-0.08	0.31	0.38	-0.07	-0.18

On the contrary, the extraction efficiency of As, Pb, Cr and Cu were affected most by the microwave parameters, and a little by sample matrix itself. The biggest value of recovery percentage between these samples in this three conditions was only 7% difference.

We can conclude that As, Pb, Cr and Cu were more suitable for accelerating extraction using microwave than Zn, Cd and Ni. Stable extraction efficiency could be obtained under certain conditions. Although the extraction efficiency of Cr and Cu was lower than 100%, the actual leaching metals content of TCLP could be calculated using extraction efficiency and dissolved metals content with microwave.

4. Conclusions

This study demonstrate that combination of conventional TCLP procedure with microwave extraction provide a promising quickly method in the field of leaching of metals from sludge.

According to the extraction efficiency of different samples under relative optimized conditions, the dissolved content of Zn, Cd and Ni was affected largely by the composition and characteristics of samples. On the contrary, the extraction efficiency of As, Pb, Cr and Cu were affected most by the microwave parameters. As, Pb, Cr and Cu were more suitable for accelerating extraction using microwave than Zn, Cd and Ni.

Application of microwave extraction reduced treatment time from 18h (TCLP procedure) to 10min. This provides rapid and useful information for the sludge toxicity.

Therefore, the microwave extraction method is recommended as a rapid and cost effective monitoring tool for samples from waste treatment plants, when combined with or supplemented by the traditional TCLP protocol.

5. Acknowledgements

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