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Determination of transition elements in bioremediated soils by ICP-OES

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Received: 27th July, 2010 ; Accepted: 6th August, 2010

ABSTRACT

In La Pampa, Argentina, soil bioremediation is one of the most widely used methods for the elimination of oil residues. Oil was treated with bacteria to degrade its organic compounds deposited in the soil. However, crude oil contains several transition elements, which can be accumulated in the soil after the bioremediation process is finished. For this reason, this paper discusses the determination of transition elements in bioremediated soils - including the concentration of Co, Cr, Cu, Fe, Mn, Mo, Ni, and Ti to evaluate its contribution to environmental impact in bioremediation zones from La Pampa, Argentina. The determinations of metals were carried out by inductively coupled plasma optical emission spectroscopy (ICP-OES) in soil samples proceeding from a remediation zone in the southwest of La Pampa. Testing samples without oil from the same zone were analyzed to determine the basal levels of elements. Results show that oil has a contribution of transition elements and can be accumulated by repeated use of soil along time, which can produce an important environmental impact in the soil for futures uses, due to the fact it can lixiviate and contaminate the Colorado River. © 2010 Trade Science Inc. - INDIA

KEYWORDS

Transition;
Elements;
Metals;
Oil;
Bioremediation;
ICP-OES.

INTRODUCTION

Bioremediation is a process frequently used to diminish the levels of oil existent in the soil by means of biodegradation; in Argentina, it is usually preferred to other remediation methods. The bioremediation process requires a prolonged period for the degradation of

oil, depending on rain levels, temperature and the incorporation of nutrients to the soil. After a bioremediation process, several quantities of heavy metals that had accumulated in the soils can infiltrate the groundwater levels or lixiviate on the surface.

At present, La Pampa province has an oil exploitation area of 1,000 km², but in the future, it will increase

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Figure 1 : (a) La Pampa province placed in Argentina. (b) Location of oil region in La Pampa. (c) Detail of the south west region of oil extraction

to 9,274 km²⁰¹. The bioremediation zone is located in a semi-arid region. Some exploitation areas was placed next to the margins of the Colorado River, fact that can be dangerous since this river supplies water to an important region of La Pampa province. In the absence of rains, metals can accumulate in the soil or if rains occur, they can lixiviate to the Colorado River. Next to the oil zone -in the margins of the Colorado River- lies the city of 25 de Mayo with a population of 6962 inhabitants²², which depends on the water supplied by the river for its subsistence. Figure 1 shows the location of La Pampa province and the oil exploitation region. In this place, although bioremediation was carried out all the year round, the preferred season is summer, because high temperatures help bacteria to grow.

It is known that oil contains transition elements, which were previously studied by several authors. Vanadium is one of most studied elements, since it is a catalyst poison and causes corrosion in furnaces and boilers during oil processing as suggested by Aucebio et al.²³. Other metals such as Cd, Cr, Zn and Cu were studied in crude oil due to their emissions to the environment²⁴. The presence of TPH and heavy metals in the vicinity of refineries was also the subject of previous studies carried out by Stigter et al.²⁵. A new analytical method for the determination of Mo, Zn, Cd, Ti, Ni, V, Fe, Mn, Cr and Co in crude oils by the ICP-OES method and micro emulsions was proposed by de Souza et al.²⁶. In addition, Vilhunen et al. used total reflection X-ray fluorescence as a method for the determination of oil samples²⁷. The determination of V²⁸ and Zn²⁹ in burned and unburned oil from Venezuela was also studied by Guidroz and Smith, respectively.

The determination of heavy metals in Arabian oil by laser spectroscopy was performed by Gondal et al.³⁰. The contamination of Cu, Pb, Zn, PAH, PCB and PCP in sediments after spilling was studied by Armenta-Arteaga et al.³¹. Iturbe et al. studied the presence of Fe, Pb, Zn and Cr in soil and water in the areas surrounding petrol stations³². Muniza et al.³³ carried out the study of several heavy metals from river oil sediments. Druyck et al.³⁴ studied the content of heavy metals in oil heavy fractions. The determination of metals from kerogens in sediments was studied by Akinlua et al.³⁵. Heavy metals were analyzed by X-ray fluorescence in zones with oil industrial activity³⁶. Toxic elements from oil were determined in cultivated lands and ore samples by laser spectroscopy³⁷. The analysis of V and Ni compounds in crude oil was carried out by graphite furnace absorption atomic spectroscopy (GF-AAS)³⁸. A biological assay was performed to determine the toxicity and leachability in flare pit soils³⁹. In another work by Amorima et al.⁴⁰ the determination of V in oil was performed by atomic spectrometric methods. The determination of heavy metals in sediments polluted with oil was carried out in the Nigeria Delta⁴¹ and Suez Gulf, Egypt⁴². In a previous work, the concentration of Mn, Cu, Co and Mo was determined to evaluate their effects on bacterial growth in the bioremediated process⁴³. On the other hand, previous works review the analysis of trace metals in oil by different spectroscopic methods^{24,25}.

This paper discusses the determination of Co, Cr, Cu, Fe, Mn, Mo, Ni, and Ti in soils used for bioremediation of oil in the southwest of La Pampa, Argentina. The levels of these elements were statisti-

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cally contrasted with soils without remediation from the same place. Measurements were carried out by inductively coupled plasma optical emission spectroscopy (ICP-OES).

EXPERIMENTAL

Reagents

HCl and HNO₃ were grade suprapure bought from Sigma (Missouri, USA) and Merck (Darmstadt, Germany) respectively. Standard solutions were prepared using Merck and Sigma reagents spectroscopic grade. Ultrapure water (18.2 MΩ cm) was obtained from a Barnstead Easy pure RF compact ultrapure water system (Dubuque, IO, USA).

Instrumental

The concentrations of eight transition elements and internal standard were determined by direct nebulization using a Varian ICP-OES model ICP-OES Vista Pro, with a Czerny-Turner monochromator, holographic diffraction grid and a Vista Chip CCD (charge-coupled device) array detector. The wavelength (nm) used to measure every element was Co (228.616), Cr (267.716), Cu (324.754), Fe (259.940), Mn (257.610), Mo (202.032), Ni (231.604) and Ti (364.321). The internal standard (In) was measured at 303.963 nm.

Sampling and sample treatment

Twenty five samples of soil were collected from the bioremediation zone, using a random systematic sampling^[20], over a surface of 40,000 m². In addition, 25

samples not used for bioremediation of oil, were collected randomly from adjacent sites.

The mineralization step was carried out following a standard method for soil analysis^[27]. A portion of every sample air dry was passed through a 250 mesh sieve. 1.00 g of sieved sample was weighted, placed in a porcelain crucible and added with 1 mL of a 1000 mg L⁻¹ In solution, used to evaluate the recovery degree. The crucibles were covered and placed in a furnace and heated to 500°C during 3 h in order to consume the oil residues and mineralize the sample. Then, the crucible was cooled at room temperature in a desiccator and added with 5 mL 5 mol L⁻¹ of HCl and 5 mL 6 mol L⁻¹ of HNO₃. The samples' solutions were filtered and transferred to a 100 mL volumetric flask and completed to mark with distilled water.

RESULTS & DISCUSSION

Recovery and validation analysis

The method of standard addition is considered as a validation method^[28,29]. In order to demonstrate the validity of the analytical procedure, a first recovery study was carried out. A synthetic solution containing all the studied elements was prepared in order to perform the recovery analysis. Portions of 1.00 g soil samples were added with the synthetic solution and then, all elements were determined following the procedure of sample preparation, after dilution of the samples to 100 mL. The results are considered satisfactory; recoveries being within the range of 99.36-103.54 %, as shown in TABLE 1.

TABLE 1 : Validation method for the recovery of transition elements

	Initial value ^a	Added ^a	Found ^{a,b}	Recovery ^c
Co	42.70	12.12	54.76	99.50
Cr	6.25	1.09	7.43	101.22
Cu	72.21	20.11	92.45	100.14
Fe	19,864.32	150.25	19,886.65	99.36
Mn	195.81	15.11	212.86	100.92
Mo	ND	2.54	2.63	103.54
Ni	20.40	5.72	26.02	99.62
Ti	444.28	15.49	462.82	100.66

^aConcentration in mg kg⁻¹. ^bMean value (n = 25). ^c[(found-initial)/added]×100

TABLE 2 : Concentrations of transition elements founded in both, bioremediated and testing soils and it difference

Element	Bioremediated soil ^{a,b}	Testing soil ^{a,b}	Difference of mean ^c
Co	42.70 ± 2.73	42.51 ± 3.02	0.19
Cr	6.25 ± 1.72	6.22 ± 2.08	0.03
Cu	72.21 ± 5.87	45.78 ± 5.24	26.43
Fe	19,864.32 ± 263.77	12,425.86 ± 248.36	7,438.46
Mn	195.81 ± 12.46	96.86 ± 10.52	98.95
Mo	ND ^d	ND ^d	-
Ni	20.40 ± 5.63	18.63 ± 5.09	1.77
Ti	444.28 ± 21.06	226.13 ± 22.18	218.15

^aConcentration in mg kg⁻¹. ^bMean ± standard deviation (n = 25).

^cNot detected

TABLE 3 : Statistical test (*t* test) for determine significant contribution

Element	<i>t</i> value ^a	<i>t</i> critic ^{a,b}	Mean contribution ^c
Cu	16.62	1.67	26.43
Fe	102.66	1.67	7,438.46
Mn	30.34	1.67	98.95
Ti	35.67	1.67	218.15

^aLevel of confidence (α) = 0.05. ^bDegree of freedom ($n_1 + n_2 - 2$) = 48. ^cConcentrations expressed in mg kg⁻¹

On the other hand, a second validation recovery method was applied, using Indium as internal standard to obtain the recovery percentage and evaluate losses in the mineralization step^[20]. Indium standard was added to samples before the mineralization step, as described in the sample preparation procedure. The recovery mean percentage obtained was 97.3 ± 3.1 % ($n = 50$).

Transition elements analysis

The concentrations of eight elements were determined in 25 samples of bioremediated soils and 25 samples of soil without oil. Calibration was performed using five levels of concentration and three replicates for each one. The regression coefficient r^2 values obtained for all elements varied from 0.995 to 0.999. TABLE 2 shows the concentrations obtained (average \pm standard deviation) for 8 elements: Co, Cr, Cu, Fe, Mn, Mo, Ni and Ti, determined in both, bioremediated and test soils and the differences found between them. Based on TABLE 2, a one sided *t* test was calculated to determine significant differences between bioremediated and not bioremediated soils. TABLE 3 shows the *t* values found for Cu, Fe, Mn and Ti, for a level of confidence $\alpha = 0.05$. These four elements were significantly contributed by oil in bioremediated soil samples in comparison with the basic levels in not contaminated soils. Mo was not detected in any sample. The remaining elements: Co, Cr and Ni were quantified but they have not shown significant differences between bioremediated and test soils.

On the another hand, the index of geoaccumulation (I_{geo}) allows for the assessment of contamination and it can also be applied to the assessment of soil contamination^[22,16]. The I_{geo} was proposed by Muller^[21] for the characterization of contamination by metals, defined by:

$$I_{geo} = \log_2 (C_s / 1.5 B_s)$$

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TABLE 4 : Determination of Co, Cr, Cu, Fe, Mn, Mo, Ni and Ti elements in contaminated samples analyzed in previous works

Sample	Co	Cr	Cu	Fe	Mn	Mo	Ni	Ti
This work (mean contribution) (mg kg ⁻¹)	-	-	26.43	438.46	98.95	ND	-	218.15
Crude oil cargoes ^[26] (µg kg ⁻¹)	-	69.6	66.0	-	-	-	-	-
Soil refinery vicinity ^[26] (µg g ⁻¹)	-	1.67	2.70	-	-	-	2.45	-
Crude oil ^[26] (µg g ⁻¹)	ND	ND	-	21.7	ND	ND	2.8	ND
Crude oil residues ^[22,27] (mg kg ⁻¹)	-	-	5	177	-	3.18	51.6	-
Sediments after oil spilling ^[22] (mg kg ⁻¹)	-	-	0.1	-	-	-	-	-
Contaminated sediments in Montevideo harbor ^[22] (µg g ⁻¹)	-	162	89	-	-	-	30	-
Karogenes from Niger Delta ^[28] (µg kg ⁻¹)	4.96	12.52	30.57	521.30	52.26	-	12.50	-

where C_n indicates the content of the heavy metal analyzed, and B_n indicates the background content of the heavy metal. The safety factor of 1.5 is used to compensate for variations in the background.

The I_{geo} values obtained in this work were Cu: 0.07; Fe: 0.09; Mn: 0.43 and Ti: 0.39. These values indicate that there exists accumulation of Cu, Fe, Mn and Ti due to the bioremediation process^[22]. Based on the I_{geo} values, the major contribution is due to Mn and Ti and to Cu and Fe, to a lesser extent. On another hand, the obtained I_{geo} values are in agreement with the statistical *t* test shown in TABLE 3.

TABLE 4 shows the concentrations of several transition elements from oil, found in this and previous works in different samples.

CONCLUSIONS

This work showed the contribution of transition elements to bioremediated soils from La Pampa, Argentina. Statistically, it showed that oil contributed significantly with four elements: Cu, Fe, Mn and Ti. Mo was not detected, while Ni, Co and Cr were not contributed by oil. The presence of transition elements, will depend on both, the actual concentration of elements in oil and the initial quantities of oil incorporated to the bioremediation process. The *t* test and the index of geoaccumulation (I_{geo}) showed that Fe, Cu, Mn and Ti are accumulated due to the bioremediation process. The intense and repetitive use of soils for bioremediation can cause environmental contamination by accumulation of metals and can also limit the ability of soils for future uses in agronomical or other activities. Also, by the lixiviation process due to intense rains, metals could

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be transported to the Colorado River and contaminate an important supply of water in the south of La Pampa.

ACKNOWLEDGEMENTS

The authors are grateful to Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Universidad Nacional de La Pampa and Universidad Nacional de San Luis that supported this research.

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