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Research Paper

ASSESSMENT OF HEAVY METAL CONTAMINATED SOIL NEAR COAL MINING AREA IN GUJARAT BY TOXICITY CHARACTERISTICS LEACHING PROCEDURE

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The concentrations of heavy metals (Cd, Cr, Co, Cu, Mn, Ni, Pb and Zn) in soils near lignite coal mine located at Surat (Gujarat) were determined and their toxicity was used to assess the risk of Cd, Cr, Co, Cu, Mn, Ni, Pb and Zn in contaminated soils and the toxicity characteristic leaching procedure (TCLP) developed by the United States Environmental Protection Agency (USEPA). The TCLP method is a currently recognized international method for evaluation of heavy metal pollution in soils. The available levels of Cd, Cr, Co, Cu, Mn, Ni, Pb and Zn were 0.41-0.77, 3-8.0, 5.6-19.0, 9.1-57.0, 47-121, 7.1-16.0, 3.4-9.0 and 13-60 mg/kg-^{1} respectively, while the international standards were 0.06, 100, 8, 30, 600, 40, 10 and 50 mg/kg-^{1}, respectively. Soils around the mine were polluted with Cd, Cr, Co, Cu, Mn, and Ni followed by Pb and Zn. Moreover, the levels of heavy metals in the soils extracted by TCLP indicated that extraction fluid 2 was more effective than extraction fluid 1 in extracting the heavy Metals from the polluted soils and there was a positive correlation between fluids1and 2. Available heavy metal contents determined by TCLP were correlated with soil total heavy metal contents.

Keywords: Soil properties, Heavy metals, Mine tailings, Risk assessment, TCLP

INTRODUCTION

Due to rapid industrialization heavy metals have been excessively released into the environment and have created a major global concern. Cadmium, zinc, copper, nickel, lead, mercury, cobalt, manganese and chromium are often detected in industrial waste waters, which originate from metal plating, mining activities, smelting, battery manufacture, tanneries, petroleum refining, paint manufacture, pesticide, pigment manufacture, printing and photographic industries, etc., (Kadirvelu *et al*., 2001a; Williams *et al*., 1988). Mining can be a significant source of metal contamination of the environment owing to activities such as mineral excavation, ore transportation, smelting and Refining, disposal of

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the tailings and waste water around mines (Adriano 2001; Jung 2001; Razo *et al*.2004; Chopin and Alloway 2007). Due to discharge and dispersion of lignite coal mine wastes from the metalliferous mines, agricultural soils, food crops and stream systems are often contaminated by elevated levels of toxic metals (McGowen and Basta 2001; Jung 2001;Lee 2006). With growing public concern throughout the world over health hazards caused by polluted agricultural products, many studies have been conducted on metal and metalloid contamination in soils, water and sediments from metalliferous mines (Merrington and Alloway 1994; Iwasaki *et al*. 1997; Jung *et al*. 2002; Lee 2006; Chopin and Alloway 2007; Anawar *et al*. 2008). It is known that serious systemic health problems can develop as a result of excessive accumulation of dietary heavy metals such as Cd, Cr, and Pb in the human body (Oliver, 1997). Heavy metals are of great concern in soil pollutants because they can threaten the health of human beings and animals through the food chain. Mining activities can produce large amounts of wastes that are a major anthropogenic source of heavy metal pollution (He 1995). The exploitation of lignite coal mines can cause severe destruction both in lignite coal mine area and elsewhere (Hu *et al*., 2002). Many investigations have been conducted in which heavy metals have been added experimentally to soils to simulate their behaviour (Wang *et al*. 2002). Evaluate heavy metals by their total concentrations in the soil and their bioavailability. Total concentrations are seldom closely related to their bioavailability which is sensitive to climate and human activities (Ren 2000; Wang 2002). The toxicity characteristic leaching procedure (TCLP) is a method that is commonly used in the United States to assess the toxicity of pollutants in the environment. The method was developed by the US Environmental Protection Agency (USEPA) as the basis for the promulgation of the best demonstrated available technologies treatment standards under the land (USEPA 1992). A study by Blackburn *et al*., (1998) indicated that the toxicity characteristic leaching procedure (TCLP) method had several advantages over other methods.

The objective of the present study was to assess the toxicity of heavy metals of soil contaminated with lignite coal mine tailings using the toxicity characteristic leaching procedure (TCLP) method in the area near lignite coal mine.

MATERIALS AND METHODS

Study Site

The experimental site was situated in Surat District (Gujarat) India. The climate is sub tropical. The highest precipitation is during monsoon period (Middle of June to sept.). The temperature ranges between 4.4^{0}C during winter and 45.5 ^{0}C during summer. The detailed descriptions of the soil collection sites were normal agricultural soil. The crops grown in this area was dominantly sugarcane of very good quality and very high yield. At Agricultural field one can also see crops like maize, jowar, tur and cotton etc. The source of irrigation was Kim River and Canals. All the eight locations were located near coal mine of Surat District (Gujarat) India.

Sampling and analysis

Eight soil samples were collected from coal mine area located at Surat District (Gujarat) (Table 1). Agricultural soil was polluted by heavy metals from the Lignite coal mine tailings. Soil samples were collected from the top depth 0-20 cm of the soil profile at various distances from the Lignite

Table 1: Sampling Locations

S. No	Sampling Location	Latitude	Longitude
1.	A-1	N- 21° 25.081'	E - 73° 06.359'
2.	A-2	N- 21° 25.268'	E - 73° 05.974'
3.	A-3	N- 21° 25.886'	E - 73° 07.650'
4.	A-4	N- 21° 25.775'	E - 73° 07.325'
5.	A-5	N- 21° 25.939'	E - 73° 07.332'
6.	A-6	N- 21° 25.193'	E - 73° 07.432'
7.	A-7	N- 21° 25.627'	E - 73° 07.858'
8.	A-8	N- 21° 25.564'	E - 73° 07.981'

coal mine tailings. The samples were air dried, ground to pass through a 2-mm sieve and stored in plastic bottles before analysis. pH of the soil samples were estimated by dipping the pH electrode meter in the saturation paste as described in USDA Hand Book No. 60 (1954). In the same suspension, conductivity swas measured using conductivity meter (Orion, EA 940 USA). The organic carbon was determined using Walkey and Black's method (Allison, 1986). Selected properties of the soil samples used were presented in Table 2.

Estimation of Heavy Metal Content

Heavy metals in soil were estimated by wet digestion with 1:4 mixtures of $HClO_4$ and conc. HNO_3 estimating metals by inductively coupled plasma spectrometer (ICP) (APHA, 1995). Heavy metal concentrations were presented in Table 3.

TCLP Method

Two different buffered acidic leaching extraction fluids were used for toxicity characteristic leaching procedure (TCLP) depending on the alkalinity and the buffering capacity of the wastes. As described

Table 2: Basic Properties of the Soil Samples

S. No.	pH1:1	ECdS/cm	Organic Carbon (%)
1	7.8±1.4	0.236±0.038	0.42±0.08
2	7.9±1.2	0.088±0.014	0.39±0.12
3	7.6±1.2	0.281±0.049	0.12±0.04
4	8.4±1.0	0.327±0.064	0.15±0.06
5	8.5±1.1	0.356±0.029	0.36±0.11
6	8.5±1.1	0.371±0.062	0.12±0.04
7	7.9±1.2	0.386±0.079	0.30±0.08
8	8.2±1.6	0.527±0.089	0.18±0.06

in toxicity characteristic leaching procedure (TCLP), if the pH of the soils was less than 5, extraction fluid 1 with a pH of about 4.93 (5.7 mL glacial CH_3CH_2OOH and 64.3 mL 1 N NaOH diluted in 1 L water) otherwise extraction fluid 2 with a pH of about 2.88 (5.7 mL glacial CH_3CH_2OOH diluted in 1 Lwater) was used. The pH values of the two solutions were adjusted with 1 mol L^{-1} HNO_3 and1 mol L^{-1} NaOH. An aliquot of 2.00 g of each sample and 40 mL extraction reagent were transferred into 100-mL plastic vessels and rotated for18 h in a horizontal shaking mixer with a speed of 30±2 rpm. At the end of the 18-h extraction period, fluid in each vessel was separated from the solid phase by vacuum-filtration through 0.8-μm- pore glass fiber filter paper. The pH of the toxicity characteristic leaching procedure (TCLP) extracts was then measured and all extracts were acidified with 1 N HNO_3 to a pH of less than 2 for long-term preservation. In this experiment, both fluids were used. The concentrations of heavy metals in extracts produced by toxicity characteristic leaching procedure (TCLP) were determined as follows. The total contents of Cd, Cr, Co, Cu, Fe, Mn, Ni, Pb and Zn were determined by digestion with HF-HNO_3-$HClO_4$, their total and available contents were determined by flame atomic absorption spectrometry (AAS) (Ru 1999). Other physical and chemical properties were analyzed according to conventional standard methods (Nanjing Agricultural University 1986).

Quality Control and Quality Assurance

The standard reference material of metals (E-Merck, Germany) was used for the calibration and quality assurance for each analytical batch. Analytical data quality of metals was ensured through repeated analysis (n=6) of EPA quality control samples for metals and the results were found to be within ± 3.57% of the certified values. The reference solution of multi-elements and single element provided by National Physical Laboratory (NPL), New Delhi, India.

RESULTS AND DISCUSSION

Effect of lignite coal mine tailings on heavy metal concentrations in the agricultural soil

Table 2 shows, the total concentrations of the heavy metals in the soil fluctuated with various distance away from the center of the lignite coal mine tailings, especially total Mn, Cu, Zn, Ni, Co, Pb and Cd. The highest concentrations of total Mn, Cu, Zn, Ni, Co, Cr, Pb, Cd were 1412, 199, 175, 83, 84, 49, 22 and 2 mg kg^{-1} respectively, indicating severe pollution of the soil in the vicinity of the lignite coal mine tailings. Table 4 shows the results of metal leachability by toxicity characteristic leaching procedure (TCLP), indicating there was a positive correlation between fluid 1 and fluid 2, and fluid 2 was more effective than fluid 1 in extracting the heavy metals from the polluted soils. This may because of the lower pH of the fluid 2, that it can dissolve more heavy metals, i.e. there was some correlation between the pH of the fluid and the contents of the heavy metals by toxicity characteristic leaching procedure (TCLP).

The Correlation of the Fluid 1 and Fluid 2 Used in TCLP

The correlation of the fluid 1 and fluid 2 used in toxicity characteristic leaching procedure (TCLP), indicating that there was a positive correlation between fluid 1 and fluid 2. The correlation coefficient of Cd, Cr, Co, Cu, Mn, Ni, Pb and Zn was found in the range of 0.9849, 0.9829, 0.9715, 0.9964, 0.9903, 0.9592, 0.9935 and 0.9973 respectively. This may because of the different buffering capacities and acidity of the two fluids.

The correlation between concentrations of extractable heavy metals and concentrations of total heavy metals

Concentrations of the heavy metals extracted by the fluid 1 and fluid 2. There was some correlation between extractable heavy metals and the total ones. The correlation between extractable Cd and total Cd was not significant; the coefficients of fluid 1 and fluid 2 were 0.9431 and 0.9384 respectively. The correlation between extractable Cr and total Cr were 0.9283 and 0.9035 respectively. The correlation between extractable Co and total Co were 0.9616 and 0.9661 respectively. The correlation between extractable Cu and total Cu were 0.9921 and 0.9846 respectively. The correlation between extractable

Table 3: Heavy Metals Concentrations

S. No.	Total Cd	Total Cr	Total Co	Total Cu mg/kg^{-1}	Total Mn	Total Ni	Total Pb	Total Zn
1	1.4±0.38	23.9±1.4	38.6±1.4	99.1±7.4	973.7±73.0	57.6±1.0	15.2±2.1	118.1±13.4
2	1.4±0.27	30.6±2.2	41.4±2.0	115.0±15.0	918.1±111.0	61.1±4.6	12.7±1.6	89.4±11.4
3	1.4±0.34	48.6±4.2	57.6±5.8	176.0±21.4	721.7±81.5	70.1±9.4	17.1±3.2	175.8±14.6
4	2.0±0.49	46.4±4.1	84.1±7.8	199.3±17.0	1411.7±144.2	82.6±8.4	22.0±1.8	155.4±4.2
5	1.6±0.24	30.4±2.0	31.8±3.2	90.3±12.4	725.4±27.8	70.2±1.4	20.7±3.1	112.5±13.8
6	1.2±0.17	29.7±3.5	27.2±1.3	68.6±4.2	611.5±71.6	50.3±1.5	15.3±1.2	69.1±1.6
7	1.1±0.14	44.6±5.0	24.7±1.2	68.3±2.1	549.6±49.4	66.9±7.4	19.1±4.4	61.2±1.3
8	2.4±0.62	49.7±6.2	27.1±2.4	67.5±1.5	623.3±61..4	65.9±6.8	20.8±1.6	75.02.6±

Table 4: Concentrations of Heavy Metals in Extractant Solutions 1 and 2 by TCLP

S. No.	Cd		Cr mg/kg^{-1}		Co		Cu	
	1	2	1	2	1	2	1	2
1	0.49±0.04	0.51±0.03	3±1.2	3.5±2.1	7±2.3	8.5±3.4	24±1.8	26±1.8
2	0.50±0.03	0.51±0.04	4±1.1	4.3±1.3	7.5±1.3	9±4.2	27±2.2	30±2.5
3	0.50±0.01	0.52±0.05	7±2.1	7.8±0.7	10±2.7	13±1.1	51±4.3	55±3.21
4	0.57±0.06	0.59±0.01	6±1.4	6.2±1.2	17±1.2	19±1.7	56±4.1	57±4.1
5	0.51±0.04	0.55±0.05	5±2.4	5.4±2.0	6.4±2.2	9±1.3	21±2.4	22±2.5
6	0.42±0.04	0.46±0.02	4±1.1	4.5±1.7	6.1±1.1	6.8±0.8	10±1.0	12±1.2
7	0.41±0.04	0.45±0.03	6.3±2.1	7±1.0	5.6±2.3	7±1.9	11±1.4	13±0.8
8	0.73±0.04	0.77±0.01	7.8±0.7	8.0±1.2	6±0.5	8±1.3	9.1±1.3	9.3±1.4

Mn and total Mn were 0.4454 and 0.4145 respectively. The correlation between extractable Ni and total Ni were 0.8107 and 0.7843 respectively. The correlation between extractable Pb and total Pb were 0.8574 and 0.8802 respectively. The correlation coefficients between extractable Zn and total Zn were 0.8246 and 0.8360 respectively. It could be seen that Cu was most significant, followed by Co, Cd, Cr, Pb, Zn, Ni, Fe and Mn.

Comparison between extractable concentration by TCLP and international standards

The critical levels or standards of the heavy metals extracted by toxicity characteristic leaching procedure (TCLP) (below which, the levels of heavy metals were considered as non toxic, US EPA 1990) were listed in Table 3. It was found that soils around the lignite coal mine were polluted with heavy metals Cd, Cr, Co, Cu, Mn, Ni, Pb and Zn, especially polluted by Cu, followed by Co, Cd, Cr, Pb, Zn, Ni and Mn.

CONCLUSIONS

Soils around the lignite coal mine were polluted. The total contents of Mn, Cu, Zn, Ni, Co, Cr, Pb, and Cd reached up to 1411.7, 199.3, 175.8, 82.6, 84.1, 48.6, 22.0 and 2.4 mg kg^{-1} respectively. If extracted by toxicity characteristic leaching procedure (TCLP), the heavy metals vary from international standards which were 600, 30, 50, 40, 8, 100, 10 and 0.06 mg/kg^{-1}. The heavy metals in the soils extracted by toxicity characteristic leaching procedure (TCLP) indicated that fluid 2 was more effective than fluid 1 in extracting the heavy metals from the polluted soils and there was a positive correlation. There were some correlations in the concentrations of heavy metals in the fluid 1, fluid 2 and total contents of heavy metals.

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