Speciation of Rubber Wood Bark Ash

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Abstract

Malaysia produces approximately 1.5 million cubic meters of rubber wood medium density fiberboards (MDF) annually. During the manufacture of the fiberboards, the floem (outer skin) of the rubber logs would be debarked and burnt. The ashes would usually be disposed in landfills. The chemical constituents of the ashes would leach and contaminate the groundwater. Therefore a sequential leaching procedure was conducted to investigate the speciation and extraction of five heavy metals (Cd, Cr, Cu, Pb and Zn) in rubber wood bark ash (RBA). The mobility and bioavailability of the metals was investigated through five fractions: (1) exchangeable, (2) bound to carbonate, (3) bound to Fe-Mn oxides, (4) bound to sulfide, and (5) residual fraction. The metal concentration of the leaching solutions was determined by inductively coupled plasma mass spectrometer (ICP-MS). In general Cd was the dominant metal in the exchangeable and carbonate fractions making up 70.2% while Cu was predominantly associated with the sulfide fraction (28.5%). Zn (11.7%) and Cd (9.2%) were also present mainly in the Fe-Mn oxide fraction while the residual fraction was dominated by Cr (40.0%) and Cu (34.0%). In addition the leachate derived through the TCLP tests indicated that the ashes may be disposed into landfills safely.

Keywords: heavy metals, rubber wood bark ash, fiberboards, sequential extraction, toxicity characteristic leaching procedure.

Introduction

The demand for rubber wood (*Hevea Brasiliensis Muell Arg*.) has been increasing rapidly in Malaysia. By the beginning of this decade, the production of rubber wood such as particleboards, medium density fiberboard (MDF), wood fiber cement-bonded particleboards (Cemboard), etc. has increased tenfold, accounting for more than 20% of the Malaysian export market capacity. There are presently 8 companies manufacturing MDF with 10 mills and a production capacity of more than 1.5 million m^3 of MDF per annum (Mcintyre 2005; Mamat 2005, NATIP 2009). The increase use of rubber wood will produce additional quantities of rubber wood bark ash (RBA), one of the waste products of burning pulverized bark and waste rubber wood. Presently, between 30 and 40 million tons of rubber wood bark ash are being collected from the incinerator of the existing rubber wood processing plants. This quantity will increase in proportion to the amounts of bark burned.

The rubber wood ash generated by these plants is and will continue to be a disposal problem. Presently less than 10% of the ash collected is utilized in some process other than direct burial. Virtually all of the disposal and utilization techniques expose ash to the water at one time or another. The exposure ranges from complete immersion of the ash such as in ponds, sluicing into drains or channels, to percolation in dumps and fill areas. Safe, long term procedures for rubber wood bark ash disposal go hand in hand with making incineration an acceptable rubber wood bark disposal alternative.

Pollution in the environment by heavy metals has received attention due to the greater understanding of their toxicological importance in the ecosystem, agriculture and human health. During combustion most of the heavy metals in the bark are retained in the ash.

Mobility and biological availability of heavy metals depend not on their total concentration but on the physicochemical form in which they occur (Filgueiras et al. 2002, Smichowski et al. 2005, Poykio et al, 2008). Therefore, in order to determine the heavy metal leachability, two different approaches can be used, a single extraction with one reagent considered to be most suitable, or a sequential extraction with various chemical reagents in an increasing order of extractive force (Iwegbue et al., 2006). A common single extraction tests commonly employed to determine the safety of waste disposal into landfills is the toxicity characteristic leaching procedure (TCLP) (US EPA Method 1311, 1992). Sequential extraction, however have been used since the early 1970s. Perhaps the most commonly employed sequential extraction tests is the one used by Tessier et al. (1979). This method allows the separation of extractable metals into five fractions i.e. exchangeable, acid soluble, reducible, oxidizable and residues; and this method is commonly applied to soil, sediment and sewage sludge (Filgueiras et al. 2002). For ashes, Polyak & Hlavay (2001) used different chemicals for the five stage sequential leaching procedure which also includes various fractions: (1) exchangeable, (2) bound to carbonate, (3) bound to Fe-Mn oxides, (4) bound to sulfide, and (5) residual fraction. The portioning of particulate metals was achieved for Cd, Cr, Cu, Pb and Zn in the rubber-wood bark ash.

The main purpose of this study was to investigate the speciation and extraction of selected metals in rubber wood bark ash and the suitability of RBA for disposal in landfills.

Materials and Methods

Sample Preparations: The ash used in this study was collected from a fiberboard manufacturer Dongwha Fibreboard Sdn Bhd (formerly known as Golden Hope Fibreboard Sdn Bhd) in Nilai, Negeri Sembilan, Malaysia. A total of 1000kg of RBA was collected and sent to the laboratory for processing. The RBA was crushed, sieved and stored in a dry place for further work. The ash was then air–dried and sieved using a 2 mm sieve and it was discovered that all the ash passed through this sieve. The ash was then kept in polyethylene bottles. All the experimental work in this study was carried out in triplicates and chemicals used were suprapure.

Major Oxides: The major oxides were determined by fusion technique using x-ray fluorescence machine (Philips PW1480, Netherlands) equipped with rhodium, Rh excitation tube and copper, Cu filter. Samples were prepared by adding 0.5 g RBA to 5 g of flux. The flux consisted of a mixture of 66.5% lithium tetraborate $Li_2B_4O_7$ and 33.5% lithium metaborate $LiBO_2$.

Loss on Ignition: Initial experiments by the authors indicated that dried rubber wood bark samples would completely burnt in an incinerator within 2 hours even at temperatures of 500^oC, leaving approximately 10% by weight as ashes. Based on this result, the loss on ignition, LOI was determined using gravimetric determination after ignition at $1000 \ ^oC$ for 20 minutes only.

Trace Elements: Selected trace elements were determined using inductively coupled plasma mass spectrometer, ICP-MS. After drying, the ash was ground up using a grinder (M20, IKA-Werke, Germany). Three samples of 0.5 g of the grounded dried ash were weighed and placed in Teflon tubes for digestion. Method 3052 (US EPA, 1996) was used to achieve total decomposition of RBA. Nine milliliters of concentrated HNO_3 (65%) and 3 ml HF (40%) was added to each tube and digested in a microwave digester, (Anton Paar GmbH Multiwave 3000) for 15 minutes**.** When the digesting cycle was completed, 18 ml of saturated boric acid H_3BO_4 (1 ml HF: 6 ml H_3BO_3) was added to each tube and a short run was performed on the microwave to complex the fluorides. The microwave digester is equipped with a sixteen-position rotor, high performance vessels, and simultaneous pressure and temperature control in all vessels. The digested samples were then analyzed by ICP-MS (Perkin Elmer ELAN 9000, Wellesley, MA, USA) which was equipped with a cross-flow nebulizer and a quadrupole mass-spectrometer with an AS-91 autosampler. Reagent blanks and internal standards (US EPA Method 6020, 1994) were used where appropriate to ensure accuracy and precision in the analysis. Internal standard solution was also spiked into the diluted sample to ensure corrections of isobaric interferences of metals.

Toxicity characteristics leaching procedure

Toxicity characteristic leaching procedure (US EPA Method 1311, 1992) was adopted to determine the suitability of RBA disposal in the landfills. This test initially requires the determination of the appropriate extraction fluid to be used. This determination is based on the inherent acidity or alkalinity of the sample.

Since RBA is alkaline, unbuffered acetic acid, CH_3COOH of pH 2.88 ± 0.05 was used. The samples inside PE extraction vessels were rotated in an agitator at 30 ± 2 rpm for 18 hours at room temperature. After the required time of agitation had elapsed, the extract was filtered through 0.45mm analytical filter papers, acidified by concentrated HNO_3, and the solutions were measured by ICP-MS.

Sequential extraction experiments

Sequential extraction was performed using the methodology of Polyak & Hlavay (2001). The sequential extraction procedure was carried out as follows:

Fraction (1): Exchangeable metals. To a 0.5 g rubber wood bark ash sample, 20 ml of 1 mol/liter Ammonium acetate, NH_4OAc (pH 6.5) solution was added in a 30 ml centrifuge tube and extraction by shaking for 16 hours at ambient temperature. The solid residue was separated from the extract by centrifugation (2500 rpm) and decantation of the supernatant liquid into 50 ml volumetric flask which was filled up with deionized water.
Fraction (2): Metals bound to carbonates. The residue from fraction (1) in the centrifuge tube was extracted for the 16 hours at ambient temperature with 0.5 mol/liter Acetic acid CH_3COOH (pH 2.7) solution. The solid residue was separated from the extract by centrifugation (2500 rpm) and decantation of the supernatant liquid into 50 ml volumetric flask which was filled up with deionized water.

Fraction (3): Metals bound to Fe-Mn oxides. The residue from fraction (2) in the centrifuge tube was extracted for 16 hours at ambient temperature with 0.1 M Hydroxylamine hydrochloride, $NH_2OH.HCl$ (pH 2, adjusted with HNO_3). The solid residue was separated from the extract by centrifugation (2500 rpm) and decantation of the supernatant liquid into a 50 ml volumetric flask which was filled up with deionized water.

Fraction (4): Metals bound to sulfide compounds. To the residue from step (3) 5 ml of 8.8 M Hydrogen peroxide, H_2O_2 (pH 2-3, adjusted with HNO_3) solution was added carefully in the centrifuge tube. Digestion was carried out in a covered vessel at room temperature for 1 hour. It was continued for 1 hour at 85ºC the volume being reduced to few ml. A further aliquot of 5 ml of 8.8 M H_2O_2 (pH 2-3, adjusted with HNO_3) solution was added to the cooled down solution and it was heated again to 85ºC and digested for 1 hour. The cover was removed and the volume was reduced to few ml. Then 25 ml of 1 M Ammonium acetate, NH_4OAc (pH 2, adjusted with HNO_3) was added to the cool moist residue and extracted for 16 hours at ambient temperature. The solid residue was separated from the extract by centrifugation (2500 rpm) and decantation of the supernatant liquid into a 50 ml volumetric flask which was filled up with deionized water.

Fraction (5): Residue. The residue from fraction (4) was digested at 100ºC for 2 hours with an acid mixture of 3.75 ml HNO_3 and 2.5 ml Perchloric acid, $HClO_4$. It was filtered into a 50 ml volumetric flask which was filled up with deionized water.

Extract except those from fraction 5 were added with 0.5 ml HNO_3 and stored at 4ºC prior to analysis. Standards were prepared from ultra pure chemicals. Analytical blanks from the same batch were placed in centrifuge tubes and in PTFE beakers. The blank is a reagent + beaker blank and the values have been subtracted from the ICP-MS measurement.

Results and Discussion

Chemical composition of RBA: The results of the chemical composition as determined by x-ray fluorescence are shown in Table 1. The main oxides of RBA are silica, SiO_2, calcium, CaO and alumina, Al_2O_3 accounting for over 76% (wt %) with the presence of Fe_2O_3, K_2O, P_2O_5 and MgO. The high CaO indicates that the ash sample is alkaline and may possess characteristics similar of a class C fly ash. The alkalinity may also inhibit the leachability of certain metals (Sorensen et al. 2001, Liu et al. 2003)

Table 1: The chemical composition (major oxides) of RBA

Composition (Major oxides)	RBA (% by weight)
SiO_2	54.48 ± 3.1
Al_2O_3	8.00 ± 1.58
Fe_2O_3	2.63 ± 0.11
CaO	13.96 ± 1.2
MgO	1.12 ± 0.83
Na_2O	0.07 ± 0.03
K_2O	5.36 ± 0.85
TiO_2	0.67 ± 0.16
P_2O_5	1.15 ± 0.77
MnO	0.14 ± 0.09
LOI (%)	11.92 ± 3.57
Total (%)	99.50

Data: mean $\pm$ standard deviation (N=3)

LOI is Loss on ignition at 1000 ^{o}C

The LOI of RBA is high indicating that some inorganic, organic and adsorbed moisture were lost due to the high temperature (Onitsuka et al. 2002). The organic in the ash may be derived from the incineration of rubber latex/resins that laced the rubber wood bark while the inorganic may came from inorganic carbons such as carbonates. Understandably, the chemical properties of RBA as shown above exhibited a wide range in constituents. This range is strongly influenced by the presence of moisture, dirt and soil on the bark before incineration. Soil properties local to the area where the rubber trees were harvested may also influence the chemical composition because of xylem transport.

Trace Metal Concentrations: The quantities of heavy metals in the ash are of key interest and are, for the most part, dictated by the makeup of waste bark. The concentrations of the trace metals of concern in the RBA as determined by ICP-MS are shown in Table 2. The total concentration of the trace metals were Cd (4.91 μg/g), Cr (38.74 μg/g), Pb (24.62 μg/g), Cu (22.62 μg/g) and Zn (178.27 μg/g). The presence of the heavy metals in RBA therefore indicated that leachability tests are necessary.

Table 2: The Concentration of total trace metals, fraction 2 of SE leachate, and TCLP leachate in RBA

Heavy Metals	Total trace metals concentration (μg/g)	Fraction 1 + Fraction 2 (Exchangeable + Oxides bound to carbonates) (μg/g)	Fraction 2 – extraction with CH_3COOH (μg/g)	TCLP concentration (μg/g) - extraction with CH_3COOH	Regulatory Level of TCLP (mg/l)
Cd	4.91 ± 1.6	3.28 ± 1.72	2.37 ± 1.63	3.05 ± 0.91	1.0
Cr	38.74 ± 3.9	16.83 ± 1.56	5.32 ± 0.23	16.22 ± 1.13	5.0
Pb	24.62 ± 2.6	19.18 ± 2.11	13.92 ± 1.2	23.00 ± 3.5	5.0
Cu	22.62 ± 0.8	6.61 ± 2.05	5.00 ± 1.93	6.27 ± 1.62	100
Zn	178.27 ± 5.3	81.17 ± 3.91	54.54 ± 1.79	80.44 ± 2.15	500

For Cu and Zn, these values were estimated from the MCL of drinking water multiplied by the dilution factor 100
Data reported as mean $\pm$ standard deviation (N = 3)

Toxicity characteristic leaching procedure: The result of the TCLP tests on the RBA is also shown in Table 2. US EPA does not publish any regulatory values for Cu and Zn. These regulatory values were estimated by a dilution factor of 100 from the Maximum Contaminant Levels (MCL) of the drinking water quality (LaGrega et al. 2001). The results indicated that all values were below the US EPA regulatory values and the estimated regulatory values for Cu and Zn. This was expected since the total heavy metal contents were low. This also indicates that the ash may be disposed safely in landfills without treatment. In addition this indicates that RBA may be used as additives in blended concrete if found suitable through other extensive physical and chemical tests.

Sequential chemical extraction: Table 3 gives the results of the sequential chemical extraction (SCE) tests. A sequential extraction test helped to explain which fraction held different metals in sample and indicate the composition in rubber-wood bark ash. The fraction in each category is also given in comparison to the sum of all fractions.

Table 3: Comparison of results for 5 trace elements using the SCE and total digestion in RBA

Fractions	Cd		Cr		Pb		Cu		Zn	
	μg/g	%	μg/g	%	μg/g	%	μg/g	%	μg/g	%
1	0.91	19.48	1.51	7.37	5.26	11.77	1.61	8.16	26.63	17.46
2	2.37	50.73	5.32	25.95	13.92	31.14	5.0	25.34	54.54	35.76
3	0.43	9.20	1.3	6.34	2.31	5.17	0.79	4.00	17.91	11.74
4	0.152	3.25	4.17	20.34	11.33	25.35	5.62	28.49	20.8	13.64
5	0.81	17.34	8.2	40	11.88	26.58	6.71	34.01	32.63	21.40
Σ1-5	4.67	100	20.5	100	44.7	100	19.73	100	152.51	100
Total	4.91		38.74		24.62		22.62		178.27	

Cadmium Distribution: The Cd association with different fractions followed the order: carbonate > exchangeable > residual > Fe-Mn bound oxides > sulfide bound as summarized in figure 1.
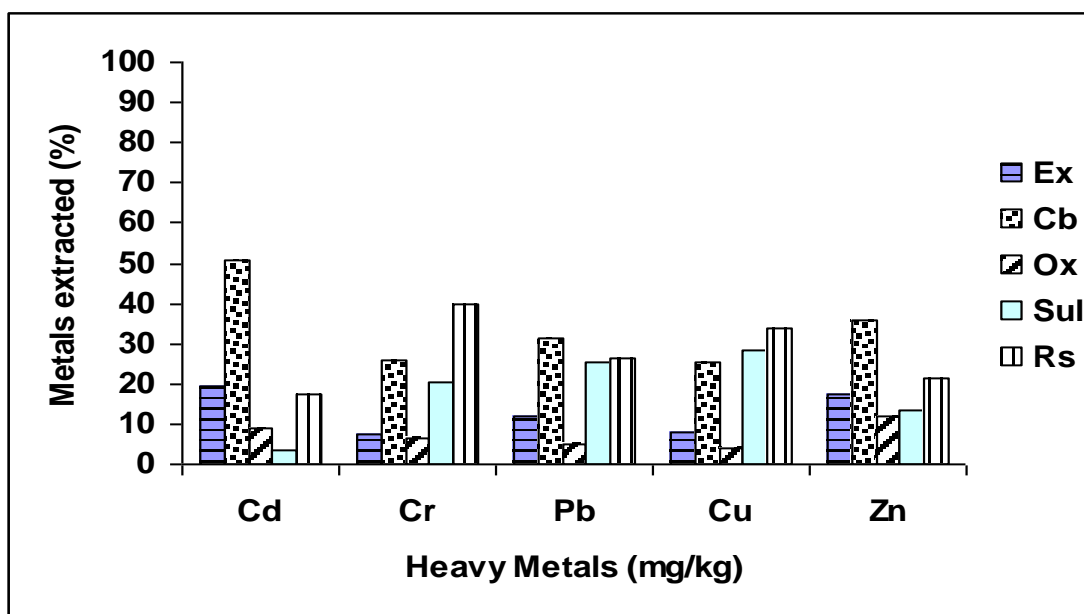

Fig. 1 Percentages of Cd, Cu, Ni, Pb and Zn in the fractioning of ash.

The total concentration of Cd in rubber-wood bark ash is 4.9 μg/g. The percentages extracted from fractions 1 to 5 were 19.5% (exchangeable), 50.7% (carbonates), 9.2% (bound to Fe-Mn Oxides), 3.3% (bound to sulfide) and 17.3% (residual) respectively. Yuan et al. (2004) and Chang et al. (2005) discovered that Cd was bound mainly in the exchangeable and carbonates in their samples. Yuan et al. (2004) explained that the high amount in the carbonate fraction, which is extractable with CH_3COOH, gives an indication of the amount of metal adsorbed on the surface of the particles, as well as on other components such as hydrated oxides and humic acids and are easily released as acid-soluble salts.

Chromium Distribution: The total amount of Cr in the rubber-wood bark ash was 38.74 μg/g. The distribution pattern of Cr in the different fractions was in the order: residual > carbonate > sulfide bound > exchangeable > Fe-Mn oxide bound as depicted in Fig 1. The highest value of Cr which was bound in the residual phase is 8.2 μg/g. This is because in the residual fraction, the high acidity condition (pH < 4.8) can leach the soluble chromium in the ash (Brigden et al, 2002). Martin et al. (1998) and Yuan et al. (2004) also discovered that Cr is commonly retained in the residual fractions. The minimum value of Cr (1.3 μg/g) was detected in Fe-Mn oxides.

The use of hydroxylamine hydrochloride, which is a strong reducing agent, as extractant in easily reduced fraction simulates anoxic conditions that are likely to occur in the natural medium (Poykio et al, 2008).

Lead Distribution: Lead in RBA showed the following order of association: carbonate > residual > sulfide bound > Exchangeable > Fe-Mn oxide bound. High amount of Pb was found in the rubber-wood bark ash, which comprises of 31.1% (13.92 µg/g) that was associated with the carbonates fraction. This may indicates that Pb may exists as $PbCO_3$ and $Pb_3(OH)_2(CO_3)_2$. Chang et al. (2005) also discovered that Pb was mainly bound in the carbonates in their fly ash samples. Morera et al. (2001) also stated that metals such as Pb and Cu were controlled by the carbonated forms in alkaline soils. Only 5% (2.31 µg/g) was bound to Fe-Mn Oxides. The distribution pattern of Pb in fraction (4), oxidizable and fraction (5), residual were close, only 25.4% and 26.6% respectively (Fig 1). This correlates well with Chang et al. (2005) who found that approximately 23% of Pb was bound in the organic matter fraction.

Copper Distribution: The amount of Cu in each fraction followed the order: residual > sulfide/organic matter bound > carbonate > exchangeable > Fe-Mn oxide bound. Most of the Cu (34.0%) was bound in the residual fraction. Bodog et al. (1996) and Yuan et al. (2004) similarly discovered that most of Cu was found to be associated with the residual phase and the smallest amount of Cu was bound to the Fe-Mn oxides phase.

Zinc Distribution: The distribution pattern of Zn in RBA in each fraction followed the order: carbonate > residual > exchangeable > bound to sulfide/organic matter > Fe-Mn oxides as shown in figure 1. Approximately 36% of the Zn content was bound to carbonates and about 21.4% in the residual phase. Chang et al. (2005) found that Zn was mainly bound in the carbonates followed by the organic matter.

TCLP and SCE

An interesting comparison may be made between TCLP and fraction 2 of the SCE test as shown in table 2. Both methods used acetic acid CH_3COOH as the extractant. The pHs of both extractants were also similar, the pH for TCLP was 2.9 and SCE was 2.7. However the TCLP tests resulted in slightly higher concentration of the heavy metals. This may be due to the TCLP's extractant that leached out both exchangeable metals and metals bound in carbonates. Upon further examination, it was found that the concentrations in the TCLP leachate were very close to the concentrations in the fraction 1 + fraction 2 (exchangeable elements + elements bound to carbonates) of the SCE test. In addition the total concentration of the elements was determined using Method 3052 and these results were compared with the sum of the 5 fractions determined by SCE. Results are shown in Table 3. The results were close enough and in general are acceptable. However the results for Pb obtained by Method 3052 were lower compared to the results obtained by SCE.

Conclusion and Recommendations

The sequential leaching procedure used in this work is useful to indirectly assess the potential mobility and bioavailability of the heavy metals in RBA. The mobility of these metals are related to their solubility and geochemical forms, and they usually decreases in the order of the extraction sequence i.e. exchangeable > carbonate > Fe-Mn oxide bound > sulfide bound > residual as shown in figure 2. This order is just a generalization and offers only qualitative information on metal mobility.

Operationally defined fraction	Extractant
Exchangeable	Ammonium acetate, NH_4OAc
Acid soluble (carbonate)	Acetic acid CH_3COOH
Easily to moderately reducible (metals bound to Fe-Mn oxides)	Hydroxylamine hydrochloride, $NH_2OH.HCl$
Oxidizable (metals bound to organic matter and sulfides)	Hydrogen peroxide, H_2O_2 + Ammonium acetate, NH_4OAc
Residual (metals bound within crystal structure of primary and secondary minerals)	Nitric acid, HNO_3 + Perchloric acid, $HClO_4$

(Left vertical axis: Metal mobility, arrow pointing up. Right vertical axis: Leachant Strength, arrow pointing down.)

Fig. 2 Relationship between metal mobility in the different operationally defined phases and leachant strength used in the SCE

The first two phases can release their metal loads by lowering the pH and are more mobile than the other phases. Accordingly, these two phases influence the mobility and hence the bioavailability. Based on this, the order of comparative mobility of the five metals is: Cd > Zn > Pb > Cu > Cr. This showed that Cd has the greatest overall affinity when compared to the rest of the metals (Table 4). Rubber-wood bark ash was mainly accumulated in the carbonate and residue fraction and the lowest concentration in heavy metals mostly in Fe-Mn oxides phase. In this study, Cu, Cr and Pb, which are all potentially toxic metals showed a clear tendency to be partitioned in this fraction.

Table 4: Comparison of heavy metal affinities in RBA

Sequential extraction fractions	Comparative heavy metal affinities
Exchangeable	Cd > Zn > Pb > Cu > Cr
Carbonate bound	Cd > Zn > Pb > Cu ≈ Cr
Fe-Mn oxide bound	Zn > Cd > Cr > Pb > Cu
Sulfide bound	Cu > Pb > Cr > Zn > Cd
Residual	Cr > Cu > Pb > Zn > Cd

The results clearly indicate that the ash may be safely disposed in monofills or landfills. However, further research should be undertaken to find better use of this material instead of disposal such as additives in other materials e.g. blended concrete or bricks and therefore reducing this material as waste. Additional physical and chemical studies should also be conducted to better understand the role of RBA in the suggested materials.

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