

THE JOURNAL OF SOLID WASTE TECHNOLOGY AND MANAGEMENT

Formerly The Journal of Resource Management and Technology (Volumes 12-22)
Formerly NCRR Bulletin (Volumes 1-11)

August 2013

Volume 39

Number 3

THE JOURNAL OF SOLID WASTE TECHNOLOGY AND MANAGEMENT

ISSN: 1088-1697

FOUNDER:

Iraj Zandi
University of Pennsylvania
U.S.A.

EDITOR:

Ronald L. Mersky
Widener University
U.S.A.

SENIOR ASSOCIATE EDITOR:

Wen K. Shieh
University of Pennsylvania
U.S.A.

ASSOCIATE EDITORS

Haluk Akgun
Department of Geological Engineering
Middle East Technical University
Ankara 06531, Turkey
Email: hakgun@metu.edu.tr

Emanuel Azmon
Prof. Emeritus
Ben-Gurion University
P.O. Box 20
Omer 84965, Israel
Email: Azmon@bgumail.bgu.ac.il

Cristina Braga
Universidade Federal do Paraná
Setor de Tecnologia
Departamento de Engenharia Química
Centro Politécnico Cx.P. 19011
Curitiba - PR - 81531-990, Brasil
Email: crisbraga@avalon.sul.com.br

Shoou-Yuh Chang
Department of Civil Engineering
North Carolina A&T State University
Greensboro, NC 27411, U.S.A.
Email: chang@ncat.edu

Mervat El-Hoz
Associate Professor
Department of Civil Engineering
University of Balamand
P.O.Box 100, Tripoli, Lebanon
Email: mervat.elhoz@balamand.edu.lb

Kasturi Gadgil
Centre for Energy Studies
Indian Institute of Technology (IIT)
New Delhi - 110016, India
Email: kgadgil2k@yahoo.com

Noah I. Galil
Department Civil Engineering
Technion—Israel Institute of Technology
Haifa 32000, Israel
Email: galilno@tx.technion.ac.il

Chukwu Onu
Department of Civil Engineering
Southern University
Southern Branch Post Office
Baton Rouge, LA 70813, U.S.A.
Email: onu@engr.subr.edu

Paul Phillips
School of Environmental Science
University College Northampton
Boughton Green Road
Northampton, NN2 7AL, U.K.
Email: paul.phillips@northampton.ac.uk

Adam Read
Knowledge Leader –
Waste & Resources Management
AEA
The Gemini Building
Harwell IBC
Didcot Oxon OX11 0QR, U.K.
Email: Adam.Read@uk.aeat.com

David Smith
The Regional Municipality of Niagara
Public Works Department
Waste Management Services Division
2201 St. David's Road, P.O. Box 1042
Thorold, Ont., L2V 4T7, Canada
Email:
david.smith@regional.niagara.on.ca

EDITORIAL BOARD

Magdy Abdelrahman
North Dakota State University
U.S.A.

Steve Bloomer
University of Teesside
U.K.

Sarvesh Chandra
Indian Institute of Technology Kanpur
India

Jess Everett
Rowan University
U.S.A.

A.J. Griffins
Cardiff University
U.K.

Patrick Hettiaratchi
University of Calgary
Canada

Gennaro J. Maffia
Manhattan College
U.S.A.

Franco Medici
University of Rome "La Sapienza"
Italy

Yusuf Mehta
Rowan University
U.S.A.

Ilan Nissim
Israel Ministry of the Environment
Israel

N.C. Vasuki
Delaware Solid Waste Authority
U.S.A.

Ming-Yen Wey
National Chung Hsing University
Republic of China

Keith P Williams
Cardiff University
U.K.

Anita Závodská
Barry University
U.S.A.

THE JOURNAL OF SOLID WASTE TECHNOLOGY AND MANAGEMENT

Formerly The Journal of Resource Management and Technology (Volumes 12-22)
Formerly NCRR Bulletin (Volumes 1-11)

August 2013

Volume 39

Number 3

- 161 DISTRIBUTION AND BIOAVAILABILITY OF METALS IN GASOLINE CONTAMINATED SITES IN LAGOS, NIGERIA
Adebola A. Oketola, Abimbola A. Adebisi, Olumide Morakinyo
- 173 MOISTURE FLOW IN LANDFILL SIMULATING BIOREACTORS CONTAINING MUNICIPAL SOLID WASTE
Sapna Sethi, NC Kothiyal, Arvind K Nema
- 182 POTENTIAL OF FUNGAL-DEGRADED MAIZE COB AS FEED FOR WEST AFRICAN DWARF RAMS FED GRADED LEVELS OF FUNGAL TREATED MAIZE COB
A. Akinfemi, O. A. Ogunwole
- 190 EFFECT OF PH ON NICKEL REMOVAL BY LEMNA MINOR
Leela Kaur, Kasturi Gadgil, Satyawati Sharma
- 197 THE APPLICATION OF SOLID OLIVE WASTE AS REINFORCEMENT IN CARBOXYLATED NITRILE BUTADIENE RUBBER /ORGANO NANO LAYERED SILICATES COMPOSITES
A. Mousa, G. Heinrich, U. Wagenknecht
- 204 A FEASIBILITY STUDY OF RECYCLING OF CONSTRUCTION AND DEMOLITION WASTE FOR STRUCTURAL PURPOSES
Leila Seleme Mariano, Marienne do Rocio de Mello Maron da Costa, Maria Cristina Borba Braga

THE JOURNAL OF SOLID WASTE TECHNOLOGY AND MANAGEMENT

Formerly The Journal of Resource Management and Technology (Volumes 12-22)
Formerly NCRR Bulletin (Volumes 1-11)

August 2013

Volume 39

Number 3

214

EXPERIMENTAL STUDY ON ABRASION RESISTANCE OF CONCRETE CONTAINING SCRAP
RUBBER POWDER

Baomin Wang, Yu Han, Ni Tu, Hongmei Ai, Tingting Zhang

DISTRIBUTION AND BIOAVAILABILITY OF METALS IN GASOLINE CONTAMINATED SITES IN LAGOS, NIGERIA

Adebola A. Oketola¹, Abimbola A. Adebisi¹, Olumide Morakinyo²

¹Analytical/Environmental Laboratory, Department of Chemistry
University of Ibadan, Ibadan, NIGERIA

²Escravos Laboratory, Chevron, Warri, NIGERIA

Email: bolaoketola@yahoo.com

Phone: +234 803 7763 961

ABSTRACT

Distribution of metals in soil of two gasoline contaminated sites in Lagos were studied. Total Concentrations of twenty-five elements were investigated in composite samples collected at different depths within the sites. The elements were determined by ICP-AES after microwave assisted acid digestion of the samples. Chemical fractionation, mobility and potential bioavailability of some of the toxic and EU priority metals e.g., Pb, Cu, Cd, and Fe were evaluated in the topsoil (0-15 cm) by sequential extraction. There were great variation in the concentrations of the elements in both sites with depth. Speciation analysis showed that Pb and Cd dominated the Fe-Mn oxide fraction while the concentrations of Fe and Cu were higher in the residual fraction in site A. In site B, Pb, Cu and Cd was mainly associated with the Fe-Mn oxide fraction, while Fe was in the residual fraction. Cd has the highest mobility factors, 33.2% (site A) and 29.5% (site B), respectively. The concentrations of most of the toxic heavy metals (e.g., Pb, Zn, Cu, Cr, Cd etc.) exceed that of the control samples and heavy metal baseline values around the world. Thus, proper management of these potentially contaminated sites is imperative to prevent human health risk.

Keywords: Soil pollution, heavy metals, sequential extraction, contaminated site, mobility factor, gasoline

INTRODUCTION

Metal contamination in soils usually results from industrial activities such as mining and smelting, electroplating, gas exhaust, energy and fuel production, fertilizer and pesticide application, and municipal waste (Kabata-Pendias and Pendias, 2001; Padmavathamma and Li, 2009). Heavy metal contamination in soil can result in loss of soil functions leading to concerns about environmental

quality protection, maintenance of human health and productivity (Bermudez et al., 2010). Soil pollution can have implications in phytotoxicity at high concentrations and results in the transfer of heavy metals to human diet from crop uptake or soil ingestion by grazing livestock (Kabata-Pendias and Mukherjee, 2007; Nicholson et al., 2003). Soil can behave as a sink for heavy metals resulting from the aerial deposition of particles emitted by urban and industrial activities (Al-Khashman and Shawabkeh, 2006), vehicle

¹Corresponding Author

exhausts (Hernandez et al., 2003), agricultural practices (Franco-Uria et al., 2008) and a host of other anthropogenic sources such as accidental discharges of substances containing heavy metals. Soil pollution by metals differs from air or water pollution because heavy metals persist in soil much longer than in other compartments of the biosphere (Lasat, 2002). Exposure to high levels of these toxic metals have been linked to adverse effects on human health and wildlife. Toxic heavy metals cause DNA damage and their carcinogenic effects in animals and humans are probably caused by their mutagenic ability (Baudouin et al., 2002; Padmavathamma and Li, 2007).

Trace metal extractability from, and mobility in contaminated soils depend not only on total concentration in the soil but also on the metal speciation in the soil solution. The mobility of trace metals is controlled by the chemical forms or complexes in which they occur in the soil (Vijver et al., 2003). This is critical in assessing both their bioavailability and their potential threat to the environment (Campbell, 1995). Studies on the distribution and speciation of heavy metals in soil can provide not only information on the degree of pollution, but especially the actual environmental impact on metal bioavailability as well as their origin (Turki, 2007). Speciation is not only very useful for determining the degree of association of the metals in the sediments and to what extent they may be remobilized into the environment (Forstner et al., 1990), but also for distinguishing metals with a lithogenic origin from those with an anthropogenic origin. Metals with an anthropogenic origin are mainly obtained in the first extraction, while in the last stage of the process, the residual fraction is obtained; corresponding to metals with lithogenic origin (Izquierdo et al., 1991; Turki, 2007). The importance of pH in metal solubility is well-known as it influences heavy metal adsorption, retention and movement (Sauve et al., 2000). de Matos et al. (2001) have demonstrated that pH and Ca concentration affect Cd, Cu, Pb and Zn mobility in soils by competing on adsorbing sites. Organic matter is another important soil component that influences metal availability. It has a nutritional function by serving as a source of N, P, and S and has a high binding capacity for cations and organic contaminants (Ostel et al., 2002).

Soils in several parts of Nigeria have accumulated considerable amount of toxic elements arising largely from different activities such as exploration, illegal mining and improper hazardous waste disposal (Ogundiran and Osibanjo, 2009), industrial emission, and vehicular exhaust etc. Petroleum production is Nigeria's largest and most important industrial sector. For operational, accidental and other reasons, some quantities of petroleum products may be released into the environment during exploration, storage, processing and distribution (Adeyemi, 2004). While all these activities have generated immense financial benefits for the country, they have also resulted in serious environmental destruction through oil spillage, wilful destruction of pipelines and accidental discharges. In the last fifty years, the country has witnessed serious environmental degradation occasioned by exploration and exploitation, refining and product marketing as well as accidental discharges and

sabotage of petroleum products. All the various activities connected with oil industry are sources of emission, causing land deterioration and reducing water quality in Nigeria most especially in the Niger-Delta region.

The harmful effects of oil spills on the environment are enormous. In Nigeria coastal environment, large areas of the mangrove ecosystem and farm land have been destroyed, polluted groundwater and drawback in fishing. While crude oil primary constituents are organics such as polycyclic aromatic hydrocarbons (PAHs), they may also contain trace concentrations of metals in the range of sub-parts per billion (ppb) to tens of parts per million (ppm) (Stacy, 1994). Trace metal concentrations in crude oil spilled can enter the soil, water and can be harmful to land, marine animals and plants, upsetting delicate ecological balances and entering the food chain (Sneddon et al., 2006). Chromium, manganese, nickel and vanadium are considered to be important from a toxic point of view and likely to occur in crude oil at some concentrations (Stacy, 1994). Accidental discharges of gasoline occurred in December 2006 and May 2008, respectively at Abule-Egba and Ijegan, suburbs of Lagos, Nigeria; which resulted in pipeline explosion and fire outbreak. The objectives of this study was to assess the concentration of metals in the soils of the gasoline contaminated sites and to determine the distribution, mobility and potential bioavailability as well as the chemical forms (speciation) of some toxic and EU priority metals (Pb, Cu, Cd) and Fe.

MATERIALS AND METHODS

Description of the study area

The study areas, Abule-Egba and Ijegan (hereafter called sites A and B) are suburbs of Lagos, Nigeria which lies between the latitude $06^{\circ}52.0''N$ and longitude $02^{\circ}53.60''E$ (site A); and latitude $06^{\circ}31.2''N$ and longitude $03^{\circ}15.24''E$ (site B). On December 26, 2006 and May 16, 2008 there was an explosion and fire outbreak which occurred when an elevated pipeline carrying petroleum product (gasoline) was vandalized (Site A) and an accidental discharged at Site B (Figure 1). In both cases, the amount of product discharged into the environment were unknown.

Sampling and sample preparation

Soil samples were collected on November 2008 in the two potentially contaminated sites in Lagos. Samples were collected randomly from twenty different points at different depths (i.e., 0-15 cm, 15-30 cm, 30-45 cm, and 45-60 cm, respectively) and mixed together to form a composite sample at each point and depth. In site A, samples were collected around the pipelines, represented by LAA1- LAA4, while in site B, samples were collected around the ruptured pipelines and 100 m away from the pipelines. These were represented by LAI1- LAI4 and LAI5- LAI8, respectively. The samples were collected in polyethylene bags, labelled accordingly and

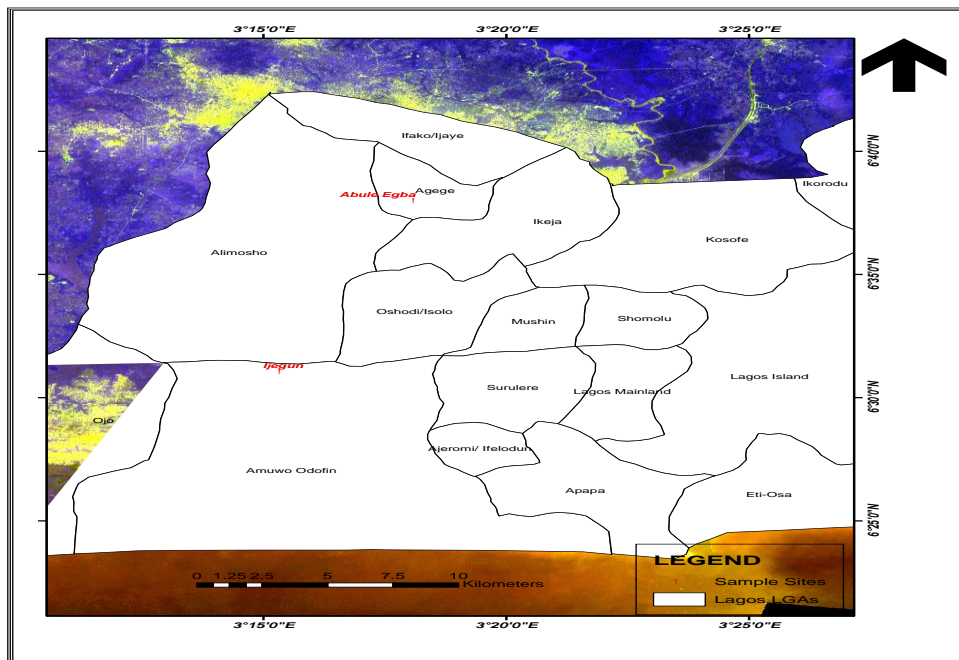


FIGURE 1
Map of Lagos showing the sampling locations

transported to the laboratory for metal analysis and general soil characteristics. The samples were air dried in the laboratory until they were properly dried and large objects (sticks, stone etc.) were removed. Samples for metal analysis were then gently ground, sieved through a 2 mm sieve and stored in air tight plastic containers until further analysis. All necessary precautions were undertaken during sampling, transportation and sample preparation to avoid cross contamination. Control samples were also collected from Lalupon, a rural village in Ibadan and the Botanical Garden, University of Ibadan.

Chemical analysis

Soil pH was measured in deionised water using a 1:1 (w/v) soil/solution and particle size distribution by hydrometer method. TOC was determined in accordance with the titration method of Walkey and Black (1934). Environmentally available metals were measured by microwave assisted acid digestion procedure (USEPA, 2007) using concentrated HNO_3 and HCl acid prior to analysis. About 0.5 g of each sample was weighed into a specially designed digestion cups made of PTFE acid resistant polymer. 9 ml of concentrated nitric acid and 3 ml of concentrated HCl were added in quick succession, and the cups were immediately capped. The digestion cups were adequately sealed by tightening the caps with the appropriate tools and the samples were arranged on the digester (Ethos Series Microwave lab station). The method program for soil digestion was set on the control software and the digestion commenced, which took about 20 minutes to complete. When

digestion was completed, the vessel was allowed to cool to room temperature and to emit all acid fumes from built up pressure. The solution was filtered into a 100 ml volumetric flask and made up to mark with distilled water.

The concentrations of Ag, Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Na, Ni, P, Pb, Se, Si, Sr, V, and Zn were analysed by Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES Thermo Scientific model number 14425501). All reagents used were of analytical grade and distilled water was used throughout. To check the analytical quality, reagent blanks and duplicate determinations were carried out since certified reference material was not available. Blank determinations were carried out and the level of the metals were below the detection limits of the instrument in all cases.

Sequential extraction for metal speciation

Selective sequential extraction was used to investigate the partitioning of some toxic and EU priority metals e.g., Fe, Cd, Cu and Pb; and to evaluate their potential mobility. This was performed on topsoil samples collected at 0-15 cm depth from both sites. The sequential extraction procedures used was modified from the scheme developed by Tessier et al., (1979). The last step was the determination of heavy metals in the residual fraction using 4 M nitric acid (Basta and Gradwohl, 2000; Yong et al., 1993). The extraction sequence is summarized as: (1) Water soluble fraction - deionised water; (2) Exchangeable fraction (readily available) – 1.0 M Mg_2Cl at pH 7; (3) Bound to carbonate - 1 M CH_3COONa adjusted to pH 5 with acetic acid; (4) Bound to Fe-Mn Oxides

- 0.04 M hydroxylamine hydrochloride (NH₂OH.HCl) in 25 % (v/v) acetic acid heated to 96±3 °C; (5) Bound to organic matter - 0.02 M HNO₃ and 30% H₂O₂ at pH 2 heated to 85±2 °C, then addition of 5 ml of 3.2 M ammonium acetate in 20 % (v/v); and (6) Residual fraction - 4 M HNO₃ heated at 80 °C . The supernatants obtained from each extraction were acidified with 0.5 ml conc. HNO₃ and stored at 4 °C until analysis with Atomic Absorption Spectrophotometer (Buck Scientific model 200A).

Statistical analysis

Data analysis was performed using SPSS 13.0 package. Correlation Coefficient was used to determine the

relationship between the metal concentrations and general soil characteristics (e.g., pH, TOC, and particle size). Comparison of total heavy metal concentrations at 0-15 cm depth with speciation data was analysed by student t-test.

RESULTS AND DISCUSSION

General soil characteristics

The general soil characteristics of the samples are presented in Tables 1 and 2, respectively. The pH ranges from 7.3-8.0 and 7.6-8.0 in Sites A and B, respectively. The soil pH in both sites were slightly alkaline, which showed

TABLE 1
Metal concentration (mg/Kg) and general soil characteristics of soil in site A (Abule-Egba)

<i>Parameters</i>	<i>LAA1 (0-15 cm)</i>	<i>LAA2 (15-30 cm)</i>	<i>LAA3 (30-45 cm)</i>	<i>LAA4 (45-60 cm)</i>
pH	8.0	7.8	7.3	7.3
% Clay	4.8	4.8	8.8	6.8
% Silt	6.0	8.0	16.0	18.0
% Sand	89.2	87.2	75.2	75.2
% TOC	0.49	0.65	2.96	2.24
Ag	1,350	1,320	1,380	1,340
Al	11,300	13,700	21,600	24,600
As	<0.04	<0.04	<0.04	<0.04
B	34.5	21.1	96.2	58.5
Ba	50.5	19.5	129	100
Ca	8,500	1,550	12,300	10,500
Cd	5.47	2.49	22.3	19.8
Co	2.68	2.11	54.2	20.4
Cr	62	99.8	77.9	125
Cu	47.1	30.9	289	130
Fe	26,300	19,100	25,400	26,600
Hg	<0.02	<0.02	<0.02	<0.02
K	338	273	662	496
Li	0.66	1.04	0.48	1.92
Mg	554	252	527	530
Mn	302	227	435	331
Na	158	100	377	289
Ni	13.0	18.4	26.3	17.3
P	278	345	373	319
Pb	235	125	285	300
Se	<0.02	<0.02	<0.02	<0.02
Si	112	85.2	47.8	95.2
Sr	35.3	11.6	26.1	29.8
V	122	152	141	262
Zn	220	93.6	364	230

TABLE 2
Metal concentration (mg/Kg) and general soil characteristics of soil in site B (Ijgun)

Parameters	Around the pipeline					> 100 m from the pipeline		
	LAI1 (0-15 cm)	LAI2 (15-30 cm)	LAI3 (30-45 cm)	LAI4 (45-60 cm)	LAI5 (0-15 cm)	LAI6 (15-30 cm)	LAI7 (30-45 cm)	LAI8 (45-60 cm)
pH	7.8	7.8	7.7	7.6	7.7	8.0	8.0	7.9
% Clay	6.8	8.8	10.8	15.8	6.8	4.8	6.8	4.8
% Silt	18.0	24.0	24.0	16.0	22.0	10.0	22.0	24.0
% Sand	75.2	67.2	65.2	68.2	71.2	85.2	71.2	71.2
% TOC	1.32	0.58	0.63	0.43	0.63	0.75	1.14	1.29
Ag	2,530	2,320	1,620	2,180	1,430	920	1,570	1,370
Al	35,400	47,800	22,300	33,600	16,000	10,000	18,200	16,500
As	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
B	48.3	34.2	21.2	47.1	12.6	10.7	13.2	19.0
Ba	89.3	25.3	29.5	31.3	18.6	17.8	22.3	22.3
Ca	7,760	1,800	3,880	1,200	1,440	1,035	1,440	2,820
Cd	5.68	2.29	1.97	3.04	0.49	<0.02	0.10	1.50
Co	48.5	30.4	1.61	2.29	31.6	30.0	31.7	<0.02
Cr	55.7	49.3	172	63.8	33.0	26.0	31.9	37.8
Cu	300	23.1	22.9	31.3	32.9	6.12	15.2	19.0
Fe	33,100	26,100	19,800	38,000	12,000	6,700	11,800	12,300
Hg	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
K	996	689	264	441	453	224	258	318
Li	<0.01	1.44	2.20	3.55	1.52	< 0.01	1.04	1.40
Mg	1,200	576	389	678	337	163	378	378
Mn	210	178	108	235	337	51.1	106	129
Na	717	601	49.4	117	516	395	29.5	821
Ni	33.1	11.2	6.36	15.5	6.60	5.47	6.26	5.53
P	739	440	190	381	362	169	222	491
Pb	656	18.5	48.8	19.8	15.0	2.76	27.7	15.5
Se	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Si	71.2	62.8	69.4	76.5	97.4	66.4	74.7	54.0
Sr	57.4	34.8	25.4	43.9	23.1	12.4	33.8	20.2
V	227	312	254	456	203	72.6	230	126
Zn	196	36.8	87.4	52.2	77.5	78.3	188	167

that humic acid content of the soil is negligible. The total organic carbon in the soil ranges from 0.43% to 2.96% in site A and 0.43% to 1.32% in site B. Variation in %TOC with depth is shown in Figure 2. The highest value of organic carbon was found in site A at depth 45-60 cm while it was at 0-15cm depth in site B. The particle grain size distribution of the topsoil (0-15 cm) composed of 89.2% sand, 6.0% silt and 4.8% clay (site A) and 75.2% sand, 18.0% silt and 6.8% clay (site B), which represent sandy texture. The high sand content of the soil suggested possible leaching of the pollutants deposited on the topsoil. However, at lower depths, the silt and clay contents of the soil will encourage retention (adsorption) of leached pollutants.

Distribution of metal concentration in soil

The concentrations of the elements (e.g., Ag, Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Na, Ni, P, Pb, Se, Si, Sr, V and Zn) determined in the soil samples from the two sites are presented in Table 1 and Table 2, respectively. There is variation in metal concentrations with depth in both sites. As, Hg and Se were below the instrument detection limits and the order of concentration of some of the toxic heavy metals in the surface soil are
 Site A: Fe > Mn > Pb > Zn > Cr > Cu > Ni > Co
 Site B: Fe > Pb > Cu > Mn > Zn > Cr > Co > Ni

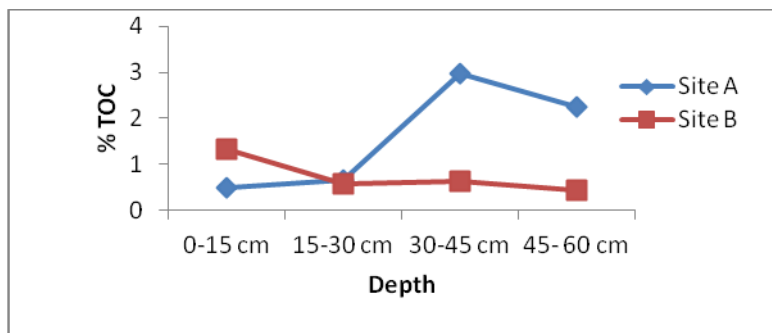


FIGURE 2
Variation %TOC with depth in site A and B

Manganese concentrations ranges from 227-435 mg/kg in site A and 51.1-337 mg/kg in site B. Methylcyclopentadienyl manganese tricarbonyl (MMT) is a fuel additives as a replacement for tetra-ethyl lead. Also, Pb and Ni are associated with gasoline (Preciado and Li, 2006). Concentrations of Mn observed in both sites are much higher than the control sample from Lalupon, a rural area in Ibadan (58.7 mg/kg). There is a significant correlation coefficient between Mn and Cu ($R^2 = 0.95$) in site A (Table 3). Lead concentration in site A and B ranges from 125-300 mg/kg and 2.76-656 mg/kg, respectively. High correlation exist between Pb and Ag in site A ($R^2 = 0.97$) while in site B, there is correlation between Pb versus Cd and Cu, ($R^2 = 0.96$ and 0.99 , respectively) (Table 4). Highest concentration of Pb was observed at 45-60 cm depth in site A and 0-15 cm depth in site B. The concentration of Pb at site B decreases as distance from the pipeline increases and also with depth. At 100 m away from the ruptured pipelines, there is no

significant correlation between all the metals except Mn and Cu ($R^2 = 0.97$). When the results obtained in this study was compared with the mean concentrations in urban soils around the world and control samples from the Botanical Garden, University of Ibadan (11.1 mg/kg) and Lalupon village (9.12 mg/kg, respectively), the values of Pb in the analysed samples from both sites were much higher than those reported for different land use areas in the world (London, Aberdeen, urban playing ground in Hong Kong and central Jordan) (Al-Khashman and Shawabkeh, 2006) and the control samples (Table 5).

The highest Ni concentration was observed at 30-45 cm and 0-15 cm with a range of 13.0-26.3 mg/kg and 5.53-33.1 mg/kg, respectively in site A and B. These concentrations were much higher than the control samples which were 6.68 mg/kg and 0.57 mg/kg, respectively (Table 5). Vanadium concentration increases with depth with highest concentration at 30-45 cm in both sites. At site B, the concentration

TABLE 3
Correlation coefficient of heavy metals in site A

	Ba	Cd	Co	Cu	Ag	Mn	Pb	Zn
Ba	1.00							
Cd	0.980*	1.00						
Co	0.911	0.873	1.00					
Cu	0.927	0.886	0.999**	1.00				
Ag	0.824	0.696	0.850	0.868	1.00			
Mn	0.954*	0.878	0.937	0.953*	0.955*	1.00		
Pb	0.799	0.664	0.741	0.768	0.974*	0.918	1.00	
Zn	0.925	0.831	0.889	0.909	0.975*	0.992**	0.960*	1.00

*Correlation is significant at the 0.01 level (2-tailed)

**Correlation is significant at the 0.05 level (2-tailed)

TABLE 4
Correlation coefficient of heavy metals in site B

	<i>Cd</i>	<i>Ba</i>	<i>Fe</i>	<i>Mn</i>	<i>Cu</i>	<i>Ni</i>	<i>Pb</i>	<i>Zn</i>
Cd	1.00							
Ba	0.972*	1.00						
Fe	0.562	0.357	1.00					
Mn	0.559	0.347	0.975*	1.00				
Cu	0.971*	0.998**	0.347	0.353	1.00			
Ni	0.995**	0.951*	0.602	0.615	0.955*	1.00		
Pb	0.955*	0.997**	0.290	0.293	0.998**	0.934	1.00	
Zn	0.882	0.965*	0.157	0.115	0.953*	0.706	0.967*	1.00

** Correlation is significant at the 0.01 level (2-tailed)

* Correlation is significant at the 0.05 level (2-tailed)

TABLE 5
Comparison of mean concentrations (mg/kg) of metals in this study with urban soils around the world and the control samples

<i>Parameters</i>	<i>London^a</i>	<i>Aberdeen^b</i>	<i>HongKong^c</i>	<i>Central^d Jordan</i>	<i>Control^e (0-15 cm)</i>	<i>Control^f (0-15 cm)</i>	<i>Site A 0-15 cm</i>	<i>Site B 0-15 cm</i>
Pb	294	94.4	93.4	62.17	11.1	9.12	235	656
Zn	183	58.5	168	146.94	29.9	ND	220	196
Cd	1	-	2.18	4.98	ND	ND	5.47	5.68
Fe	-	-	-	-	1549	2,550	26300	33100
Cu	73	27	24.8	-	3.88	4.57	47.1	300
Cr	-	23.9	-	83.93	4.32	4.83	125	55.7
Ni	-	-	-	-	6.68	0.57	13.0	33.1
Mn	-	-	-	-	-	58.7	302	210

^a Thornton (1991), ^b Paterson et al. (1996), ^c Li et al. (2001), ^d Banat et al. (2005), ^e Control sample from Botanical Garden, University of Ibadan, ^f Control sample from Lalupon, a rural area in Ibadan, ND = Not Detectable

decreases as distance from the pipeline increases with depth. Chromium concentration was lowest at 0-15 cm and increases to 30-45 cm in site A while it was lowest at 15-30 cm in site B. The concentration in both sites ranges from 62.0-125 mg/kg and 26.0-172 mg/kg, respectively which were higher than the mean concentration in urban soils from different part of the world and the control samples (Table 5). The range of Zn concentration were 93.6-364 mg/kg and 36.8-196 mg/kg, respectively. These were higher than the mean concentration in urban soils from different parts of the world and control samples (i.e., 29.9 mg/kg and below the instruments detection limit in samples from Botanical Garden and Lalupon, respectively). There is high significant correlation between

Zn versus Mn, and Pb in site A ($R^2 = 0.99$ and 0.96 , respectively). In site B, high correlation was observed between Pb versus Cu, and Cd around the ruptured pipeline ($R^2 = 0.99$ and 0.96 , respectively). Metal production (drying of zinc concentrates and roasting, smelting, and refining of ores) is the largest source of anthropogenic atmospheric cadmium emissions, followed by waste incineration and by other sources, including the production of batteries, fossil fuel combustion and generation of dust by industrial processes (Yamagata, 1970). Variation in metal concentrations as a function of depth at both sites are presented in Figures 3 and 4, respectively.

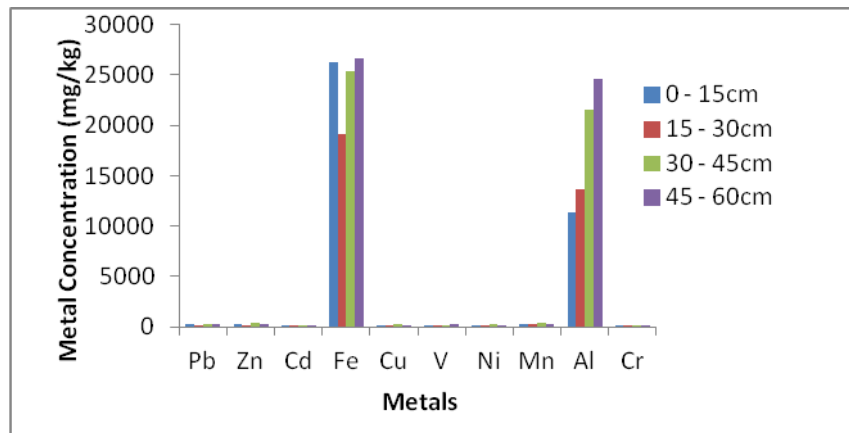


FIGURE 3
Variation in heavy metal concentrations with depth in site A

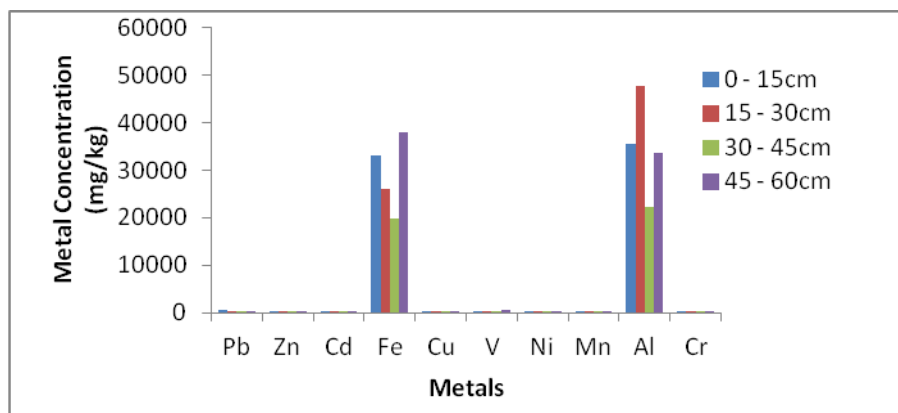


FIGURE 4
Variation in heavy metal concentrations with depth in site B

Soil sequential extraction

Partitioning results expressed on percentage basis show the effectiveness of the sequential extraction procedure in identifying possible anthropogenic inputs of metals. The sequential extraction procedure assumes that the residual fraction corresponds to metals tightly bound to the crystal lattice of primary or secondary minerals and therefore environmentally unavailable (Tiessier et al., 1979; Preciado and Li, 2006). The sum of the fractions with the exception of residual is termed non-residual (Hickey and Kittrick, 1984). Metals in the non-residual fractions are assumed to be more available than metals associated with the residual. The association between heavy metals and soil components increases from water soluble to residual, thus making the water soluble and the exchangeable fractions the most soluble and mobile forms (Ogundiran and Osibanjo, 2009). Soil partitioning result showed a consistent distribution of metals with Fe and Cu dominating the residual fraction while Cd and Pb are mostly attached to Fe-Mn oxide in site A. In site B, Fe was largely associated with residual fraction while Cu, Cd

and Pb dominated the Fe-Mn oxide fraction. Associations of Pb with Fe-Mn oxide fraction in both sites can be attributed to high affinity of Pb to sorb to Fe-Mn oxide in soil and also to the formation of stable complex (Ramos et al., 1994). The rank of bioavailability based on the water soluble + exchangeable metal fractions are:

Site A: Fe > Pb > Cd > Cu; and Site B: Fe > Pb > Cu > Cd

The sum of water soluble and exchangeable metal fractions is generally used to indicate bioavailable metals and equally the forms that can leach into groundwater (Ogundiran and Osibanjo, 2009). The concentrations of Pb, Cu, and Cd in the non-residual form was higher than the residual fraction in both sites except Cu in site B, which showed higher concentration in the residual form. Thus, these metals are mostly from anthropogenic origin and have the tendency to leach into groundwater as well as available to plants, bioaccumulate and gets to human and other animals through the food chain. The % metals (exchangeable + water soluble) forms in both sites are 1.07 % and 1.14 %, respectively. These indicated that the metals in site B are readily available

than that in site A. The % metal fractions is shown in Figures 5 and 6.

Metal mobility factor

Mobility factor describes the potential movement of metals out of the contaminating medium (Kabala and Singh, 2001). It can be calculated as

$$MMF = \frac{F_1 + F_2 + F_3}{F_1 + F_2 + F_3 + F_4 + F_5 + F_6}$$

Where, MMF = metal mobility factor; F = concentration of metal in different fractions

The result of the mobility factor is presented in Table 6. The potential of a metal to become mobile in the environment and to be bioavailable has been connected with high percentage of MMF. The mobility factors of Cd, Cu and Pb revealed that when the metals are present in soil as metals of anthropogenic origin, they have high potentials to be mobile

and consequently bioavailable. Fe which showed significant high total metal concentration indicated the least mobility factor in both sites while Cd with low concentrations (Tables 1 and 2) have the highest mobility factor. The relative high mobility factors of Pb, Cd and Cu can pose potential hazards to the ecosystem.

Statistical analysis and data treatment

Student t-Test (2-tailed) of the results obtained from direct analysis using ICP-AES for total metal and speciation analysis using AAS (Table 7) showed that there is no significant difference between them at 95% confidence interval.

CONCLUSION

The distribution of heavy metals in the soils of the study

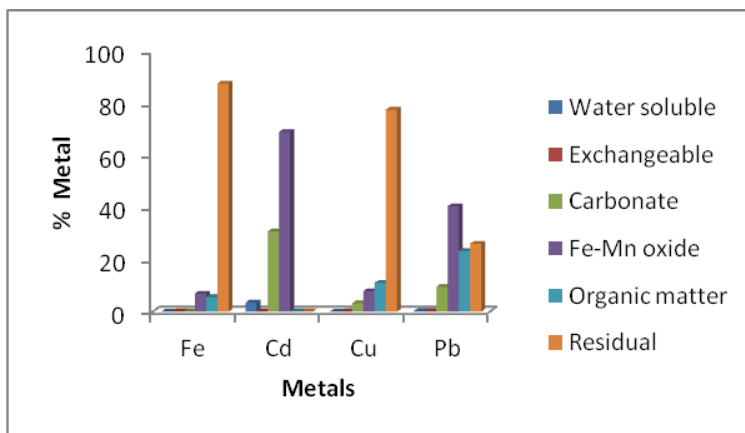


FIGURE 5
% Metal in soil fraction in site A

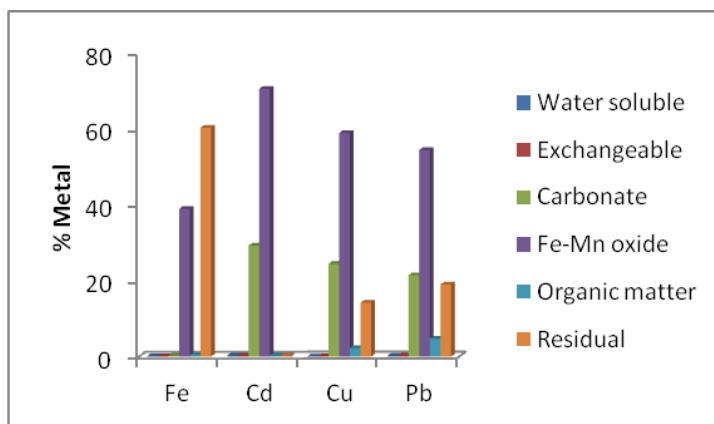


FIGURE 6
% Metal in soil fraction in site B

TABLE 6
Mobility factors of metals in Sites A and B

<i>Location</i>	<i>Fe (%)</i>	<i>Cd (%)</i>	<i>Cu (%)</i>	<i>Pb (%)</i>
A	0.21	33.2	3.34	10.0
B	0.39	29.5	24.5	21.8

TABLE 7
Student t-Test of heavy metals from direct and speciation analysis

0 – 15cm (site A)			0 – 15cm (site B)		
<i>Heavy metals</i>	<i>Direct analysis</i>	<i>Speciation</i>	<i>Heavy metals</i>	<i>Direct analysis</i>	<i>Speciation</i>
Fe	26300	17800	Fe	33100	13600
Cd	5.47	5.79	Cd	5.68	4.03
Cu	47.1	187	Cu	300	398
Pb	235.42	233	Pb	656	475
	<i>Direct analysis</i>	<i>Speciation</i>		<i>Direct analysis</i>	<i>Speciation</i>
Mean	6646.9975	4556.4475	Mean	8515.42	3619.2575
Variance	171672455.9	77961478.7	Variance	268693619.1	44315981.95
Observations	4	4	Observations	4	4
Pearson Correlation	0.9999749		Pearson Correlation	0.999846148	
Hypothesized Mean Difference	0		Hypothesized Mean Difference	0	
Df	3		Df	3	
t Stat	0.978382182		t Stat	1.005725726	
P(T<=t) one-tail	0.200019038		P(T<=t) one-tail	0.194320711	
t Critical one-tail	2.353363435		t Critical one-tail	2.353363435	
P(T<=t) two-tail	0.400038077		P(T<=t) two-tail	0.388641421	
t Critical two-tail	3.182446305		t Critical two-tail	3.182446305	

areas showed that the areas have been affected by anthropogenic activity, particularly from the discharge of gasoline which resulted in fire outbreak that destroyed different structures (such as vehicles, building etc.) in the areas. These have resulted in the accumulation of heavy metals in the areas compared with the natural background levels around the world and the control samples. Generally, there is no regular trend in the concentration of the metals as a function of depths, the distribution of the metals showed high concentration close to the ruptured pipelines. The speciation study showed that the level of the heavy metals in

the non-residual forms can be potential sources of soluble, mobile and available forms of the metals thereby posing potential risks to human, animals and the environment. Metals in site B have higher mobility than in site A except Cd in site A where the reverse is the case. With regards to health risks, bioavailability and mobility of metals can be stated to be of major significance in the soil. Hence, there is need to reduce the introduction of heavy metals into the environment from anthropogenic sources since metals are persistent, toxic and non- biodegradable.

REFERENCES

- Adeyemi, O.T. (2004). "Oil exploration and environmental degradation: the Nigerian experience." *Environmental Informative Archives*, Volume 2, pp. 387-393.
- Al-Khashman, O.A., and R. Shawabkeh, (2006). "Metals distribution in soils around the cement factory in Southern Jordan." *Environ. Pollut*, Volume 140, pp. 387-394
- Banat, K.M., F.M. Howari, A.A. Al-Hamad, (2005). "Heavy metals in urban soils of central Jordan: should we worry about their environmental risks." *Environmental Research*, Volume 97, pp. 258 -273.
- Basta, N.T, and R. Gradwohl, (2000). "Estimation of cadmium, lead and zinc bioavailability in smelter contaminated soils by a sequential extraction procedure." *Journal of Soil Contamination*, Volume 9(2), pp. 149-164.
- Baudouin, C., M. Charveron, R. Tarrouse, and Y. Gall, (2002). "Environmental pollutants and skin cancer." *Cell Biology and Toxicology*, Volume 18, pp. 341-348.
- Bermudez, G.M.A., M. Moreno, R. Invernizzi, R. Pla, and M.L. Pignata, (2010). "Heavy metal pollution in topsoil near a cement plant: the role of organic matter and distance to the source to predict total and HCl extracted heavy metal concentrations." *Chemosphere*, Volume 78, pp. 375-381.
- Campbell, P.G.C., 1995. Interactions between trace metals and aquatic organisms: A critique of the free-ion activity model. In: Tessier, A., Turner, D.R. (Eds.), *Metal Speciation and Bioavailability in Aquatic Systems*. John Wiley and Sons, Chichester.
- de Matos, A.T., M.D.F. Fontes, L.M. da Costa, and M.A. Martinez, (2001). "Mobility of heavy metals as related to soil chemicals and mineralogical characteristics of Brazilian soils." *Environ. Pollut*, Volume 111, pp. 429-435.
- Forstner, U., W. Ahlf, W. Calmano, M. Kersten, and J. Schoer, (1990). Assessment of metal mobility in sludges and solid wastes, In , J.A.C. Broeckaert, S. Gucer and F. Adams. Seies (Eds.), *Metal speciation in the environment*, (pp. 106), Berlin: Springer,.
- Franco-Uria, A., C. Lopez-mateco, E. Roca, and M.L. Fernandez-Marco, (2008). "Source identification of heavy metals in pasturelands by multivariate analysis in NW. Spain." *J. Hazar. Mater*. Volume 165, pp. 1008-1015.
- Hernandez, L., A. Probst, J.L. Probst, and E. Ulrich, (2003). "Heavy metal distribution in some French forest soils: evidence for atmospheric contamination." *Sci. Total Environ*. Volume 312, pp. 195-219.
- Hickey, M.G. and J.A. Kittrick, (1984). "Chemical partitioning of cadmium, copper, nickel, and zinc in soils and sediments containing high levels of heavy metals." *J. Environ. Qual.*, Volume 13, pp. 372-376.
- Izquierdo, C., J. Usero, and I. Gracia, (1997). "Speciation of heavy metals in sediments from salt marshes on the Southern Atlantic coast of Spain." *Marine Pollut. Bull.*, Volume 34, pp. 123-128.
- Kabala, C. and B.R. Singh, (2001) "Fractionation and mobility of copper, lead, and zinc in soil profiles in the vicinity of a copper smelter." *J. Environ. Qual.*, Volume 30, pp. 485 -492.
- Kabata-Pendias, A., and A.B. Mukherjee, (2007). *Trace elements from soil to human*. Berlin: Springer-verlag.
- Kabata-Pendias, A. and H. Pendias, 2001. *Trace Elements in Soils and Plants*. Boca Raton, CRC Press.
- Lasat, M.M. (2002). Phytoextraction of toxic metals – A review of biological mechanisms. *J. Environ. Qual.* Volume 3, pp. 109-120.
- Li, X.D., C.S. Poon, S.L. Pui, (2001). "Heavy metal contamination of urban soils and street dusts in Hong Kong." *Applied Geochemistry*, Volume 16, pp. 1361-1368.
- Nicholson, F.A., S.R. Smith, B.J. Alloway, C. Carlton-Smith, and B.J. Chambers, (2003). "An inventory of heavy metals inputs to agricultural soils in England and Wales." *Sci. Total Environ*, Volume 311, pp. 205-219.
- Ogundiran, M.B. and O. Osibanjo, (2009). "Mobility and speciation of heavy metals in soils impacted by hazardous waste." *Chemical Speciation and Bioavailability*, Volume 21(2), pp. 59-69.
- Ostel, L.A., E.J.M. Temminghoff, and van W.H. Riemsdijk, (2002). "Solid-solution partitioning of organic matter in soils as influenced by an increase in pH or Ca concentration." *Environ. Sci. Technol*, Volume 36, pp. 208-214.
- Padmavathamma, P.K. and L.Y. Li, (2007). "Phytoremediation technology: hyper-accumulation metals in plants." *Water Air Soil Pollut*, Volume 184, pp. 105-126.
- Paterson, E., M. Sanka, L. Clark, (1996). "Urban soils as pollutant sinks – a case study from Aberdeen, Scotland." *Applied Geochemistry*, Volume 11, pp. 129-131.
- Preciado, H.F and Y. Li, (2006). "Evaluation of metal loadings and bioavailability in air, water and soil along two highways of British Columbia," *Canada. Water, Air, and Soil Pollution*, Volume 172, pp. 81-108.
- Ramos, I. L.M. Hernandez, and M.J. Gonzalez, (1994). "Sequential fractionation of copper, lead, cadmium and zinc in soils from or near Donnal Park." *J. Environ. Qual.* Volume 23, pp. 20-57.
- Sauve, S., W. Hendershot, and H.E. Allen, (2000). "Solid-solution partitioning of metals in contaminated soils dependence on pH, total metal burden, and organic matter." *Environ. Sci. Technol*, Volume 34, pp. 1125-1131.
- Sneddon, J., C. Hardaway, K.K. Bobbadi, and J.N. Beck, (2006). "A study of a crude oil spill site for selected metal concentrations remediated by a controlled burning in Southwest Louisiana." *Microchemical Journal*, Volume 82, pp. 8-16.
- Stacy, G. III. (1994). *Symposium Proceedings; Gulf of Mexico and Caribbean oil spills in coastal ecosystems; assessing effects, natural recovery, and progress in remediation research, in-situ burns as an oil response technique*. pp. 191-194.

- Tessier, A., P.G.C. Campbell, and M. Benon, (1979). "Sequential extraction procedure for the speciation of particulate trace metals." *Analytical Chemistry*, Volume 51, pp. 844- 851.
- Thornton, I. (1991). "Metal contamination of soils in urban area. In: Bullock, P., Gregory, P.J. (Eds.)," *Soil in the Urban Environment*. Blackwell, pp. 47-75.
- Turki, A.J. (2007). "Metal speciation (Cd, Cu, Pb and Zn) in sediments from Al-Shabab Lagoon, Jeddah, Saudi Arabia". *Mar. Sci*, Volume 18, pp. 191-210.
- USEPA (2007). Method 3051A, Microwave assisted acid digestion of sediments, sludges, soils and oils. Washington, DC.
- Vijver, M., T. Jager, L. Posthuma, W. Peijnenburg, 2003. "Metal uptake from soils and soil-sediment mixtures by larvae of *Tenebrio molitor* (L.) (Coleoptera)." *Ecotoxicology and Environmental Safety*, Volume 54, pp. 277-289.
- Walkey, A. and I.A. Black, (1934). "Methods of soil analysis." *Soil Science*, Volume 37, p. 29.
- Yamagata, N. (1970). "Cadmium pollution in perspective. In: Koshu Eisein Kenkyi Hokoku," *Institute of Public Health, Tokyo*, Volume 19, pp. 1-27.
- Yong, R.N, R. Galvez-Cloutier, Y. Phadungchewit, (1993). "Selective sequential extraction analysis of heavy metal retention in soil." *Canadian Geotechnical Journal*, Volume 30, pp. 834-847.

MOISTURE FLOW IN LANDFILL SIMULATING BIOREACTORS CONTAINING MUNICIPAL SOLID WASTE

Sapna Sethi^{1*}, NC Kothiyal², Arvind K Nema³

¹Research Scholar, Department of Chemistry
Dr. B. R. Ambedkar National Institute of Technology, Jalandhar-144008, INDIA
Email: sethisapna@yahoo.co.in

²Professor, Department of Chemistry
Dr. B. R. Ambedkar National Institute of Technology, Jalandhar, INDIA

³Associate Professor, Department of Civil Engineering
Indian Institute of Technology, New Delhi, INDIA

ABSTRACT

Heterogeneous nature of municipal solid waste creates complex hydraulic conditions in landfills and leads to non-uniform moisture flow through the waste. Maintenance of uniform moisture in landfills is prerequisite for success of bioreactor technology. The present study focuses on moisture flow conditions in landfill simulating bioreactors containing municipal solid waste and organic solid waste. The organic solid waste was selected with an aim to observe the effects of minimization of heterogeneity of waste on moisture movement. The moisture flow through waste samples was studied with the help of tracer tests. The positively skewed tracer distribution confirmed short circuiting or channelization of moisture flow through both types of waste samples. However, the extent of channelization was found to be less in organic solid waste as compared to municipal solid waste. The hydraulic retention time for pure organic waste was found to be higher due to its lesser heterogeneity and channelization as compared to municipal solid waste. The values of field capacity and wet moisture content indicated that both types of waste samples would require absorbing additional liquids to reach their field capacities for optimum degradation in bioreactor landfills. But the additional liquid requirement would always be higher for municipal solid waste as compared to organic solid waste.

Keywords: Municipal solid waste; organic solid waste; moisture flow; channelized flow; hydraulic retention time

INTRODUCTION

Moisture is considered as one of the most critical parameter affecting biodegradation of municipal solid waste (MSW)

in landfills [1]. Municipal solid waste is a highly heterogeneous and complex mixture of organic and inorganic fractions. Heterogeneous nature of MSW leads to non-uniform moisture flow in the landfills. The channeled flow through solid waste has been considered as a major leachate or moisture

* Correspondence author

movement mechanism in landfills [See 2-10]. The channelized flow results in limited participation of total waste mass taking part in water movement [11]. Therefore, it creates a major hurdle in uniform saturation and biodegradation of waste in landfills which are designed to operate as bioreactors.

Time taken by water while percolating through a landfill is estimated as mean residence time (water holding time) or hydraulic retention time (HRT). Leachate routing and mean residence time in landfills is dependent upon many factors including the nature of waste, its particle size and compaction density [12]. Tracer tests have been successfully used in several investigations to follow the hydraulic path and also to calculate mean residence time in landfills [See 7, 9-15]. Tracer travel time distributions are derived from breakthrough curves (BTCs).

The present study describes laboratory investigations of moisture flow in landfill simulating reactors containing municipal solid waste and organic solid waste (OSW). Solute transport in laboratory scale reactors containing two types of wastes was considered and compared by means of breakthrough curves obtained by conducting tracer tests. The objective of this investigation is to compare moisture transport in MSW and OSW loaded in the reactors. The organic solid waste contributes as a major fraction of MSW in developing countries. The aim to select OSW for this study is to observe the effects of minimization of heterogeneity of waste on moisture movement.

MATERIALS AND METHODS

Solid waste material

Fresh solid waste samples were collected from the Wariana dump site located at Jalandhar in Punjab, India. The city observes brief south-west monsoon season with average annual rainfall of about 700 mm which is spread over 35 rainy days. Samples were prepared by mixing municipal solid waste collected from different areas of the city. Sample selection was done by coning and quartering method in respect to ASTM D 6323-98 [16]. Two types of waste samples were used for the present study. The shredded MSW samples consisted of compostable material, paper, plastic, rags etc. and the OSW samples contained fruit, vegetable and yard waste (Table 1).

Components of OSW were collected and separated manually at the dump site. The size reduction of waste materials approximately to particle size (d_p) of 1.5cm was achieved using knives and scissors so that moisture content of waste was not affected. After shredding, the fresh waste samples were immediately stored in black polybags and transferred to laboratory where these were refrigerated at 4°C before loading them into the respective reactors. Initial moisture contents of wet waste samples were determined using ASTM standard test method E790. The specific gravity of both the samples was determined in accordance with ASTM D 854. The coefficient of permeability of solid waste samples was determined

TABLE 1
Composition of MSW and OSW

<i>Waste type</i>	<i>Waste Fraction</i>	<i>Percentage</i>
MSW→	Fruits and Vegetables	35
	Plastic	9
	Paper	6
	Rubber	0.5
	Rags	8.5
	Yard waste	12
	Inerts	29
OSW→	Fruits and Vegetables	96
	Yard waste	4

by using constant head method (ASTM D 2434-68). It was reported in cm/sec at 27°C.

Landfill simulating reactors

Experiments were conducted using three symmetrical cylindrical reactors made of plexiglass with diameter (D) of 17cm and height of 60cm (Figure 1). Each reactor had a metallic lid connected to overhead funnel of one litre capacity with a flow regulator to control flow of liquid inside the container. A water distribution system in the form of circular shower having pores was installed just below the lid of reactor to add liquid in the form of spray to waste. Leachate was collected through the collection port installed at the bottom of reactor with a stopper.

Preferential sidewall flow may occur in small-scale reac-

tor systems, due to variation in behaviour at the mixture/wall interface. The effect depends on the ratio of container diameter to particle diameter. Preferential sidewall flow could be assumed negligible in the reactors with diameter/particle diameter (D/d_p) ratio greater than 10 [17]. Here in the study, the reactor's diameter was 17cm and the particle size was reduced to 1.5cm. In actual waste disposal facilities, the diameter of a landfill is quite large. Though shredding may be helpful in enhancing waste decomposition, but the size reduction up 1.5cm is not required in actual landfills.

Filling of reactors

A 7cm thick layer of gravel, consisting of 2.0cm sized gravel pieces was placed at the bottom of each reactor for leachate drainage. Two nylon screens of 1mm diameter were

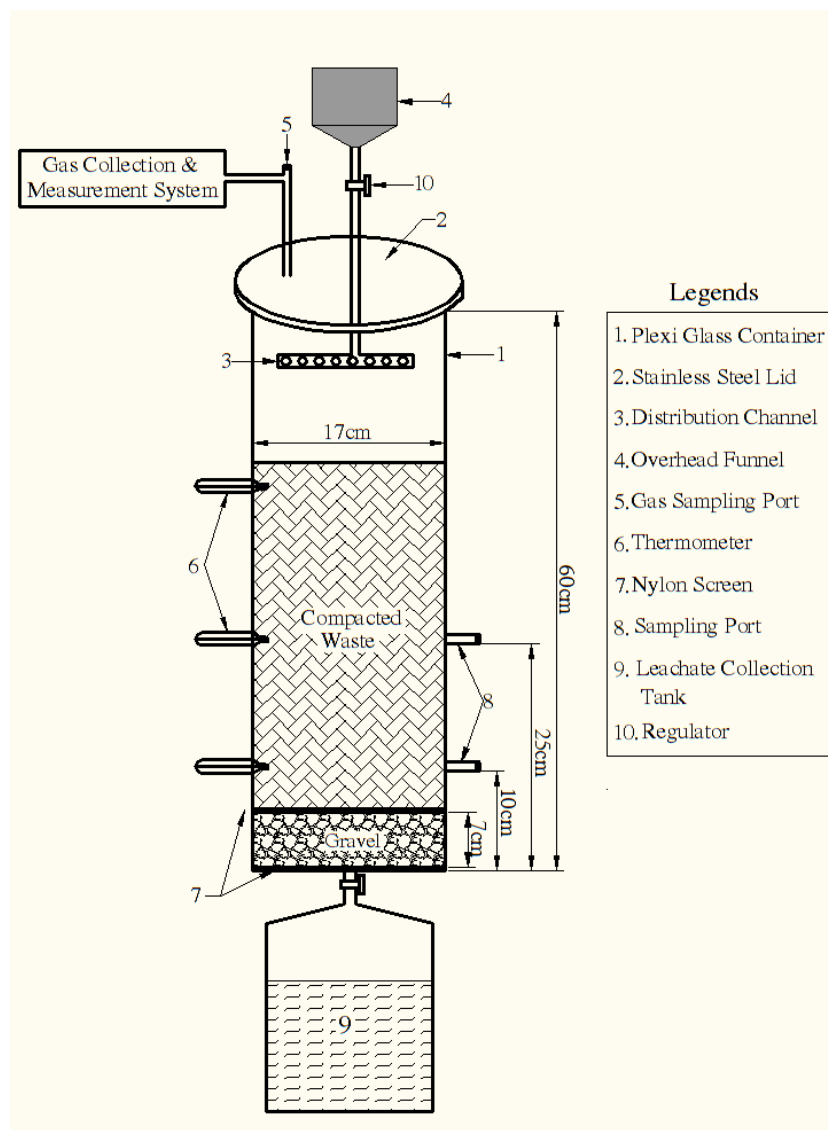


FIGURE 1
Landfill simulating bioreactor

placed above and below the drainage layer to retain solid waste and stop particles from leaching out. Waste samples of 7.0kg were compacted manually in the reactors in 40cm layers to the bulk densities of 771kg/m³. Initially all the three reactors were filled with MSW. After conducting first set of tracer experiments with MSW, the reactors were filled with OSW of the composition mentioned in Table 1 and another set of tracer experiments was performed.

Field capacity or volumetric moisture content (θ)

Field capacity which essentially means the amount of water which waste can store against the force of gravity before it drains was measured in both waste samples by conducting a separate experiment. Field capacity is a function of the waste composition, age, density and porosity. The optimum degradation of refuse takes place in a bioreactor landfill only when the waste is held at its field capacity [1].

Initial moisture contents of samples were determined using ASTM standard test method E790. Undisturbed samples (7.0kg) of 17cm in diameter and 40cm in height in reactors were first saturated with water and then left to drain until the drainage ceased. Field capacity was determined using the equation (1) mentioned in [18].

$$\Delta F_{SW} = W_{SW} + W_A - W_L \quad (1)$$

Where ΔF_{SW} = solid waste field capacity, W_{SW} = initial moisture content of the refuse, W_A = added water, W_L = percolated water.

Field capacity determination of MSW and OSW was carried out in duplicate and an average value of field capacity was reported for each waste sample.

Hydraulic retention time

Theoretical Hydraulic retention time (HRT) of a landfill was calculated by the equation (2) given in [12].

For an unsaturated landfill

$$HRT = S/Q \quad (2)$$

Where S = Volumetric water holding capacity of the waste or field capacity (θ) x Volume of waste sample in the landfill; Q = Flow rate through the landfill.

Average flow rate of water through the waste in a reactor was determined by measuring flow of collected leachate (out-flow) while conducting tracer tests under saturated conditions. Average flow rate of leachate was measured as 0.20 L/min for MSW as well as OSW reactors. Volume of waste sample was 9.08 L in each reactor.

The (actual) mean retention time and variance of tracer curves was calculated using equations (3) and (4) as given below.

$$t_{\Delta c} = \frac{\sum t_i c_i \Delta t_i}{\sum c_i \Delta t_i} \quad (3)$$

$$\sigma_{\Delta c}^2 = \frac{\sum t_i^2 c_i \Delta t_i}{\sum c_i \Delta t_i} - t_{\Delta c}^2 \quad (4)$$

Where $t_{\Delta c}$ = Mean retention time; t_i = i^{th} time the concentration of tracer measured;

c_i = Concentration of tracer at t_i ; σ^2 = Variance.

Tracer tests

Tracer study was conducted to determine the flow conditions within simulated landfill bioreactors using a non-reactive chemical called tracer whose mobility was exclusively determined by flow of water and it was completely soluble in water. For each waste sample, three different types of experiments were performed: firstly by the addition of water to reactor without tracer application with the sole purpose to determine background mass of sodium chloride in waste samples, i.e. Experiments 1 and 4; secondly, the tracer application without prior flushing of reactors to get an idea about total mass of sodium chloride (sum of background mass and the mass applied to reactor by pulse application of tracer), i.e. Experiments 2 and 5; and lastly by flushing of reactors with water followed by tracer application to determine mass of tracer recovered after flushing i.e. Experiments 3 and 6 (Table 2). For experiments 3 and 6, the reactors were flushed with water to establish steady state flow in reactors. The other purpose was to flush out background concentration of sodium chloride from the waste. Flushing decreased sodium chloride concentration in background to less than 5% of the concentration introduced in reactor in the form of tracer afterward.

For this study, sodium chloride was used as tracer. 11g of NaCl was dissolved in 0.20 L of water and applied as tracer to waste samples in reactors. The concentration of NaCl required for the present tracer study was calculated on the basis of tracer concentration used in [14]. Pulse of NaCl was applied at the flow rate of 0.2 L/min. The flow rate was decided based on the annual precipitation data for Jalandhar city. The mean rainfall and mean rainy days in the city along with cross sectional area of reactor were utilized to calculate the flow rate [19].

After the pulse application, water was applied at the same rate till electrical conductivity of leachate became same as it was before applying the tracer on to the refuse. Leachate samples were collected at regular intervals. Chloride concentrations in leachate samples were determined by argentometric titration method [20]. Breakthrough curves were plotted for concentrations of tracer in leachate samples versus time.

RESULTS AND DISCUSSION

The average values of initial moisture content were de-

TABLE 2
Methodologies of different experiments

<i>S.No.</i>	<i>Method</i>
Experiment 1(MSW),4(OSW)	Double distilled water (12 L) was added to MSW/OSW at the rate of 0.20 L/min for 60 min. Leachate samples were collected at regular intervals.
Experiment 2 (MSW),5(OSW)	Tracer was applied to MSW/OSW at the rate of 0.20 L/min, followed by the addition of 6 L of water for 30 min. Leachate samples were collected at regular intervals.
Experiment 3(MSW),6(OSW)	Water was sprinkled to MSW/OSW at the rate of 0.20 L/min till the background concentration of sodium chloride in waste decreases to 5% of the total concentration of tracer applied in the reactor. Continuous flow of water created steady state flow conditions inside the reactor and steady discharge rate was attained. After that, tracer was applied at the rate of 0.20 L/minute. It was followed by the addition of 6 L of water for 30 min for MSW and 8 L of water for 40 min for OSW. Leachate samples were collected at regular intervals.

terminated as 30% and 59% for wet samples of MSW and OSW, respectively. The specific gravity of 1.03 ± 0.055 was determined for MSW and 0.85 ± 0.154 for OSW. The coefficient of permeability was found between $3.9-4.5 \times 10^{-3}$ cm/s and $1.0-1.3 \times 10^{-2}$ cm/s for MSW and OSW, respectively.

Field capacity

The value of field capacity was calculated to be 0.45(v/v) and 0.65(v/v) for MSW and OSW, respectively, using the methodology enumerated in materials and methods section. Field capacity of MSW in the present study was found to be in the same range as reported in the previous literature [13]. Higher moisture retention capacity of organic solid waste as indicated by its higher field capacity would help it to degrade at a faster rate in an anaerobic bioreactor. The moisture contents of both MSW and OSW were found to be below their field capacity values. The difference between moisture content and field capacity was found to be higher for MSW as compared to OSW. The moisture content of 40-70% is required to optimize decomposition of waste and for enhancing bioreactor effectiveness [1]. Therefore, the addition of liquids to municipal solid waste would be necessary to meet the desired moisture content for optimal decomposition and the additional liquid requirement would always be higher for MSW as compared to OSW in a bioreactor landfill.

Field capacity decreases with age due to the degradation of organic fractions that contributes to most of the absorption capacity of waste. In the present study effect of changing field capacity has not been studied. Higher field capacity helps in retaining moisture which further helps in degradation of organic components of the waste. It is to be noted that in case of older waste disposal facilities, most fraction of the organics would be already in degraded state; hence the role of moisture is limited.

Hydraulic retention time

The theoretical values of HRT for MSW and OSW reactors were found to be 15.5 min and 19.7 min, respectively. Actual hydraulic retention time of MSW and OSW were found to be 11.1 min and 13.4 min, respectively. Actual retention times for both types of wastes were less than what was predicted theoretically by the Equation (2). The lesser value of actual solute travel time was due to short-circuiting of moisture. To achieve effective recirculation rates in bioreactor landfill, the required hydraulic retention time has to be achieved successfully. Otherwise lower moisture retention time could affect the methanogens growth and multiplication and hence stabilization of the waste in a landfill. The required HRT could be attained by reducing or breaking the channeling effect. In comparison to MSW, the hydraulic retention time was found to be higher for OSW. Better permeability and moisture retention capacity of organic fraction resulted in higher retention time for OSW. A nonzero value of variance i.e. 48.7 min^2 for MSW and 44.2 min^2 for OSW again indicated dispersion/diffusion along the path of fluid in the reactor.

Tracer tests

The first and fourth experiments with MSW and OSW were performed simply by flushing them with water without the application of tracer in the reactors. The objective of this experiment was to get an idea of background mass of sodium chloride in waste samples. Concentration of sodium chloride in g/L in the collected leachate samples versus time was plotted as shown in (Figures 2 and 3) for MSW and OSW, respectively. The concentration of sodium chloride in the leachate samples was found to be decreasing with time for both types of wastes. The area under the solute concentration time curve (AUC) was calculated for plots 2 and 3 using the trapezoidal rule. The area under curve represented 23.16

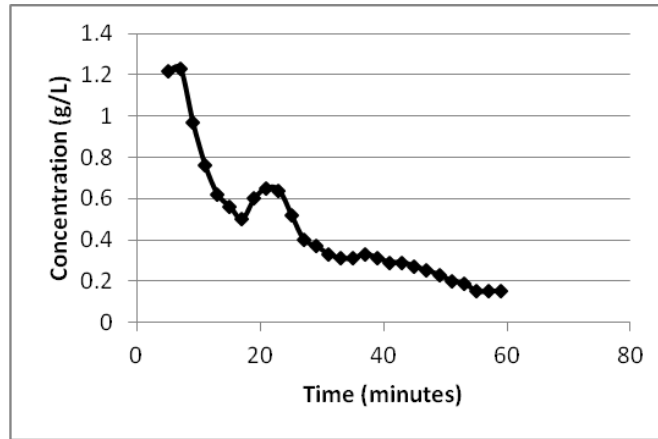


FIGURE 2
Concentration vs. time plot for experiment 1 with MSW

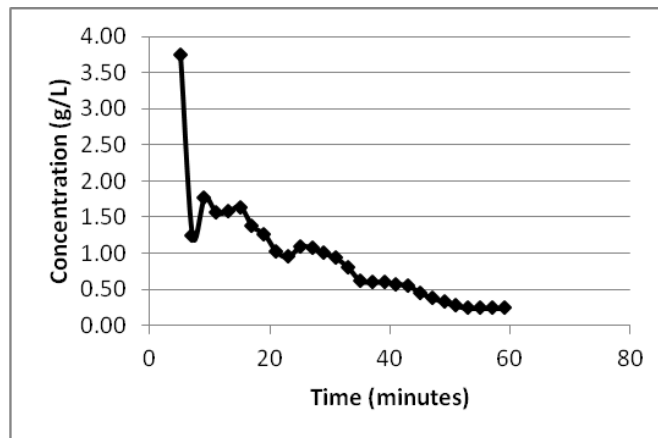


FIGURE 3
Concentration vs. time plot for experiment 4 with OSW

g.min/L of sodium chloride for MSW and 45.35 g.min/L of sodium chloride for OSW. In order to estimate the total mass of solute recovered in the leachate samples, the solute concentration in g.min/L was multiplied with average flow rate (L/min) of leachate. The higher mass of solute was recovered for OSW (9.07 g) as compared to MSW (4.63 g). The presence of higher background concentration of sodium chloride in OSW in comparison to MSW could be a reason for its additional mass recovery in leachate samples.

The second and fifth experiments with MSW and OSW were carried out by adding tracer to the refuse in order to determine the total mass of sodium chloride in the reactors. The total sodium chloride must be the sum of background mass of sodium chloride in the waste and mass introduced in the reactor by the application of tracer pulse. The measured sodium chloride concentrations in the collected leachate samples were plotted against time both for MSW and OSW (Figures 4 and 5). It can be seen from these plots that concentration of sodium chloride gradually decreased in both cases after attaining a peak. AUC for plots 4 and 5 were calculated

as 91.0 g.min/L and 115.24 g.min/L for MSW and OSW, respectively. The total solute mass recovered in leachate samples was calculated as 18.2 g for MSW and 23.05 g for OSW. Although same tracer mass was introduced in both reactors, but higher mass of the recovered solute in OSW leachate samples at this point was again due to its higher background concentration of sodium chloride as compared to MSW.

The third and sixth experiments with MSW and OSW were conducted to determine mass of tracer recovered after flushing the reactors, which was applied by the pulse application. Tracer concentration versus time curves (BTCs) were plotted for both types of wastes (Figures 6 and 7). Areas under curves for these breakthrough curves were calculated as 56.07 g.min/L for MSW and 89.08 g.min/L for OSW. The total tracer mass recovered in leachate samples was 11.0 g for MSW and 17.8 g for OSW. Initially a pulse of 11.0 g was applied as tracer for conducting these experiments. But the results indicated the recovery of higher mass of tracer from OSW reactor. The contribution of background mass of sodi-

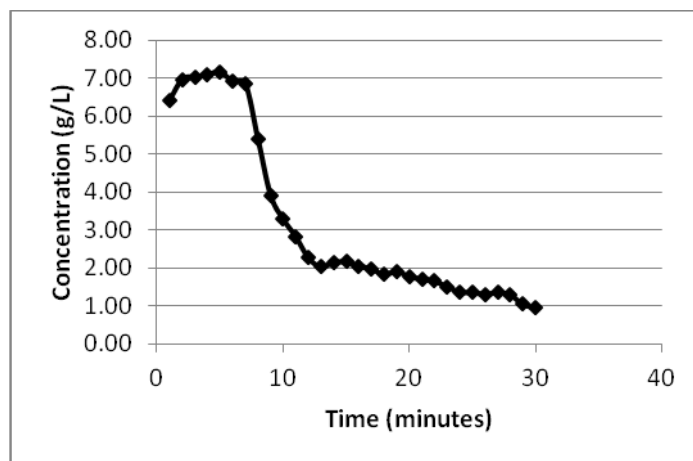


FIGURE 4
Concentration vs. time plot for experiment 2 with MSW

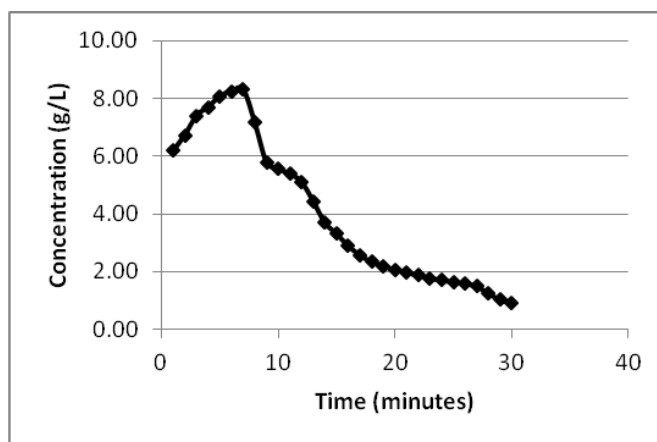


FIGURE 5
Concentration vs. time plot for experiment 5 with OSW

um chloride in refuse to the retrieved tracer could be the reason for higher tracer mass recovery. It seems that flushing of waste prior to the tracer study could not remove the entire sodium chloride from different pockets of OSW reactor.

Break through curves (BTCs) as shown in Figures 6 and 7 are positively skewed. While the peak in the initial part of curve suggested the preferential flow of moisture through domains with more mobile water whereas the tail of the curve revealed slow and sluggish flow through domains of less mobile water in the waste [11]. Earlier part of the peak pointed out the real hydraulics of reactor and confirmed the channelized flow through heterogeneous waste in reactors.

Maximum concentration of tracer in leachate sample for MSW reactor and in OSW reactor was observed at 9 minutes and 15 minutes, respectively. It was observed that the extent of skewness of measured tracer concentration distributions was greater for MSW in contrast to OSW. The calculated values of skewness of concentration distributions were 0.85

for MSW and 0.13 for OSW. Lesser degree of skewness observed for OSW could be an indication of relatively symmetrical distribution and limited channelized flow as compared to MSW. Organic solid waste with less heterogeneity might have helped to reduce channels and to distribute uniform moisture in reactors. Since both materials were shredded to similar extent, the cause of difference could be due to some MSW components like plastic, rubber etc. which were impermeable to moisture. However, almost all OSW constituents were permeable to some extent. As the moisture flow was less heterogeneous in OSW, it could be useful in anaerobic bioreactors digesting organic waste for enhancement of uniform degradation and stabilization.

Even though the gas flow through waste channels is not discussed in the present study, but owing to its heterogeneity and thus more channels, MSW is likely to facilitate the gas distribution and collection as compared to OSW.

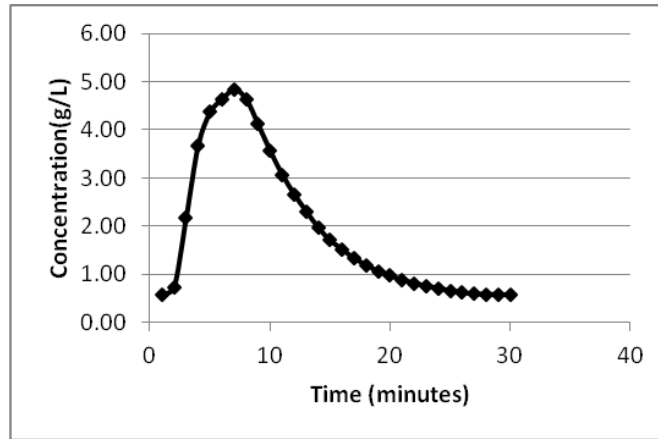


FIGURE 6
Tracer concentration vs. time plot for experiment 3 with MSW

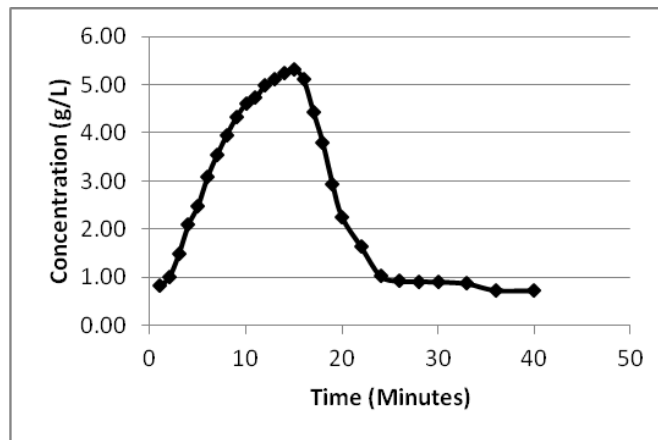


FIGURE 7
Tracer concentration vs. time plot for experiment 6 with OSW

CONCLUSIONS

The study was conducted utilizing tracer tests with the purpose to compare the moisture flow in reactors loaded with two types of wastes i.e. municipal solid waste and organic solid waste. In line with the previous studies, the channeling of moisture movement was indicated through both kinds of wastes in the reactors. Extent of channeling was lower for organic waste in contrast to municipal solid waste. Lesser heterogeneity and higher permeability of organic waste as compared to municipal solid waste possibly helped it to reduce channels in the reactor. This implies that a slight concern for selection of materials to be deposited and placing them at appropriate density could reduce channeling in landfills. Otherwise wetting of waste would never be uniform due to preferential flow.

Further, the different characteristics of the waste samples affected hydraulic retention time and leachate routing in the reactors. The hydraulic retention time for pure organic waste was higher again due to its lesser heterogeneity and channel-

ing as compared to municipal solid waste.

Optimum degradation of municipal solid waste and organic solid waste in bioreactor landfills would require absorbing additional liquids by the waste samples to reach their field capacities as indicated by their lower moisture contents as compared to field capacity values in the present study. The additional liquid requirement to meet the desired waste moisture content for optimal decomposition would be higher for municipal solid waste as compared to organic solid waste in a bioreactor landfill. The physical composition of the city waste indicated biodegradables and inerts as its major fractions. Segregation of inerts and recyclables from municipal solid waste before placing it in a bioreactor landfill would be helpful in reducing channelization of moisture movement and enhancing uniform degradation of the waste. Though shredding of waste has been considered to be high price activity but it could also be helpful in reducing moisture channels in landfills.

The transport processes of liquids are affected by local material degradation and mechanical deformation in landfills.

Uniform moisture distribution attained in bioreactor landfills at the starting phase would definitely be helpful in uniform degradation of the waste, but it might not persist in the subsequent phases due to change in behaviour of waste with degradation. So this kind of time dependent behaviour must be addressed to designers and operators of landfills for better end results.

REFERENCES

- [1] Reinhart, D. and T.G. Townsend, "Landfill Bioreactor Design and Operation." Lewis Publisher, Boca Raton, New York, 1998.
- [2] Korfiatis, G.P., A.C. Demetracopoulos, E.L. Bourodimos, and E.G. Nawy, "Moisture transport in a solid waste column." *Journal of Environmental Engineering*, 1984. Volume 110: pp. 789–796.
- [3] Zeiss, C. and W. Major, "Moisture flow through municipal solid waste: patterns and characteristics." *Journal of Environmental Systems*, 1992. Volume 22: pp. 211–231.
- [4] Wall, D.K. and C. Zeiss, "Municipal landfill biodegradation and settlement." *Journal of Environmental Engineering*, 1995. Volume 122: pp. 214–224.
- [5] Zeiss, C. and M. Ugucioni, "Mechanisms and patterns of leachate flow in municipal solid waste landfills." *Journal of Environmental Systems*, 1995. Volume 23: pp. 247–270.
- [6] McCreanor, P.T. and D.R. Reinhart, "Hydrodynamic modeling of leachate recirculating landfills." *Waste Management and Research*, 2000. Volume 17: pp. 465–469.
- [7] Rosqvist, H. and G. Destouni, "Solute transport through preferential pathways in municipal solid waste." *Journal of Contaminant Hydrology*, 2000. Volume 46: pp. 39–60.
- [8] Capelo, J. and M.A.H. de Castro, "Measuring transient water flow in unsaturated municipal solid waste - a new experimental approach." *Waste Management*, 2007. Volume 27: pp. 811–819.
- [9] Oni, O.A.G., "Studying pollutant solute transport in saturated MSW using multi-tracer tests." *Australian Journal of Basic and Applied Sciences*, 2009. Volume 3: pp. 3727–3740.
- [10] Fellner, J., D. Laner, and P.H. Brunner, "Landfill simulation reactors – A method to predict the behaviour of field-scale landfills?" Fourth international workshop on Hydro-Physico-Mechanics of Landfills, Santander, Spain; April 27 – 28, 2011.
- [11] Rosqvist, N.H., L.H. Dollar, and A.B. "Fourie, Preferential flow in municipal solid waste and implications for long-term leachate quality: valuation of laboratory-scale experiments." *Waste Management and Research*, 2005. Volume 23: pp. 367–380.
- [12] Munasinghe, R., "Effect of hydraulic retention time on landfill leachate and gas characteristics." Ph.D. thesis. The University of British Columbia, Vancouver, Canada, 1997.
- [13] Rosqvist, H. and D. Bendz, "An experimental evaluation of the solute transport volume in biodegraded municipal solid waste." *Hydrology and Earth System Sciences*, 1999. Volume 3: pp. 429–438.
- [14] Fellner, J., G. Doberl, G. Allgair, and P.H. Brunner, "Comparing field investigations with laboratory models to predict landfill leachate emissions." *Waste Management*, 2009. Volume 29: pp. 1844–1851.
- [15] Oni, O.A.G. and R.P. Beaven, "Quantifying the solute transport water in a MSW fill in varied saturated conditions with different tracers." *American Journal of Science*, 2010. Volume 6: pp. 419–430.
- [16] "Standard test method for determination of the composition of unprocessed municipal solid waste." American Society for Testing and Materials (ASTM), US, 2003.
- [17] Mason, I.G. and M.W. Milke, "Physical modelling of the composting environment: A review. Part 1: Reactor systems." *Waste Management*, 2005. Volume 25: pp. 481–500.
- [18] Hernandez-Berriel, Ma.C., L. Marquez-Benavides, D.J. Gonzales-Perez, and O. Buenrostro-Delgado, "The effect of moisture regimes on the anaerobic degradation of municipal solid waste from Metepec (Mexico)." *Waste Management*, 2008. Volume 28: pp. 14–20.
- [19] Sanphoti, N., S. Towprayoon, M. Ritzkowski, and R. Stegmann, "Seasonal influence on emission behavior of simulated tropical landfill operated with leachate recirculation." The 2nd Joint International Conference on Sustainable Energy and Environment, Bangkok, Thailand, 2006.
- [20] "Standard methods for the examination of water and wastewater." 20th ed. American Public Health Association (APHA), Washington DC, USA, 2005.

POTENTIAL OF FUNGAL-DEGRADED MAIZE COB AS FEED FOR WEST AFRICAN DWARF RAMS FED GRADED LEVELS OF FUNGAL TREATED MAIZE COB

¹A. Akinfemi, ²O. A. Ogunwole

¹Faculty of Agriculture, Department of Animal Science, Nasarawa State University, Shabu-lafia Campus, PMB 135, Lafia, Nasarawa State

²Department of Animal Science, University of Ibadan, Ibadan
NIGERIA

ABSTRACT

Maize cobs (MC) were treated with *Pleurotus tuber-regium* (Pt) and thereafter used for *in-vivo* studies in which twenty rams were allotted to five groups of four rams per treatment in a completely randomized design. Each group was fed any of the diets in which MC (g/100g) treated with Pt replaced wheat offal at 0 (A), 25 (B), 50 (C), 75 (D) and 100 (E) as supplement to a basal *Panicum maximum* in an experiment lasting 114 days. Parameters measured were Voluntary Dry Matter Intakes (VDMI), Average Daily Weight Gain (ADWG), Feed Conversion Ratio (FCR), ruminal pH, Total Volatile Fatty Acids (TVFA) and Ammonia Nitrogen (NH₃-N). Fungal-degradation significantly improved the VDMI (g) which increased consistently from 676.8 in rams on control diet to 709.4 for rams on diet E. The ADWG (g/d) recorded for rams ranged from 67.7 for rams on control diet to 88.8 for animals on diet E. Treatment effect on FCR and ruminal-pH was significant. The TVFA (meq/L) ranged from 10.1 in Diet A to 12.8 in Diet B. The NH₃-N (mg/ml) also increased from 18.2(A) to 26.4(E). Inclusion of MC treated with (Pt) in the diet of rams improved the voluntary feed intake and digestibility.

Keywords: *Pleurotus tuber-regium*, *Panicum maximum*, *in-vivo*, Supplementation, Biodegraded

INTRODUCTION

In developing countries of the world, natural pastures make up the bulk of the feed consumed by grazing animals. This is because ruminants are endowed with the ability to degrade and utilize forages with the help of microbes in their rumen. However, the major constraint to livestock production in Nigeria, is inadequate all year-round supply of pastures. There is therefore, the need to search for more available

roughage particularly agricultural by-product such as maize cob. However, most agricultural by-products are usually bulky with high fibre, low protein, vitamins and minerals. Therefore, sustainability of livestock on grasses and crop residues alone becomes difficult, hence the need for alternatives. Fungal treatment is preferable to other treatment, such as application of chemical (Salman *et al.*, 2008). Burning of crop residues and by-product leads to environmental pollution, consequently health hazards.

*Corresponding author: akinfemiabayomi@gmail.com

Recently, the production of microbial protein from agricultural wastes and by-products has received the attention of several workers (Bellany, 1975; Dunlop, 1975; Han and Anderson, 1975; Moo-Young *et al.*, 1978; Garg and Neolantan, 1981). Much interest has been evinced in new biotechniques for improving the nutritive value of lignocellulose using biological treatment in solid substrate fermentation under non-sterile conditions (Gupta *et al.*, 1985). Such scientists (Shoukry *et al.*, 1985; Khorshed 2000; El-Ashry *et al.*, 2003, and El-Kady *et al.*, 2006) used biological treatments like *Trichoderma viride* to improve the nutritive value and digestibility of poor quality roughages.

Fungal treatment lead to the beneficial effects in ruminant performance and such treatments are most likely to be of great value for livestock in positive nitrogen balance. *Pleurotus tuber-reguim* was used to improve the nutritive value of maize cobs. The aim of this study was to investigate the nutritive potential of fungal treated maize cob as a supplement to a complete feed mixtures for West African dwarf (WAD) rams. Nutrient digestibility, nitrogen balance, NH₃-N, TVFA and pH were the criteria for evaluation

MATERIALS AND METHODS

Fungal treatments of maize cob in large scale (on-farm condition)

The experiment was carried out at the Small Ruminant Unit of Research Farm, National Cereal Research Institute (NCRI), Moore Plantation, Ibadan from August to December, 2009.

A heap of 500kg of milled maize cob was moistened with water on a concrete floor, covered with cellophane sheet and allowed to ferment for two weeks. The fermenting heap of milled maize cob was turned every third interval to allow even distribution of heat. After the completion of the composting process, the fermented substrate was then transferred to 3-tier inoculation trays (2ft x 6ft) and allowed to cool before inoculating with active fungal culture (spawn). The mixture of active fungal culture prepared in bags was used at 10% w/w, mixed well into the cool fermented maize cobs and allowed to ferment for 40 days.

At the end of the fermentation period, the treated maize cob was sun dried until the substrate attained less than 10% moisture content. It was then bagged and stored until required for feeding trials with West African dwarf (WAD) rams.

Preparation of active fungal culture for on-farm inoculation of maize cob

The active fungal culture of *Pleurotus tuber-reguim* obtained from Culture Bank of the Department of Botany and Microbiology, University of Ibadan was reproduced in bags for on-farm inoculation. Each 5kg bag of sterilized guinea corn grains was inoculated at 5% w/w, and immediately the bag was sealed and kept in a dark room for two

weeks to allow total ramification of the guinea corn grains by the active fungal culture. The treated substrates were subsequently used for inoculation on large scale.

T₁ = 0% Fungal treated maize cob, T₂ = 10% fungal treated maize cob, T₃ = 20% fungal treated maize cob, T₄ = 30% fungal treated maize cob, T₅ = 40% fungal treated maize cob, PKC = Palm kernel cake, GNC = groundnut cake, FTMC = Fungal treated maize cob, DCP = dicalcium phosphate, SBM = soybean meal, Vit.Premix = Vitamin-Mineral Premix.

Formulation and composition of the experimental diets

Five experimental diet supplements feed mixtures were formulated as follows:

T₁ = the first mixture contained 0% fungal treated maize cob

T₂ = the second mixture contained 10% fungal treated maize cob

T₃ = the third mixture contained 20% fungal treated maize cob

T₄ = the fourth mixture contained 30% fungal treated maize cob

T₅ = the fifth mixture contained 40% treated maize cob.

The dietary ingredients were mixed fortnightly and packed in sacks lined with polythene sheets to avoid rancidity and loss of palatability. Formulation of diets, proximate composition and gross energy of diets, and proximate composition of guinea grass (*Panicum maximum*), wheat offal and fungal treated maize cob (FTMC) are presented in Tables 1, 2, and 3.

DM = Dry matter, CP = Crude protein, CF = Crude fibre, EE = ether extract, NFE = Nitrogen free extract, GE = Gross energy, T₁ = 0% Fungal treated maize cob, T₂ = 10% fungal treated maize cob, T₃ = 20% fungal treated maize cob, T₄ = 30% maize cob, T₅ = 40% fungal treated maize cob,

Experimental animals

Twenty (20) West African dwarf (WAD) – growing rams aged between 5-6 months weighing 15.6-16kg were used for the experiment. They were purchased from the sheep market in Iwo, Oyo state. On arrival, the rams were given prophylactic treatments, which consisted of intramuscular application of oxytetracycline and vitamin B complex, at the dosage of 1ml/10kg body weight of the animal. They were also drenched with 10% lavasol to control endoparasite, and treated for mange and other ectoparasites using ectopore. A preliminary period of 14 days was allowed to acclimatize the animals to their new environment and feed.

Housing

Each WAD-ram was housed individually in a paired well ventilated metabolic cage made of wood and partitioned. Each metabolic cage was equipped with wooden feed troughs

TABLE 1
Gross composition (%) of experimental diets

<i>Ingredient</i>	<i>T₁</i>	<i>T₂</i>	<i>T₃</i>	<i>T₄</i>	<i>T₅</i>
Maize bran	30	30	30	30	30
PKC	10	10	10	10	10
GNC	10	10	10	10	10
Wheat offal	40	30	20	10	-
FTMC	-	10	20	30	40
Common salt	1.0	1.0	1.0	1.0	1.0
DCP	3.75	3.75	3.75	3.75	3.75
SBM	3.75	3.75	3.75	3.75	3.75
Vit. Premix	1.50	1.50	1.50	1.50	1.50
Total	100	100	100	100	100

TABLE 2
Proximate composition and gross energy of experimental diets

<i>Parameters</i>	<i>T₁</i>	<i>T₂</i>	<i>T₃</i>	<i>T₄</i>	<i>T₅</i>
DM	89.88	89.66	89.83	89.76	89.21
CP	16.56	16.74	16.38	15.96	16.14
CF	22.14	17.89	19.21	20.69	21.76
Ash	8.21	10.28	11.26	9.28	10.81
EE	3.87	3.64	3.61	3.76	3.58
NFE	49.22	51.00	49.54	50.31	48.21
GE Kcal/kg	3985	3978	3876	3787	3724

and plastic drinkers.

Feeding of WAD-rams

On arrival, the rams were allowed six weeks to acclimatize to the experimental diets with gradual withdrawal of their usual diets which they were used to. The twenty (20) WAD rams were weighed and randomly allotted to five groups of four replicates in a completely randomized design (CRD). For easy identification and separation, labeled tag was placed on each animal corresponding to the pen number. The rams were fed first with supplemental diet (Table1) at 5% body weight and thereafter released to zero graze on *Panicum max-*

imum. Refusals were weighed the following morning and deducted from the total amount served, for the determination of feed intake. Daily feeds were served to meet 5% of rams' body weight and were frequently adjusted to ensure that each animal received about 20% of feed above its previous day's consumption. Samples from refusal were taken for proximate composition. Fresh water was served daily; Salt licks were placed permanently in each pen. Weights of rams were taken before the commencement of the experiment and subsequently once weekly. The rams were weighed in the morning before feeding. The feeding trial lasted one hundred and five days (105).

TABLE 3
Proximate composition of Guinea grass, wheat offal and fungal treated maize cob

Parameters	Guinea grass	Wheat offal	FTMC
Dry matter	42.03	90.00	92.50
Crude protein	6.93	17.13	18.80
Crude fibre	43.49	12.17	19.36
Ether extract	3.21	5.56	8.73
Ash	10.15	6.30	7.85
Nitrogen free extract	36.22	31.16	37.41

Digestibility trials

Twenty WAD-rams used for growth studies were randomly selected for determining the digestibility and N-balance of the diets. The rams were confined in individual modified metabolism cages (Akinsoyinu, 1974) for separate collection of faeces and urine in a completely randomized design. The rams were offered the experimental diets prior to 7 days digestibility period. The animals were weighed both at the beginning and the end of digestibility trials. During 7 days of collection period, total faeces were weighed daily. A 10% sample of total faeces was stored in a freezer at -4°C . The sample of each day was bulked together at day 7 of collection. The bulk for each animal was mixed thoroughly, dried in the oven at 60°C and stored for chemical analysis. Individual urine sample was collected and weighed daily in the morning using measuring plastic container. At collection, 2ml of 10% Tetraoxosulphate VI acids (H_2SO_4) was added to each container to prevent microbial growth and loss of nitrogen. Ten percent of total urine was taken daily and stored at -4°C for subsequent analysis for nitrogen. Daily feed was served at 5% body weight. Feed refusals were taken and mixed for the entire collection period on individual basis using an air tight plastic bag. On the last day of digestibility trial, samples of ruminal contents were taken at 3hr post feeding via stomach tube and strained through four layer of cheese cloth. Samples were separated into 2 portions; the first was used for immediate determination of ruminal-pH using digital pH meter and ammonia-nitrogen ($\text{NH}_3\text{-N}$) by AOAC. (1991), while the second portion was stored at -20°C after adding two drops of toluene and a thin layer of paraffin oil till analysis for TVFA's according to Warner (1964).

CHEMICAL ANALYSIS

The supplemental feeds refusals and dried faeces for each animal were ground through a 1mm mesh screen for analysis. Two grams of milled samples in duplicate was taken for proximate analysis. Nitrogen (N) content of each milled sam-

ple was determined by the use of standard Kjeldhal method (AOAC, 1991) and the crude protein (CP) calculated (using $\text{N} \times 6.25$). Neutral detergent fibre (NDF), acid detergent fibre (ADF), acid detergent lignin (ADL) and crude fiber (CF) were assessed using the methods proposed by Van Soest *et al.* (1991).

STATISTICAL ANALYSIS

Data were subjected to analysis of variance using procedure of SAS (1999). Significant means were separated using the Duncan Multiple range test of the same package.

RESULTS

Gross composition

The gross composition of the experimental diets and the proximate composition of Guinea grass, wheat offal and fungal treated maize cob are shown in Tables 1 and 2.

Also presented in Table 4 is the growth performance of WAD rams fed graded levels of FTMC. The results showed that treatment effect on DMI, MWG and AVDG differ ($P < 0.05$) between treatments. Animals on T_5 which was 100% replacement of wheat offal recorded the highest DMI, MWG and AVDG. However, variations in the FCR between T_2 , T_3 , T_4 and T_5 did not differ significantly ($P > 0.05$).

Apparent digestibility

Apparent digestibility by WAD rams fed graded levels of fungal treated maize cobs (FTMC) are shown in Table 5. Treatment effects obtained for apparent digestibility of CP, CF, EE, Ash, NFE, ADF, NDF, cellulose and hemicellulose differed among treatments ($P < 0.05$). In the entire treatments, apparent digestibility increased with increasing levels of supplementation with FTMC, compared with those on control

TABLE 4
Growth Performance of West African dwarf rams fed experimental diets

Parameters	T ₁	T ₂	T ₃	T ₄	T ₅	SEM
DMI g/d W ^{0.75}	132.68 ^e	134.48 ^d	136.46 ^c	139.41 ^b	141.45 ^a	0.003
Initial body weight, kg	13	12.75	13	13	12.75	-
Final body weight, kg	21.13 ^e	22.33 ^d	23.57 ^c	26.01 ^b	27.33 ^a	0.003
Mean weight gain, kg	8.13 ^e	9.58 ^d	9.67 ^c	10.33 ^b	11.58 ^a	0.003
Total DMI/BW%	3.03 ^e	3.08 ^a	3.04 ^{bc}	3.05 ^b	3.08 ^a	0.020
Feed conversion ratio	9.99 ^a	8.83 ^b	8.34 ^b	8.28 ^b	7.79 ^b	0.210

^{abcd} Row means with different superscripts differ significantly at ($P < 0.05$), T₁ = 0% Fungal treated maize cobs, T₂ = 10% fungal treated maize cobs, T₃ = 20% fungal treated maize cobs, T₄ = 40% fungal treated maize cobs, SEM = Standard error of mean.

TABLE 5
Apparent digestibility of West African dwarf rams fed graded levels of fungal treated maize cob

Parameters	T ₁	T ₂	T ₃	T ₄	T ₅	SEM
CP	60.00 ^e	65.90 ^d	67.21 ^c	69.47 ^b	71.83 ^a	0.21
CF	60.08 ^e	62.32 ^d	64.49 ^c	66.23 ^b	67.34 ^a	0.003
EE	66.55 ^e	67.12 ^d	68.72 ^c	71.01 ^b	73.91 ^a	0.003
Ash	68.16 ^e	70.42 ^d	72.38 ^c	76.50 ^b	77.50 ^a	0.02
NFE	72.75 ^d	78.98 ^c	79.11 ^c	80.47 ^b	82.13 ^a	0.15
DM	64.57 ^e	66.03 ^d	67.67 ^c	69.47 ^b	70.58 ^a	0.003
ADF	71.45 ^e	76.86 ^d	77.28 ^c	78.62 ^b	81.81 ^a	0.003
NDF	70.10 ^e	73.60 ^d	77.76 ^c	81.00 ^b	81.91 ^a	0.15
Cellulose	66.97 ^d	75.20 ^c	75.44 ^c	78.59 ^b	81.83 ^a	0.02
Hemicellulose	62.40 ^e	69.25 ^d	70.33 ^c	72.85 ^b	74.19 ^a	0.02

^{abcd} Row means with different superscripts differ significantly at ($P < 0.05$), T₁ = 0% Fungal treated maize cobs, T₂ = 10% fungal treated maize cobs, T₃ = 20% fungal treated maize cobs, T₄ = 40% fungal treated maize cobs, DM = Dry matter, CP = Crude protein, CF = Crude fibre, EE = ether extract, NFE = Nitrogen free extract, ADF = Acid detergent fibre, NDF = Neutral detergent fibre, SEM = Standard error of mean.

diet.

Nitrogen balance and rumen liquor parameters

Data on nitrogen utilization and rumen fluid parameters are presented in Table 6. Treatments effect as affected by N-intake of FTMC differed ($P < 0.05$). Faecal-N of animals on T₁ (1.99 g/d kgW^{0.75}), T₂ (1.65 g/d kgW^{0.75}) and T₄ (1.55 g/d kgW^{0.75}) differed from those on T₃ (0.94 g/d kgW^{0.75}) and T₅ (0.99 g/d kgW^{0.75}). Variations in urinary nitrogen were simi-

lar ($P > 0.05$) for rams on T₁, T₂, T₃ and T₅. The highest (4.18g/d kgW^{0.75}) and least (2.49g/d kgW^{0.75}) nitrogen balance were observed for animals on T₅, which was 100% replacement of wheat offal. The ruminal-pH values recorded ranged from 6.76 to 9.08. The variables observed differed ($P < 0.05$) between treatments. The TVFA's (meq/mL) obtained in this study were 10.10, 10.30, 11.92, 12.37 and 12.84 for rams on T₁, T₂, T₃, T₄ and T₅ respectively. Variations in TVFA's were generally better in all the fungal supplemented treatments compared with control. Similarly, NH₃-N differed ($P < 0.05$) with increasing levels of supplementation. The val-

TABLE 6
Nitrogen utilization and rumen fluid parameters of WAD rams fed experimental diet

Parameters	T ₁	T ₂	T ₃	T ₄	T ₅	SEM
N – intake g ^d ⁻¹ /kgW ^{0.75}	8.71 ^d	8.76 ^b	8.76 ^b	8.55 ^c	9.08 ^a	0.003
Faecal-N (g/d ¹) kgW ^{0.75}	1.99 ^a	1.65 ^{ab}	0.94 ^b	1.55 ^{ab}	0.99 ^e	0.15
Urinary-N (g/d ¹) KgW ^{0.75}	4.25 ^a	3.99 ^{ab}	4.20 ^{ab}	3.00 ^b	4.45 ^a	0.21
N-balance (g/d ¹) KgW ^{0.75}	2.49 ^b	3.46 ^a	3.62 ^a	4.00 ^a	4.18 ^a	0.21
<i>Rumen fluid parameters at 6hrs post feeding</i>						
pH (g/d ¹)	6.76 ^a	7.74 ^b	8.76 ^b	8.55 ^c	9.08 ^a	0.003
TVFA meq mL ⁻¹	10.10 ^e	10.30 ^d	11.92 ^c	12.37 ^b	12.84 ^a	0.02
NH ₃ -N mg/ mL ⁻¹	18.20 ^e	19.60 ^d	23.75 ^c	24.20 ^b	26.40 ^a	0.03

^{abcd} Row means with different superscripts differ significantly at ($P < 0.05$), T₁= 0% Fungal treated maize cobs, T₂ = 10% fungal treated maize cobs, T₃ = 20% fungal treated maize cobs, T₄ = 40% fungal treated maize cobs, TVFA = Total volatile fatty acid, N = nitrogen, SEM = Standard error of mean.

ues (mg/mL) recorded were 18.20, 19.60, 23.75, 24.20 and 26.40 for animals on T₁, T₂, T₃, T₄ and T₅ respectively.

DISCUSSION

Growth performance

The increased DMI with increasing fungal inclusion may be due to beneficial effects of fermentation. The DMI is a basic limiting factor in feed utilization as it affects the overall performance of farm animals (Mako, 2009). These results were in agreement with other reports (Mahrous and Abou-Ammou, 2005; Bassuny *et al.*, 2005; and El-Kady *et al.*, 2006). They indicated that DMI of biologically treated roughage improved compared with untreated roughage. Similarly, the increased MWG and AVDG obtained for rams on treated diets may also be due to higher DMI utilization which affects overall performance. However, rams on control (T₁) recorded the lowest MWG and AVDG, which might be due to 0% FTMC having high lignocelluloses bonding that limits digestibility. The higher AVDG of rams on treated ration could also be attributed to higher and rapid by-pass of protein from rumen and subsequent digestion and absorption in the abomasums and duodenum. The FCR is the quantity of feed required to produce a unit increase in body weight, thus, the lower the FCR, the better the feed. The lowest FCR obtained for rams on T₅ may be due to the influence of DMI more so that the relationship between total DMI and total weight gain of rams on FTMC was proportional and highly significant ($P < 0.05$) indicating that DMI for rams on FTMC directly influenced the growth of rams.

Apparent digestibility

The high values of all apparent digestibility parameters obtained in the entire supplemented ration, especially for the rams on T₅ may be indicative of proper utilization of feedstuffs. Several authors (Titi and Lubbadah, 2004; Wang *et al.*, 2004; Dean *et al.*, 2005; Eun and Beauchemin, 2005; Yu *et al.*, 2005; Mohammed *et al.*, 2005; El-Kady *et al.*, 2006) reported an increase in DM, CP, CF and NFE digestibility when fungal treated beet bulb were supplemented in animal diets. Others (Deraz and Ismail, 2001) reported that Trichoderma treatments had the effect of loosening lignocellulotic bonds and sulubilizing some of the hemicelluloses content. The highest apparent digestibility of CP, CF, Ash, NFE, Cellulose, hemicelluloses, ADF and NDF could be indicative of increased microorganism's biomass, while the highest digestibility of CF may be due to increased activity of enzymes produced by microorganisms (Gado *et al.*, 2007a). It was observed in this study that diet T₅ (100% replacement of wheat offal) was most suitable of the test diets.

Nitrogen balance

The improved positive nitrogen was consistent with other reports (Langer *et al.*, 1982; Marwaha *et al.*, 1990 and Bakshi and Jander, 1991) that growing Jersey calves fed fungal treated wheat retained 29% of nitrogen N-intake. However, Walli *et al.* (1991) noticed a positive N-balance when calves were fed on fungal treated wheat straw. Generally, the superiority of N-retention in a specific ration is affected by several factors. These include possible production of microbial protein synthesis, increased presence of fermentable energy (Hagemeister, *et al.*, 1981), differences in availability of fermentable energy (Tagari *et al.*, 1976), variability in nitrogen

which might escape fermentation from the rumen, increased utilization of ammonia in the rumen (Holzer *et al.*, 1986) and the effect of free fats in protein synthesis (Sutton *et al.*, 1983). This may further explain the observed variations in nitrogen retention as affected by treatment.

Rumen liquor parameters

The lower pH obtained in diets T₃ and T₅ might be due to fermentation process of both non-structural and structural carbohydrate, and production of volatile fatty acids, which affected the pH to some limit until they were proportionally and relatively absorbed from the rumen wall. This assumption agreed with report elsewhere (Reddy and Reddy, 1985) that pH values were inversely related to TVFA's concentration in the rumen. The anaerobic fermentation of fungal treatment (T₄ and T₅) was more efficiently faster yielding more TVFA's than diets T₂, T₃ and control (T₁) groups. The TVFA's concentration in the rumen might also be affected by other factors such as DM digestibility, rate of absorption, rumen pH, transportation of the digestion from the rumen to other parts of the digestive tract and the microbial population in their activities (Salman *et al.*, 2008). Higher values of rumen liquor ammonia-nitrogen observed with fungal treated rations especially diet T₅ indicated that the release of ammonia-nitrogen from those rations were easier (Pujso, 1964) than the control or that the treated ration were well utilized by rumen microbes.

Some reports (Smith *et al.*, 1980; Ikwuegbu and Sulston, 1980) attributed increase in ammonia-nitrogen concentration in the rumen to reduction of ammonia-nitrogen absorption by rumen epithelium or to a decrease in the efficiency of microbial protein synthesis. Others (Salman *et al.*, 2008; Khorshed (2000) and El-Ashry *et al.*, 1997) observed significant increase in rumen ammonia-nitrogen concentration with fungal treated residues. Yadav and Yadav (1988) observed that increased ruminal ammonia nitrogen concentration might be due to higher intake of nitrogen and higher crude protein digestibility. Their findings were consistent with the present results.

CONCLUSION

Inclusion of maize cob treated with *Pleurotus tuber-regium* in the diet of rams improved the voluntary feed intake, digestibility and average daily weight gain. Biodegraded maize cob completely replaced wheat offal in the diet of West African Dwarf rams and can thus be used in the developing countries where ruminant feeds is limiting.

REFERENCES

- Akinsoyinu, A.O. (1974). Studies on Protein and energy utilization by West African dwarf goats. PhD, Thesis University of Ibadan, Nigeria.
- AOAC (1991). The official methods of Analysis. Association of Official Analytical Chemist, 15th Edn., Washington DC.
- Bakish, M.P.S and P.N, Janger 1991. "Agaricus bisporus harvested spent wheat straw as livestock feed." *Indian Journal of Animal Science*. Volume 61 (6): pp. 653-645
- Bassuny, S.M., Abdel-Aziz, A.A, Abdel-Fattah, H.J and Abdel-Aziz, M.Y.S. (2005). "Fibrous Crop by-products as Feeds. 4. Effect of biological treatments for rice straw and bean straw on chemical composition, digestibility and some ruminal and blood constituents of sheep." *Egypt J. Nutr. Feeds*, Volume 8: pp. 541-54.
- Bellany, W.D., (1975). Production of single cell protein from insoluble agricultural wastes by Mesophiles. *In: Single Cell Protein, Vol. 2 edition by S.R. Trannenboun and D.I.C. Nong*, MIT Press, Cambridge, London.
- Dean, A.T., Adesogan, N. Krueger and R.C. Little, (2005). "Effect of fibrolytic enzymes on the fermentation characteristics, aerobic stability and digestibility of Bermuda grass silage." *J. Dairy Sci.*, Volume 88: pp. 994-1003.
- Deraz, T.A. and Ismail, H. (2001). "Cotton stalks treated with white-rot fungus for feeding sheep." *Egypt J. Nutrition Feeds*, Volume 4: pp. 423-34.
- Dunlop, G.E., (1975) Production of single Cell protein from insoluble agricultural wastes by Mesophiles. *In: Single Cell Protein, Vol: 2 editions by S.R.*
- El-Ashry, M.A., Kholif, A. M, Fadel, M., El-Alamy, H. A, El-Sayed, H. M. and S.M. Kholif, (2003). "Effect of biological treatments on chemical composition and *in vitro* and *in vivo* digestibility of poor quality roughages." *Egyptian J. Nutr. Feeds*, Volume 6: pp. 113- 26.
- El-Kady, R.I., Awadalla, I.M., Mohammed, M.I, Fadel, M. and Abd El-Rahman, H.H. (2006). "Effect of exogenous enzymes on the growth performance and digestibility of growing Buffalo calves." *Int. J. Agric. Biol.*, Volume 8: pp. 354-69.
- Eun, S. and Beauchemin, K.A. (2005) "Effect of proteolytic feed enzyme on intake, digestion, ruminal fermentation and milk production." *J. Dairy Sci.*, Volume 88: pp. 2140-53.
- Gado, H.M, Ramadan, F., Mourad, M. and Matter, B.B. (2007a). "Effect of biological treatment of some agricultural by-products in ration digestibility and lamb performance." *Egypt J. Nutr. Feeds*, Volume 10: pp. 509-16.
- Garg, S.K. and Neolantan, S. (1981). "Effect of cultural on cellulose activity and protein production by *Aspergillus Terrues*." *Biotechnol. Biorig.*, Volume 23: pp. 1653-9.
- Gupta, R., Sinha, A.P., Gupta, B.S., Srivastava, J.P. and Maheshawi, P.K. (1985). "Effect of ammonia (generated from urea) on proximate constituents of paddy straw." *Indian J. Anim. Health*, Volume 24: pp. 101-4.
- Hagemeister, H., W. Lipping and W.K. Kaufmann, (1981). *Microbial Protein Synthesis and Digestion in the High Yielding Dairy Cow*. In Recent Advances in Animal Nutrition. Haresign. 67. Butterworth, London.
- Han, Y.W and Anderson, A.W. (1975). "Some solid fermentation of rye grass straw." *Appl. Microbial*. Volume 30: p. 930.
- Holzer, Z., D. Levy and V. Samule, (1986). "Interactions between supplementary nitrogen source and ration energy

- density on performance and nitrogen utilization in growing and fattening male Cattle. *Anim. Prod.*, 42: 19 linseed oil supplementation on rumen in sheep." *British J. Nutr.*, Volume 48: p. 365.
- Ikwegbu, O.A and Sutton, J.D. (2008). "The effect of varying linseed oil supplementation on rumen metabolism in sheep." *British Journal of Nutrition*. Volume 48: p. 365.
- Khorshed, M.M.A. (2000). Different treatments for improving nutritional quality of some crop residues used in ruminant nutrition. *Ph.D. Thesis*, Faculty of Agriculture, Ain Shams University.
- Langer, P. N., Sebgal, J. P, Rana, V. J, Silgh, M.M. and Garcha, K (1982). "Utilization of Agaricus bisporus-cultivated spent stew in the ruminant diet." *Indian J. Anim. Sci.*, Volume 52: pp. 627-43.
- Mahrous, A.A. and Abou Ammou, F.A. 2005. "Effect of biological treatments for rice straw on the productive performance of sheep." *Egyptian J. Nutr. Feeds*. Volume 8: pp. 529-40.
- Mako, A.A. (2009). Evaluation of Water Hyacinth (*Eichornia crassipes* Mart Solms-lau bach) As a potential feed for the West African Dwarf Goats. Ph.D. Thesis. University of Ibadan, Ibadan.
- Marwaha, C.I., M. Sharma, B. Singh and B.S. Katoch, 1990. "Comparative feeding value of un-treated, urea treated and fungal treated wheat straw in growing Jersey calves." *Indian J. Dairy Sci.*, Volume 43: pp. 3-11.
- Mohamed, A.H., El-said, B.E, Ibrahim, Y.K, Tejido, M.L. and Carro, M.D. 2005. "Effect of exogenous enzymes on in vitro ruminal fermentation of a high forage diet and productive response of lactating ewes." *Egypt. J. Nutr. Feeds*. Volume 8: pp. 591-602.
- Moo-Young, M., Chahol, D.S. and Vlach, D. (1978). "Single cell protein from barious chemically pretreated wood substrate using chactonium celluloytican." *Biotechnol. Bioeng.*, 20?107-18.
- Pujso, K, 1964. Zasz proble. Postep. Nukroin 54:91. In: *Tracer Studies on Non-protein Nitrogen for Ruminants*, P: 53. Taea. Vienna, 1972 pulse legumes. *Comm. Appl. Biol. Sci. Ghent University*. Volume 69(1): pp. 103-110.
- Salman, F.M, EL-Kadi, R.I, Abdel-Rahman, H, Ahmed, S.M, Mohamed, M.I and Shoukry, M.M. (2008). "Biologically treated sugar beet pulp as a supplement in goat rations." *International Journal of Agriculture and Biology*. Volume 10: pp. 412-416 .
- SAS. (1999). Statistical Analytical System. SAS/STAT. User's guide. Version 6,3rd edition. Carry, North Carolina, USA, 943pp
- Shoukry, M.M, Hamissa, F.A., Sawsan, M., Ahmed, A.H., El-Refai, H.M., Ali and Abdel-Motagally, Z. M. Z. (1985). Nutritive improvement of some low quality roughages for ruminants. I. "Effect of different microbial and chemical treatments on the quality of sugarcane bagasse." *Egypt J. Anim. Prod*. Volume 25: pp. 329-42.
- Smith, N.E., Collar, I.S., Bath, D.L., Dunkley, W.L. and Franke, A.A., (1980). "Whole cotton seed and extruded soybean for cows in early location." *J. Anim. Sci.*, Volume 53: pp. 217-26.
- Sutton, J.D., R. Knight, A.B. Mc. Allan and R.H. Smith, (1983). "Digestion and Synthesis in the rumen of Sheep given diets supplemented with free and protected oils." *British J. Nut.*, Volume 49: p. 419.
- Tagari, H., D., Lery, Oizer, Z.H and Jian, D. (1976). "Poultry litter for intensive beef production." *Anim. Prod.*, Volume 23: p. 317.
- Titi, H. and W.F. Lubbadah, (2004). "Effect of feeding cellulose enzyme on productive responses of pregnant and lactating ewes and goats." *Small Ruminant Res.*, Volume 52: pp. 137-43.
- Van Soest, P.J, Robertson, J.B and Lewis, B.A (1991) "Methods for dietary fibre, neutral detergent fibre and non-starch polysaccharides in relation to animal nutrition." *Journal of Dairy Science*. Volume 74: pp. 3583-3597.
- Walli, T.K., Rai, S.N., Gupta, B.N. and Singh, K. (1991). "Influence of fungal treated and urea treated wheat straw on nutrient utilization in calves." *India J. Anim. Nutr.*, Volume 8: p. 227.
- Wang, Y., Spratling, B.M., Zobell, D.R., Wiedmeier, R.D. and Allister, M.C. (2004). "Effect of alkali pretreatment of wheat straw on the efficacy of exogenous fibrolytic enzymes." *J. Anim. Sci.*, Volume 82: pp. 198-208.
- Warner, A.C.J. (1964). "Production of volatile fatty acids in the rumen. Methods of measurements." *Nutr. Abst. Rev.* Volume 34: p. 339.
- Yadav, B.P.S. and I.S. Yadav, (1988). "Incubation studies with strained rumen liquor of cattle for *in vitro* evaluation of ammoniated straw." *Indian J. Anim. Sci.*, Volume 58: p. 398.
- Yu, P.J.J, Kimon, M.C. and Christenson, D.A (2005). "Improving the nutritional value of out hulls for ruminant animals with pretreatment of a multienzyme cocktail: *In vitro* studies." *J. Anim. Sci.*, Volume 83: pp. 1133-41.

EFFECT OF PH ON NICKEL REMOVAL BY LEMNA MINOR

Leela Kaur^{1*}, Kasturi Gadgil², Satyawati Sharma³

¹Department of Environmental Science, Maharaja Ganga Singh University
Bikaner (Rajasthan) – 334004, INDIA

²ABES Engineering College, Ghaziabad, U.P., INDIA

³Centre for Rural Development & Technology, Indian Institute of Technology (IIT) Delhi
Hauz Khas, New Delhi – 110016, INDIA

ABSTRACT

The presence of heavy metals in water is wide spreading all over the world. Aquatic plants are being used to remediate heavy metal contaminated wastewater. The present study evaluated the effect of pH on the uptake of nickel from nickel contaminated water by "Common duckweed" (*Lemna minor*). *Lemna minor* demonstrated the ability to remove nickel passively by root absorption and bioaccumulation. 10 mg/l nickel was used through out the experiments. Removal was studied in both the acidic and alkaline ranges of pH, maintained by using HCl and NaOH. The results indicated that *Lemna minor* grows best at pH 6-8 range. Growth of *Lemna* plants helped in the accumulation of Ni. The removal of nickel was dependent on the pH parameter. Maximum nickel removal was observed at pH 6. The efficiency of common duckweed for nickel removal was 98.8% at pH 6 for 28 days. At pH >8, the nickel ions get precipitated due to hydroxide anions forming a nickel hydroxide precipitate. Ni accumulation increased with the increasing exposure time. The results revealed that duckweed may efficiently be used for the removal of nickel from industrial effluents with pH around 6.

Keywords: Nickel; pH; *Lemna minor*; phytoremediation

INTRODUCTION

The removal of toxic heavy metals such as cadmium, copper, lead, nickel, mercury, and zinc from aqueous environment has received considerable attention in recent years due to their toxicity and carcinogenicity which may cause damage to human system [1]. Nickel ions are non-biodegradable toxic heavy metals and may cause dermatitis and allergic sensitization [2, 3]. The tolerance limit of nickel in drinking water is 0.01 mg/l, and for industrial wastewater it is 2.0 mg/l [4]. The parameter set for tolerance limit of inland

surface waters subjected to nickel pollution is 3.0 mg/l according to Indian Standard [5]. The major sources of nickel contamination to water comes from industrial process such as electroplating, batteries manufacturing, mine, metal finishing and forging. Therefore, different methods were investigated and applied to remove nickel ions from water such as adsorption, chemical precipitation, ion exchange, filtration, membrane separation, and reverse osmosis [6-8]. However, most of these methods have some disadvantages including incomplete metal removal, toxic sludge generation and high cost. This has led to a search for simple and cost-effective method [9-11]. Phytoremediation is such an alternative which is the

*Corresponding author: Phone: 911512212044; Fax: 911512212042; Email: leela.kaur@gmail.com

use of plants for removal of contaminants from water, air or soil matrix. Various mechanisms of phytoremediation are phytoabsorption, phytovolatilization phytoextraction, and phytostabilization. Aquatic plants like water hyacinth, duckweed, *Azolla filiculoides*, *Ceratophyllum demersum*, *Nymphaea alba L.*, *Myriophyllum spp.*, *Salvinia spp.*, and *Pistia stratiotes* are potential candidates for the removal of heavy metals from contaminated water or wastewaters [12].

Nickel (Ni) is easily accumulated in the biota, particularly in the phytoplankton or other aquatic plants. *Lemna minor*, also known as common duckweed, is chosen for our study because it is easy to culture and harvest, having fast growth rate and is highly sensitive to different pollutants [13-17].

In plants, Ni is a component of the enzyme urease and is considered an essential micronutrient for growth [18]. However, excess Ni is known to be toxic and many studies have been conducted concerning Ni toxicity of various species [19-20]. Higher Ni concentrations cause weak plant growth, yield depression, disorder in plant metabolism and chlorosis [21].

The aim of the present study was to determine the range of Ni removal potential of *Lemna minor* under different pH conditions in Ni contaminated water.

EXPERIMENTAL

Duckweed plants were picked up from a stream of water from the main campus. They were identified as *Lemna minor* as *Lemna minor* is readily identified by its smooth dorsal surface and three veins arising from point of root attachment, without dorsal row of papules and reddish anthocyanin on ventral side and without winged root sheath [22]. *L. minor* plants were cultured in a water tank in micro model IIT Delhi (the experimental site). In water tank, tap water along with farm yard manure in 1:2 ratios was added for proper growth of *Lemna* plants. Farm yard manure (organic C 12.2%, total N 0.55%, total P 0.75%, total K 2.30% and pH 7.2) was added for providing nutrients to plants. Table 1 shows the physico-chemical characteristics of tap water. Culturing tanks were kept in an open environment to get enough sunlight.

A stock solution was prepared by using nickel nitrate salt [as $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Qualigens)]. 10 mg/l of nickel as nickel nitrate was prepared. Plastic containers of six litre capacity were filled with water. These containers were kept in an open environment to get enough sunlight. A known quantity (6.0 g) of *L. minor* was taken out of culturing tank and treated with different pH (range pH 4-10). pH of the solutions were

TABLE 1
The physico-chemical characteristics of tap water

Parameters	Values
pH	7.1
EC	4.23 mmho/cm
TDS	350 mg/l
BOD	130 mg/l
COD	208 mg/l
Phosphate	13 mg/l
Nitrate	40 mg/l
K	12 mg/l
Na	180 mg/l
Chloride	100 mg/l
Total hardness	250 mg/l
Alkalinity	330 mg/l
Ca	50 mg/l
Mg	20 mg/l

maintained by using HCl and NaOH. A black line was drawn on the containers so that a six litre water level could be maintained. The plants were checked everyday and tap water was added to each container so that the six litre water level line remained constant. Samples were collected at an interval of 7, 14, 21 and 28 days.

The biomass weight was taken by drying duckweed plants on filter paper for 10 minutes and then the biomass was oven-dried to constant weight, at 60°C for 24 hours.

Plants were analyzed for relative growth and metal accumulation. In addition, the metal that remained in the solution was also analyzed to assess the removal potential of *L. minor*.

Relative growth of control and treated plants were calculated as follows [23]:

$$\text{Relative growth} = \frac{\text{Final fresh weight (g)}}{\text{Initial fresh weight (g)}}$$

Quantification of Ni was done by the following procedure: The dried plant samples were heated in a muffle furnace at 500°C for 6 hours. The ash of each sample was dissolved in 5 ml of 20 % HCl to dissolve the residue. Samples were heated on a hot plate to boiling. Required amount of HCl (20 %) was added to avoid sample drying. The resulting solutions were filtered and diluted to 50 ml with deionized water in volumetric flasks. Ni content of these plant samples and water samples were determined using flame atomic absorption spectrophotometry (Electronics Corporation of India Limited AAS4129) with the following settings: wavelength 232 nm, lamp current 3.5 mA, slit 0.2 nm, fuel – acetylene and oxidant air.

Ni concentration in the samples was calculated using the following formula:

$$\text{Ni accumulation (mg/kg)} = \frac{\text{Reading of Ni in Sample (mg/l)} \times \text{Total volume of the Sample (ml)}}{\text{Dry weight of the Sample (g)}}$$

Nickel removal was calculated by the following formula:

$$\text{Percentage Nickel Removal} = \frac{\text{Concentration of Ni in } Lemna \text{ biomass} \times 100}{\text{Concentration of Ni in water solution}}$$

RESULTS

The results obtained, out of the experiments, are shown in Figures (1-3). The *Lemna* biomass was harvested to get its yield and the metal analysis after 7, 14, 21 and 28 days of experiments. The water remaining in the tub was also analyzed for Ni content. All these parameters are discussed here.

Relative growth

Effect of different pH on relative growth of *L. minor* in Ni contaminated water with different exposure time is shown in Figure 1. *L. minor* showed good growth in the pH range from 6-8. Toxicity symptoms like pigment decolorization and chlorosis are observed at pH 4 and pH 10. Relative growth showed dependence on the pH and exposure time. Relative growth increased with the increase in exposure time. For the 7 days treatment test, the highest value of relative growth was at pH 6 (1.74±0.35) and the lowest value was at pH 10 (1.29±0.13). Control is pH 7 without Ni content. However, the highest and the lowest value of relative growth for 28

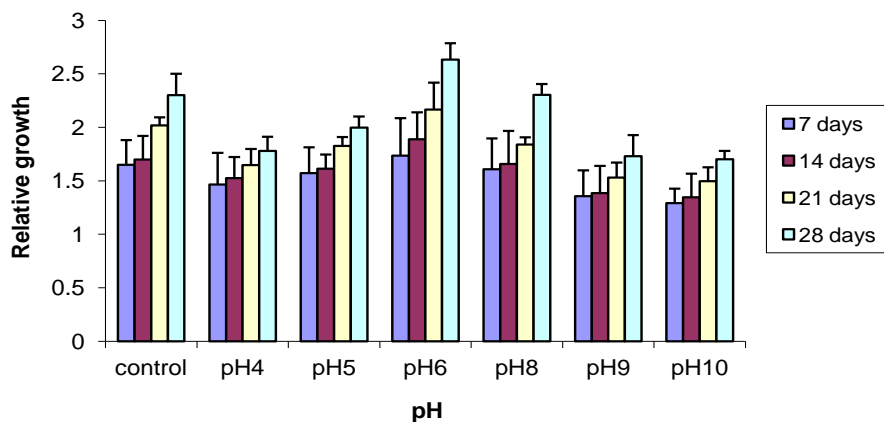


FIGURE 1
Effect of pH on relative growth of *L. minor* at Ni concentration 10 mg/l

days treatment test were at pH 6 (2.63 ± 0.15) and pH 10 (1.70 ± 0.07) respectively.

Metal accumulation

Accumulation of Ni by *L. minor* at different pH is shown in Figure 2. Accumulation of Ni by *Lemna* increased with time. Plants treated for 7 days showed the highest and the lowest Ni accumulation at pH 6 (285 ± 38 mg/kg dry weight) and pH 10 (203 ± 42 mg/kg) respectively. Plants treated at pH 6 for 28 days accumulated the highest level of metal (400 ± 10 mg/kg). The lowest Ni accumulation was found to be 285 ± 5 mg/kg for *L. minor* treated with pH 10 for 28 days.

Metal remained in the residual solution

Graphical representation of concentration of Ni (mg/l) remained in the water samples at different exposure time is

shown in Figure 3. Ni in the solution decreased with time. The lowest value of Ni remained in the residual solution was 0.12 ± 0.03 mg/l at pH 6 while the highest value was shown by pH 10 (0.85 ± 0.05) for 28 days treatment. Plants treated for 7 days showed the highest and the lowest Ni remained in the residual solution at pH 10 (1.83 ± 0.18 mg/l) and pH 6 (1.0 ± 0.005 mg/l) respectively.

Figure 4 shows Ni removal potential of the *L. minor*. From these results it is evident that maximum removal of Ni was 98.8% at pH 6 for 28 days. The maximum and the minimum removal potential for 7 days were obtained in plants treated with pH 6 (90%) and pH 10 (82%). The minimum removal potential after 28 days were obtained in plants treated with pH 10 (91%). Optimum pH was found to be in the range of 6-8, at which maximum removal of nickel was observed. The percentage Ni removal increased with pH to attain a maximum at pH 6 and thereafter the percentage removal did not increase significantly. The basic mechanism that governs the accumulation characteristics of *Lemna* at pH

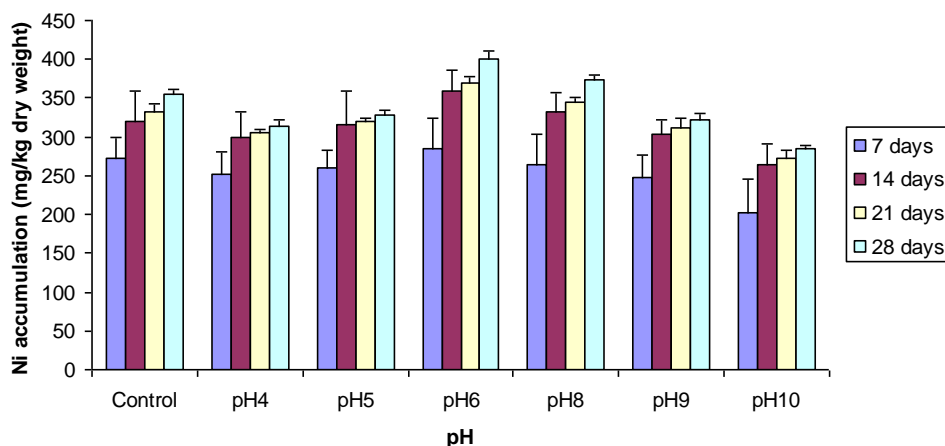


FIGURE 2
Effect of pH on Ni accumulation by *L. minor*

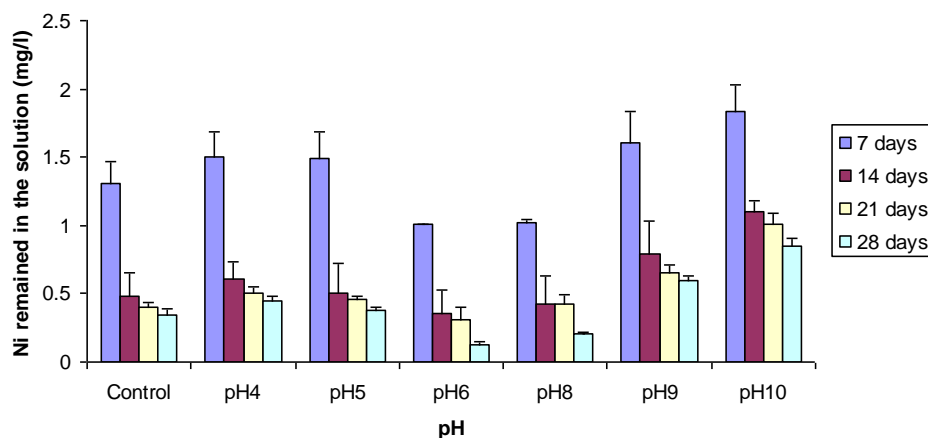


FIGURE 3
Effect of pH on Ni remained in the solution

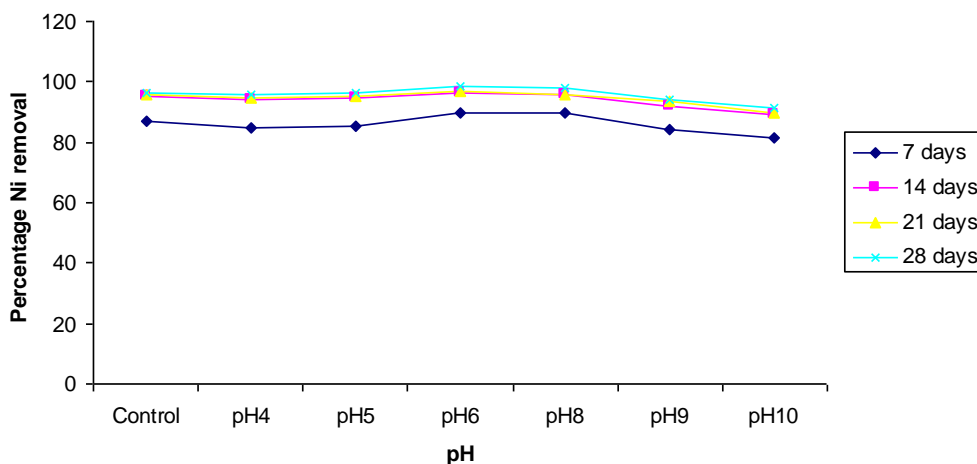


FIGURE 4
Percentage Ni removal potential of *L. minor*

ranging between 6 to 9 might be due to adsorption and ion exchange. At these pH levels transferable cations present at the exchangeable sites are substituted with Ni^{2+} cation in the aqueous solutions [24]. The lowest Ni removal was at pH 4 in acidic pH. This could be due to the increase in competition for adsorption sites by hydrogen ions.

DISCUSSION

pH is one of the most important parameters controlling uptake of heavy metals by plants from wastewater and aqueous solutions [25]. The dependence of metal uptake on pH is related to both the surface functional groups on the cell walls of the biomass and the metal chemistry in solution [26]. This implies that the functional groups on the cell walls and its ionic state in the pH range determine the extent of biosorption. Therefore adsorption studies are required. The positively charged hydrogen ions may also compete with nickel ions for binding on the ligands on the cell wall. At lower pH, the higher concentration of the hydrogen ions effectively leads to fewer ligands being available for the binding of the nickel ions. As the pH is increased (i.e. fewer H^+ ions), more ligands are available for these two cations, thus resulting in an enhanced nickel ions removal.

At pH 6, the Nickel uptake reaches the maximum due to the effect of the functional groups formed on the surface of *Lemna minor* plants. At pH value 4, the nickel uptake was very weak due to the competition between Ni^{2+} and H^+ in the solution. At higher pH value (pH 8), Ni is less soluble and there is an increasing negative charge density on the surface of *Lemna* plants [27]. Hence, more Ni^{2+} could easily be adsorbed as the pH increases. The decrease at pH 9 and pH 10 may be due to the abundant OH^- ions causing increased hindrance to diffusion of nickel ions. Similar observations have been reported by Wang and Qin [28], Kandaha and Meunier [29], Olayinko et al. [30] and Bansal et al. [31]. It is to be

expected that with increase in pH values, more and more ligands having negative charge would be exposed which result in increase in attraction of positively charged metal ions [32]. In addition at higher pH the lower binding is attributed to reduced solubility of the metal and its precipitation [33].

Nickel can be removed from industrial wastewaters by precipitation as hydroxide at pH ranging from 10 to 11 (solubility is 0.12 mg/l), and as sulfate or carbonate [34]. Every dissolved metal has a distinct pH at which the optimum hydroxide precipitation occurs e.g. Nickel has pH 10.8. It is seen that at a pH of 8.0 nickel has solubility of 70 mg/l and at a pH of 10.2 the solubility is 0.1 mg/l [35]. The effluent limitation for nickel is 2.4 mg/l to discharge to a city sewer in the U.S. A pH value of 9.0-9.5 will usually precipitate nickel ions to their required level [35].

Toxicity symptoms like chlorosis (a progression of green to yellow colour on the frond) and frond disconnection (detachment of fronds from colonies) were observed at the start of exposing *Lemna* fronds to Ni at pH 4 and pH 10 and these signs progressed to necrosis at the end of the treatment. A study by Kaur et al. [36] showed that 1 mg/l of Ni enhanced the plant growth whereas Ni caused visible damage to *L. minor* at concentration of 5.0 mg/l. Similarly, Khellaf and Zerdaoui [37] found that duckweed tolerated Ni at concentrations of 3.0 mg/l without showing any visible signs of toxicity. Kara [38] had shown that *L. minor* acts as a hyperaccumulator for Ni and thus is likely suitable for the use in accumulating Ni. Axtell et al. [39] also reported a comparative study of the absorption of Pb and Ni by *L. minor* and it showed a preference to remove Ni. All these studies support the good phytoremediation potential of *L. minor* for Nickel polluted water.

CONCLUSION

The results showed *Lemna minor* grows best at pH 6-8

range. Growth of *Lemna* plants helped in the accumulation of Ni. The present study indicated that Ni uptake by *L. minor* was dependent upon pH values of the solutions. Descending order of Ni accumulation by *L. minor* was as follows: pH6> pH8> pH7> pH5> pH4> pH9> pH10. *L. minor* was quite effective for Ni removal and practical implementation of duckweed system would help in waste water treatment plants especially in the treatment of metal finishing effluents. After duckweed phytoremediation a high quality effluent could be generated that meets discharge standards and generates non-hazardous waste which would not endanger the environment or public health.

ACKNOWLEDGMENT

The authors wish to acknowledge the financial support from the University Grants Commission (U.G.C.), New Delhi, India.

REFERENCES

- [1] Lin, S.H., S.L. Lai, H.G. Leu, 2000. "Removal of heavy metals from aqueous solution by chelating resin in a multistage adsorption process." *J. Hazard. Mater.* Volume B76, pp. 139–153.
- [2] Abu Al-Rub, F.A., M. Kandah, N. Al-Dabaybeh, 2002. "Nickel removal from aqueous solutions using sheep manure wastes." *Eng. Life Sci.* Volume 2, pp. 111–116.
- [3] Abu Al-Rub, F.A., M. Kandah, N. Al-Dabaybeh, 2002. "Competitive adsorption of nickel and cadmium on sheep manure wastes; experimental and prediction studies." *Sep. Sci. Technol.* Volume 38, pp. 483–497.
- [4] Sharma, Y.C., V. Srivastav, S.N. Upadhyay, C.H. Weng, 2008. "Alumina nanoparticles for the removal of Ni(II) from aqueous solutions." *Ind. Eng. Chem. Res.* Volume 47, pp. 8095–8100.
- [5] Anonymous, 1974. Indian standard. Tolerance limits for inland surface waters subject to pollution. IS: 2296. Indian Standards Institution, New Delhi.
- [6] Feng, D., C. Aldrich, H. Tan 2002. "Treatment of acid mine water by use of heavy metal precipitation and ion exchange." *Mineral. Eng.* Volume 13(6), pp. 623–642.
- [7] Matlock, M.M., B.S. Howerton, D.A. Atwood, 2002. "Chemical precipitation of heavy metals from acid mine drainage." *Water Research.* Volume 36(19), pp. 4757–4764.
- [8] Mohammadi, T., A. Moheb, M. Sadrzadeh, A. Razmi, 2005. "Modeling of metal ion removal from wastewater by electrodialysis." *Sep. Puri. Technol.* Volume 41(1), pp. 73–82.
- [9] Özcan, A., A.S. Özcan, S. Tunali, T. Akar, I. Kiran, 2005. "Determination of the equilibrium, kinetic and thermodynamic parameters of adsorption of copper (II) ions onto seeds of *Capsicum annum*." *J. Hazard. Mater.* Volume 124, pp. 200–208.
- [10] Ahalya, N. and T.V. Ramachandra, 2006. "Phytoremediation: Processes and Mechanisms." *J. Ecobiol.* 18(1), pp. 33–38.
- [11] Soudani A., M. Chiban, M. Zerbet, F. Sinan, 2011. "Use of Mediterranean plant as potential adsorbent for municipal and industrial wastewater treatment." *J. Environ. Chem. Ecotoxicol.* Volume 3(8), pp. 199–205.
- [12] Anawar, H.M., A. Garcia-Sanchez, M. Tari Kul Alam, M. Majibur Rahman, 2008. "Phytofiltration of water polluted with arsenic and heavy metals." *Int. J. Environ. Pollut.* Volume 33(2/3), pp. 292–312.
- [13] Bassi, M., M.G. Corradi, M. Realini, 1990. "Effects of chromium (VI) on two fresh water plants, *Lemna minor* and *Pistia stratiotes*." *Cytobios.* Volume 62, pp. 27–38.
- [14] Kwan, K.H.M., S. Smith, 1991. "Some aspects of the kinetics of cadmium and thallium uptake by fronds of *Lemna minor* L." *New Phytol.* Volume 117, pp. 91–102.
- [15] Jain, S.K., P. Vasudevan, N.K. Jha, 1989. "Removal of some heavy metals from polluted water by aquatic plants: studies on duckweed and water velvet." *Biol. Wastes.* Volume 28, pp. 115–126.
- [16] Jain, S.K., P. Vasudevan, N.K. Jha, 1990. "*Azolla pinata* R.Br. and *Lemna minor* for removal of lead and zinc from polluted water." *Water Resource.* Volume 24, pp. 177–183.
- [17] Rahmani, G.N.H., S.P.K. Sternberg, 1999. "Bioremoval of lead from water using *Lemna minor*." *Bioresource. Technol.* Volume 70, pp. 225–230.
- [18] Brown, P.H., R.M. Welch, E.E. Cary, 1987. "Nickel: A micronutrient essential for higher plants." *Plant Physiol.* Volume 85, pp. 801–803.
- [19] Mishra, D., M. Kar, 1974. Nickel in plant growth and metabolism. *Bot. Rev.* Volume 40, pp. 395–452.
- [20] Seregin, I.V., A.D. Kozhevnikova, 2006. "Physiological role of nickel and its toxic effects on higher plants." *Russ. J. Plant Physiol.* Volume 53, pp. 257–277.
- [21] Yang, X., V.C. Baligar, D.C. Martens, R.B. Clarks, 1996. "Plant tolerance to Ni toxicity.1. Influx, transport and accumulation of Ni in four species." *J. Plant Nutr.* Volume 19, pp. 73–85.
- [22] Waynesword. 2012. Retrieved from: <http://waynesword.palomar.edu/lemi.htm>
- [23] Lu, D., P. Mausel, E. Brondizio, E.F. Moran, 2004. "Relationships between forests stand parameters and Landsat TM spectral responses in the Brazilian Amazon Basin." *For. Ecol. Manage.* Volume 198, pp. 149–167.
- [24] Ramamurthi, V., P.G. Priya, S. Saranya, C.A. Basha, 2009. "Recovery of nickel (II) ions from electroplating rinse water using hectorite clay." *Mod. Appl. Sci.* Volume 3 (9), pp. 37–51.
- [25] Sheng, P.X., L.H. Tan, J.P. Chen, Y.P. Ting, 2004. "Biosorption performance of two brown algae for removal of chromium and cadmium." *J. Disper. Sci. Technol.* Volume 25, pp. 681–688.
- [26] Chawla, G., J. Singh, P.N. Viswanathan, 1991. "Effect of pH and temperature on the uptake of cadmium by *Lemna minor* L. Bullet." *Environ. Contamin. Toxicol.* Volume 47(1), pp. 84–90.
- [27] Congeevaram, S., S. Dhanarani, J. Park, M. Dexilin, K. Thamaraiselvi, 2007. "Biosorption of chromium and nickel"

- el by heavy metal resistant fungal and bacterial isolates.” *J. Hazard. Mater.* Volume 146, pp. 270-277.
- [28] Wang, X.S., Y. Qin, 2006. Removal of Ni(II), Zn(II) and Cr(VI) from aqueous solution by *Alternanthera philoxeroides* biomass. *J. Hazard. Mater.* Volume B138, pp. 582-588.
- [29] Kandaha, M.I., J.L. Meunier, 2007. “Removal of nickel ions from water by multi-walled carbon nanotubes.” *J. Hazard. Mater.* Volume 146, pp. 283-288.
- [30] Olayinka, K.O., B.I. Alo, T. Adu, 2007. “Sorption of heavy metals from electroplating effluents by low cost adsorbents II: Use of waste tea, coconut shell and coconut husk.” *J. Appl. Sci.* Volume 7 (16), pp. 2307-2313.
- [31] Bansal, M., D. Singh, V.K. Garg, P. Rose, 2009. “Use of agricultural waste for the removal of nickel ions from aqueous solutions: equilibrium and kinetics studies.” *Int. J. Environ. Sci. Engg.* Volume 1 (2), pp. 108-114.
- [32] Sekher, K.C., S. Subramanian, J.M. Modak, K.A. Natarajan, 1998. “Removal of metal ions using an industrial biomass with reference to environmental control.” *Inter. J. Miner. Process.* Volume 53, pp. 107-120.
- [33] Zhou, J.L., R.J Kiff, 1991. “The uptake of copper from aqueous solution by immobilized fungal biomass.” *J. Chem. Technol. Biotechnol.* Volume 52, pp. 317-330.
- [34] Haas, C.N., R.J. Vamos, 1995. Hazardous and industrial waste treatment. Prentice Hall, Englewood Cliffs, NJ, pp. 147-152.
- [35] Hoffland Environmental, 2012. Retrieved from: <http://www.hoffland.net/hydroxide-precipitation.html>
- [36] Kaur, L., K. Gadgil, S. Sharma, 2008. “Phytoaccumulation of nickel from contaminated water by duckweed (*Lemna minor*).” *J. Environ. Res. Develop.* Volume 3 (2), pp. 388-394.
- [37] Khellaf, N., and M. Zerdaoui, 2009. “Growth response of the duckweed *Lemna minor* to heavy metal pollution.” *Iran. J. Environ. Health. Sci. Eng.* Volume 6 (3), pp. 161-166.
- [38] Kara, Y., D. Basaran, I. Kara, A. Zeytunluoglu, H. Genci, 2003. “Bioaccumulation of nickel by aquatic macrophyta *Lemna minor* (duckweed).” *Int. J. Agricul. Biol.* Volume 5 (3), pp. 281-283.
- [39] Axtell, N.R., S.P.K. Sternberg, K. Claussen, 2003. “Lead and nickel removal using *Microspora* and *Lemna minor*.” *Bioresource Technol.* Volume 89 (1), pp. 41-48.

THE APPLICATION OF SOLID OLIVE WASTE AS REINFORCEMENT IN CARBOXYLATED NITRILE BUTADIENE RUBBER /ORGANO NANO LAYERED SILICATES COMPOSITES

A. Mousa^{1,2}, G. Heinrich², U. Wagenknecht²

¹Department of Materials Engineering, Faculty of Engineering
Al-Balqa Applied University, Salt 19117 JORDAN

²Leibniz-Institut für Polymerforschung Dresden e.V. Hohe Strasse 6, D-01069 Dresden, GERMANY

ABSTRACT

The surface energy of organic biomaterial based olive solid waste (OSW) was measured and compared with that of organic nano layered silicates (NLS). The measured surface energy value of the OSW was approximately similar to that of the NLS. Such fact provided the organic nature of both compounds were the trigger to produce hybrid filler that is a combination between OSW and NLS. The hybrid filler was incorporated into carboxylated Nitrile Butadiene Rubber (XNBR). The samples were inspected with respect to their mechanical properties. It has been found that the hybrid filler was able to improve the tensile strength at break and the Young's Modulus as compared to the pristine control. The improvement in the tensile strength was attributed to: firstly; the exfoliation-intercalation dispersion state of the nanosilicates as evidenced by transmission electron microscope (TEM) pictures. Secondly: the good interaction between the hybrid filler and the matrix being related to the polar nature of the hybrid filler and the matrix had increased the degree of crosslinking. The increased crosslink density was evidenced by the increased state of cure which is the difference between the maximum torque, S_{max} and minimum torque, S_{min} , (ΔS) derived from the moving die rheometer (MDR). The increased degree of crosslinking was accompanied by a decreased swelling index data. The cure rate index (CRI) was increased with the addition of the bio-waste material highlighting the role of the OSW to promote the crosslinking reaction. Dynamic mechanical analysis (DMA) revealed that the storage Modulus (E') has been increased after the incorporation of hybrid filler, while the mechanical loss factor i.e. glass transition temperature ($\tan\delta$) has been reduced reflecting the reinforcing efficiency of the bio-waste material.

Keywords: Olive solid waste, Environment, Strength, Hybrid filler, Composite, Elastomer

INTRODUCTION

Hybrid composites are becoming more commercially significant in their own right for a number of reasons. Firstly, they are capable to dilute expensive reinforcements with cheaper materials that are very important economically. Secondly, it is possible for wider spectrum of physical and me-

chanical properties, thus easing design of materials with specific characteristics. Thirdly, the hybrids give rise to achieve synergistic effects by the improvement in mechanical characteristics and functional properties, since composites can be tailored to meet the demanded properties. The combination of specific filler with the polymer matrix will ease the various composites applications that vary from construction materials

¹Corresponding author: Email: mousa@rocketmail.com

to aerospace industries [1]. In general fillers are utilized into polymer system to enhance the performance of the polymer system or for economical reasons; the fillers could be either organic or inorganic fillers. The organic fillers emerge from renewable resources that are normally naturally occurring biomaterials of woody nature and are gaining attention due to economical and ecological reasons. Examples on this type are but not limited to rice husk, sisal, jute...etc.. The naturally occurring materials have many advantages such as easy process ability, environmental friendly, low cost and reduced wear on the processing machine [2-6]. Recently it is our concern to find out new application for biomaterial known as olive solid waste which is very common in the Mediterranean countries as agrowaste material produced by the olive oil industry. The produced residue is thrown into the nearby landfills or near the oil refineries. The main application is burning to generate heat during winter, this again is of negative impact on the environment. Recently we implemented this material in various polymer systems as an attempt to check its potential application as a polymer additive. The material displayed some shortcomings in term of reinforcing potential. To compensate for such shortcoming of such green material it is intended to hybrid it with common filler that is organo nano layered silicates (NLS) without any chemical modification of the raw OSW. Further information on NLS can be found in the open literature [7-12]. Two reasons triggered us to hybrid OSW with NLS, the former is the hydroxyl groups of the biomaterial that render it polar, the latter is the comparable surface energies. Thus the potential of such hybrid filler on the mechanical performance of XNBR composites will be reported. The application of the OSW into the XNBR will have dual purposes economical and ecological.

EXPERIMENTAL

Materials

LANXESS Deutschland GmbH supplied Carboxylated nitrile rubber, Krynac X 740. Quaternary ammonium salt modified natural Montmorillonite; Nanofil 15 donated by

Süd-chemie AG, Germany. ACROS Organics, Belgium, supplied stearic acid and zinc oxide powder. Mercapto Benzo-thiazole Sulfinamide (MBTS) and sulfur were donated from a local rubber factory in Jordan. The olive solid waste (OSW) was obtained from a local olive refinery in Jordan, the particle size of which was $\leq 45\mu\text{m}$. The process of the OSW treatment was reported in our previous works [13-14].

Formulation

The recipe used to produce the rubber hybrid composites is shown in Table 1. Recall that the XNBR was used as matrix, the vulcanization system was sulfur based one as follows, zinc oxide as activator, MBTS as accelerator of the vulcanization reaction, the crosslinking agent was sulfur. Hybrid filler (NLS/OSW): 5/15. Three formulations were prepared in this work these are: The control, which is XNBR vulcanizate and designated as C; the control with organo-nanosilicates and designated as CS; and the control with hybrid filler being designated as CH.

Filler Surface Energy Determination

The surface energy of the OSW was measured according to Wilhelmy-method (advancing, receding and mean contact angle).

Sample preparation

The samples were fabricated by Brabender two roll mill (C.W. Brabender instruments, Hackensack, NJ; 230 V, 40 A) at room temperature and 25rpm for 10 min. The degree of crosslinking was determined using an Ekktron oscillating disc rheometer at 160 °C, 1.66 Hz frequency and 0.5 arcs. The degree of crosslinking was taken as the difference between the maximum torque, S_{max} and minimum torque, S_{min} , (ΔS).

Where: $\Delta S = S_{\text{max}} - S_{\text{min}}$. (1)

The cure rate index, *CRI*, expressed as

TABLE 1
Recipe used to produce XNBR hybrid composites in (php)*

XNBR	100
Stearic acid	1
zinc oxide	3
MBTS**	0.7
Sulfur	1.5
NLS	5

*php is part per hundred part polymer

** MBTS is 2-Mercaptobenzothiazyl Disulfide

$$CRI = \Delta S / (t_{90} - t_2) \quad (2)$$

where t_2 is the scorch time and t_{90} is the optimum cure time.

Compression molding

Rectangular sheets of 2mm thickness were molded at 10MPa and 160 °C using Carver Auto Series compression molding machine according to their t_{90} as derived from Ekktron moving die rheometer.

Swelling studies

2mm thick circular discs with 20 mm diameter were immersed in xylene. Swelling index was determined by weighing the polymer sample ahead to submerging in the required solvent (W_i). The samples were immersed into vials for 36h in the solvent which was enough to reach the equilibrium state. The percentage of solvent absorption, $Q(t)$, was calculated using the following formulation:

$$Q(t) = \frac{W_t - W_i}{W_i} \times 100 \quad (3)$$

The same procedure was repeated in the case of water absorptivity.

Dynamic Mechanical Analysis

Rheometric scientific thermal analyzer was run in the temperature/time scan mode to determine the storage Modulus (E') and the mechanical loss factor ($\tan\delta$). The specimens were scanned from -40 to 100°C at a heating rate of $4^\circ\text{C}/\text{min}$ at frequency of 10 Hz. Two runs were scanned and the second run is reported.

Tensile Properties

Tensile tests were performed on 2 mm thick dumbbells at ambient temperature on a Zwick 1456 universal testing machine at a deformation rate of 500 mm/min according to ASTM D412. The dumbbell specimens were cut from molded rubber sheets. Five specimens were tested and the median value was taken for each formulation.

TEM

Tensile strength fractured samples were viewed under transmission electron microscope to inspect the dispersion state of the layered nanosilicates within the composites. The Samples were cut at -130°C and the thickness was near 60nm.

RESULTS AND DISCUSSIONS

Mechanical Properties

Table 2 compares the influence of single and hybrid filler on the tensile strength at break of XNBR composites. It can be seen that the addition of the layered nanosilicates has increased the tensile strength at break of the XNBR composite. This should be due to the high surface area of the silicates and the dispersion state (intercalation/exfoliation) of the silicates as well. The dispersed platy nanosilicates are expected to contribute to the stress transfer mechanism, which will increase the ability of the matrix to resist rupture where the role of surface area give better chance for improved interaction with the matrix. This is in line with earlier reports on the influence of nanosilicates on various polymer systems (10-12). The effect of the hybrid filler on the tensile strength at break of the XNBR composite is shown in Table 2 as well. It is obvious that the hybrid filler has further increased the tensile strength of the composite compared to the plain counterpart not only this but also exceeds that of the nanosilicates filled composite. Such observation should be traced to the fact that the hybrid filler is fully accessible by the XNBR matrix. The accessibility posed by the organic nature of the biomaterial OSW, the ammonium ion covered silicate platelets last but not least is the polarity of the hybrid and the XNBR, the polarity was brought about by the various reactive functional groups within the structure of these materials namely the carboxylic acid group ($-\text{COOH}$) of the XNBR and the hydroxyl group ($-\text{OH}$) of the OSW, in other words rubber-filler interactions was responsible for the observed trend. One should not oversight the expected filler-filler interactions in this case, which is due to the comparable surface energy of both fillers and their polar nature. *The data was obtained at a fixed layer of particles at adhesive tape with seven test liquids of different surface tension and polarity. During the measurements we noticed that the surface tension of most test*

TABLE 2
Effect of filler type on mechanical properties of XNBR composites

Sample	Stress at break (MPa)	Mod.100 (MPa)	Strain at break (%)	Hardness
C	9	3.5	694	48
CS	10	4	720	55
CH	10.5	7	668	57

liquids was changed, most probably due to the leakage of oil from the wood powder. The value of the surface energy was found to be 24.8 MJ/m^2 . This value is comparable to that of organo layered nanosilicates (Nanofil) measured earlier [13]. This was the key factor behind the formation of the hybrid material. Thus, it is expected that sort of filler-filler interactions were capable to contribute to the stress transfer process, hence higher tensile strength of the composites before rupture. In line with tensile strength course the modulus at 100% elongation (M100) of the composite with single and hybrid filler is shown in Table 2. It is noted that M100 of the composite filled nanosilicates has been increased which is also an indicator on increased stiffness. The (M100) of the composite with the hybrid filler displayed higher values compared to the control. The same reasons used to explain the tensile strength hold in this case as well. Table 2 also illustrates the influence of single and hybrid filler on the strain at break of the vulcanizate. It is obvious that the organo layered nanosilicates addition has increased the strain of the XNBR vulcanizate as compared to the plain counterpart. This scenario can be due to two main reasons the former is the intercalated/exfoliated structure of the nanosilicates, which allows an easy reorientation of the platelets. The latter is the lubricating role acted by the platy nanoclay that will enhance the molecular retractability of network. It is clear that hybrid filler decreased the strain of the composites as shown in Table 2, due to the increased rigidity and stiffness after hybrid filler incorporation, hence strong materials with reduced ability to be elongated. Summing up the improved tensile strength was related to the enhanced rubber-filler interactions, in other words improved crosslink density of the XNBR composites after either single or hybrid filler incorporation. Table 1 depicts the dependence of XNBR composite on the filler type either single or hybrid. Note that the incorporation of the nanosilicates has increased the hardness of the composite. This should be due to the volume fraction reduction of the matrix after the addition of the silicates in addition to the increased strength of the whole composite after the intercalation/exfoliation of nanosilicates. The hybrid filler addition has further increased the hardness because of the further reduction in the volume fraction of the matrix upon the addition of the hybrid filler as well as the increased degree of crosslinking. This trends concurs similar work on the effect of effect of processing time on the tensile, morphological, and thermal properties of rice Husk powder-filled polypropylene composites (14). As evidence on this fact, the extent of cure, which indicates the crosslink density, is presented in Table 3. It can be seen that the addition of the nanosilicates as well as the addition of the hybrid filler has increased the state of cure (ΔS) which is an indication on the degree of crosslinking. This suggests that the XNBR became more crosslinked in the presence of single and hybrid filler. The same reasons discussed under tensile strength hold to explain this observation. The increase in crosslink density was accompanied by a decreased swelling index as compared in Table 3, recall that swelling index is an indirect indication of the degree of crosslinking. The observed trend was harmony with the extent of cure results reported in the same Table as

well. This conclusively proves that the incorporation of either single or hybrid filler has facilitated the formation of new crosslinks. The conclusion is that besides the sulfur crosslinks initiated by the sulfur curing system the active functional groups of the fillers were capable to form secondary physical bonds with the matrix due to polar-polar interactions, which is in line with earlier work on polymer-lignocelluloses composites [15, 16]. The effect of single and hybrid on the curing rate index (CRI) of the XNBR composites is shown in Table 3 as well. It is clear that the incorporation of both fillers has increased the rate of the curing reaction. This is due to the amine functionality with the structure of the NLS after the modification process. This is well know and had been reported in previous work (10-12, 16). The new finding is the role of the organic bio-waste material (OSW) to facilitate the crosslinking reaction, which is also due to the amine functionality within the structure of this material as reported by us earlier (17).

DMA

To support the fact that the hybrid filler was capable to reinforce the matrix through interactions between the filler and the matrix, perhaps some important information could be comprehended from Figure 1. The storage modulus reflects the actual strength of the material, is shown in Figure 1. The storage modulus data is in line with that shown in Tables 1 and 2 respectively. It can be noticed that at higher temperature the hybrid filler displayed higher E' which is a hint on the ability of the hybrid filler to retard the softening temperature of the composite. This is attributable to the thermal conductivity of nanosilicates as well as the phenolic hydroxyl group of the biomaterial acting as antioxidant. Considering $\tan\delta$ curves shown in Figure 1 as well, it can be seen that the incorporation of the nanoclay has further decreased the peak intensity of the $\tan\delta$ compared to the control, which highlights the higher reinforcing ability of nanoclay via more interactions as mentioned earlier. The lowest peak intensity was shown in the case of hybrid filler collaboration due to excessive interaction between the hybrid filler and the matrix. The data shown in Figure 1 reconfirms the fact that the hybrid filler was able to reinforce the matrix. Furthermore the decreased $\tan\delta_{\max}$ at the T_g value indicates quite well lesser damping characteristics of the composites with the incorporation of the hybrid filler. The enhanced degree of interaction was reconfirmed by the shift to right of the T_g value shown in the same figure. Similar results were reported earlier on unsaturated polyester/kenaf hybrid composites and thermoplastic natural rubber filled empty fruit bunch hybrid composites (18,19).

Water Absorption

The water absorption pattern of the XNBR composites as a function of single and hybrid filler at room temperature is

TABLE 3
Swelling index and degree of crosslinking of XNBR vulcanizate and its composites

Sample	Deg of crosslinking (dN.m)	Cure rate index (dN.m/min.)	Swelling ratio
C	6	0.38	1.3
CS	8	0.55	1
CH	11	0.61	0.96

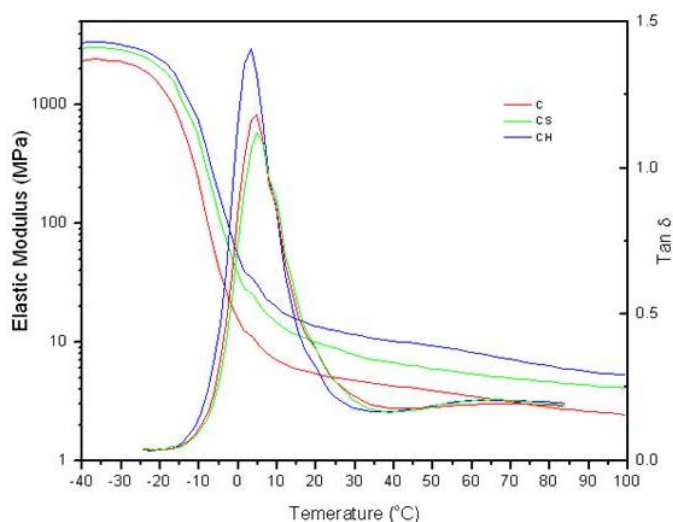


FIGURE 1

The effect of filler type on E' and $\tan\delta$ of XNBR composites

shown in Figure 2 as well. Obviously the silicates addition has decreased the water absorption of the composites with reference to the unfilled counterpart. This could be due to the high aspect ratio of the nanosilicates platelets where the solvent (water in this case) has to travel longer distance to penetrate into the matrix; this is expected to hinder the water penetration into the matrix. This agrees quite well with earlier report on long-term water absorption behaviour of polypropylene/wood flour/organoclay hybrid nanocomposite (20). Note that the hybrid filler has also increased the hygroscopic pattern of the matrix compared to the plain composite. This should be traced to the contribution triggered by the OSW powder where the hydroxyl groups of the OSW being involved in the hydrogen bond formation. In other words the water uptake has been increased after the addition of the OSW.

TEM

TEM pictures of tensile strength fractured surfaces of the composite with single and hybrid filler is shown in Figure 3a. The dispersion state of the nanosilicates filled XNBR revealed dark lines, which correspond to the bundles of stacked

silicate platelets within the XNBR. The addition of OSW has improved the dispersion state of the nanosilicates. The plausible explanation is the addition of the OSW will increase the material resistance to deformation during mixing, hence the torque which is an indirect indication of the stress will increase, this will favor the exfoliation of the nanosilicates or improve the better intercalation/exfoliation dispersion state which is the case shown in Figure 3b. The intercalation/exfoliation dispersion state could be correlated with the improved tensile properties of the XNBR composite containing either single or hybrid filler.

CONCLUSIONS

Based on the aforementioned results the following conclusions might be drawn:

The incorporation of either single or hybrid filler into the XNBR composites has improved the mechanical properties. The improved mechanical properties were related to the reinforcing ability of the nanosilicates due to many reasons, dispersion state of the nanosilicates, high surface area of the nanosilicates and enhanced interactions between the matrix and the filler, in other word increased overall crosslink densi-

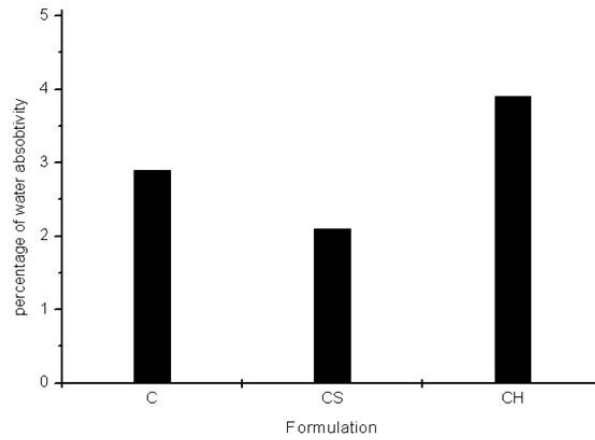


FIGURE 2

The effect of filler type on the % water uptake of XNBR composites

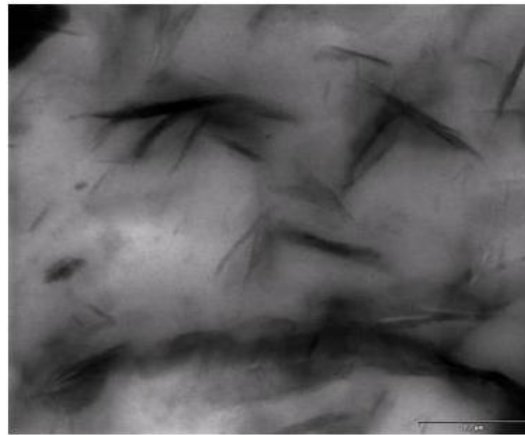


FIGURE 3a

TEM Picture of the Tensile strength Fractured specimen of the XNBR Composite with Layered nanosilicates

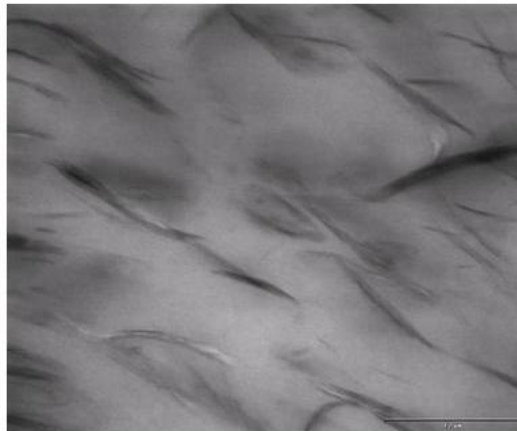


FIGURE 3b

TEM Picture of the Tensile strength Fractured specimen of the XNBR Composite with hybrid filler

ty. The enhanced crosslink density was evidenced by the increased extent of cure, decreased swelling index and the DMA studies. The hybrid filler has further enhanced the mechanical performance of the materials. This was due the

increased crosslink density and the improved dispersion state (exfoliation/intercalation) of nanosilicates. In conclusion successful hybrid filler was achieved with the fact that OSW is of added value that is can be used as co-curing agent.

ACKNOWLEDGMENT

Ahmad Mousa is thankful to the Leibniz-Institut für Polymerforschung Dresden e.V., for the research stay during the June-August 2009. I am also grateful to the Alexander von Humboldt Foundation for the research scholarship to carry out this research.

REFERENCES

1. Bledzki, A.K., J.Gassan, Composites reinforced with cellulose based fibres *J. Progress in Polymer Science*, Volume 24, pp. 221–274 (1999).
2. Rowell, R.M.; A.R. Sanadi, D.F. Caulfield, Jacobson, E. Utilization of Natural Fibers in Plastic Composites: Problems and Opportunities. In: Leão, A.L.; Carvalho, F.X. & Frollini, E. eds. *Lignocellulosic-Plastic Composites*, São Paulo, USP & UNESP, 1997. pp. 23-51.
3. Bledzki, A.K., S. Reihmane, J. Gassan, Thermoplastics Reinforced with Wood Fillers: A Literature Review. *Polymer-Plastic Technology Eng.*, Volume 37, (4) pp. 451-468 (1998).
4. Bogoeva-Gaceva, G., M. Avella, M. Malinconico, A. Buzarovska, A. Grozdanov, G. Gentile, and M.E. Errico, "Natural Fiber Eco-Composites," *Polymer Composites*, Volume 28, pp. 98-107 (2007) .
5. Khan, M.A., K.M.I. Ali, C. Koppe and G. Hinrichsen, "Study of Tensile Properties of Biopol-Jute Composites," *Journal of Polymer Plastics Technology and Engineering*, Volume 38(1), p. 99, 1999.
6. Khan, J.A., M.A. Khan, R. Islam, Abdul Gafur, Mechanical, "Thermal and Interfacial Properties of Jute Fabric-Reinforced Polypropylene Composites," *Materials Sciences and Applications*, Volume 1, pp. 350-357, 2010.
7. Hoffmann, B, C. Dietrich, R. Thomann, C. Friedrich, R. Mulhaupt, "Melt compounding of different grades of polystyrene with organoclay. Part 2: rheological properties." *Macromol. Rapid Commun.*, Volume 21, p. 57 (2000).
8. Reichert, P., H. Nitz, S. Klink, R. Brandsch, R. Thomann, R. Mulhaupt, "Poly (propylene)/organoclay nanocomposite formation: Influence of compatibilizer functionality and organoclay modification *Macromol. Mater. Eng.*, Volume 275, p. 8 (2000).
9. Tripathy, S.S., G. Levita and L.D. Landro, "Interfacial Adhesion in Jute-Polyolefin Composites," *Journal Polymer Composites*, Volume 22, No. 6, 2001, pp. 815-822.
10. Mousa, A; G. Heinrich and U. Wagenknecht, "The Potential of O-MMT as a Reinforcing Filler for Uncured and Dynamically Cured PVC/XNBR Composites." *J. of Macromolecular Science*, Part A Pure and Applied Chemistry: Volume 45, pp. 733-741(2008).
11. Mousa, A., J. Karger-Kocsis, "Rheological and Thermodynamic Behavior of SBR/Organoclay nanocomposites," *Macromolecular Engineering J*, Volume 286, pp. 260-266 (2001).
12. Teh, P.L., Mohd Ishak Z.A., Hashim, A.S., Karger-Kocsis, J., Ishiaku, U.S., "Physical properties of natural rubber/organoclay nanocomposites compatibilized with epoxidized natural rubber." *J. Appl. Polym. Sci*; Volume 94: pp. 2438-2445 (2004).
13. Stöckelhuber, K.W., A. Das, R. Jurk, G. Heinrich, "Contribution of physico-chemical properties of interfaces on dispersibility, adhesion and flocculation of filler particles in rubber." *Polymer*, Volume 51, p. 1954 (2010) .
14. Hattotuwa, G.B. , H. Ismail, and A. Baharin, "Effect of Processing Time on the Tensile, Morphological, and Thermal Properties of Rice Husk Powder-Filled Polypropylene Composites," *Polymer-Plastics Technology and Engineering*, Volume 42: 5, pp. 827- 851 (2003).
15. Mousa, A., G. Heinrich, U. Wagenknecht, "Thermoplastic Composites Based on Renewable Natural Resources: Unplasticized PVC/Olive Husk." *International Journal of Polymeric Materials*, Volume 59, pp. 843-853 (2010).
16. Mousa, A., G. Heinrich, U. Gohs, R. Hassler and U. Wagenknecht, "Application of Renewable Agro-waste Based Olive Pomace on the Mechanical and Thermal Performance of Toughened PVC." *Polymers-Plastics Technology and Engineering J*; Volume 48, pp. 1030-1040 (2009).
17. Mousa, A., G. Heinrich, U. Wagenknecht, "Cure Characteristics and Mechanical Properties of Carboxylated Nitrile Butadiene Rubber (XNBR) vulcanizate reinforced by Organic Filler," *Polymers-Plastics and Technology and Engineering*, Volume 50, pp. 1388-1392 (2011).
18. Din, R.H., L. Musa, A.A Aziz and G.-S. Tay, "Unsaturated Polyester-Kenaf Composites: The Effects of a Modified Montmorillonite Filler on the Tensile Properties," *Polymer-Plastics Technology and Engineering*, Volume 49: 9, pp. 929-937 (2010).
19. Anuar, H., Ahmad, S.H. , Rasid, R. and Daud, N.S. Nik, "Tensile and Impact Properties of Thermoplastic Natural Rubber Reinforced Short Glass Fiber and Empty Fruit Bunch Hybrid Composites," *Polymer-Plastics Technology and Engineering*, Volume 45: 9, pp. 1059-1063 (2006).
20. Ismaeil, Ghasemi and Behzad Kord. "Long-term water absorption behaviour of polypropylene/wood flour/organoclay hybrid nanocomposite," *Iranian Polymer Journal*, Volume 18 (9), pp. 683-691 (2009).

A FEASIBILITY STUDY OF RECYCLING OF CONSTRUCTION AND DEMOLITION WASTE FOR STRUCTURAL PURPOSES

Leila Seleme Mariano

Brasilian Air Force – Integrated Air Traffic and Control Center – CINDACTA II

Marienne do Rocio de Mello Maron da Costa

Parana Federal University / Department of Civil Engineering / Civil Engineering Post-Graduate Program

Maria Cristina Borba Braga*

Parana Federal University / Department of Hydraulics and Sanitation / Water Resources and Environmental Engineering Post-Graduate Program

ABSTRACT

The environmental problems related to construction and demolition waste involve their final disposal and the use of raw materials. The main goal of this research was to manage on site construction and demolition waste and generate concrete for structural purposes by processing concrete and mortar wastes. A Construction and Demolition Waste Management Plan (CDWMP) was developed for this study and applied by means of the implementation of recycling procedures. This plan included quantifying wastes and analyzing their generation. The concrete and mortar wastes were separated for recycling to produce concrete in which these wastes, respectively, replaced fractions of coarse aggregate (crushed stone) and fine aggregate (sand). Tests were carried out to characterize the resulting concrete and the aggregates used. The strength of the concrete generated varied from 6 MPa to 21.4 MPa, for the same mixture. It was observed that structural concretes can be produced using recycled aggregates, however this cost is higher compared to that of concrete produced with conventional aggregates. It was also concluded that despite the cost of concrete production, there were environmental and economic advantages to performing and applying the CDWMP to this specific construction site.

Keywords: construction and demolition waste, CDW management, CDW recycling, large CDW generators, structural concrete

INTRODUCTION

Construction is one of the industries that use major quantities of non renewable resources and also generates the greatest amount of wastes. However, CDW disposal is not the only

environmental problem related to construction sites because the use of raw materials also causes environmental impacts.

The importance of sustainable waste management is evident, but its implementation also depends on public policies and the ability of governments to retrace responsibilities to potential generators (Costa *et al.*, 2007; Nitivattananon,

*Correspondence author: Universidade Federal do Paraná, Setor de Tecnologia, Departamento de Hidráulica e Saneamento, Centro Politécnico – Jardim das Américas, CxP 19011, 81531-980 Curitiba – Paraná – BRAZIL, Email: crisbraga@ufpr.br

Borongan, 2007). Waste management provides environmental benefits, economic optimization, acceptability and equity. In particular, governments that do not have the strength to lead the CDW management ultimately bear the consequences of a production of large amounts of these wastes and the depletion of landfills, rather than ensuring the well being of future generations, as it occurred in Hong Kong, for instance (Chung and Lo, 2003).

In Brazil, CONAMA Resolution nº 307/02 establishes criteria and guidelines for the management of construction and demolition waste. This legal instrument, as specified, should be used as a basis for the Federal District as well as municipal administrations to write decrees or laws aiming at waste generators, especially those responsible for the production of large amounts. Thus, in order to comply with legal specifications, those waste generators should prepare and present to the local environmental agency Construction and Demolition Waste Management Plans (CDWMP) (CONAMA, 2002).

According to the results produced by the census of sanitation (IBGE, 2008), in Brazil, approximately 28% of the municipalities dispose of their wastes in sanitary landfills and 29% collect and recycle construction and demolition waste. Thus, it could be assumed that most of the CDW are disposed of inappropriately.

An alternative to avoid CDW inadequate disposal is their recycling to produce concrete. However, it has to be established appropriate amounts of waste aggregates to substitute raw materials in the production of structural concrete (Richardson *et al.*, 2010). The importance of this consideration is related to some factors that affect the workability of concrete, such as size distribution of the aggregate, shape of the aggregate particles, gradation and relative proportions of the fine and coarse aggregate, plasticity, cohesiveness, and consistency of the mix (DOT, 2003).

Other option for CDW utilization would be in paving as base and sub-base layers. Another use could be the disposal in landfills, as cover material. Nevertheless, in order to avoid diminishing the useful life time of landfills the latter option should be considered with caution (Huang *et al.*, 2002).

Therefore, management, preparation and recycling of construction waste for structural reuse are important when the environmental, economic and the legal perspectives are considered.

The main goals of this research was to define and implement waste management actions in a 4,000 m² construction site, as well as to produce concrete for structural purposes by processing concrete and mortar wastes.

MATERIALS AND METHODS

The site used as a case study for this research was a school, which was built in Campo Largo – State of Parana, Brazil, with a total area of 4,465,45 m².

Firstly, the Waste Management Plan for the construction site was prepared. For this the construction wastes were characterized as class A, B, C and D according to a Brazilian legal instrument, the Resolution CONAMA 307/02

(CONAMA, 2002). Secondly, a talk was given to the workers at the construction site to provide information about the activities to be performed in order to implement the Management Plan.

In a following stage, a reduction of waste generation was studied for each type of waste. A broad study was carried out in order to purchase materials in such a way as to reduce the amount of waste produced in relation to appropriate use, transport and storage. On the other hand, the possibility of recycling was studied individually, for instance, concrete and ceramic wastes were recycled for non-structural filling; mortar waste was reused to make new mortars; wood waste was classified as reusable and stored, whereas those considered either non-reusable or non-recyclable were donated to third parties. Wastes such as plaster, glass, PVC and acrylic were considered of being related to the responsibility of the suppliers and were disposed of according to specific legislation. Other wastes were evaluated, identified as reusable/recyclable or non-reusable/non-recyclable, and disposed of according to Resolution CONAMA 307/02 (CONAMA, 2002). It should be pointed out that to comply with the established management plan, the construction wastes were segregated as they were being generated and, when necessary, identified and disposed of at separate sites.

The wastes were quantified by calculating the amount of waste generated, or by determining the mass, using a Filizola anthropometric scale, model 34, with a capacity for 150 kg and 100g graduation.

The aggregates and concrete were characterized according to the flowsheet shown in Figure 1.

Flowcheet for the Characterization of Concrete Aggregates

The materials selected were type I sand, type II sand, crushed stone, mortar waste and concrete waste. The concrete made using these aggregates contained natural and recycled aggregates in its composition. Analyses were performed to characterize the natural and recycled aggregates and tests were performed to characterize the concrete made based on these aggregates.

Thus, the analyses of seven parameters were carried out for the aggregates selected, as follows: grain size, grain morphology, thermogravimetry (TG), X-ray diffraction (XRD), potential reactivity, compressive strength and permeability.

The determination of the grain size was used to set grain size distribution due to the expectation that the particles of mortar waste were to be within the limits of the grain size of sand, and the particles of concrete waste was to be within the limits of the grain size of crushed stone. The limits are specified by a Brazilian technical standard, the NBR 7211:2009 (Aggregates for Concrete / Specification). In order to characterize the aggregates, mechanically shacked sieves were used. Coarse aggregates were sieved using a Soloteste equipment, whereas fine grained aggregates were sieved using a Bertel equipment. The mesh of the sieves varied from 4.8mm to 0.15mm for coarse aggregates and from 38mm to 4.8mm for fine grained aggregates.

As aggregate grain shape affects different features of

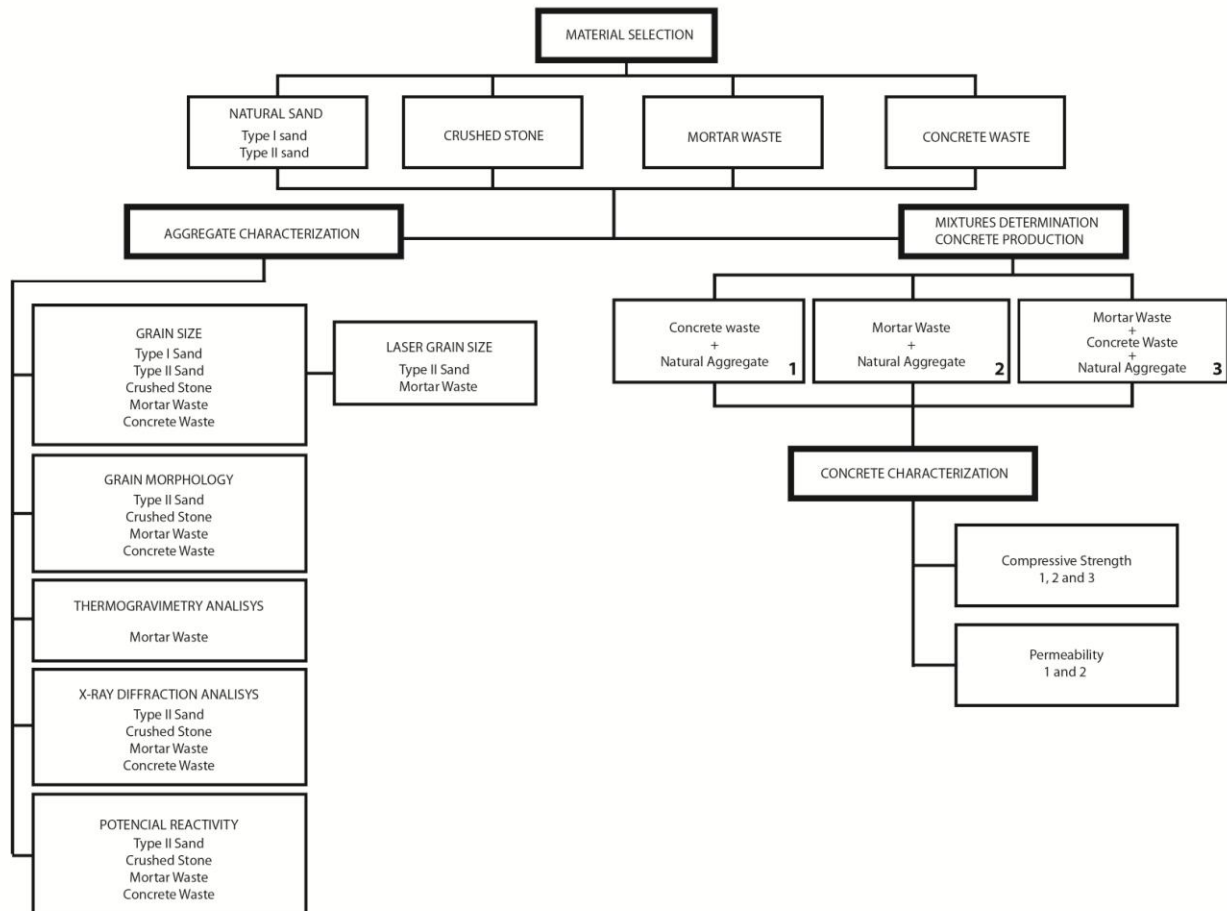


FIGURE 1
Flowcheet for the Characterization of Concrete Aggregates

material structure, and as a consequence affects mechanical properties of the concrete, it was necessary to determine grain morphology of the materials used. Thus, to carry out this test a Leica stereomicroscope was used. Through the determination of these parameters it can be evaluated the effect of the use of this aggregates on the workability of concrete.

The TG analysis was used to pre-identify components of the aggregates. In a controlled atmosphere, this test allows the assessment of material thermal stability through the determination of the temperature at which the materials change weight. This test was carried out using a Mettler-Toledo equipment, TGA/SDTA851, at 1 atm of oxygen, with temperature varying from 30° C to 1000° C at a heating rate of 10° C per minute.

The XRD analysis is used to determine the arrangement of atoms within a crystal. This characteristic can influence the quality of the concrete. To carry out this test, a Phillips Analytical equipment, PW2273/20, was used.

The potential reactivity determines the reactivity between cement and the aggregates utilized in concrete preparation. This parameter is evaluated through the percentage of expansion of concrete test specimens. Samples of cement, raw and recycled materials were used to carry out this test and the method ASTM C1260-07 (Standard Test Method For Poten-

tial Alkali Reactivity of Aggregates / Mortar-Bar Method) was used.

In order to characterize the concrete produced by waste recycling compressive strength and permeability tests were performed. According to a Brazilian technical standard, the NBR 19431:2004 (Execution of Concrete Structures / Procedure), for the production of structural concrete a resistance less than or equal to 15 MPa is specified. In order to comply with this specification another Brazilian technical standard should be considered, the NBR 10786:1989 (Hardened Concrete - Determination of the Water Permeability Coefficient / Method of Test), which specifies a range for the permeability coefficient (k) varying from 10⁻⁷ cm/s to 10⁻⁹ cm/s.

Regarding concrete production, masonry and concrete wastes replaced either partially or completely, sand and crushed stones, respectively. The quality of these materials was verified by visual inspection, and sieving was performed for the mortar wastes. Concrete traces, i. e., the proportion of sand and cement used in the mixture, were determined for the cases in which the recycled wastes replaced the natural aggregates by 33%, 66% and 100%.

The construction was monitored for a period of twelve months and the implementation of the On Site Construction Waste Management Program was conceived to comply with

Decree n° 1.111/06 of the Municipality of Ponta Grossa, State of Parana, Brazil.

RESULTS AND DISCUSSION

In order to compare the amount of waste produced by this work with those generated elsewhere, a generation index, which is calculated by dividing the mass of residues (kg) and the worked area (m²), was calculated.

Waste quantification resulted in a generation index of 34.2 kg/m², which was compared to other references (Table 1).

Comparison of Results of CDW Produced

The results produced by Tozzi and Braga (2007), which only concerned construction, presented an index of 42.9 kg/m², whereas results presented by Monteiro (2001), considering both construction and demolition waste, presented an index of 300 kg/m². According to this author, construction sites that implement waste management programs produce a significantly smaller amount than the Brazilian average,

which is 300 kg/m². Therefore, in this case, the results produced by Tozzi and Braga (2007) are more appropriate for comparison.

When the value obtained by this research is compared to that of Bohne (2005), who obtained a generation index of 30.8 kg/m² for constructions of similar sizes, it can be observed that almost the same total amount of waste was generated, and the difference between them is approximately 10%. Another example is the result produced by Kibert (2002), which presented a waste generation index of 27 kg/m², a 20.9% difference in generation, when compared to those produced by this research (34.2 kg/m²). However, an analysis of waste generation in construction sites managed both in Brazil and abroad shows that the construction procedures and the materials used are different, and therefore the comparison between national and international references is inappropriate.

The efficiency of the program was measured by the percentage of the materials that was not discarded, but on the other hand, was recycled or reused. The results produced by this study allow to point out that a total efficiency of waste reduction and recycling of approximately 96% was achieved, when compared to the total amount of purchased material, as

TABLE 1
Comparison of Results of CDW Produced

<i>Material</i>	Amount of CDW produced (kg/m ²)			
	<i>The studied site</i>	<i>Monteiro, 2001</i>	<i>Bohne et al., 2005</i>	<i>Tozzi & Braga, 2006</i>
Concrete	9.08		19.11	3.02
Ceramic	2.55	87.00	--	17.65
Mortar	2.93	189.00	--	18.33
Wood	16.82	3.00	2.75	0.87
Toxic wastes	--	--	0.07	--
Gypsum	--	--	1.38	--
Glass	--	--	0.12	--
Insulation materials	--	--	0.21	--
Metals	--	--	0.48	--
Paper	0.16			0.58
Plastics	0.04		0.46	
Asbestos cement	0.63		0.00	
Other/unknown	1.94	21.00	6.19	2.43
<i>Total</i>	34.15	300.00	30.77	42.89

TABLE 2
Program Efficiency and Savings Generated by the Implementation of Onsite CDWMP

Program Efficiency			
<i>Material</i>	<i>Amount Gained (t)</i>	<i>Amount Wasted (t)</i>	<i>Efficiency (%)</i>
Concrete	2,175.38	40.54	98.14
Ceramic	508.72	11.38	97.76
Mortar	629.78	13.07	97.92
Asbestos cement	27.55	2.81	89.80
Wood	88.34	75.10	14.98
<i>Total</i>	3,429.77	142.90	95.83

Savings Generated by the Implementation of the Cdwmp			
<i>Waste</i>	<i>Amount Gained as a Result of Reuse of Materials (US\$)</i>	<i>Amount Gained as a Result of Non-payment for Collection and for Non- disposal (US\$)</i>	<i>Total Amount Saved per Tipe of Waste (US\$)</i>
Concrete	720.93	376.13	1,097.06
Ceramic	413.39	215.67	629.06
Mortar	157.64	64.54	222.18
Asbestos cement	--	42.50	42.50
Wood	3,720.96	375.91	4,096.87
Paper	--	10.23	10.23
Plastic	--	1.59	1.59
<i>Total amount saved (US\$)</i>			6,099.49
<i>Amount saved per area (US\$/m²)</i>			1.36

shown in Table 2.

Program Efficiency and Savings Generated by the Implementation of Onsite CDWMP

Analyzing each material separately, wood was related to the lowest recycling and reutilization efficiency, with an efficiency of 15 %. Therefore, it is worth mentioning that the procedures involving this material must be studied to diminish its generation. The other materials reached higher efficiency, above 85%, which was considered satisfactory.

The economy generated by the implementation of the recycling program was US\$ 6,099.49, as a total amount saved, and US\$ 1.36 per square meter constructed, which was

not a significant value compared to the overall value of the construction site. Nevertheless, it is environmentally very important, since it is related to a reduction of raw materials extraction and a more appropriate disposal of wastes (Table 2).

As presented in the material and methods section, the aggregates used in concrete production were characterized by analyses of grain size, morphology, TG, XRD and potential reactivity. However, it has to be mentioned that due to the different characteristics in the fresh state, the larger amount of fines present in the aggregates from recycled wastes affected the workability of the concretes produced using these materials.

The results obtained from the analysis of particle grain size are presented in Figures 2 and 3.

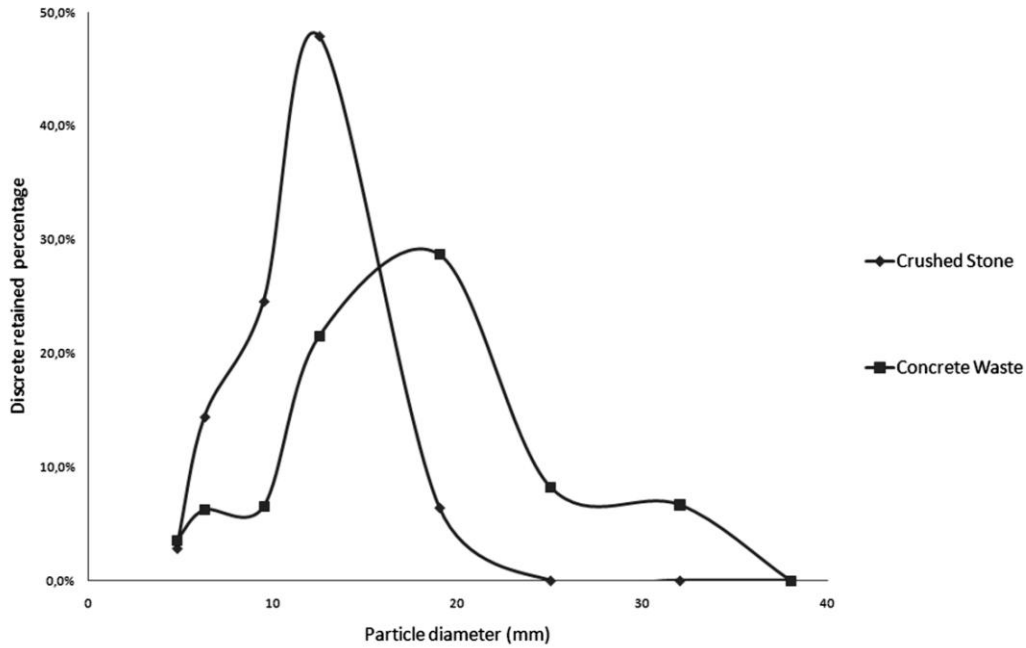


FIGURE 2
Grading of Concrete Aggregates - Crushed Stone *Versus* Concrete Waste

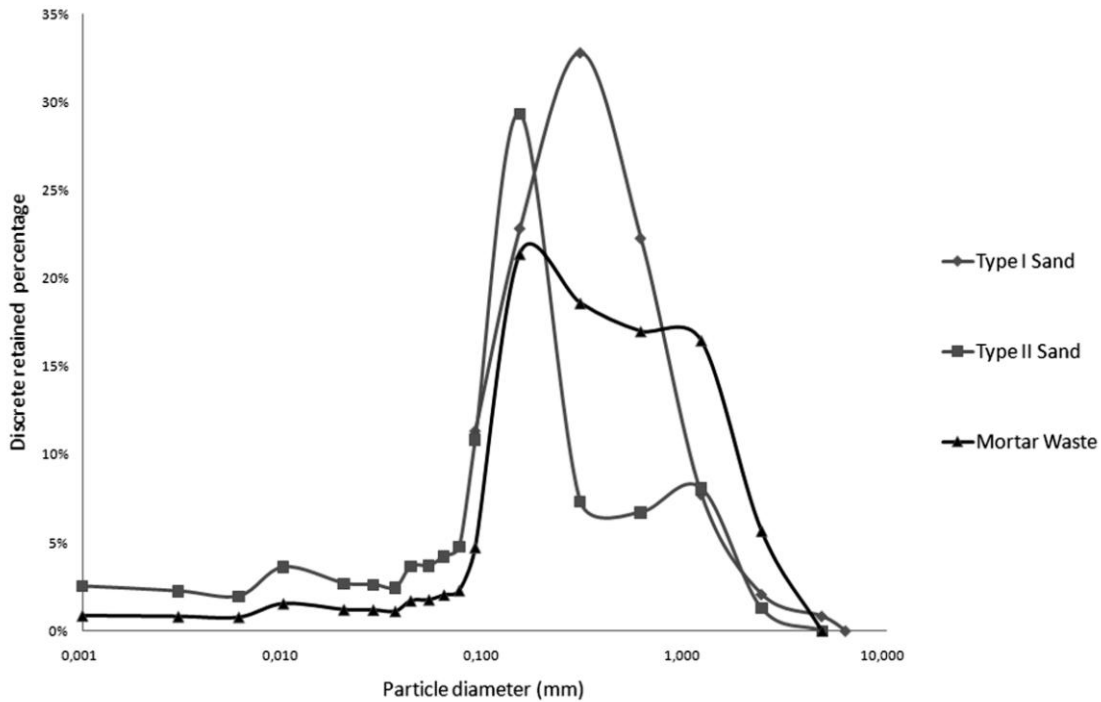


FIGURE 3
Grading of Concrete Aggregates - Sand Type I, Sand Type II and Mortar Waste

Grading of Concrete Aggregates - Crushed Stone *Versus* Concrete Waste

Morphological analysis showed that the natural and recycled aggregates presented the same characteristics of sphericity, roundness and grade designation. The sand and mortar wastes presented high sphericity, sub-angulous roundness and, in terms of grade designation, their selection was designated as well-graded. Morphological analysis made possible to observe the roughness of the materials analyzed, and that

ricity, roundness and grade designation. The sand and mortar wastes presented high sphericity, sub-angulous roundness and, in terms of grade designation, their selection was designated as well-graded. Morphological analysis made possible to observe the roughness of the materials analyzed, and that

recycled aggregates are rougher than natural aggregates (Figure 3), which influences the workability and strength of the concrete.

Grading of Concrete Aggregates - Sand Type I, Sand Type II and Mortar Waste

Quartz, calcite, dolomite, gypsite, portlandite, and hydrated calcium silicate were identified in the mortar waste by means of TG and XRD tests. Through X-ray diffraction, quartz was identified in sand, crushed stone and quartz, portlandite and hydrated calcium silicate were identified in the concrete waste. These results show that the natural and recycled aggregates have different chemical compositions, and therefore, when the production of structural concrete is considered these characteristics have to be carefully considered.

The results of the potential reactivity test showed that only crushed stone is inert, the type II sand, the concrete waste and the mortar waste are reactive and need further studies to de-

termine whether they are deleterious to the resulting concrete to be composed.

In order to determine the compressive strength of the concrete generated with recycled and reused materials, the breakdown of test specimens at 7, 14 and 28 days was performed with simple compression. The results presented values which varied from 6 MPa to 21MPa at a 28-day interval. Concrete generated with type I sand showed a better result, 21.4 MPa at 28 days for the trace that replaced 66% of the crushed stone by concrete waste. The results of compressive strength of the concretes generated with type I sand are shown in Table 3.

Compressive Strength of Various Trace Base Tested for Concrete Production

In order to plot the concrete behavior curves, the concretes produced with a 66% replacement of crushed stone were re-elaborated. It has to be mentioned that these were the concretes that attained an approximate compressive strength of

TABLE 3
Compressive Strength of Various Trace Base Tested for Concrete Production

<i>Mixture</i>	Compressive strength at 7 days (MPa)		Compressive strength at 28 days (MPa)	
	<i>Series 1</i>	<i>Series 2</i>	<i>Series 1</i>	<i>Series 2</i>
Trace Base	11.7	--	19.4	--
concrete 33%	9.8	13.5	16.6	19.1
concrete 66%	15.0	12.2	21.4	16.6
concrete 100%	11.8	10.7	18.8	14.3
mortar 33%	10.2	--	13.8	--
mortar 66%	12.0	--	16.6	--
mortar 100%	8.9	--	10.9	--
mortar 33% and concrete 100%	6.4	--	10.2	--
mortar 33% and concrete 66%	8.1	--	10.9	--
mortar 33% and concrete 33%	10.3	--	15.3	--
mortar 66% and concrete 100%	4.6	--	5.1	--
mortar 66% and concrete 66%	8.1	--	9.7	--
mortar 66% and concrete 33%	8.9	--	11.5	--
mortar 100% e concrete 100%	3.8	--	5.1	--
mortar 100% and concrete 66%	5.9	--	6.4	--
mortar 100% and concrete 33%	6.9	--	8.7	--

20 MPa.

The lowest values (Table 4) were obtained in this trace using type II sand, and compressive strength curves as a function of time indicated stabilization with increased compressive strength (Figure 4).

Compressive Strength Determined for the Concrete Mixture Produced with 66% Replacement of Crushed Stone

Compressive Strength versus Time

The concretes generated using type II sand presented a low performance, i.e., a compressive strength lower than specified by the Brazilian standard (15 MPa) was not reached. This was due to the high presence of fines in the aggregates replaced and in the sand. When these fines absorb water they may impair the workability of concrete, increase the void index and partly prevent hydration of the cement. Taking the morphological characteristics and differences in the aggregate grain size into account, their workability were certainly different, determining different performances in molding the test specimens. In this case voids were clearly observed in the test specimens, which affected the uniformity of the strength among them, as well as the strength of the concretes. It should be mentioned that the water/cement ratio was kept constant for all concretes.

For the permeability tests, the concrete generated with masonry wastes presented a value of 2.12×10^{-7} cm/s, whereas the result for the concrete generated with concrete wastes was 1.88×10^{-7} cm/s, both produced at 32 days. The concrete generated using wastes absorbed more water due to their larger specific surface and higher content of fines in the wastes. Water absorption is undesirable, since it impairs the workability of concrete and generates a high void index. The concrete generated with mortar wastes is more pervious since the specific surface present in the mixed aggregates is quantitatively larger compared to the concrete generated with con-

crete wastes. Therefore, the increase in the void index of the mixture resulted in a reduction of the workability of concrete, noticed when difficulties in molding occurred. Comparing these results with the permeability of conventional concrete, which varies from 10^{-7} cm/s to 10^{-9} cm/s, it can be deduced that the concrete generated from recycled aggregates is of a similar quality.

The advantage related to the implementation of this program could be observed when a total amount of US\$ 6.099,49, and a value of US\$ 1.36 per square meter constructed were considered. Thus, it is worth mentioning that 125 m³ of wastes were not disposed of in landfills or other areas, and that 45.5 m³ of natural aggregates were not exploited.

CONCLUSIONS

If the size of the construction site is taken into account and also considering that the wastes had a low specific generation (34.2 kg/m²), it can be pointed out that the method adopted for the management of the 4,000 m² construction waste was effective. The implementation of the On Site Construction Waste Management Program allowed waste recycling of approximately 96%. The lowest result was obtained for wood, which was only 15%.

The results of grain size analyses showed that the natural and recycled aggregates presented similar sizes, however, it was observed that the recycled presented larger amounts of fines, which affected the workability of the concrete. Results of morphology tests showed that the recycled aggregates presented the same sphericity, roundness and grade designation. These analyses classified the aggregates as well-graded, and showed that recycled aggregates presented higher roughness than natural aggregate, which influences the workability and compressive strength of the concrete. TG and XRD showed that the natural and recycled aggregates presented different chemical compositions, thus necessitating being

TABLE 4
Compressive Strength Determined for the Concrete Mixture Produced with 66% Replacement of Crushed Stone

Mixture	Series	Compressive strength (MPa)		
		7 Days	14 days	28 days
Concrete waste 66%	1	4.6	4.6	6.3
	2	5.0	5.0	6.4
	3	4.6	4.6	6.3
	4	4.3	4.3	6.5
	5	4.6	4.6	6.1
	Average	4.6	4.6	6.3

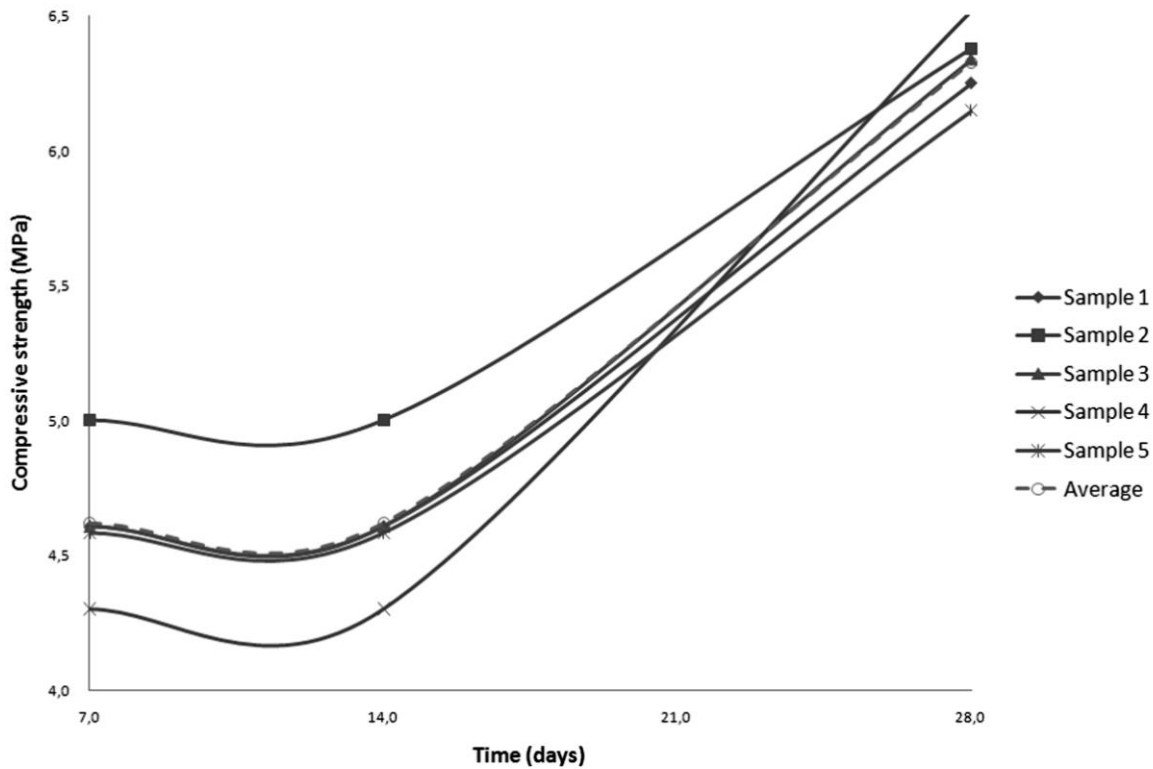


FIGURE 4
Compressive Strength versus Time

considered differently when concrete composition is to be defined. The results of the potential reactivity test showed that only crushed stone were inert. The type II sand, the concrete waste and the mortar waste were reactive and further studies are needed to determine whether they are deleterious to the composition of structural concrete.

The permeability test, applied on concrete, showed that the concrete produced with recycled and reused materials were the same quality as the concrete produced with natural materials. The compressive strength of the concrete reached values which varied from 6 MPa to 21MPa, at a 28-day interval. Concrete generated with type I sand showed a better result, 21.4 MPa at the same period of time for the trace that replaced 66% of the crushed stone by concrete waste.

The results of this research allow concluding that the concrete generated from recycled aggregates can be produced with structural characteristics. However, it is more expensive than the concrete from natural aggregates. This can be explained by the fact that to produce concrete from recycled aggregates a major amount of cement is needed to achieve the same compressive strength. It has also to be mentioned that the concrete produced from recycled aggregates is less durable. Thus, a prior study to determine the additives to be used to improve concrete workability as well as physical and chemical characteristics of the aggregates used is of great importance.

It should be pointed out that the natural aggregates are finite, that the disposal of construction waste also incurs costs, and that options to replace them should be considered,

since they soon will no longer be optional, and recycling will become mandatory.

REFERENCES

- Bohne, R.A., "Dynamic eco-efficiency Modeling for Recycling of C&D Waste," Norwegian University of Science and Technology - Industrial Ecology Programme, 2005.
- Costa, N., N. Costa Jr., M. Luna, P. Selig, J. Rocha, "Planejamento de Programas de Reciclagem de Resíduos de Construção e Demolição no Brasil: uma Análise Multivariada (Planning of Construction and Demolition Waste Recycling Programs in Brazil: a Multivariate Analysis)," *Engenharia Sanitária e Ambiental*, Volume 12, No. 4, 2007, pp. 446-456. (in Portuguese).
- DOT - Minnesota Department of Transportation, Concrete Manual, "Chapter 2: Properties and Mix Designations," series 6-694.200, 2003, [<http://www.dot.state.mn.us/materials/manuals/concrete/Chapter2.pdf>]. May 2011.
- IBGE - Instituto Brasileiro de Geografia e Estatística (Brazilian Institute of Geography and Statistics). "Pesquisa Nacional de Saneamento Básico 2008 (Census of Sanitation 2008)."[http://www.ibge.gov.br/home/estatistica/populacao/condicaodevida/pnsb2008/PNSB_2008.pdf], May 2011. (in Portuguese)
- Kibert, C.J., "Policy Instruments for a Sustainable Built Envi-

- ronment,” *J. Land Use and Environmental. Letters*, Volume 17, No 2, 2002, pp. 379-394.
- CONAMA - Conselho Nacional do Meio Ambiente (Brazilian Council of Environment), Resolução CONAMA nº 307 - Diretrizes, Critérios e Procedimentos para a Gestão dos Resíduos da Construção Civil (Resolution nº 307/02 – Directives, Criteria and Procedures for CDW Management, 2002. (In Portuguese)
- Chung, S., C.W.H. Lo, “Evaluating sustainability in waste management: the case of construction and demolition, chemical and clinical wastes in Hong Kong.” *Resources. Conservation and Recycling*, Volume 37, 2003, pp. 119-145.
- Huang, W., D. LIN, N. Chang, K. LIN, “Recycling of Construction and Demolition Waste Via a Mechanical Sorting Process,” *Resources Conservation and Recycling*, V.37, 2002, pp.23-37.
- Monteiro, J.H.P., C. E.M. Figueiredo, A.F. Magalhães, M.A.F. Melo, J.C.X. Brito, T.P. Almeida, G.L. Mansur, “Manual de Gerenciamento Integrado de Resíduos Sólidos (Handbook of Integrated Solid Waste Management).” Rio de Janeiro: IBAM, 2001.
- Nitivattananon, V., G. Borongan, “Construction and Demolition Waste Management: Current Practices in Asia,” *Proceedings of the International Conference on Sustainable Solid Waste Management*, September 2007, pp.97-104.
- PMPG - Prefeitura Municipal de Ponta Grossa (Municipality of Ponta Grossa), “Decreto nº 1.111 - Plano Integrado de Gerenciamento de Resíduos da Construção Civil do Município de Ponta Grossa (Decree 1.111 – Integrated Construction and Demolition Waste Management Plan,” 2006. (In Portuguese)
- Richardson, A., P. Allaim, M. Veuille, “Concrete with Crushed, Graded and Washed Recycled Construction Demolition Waste as a Coarse Aggregate Replacement.” *Structural Survey*, Volume 28, 2010, pp. 142-148.
- Tozzi, R.F., M.C.B. Braga, “Caracterização, Avaliação e Gerenciamento da Geração de Resíduos da Construção Civil (RCC) em Duas Obras no Município de Curitiba, Brasil (CDW Characterization, Evaluation and Management in two construction sites in Curitiba, Brazil,” *Engenharia e Construção*, Volume 10, No. 2007, 127, 35-40. (in Portuguese)

EXPERIMENTAL STUDY ON ABRASION RESISTANCE OF CONCRETE CONTAINING SCRAP RUBBER POWDER

Baomin Wang^{1*}, Yu Han¹, Ni Tu¹, Hongmei Ai¹, Tingting Zhang^{1,2}

¹Faculty of Infrastructure Engineering, Dalian University of Technology
Dalian 116024, CHINA

²Department of Civil and Environmental Engineering, Imperial College London
London SW7 2AZ, UK

ABSTRACT

The abrasion resistance of cement concrete containing scrap rubber particles by use of the test method specified in *Chinese Test Method of Cement and Concrete for Highway Engineering JTGE30-2005* was researched in this paper. The test results showed that rubberized concrete had higher abrasion resistance compared with ordinary concrete, and its abrasion resistance had no inevitable relation with compressive strength. The abrasion resistance of rubberized concrete was reduced along with the increasing of water-cement ratio; the abrasion loss per unit area of rubberized concrete with water-cement ratio of 0.42 was decreased by 27% and 100% respectively compared with the rubberized concrete with water-cement ratio of 0.54 and 0.66. Along with the addition of rubber powder, the abrasion resistance of concrete was improved first and then reduced; when the content of rubber powder was more than 10kg/m³, the abrasion resistance of concrete would be reduced. Among the three different rubber powder with particle size of 80-mesh, 100-mesh and 120-mesh respectively, the concrete containing 100-mesh rubber powder had the best abrasion resistance, with abrasion loss per unit area decreased by 39% and 4% respectively compared with the concrete containing 80-mesh and 120-mesh rubber powder.

Key Words: Rubber powder, concrete, abrasion resistance

INTRODUCTION

The abrasion is a degradation phenomenon unique to cement concrete pavement, also an important topic in the durability of concrete research [1]. The abrasion resistance is not only the prerequisite to skid resistance, but also the important index of influencing safety and durability. In recent years, along with the development of Chinese national economy and transportation business, massive cement concrete pavements

had been built, however, many pavements suffered from bare surface, concrete stripping even pot holes soon after being open to traffic, which seriously influence the use of concrete pavements. As a result, it is of great significance to research the abrasion mechanism, degradation process of concrete and putting forward the improvement measures.

Rubberized concrete was a new-type concrete which has drawn wide attention in recent 20 years. Some researches showed that special advantages of cement concrete, such as

Corresponding author: Tel.: +86 137 0494 3503; Fax: +86 411 8470 7171; Email address: wangbm@dlut.edu.cn

Address: The First Comprehensive Experimental Building NO.217, Dalian University of Technology, Linggong Road No.2, Ganjingzi district, Dalian city, Liaoning Province, P.R.CHINA

better crack resistance^[2-4], higher toughness^[5-6], good frost resistance^[7-8] and impact resistance^[9-11], can be realized by admixing the rubber powder made of scrap tire. Recycling of massive scrap rubber can solve worsening black pollution.

Admixing rubber powder into cement concrete was a way of modifying cement concrete pavement. The abrasion resistance of concrete has direct influence on expanding its application range in pavement, but there were less literatures regarding the abrasion resistance of rubberized concrete. The influences of water-cement ratio, content and particles size of rubber powder on abrasion resistance of rubberized concrete was researched in this paper, and provided some references for the further application of rubberized concrete to practical engineering projects.

MATERIALS AND METHODS

Cement. P·O42.5R, made by Dalian Onoda Cement Co., Ltd., see Table 1 and Table 2 for detailed indexes.

Coarse Aggregate. 5-25mm continuously graded, apparent density of 2810kg/m³, bulk density of 1540 kg/m³, packed density of 1660kg/m³, crushing index of 3.05%. Coarse aggregate was cleaned by tap water and dried before test, and its silt content and moisture content could be ignored.

Fine Aggregate. river sand, with fineness modulus of 2.7, medium sand of Zone II, apparent density of 2630kg/m³, bulk density of 1270kg/m³, packed density of 1460 kg/m³, silt content of 2.8%. Fine aggregate was dried before test, and its moisture content could be ignored.

Admixture. SW-4 super-plasticizer made by Dalian Shenwei Building Materials Co., Ltd.

Rubber Powder. 80-mesh, 100-mesh and 120-mesh scrap tire

rubber powder, made by Sichuan Luyuan Science & Technology Co., Ltd., with density of 1.116g/cm³, average particle size of 173μm, 140μm and 119μm respectively, rubber powder surface is not smooth and appears to be burr-shape connected.

Mix Proportion. The mix proportion adopted in this test is shown in Table 3:

Test method. The concrete was mixed by forced mixer and molded by vibration; the workability of concrete mixture was tested according to GB/T50080-2002 *Standard for Test Method of Performance on Ordinary Fresh Concrete* before molding. In this test, 8 groups of concrete samples were all of the slump of 150mm~180mm.

The sample for abrasion test was cubic with dimensions 150mm×150mm×150mm, each group included 3 samples.

The sample for strength test was cubic with dimensions 100mm×100mm×100mm, each group included 3 samples. The test was conducted according to GB/T50081-2002 *Standard for Test Method of Mechanical Properties on Ordinary Concrete*.

The test method was as follows: after standard curing of 27 days, taken out the abrasion sample from the curing place, air-dried it for 12h indoors after removing surface moisture, then putted it in 60°C±5°C drying oven for 12h up to constant weight. Clamped the sample firmly on the abrasion wear test machine with knurl wheel grinding head and grinded it for 30 revolutions at the load of 200N, removed the sample and weigh it after eliminating surface dust, recorded the related mass m₁ as initial mass of sample, then grinded it for 60 revolutions at the load of 200N, removed the sample and weighed it after eliminating surface dust, recorded the remaining mass m₂. Calculated the abrasion loss of each sample according to the following formula, indicated it by abrasion loss per unit

TABLE 1
Chemical composition of the cement (w%)

CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	SO ₃	MgO	Na ₂ O _{eq}
61.13	21.45	5.24	2.89	2.50	2.08	0.77

TABLE 2
Physical properties of the cement

Loss on ignition (%)	Specific surface area (m ² /kg)	Setting time (min)		Soundness	Compressive strength (MPa)		Flexural strength (MPa)	
		Initial setting	Final setting		3d	28d	3d	28d
3.52	330	187	239	Qualified	28.5	52.5	6.0	8.2

TABLE 3
Mix proportion of concrete

No.	Water-cement ratio	Sand percentage (%)	Water (kg)	Cement (kg)	Sand (kg)	Gravel (kg)	Plasticizer (%)	Rubber powder (kg)
1	0.42	39	190	452	678	1060	0.7	0(100-mesh)
2	0.42	39	190	452	678	1060	0.8	10(100-mesh)
3	0.42	39	190	452	678	1060	1.0	20(100-mesh)
4	0.42	39	190	452	678	1060	1.2	30(100-mesh)
5	0.42	39	190	452	678	1060	1.0	20(80-mesh)
6	0.42	39	190	452	678	1060	1.0	20(120-mesh)
7	0.42	39	190	288	718	1124	0.7	20(100-mesh)
8	0.42	41	190	352	733	1055	0.8	20(100-mesh)

area.

$$G_c = \frac{m_1 - m_2}{0.0125}$$

In which: G_c —abrasion loss per unit area (kg/m^2); m_1 —initial mass of sample (kg); m_2 —mass of sample after abrasion (kg); 0.0125—abrasion area of sample (m^2).

The arithmetic mean value of abrasion losses of three samples was taken as the test result, which accurate to $0.001\text{kg}/\text{m}^2$. If the abrasion loss of one sample was 15% higher than mean value, this loss value should be abandoned, then the mean value of abrasion losses of the remaining two samples should be taken as the test result. If the abrasion losses of the two samples were both 15% higher than mean value, the test should be conducted again.

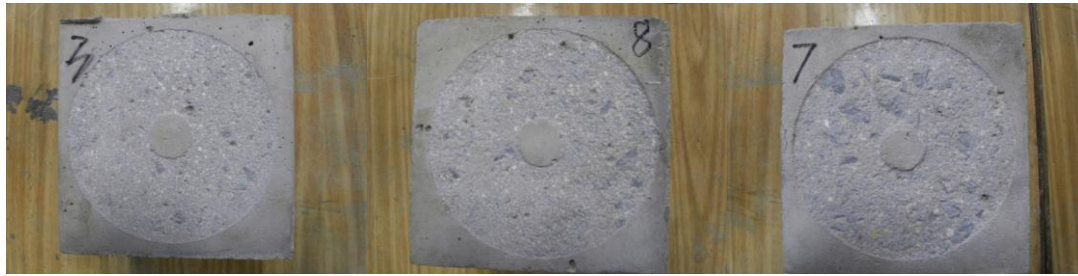
Influence of Water-cement Ratio on Abrasion Resistance of Rubberized Concrete

The abrasion mechanism of concrete may be summarized as follows: firstly, the mortar on the surface of concrete was abraded by knurl wheel with the abrasion depth of several millimeters, then the fine aggregate strips away with the stripping depth of dozens of millimeters, and the coarse aggregate was bared; in this case, abrasion effect was borne by both the mortar and coarse aggregate. Generally the abrasion resistance of coarse aggregate was better than that of the mortar, so coarse aggregate gradually stands out and the cement mortar was worn to be concave; the abrasion effect on convex coarse aggregate was strengthened while the abrasion effect on concave mortar was reduced to some degree. Along with the continuation of abrasion process, coarse aggregate would

easily break away from the matrix in the form of abrasive wear since it cannot connect with mortar due to unsmooth concrete surface, then new mortar would bear the increasing abrasion effect and be gradually abraded. A new round of abrasion begins until next layer of coarse aggregate was bared^[12-14].

Seen from Figure 1, an annular abrasion face with ID of about 30mm and OD of 130mm occurs on the sample surface; the concrete sample 3 only bared a little coarse aggregate with low concavity, the sample 7 bared a lot of coarse aggregate with high concavity, the sample 8 were between them in surface abrasion conditions. It can be seen that the abrasion loss per unit area decreases along with the decreasing of water-cement ratio. While the rubber powder particle size was 100-mesh and the content of rubber powder was $20\text{kg}/\text{m}^3$, the abrasion loss per unit area of rubberized concrete with water-cement ratio of 0.42 was decreased by 27% and 100% respectively compared with the rubberized concrete with water-cement ratio of 0.54 and 0.66, and its compressive strength at 28d curing age was also reduced to 28.3 MPa and 22.3 MPa from 40.0 MPa.

Water-cement ratio had close relation with both compressive strength and abrasion resistance of rubberized concrete. When water-cement ratio decreased, the strength and elastic modulus of concrete were improved to decrease the elastic modulus difference between hardened cement paste and aggregate. The size of hydrate crystalline particle was reduced because of the decreasing of free space for crystal growth, its enrichment degree and orientation degree decreased, and the porosity on the interface zone decreased, which helped to improve the abrasion resistance of concrete. But water-cement ratio cannot decrease without limitation, because it should offered the water content required for complete hydration of cementing materials and ensured the workability in the process of construction.



No.3 specimen

No.8 specimen

No.7 specimen

FIGURE 1

Post-abrasion concavity of rubberized concrete with different water-cement ratios

Influence of rubber powder content on abrasion resistance of rubberized concrete

There were two different viewpoints on the relationship between abrasion resistance and compressive strength of concrete. Some researchers think that the abrasion resistance of concrete was improved along with the increasing of compressive strength, for example Naiqian Feng^[15] mention that the abrasion coefficient would decrease in the form of exponential relationship along with the increasing of compressive strength; some ones^[16-17] thought that linear relation existed between compressive strength and abrasion resistance of concrete, others^[18] thought that there was no inevitable relation between abrasion resistance and compressive strength.

Seen from Figure 2, the compressive strength of concrete was reduced along with the addition of rubber powder, and the strength was in inverse proportion to the content of rubber powder. While rubber powder particle size was 100-mesh and the content of rubber powder was 10kg/m³, 20kg/m³ and 30kg/m³ respectively, the compressive strength of rubberized concrete at 28d curing age would decrease by 14%, 19% and 30% respectively, compared with the ordinary concrete. The reason thereof was that rubber powder, similar to micro-pores of concrete, cannot act as the framework to bear the pressure on concrete. Furthermore, rubber powder was different from the mortar in elastic modulus, the elastic modulus of rubber powder was less than 1/200 of elastic modulus of concrete mortar, and thus the large stress concentration easily happened at the surrounding mortar matrix to result in sample damage. The stress concentration would be increasingly serious along with the increasing of rubber powder content^[19].

It was shown in Figure 3 that, along with the addition of rubber powder, the abrasion resistance of concrete was improved first and then reduced; when the content of rubber powder was more than 10kg/m³, the abrasion resistance of concrete would be reduced. But compared with the ordinary cement concrete without rubber powder, the rubberized concrete types with rubber powder content of 10kg/m³, 20kg/m³ and 30kg/m³ respectively all had higher abrasion resistance, and their abrasion losses per unit area decreased by 64%, 46% and 4% respectively. When the rubber powder content was 20 kg/m³ and 30kg/m³ respectively, the abrasion loss per unit area of rubberized concrete increased by 50% and 167% respectively, compared with the rubberized concrete with rubber powder content of 10 kg/m³. The above analysis showed that the compressive strength of rubberized concrete had no inevitable relation with abrasion resistance.

After been admixed, rubber powder did not participate in chemically react with other components of concrete, and it could be seen as inert filler of concrete. Rubber powder as a highly elastic substance; a certain amount of rubber powder

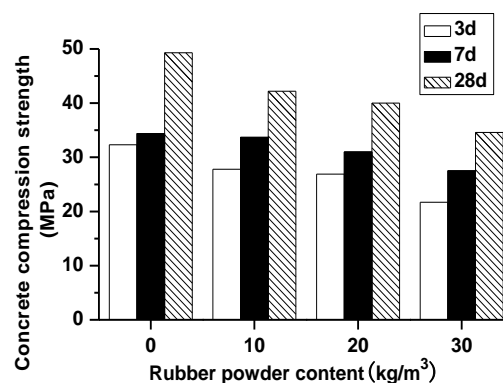


FIGURE 2

Influence of rubber powder content on compressive strength

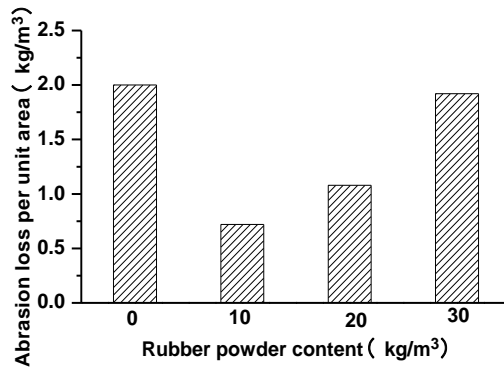


FIGURE 3
Influence of rubber powder content on abrasion resistance

could reduce the stiffness and toughness of concrete, improve the deformability of concrete, effectively decrease and mitigate the friction force caused by friction effect of knurl wheel, and reduce the abrasion of concrete. When the content of rubber powder increased, the interface between rubber powder and the mortar would increase. It was just the weak zone with low adhesive force under the influence of external pressure on rubberized concrete. Under the influence of knurl wheel, it was easily taken away by the friction force and accordingly the abrasion of concrete was worse. It showed that there was a reasonable range for rubber powder content, the abrasion resistance of rubberized concrete would be optimal when the rubber powder content was about 10kg/m³.

Influence of Rubber Powder Particle Size on Abrasion Resistance of Rubberized Concrete

The test results showed(as shown in Figure 4) that the compressive strength of rubberized concrete with rubber powder particle sizes of 80-mesh, 100-mesh and 120-mesh

reaches 41.4MPa, 40.0MPa and 39.8MPa respectively at 28d curing age, all lower than 49.3 MPa, which was the compressive strength of concrete without rubber powder. The smaller the particle size of rubberized powder was, the lower compressive strength of rubberized concrete would be, but only smaller difference existed. If the water-cement ratio was the same and the content of rubber powder was 20kg/m³, the concrete types with rubber powder particle sizes of 80-mesh, 100-mesh and 120-mesh all had higher abrasion resistance and their abrasion losses per unit area were reduced by 12%, 46% and 44% respectively, compared with ordinary concrete without rubber powder. In this case, the relationship that the abrasion resistance of concrete was in direct proportion to compressive strength would not apply.

Among the three kinds of rubber powder with particle size of 80-mesh, 100-mesh and 120-mesh respectively, the concrete containing 100-mesh rubber powder had the best abrasion resistance, with abrasion loss per unit area decreased by 39% and 4% respectively compared with the concrete containing 80-mesh and 120-mesh rubber powder. While the rubber powder had smaller particle size, rubber powder could be evenly mixed into concrete to strengthen internal com-

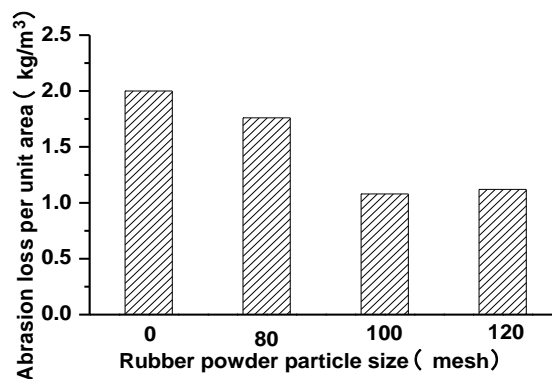


FIGURE 4
Influence of rubber powder particle size on abrasion resistance

pactness; on the other hand, while the particle size was smaller, more rubber powder would be distributed on the binding surface between paste and aggregate, and impaired the binding power thereof, these two effects interacted. Seen from the test results, the concrete had the optimal abrasion resistance when the particle size of rubber powder was 100-mesh.

CONCLUSION

- Rubberized concrete has higher abrasion resistance compared with ordinary concrete, in which water-cement ratio is the major factor influencing its abrasion resistance. The abrasion resistance of rubberized concrete is improved along with the decreasing of water-cement ratio; the abrasion loss per unit area of rubberized concrete with water-cement ratio of 0.42 is decreased by 27% and 100% respectively compared with the rubberized concrete with water-cement ratio of 0.54 and 0.66. The abrasion resistance of rubberized concrete is optimal when the content of rubber powder is 10kg/m^3 , which will be reduced after the content of rubber powder is more than 10kg/m^3 . Among the three kinds of rubber powder with particle size of 80-mesh, 100-mesh and 120-mesh respectively, the concrete containing 100-mesh rubber powder has the best abrasion resistance, with abrasion loss per unit area decreased by 39% and 4% respectively compared with the concrete containing 80-mesh and 120-mesh rubber powder.
- For evaluating the abrasion resistance of rubberized concrete, the compressive strength sometimes can explain the reason thereof, for example, it has close relation with water-cement ratio. But the abrasion resistance has no inevitable relation with the strength. Along with the addition of rubber powder, the abrasion resistance of concrete is improved first and then reduced; when the content of rubber powder is more than 10kg/m^3 , the abrasion resistance of concrete will be reduced. The compressive strength of concrete will be reduced after the addition of rubber powder, and it is in inverse proportion to the content of rubber powder. Furthermore, if the particle sizes of rubber powder are different, the relationship that the abrasion resistance of concrete is in direct proportion to compressive strength will not apply.

ACKNOWLEDGEMENTS

The author would like to express appreciation for the financial support by the National Natural Science Foundation of China (51178085), the financial support by the National Natural Science Foundation of China (51278086), the Coastal and Offshore Engineering State Key Laboratory Open Fund (LP1109), Liaoning Provincial Scientific Research Program of Higher Education (LS2010045), construction safety and environmental state key laboratory open topics(201202), and

Liaoning Provincial Doctor Foundation (20101017).

REFERENCES

- [1] Yu Chen, Daqian Zhang. "Abrasion Mechanism and abrasion resistance on cement concrete pavement[J]." *China Concrete And Cement Products*, 2004 (2): pp. 16-19.
- [2] Yunfang Meng, Dezhi Wang, Jingyun Han. "Adding the powder of rubber waste and fly-ash to raise the cracking resistance properties of concrete[J]." *Concrete*, 2006 (6): pp. 49-55.
- [3] Raghvan D., H. Huyuh, C.F. Ferraris, "Workability, mechanical properties, and chemical stability of a recycled tyre rubber-filled cementitious composite[J]." *Journal of Materials Science*, 1998, Volume 33 (7): pp. 1745-1752.
- [4] Jingfu Kang, Pingzu Zhang. "Effects of scrap tire rubber on the cracking properties of cement paste and mortar[J]." *Journal of Tianjin University*, 2006 (9): pp. 1026-1030.
- [5] Tantara M.W., J.A. Lepore, I. Zandi Quasi-Elastic Behavior of Rubber Included Concrete[C].In: Ronald Meraky(Ed.),Proceeding of the 12th International Conference on Solid Waste Technology and Management, Philadelphia, PA, 1996.
- [6] Jing Li. The performance Research of cement concrete with waste tire rubber[D].Dalian University of Technology, 2010.
- [7] Paine K.A., R.K., Dhir R Moroney, K. Kopasakis Use of Crumb Rubber to Achieve Freeze/Thaw Resisting Concrete[C]. Proc. Intl Congress Concrete for Extreme Conditions, (Eds R K Dhir, M J Mccarthy and M D Newlands), 2002. pp. 485-498.
- [8] Yamei Zhang, Zhiyuan Zhao, Shenxia Chen, Wei sun. "Impact of rubber powder on frost resistance of concrete in water and NaCl solution[J]." *Journal of Southeast University* (Natural Science Edition), 2006 (11): pp. 248-252
- [9] Eldin N.N., A.B. Senouci, "Rubber tire particles as concrete aggregate [J]." *Journal of Materials in Civil Engineering*, 1993(5): pp. 478-496.
- [10] Shaomin Song, Juanhong Liu, Shuxin Jin. "Study on toughness of rubber modified concrete[J]." *China Concrete And Cement Products*, 1997(1): pp. 10-12.
- [11] Qi Luo. Research on the physico-mechanical properties and durability of crumb rubber-modified concrete[D]. Nanchang University, 2007.
- [12] Songxiao Peng. Experimental study on abrasion resistance of recycled concrete[D].Central South University,2009.
- [13] Naiqian Feng, Feng Xing. Durability of concrete and concrete structure[M].Beijing:China machine press,2008.
- [14] Naiqian Feng. High performance concrete structure [M].Beijing: China machine press, 2004.
- [15] Naik T.R., S.S. Singh, B.W. Ramme, "Mechanical Properties and Durability of Concrete Made with

- Blended Fly Ash[J].” *Materials Journal*,1998, Volume 95, (4): pp. 454-462
- [16] Gjorv O.E., T. Baerland, H.R. Ronning, “Abrasion resistance of high-strength concrete pavements[J].” *Concrete International*,1990,12(1):45-48
- [17] Langan B.W., Joshi R.C., Ward M.A. “Strength and durability of concrete containing 50% Portland cement replacement by fly ash and other materials[J].” *Canadian Journal of Civil Engineering*,1990, Volume 17(1): pp. 19~27.
- [18] Zhu H. *Crumb Rubber Concrete*, *Papra Handbook on Polymers Use in Construction[M]*. Shawbury, SY44NR,UK: Rapra Technology, 2004.