Assessing the Suitability of the Composting Process in Treating Contaminating Pesticides and Pathogenic Wastes

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ABSTRACT

Composting is a treatment which has been employed for organic wastes such as household wastes, yard wastes, manure and municipal solid wastes. More and more, wastes, hazardous in nature, such as polychlorobiphenyls (PCBs), contaminated soils, oily/petroleum wastes and explosives are nowadays being treated through composting. By the inherent characteristics of the composting process, the toxicity of hazardous wastes is strongly reduced and the compost can be safely disposed as landfill cover or other less expensive methods. This paper assesses the suitability of the composting process in treating hazardous wastes, mainly livestock wastes and pesticide-contaminated wastes. It analyses in general the parameters involved in the degradation of the hazardous wastes. For livestock wastes composting, it focuses on the heat/temperature inactivation of microorganisms and the use of indicators to judge the outcome of the process. In the case of pesticide-contaminated green wastes composting, the degradation of the pesticide molecules during the composting process is studied. The composting of green wastes contaminated with chlorinated herbicides has shown that the composting process was favourable to the microbial metabolism of 2,4-dichlorophenoxyacetic acid (2,4-D) and atrazine. Various parameters contributed to the biodegradation such that loss of 2,4-D occurred at a faster rate than atrazine. The biodegradation of atrazine was initiated by nucleophilic displacement of chloride ion. During composting of livestock wastes, hygienisation was attained at a maximum temperature of 66.4°C and log10 reductions of –8.03, –8.18 and –5.96 were noted for faecal coliforms (FC), Escherichia coli (EC) and faecal enterococci (FE). Hence, it has been demonstrated that FC and EC could be more rapidly destroyed at elevated temperatures compared to FE.

Keywords: hazardous wastes, microbial activity, pesticides, pathogens, sanitization

Abbreviations: D, decimal reduction time; EC, Escherichia coli; FC, faecal coliforms; FE, faecal enterococci; HMX, octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine; MPN, most probable number; MSW, municipal solid wastes; PAH, polycyclic aromatic hydrocarbon; PCB, polychlorobiphenyl; PCP, pentachlorophenol; RDX, N-methyl-N,2,4,6-tetranitroaniline (tetryl) and hexahydro-1,3,5-trinitro-1,3,5-triazine; STEC, Shiga toxin-producing Escherichia coli; SVOC, semi-volatile organic compound; TNT, 2,4,6-trinitrotoluene

INTRODUCTION

Composting is defined as the biological decomposition and stabilization of organic substrates under conditions that allow the development of thermophilic temperatures as a result of biologically produced heat, to produce a final product that is stable, has a limited number of bacterial counts as compared to the raw materials or waste, and can be beneficially applied to land (Haug 1993). A composting system is inherently complex and therefore dynamic, with very intense biological activity and various interdependent interactions amongst the various process parameters (Agnew and Leonard 2003). Many factors that affect the composting process performance are determined by process design and substrate preparation, but some can be influenced by external control during the process.

The main interest with composting as a waste management option lies in its capacity to both stabilize exogenous organic matter and its potential for sanitization, resultant of the self-heating characteristic based on time-temperature relationships with other factors including, ammonia concentrations, microbial inhibition and antagonism (Haug 1993). Composting and sanitization are not necessarily synonymous, for sanitization requires that certain specific conditions be followed strictly. Dumontet et al. (2001) rated composting among the best available technologies for sanitizing and stabilizing biosolid organic fractions. The stabilization potential of composting on livestock wastes has already been established through several works where the trends in temperature, volatile solids, pH and nitrogen, turning effect, phospholipid fatty acid profiling of microbial succession revealed stability of the end-products (Elwell et al. 1996; Michel et al. 1996; Tiquia et al. 2000, 2002; Kato and Miura 2008).

The composting process has shown significant potential to reduce the toxicity of hazardous wastes by degrading toxic organic substances which are present in the waste stream (Khan and Anjaneyulu 2006). Composting is one among the bioremediation technologies applied commercially at hazardous-substance-contaminated sites (Khan et al. 2004). Composting matrices and composts are rich sources of microorganisms, which can efficiently degrade chemical and hazardous contaminants to innocuous compounds such as carbon dioxide and water (Khan and Anjaneyulu 2006). Composting is now emerging as an ex-situ biological technology that is potentially applicable to non-volatile and semi-volatile organic compounds (SVOCs) in soils. Composts derived from green wastes (Antizar-Ladislao et al. 2005), lagooning sewage sludge (Amir et al. 2005; Atagana 2008), spent mushrooms (Lau et al. 2003), yard wastes (Carlstrom and Tuovinen 2003) and municipal solid wastes (Lourencetti et al. 2007) have been applied in the degradation and disposal of polycyclic aromatic hydrocarbons (PAHs), polychlorobiphenyls (PCBs), naphthalene, phenanthrene, anthracene, fluorethene, pyrene (Kästner and Mahro 1996; Parrish et al. 2004), explosives (Williams...
et al. 1992; Jarvis et al. 1998; Gray 1999; Boopathy 2000a; Gustavsson et al. 2004), hydrocarbons, petroleum and some pesticides (Antizar-Ladislao et al. 2005). Much of the work on treatment of contaminated soils by composting has been done on soils with low concentrations of the contaminating substances in spite of the fact that composts produced from cattle manure and vegetable wastes (Atagana et al. 2003), yard trimmings (Block 1998) and organic household waste (Brändli et al. 2005) have been reported to have potential for remediation of heavily contaminated sites (García-Gomez et al. 2003; Marin et al. 2006).

Mohee and Mootooosawmy (2004) assessed the feasibility of bioremediating oil-contaminated soils with the final compost produced from sewage sludge composting. The authors observed that frequent turning and mixing of the compost pile was required and that after 30 days of composting, 51% of oil could be degraded and volatile solids content could be lowered by 25%, showing that degradation of oils could be achieved by finished compost. Michel et al. (2001) studied the remediation of a PCB-contaminated soil from a former paper mill by composting with yard wastes in field scale piles. The PCBs in the contaminated soil had an average of 4 chlorines per biphenyl. The less chlorinated PCB congeners, with 1–3 chlorines per biphenyl, were preferentially degraded and the loss due to volatilization amounted to only 1%. Michel et al. (2001) observed that subsequent yard trimmings amendment levels of 60% or higher caused a 40% loss of PCBs. Antizar-Ladislao et al. (2005) studied the biodegradation of 16 PAHs from a coal-tar contaminated soil by in-vessel composting. They observed a decrease in the PAH concentration during the composting process. The two- and three-ring PAHs were removed to a greater extent during the composting process, with removal efficiencies of 91.8% at 38°C, 72.8% at 55°C and 81.9% at 70°C.

**IN-VESSSEL COMPOSTING OF GREEN WASTES CONTAMINATED WITH CHLORINATED HERBICIDES**

The composting process is considered to provide optimum conditions for destruction of xenobiotics through enhanced microbial activity. The capacity of microorganisms to degrade organic matter depends on their ability to produce specific enzymes to act on the substrate (Tuomela et al. 2000). Proteins, lipids and fats are found to be degraded by thermophilic bacteria whereas complex organics and cellulose will be degraded by both mesophilic and thermophilic fungi and actinomycetes. The molecular structure and concentration of the contaminant will determine the use of the compound as either a primary, secondary or co-metabolic substrate and thus, affect the type of microbial transformation occurring (Boopathy 2000b). There are a number of possible routes of removal of organic contaminants from a compost environment. These include mineralization, biotransformation, assimilation as nutrient into microbial biomass, polymerization, volatilization, leaching and sorption (Fogarty and Tuovinen 1991). Fig. 1 is an illustration of the possible interactions between the compost and the organic contaminant.

Pesticides encompass a wide variety of chemicals including herbicides, insecticides, fungicides and rodenticides. These chemicals have found extensive use in the field of agriculture as they increase crop production by killing weeds and suppressing plant diseases. The presence of herbicides such as clopyralid and picloram in composts has raised concern over the use of herbicide-contaminated composts for plant growth and the fate of these compounds during the composting process. The susceptibility of pesticides to biological degradation is extremely variable because of differences in molecular structure as well as in chemical and physical properties (Fogarty and Tuovinen 1991). In soil systems, degradation of pesticides is considered to be the result of a combination of chemical and biological events. As a rule, it has been stated that pesticide-degrading bacteria exhibit preferential utilization of sugars and organic acids which are readily metabolized through common intermediate pathways to yield tricarboxylic acid cycle metabolites (Fogarty and Tuovinen 1991). The factors influencing the fate of pesticides throughout the composting process include the composting system, temperature, moisture, C/N ratio, pH, volatility, biological degradation, adsorption and leaching (Büyüksoymez et al. 1999, 2000).

According to the study of Hartlieb et al. (2003), the fates of pyrene and simazine during the composting of municipal biowaste in pilot-scale bioreactors were asso-

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**Fig. 1 Intra-compost and pollutant interactions.** Adapted and modified from Semple et al. (2001).
associated with mineralization and the formation of non-extractable residues upon binding with the compost humic matrix. However, humic and fulvic acids play a minor role in binding simazine residues in compost (Hayar et al. 1997). Acidic and anionic pesticides such as phenoxyacetic acids and esters, asulam and dicamba could, in turn, interact with organic matter by H-bonding at pH values below their p\text{K}_a when the agrochemicals are in their non-ionised forms. The role played by the soil component and high temperature on degradation of 2,4-D have been reported to be significant (Michel et al. 1995). These studies emphasize the fact that the degradation of pesticides during composting is a combination of various factors and it differs from one contaminant to the other. Due to variation in the chemical structures and properties of pesticides, the mechanistic pathways of degradation that most pesticides follow during composting remain to be elucidated. Some studies have attempted to understand the factors controlling mineralization and the formation of non-extractable residues. Atrazine, simazine, terbutryn, pendimethalin, and dimetfuron were among the most highly sorbed herbicides.

The persistence of chlorpyrifos, diazinon, isofenphos, and pendimethalin after composting with grass clippings was investigated (Lemmon and Pylypiw Jr 1992). They found these pesticides undetectable after 3 weeks of composting at a lab-scale and that their rate of degradation was enhanced during composting. The fate of 14C-diazinon in compost and compost-amended soil has been evaluated (Leland et al. 2003). This study demonstrated considerable degradation of 14C-diazinon, an increase in its primary hydrolysis product and incorporation of radiolabelled diazinon into the non-extractable fraction within 60 days of composting. Little mineralization of the pesticide was also reported. Soil amended with 60 day-composted diazinon exhibited no toxicity. Petruska et al. (1985) studied the transformation of two radio-labeled pesticides, diazinon and chlordane within a bench-scale composting system. The pesticides were found to follow two major routes, volatilization and hydrolysis. Atrazine and chlordane were volatilized but no derivatization into the footnotes were noted. Only 15% of diazinon was found to volatilize. The remaining percentage of diazinon was partially hydrolyzed due to the conditions present in the composting system. 49.6% of chlordane was volatilized and 47.8% remained in the compost media. Chlorpyrifos-methyl, malathion, and lindane were almost fully degraded (>99%) whereas endosulfan was only partially degraded during composting (French et al. 2005). The authors suggested that a longer maturation time is required to allow for the disappearance of high levels of persistent pesticides. Further, Rao et al. (1995) found minimal mineralization of atrazine during composting with different wood-derived substrates. After 160 days of composting, there was no detectable atrazine and up to 11% of the chemical had been mineralized. It was suggested that the unmineralised atrazine had leached or complexed with the humic components, thus preventing further transformation. The authors also noted that the leaching potential (<1%) and very little volatilization of the pesticide is not always favourable (Barker and Bryson 2002). This is because some pesticides undergo partial degradation (Bricco et al. 2007), mineralization, transformation to other noxious chemical compounds, volatilization and adsorption onto the humic fractions of compost (Elkhattabi et al. 2010). This contributes to an increase in the leaching of pesticides in composts. In their study, Kupper et al. (2008) investigated the concentration levels and dissipation of modern pesticides during composting at a full-scale plant level. Of the 271 pesticides analyzed, only 28 were detected. Within the three windrows studied, total concentrations were between 36 and 101 µg/kg of dry matter (d.m.) in input materials and between 6 and 20 µg/kg in composts after 112 days of treatment. More than two-thirds of all pesticides detected in the input materials showed dissipation rates higher than 50% during composting, while levels of the most triazoles decreased slightly or remained unchanged.

**PREVIOUS STUDIES ON MICROBIAL SURVIVAL DURING IN COMPOSTING**

The poultry industry in Mauritius, representing the largest share of the local livestock sector, is fully developed with a production of 36,000 tonnes of processed chicken produced annually. Total poultry population is 1 million with growth rate of 5.7% per annum. This indicates a considerable amount of waste generated from the poultry rearing facilities. Animal waste-related environmental problems, particularly regarding the poultry subsector have been exacerbated by the organizational structure of the industry, notably its high degree of vertical integration and the rise of contract farming (Rajkomar and Driver 2003). In line with the industrial ecology concept, clean practices that allow transformation and re-use of livestock wastes need to be researched and applied to prevent environmental and sanitation hazards associated with wastes presenting zoontic significance and high potential for non-point source pollution. Uncontrolled disposal and land application of raw manure may potentially spread pathogens to non-target environments (Bach et al. 2002) as animal wastes in the form of manure are largely recycled to agricultural land as the most economical and environmentally sustainable means of treatment and reuse. These materials have a beneficial fertilizer value and can help maintain soil quality and fertility. However, animal manures frequently contain enteric pathogenic microorganisms (Pell 1997) and land spreading can lead to pathogen proliferation and occupational and environmental exposures and infections. Thus, the practice is still fraught with pitfalls. Table 1 summarizes some of the dangerous pathogens that have been detected in poultry wastes and their associated health impacts that may be observed in humans following handling and land spreading of these wastes. Table 2 summarizes the safe pathogen reduction levels relevant to land application for a number of regions and countries.

Traditionally, because the environmental aspects of chemical contamination are obvious in the short term, prevention of such pollution was the most important consideration during waste disposal. Hutchinson et al. (2005) and earlier reports (Jones et al. 1999; Bicudo et al. 2003) have shown there are also significant microbiological risks, which need to be taken into account when animal wastes are spread onto land. Although mean reduction time (D) values are useful for comparing initial linear rates of pathogen decline, the rate falls as the least hardy organisms are removed from the population and leave behind only those organisms that are better equipped for survival. Since the decline is not fully linear, it is not possible to extrapolate pathogen survival from initial levels of zoonotic agents. A typical D value for the initial decline is 2 to 3 days. *L. monocytogenes* could, however, be recovered from some plots for up to 128 days. Given that *L. monocytogenes* is a ubiquitous soil organ...
nism, the risks to food safety posed by its extended survival are currently unclear. Earlier, Gagliardi and Karns (2000) demonstrated the possibilities for Escherichia coli (EC) to survive, replicate and move downwards in soil for up to two months through manure spreading. Likewise, Kudva et al. (1998) reported the survival of EC O157:H7 for more than one year in stockpiled non-aerated ovine manure pile that was exposed to environmental conditions. Vernoyoz-Rozend et al. (2004) demonstrated that the environment is a reservoir in which new clones of Shiga toxin-producing EC (STEC) that is pathogenic for humans could emerge. Their results emphasize that appropriate handling and use of manure, slurry, and sewage sludge are necessary so that contamination of the environment and food by STEC can be prevented. Such facts have highlighted the priorities associated with seeking efficient manure treatment processes.

The use of indicator pathogens for detection is highly justifiable. The survival times and the resistance of pathogens outside their hosts depend on the susceptibility of the microorganisms to the environment and the treatment process. Microbiological investigations have verified the sanitization effect of composting and have showed a considerable reduction in densities of microorganisms (Haug 1993). Ugwuanyi et al. (1999) showed that EC was more sensitive to elevated temperature of 55°C at pH 8 than 7. Parmar et al. (2001) reported that the combination effects of enzyme, pH and temperature played a significant role in pathogen removal from sewage sludge. Several guidelines have been established regarding pathogen elimination during windrow composting with the major aspects requiring temperatures to be maintained at 55°C for 15 days or longer with a minimum of five pile rotations (USEPA, 1999) or that final composts should contain <log106 cells/g dry wt of faecal coliforms. However, even though pathogen elimination by composting has been well documented (Table 3), composting regimes required to achieve elimination of pathogen indicators and pathogens vary widely principally due to the highly dynamic singularity of the composting system, for instance, the scale of composting amongst others. Hence, the effect of higher temperatures on reducing the time required for pathogen reduction was reported by Himathongkham et al. (1999), where a 10-fold reduction in EC O157:H7 after 105 days at 4°C or 45 days at 37°C in a laboratory incubation with cattle manure was shown. Turner (2002) indicated that pathogen inactivation was also affected by water content and nature of the substrate. Moreover, if incomplete inactivation occurred due to low temperatures or excessive drying tendency, recovery and upsurge of the damaged pathogenic populations may be highly probable. Hassen et al. (2001) found that following an initial tendency for decline of faecal coliforms (FC) and faecal streptococci under promising process conditions, resurgence occurred explosively without re-inoculation during composting of MSW.

Lung et al. (2001) reported that Salmonella enteritidis and EC O157:H7 were not detected after 48 h and 72 h at 45°C during cow manure composting. According to Turner (2002), EC can be inactivated in either farm yard manure or

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**Table 1** Pathogens detected in poultry wastes, their associated health impacts observed in humans

<table>
<thead>
<tr>
<th>Pathogen/Pathogen type</th>
<th>Impacts on health due to land spreading and handling</th>
<th>Reference (stated for pathogen/pathogen type only)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salmonella spp.</td>
<td>Abdominal pain, diarrhea, nausea, chills, fever, headache</td>
<td>Cai et al. 1994</td>
</tr>
<tr>
<td>Campylobacter jejuni</td>
<td>May lead to paralytic condition, Guillain-Barr Syndrome (GBS); acute flaccid paralysis (AFP); zoonotic enteric infections; arthritis, and septicemia</td>
<td>Cai et al. 1994; Wassenaar et al. 1998; Duggan et al. 2001</td>
</tr>
<tr>
<td>Fecal streptococci</td>
<td>Impetigo, cellulitis, Toxic shock syndrome, Necrotizing fasciitis</td>
<td>Cai et al. 1994</td>
</tr>
<tr>
<td>Pseudomonas aeruginosa; Acronomas hydrophila; Yersinia enterocolitica</td>
<td>Bacteremia (infections of the blood), skin infections, ear infections, urinary tract infections, and in some cases even pneumonia</td>
<td>Kelley et al. 1995</td>
</tr>
<tr>
<td>Staphylococcus</td>
<td>Pimples, folliculitis, furuncles, boils, swimmer’s ear (an infection of external ear canal), sinusitis, epiglottis, whitlow, breast infection, impetigo, cellulitis, genital infection, or scaled skin syndrome. Infections of internal organs include urinary tract infections, arthritis, pneumonia, infection of veins (thrombophlebitis), lymph nodes (lymphadenitis) or lymph vessels (lymphangitis), bone infection (osteomyelitis) or life threatening sepsis (staph blood invasion), infection of heart valves (endocarditis), meningitis</td>
<td>Terzich et al. 2000</td>
</tr>
<tr>
<td>Escherichiacoli</td>
<td>Diarrhea, abdominal gas</td>
<td>Terzich et al. 2000; Duggan et al. 2001</td>
</tr>
<tr>
<td>Chryseobacterium sp.</td>
<td>Septic arthritis, elbow and other joint infections</td>
<td>Riffel and Brandelli 2006</td>
</tr>
<tr>
<td>Acinetobacter sp; Flavobacterium sp; Klebsiella sp; Micrococcus sp; Nocardia spp.</td>
<td>Pneumonia, urinary tract infections, sepsis, meningitis, trach site infections, wound infections, skin infections, endophthalmitis</td>
<td>Akinde and Obire 2008</td>
</tr>
</tbody>
</table>

**Table 2** Safe pathogen reduction levels relevant to land application for a number of regions and countries

<table>
<thead>
<tr>
<th>Pathogen</th>
<th>Region and/or country</th>
<th>Pathogen level</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Faecal coliform</td>
<td>Ontario (Canada)</td>
<td>&lt;2 million MPN/g</td>
<td>For field management practices</td>
</tr>
<tr>
<td></td>
<td>Quebec (Canada)</td>
<td>&lt;2 million MPN/g</td>
<td>For field management practices</td>
</tr>
<tr>
<td></td>
<td>Alberta (Canada)</td>
<td>&lt;1000 MPN/g</td>
<td></td>
</tr>
<tr>
<td>Salmonella</td>
<td>Quebec (Canada)</td>
<td>&lt;15 MPN/20 g</td>
<td></td>
</tr>
<tr>
<td>Sweden</td>
<td>None in 25 g samples of 25 g</td>
<td>Compiled from EU (2001)</td>
<td></td>
</tr>
<tr>
<td>Spain</td>
<td>None in 25 g of treated waste</td>
<td>Compiled from EU (2001)</td>
<td></td>
</tr>
<tr>
<td>Total count of pathogens</td>
<td>Italy</td>
<td>1000 MPN/g of dry solids</td>
<td>Compiled from NRC (2002) and EU (2001)</td>
</tr>
<tr>
<td>Total count of pathogens</td>
<td>Poland</td>
<td>Biosolids cannot be used in agriculture if it contains Salmonella; Parasites: 10/kg of dry solids</td>
<td>Compiled from NRC (2002) and EU (2001)</td>
</tr>
<tr>
<td>Total count of pathogens</td>
<td>France</td>
<td>8 MPN/10 g of dry solids</td>
<td>Compiled from NRC (2002) and EU (2001)</td>
</tr>
<tr>
<td>Faecal Streptococci</td>
<td>Spain</td>
<td>1000 MPN/g</td>
<td>Compiled from EU (2001)</td>
</tr>
<tr>
<td></td>
<td>Quebec</td>
<td>&lt;1000 MPN/g of dry solids faecal coliforms</td>
<td>For fertilizer use and in compost (Compiled from EU, 2001)</td>
</tr>
<tr>
<td>E. coli</td>
<td>Spain</td>
<td>&lt;1000 MPN/g of treated waste</td>
<td>Compiled from EU (2001)</td>
</tr>
</tbody>
</table>

The above studies show that composting can be appropriate in treating hazardous wastes of a particular nature, mainly those susceptible to biological degradation. Active composting uses biological microorganisms to build up stable organic compounds through humification and reduces concentrations of organic pollutants. This paper revisits the first studies conducted at the University of Mauritius on the application of composting in the treatment of green wastes contaminated with chlorinated herbicides and livestock wastes. This paper presents a discussion, in particular, on the mechanisms of degradation of chlorinated herbicides during composting process and the fate of sanitization indicators during composting of spent broiler litter (SBL) or livestock wastes.

**OBJECTIVES**

Uncontaminated and chlorinated herbicide-contaminated green wastes were composted in rotary drum composters at the University of Mauritius by Mohee and Jumnoodoo (unpublished data, 2008), each of a capacity of 200 L, with the aim of studying the fate of the herbicides during composting. A self-heating reactor design has been used for the composting experiments carried out in this study. The pilot-scale batch composter was designed of polyvinyl chloride (PVC) plastic (thermal conductivity of 0.171 W/m.K) with a thickness of 4 mm, an internal diameter of 550 mm and a length of 880 mm (Mudhoo and Mohee 2008). Two adjacent holes had been made in both sides of the drum through which two PVC pipes of 1 mm thickness and 50 mm internal diameter were passed. The pipes were perforated at about 20 mm intervals along the circumference and 40 mm intervals along the length of the pipes with holes 5 mm in diameter, and allowed the diffusion of air through the compost mixture thus ensuring aerobic conditions (Mudhoo and Mohee 2008). The upper side of the drum had been perforated with 3 holes of 50 mm diameter and spaced at 220 mm along the length of the drum. They allowed temperature measurements to be effected and allowed free exchange of air between the compost pile and the atmosphere. The main mode of air flow into the bioreactor was passive aeration (Sartaj et al. 1997). Depending on the temperature being reached in the reactor as a result of biodegradation and heat release, the air flow rate would also be varying. The passive aeration system was similar to natural aeration, except that perforated pipes have been used to facilitate air delivery and distribution to the matrix of composting substrates. Air was drawn into the perforated pipes by convection currents developed by temperatures differences (Sartaj et al. 1997) from the point of entry to the warmer decomposing compost mass. A detailed diagram of the composting reactor may be consulted in Mudhoo and Mohee (2008).

Four composting systems, Composts A, B, C and D, were set up with the following material compositions: grass clippings (turf-type tall fescue - *Festuca arundinacea*) – 25 kg, brown leaves and branches – 4.5 and 5.5 kg, respectively and finished compost of mixed municipal solid wastes and broiler litter – 5 kg. The composts differed in the type of grass clippings used. The characteristics of four composting mixes prepared for the composting experiments in this study have been provided in Table 4. Compost A was the control, with uncontaminated grass clippings. Compost B was contaminated with atrazine (Atrazine 500 SC, and 500 g/L of atrazine as active ingredient) obtained from Chemical House, Port-Louis, Mauritius. Composts C and D were spiked with 2,4-dichlorophenoxyacetic acid (2,4-D) amine salt 720 g/L (72.0% of 2,4-D as active ingredient) from Fertiagro Pte. Ltd., Singapore and tordon 101 (Tordon 101™) with 65 g/L of picloram and 240 g/L of 2,4-D as active ingredients (both present as trisopropylamine salt), purchased from IBL Agrochemicals, Port-Louis, Mauritius, respectively. The experiment lasted for 89 days, within which the compost maturity was reached based on the cumulative carbon dioxide evolution data presented later in this paper. Temperature, piggery wastes composting amended with straw if kept at 55°C for more than 2 h and that both mesophilic and thermophilic conditions are crucial to bring about inactivation of coliforms including EC O157 and *Salmonella*. Fremaux et al. (2007) detected non-O157:H7 Shigatoxin-producing EC in cow manure during 42 days in turned manure piles and during at least 90 days in unturned piles, thereby emphasizing the importance of implementing good management practices during composting.

Concern about the environmental impact of repeated pesticide and herbicide use and the contamination of soil and other solid substrates has prompted research into the environmental fate of these agents, which can emigrate from treated fields to air, other land and water bodies. How long the contaminant remains in the soil or containing medium depends on how strongly it is bound by the components in the medium and how readily it is degraded. It also depends on the environmental conditions at the time of application. Bioremediation encompasses *ex situ* engineered methods like bioreactors and enzyme catalyzed breakdown. The success of bioremediation is governed by three important factors – availability of microbes, accessibility of contaminants, and a conducive environment. There are many well-established bioremediation technologies applied commercially at contaminated sites. One such technology has been seen to be the use of compost material. Composting matrices and composts are rich sources of microorganisms, which can both degrade contaminants to innocuous compounds such as carbon dioxide and water and reduce pathogens to safe levels. The above discussion and the many research papers available in the literature on research concerning composting as a viable bioremediation and on the use of composts to degrade organic pollutants indicates its appropriateness in degrading herbicides.

**MATERIALS AND METHODS**

**Mechanisms of degradation of chlorinated herbicides during composting**

1. **Chemicals used in composts**

Uncontaminated and chlorinated herbicide-contaminated green wastes were composted in rotary drum composters at the University of Mauritius by Mohee and Jumnoodoo (unpublished data, 2008), each of a capacity of 200 L, with the aim of studying the fate of the herbicides during composting. A self-heating reactor design has been used for the composting experiments carried out in this study. The pilot-scale batch composter was designed of polyvinyl chloride (PVC) plastic (thermal conductivity of 0.171 W/m.K) with a thickness of 4 mm, an internal diameter of 550 mm and a length of 880 mm (Mudhoo and Mohee 2008). Two adjacent holes had been made in both sides of the drum through which two PVC pipes of 1 mm thickness and 50 mm internal diameter were passed. The pipes were perforated at about 20 mm intervals along the circumference and 40 mm intervals along the length of the pipes with holes 5 mm in diameter, and allowed the diffusion of air through the compost mixture thus ensuring aerobic conditions (Mudhoo and Mohee 2008). The upper side of the drum had been perforated with 3 holes of 50 mm diameter and spaced at 220 mm along the length of the drum. They allowed temperature measurements to be effected and allowed free exchange of air between the compost pile and the atmosphere. The main mode of air flow into the bioreactor was passive aeration (Sartaj et al. 1997). Depending on the temperature being reached in the reactor as a result of biodegradation and heat release, the air flow rate would also be varying. The passive aeration system was similar to natural aeration, except that perforated pipes have been used to facilitate air delivery and distribution to the matrix of composting substrates. Air was drawn into the perforated pipes by convection currents developed by temperatures differences (Sartaj et al. 1997) from the point of entry to the warmer decomposing compost mass. A detailed diagram of the composting reactor may be consulted in Mudhoo and Mohee (2008).

Four composting systems, Composts A, B, C and D, were set up with the following material compositions: grass clippings (turf-type tall fescue - *Festuca arundinacea*) – 25 kg, brown leaves and branches – 4.5 and 5.5 kg, respectively and finished compost of mixed municipal solid wastes and broiler litter – 5 kg. The composts differed in the type of grass clippings used. The characteristics of four composting mixes prepared for the composting experiments in this study have been provided in Table 4. Compost A was the control, with uncontaminated grass clippings. Compost B was contaminated with atrazine (Atrazine 500 SC, and 500 g/L of atrazine as active ingredient) obtained from Chemical House, Port-Louis, Mauritius. Composts C and D were spiked with 2,4-dichlorophenoxyacetic acid (2,4-D) amine salt 720 g/L (72.0% of 2,4-D as active ingredient) from Fertiagro Pte. Ltd., Singapore and tordon 101 (Tordon 101™) with 65 g/L of picloram and 240 g/L of 2,4-D as active ingredients (both present as trisopropylamine salt), purchased from IBL Agrochemicals, Port-Louis, Mauritius, respectively. The experiment lasted for 89 days, within which the compost maturity was reached based on the cumulative carbon dioxide evolution data presented later in this paper. Temperature,
moisture, pH, volatile solids (VS), electrical conductivity, carbon dioxide evolution rate and chloride content were monitored on a weekly basis and in triplicate. The experimental procedure is summarized in Fig. 2. All samples were collected as grab samples of masses 15–20 g. Samples were taken in triplicate (one sample from the middle and a sample from every of the two ends along the reactor length, all from roughly at mid-depth of the remaining compost bed depth.

2. Measurement of physical parameters

Temperature was measured using the Checktemp 1 temperature probe on a daily basis as far as possible. The temperature was measured at three main points [left end, centre and far right end] of the rotary drum composter and the average value was recorded. The moisture content was determined on drying 100-200 g of fresh materials in the STABIL-THERM (BlueM electric company, USA) oven at 105°C until constant loss in weight was achieved. As for pH determination, 200 mL of 0.01 M CaCl₂ (Laboratory Reagent, BDH Limited, UK) oven at 105°C until constant loss in weight was achieved. As for pH determination, 200 mL of 0.01 M CaCl₂ (Laboratory Reagent, BDH Limited, UK) solution was added to 20 g of sample material and the mixture was shaken for 1 hr on the ks 501 digital IKI-Labortechnik apparatus for 15 min. The samples were then titrated against 1 M HCl (SG 1.18, Fisons scientific equipment, England) solution using phenolphthalein as the indicator. A blank was set up with the NaOH trap only. The amount of CO₂-carbon generated was calculated as follows:

\[ \text{CO}_2 \text{C (mg) = (HCl}_b - \text{HCl}_s \times 12 \]

where \( \text{HCl}_b \) = volume of HCl used for titrating the blank and \( \text{HCl}_s \) = volume of HCl used in titration of compost samples.

Since the biodegradation of atrazine is believed to be initiated by the nucleophilic displacement of chloride ion (Erickson et al. 1989; Laturnus et al. 2005), the chloride content of the composts was determined by the argentometric method (Adoki and Odo-kuma 2007; Gavlasova et al. 2008) as per APHA (1998). The compost extracts were prepared by shaking a mixture of the compost samples and de-ionised (DI) water at a ratio of 1:3 (compost: DI water) in stoppered 500 mL Erlenmeyer flasks on the ks 501 digital IKI-Labortechnik apparatus for 15 min. The samples were left to stand for overnight. 25 mL of the aliquots were pipetted to each flask and titrated against the standardized AgNO₃ solution in a similar way. The chloride content in the sample was calculated by the following formula:

\[ \text{Cl}^- (\text{mg/L}) = \frac{(A - B) \times M \times 35.5}{25/1000} \times 3 \]

where \( A = \) mL titrant used for sample, \( B = \) mL titrant used for blank and \( M = \) molarity of silver nitrate.

Experimental procedures for spent broiler litter composting study

Windrow composting was carried out with broiler litter, and sugar cane bagasse as bulking agent. The broiler litter was obtained from...
a commercial facility consisting of 10 pens per broiler house with rearing capacity of 2000 birds per pen. Ingredient analysis was performed to obtain basic data on the component ingredients needed for the identification of an optimal feedstock recipe, followed by adjustment of moisture content. Three experimental windrows were set up, in order to eliminate sources of errors, with an approximate size of windrows of the order of 0.6 m height, 0.7 m width and 1.2 m length. The experiment was run in a covered shed with concrete flooring on the University Farm for 110 days. Process control was based on temperature development and the windrows were manually turned 6 times (Days 7, 14, 21, 27, 42 and 56).

Temperature was recorded using a digital temperature probe of 0.3 m (Model 3320, England) along the windrows, at three levels 1, 2, 3 (bottom, middle, top respectively) at 24 specified locations. The compost feedstock was analysed for moisture content (105°C for 24 h; Memmert, Germany), volatile solids and total C using loss on ignition technique (550°C for 5 h, Carbolite muffle furnace), total nitrogen (macro-Kjeldahl technique; Gerhardt Kjeldatherm, Germany), pH (1: 10 calcium chloride extract). C: N ratios were calculated from organic C and Kjeldahl-N.

There is a varied and important number of pathogens in poultry related wastes. If only sanitation efficiency has to be considered, evaluation of the efficiency of treatments should be based on the monitoring of pathogenic micro-organisms. However, it is not possible to monitor all these micro-organisms because of their high number but also because there are not always specific techniques for their quantification or identification. There is a few number of micro-organisms for which quantification of the population is possible: Salmonella spp., some enteric viruses, faecal coliforms, Escherichia coli and faecal enterococci, cysts of protozoa and helminth eggs. This explains why FC, presumptive EC, Salmonella spp., some enteric viruses, faecal coliforms, Escherichia coli and faecal enterococci, cysts of protozoa and helminth eggs. This explains why FC, presumptive EC, E. coli, S. typhimurium, some enteric viruses, faecal coliforms, Escherichia coli and faecal enterococci, cysts of protozoa and helminth eggs. This explains why FC, presumptive EC, Salmonella spp., some enteric viruses, faecal coliforms, Escherichia coli and faecal enterococci, cysts of protozoa and helminth eggs.

The electrical conductivity for all compost mixes in-

\[ \text{Table 5} \]

<table>
<thead>
<tr>
<th>Compost</th>
<th>pH range</th>
<th>Electrical conductivity (mS/cm)</th>
<th>Overall volatile solids decrease (%)</th>
<th>Moisture range (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>6.4–8.3</td>
<td>0.58–1.38</td>
<td>15.89</td>
<td>66.7–72.4</td>
</tr>
<tr>
<td>B</td>
<td>6.7–8.4</td>
<td>0.40–1.49</td>
<td>18.82</td>
<td>48.1–66.0</td>
</tr>
<tr>
<td>C</td>
<td>6.4–8.1</td>
<td>0.59–1.27</td>
<td>14.26</td>
<td>46.0–63.1</td>
</tr>
<tr>
<td>D</td>
<td>6.5–8.2</td>
<td>0.58–1.32</td>
<td>23.95</td>
<td>55.3–73.2</td>
</tr>
</tbody>
</table>

**RESULTS AND DISCUSSION**

**Degradation of chlorinated herbicides**

*1. Evolution of parameters during composting*

The physicochemical characteristics of the four composts were suggestive of successful aerobic composting. The variation of the average compost matrix temperature is given in Fig. 3 and the results for pH, electrical conductivity, overall volatile solids change and moisture contents are summarized in Table 5.

One of the main characteristics of composting is the production of heat due to exothermic oxidation reactions (Lhadi et al. 2004). This microbial heat production represents an indirect yet reliable measure of microbial activity since there is a linear correlation between rate of heat production and rates of oxygen consumption and carbon dioxide production (Cooney et al. 1969). Fig. 3 shows the typical temperature trends during aerobic composting for the four composts (A, B, C and D) during the high rate composting phases. All the composting matrices show a rapid increase in average temperature from an average ambient temperature of 24.6 ± 0.3°C up to a peak temperature during the first 4 days of the composting. The peak temperature recorded were as follows: 55.4°C for compost A, 55.1°C for compost B, 55.4°C for compost C and 55.2°C for compost A. It may be observed that the maximum temperature reached by the four composts do not vary significantly. Thereafter the high rate thermophilic composting stage, temperatures started to decrease for all four composts. The cooling phases in all four experiments lasted for 23–28 days until room temperature was reached on day 35–40. The curing phases continued at 25.5–27.0°C till the end.

The pH increased to a value greater than the final values given in Table 5 for the composts after 13 days of composting. The high pH values detected here were consistent with those obtained by other authors with this type of organic materials (Charest and Beauchamp 2002; Lhadi et al. 2004; Arvanitoyannis and Varzakas 2008; Mohee et al. 2008b). These increases are the consequences of complex chemical and biological reactions which occur during mineralization of organic matter, proteins and amines that produced ammonia gas that was detected by its characteristic irritating smell. Ammonia, being alkaline in nature, caused the pH to rise. The accumulation of volatile fatty acids early during composting can also contribute to occasional drops in pH (Ugwuanyi et al. 2005; Iyengar and Bhave 2006) as was observed between days 31 and 37 in composts A and C. These results, therefore, show that the average pH (for all four composts varying from 6.4-8.4) of the composting materials was acceptably within the normal range of 6.5–8.5 (Haug 1993) for optimum microbial activity. pH was thus not a limiting factor for the compost set-ups studied for the degradation of the chlorinated pesticides.

The electrical conductivity for all compost mixes increased from their respective starting value (lower limit value for each range given in Table 5) to an average maximum value of 1.59 ± 0.11 on days 15–17. Electrical conductivity is expected to generally increase during composting (Sánchez-Monero et al. 2001) due to the concentration of ions as the weight of the pile decreases although it can decrease if the loss of soluble salts by leaching is not prevented. After day 18, the electrical conductivity started to decrease in the composts due to losses by gradual
leaching as the piles had relatively high moisture contents, or due to decomposition of the most labile fractions of the organic matter (Cayuela et al. 2004). During the composting processes, the volatile solids content decreased for all composts, especially so during the high-rate phase around day 4–7. The overall decreases in volatile solids for the composts have been calculated and are given in Table 5. The overall change in volatile solids has been determined as follows:

\[
\text{Overall change in VS (\%) = } \left( \frac{\%VS_i \times M_i - \%VS_f \times M_f}{\%VS_i \times M_i} \right) \times 100
\]

where the subscripts i and f denote the initial parameter values and the final parameter, respectively and M, the wet mass of each compost mix. Since the decrease in volatile solids is a good indicator of biodegradation for composting (Briski et al. 2003; Mohee et al. 2008b), it is hence deduced that all four composting experiments have undergone relatively high degradation of the available biodegradable volatile solids matter, the highest being for compost D, second most for compost B and the least for compost C. Fig. 4 shows the profiles for the cumulative CO₂ evolved during the composting experiments for the composts. The CO₂ evolution rate has been the most in compost D and the least in compost C as depicted from the relative final cumulative evolution rate has been the most in compost D and the least for compost C. It is supposed that the presence of the three types of pesticide molecules might have influenced the microbial activity in the composting substrates and hence brought about the biodegradation of the substrates to different extents. However, at this stage of the study, the specific factors having influenced the microbiological utilization of the biodegradable fractions of the inoculated organic compounds and of the substrates in the composting mixes remain unknown (Fogarty and Tuovinen 1991).

2. Pesticides degradation mechanism

The herbicides investigated were chlorine derivatives and they varied in the degree of persistency in the environment. Microbial metabolism of the herbicides was expected to predominate during the composting process. Though the chloride ion (Cl⁻) is a labile group, it was not responsible for initiating the biodegradation of all the herbicides, except for atrazine. Steric hindrance, the types of microbes and the presence of other molecules that can be utilized as carbon or energy sources by microorganisms might have inhibited nucleophilic displacement of the halide. Results have been based on the respiration measurements, chloride content and electrical conductivity. According to Fig. 5, the mean cumulative chloride content showed a clear demarcation for the uncontaminated compost than the contaminated ones. A probable explanation could be that the breaking of the C-Cl bond contributed poorly to the loss of the herbicides in the composting systems. Mechanisms such as oxidative cleavage and loss of carbon dioxide contributed to the degradation of the herbicides. However, in the case of the atrazine, degradation was observed after 24 days of composting and the isolation of hydroxyatrazine confirmed the biologically mediated hydrolytic dechlorination of atrazine as has been observed by Topp (2001) and Wackett et al. (2002). Basic tests of functional groups of the proposed degradation intermediates or products were also performed after isolation for further confirmation of the results on degradation.

Fig. 4 Cumulative carbon dioxide evolution during composting process of composts A, B, C and D.

Fig. 5 Cumulative chloride content of composts A, B, C and D.
Benchmark stages of composting, were highly significant resistance to high temperature compared to EC especially FE concentrations, respectively. As expected, FE exhibited 6 tics, while FE reduction followed first-order decay (Table 1). EC reductions were expressed by second-order decay kinetics and hygienization. Temperature histories (Fig. 6) revealed hygienisation attainment with maximum temperature of 66.4°C Log 10 reductions of −8.03, −8.18 and −5.96 occurred in FC, EC and FE concentrations, respectively. As expected, FE exhibited resistance to high temperature compared to EC especially for the first 21 days. Differences in mean, representing benchmark stages of composting, were highly significant (P < 0.05) for all pathogen indicators. VSRcl (%), 88.50 reduction was effective in depicting substrate degradability under thermophilic conditions. The rate equations showed that FC and EC reductions were expressed by second-order decay kinetics, while FE reduction followed first-order decay (Table 6). Based on the conclusions of several researchers (Haug 1993; Christensen et al. 2002), Gram positive faecal enterococci or fecal streptococci as it was formerly known, demonstrate elevated thermal resistance than Gram negative EC. Effectively, the present findings showed that FC and EC were rapidly destroyed while FE was more resistant. The trends for the two parameters are as follows: (1) for temperature and ▪ for moisture.

Temperature dependency of the stabilization rate was equally verified by Sobrataee et al. (2008) by applying empirically derived rate equations. Decomposition rate according to the equation of Haug (1980) showed a definite tendency to increase rapidly with temperature elevation while the results from Mohee (1998) and Nielsen and Berthelsen (2002) have emphasized on the reduction in decomposition rate beyond 55°C. The structured model proposed by Nielsen and Berthelsen (2002), based on the application of theoretical assumptions about enzyme catalysis and high activation energy-induced spontaneous deactivation, has indicated system progress rate and where it can be optimized hence, revealing the relevance of such results for practical purposes in the technical management of composting facilities. The main implication hence resides in the ability to plan the process runs for spent broiler litter composting in Mauritius in such a way to maximize on both the attainment of stability and hygienization.

**Table 6** Rate equations and order of decay rate of faecal and decomposition indicators.

<table>
<thead>
<tr>
<th>Software generated rate equations</th>
<th>Simplified rate equations</th>
<th>Order of decay rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{dFC}{dt} = -c(a^2 - bFC)(b - FC)$</td>
<td>$\frac{dFC}{dt} = -0.00145FC^2 + 0.0729FC - 0.185$</td>
<td>Second</td>
</tr>
<tr>
<td>$\frac{dEC}{dt} = -c(a^2 - bEC)(b - EC)$</td>
<td>$\frac{dEC}{dt} = -0.0020EC^2 + 0.105EC - 0.253$</td>
<td>Second</td>
</tr>
<tr>
<td>$\frac{dFE}{dt} = -b(FE) + c(a - FE)$</td>
<td>$\frac{dFE}{dt} = -0.003(4.17 + FE)$</td>
<td>First</td>
</tr>
<tr>
<td>$\frac{dVSR_{cl}}{dt} = -c(C_{org} - b)$</td>
<td>$\frac{dVSR_{cl}}{dt} = 0.00083 × 0.0201 × 0.0101 × 0.00326 × 0.01 × 0.0083 × 0.02 = 0.000132/tonne$</td>
<td>Pseudo-first</td>
</tr>
</tbody>
</table>

**Fig. 6** Evolution of physico-chemical parameters during composting.

The trends for the two parameters are as follows: □ for temperature and ▪ for moisture.
As expected, the greatest pathogen reduction effect (PRE) occurred during the thermophilic phase. Thus, in the absence of composting the net PRE at point of harvest is estimated at 5.30 log removal for EC, assuming a 1-log dilution effect of the enterobacteria. It can be concluded that there is a definite advantage in optimally composting SBL mix before land application since the composting process effectively confers an escalating dilution effect of the enterobacteria.

CONCLUSION

The composting of green wastes contaminated with chlorinated herbicides has shown that the composting process was favourable to the microbial metabolism of 2,4-dichlorophenoxyacetic acid (2,4-D) and atrazine. The biodegradation of picloram was slow due to its higher persistency. Various parameters contributed to the biodegradation of the herbicides such that loss of 2,4-D occurred at a faster rate than atrazine. The biodegradation of atrazine was initiated by nucleophilic displacement of chloride ion. The paper has also demonstrated the success of livestock wastes sanitization through composting. During composting of spent broiler litter, hygienisation was attained at a maximum temperature of 66.4°C and log10 reductions of –8.03, –8.18 and –5.96 were noted for faecal coliforms, Escherichia coli and faecal enterococci, respectively. Hence, it was demonstrated that FC and EC could be more rapidly destroyed at elevated temperatures compared to FE. The studies hence presented and discussed confirm that composting can be very suitable in treating pesticides contaminated and pathogen containing wastes.

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