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Polyvinyl chloride degradation by hybrid (chemical and biological) modification

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ABSTRACT

Chemical and microbial modifications are not common with polyvinyl chloride (PVC). This paper presents a novel green hybrid technique for the PVC degradation using biodegradation followed by chemical modification, using glycerol and urea (C-PVC). *Mucor rouxii* specie is found to be susceptible towards C-PVC bio-degradation. Chemical change in PVC was monitored by observing change in the C–C, C–H and C–Cl bond environment using IR spectroscopy followed by dechlorination study. Role of ZnO in chemical modification was observed by elemental analysis. Thermogravimetric with IR study justified microbial participation in the degradation and found that *M. rouxii* modified C-PVC (M-PVC) considerably reduces degradation time and temperature. Degradation temperature for C-PVC and M-PVC was noted as 550 °C and 450 °C, as compared with PVC 600 °C. Degradation pattern was also investigated by surface morphological using AFM analysis.

1. Introduction

Due to excellent mechanical and thermal properties polyvinyl chloride (PVC) received a great acceptance in various fields like building, household appliance, packaging, electric and electronic products, automotive, furniture etc. Huge amount of PVC waste was discharged both in post-manufacturing and post-consumer stages. Worldwide PVC waste can be principally managed by landfilling (82%) and incinerator (15%). Other techniques like mechanical recycling, chemical and biological degradation contributes 3% of total recycling. Land filling has the limitation of space and associated soil infertility [1,2]. Poor product quality restricts the applicability of mechanical recycling techniques [3]. PVC incineration techniques involve both thermal, catalytic, radiofrequency [4] with pyrolysis and steam gasification process (Table 1). Chemical modification techniques targets chlorine as nucleophiles (Nu) and reduce the dechlorination temperature [5] and involves the use of various chemicals like as NaOH, $Ca(OH)_2$, SCN^-, OH^-, N_3^-, ethylenediamine [5–8]. These processes were improved and degradation was performed by using green solvents like ethylene glycol, polyglycols [9] and microbial strains like *M. Luteu*, *Aspergillus fischeri* and *Paecilomyces species* [10].

Glycerol is now recognized as renewable, inexpensive, green chemical and research is concentrating towards its efficient utilization as value added materials in various processes. The present paper presents a novel green biodegradation method for PVC using combination of chemical and biological technique.

2. Material and method

Poly (vinyl chloride) (PVC, Mw = 80,500 g mol^{-1}) urea (NH_2CONH_2) and sodium carbonate (Na_2CO_3) were obtained from High media. Each of these materials and chemicals was purchased in powder form. Glycerol (AR grade) was utilized without further purification.

2.1. Chemical modification of PVC (C-PVC)

Take a 250 mL three-necked flask equipped with a magnetic stirrer, reflux condenser and thermometer, charge it with glycerol (182.0 g; 2.0 mol), urea (30.0 g; 0.5 mol) and Na_2CO_3 (0.4 g), ZnO

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Table 1
Chemical and Biological method for PVC degradation.

Technique	Condition	Dechlorination/degradation	Reference
Steam pyrolysis	250 °C; 1 h	75% dechlorination	11
Gas- liquid fluidized bed reactor	280–320 °C, 1 min after melting	99.5% dechlorination	12
Zinc(II) oxide/Chemical recycling	453 and 673 K for 0.5–5 h	70% dechlorination	13
Poly(ethylene glycol)/Chemical recycling	210 °C; 1 h	74.2% dechlorination	9
1.0 M NaOH/EG solution/Chemical recycling	150–190 °C; 15 min	close to 100% dechlorination	6
NaOH in DMSO/Chemical recycling	80 °C; 1–3 h.	98-99% dechlorination	14
Co-milling with eggshell	550 rpm; 4 h	95% dechlorination	15
1-butyl-3-methylimidazoliumhydroxide/Chemical recycling	180 °C; 1 h	91.2% dechlorination	16
nucleophilic substitution OH/EG solution	190 °C 0.5 h	90% dechlorination	5
1.0 M NaOH/EG	130-190 °C; 15 min	97.8% dechlorination	17
P.chrysosporium PV1	starch blended polyvinyl chloride films; soil burial; 90 days.	Molecular weight decreases from 80,275 to 78,866 Da; CO_2 release 7.85 g/l	18
Micrococcus species	enrichment culture technique	0.36% release of chloride; 8.87% carbon dioxide evolution	10

(0.2 g) as catalyst. Add 62.2 g PVC (1.0 mol/vinyl unit) and heat at 170 °C for 4 h with ZnO (0.2 g) as carbonylation catalyst. Suitable reaction temperature was decided by the following facts: (*i*) 170–190 °C was the optimum temperature for the chemical modification of PVC using polyol under alkaline condition [6]; (*ii*) glycerol to acrolein conversion started after 180 °C [19]. These facts indicate 170 °C as suitable reaction temperature. Amination provides biocompatibility of PVC and it involves the use of alkyl amine like reagent [20], so efforts has been made to use inexpensive reagent like urea to improve the commercial feasibility. Furthermore, urea controls the dehydration of glycerol by the formation of glycerol urethane and glycerol carbonate and improves the application of glycerol as reagent. Suitable reaction time was decided by using IR spectroscopy. Effervescence with color change from yellow to black indicates the chemical modification. The reaction was cooled at room temperature. The resultant C-PVC was filtrated, washed with ethanol and deionised water, and dried in a vacuum at room temperature.

2.2. Biological modification of C-PVC (M-PVC)

In order to isolate compatible microbes for degradation, 0.5 g of C-PVC powder was placed in an Erlenmeyer flask of 500 mL capacity containing growth media (in g/l): K_2HPO_4 (5 g), KH_2PO_4 (2 g), $MgSO_4$ (2 g), NaCl (0.1 g), $NaNO_3$ (5 g) and yeast extract (3 g), with 0.5 g with soil collected from the polymer collection/recycling site at Satto Wali Gathi, Near Patel Nagar, Dehradun (India). This sample was kept under shaking conditions (150 rpm) at 37 °C for a period of 30 days. Subsequently, 1 ml of sample was withdrawn and transferred to fresh media with C-PVC powder and incubated for further 30 days. This was repeated for 3 cycles and subsequently 1 ml of sample was withdrawn and transfer to 5 ml of nutrient broth. The tube was incubated at 37 °C under shaking conditions for 24 h and spread on nutrient agar plate (peptone 5.0 g/l, yeast extract 5 g/ml NaCl 2.5% and 2% agar). Morphologically different colonies were picked up and further purified, by streaking on nutrient agar plate.

The microbial identification was carried out by determining the gene sequence coding for 16S rRNA and biochemical analysis. The PCR was carried out using 16S rRNA gene universal primer as conditions and temperature program described by Kumar et al. (2006) [21]. The PCR product was separated by agarose gel electrophoresis and visualized by SYBR*1* Green 1 staining (Sigma, St. Louis, USA) and, finally purified by using a Wizard PCR Preps Purification System (Promega Corp., Madison, USA) according to the manufacturer's instructions. The purified DNA was sequenced using an ABI PRISM Big Dye Terminator Cycle Sequencing Kit (Applied Biosystems, CA, USA) and the sequencing products were separated by capillary electrophoresis by using a 313Xl Sequencer (Applied Biosystems, USA).

To identify the different isolated microbes, the 16S rDNA consensus sequence, obtained by analyzing with DNAMAN version 5.2.9 (Lynnon BioSoft, Quebec, Canada), was then compared with 16S rRNA gene sequences from the public GenBank, EMBL, and DDBJ databases using the advanced gapped n-BLAST program, version 2.1. The program was run *via* Internet through the National Centre for Biotechnology Information website (http://www.ncbi.nlm.nih.gov/blast/). Multiple-sequence alignments were performed using the CLUSTAL program [22]. Sequence distance matrices were established in pairwise comparisons by use of the Kimura algorithm [23]. Phylogenetic trees were constructed by the neighbor-joining method using the PHYLIP software package. Statistical significance was evaluated by bootstrap analysis with 100 repeats of bootstrap samplings [24]. Sequences with more than 98% identity with a GenBank sequence were considered to be the same species as the highest score-matching sequence on the public sequence databases.

Gram's staining and biochemical reactions like *IMViC*, catalase, oxidase, gelatin and urea hydrolysis, sugar fermentation, enzyme production, H_2S production etc. were also carried out according to Bergey's Manual of Determinative Bacteriology. Microbes thus evaluated for their ability to grow in presence of C-PVC in growth media (described above) by measuring absorbance at 600 nm using spectrophotometer at time intervals. The potential microbe having higher growth on C-PVC is used for further study.

For biological modification 0.5 g C-PVC powder in DI water was charged in 100 ml of growth media and inoculated with 10% (v/v) inoculums. The flask was incubated at 37 °C in a shaking incubator for a period of 30-days to obtain M-PVC.

2.3. Degradation experiment

Thermal degradation pattern of C-PVC and M-PVC different experiments were performed at 100–800 °C and compared with the degradation pattern of PVC. 0.5 g of material at every 100 °C variation was analyzed by Bruker FT- 200 FTIR spectrophotometer in the 4000–400 cm^{-1} absorption range. All the experiments were performed in triplicate and repeated at least three times to ensure reproducibility.