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Biological Remediation and Removal of Radioactive Metals and Complex Aromatic Compounds from Nuclear and Radioactive Waste

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In pursuing carbon emission free technologies in the energy industry, interest in nuclear energy has grown. However, technology for handling radioactive waste containing organic materials are lacking. Methods are required for biodegradation of often recalcitrant irradiated organic compounds which are persistent in radioactive waste from the nuclear industry. In this study, a bioseparation process for extraction of ^{14}C and de-radiation of nuclear graphite was investigated in a continuous flow sequencing-batch/biofilm reactor. Dehalogenation and mineralisation of aromatic halogenated compounds in the waste stream of a pebble bed manufacturing process was simulated by the photocatalytic/biological hybrid system in the 50 to 1,000 4-CP mg.L^{-1}. The efficiency of degradation of the irradiated compounds was compared to conventional degradation using PAH degrading microorganisms. The Pathway of degradation was established for both systems by evaluating the intermediates of degradation of radiolabelled phenolic compounds with ortho-^{13}C-ortho and para-^{13}C phenol. Phenol degradation under photocatalytic conditions was shown to follow the catechol→ hydroquinone→ hydroxyhydroquinone→benzene-1,2,3-triol pathway, whereas the degradation in the biological stage followed the meta-cleavage pathway via catechol→ 2-hydromuconic semialdehyde→ pyruvate under aerobic conditions. This study demonstrates the potential of efficiently managing the organic component of nuclear waste using a cleaner, environmentally friendly biological process.

1. Introduction

The exponential increase in the world population in the last 200 years and the fast depletion of fossil fuel reserves has resulted in renewed interest in nuclear energy (Wang and Li, 2016). Additionally, the increased pressure to cut down on the burning of coal as a primary energy source due to its effects on global warming has caused many governments to re-open research into carbon free sources of energy such as solar, wind, nuclear and geothermal energy (McCauley, 2018). The main impeding factor in the implementation of nuclear energy is mainly due to the shortage of solutions for treatment and disposal of radioactive waste (Ismagilov et al., 2000). The buck of radioactive waste contains low and intermediate level waste (LLW, ILW) and a small amount of Transuranic (TU) elements. Low Level Waste (LLW) is generated from hospitals and industry, as well as the nuclear fuel cycle (Chirwa, 2011). LLW does not require shielding during handling and transport and is suitable for shallow land burial. To reduce its volume, it is often compacted or incinerated before disposal. The bulk of graphitic waste from Generation IV fast reactors could fall into this category. In this case, the limitation is space requirements rather than shielding and treatability.

Wastewater from the general waste stream contains a large amount of organic pollutants. These radioactive organic compounds are recalcitrant and represent the highest risk to the environment through increase in total organic carbon (TOC) and toxicity. Physical and chemical treatment of organic aromatic pollutants has been shown to produce secondary radioactive waste which requires further treatment (IAEA, 2004). In this study, bioseparation of ^{14}C from a $^{12}C/^{14}C$ nuclear graphite was attempted using locally isolated microorganisms.

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Irradiated compounds were degraded in a photocatalytic/bioreactor hybrid system to achieve complete mineralisation of the compounds to CO_2 and H_2O.
The study demonstrated that radiation tolerant consortia of bacteria can be isolated and optimised to efficiently degrade recalcitrant compounds under radiotoxic conditions.

2. Configuration of the Generation IV Nuclear Reactor

In order to free itself from reliance on coal as the principal source of energy, a country such as South Africa will need an energy source as dependable as coal while at the same time be able to remedy the potential environmental impacts of the chosen energy source. Nuclear energy has been discussed as the potential replacement of the coal generation capacity of South Africa. Nuclear energy offers a source with lower carbon emissions. However, it comes with the problem of radioactive waste which could create an environmental burden for thousands of years. Additionally, like coal, uranium on which nuclear energy is based, is a non-renewable resource on earth. The minimum requirement for new nuclear reactors is that they must be safe. Reactors with graphite as the neutron regular have been proposed. These reactors are able to self-regulate and shut down if the cooling agent – mostly a noble gas – is depleted. This reduces the risk of accidents such as those that occurred in Chernobyl (Ukraine) in 1986 and Tukushima (Japan) in 2011. One such technology is the Pebble Bed Modular Nuclear Reactor (PBMR). The PBMR is a Generation IV reactor capable of operating at very high temperatures (700 - 1,300 ºC). The reactor is cooled by helium through the Brayton cycle (Figure 1a) (PBMR Pty Ltd, 2008). The core is filled with graphite pebbles the size of golf balls containing uranium kernels as the reactive component. The flux of neutrons is moderated by the TRISO oxide layer surrounding each fuel kernel and the graphite matrix surrounding the kernels (Figure 1b).

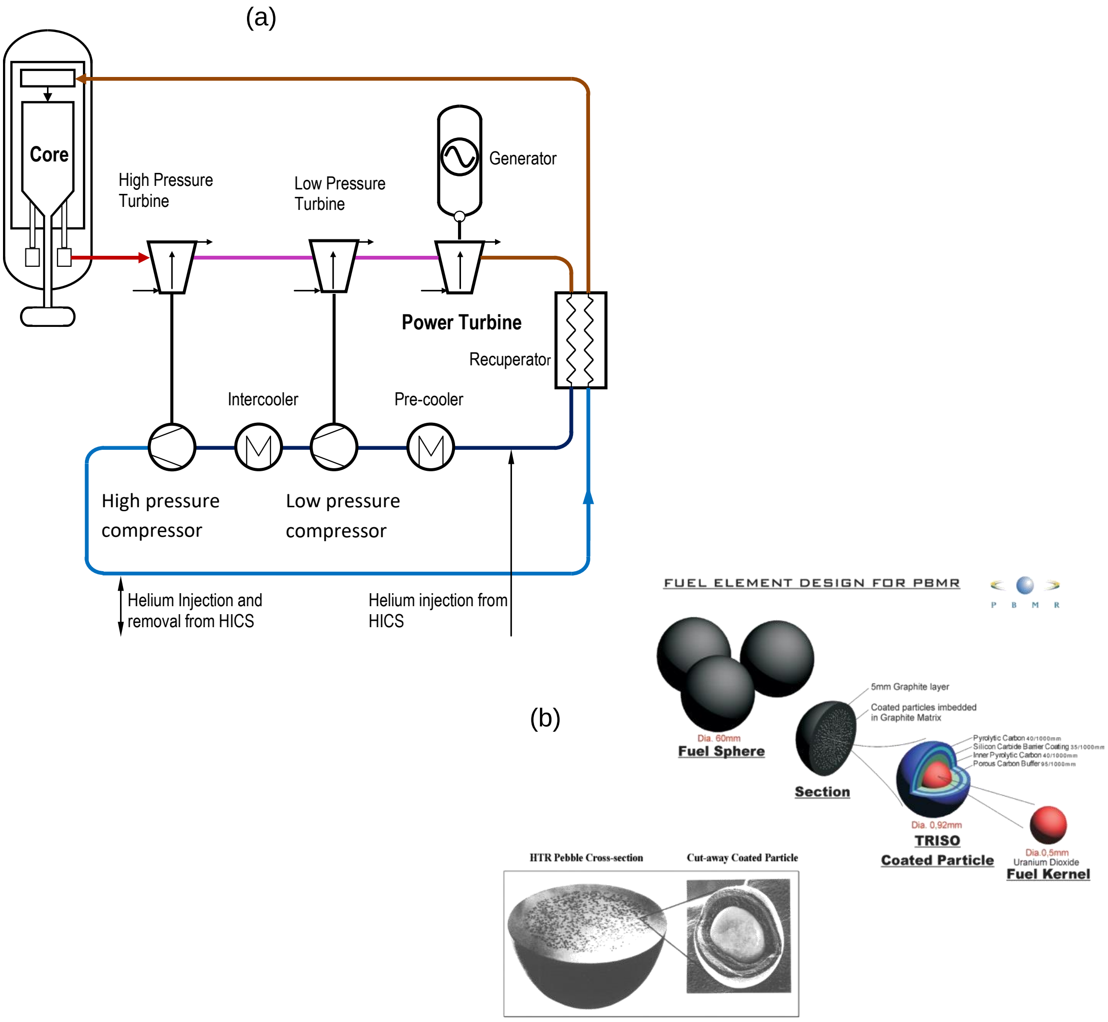

Figure 1: (a) Schematic layout of the PBMR system and (b) anatomy of the pebble [Courtesy, PBMR (PTY) Ltd, SA].

3. Carbon-14 study

Biomass has long been suspected of being capable of preferential sequestration of the carbon atom based on mass. Fossils from the earlier earth suggest higher concentrations of ^{13}C concentration in plants in an atmosphere with both ^{13}C and ^{12}C (Yim and Caron, 2006). This phenomenon is not evident in the modern plants; the presence of this capability in microorganisms from extreme environments may be likely due to preservation of archaic mechanisms in these organisms.

In this study, a consortium of organisms was isolated from oil contaminated sites and radioactive wastewater storage ponds from radioisotope processing facilities in South Africa (Oboirien and Chirwa, 2007). Cultures from the different sources were characterised using the standard 16S rRNA genotype fingerprinting of sequenced DNA and DNA seprated by DGGE of amplified DNA. Initial analysis showed the presence of Klebsiella oxyoetica*,* Ponteae agglomerans, Klebsiella stutseli and Pseudomonas putida as the predominant active agents in the wastewater and sludge sources. K oxyoetica, K stutseli and P agglomerans showed resistance to radiation from nuclear graphite at levels up to 1.055 ± 0.067 Bq·µL^{-1}, enough to inhibit metabolic activity in most mesophilic bacteria from the natural environment (Kudryasheva et al., 2008).

The study was conducted in a continuously mixed reactor (growth vessel) constructed from Pyrex panels (30 cm × 20 cm × 15 cm) with finely ground graphite as the principal carbon source (1,500 - 2,000 mg.L^{-1}) and spikes of glucose (500 mg.L^{-1} every 48 h). The growth vessel was connected to a biofilter unit by submersible pump where particulate matter was isolated for further analysis as described earlier by Molokwane and Chirwa (2007) (Figure 2). The pump was also used for recirculation and mixing.

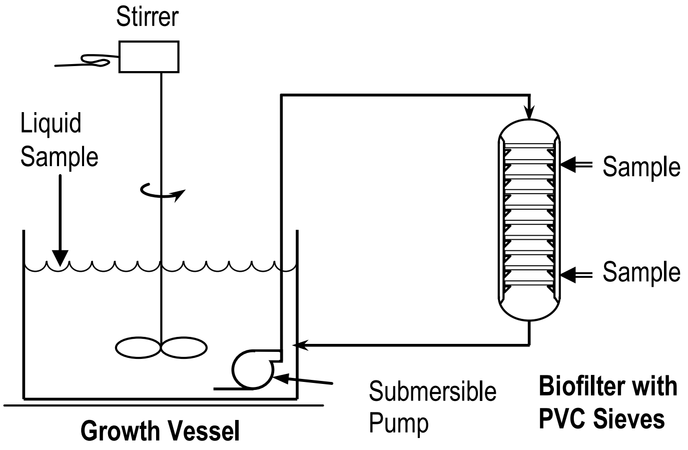

Figure 2: Experimental setup for bioseparation of ^{14}C from $^{12}C/^{14}C$ nuclear graphite (Adopted from Molokwane and Chirwa, 2007).

The samples collected from the aeration chamber (Sample A) and PVC trays (Sample B) were analysed for ^{14}C content by the Tri-Carb 2900TR Liquid Scintillator (Perkin-Elmer, Shelton, Connecticut, USA). The results from detailed analysis after operating the bioreactor for 5 days after adding ^{14}C containing graphite showed a higher ^{14}C count in Sample B from the biofilter racks where the bacteria cells were mostly concentrated (Table 1).

Table 1: Results of the C-14 bioseparation experimental in the fed-batch continuous flow mixed reactor after operation for 5 days.

		Sample A (from reservoir)	Sample B (from biofilter)
CO_2 measurement (torr)			
	Filter	254	171.8
	Bacteria	80	338.2
	Filler	176	0
	Total	510	510
^{14}C measurement			
	Detection time (min)	940	1,124
	Total counts	5,157	10,818
	Sample Activity (cpm)	5.48	11.51

4. Photocatalytic degradation pathway

The degradation pathway in non-radioactive phenolic sample during a photocatalytic process showed than phenol mineralised in a stepwise process with organic intermediate observed at different times until all compounds were degraded (Figure 3) (Chirwa and Bamuza-Pemu, 2010). For higher radioisotopes of C, the

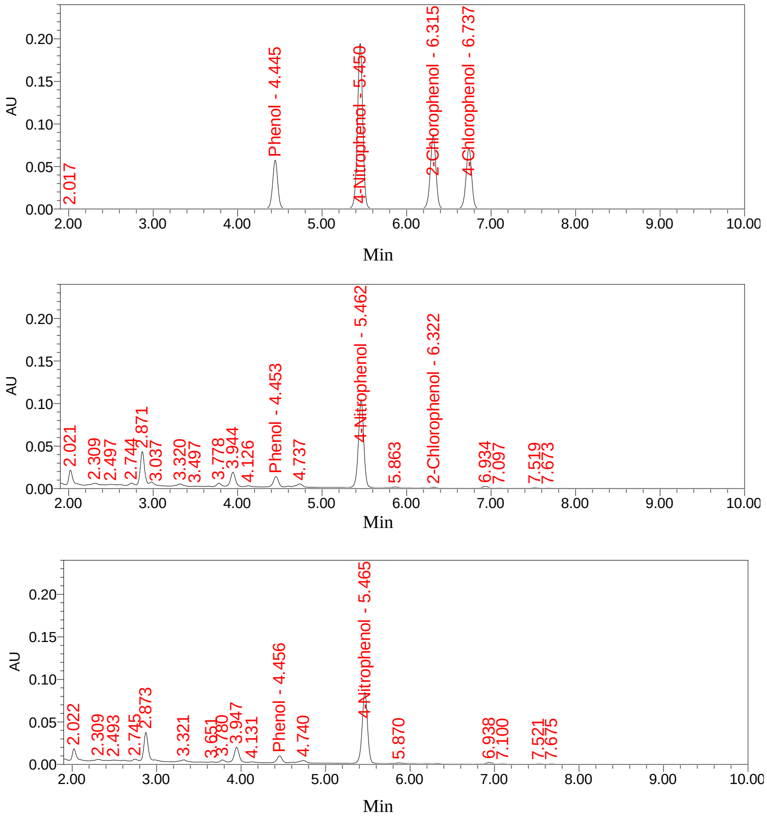

Figure 3: Chromatograms showing intermediates formed at different times during the photocatalytic degradation of mixture of Phenol, 2-CP, 4-CP,and 4-NP.

process was evaluated using ^{13}C-ortho and ^{13}C-para phenol and it showed that the degradation pathway followed the oxidative process involving the intermediate formation catechol → hydroquinone → hydroxyhydroquinone → benzene-1,2,3-triol (Figure 4). These results suggest that, for most of the irradiate compounds, accumulation of intermediate less toxic compounds could benefit the microbial cultures that could be used in the second stage after initial exposure to photocatalytic degradation.

5. Biological degradation pathway

In nuclear fuel processing, the problem is the generation of large volumes of partially water soluble wastes that often contain toxic organic compounds. The use of decontamination reagents such as carbon tetrachloride (CCl_4) together with phenolic tar results in wastewater with a high content of chlorophenols. Chlorophenols cause serious environmental concerns because of their toxic and carcinogenic effects on living organisms (Olaniran and Igbinosa, 2011). Overall, there are 19 possible configurations of chlorinated phenols in nature. One of these, 4-chlorophenol (4-CP), represents the most basic structure and its degradation pathway has been extensively studied in several organisms (Bian et al., 2011). 4-CP was thus used as a model compound representing in the evaluation of the biological degradation of recalcitrant aromatic pollutants in heavily polluted wastewaters such as effluents from nuclear fuel processing and radioisotope manufacturing plants.

The dehalogenation of the phenolic compound happened rather quickly as shown in the photo-oxidation process (Figure 4). The biological degradation of the remnant compound will follow the meta-cleavage pathway under aerobic conditions or the ortho-cleavage pathway under anaerobic conditions. When the conditions are transitional, a truncated meta-cleavage pathway exists in which phenol is converted to HMSA followed by conversion to Acetate and Succinic acid. Evidence of the existence was of the truncated meta-cleavage pathway was demonstrated earlier by Nkhalambayausi-Chirwa and Wang (2001) in reaction where the final products were acetate and succinate in an oxygen-stressed biofilm environment (Figure 5).

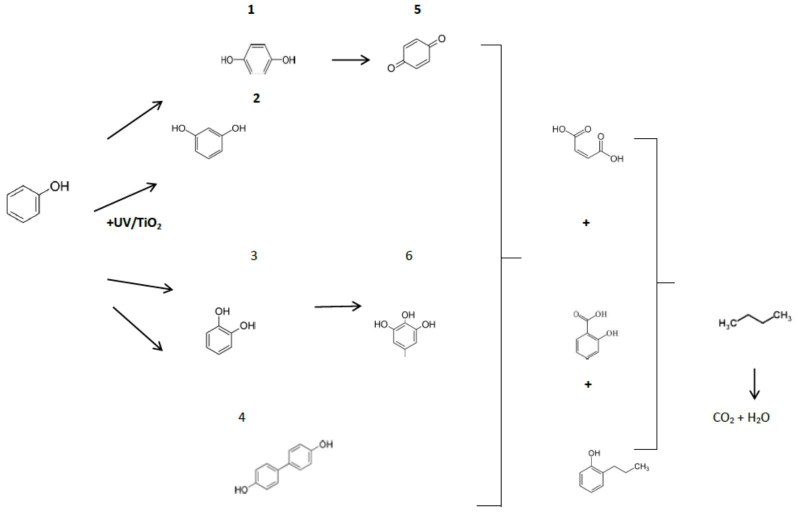

Figure 4: The pathway tracking of degradation products during photolytic degradation of radiocarbon labelled ^{13}C phenol using GC-MS analysis.

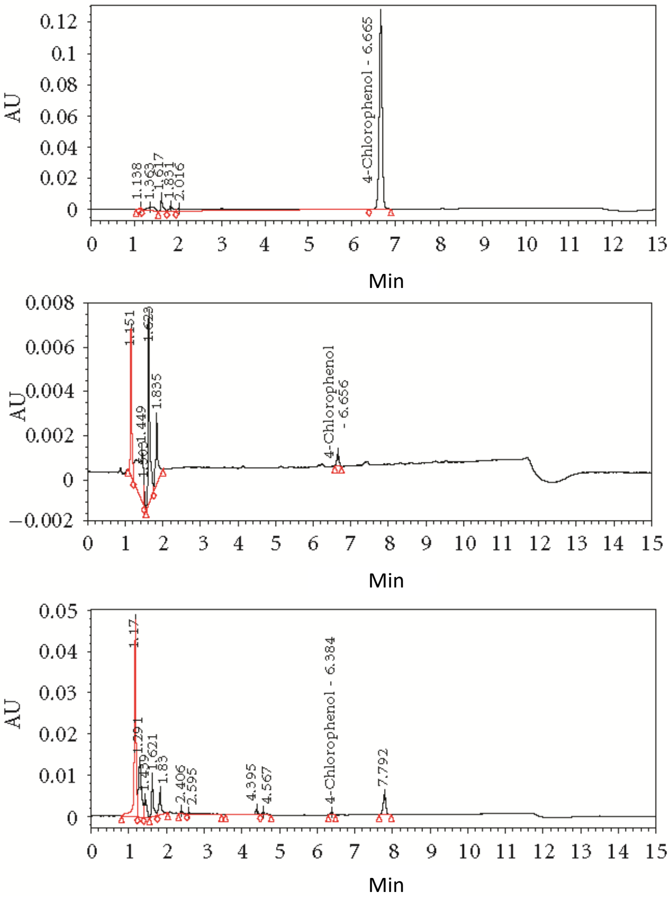

Figure 5: Chromatograms showing the degradation and mineralisation levels during photolytic degradation and biodegradation in a CSTR as the second stage.

6. Conclusion

For the first, the bioseparation of 14C from a 14C/12C graphitic matrix was demonstrated. The microbial consortium that achieved the bioseparation process contained some archaebacterial Panteae agglomerans and Klebsiella stutseli species. Degradation of aromatic compounds was most probably facilitated by Pseaudomansa putida serotypes. The processes investigates show the potential of lowering radiotoxicity of evolved irradiated waste followed by mineralisation of complex aromatic organic compounds using a two-stage photocatalytic-biological process.

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