

Comparison of granular activated carbon bio-sorption and advanced oxidation processes in the treatment of leachate effluent

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Abstract—Landfill leachate is a toxic effluent of a decomposing landfill that is produced when rainwater percolates through the landfill leaching out contaminants and pollutants. Untreated leachate is a potential source for the contamination of soil, surface and ground water. In this study, the treatment processes such as granular activated carbon (GAC) adsorption/bio-sorption (batch), and advanced oxidation processes (AOP) viz. photocatalysis and Fenton's process were evaluated and compared by using synthetic landfill leachate (SLL) as a contaminant. TiO₂ was used as a catalyst in photocatalysis, and Fenton's reagent (H₂O₂/Fe⁺²) was used in Fenton's process. The degradation of SLL effluent by the three above-mentioned processes was characterized by the % TOC removal. The % TOC removed by photocatalysis, Fenton oxidation and bio-sorption (which includes adsorption and biodegradation) was 30, 60 and 85%, respectively. The bio-sorption increased with the increasing GAC dose. The optimum dose of Fenton's reagent in advanced oxidation was 15 and 400 milli moles of Fe⁺² and H₂O₂, respectively. The Fenton's process showed faster degradation kinetics compared to biodegradation and photocatalysis.

Key words: Landfill Leachate, Bio-sorption, Advanced Oxidation, Photocatalysis

INTRODUCTION

Australia is among the highest producers of waste in the world [1]. It generates waste at a rate of 2.25 kilograms per person per day, the majority of which ends up in landfill. During 2002-03 over 17 million tons of waste was disposed in landfills in Australia [2].

As the landfills are open places, the rain water infiltrating through a landfill leaches with it the decomposing organic matter, inorganic ions and heavy metals by physical extraction, hydrolytic and fermentative processes. This contaminant-laden concentrated effluent from the landfill is called landfill leachate. Landfill leachate can be regarded as a high strength wastewater with acute and chronic toxicity. Its composition will vary from site-to-site, depending on many factors including; the nature of the waste in the landfill, the filling method, the level of compaction, the engineering design of the landfill, the rainfall of the region, and the stage of decomposition of the waste [3,4]. Untreated leachate can percolate through the soil, mix with surface or permeate through the ground water and can contribute to the pollution of soil, surface and ground water.

A range of biological and chemical treatment processes for landfill leachate have been studied and shown in Table 1. Biological processes are more effective for young leachate with a high BOD₅/COD ratio. Biological processes are less effective in treating leachates from intermediate or stabilized landfills with a low BOD₅/COD ratio, or with high concentrations of toxic constituents. Bio-sorption is an environmentally friendly process in removing organic matter from wastewater of biological nature, although it has not been tested specifically with landfill leachate effluent [5,6]. To treat these refractory leachates, physico-chemical processes appear viable. These

processes include evaporation, sedimentation, flocculation/precipitation [7,8] ion exchange, activated carbon adsorption [9] chemical oxidation [10-12] membrane filtration including reverse osmosis (RO) [13] and nano filtration (NF) [14]. They are applied as either pre/post-treatments or complete treatments. Advanced oxidation processes such as conventional Fenton, photo-Fenton and electro-Fenton are powerful advanced oxidation processes (AOP) that effectively degrades refractory organics and persistent organic pollutants (POPs), which are difficult to degrade by other processes such as bio-degradation. Furthermore, they can be used as a pretreatment step to facilitate other degradation processes. The important parameters that govern the Fenton process are pH, ratio of Fe⁺²/H₂O₂, and reaction temperature. In fact, Fenton's process is a combination of two processes, chemical oxidation and coagulation. At pH 4 and below the main process is an oxidation process where the organics are degraded by the produced hydroxyl radicals. At higher pH, pH above 5, it is a coagulation process. Ferric hydroxo complexes (precipitates) are formed at higher pH (>5) and these complexes coprecipitate organics from the solution. However, chemical oxidation is the primary objective of Fenton's process. Hence, the Fenton reagents dose optimization and reaction parameters are keys in the success of Fenton's process. Fenton processes are faster, economical and increase the biodegradable fraction of organic constituents in leachate, particularly in mature or biologically recalcitrant leachate [15]. A multivariate approach for the treatment of landfill leachate by Fenton's process was studied, and it was concluded that a low pH and high ratio of H₂O₂/Fe⁺² was desirable for Fenton's process [16].

Another emerging technology is bio-sorption. which was found to effectively remove organic matters from water and wastewater. In bio-sorption, microbial communities establish and grow on the media such as GAC. Organic substances are first adsorbed onto media

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Table 1. Treatment processes for landfill leachate

Treatment processes	Inferences	References
Activated carbon fluidized beds	Adsorption isotherms of three different activated carbons were studied	Rivas (2006)
Biodegradation	The removal mechanism of low molecular weight organics was by biodegradation	Imai (1995)
Coagulation and flocculation as a pretreatment for biodegradation	Comparison of two biological treatment processes	Loukidou (2001)
	Landfill leachate treatment with submerged biofilters	Alvez (2006)
Advanced oxidation	Coagulation removed complex and recalcitrant organic matter reducing the ozone demand	Orta de Velasquez (2006)
	Different coagulant were used to study to decrease COD of landfill leachate	Alvez (2005)
Membrane process	Advanced oxidation by iron coated GAC /H ₂ O ₂	Morais (2005)
	Electro Fenton method	Zhang (2006)
Combined treatment	Advanced oxidation by iron coated GAC /H ₂ O ₂	Huan-Jung Fan (2007)
	Membrane bioreactor (MBR) and reverse osmosis (RO)	Won-Young Ahn (2002)
Combined treatment	Ultrafiltration treatment of landfill leachates	Tabet (2002)
	Nano-filtration treatment landfill leachate	Wahab (2004)
Combined treatment	Biodegradation followed by chemical oxidation using ozone and Fenton methods	Iaconi (2006)

Table 2. Composition of synthetic landfill leachate (SLL)

Component	Per liter	Composition of trace metal solution (TMS)	
Acetic acid	7 mL	FeSO ₄	2,000 mg
Propionic acid	5 mL	H ₃ BO ₄	50 mg
Butyric acid	1 mL	ZnSO ₄ ·7H ₂ O	50 mg
K ₂ HPO ₄	30 mg	CuSO ₄ ·5H ₂ O	40 mg
KHCO ₃	312 mg	MnSO ₄ ·7H ₂ O	500 mg
K ₂ CO ₃	324 mg	(NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O	50 mg
NaCl	1,440 mg	Al ₂ (SO ₄) ₃ ·16H ₂ O	30 mg
NaNO ₃	50 mg	CoSO ₄ ·7H ₂ O	150 mg
NaHCO ₃	3,012 mg	NiSO ₄ ·6H ₂ O	500 mg
CaCl ₂	2,882 mg	96% H ₂ SO ₄	1 mL
MgCl ₂ ·6H ₂ O	3,114 mg		
MgSO ₄	156 mg		
NH ₄ HNO ₃	2,439 mg		
Urea CO(NH ₂) ₂	659 mg		
Na ₂ S·9H ₂ O	Titrate to Eh-120 mv:-180 mv		
NaOH	Trite to pH=5.8-6.0		
Trace metal solution	1 mL		
Distilled water	to make 1 L		

and then biodegraded by the microbial communities. Bio-sorption can be performed in fixed beds (bio-filters) or batch reactors.

In this study, the treatment of landfill leachate effluent (percolated through the soil) by GAC bio-sorption, (simulating a batch reactor) and AOP processes such as photocatalysis and advanced oxidation (Fenton's process) was investigated and compared.

EXPERIMENTAL METHODOLOGY

1. Synthetic Landfill Leachate (SLL)

The study was conducted with SLL. The composition of the SLL

is given elsewhere [17] and is shown in Table 2. It should be noted that the TOC concentration (64 mg/l) was selected to simulate the contaminated ground water by leachate percolating through soil and reaching the ground water. The contribution of fatty acids, viz. acetic acid, propanoic acid and butyric acid of SLL, towards % TOC is shown in Fig. 1.

2. Materials

GAC manufactured by Calgon Carbon Corporation, USA was used as media in adsorption/bio-sorption experiments and its properties are shown in Table 3.

3. GAC Adsorption/Bio-sorption

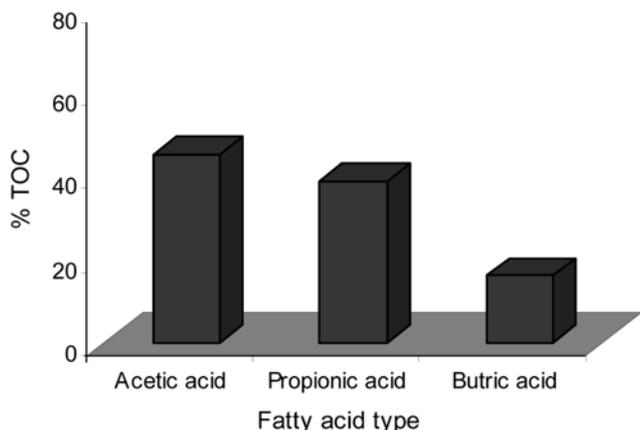


Fig. 1. Contribution of organic matter of SLL towards % TOC.

Table 3. Characteristics of granular activated carbon (GAC) used in this study (Calgon Carbon Corp., USA)

Specification	GAC
Surface area (m ² /g)	1001.2
Mean pore diameter (Å)	22.55
Micropore volume (cm ³ /g)	0.269
Mean diameter (µm)	750
Bulk density (kg/m ³)	600
Product code	F-400

Batch adsorption/bio-sorption study was performed in 1 L beakers with 20, 40 and 60 g/l of GAC. A control sample containing 20 g/l of GAC with 0.05% sodium azide was used to check the bio growth. The sodium azide suppresses/or eliminates the bio-growth. SLL with a TOC concentration of 64 mg/l was used. The solutions were continuously stirred and aerated. The SLL was replenished with fresh SLL every day (20% of fresh TOC was added daily) to provide continuous organic carbon and nutrient supply for bio growth.

4. Microbiological Analysis

GAC particle samples were taken on a periodic basis to perform a quantitative microbiological analysis. The spread-plate technique with a medium of nutrient agar was used to determine the viable counts and give an estimate the number of viable microbial mass in these samples.

5. Advanced Oxidation

Advanced oxidation of SLL was carried out by using Fenton's reagent (FeSO₄/H₂O₂). The degradation of SLL was characterized by determining the total organic carbon (TOC) in the effluent samples. The reduction of TOC in the effluent samples denotes mineralization of organic matter. The TOC was measured by TOC analyzer (Multi N/C 200 analyzer, Analytica Jena AG). The advanced oxidation experiment was performed in a jar test at room temperature (22-24 °C). Dose optimization of Fe⁺² (FeSO₄·7H₂O) was determined in a series of experiments containing different concentration of Fe⁺². The optimized dosage of Fe⁺² (FeSO₄·7H₂O) was 15 milli moles. A known concentration of SLL (64 mg/L TOC) was added to different beakers containing optimized dosage of Fe⁺² ions. The pH of the solution was maintained at 2.5 (a prerequisite for Fenton reaction) through the addition of required amount of dilute H₂SO₄.

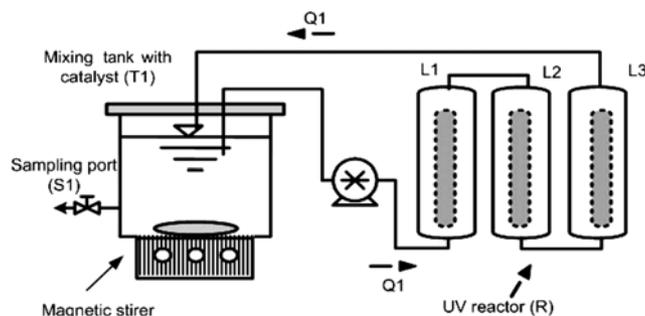


Fig. 2. Photo-catalytic batch reactor system (T1, mixing tank with catalyst 1.5 L; S1, sampling port; Q1, flow line; R, UV reactor unit; L1, L2, L3, 70 mL each with total 210 mL UV lamps 8 watts each, Q1=200 mL/min).

An increasing concentration of H₂O₂ was added to each beaker. The consumed and residual amounts of H₂O₂ were determined by iodometric method. The ferrous, ferric and total iron of SLL effluent was determined by 5-sulfosalicylic method [18].

6. Recirculated Photocatalysis Reactors

In the photo-catalysis process with TiO₂ as catalyst. Hydroxyl radicals (strong oxidizing agents) are produced due to the interaction of UV with TiO₂. A comprehensive review of photocatalysis processes using UV/TiO₂ has been documented [19]. The photocatalysis reactor system comprised of three stainless steel reactors (L1, L2 and L3 as shown in Fig. 2) each with a volume of 70 mL. TiO₂ was dosed directly into a holding tank (T1) containing 5 L of stock solution. The solution was mixed with a magnetic stirrer. Air sparging was also provided. The temperature in the circulation tank was controlled by a thermoline. The solution containing TiO₂ was pumped to the photo-catalytic reactor at flow rates of 200 mL/min.

7. SEM/EDX of TiO₂, and PAC Coated TiO₂

Photocatalysis experiments were conducted both with TiO₂ and TiO₂-coated PAC (TiO₂/PAC). The Figs. 3(a) and 3(b) shows scanning electron microscopy (SEM) images of PAC and TiO₂/PAC, respectively. The PAC surface consisted of a clean surface area, while the TiO₂/PAC surface was coated with TiO₂. The majority of particles were found to be less than 1 µm, which were constituted by agglomerates of 0.05 µm TiO₂ particles. The deposition of TiO₂ on PAC was not uniformly distributed.

Energy dispersive X-ray (EDX) analysis was performed to determine the presence of the different elements in PAC and TiO₂/PAC (Figs. 4(a) and 4(b)). EDX mapping technique showed that different elements were spread in/on PAC and TiO₂/PAC. The elements on the PAC were C (92%), O (7%) and K (1%). The elements on the TiO₂/PAC were C, O, Na, Si, S, K and Ti. The Ti content on TiO₂/PAC was only 6.8% in terms of weight percentage. The characteristics of P25-TiO₂ are as follows: non-porous, 65% anatase, 25% rutile, size=25 nm and surface area=42.3 m²/g. The details can be found elsewhere [20].

RESULTS

1. GAC Bio-sorption

The adsorption equilibrium of organic matter onto the GAC was attained within three hours of experimental operation and the per-

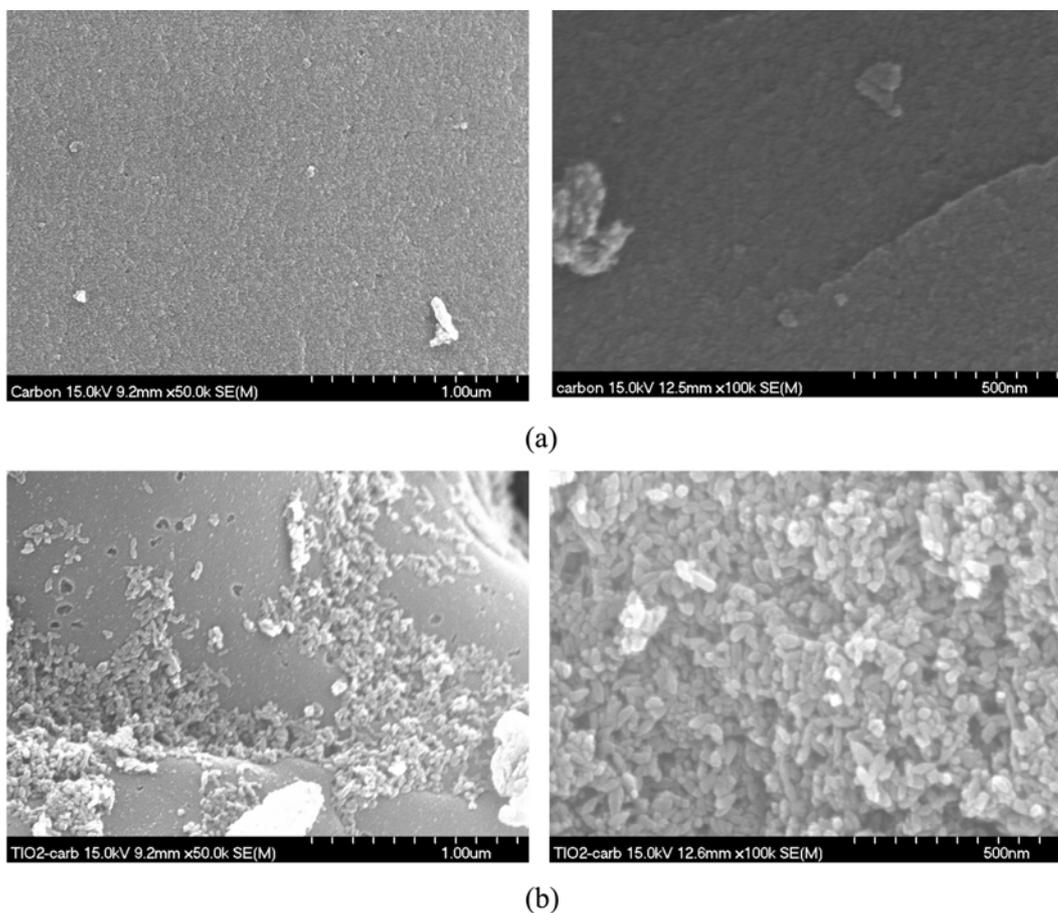


Fig. 3. (a) SEM image of PAC, (b) SEM image of TiO₂ coated with PAC (TiO₂/PAC).

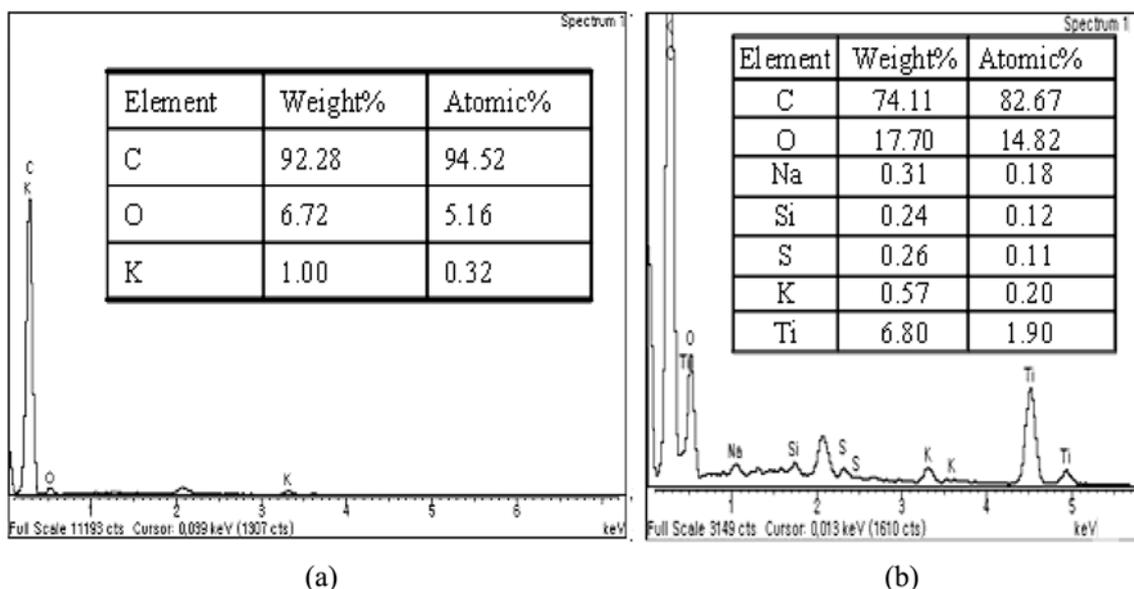


Fig. 4. (a) EDX results on PAC, (b) EDX results on TiO₂/PAC.

cent TOC removed (due to adsorption) by 20, 40, 60 g/l GAC was 44, 48 and 63 percent, respectively (Fig. 5(a)). The pH, total alkalinity and TOC were regularly monitored throughout the experiments. The adsorption equilibrium concentration was maintained for the

first two days and TOC concentration in SLL remained unchanged. After two days, the concentration of TOC started to decrease in SLL and the solution became turbid. The TOC concentration in the control sample (in which sodium azide was added) remained unchanged.

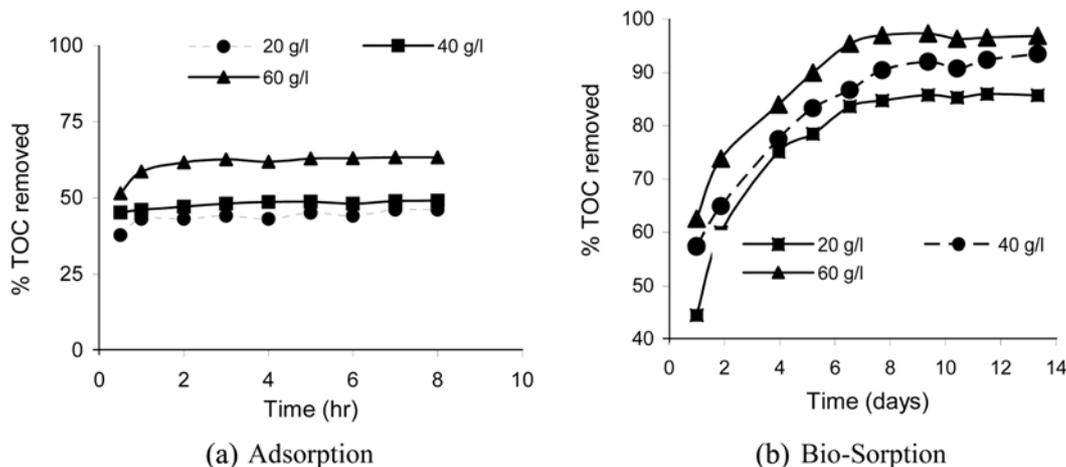


Fig. 5. Removal of organic matter by GAC (TOC of SLL=64 mg/l).

The decrease in TOC concentration could be attributed to the adsorption of bulk TOC onto the GAC due to the degradation of adsorbed organic matter (on GAC) by microbial communities. Bio-degradation and bio-sorption alternates on GAC surface are a function of bioactivity. Hence, the organic content and nutrient supply are important in sustaining the microbial activity (biodegradation).

Every day, the organic matter in the jar was replenished by replacing 20% of TOC concentration. From day 6 onwards, the TOC removal efficiency was practically constant and highest. The total percent TOC removed (including adsorption and bio-sorption) during this bio-degradation phase was 85, 92 and 97% for the 20, 40 and 60 g/l GAC, respectively (Fig. 5(b)). The replenishment decreased the pH of the solution to 6 (because the pH of SLL was 6). The pH then increased with time and reached a maximum of 8.2 during the day (Fig. 6). The increase in pH with time was due to the increase in total alkalinity and HCO_3^- concentration of the SLL. The pH in the control sample (containing sodium azide) was practically unchanged due to limited or no bioactivity. The mineralization of organic compounds in SLL, hence, could be attributed to bio-degradation.

2. Microbiological Analysis

A quantitative microbiological analysis was carried out on GAC

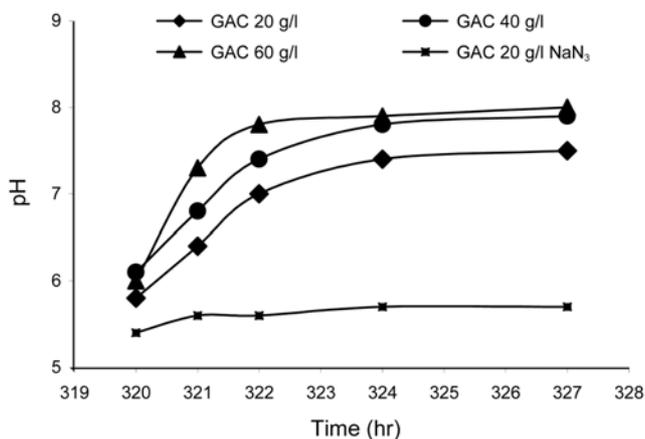


Fig. 6. pH increase with time from 318 to 328 hr.

particle samples on a periodic basis by using the spread-plate technique with a medium of nutrient agar. This method gives an estimate of the viable microbial mass in each sample. The SLL used in these experiments was rich in carbon, nitrogen and other nutrient sources. As a result, the number of viable bacteria increased uniformly during the initial period. Fig. 7 shows a similar rate of microbial growth for both GAC samples taken from experiments with

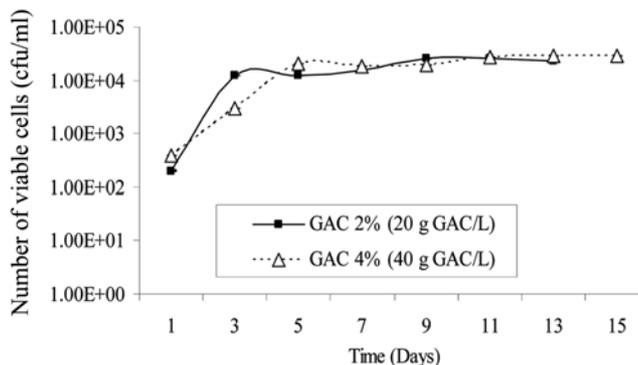


Fig. 7. Microbial analysis of bio-sorbed GAC.

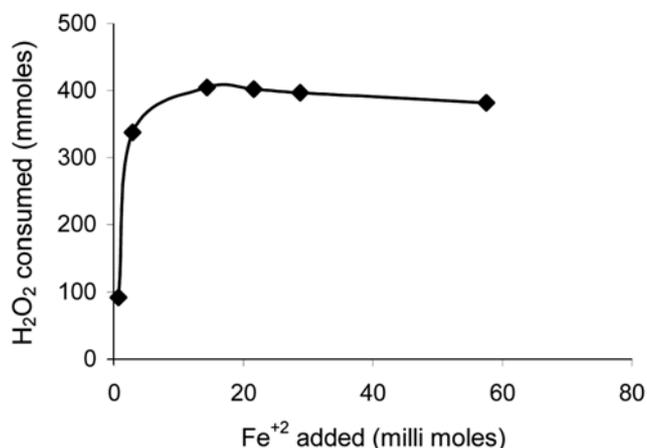
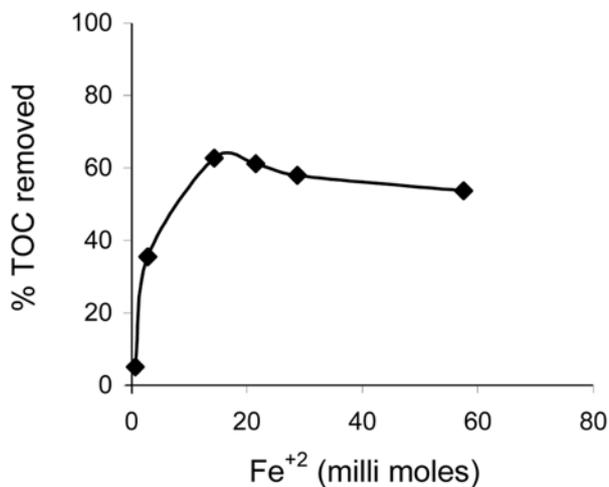
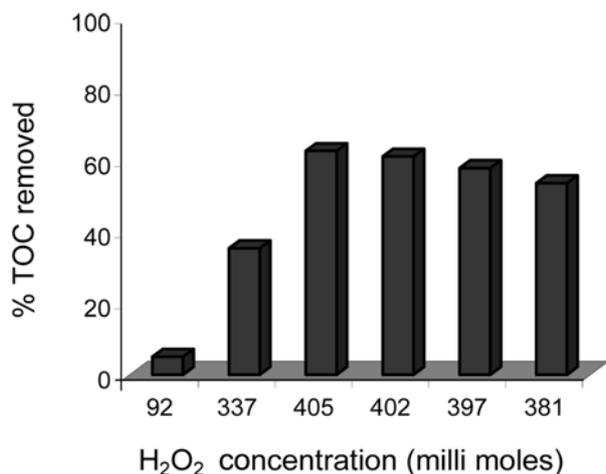


Fig. 8. Fenton's reagent (Fe^{+2} and H_2O_2) dose optimization.



(a) Effect of Fe^{2+} concentration in milli moles (H_2O_2 concentration = 400 millimoles)



(b) Effect of H_2O_2 concentration in milli moles (Fe^{2+} concentration = 15 milli moles)

Fig. 9. Percent TOC removed by advanced oxidation (Fenton process).

a concentration of 2% and 4% GAC (20 g GAC/L and 40 g GAC/L). However, the bio-degradation increased with the weight of the GAC as can be seen from Fig. 5(b). The viable numbers increased rapidly and reached stationary phase in a period of 15 days.

3. Advanced Oxidation

The optimum Fe^{2+} and H_2O_2 dose was 15 and 400 milli moles (Fig. 8). Advanced oxidation removed TOC by 60% at an optimum dose of Fenton's reagent (Fig. 9(a) and 9(b)). The faster reaction kinetics of Fenton's processes is an advantage compared with biodegradation and photocatalysis. The rate of degradation and percent H_2O_2 consumption was a function of initial TOC (organic loading) concentration of the leachate effluent. The percent TOC removal in both cases (66 and 660 mg/l initial TOC) was 60%, but the rate of degradation was slower in case of 660 mg/l initial TOC (Fig. 10). The effect of oxidation state of catalyst (Fe) in Fenton processes was also studied by using FeCl_3 (Fe^{3+}) and FeSO_4 (Fe^{2+}). The results suggested that the TOC removal efficiency was not affected signif-

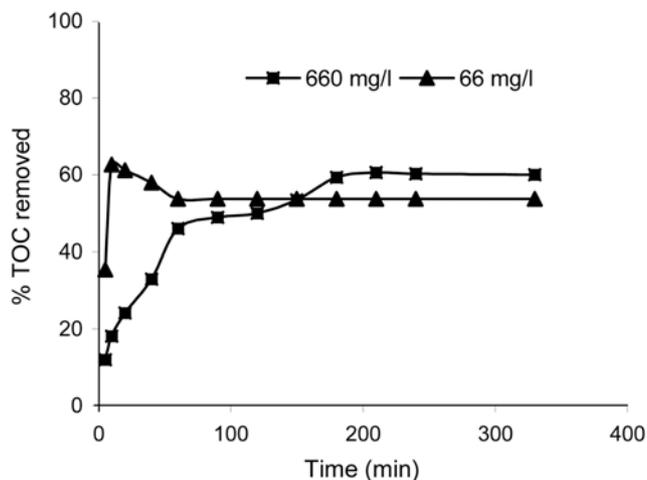


Fig. 10. Comparison of TOC removal rate for different initial TOC concentrations of leachate; (H_2O_2 concentration=400 millimole, Fe^{2+} concentration=15 milli-moles).

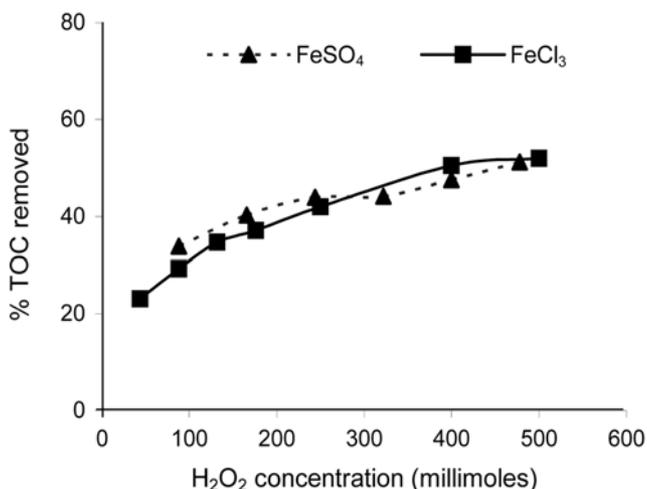


Fig. 11. The effect of oxidation state of iron and % TOC removal in Fenton reaction (Reaction time 2 hrs).

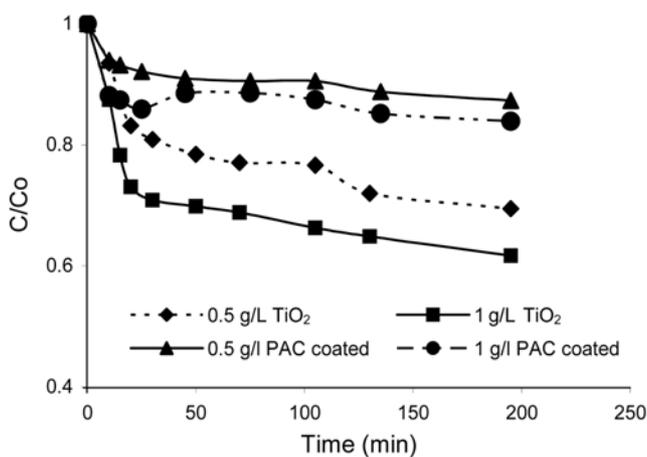


Fig. 12. Organic matter removal (as DOC) from SLL in a recirculated photocatalysis reactor.

Table 4. Comparison of treatment efficiencies in the three different processes used

Treatment process	Reagents concentration	% TOC removed
Photocatalysis	1 gm/L TiO ₂	30
Advanced oxidation	(H ₂ O ₂ 400 millimoles; Fe ⁺² 15 millimoles; Initial TOC concentration 64 mg/L)	60
Bio-sorption	GAC (20 g/L)	85
	GAC (40 g/L)	92
	GAC (60 g/L)	97

icantly by the oxidation state of Fe catalyst (Fig. 11). Similar findings were reported. It was verified that the oxidation state of the catalyst does not influence the efficacy of the process in terms of removal of chemical oxygen demand [22].

4. Photocatalysis

Fig. 12 presents the removal of organic matter from SLL at different concentrations of TiO₂ and TiO₂/PAC in a photocatalysis reactor. The photocatalysis with TiO₂ led to only 30% of DOC removal at a TiO₂ dose of 1 g/L. The TiO₂/PAC was not efficient in removing DOC from SLL. This may be due to PAC pore blockage by TiO₂ nano-particle. Also, the amount of TiO₂ deposited on the PAC was marginal (<7%). A comparison of % removal by bio-sorption, photocatalysis and advance oxidation is shown in Table 4.

CONCLUSIONS

The degradation of SLL effluent by biological and advanced oxidation treatment processes, namely photocatalysis and Fenton process, was investigated and compared. The percent TOC removal by photocatalysis, Fenton oxidation and bio-sorption was 30, 60 and 85%, respectively. However, the degradation kinetics by Fenton processes was faster than photocatalysis and GAC bio-sorption. In this study the optimum dose of Fenton's reagent was 15 and 400 millimoles of Fe⁺² and H₂O₂, respectively. The degradation kinetics and oxidant (H₂O₂) consumption in Fenton's process was a function of initial TOC concentration. In photocatalysis process, the TiO₂-coated PAC did not significantly enhance the degradation compared to uncoated PAC.

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