

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. It 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 were evaluated using synthetic landfill leachate (SLL) as a contaminant. Advanced oxidation of SLL was studied using Fenton's reagent ($\text{H}_2\text{O}_2/\text{Fe}^{+2}$). The total organic carbon (TOC) removal efficiency (of landfill leachate) was evaluated for sequential adsorption/bio-sorption (on GAC) and Fenton process and compared with photocatalysis. The percent TOC removed by GAC bio-sorption at the peak bio-growth was 85, 92 and 97 % for the 20, 40 and 60 g/l GAC respectively. The Advanced oxidation process removed 60% of the TOC at an optimum dose of Fenton's reagent (15 and 400 milli moles of Fe^{+2} and H_2O_2). Photo-catalysis with TiO_2 removed only 30% of the TOC. The TiO_2 coated on powdered activated carbon (PAC) as a photo catalyst led to even lower TOC removal of less than 7%.

Keywords: Landfill leachate, biofilters, 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 tonnes 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 a 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 the ground water and can contribute to the pollution of soil, surface water 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 leachate 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 and 6]. To treat these refractory leachates, physico-chemical processes appear viable. These processes

include evaporation, sedimentation, flocculation/precipitation [7 and 8] ion exchange, activated carbon adsorption [9] chemical oxidation [10, 11 and 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 effective in reducing concentrations of refractory organic contaminants and colour. Fenton process involves oxidation of organic compounds by hydrogen peroxide (H_2O_2) and Fe^{+2} ions. 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 treatment of landfill leachate by Fenton's process was studied. It was concluded that a low pH and high ratio of $\text{H}_2\text{O}_2/\text{Fe}^{+2}$ 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 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 (percolated through the soil) by GAC bio-sorption (simulating a batch reactor) and advanced oxidation using Fenton's reagent ($\text{FeSO}_4/\text{H}_2\text{O}_2$) was investigated and compared with photocatalysis.

EXPERIMENTAL METHODOLOGY

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 percolated through soil and reached the ground water. The contribution of fatty acids viz. acetic acid, propionic acid and butyric acid of SLL towards % TOC is shown in Figure 1.

Materials

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

GAC Adsorption/Bio-sorption

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.

Advanced Oxidation

Advanced oxidation of SLL was carried out using Fenton's reagent ($\text{FeSO}_4/\text{H}_2\text{O}_2$). The degradation of SLL was characterized by determining the total organic carbon (TOC) in the effluent samples. The TOC was measured by TOC analyzer. The advanced oxidation experiment was performed in a jar test at room temperature. Dose optimization of Fe^{+2} ($\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$) was determined in a series of experiments containing different concentration of Fe^{+2} . The optimized dosage of Fe^{+2} ($\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$) was 15 milli moles. A known concentration of SLL (TOC) was added to different beakers

containing optimized dosage of Fe^{+2} . The pH of the solution was maintained at 2.5 (a prerequisite for Fenton reaction) through the addition of required amount of dilute H_2SO_4 . An increasing concentration of H_2O_2 was added to each beaker. The consumed and residual amounts of H_2O_2 were determined by iodometric method.

Recirculated Photocatalysis reactors

In photo-catalysis process TiO_2 as catalyst. Hydroxyl radicals (strong oxidizing agents) are produced due to the interaction UV with TiO_2 . A comprehensive review of photocatalysis processes using UV/ TiO_2 has been documented [18]. The photocatalysis reactor system comprised of three stainless steel reactors (L1, L2 and L3 as shown in Figure 2) each with a volume of 70 mL. TiO_2 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 TiO_2 was pumped to the photo-catalytic reactor at flow rates of 200 mL/min.

SEM/EDX of TiO_2 , and PAC coated TiO_2

Photocatalysis experiments were conducted both with TiO_2 and TiO_2 coated PAC (TiO_2/PAC). The Figures 3 and 4 show scanning electron microscopy (SEM) images of PAC and TiO_2/PAC respectively. PAC surface consisted of clean surface area, while TiO_2/PAC surface was coated with TiO_2 . The majority of particles were found to be less than 1 μm , which were constituted by agglomerates of 0.05 μm TiO_2 particles. The deposition of TiO_2 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 (Figures 5 and 6). 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 [19].

RESULTS

GAC Bio-sorption

The adsorption equilibrium of organic matter onto the GAC was attained within three hours of experimental operation and the percent TOC removed (due to adsorption) by 20, 40, 60 g/l GAC was 44, 48 and 63 percent respectively (Figure 7). The pH, total alkalinity and TOC were regularly monitored through out the experiments. This adsorption equilibrium concentration was maintained for the first 2 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. As mentioned before, 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 percent TOC removed during this bio-degradation phase was 85, 92 and 97 % for the 20, 40 and 60 g/l GAC respectively (Figure 8). The replenishment decreased the pH to 6 (because the pH of SLL was 6). The pH then, increased with the time and reached a maximum of 8.2 during the day (Figure 9). The pH in the control sample (containing sodium azide) was practically unchanged. The increase in pH with time could be attributed to the increase in total alkalinity and HCO₃ concentration of the SLL. The mineralization of organic compounds in SLL hence, was due to bio degradation. **Our previous study confirmed this phenomenon [6]. Biogrowth in terms of viable microbial cells is discussed**

elsewhere [6].

Advanced Oxidation

The effect of Fenton oxidation in removing organic matter (TOC of SLL) was also studied. The optimum Fe^{2+} dose was observed to be 15 milli moles (Figure 10). The results also showed that the optimum dose of H_2O_2 was 400 milli moles (Figure 13). Also, more than 95 % of H_2O_2 used was consumed in the oxidation. Advanced oxidation removed the TOC by 60% at an optimum dose of Fenton's reagent (Figure 11). The oxidation was completed with 10 minutes of reaction time (Figure 12). The effect of oxidation of oxidation state of catalyst (Fe) in Fenton processes was also studied using FeCl_3 (Fe^{+3}) and FeSO_4 (Fe^{+2}). The results suggested that the TOC removal efficiency was not affected greatly by the oxidation state of Fe catalyst (Figure 14). Similar finding 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 [20].

Photocatalysis

Figure 15 presents the removal of organic matter from SLL at different concentrations of TiO_2 and TiO_2/PAC in photocatalysis reactor. The photocatalysis with TiO_2 led to only 30% of DOC removal at a TiO_2 dose of 1 g/L. The TiO_2/PAC was not efficient in removing DOC from SLL. This may be due to PAC pore blockage by TiO_2 nano-particle. Also, the amount of TiO_2 deposited on the PAC was marginal (< 7%).

CONCLUSIONS

GAC bio-sorption led to a consistent TOC removal without the need to regenerate the activated carbon. The bio-sorption followed a bio-growth curve. The percent TOC removed at the peak bio-

growth was 85, 92 and 97 % for the 20, 40 and 60 g/l GAC. The pH and total alkalinity increased during the biodegradation. The increase in pH and total alkalinity was due to the formation of bicarbonate (HCO_3). Advanced oxidation using Fenton reagent led to 60% of TOC removal. The Fe^{2+} and H_2O_2 doses were 15 and 400 milli-mole/L. A pre-treatment of bio-sorption led to an organic removal in SLL of 75% even with a small concentration of H_2O_2 as low as 200 millimole/L. A comparative study made with photocatalysis showed that the advanced oxidation was better than photocatalysis in treating landfill leachate.

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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 Comparison of two biological treatment processes Landfill leachate treatment with submerged biofilters	Imaii (1995) Loukidou (2001) Alvez (2006)
Coagulation and flocculation as a pretreatment for biodegradation	Coagulation removed complex and recalcitrant organic matter reducing the ozone demand Different coagulant were used to study to decrease COD of landfill leachate	Orta de Velasquez (2006) Alvez (2005)
Advanced oxidation	Advanced oxidation pre-treatment to improve biodegradability Electro Fenton method Advanced oxidation by iron coated GAC /H ₂ O ₂	Morais (2005) Zhang (2006) Huan-Jung Fan (2007)
Membrane process	Membrane bioreactor (MBR) and reverse osmosis (RO) Ultrafiltration treatment of landfill leachates Nano-filtration treatment landfill leachate	Won-Young Ahn (2002) Tabet (2002) 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	7mL	FeSO ₄	2000mg
Propionic acid	5mL	H ₃ BO ₄	50mg
Butyric acid	1mL	ZnSO ₄ •7H ₂ O	50mg
K ₂ HPO ₄	30mg	CuSO ₄ •5H ₂ O	40mg
KHCO ₃	312mg	MnSO ₄ •7H ₂ O	500mg
K ₂ CO ₃	324mg	(NH ₄) ₆ Mo ₇ O ₂₄ •4H ₂ O	50mg
NaCl	1440mg	Al ₂ (SO ₄) ₃ •16H ₂ O	30mg
NaNO ₃	50mg	CoSO ₄ •7H ₂ O	150mg
NaHCO ₃	3012mg	NiSO ₄ •6H ₂ O	500mg
CaCl ₂	2882mg	96% H ₂ SO ₄	1mL
MgCl ₂ •6H ₂ O	3114mg		
MgSO ₄	156mg		
NH ₄ HNO ₃	2439mg		
Urea CO(NH ₂) ₂	659mg		
Na ₂ S•9H ₂ O	Titrate to Eh-120mv:- 180mv		
NaOH	Trite to pH=5.8-6.0		
Trace metal solution	1mL		
Distilled Water	to make 1L		

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

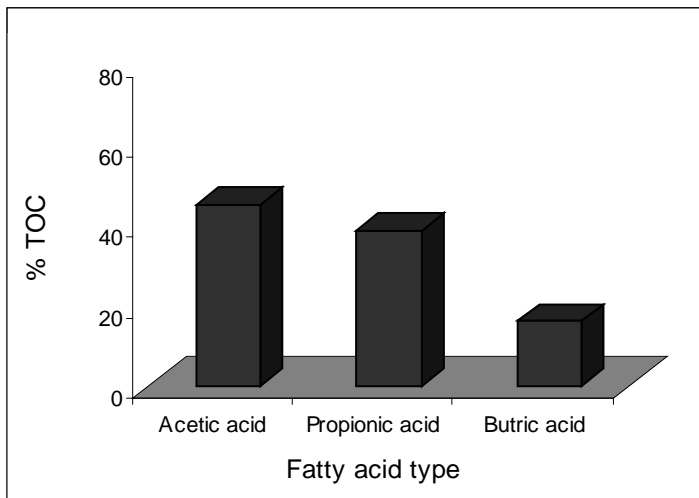


Figure 1. Contribution of organic matter of SLL towards % TOC

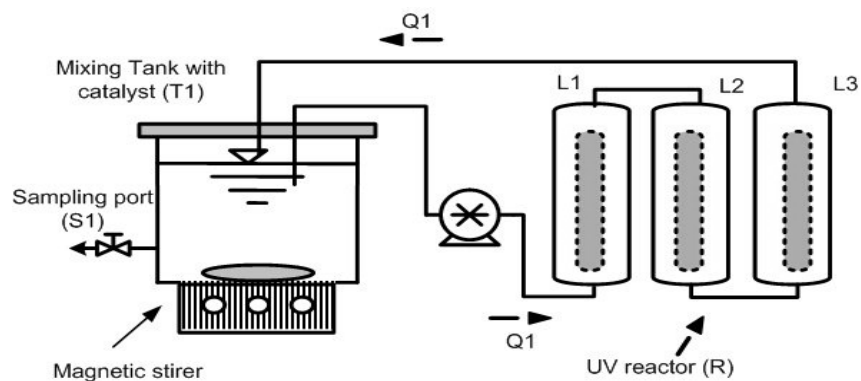


Figure 2. Photo-catalytic batch reactor system (T1; mixing tank with catalyst 1.5 L, S1; sampling port, Q1; flow line, R; UV reactor unit, L1, L2, L3, 70 mL each with total 210 mL UV lamps 8 watts each, $Q1=200$ mL/min)

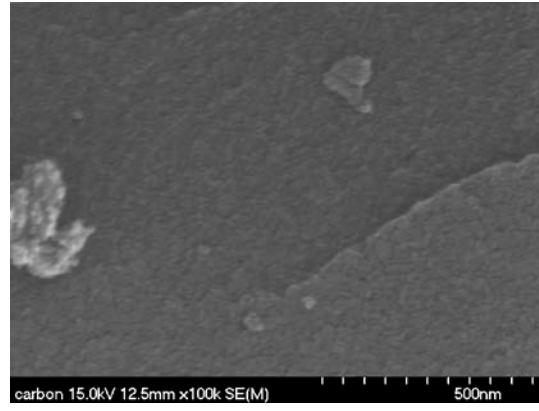
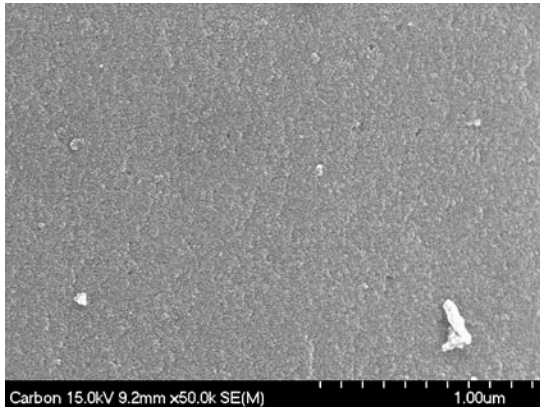


Figure 3. SEM image of PAC

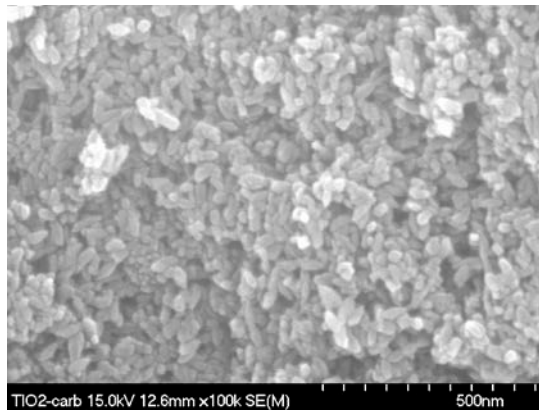
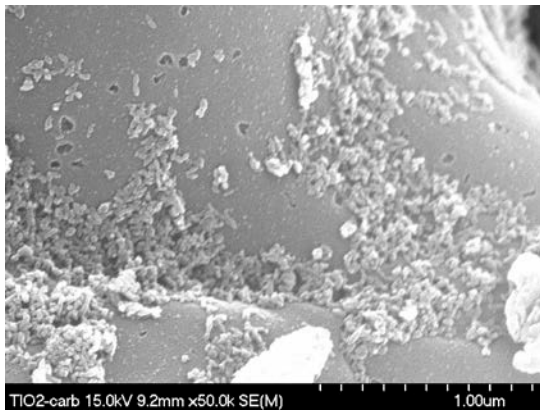


Figure 4. SEM image of TiO₂ coated with PAC (TiO₂/PAC)

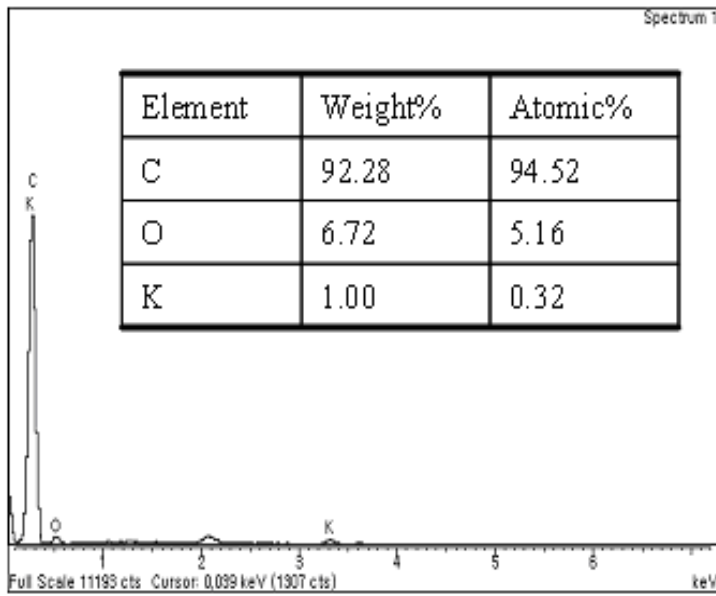


Figure 5. EDX results on PAC

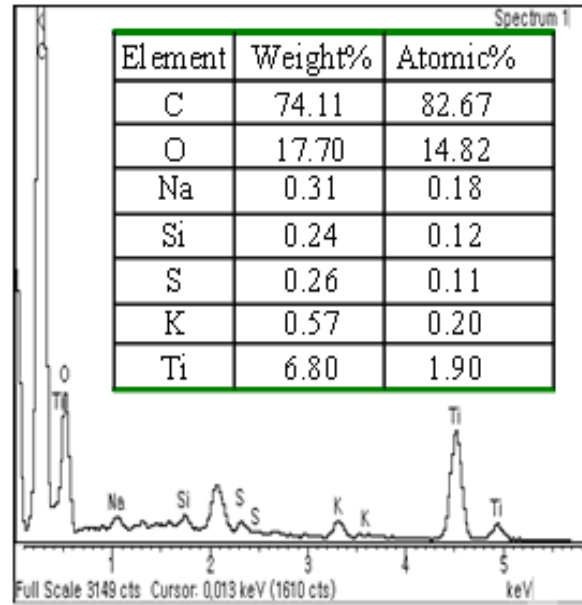


Figure 6. EDX results on TiO₂/PAC

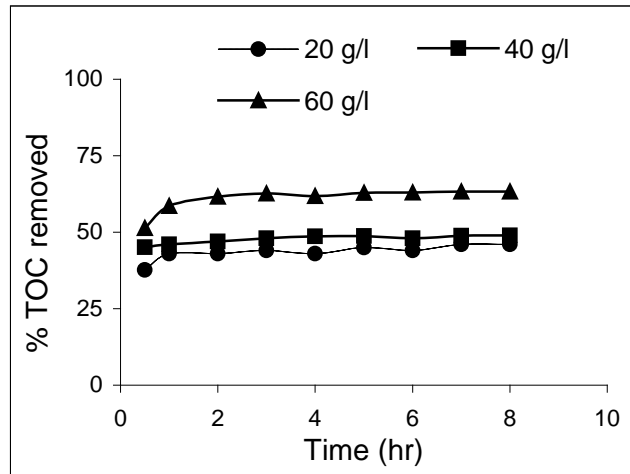


Figure 7. Adsorption of organic matter on GAC g/l (TOC of SLL = 64mg/l)

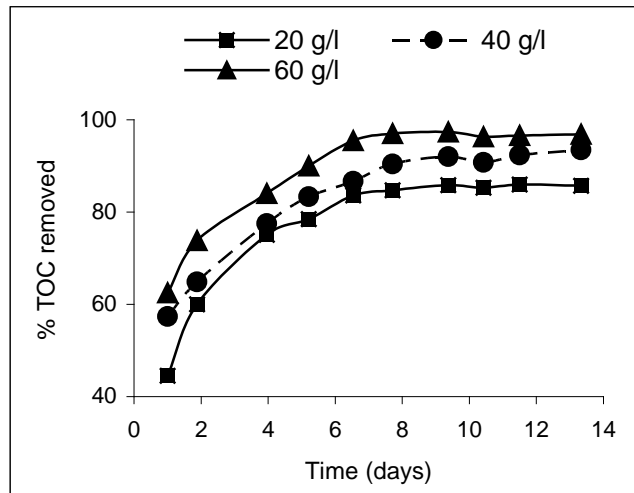


Figure 8. Bio-sorption of organic matter on GAC g/l (TOC of SLL = 64mg/l)

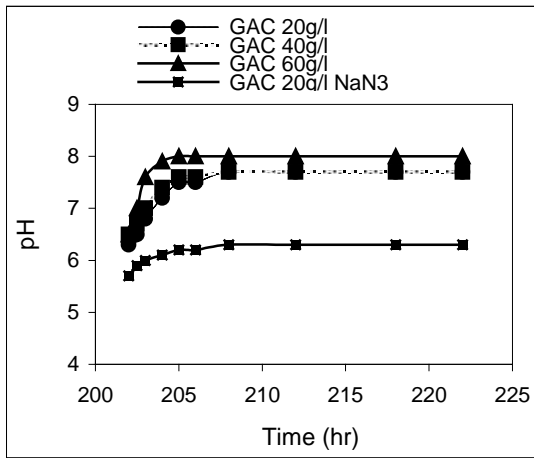


Figure 9 (a). pH increase with time from 200 to 225hr (NaN₃= sodium azide)

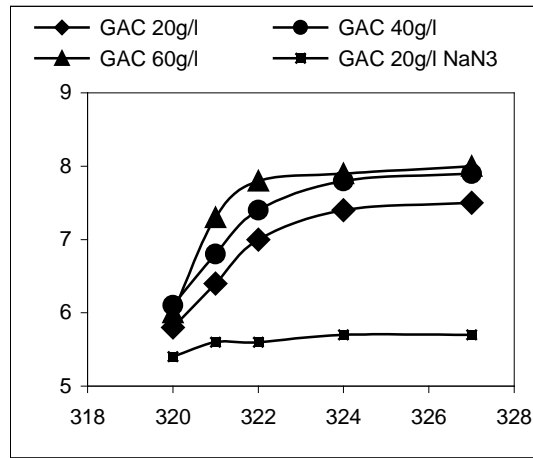


Figure 9 (b). pH increase with time from 318 to 328hr

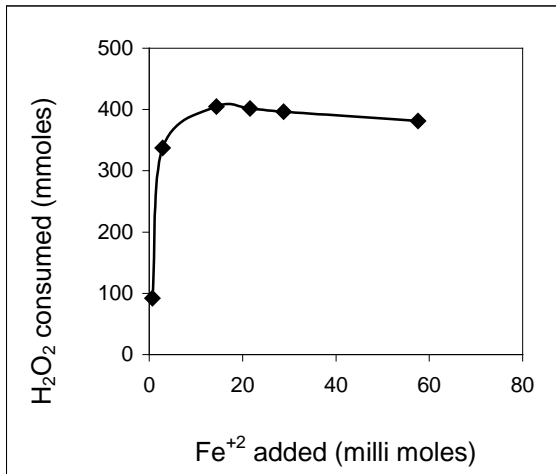


Figure 10. Fe⁺² dose optimization of Fenton's reagent (H₂O₂ concentration = 400 milli moles)

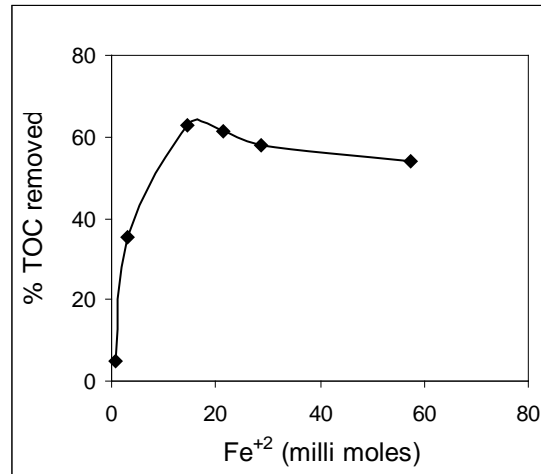


Figure 11. Fe⁺² (milli-moles) consumed and %TOC removed (H₂O₂ concentration = 400 milli moles)

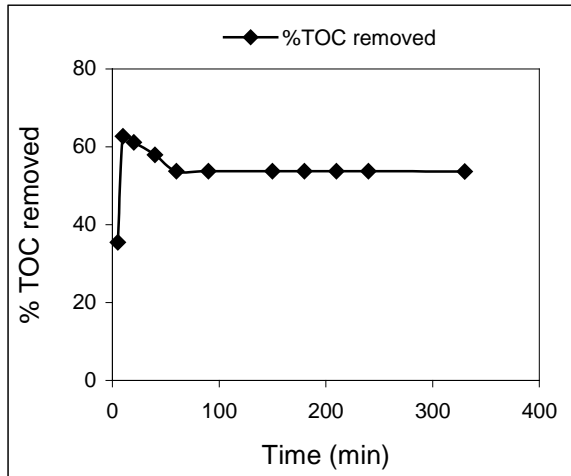


Figure 12. % TOC removal with time in Fenton's process (H₂O₂ concentration = 400 milli-mole, Fe⁺² concentration = 15 milli-moles)

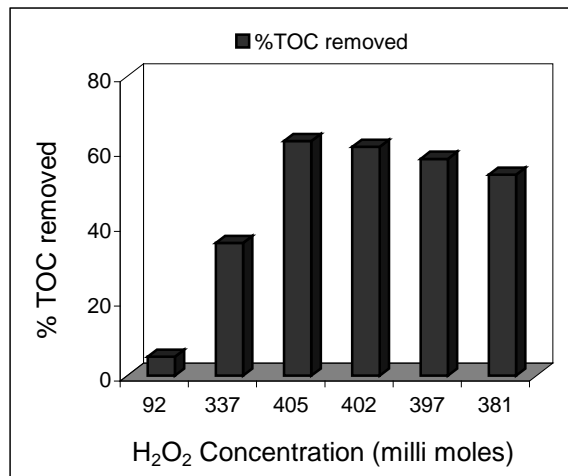


Figure 13. H₂O₂ (milli-moles) consumed and % TOC removed (Fe⁺² concentration = 15 milli-moles)

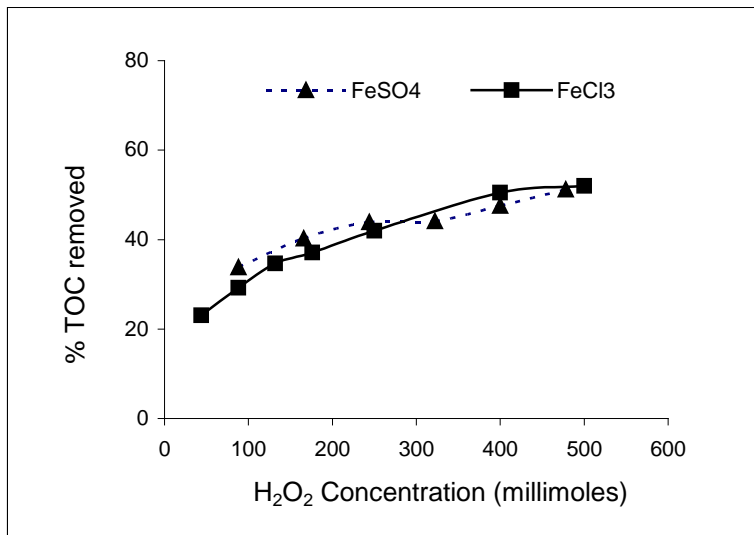


Figure 14. The effect of oxidation state of iron on % TOC removal in Fenton reaction
(Reaction time 2hrs)

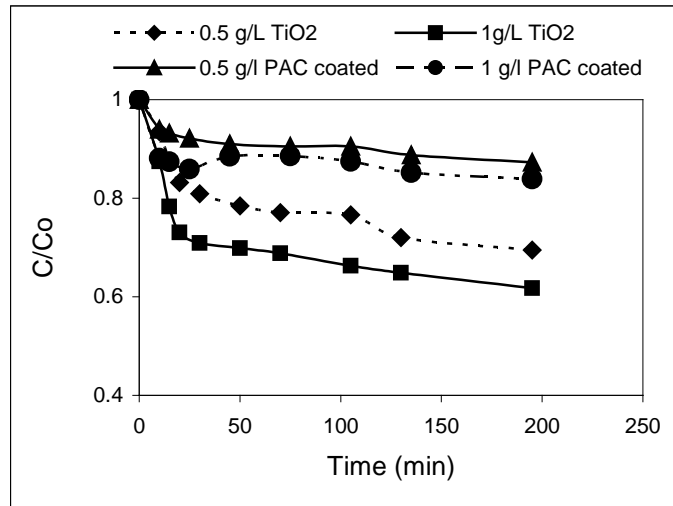


Figure 15 Organic matter removal (as DOC) from SLL in a recirculated photocatalysis reactor

