Photoremediation of natural leachate from a municipal solid waste site in a pilot-scale bubble column reactor

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Abstract

An 18-litre pilot-scale bubble column photoreactor has been used to carry out the mineralisation of a municipal solid waste dirty brown leachate. Rate data collected at 300 K and atmospheric pressure with titania particles suspended in upward flowing oxidising air through a stationary liquid phase suggested that the mineralisation of humic compounds was accompanied by a parallel hydrolytic photodecomposition of nitrogenous matter to NH_4^+ ions. The total organic carbon (TOC) reduction rate followed a Langmuir–Hinshelwood kinetics, while NH_4^+ ions production is competitively inhibited at high TOC concentration (>35 mM). Photoremediation was also attended by significant (50–70%) decolourisation. The treated leachate may be recycled for agricultural use.
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1. Introduction

Municipal landfill is a receptacle for various domestic, industrial and agricultural wastes and as a result of the various microbiological processes taking place, the associated percolated liquid (leachate) contains toxic, non-biodegradable humic substances and nitrogenous species. These pollutants, however, have to be removed or rendered harmless in order to meet NSW-EPA requirements before eventual discharge into the public water system. Research within the last two decades has shown that oxidative photocatalytic degradation is an effective technique for the removal of biologically-recalcitrant organic pollutants from wastewater even at very low concentrations under essentially ambient conditions [1]. Although, the composition of leachate from a municipal dump-site is complex, the aqueous phase contains essentially phenolic (humic) substances and nitrogeneous products of bacterial activity on the solid waste. Research in the literature has mostly dealt with syn-

thetic, single-component pollutant solutions [2,3]. Nevertheless, recent studies in our laboratory have yielded encouraging results even with complex industrial aqueous effluents, for example, the photocausticisation of spent Bayer liquor [4,5]. The present paper reports the application of photocatalysis to the decontamination of a batch liquid waste containing a matrix of natural pollutants.

2. Experimental

Leachate samples collected from a Sydney solid waste dump-site were used in all runs. The dirty brown smelly raw leachate was subsequently diluted with nanopure water to various compositions – from 150 ppm (0.150 g L^{-1}) to 900 ppm – for the purpose of this investigation.

Experiments were conducted with 5 g L^{-1} TiO_2 particles (average $d_p = 120\mu m$) in the stationary liquid phase, while air was sparged upwards (at flow rates between 2 and 20 L min^{-1}) through a stainless steel 70 μm mesh distributor to keep the catalyst particles in suspension and ensure hydrodynamics in the pseudo-homogeneous regime and excellent solid recirculation for effective light-harvesting.

Nomenclature

$C_{TOC_{initial}}$	initial concentration of total organic carbon (M)	g	acceleration due to gravity (cm s^{-2})
C_{TOC}	concentration of total organic carbon (M)	ρ_L	liquid density (g cm^{-3})
k_{obs}	observed reaction constant rate (min^{-1})	σ	surface tension dyne (cm^{-1})
d_{vs}	bubble size (cm)	v_L	liquid kinematic viscosity (cm^{2}s^{-1})
D_c	column diameter (cm)	u_g	superficial gas velocity (cm s^{-1})

A Primarc (AVP06C) lamp with variable power supply (200–400 W) was used as the ultraviolet light source. The photon emission of the lamp in the ultraviolet range (250–400 nm) was about 1×10^{-4} Einstein s^{-1} (at 300 W input power). A schematic diagram and detailed description of the pilot-scale bubble column photoreactor have been given by Pareek et al. [4]. Pollutant degradation was monitored by total organic carbon (TOC) content analysis of 10-ml aliquots taken at 10-min intervals over the 48-h period as well as in situ pH measurements using a TPS Digital pH probe.

3. Results and discussion

3.1. Hydrodynamics and mass transfer

In general, a bubble column reactor is assumed to be operating in the pseudo-homogeneous regime if the gas velocity is less than 5 cm s^{-1} and the liquid phase contains a solid loading not exceeding 15 wt% [6]. These conditions were met in the photoreactor with air flow rates (2–20 L min^{-1} i.e. 0.166–1.66 cm s^{-1}) and catalyst loading of 5 g L^{-1}. Indeed, visual inspection (through any of the four equally-spaced light intensity monitoring ports) revealed a distribution of fine well-dispersed bubbles in the stationary liquid column and thus excellent gas–liquid mass transfer may be expected. This was confirmed using correlations provided by Akita and Yoshida [7] for the average bubble diameter, d_{vs}, gas hold-up, ε_G, and mass transport coefficient, k_L, as outlined below.

For the average bubble size,

$$\frac{d_{vs}}{D_c} = 26 \left(\frac{D_c^2 g \rho_L}{\sigma_L} \right)^{-0.5} \left(\frac{g D_c^3}{v_L^2} \right)^{-0.12} \left(\frac{u_G}{\sqrt{g D_c}} \right)^{-0.12} \quad (1)$$

confirmed that the bubble diameter varied only slightly from 0.623 cm to 0.822 cm over the range of gas flow rate used.

For the gas phase hold-up, ε_G, the appropriate correlation is

$$\frac{\varepsilon_G}{(1-\varepsilon_G)^4} = 0.2 \left(\frac{D_c^2 g \rho_L}{\sigma_L} \right)^{\frac{1}{8}} \left(\frac{g D_c^2}{v_L^2} \right)^{\frac{1}{12}} \left(\frac{u_G}{\sqrt{g D_c}} \right) \quad (2)$$

which yielded $0.0055 \leqslant \varepsilon_G \leqslant 0.0465$ over the same gas flow rate spectrum. The corresponding gas-to-liquid mass transfer coefficient namely

$$k_L a = 0.6 D_{O_2-water}^{0.5} v_L^{0.12} \left(\frac{v_L}{\sigma_L} \right)^{-0.62} D_C^{0.17} g^{0.93} \varepsilon_G^{1.1} \quad (3)$$

gave values 0.123–1.285 s^{-1} with associated axial dispersion coefficient [8] of 35–175.2 cm^2 s^{-1} which suggest excellent gas–liquid mixing ($Pe < 5$). Thus, subsequent kinetic data were treated as those obtained from a CSTR. Indeed, Fig. 1 shows that beyond an air flow rate of 4 L min^{-1}, the reaction rate was independent of the system hydrodynamics and hence subsequent runs to examine the leachate photoremediation kinetics was carried out with gas flow rate of 5 L min^{-1}.

3.2. Reaction analysis

Fig. 2 shows representative TOC concentration profiles obtained during the photodegradation of the leachate pollutants. This exponential decrease indicates that the data may be fitted to

$$-r_{TOC} = -\frac{dC_{TOC}}{dt} = k_{int} C_{TOC}^n \quad (4a)$$

from which

$$-r_{TOC} = -\frac{dC_{TOC}}{dt} = k_{obs} C_{TOC} \quad (4b)$$

where $k_{obs} = k_{int} C_{TOC}^{n-1}$, and upon integration, Eq. (4b) yields:

$$\ln \frac{C_{TOC_{initial}}}{C_{TOC}} = k_{obs} t \quad (5)$$

In general, k_{obs} would be a function of C_{TOC} unless the reaction is intrinsically first-order. Interestingly, spectrophotometric measurements of the aliquots also revealed substantial reduction (between 50% and 77%) in the colour of the reacting mixture with time-on-stream. This implicated the removal of humic compounds consistent with TOC analysis although the percentage reduction in colour removal was generally higher than that obtained from TOC measurements (27–45%). TOC removal is proof of photomineralisation (total oxidation of the phenolic derivatives to CO_2), while colour reduction simply reflects oxidative opening benzene ring in the phenolic substances to other straight chain compounds which would still register as part of the total organic carbon content in liquid phase. Thus, reaction rate based on TOC data is a more conservative