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Contaminant effects on the photo-oxidation of greywater over titania film catalysts

Lorena Lopez [a], Barbara C. Panther [b], Terence W. Turney [c,*]

[a] Faculty of Science, Monash University, Clayton, VIC 3800, Australia
[b] Faculty of Science and Technology, Federation University, Northways Road, Churchill, VIC 3842, Australia
[c] Department of Materials Science & Engineering, Monash University,Clayton, VIC 3800, Australia

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ABSTRACT

One strategy for reducing water demand is by matching water quality to water need, through increased use of treated greywater to replace potable water in non-potable applications. Greywater processing, using photo-oxidation over TiO_2 films, results in catalytic activity, which can be either enhanced or inhibited by xenobiotic contaminants found within the greywater stream. Analysis of film pre-treatment and reaction conditions indicated that photoactivation was caused in part by contact of the films with water and in some instances by degradation products produced during the initial cycle of photodegradation. Using a model probe for photoactivity, degradation over such films exhibited pseudo-first order kinetics. However, after catalyst re-cycling, the kinetics deviated from first order, with the films becoming increasingly more photoactive. Aging of these films over a prolonged period of time did not alter film photocatalytic activity and prior exposure of the films to UV irradiation in water actually decreased subsequent photocatalytic activity of the films compared with the un-irradiated films. Some greywater components, such as polyethylene glycol, enhanced the photodegradation rate of the model probe in both the initial and subsequent cycles, whereas others, such as sodium stearate, were more complex; the initial photodegradation rate was initially inhibited but then enhanced over subsequent photocatalytic cycles. Ionic phosphate has a strong inhibitory effect under all conditions tested. The results indicate that even minor components, at concentrations typically found in household effluents, may have a critical effect on the photocatalytic activity of titania films during processing of greywater.

1. Introduction

As the global need for safe and clean water is increasing, recycling wastewater is becoming essential [1,2]. The drivers are partly economic but they also represent an opportunity to reduce added environmental burdens on pristine water sources, through the treatment and re-cycling of water for non-potable applications. In this regard, domestic greywater is seen as one of the most appropriate and promising sources of wastewater, with great potential for treatment and reuse, as it represents between 60% and 75% of the domestic wastewater daily volume in developed economies and contains a lower concentration of organic compounds and fewer pathogens when compared to many other wastewater sources [3–5]. A wide range of technologies have already been tested and used for greywater treatment, from very simple to quite complex systems, based on single or combinations of physical, biological and chemical treatments [4,6–9].

The chemical processing of organic contaminants in waste waters has been widely examined using photodegradation over active catalysts, such as the rutile or anatase forms of titanium dioxide (TiO_2) [10,11]. Although photocatalytic processing is considered a promising chemical treatment for different types of wastewater streams and has been subject to numerous studies for environmental applications, its implementation has been limited by process complexity and inherent variations in composition of such effluent streams. For example, the use of such catalysts in suspension requires the need for physical separation of the TiO_2 particles from the treated water after treatment. Loss of catalyst and fouling by suspended solids, which accumulate with the recycled catalyst particles, decrease its efficiency upon reuse. It is

* Corresponding author. Tel.: +61 3 99051762; fax: +61 3 99054940.
E-mail addresses: lorena.lopez-vanegas@monash.edu (L. Lopez), barbie.panther@monash.edu (B.C. Panther), terry.turney@monash.edu (T.W. Turney).

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also not clear how these photocatalysts change in performance in the presence of a plethora of different chemicals typically found in greywater [5,12,13]. These difficulties combine to make TiO_2 photocatalytic processing of greywater a challenging processing problem.

The photocatalytic activity of TiO_2 in aqueous media is dependent on its ability to generate free radicals (mainly hydroxyl radicals, $OH^{\bullet}$), which can participate in oxidation reactions [14]. This process is strongly influenced by the intrinsic properties of the TiO_2, including phase type, crystallinity, surface area, surface hydroxyl groups, particle size and surface morphology [15,16]. Moreover, photocatalytic activity is further dependent on reaction conditions, including solution pH, reaction temperature, the composition of the substrates in solution, the intensity and wavelength of the radiation and the presence of competing electron/hole scavengers [17–20]. As photocatalytic reactions are strongly believed to occur at the surface of the TiO_2 catalyst, any change in the surface chemistry, through adsorption of the reactants or reaction products, may have an additional impact on photocatalytic activity. Such effects may persist or even be enhanced during catalyst recycling. Thus, many factors can play a role in the photocatalytic process and they will ultimately determine practical utility of such photocatalysts.

The huge variability in composition and the complexity of domestic greywater streams make the general assessment of TiO_2 film photocatalysis difficult. Furthermore, many of the xenobiotic greywater components have the potential to deactivate (or indeed some, to activate) the TiO_2 catalyst. Rather than adopting the conventional approach of addressing the photodegradation of multiple greywater streams, this paper examines how individual greywater components could alter the photocatalytic ability of anatase thick films towards a constant probe substrate. Such an approach serves to decouple issues around variations in greywater composition from the inherent activity of the catalyst. This study seeks to determine which xenobiotic greywater contaminants may be amenable to photocatalytic processing, without having to address each greywater composition on an *ad hoc* basis.

2. Materials and methods

2.1. Individual greywater components

The composition of greywater exhibits significant regional and temporal variation as a result of national preferences, the habits of individual households and the use of different personal care and other products within each household. According to Katukiza et al., the characteristics of the greywater generated by laundry, in the kitchen and in the bathroom can vary significantly [21]. In our study, the identification of the individual xenobiotic greywater components was carried out through a detailed survey of the chemical composition of products found in Australian supermarkets for the use in laundries and for personal care in showers and sinks in an average household, in a manner similar to that reported by Eriksson et al. in 2003. [22]. The current list, broken up into various component classes, is outlined in the Supplementary information.

Given the wide variations in greywater composition, this paper seeks to establish a predictive model to determine which xenobiotics will have substantial effect on the photocatalytic activity of anatase thick films. The assessment is achieved not by measuring the photodegradation of individual components, but by assessing the photooxidation of a single common probe substrate in the presence of individual greywater components. This approach enables identification of those greywater components which may poison (or indeed enhance) the photocatalyst. Methyl orange appeared an obvious probe species as it has been subject to numerous photooxidation studies over titania [23–25]. Photodegradation data, for individual greywater components are given in Table 1, with the effect of three of these components discussed in more detail.

2.2. Materials

Sodium stearate (SS), polyethylene glycol (PEG) and disodium phosphate (DSP) were chosen because of their prevalence in a wide range of the surveyed products. Sodium stearate was

Table 1
The effect of xenobiotic greywater components on the photodegradation of methyl orange over anatase films.

Initial run	Subsequent runs	Activation	Contaminant
Increased photodegradation rate of methyl orange	Deviation from 1st order in 2nd and subsequent runs	Enhanced activation	Sodium laureth sulphate Polyethylene glycol Pyrithione zinc 4-Methylbenzylidene camphor
		Inhibited activation	Citronellol Citral Diethylene glycol monobutyl ether
No effect on photodegradation rate of methylorange	Deviation from 1st order in 2nd and subsequent runs	Enhanced activation	Linalool Xanthan gum Benzophenone-4
		Inhibited activation	1,2-hexanediol Oxybenzone Octyl methoxycinnamate
Decreased photodegradation of methyl orange	Deviation from 1st order in 2nd and subsequent runs	Enhanced activation	Sodium stearate Blue-1 Formaldehyde Methylparaben
		Inhibited activation	Sodium dodecylbenzenesulfonate Yellow-5 Benzyl salicylate
	Conserved linearity in all runs	Strongly inhibited activation	Sodium tripolyphosphate Dipotassium hydrogen orthophosphate Disodium hydrogen orthophosphate