

Photocatalytic Degradation of Taste and Odour Causing Compounds in Natural Water Sources

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The aesthetic quality of drinking water from surface water sources is often compromised by the presence of odour causing compounds, (particularly geosmin and MIB. These compounds are a major concern in the drinking water industry in South Africa and globally. They lower the potability of the water and may serve as precursors of carcinogenic disinfection byproducts (DBPs during disinfection. Taste and odour causing compounds have been shown to survive conventional treatment unit operations such as sedimentation and filtration. This study highlights the optimisation of a photocatalytic system of irradiated anatase titanium dioxide for the degradation of geosmin at environmentally significant levels obtained from the analysis of source waters of the Rietvlei and Roodeplaat Water Treatment Plants supplying drinking water to the capital city of Pretoria and its environs. Effect of UV radiance flux on the degradation efficiency was evaluated using a low pressure 9 W lamp and a medium pressure 400 W UV lamp. Photocatalytic degradation was carried out with a TiO_2 /UV batch system using both lamps. Effect of catalyst concentration on the process was also evaluated over a wide range of TiO_2 concentrations. Complete degradation of environmentally significant levels of geosmin was achieved with the photocatalytic system (medium pressure UV and catalyst concentration of 60 mg/l within 40 minutes. of treatment with initial degradation rates of 14.8 ng/l.min⁻¹. The results of the study for the degradation of geosmin is very encouraging and can be adopted for the treatment of other taste and odour compounds like 2-MIB and 2,4,6-TCA

1. Introduction

The presence of taste and odour in drinking water results in consumer rejection due to misconceptions about its safety for drinking. Two compounds responsible for earthy and musty taste and odour in drinking water supplies are geosmin and 2-methylisoborneol (2-MIB. They are secondary metabolites of blue green algae (Lawton et al., 2003, and are detectable by humans at concentrations as low as 4 and 10 ng/l (Park et al., 2007.

Occurrence of taste and odour problems in drinking water is on the increase with the dependence on surface water sources for the production of drinking water. In the face of increased agricultural activities, eutrophication of surface water especially during the summer months results in algae blooms caused by nutrient enrichment. Although South Africa has no clear sensory quality standards with regards to taste and odour, consumer complaints resulted in a survey of water bodies in South Africa in the early 1990's, which revealed that 30% of water bodies examined had odour problems and 50% of these problems were attributed to geosmin (Wnorowski, 1992). The situation has grown worse over the years with one of the worst cases in recent years experienced by Rand Water between September and November 2005, where high cyanobacteria concentrations in the source water resulted in high concentrations of geosmin in drinking water with a resultant consumer rejection ((Swanepoel and du Preez, 2006

1.1 Drinking Water Sources in Gauteng Province in South Africa

In the Gauteng Region of South Africa, drinking water is supplied by Rand Water (Zuikerbosch Water Treatment Plant, Johannesburg Water, City of Tshwane (Rietvlei Water Purification Works, and Magalies Water (Roodeplaat Water Treatment Plant. Johannesburg Water supplies the City of Johannesburg and its environs including Midrand and Soweto; Rietvlei Plant supplies the Eastern parts of Pretoria; whereas Roodeplaat Plant supplies the Northern parts of Pretoria (Montana and environs and Rand Water, the biggest of the four supplies parts of Pretoria and the rest of Gauteng Region. All four treatment plants receive water from surface water sources, Zuikerbosch Water Treatment Plant, receives water from the Vaal Dam, Johannesburg purchases the bulk of its water from Rand Water, Rietvlei Treatment Plant from the Rietvlei Dam, and Roodeplaat Treatment Plant from the Roodeplaat Dam.

1.2 Treatment Options for Taste and Odour Compounds in Water

Several treatment methods have been investigated for the removal of taste and odour compounds from water among which are: ozonation (Ho et al., 2002, adsorption on powdered activated carbon (PAC or granular activated carbon (GAC (Ng et al., 2002, control of cyanobacterial by the use of algacides or by microbial oxidation (Saito et al., 1999. Conventional treatment methods such as chemical, biological and physical methods have limited success in treating taste and odour compounds. Geosmin and MIB are both virtually resistant to oxidation by ozone and have been reported to react very slowly with ozone (Peter and Gunten, 2007, their resistance to ozonation was attributed to their tertiary structure. Geosmin is reported to be extremely difficult to degrade microbially. Although some level of success in geosmin removal has been reported with GAC, in most cases residual amounts left are above the human detection threshold. It is therefore important to evaluate the process efficiency of the newer treatment methods for the removal of geosmin. Advanced oxidation processes such as semiconductor photocatalysis have been used successfully to degrade other aromatic compounds, thus are proposed for use in degradation the taste and odour causing compounds .

1.3 Photocatalysis as a Treatment Option for Taste and Odour Compounds

Semiconductor photocatalysis is an advanced oxidation process based on the generation of reactive electron hole pairs (h^+ e^-) by photoactivation of semiconductor materials acting as catalysts utilising low energy ultraviolet (UV) light (Herrmann, 1999.

Photogenerated positive holes are powerful oxidants while the negative electrons are very good reductants. Both elements can either react directly with organic compounds or indirectly through the action of hydroxyl radicals generated from reduction of oxygen on the surface of the catalyst. In water purification the electron acceptor is oxygen and the pollutant is the electron donor and the process most often achieves complete mineralization of the organic pollutants to carbon dioxide and water (Mills and Lee, 2004).

Of all the tested semiconductor materials, titanium dioxide (anatase form is the most widely used catalyst due to the existence of the band-gap energy in the crystal which results in high photoactivity. Titanium dioxide has wide band gap energy of 3.25 – 3.05 eV, absorbing light of wavelength 380 to 405 nm. Other desirable properties of TiO_2 include its resistance to photo or chemical corrosion, non toxicity, non carcinogenic nature, and its insolubility under operational conditions (Mills and Lee, 2004).

Though photocatalysis has been widely applied for the destruction of a very wide range of organic pollutants, until now, there has no reported successful application in the drinking water industry. The current study aims at evaluating a photocatalytic process for the degradation of geosmin to levels below human detection threshold.

2. Materials and Methods

2.1 Chemicals

Geosmin (Sulpeco) was purchased as a standard solution of 100 µg/ml in methanol from Sigma-Aldrich, Germany. Tertiary butanol was obtained from Merck, South Africa. All solutions were prepared using ultrapure water from Milli-Q (Millipore Direct Q3 from Waters supplied by Microsep, South Africa).

2.2 Materials

Radiation sources were (a) long-arc 400W medium pressure (Lamp A; and (b) a 9W low pressure (Lamp B, UV lamps. Both were from Philips, Netherlands and were supplied by Technilamps, South Africa. UV radiation intensity was measured with Goldilux UV Smartmeters, Model GRP-1 (USA, supplied by MIT, South Africa, calibrated at the National Metrology Institute of South Africa (NMISA). Radiance intensity of lamps A and B measured at the wall of the reactor, with contribution for the cooling water taken into consideration were 34 mW/cm² and 1326 µmW/cm² respectively. Anatase titanium dioxide powder was purchased from Sigma-Aldrich, Germany.

2.3 Photocatalytic Degradation Experiments

Photocatalytic degradation of geosmin was conducted in batch with 1L of geosmin solution (220 ng/ℓ, representing highest levels obtained from analysis of water samples from Rietvlei and Roodeplaat Dams. Geosmin solutions were treated with: (a) TiO_2 - 40 mg/ℓ, irradiated with (i) lamp B and (ii) lamp A; (b) TiO_2 - 40-100 mg/ℓ, irradiated with lamp A and (c) with TiO_2 - 100 mg/ℓ in the absence of UV radiation (used as control). The reactor contents were aerated at a flow rate of 10 ml/min through a glass tube. UV lamps were cased in double walled quartz sleeves, and cooled by circulating cold water

through the outer jacket of the sleeves. 12 ml aliquots were withdrawn from the reactor at intervals, filtered, and 10ml of the filtered solution was analysed after the addition 3 g of NaCl and 0.5 ml of t-butanol. Total reaction time was 60 minutes.

2.4 Analysis

Geosmin concentrations was analysed with Perkin Elmer, Clarus 600T GC/MS. Geosmin was extracted and introduced into the GC column by Turbo Matrix 40 Headspace equipped with a trap. Geosmin concentrations were obtained from calibration curves of standards, from the SIR of 3 ions (55, 112 -base peak and 125 ($r^2 = 0.99$). Method detection limit obtained was 0.5 ng/l. Fresh standards were analysed with each batch of compounds on the GC/MS.

3. Results and Discussion

3.1 Effect of variation of light intensity on the kinetics of geosmin degradation

Higher degradation rates were achieved with the medium pressure lamp (95.8% removal than with the low pressure lamp (49.6% with TiO_2 concentration of 40 mg/l in 60 minutes. Under these conditions geosmin levels below human detection threshold were obtained with the medium pressure lamp. Based on its superior performance, catalyst concentration optimization studies were performed with the medium pressure lamp.

3.2 Effect of catalyst loading

The degradation profiles for the various systems are presented in Figure 1.

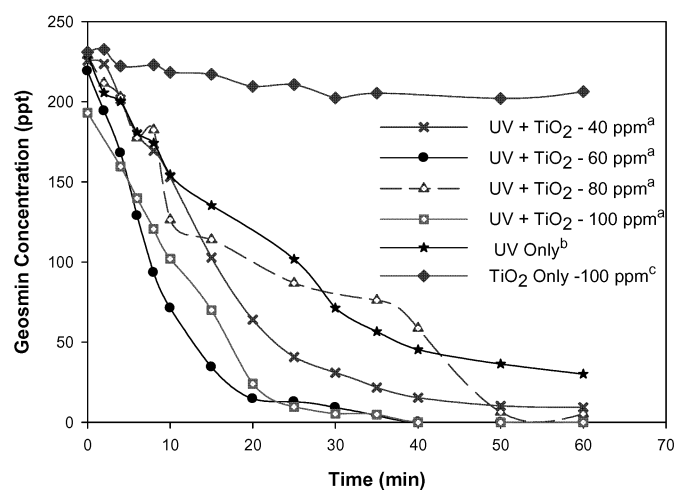


Figure 1: Degradation profile of geosmin (220 ng/l): Conditions (a Photocatalysis - UV and TiO_2 (40-100 mg/l), (b Photolysis - UV Only and (c TiO_2 only

Rapid degradation was obtained at all catalyst concentrations. Complete degradation was achieved at the optimum catalyst concentrations of 60 mg/l after 40 minutes of treatment. The control achieved only about 10% degradation, which is an indication that UV irradiation is a key factor to an efficient photocatalytic system. Though the

photolytic (UV only system achieved about 86% degradation, residual levels (30 ng/l after 60 minutes of treatment were above the human threshold.

Literature showing effect of catalyst loading for geosmin is lacking, the general observed trend reflects an increase in organic degradation rates with increasing catalyst concentration to a maximum of 60 mg/l, beyond which a negative effect is observed due screening of photons of light by excess catalyst particles dispersed in water (Herrmann, 1999. Trend on effect of catalyst loading is in line with findings from other studies on photocatalytic degradation of phenolics (Barakat et al., 2005.

3.3 Kinetics of Degradation

Kinetics of Photocatalysis of organic compounds can be described by the Langmuir-Hinshelwood kinetic scheme (Mills and Lee, 2004; Hofmann, et al., 1995 represented by:

$$R_i = \frac{-d[C]_o}{dt} = \frac{kK[C]_o}{1 + K[C]_o} \quad [1]$$

Where: R_i = initial rate of geosmin degradation (ppt .min⁻¹, $[C]_o$ = initial concentration of geosmin (ppt, K is equilibrium adsorption constant (ppt⁻¹, and k =pseudo first order reaction rate constant (min⁻¹.

The variations in $\ln C_o/C$ as a function of time for the data in Figure 1 gave linear plots typical of pseudo first order kinetics of photocatalytic as shown in Figure 2.

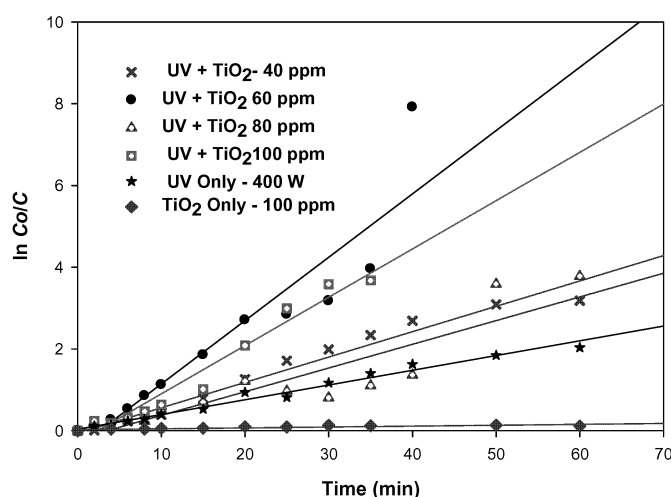


Figure 2: First order linear transform $\ln(C_o/C) = f(t)$ of the kinetics of geosmin degradation for degradation profile in Figure 1 .

Pseudo first order rate constants were obtained from linear transforms of the plot of $\ln C_o/C$ as a function of time from apparent first order kinetic equation.

4. Conclusion

Environmentally significant levels of geosmin can be degraded to levels below the human detection threshold using titanium dioxide photocatalysis with very low catalyst concentrations of 60 mg/l. UV photolysis alone is inefficient for the degradation of geosmin to environmentally insignificant levels. Lessons learnt from the study can also be applied to the degradation of other taste and odour causing compounds like 2-MIB.

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