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FULL LENGTH ARTICLE

Effect of ozonation combined with heterogeneous catalysts and ultraviolet radiation on recycling of gas-station wastewater

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Abstract Ozonation is extensively applied in the treatment of drinking water and wastewater due to the powerful oxidation potential of ozone. Heterogeneous catalytic ozonation (HCO) of wastewater proceeds through hydroxyl radicals as the oxidation species. The effect of ozonation alone and combined with catalysts in the presence and absence of UV-radiation was investigated to reuse the biologically pretreated gas-station wastewater instead of fresh water. Two types of catalysts: titanium dioxide (TiO_2) and activated carbon (AC) were studied. The concentration of catalyst, dark adsorption, reaction time and the improvement of biodegradability were studied. The combination of catalysts and ozonation reveals a significant improvement in the removal of contaminants present in wastewater by using the ozonation, adsorption or photocatalysis systems. Maximum dissolved organic carbon (DOC) removal of 91% was achieved by the combination of ozone, TiO_2 and the UV-radiation system. But, an increase in biodegradability from 0.12 to 0.33 was realised with ozone and the TiO_2 system. Furthermore, the biodegradability was increased with increasing catalyst concentration combined with ozone up to 1 g/L with TiO_2 and 0.5 g/L with AC.

1. Introduction

Gas-stations usually consume large volumes of water in many activities such as car washing, floor cleaning, toilet, cafeteria use, etc. Many particles and chemicals are found in the wash water. The concentration and severity of these particulates are usually extrapolated or not considered [1]. Many contaminants of gas-station wastewater have an impact on the environment. Several treatment methods have been employed for the reuse of gas-station wastewater [1,2]. The conventional treatment processes do not allow complete removal of detergents and dissolved solids or heavy metals. Therefore, additional treatment steps are required to eliminate refractory and harmful contaminants to the environment and also to reduce the consumption of fresh water. Because of the large

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variety of chemicals applied in gas-station, the organic content of wastewater is normally measured using integral parameters such as biochemical oxygen demand (BOD), chemical oxygen demand (COD) and dissolved organic carbon (DOC) or hydrocarbon content.

Ozonation is a green processes widely used to destroy or degrade many toxic organic compounds, in water and wastewater with the resulting formation of more biodegradable molecules. Ozone reacts through a direct mechanism that involves the O_3 molecule and/or an indirect mechanism that involves hydroxyl radicals ($OH^{\cdot}$). It has been shown that ozone system achieves limited mineralisation of organics in drinking water and little COD removal in wastewaters. Consequently, ozone-based advanced oxidation processes were employed to enhance ozone reactivity. Catalytic systems such as O_3/H_2O_2, O_3/UV, and O_3/catalyst have been used for the removal of various water pollutants [3–5]. Mechanisms of $OH^{\cdot}$ production from ozone combined with hydroxide ion, hydrogen peroxide and UV-radiation are well established but to a lesser extent than those of heterogeneous catalytic ozonation [6,7].

The combination of ozone and UV-radiation (O_3/UV) is an effective catalytic system for oxidation and destruction of toxic and refractory organics in water; the process is initiated by photolysis of ozone. Ultraviolet lamps should have their maximum radiation output at 254 nm for an efficient ozone photolysis [8]. A two step mechanism has been proposed involving light-induced homolysis of O_3 and subsequent production of $OH^{\cdot}$ radicals by the reaction of $O^{\cdot}$ with water [9,10].

$$O_3 + h\nu \rightarrow O_2 + O^{\cdot} \quad (1)$$

$$O^{\cdot} + H_2O \rightarrow 2OH^{\cdot} \quad (2)$$

The use of ozone in combination with heterogeneous catalysts [11,12] has been recently investigated in liquid phase reactions with aniline [13], phenol [14], formic acid [15], and cyanide ions [16]. In all cases a significant improvement of the oxidation process performance has been reported as the mineralisation rate of organic and inorganic substances is greatly enhanced.

Activated carbon (AC) has high surface area and possesses good porous texture allowing the high adsorption capacity of some substances, which allow the efficient use of AC in the removal of aqueous and/or gaseous pollutants. In addition, the use of activated carbon can accelerate the decomposition rate of O_3 and result in higher concentration of active radicals [17,18]. Based on these remarks, the combination of O_3 and AC has been used in wastewater treatment.

Titanium dioxide (TiO_2) is extensively used as photocatalyst. To improve the performance of the photocatalytic system is to change the reaction ambient by adding strong a oxidant species such as hydrogen peroxide [19] also in the presence of Fe(II) ions [20], or ozone. Furthermore, TiO_2 was studied as an adsorbent to remove contaminants from wastewater without UV-radiation in order to access the effect of dark adsorption.

The aim of this study is the efficient removal of refractory contaminants in biologically pre-treated gas-station wastewater to minimise the use of fresh water through the recycling process. The influence of ozone alone and/or combined with ultraviolet (UV) radiation and catalysts was investigated to compare the different studied systems: ozone (O_3 alone), ozone/titanium dioxide (O_3/TiO_2), ozone/activated carbon (O_3/AC), UV/O_3, UV/TiO_2, UV/O_3/TiO_2 and UV/O_3/AC. The influence of the concentration of catalyst, dark adsorption, reaction time and the improvement of biodegradability was investigated.

2. Experimental

2.1. Wastewater characteristics

Biologically pre-treated wastewater was collected from a gas-station. Wastewater was stored at 20 ± 1 °C. The properties of the investigated wastewater are listed in Table 1.

2.2. Materials

A commercial activated carbon from NORIT Nederland B.V. type NRS CARBON EA 0.5–1.5 was used with: 350 kg/m^3 apparent density, 13 wt% ash content, 10 wt% moisture content (as packed) and min. 850 Iodine number. All analyses are based on NORIT Standard Test Methods (NSTM).

A commercially titanium dioxide catalyst (Degussa P25) was used; characterised by: 50 ± 15 m^2/g, specific surface area, 20–30 nm, particle size and crystal structure shows 70% anatase and 30% rutile.

2.3. Experimental set-up

A 1.8 L glass reactor was used (1) as showed in Fig. 1. The reactor was operated in the batch mode. A magnetic stirrer (3) was used to ensure well mixing and prevent gas bubbles coalescence. A light source (4) was placed in the centre of the reactor composed of a medium pressure mercury vapour lamp (UV-H1022, BLV Licht- und Vakuumtechnik, Germany) housed in a double quartz sleeve with a cooling jacket. The lamp was constantly cooled by circulating distilled water through the cooler (5) to keep a constant temperature and protect the lamp from overheating.

Ozone was supplied by an Ozomat ozone generator (Ozomat COM/R, Anseros, Tübingen, Germany) from dry oxygen used as the feed with a maximum ozone concentration of 150 g/m^3. Online analysers were used to measure the ingoing and outgoing ozone concentration (Ozomat GM, Fa. Anseros, Tübingen, Germany). The oxygen–ozone mixture was supplied at the end bottom of the reactor through a microporous distributor which permits for a good gas distribution (6). Teflon tubing was used for the ozone gas lines. Ozone consumption was determined as the difference between the initial and residual ozone concentration in the gas phase. The operating conditions for the experiments are summarised in Table 2.

All experiments were carried out at an initial pH of 7.2 (the pH of wastewater) (see Table 1). For all the experiments carried out with UV-radiation, the light was immediately turned

Table 1 Characteristics parameters of biologically pre-treated gas-station wastewater.

Parameter	Unit	Value
pH	–	7.2
DOC	mg/L	45
COD	mg/L	112
BOD_5	mg/L	14
Colour	–	Light yellow