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Photocatalytic degradation of 4-nitroaniline using solar and artificial UV radiation

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Abstract

The photocatalytic degradation (PCD) of 4-nitroaniline was studied in the presence of TiO_2 suspensions in a batch and continuous annular reactor. Artificial and solar radiation was employed as sources of UV radiation. The effect of catalyst loading, pH, presence of anions and initial concentration on the rate of photocatalytic degradation was investigated. *p*-Aminophenol, *p*-benzoquinone and hydroquinone were identified as the intermediates during the degradation process. A kinetic expression for PCD of 4-NA is provided.

Keywords: Nitroaniline; Photocatalysis; TiO_2; Kinetics

1. Introduction

Purification of water by semiconductor photocatalysis is a rapidly growing area of interest. Many organic compounds are resistant to conventional chemical and biological treatments, making it necessary to devise new treatment methods which can act as alternative to biological and classical physico-chemical processes. Photocatalytic degradation process can be defined broadly as an aqueous phase oxidation process, which is based primarily on the attack of the hydroxyl radical, resulting in the destruction of the target pollutant or contaminant compound. The distinct advantages of PCD such as complete mineralization, low cost, mild operating conditions and immunity to solution toxicity, over the other destructive and non-destructive technologies has attracted the attention of many researchers [1–2].

p-Nitroaniline (4-NA) is highly toxic with a TLV of $0.001\,kg\,m^{-3}$. 4-NA is found in wastewater discharges from industries where it is either manufactured or used as an intermediate such as in the synthesis of dyes, antioxidants, pharmaceuticals, in gum inhibitors, poultry medicines, and as a corrosion inhibitor. 4-NA has been found to be harmful to aquatic organisms and may cause long-term damage to the environment [3].

The present work deals with photocatalytic degradation of *p*-nitroaniline using solar radiation as well as artificial radiation, in batch and continuous mode. A very limited literature is available on photocatalytic degradation (PCD) of 4-NA. Bauer and Spaeek [4] have compared degradation of 4-NA using photocatalysis and photo Fenton reaction. However, no literature is available with regard to the effect of the various parameters on the rate of photocatalytic degradation. In view of this, batch reactor studies using solar radiations were carried out to study the effect of the various parameters such as catalyst loading, initial 4-NA concentration, pH, presence on anions, and catalyst reusability on the rate of PCD. The kinetics of the photocatalytic degradation was also investigated.

The PCD of 4-NA in a continuous annular reactor was also an integral part of our present study. Notwithstanding the substantial advantages of photocatalytic degradation, the technique of PCD is yet to be implemented on large scale for treatment of industrial wastes. The biggest hurdle has been catalyst filtration/recovery owing to the fine particle size of the TiO_2, the most widely photocata-

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Nomenclature

C_0	initial concentration of 4-nitroaniline (kg m^{-3})
C_ℓ	concentration of intermediates (kg m^{-3})
C_t	concentration of 4-nitroaniline at time t (kg m^{-3})
$C_{t=0}$	concentration of 4-nitroaniline at time $t = 0$, before the 4-nitroaniline solution was exposed to sunlight (kg m^{-3})
I	rate of light absorption
k_1, k_2, k_r	reaction rate constant (s^{-1})
k_{obs}	pseudo-first-order rate constant (m^3 kg^{-1})
K	equilibrium adsorption constant of 4-nitroaniline
K_c	second order rate constant (kg s^{-1})
$TOC_{t=0}$	total organic carbon at time t, before the 4-nitroaniline solution was exposed to sunlight (kg m^{-3})
TOC_t	total organic carbon at time t (kg m^{-3})

Greek letters

λ	wavelength of light (nm)
θ	power term
$\theta_{OH^\bullet}$	fractional site coverage by hydroxyl radicals
θ_C	fraction of sites covered by 4-NA

lyst. In view of this, most investigators have used the catalyst in immobilized forms [5–8]. However, limited surface area and potential losses of catalyst by attrition are main drawbacks. Further, higher catalyst loading leads to solution opacity and poor photon penetration, thereby poor reactor response. One alternative, which can overcome this problem, lies in the use of candle filters relying on surface filtration under conditions such that there is a zone of high shear near the filter surface that prevents solid deposition and plugging of the candle filter [9–10]. The high surface area per unit mass of this catalyst allows low catalyst loading (<0.5 wt%) without affecting the space-time yield. For instance, 0.5 wt% loading of the catalyst affords a surface area of about 200 m^2 m^{-3} of the reactor volume, which is far greater than what can be achieved with an immobilized catalyst. Further, the low photocatalyst loading can allow better penetration of the incident photons. Fig. 1 shows the configuration of the annular reactor used in the present experimental studies. The liquid hydrostatic head in the column serves as the driving force for filtration allowing retention of the catalyst in the reactor. The low particle size and catalyst loading allow ease of solid suspension at relatively low (0.03–0.05 m s^{-1}) air sparging rates. Thus, the energy requirement for air sparging can be kept low.

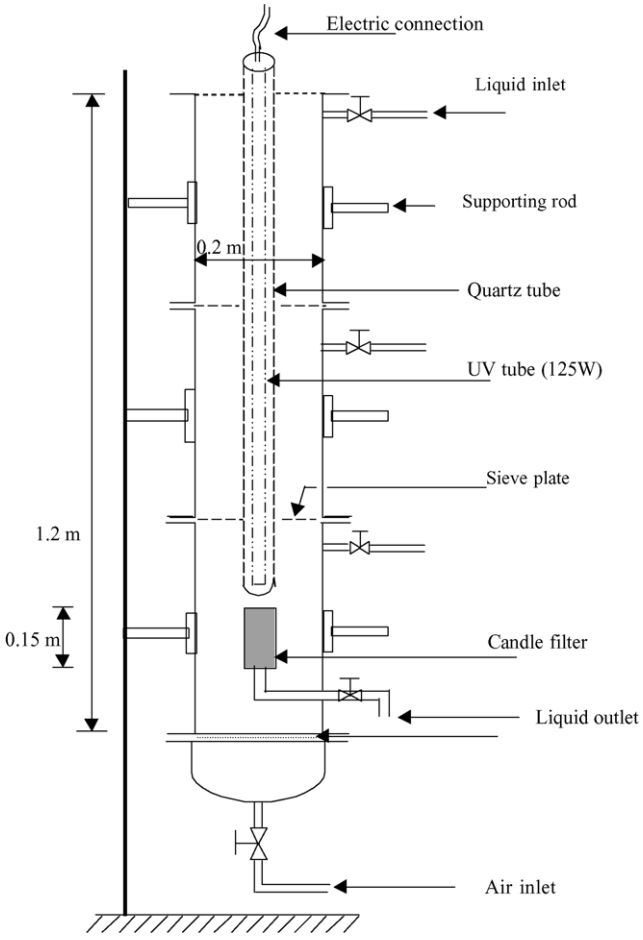

Fig. 1. Novel annular bubble column reactor for continuous photocatalytic degradation of 4-nitroaniline using artificial UV radiations.

2. Experimental

2.1. Materials

All the reagents used for experimental studies were analytical reagent grade. Degussa P-25 TiO_2 was supplied as free sample by Degussa Co., Germany. 4-Nitroaniline, sodium chloride, sodium carbonate, sodium bicarbonate, sodium sulfate of analytical reagent grade were obtained from S.D. Fine Chemicals Ltd., Mumbai, India. All the reaction mixtures and HPLC mobile phase solutions were prepared in deionized water. Plain solar radiation intensity was measured in W m^{-2} by 'Daystar meter' (daystar Inc., Las Cruces, NM, USA) working on photocell principle. Solar radiation intensity at ground level is referred to as plain intensity henceforth.

2.2. Batch experiments

All the experiments were carried out in a quartz cylindrical reactor, similar to that employed by Kamble et al. [9]. The initial temperatures of the reaction mixtures were in the range of 28–32 °C and the final temperature was in the range of 32–35 °C during the PCD of 4-NA. The temperature of the