Hydrodynamic Conditions and Photodegradation of Methyl Orange in a Fluidized Bed Photoreactor

Reliance J. Mhlanga[1], Nhlanhla Nyembe[2], Haleden Chiririwa[3] and Ochieng Aoyi[4]

Abstract—Advanced oxidation processes (AOPs) have emerged as promising techniques for the treatment of wastewater containing complex organic compounds. In this study, experiments were carried out to determine the effect of superficial gas velocity on the hydrodynamic conditions (average gas hold-up & bubble size) and the effect of operating conditions on the photodegradation of methyl orange (MO) in a fluidized bed photoreactor. Optimum operating parameters were found to be: time of 120 min, catalyst loading of 1.5 g/L and the superficial gas velocity being 212.23 mm/s. An increase in the superficial gas velocity increases the average gas hold-up and bubble size. The effect of hydrodynamic conditions on photodegradation showed that an increase in the superficial gas velocity results in an increase in the removal of color and total organic carbon (TOC) removal.

Keywords— Hydrodynamics, Methyl orange, Photodegradation, Photoreactor.

I. INTRODUCTION

IN recent times, one of the major global problems is the access to clean water and only a few people in the world have access to clean water and sanitation. Freshwater is a fundamental resource for human well-being and the natural environment; it is regarded as the most essential natural resource in the world [1]. Over the past few decades, climate change and human socioeconomic development have greatly changed the global hydrological cycles, threatening human water security, the health of aquatic environments and river biodiversity [2]–[4]. The discharge of textile effluents to the water bodies has raised much concern because of potential health hazards associated with the entry of toxic components into the food chains of humans and animals [5]. The need to purify water previously considered clean has attracted a lot of interest from a lot of researchers recently, with various techniques having come into view [6].

Methyl orange (MO) is an azo dye that has been widely used in textiles, foodstuffs, paper and the leather industries [7]–[9]. However, the release of MO and its products into the environment causes serious pollution problems [10]. The effluent streams coming from textile plants must be treated in order to remove the toxic or carcinogenic dye residues and their by-products, whereas an effective effluent decolorization is usually required by most government regulations. Various methods of water treatment exist for treating industrial water contaminated with MO [11]. The photocatalytic treatment of wastewater containing dyes has also been widely reported as an alternative method of wastewater treatment [12]–[13].

The presence of MO in the environment causes pollution and threatens the aquatic species. There are various technologies available for the removal of MO from water. Most of these technologies are energy intensive and introduce chemicals which are not wanted in the first place. They also concentrate the pollutants into solid or liquid side streams which require additional treatment or disposal thus escalating the cost of effluent treatment [5]. As a result, the application of the heterogeneous photocatalytic oxidation (HPO) process as an advance oxidation process (AOP) to degrade toxic organic pollutants has emerged as a robust and cost effective treatment method. The attractiveness of the HPO process to many researchers is due to its flexibility to employ ultraviolet (UV) light or solar and titanium dioxide (TiO2) to completely degrade toxic organic pollutants into biodegradable and less harmful products.

In this work, the photocatalytic degradation of MO contaminated water was investigated using solar as a UV source and TiO2 as a photocatalyst. The aim of the study was to investigate the hydrodynamic conditions and optimize the operating conditions that affect the photodegradation of MO in a fluidized bed photoreactor. The main drawbacks in the commercialization of the HPO process are the cost of: UV light lamps and the separation of the catalyst post-treatment. These challenges were addressed, in the current study, by using sunlight as a UV source and by attaching the catalyst onto colloidal silica so as to form denser particle sizes. The act of forming denser particle sizes facilitates the post separation process. The use of solar energy may prove to be economically and technologically feasible, for water treatment and detoxification of wastewater [14]–[15].

II. METHODOLOGY

A. Materials

Methyl orange was used as a model pollutant due to the fact

[1]Department of Chemical Engineering, Vaal University of Technology, Vanderbijlpark, 1900, RSA (phone: +27169509059; email: reliance.josephina@yahoo.com)

[2,3,4]Centre for Renewable Energy and Water, Vaal University of Technology, Vanderbijlpark, 1900, RSA (e-mail: nhlanhlan@vut.ac.za, harrychiririwa@yahoo.com, ochienga@vut.ac.za).

that it is the most commonly present pollutant in textile wastewater. Hydrochloric acid [32% (v/v)] and sodium hydroxide (NaOH) were used to adjust the initial pH level of the solution and were obtained from Sigma Aldrich (South Africa). Commercial grade TiO_2 Degussa P25 was used as a photocatalyst, with surface area of 60-80 m^2/g, particle size of 30 nm and was obtained from Merck (South Africa). A compressor was used to supply air for agitation. The pH level was measured using an Orion Star A111 pH meter (Thermo Scientific). The concentration of methyl orange was determined using the UV-vis spectrophotometer. The total organic carbon (TOC) in solution was determined by using the Teledyne Tekmar TOC Torch analyser. Solution turbidity was measured using a Hach DR2000 photometer using the FAU turbidity function.

B. Solution Preparation

A stock solution of known concentration was prepared by dissolving the appropriate amount of MO powder in a determined amount of de-ionized water.

C. Catalyst Preparation

The composite catalyst was prepared by binding TiO_2 using silica xerogel. A Suitable quantity of TiO_2 and colloidal silica were magnetically stirred until the mixture was homogeneous. The mixture was then laid on glass plates and dried at 60°C to remove the moisture. The dry sample was then sieved to a particle size range of 38 to 75 μm. The screened powder was then washed using 0.1 M HCl to remove the excess alkalinity and the excess acidity was neutralized by washing the catalyst particles several times with de-ionized water. Between each wash, the pH of the wash was monitored and the washing stopped when the pH value remained constant at about 6.5. The final composite catalyst product was obtained after drying at 60°C.

D. Experimental Setup

The experimental setup consisted of a fluidized bed photoreactor as shown in Fig. 1.
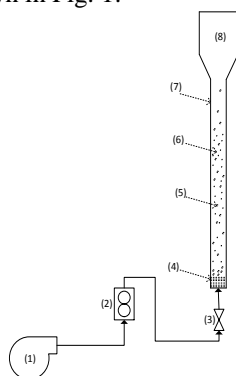

Fig. 1 Experimental setup. (1) Compressor; (2) Flowmeter; (3) Non-return valve; (4) Gas distributor; (5) Air bubbles; (6) Catalyst particles; (7) Fluidized bed photoreactor and (8) Degassing zone

E. Experimental Design

According to literature, the photocatalytic degradation of organic pollutants is significantly affected by these operating parameters: reaction time, catalyst loading [18], and superficial gas velocity [16] and these are shown in Table I. The method used to conduct the experiments is called the one-factor-at-a-time approach, where others variables are kept constant to determine the optimum level for each variable studied.

TABLE I
ONE FACTOR AT A TIME EXPERIMENTAL

Parameter	Levels		
Reaction time (min)	60	90	120*
Catalyst loading (g/L)	0.5	1*	1.5
Superficial gas velocity (mm/s)	70.74	141.49*	212.23

*Parameters that were kept constant.

F. Photodegradation Experiments

The photocatalytic activity of the prepared composite catalyst was tested for the degradation of MO with an initial concentration of 13 ppm. The photodegradation reaction was carried out in a fluidized bed photoreactor with a volume of 400 mL in the presence of air bubbling system. The following variables were studied: catalyst loading, superficial gas velocity and reaction time (Table I). Sampling was done at the beginning and end of each experiment. Before analysis, the samples at the end of each experiment were filtered through a 0.45 μm membrane syringe filter [17]. The amount of MO was quantified using a UV-Vis spectrophotometer at a wavelength of 464 nm.

G. Hydrodynamics Experiments

The hydrodynamic experiments were carried out to determine the effect of superficial gas velocity on the average gas hold-up and bubble size. The photoreactor consisted of a sintered-plate type bubble distributor with a pore size of 10-15 μm. The bubble size and average gas hold-up measurements were carried out to characterize the fluidization behavior of the photoreactor. The average gas hold-up (ε_G) measurement was carried out by using the quick stop method [16] and was calculated by using (1):

$$\varepsilon_G = \frac{H_D - H}{H} \qquad (1)$$

where H is the liquid height with no gas sparging and H_D is the displaced height during gas sparging.

III. RESULTS AND DISCUSSION

A. Hydrodynamics

The hydrodynamic conditions such as the average gas hold-up and bubble size in the fluidized bed photocatalytic reactor had a great influence in the photodegradation of MO. The gas hold-up plays a huge role in the rate of gas-liquid mass transfer which controls the amount of oxygen dissolved in solution. The oxygen behaves like an electron scavenger which prevents electron-hole recombination during photocatalysis. This suggests that high oxygen mass transfer results in efficient photodegradation rates. The hydrodynamic experiments were

carried out to determine the average gas hold-up and the bubble size distribution at different superficial gas velocities. The bubble size also has an effect on the rate of mixing in the system.

1) Effect of Superficial Gas Velocity on the Average Gas Hold-up

The effect of superficial gas velocity on the average gas hold-up was investigated and the results are shown in Fig. 2. The results showed that an increase in the superficial gas velocity results in an increase in the average gas hold-up. This was caused by the decrease in the buoyant force experienced by the bubbles, thereby reducing the bubble slip velocity [20]. The average gas hold-up increased from 0.02 to 0.15 when the superficial gas velocity was increased from 70.74 to 282.97 mm/s. This was due to the fact that increasing superficial gas velocity increased the number of bubbles present in solution which resulted in an increase in the average gas hold-up. The same trend was also seen in the bubble size results (Fig. 4). Reference [19] obtained a similar trend when they studied the effect of superficial gas velocity on the overall gas hold-up.
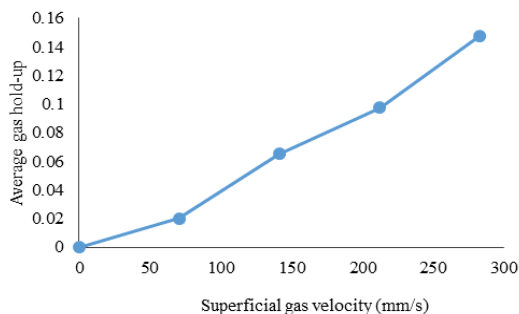

Fig. 2 Average gas hold-up against superficial air velocity

2) Effect of Superficial Gas Velocity on the Bubble Size

The effect of superficial gas velocity on bubble size was determined by varying the superficial gas velocity (70.74 to 282.97 mm/s). The results showed an increase in the bubble size with an increase in the superficial gas velocity. There are two operating regimes namely: homogeneous bubble flow regime where the bubble size ranges from 1-7 mm and the heterogeneous bubble flow regime which ranges from 20-70 mm. Fig. 3a to 3c shows that a homogeneous bubble flow regime exists and Fig. 3d shows a transitional bubble flow regime. When increasing the superficial gas velocity, the static liquid column expands and the volume fraction of bubbles increases with superficial gas velocity. Increasing the superficial gas velocity further results in a decrease in the photon efficiency in spite of the vigorous mixing of bubbles. Also the larger number of bubbles may hinder absorbance of solar light to the photocatalyst. Therefore, it is necessary to operate at an optimum superficial gas velocity that provides adequate mixing with minimal photon deficiency.
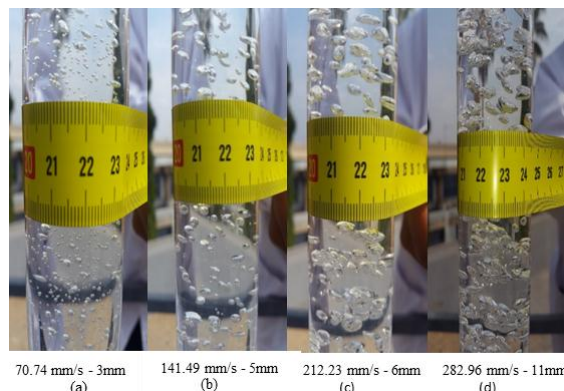

| 70.74 mm/s - 3mm | 141.49 mm/s - 5mm | 212.23 mm/s - 6mm | 282.96 mm/s - 11mm |
| (a) | (b) | (c) | (d) |

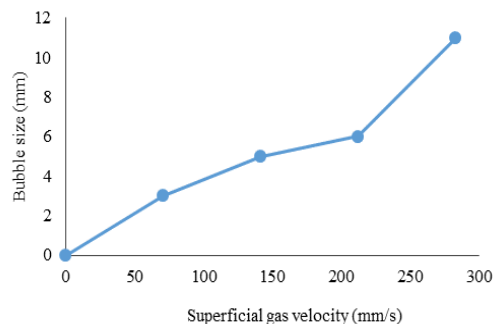Fig. 3 Bubble size distribution

Fig. 4 Bubble size against superficial gas velocity

B. Photodegradation

1) Effect of Irradiation Time on the Removal of Color and TOC

Fig. 5 shows the effect of reaction time on the removal of color and TOC. It can be seen that as the reaction time increases the solution becomes decolorized (reduction of color). Since the presence of color is directly proportional to the presence of MO, due to the fact that it is the pollutant that causes color. Therefore, the decolorization of the solution simply implies that there is removal of MO. The same decrease was seen on the TOC reduction results, the only difference is that TOC represents the degradation of the various organic compounds present in the solution. The results show that 80% of color was removed in 60 min, whereas, only 33.97% of TOC was removed at the same time. This suggests that most of the MO was degraded in 60 min, although, other MO derivatives are still present in solution as shown by the TOC reduction results. Reference [7] studied the photocatalytic degradation of MO in water using Ag/ZnO as a catalyst. They reported that irradiation of MO after 10 min produces other forms of methyl groups such as monohydroxlated products. Consequently, monitoring the reduction of TOC gives a clear indication on the degradation of MO and its derivatives.
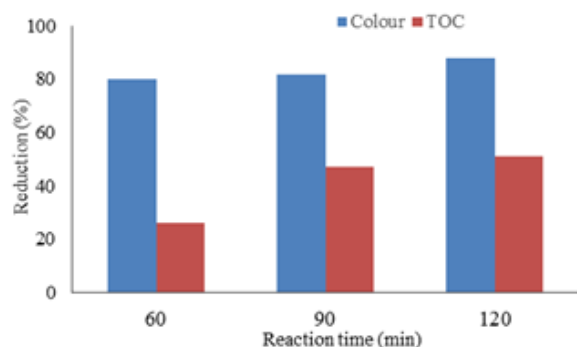
Fig. 5 Effect of reaction time on the removal of color and TOC

2) Effect of Catalyst Loading on the Removal of Color and TOC

The removal of color and TOC increased with an increase in the amount of catalyst as shown in Fig. 6. An increase in the catalyst loading results in an increase in the amount of catalyst particles present in the photoreactor. This, however, increases the amount of active sites available for MO adsorption and photodegradation [14]. Considering the range (0.5–1.5 g/L) of catalyst loading that was used in this study, 1.5 g/L was found to be the optimum loading since it achieved the highest color removal (~98 %) and TOC reduction (~79 %). Extrapolation of the data shows that increasing the catalyst loading beyond 1.5 g/L will cause a decrease in the removal of TOC and color. According to literature, this is referred to as the liming factor. This means that increasing the catalyst loading beyond the limiting factor will cause obstruction to the energy photons (UV light) from reaching the surface of the catalyst particles due to an excessive amount of catalyst particles present in the photoreactor [14]. Reference [18] obtained an optimum catalyst concentration of 100 mg/L (limiting factor) and showed that an increase in catalyst loading beyond this value results in the decrease in the total chemical oxygen demand (TCOD). It is therefore, recommended to operate at the limiting factor which gives maximum photodegradation and reduces the cost of catalyst loading.
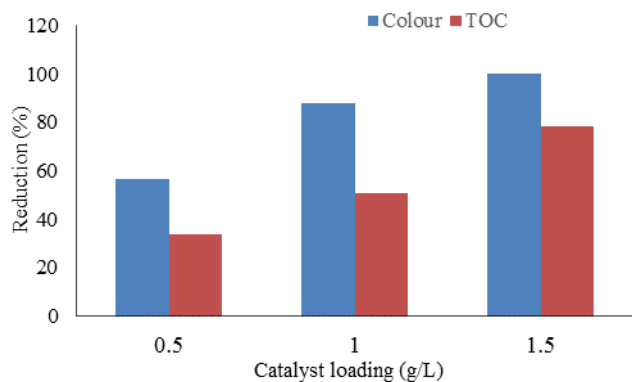

Fig. 6 Effect of catalyst loading on the removal of color and TOC

3) Effect of Superficial Gas Velocity on the Removal of Color and TOC

The introduction of air in a fluidized bed photoreactor is essential due to the fact that air plays two major roles in the photodegradation of pollutants. Air is used for mixing inside the reactor (hydrodynamics) and the oxygen is used to prevent electron-hole recombination. Therefore, Fig. 7 showed that, as the superficial gas velocity is increased, the removal rate of color and TOC increases. This indicates that an increase in the superficial gas velocity results in an increase in the number of bubbles, thus mixing between the TiO$_2$ catalyst and methyl orange is enhanced and a higher mass transfer rate is obtained. At higher superficial gas velocities, the bubble size increases (Fig. 4) which leads to a vigorous mixing inside the photoreactor. The optimum superficial gas velocity was found to be 212.23 mm/s. The hydrodynamic study revealed that at this superficial gas velocity (212.23 mm/s), the transitional bubble flow regime exists. It is evident from Fig. 7 that the hydrodynamics play a significant role in the photodegradation of MO.
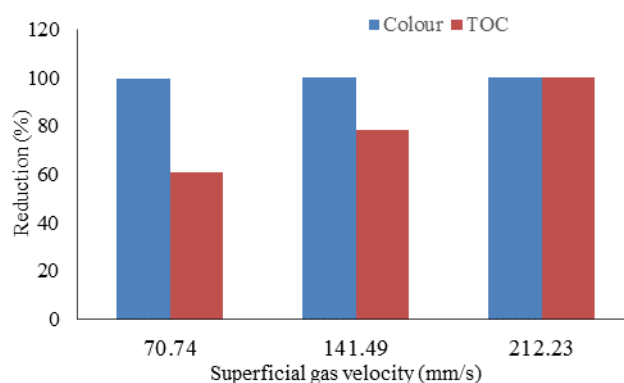

Fig. 7 Effect of air velocity on the removal of color and TOC

IV. CONCLUSION

The purpose of this study was to investigate the hydrodynamic conditions and to obtain optimum conditions for methyl orange photodegradation in a fluidized bed photoreactor. It was shown that the photodegradation efficiency is significantly influenced by the hydrodynamics (superficial gas velocity), catalyst loading and reaction time. It was also shown that the superficial gas velocity affects the bubble size and average gas hold-up. The average gas hold-up increased from 0.02 to 0.15 when the superficial gas velocity was increased from 70.74 to 282.96 mm/s. The effect of hydrodynamic conditions on photodegradation showed that an increase in the superficial gas velocity results in an increase in decolorization and the removal of TOC. The optimum photocatalytic operating conditions were found to be: superficial gas velocity of 212.23 mm/s, catalyst loading of 1.5 g/L and reaction time of 60 min. It was evident that solar, as a renewable energy source, can be effectively applied in the photodegradation of MO. This study has revealed that the heterogeneous photocatalytic oxidation process can be effectively applied for the degradation of MO in wastewater. Although it was shown that the hydrodynamics significantly affect the photodegradation efficiency, a more in-depth study on the hydrodynamics is necessary for more transparency. Further work can be done to use computational or numerical

techniques to study hydrodynamic phenomena, light distribution in the reactor and photodegradation reaction kinetics.

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