



Photocatalytic degradation of indole in a circulating upflow reactor by UV/TiO₂ process—Influence of some operating parameters

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ABSTRACT

The present work involves the photocatalytic degradation of indole on a recirculating reactor. The effects of various factors as initial concentration of indole, catalyst-loading, pH, agitation and flow rate of the solution on the photodegradation were examined. The experimental results indicate that the optimal pH for indole elimination is about 6–7; the effect of catalyst loading shows an optimal value (1 g/L) which is necessary to degrade indole; the increase of recirculating rate leads to a decrease of degradation rate due to the reduction of the residence time; the agitation speed has a slight influence on the indole degradation by improving the mass transfer step. Finally, L–H model was used to fit experimental results concerning the influence of experimental data. L–H model constants' were determined also.

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1. Introduction

The industrial and agricultural activities contribute to increasing the contamination (pollution) of soil, water surface and groundwater. Wastewater treatment is usually based on physical and biological processes. After elimination of particles in suspension, the usual processes are biological treatment (natural decontamination) [1,2]. To perform the wastewater treatment, unfortunately, the conventional chemical and physical methods are not destructive, but only transfer the pollutant from one phase to another. Therefore, a new and different kind of pollution is faced and further treatments are required [3]. The ideal wastewater treatment method will not only completely degrade the primary pollutant, but will also mineralise all organics and also be cost effective [4].

In the near future, advanced oxidation techniques (AOT's) are promising methods for wastewater treatment [5,6]. The AOT's can be used alone or in combination with biological steps in order to insure an efficient level of pollutants abatement [7,8]. Such advanced oxidation processes (AOPs) include, amongst others, ozone oxidation, hydrogen peroxide, hydrogen peroxide/ferrous or ferric ion (the so-called Fenton's reagent), UV irradiation,

photocatalysis, electrochemical oxidation, as well as various combinations of them [9,10]. Usually AOT's lead, in aqueous phase, to OH• radicals production having a very high oxidative potential. The hydroxyl radical is able to mineralise the majority of organic compounds. Among the AOT's, photocatalysis use semiconductors to produce hydroxyl radicals by irradiation. The mechanisms of photocatalysis are well documented [11–13]. Photocatalytic oxidation involves the use of a semiconducting material, such as TiO₂, along with enough light energy to promote an electron from the valance band to the conduction band [14]. The energy requirement for this reaction is equivalent to the band gap energy of the material used. The produced electron/hole pairs are used as reducing/oxidizing agents. The positively charged holes oxidize the organic compounds adsorbed on the catalyst surface. In addition, hydroxyl radicals are produced in aqueous system. The hydroxyl radicals serve as a strong oxidizing agent for the conversion of organic molecules to carbon dioxide [15,16]. To prevent electron/hole recombination from occurring, the electrons must also be consumed. Oxygen molecules are converted to superoxide molecules upon reacting with electrons. Therefore, oxygen is added, as an electron acceptor, to the reaction mixture as a way to minimize the recombination of electrons and holes [17].

TiO₂ is one of the suitable semiconductors for photocatalysis and has been applied into various photocatalytic reactions [18,19]. Its use, on wastewater remediation, is based on several factors: (1) the process occurs under ambient conditions; (2) the formation of photocatalysed intermediate stable products, unlike direct photol-

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ysis techniques, is avoided; (3) oxidation of the substrates to CO_2 is complete; (4) it is inexpensive and has a high turnover; (5) the process offers great potential as an industrial technology to detoxify wastewaters [20].

Indole and methyl indole produced by biodegradation of proteins are found as characteristic substances in wastewater from cattle farm and in liquid manure. Level as high as several mg/L are observed in pig-breeding manure [21]. Indole and its derivatives have unpleasant smell but can cause more important damage to living organisms. They are highly toxic and are even mutagenic and carcinogenic [22].

Indole belongs to nitrogen-heterocyclic compounds (NHCs) family. Some studies concerning its removal by biological or chemical methods are reported in the literature [23]. AOPs seem to be more effective. However, some residual chemicals (as O_3 or H_2O_2) used can induce environmental risk or toxicity [23]. The photocatalysis of indole and its derivatives can be an interested challenge since there are no chemicals used and by-products are essentially H_2O and CO_2 [24,25].

The aim of the present work is to study the photodegradation of indole, as a model molecule, in order to define the basic data for the design of a pilot unit of solar wastewater treatment in “Unité Avicole de Taboukert” (poultry), Algeria. The Effects of parameters like the initial concentration of indole, catalyst loading, pH, airflow rate, agitation of the solution, and the flow rate of solution will be studied.

2. Experimental

2.1. Materials and products

All the experiments were carried out on a recirculating plant (Fig. 1). The glass jacket reactor used has an internal volume equal to 0.9 L. A UV lamp (emission spectra between 340 and 400 nm, Phillips PL-L24W/4P) with a power of 24 W was used. The UV lamp was positioned centrally in the reactor, inside a quartz tube (jacket), surrounded by the indole solution (see Fig. 1).

The lamp was totally immersed in the reactor and therefore the maximum light irradiation was achieved. Diameter of the quartz tube (jacket) was the minimum to hold the lamp and thus the adsorption of light photons by oxygen molecules in the air around the lamp was minimized. A pump, located below the reactor, pro-

vides an adjustable circulating flow. The reactor is equipped with a water-flow jacket for regulating the temperature by means of an external circulating flow (JULABO) with an accuracy of $\pm 0.1^\circ\text{C}$. Air was supplied at a constant flow-rate using an air pump (micro-air compressor). The whole reactor was covered with an aluminium thin layer to prevent UV emission.

The indole used was purchased from Fluka and its purity is higher than 99%. All the solutions were prepared by dissolving the pollutant in bi-distilled water. A volume of 1.2 L was used in each experiment.

The medium provided by Ahlström is a perforated nonwoven textile composed of cellulosic fibres coated with a mix of catalyst (TiO_2 Millennium PC 500, specific area = $317\text{ m}^2\text{ g}^{-1}$). It is referenced as Media 1048 by Ahlström. The quantity of catalyst deposited is equal to 25.5 g m^{-2} . The use of immobilised catalyst permits to avoid the separation step of the particles.

The evolution of indole concentration is followed by UV-visible spectrophotometer (Shimadzu mini 1240) by sampling 5 mL of solution. Absorbance of the samples is measured after 5 min of centrifugation. Sulphuric acid and sodium hydroxide, used to adjust the pH solution were Merck products. The pH and temperature of the solution were monitored during the runs (Inolab system).

2.2. Experimental procedure

A desired quantity of the photocatalyst is placed in the reactor then indole solution (1.2 L) is added in the tank. Before irradiation, the solution is flowing during a period of 60 min in the dark. We note a decrease of the concentration during the first minutes. This is due to the adsorption, on the catalyst surface, which is the first step on the heterogeneous catalysis. After 50 min, the steady state is reached.

Then the UV lamp is switched on to initiate the irradiation and the photocatalysis process.

It should be noted that indole on TiO_2 (in our conditions) leads in all cases to very low adsorbed level (<1% of the indole). Experimental results demonstrate also that in our system the disappearance of indole by evaporation is negligible.

During the photodegradation, aeration rate of 1 L/min was maintained. The duration of all the experiences was fixed at 120 min.

3. Results and discussion

As reported above, the influence of some experimental parameters will be studied and discussed.

3.1. Effect of catalyst concentration

The optimal amount of photocatalyst to achieve the maximum efficiency of the process depends on the nature of the catalyst, the geometry of the reactor, the incident radiant flux and the mean optical pathway within the suspension [26]. The catalyst dosage as an important parameter has been extensively studied in many photocatalytic reactions suggesting that the optimal TiO_2 dosage varies from 0.15 to 2.5 g/L [27].

In the present study, degradation of indole (10 mg/L) with different amounts of TiO_2 (from 0.5 to 2 g/L which correspond to a surface sample varying from 0.0196 to 0.0784 m^2 , respectively) was carried out during 2 h. The experimental results are shown on Fig. 2. We note that, in a first time, the rate of indole degradation increases with increasing TiO_2 concentration up to a certain value. Then the increase of TiO_2 leads to a decrease of degradation efficiency. The initial rates at varying TiO_2 concentrations are determined from the initial slopes and are plotted against the TiO_2 concentrations (Fig. 3). We note the existence of an optimum value. This is because catalyst loading exhibits conflicting effects on the photocatalytic process.

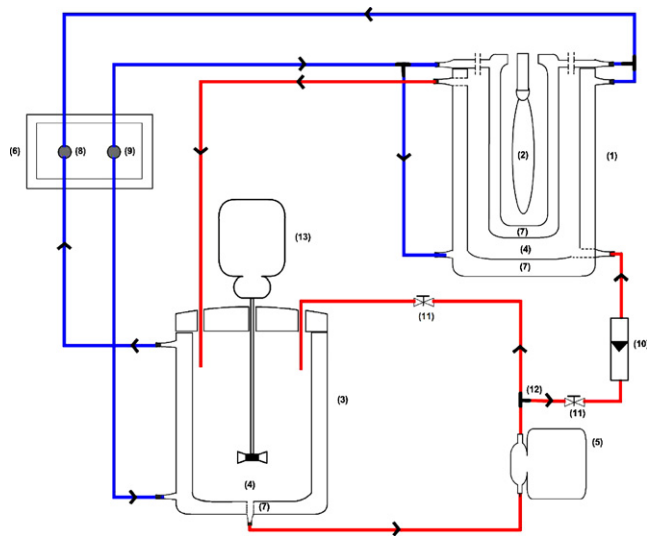


Fig. 1. Experimental system. 1: Glass jacket reactor; 2: UV lamp; 3: tank; 4: solution; 5: centrifugal pump; 6: cryostat of circulation water; 7: quartz jacket; 8: water inlet; 9: water outlet; 10: flow meter; 11: valve; 12: by pass; 13: air pump.

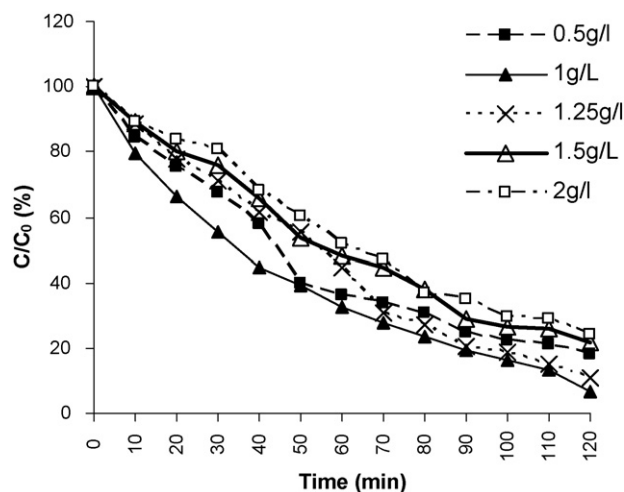


Fig. 2. Effect of catalyst concentration on the indole photodegradation.

At lower loading levels, photonic adsorption controls the reaction extent due to the limited catalyst surface area, while at higher loading levels; light scattering by catalyst particles predominates over photonic adsorption [3,28,29].

To take into account these two opposite effects, Wu et al. [30], have proposed a three constants model to represent the variation of initial degradation rate:

$$-r_0 = k_1 C_S \exp(-k_2 C_S - k_3 C_S^2) \quad (1)$$

where C_S represents catalyst concentration and k_1 , k_2 and k_3 are a proportional constants. They are determined by considering that the degradation kinetic is proportional to $[h^+]$ vacancy concentration and this last is proportional to energy received by the catalyst. More details about the model are given in the publication pre-cited [30].

A non-linear regression method (Excel Solver) was used to find the best values of the constants. Even if the maximum value of the degradation rate is overstated, the model fits satisfactorily the experimental results (Fig. 3).

In our case, an optimal catalysts concentration of 1 g/L was selected corresponding to the maximum of the degradation rate. This concentration will be used for the rest of experimental runs.

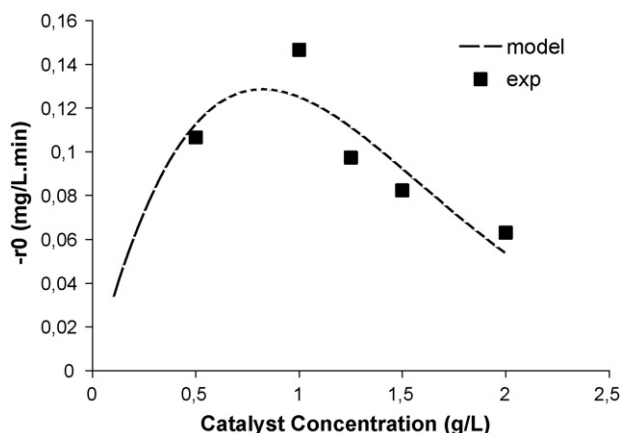


Fig. 3. Effects of TiO_2 concentration on the indole initial photodegradation rate (solution volume: 1200 mL, UV lamp: 24 W, flow rate of solution = 0.5 mL/s, temperature: 25 °C, initial indole concentration: 10 mg/L, airflow rate: 2 L/min, natural pH: 6.8).

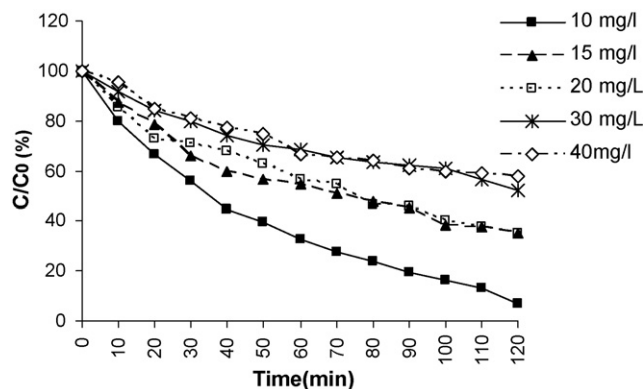


Fig. 4. Effect of initial indole concentration on photodegradation using TiO_2 (solution volume: 1200 mL, UV lamp: 24 W, temperature: 25 °C, airflow rate: 2 L/min, natural pH: 6.8, flow rate of solution = 0.5 mL/s, catalyst concentration = 1 g/L).

3.2. Effects of initial indole concentration

Some experiments were carried out at different concentrations varying from 10 to 40 mg/L. The values of the latter are given in the legend of Fig. 4. All other parameters are kept constant. We note (Fig. 4) that the increase of initial indole concentration leads to an increase of residual indole concentration at different processing time. Similar results have been reported concerning the photocatalytic oxidation of others pollutants [31–33]. Kamble et al. [34] suggest that as the initial concentration increases, the adsorption on the catalyst surface also increases. Since irradiation time and the amount of catalyst are constant, the OH^* (primary oxidant) concentration remains practically same. Thus, although bulk liquid concentration increases, the rate of photocatalytic degradation decreases due to a lower $OH^*/$ indole ratio. On the other hand, the penetration of light decreases when the pollutant concentration increases, this leads to less active sites creation.

The Langmuir–Hinshelwood (L–H) model is commonly used to rationalize the mechanisms of reactions occurring on solid surfaces [35–38]. According to the L–H kinetic model, the initial rate of the photocatalytic reaction is given as

$$r_0 = \frac{kKC_0}{1 + KC_0} \quad (2)$$

where k and K are the kinetic rate constant and the adsorption equilibrium constant, respectively. And C_0 is the initial indole concentration.

By plotting $1/r_0$ versus $1/C_0$, we can confirm the validity of the model if the linearization is correct. Moreover, the values of reaction rate constant k and adsorption equilibrium constant K can be determined by linear regression. The reported results on Fig. 5 show that the L–H model can approach correctly the experimental data. This means that the kinetic reaction step is probably the limited step.

The obtained values of k and K are: $k = 0.281$ mg/(L min) and $K = 0.083$ L/mg.

These constant values are the same order of magnitude than those reported in the literature concerning the photocatalysis of organic pollutants [31,39–41].

It is important to note that the mineralisation of the pollutant is not complete. This means that a possible by-product is generated. A more detailed study concerning this aspect will be done later.

3.3. Effect of pH

An important parameter in the heterogeneous photocatalysis is the reaction pH, since it influences the surface charge properties

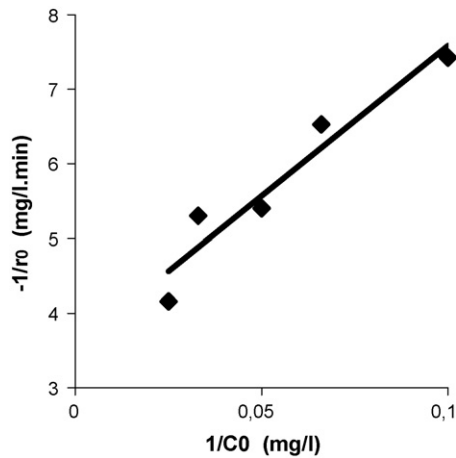


Fig. 5. Linearization of the L-H model.

of the photocatalyst and therefore the adsorption behaviour of the pollutant and also the size of aggregates it forms [28,42]. In wastewater treatment it is also an important operational parameter. To study the effect of pH on the degradation efficiency, experiments were carried out at various pH values, ranging from 2.23 to 10.39. All the other parameters are maintained constant.

We note (Fig. 6) that the pH influences strongly the degradation efficiency of indole. When increasing pH from 2.23 to 7, the photodegradation efficiency increases. Then it decreases beyond this value. The pH 7 value seems to be the optimum pH for the photodegradation of indole. It is interesting to note that both in acid and basic solution, the photodegradation are less successful.

According to literature reports [9,43], it is well known that TiO_2 possesses an amphoteric surface and its point of zero charge (PZC) is equal to 6.3. In other words, this means that the TiO_2 surface is positively charged (Ti-OH_2^+) when the pH is lower than this value and negatively charged (Ti-O^-) when the pH is higher than PZC.

The molecule of indole is positively charged at acidic pH. This is due to the free doublet of nitrogen atom which is a captor of proton. This leads to repulsion between catalyst surface and indole due to the same charge. As a basic molecule, indole is also negatively charged on basic solution. Then the same repulsion phenomenon occurs. So the optimum pH value which gives a maximum degradation rate is about 6–7.

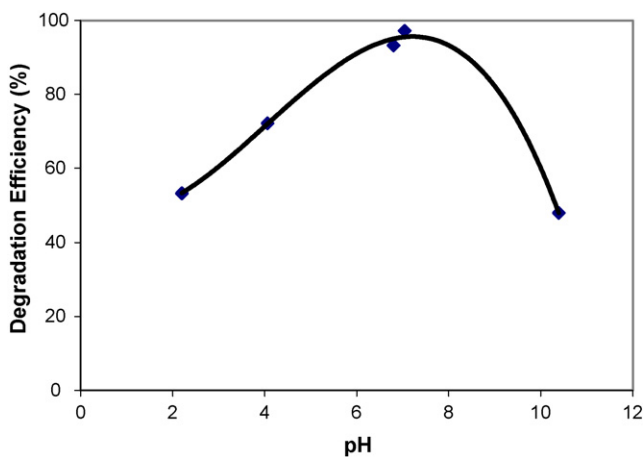


Fig. 6. Effect of pH on photodegradation efficiency of indole (solution volume: 1200 mL, airflow rate: 2 L/min, $\text{TiO}_2 = 1 \text{ g/L}$, $T = 25^\circ\text{C}$ and UV lamp = 24 W, flow rate of solution = 0.5 mL/s).

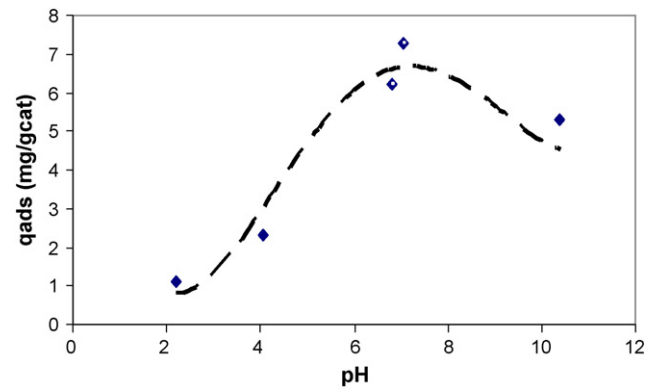


Fig. 7. Effect of pH on adsorption capacity of TiO_2 (solution volume: 1200 mL, airflow rate: 2 L/min, $\text{TiO}_2 = 1 \text{ g/L}$, $T = 25^\circ\text{C}$ and UV lamp = 24 W, flow rate of solution = 0.5 mL/s).

The adsorption is expected to enhance the process since the photodegradation is a surface-oriented reaction [44]. A study on the adsorption of indole on TiO_2 surface was carried out. The same behaviour is observed (Fig. 7) which confirm the existence of the repulsive forces between the TiO_2 surface and the adsorbate at low and high pH.

3.4. Effect of flow rate

Flow rate is an important factor that affects photocatalytic reaction by changing the convective mass transfer and residence time in the reactor. The influence of the flow rate on the degradation of indole is summarized in Fig. 8. We note that increasing the flow rate from 0.5 to 4.03 mL/s, leads to a decrease of the indole degradation from 93% to 58% (Fig. 9). It is well known that the flow rate has dual effects on the photocatalytic reaction [45]. The increased flow rate improves the photocatalytic reaction by increasing diffusion between indole and TiO_2 catalyst. It can also influences agglomeration of catalyst particles in the case of non supported media [46]. The opposite effect which is observed is the reduction of the residence time which leads to less degradation amount of indole by affecting the adsorption on the surface of TiO_2 and the photocatalytic reaction. In our experiments, the effect of the reduction of the residence time seems to be more predominant than the improvement of the diffusion. This is probably due to the fact that photodegradation of indole is under pure kinetic regime. These results confirm the validity of L-H model used previously to represent the influence of initial indole concentration.

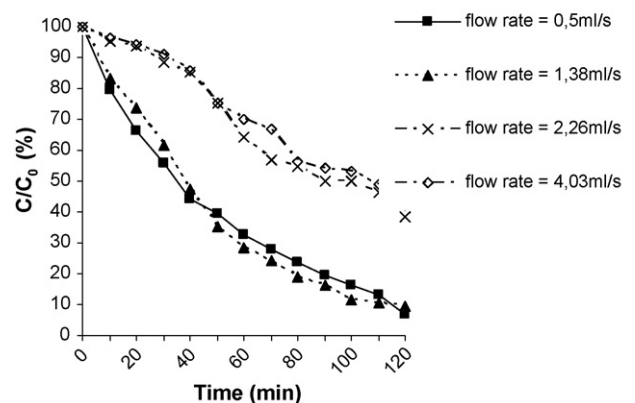


Fig. 8. Effect of flow rate on degradation of indole ($[\text{TiO}_2] = 1 \text{ g L}^{-1}$, $T = 25^\circ\text{C}$, solution volume: 1200 mL, airflow rate: 2 L/min, and UV lamp = 24 W).

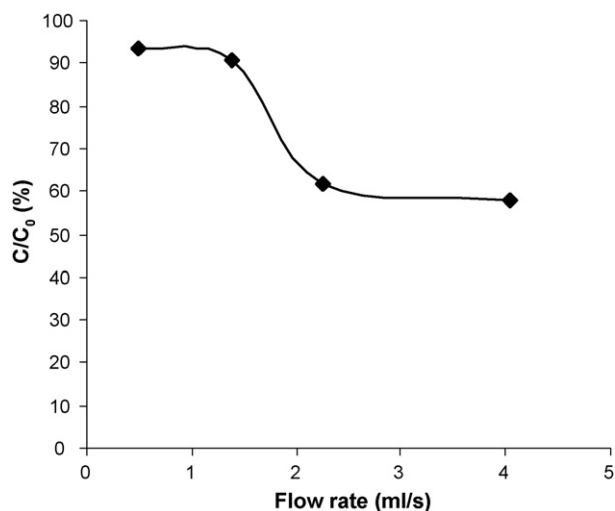


Fig. 9. Effect of flow rate on degradation of indole at irradiation time of 120 min; ([TiO₂] = 1 g L⁻¹, T = 25 °C, solution volume: 1200 mL, airflow rate: 2 L/min, and UV lamp = 24 W).

The plateau observed at the value of flow rate up to 2 mL/s is probably due to the fact that the decrease of residence time is compensated by the increase of diffusion. However, this aspect needs more investigation.

3.5. Effect of agitation speed

A series of experiments were carried out by varying the agitation speed while keeping all other factors constant. The results are summarized in Fig. 10. We note that the indole photodegradation increases when increasing agitation speed from 0 to 350 rpm. The initial reaction rates at varying agitation speeds are computed from the initial slopes and the results are represented in Fig. 11. The results confirm that the indole photodegradation is also dependent on the agitation speed, even if the process is chemical step controlled. Two reasons can be cited to explain this behaviour.

Firstly, it is well known that heterogeneous photocatalysis is governed by two steps in series. Then the overall mass transfer is the summation of the mass-transfer resistance and the chemical reaction resistance:

$$\frac{1}{k} = \frac{1}{k_c} + \frac{1}{k_r} \quad (3)$$

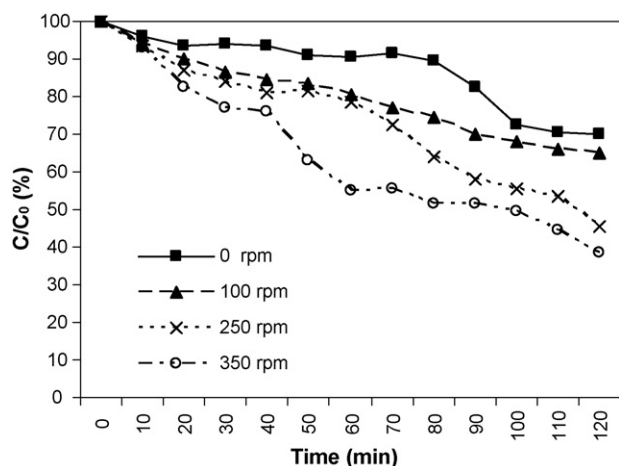


Fig. 10. Effects of agitation speed on the indole initial concentration rate.

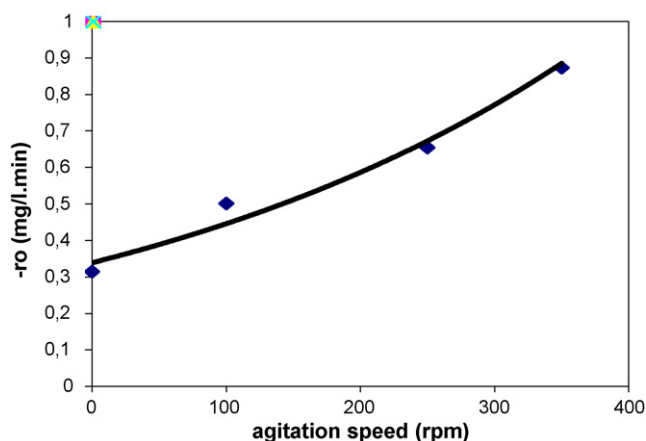


Fig. 11. Effects of agitation speed on the initial degradation rate.

where k_c is the mass transfer coefficient, k_r the reaction rate constant and k is the overall rate constant [47,30].

Using the correlation of the Schmidt number and Reynolds number we can see that the mass transfer step, and then k_c , is influenced by the agitation speed. So the increase of the agitation speed leads to high mass transfer and then to high degradation rate of indole.

Secondly, the increase of the agitation speed can promote the oxygen transfer on the liquid phase. And thereby increase the degradation kinetics.

4. Conclusion

The current work has examined the influence of some experimental parameters on the photodegradation of indole. The results confirmed that photocatalysis is a convenient means of decontamination of wastewaters. The main results concerning the indole photodegradation on a slurry recirculating reactor are

- The optimal loading of TiO₂ is equal to 1 g/L.
- Due to the nature of the pollutant, an optimal pH value was found to be equal to 6–7.
- A high flow rate of recirculation has a negative effect on the pilot performance. The reduction of the residence time seems to be the predominant factor which can explain this behaviour.
- On the contrary, the agitation speed leads to the improvement of the degradation due to the reduction of the mass transfer step.
- Finally, the influence of initial concentration was tested and represented by the means of Langmuir–Hinshelwood model. This allows us to determine the values of the constants' model and to verify its validity.

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