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Original Research Article

Photocatalytic Activity of Aluminium Oxide Nanoparticles on Degradation of Ciprofloxacin

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Abstract

In this research, Al_2O_3 nanoparticles were successfully synthesized using facile chemical precipitation method as a photocatalyst. The synthesized photo catalyst was characterized using scanning electron microscopy. The photocatalytic activity of the synthesized $Al_2O_3$was studied on the degradation of ciprofloxacin as a model pollutant in UV light irradiation by conductometry method. The experiments were carried out by varying contact time from 1- 5 hours and catalyst load from 0.5 – 2.5g. The optimum catalyst dose and contact time were found to be 1g and 1 hour respectively for the drug degradation. The result exhibited photocatalysis activity. The photocatalytic activity can be attributed to higher absorption of Ultra-Violet light by the synthesized Al_2O_3 that led to formation of a large number of reactive species. The Kinetics study of the photodegradation process was explained in terms of the modified Langmuir Hinshelwood model. The values of the kinetic rate constant (k) of the photodegradation were $8.0x10^{-3}min^{-1}$ and $5.0x10^{-2}min^{-1}$in the absence and presence of the synthesized photocatalyst respectively.

Keywords: Photocatalysis, Al_2O_3 Nanoparticle, Ciprofloxacin, Conductometry, Photodegradation.

1.0 INTRODUCTION

Recent studies in environmental science have focused on the removal of pharmaceuticals and their metabolites in water bodies [1]. The occurrence of pharmaceuticals in the environment results in exposure to non-target organisms which have led to antibiotic resistance in bacteria [2]. There are large numbers of harmful pharmaceutical drugs detected in environmental waters that badly affects human health and animals [3,4]. Moreover, pharmaceuticals such as ciprofloxacin and fluoroquinolone have been reported to cause adverse toxicity towards green algae [5]. These compounds get to water bodies from various sources, such as disposals from hospitals and households, excretions by humans and animals and it is important to develop new and effective technologies for their removal from wastewaters and aquatic ecosystems [6].

Various advanced waste water treatment techniques such as membrane based processes, advanced oxidation processes (AOP) and UV illuminated processes are utilized for removal of organic pollutants [7].

The application of advanced oxidation processes (AOPs) has shown promising results in removal of pharmaceutical pollutants because of its effectiveness in degrading aqueous pollutants with in situ highly reactive hydroxyl radical ($^{\cdot}OH$) which is responsible in initiating the oxidation of organic compounds in the waste water [8-11]. Many AOPs such as UV/H_2O_2, ozone based and semiconductor based catalytic processes are employed for effective degradation of organic pollutants in wastewater. Semiconductor based photocatalytic process is extensively used compared to other AOPs due to less input of chemical components, low cost, easy recovery of catalyst, multiple active sites and the heterogonous nature of the catalyst [3, 8].

TiO_2, ZnO, Fe_2O_3, Fe_2O_4 and Al_2O_3 and many other semi-conductor materials are employed as photocatalyst for different applications like environment, energy and chemical synthesis [9,12-13]. Aluminium oxide (Al_2O_3) is not extensively used in treatment of pharmaceutical wastewater even being chemically stable, non toxic and also comparatively economical as it can be synthesized from waste aluminium cans.

There are no reports found on photocatalytic degradation of ciprofloxacin by aluminium oxide (Al_2O_3). In the present study, aluminium oxide nanoparticles were synthesized via facile precipitation method from waste aluminium cans. The synthesised Al_2O_3 nanoparticles photocatalyst were characterised using scanning electron microscope (SEM) and its photocatalytic activity was evaluated based on the degradation of ciprofloxacin under ultra-violet light irradiation.

2.0 MATERIALS AND METHODS

2.1 Materials

All chemicals and reagents used for the synthesis were of analytical grade and were used without former purification.

2.2 Synthesis of Aluminium Oxide

Empty aluminium beverage cans were collected from waste bins. The collected materials were thoroughly washed with detergents and rinsed extensively with deionsed water after removing the polymer coating on the aluminium can. The aluminium empty cans were cut into smaller pieces. 5.32g of the aluminium waste was accurately weighed using Top-loading balance (Model- Atom-A110C) into 100ml beaker and 100ml of 10% solution of NaOH was added and heated, but not to boiling point. The reaction is completed when the hydrogen evolution ceases and a clear solution appears without any visible pieces of aluminium metal. The solution was filtered under vacuum filtration into a 500ml flask and allowed to cool in a cooling bath.

250ml of cold 3M $NaHCO_3$ solution was slowly and carefully added from the burette with constant stirring. Then the reaction mixture was heated upto 60℃ and was kept in the ice bath to cool. A white precipitate of aluminium carbonate was filtered and washed with distilled water and 70% ethanol, and were dried in hot air oven at 105 ℃ for 3 hours. The aluminium carbonate crystals obtained was calcined at 400℃ for 8 hours to obtain aluminium oxide particles and was ground into fine particles to give aluminium oxide nanoparticle.

2.3 Characterization of the Aluminium Oxide Nanoparticles

The Surface morphology of synthesized Al_2O_3 nanoparticles was done by scanning electron microscope (SEM) PhonorxProx model Q15OR.

2.4 The Photocatalytic Degradation Study

The photocatalytic degradation process was studied using the method described in our earlier study [9].The effect of catalyst load was carried out using Al_2O_3 in 100ml of 200mg ciprofloxacin solution and exposed to 254nm 220V-15W UV-lamp in a photoreactor for 3 hours. The solution was separated by filtration and the conductance reading of the ciprofloxacin was taken using conductivity reading (Model: Jonway 4510). In order to determine the effect of exposure time the experiment were performed by varying exposure time from 1 to 5 hours with 1.0g Al_2O_3 in 100ml of 200mg ciprofloxacin solution. The percentage degradation of the ciprofloxacin was evaluated using equation 1.

$$\mathrm{PD}(\%) = \frac{\wedge_1 - \wedge_0}{\wedge_1} \mathrm{x}\, 100 \qquad \ldots \quad (1)$$

Where $\wedge_0$ represent the initial conductance reading before UV lamp irradiation, $\wedge_1$ is the conductance at time interval and PD is the percentage degration of ciprofloxacin.

Similarly, the kinetics of the reaction for the degradation of ciprofloxacin was calculated using modified Langmuir – Hinshelwood equation 2 [1].

$$In\left(\frac{\wedge_0}{\wedge}\right) = -k_t \quad \ldots \quad (2)$$

Where k is the reaction rate (min^{-1}), t is the irradiation time, ∧ and ∧ retains their earlier meaning respectively.

3.0 RESULTS AND DISCUSSION

The surface morphology of the synthesized Al_2O_3 nanoparticle catalyst was examined using scanning electron microscope (SEM), and the micrograph is shown in Fig 1. It can be seen from the image of the synthesized Al_2O_3 nanoparticles shows regular sphere like morphology.

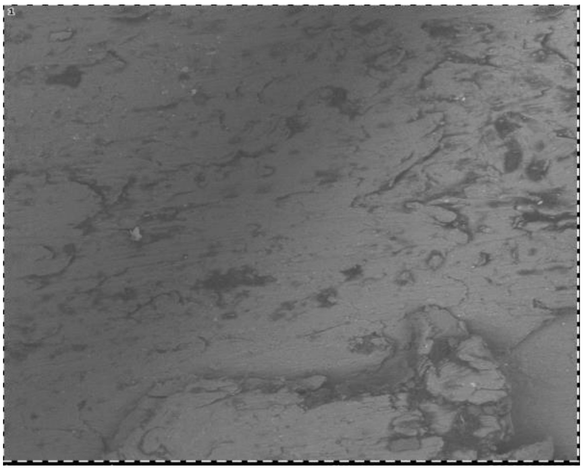

Fig-1: 500 times magnification of aluminium oxide

3.1 Photo Catalytic Degradation of Ciprofloxacin

3.1.1 Effects of Catalyst Load on the Rate of Photocatalytic Degradation Reactions

The effect of Al_2O_3 nanoparticles on the photodegradation of ciprofloxacin was studied by adding different quantities of the photocatalyst varying from 0.5g to2.5g/100ml into the reaction vessel and placed it in a photo-reactor at fixed 220ppm of ciprofloxacin. The experimental result shows that there is an increase in the rate of photocatalytic degradation from 0.5g to 2.5g as presented in Fig 2. The results of the study revealed that the introduction of the photocatalyst increases the rate of degradation when compared with the blank study, indicating the stability of ciprofloxacin and UV light irradiation in the absence of catalyst. The catalytic activity of Al_2O_3 nanoparticle shows that the photocatalyst played a major role in the mineralization of the studied compound.

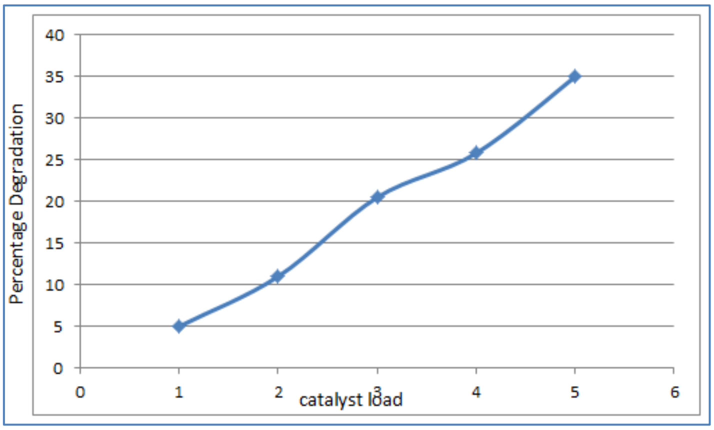

Fig-2: Effect of catalyst load photocatalytic degradation of ciproloxacin

The presence of active sites on catalyst surface plays an important role in explaining the high percentage of degradation obtained in thecurrent result. This can be demonstrated on the basis of increase in the amount of active sites on the catalyst surface. The increase in active sites on the Al_2O_3 nanoparticle surface leads to the increase on the number of ciprofloxacin molecules adsorbed on the catalyst surface. This also leads to increase in the area of illumination and an increase in the amount of catalyst leading to an increase in the number of absorbed photon. This causes an increase in percentage degradation [9, 14].

3.1.2 Effect of Contact Time

The influence of contact time of exposure on the photodegradation of ciprofloxacin in the absence and presence of Al_2O_3 nanoparticles was studied by varyingthecontact time of exposure in UV light from 1 hour to 5 hours in the reaction mixture, placed in a UV photo-reactor of fixed ciprofloxacin concentration of 100mg/100ml and photocatalyst of 1.0g. The experimental data of effect of time on photocatalytic degradation rate of Al_2O_3 nanoparticles indicated that the optimal time is 1 hour.

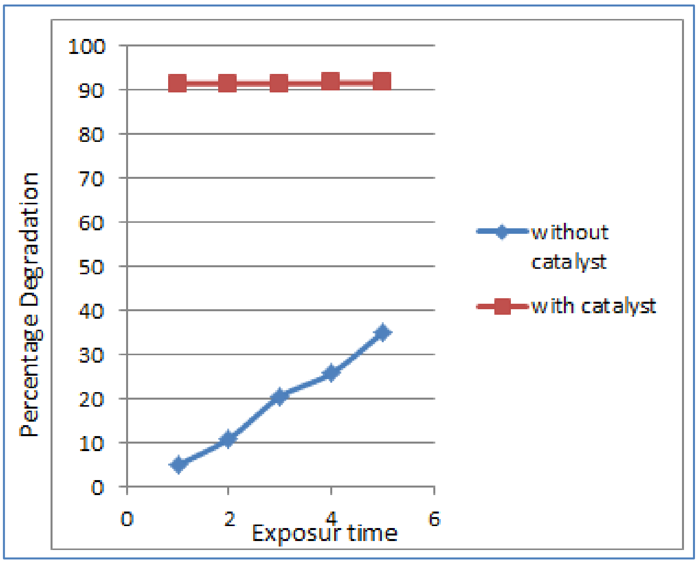

Fig-3: Effect of exposure time onphotocatalytic degradation of ciproloxacin

The results revealed the percentage degradation rate had no significant effect with increase in contact time as plotted in figure 3. Furthemore, in order to quantitatively compare the photocatalytic efficiency of the synthesized Al_2O_3 nanoparticles, the rate of ciprofloxacin degradation was evaluated by plotting graph of $In\ \frac{\Lambda_0}{\Lambda_1}$ against time (mins). The evaluated rate constant (K) for the degradation of ciprofloxacin in the absence and presence of Al_2O_3 nanoparticle photocatalyst are $8.0 \times 10^{-3} min^{-1}$ and $5.0 \times 10^{-2} min^{-1}$ with correlation coefficient of 0.945 and 0.892 respectively. Moreover, the high values of correlation coefficients (R^2) indicate that the photocatalytic degradation process follows Pseudo-First Order Kinetic Model. The photocatalytic activity and degradation efficiency of studied synthesized aluminium oxide nanoparticles from waste aluminium cans on ciprofloxacin shows apromising future for its utilization as heterogeneous photocatalyst in an oxidation process for waste water containing pharmaceuticals compounds.

3.2 Photocatalytic Degradation Mechanisms of Al_2O_3 Nanoparticles

When a semiconductor photocatalyst such as $Al_2O_3$is irradiated by photon energy, which is greater or equal to its ban gap energy, electron (e-) is excited form its valence band to the conduction band [1]. This causes the formation of an electron vacancy called hole (h^+) in the valence band. The photogenerated positive holes (h^+) react with water to produce hydroxyl radical ($^{\bullet}OH$), while the photo-generated electrons (e-) react with dissolved oxygen to produce superoxide radicals($O_2^{\bullet-}$). The generated primary products ($^{\bullet}OH$ and $O_2^{\bullet-}$) are strong oxidizing agents that interact with the ciprofloxacin to degrade it into simple substances (CO_2, H_2O and Mineral acids). The proposed mechanisms are illustrated in equations 3 – 6.

$$Al_2O_3 + hv \rightarrow Al_2O_3(e^- + h^+) \qquad --- 3$$
$$e^- + O_2 \rightarrow O_2^{\bullet-} \qquad --- 4$$
$$h^+ + H_2O \rightarrow OH^{\bullet} \qquad --- 5$$
$$OH^{\bullet} + O_2^{\bullet-} + ciprofloxacin \rightarrow CO_2 + H_2O + mineral\ acid \ ----6$$

CONCLUSION

Aluminium oxide (Al_2O_3) nanoparticles have been successfully synthesized using facile chemical precipitation method. The synthesized Al_2O_3 was characterized using scanning electron microscopy. Its photocatalytic activity was evaluated using ciprofloxacin as a model wastewater pollutant under ultraviolet light irradiation. The Al_2O_3 nanoparticles demonstrated remarkable improvement in the photocatalytic degradation. The demonstration of Al_2O_3improvement in degradation of ciprofloxacin can be attributed to the higher absorption of UV light that led to formation of a large number of oxidizing agents such as •OH and $O_2^{\bullet-}$.

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Conflict of Interest

The authors have not declared any conflict of interest.

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