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Full Length Research Paper

Kinetic studies of BOD_5, COD and Chromium removal in tannery effluent using $ZnO-ZnFe_2O_4$ composite photocatalyst supported on activated carbon

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Abstract

The kinetics studies of the adsorption and degradation phenomena involving tanning wastewater containing high BOD_5, COD and chromium were investigated using a batch reactor and UV light irradiation under ambient conditions of temperature and pressure. Experiments were performed in a suspended $ZnO-ZnFe_2O_4$/20g AC system at natural pH of 6.93 and catalyst concentration of 0.1 mg/100ml. The initial concentration of tannery wastewater was varied between 0.1mg/10ml-0.1mg/100ml. The kinetic analysis of the photodecomposition of tannery wastewater showed that the disappearance followed satisfactorily the pseudo first-order according to Langmuir— Hinshelwood model. The plots obtain from this model were then used to determine the values of r_o, $1/C_o$ and $1/r_o$. The photocatalytic removal of BOD_5, COD and Cr nicely fitted the Langmuir – Hinshelwood kinetic model (R^2 = 0.9364 for BOD5, 0.9673 for COD, and 1 for Cr). The adsorption of the three parameters was found to be the rate controlling step of the photocatalytic processes.

Keywords: Photocatalyst, COD, BOD_5, Chromium, $ZnO-ZnFe_2O_4$, Tannery wastewater

INTRODUCTION

The removal of hazardous chemicals from wastewater is presently one of the most important subjects in pollution control. These pollutants may originate from industrial applications such as textile processing and Leather manufacture. Photocatalytic oxidation (PCO) is a highly effective process for the degradation of a wide variety of priority pollutants in water and wastewater (Hoffmann et al.,1995, Tatsuma et al., 2002). PCO occurs as a result of the interaction of a semiconductor photocatalyst and UV radiation that yields highly reactive hydroxyl radicals, which are believed to be the main species responsible for the oxidation of organic substrates (Hoffmann et al., 1995, Tatsuma et al., 2002). Photocatalytic oxidation in the presence of semiconducting materials, of organic compounds with environmental concern has been studied extensively during the last 20 years and it has been demonstrated that heterogeneous photocatalysis can be an alternative to conventional methods for the removal of organic pollutants from water and wastewater (Galindo et al., 2001). The catalyst may be used either as an aqueous slurry or it may immobilize onto a supporting substrate (Matthews, 1992). Suspension or slurry type reactors have been reported to be efficient due to the large surface area of catalyst available for reaction and the efficient mass transfer within such systems (Dijkstra, 2001).

However, due to the small particle size of the ZnO particles, a post-treatment catalyst recovery stage is necessary. In the last decade, the mechanism of heterogeneous photocatalysis has been investigated by many researchers (Fu et al., 1996, Li et al., 2011). A photocatalytic reaction proceeds on the surface of semiconductors via several steps: (i) production of electron– hole pairs by irradiating the semiconductor with light having an energy content higher than the band gap energy of the semiconductor; (ii) separation of the

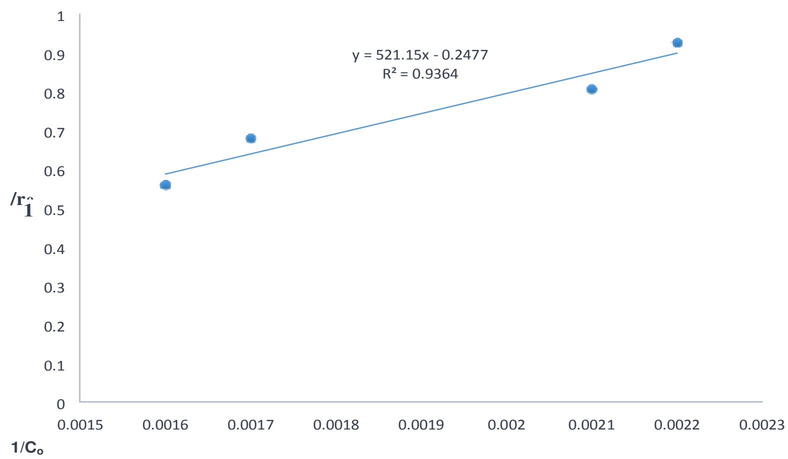

Figure 1. Plot of $1/r_o$ versus $1/C_o$ for BOD_5 Removal with Effluent Treated with $ZnOZnFe_2O_4$/ AC Photocatalyst

photogenerated electrons and holes due to trapping by species that are adsorbed on the semiconductor; (iii) redox reactions between the trapped electrons and holes and the adsorbents; (iv) desorption of reaction products and reconstruction of the surface (Fu et al.,1996, Li et al.,2011). PCO kinetics of many organic substrates has been analyzed in terms of Langmuir–Hinshelwood (L–H) rate equations (Saien, Khezrianjoo 2008- Krishnakumar, Swaminathan 2011). Langmuir–Hinshelwood rate expression has been successfully used for heterogeneous photocatalytic degradation to determine the relationship between the initial degradation rate and the initial concentration of the organic substrate (Saien, Khezrianjoo 2008- Krishnakumar, Swaminathan 2011).

MATERIAL AND METHODS

The actual tanning wastewater (composite sample) was collected in a plastic container from a tanyard of Nigeria institute of leather and Science Technology Zaria. This sample was analysed for COD, BOD_5 and Cr using standard methods. The photocatalyst employed in this work $ZnOZnFe_2O_3$/20gAC, was synthesized in the laboratory using co-precipitation method.

Firstly, the effect of initial concentration of COD, BOD_5, and Cr were determined.100 ml of the effluent was measured with a cylinder and poured into a beaker and samples are taken for analysis to determine the COD, BOD_5 and Cr. 0.1 g of activated carbon was then added to the effluent which was then stirred for 2 hours and again samples were taken for analysis of the aforementioned parameters which were later recorded. Another 50 ml of the effluent was also measured and poured in a beaker and 50 ml of water was added to it and samples were taken for analysis, again 0.1 g of activated carbon was added to it and it was stirred for 2 hours and samples were taken for analysis of aforementioned parameters. This was repeated for 25ml of effluent/75 ml of water, 10 ml of effluent/90 ml of water and samples were in each case taken for analysis.

Similarly, 100 ml of effluent was measured and 0.1 g of 20 g AC ZnO-$ZnFe_2O_4$ catalyst was added and photocatalysed for two hours after 2 hours adsorption without light, after which samples were taken for analysis in each case for COD, BOD_5 and Cr. The same procedure was repeated for 50 ml of effluent/50 ml of water, 25 ml of effluent/75 ml of water, 10 ml/90 ml of water and samples were taken for after adsorption for 2 hours without light and after adsorption for 2 hours with light.

The kinetics of heterogeneous photocatalytic process is often described by Langmuir-Hinshelwood kinetic model (Sleiman et al.,2007, Silva, Faria 2003)

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$$r = -\frac{dC}{dt} = \frac{KrKeC}{1+KeC} \qquad (1)$$

Where r is the reaction rate, C is the concentration BOD_5, COD and Cr. Kr and Ke are the apparent reaction rate constant and the apparent equilibrium of adsorption constant, respectively. By replacing r with the initial reaction rate ro and C with the initial concentration of BOD_5 in the raw effluents, Co, Eq. (3) can be written in the following linearized form:

$$\frac{1}{ro} = \frac{1}{Kr\,Ke\,Co} + \frac{1}{Kr} \qquad (2)$$

RESULT AND DISCUSSION

Langmuir-Hinshelwood Kinetics

From the experiment that was carried out for Langmuir-Hinshelwood plot, values for r_o, $1/C_o$ and $1/r_o$ were obtained and were later used to plot graphs (Figures1- 2).

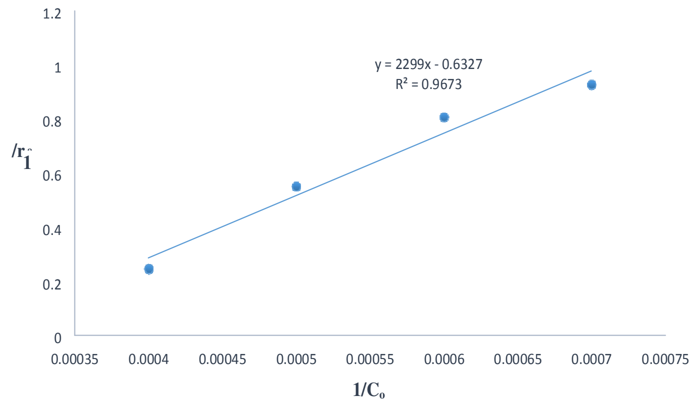

Figure 2. Plot of $1/r_o$ versus $1/C_o$ for COD Removal with Effluent Treated with ZnO-$ZnFe_2O_4$ / AC Photocatalyst

Table 1. Calculated Values of r_o, $1/C_o$ and $1/r_o$ for the Langmuir-Hinshelwood Kinetic Plot.

Composition of Effluent/water Ratio	r_o (m g/lmin)			$1/C_o$			$1/r_o$		
	COD	BOD_5	Cr	COD	BOD_5	Cr	COD	BOD_5	Cr
100ml/0ml	4.075	1.79	0.027	0.0004	0.0016	0.303	0.245	0.559	37.04
50ml/50ml	3.167	1.48	0.015	0.0005	0.0017	0.400	0.550	0.676	66.67
25ml/75ml	3.100	1.24	0.010	0.0006	0.0021	0.476	0.806	0.806	100.00
10ml/90ml	2.533	1.08	0.006	0.0007	0.0022	0.526	0.926	0.926	166.67

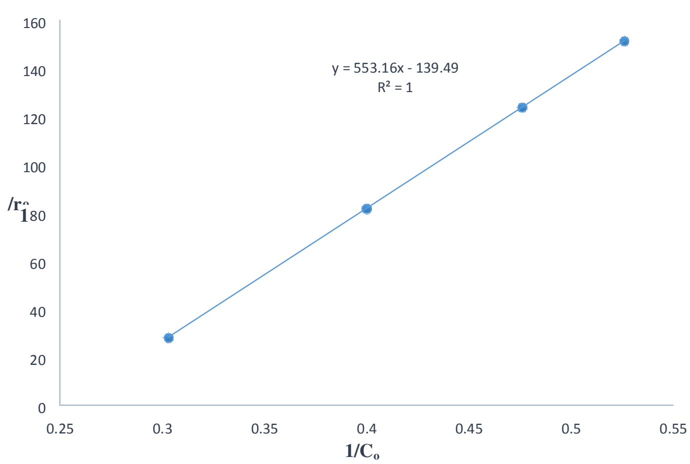

Figure 3. Plot of $1/r_o$ versus $1/C_o$ for Cr Removal with Effluent Treated with ZnO-$ZnFe_2O_4$ / AC Photocatalyst

The equations for these graphs shows a very good R^2 after their linearization and subsequently their slope and intercept were used to calculate rate constants k_r and equilibrium adsorption constant K_e. The values for the K_e

and k_r are very low and from literatures, it indicate that photocatalysis as a treatment technology for tannery effluent is very effective**.** The k_r value is highest for chromium removal while the K_e is lowest and this indicate that of the parameters considered the rate of chromium removal is the
fastest.

CONCLUSIONS

The photocatalytic removals of BOD_5, COD, and Cr nicely fitted the Langmuir-Hinshelwood kinetic model. The calculated values of the apparent reaction rate constants (Kr) and apparent equilibrium of adsorption constants (Ke) are 4.729 $*10^{-4}$ mg/lmin, 2.752 $*10^{-4}$mg/lmin 2.548 $*10^{4}$mg/lminand
4.037lmin/mg,1.5805lmin/mg,7.267lmin/mg for BOD_5, COD and Cr respectively. The BOD_5, COD and Chromium adsorptions are the controlling step of the photocatalytic process because the value of Kr is substantially higher than that of Ke.

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