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BOD_5 removal from tannery wastewater over ZnO-$ZnFe_2O_4$ composite photocatalyst supported on activated carbon

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Tannery wastewater with high biological oxygen demand (BOD_5) was treated with ZnO-$ZnFe_2O_4$ composite photocatalyst supported on activated carbon under visible light irradiation. Only 9% of BOD_5 in the raw effluent were removed via adsorption on the surface of the photocatalyst in the dark for two hours. Photocatalysis with ZnO-$ZnFe_2O_4$ composite photocatalyst on activated carbon support removed 90% of BOD_5 in two hours. For all the photocatalysis, complete BOD_5 removal of the wastewater sample could not be achieved. The photocatalytic effiency was found to increase with increase in the power of the light sources employed. The kinetics of decrease of the value of BOD_5 fitted to the pseudo first order kinetic model (R^2 = 0.9601). The derived value of the apparent rate constant for the photocatalytic decrease of the value of BOD_5 was 0.049 min^{-1}.

Key words: Photocatalyst, BOD_5, ZnO-$ZnFe_2O_4$, tannery, wastewater.

INTRODUCTION

In Nigeria, there are over 496 tanneries in the formal sector and a large number of small and medium-scale tanneries exist in the informal sector. Most of the tanneries are located in the industrial estates of Kano, Sokoto, Jos, Zaria, and Maiduguri. Many of the big tanneries are well-mechanized and export oriented especially in Kano. Leather tanneries produce wastewater, solid waste and air emissions. However, wastewater is by far the most important environmental challenge being faced by tanneries worldwide (Sarkar, 1981). Tannery wastewater are particularly characterized by high chemical oxygen demand (COD) and biochemical oxygen demand (BOD). Their main source is the organic contents derived from hides and skins. Wastewater of tanneries carries BOD_5 values in the range of 400 to 1200 mg/L, whereas BOD_5 limit set by the Nigerian Environmental Standards and Regulations Enforcement Agency (NESREA) is only 150 mg/L. In about 80% of the cases untreated tannery wastewater is discharged directly into recipient water bodies or onto open land (Wang et al., 2009).

At tannery wastewater treatment facilities, BOD_5 is usually reduced either by adsorption on activated carbon or by biological treatment (Di Iaconi, 2002). Yakubu et al. (2008) prepared activated carbon from date seeds and use it to remove 91% of the COD of a real tannery effluent. However, these methods have some real limitations. These methods for treating tannery effluents are characterized by high capital and operating costs (Hany et al., 2007). Adsorption process concentrates the pollutants present in wastewater by transferring them to activated carbon. Biological treatment of wastewater is very slow and often characterized by low reduction efficiency. Adsorption and biological methods of treating effluents generate sludge which is very difficult and

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costly to treat (Schrank et al., 2004).

Photocatalysis utilizes light and semiconducting photocatalysts to destroy various environmental pollutants. Irradiation of photocatalysts by visible and/or ultraviolet light lead to the generation of electrons and holes which subsequently generate highly active hydroxyl radical that are capable of oxidizing various organic materials into water and CO_2. Photocatalysis has been applied for the disinfection and detoxification of effluents of various industries. The most widely used photocatalyst are TiO_2 and ZnO due to their high activity, stability and low cost. However, their large band gap makes them effective only in the presence of UV light. Generation of UV light is expensive and utilization of UV light poses more health hazards than visible light. Presently, the development of visible light active photocatalysts is a topic of considerable research interest. Visible light responsive photocatalysts can be developed by coupling high band gap semiconductors such as ZnO with low high band gap semiconductors such as α-Fe_2O_3 and $ZnFe_2O_4$ (Shao et al., 2013). The photocatalytic activity of $ZnFe_2O_4$ - TiO_2 nanocomposite was synthesized and investigated by Yuan et al. (2001) and found that the $ZnFe_2O_4$ - TiO_2 nanocomposite is more effective than pure TiO_2 in the degradation of phenol.

Photocatalytic activity is usually enhanced by supporting the photocatalyst particles on inert support such as clays and activated carbons (Montaser et al., 2011; Sarwan et al., 2012). Recently, ZnO-$ZnFe_2O_4$ composite photocatalyst supported on activated carbon synthesized via co-precipitation method was found to be very effective for the removal of chromium ions from a raw tannery effluent (Fahim et al., 2006). This work investigates the feasibility of using the same ZnO-$ZnFe_2O_4$ composite photocatalyst supported on activated carbon for the decrease of the value of BOD_5 from tannery effluent.

MATERIALS AND METHODS

The tannery wastewater used was collected in a plastic container from the tannery of the Nigerian Institute of Leather and Science Technology, Zaria, Kaduna State, Nigeria. The tannery effluent was filtered to remove suspended solids. All reagents used were of analytical grade.

Synthesis of photocatalysts

ZnO-$ZnFe_2O_4$ composite photocatalyst on activated carbon support was prepared by co-precipitation of 222 mmol of $Zn(NO_3)_2.6H_2O$ and 17 mmol of Fe $(NO_3)_3.9H_2O$ with 613 mmol of aqueous solution of NH_4OH in the presence of 20 g of activated carbon at 50ºC at a pH of 8. The formed precipitate was aged for 24 h. The ZnO:$ZnFe_2O_4$ molar ratio is 25:1. The solid product was washed with deionised water filtered using man filter paper and buchner funnel. The precipitate was further drain with vacuum pump to remove water and other products. The filtrate obtained after vacuum filtration was dried overnight in the oven at a temperature of 120ºC and then calcined in a furnace at 1000ºC for four hours to yield ZnO-$ZnFe_2O_4$ composite on activated carbon support.

Adsorption on activated carbon

100 ml of the effluent was collected and placed in a beaker, 0.1 g of activated carbon was then added, placed on a hot plate and magnetically stirred for two hours under ambient conditions. Sample of the adsorbed effluent after 2 h of adsorption was taken and analysed for BOD_5 at intervals of 5, 10, 15, 20, 30, 60 and 120 min.

Photocatalytic experiments

Effect of contact time on the decrease of the value of BOD_5

100 ml of the effluent was collected and placed in a beaker, 0.1 g of the photocatalyst was then added, placed on a hot plate and magnetically stirred for two hours in the dark. Sample of the adsorbed effluent after 2 h of adsorption in the dark was taken and analysed for BOD_5. Immediately after adsorption in the dark stage for two hours, the mixture of effluent and the photocatalyst in the beaker was exposed to visible light irradiation by a 500W halogen lamp under stirring. Samples were taken after 5, 10, 15, 20, 30, 60 and 120 min from the start of irradiation and analysed for BOD_5. All the experiments were performed at the pH of 3.0 which is the pH of the raw tanyard effluent.

Effect of catalyst dosage on the decrease of the value of BOD_5

To determine the effect of catalyst dose, 100 ml of the effluent was measured and placed in a beaker, 0.05 g of the catalyst was then measured and added to content of the beaker, the beaker was then placed in a hot plate and magnetic stirrer was introduce into the beaker, the content of the beaker was continuously stirred in the dark for two hours after which a 5 ml of the sample was taken for analysis. The all content of the beaker was then exposed to light while it was continuously stirred for another two hours and again 5 ml sample was then collected for analysis, the same procedure was repeated for 0.10, 0.15 and 0.20 g of catalysts.

Effect of pH on the decrease of the value of BOD_5

100 ml of the effluent was measured and placed in a beaker, sodium hydroxide solution whose concentration is known was added to it to adjust the pH of the effluent. For any addition of sodium hydroxide, a pH meter was used to determine the pH of the effluent until the pH of 4 is obtained, a 5 ml of effluent was then taken for analysis, the effluent was then magnetically stirred in the dark for two hours and again 5 ml sample was collected for analysis. The effluent was further exposed to light for another two hours and again 5 ml sample of the effluent was taken for analysis. The same procedure was repeated for pH 7 and pH 9.

Effect of light Intensity on the decrease of the value of BOD_5

To determine the effect of light, 100 ml of the effluent was measured and placed in a beaker, exposed to 100 W tungsten lamp and continuously stirred for two hours, 5 ml of the sample of the effluent was then taken for analysis. This procedure was repeated for 200 W tungsten lamp.

Analysis of effluent for BOD_5

The BOD_5 was determined by an open reflux method. Analysed sample of the effluent was diluted in water, the pH adjusted to 6 and it seeded with microorganism, the sample was then incubated in the dark for five days at 20ºC. The microorganism uses the oxygen dissolved in the water as they degrade the organic matter. The oxygen remaining after five days is determined and the BOD_5 was calculated by comparison with the oxygen in the effluent-free reference sample. The BOD_5 content of the raw tannery effluent was 650 mg/L. The analyses of BOD_5 were carried at National Research Institute for Chemical Technology (NARICT), Zaria.

Determination of photocatalytic efficiency (PE)

The photocatalytic efficiency of the decrease of the value of BOD_5 (PE) was calculated using Equation 1:

$$PE = \frac{(C_0 - C_t) \times 100\%}{C_0} \quad (1)$$

Where Co and C_t are the initial concentration of BOD_5 and the concentration of BOD_5 after irradiation time (t) respectively.

Langmuir–Hinshelwood model

The photocatalytic reaction kinetics of organic compounds is often described by the pseudo first order approximation of the Langmuir–Hinshelwood model (Laoufi et al., 2008; Xiao et al., 2012).

$$Ln\left(\frac{C_0}{C_t}\right) = k_{app}t \quad (2)$$

Where (k_{app}) is the apparent rate constant for the photocatalytic reduction of BOD_5 and (t) is the irradiation time.

RESULTS AND DISCUSSION

Chemical composition of the synthesized photocatalysts

The composition of the synthesized ZnO-$ZnFe_2O_4$ photocatalyst is summarized in Table 1. It shows that aside the major components (Zinc and Iron), there are other components which constitute impurity, this is expected as there were certain amount of impurity in the substances used in their synthesis.

Comparison of the efficiency of decrease of the Value of BOD_5 using activated cabon (AC), ZnO-$ZnFe_2O_4$, ZnO- $ZnFe_2O_4$ /AC

Figure 1 shows the effect of contact time on the percentage decrease of the value of BOD_5 via adsorption on activated carbon (AC). It also shows the effect of irradiation time on the decrease of the value of BOD_5 content of the raw tannary effluent using ZnO- $ZnFe_2O_4$ composite photocatalyst and ZnO-$ZnFe_2O_4$ composite photocatalyst on activated carbon support (ZnO-$ZnFe_2O_4$ /AC).

It can be clearly observed from Figure 1 that the decrease of the value of BOD_5 was very fast in the first 30 min of irradiation. Thereafter, the process becomes slower most likely due to the formation of some products of the photocatalytic reaction that may alter cause of the BOD_5 reduction. The percentage decrease of the value of BOD_5 reaches 80% within 30 min when using ZnO-$ZnFe_2O_4$ composite photocatalyst on activated carbon support (ZnO- $ZnFe_2O_4$ /AC). The percentage removal increases from 80 to 90% when the irradiation time was increased from 30 to 120 min. Only 9% of the BOD_5 in the raw effluent were removed via adsorption on the surface of the ZnO-$ZnFe_2O_4$ composite photocatalyst supported on activated carbon in the dark for 120 min. Similar observations were made in the case of photocatalytic reduction of Hg^{+2} by Dou and Chen (2011). Organic molecules in the effluent are oxidized by the highly reactive photogenerated $O_2^{\bullet-}$ and $^{\cdot}OH^{\bullet}$ radicals on the surface of the phototatalyst to form various intermediates which are subsequently oxidized to CO_2 and H_2O (Konstantinou and Albanis, 2004). The nature of the intermediates is often difficult to establish. Moreso, it is observed that ZnO-$ZnFe_2O_4$ composite photocatalyst on activated carbon support (ZnO-$ZnFe_2O_4$ /AC) has the highest efficiency in the reduction process. Hence it is selected for the study of the effect of catalyst dosage, pH and lamp power on the photocatalytic treatment of the effluent.

The effect of photocatalytic dosage on the photocatalytic efficiency of decrease of the value of BOD_5 is presented in Figure 2. The percentage reduction of BOD_5 increased from 88.28 to 91.02% when the photocatalyst dosage was increase from 0.05 to 0.10 g/L. The increase in photocatalytic dosage led to an increase in the active surface of the photocatalyst which result in enhanced BOD_5 removal (Montaser et al., 2011). However, further increase of the photocatalyst dosage resulted in the decrease in percentage reduction of BOD_5. This is attributed to the increased turbidity of the suspension, which reduces light penetration and inhibits the photocatalytic process (Jaafar et al., 2012). The optimum catalyst is found to be dependent on the initial solute concentration. Hence, higher amount of catalyst may not be useful both in view of possible aggregation as well as reduced irradiation due to increase in light Scattering. Similar observations were made by other researchers (Yakubu et al., 2008; Montaser et al., 2011).

The pH of the effluent was varied between 3 and 10 as shown in Figure 3. The photocatalytic activity was found to increase with increase in pH up to 9 and then it was almost constant even though the photocatalytic reduction

Table 1. Chemical composition of the synthesized photocatalysts (% wt.).

Synthesized catalysts	Zn	Fe	Si	P	Ca	Cr	Ni	Total
ZnO-$ZnFe_2O_4$	93.06	5.81	0.72	0.24	0.12	0.044	0.026	100
ZnO-$ZnFe_2O_4$/ AC	91.87	6.81	0.42	0.53	0.31	0.052	0.032	100

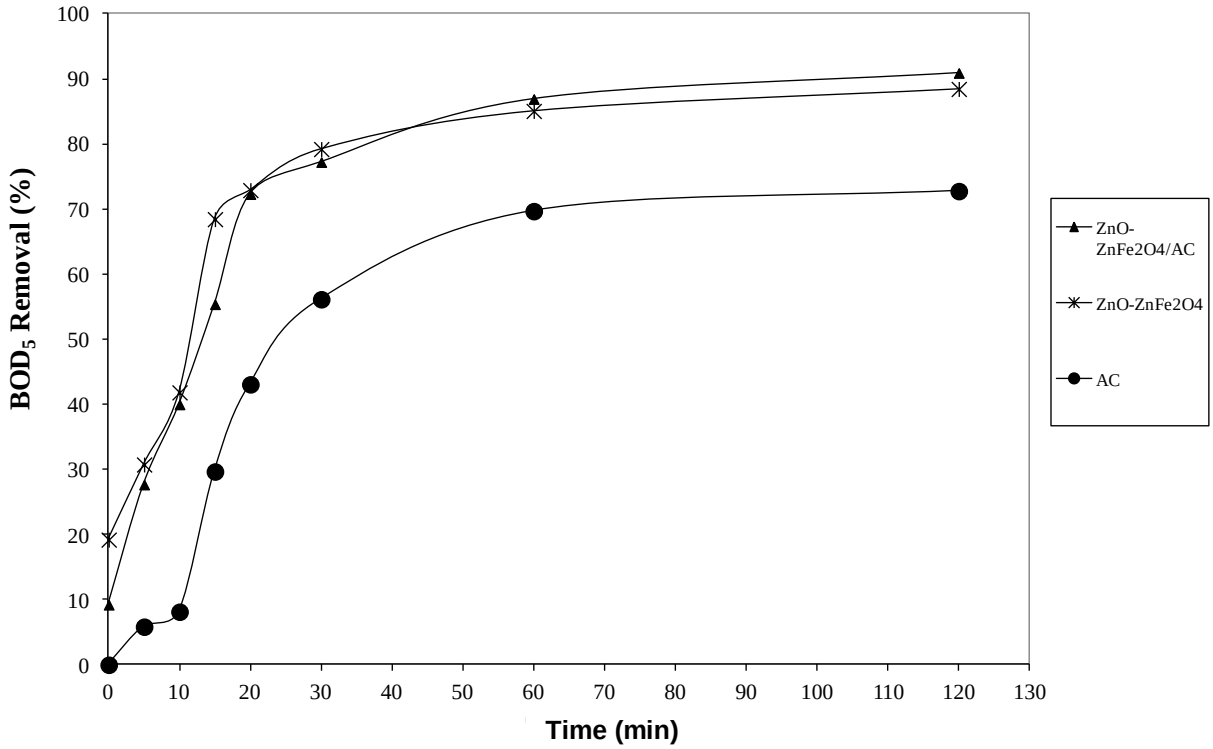

Figure 1. Percentage decrease of the value of BOD_5 using AC, ZnO- $ZnFe_2O_4$, ZnO- $ZnFe_2O_4$ / AC Catalyst.

of the effluent is low at alkaline pH. It is thus concluded that photocatalytic reaction occur not only on the catalyst surface but also in the close vicinity of the catalyst surface. The acid-base property of the metal oxide surface can have considerable implication on their photocatalytic activity. The point of zero charge is pH 9 and above this value, ZnO-$ZnFe_2O_4$ is negatively charged by means of adsorbed OH^- ions.

The influence of light intensity on the BOD_5 reduction was examined using three different lamps (100, 200 and 500 W) as shown in Figure 4, from where it is clearly seen that the photocatalytic efficiency increased with increase in the light intensity. The overall energy input to a photocatalytic process is dependent on light intensity. The photocatalytic efficiency increases when more quanta of radiations fall on the photocatalyst surface because more reactive $O_2^{\bullet-}$ and $^{\cdot}OH^{\bullet}$ radicals are produced (Shafaei et al., 2010).

The photocatalytic reaction kinetics was modeled by the pseudo first order approximation of the Langmuir–Hinshelwood model as shown in Figure 5. Experimental data is assumed to be well modeled by a given equation if the squared correlation coefficient (R^2) is greater than 0.95 and averagely modeled if R^2 is between 0.75 and 0.95 (Adie et al., 2010). As seen in Figure 5, the R^2 is 0.961. The apparent rate constant (k_{app}) for the photocatalytic decrease of the value of BOD_5 was obtained from the slopes of the linear plots of $Ln(C_0/C)$ versus the corresponding irradiation time (t) as presented in Figure 5. The derived value of the apparent rate constant for the photocatalytic decrease of the value of BOD_5 was 0.049 min^{-1}. These results indicate the feasibility of photocatalysis for the decrease of the value of BOD_5 from raw tannery effluents.

Conclusions

Only 9% of the BOD_5 in the raw effluent were removed via adsorption on the surface of the ZnO-$ZnFe_2O_4$ composite photocatalyst supported on activated carbon

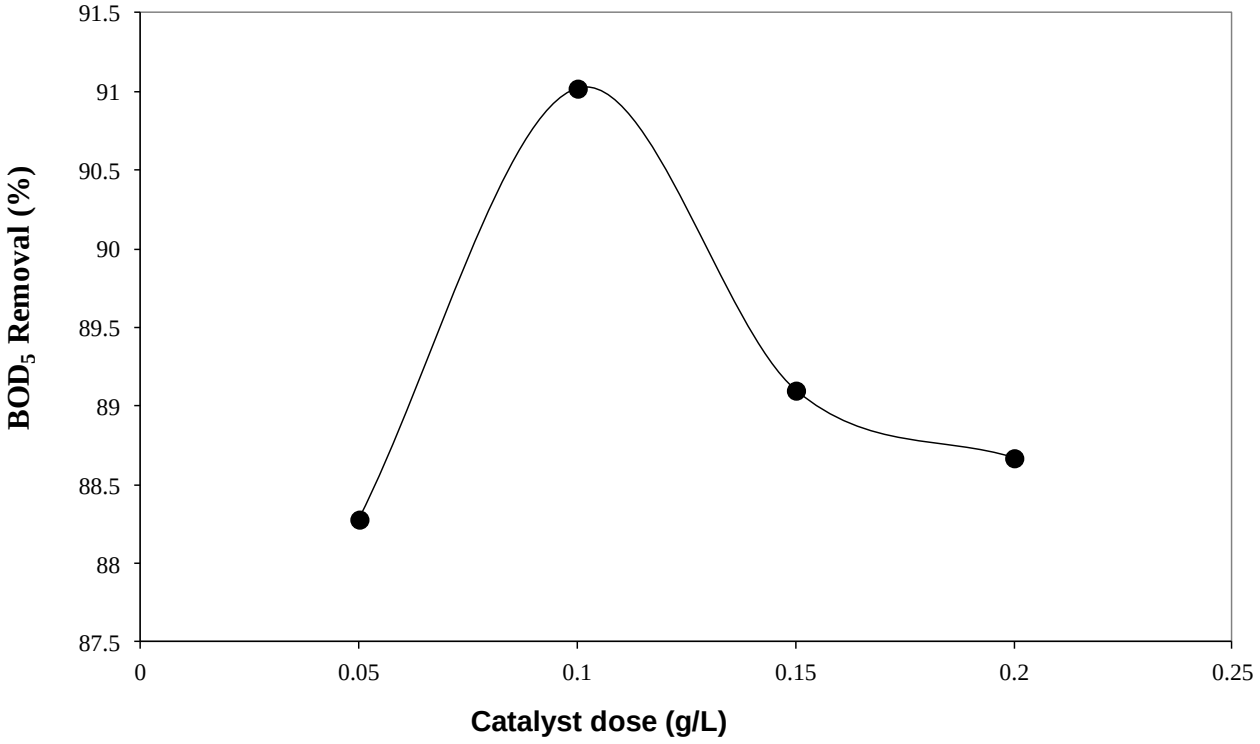

Figure 2. Effect of catalyst dose on the photocatalytic decrease of the value of BOD_5 from tannery effluent using ZnO-$ZnFe_2O_4$ composite photocatalyst on activated carbon support.

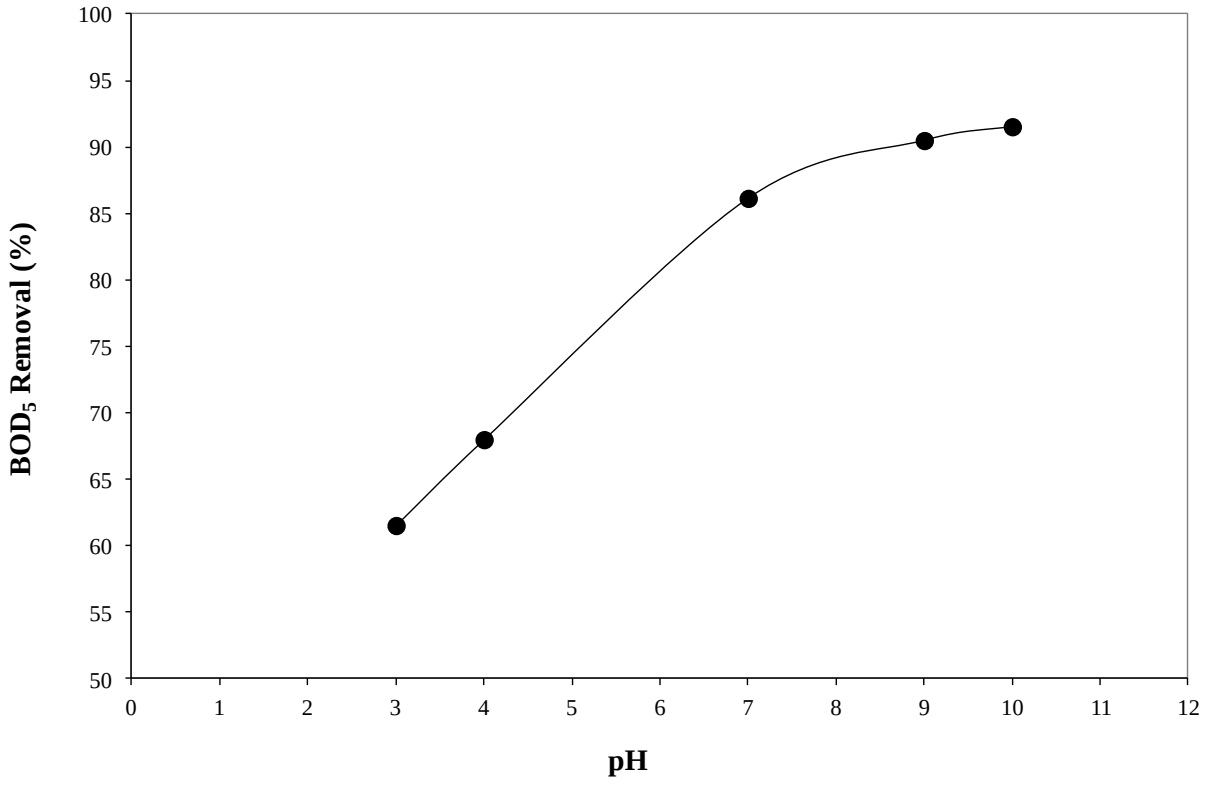

Figure 3. Effect of pH on the photocatalytic decrease of the value of BOD_5 from tannery effluent using ZnO-$ZnFe_2O_4$ composite photocatalyst on activated carbon support.

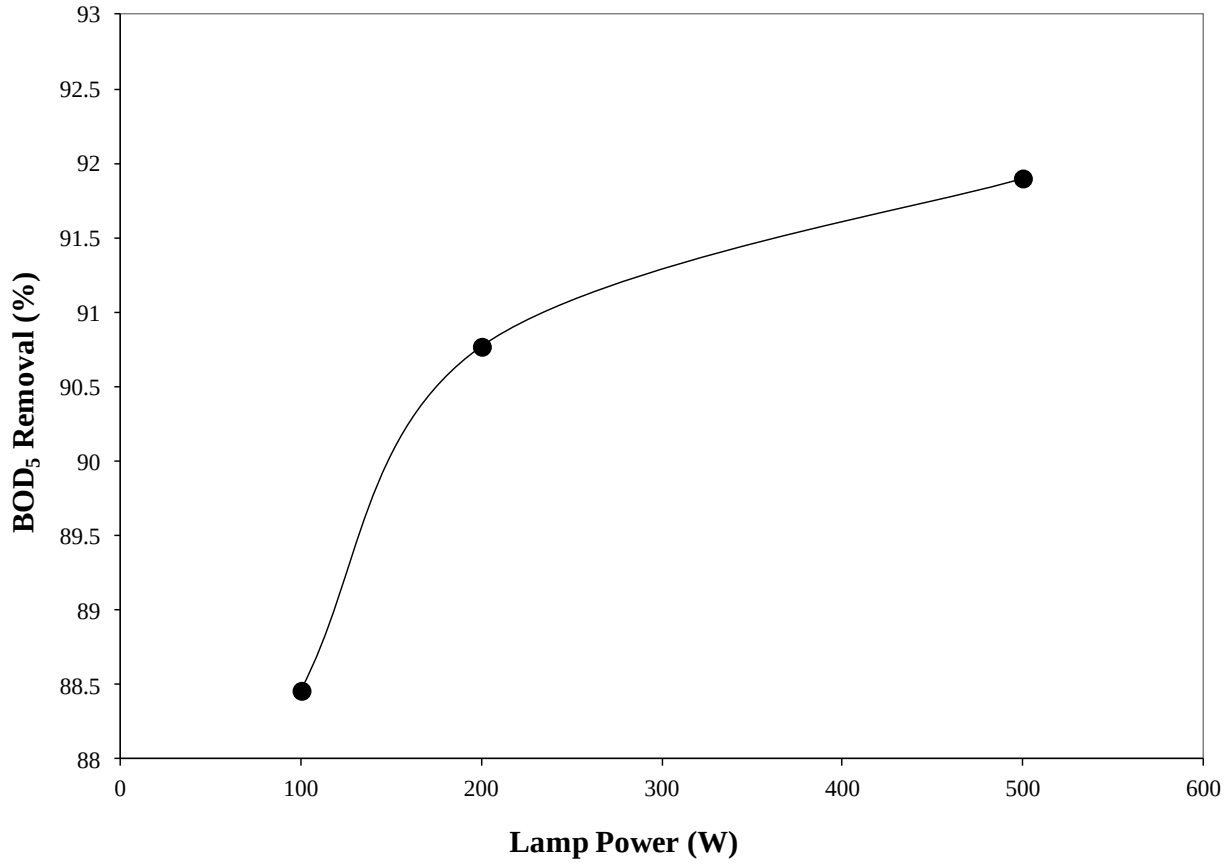

Figure 4. Effect of light Intensity on the photocatalytic decrease of the value of BOD_5 from tannery effluent using ZnO-$ZnFe_2O_4$ composite photocatalyst on activated carbon support.

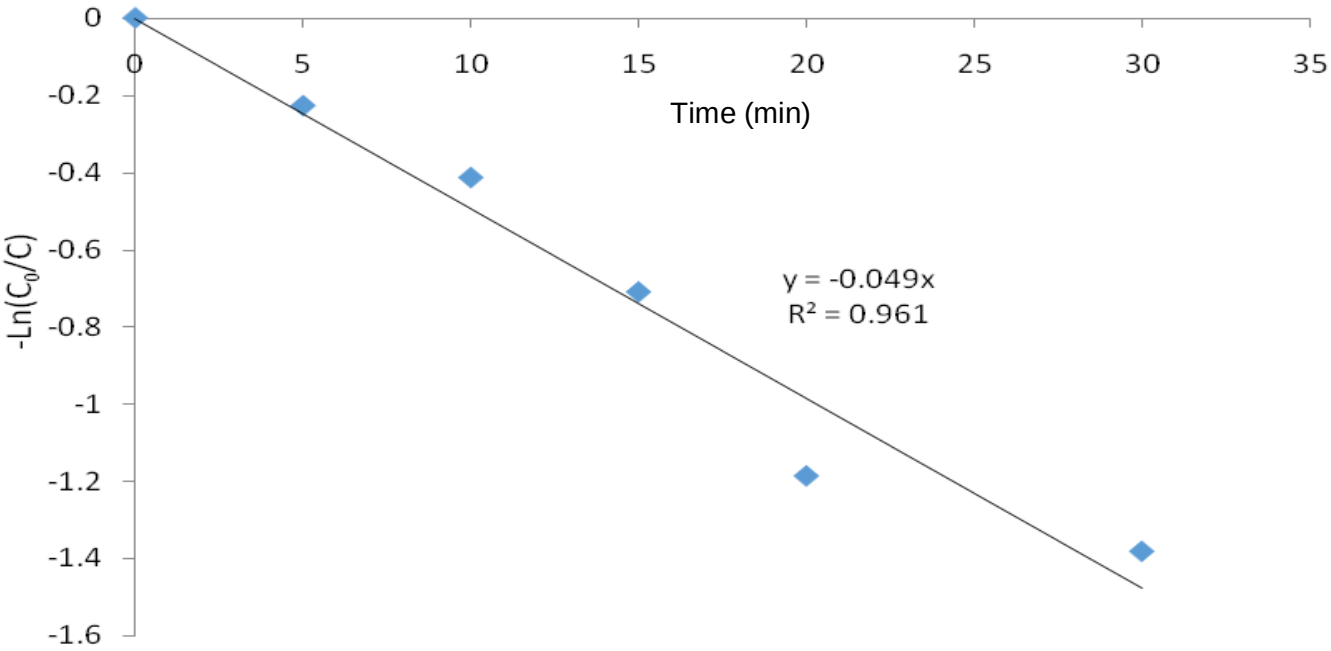

Figure 5. Pseudo first order kinetic plot for the decrease of the value of BOD_5 from tannery effluent using ZnO-$ZnFe_2O_4$ composite photocatalyst on activated carbon support.

in the dark for 120 min. Photocatalysis with ZnO-$ZnFe_2O_4$ composite photocatalyst supported on activated carbon achieves 80% decrease of the value of BOD_5 in 30 min and 91% in 120 min. The photocatalytic efficiency was found to increase with increase in the light intensity. The kinetics of photocatalytic decrease of the value of BOD_5 follows pseudo first order kinetic model with an apparent rate constant of 0.049 min^{-1}.

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