COMPARATIVE ANALYSIS OF PHOTO DEGRADATION KINETICS USING LINEAR AND NON-LINEAR KINETIC MODELS

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ABSTRACT

The present studies demonstrate the synthesis of nanocarbon ball-like structures with an approximate size of 50 to 80 nm diameter. A visible light active photocatalyst was achieved by co-doping Y/Fe/TiO₂ on the nanocarbon structure. The carbon nanostructure acts as a host material for the Y/Fe/TiO₂ composite and its synergetic effect makes the titania to generate electron-hole pair under the irradiation of visible light. The composition and morphological structures were studied using XRD and FESEM. From UV-DRS analysis, the calculated optical band gap for the composite catalyst is 2.73 eV. The photo-induced fragmentation of the Rhodamine-B dye was studied and the actual kinetics was evaluated using linear and non-linear methods. The non-linear kinetic model found more appropriate to describe the kinetics and the linear model has some limitations.

Keywords: *Alternanthera sessilis*, Waste engine oil, Carbon balls, Rhodamine-B and Band gap.

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INTRODUCTION

Disposal of polluted wastewater from industries and domestic activities are of great concern around the world³. Effective removal of the dissolved impurities in the wastewater is a highly complicated and costly affair. Already the majority of the population around the world are facing acute and chronic toxicity due to the discharge of untreated effluents into the freshwater bodies, which are being utilized by human being for their day-to-day activities². Along with overutilization, waste disposal also makes many folds increase in the freshwater shortage.

In view of this, many technologies are developed and some existing technologies are modified to reduce, reuse and recycle the wastewater generated from industries and domestic applications⁵. The treatment technologies which were studied and reported by the past researchers include biological treatment, ultrafiltration, ion exchange, chlorination, ozonization, adsorption, reverse osmosis, coagulation with chemical agents etc.^{7,8,10-14} Most of the above-said technologies transfer the solute from one component to other, which necessitates additional treatment for the generated secondary wastes thereby making the processes further costlier¹⁶.

Photoinduced generation of free radical and effective utilization of the generated free radical for the complete mineralization of the complex organic dye molecule has been proved to be a state-of-art technology⁷. Among the available oxidation technologies, the generation and utilization of hydroxyl radical have many advantages like wide selectivity, reaction with complex molecules without additives and good reactivity with a variety of contaminants. The great potential of hydroxyl radical was proved from its degradation rate constant having the order of 10⁶ to 10⁹ mol/L/s¹⁵.

After the invention of photoinduced water splitting by titania by Fujishima and Honda⁹, there is a tremendous increase in the number of publications based on titania every year. Though there are many people are working in titania photocatalysis, the mission will be fulfilled when the titania made active

under the entire range of visible radiation with maximum efficiency. Doping the nano titania crystallites on a carbon-based host material like CNT, graphene oxide, 2D and 3D graphene structures and nano-sized fullerene-like carbon balls was proved to enhance the generation of electron-hole pair by preventing the electron-hole recombination due to synergic effect^{1,6}. In this work, the objective is to analyze the photo-induced fragmentation of Rhodamine-B dye using Y/Fe/TiO₂@NCS (Nano Carbon Spheres). For the analysis of degradation kinetics, the results of the existing linear model were compared with the results of non-linear models based on the standard deviation.

EXPERIMENTAL

Preparation of Green Catalyst

The multi-metal catalyst was prepared in a green procedure by the following steps. The carbonized stems of *Alternanthera sessilis* were drenched with waste engine oil for about 30 min and then air-dried for about 1 h. The air-dried, oil-drenched carbonized stems were kept on a stainless steel grill and it is burnt from the bottom using LPG as fuel mixed with air. The soot formed during the combustion was collected using a dome-shaped surface of the chromium oxide layer of Stainless steel lid (316SS) which is kept over the combustion chamber. The carbon deposited at the inner surface of the stainless steel dome was carefully collected and washed with double distilled water and finally with alcohol¹.

The Y and Fe co-doped TiO₂ photocatalyst were synthesized by sol-gel process. About 17 mL of (Ti(OBu)₄) was dissolved in 22 mL of ethanol with constant stirring. To this 1.5 mL of acetic acid was added drop by drop to suppress the hydrolysis. The solutions were stirred for 30 min using a magnetic stirrer to get the solution A. The solution B was prepared by adding 20 mL of 0.1M Y(NO)₃·6H₂O to 20 mL of 0.1M Fe(NO)₃. The prepared solutions A and B were thoroughly mixed and the contents were hydrolyzed at 25°C for about 30 min under agitation which yielded a transparent sol. Exactly 0.5g of NCS is stirred well separately by using a magnetic stirrer for about half an hour. To this suspension, transparent sol containing Y/Fe/TiO₂ was slowly added with constant stirring, the supernatant solution was decanted off and the contents were dried at 120°C until to get a solid mass. The solid composite was powdered well using mortar and pestle, and calcined for 3h at a temperature of 450°C under a constant flow of N₂ gas. The powdered composite was used for the photocatalytic studies¹.

Photocatalytic Studies

The photocatalytic degradation study of the dye in an aqueous phase was done in an annular type photoreactor. This has a central lamp surrounded by 16 reaction cells. The light source is obtained from a one foot long LED lamp (20 W, 210–240 V Philips India make) at the central axis. Y/Fe/TiO₂@NCS photocatalyst of known quantity was added to 100 mL of Rho-B solution of a particular concentration in the sampling tube. The temperature of the reaction was maintained at 30 ± 3°C (room temperature) for all the experiments and the system was irradiated with a light source. For a particular time interval, the sample tube was removed from the slot, centrifuged using Universal make centrifuge at 5000 rpm for 5 min. Double beam UV–Vis spectrophotometer (Systronics make, model: 2201) was used to measure the final concentration of the dye solution by measuring the absorbance at the 594 nm (λ max of Rhodamine-B dye).

Characterization Studies

The Scanning Electron Microscope (SEM) image was taken using the QUANTA 250 FEG Field Emission Scanning Electron Microscope (FESEM). The X-ray diffraction (XRD) patterns were studied by X-ray diffractometer with Cu K α radiation, operated at 40 kV and 30 mA.

RESULTS AND DISCUSSION

Characteristics of NCS and Y/Fe/TiO₂@NCS

The prepared samples were analyzed with XRD to ascertain the various crystallographic planes and evaluated the crystal forms of the composite catalyst (Fig.-1). The XRD pattern of NCS has a broad peak at 25° which is generated due to the reflections of (002) graphitic plane. This is a typical pattern of amorphous structure with a d_{002} of 0.036 nm based on Bragg's equation (JCPDS 41-1487), which gives a

quantitative measurement for the graphitic network¹⁷. Presence of another peak with low intensity is observed around 44° which is generated by the reflection of (100) graphitic plane¹⁸. The peaks pertaining to graphitic carbon are not present in the XRD pattern of the composite catalyst. However, a sharp and high-intensity peak for the (101) plane of anatase form of titania is observed at 25.5° .

Other XRD peaks were generated due to the reflections of (004) plane of anatase TiO_2 at 38.17° , peak at 48.12° for (200) plane of anatase TiO_2 and peak at 54.57° for the (105) plane of anatase showed the confirmation of the presence of doped Titania on the NCS surface. The characteristic peaks for Fe_2O_3 were observed at a 2θ angles of 31.2° and 63.0° corresponding to the (206) and (4,0,12) planes respectively (JCPDS card No. 25-1402)¹⁹. The doping of Y_2O_3 is proved (JCPDS 88 – 1040) by the XRD peaks at a 2θ values of 36.0 , 69.27 and 75.82° related to the reflections in (411), (800) and (811) planes respectively²⁰.

Fig.-1: XRD Pattern of NCS and Y/Fe/TiO₂@NCS

The scanning electron microscopic images of NCS and Y/Fe/TiO₂@NCS were shown in Fig.-2. It was observed from the SEM images of the pure carbon samples, the clusters of nano carbon spheres of sizes ranging between 50 and 80 nm were present. When the carbon is co-doped with Y/Fe/TiO₂, the composite grains are uniformly distributed over the surface of NCS.

Fig.-2: SEM images (a) Pure NCS (b) Y/Fe/TiO₂@NCS

Based on the UV-DRS studies, the calculated optical band gap for the composite catalyst is 2.73 eV. There is a considerable cutback in the band gap of the Y/Fe/TiO₂@NCS when compared with that of pure TiO₂ (3.2eV). This reduction will bring the absorption wavelength of the Y/Fe/TiO₂@NCS well within

the visible region. Further, the photocatalytic decomposition ability of the Y/Fe/TiO₂@NCS is analyzed using solar light.

Photocatalytic Studies

The ability of TiO₂ towards the photo fragmentation of large size organic molecules depends mainly on the size of titania, the particular shape and also the crystallite construction. The Semiconductor nature of TiO₂ is a proficient photocatalyst under solar light irradiation^{21,23}. The doping of semiconductor titania with nano carbon host has tremendous photocatalytic behavior under solar light irradiation²². The clear mechanism for the enrichment of photocatalytic activity of nano titania by carbon hosting is not properly proved yet, still, many investigators are operating for the development of carbon hosted nano-sized TiO₂ photocatalyst. The decomposition of Rho-B dye using Y/Fe/TiO₂@NCS is demonstrated in the following section.

Effect of pH

All the heterogeneous photocatalysis systems are well controlled by the solution pH. The function of photocatalyst depends upon the extent of dye molecules which are exposed on the catalyst surface. The surface charge of catalyst depends on the solution pH, which can further influence the adsorption of dye molecules on the catalyst surface²⁴. The extent of dye degradation is related to the point of zero charges (pH_{zpc}) of the catalyst, which is related to the surface charge properties. The pH_{zpc} of the composite catalyst Y/Fe/TiO₂@NCS is 6.8. It is evident that when the solution pH is below the pH_{zpc}, the surface of the composite catalyst acquires a positive charge and it acquires a negative charge at pH > pH_{zpc} of catalyst as shown in Fig.-3.

Fig.-3: Variation of Surface Charge of Y/Fe/TiO₂@NCS with Solution pH

The selected dye Rhodamin-B is a cationic dye that ionizes into Rho-B⁺ and Cl⁻ in aqueous solution. The cationic dye experience a repulsive force when the solution pH < pH_{zpc}, which leads the poor activity of the catalyst at lower pH. At higher pH, (ie pH > pH_{zpc}) the negative charge catalyst surface will attract the Rho-B⁺ ions and the photocatalytic activity is greatly enhanced. The variation of Rho-B degradation with a change in solution pH is graphically shown in Fig.-4.

Unlike adsorption, the solution pH greatly affects the photocatalytic activity by controlling positive holes and hydroxyl ions generated at the catalyst surface. At lower pH the dyes are oxidized by the holes generated at the catalyst surface and at privileged or basic pH, the hydroxyl ions are dependable for the photodegradation of Rho-B by Y/Fe/TiO₂@NCS catalyst²⁵. As in the present case, Rho-B degradation rate is controlled greatly by the modification of the electrical double layer formed between solid-liquid interfaces²⁶. The electrical double layer affects the solute adsorption on a solid surface and also modifies the recombination rate of photogenerated electron-hole pair²⁶.

Effect of Catalyst Load

During the formulation of a photocatalytic system, it is important to optimize the catalyst load for a particular dye. For effective and efficient use of catalyst, it is essential to fix the optimal catalyst dose.

The optimum amount of catalyst requirement may vary based on the nature of the dye, the property of the catalyst and the nature of photo reactors used and also the intensity of light used²⁷. In the present case, the decomposition of Rho-B increases with increasing the catalyst dose upto 50 mg and then further raise in the catalyst dose reduces the rate of degradation as shown in Fig.-5.

Fig.-4: Variation of Rho-B Degradation with Varying pH

Fig.-5: Effect of Y/Fe/TiO₂@NCS Dosage on the Degradation of Rho-B

This kind of variation can be explained based on the following three possibilities.

1. When all the dye molecules are adsorbed on the catalyst surface, further addition of catalyst will not have any impact on the degradation rate.
2. When the concentration of particles in a solution exceeds some level, the particle-particle interaction is more significant, which will deactivate the activated molecules through collision with ground state catalyst which will reduce the degradation rate²⁸.
3. The third possible reason is that the catalyst does exceed the optimum level, the effective penetration light is prevented by the opacity of the suspension and then by the degradation efficiency decreases³¹. Based on this the optimum dose of Y/Fe/TiO₂@NCS is fixed as 50 mg/100 ml of Rho-B dye solution.

Kinetics of Rho-B Degradation

In order to evaluate the real mechanism of photodegradation as well as the number of molecules which actually determines the degradation rate, the kinetic data analyzed using the linear and non-linear first-order kinetic equation.

The first-order kinetic expression is given as

$$C_t = C_0 e^{-k_{app} \cdot t} \quad (1)$$

Where C is the concentration of dye at time t and C_0 is the concentration of dye at time $t=0$ in mg/L.

Linearizing the above equation,

$$\ln a = \ln C_0 - k_{app} \cdot t \quad (2)$$

$$-\ln \frac{C_t}{C_0} = k_{app} \cdot t \text{ or } \ln \frac{C_0}{C_t} = k_{app} \cdot t \quad (3)$$

A plot of $\ln \frac{C_0}{C_t}$ Vs Time gives a linear trace with a slope of k_{app} .

The linear first-order kinetic plot for the photo degradation Rho-B onto Y/Fe/TiO₂@NCS at various concentrations is made known in Fig.- 6 and the results are given in Table-1. The first-order rate constant increases from 0.0414 to 0.0751 on raising the initial concentration of Rho-B from 25 to 100 mg/L. As the concentration increases the number of Rho-B molecules available for degradation also increases, which ultimately increases the degradation rate. The linear plot has a correlation coefficient value of $0.9604 < r^2 < 0.9819$.

Table-1: Results of Linear First-Order and L-H Kinetic Studies

First Order Linear Plot Results			L-H Plot		
Initial Dye Concentration, mg/L	k_{app}	r^2	k_r	K	r^2
25	0.0414	0.9653	0.040	398.53	0.8722
50	0.0451	0.9704			
75	0.0486	0.9819			
100	0.0751	0.9604

Fig.-6: A Plot of a Linear First-Order Kinetic Model for the Degradation of Rho-B

Generally linearizing any kinetic equation will lead to many errors in the calculated rate constants²⁹. In order to minimize the error generated due to linearization could be minimized by analyzing the data using non-linear methods using Data Solver tool in MS Excel. The C_t calculated using the non-linear model is compared with that of experimental C_t . The square of the difference between experimental and calculated model C_t is set as a goal for the minimization of error. For each concentration, the square of deviation is minimized by varying 1) both n and k_{app} 2) by fixing $n=0.99$ and k_{app} is optimized 3) by fixing k_{app} equal to the result obtained in the linear model and n is optimized. Table-2 shows the results of derived using non-linear first-order kinetics using Data Solver Method with an initial Rho-B concentration of 25, 50, 75 and 100 mg/L respectively.

Table-2: Results of Non-linear First-Order Kinetic Studies

S. No.	Concentration of Rho-B	Both n and k_{app} are optimized			n is Fixed Constant = 0.99		k_{app} is Fixed Constant, which is equal to the Linear Model	
		N	k_{app}	Sd^2	k_{app}	Sd^2	n	Sd^2
1.	25	0.660	0.134	0.565	0.0581	8.686	1.1181	17.531
2.	50	0.9427	0.0627	27.011	0.0537	27.630	1.0438	29.451
3.	75	0.9135	0.0654	34.502	0.0494	37.854	0.9950	33.001
4.	100	1.0473	0.0381	47.246	0.0479	50.124	0.8782	40.851

When $n=0.99$, i.e., it is imagined that the order is 1, the k_{app} decreases from 0.0581 to 0.0479 when the data solver is performed by optimizing both n and k_{app} , the order of degradation varies from 0.66 to 1.0473, which indicate that the degradation is not pure first order. As some of the degradation products also participate as a reactant and the degradation order found to be fractional. When k_{app} is fixed (equal to the results of the linear model), the order is evaluated. In such conditions, the order decreased from 1.1181 to 0.8782, indicating that the order is fractional at higher concentrations and the order decreases with the increase of concentration.

Langmuir-Hinselwood kinetics

The Langmuir-Hinselwood kinetic model is also one of the useful models to illustrate the kinetics of heterogeneous photocatalytic system³⁰. In the present study, the L-H-kinetic model is used without approximating it to first-order kinetic expression. As the approximation of L-H model to first-order kinetics is not correct for the estimation of L-H model parameters.

The L-H kinetic expression is given by

$$r_0 = \frac{-dc}{dt} = \frac{K_r K C_0}{1 + K C_0} \quad (4)$$

Where K_r is the limiting rate constant of reaction at maximum coverage and K is the adsorption equilibrium constant. The L-H plot, for the Rho-B degradation by Y/Fe/TiO₂@NCS is revealed in Fig.-7 and the constants are given in Table-1. The poor r^2 for the L-H isotherm indicates that the L-H isotherm is not fit enough to describe the heterogeneous photo-induced degradation of Rho-B by the prepared Y/Fe/TiO₂@NCS composite.

Fig.-7: L-H Plot for the Photodegradation of Rho-B by Y/Fe/TiO₂@NCS

CONCLUSION

The nano carbonaceous ball-like structure was successfully prepared using an economically unimportant material (exhausted engine oil from truck maintenance industries). The prepared nanostructures have a uniform size of 50 to 80 nm diameter. Y/Fe/TiO₂ co-doped carbon structure was characterized using

XRD, which imparts the presence of Y, TiO₂ and Fe on the carbon network. The string-like carbon spheres were viewed using FESEM, which give a clear surface topography of the carbon network. The synergetic effect of the carbon network greatly enhances the optical band gap of TiO₂ from 3.2 eV to 2.73 eV. Linearization of kinetics models produces an inaccurate result when compared with that of non-linear models as proved from this study.

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