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Photocatalytic degradation of Acid Red dye stuff in the presence of activated carbon-TiO_2 composite and its kinetic enumeration

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ABSTRACT

The present paper deals with photocatalytic degradation of effluents from dye industries which have known toxic impacts on flora and fauna. Nano composite of titanium dioxide having activated carbon (TiO_2/AC) base was synthesized using sol-gel method. The synthesized catalyst was then characterized by Fourier Transform-Infrared (FT-IR) spectroscopy, Scanning Electron Microscopy (SEM), X-ray Diffractometry (XRD) and Brunauer Emmet Teller (BET) surface area analyzer. A synthetic solution of AR-131 dye was subjected to photocatalytic degradation using TiO_2/AC nano composite as catalyst. The degradation mechanisms of dye (AR-131) via photo-catalysis were found to follow a first order kinetics mechanism (vis. Langmuir- Hinshelwood Model). Toxicity of spent catalysts was further investigated in seed germination of *Vigna radiata*. Enhanced seed germination along with elongation of root and shoot was noticed up to the concentration of 500 ppm confirming its non toxicity.

1. Introduction

Synthetic dyes find broad applicability in textile, paper, fabric, leather,cosmetic industries etc due to their numerous fast colouring shade, efficient binding capacities, tolerance to extreme environmental conditions and so on [1–3]). The diverse chemical composition and complex structures of these dyes, (which provide durability to the applications, is greatest threat to environment even at lower concentration as they are toxic, carcinogenic, mutagenic and teratogenic [4,5,3,2]). The aquatic ecosystem is greatly being damaged as 10–20% of these dyes remain in discharged effluents [6–8]).

The stringent regulation enforced in the recent past compelled researchers to look for cost effective treatment of these complex natured effluent [9,3]. Several physico chemical treatments are applied for the degradation of these effluents. However, the biggest disadvantage of these techniques is the transfer of one kind of pollutant to another kind [10,11]. Among these various physico chemical treatments “adsorption” is absorb to be the most favorable technique [2]. In order to address this issue, advance techniques such as bioremediation, ozonation, ultrasonication, oxidation etc have been tested for their efficacy in dye waste water treatment [12–14]. Intermediates and secondary pollutants generated during these processes still pose a challenge to environment even after these advance techniques [15–18].

Recently, the focus has been shifted to photocatalysis as it is has proven to be an available tool for the degradation of a wide range of organic pollutants [19–23]. Low cost non carcinogenic oxidizing agents such as TiO_2 are being used for degradation of dyes under UV irradiation [24–26,19,27]. The major disadvantage in using TiO_2 based catalysts is their low light utilization ratio and their activity increases only in UV range (anatase 3.3 eV and rutile 3 eV) [28]. As a consequence it shows photo-catalytic activity only in a small fraction *i.e.* <5% of incident solar irradiation [29,13,27]. So the processes can be made more effective through either of these two strategies:(1) utilization of cost effective support materials such as activated carbon (AC) having high adsorption surface area, rapid adsorption kinetic and regenerability [11–30] .And (2) doping of semiconductors such as graphene to make it active even in the visible range. Therefore, TiO_2 is now being used with Carbon materials [31,32].

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Nomenclature

AR-131	Acid Red 131
Ac	Activated carbon
TiO2/AC	Photo-catalyst of TiO_2 over activated charcoal
UV	Ultraviolet irradiation
θ	Fractional sites vacant over the catalyst
θ'	Fractional sites occupied by un-degraded dye molecule
θ_D	Fractional site covered by degraded dye molecule
A_t	Adsorbed quantity of dye at a particular time
A_{max}	Maximum quantity of dye that can be adsorbed
K_a	Langmuir adsorption constant for reactant
A_{eq}	Equilibrium adsorption quantity
C_{eq}	Equilibrium concentration of the dye
r_o	Initial rate of reaction at initial concentration (At C_o)
r	Rate of reaction at any concentration of dye (At C)
k_f	Apparent I order rate constant for photo-catalytic reaction

In the present paper, investigation has been made to treat Acid Red 131 dye using TiO_2/Ac as photocatalyst. TiO_2-activated carbon (TiO_2/AC) nano-composite, are generally prepared through sol gel process, whereas the activated carbon is generally derived from low cost waste such as coconut shell bamboo, vegetable fibers, corn shell, rice husk and bagasse [27]. The enhanced catalytic activity of TiO_2 with the addition of activated carbon might be due to (1) inhibitory effect to recombination of free electron hole pair, (2) more radiant energy due to large surface areas and (3) involvement of hydrolysis and condensation reaction in processes [33,34,19,30]. Finally, a comparative kinetic evaluation of degradation is done using both pure TiO_2 and TiO_2 –Ac composite. Then the spent catalyst is also subjected to a seed germination test to investigate its toxicity on environment.

2. Materials and methods

2.1. Chemical and reagent

Acid Red 131 dye ($C_{30}H_{23}N_3O_9S_2$-H) with molecular weight 645 amu (Fig. 1) was procured from MILI Industries, Gujarat (CAS No. – 2234-99-0). Activated carbon (<20 µm) for the preparation of TiO_2/Activated-C (TiO_2/AC) nano-composite was purchased from Rankem chemicals, India. Titanium tetra-isopropoxide (TTIP), 95.9%(v/v), and hydrogen peroxide (H_2O_2), 90%(v/v), were procured from Sigma Aldrich, India. All other chemicals used where also of analytical grade procured from Merck, India.

2.2. Synthesis of catalyst

Ac/TiO_2 composite was synthesized by using sol-gel technique. Titanium tetra- isopropoxide (TTIP) was used as binder. Preparation technique in line with [35–39] was adopted. 35.8 gm of TTIP was dissolved in 180 ml of 98% propanol and 20 ml of 34% HCl (w/v) was added to it. This mixture was homogenized through stirring for an hour and diluted further to 1000 ml. The solution pH was maintained at 3 by addition of NaOH and HCl. 10 g each of P25 TiO_2 and activated carbon were mixed in diluted solution and again stirred for three hours. Thus, the final solution obtained was filtered through (45 µm) filter and oven dried for 24 h at 85 °C. The resulted sample was powdered and calcinated at 350 °C [39–49]. The photocatalyst finally obtained with the specific surface area (SSA) of 288.70 m^2/g was used for further experimental process.

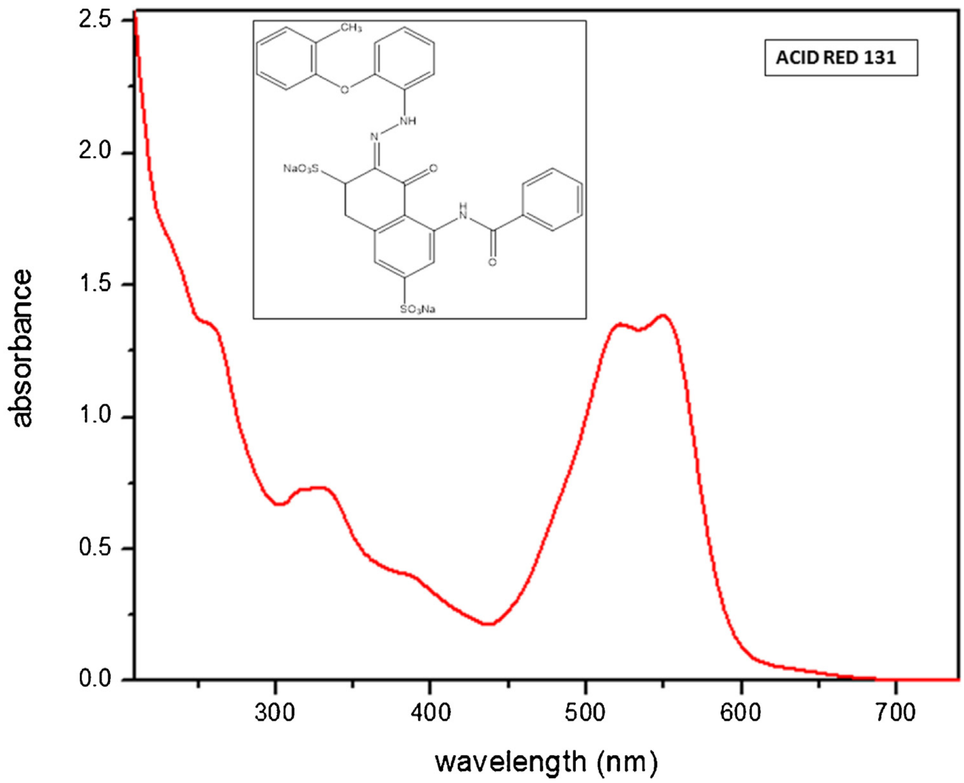

Fig. 1. Figure showing the UV–vis spectra and the structure of Acid Red-131 dye.