PHOTOCATALYTIC DEGRADATION OF DYES IN PHOTOCHEMICAL FOAM-BED REACTOR USING TITANIUM-DIOXIDE (TiO_2) NANOPARTICLES AS CATALYST

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by

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Submitted in fulfilment of the requirements of the degree of Doctor of Philosophy

to the

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DEDICATED TO MY PARENTS

CERTIFICATE

This is to certify that the thesis entitled "**Photocatalytic Degradation of Dyes in Photochemical Foam-Bed Reactor Using Titanium-Dioxide (TiO_2) Nanoparticles as Catalyst"** being submitted by **Guncha Munjal** to the Department of Chemical Engineering, Indian Institute of Technology, New Delhi, in partial fulfillment of the requirements for the award of the degree of **Doctor of Philosophy** in Chemical Engineering, is a record of bonafide work carried out by her. She has worked under my guidance and supervision and has fulfilled the requirements, which to my knowledge have reached the requisite standard for the submission of the thesis.

The research report and results presented in this thesis have not been submitted, in part or full, to any other university or institute for the award of any degree or diploma.

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ABSTRACT

The present work is primarily related to the photo-degradation of a model dye (methylene blue) in a foam-bed reactor in the presence of TiO_2 nanoparticles serving as a semiconductor photocatalyst. Foam-bed reactor, which offers high gas-liquid interfacial areas, permits large contact times between the gas and liquid with moderate pressure drops is used for the first time for the purpose of practically executing a photochemical gas-liquid reaction.

It was observed that when the cationic dye (methylene blue) was mixed with an anionic surfactant (sodium lauryl sulfate) partitioning of the dye occurred between the foam and storage sections of the photo-reactor. Even in the absence of irradiation, depletion of the dye in the storage section, with an accompanying build-up of concentration of methylene blue in the foam section, was observed. Also, the TiO_2 nanoparticles moved out of the storage section to accumulate in the foam section which not only solved the problem of post-treatment separation of photocatalyst particles from the treated water, but also brought the dye and photocatalyst nanoparticles in close proximity to each other in the region of high irradiation intensity leading to a rapid dye degradation. Similar phenomena of simultaneous partitioning and photo-degradation of dyes were realized for other types of dyes, and their mixtures in given ratios, through the choice of an appropriate surfactant. Further experiments on the photocatalytic degradation of methylene blue were performed in a bubble-column reactor and, in a photochemical foam-bed reactor. These experiments showed a dye degradation efficiency of 33.2% in 90 minutes with a 15 W UV irradiation source in a bubble-column reactor whereas, the combined phenomena of partitioning and photo-degradation of the dye in a photochemical foam-bed reactor, showed a dye degradation efficiency of 96.2% in 90 minutes. Other dyes' degradation profiles in a photochemical foam-bed reactor were also compared with those in a

bubble column. For anionic dyes, such as orange g and congo red a suitable surfactant is cationic (like CTAB). Mixtures of two oppositely charged dyes methylene blue (cationic) and congo red (anionic) taken in equal proportion got partitioned into foam section when mixed with a zwitterionic surfactant (like CHAPS), and thus could also be effectively, degraded photo-catalytically. Effects of variation in catalyst loading, initial dye concentration, light intensity, air flow rate and foam height ranging from 0.1-1 kg/m^3, 0.16-0.94 moles/m^3, 10.4-48.4 μW/cm^2, (0.835-2.1) × 10^{-4} m^3/sec, 0.55-0.8 m respectively on the performance of photochemical foam-bed reactor was studied.

Finally, a kinetic invariance approach, based on the uniqueness of dimensionless representation of the conversions in terms of non-dimensionalized dye concentration (C_D/C_{D0}) and non dimensionalized time ($t/t_{0.99}$), used for the representation and prediction of experimental data in bubble-column as well as in photochemical foam-bed reactor.

सार

वर्तमान काम प्राथमिक रूप से एक फोम-बेड रिएक्टर में एक मॉडल डाई (मेथिलिन नीला) के फोटो-डिग्रेडेशन से जुड़ा हुआ है जो TiO_2 नैनोकणों की उपस्थिति में अर्धचालक फोटोकैटालिस्ट के रूप में कार्य करता है। फोम- बेड रिएक्टर, जो उच्च गैस-तरल इंटरफेसियल इलाकों की पेशकश करता है, गैस और तरल पदार्थ के बीच मध्यम दबाव की बूंदों के बीच बड़े संपर्क के समय की अनुमति देता है, एक फोटोकैमिकल गैस-तरल प्रतिक्रिया को व्यावहारिक रूप से निष्पादित करने के उद्देश्य के लिए पहली बार उपयोग किया जाता है।

यह पाया गया कि जब कैथिक डाई (मिथाइलन नीला) को एक एनोनिक सर्फेटेंट (सोडियम लॉरिल सल्फेट) के साथ मिलाकर डाई गया था, तो फोटो रिएक्टर के फोम और स्टोरेज अनुभागों के बीच रंगा हुआ था। यहां तक कि विकिरण की अनुपस्थिति में, फोम अनुभाग में मैथिलीन नीले रंग की एकाग्रता के साथ भंडारण खंड में डाई की कमी देखी गई थी। इसके अलावा, TiO_2 नैनोकैक्टिक्स फोम अनुभाग में जमा करने के लिए स्टोरेज से बाहर निकल गए, जिससे न केवल उपचारित जल से फोटोकैटिलेस्ट कणों के बाद के उपचार से जुदाई की समस्या हल हो, बल्कि एक दूसरे के करीब में डाई और फोटोकैटालिस्टिक नैनोकणों को भी लाया उच्च विकिरण तीव्रता के क्षेत्र में एक तेजी से डाई गिरावट के लिए अग्रणी। एक प्रकार की विभाजन की तस्वीर और रंजक के फोटो-गिरावट, एक उपयुक्त सर्फटेन्ट की पसंद के माध्यम से, अन्य प्रकार के रंगों के लिए, और उनके अनुपात को दिए गए अनुपात में प्राप्त किया गया था। मेथिलिन नीले रंग के फोटोकेटलाइटिक डिग्रेडेशन पर आगे के प्रयोगों को एक बबल-कॉलम रिएक्टर में किया गया था और, एक फोटोकैमिकल फोम-बेड रिएक्टर में। इन प्रयोगों में एक बुल-कॉलम रिएक्टर में 15 डब्लू यूवी विकिरण स्रोत के साथ 9 0 मिनट में 33.2% की डाई डिग्रेडेशन दक्षता दिखायी गई,

जबकि एक प्रकाश रासायनिक फोम-बेड रिएक्टर में डाई के विभाजन और फोटो-गिरावट की संयुक्त घटनाएं दिखायी गयीं 90 मिनट में 96.2% की डाई डिग्रेडेशन क्षमता। एक प्रकाश-रासायनिक फोम-बिस्तर रिएक्टर में अन्य रंगों के डिग्रेडेशन प्रोफाइल को बबल कॉलम में उन लोगों के साथ तुलना की गई थी। एनोनिक रंगों के लिए, जैसे कि ऑरेंज जी और कांगो रेड एक उपयुक्त सर्फैक्टिक है (जैसे CTAB)। दो विपरीत रूप से चार्ज किए गए रंगों के मिश्रित मिथाइलें नीले (cationic) और कांगो लाल (anionic) समान अनुपात में लिया गया फोम अनुभाग में विभाजित किया गया था, जब एक झ्विडटरियन सर्फैक्टेंट (जैसे CHAPS) के साथ मिलाया जाता है, और इस प्रकार यह भी प्रभावी रूप से अवक्रमित फोटो-कैटलास्टिक रूप से हो सकता है। उत्प्रेरक लोडिंग, प्रारंभिक डाई एकाग्रता, हल्की तीव्रता, वायु प्रवाह दर और 0.1-1 kg / m^3, 0.16-0.94 $moles / m^3$, 10.4-48.4 $\mu W / cm^2$, (0.835-2.1) $\times 10^{-4}$ m^3/sec से लेकर फोम ऊंचाई में भिन्नता के प्रभाव, फोटोरैमिकल फोम-बेड रिएक्टर के प्रदर्शन पर क्रमशः 0.55-0.8 मीटर का अध्ययन किया गया।

अंत में, गैर-आयामी डाई एकाग्रता (C_D/C_{D0}) और गैर-आयामी समय ($t/ t_{0.99}$) के संदर्भ में रूपांतरणों के आयामहीन प्रतिनिधित्व के विशिष्टता के आधार पर एक गतिज अपरिवर्तक दृष्टिकोण, प्रतिनिधित्व और पूर्वानुमान के लिए उपयोग किया जाता है बबल-स्तंभ में प्रयोगात्मक डेटा के साथ-साथ फोटोकैमिकल फोम-बेड रिएक्टर।

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS

2a	Thickness of liquid foam film (m).
A	Total surface area of bubble (m^2).
AFR	Air flow rate.
C_A	Concentration of species A in the liquid phase in the foam film (moles/m^3).
C_A^*	Saturation concentration of O_2 at interface (moles/m^3).
C_{Ag}	Concentration of A in the gas pockets surrounding the liquid film (moles/m^3).
C_{AI}	Concentration of air at gas-liquid interface (moles/m^3).
C_B	Concentration of liquid phase reactant B (moles/m^3).
C_{BO}	Initial concentration of liquid phase reactant B (moles/m^3)
C_{B1}, C_{B2}, C_{B3}.... and C_{Bm}.	Concentration of liquid phase reactant B at the end of the subsections 1,2,3 and m respectively (moles/m^3).
C_{B1}	Concentration of liquid phase reactant B in the liquid draining into the foam section (moles/m^3).
C_D	Concentration of dye (moles/m^3).
C_{DO}	Initial dye concentration (moles/m^3).
C_{DE}	Equilibrium dye concentration (moles/m^3).
CMC	Critical micellar concentration (dimensionless).
C_{NP}	Mass concentration of TiO_2 nanoparticles (kg/m^3).
D_B	Diameter of bubble (m).
D_A	Diffusion coefficient of reactant A in the liquid phase (m^2/sec).
D_{AO}	Diffusivity coefficient of O_2 in water (m^2/sec).

G	Acceleration due to gravity (m/sec^2).
H	Height of tube (m).
I_a	Intensity of light absorbed in the film section (E/m^2sec).
I_o	Intensity of light source ($\mu W/cm^2$).
I_{on}	Intensity of light after passing through 'n_f' films (E/m^2sec).
K	First order rate constant (sec^{-1}).
KV	Kinematic viscosity (m^2/sec).
K_2	Second order rate constant ($g.m^3/sec$).
K_a	Mass transfer coefficient (m/sec).
K_e	Equilibrium distribution factor (dimensionless).
K_H	Henry constant (m^3.atm/moles).
K_n^2	Equals $[-(p_n*+\lambda)/D_A]$.
L	Representative length of the gas pocket in a foam (m).
m	Number of subsections of the foam layers.
M	Total amount of reactant A, both free to diffuse and immobilized, in half the liquid film of surface area S at contact time t_c* (moles).
M_g	Mass of the TiO_2 nanoparticles (g).
M_∞	Total amount of reactant A, both free to diffuse and immobilized, in half the liquid film of surface area S after infinite time (moles).
n_f	Number of films above a given film (dimensionless).
N	Number of moles (moles).
N_p	Number of particles.
P_i	Partial pressure of O_2 (atm).

q_1, q_2, q_3….and q_m	Flow rates of liquid drained from subsections 1,2,3…..and m respectively (m^3/sec).
q_e	Mass of dye adsorbed per gram of adsorbent at equilibrium (moles/g).
q_t	Mass of dye adsorbed per gram of adsorbent at any time (moles/g).
Q	Flow rate of liquid entering the foam bed reactor (m^3/sec).
Q_g	Air flow rate (m^3/sec).
RPM	Rotation per minutes.
S	Surface area of a liquid film (m^2).
t	Time (seconds).
t_c	Time of contact between the liquid film and gas pockets in the foam section (sec).
t_c*	Total time of contact in the foam section (sec).
t_i	Time node corresponding to the i^{th} interval (sec).
u_B	Bubble rise velocity (m/sec).
V	Volume of the solution (m^3).
V_B	Volume of 1 bubble (m^3).
V_S	Volume of liquid in the storage section (m^3).
V_1	Volume of the liquid in the foam section (m^3).
x	Spatial coordinate of a system with origin placed at the center of the foam film (m).
Y	Stoichiometric factor for B (moles of aqueous phase reactant B consumed per mole of A) (dimensionless).
Z	Depth in liquid, vertical position of the film (m).

δ_f	Thickness of the liquid film (m).
δp	Thickness of gas pocket (m).
α_λ	Molar extinction coefficient at wavelength of light (m^2/mole).
α'_λ	Effective extinction coefficient for film section (m^2/mole).
ε	Average liquid hold up in the foam section (dimensionless).
$\varepsilon_1,\varepsilon_2,\varepsilon_3$…and $\varepsilon_{m.}$	Liquid holdup of an individual subsections of 1,2,3…and m respectively.
λ	Pseudo first order rate constant for absorption (g/sec.m^3).
λ_{max}	Maximum absorbance at the wavelength (nm).