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Biosynthesis of ZnO/SiO_2 nanocatalyst with palash leaves' powder for treatment of petroleum refinery effluent

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A B S T R A C T

This work aims the synthesis and characterization of ZnO/SiO_2 nanocatalyst from plant waste material by green route and application of this ZnO/SiO_2 nanocatalyst for the treatment of petroleum refinery effluent. Butea monosperma (Palash) leaves' powder was used as reducing and stabilizing agent for synthesis of ZnO/SiO_2 nanocatalyst. Palash leaves contain broad variability of biomolecules which work as reducing and capping agent. In this research work, COD and acenaphthylene which is Polycyclic Aromatic Hydrocarbons (PAH) were degraded by synthesizing ZnO/SiO_2 nanocatalyst under UV-light in an annular photocatalytic reactor. X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), FIELD emission gun-Scanning electron microscopy (FEG-SEM), Energy dispersive X-ray (EDX) and Transmission electron microscopy (TEM) analysis confirmed the formation of ZnO/SiO_2 nanocatalyst. Characterization studies revealed that spherical and hexagonal nanoparticles with particle size ranging from 8 ± 5 nm to 40 ± 5 nm and mean particle with diameter of 20 ± 5 nm were synthesized using this method which is stable in the environment. Brunauer, Emmett and Teller (BET) surface area of ZnO/SiO_2 nanocatalyst is found to be 150.25 m^2/g. Fractional Factorial design was applied to find optimum condition of process parameters and found that optimum percent. Removal of COD (mg/l), and acenaphthylene were achieved at reaction condition of 1 g/L of ZnO/SiO_2 nanocatalyst loading, 30 °C temperature and 4 h reaction time and found that optimum percent removal of COD (mg/l), and acenaphthylene is 75%, and 73% respectively. Various metals, naturally present in palash leaves' powder, decrease band gap of energy and improve photocatalytic activity of nanocatalyst.

1. Introduction

Petroleum refinery industries discharge highly polluted water, which creates health problems for human beings, disturbs ecosystem and also pollutes ground water so treatment of petroleum refinery effluent is a very big challenge before discharging of the contaminated water into the water bodies or environment. Petroleum refinery effluent contains Chemical Oxygen Demand (COD), Biological oxygen demand (BOD), total petroleum hydrocarbon (TPH), oil and grease (O & G), Sulphate and phenols as pollutants [1,2]. Petroleum refinery effluent contains many polycyclic aromatic hydrocarbons such as naphthalene, anthracene, acenaphthylene, acenaphthene, fluorene, phenanthrene etc. Photocatalytic degradation is a very effective treatment method which reduces an efficiently COD and hydrocarbons from wastewater [3,4]. The characteristics of some petroleum refineries wastewater are given in Table 1.

The conventional treatment of refinery wastewater depends on the physicochemical and mechanical techniques and further biological treatments in the integrated activated sludge treatment units. Concerning the way that distinctive concentrations of aliphatic and aromatic petroleum hydrocarbons are available in refinery wastewaters, among which the aromatic fraction is not readily degraded by the conventional treatments and is more toxic, there is still a requirement for cutting edge strategies to reduce this kind of pollutants however much as could reasonably be expected. The photocatalysis is one of the procedures which can totally degrade the organic contaminations into safe inorganic substances, for example, CO_2 and H_2O under mild conditions.

Palash leaves have been using for biomedical purposes but it was not used for synthesis of nanocatalyst yet. Palash leaves contain many biomolecules these are Alkaloids, Phenolic acid, Flavonoids Carbohydrate and Protein which make it strong

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Table 1
Typical composition of some petroleum refinery effluents [23]. (Composition (mg/L).

Parameters	Refinery −1	Refinery −2	Refinery-3	Refinery- 4
pH	7–9	6.5–7.5	8.0	10
COD	300–600	170–180	80–120	80.8
BOD	150–360	–	40.25	8.0
PAH	50–100	20–60	20–30	10–20
O&G	<50	NR	–	45
SS	< 150	420–650	22.8	NR
Ammonia	15	–	–	22
Phenols	–	–	–	30
Sulphides	22	887	–	10

Table 2.
Characteristics of petroleum refinery wastewater Composition (mg/L).

pH	COD	BOD	SS	PAH	Phenol	Sulphide	Oil-grease
8.76	550	250	110	50–100	90	5	500

Table 3.
The operative conditions of experiments.

Parameter	Value
COD Concentration in refinery wastewater	Up to 550 mg/L^{-1}
Acenaphthylene in synthesis aqueous solution	Up to 100 mg/L^{-1}
pH	3–11
Temperature	25–45 °C
Irradiation time	Up to 6 h
Light intensity	11 W/m^2
Catalyst dose	0.5 to 1.5 g/L

Fractional Factorial Design
Factors: 5 Base Designs: 5, 8 Resolution: III
Runs: 24 Replicates: 3 Fraction: 1/4
Blocks: 1 Center pts (total): 0

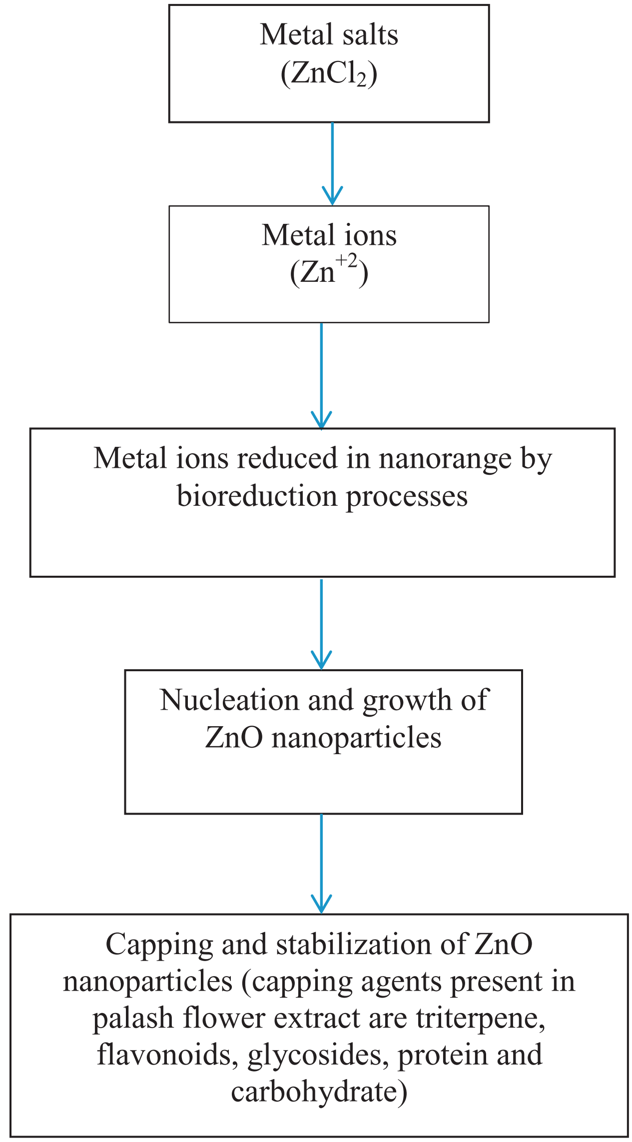

Fig. 1. Mechanism and role biomolecules present in palash leaves powder for nanocatalyst synthesis.

biomass for synthesis of nanocatalyst. Functional groups present in flavonoids, carbohydrate, proteins work as reducing and stabilizing agent in chemical method coating surfactance are used for coating of functional group as stabilizing agent but in this method functional groups coated naturally. So in this experiments palash leaves powder has been used as reducing and stabilizing agent [5-9].

The object of the current research work is the green synthesis of enhanced photocatalyst of ZnO/SiO_2 nanocatalyst by using palash leaves' powder as reducing and stabilizing agent. After synthesis of nanocatalyst, various characterizations like XRD, FEG-SEM, TEM, FTIR, EDX, and BET were also carried out to know the size, morphology, and functional groups present in the nanocatalyst. To treat petroleum refinery effluent and increase the efficiency of nanocatalyst to reduce the concentration of acenaphthylene as PAH, and COD as pollutants from the petroleum refinery effluent .Palash leaves contain a wide range of biomolecules which work as reducing and stabilizing agent and thus increase the reaction rate of the synthesis of nanocatalyst. Palash leaves contain Protein, Carbohydrate etc. as biomolecules. Palash leaves also contain Si, Mg, S, K, Ca, and Cu, Zn metallic and nonmetallic elements naturally and thus increase photocatalytic activity of nanocatalyst [6].The objective of this study is to optimize the operating parameters in photocatalytic degradation of COD and acenaphthylene using an annular reactor. ZnO/SiO_2 nanocatalyst was used in this study for refinery wastewater treatment. The operating parameters which include initial pollutant concentration, catalyst loading, initial wastewater pH, UV light intensity and operating temperature. Optimum parameter values depends on the target pollutant, type of catalyst and design of reactor used; hence there is a need to evaluate optimum operating parameter values for every new photocatalytic pol-

Table 4.
Factors and their levels used for two-levels used for two-level fractional factorial design for acenaphthylene.

Factor name	Factor Code	Low level (−1)	High level (+1)
pH	A	9.0	11.0
Time (h)	B	4	6
Catalyst loading (g/L)	C	1.0	1.5
Initial concentration (mg/L)	D	50	100
Temperature (°C)	E	25	30
UV- Intensity (W/cm^2)	Constant	11	11