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Novel pebble bed photocatalytic reactor for solar treatment of textile wastewater

Nageswara Neti Rao[a,*], Vibha Chaturvedi[b], Gianluca Li Puma[c]

[a] Wastewater Technology Division, National Environmental Engineering Research Institute (Council of Scientific & Industrial Research), Nehru Marg, Nagpur 440020, India
[b] Department of Chemistry, Krishna Engineering College, Ghaziabad, India
[c] Photocatalysis & Photoreaction Engineering, Department of Chemical Engineering, Loughborough University, Loughborough LE11 3TU, United Kingdom

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ABSTRACT

A novel, low cost, pebble bed photocatalytic reactor (PBPR) having a horizontal or inclined solar trough collector is presented. The collector contains TiO_2 coated, silica rich, white pebbles fixed on a flat surface in an ordered configuration to facilitate the contact between the liquid and the photocatalyst. The reactor efficiency was evaluated for the decolorization of selected reactive dye solutions: Reactive Black 5 (RB5), Reactive Orange 16 (RO16), Reactive Red 2 (RR2), Reactive Red 141(RR141), Reactive Yellow 84 (RY84) and Reactive Violet 13 (RV13) as well as, for the treatment of textile wastewater (synthetic dye house effluents) under sunlight. The rate of decolorization of chlorotriazine reactive dyes was found to be faster than that of vinylsulfone based dyes. The decolorization rate of the dyes followed pseudo first-order kinetics. The first order rate constant of color removal was in the range from 2.479×10^{-2} to $7.858 \times 10^{-2}\ \text{min}^{-1}$, with a maximum mineralization efficiency (k_{TOC}/k_{dye}) of 28%. The figure of merit of this reactor as recommended by IUPAC (the collector area per mass A_{CM}) and (the collector area per order A_{CO}) was in the range of 0.30–0.37 m^2/g dye and 8.6–12.2 m^2/m^3/order, respectively, with the exception of RO16 which degraded at a much slower rate. The treatment of simulated textile wastewater showed 72% (Batch I) and 54% (Batch-II) color reduction and 3–35% total organic carbon (TOC) reduction. The results indicate that the PBPR can be successfully used for the decolorization of dyes from dyeing wastewater under sunlight.

1. Introduction

Recent studies have demonstrated that heterogeneous photocatalysis using semiconductors such as titanium dioxide (TiO_2) and UV light irradiation can be used to destroy a wide range of organic pollutants dissolved in water [1–5]. The possibility of integrating photocatalysis and solar technologies [6–9] has triggered further attention because of lower treatment costs due to the use of renewable solar energy.

Matthews [10] reported the use of suspended TiO_2 in a solar illuminated tubular reactor equipped with a parabolic trough concentrator (PTC) for the degradation of a variety of organic compounds. However, the need for a catalyst recovery system led to the conclusion that scaling up of such a design may be complex. Light-concentrating reactors require reflectors and solar tracking devices, which are expensive and difficult to maintain. Further, they can only concentrate the direct component of the solar radiation. In contrast, non-concentrating reactors utilize both the direct and the diffuse components of solar light, they usually involve low cost devices but the footprint of these reactors is larger [11].

An efficient type of concentrating (one- to three-sun) solar photoreactor is the compound parabolic concentrator (CPC) [9,11,12]. Designs of non-concentrating solar reactors (one sun) include tubular [13], double-skin [8], shallow pond [14], falling film [8], coated mesh [15], cascade [16–18] and fountain [19,20]. In these configurations the TiO_2 catalyst is either suspended in the liquid or supported on the walls of the reactor. The reactor configurations utilizing slurry suspensions of TiO_2 in general outperform those using supported photocatalysts but a catalyst recovery system is needed which may increase treatment costs. In contrast, if the catalyst is supported directly on the reactor wall it makes replacement of the catalyst unpractical should this deactivate over time. Therefore, it is desirable to have a supported photocatalyst that can be easily replaced, economical and easy to produce.

An alternative, low cost method for supporting the catalyst involves coating TiO_2 on pebbles. Recent studies have shown the potential of using TiO_2 coated pebbles for the degradation of reactive dyes under solar radiation [21]. TiO_2-coated white pebbles which are rich in silica outperformed red and black pebbles due to the interaction of the stable and inert native quartz/silica on the pebble support with titania. The presence of a higher concentration

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[*] Corresponding author. Fax: +91 712 2249900/885x402.
E-mail address: nn_rao@neeri.res.in (N.N. Rao).

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of native metal oxides and ions (e.g., iron and manganese) on the surface of red and black pebbles was found to inhibit the photocatalytic rates. In the present paper, we investigate a novel configuration of low cost, non-concentrating solar photoreactor made of a bed of orderly distributed pebbles (PBPR) having a horizontal or inclined trough with TiO_2 coated, silica rich, white pebbles fixed on its surface. The pebbles distributed in a triangular pattern allow for maximum contact of the water with the supported TiO_2 and promote mixing. The reactor efficiency was evaluated for the decolorization and mineralization of textile wastewater containing reactive dyes under both sunlight and artificial sources of irradiation. The dyes and the composition of the wastewater were selected to simulate real hazardous effluents in the textile industry.

2. Materials and methods

2.1. Chemicals and materials

1-Amino-8-hydroxy-2,7-bis azo[(p-vinylsulfonic acid)]-naphthalene-(3,6-disulfonic acid) tetra sodium salt, $C_{26}H_{21}O_{19}N_5S_6Na_4$ (C.I. Reactive Black 5, RB5, M.W. = 986) was purchased from M/s Atul Dyes, Ahmedabad (India). Some other reactive dyes used for testing viz. C.I. Reactive Orange 16 (RO16; Commercial name, Orange3R; M.W. = 650), C.I. Reactive Yellow 84 (RO84; Commercial name, Yellow HE4R; M.W. = 1922), C.I. Reactive Red 141 (RR141; Commercial name, Red HE7B; M.W. = 1634), C.I. Reactive Red 2 (RR2; Commercial name, Red M5 B; M.W. = 595) and C.I. Reactive Violet 13 (RV13; Commercial name, Magenta B; M.W. = 715) were kindly supplied by M/s Color Chem., Ahmedabad. The observed wavelength of maximum absorption ($\lambda_{max,nm}$) and calculated absorption coefficient (ε, $mg^{-1}\,L\,cm^{-1}$) are as follows: RB5, 597 (3.21×10^{-2}); RO16, 493 (2.14×10^{-2}); RR2, 538 (1.90×10^{-2}); RR141, 547 (2.20×10^{-2}); RY84, 409 (1.22×10^{-2}) and RV13, 538 (2.37×10^{-2}). The dyes were used at their commercially available purity level of >95% dye content.

Titanium dioxide photocatalyst (80:20, anatase: rutile) was purchased from Degussa AG, Germany. Its specific BET surface area and mean particle diameter were 50 m^2/g and 30 nm, respectively. Ethylenediaminetetraacetic acid disodium salt (Na_2EDTA) was a reagent grade chemical (E Merck India Pvt. Ltd., Mumbai). Deionized water (Millipore Elix 3 Water Purifier) was used for preparing all aqueous solutions.

2.2. Selection and pretreatment of pebbles

Pebbles were collected from the rejects of sand at a construction site. The sand was quarried from Kanhan riverbed that falls under the Kamthi region, Maharashtra, India. This region is overlaid by coarse grained, ferruginous sandstone with quartz pebbles [22]. Although, three types of pebbles, i.e. black (B), red (R) and white (W) were present on the site, only white pebbles based on their size (at least 0.5–1.0 cm cross-sectional length) were selected for this study. In a previous study we have characterized the pebbles and demonstrated that the white pebbles coated with TiO_2 have higher photocatalytic activity than TiO_2 coated black or red pebbles [21]. Initially the pebbles were washed under tap water to remove the soil present on the surface. They were then subjected to leaching in EDTA solution. Typically, 150-g sample of pebbles were immersed in 300 ml of 0.1 M EDTA and the solution was agitated by a mechanical shaker for 12 h. The pebbles were thoroughly rinsed in water and dried in a hot air oven at 80 °C.

2.3. Preparation of TiO_2 coated pebbles (TiO_2/pebbles)

The photocatalyst coated pebbles were prepared according to previously made titania powder (PMTP) method [23,24]. The method consisted of spraying the pretreated pebbles with a 2% TiO_2 suspension in 80:20 ethanol–water mixture followed by air flow drying at 60–70 °C. The spray coating-drying method was repeated five times until a satisfactory coating on the entire surface of the pebbles was achieved. The TiO_2/pebbles were then kept in an oven at 150 °C for 8 h. The amount of TiO_2 loaded on the pebble bed reactor was estimated to be 0.79 g. The photograph (A) in Fig. 1 illustrates the pebbles before and after TiO_2 coating.

Table 1
Specifications of the pebble bed photo reactor (PBPR).

Details of pebble bed reactor	
Inner length of trough, m	0.52
Inner width of trough, m	0.45
Depth of the trough, m	0.008
Average pebble diameter, cm	0.9
Approximate number of pebbles in each row (across 0.47 m width)	32
Inter-pebble distance, cm	0.5
Total number of pebbles across 0.52 m × 0.45 m reactor	1300 ± 25
Estimated TiO_2 coated surface area, cm^2	6090
Total amount of TiO_2 present on pebble bed reactor	0.790 ± 0.010 g
Estimated volume of liquid required for submergence of pebbles when PBPR is positioned horizontal, l	0.66

2.4. Pebble bed photo reactor

The photograph in Fig. 1(B) depicts solar photocatalytic pebble bed reactor and the close-up of pebbles. The photo reactor comprised an inclined trough with the pebbles fixed on its surface. The trough (inner length, 52 cm; inner width, 45 cm; height, 0.8 cm) was fabricated using a transparent Perspex™ sheet. Pebbles were fixed onto the surface of the trough using a mixture of Araldite$^{(R)}$ and M-Seal$^{(R)}$. They were positioned in an ordered configuration as depicted in Fig. 1(C) with pebbles in a row forming equilateral triangles with the pebbles in the row immediately above. This configuration allows the optimal distribution of the liquid over the pebbles avoiding preferential channeling. The trough was fixed on to a galvanized iron frame. The metal frame had provisions for tilting the trough at predefined angles between 0 and 60°. The volume of liquid contained in the PBPR when positioned in the horizontal position was 0.66 L with all the pebbles just submerged under the water. In contrast, when the reactor was inclined over the horizontal, the pebbles summits emerged through the liquid, and the liquid flow channeled through the canyons formed by the pebbles. Further specifications of the pebble reactor are reported in Table 1. An inlet pipe having closely spaced holes was positioned transversally at the inlet of the trough to distribute the liquid across the pebbles uniformly. The liquid flow rate was controlled by a peristaltic pump. Batch experiments were carried out with recirculation of the liquid between the reactor and a holding tank. The duration of each experiment was 5 h. The water distribution pattern through the pebbles followed the directions indicated in Fig. 1(C). The arrows indicate the direction of flow diversion at each pebble. The thin film design and water flow pattern allowed for natural aeration of the water, providing the oxygen necessary for the oxidation of the dyes dissolved in the water, therefore eliminating the need of air bubbling the feed water.

The reactor was irradiated with either solar radiation (Nagpur, India, 21°06′N latitude and 79°03′E longitude, between 10.00 and 15.00 h) or with a UV lamp. The irradiance measurements for the two irradiation arrangements are presented in Table 2. The lamp was placed in the center, parallel to the reactor bed and in the longitudinal direction fixed by a metal support at a 30 cm distance. The reactor was covered with thermocol having aluminum foil wrapped around it, which also reflected UV light. The UV lamp was removed in the experiment performed using solar radiation.