



Invited feature article

Bare, gold and silver nanoparticle decorated, monodisperse-porous titania microbeads for photocatalytic dye degradation in a newly constructed microfluidic, photocatalytic packed-bed reactor

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ABSTRACT

Monodisperse porous titania microbeads were synthesized by a sol-gel templating protocol. Gold nanoparticles (AuNPs) synthesized by Turkevich and Martin methods 16 and 5 nm in size, respectively and silver nanoparticles (AgNPs) 12 nm in size were decorated onto the primary amine attached titania microbeads. Both size and porous properties of bare or AuNP/AgNP decorated monodisperse-porous titania microbeads were suitable for using them as a photocatalyst in a “**Microfluidic, Photocatalytic Packed Bed Reactor (MPPBR)**” with reasonable pressure drops in the microflow rate range. Then, a MPPBR system for “**continuous photocatalytic dye degradation**” was first constructed by slurry packing of bare or AuNP/AgNP decorated titania microbeads into a fused silica capillary 320 μm in diameter. The photocatalytic activities of bare and AuNP/AgNP decorated titania microbeads were determined in MPPBR using a textile dye, Remazol Black 5 (RB5). The complete removal of RB5 was achieved in continuous mode and an appreciable enhancement in the photoremoval rate of RB5 was observed with the MPPBR containing Martin AuNP decorated titania microbeads. The system constructed can be evaluated as a promising tool for both pre-column and post-column applications involving the removal of coloured contaminants in the assays conducted in micro-liquid chromatography systems.

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1. Introduction

Wastewaters generated by textile industries contain large amounts of toxic aromatic compounds, especially azo dyes. Various combinations of conventional methods like biological, physical and chemical processes have been used to deal with textile wastewaters [1,2]. Due to the limitations of these processes, investigations have been focused on the treatment of wastewater using heterogeneous photocatalysis (UV/TiO₂) [1,3]. This process, in which semiconductor metal oxides are used, is based on the formation of hydroxyl radicals and reaction of these hydroxyl radicals with organic contaminants. Due to high activity, low cost and non-toxicity, TiO₂ is one of the most suitable semiconductors that have been used for photocatalysis [4,5–7]. Among the other

noble metal nanoparticles, gold nanoparticles (AuNPs) have received great attention due to their effectiveness in the enhancement of the photocatalytic activity of TiO₂. Referring to literature, there has been an increasing research on using AuNPs for the modification of TiO₂ and the results showed that the band gap energy of TiO₂ was decreased by AuNPs which resulted in a better photocatalytic activity [8–13]. By considering this, we planned to apply Au nanoparticle decoration onto the monodisperse-porous titania microbeads synthesized in our recent studies for obtaining a high performance new photocatalyst.

Most of reported studies on using heterogeneous photocatalysis were carried out in batch reactors [14–21]. However, several studies were reported in which the decolorization of azo dyes was performed in continuous processes. Merzouk et al. [22] used continuous electro-coagulation for decolorization of a synthetic textile wastewater by aluminum electrodes. In another study, Li and Jia [23] designed a packed-bed bioreactor for continuous decolorization of synthetic dyes using rice hull *Schizophyllum* sp. F17. Rahimi et al. designed a continuous Y-shaped microreactor in

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which the Fenton degradation of an azo dye was taken place [24]. Sun et al. proposed a microporous tube-in-tube microchannel reactor for the decolorization of azo dye Acid Red 14 [25].

In most of the photocatalytic processes, titania nanoparticles were used in batch reactors since both their size and porous properties are not suitable to work in continuous reactors by forming packed beds within the tubular systems. In this work, we synthesized bare and AuNP/AgNP decorated forms of monodisperse-porous titania microbeads with size and porous properties extremely suitable for the construction of packed-beds in a tubular reactor with reasonable column-permeabilities. Then, a “**Microfluidic, Photocatalytic Packed Bed Reactor**”, MPPBR system was first constructed by slurry-packing of bare and AuNP/AgNP decorated, monodisperse-porous titania microbeads into fused silica capillary tubing. By using the microfluidic system, the complete removal of a textile dye, Remazol Black 5 (RB5) was achieved under UV-irradiation in continuous mode with different flow mobile phase rates and dye feed concentrations.

2. Experimental

2.1. Materials

All the chemicals used for the preparation of sodium sulfonate attached-poly(3-chloro-2-hydroxypropyl methacrylate-co-ethylene glycol dimethacrylate) ($-\text{SO}_3\text{Na}$ attached-poly(HPMA-Cl-co-EDMA)) microbeads were purchased from Sigma Chemical Co., St. Louis, MO, USA, as reported in earlier studies [26]. Titanium chloride (TiCl_4) as precursor, ammonium hydroxide solution (NH_4OH , 26%w/w) and hexadecyltrimethylammonium bromide (CTAB) were also purchased from Sigma. For the derivatization of monodisperse-porous titania microbeads with amine groups aminopropyltriethoxysilane (APTES) and triethylamine (TEA) were purchased from Sigma Chemical Co., St. Louis, MO, USA with groups. For the synthesis of gold nanoparticles (AuNPs), chloroauric acid-trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, Sigma Chemical Co., St. Louis, MO, USA), trisodium citrate (TSS, Sigma Chemical Co., St. Louis, MO, USA), sodium borohydride (NaBH_4 , Sigma Chemical Co., St. Louis, MO, USA) were used. Sodium hydroxide (NaOH , Sigma Chemical Co., St. Louis, MO, USA) and hydrochloric acid (HCl , 37%w/w, Sigma Chemical Co., St. Louis, MO, USA) were used for the preparation of NaBH_4 and HAuCl_4 solutions, respectively. For the synthesis of silver nanoparticles (AgNPs), silver nitrate (AgNO_3 , Sigma Chemical Co., St. Louis, MO, USA) was used. The dye used in the photocatalytic activity runs, Remazol Black 5 (RB5) was purchased from Aldrich. Distilled deionized (DDI) water (Direct-Q 3 UV (Type 1), Millipore, USA) with a resistivity of $18 \text{ M}\Omega \text{ cm}$ was used during all synthesis runs.

2.2. Synthesis of monodisperse porous bare and AuNP/AgNP decorated titania microbeads

The titania microbeads were synthesized by sol-gel templating method using $-\text{SO}_3\text{Na}$ attached-poly(HPMA-Cl-co-EDMA) microbeads as template, according to the methods reported in our earlier research [26]. Monodisperse porous $-\text{SO}_3\text{Na}$ attached-poly(HPMA-Cl-co-EDMA) microbeads were synthesized by a multi-step microsuspension polymerization [26]. The synthesis of titania microbeads consists of hydrolysis and condensation steps. In the hydrolysis step, $-\text{SO}_3\text{Na}$ attached-poly(HPMA-Cl-co-EDMA) microbeads (0.4 g) were dispersed within the precursor solution (TiCl_4 solution, 60 mL, 0.1 M) and stirred at 250 rpm at room temperature for 24 h for the adsorption of hydrous titanium dioxide ($\text{TiO}_2 \cdot n\text{H}_2\text{O}$) nanoparticles into the polymeric template. In the condensation step, microbeads were treated with ammonia solution (60 mL, 1 M) containing CTAB (0.3 g) and the solution was

stirred at 250 rpm at room temperature for 6 h. In order to obtain integrated titania microbeads, the hydrolysis and ammonia precipitation steps were repeated twice. The polymeric templates were removed from the titania-polymer composite microbeads by calcination at 450°C for 4 h with a heating ramp of $2^\circ\text{C}/\text{min}$, under air atmosphere.

The amine attachment on titania microbeads was obtained by the derivatization with APTES. Briefly, the monodisperse-porous titania microbeads (0.4 g) degassed at 250°C for 6 h before reaction with APTES were dispersed within Iso-PrOH (20 mL), to which APTES (3 mL) and TEA (0.3 mL) were added by ultrasonication, in a sealed glass reactor. Then, the reactor was kept in a temperature-controlled shaking water bath at 80°C for 24 h. After derivatization, to remove the excess APTES the amine attached titania microbeads were washed with Iso-PrOH by centrifugation (5000 rpm, for 3 min) and decantation for several times. Turkevich AuNPs, Martin AuNPs and AgNPs were synthesized and then the decoration of AuNPs/AgNPs on amine attached titania microbeads with an Au/Ag loading percent of 5.0%w/w was carried out according to the methods given in Supplementary material.

2.3. Photocatalytic degradation of RB5 in a microfluidic, photocatalytic packed-bed reactor (MPPBR)

The photocatalytic degradation of RB5 dye was performed in a microfluidic, photocatalytic packed-bed reactor (MPPBR) operated in continuous mode. The microfluidic packed-bed reactor was constructed by slurry-packing of bare titania, Turkevich AuNP or Martin AuNP decorated titania and AgNP decorated titania microbeads into a polyimide coated fused silica capillary (12 cm, ID: $320 \mu\text{m}$, OD: $432 \mu\text{m}$, Polymicro Technologies, U.S.A.) with a UV transparent window, 6 cm in length. Bare titania, Turkevich or Martin AuNP decorated titania and AgNP decorated titania microbeads were slurry packed into the polyimide coated fused silica capillary under high pressure by using a packing system containing a stainless steel column (ID: 4.6 mm, Length: 100 mm) filled with the slurry of microbeads and an HPLC pump (Schimadzu, LC-10AD, Japan). By means of HPLC column, DDI water was pumped into the HPLC column containing the slurry of the microbeads and the slurry was transferred from the column into the fused silica capillary containing a stainless steel frit (diameter: 0.5 mm, pore size: $2 \mu\text{m}$) on one end. The formation of packed-bed by the entrapment of the microbeads within the fused silica capillary was monitored by optical microscope. The packing operation was continued under high pressure (70 bar) till a stable bed formation was obtained.

The microfluid photodegradation system consists of an HPLC pump (Schimadzu, LC-10AD, Japan), a polyimide column (ID: 4.0 mm, Length: 250 mm) filled with the RB5 feed solution and the microfluidic packed bed reactor (MPPBR) connected to the polyimide column. By means of the HPLC pump, DDI water was pumped at a prescribed flow rate ($1\text{--}10 \mu\text{L}/\text{min}$), into the polyimide column completely filled with the RB5 feed solution and the RB5 feed solution within the column was simultaneously transferred into the MPPBR with the same flow rate. The photograph of the continuous MPPBR system is given in Fig. 1. As seen from Fig. 1, silica capillary columns packed with bare and AuNP/AgNP decorated titania microbeads were irradiated 30 cm away from the top of the UV transparent window with a UV light-source (Osram, Ultra-vitalux lamp, 300 W) at 25°C within a closed metal box equipped with a temperature-control system. During the photocatalytic degradation the samples were collected at certain times from the porous frit located at the end of the silica capillary. RB5 dye concentration at any time was determined by measuring the absorption of sample in visible-region at 598 nm using Nanodrop 1000 (Thermo Scientific, ND1000, USA).



Fig. 1. A photograph of the microfluidic packed bed reactor (MPPBR) system used for continuous photodecolorization of RB5 solution.

2.4. Characterization

The size distribution properties and the surface morphology of poly(HPMA-Cl-co-EDMA) microbeads, bare and AuNP/AgNP decorated titania microbeads were determined by scanning electron microscopy (SEM; JEM 1200EX, JEOL, Akishima, Tokyo, Japan).

3. Results and discussion

The TEM photographs of Turkevich AuNPs, Martin AuNPs and AgNPs are given in Fig. S1 in Supplementary material. As seen in Fig. S1, Turkevich AuNPs, Martin AuNPs and AgNPs were synthesized with narrow size distribution and 16, 5 and 12 nm in size, respectively. Bare titania microbeads, Turkevich AuNP decorated titania, Martin AuNP decorated titania and AgNP decorated titania microbeads were synthesized. The gold and silver contents of decorated microbeads were measured by EDAX and the results are given in Fig. S2 and Table 1, respectively. As seen here, the resulting gold and silver contents of decorated microbeads were lower when compared with the theoretical loading percent (5%w/w). The reason for this could be the incomplete adsorption of AuNPs/AgNPs onto the titania microbeads.

The catalysts were then packed into a polyimide coated fused silica capillary used for the complete removal of RB5 in continuous mode under UV light irradiation. The representative SEM photographs of bare titania, Turkevich AuNP decorated titania, Martin AuNP decorated titania and AgNP decorated titania microbeads prepared with an Au/Ag loading percent of 5% (%w/w) are exemplified in Fig. 2. The difference between the surface morphologies of titania, Turkevich AuNP decorated titania, Martin AuNP decorated titania and AgNP decorated titania microbeads was a visual proof for the presence of AuNPs/AgNPs on the titania microbeads.

In the literature, titania has been mostly used as photocatalyst in the form of nanoparticles to obtain sufficient surface area providing a satisfactory photocatalytic activity [16–21]. However, the pressure drop that can be considered as the flow resistance formed in a packed-bed is inversely proportional with the particle

size according to Ergun Equation [27]. For this reason, the nanoparticle form of titania is not suitable for using in continuous packed-bed reactors since the back-pressure generated by a packed-bed formed with the titania nanoparticles should be too high and not practical for the operational point of view. Both the particle size and the porous properties (i.e. the porosity, mean pore size, pore-size distribution, specific surface area) of titania microbeads produced by “sol-gel templating method” proposed in this study are convenient to construct a “Microfluidic, Photocatalytic Packed Bed Reactor, MPPBR” that can be operated with reasonable pressure-drops in a selected microflow rate range (i.e. 1–10 $\mu\text{L}/\text{min}$). In other words, bare titania microbeads or AuNP/AgNP decorated titania microbeads produced in this study can be easily slurry packed into fused silica capillaries with internal diameters ranging between 100 and 500 μm or HPLC columns with internal diameters ranging between 2.0–7.8 mm [28,29]. Then, these columns/micro-columns can be operated with the back-pressures easily tolerable with conventional/micro-HPLC pumps. Typical back-pressure-flow rate relationships of the capillary columns (internal diameter: 320 μm , length: 120 mm) packed with the monodisperse-porous bare titania, Turkevich AuNP decorated titania, Martin AuNP decorated titania and AgNP decorated titania microbeads 5 μm in size, used as MPPBRs in our study are given in Fig. 3.

The mean particle size and specific surface area values of bare and AuNP/AgNP decorated titania microbeads and the micro-column-permeability values calculated according to the Darcy's equation for the microcolumns constructed using these microbeads are given in Table 2 [30]. As seen here, the permeability values determined by passing DDI water from the microcolumns packed with bare titania or AuNP/AgNP decorated porous titania

Table 1
The content of gold and silver on the titania microbeads measured by EDAX.

Microbead type	Au or Ag content (%w/w)
Turkevich AuNP decorated Titania Microbeads	3.68
Martin AuNP decorated Titania Microbeads	4.05
AgNP decorated Titania Microbeads	3.75

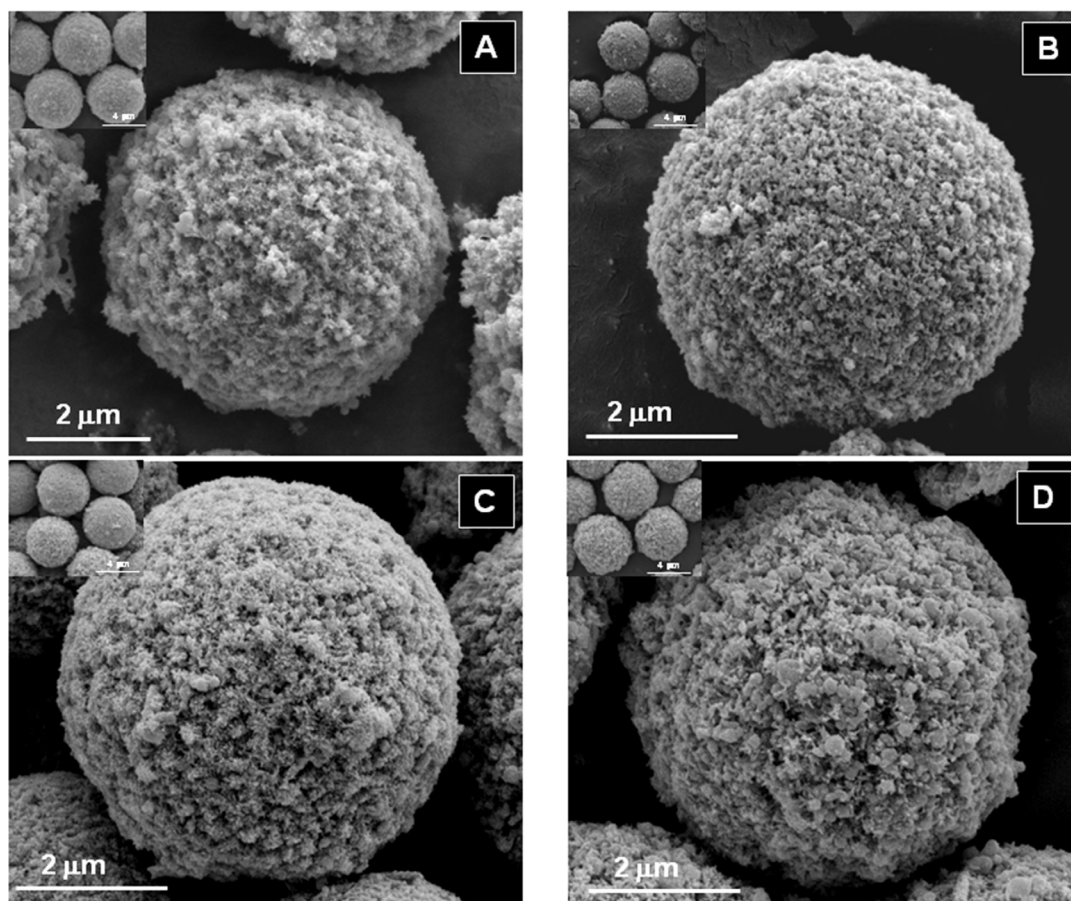


Fig. 2. SEM photographs of (A) bare titania (B) Turkevich AuNP decorated titania (C) Martin AuNP decorated titania (D) AgNP decorated titania microbeads with an Au/Ag loading percent of 5% (%w/w). The scale bar is given on each photograph.

microbeads for satisfactorily high and suitable for the evaluation of all microbead types within the photocatalytic reactors designed in the form of continuous packed-beds.

As seen in Fig. 3, the back-pressure varied linearly between 0.3–6.6 MPa by changing the flow rate of mobile phase between 0.1–10 $\mu\text{L}/\text{min}$ for MPPBR packed with the bare titania microbeads. The back-pressure at constant flow rate was slightly higher for the microcolumn containing Turkevich AuNP decorated titania

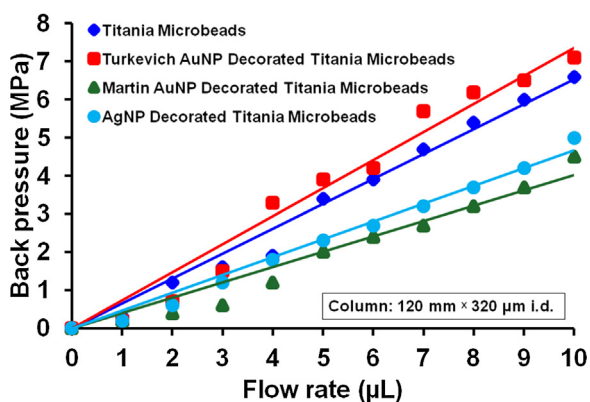


Fig. 3. The back-pressure-flow rate relationship for the MPPBRs packed with bare titania, Turkevich AuNP decorated titania, Martin AuNP decorated titania, AgNP decorated titania microbeads. (Mobile phase: 25 ppm RB5 solution, Column size: ID: 320 μm , length: 120 mm).

microbeads, while it was lower for the microcolumn containing Martin AuNP decorated titania microbeads compared to bare titania and AgNP decorated titania microbeads. This result may be attributed to the matching of AuNPs with Turkevich method to the median size of mesopores of bare titania microbeads. Hence, the porosity may decrease due to the filling of the most of the mesopores by Turkevich AuNPs. As a conclusion, reasonable back-pressure values easily tolerable by the conventional micro-flow pumps were obtained within a micro-flow rate range that can be particularly utilized in liquid-chromatography devices. This behavior showed the suitability of porous titania microbeads produced in our study for column applications involving the use of packed-beds. By considering this property of the porous titania microbeads produced in this study, different MPPBRs were constructed for the continuous photocatalytic degradation of selected dye.

3.1. Kinetics of continuous photocatalytic decolorization

Before performing the photocatalytic decolorization experiments, control experiments without catalyst and without UV light were done and the results are given in Fig. S3 in Supplementary material. As seen in Fig. S3, the concentration of RB5 was constant and 125 ppm during without catalyst experiment, as there was no interaction between the fused silica capillary column and RB5. However in without light experiment, RB5 concentration reached its inlet value by showing a continuous increase within 120 min

Table 2

The mean particle size, mean pore size and specific surface area values of bare and AuNP/AgNP decorated titania microbeads and the microcolumn-permeability values.

Microbead type	MMS (μm) ^a	CV (%) ^a	SSA (m^2/g) ^a	Column-permeability ($\ast 10^{-11} \text{m}^2$)
Bare Titania Microbeads	5.4	4.9	91.0	3.2
Turkevich AuNP decorated Titania Microbeads	5.5		72.2	2.6
Martin AuNP decorated Titania Microbeads	5.4		66.2	5.2
AgNP decorated Titania Microbeads	5.5		59.8	4.6

MMS: Mean microbead size, CV: Coefficient of variation, SSA: Specific surface area.

^a The values were taken from Ref. [20].

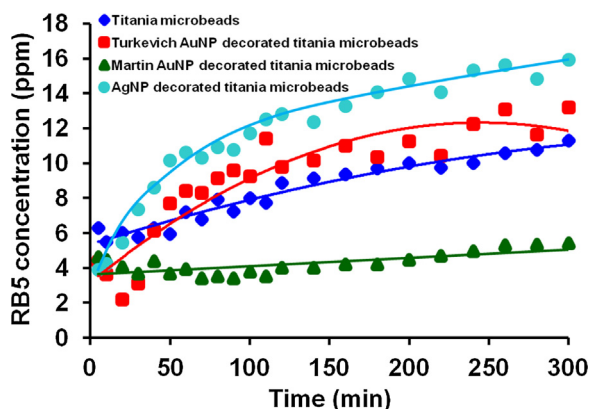


Fig. 4. Effect of AuNP/AgNP on the continuous photocatalytic degradation of RB5 dye in MPPBR. (Conditions: Flow rate: $5 \mu\text{L}/\text{min}$, Au loading (% w/w): 5%, RB dye solution: 125 ppm, pH: 7).

due to the adsorption of RB5 onto Martin AuNP decorated titania microbeads.

The variation of RB5 outlet concentration with the time during the continuous decolorization of RB5 solution with a flow rate of $5 \mu\text{L}/\text{min}$ is comparatively given in Fig. 4 for the MPPBRs packed with bare titania, Turkevich AuNP decorated titania, Martin AuNP decorated titania and AgNP decorated titania microbeads. As seen here, the lowest outlet dye concentration at constant time was obtained with the MPPBR packed with Martin AuNP decorated titania microbeads compared to the MPPBRs containing bare titania microbeads, Turkevich AuNP decorated and AgNP decorated titania microbeads. AgNP decorated titania microbeads gave

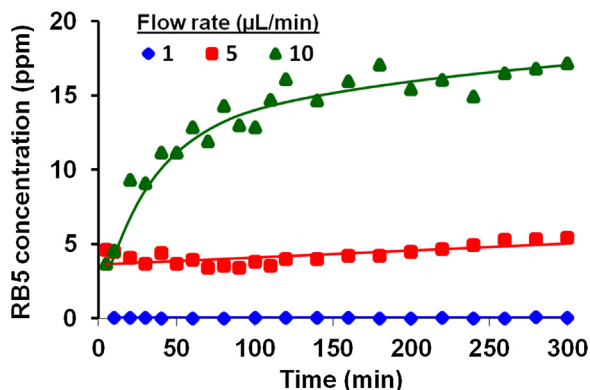


Fig. 5. Effect of flow rate on the continuous photocatalytic degradation of RB5 dye in MPPBR (Conditions: Au loading (%w/w): 5%, RB dye solution: 125 ppm, pH: 7).

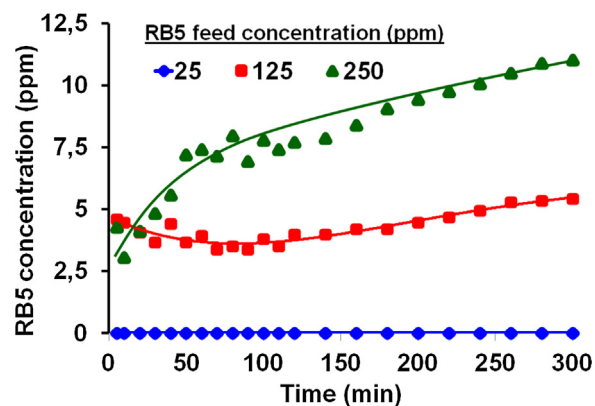


Fig. 6. Effect of dye concentration on the continuous photocatalytic degradation of RB5 dye in MPPBR (Conditions: Au loading (%w/w): 5%, flow rate: $5 \mu\text{L}/\text{min}$, pH: 7).

reasonably lower photocatalytic activity with respect to the bare and AuNP decorated microbeads. Hence, a clear enhancement in photocatalytic degradation rate was observed in MPPBR packed with the Martin AuNP decorated titania microbeads. Similar behavior was also obtained in the batch reactor and explained by the better electron transfer capability of AuNPs with smaller size [31].

The effect of flow rate on the photocatalytic degradation of RB5 in MPPBR prepared with the Martin AuNP decorated titania microbeads is shown in Fig. 5. As seen here, the almost zero outlet dye concentration (i.e. quantitative decolorization) was obtained at a flow rate of $1 \mu\text{L}/\text{min}$. Higher outlet dye concentrations corresponding to lower decolorization yields of 96 and 86% (%w/w) were obtained with the flow rates of 5 and $10 \mu\text{L}/\text{min}$, respectively. The decrease in the retention time by increasing the flow rate should be of course the reason of this behaviour.

The effect of dye feed concentration on the photocatalytic degradation of RB5 in MPPBR prepared with the Martin AuNP decorated titania microbeads is shown in Fig. 6. The amount of RB5 that should be converted by per unit mass of photocatalyst (Martin AuNP decorated titania microbeads) increases with the increasing dye feed concentration. This case is the reason of the decrease in RB5 decolorization yield observed (i.e. higher outlet dye concentration) by increasing the feed concentration of RB5 (Fig. 6). However, an outlet concentration of ca. 11 ppm corresponding to a decolorization yield of 95.6% (%w/w) could be achieved even the feed concentration of RB5 was kept at a high level like 250 ppm.

4. Conclusion

The size and porous properties of bare or AuNP/AgNP decorated titania microbeads are very suitable for being used as a photocatalyst in the microfluidic reactors. The microfluidic columns with suitable column-permeability values were obtained by slurry-packing of bare or AuNP/AgNP decorated titania microbeads into the fused silica capillary tubings. Hence, “microfluidic, photocatalytic packed bed reactor, MPPBR” was first constructed as a new tool for continuous photocatalytic dye degradation in a microfluidic system. The results of the kinetic study indicated that, the new reactor could be successfully operated for continuous photocatalytic decolorization of textile-dyes. We believe that the microcolumns in the form of “microfluidic photocatalytic packed bed reactor” can be used as “pre-column” or “post-column” particularly in the micro-liquid chromatography applications involving the removal of coloured contaminants before or after the chromatographic separation.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jphotochem.2016.08.015>.

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