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TITANIUM DIOXIDE SOL-GEL/ZINC OXIDE POWDER-COATED CLAY BEADS IN PHOTOCATALYTIC REACTOR

Thurgadewi Krishnan, Ng Con Nie, Wan Rafizah Wan Abdullah, Mohamad Awang, Wan Salida Wan Mansor*

Faculty of Ocean Engineering Technology and Informatics, Universiti Malaysia Terengganu, 21030 Kuala Nerus, Terengganu, Malaysia

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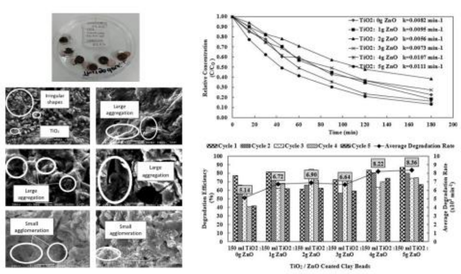
*Corresponding author
wansalida@umt.edu.my

Graphical abstract



Abstract

Catalyst Immobilization methods are important for providing better recovery of catalyst in photocatalytic treatment. The aim is to characterize and evaluate the photocatalytic performance of TiO_2/ZnO-coated clay beads. The titanium dioxide/zinc oxide (TiO_2/ZnO)-coated clay beads were prepared via the sol-gel process. Various ZnO powder ratios gave different TiO_2/ZnO composites sol. Four layers of TiO_2/ZnO sol were coated on clay beads and dried in the oven at 100°C for 30 min. The coated clay beads were calcined at 500°C for one hour for every two layers. Characterization of coated clay beads was done using a scanning electron microscope and energy dispersive spectroscopy. The increased surface area on small agglomeration and optimum loading of ZnO (5 g) resulted in the highest degradation efficiency recorded at 86.57%. An effective catalyst immobilization achieved a good recycling performance on clay beads. Degradation rate data were presented by pseudo-first-order kinetics. It was observed that the average degradation rate for TiO_2/5 g ZnO is 0.00836 min^{-1}. The actual results in this work can be applied as a guideline for the preparation of TiO_2/ZnO-coated clay beads with high photocatalytic performance.

Keywords: TiO_2/ZnO clay beads, sol-gel, photocatalysis, degradation rate, beads recyclability

Abstrak

Kaedah imobilisasi pemangkin adalah penting untuk menyediakan cara pemulihan pemangkin yang lebih baik dalam rawatan fotomangkin. Matlamat kajian ini adalah untuk mencirikan dan menilai prestasi fotopemangkin bagi manik tanah liat bersalut TiO_2/ZnO. Manik tanah liat bersalut titanium dioksida/zink oksida telah disediakan melalui kaedah 'sol-gel'. Nisbah serbuk ZnO yang berbeza telah memberikan sol komposit TiO_2/ZnO yang berbeza. Empat lapisan sol TiO_2/ZnO telah disalutkan pada manik tanah liat dan dikeringkan dalam ketuhar pada suhu 100^0C selama 30 minit. Manik tanah liat yang bersalut telah dikalsinasi pada 500^0C selama satu jam bagi setiap dua lapisan. Pencirian manik tanah liat bersalut telah dilakukan menggunakan 'scanning electron microscope dan 'energy dispersive spectroscopy'. Pertambahan luas permukaan pada penggumpalan kecil dan pemuatan optimum ZnO (5 g) telah menghasilkan kecekapan degradasi tertinggi dicatatkan pada 86.57%. Kaedah imobilisasi pemangkin yang berkesan telah mencapai prestasi kitar semula yang baik pada manik tanah liat. Data kadar degradasi telah menunjukkan mengikut kinetik tertib pertama. Diperhatikan bahawa purata kadar degradasi untuk TiO_2/5 g ZnO adalah

0.00836 min^{-1}. Hasil sebenar dalam kajian ini boleh diaplikasikan sebagai panduan bagi penyediaan manik tanah liat bersalut TiO_2/ZnO yang memberikan prestasi fotomangkin yang terbaik.

Kata kunci: Manik tanah liat TiO_2/ZnO, *sol-gel*, fotomangkin, kadar degradasi, kebolehkitar semula manik

1.0 INTRODUCTION

Semiconductor nanocomposites provide high interest in photocatalytic applications because of their improved properties [1, 2]. Titanium dioxide (TiO_2), a semiconductor from abundantly available metal, has been investigated as one of the most promising photocatalyst candidates due to its non-toxicity, cheapness, and highly reactive properties [3, 4]. Applications of TiO_2 in environmental remediation relating to wastewater treatment, air purification, and disinfection were also observed [5]. For instance, Hachem *et al.* (2001) reported that textile dyes decolourisation performed by commercial Dequssa P25 TiO_2 using homemade reactor under 18 W UV fluorescent lamp irradiation [6]. In a recent study, methylene blue degradation was executed by flowerlike rutile phase TiO_2 film on a photocatalytic reactor under a 300 W xenon lamp [7]. Moreover, Zinc oxide (ZnO) also has a comparable band gap with TiO_2, making it an equally efficient photocatalyst [8]. In 1994, kraft black liquor effluent from the paper and pulp industry was treated with a 250 W mercury lamp by commercial ZnO catalyst [9]. Recently, photocatalytic degradation of phenol was performed by fabricated ZnO nanorods under 1000 W/m^2 solar simulator [10]. ZnO offers a great photocatalytic activity even in small quantities [11, 12]. The similarity indicates the suitability of ZnO to be coupled with TiO_2.

The coupling of two photocatalysts has become a new method for enhancing photocatalytic activity [13, 14]. The semiconducting material absorbs the light energy and becomes an excited state that further produces a pair of electrons and holes (e–/h+). The holes (h+) produced is a potent oxidizing agent that will react with a water molecule (H_2O) to create super reactive hydroxyl radicals (HO•) [15]. These hydroxyl radicals will react with dyes or organic pollutants and decompose them into smaller intermediates, such as carbon dioxide (CO_2) and water (H_2O) [16, 17]. Several methods have been executed for coupling of these photocatalysts, such as hydrothermal [18], solvothermal [19], spray pyrolysis [20], chemical vapor deposition [21], electrodeposition [22, 23], magnetron sputtering [24], sol-gel [25, 26], and incipient wet impregnation [27]. Among these above-mentioned methods, the sol-gel method is a cost-effective practice with low-temperature synthesis [28-30].

Moreover, photocatalytic treatment has a problem in recovering and recycling powdered catalysts from treated effluent in slurry reactors [31, 32]. Alternatively, catalyst immobilization into solid support material will solve the problem of recovery and recycling of the catalyst. Meanwhile, several studies used quartz glass [33], zeolites [34], chitosan gel beads [35], polymeric beads [36], and clay beads [37]. Few studies have been done on TiO_2/ZnO-coated clay beads. In Bel Hadjltaief *et al.* research, tunisian clay supported ZnO-TiO_2 were used to assess photocatalytic degradation of methyl green under 100 W UV lamp [38]. Vaizogullar *et al.* was used TiO_2/ZnO-supported on sepiolite clay for the photocatalytic degradation of flumequine antibiotic under a 2mW/cm^2 spectro line UV lamp [39]. In addition, methylene blue photocatalytic degradation performance was conducted by synthesis of rectorite clay-based ZnO and TiO_2 under simulated sunlight irradiation [40]. The advantages of clay beads over other supporting materials are their vast availability in nature, cheapness, and environmentally friendly [41]. Furthermore, their high porosity is useful, making them great adsorbents [42, 43]. Therefore, the present work aims to characterize and evaluate the photocatalytic performance of TiO_2/ZnO-coated on clay beads.

2.0 METHODOLOGY

2.1 Preparation of TiO_2/ZnO Composites Sol

In the current study, TiO_2/ZnO composites sol were prepared by directly mixing ZnO powder into TiO_2 sol-gel, synthesized by the sol-gel process. Titanium isopropoxide (Sigma-Aldrich India, 97% v/v) was used to prepare transparent TiO_2 sol at room temperature. Firstly, 101ml of titanium isopropoxide was dissolved in 208ml of 2-propanol (R&M Chemical India, 99.5% v/v). The solution was under continuous stirring by a magnetic stirrer for 2 hours to acquire a precursor solution. Then, a combination of distilled water (7 ml), and acetic acid (1 ml) (R&M Chemical India, ≥99.7% v/v) was dropped into the precursor solution at a speed of 1 drop/s under vigorous stirring. Next, the solution was continuously stirred for 10 min to attain a yellow transparent sol. Then, 105 ml of triethanolamine (Sigma-Aldrich Germany, 99% v/v) was added and stirred for 30 min to increase the mixture's stability. Subsequently, various amounts of ZnO powder (Aldrich USA, <100 nm particle size w/w) were mixed with a fixed volume of 150 ml TiO_2 sol to form different mass ratios of ZnO (1 g/L, 2 g/L, 3 g/L, 4 g/L, and 5 g/L).

2.2 Catalyst Immobilization

The TiO_2/ZnO-coated clay beads were prepared by the dip-coating method. Before the coating procedure, the clay beads, also known as lightweight expanded clay aggregate (LECA), were washed a few times with water (1000 ml) and acetone (20 ml) for 10 min before being dried in the oven. The clean clay beads were immersed in TiO_2/ZnO sol at a speed of 1 mm/s. The dip-coated beads were allowed to air dry for 5 min in the fume-hood. Then, those coated clay beads were shifted to an oven at 100°C for 30 min. This process was repeated before the beads moved to a furnace for calcination. The ramp-up heating rate was 2°C/min, and the temperature was held at 500°C for 1 hour before cooling down naturally to minimize cracking. The procedure was repeated to acquire four TiO_2/ZnO layers, with calcination every two layers.

2.3 Characterization of TiO_2/ZnO-coated Clay Beads

Analytical Scanning Electron Microscopy (SEM) (model: JSM-6360 LA; JEOL) was used to observe the bare and TiO_2/ZnO-coated clay beads surface morphology. Before SEM imaging, samples were sputter-coated with a gold layer (JFC-1600 Auto fine coater). The surface elemental composition of the samples was determined via Energy Dispersive Spectroscopy (EDS) attached to the SEM. An acceleration voltage of 20.0 kV was applied for imaging for all samples.

2.4 Photocatalytic Experiment

Photocatalytic experiments were carried out in a column-shaped glass reactor with a 500-ml capacity. A 13 W UV lamp (WK-X2) was applied as a light source. It was placed vertically inside the reactor (Figure 1). The photocatalytic decolorization experiments were carried out at a known amount of TiO_2/ZnO-coated clay beads with 500 ml of methylene blue (MB) solution. All mixtures were agitated at 1500 rpm using a magnetic stirrer at room temperature. The effect of varying TiO_2/ZnO-coated clay beads was carried out in the range of 1 g to 5 g of ZnO mass ratios.

Meanwhile, TiO_2 sol volume was used with a fixed volume. During 180 min reaction time, samples were taken at certain time intervals from the reactor. Those samples were observed with spectrophotometric analysis using UV-Vis spectrophotometry (UV-1800; Shimadzu). The experiments were conducted under degradation kinetics and efficiency studies. The degradation rate follows Langmuir pseudo-first-order kinetics [44, 45] was calculated by the following equation:

$$\ln (C/Co) = -k \times t \quad (1)$$

The degradation efficiency was calculated as follows:

$$\% \text{ Degradation efficiency} = [C0 - Ct]/C0 \times 100\% \quad (2)$$

where, k is the pseudo-first-rate kinetic constant, Co is the initial concentration, and C is the concentration after the methylene blue degradation for time (t).

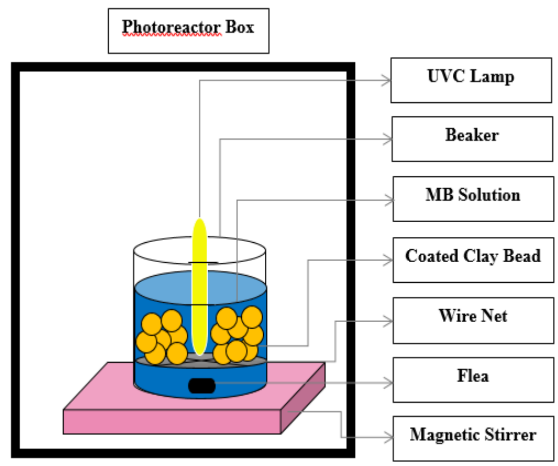


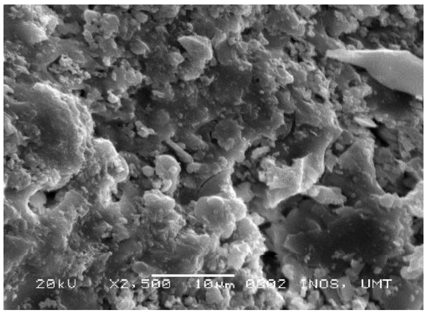
Figure 1 Experimental setup of photoreactor for photocatalytic experiments

3.0 RESULTS AND DISCUSSION

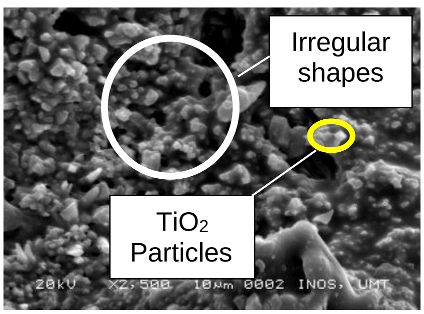
3.1 Scanning Electron Microscopy (SEM) Images of TiO_2/ZnO-coated Clay Beads

Surface morphology analysis of the bare clay bead and TiO_2/ZnO-coated clay beads at 2500× magnification was performed, and the results are shown in Figure 2. The SEM image of Figure 2(a) indicates the surface morphology of bare clay beads as compared to that of TiO_2/ZnO-coated clay beads (Figures 2(b–g)). The surface of the bare clay bead has smooth surfaces with irregular morphological shapes (Figure 2(a)). Figures 2(b–g) are micrographs of coated clay beads that show dispersed TiO_2 and TiO_2/ZnO nanocomposites on the surface of the clay beads. After the accumulation of nanoparticles, the bare bead morphology modification indicated that the active species (TiO_2 and ZnO) were uniformly scattered on the bead surface [46].

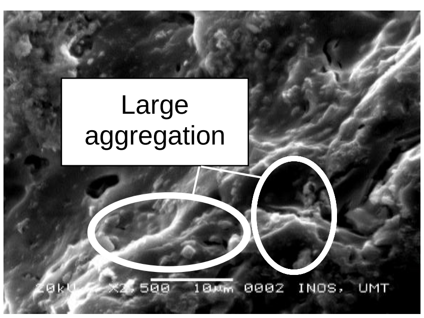
Figure 2(b) reveals TiO_2 nanoparticles synthesized from titanium isopropoxide hydrolysis without adding any ZnO powder. It can be seen that pure TiO_2 nanoparticles aggregates in irregular cubic shapes, where triethanolamine was utilized as a stabilizer which acts as a shape controller [47, 48]. The aggregation could be formed due to the high viscosity of the sol-gel, thus minimizing the dispersion of particles [49]. Figures 2(c–g) exhibit the TiO_2/ZnO nanocomposite at different mass ratios of ZnO powder. TiO_2 nanoparticles morphology was affected by ZnO addition [50], and the size of distribution of TiO_2/ZnO nanocomposites was improved in Figures 2(f–g). TiO_2/ZnO nanocomposites have regular morphology comprised of small agglomerates and nanoparticles. It displays a well-ordered structure and good particle distribution [51]. Figures 2(c–e), TiO_2/ZnO nanocomposites reveal some large aggregation with different particle size dispersion. Other work reported that the particle size distribution and agglomeration level appeared to be determined by the TiO_2/ZnO ratio [52].



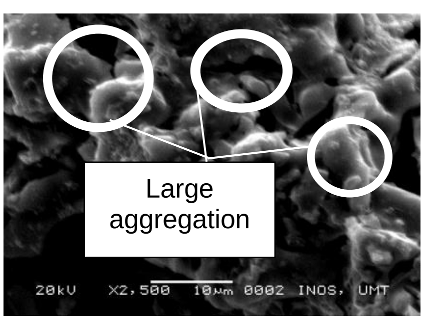
(a) bare beads



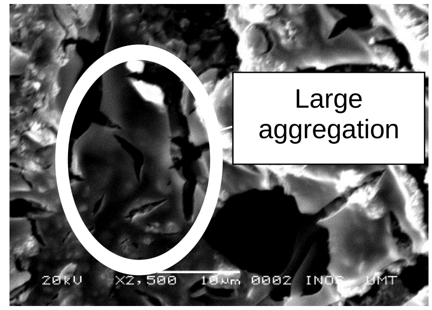
(b) TiO_2 only



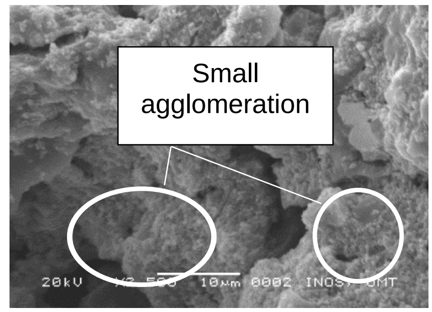
(c) TiO_2/1 g ZnO



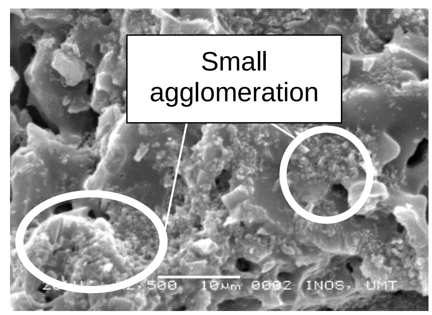
(d) TiO_2/2 g ZnO



(e) TiO_2/3 g ZnO



(f) TiO_2/4 g ZnO



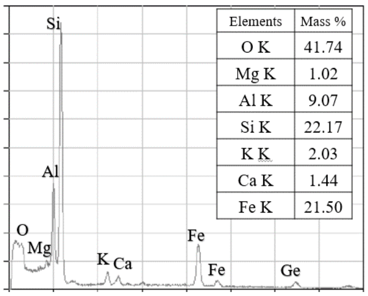
(g) TiO_2/5 g ZnO

Figure 2 SEM micrographs of the bare and TiO_2/ZnO coated clay beads

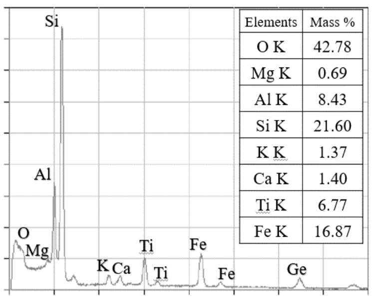
3.2 Energy Dispersive Spectroscopy (EDS) Analysis of TiO_2/ZnO-coated Clay Beads

Figure 3 shows the energy dispersive spectroscopy (EDS) of bare clay bead and TiO_2/ZnO-coated clay beads with the elemental composition of composites [53]. Presence of elements of oxygen (O), magnesium (Mg), aluminum (Al), silicon (Si), potassium (K), calcium (Ca), and iron (Fe) were detected in clay beads (Figure 3(a–g)). These elements were obtained from the clay beads. Figure 3(b–g) shows the energy dispersion spectra of TiO_2/ZnO composite nanoparticles on clay beads at different ZnO mass ratios. The nanocomposites were mainly composed of Ti, Zn, and O elements. Another study demonstrated that pure TiO_2 has titanium (Ti) and oxygen (O) signals, but the TiO_2/ZnO nanocomposite has an additional indication of zinc (Zn). This composition indicated that ZnO was successfully incorporated into TiO_2 nanoparticles to entrap into clay beads [54]. The composition of the

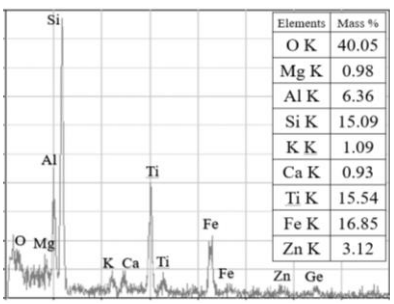
Zn element increases with an increase in ZnO mass ratio.



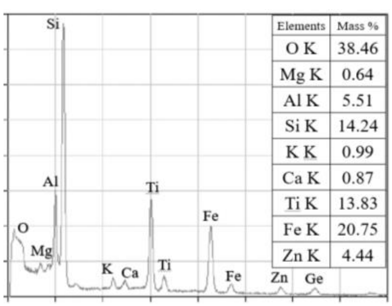
(a) bare beads



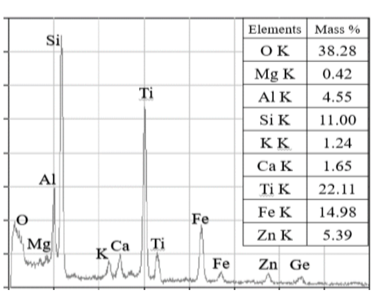
(b) TiO_2 only



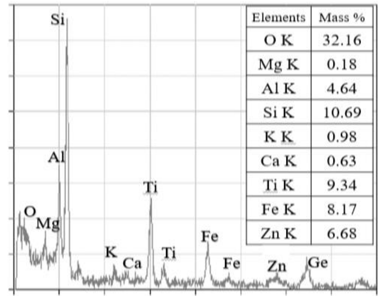
(c) TiO_2/1 g ZnO



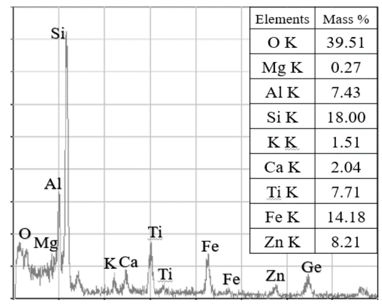
(d) TiO_2/2 g ZnO



(e) TiO_2/3 g ZnO



(f) TiO_2/4 g ZnO



(g) TiO_2/5 g ZnO

Figure 3 EDS analysis of the bare and TiO_2/ZnO coated clay beads

3.3 Photocatalytic Properties of TiO_2/ZnO-coated Clay Beads

The ZnO mass ratio is the parameter that indicates the performance of photocatalytic degradation. Figure 4 shows the effect of the ZnO mass ratio on photocatalytic degradation of MB (25 mg/l) in water under UV irradiation in a batch reactor at different time intervals. The displayed k-values in Figure 4 are from fitting curves of the data for a 0–180 min period. These values represent a valid measurement of all the TiO_2/ZnO-coated clay beads' photocatalytic degradation rates. TiO_2/2 g ZnO showed the lowest photocatalytic activity with $k = 0.0056$ min^{-1}. Moradi *et al*. mentioned that the large aggregation of nanocomposites decreased photocatalytic degradation activity [55]. Meanwhile, TiO_2:5 g ZnO, with $k = 0.0111$ min^{-1}, has the fastest MB degradation rate, respectively. More active sites are available in small aggregation due to increased surface area at a higher mass ratio of ZnO than lower mass ratio, which enhance photocatalytic degradation [56].

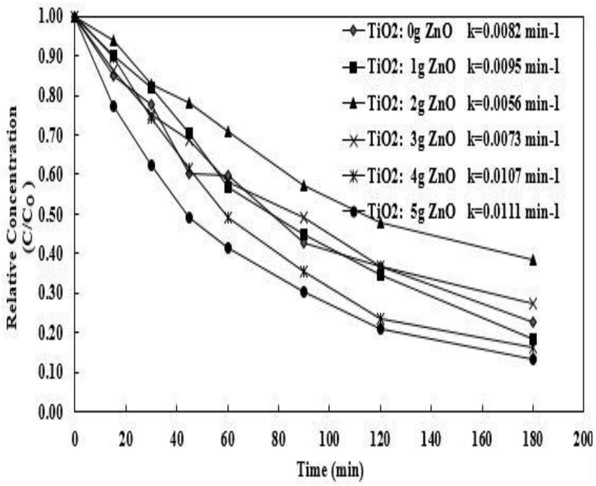


Figure 4 Photocatalytic degradation of MB under UVC irradiation by TiO_2/ZnO-coated clay beads.

3.4 Recycling Performance of TiO_2/ZnO-coated Clay Beads

Beads recycling was performed under UV light using a batch photocatalytic reactor with varying TiO_2/ZnO-coated clay beads for treating 25 mg/l MB solution at a time to evaluate photocatalyst regeneration performances [57]. Figure 5 shows that about five cycles were performed in three hours each, with the highest and lowest degradation efficiency of MB in the 1st and 5th cycles by TiO_2/5 g ZnO-coated clay beads at 86.57% and 66.81%, respectively; this results in the highest average degradation efficiency of 76.48%.

Moreover, in the literature experimental observation [40], 0.7 g/L of rectorite clay/ZnO/TiO_2 (2:1:0.067) recycling performance was maintained at higher than 60% for five repetitive experiments in photocatalytic degradation of 5 mg/L methylene blue. In another literature experimental observation [38], the recycling performance of 0.8 g/L ZnO-TiO_2/Tunisian clay photocatalyst was maintained at higher than 95% degradation efficiency for five consecutive cycles in treatment of 75 mg/L of methyl green. In this study, the average MB degradation rate for the TiO_2/5 g ZnO was calculated to be 0.00836 min^{-1}, which portrays an increase in ZnO content incorporated with TiO_2 increases recycling performance [58].

TiO_2/4 g ZnO-coated clay beads showed a slight decrease in the MB degradation efficiency from Cycle 1 to Cycle 3, but it remained higher than 60% for five cycles with an average degradation rate of 0.00822 min^{-1}. On the other hand, recyclability of TiO_2/ZnO-coated beads with the mass ratio of 1 g to 3 g ZnO displayed the same trend in the average degradation rate (0.00672 min^{-1}, 0.00690 min^{-1}, and 0.00664 min^{-1}), respectively. TiO_2/ZnO-coated beads without any ZnO powder showed the lowest average MB degradation efficiency, 57.97%, for five cycles with k = 0.00514 min^{-1} because less active sites are available in TiO_2 only-coated clay beads, causing a lower percentage of MB degradation [59]. Moreover, cubic TiO_2 has lower energy of binding that specifies a less oxidizing state than anatase TiO_2 [60]. Optimum loading of ZnO in the TiO_2/ZnO composites enhances the generation rate of electron/hole pairs to increase photocatalytic efficiency [61]. Concurrently, it increases the formation of hydroxyl radicals to improve photocatalytic performances [62].

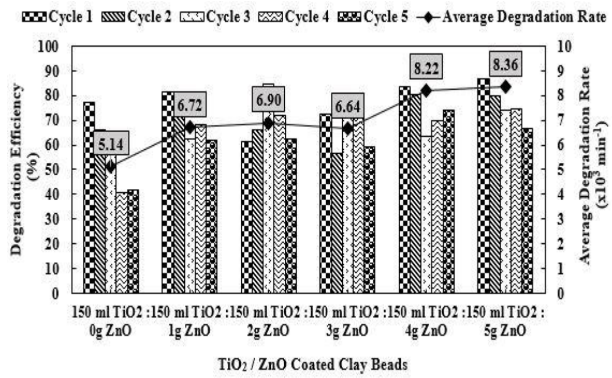


Figure 5 Recycling of TiO_2/ZnO-coated clay beads in terms of MB degradation efficiency and average rate constant

4.0 CONCLUSION

In this study, Preparation of the TiO_2/ZnO-coated clay beads was conducted via a sol-gel process using clay beads as substrate, where characterization of the prepared beads was done via SEM and EDS. The results demonstrate that coated clay beads were composed of nanoparticles. Small agglomerates are dispersed homogeneously in the TiO_2/5 g ZnO-coated clay beads. An optimal TiO_2/ZnO ratio of TiO_2/5 g ZnO was found to achieve a higher degradation efficiency with a k-value of 0.00836 min^{-1}. Furthermore, the immobilized TiO_2/ZnO recyclability over clay beads up to five cycles without any catalyst reactivation proves the acceptability of clay beads in photocatalytic treatment. In the future, more studies and research on catalyst immobilization of LECA clay beads remain necessary to upgrade the photocatalytic activity. Furthermore, researchers should further investigate the benchmark for raw chemicals used to prepare synthesis sol-gel since every ratio will give different results. This application will help convert lab-scale practices into pilot scales in the industrial plant.

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