Kinetic Investigation of Hg(II) Photoreduction using TiO_2-immobilized on Calcium Alginate Beads: Effect of Ferric ion and Organic Compound

Jeffrey Baloyi, Tumelo Seadira, Richard Moutloali, Mpfunzeni Raphulu, and Aoyi Ochieng

Abstract**—**To overcome the separation problems of powder TiO_2, the TiO_2 was immobilized on calcium alginate beads (Alg/TiO_2). These synthesized beads were applied to reduce toxic Hg(II) to Hg(0) in aqueous solution under ultraviolet irradiation. In the system without Alg/TiO_2 or UV light, no Hg(II) reduction was observed. The reduction of Hg(II) was approximately 9.9 and 78% when the system was exposed to ultraviolet irradiation with blank beads and Alg/TiO_2, respectively. Photoreduction of Hg(II) increased with increasing pH, initial Hg(II) concentration, catalyst dosage. Addition of Fe(III) ions and citric acid improved the photoreduction of Hg(II). The kinetic analysis of the photoreduction showed that the removal of Hg(II) best fitted with the pseudo first-order kinetic. The optimal conditions for Hg(II) photoreduction were found to be: pH 8, 2 g/L of the photocatalyst and 100 mg/L of initial Hg(II) concentration. Moreover, Alg/TiO_2 can achieve 75% photoreduction activity up to the third cycles. The results show that Alg/TiO_2 are promising materials to effectively treat wastewater containing Hg(II).

Keywords**—** Hg(II), Alg/TiO_2, photoreduction, citric acid, Fe(III)

I. Introduction

FOR the last few decades, the pollution of water resources due to the increase in the level of global industrialization, urbanization and inadequate effluents treatment due to lack of awareness and insufficient treatment facility has become a serious health hazard in the world [1]. This has led to the transport and introduction of various contaminants into aquatic environment. Metals found in industrial wastewater are toxic in some of their valance states. For example mercury in water is mainly seen in the +2 oxidation state. Hg(II) is a priority metal pollutant introduced into natural water from many industrial processes including agricultural materials, mining, coal combustion, chloro-alkali, military operations, medical antiseptic, pharmaceuticals, pulp and paper and production of plastics [2]. Hg(II) has universally been considered to be very toxic at low and high concentrations and causes rheumatoid arthritis, diseases of the kidneys, liver, effects on reproduction ,circulatory system, central nervous system and cause sensory and psychological impairments in human [3]. Nowadays, most of these industries are facing the difficult problem of disposal of Hg(II) in wastewater produced in large quantity. Therefore, due to its high toxicity level it is essential to develop the effective and robust wastewater treatment technology to treat Hg(II) prior to its discharge to the environment.

Several methods such as chemical precipitation, ion exchange, adsorption, membrane filtration, electrochemical treatment technologies, liquid extraction and biological treatment are employed for the removal of Hg(II) in wastewater [4]. However, these methods have certain disadvantages such as higher operational cost, requiring additional chemical, high energy consumption, residual metal sludge disposable and often ineffective at low concentrations. Therefore, it is clear that the prospect of developing more efficient and durable systems become necessary [5]. Compared with the conventional chemical reduction methods, the photocatalytic reduction of Hg(II) has some advantages, such as simple operation, ambient conditions, low cost, high efficiency, reusability, direct use of infinite, clean and safe natural solar energy, and no use and no release of sludge [6]. As a friendly environmental treatment process, photocatalysis has proved to be quite promising in the elimination of Hg(II) ions, which can comply with the World Health Organization (WHO) guidelines: to decrease the maximum concentration at less than 0.005 mg/L [7].

Titanium dioxide (TiO_2) is an effective catalyst and is the most widely used photocatalyst because of its favourable chemical property, physical sunblock in sunscreens, high degree of photocatalytic activity, non-toxicity, high stability, and low cost [8]. However, the use of free-suspended TiO_2 is impractical due to the difficult in separation of TiO_2 particles in water after use.

In the present work, the removal of Hg(II) ions from aqueous solutions using immobilized TiO_2 on calcium alginate was investigated. The aim of this work was to study the influence of operating parameters such as pH, initial concentration, photocatalyst dosage on Hg(II) removal and to determine the reaction kinetics. Furthermore, effect of Fe(III), citric acid, and reusability of presented materials was further studied.

II. Experimental

A. Materials and photocatalysts

Nitric acid (99.99% HNO_3), Sodium hydroxide (99% NaOH), mercury-chloride (99.99% $HgCl_2$), Iron(III)Chloride

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Hexahydrate (99.99% $FeCl_3.6H_2O$) and citric acid (99.5% $HOC(COOH)(CH_2COOH)_2$), were purchased from Merck Chemicals (Pty) Ltd., R.S.A. Sodium alginate (99% $NaC_6H_7O_6$) and calcium chloride (99.99% $CaCl_2$), purchased from Sigma Aldrich South Africa, were used to prepare immobilized TiO_2-alginate beads (amorphous, BET surfacce area of 62 m^2/g, particle size 1 - 2 mm). All of the chemicals were analytical grade and employed as received. High purity water (resistivity 18.2 MΩcm) purified by a Milli-Q water system (Millipore) was used throughout. Synthesized pure rutile dandelion TiO_2 sample, (anatase: rutile 0:100, BET surfacce area of 81 m^2/g, particle size 17 nm), was employed as photocatalyst in immobilized forms. Details on the procedures used for preparation and characterization of the pure rutile dandelion TiO_2 sample can be found on the previous work [9].

B. Immobilization of TiO_2 on biopolymer- Calcium Alginate

The immobilization of photocatalyst was carried out according to the procedures described by Harikumar et al. [10]. One step encapsulation method for immobilization of nanoparticles in semi permeable alginate beads was used. A solution containing TiO_2 nanoparticles (40 g) and sodium alginate (40 g) was prepared with high purity water, and stirred for 30 min at 23 ± 2°C using overhead stirrer. After thoroughly mixing, the calcium alginate beads were prepared by dropping the suspension in an aqueous solution of $CaCl_2$ (8 wt. %) with the aid of a peristaltic pump, where spherical gel beads were formed with a size of 1-2 mm. The gel beads were retained in the $CaCl_2$ solution for 12 h for hardening and then washed with high purity water. The excess water in the beads was removed by filtering with filter paper and air-dried at ambient temperature (23 ± 2°C) for 10 h [11]. To prepare alginate blank beads, (beads without TiO_2) similar procedures were employed except that the addition of TiO_2 suspension only sodium alginate was used.

C. Experimental setup

The cylindrical glass batch photoreactors were used for experimental purpose. The ultraviolet light source used was a mercury UV-C lamp (HPR 125 W) of predominant wavelength 300-400 nm developed by Philips Lighting. The lamp was placed inside a reactor box at about 4 cm above the cylindrical glass batch reactors containing 250 mL of $HgCl_2$ (shown in Fig. 1). The TiO_2 nanoparticles immobilized in calcium alginate, which was in the form of spherical beads were used as the photocatalyst. The lamp and reactor were placed inside a dark box, which was covered with aluminium foil so that no stray light could enter the reactor.

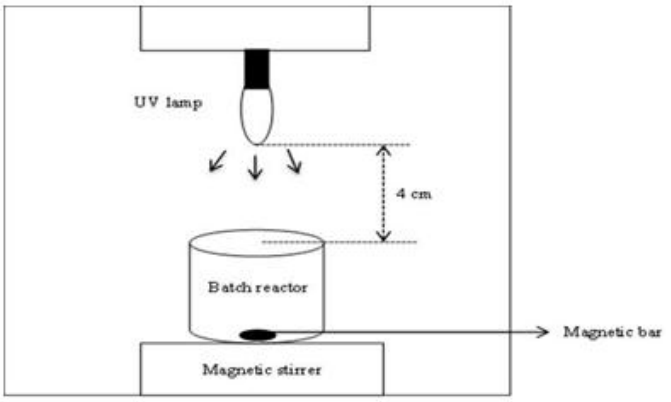

Fig. 1 Experimental set up of batch photocatalytic reactor system [12].

D. Photocatalytic treatment

Photocatalytic experiments were carried out in a batch type photoreactor at room temperature (25 ± 2°C). Batch experiments were carried out to investigate the effects of photocatalyst dosage, initial pH, initial Hg(II) concentration, Fe(III) and citric acid on the reduction of Hg(II). A desired amount of photocatalyst was added to a reaction flask containing 250 mL of an aqueous solution of $HgCl_2$, Fe(III) and citric acid with defined concentrations (20 to 100 mg/L). The stock solutions of Hg(II), citric acid and Fe(III) were prepared (1000 mg/L) by dissolving $HgCl_2$, citric acid and $FeCl_3.6H_2O$, respectively in 1L of high purity water. The stock solutions were diluted with high purity water to obtain the desired concentration range of Hg(II), citric acid and Fe(III) solutions. The initial pH of solution was adjusted by HNO_3 or NaOH aqueous solutions. Prior to photocatalytic experiments, the UV-C lamp was preheated for 30 min to obtain a constant light intensity. At different time intervals during the runs, 5 mL samples of the suspension were withdrawn from the batch reactors and centrifuged employing a 5810-R Eppendorf centrifuge before the absorption spectrum was taken. The absorbance of Hg(II) was measured spectrophotometrically at 478.4 nm, by UV-vis spectrophotometer using APHA, standard methods for examination of water and wastewater [13]. The photocatalytic activity was evaluated by analyzing the Hg(II) reduction after a fixed contact time.

E. Kinetic studies

The pseudo-first-order model was usually used to describe the kinetics of photocatalytic reduction of inorganic pollutants [14], being the kinetic equation given by (1):

$$r = \frac{-d[C]}{dt} = k.C^n, \quad (1)$$

where r is the reduction rate, C is the pollutant concentration and n order of reaction. The intergrated form of the Eq.(1) is presented by

$$\ln\left(\frac{C_0}{C}\right) = k_{app}.t \quad (2)$$

where *Kapp* is the apparent rate constant and C_0 is the concentration at t = 0 was used to fit the experimental data. The apparent rate constant was used as the basic kinetic parameter for different photocatalytic reactions in which the determination of photoreduction activity was independent of the previous adsorption period in the dark and the concentration of Hg(II) ions remaining in the solution [15].

III. Results And Discussion

A. Control experiments

Control experiments were carried out without the Alg/TiO_2, with Alg/TiO_2 in the dark and blank beads without TiO_2 under UV. The control experiments were designed to exhibit possible effects of photolysis, adsorption, precipitation and photocatalytic activity of the beads alone in the system. The results of the Hg(II) ions removal control experiments are shown in Fig. 2 and 3.

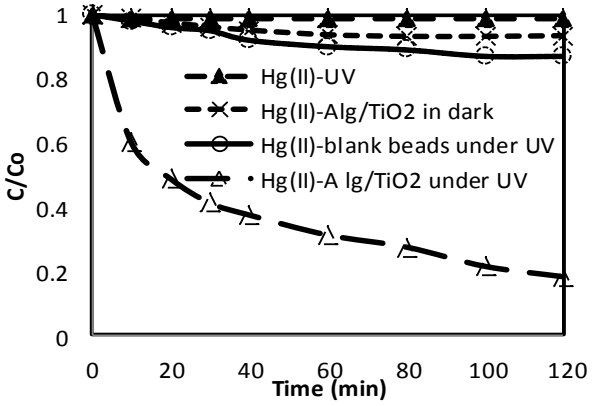

Fig. 2 Comparison of the photoreduction performance with UV (without Alg/TiO_2), Alg/TiO_2 in dark, blank beads and Alg/TiO_2 under UV. (Experimental conditions: initial pH, 8; initial Hg(II) concentration, 100 mg/L; catalyst dosage, 2 g/L).

Photolytic experiments were performed without addition of Alg/TiO_2 in order to determine whether any photochemical reactions could occur in the absence of catalyst. As shown in Fig. 2 there is no photolytic reduction of Hg(II) observed in the absence of Alg/TiO_2 under UV light after 120 min of irradiation at pH 8. As it can be seen in Fig. 2 approximately 9.2% of Hg(II) was reduced using blank beads under UV irradiation. These results can be attributed to the photoreduction via the photo induced electron transfer between the excited Hg(II) ion and the blank beads [16]. The adsorption of Hg(II) onto the Alg/TiO_2 surface was evaluated by analyzing the Hg(II) reduced in the solution after stirring 2 g of Alg/TiO_2 and 100 mg/L of Hg(II) solution for 120 min in the dark at pH 8. The results indicated negligible dark adsorption of Hg(II) onto the Alg/TiO_2 surface. However, when the system was exposed to UV light, rapid decrease in Hg(II) concentration was observed. The results indicates that the UV light energy is important in Hg(II) reduction.

In order to verify whether or not the decrease of the Hg(II) concentration could be due to the precipitation of the metal ions in the forms of metal hydroxides, a control experiment was carried out on the Hg(II) ions solution without photocatalyst. As shown in Fig. 3, when comparing the control (without a photocatalyst) and the sample (with photocatalyst) from pH 2 to 9, it is clear that the removal of Hg(II) ions from pH 2 to 8 was due to the photoreduction rather than by precipitation and which accounted for 0 %. This observation is supported by [16], who reported that when the pH is raised above 8 the Hg(II) ions precipitate to form hydroxyl species such as $Hg(OH)_2$ within the solution. Kannan and Malar [17], also observed the precipitation of Hg(II) ions to form $Hg(OH)_2$, when the pH is raised above 9. Photoreduction at pH above 8 was not considered in this study in order to avoid any possible interference from metal precipitation in solution. Hence the pH of 8 for the removal of Hg(II) from aqueous solution was used in all experiments in this work.

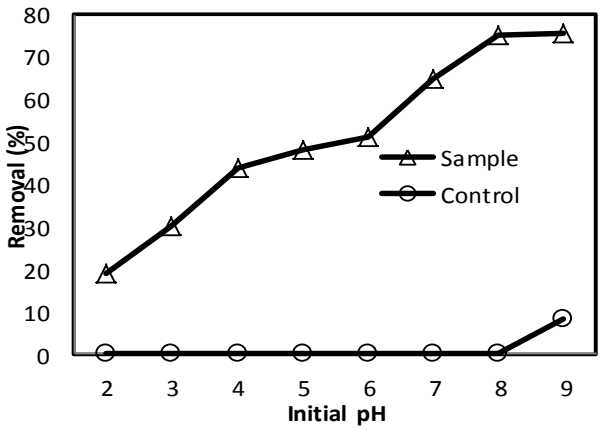

Fig. 3 Influence of initial pH on the Hg(II) photoreduction and precipitation. Experimental conditions: [initial pH (2 - 9); initial Hg(II) concentration (100 mg/L) and catalyst dosage, 2 g/L].

B. Effect of initial pH

In this work, pH of Hg(II) solution was adjusted to a range of values from 2 to 9, all other parameters were kept constant, and the results are shown in Fig. 4A. At low pH, the reduction of Hg(II) was found to be lower than that at high pH. Photoreduction of Hg(II) onto Alg/TiO_2 increased from 18.7 to 78% when pH of the solution was increased from 2 to 8. This can be attributed to the surface sites of Alg/TiO_2 which are protonated at low pH and deprotonated at high pH. The low reduction efficiency of Hg(II) observed at low pH, might be due to the competition between Hg(II) and H^+ cations for electrons at this pH. Smilar observation has been reported by [17]. Moreover, the like-charges of the Alg/TiO_2 and Hg(II) ions will repel each other due to the surface charges of the Alg/TiO_2 and that of Hg(II) ions which are both positive in the solution. However, as the pH increases, there is a greater possibility for the positive Hg(II) ions to be attracted to increasingly negatively charged Alg/TiO_2 catalyst. Moreover,

there are also a possible decrease in competition between H^+ and Hg(II) cations for the electrons. At pH values greater than 8, higher reduction of Hg(II) can be attributed to the possible precipitation of Hg(II) to $Hg(OH)^+$ or $Hg(OH)_2$ which can then leads to a higher reduction of Hg(II) within the solution [19].

The linear trend of Hg(II) rate constant as function of pH shown in Fig. 4B, this indicates that the reaction obeys a pseudo first-order kinetics. As it can be seen in Fig. 4B increasing the pH values led to the enhancement of the rate constant *k*. Similar results have been previously reported by [19].

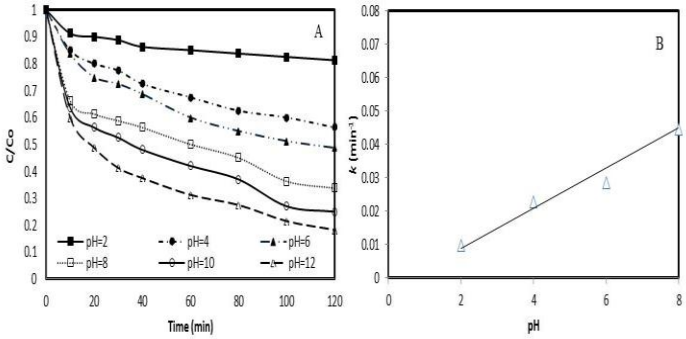

Fig. 4B Effect of initial pH on the reduction of Hg(II) (A) and the effect of initial pH value on the rate constant in solution (B). (Experimental conditions: initial Hg(II) concentration of 100 mg/L and 2 g/L of Alg/TiO_2 catalyst).

C. Effect of photocatalyst dosage

In order to determine the effect of catalyst mass on Hg(II) phodoreduction efficiency, 250 mL of solution (100 mg/L) was used with each of 0.5, 1.5, 2 and 2.5 g/L of Alg/TiO_2 for 120 min. The results in Fig. 5A indicate that the photoreduction of Hg(II) increased with an increase in catalyst dose from 1 to 2 g/L. Further increment in catalyst concentration to 2.5 g/L lead to a decrease in photoreduction efficiency. The observed increment in the photoreduction efficiency at a catalyst concentration of 2 g/L can be attributed to the increase of the total number of active sites on the photocatalyst surface thus resulting in an increase in the number of electrons which can take part in the photoreduction Hg(II). At a higher catalyst dosage beyond the 2 g/L, there is a decrease in the number of surface active sites due to the aggregation of Alg/TiO_2 particles. Thus resulting in a reduction in surface area available for light absorption and hence a drop in photoreduction. The kinetic relationship between Hg(II) rate constant and catalyst dosage is given in Fig. 5B. The Hg(II) rate constant depends on the amount of catalyst and the experimental data fits well pseudo-first order kinetic model.

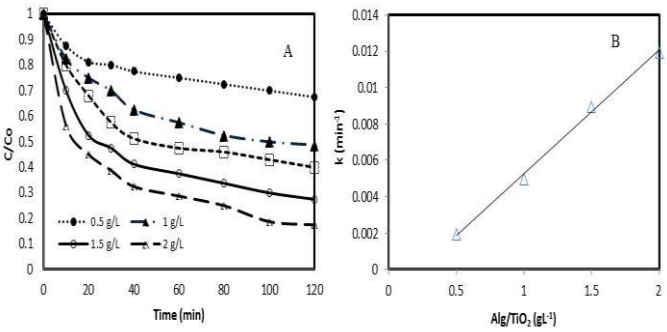

Fig. 5 Effect of photocatalyst dosage on the reduction of Hg(II) and the effect of photocatalyst dosage on the rate constant in solution (100 mg/L, 250 mL) with pH 8.

D. Effect of initial concentration

The influence of initial Hg(II) concentration and contact time on the photoreduction efficiency of Hg(II) was examined by irradiating the 2 g/L of TiO_2 at pH 8 with initial Hg(II) concentrations ranging from 20 to 100 mg/L. The photoreduction efficiency of Hg(II) at different initial concentrations is summarized in Fig. 6A. After 120 min irradiation, 45% and 81.5% of Hg(II) initially present in solution was reduced at initial Hg(II) concentrations of 20 and 100 mg/L, respectively. According to the results, photoreduction efficiency increased with increasing initial concentration of Hg(II) and the increase being more pronounced during the first 60 min of irradiation time. This can be explained by the increase in initial concentration of Hg(II) ions which causes a decrease in the number of photons reaching the catalyst surface [20]. As the concentration of Hg(II) increases above 80 mg/L low photoreduction efficiency was observed. This can be attributed to the deactivation of the active sites of the catalyst, resulting in a reduction of the photoreduction efficiency. The slope and the intercept of the linear plot of Hg(II) rate constant *k* as function initial Hg(II) concentration is shown in Fig. 6B. As indicated in Fig. 6B increasing initial Hg(II) concentration enhanced the reaction rate constant *k*.

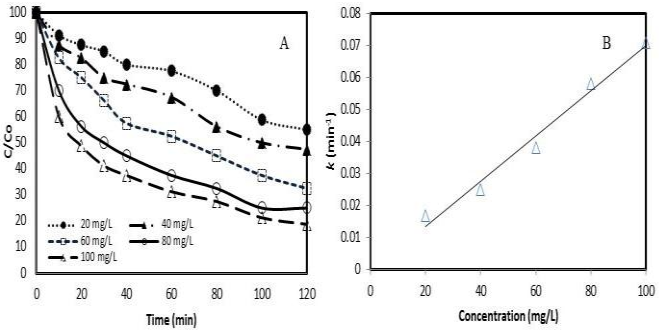

Fig. 6 Effect of initial Hg(II) concentration on the reduction of Hg(II) (A) and the effect of initial concentration on the rate constant (B) in solution (250 mL) with optimum catalyst dosage of 2 g/L and pH 8.

E. The influence of citric acid on the photoreduction of Hg(II)

The influence of citric acid on the photoreduction of Hg(II) is illustrated by Fig. 7A. As can be clearly seen from Fig. 7, the irradiation time required for complete removal of Hg(II) was extended as the initial citric acid concentration decreases. From Fig. 7A the Hg(II) reduction at initial citric acid concentration of 20 and 40 mg/L was about 60 and 76.25% at 120 min irradiation time. While, after 100 min irradiation time, 98 and 100% was removed in the presence of 60 and 80 mg/L, respectively. These results indicated that the Hg(II) photoreduction efficiency was enhanced by citric acid concentration. This can be attributed to initial citric acid concentration which sufficiently enhances charge separation of photo-induced hole/electron pairs by simultaneous redox reactions [4]. Citric acid acts as sacrificial electron donor, accelerating the reduction of Hg(II) to Hg(0).

The plot of Ln (*Co/C*) against the irradiation time (*t*) in the presence and absence of citric acid is shown in Fig. 7B, demonstrating a linear relationship both in the single system and binary system. The experimental data both in the single system and binary system obeys a pseuso-first order kinetic model. It can be pointed out that the addition of citric acid led to the enhancement of the reaction rate constant. This fact could be ascribed to the oxidation of citric acid which consumes photo-excited holes efficiently and thereby supressing the electron-hole recombination. Similar results have been reported by Bussi et al. [21].

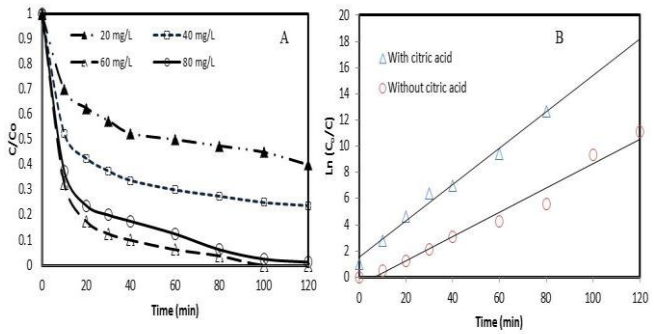

Fig.7 Influence of citric acid concentration on the Hg(II) photoreduction and in solution (Experimental conditions; pH 8, 100 mg/L initial Hg(II) concentration and 2 g/L catalyst dosage).

F. Effect of Fe(III) on the photocatalytic reduction of Hg(II) by citric acid

In the present study, Fe(III) precipitation experiment was carried out to check if precipitation was likely to occur in the solution at pH of 8. As can be seen in Fig. 8, Fe(III) was found not precipitating to $Fe(OH)_3$ at pH of 8. Similar observation has been reported by [24], who observed the precipitation of Fe(III) ions to $Fe(OH)_3$ over the pH range of 3.5 to 7.

To investigate the effect of Fe(III) ions on reduction of Hg(II), the initial concentration of Hg(II) and citric acid were kept at 100 and 60 mg/L, respectively in the solution at initial pH of 8. The presence of Fe (III) accelerated the photoreduction of Hg(II), which increased from approximately 93 to 100% after 60 min irradiation as shown in Fig. 8. The fast reaction between Hg(II) and citric acid in the presence of Fe(III) can be attributed to photoreaction products generated during photoreduction process. These products like Fe(II), $HO_2/O_2^{\bullet-}$ or $CO_2^{\bullet-}$, catalyze the reduction of Hg(II) [23]. Previous study reported by [22] also observed that Hg(II) can be reduced to much lower concentration in the presence of Fe(III). They further suggested that Fe(III) can be absorbed by TiO_2 and, subsequently, easily photoreduced to Fe(II) by accepting photo-reduced electrons on the surface of the TiO_2 catalyst. In the presence of Fe(III), Hg(II) is also reported by [23] to be photoreduced by the following redox reactions:

$$Fe(III) + e^- \rightarrow Fe(II) \quad (3)$$

$$Hg(II) + 2Fe(II) \rightarrow Hg + 2Fe(III) \quad (4)$$

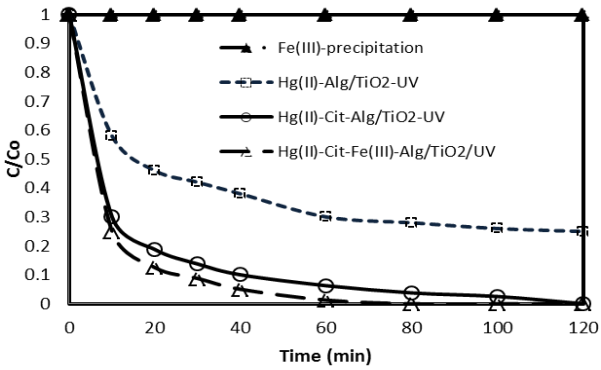

Fig.8 Effects of Fe(III) on the Hg(II) photocatalytic degradation in solution (Experimental conditions; pH, 8; 100 mg/L, initial Hg(II) concentration; 100 mg/L, Fe(III) and 2 g/L, catalyst dosage).

G. Reusability of photocatalyst

As shown in Fig.9 Alg/TiO_2 demonstrated good stability after recovery and catalyst reuse is effective for photoreduction of Hg(II). The first cycle reduced 100% of Hg(II) ions after 120 min of irradiation. Subsequently, the second cycle reduced 85% of Hg(II) ions. While the third cycle reduced 75% of Hg(II) ions. After these cycles, the efficiency markedly decreased, as illustrated in the fourth cycle, where the reduction efficiency decreased to 63% for Hg(II) ions. However, the reduction efficiency of Hg(II) ions was still significant after four times of Alg/TiO_2 reuse. Agglomeration and sedimentation of the Hg(II) on the surface of the Alg/TiO_2 particles after each cycle of photoreduction is a possible cause of the observed decrease on the reduction efficiency, because each time the photocatalyst is reused new parts of the catalyst surface become unavailable for Hg(II) adsorption. This prevents excitation of photons during photocatalytic reduction process, reducing the efficiency of the catalytic reaction. Furthermore, the decrease in the removal efficiency may be due to the non-negligible adsorbed molecules on the Alg/TiO_2 surface and thus hinder the

formation of electron-hole pairs which is crucial in photoreduction of Hg(II). Liu et al. [26] utilized a pure recycled TiO_2-impregnated glutaraldehyde crossslinked alginate beads in the reduction of toxic heavy metals and observed that the reduction ratio kept 100% after three times of reuse. Therefore, it can be concluded that, the reusability of Alg/TiO_2 in Hg(II) photoreduction goes towards green chemistry key principles.

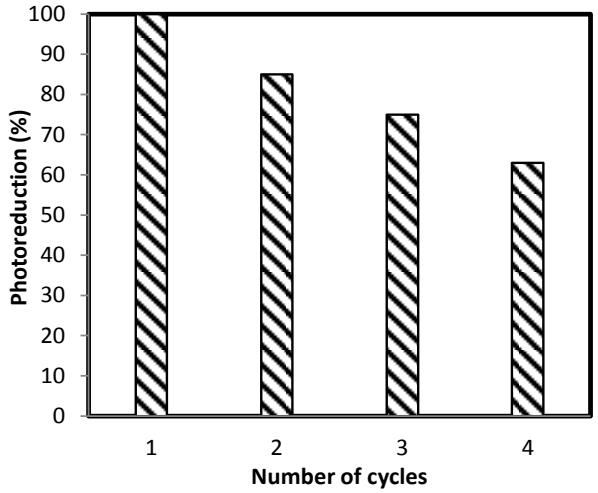

Fig.9 Reusability of Alg/TiO_2 photocatalyst. Photocatalytic conditions for Hg(II) reduction: initial Hg(II) concentration, 100 mg/L; initial citric acid concentration, 100 mg/L; Alg/TiO_2 dosage, 2 g/L; initial pH, 8. Regeneration conditions: regeneration solution, 100 mL of $CaCl_2$ (4%); temperature, 25ºC; contact time, 120 min.

IV. Conclusions

The photoreduction of Hg(II) in aqueous solution was successfully achieved using TiO_2 immobilized on calcium alginate under UV irradiation. The results of control experiments showed that both Alg/TiO_2 and UV light are important in the photoreduction of Hg(II). The photocatalyst dosage, initial Hg(II) concentration and pH values of the solution greatly influence the photoreduction of Hg(II). The photoreduction of Hg(II) fits well the pseudo-first-order kinetic and the dependence of the apparent rate constant on the initial Hg(II) concentration, initial pH and catalyst dosage is expressed by a linear equation. It can be concluded that the presence of Fe(III) and citric acid significantly improves the photoreduction of Hg(II) ion. Finally, Alg/TiO_2 can be reused without losing effectiveness for at least four cycles.

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