

Photocatalytic Degradation of Some Charges Aqueous Phase Pollutants using Nafion and Silica Modified TiO₂

(Kemusnahan Fotomangkinan Beberapa Pencemar Tercas Fasa Akueus
menggunakan TiO₂ Terubahsuai Nafion dan Silika)

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ABSTRACT

The present study investigated the use of modified titanium dioxide (TiO₂) based photocatalytic degradation (PCD) process for the removal of some critical charged aqueous phase pollutants. First of all, the use of Nafion TiO₂ (Nf-TiO₂) and silica TiO₂ (Si-TiO₂) for the removal of aqueous phase ammonia (NH₄⁺/NH₃) species employing near UV lamp as energy source was studied. The use of Nf-TiO₂ enhanced NH₄⁺/NH₃ PCD with optimum removal noted for 1 mL of Nafion solution coating per g of TiO₂ and respective overall NH₄⁺/NH₃ removal was about 1.7 times higher compared to plain TiO₂ at 6 h reaction time. Similarly the 0.5 mL silica solution coating per g TiO₂ sample, also enhanced NH₄⁺/NH₃ removal with optimum efficiency similar to Nf-TiO₂. The results from effect of ammonia concentration on to its PCD using Nf-TiO₂ indicated that overall mass based NH₄⁺/NH₃ removal was higher at greater NH₄⁺/NH₃ amounts indicating high efficiency of Nf-TiO₂. Similar trends were noted for Si-TiO₂ as well. Furthermore, the results from modified TiO₂ and mixed NH₄⁺/NH₃ and cyanide (CN⁻) systems indicated successful removal of co-pollutant CN⁻ along with simultaneous degradation of NH₄⁺/NH₃ species at rates that were still higher than plain TiO₂. Nevertheless application of Nf-TiO₂ for the treatment of cationic dye methylene blue (MB) indicated slower MB removal compared to plain TiO₂ though significant MB degradation using Nf-TiO₂ could still be achieved at pH3. Additionally the results from solar radiation energized PCD process indicated positive role of solar radiation for the removal of NH₄⁺/NH₃ species under a varying set of conditions.

Keywords: Cationic pollutants; Nafion TiO₂; photocatalysis; solar energy; silica TiO₂

ABSTRAK

Penyelidikan ini mengkaji tentang penggunaan titanium dioksida terubah suai (TiO₂) berasaskan proses pemusnahan fotomangkinan (PCD) untuk sesetengah bahan pencemar tercas fasa akueus kritikal. Pertama ialah penggunaan semua TiO₂ Nafion (Nf-TiO₂) dan TiO₂ silika (Si-TiO₂) untuk penyingkiran ammonia fasa akueus spesies (NH₄⁺/NH₃) yang menggunakan lampu dekat UV sebagai sumber tenaga telah dikaji. Penggunaan Nf-TiO₂ mempertingkatkan NH₄⁺/NH₃ PCD dengan penyingkiran optimum bagi 1 mL salutan penyelesaian Nafion untuk setiap g TiO₂ dan keseluruhan penyingkiran NH₄⁺/NH₃ adalah 1.7 kali lebih tinggi berbanding dengan TiO₂ plain pada masa tindak balas 6 jam. Lapisan larutan silika 0.5 mL untuk setiap g sampel TiO₂, juga mempertingkatkan penyingkiran NH₄⁺/NH₃ dengan kecekapan optimum menyerupai Nf-TiO₂. Hasil daripada kesan kepekatan ammonia kepada PCD dengan menggunakan Nf-TiO₂ menunjukkan bahawa jisim keseluruhan berasaskan penyingkiran NH₄⁺/NH₃ adalah lebih tinggi daripada jumlah NH₄⁺/NH₃ yang menunjukkan kecekapan tinggi Nf-TiO₂. Trend serupa dilihat pada Si-TiO₂. Selain itu, hasil daripada TiO₂ diubah suai dan campuran NH₄⁺/NH₃ dan sistem sianida (CN⁻) menunjukkan penyingkiran berjaya bersama pencemar CN⁻ bersama-sama dengan kemerosotan serentak spesies NH₄⁺/NH₃ pada kadar yang telah masih lebih tinggi daripada TiO₂ biasa. Walau bagaimanapun, aplikasi Nf-TiO₂ untuk rawatan kationik pencelup metilena biru (MB) menunjukkan penyingkiran MB lebih perlahan berbanding TiO₂ plain walaupun kemerosotan MB secara bererti menggunakan Nf-TiO₂ masih boleh dicapai pada pH3. Tambahan pula keputusan daripada sinaran suria yang mengecahkan proses PCD menunjukkan peranan positif radiasi solar untuk penyingkiran spesies NH₄⁺/NH₃ di bawah satu set keadaan yang berbeza.

Kata kunci: Bahan pencemar kationik; fotomangkinan; tenaga solar; TiO₂ Nafion; TiO₂ silika

INTRODUCTION

It has been well established that Titanium dioxide (TiO₂) is an effective photocatalyst for diverse and complex set of environmental applications and thus TiO₂ based photocatalytic degradation (PCD) process has been extensively studied for the removal of several toxic aqueous environmental pollutants that are specifically

present in industrial waste streams. TiO₂ is ideally suited as a photocatalyst because it is extremely stable, non-toxic, safe to handle, inexpensive and also photoactive under natural solar irradiation (Hoffmann et al. 1995). Furthermore the PCD process has been noted to degrade both neutral and charged aqueous phase pollutants such as ammonia or NH₄⁺/NH₃ (Lee et al. 2002). To that end,

altering the surface properties of TiO_2 that induce specific functional groups at the photocatalyst's surface and also alter the surface charge and pH_{zpc} value has been shown to play a significant role during photocatalysis of charged pollutants and hence different methods of surface modification of TiO_2 have been used to increase the effectiveness of photocatalytic process (Choi 2006; He 2009). To that end, $\text{NH}_4^+/\text{NH}_3$ species with pK_a of 9.26 (Sawyer et al. 2003) that is noted in several wastewater streams requires an appropriate treatment before disposal to avoid the respective negative environmental consequences. Considering this, treatment of $\text{NH}_4^+/\text{NH}_3$ species has been an active environmental engineering research area. Though the TiO_2 photocatalytic degradation of aqueous $\text{NH}_4^+/\text{NH}_3$ under UV illumination and basic pH values does transpire, however lower removals using plain TiO_2 as photocatalyst have been noted (Bonsen et al. 1997; Kim & Choi 2002; Lee et al. 2002; Low et al. 1991; Vohra et al. 2010). In that regard several studies have reported use of Nafion modified TiO_2 [Nf- TiO_2] and silica modified TiO_2 [Si- TiO_2] for the PCD of several cationic and anionic pollutants (Chen et al. 2010; Lee et al. 2005; Park & Choi 2005; Vohra & Tanaka 2001; Vohra et al. 2005; Wang et al. 2007). Generally, the use of such modified photocatalysts during the PCD process is noted to enhance the removal of charged cationic pollutants (Vohra & Tanaka 2003). However anionic pollutants have shown either reduced or no significant change in their PCD initiated removal using respective modified photocatalysts during the PCD process (Park & Choi 2005; Wang et al. 2007). As $\text{NH}_4^+/\text{NH}_3$ species degradation and removal from respective wastewater streams typically required for environmental protection, the present study investigated the use of Nafion modified TiO_2 [Nf- TiO_2] and silica modified TiO_2 [Si- TiO_2] for the PCD of $\text{NH}_4^+/\text{NH}_3$ using both UV lamp and solar irradiation as the energy source. Furthermore several dyes that are widely used for different applications in industries are also significant source of pollution, such as methylene blue (MB) which is also a cationic dye. However it is difficult to remove and degrade MB from the respective effluent streams using conventional wastewater treatment systems alone (Kannan et al. 2001). Most PCD studies also focused on MB degradation using plain TiO_2 (Hasnat et al. 2005; Lakshmi et al. 1995) except Park and Choi (2005) who used Nf- TiO_2 , however, the energy source was visible-light (with wavelength > 420 nm) that employed the dye sensitization based mechanism for MB degradation. Hence as summarized previously, the though PCD initiated removal of various charged pollutants using the PCD process and modified TiO_2 has been studied, however, to the best of our knowledge, the use of Nafion modified TiO_2 [Nf- TiO_2] and silica modified TiO_2 [Si- TiO_2] for the removal of $\text{NH}_4^+/\text{NH}_3$ using both UV lamp and solar irradiation as the energy source has not investigated. Furthermore methylene blue dye (MB) degradation using Nf- TiO_2 employing near UV radiation as the energy source also needs to be explored. The present work thus reports

on the two subjects along with the results from solar PCD initiated removal of $\text{NH}_4^+/\text{NH}_3$, considering the use of solar energy will also add to PCD process efficiency by using a natural and green energy source. Detailed findings are reported in the following sections.

MATERIALS AND METHODS

CHEMICALS AND MATERIALS

All chemical used were of high purity Titanium dioxide powder (P25 TiO_2 - DEGUSSA), tetraethylorthosilicate ($\text{C}_8\text{H}_{20}\text{O}_4\text{Si}$ - ALDRICH), Nafion perfluorinated ion-exchange resin 5% w/w solution (ALDRICH), ammonium chloride (NH_4Cl - BDH), sodium cyanide (NaCN - FISHER), methylene blue (FISHER), sodium carbonate (Na_2CO_3 - BDH), sodium bicarbonate (NaHCO_3 - BDH), hydrochloric acid (HCl - BAKER), sodium hydroxide (NaOH - FISHER) and pH calibration standards (FISHER).

EXPERIMENTAL DETAILS

Modified TiO_2 Preparation For Nafion TiO_2 (Nf- TiO_2) preparation, we added a given volume of Nafion 5% w/w solution per 1 g plain TiO_2 sample, followed by vigorous mixing to have an appropriate coating of TiO_2 by the Nafion polymer solution. The respective Nf- TiO_2 sample was then dried overnight before use. For silica TiO_2 (Si- TiO_2) preparation, the desired volume of tetraethylorthosilicate/TEOSi solution was added to 1 g plain TiO_2 sample followed by vigorous mixing for an appropriate silica coating on to TiO_2 . The respective sample was dried overnight and then transferred to furnace that was gradually ramped to temperature of 700°C and then maintained at 700°C for 5 h, followed by gradual cooling to room temperature. The respective Si- TiO_2 sample was used without any further treatment.

Photocatalysis Experiments Figure 1(a) provides the layout of batch type Pyrex glass reactor that was used for the UV lamp energized experiments. Batches of synthetic wastewater samples were prepared using high purity water (CORNING Mega Pure™ System) and stock solutions of respective chemicals. For all UV lamp PCD experiments, 1 L of synthetic wastewater sample was mixed with given weight of photocatalyst (plain or modified) and the system was kept in suspension using a magnetic stirrer setup. A 15 W UV lamp (F15T8-BLB 15W, Sankyo Denki, Japan) with 315-400 nm wavelength range (peak at ~ 352 nm) was used to excite the photocatalyst; the UV lamp was separated from the synthetic wastewater sample using a glass sleeve (Figure 1(a)). The photocatalytic reactor remained covered with aluminium foil during experiment to avoid exposure to other light sources. The initial pH was measured and adjusted to the desired value using HCl and/or NaOH solution. Several samples were collected during the course of experiment at different intervals and analysed for target pollutant. The reactor used for solar photocatalysis experiments is a

re-circulating one-sun plug flow type reactor made from Pyrex glass (Figure 1(b)), in which a series of parallel and thin pipes were connected to influent and effluent header pipes. For the solar photocatalysis experiments, given weight of photocatalyst was suspended in 2 L of synthetic wastewater sample and pH was adjusted to the desired value. Synthetic wastewater (with photocatalyst in suspension) was constantly passed through the reactor tubes, using a pump and magnetic stirrer setup (Figure 1(c)). Several samples were collected during the course of experiment at different intervals and analysed for target pollutant. The intensity of incoming solar radiation was quantified using a standard optical power meter and photo-detector setup (Newport, U.S.A.) in mW/cm^2 . An average value of the solar radiation exposure intensity in the study area is around $100 \text{ mW}/\text{cm}^2$.

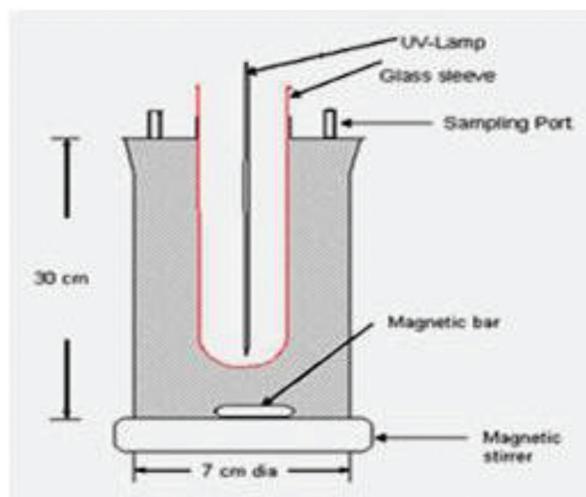


FIGURE 1(a). The reactor layout/details used for UV lamp based photocatalysis experiments

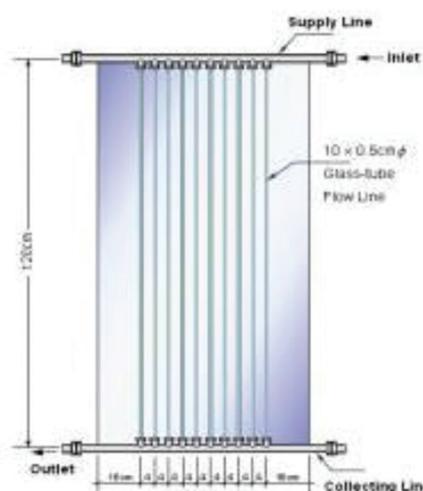


FIGURE 1(b). Pyrex glass reactor used for the solar photocatalysis experiments

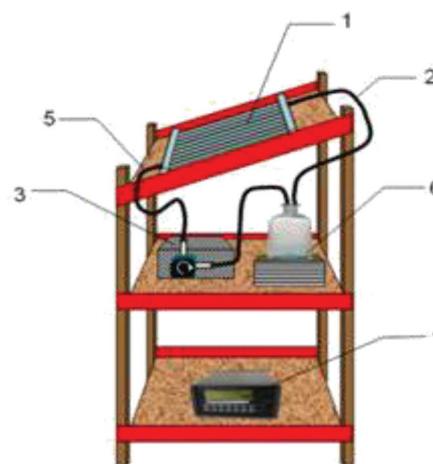


FIGURE 1(c). Solar photocatalysis reactor and support hardware (1 - Glass Reactor; 2 - Effluent Header; 3 - Pump; 4 - Solar Intensity Meter; 5 - Influent Header; 6 - Storage Tank)

ANALYTICAL METHODS

The solution/suspension pH was adjusted using a pH electrode (AccuTupH⁺ 13-620-185) and Accumet XL15 pH meter which was also regularly calibrated using pH calibration standards. Each sample was first filtered using a $0.2\text{-}\mu\text{m}$ pore size filter (Whatman, Germany) and then analyzed for the respective pollutants. An ion specific electrode (Orion 65-12, USA) and a meter setup with mV readings option (Orion, USA) were used for aqueous phase ammonia analysis. Each sample was transferred into a mini size beaker and few drops of NaOH solution were added to raise pH; the specific electrode was then dipped into the sample (with ongoing stirring) and meter-mV reading was noted after reaching equilibria. The respective concentration of ammonia was then determined using standard calibration curve procedure. The ammonia analysis setup was regularly calibrated using appropriate calibration standards. The cyanide (CN⁻) species was analyzed using a cyanide specific electrode (96-06 Cyanide Electrode, ORION, USA). The rest of the procedure is the same as reported before for ammonia analysis using electrode. Methylene blue analyses were completed using a UV-Vis spectrophotometer system (Shimadzu, Japan). For each analysis, the respective sample was transferred into a clean cuvette and the absorption value at wave length of 663 nm was noted for further processing using standard procedures. The respective UV-Vis spectrophotometer system was duly calibrated using methylene blue standards.

RESULTS AND DISCUSSION

We initially conducted a few preliminary $\text{NH}_4^+/\text{NH}_3$ PCD experiments using the UV lamp based reactor setup (Figure 1(a)) with results given in Figure 2. Respective findings from photocatalytic degradation of $\text{NH}_4^+/\text{NH}_3$ using Nafion-TiO₂ (Nf-TiO₂) at pH10 and pH12 indicate pH12

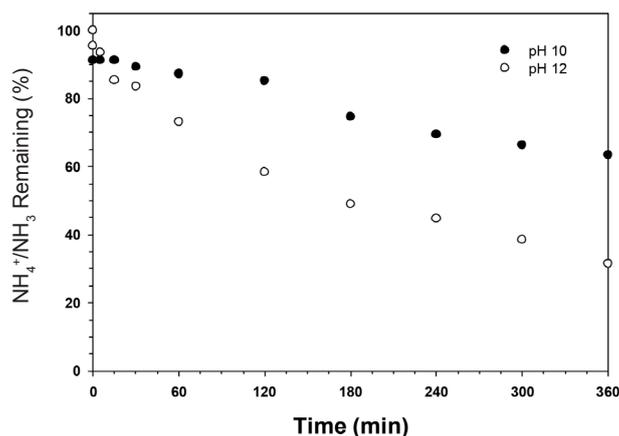


FIGURE 2. $\text{NH}_4^+/\text{NH}_3$ photocatalytic degradation using Nf-TiO₂ at pH10 and pH12 ($\text{NH}_4^+/\text{NH}_3$ 10 ppm, Nf-TiO₂ 1 g/L (Nf:TiO₂ - 1 mL per 1 g)

to yield higher $\text{NH}_4^+/\text{NH}_3$ removal, which is similar to previously noted $\text{NH}_4^+/\text{NH}_3$ degradation trends using plain TiO₂ (Bonsen et al. 1997; Zhu et al. 2007, 2005). (It should be noted that an experiment in the absence of UV/TiO₂ at pH12 showed insignificant ammonia removal which confirmed that the noted decrease in $\text{NH}_4^+/\text{NH}_3$ (Figure 2) resulted from PCD and not because of stripping). Higher $\text{NH}_4^+/\text{NH}_3$ PCD rate at pH12 was ascribed to higher OH⁻ ions concentration, which were precursors for the OH[•] radicals that are dominant oxidant species in advanced oxidation systems (Ogata et al. 1981; Turchi & Ollis 1990; Wei et al. 1990). Hence, we further investigated the efficiency of Nf-TiO₂ for $\text{NH}_4^+/\text{NH}_3$ PCD at pH12, at several different ratios of Nafion to TiO₂. This was done to ascertain the efficiency of Nf-TiO₂ compared to plain TiO₂ for $\text{NH}_4^+/\text{NH}_3$ PCD and also to find the optimum Nafion amount for $\text{NH}_4^+/\text{NH}_3$ removal. The respective results provided in Figure 3 indeed showed that for $\text{NH}_4^+/\text{NH}_3$ PCD, the Nf-TiO₂ efficiency was higher compared to plain TiO₂ (i.e. 0 mL Nafion per g TiO₂). Figure 3 also shows about 50% $\text{NH}_4^+/\text{NH}_3$ removal using 0.1 mL Nafion per g of TiO₂ photocatalyst whereas the 1 mL Nafion per g of TiO₂ photocatalyst yields highest $\text{NH}_4^+/\text{NH}_3$ removal, i.e. approximately 69% at 6 h reaction time. On the other hand, the use of 2 mL Nafion per g of TiO₂ photocatalyst results in lesser ammonia removal efficiency in comparison to 1 mL of Nafion per g of TiO₂ (Figure 3). Hence the Nf-TiO₂ yield higher $\text{NH}_4^+/\text{NH}_3$ removal efficiency compared to plain TiO₂ with optimum removal noted for 1 mL of Nafion per g of TiO₂. These results clearly indicate that surface modification of photocatalyst TiO₂ using Nafion enhances $\text{NH}_4^+/\text{NH}_3$ PCD initiated removal. Also for the present study the initial $\text{NH}_4^+/\text{NH}_3$ adsorption (at time zero; Figure 3) was noted be higher for the Nf-TiO₂ compared to plain TiO₂ which could explain the enhanced efficiency of Nf-TiO₂ for $\text{NH}_4^+/\text{NH}_3$ removal. Earlier studies have indicated an acidic shift in pH_{zpc} of Nf-TiO₂ compared to plain TiO₂ (Lee et al. 2005; Park & Choi 2005), which could enhance

electrostatic interactions between the negatively charged Nf-TiO₂ surface sites and cationic substrates. Nevertheless at pH12, the cationic NH_4^+ species will mostly convert to neutral NH_3 species considering $\text{NH}_4^+/\text{NH}_3$ pKa of 9.26 (Sawyer et al. 2003) and therefore enhanced electrostatic interaction between $\text{NH}_4^+/\text{NH}_3$ species and Nf-TiO₂ argument cannot be invoked to explain the noted increase in $\text{NH}_4^+/\text{NH}_3$ PCD (Figure 3). Regarding Nf-TiO₂ initiated PCD of pollutants with pH dependent speciation, Vohra and Tanaka (2001) noted that though degradation of cationic-paraquat and neutral-phenol (at experimental pH < 6) in a mixed system started simultaneously, however paraquat removal was slower which indicated preferential removal of neutral-phenol species (at the given pH). Also Nf-TiO₂ samples are indicated to have higher specific surface area compared to plain TiO₂ (Lee et al. 2005). Typically catalyst with higher specific surface area exhibit enhanced PCD rate either because of more substrate-adsorption sites or higher surface bound OH⁻ species that were precursors to OH[•] radicals as mentioned earlier were dominant oxidant species in the PCD systems (Turchi & Ollis 1990; Vohra et al. 2011). Thus higher initial accumulation of ammonia species on to Nf-TiO₂ could result either because of Nf-TiO₂ higher specific surface area and/or micro-scale interactions between the sulfonate groups at the Nafion polymer sites and $\text{NH}_4^+/\text{NH}_3$ species as the pH within the Nafion matrix is lower compared to the bulk solution (Lee et al. 2005). In any case such an enhanced initial $\text{NH}_4^+/\text{NH}_3$ accumulation possibly causes faster $\text{NH}_4^+/\text{NH}_3$ PCD using Nf-TiO₂. Based on successful application of Nf-TiO₂ for $\text{NH}_4^+/\text{NH}_3$ photocatalysis, we then explored the use of silica modified TiO₂ (Si-TiO₂) for $\text{NH}_4^+/\text{NH}_3$ PCD using the same reactor setup. Similar to Nf-TiO₂ findings, Si-TiO₂ also showed higher $\text{NH}_4^+/\text{NH}_3$ removal compared to the plain TiO₂ (Figure 4). The 0.5 mL silica per g TiO₂ sample, showed about 68% $\text{NH}_4^+/\text{NH}_3$ removal at 6 h reaction, which is close to previously noted highest Nf-TiO₂ $\text{NH}_4^+/\text{NH}_3$ degradation result (Figure 3). Furthermore the 0.5 mL silica per g TiO₂

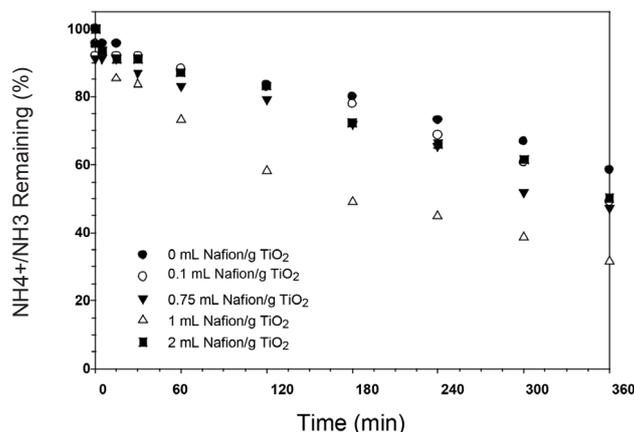


FIGURE 3. $\text{NH}_4^+/\text{NH}_3$ photocatalytic degradation at pH12: Effect of Nafion amount ($\text{NH}_4^+/\text{NH}_3$ 10 ppm, Plain TiO_2 or Nf- TiO_2 1 g/L)

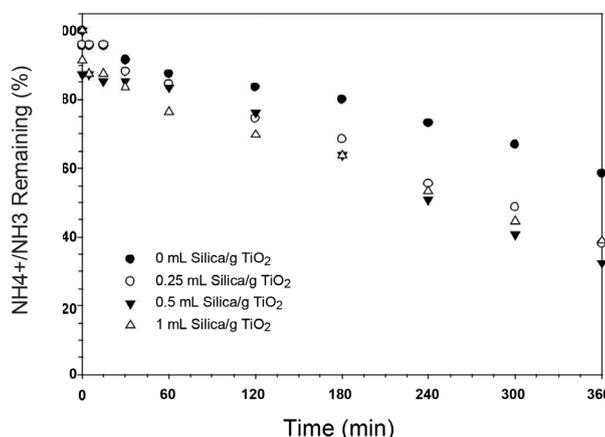


FIGURE 4. $\text{NH}_4^+/\text{NH}_3$ photocatalytic degradation at pH12: Effect of silica amount ($\text{NH}_4^+/\text{NH}_3$ 10 ppm, Plain TiO_2 or Si- TiO_2 1 g/L)

sample yields optimum $\text{NH}_4^+/\text{NH}_3$ removal compared to other two Si- TiO_2 samples (i.e. 0.25 mL Si per g TiO_2 and 1 mL Si per g TiO_2). Surface modification of TiO_2 particles by silica causes the following changes to TiO_2 surface: lowering of pH_{zpc} ; increases in specific surface area; and increase in surface OH functional groups which were precursors for OH^\bullet radicals (Vohra et al. 2005). Furthermore, according to Ding et al. (2000) silica modified TiO_2 enhances electron/hole (e^+/h^-) charge separation efficiency by providing electron/hole trap sites, which in turn leaves more hole species for OH^\bullet radicals formation thus accelerating the mineralization of target pollutants. In summary the above mentioned results clearly show higher photocatalytic efficiency of both Nf- TiO_2 and Si- TiO_2 for $\text{NH}_4^+/\text{NH}_3$ degradation, as compared to plain TiO_2 . To further explore this subject specifically for practical applications, we investigated the effect of ammonia concentration on to its PCD using the respective modified TiO_2 samples. Figure 5(a) that summarizes the respective photocatalytic degradation results using Nf- TiO_2 indicates that maximum percent based $\text{NH}_4^+/\text{NH}_3$ PCD (at 6 h reaction time) transpires at

10 ppm and with an increase in its initial concentration the respective overall percent removal decreases. Nevertheless, overall mass based $\text{NH}_4^+/\text{NH}_3$ removal is still higher at greater $\text{NH}_4^+/\text{NH}_3$ amounts with respective mass removed amounts for 50, 20 and 10 ppm $\text{NH}_4^+/\text{NH}_3$ systems noted to be 27.2, 11.45, and 6.85 ppm, respectively (Figure 5(b)), indicating high efficiency of Nf- TiO_2 . Furthermore, the mass based $\text{NH}_4^+/\text{NH}_3$ removal for Nf- TiO_2 at higher $\text{NH}_4^+/\text{NH}_3$ amounts was also noted to be higher compared to plain TiO_2 . For example plain TiO_2 study at 50 ppm $\text{NH}_4^+/\text{NH}_3$ showed 37.3% removal at 6 h reaction time that is equivalent to approximately 18.65 ppm overall mass based $\text{NH}_4^+/\text{NH}_3$ removal, whereas as also mentioned before for Nf- TiO_2 the overall $\text{NH}_4^+/\text{NH}_3$ mass removal for 50 ppm $\text{NH}_4^+/\text{NH}_3$ study is 27.2 ppm. Also Si- TiO_2 photocatalyst shows about 45.2% $\text{NH}_4^+/\text{NH}_3$ removal at 6 h reaction time for 50 ppm $\text{NH}_4^+/\text{NH}_3$ PCD (Figure 5(c)) that is equivalent to approximately 22.6 ppm $\text{NH}_4^+/\text{NH}_3$ mass-based removal. In summary, both Nf- TiO_2 and Si- TiO_2 showed not only enhanced $\text{NH}_4^+/\text{NH}_3$ mass-based removal efficiency with an increase in $\text{NH}_4^+/\text{NH}_3$ concentration but noted efficiencies

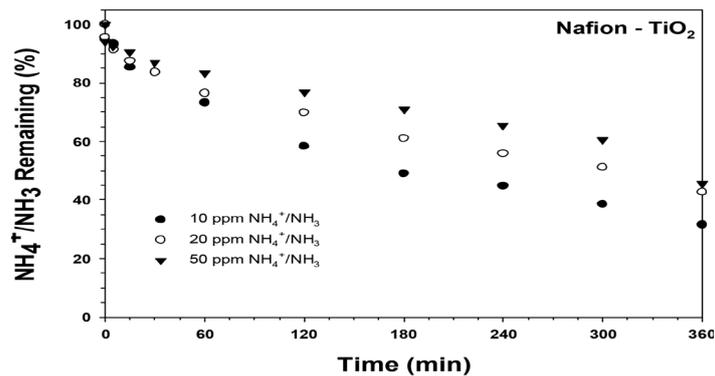


FIGURE 5(a). Photocatalytic degradation of NH₄⁺/NH₃ using Nf-TiO₂: NH₄⁺/NH₃ initial concentration effect (pH12, 1 g/L Nf-TiO₂ (Nf:TiO₂ - 1 mL per 1 g)

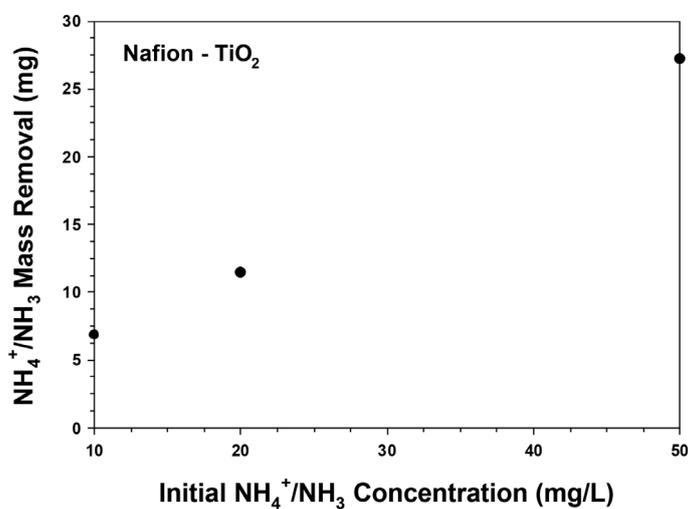


FIGURE 5(b). Overall NH₄⁺/NH₃ mass removal at 6 h reaction time at varying initial NH₄⁺/NH₃ concentrations using Nf-TiO₂ (pH12, 1 g/L Nf-TiO₂ (Nf:TiO₂ - 1 mL per 1 g)

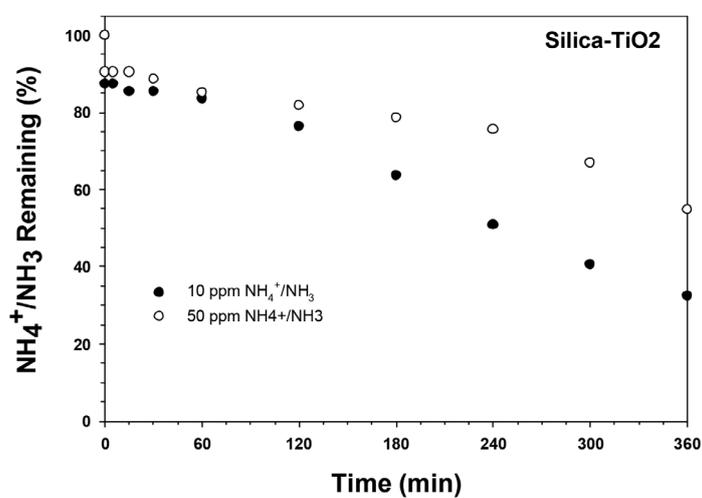


FIGURE 5(c). Photocatalytic degradation of NH₄⁺/NH₃ at two different initial concentrations using Si-TiO₂ (pH12, 1 g/L Si-TiO₂ (Si: TiO₂ - 0.5 mL per 1 g)

were also higher compared to plain TiO_2 . These findings are indeed promising, for respective practical applications with faster reaction kinetics. Furthermore, another aspect that needs attention is the effect of common co-pollutants such as cyanide (CN^-) on the noted efficiency of Nf- TiO_2 and Si- TiO_2 for $\text{NH}_4^+/\text{NH}_3$ removal. For example CN^- is often noted to be present along with $\text{NH}_4^+/\text{NH}_3$ in industrial wastewaters from sources as petroleum refineries (Berne & Cordonnier 1995; Chao et al. 2006). The results in Figure 6(a)-6(c) shows that in the presence of 5 ppm cyanide the efficiency of Nf- TiO_2 is somewhat reduced (Figure 6(a)) whereas for Si- TiO_2 the change is insignificant (Figure 6(b)). Also for both cases we note significant cyanide removal as well (Figure 6(c)), indicating that the respective decrease in $\text{NH}_4^+/\text{NH}_3$ removal using modified Nf- TiO_2 results from competitive degradation of CN^- . Nevertheless these results were supportive indicating successful removal of co-pollutant

CN^- along with simultaneous degradation of $\text{NH}_4^+/\text{NH}_3$ species at rates that are still higher than plain TiO_2 .

With the previously mentioned promising $\text{NH}_4^+/\text{NH}_3$ removal results, we further explored the PCD of another cationic pollutant, i.e., methylene blue dye (MB) employing Nf- TiO_2 considering that MB is a widely used cationic dye and respective wastewater discharges pose a serious environmental concern (Kannan et al. 2001). The effect of pH on MB degradation using Nf- TiO_2 is reported in Figure 7(a) whereas Figure 7(b) provides qualitative changes during MB degradation. At pH3 approximately 93% MB is degraded at 2 h reaction time whereas at pH6 we note about 78% MB removal. Hence Nf- TiO_2 is more efficient at lower pH of 3 than pH6 for the MB degradation, unlike $\text{NH}_4^+/\text{NH}_3$ results that showed an increase in degradation with an increase in pH from 10 to 12 (Figure 2). In contrast, the initial adsorption of MB on to Nf- TiO_2 is lower at pH3 compared to pH6. The aforementioned acidic shift

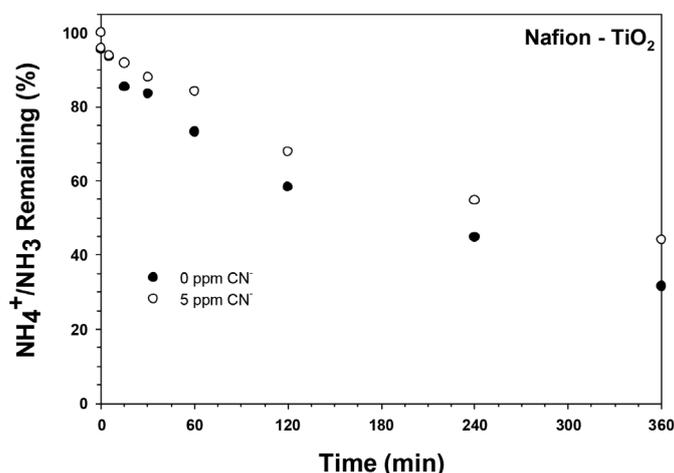


FIGURE 6(a). Photocatalytic degradation of $\text{NH}_4^+/\text{NH}_3$ using Nf- TiO_2 : Effect of 5 ppm CN^- ($\text{NH}_4^+/\text{NH}_3$ 10 ppm, pH12, 1 g/L Nf- TiO_2 (Nf: TiO_2 - 1 mL per 1 g)

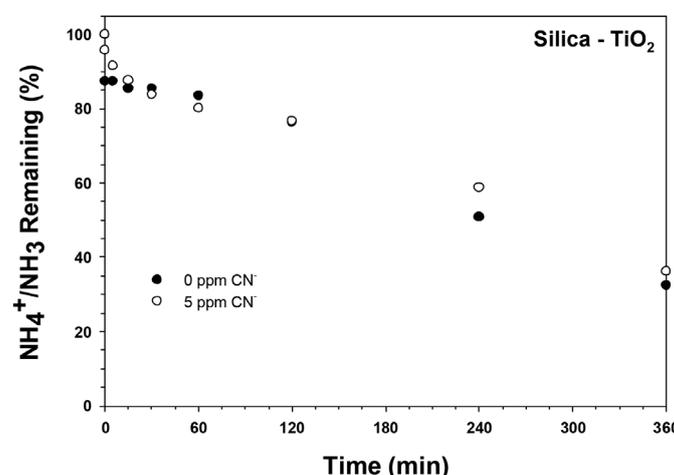


FIGURE 6(b). Photocatalytic degradation of $\text{NH}_4^+/\text{NH}_3$ using Si- TiO_2 : Effect of 5 ppm CN^- ($\text{NH}_4^+/\text{NH}_3$ 10 ppm, pH12, 1 g/L Si- TiO_2 (Si: TiO_2 - 0.5 mL per 1 g)

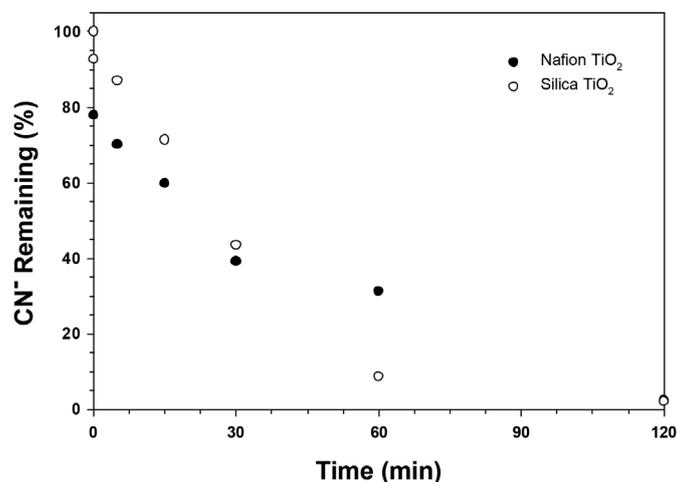


FIGURE 6(c). Photocatalytic degradation of CN^- from mixed CN^- and $\text{NH}_4^+/\text{NH}_3$ systems using 1 g/L of Nf-TiO₂ or Si-TiO₂ (CN^- 5 ppm; $\text{NH}_4^+/\text{NH}_3$ 10 ppm, pH12 (Nf:TiO₂ - 1 mL per 1 g and Si:TiO₂ - 0.5 mL per 1 g)

in pH_{zpc} of Nf-TiO₂ (Lee et al. 2005, Park & Choi 2005) possibly influenced the electrostatic attraction between its surface and cationic MB species resulting in higher MB adsorption on to Nf-TiO₂ at pH6. However such an increase in initial MB adsorption does not seem to influence its PCD initiated degradation (Figure 7(a)). Hasnat et al. (2005) who investigated the PCD of MB using visible light and plain TiO₂ noted poor MB adsorption and degradation in the acidic pH range, however, at basic pH values MB degradation was indeed noted. The same was observed by Lakshmi et al. (1995) who noted that MB PCD rate increased with an increase in pH, exhibiting a maximum at pH7-8 range. On similar lines Mulvaney et al. (1990) indicated that a rapid electron injection from cationic methyl viologen radical ($\text{MV}^{+\bullet}$) into valence band of photocatalyst TiO₂ particle transpired above photocatalyst's pH_{zpc} , which could possibly explain methyl viologen higher PCD at higher pH values. We also noted the same for plain TiO₂ as shown in Figure 7(c), with all other conditions same as in Figure 7(a). Furthermore respective results as given in Figure 7(c) indicate higher MB removal at respective pH values using plain TiO₂ compared to Nf-TiO₂ (Figure 7(a)). Wang et al. (2007) who studied PCD of cationic dye Basic Red 2 also noted higher adsorption of Basic Red 2 dye on Nf-TiO₂ compared to plain TiO₂ at alkaline pH values. Nevertheless the degradation rate of cationic Basic Red 2 dye using Nf-TiO₂ was still lower as compared to plain TiO₂ which is similar to what we have noted in the present work (i.e. Figure 7(a) and 7(c)). Park and Choi (2005) who employed visible-light as the energy source ($\lambda > 420$ nm), report that though adsorption of anionic dye AO7 onto Nf-TiO₂ decreased with an increase in Nafion coating (because of electrostatic repulsion) still the rate of AO7 PCD initiated removal showed an increase with an increase in Nafion coating. The above reported conflicting trends as noted for Dye/Nf-TiO₂ systems are intriguing. We suggest that comparatively slower MB degradation using Nf-TiO₂ could result because of competitive adsorption of H and

MB cations onto Nf-TiO₂ (unlike plain TiO₂ which will be mostly positively charged at pH6 considering Degussa P25 TiO₂ pH_{zpc} of 6.5), which in turn will reduce the formation of OH^\bullet radicals. Also unlike the other previously mentioned studies that used the sensitization pathway for dye molecule degradation, the present work used near UV light source that would involve the use of either OH^\bullet radicals or hole (h^+) species for target pollutant degradation. Nevertheless Nf-TiO₂ under acidic conditions can successfully degrade MB dye as reported in Figure 7(a) albeit at a slower rate compared to plain TiO₂.

Solar energy has also been widely used as an alternative UV radiation source in the PCD processes and is attractive especially in solar energy rich regions across the globe (Asahi et al. 2001; Collazzo et al. 2012; Mangrulkar et al. 2012; Sakthivel et al. 2003; Zou et al. 2001). However the use of solar energized Nf-TiO₂ and Si-TiO₂ based photocatalysis for $\text{NH}_4^+/\text{NH}_3$ PCD is rare and considering this we also investigated this subject. The layout of solar reactor used for this purpose is shown in Figure 1(b) whereas Figure 1(c) provides the general layout of whole solar photocatalysis setup, with details already given in section 2.2. An average value of the solar radiation exposure intensity in the study area is around 100 mW/cm². The results from respective experimental work as provided in Figure 8 shows higher $\text{NH}_4^+/\text{NH}_3$ removal using Nf-TiO₂, i.e. up to 54%, compared to both plain TiO₂ and Si-TiO₂ that show near 45% $\text{NH}_4^+/\text{NH}_3$ removal. It should be noted that overall $\text{NH}_4^+/\text{NH}_3$ removal using solar energy and modified TiO₂ is though lower compared to respective UV lamp results (Figure 8). Though the amount of Nf-TiO₂/Si-TiO₂ used in the solar experiments was kept lower i.e. 0.25 g/L to maximize the penetration of solar radiation through the plug flow reactor tubes (Figure 1(b)) however another set of solar experiments completed at 0.5 g/L Nf-TiO₂ or Si-TiO₂ did not show a significant change in $\text{NH}_4^+/\text{NH}_3$ removal efficiency. In summary, findings reported in this study showed positive role of both modified Nf-TiO₂

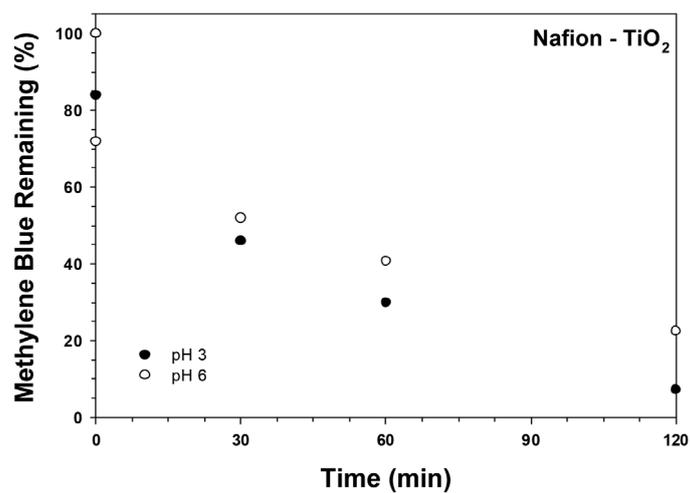


FIGURE 7(a). Photocatalytic degradation of methylene blue (MB) using Nf-TiO₂: pH effect (MB 10 ppm, Nf-TiO₂ 0.1 g/L ((Nf:TiO₂ - 1 mL per 1 g)

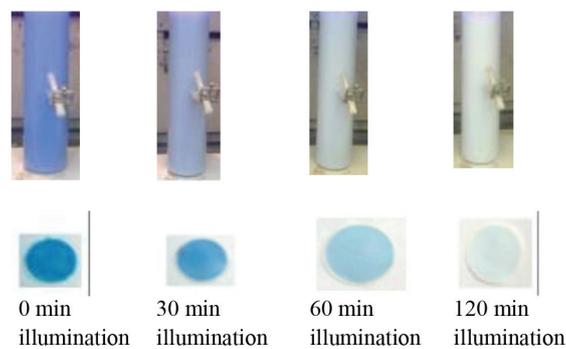


FIGURE 7(b). View of PCD reactor and 0.2 μm filter papers during PCD of methylene blue (MB) using Nf-TiO₂ (0.1 g/L)

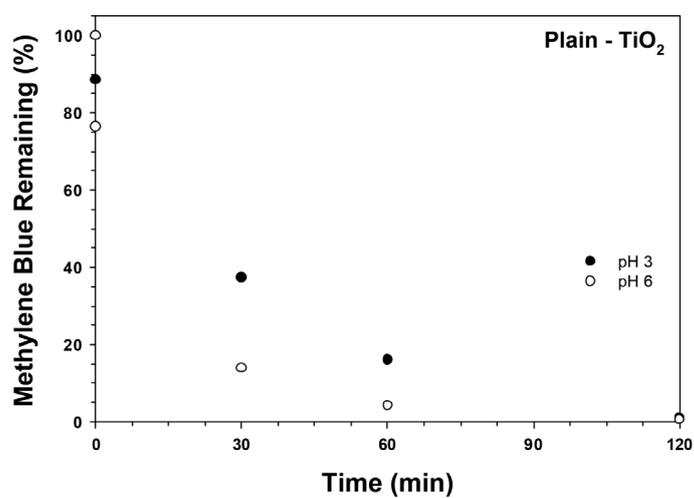


FIGURE 7(c). Photocatalytic degradation of methylene blue (MB) using plain TiO₂: pH effect (MB 10 ppm, TiO₂ 0.1 g/L)

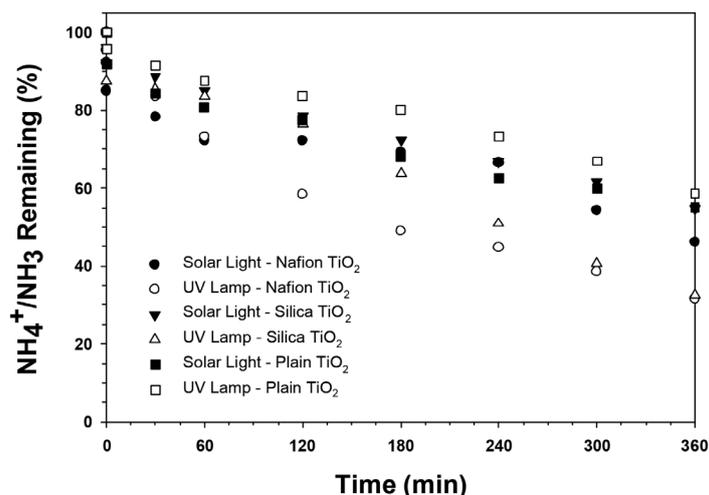


FIGURE 8. $\text{NH}_4^+/\text{NH}_3$ degradation using different photocatalysts: Effect of light source (pH12, $\text{NH}_4^+/\text{NH}_3$ 10 ppm, photocatalyst amount 0.25 g/L for solar experiments and 1 g/L for UV lamp experiments, Nf:TiO₂ - 1 mL:1 g, Si:TiO₂ - 0.5 mL: 1 g)

and Si-TiO₂ samples for degrading $\text{NH}_4^+/\text{NH}_3$ species using artificial UV lamp as energy source, at significantly higher rates compared to plain TiO₂. Furthermore, $\text{NH}_4^+/\text{NH}_3$ can also be successfully removed using Nf-TiO₂ and solar radiation as the energy source, with overall removal efficiency noted to be somewhat high than respective plain TiO₂ and Si-TiO₂ solar PCD studies.

CONCLUSION

The results from the present photocatalysis studies showed that positive role of both Nafion modified TiO₂ [Nf-TiO₂] and silica modified TiO₂ [Si-TiO₂] samples for degrading $\text{NH}_4^+/\text{NH}_3$ species using artificial UV lamp as energy source, at higher rates compared to plain TiO₂. The use of Nf-TiO₂ enhance $\text{NH}_4^+/\text{NH}_3$ PCD with optimum removal noted for 1 mL of Nafion solution coating per g of TiO₂ and respective overall $\text{NH}_4^+/\text{NH}_3$ removal about 1.7 times higher compared to plain TiO₂ at 6 h reaction time. Similarly the 0.5 mL silica solution coating per g TiO₂ sample, also enhanced $\text{NH}_4^+/\text{NH}_3$ removal with efficiency similar to previously mentioned Nf-TiO₂. Furthermore, the results from effect of ammonia concentration on to its PCD using Nf-TiO₂ and Si-TiO₂ indicated that overall mass based $\text{NH}_4^+/\text{NH}_3$ removal was higher at greater $\text{NH}_4^+/\text{NH}_3$ amounts. Also the results from mixed $\text{NH}_4^+/\text{NH}_3$ and cyanide (CN⁻) systems indicated successful removal of co-pollutant CN⁻ along with simultaneous degradation of $\text{NH}_4^+/\text{NH}_3$ species using modified TiO₂ at rates that were higher than plain TiO₂. Furthermore $\text{NH}_4^+/\text{NH}_3$ could also be successfully removed using Nf-TiO₂ and solar radiation as the energy source, with overall removal efficiency noted to be somewhat high than respective plain TiO₂ and Si-TiO₂ solar PCD studies.

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