

PHOTOCATALYTIC TREATMENT OF AQUEOUS PHASE
POLLUTANTS USING MODIFIED TiO₂

BY

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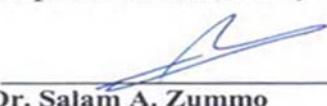

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Dedicated to
My
Beloved Parents

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ABSTRACT

NAME : Mohammad Monirul Islam Chowdhury
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Photocatalytic degradation (PCD) of aqueous phase pollutants was investigated using modified TiO₂. The use of Nafion modified TiO₂ and silica modified TiO₂ resulted in increased NH₄⁺/NH₃ PCD compared to the plain TiO₂. The ratio of 1:1 ml-Nafion-Solution/gm-TiO₂ for Nf-TiO₂ and 0.5:1 ml-Silica-Solution/gm-TiO₂ for Si-TiO₂ maximized the photocatalytic degradation (PCD) of NH₄⁺/NH₃. The PCD trends were also noted to be a function of pH, and same as plain TiO₂, Nafion modified TiO₂ also showed higher NH₄⁺/NH₃ removal efficiency at pH 12 compared to pH 10. However the role of electrostatic attraction, because of pH dependent speciation of NH₄⁺/NH₃ and TiO₂ surface sites, was found not to play any significant role and could not explain respective enhanced NH₄⁺/NH₃ PCD at higher pH. Rather higher OH⁻ radicals formation because of higher OH⁻ ions concentration at elevated pH, was postulated to initiate the noted enhanced PCD at pH 12. Nevertheless for the silica modified TiO₂ that showed enhanced NH₄⁺/NH₃ PCD was noted to have comparatively higher adsorption initiated substrate uptake at time zero, thus indirectly suggesting a possible role of adsorption in NH₄⁺/NH₃ PCD. Surface modification of TiO₂ also yielded a better removal efficiency till 50 ppm NH₄⁺/NH₃, with Nf-TiO₂ showing 19% and Si-TiO₂ showing 7% more NH₄⁺/NH₃ removal, as compared to plain TiO₂. However, the overall percent based NH₄⁺/NH₃ removal gradually reduced with any further increase in NH₄⁺/NH₃ concentration using both plain and modified TiO₂ catalysts. For mixed NH₄⁺/NH₃ and CN⁻ systems, PCD rates were found to be comparatively faster for Si-TiO₂ as compared to Nf-TiO₂. Furthermore, approximately 99% of CN⁻ was also removed after 120 min. However, decrease in the overall NH₄⁺/NH₃ removal was noted as the CN⁻ concentration was increased (from 0 till 10 ppm) in the mixed systems. Furthermore, PCD of methylene blue (MB) using modified TiO₂ samples also yielded successful removal.

الاسم : محمدمنير الإسلام شودري
عنوان الرسالة : استخدام الطريقة الكهروضوئية لمعالجة المياة الملوثة وذلك باستعمال

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الأهداف الرئيسية لهذه الدراسة هي البحث عن تأثير ثاني أكسيد التيتانيوم المعدل في إزالة الملوثات من المياة مثل الأمونيا و الأمونيوم والسيانيد وذلك باستخدام الطريقة الكهروضوئية والمياة المقطرة والمضاف لها الملوثات في المختبر.

أظهرت الدراسة أن أفضل إزالة للأمونيا من المياة كانت عند استخدام محفزات ثاني أكسيد التيتانيوم والنافيون بنسبة 1:1 وأيضاً ثاني أكسيد التيتانيوم وثاني أكسيد السيلكون بنسبة 0.5 على التوالي وقد كان تركيز الأمونيا 10 جزء بالمليون عند بداية المعالجة كما أنه لوحظ أن للإزالة علاقة بدرجة الحموضة (الأس الهيدروجيني) وأن أفضل إزالة للأمونيا تحققت عند درجة الحموضة 12 بدلاً من 10 وذلك عند استخدام نافيون وثاني أكسيد التيتانيوم.

أن مما أوجنته الدراسة أن المجموع الكلي لإزالة الأمونيا ينقص تدريجياً بزيادة تركيز الأمونيا كما وأنه باستخدام ثاني أكسيد السيلكون وثاني أكسيد التيتانيوم كمحفزات لإزالة الأمونيا والسيانيد من المياة الملوثة فإن نسبة الإزالة بلغت 99% بعد مرور 120 دقيقة من المعالجة .

ومن المتوقع أن تسهم نتائج هذه الدراسة في حل مشكلة إزالة الملوثات العضوية ، وتعزيز الجهد البيئي لإزالتها من مياه الصرف الصحي والصناعي.

ماجستير الهندسة
جامعة الملك فهد للبترول والمعادن
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CHAPTER 1

1. Introduction

Photocatalytic reactions at the surface of titanium dioxide (TiO_2) have attracted much attention in view of their practical environmental cleanup applications such as self cleaning surfaces, wastewater treatment, air purification, bacteria inactivation, and hydrogen generation. Furthermore the TiO_2 based photocatalytic degradation (PCD) process has also been extensively studied for the removal of several toxic aqueous phase environmental pollutants, as an alternative to other wastewater treatment technologies such as air stripping or carbon adsorption. The PCD process is an Advanced Oxidation Process (AOP) that utilizes either artificial or solar light along with TiO_2 , for environmental cleanup. This process has been successfully used for the removal and mineralization of a variety of aqueous phase pollutants that are specifically present in many industrial waste streams [Fabbri et al., 2006].

It has been well established that TiO_2 is the most effective photocatalyst for environmental applications compared to other photocatalysts such as CdS , ZnO , or Fe_2O_3 . TiO_2 is ideally suited as a photocatalyst because it is extremely stable, non-toxic, safe to handle, inexpensive, and photoactive under near UV light [Choi 2006]. According to Hoffmann et al. [1995], TiO_2 photocatalyst has shown excellent performance in oxidizing and subsequently mineralizing various aqueous pollutants [Hoffmann et al., 1995]. The surface properties of TiO_2 play a significant role in determining the photocatalytic reaction efficiency. Thus, different methods of surface modification of TiO_2 such as silica loading on TiO_2 , Nafion coating on TiO_2 , titania deposited with Pt

nanoparticles, Ag/TiO₂ and surface fluorination of TiO₂ have been used to increase the effectiveness of photocatalytic process. It has also been found that the surface acidity of TiO₂ could be more enhanced by coating Nafion polymer on TiO₂ surface (Nf- TiO₂) [Lee et al., 2005]. It is well known that TiO₂ surface in an aquatic environment takes electric charge which is dependent on pH. For example Degussa P25 TiO₂ at pH < 6.5 has positive surface charge due to the presence of $\equiv\text{TiOH}_2^+$ groups where negative surface charge is noted at higher pH value (pH > 6.5) owing to $\equiv\text{TiO}^-$ groups [Lee and Choi, 2005]. This pH-dependent surface charge affects the adsorption of substrates and consequently photocatalytic reactions. For example, enhanced aqueous phase degradation of cetylpyridinium bromide and rhodamine 6G (R-6G) was found while using silica-coated TiO₂ used during photocatalytic degradation [Tada et al., 1998]. Moreover, Vohra and Tanaka [2003] have found that the use of silica-modified TiO₂ catalyst results in enhanced photocatalytic degradation (PCD) of cationic pollutants. The modification of TiO₂ causes an increased specific surface area (SSA), which in turn causes enhanced substrate adsorption onto TiO₂ [Vohra and Tanaka, 2003]. Beside these, it was also reported in the same study that the enhanced electrostatic attraction of cationic aqueous phase pollutants onto the negatively charged Si-O⁻ groups onto TiO₂ surface seems to be the main reason for the enhanced photoactivity of Si-TiO₂. In general higher adsorption of charged aqueous molecules results onto modified TiO₂.

In view of its practical environmental applications, the photocatalytic degradation using titanium dioxide under UV illumination has been suggested as an alternative treatment processes for the removal of several pollutants that are noted in industrial wastewaters. Though the TiO₂ photocatalytic degradation of aqueous pollutants under UV illumination

has proven to be effective but low efficiencies using plain TiO₂ as photocatalyst remains a concern. Considering this several studies have explored TiO₂ surface modification to improve its efficiency [Choi, 2006]. Modified TiO₂ can be very different from the pure TiO₂ in many aspects such as light absorption, charge recombination dynamics, interfacial charge transfer kinetics, surface charge, and adsorption of substrates. According to Wen and Young [2007], surface modification of TiO₂ typically reduces the zeta potential and shifts it to negative range under typical pH values. Moreover, Vohra et al. [2005] have found enhanced photocatalytic degradation of tetramethylammonium (TMA) using silica-loaded titania. This research intends to find out the performance of Nafion and Silica modified TiO₂ for the removal of some aqueous phase pollutants including NH₄⁺/NH₃. Specifically, the effect of different variables including pH, Nafion amount, silica amount, and NH₄⁺/NH₃ and co-pollutants' concentration, onto photocatalytic degradation of NH₄⁺/NH₃, will be investigated. No such study has been completed before. The detailed results are listed later in this document.

CHAPTER 2

2. Literature Review

2.1 General Background

Photocatalysis basically refers to the acceleration of a photoreaction by the presence of a catalyst. It can be said that the catalyst may accelerate the photoreaction by interaction with the substrate in its ground or excited state and/or with a primary photoproduct, depending upon the mechanism of the photoreaction. Besides this, catalysis implies a catalytic entity that participates and accelerates the chemical transformation of a substrate while it remains unaltered at the end of each catalytic cycle [Kutul et al., 1993]. In photocatalysis, no energy is stored; there is merely an acceleration of a slow event by a photon- assisted process.

TiO₂ photocatalysis is one such technology for the destruction of toxic pollutants that are present in wastewater. Different studies have reported the significance of TiO₂ surface properties in the photocatalytic degradation process (PCD) [Pichat et al., 1993]. Also the TiO₂ surface and several substrates speciation is pH-dependent and for this reason markedly altered PCD trends are noted with changing pH [Vohra et al., 2003; Kim & Choi 2002]. Kormann et al. [1991] found that cationic substrates show increased adsorption and degradation at higher pH while an anionic substance has high adsorption and degradation rate at lower pH. Vohra et al. [2001] also found that modification of TiO₂ surface properties yields faster adsorption and degradation in aquatic environment.

In photocatalytic oxidation of organic substances, pollutant molecules are typically mineralized to inorganic species like CO₂, H₂O, halide ions, sulfate, and phosphates [Kim & Choi, 2002]. Nitrogen-containing organic compounds lead to two main inorganic species during their photocatalytic degradation such as ammonium (NH₄⁺) and nitrate (NO₃⁻). The relative concentration of the two product ions depend on the molecular structure of the substrates, the oxidation state of nitrogen, pH, the illumination time, and the adsorption behavior of the substrates on photocatalysts. Schmelling and Gray [1995] report the formation of nitrite (NO₂⁻) as an intermediate product in case of incomplete oxidation process.

2.2 Photocatalysis as an advance oxidation process

Photocatalysis or photocatalytic degradation is one of the pollutant degradation techniques known as advanced oxidative processes (AOPs). This processes also include some techniques such as Fenton's reagent oxidation, ultraviolet (UV) and H₂O₂ process are capable of degrading organic contaminants at ambient temperature and pressure [Hudgins & Robert, 1996]. The PCD process has been paid much attention because of its low energy consumption, simple operation, mild reaction conditions and no secondary pollution [Kenneke, 1993]. Titanium dioxide (TiO₂) that is used during the PCD process is a powerful photocatalyst that can break down many aqueous phase pollutants. When exposed to sunlight or artificial UV irradiation, it generates a pair of conduction band (CB) electron (e⁻) and a valence band (VB) hole (h⁺) in the solid oxide lattice, because of absorbing a photon with energy greater than 3.2 eV. The CB electrons and VB holes in TiO₂, are moderate reductants and strong oxidants respectively. This subsequently causes charges transfer at the interface that initiates various kinds of redox reactions. Therefore,

several studies have reported the effectiveness of TiO₂ as a photocatalyst for treating the organic and inorganic pollutant from water. Hence the photocatalytic destruction of organic and inorganic pollutants begins with TiO₂ excitation by suprabandgap photons, and continues through OH radical formation at the photocatalyst surface that eventually degrades the target pollutants.

2.3 Mechanism of TiO₂ as a photocatalyst under UV illumination

As briefly mentioned above, initial process for heterogeneous photocatalysis of organic and inorganic pollutants by semiconductors is the generation of electron-hole pairs in the semiconductor particles. The TiO₂ photo-catalyst normally absorbs photons with energy equal or higher than its band gap energy (<385nm) under UV illumination process. This delocalizes the valence electron and excites it to the conduction band of the semiconductor. These photo excited charge carriers can initiate the degradation of the adsorbed chemical species by one or more forms of electron transfer reactions. It is important that UV light source has sufficient high photon energy (proper wavelength) at the required intensity.

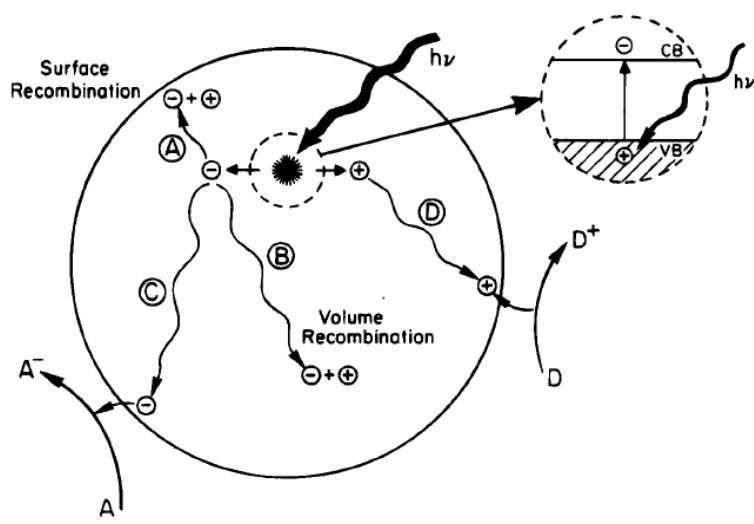


Figure 2.1: Schematic of photoexcitation in a semi conductor [Amy et al. 1995]

It is seen from Figure 2.1 that the photoinduced electron transfers to adsorbed organic or inorganic species or to the solvent from migration of electrons and holes to the semiconductor surface. Pathway C describes the surface of semiconductor can donate electrons to reduce an electron acceptor and pathway D focus that a hole can migrate to the surface where an electron from a donor species can combine with the surface hole oxidizing the donor species. Recombination of the separated electron and hole can occur in the volume of the semiconductor particle (pathway B) or on the surface (pathway A) with the release of heat [Amy et al. 1995].

2.4 Photocatalytic degradation of some pollutants

$\text{NH}_4^+/\text{NH}_3$ is a common aqueous phase pollutant of much concern. Considering this, the treatment of $\text{NH}_4^+/\text{NH}_3$ nitrogen in wastewater has been an active environmental engineering research area. For example, Bonsen et al. (1997) who investigated PCD of $\text{NH}_4^+/\text{NH}_3$ using TiO_2 , and UV lamp ($\lambda > 300 \text{ nm}$), found that no degradation takes place up to pH 7.2. It is noted that the pK value for ammonia is 9.26 [Sawyer et al., 2003]. $\text{NH}_4^+/\text{NH}_3$ speciation trends with respect to aqueous pH is given in figure 2.2. This specific notation has been used considering pH dependent speciation. Ogata et al. [1981] have investigated the pH effect of NH_3 degradation in the presence of H_2O_2 under irradiation and found that degradation of NH_3 was closely related to the dissociation equilibrium of NH_3 (pK_a 9.26). It was also found that the degradation trend was very slow at low pH, while the rapid degradation trend of NH_3 was seen as the pH of solution was increased from 8 to 10, and only slight degradation trend was observed for $\text{pH} > 10$, where most of the ammonia was unprotonated [Ogata et al. 1981]. Nevertheless, at pH values higher than 9.9 no further enhanced PCD was noticed. Furthermore, the authors

also found that the concentration of TiO₂ could be decreased to 0.05% (w/v) without any noticeable reduction in the degradation efficiency. On the other hand an increase of the TiO₂ concentration above 0.5% showed deposition of TiO₂ in the tubes. In another study, Sugiyama et al. [2009] found the PCD initiated removal rate of aqueous NH₄⁺/NH₃ increased with an increase in initial solution pH. It was also found from another study that ammonium ion was a significant reaction product at pH 3.4, whereas nitrite and nitrate were dominant at pH 11 which also indicates higher NH₄⁺/NH₃ oxidation at higher pH [Kim and Choi, 2002]. Schmelling and Gray [1995] also did not observe the PCD of ammonium to nitrate in TiO₂ suspension at pH 5. Moreover, no significant NH₄⁺/NH₃ PCD was observed even after 1000 min of UV illumination at pH of 5 and 9 [Malik, 2005]. The author however noted an enhanced degradation when the solution pH was raised to pH 11.

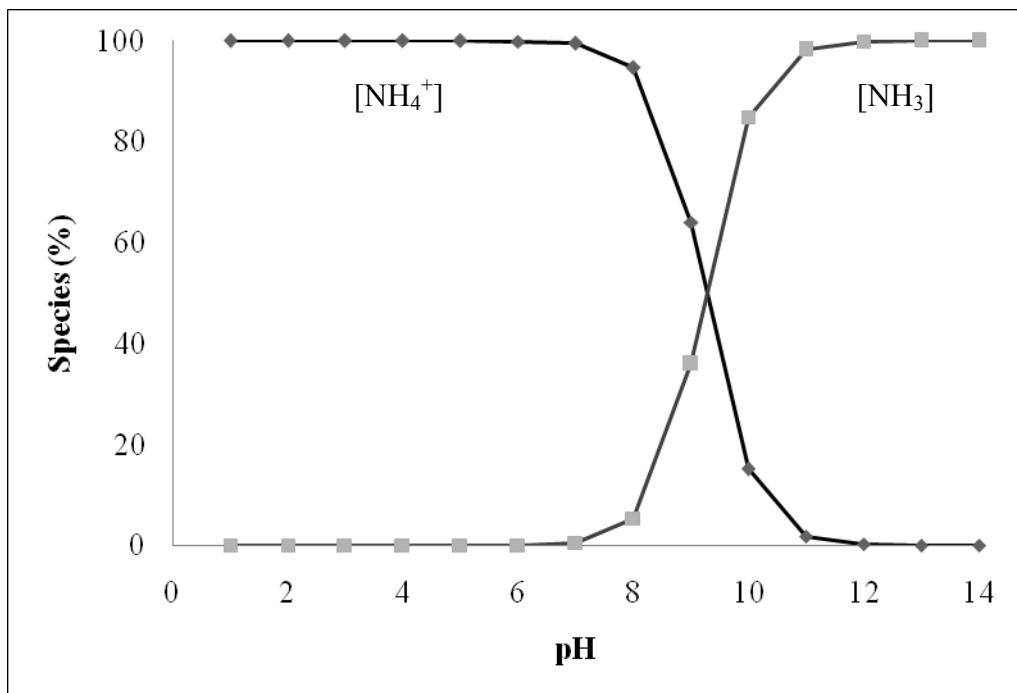


Figure 2.2: $\text{NH}_4^+/\text{NH}_3$ speciation trends with respect to pH

To further explore the PCD initiated removal of cationic pollutants, we quote example of tetramethyl ammonium (TMA) that depicts a sole case of recalcitrant organic cations whose surface interaction on TiO_2 surface is mostly electrostatic and direct electron transfer reactions on TiO_2 is insignificant. Vohra et al. [2003] investigated the PCD of TMA with surface fluorination of TiO_2 and found that PCD rate was decreased at pH 3 and increased at pH 5 and 7. Basically, the preferential formation of free OH radicals on F– TiO_2 is the main cause of increased photoreactivity [Minero et. al., 2000]. However, Kim and Choi [2002] who investigated photocatalytic degradation of TMA both at high and low pH, noted no significant adsorption of cation TMA onto TiO_2 surface. They suggested that the photocatalytic degradation of TMA was initiated by free OH radicals.

Several cationic dyes are also widely used for different industrial applications, and effluents from textile, leather, food processing, dyeing, cosmetics, paper, and dye manufacturing industries are significant sources of dye pollution. From an environmental point of view, the removal of synthetic dyes is of great concern, since some dyes and their degradation products may be carcinogens and toxic. Among the different type of dyes, methylene blue (MB) is one of the major pollutants in dying industries. MB and its break down products are generally toxic for living organisms. Therefore, decolourisation of MB is an important aspect of wastewater treatment before discharge into the water. It is difficult to remove MB from the respective effluent using conventional wastewater treatment systems, because it is hard to degrade using bio-degradation alone [Kannan et al., 2001]. Hasnath et al. [2005] have investigated the PCD of MB under visible light and found its concentration decreases gradually causing degradation at pH 9.5. Like most semiconductors the photocatalytic nature of TiO_2 is pH dependent because of its

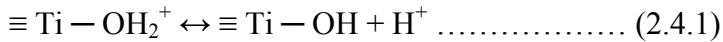
amphoteric nature. Hence at higher pH electrostatic interactions between the negative TiO_2 surface and MB cations lead to strong adsorption that enhances degradation rate as well. Therefore it can be said that once MB is adsorbed onto TiO_2 , it then readily degrades photocatalytically. However, only little degradation was obtained under visible light illumination in the acidic solutions. In the acidic pH ($\text{pH} < 6.8$) there was a poor MB adsorption, because the TiO_2 surface and MB were both positively charged in the acidic media. Therefore, decrease in pH causes decrease in degradation rate. Same was observed by Lakshmi et al. [1995] during the investigation of TiO_2 -mediated PCD of MB. They also found that the rate increased with an increase in pH, exhibiting a maximum around pH 6.9-8.0. The observed increase in the rate of the photocatalytic degradation of MB with an increase in pH seem to indicate that surface property of TiO_2 plays a significant role in PCD of cationic dye. Thus the pH dependent acid-base property of the metal oxide surface has a considerable influence on the photocatalytic activity.

2.5 Surface modification of photocatalyst TiO_2

One of the most active fields in using TiO_2 as a photocatalyst is the development of a system capable to degrade a large number of organic and inorganic contaminants in wastewater under UV light. As mentioned earlier the overall photocatalytic performance of a particular semiconductor is measured by several factors including stability of the semiconductor under illumination, the efficiency of the photocatalytic process, the wavelength range, pH, and the surface modification. Besides these, two important parameters like specific surface area (SSA) and surface charge also determine the photoactivity of catalysts. SSA increases due to surface modification of catalyst and a higher SSA exhibits a higher PCD rate because of more substrate-adsorption sites

availability [Vohra et al., 2005]. Three benefits noted because of TiO₂ surface modification in a PCD system include (1) reduced e⁻ / h⁺ recombination by increased charge separation during the photocatalytic process; (2) increased wavelength response range (i.e. excitation of wide band gap semiconductors by visible light); and (3) changed selectivity or yield of a particular product [Amy et al., 1995]. All these advantages ultimately assist to achieve a higher degradation rate.

The modification of surface charge of TiO₂ influences the photocatalytic reactivity for ionic substrates by altering the electrostatic interaction between the catalyst surface and the substrate [Choi, 2006]. The surface charge on TiO₂ in pure water results from the pH-dependent speciation of surface hydroxyl group. The following reactions describe how does TiO₂ reacts in pure water.



It has been reported that the point of zero charge of Degussa P25 TiO₂ is 6.5 [Park & Choi, 2005, Vohra et al., 2005]. Therefore, the surface charge of plain TiO₂ is positive at pH ≤ 6.5 due to presence of $\equiv \text{Ti} - \text{OH}_2^+$ groups and dominantly negative at pH ≥ 6.5 owing to $\equiv \text{Ti} - \text{O}^-$ groups [Choi, 2006, Vohra et al., 2005]. However, the zeta potential of TiO₂ particles can vary with surface modification. For example zeta potential of Degussa P25 TiO₂ shifted to more acidic values with the addition of Nafion. The negative shift of zeta potential was larger at higher Nafion concentration. It indicates to the fact that the anionic sulfonate groups (SO₃⁻) in the Nafion layer outnumber the positively charged surface functional groups on TiO₂ ($\equiv \text{TiOH}_2^+$). On the Nafion-coated TiO₂ film,

the side chains ($-\text{CF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2-\text{SO}_3^-$) of Nafion is attached to the surface of TiO_2 using the hydrophobic backbone ($-(\text{CF}_2\text{CF}_2)_n-\text{CFCF}_2-$) [Wang & Ku, 2007]. The surface charge of TiO_2 modified by Nafion directly influences the electrostatic interaction between charged substrates and the catalyst surface i.e., negatively charged molecules would be repelled from the surface of Nf/TiO_2 , whereas positively charged species are attracted [Park & Choi, 2005]. Chen et al. [2010] have investigated the photocatalytic degradation of Victoria Blue R (VBR) using Nafion modified TiO_2 and found that attachment of the anions to the TiO_2 surface using the Nafion-coated- TiO_2 results in increased degradation of the cationic dye. Their results indicate that the Nafion- TiO_2 surface is negatively charged, and the VBR adsorbs onto the Nafion- TiO_2 surface through the positive ammonium groups. The most important finding from this literature is that though at a certain coating of Nafion onto Degussa TiO_2 results in maximum removal efficiency of cationic dye, further coating of Nafion onto TiO_2 reduced photocatalytic degradation. It is due to the fact that excess coating of Nafion decreased adsorption and produce a hydrophobic surface. The presence of the optimum Nafion deposits led to a positive effect on the removal rate. From literature review the following advantages can be listed for Nf-TiO_2 :

- Nafion is chemically inert in both oxidative and reductive environments, even under UV illumination [Vohra et al., 2001; Choi et al., 2005; Park & Choi, 2005].
- Nafion- TiO_2 promotes the photocatalysis of several pollutants such as paraquat [Vohra & Tanaka, 2001; Park & Choi, 2005; Choi, 2006].

The modification of TiO_2 with silica also changes the surface charge characteristics and yields higher specific surface area. An increased surface area causes an enhanced

adsorption which ultimately leads to rapid degradation of substrate under UV or visible light. Silica loading onto TiO₂ surface causes the surface highly negative which was confirmed by Vohra et al. [2005]. They found that zeta potential of Si-TiO₂ significantly shifted to lower pH which leads to more negative surface charge of Si-TiO₂ than the pure TiO₂ over the given pH range. It was also found by them that the negative charge density on Si-TiO₂ surface was saturated above pH 7. Beside this, the loading of silica on TiO₂ may also have influence on the band gap transition. For example significant blue shift of absorption edge in the diffuse reflectance UV spectra of Si-TiO₂ samples was observed with increasing silica content [Liu & Davis, 1994].

Tada et al. [1998] have also studied the use of silica-coated TiO₂ (Si-TiO₂) as photocatalyst during PCD of cetylpyridinium bromide and rhodamine 6G (R-6G). They noted increased electrostatic interactions between the anionic catalyst surface and the cationic substrate moieties which lead to an enhanced PCD. Anderson and Bard [1997] found in their study that Si-TiO₂ catalyst yields higher PCD rates only for the cationic pollutants and no such increase results for neutral or anionic species, which is different from the other mixed-oxides studies. Typically the silica coating causes an increased TiO₂ surface area because SiO₂ surface is more porous than the plain TiO₂ which leads to an enhanced adsorbing capacity of substrate moieties and hence yields higher degradation rates [Vohra & Tanaka, 2003]. Moreover, Si-TiO₂ also accelerated the PCD of neutral substrate like trichloroethylene during its PCD, which was ascribed to enhanced surface OH group density and reduced bulk defects [Jung & Park, 2001]. It is noted that the increasing rate of SSA is related to the addition of silica or Nafion content. Table 1 shows that the increasing rate of SSA is high at a specific content of silica per gm of TiO₂ and

further addition of silica, the rising trend of SSA remain stable [Vohra and Tanaka, 2003]. As mentioned previously that $\text{NH}_4^+/\text{NH}_3$ degradation and removal from respective wastewater is typically required for environmental protection. The present study investigated the use of Nf-TiO₂ and Si-TiO₂ specifically for the PCD of $\text{NH}_4^+/\text{NH}_3$. To the best of our knowledge no detailed investigation on said topic has yet been reported. However, it was evident from the above given literature review that photocatalytic degradation of several aqueous pollutants using modified TiO₂ photocatalyst yields better substrate removal. Considering this, the present work intends to explore the photocatalytic degradation of aqueous phase $\text{NH}_4^+/\text{NH}_3$ using surface modified catalysts. The PCD of cyanide and MB has also been briefly studied.

Table 1: Specific surface area (SSA) values for $\text{SiO}_2\text{--TiO}_2$ [Vohra and Tanaka, 2003]

SiO_2 (g/g TiO_2)	SSA (m^2/g)
0.000	14.9
0.012	14.4
0.060	24.7
0.120	32.9
0.190	39.0
0.240	42.9

CHAPTER 3

3. Research Objectives

It was attempted to examine a number of variables, which can affect the photocatalytic activity of surface modified TiO₂ during PCD of aqueous phase NH₄⁺/NH₃. Some specific objectives of this research work are provided below:

- To investigate the effect of modifying TiO₂ using Nf-TiO₂ and Si-TiO₂ on the removal of NH₄⁺/NH₃
- To optimize the above mentioned ammonia removal using Nafion and silica amount, pH, and NH₄⁺/NH₃ concentration as the variables
- To study the mass removal efficiency of NH₄⁺/NH₃
- To study NH₄⁺/NH₃ removal in presence of co-pollutant cyanide
- To study the PCD of methylene blue using modified TiO₂

CHAPTER 4

4. Methodology & Description of Research

4.1 Chemical, Materials and Equipments

The following reagent-grade chemicals were used for the research: TiO₂ (Degussa P25), NH₄Cl, HClO₄, NaOH, HCl, NaCN (Sodium Cyanide), Nafion (perfluorinated ion-exchange resin), organic silica solution, methylene blue (MB).

Some basic materials and equipment which were used in this research work included: Magnetic stirrer, 15W UV lamp, 0.2-μm filter papers, pH meter, ion selective electrodes, furnace, TOC analyzer (Shimadzu, Japan), UV-vis spectrophotometer (Shimadzu Japan) etc. All PCD experiments were carried out using a Pyrex-glass batch type reactor (30 cm long and 7 cm dia), holding 1000 ml of the synthetic wastewater sample with plain and modified TiO₂. Figure 4.1 presents the schematic view of experimental setup. A 15W black light lamp was used as a UV light source. Aluminium foil was also used for protecting the reactor from external light source. Samples were collected through the specific sampling port. Aerated deionized water was used throughout the study.

4.2 Experimental Procedure

The nafion-coated TiO₂ (Nf-TiO₂) samples were prepared by adding the desired amount of Nafion solution to 1gm of TiO₂ powder with rigorous mixing and to ensure a homogeneous coating of Nafion onto TiO₂. After being mixed manually, the mixture was dried overnight at room temperature. No further treatment of Nf-TiO₂ sample was followed. The silica-coated TiO₂ (Si-TiO₂) sample were also prepared by adding the

desired amount of silica solution to 1 gm of TiO₂ powder with appropriate mixing to ensure a homogeneous silica coating on the surface of TiO₂. After the mixture the modified photocatalyst was air dried overnight, the sample was calcined at 700°C for 5 hrs and then crushed to powder form. For the photocatalytic degradation experiments, pure TiO₂, Nf-TiO₂, and Si-TiO₂ were used as photocatalyst.

Synthetic wastewater was prepared using various concentrations of target pollutants. 1 gm of TiO₂ which was suspended in 1 L of synthetic wastewater sample, and the initial pH value of synthetic wastewater was then adjusted to the desired value. The pH was adjusted using HClO₄ and NaOH as needed. The solution was then stirred for 30 min by magnetic stirrer for adsorption-desorption equilibrium to be reached. For all experiments, two blank samples were collected. The first sample was collected before the addition of TiO₂ and pH adjustment and the other one was collected after the addition of catalyst and pH adjustment. The first sample provided the initial concentration of target species and second one indicated the possible adsorption of target pollutant. The synthetic wastewater was transferred into the reactor after the addition of TiO₂ and pH adjustment and the UV light was then turned on. A 15 W black light lamp was used as the UV light source with wave length peak at 352 nm. The lamp was positioned at the centre of the reactor and separated from the synthetic wastewater using a glass sleeve. This glass sleeve was inserted into the reactor through a female-joint that helped to secure it. This arrangement also covered the top of reactor, except the sampling port. After turning on the lamp with continuous stirring, samples were collected at specific time interval. Each sample collected from the port of the reactor was filtered using 0.2µm filter paper. Finally the respective sample was analyzed for the specific pollutants.

The $\text{NH}_4^+/\text{NH}_3$ concentration was measured by Orion ammonium electrode. On the other hand, the MB concentration was obtained using UV-visible spectrophotometer (Shimadzu) and measuring absorbance at 664 nm (λ max). Cyanide was analyzed using Orion cyanide electrode.

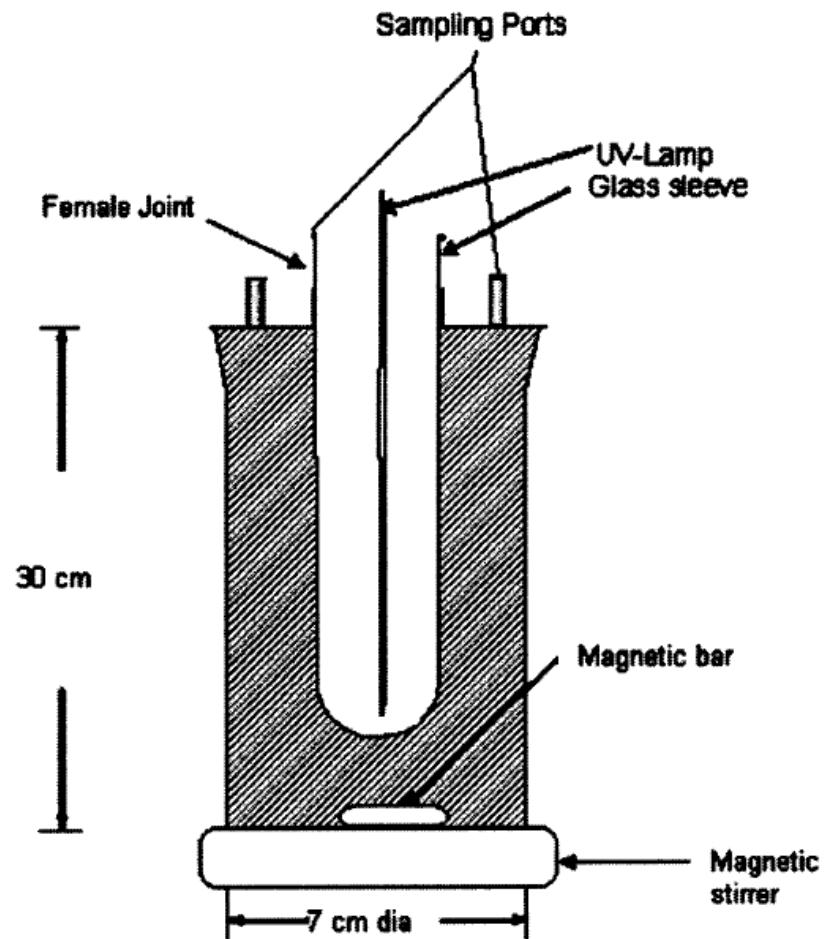


Figure 4.1: Layout of the photoreactor

CHAPTER 5

5. Results and discussion

5.1 PCD of $\text{NH}_4^+/\text{NH}_3$ with plain TiO_2

The solution pH has a dominant effect on the photocatalytic reaction efficiency because of many properties, such as the semiconductor's surface charge state, the flat-band potential, and the speciation of $\text{NH}_4^+/\text{NH}_3$, are all strongly pH dependent. Figure 5.1 illustrates the photocatalytic degradation of $\text{NH}_4^+/\text{NH}_3$ as a function of pH. The experiment was conducted at two different pH values and the initial concentration of $\text{NH}_4^+/\text{NH}_3$ was 10 ppm. The results show only 20% $\text{NH}_4^+/\text{NH}_3$ removal at pH 10 after 6 hour illumination. However an increase in $\text{NH}_4^+/\text{NH}_3$ removal is noted at pH 12 amounting to more than 40% at 6 hour period which is higher than the PCD of $\text{NH}_4^+/\text{NH}_3$ at pH 10. From figure 5.1, 5% $\text{NH}_4^+/\text{NH}_3$ adsorption is seen at time zero. It was previously discussed that dominant species will be NH_3 at pH 12, and hence it cannot expect significant electrostatic attraction at that pH 12. The higher PCD rate at pH 12 can be ascribed to high OH^- ions concentration, that generates OH^\bullet radical.

It was also conducted an experiment in absence of UV/ TiO_2 as well to make sure that the loss of $\text{NH}_4^+/\text{NH}_3$ as noted in Fig 5.1, because of PCD, and not for simple stirring. The respective results are given n Figure 5.2. It is clear that even at 24 hr, no significant decrease in $\text{NH}_4^+/\text{NH}_3$ is noted. Hence it can be said that $\text{NH}_4^+/\text{NH}_3$ removal in Figure 5.1 is because of PCD. However, the initial $\text{NH}_4^+/\text{NH}_3$ adsorptions for pH 10 and 12 were same amounting to near about 5% (Figure 5.1). The adsorption of $\text{NH}_4^+/\text{NH}_3$ on TiO_2 could also result from other mechanism rather than electrostatic attraction such as

specific bonding [Hoofmann et al., 1995]. It was found by Linsebigler [1995] that the surface of TiO₂ first adsorbed the ammonium ion which dissociated to produce NH₃ species and followed by desorption of end products N₂ and H₂.

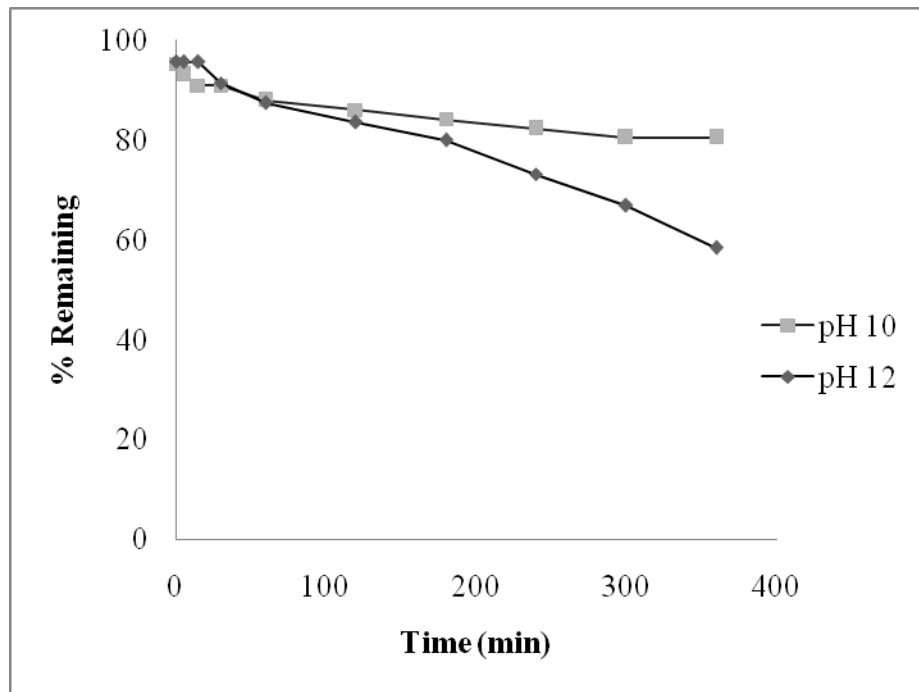


Figure 5.1: Effect of pH during PCD of $\text{NH}_4^+/\text{NH}_3$ with plain TiO_2

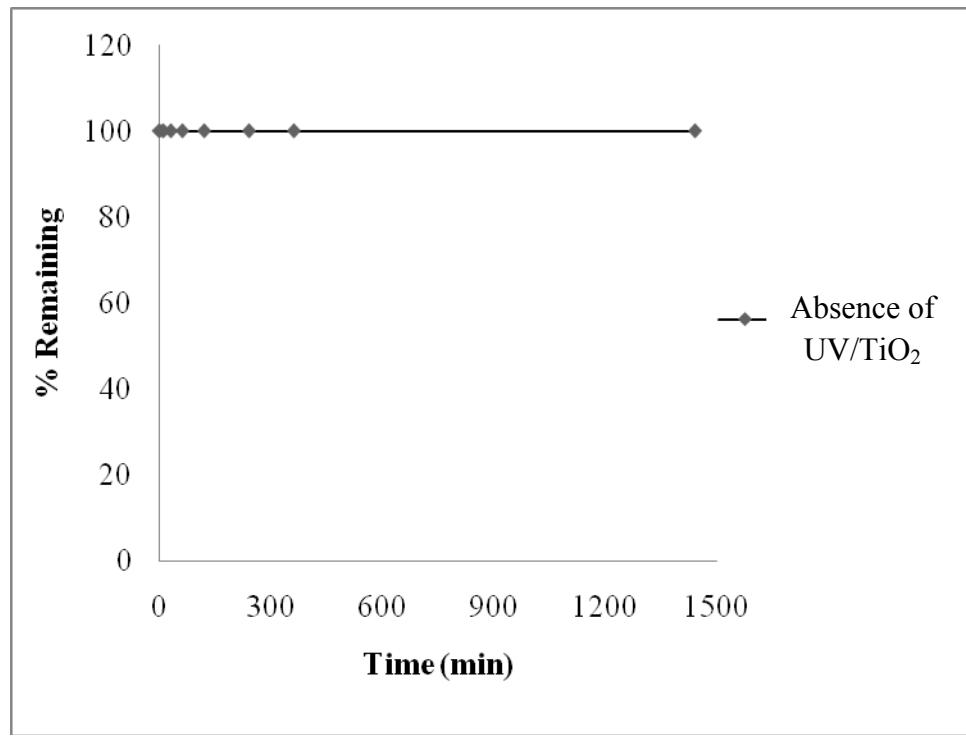


Figure 5.2: PCD of $\text{NH}_4^+/\text{NH}_3$ in absence of UV/TiO₂ at pH 12

5. 2 PCD of NH₄⁺/NH₃ using Nafion modifiedTiO₂

The PCD initiated NH₄⁺/NH₃ removal trends using Nafion modified TiO₂ at different pH values are given in Figures 5.3, 5.4, and 5.5. It is clear from the Figure 5.3 and 5.4 that Nf-TiO₂ is more efficient catalyst compared to plain TiO₂ at pH 10 and pH 12. Furthermore the Nf-TiO₂ also shows two distinct pH dependent trends (Figure 5.5). This is similar to what was observed previously for pH effect on NH₄⁺/NH₃ PCD using plain TiO₂. The Nf-TiO₂ results show higher removal efficiency for pH 12 than pH 10. Nevertheless, Nafion modified TiO₂ is an efficient catalyst in comparison to plain TiO₂ with removal efficiency about 65% at pH 12. On the other hand, the removal efficiency of NH₄⁺/NH₃ at 6 hr period for Nafion modified TiO₂ at pH 10 is 37% which is nearly twice of plain TiO₂. These results indicate that surface modification of photocatalyst TiO₂ with Nafion increased the substrate PCD rate. It is also seen that the overall PCD of NH₄⁺/NH₃ at pH 12 from 5 minute to 120 minute is higher than the respective later portion of PCD trend.

It was expected that the electrostatic interaction between the cationic NH₄⁺/NH₃ species and charged catalyst surface will be important as also indicated for tetramethylammonium (TMA) by Park and Choi investigation [2005]. The experimental results agree with this statement, i.e., the initial NH₄⁺/NH₃ adsorption is high for Nf-TiO₂ which is also expected to increase the removal efficiency of NH₄⁺/NH₃. Nevertheless, the initial adsorption for pH 10 is high as compared to pH 12 which indicates the specific adsorption of cationic species NH₄ on the respective TiO₂ sites is high at low pH value. This observation is in lies with NH₄⁺/NH₃ speciation and TiO₂ surface charge which will be negative at pH above 6.5. The PCD results at pH 10 and pH 12 somehow negate the

effect of adsorption onto PCD of $\text{NH}_4^+/\text{NH}_3$. However the concentration of OH^- ions, the precursor OH radicals, would also increase with an increase in pH [Wei & Wan, 1991]. This would possibly explain the noted discrepancy between initial adsorption and PCD trends at pH 10 and 12.

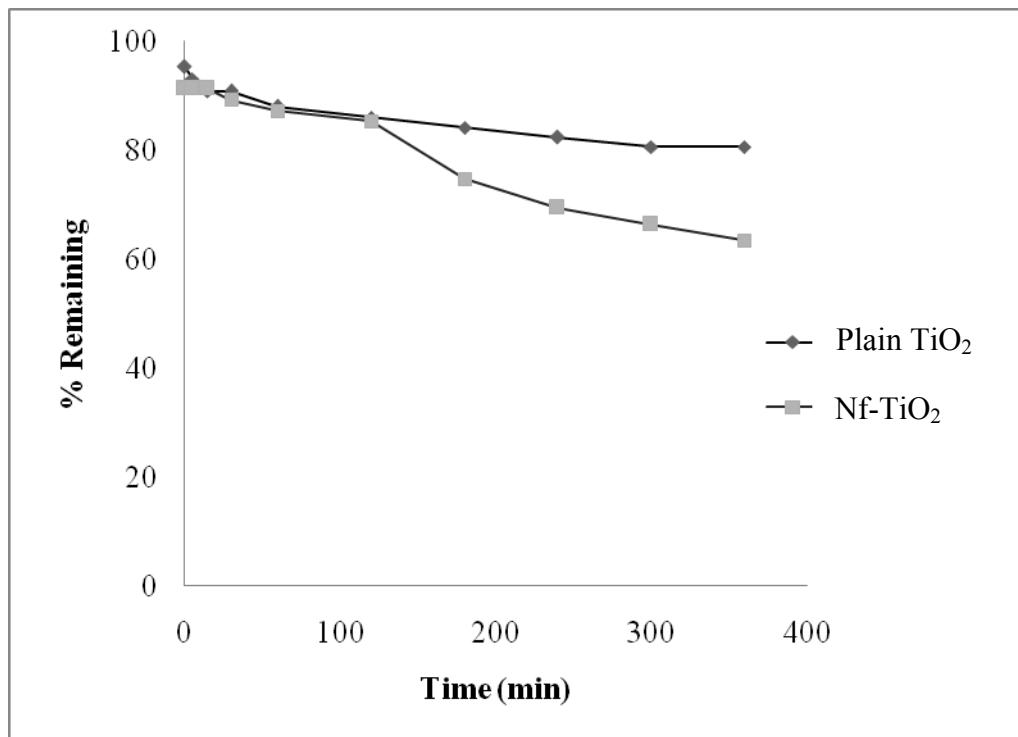


Figure 5.3: PCD of 10 ppm NH₄⁺/NH₃ using plain and Nf-TiO₂ at pH 10

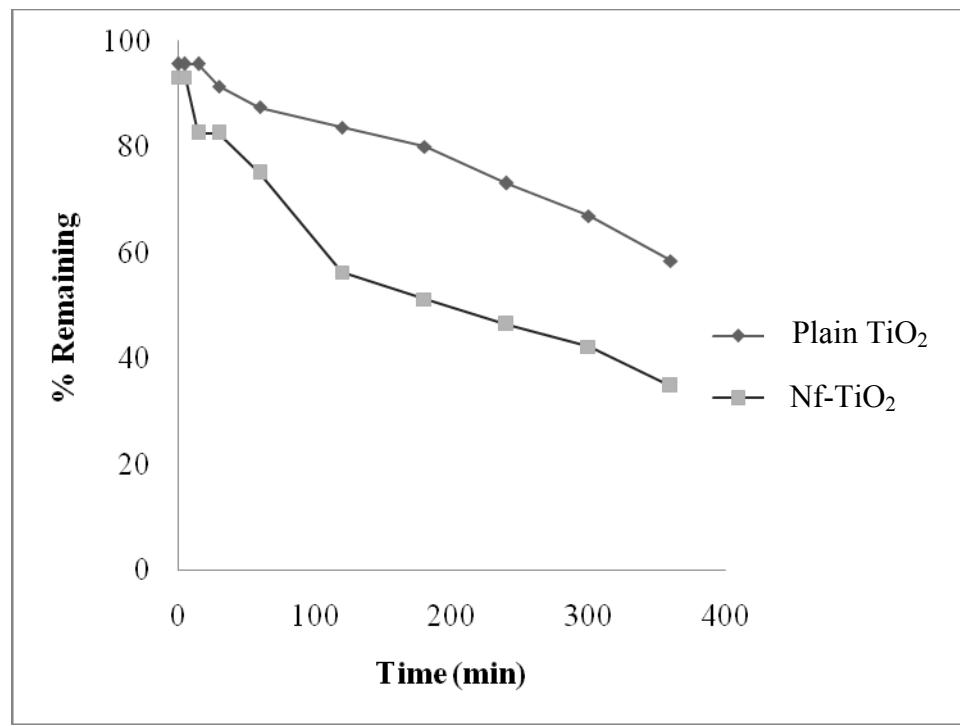


Figure 5.4: PCD of 10 ppm $\text{NH}_4^+/\text{NH}_3$ using plain and Nf- TiO_2 at pH 12

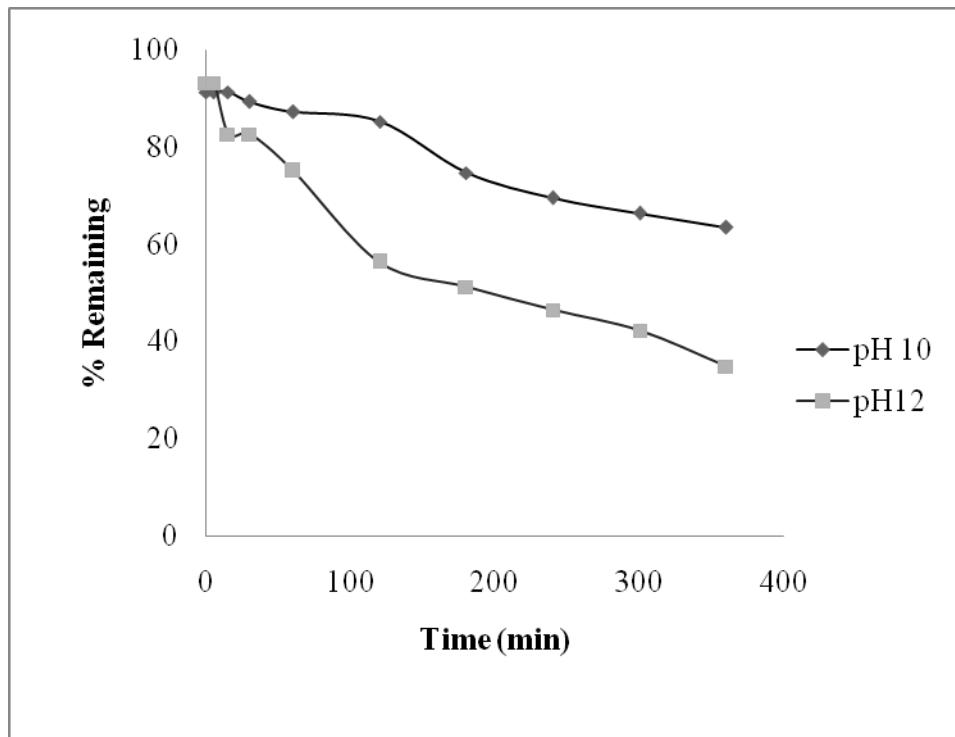


Figure 5.5: PCD of 10 ppm NH₄⁺/NH₃ using Nf-TiO₂: pH effect

Four different ratio of Nafion to TiO_2 , were further investigated at pH 12 to find the optimum Nafion amount for getting maximum removal efficiency of $\text{NH}_4^+/\text{NH}_3$. The respective results are provided in Figures 5.6 to 5.10. It is seen that the higher Nf- TiO_2 efficiency is noted at any content of Nafion. Typically the specific surface area (SSA) values increase due to surface modification of catalyst and higher SSA exhibits higher PCD rate because more substrate-adsorption sites would be available onto the photocatalyst surface [Vohra et. al., 2005]. Furthermore the surface modification of TiO_2 with Nafion has also been reported to increase the SSA [Lee et al., 2005]. It was also stated Lee et al. (2005) that the sulfonate groups in the Nafon coating induce highly negatively surface charges on TiO_2 which enable the accumulation of cationic species within the Nafion matrix. Though Nf- TiO_2 shows somewhat higher $\text{NH}_4^+/\text{NH}_3$ adsorption but the difference is not large. The adsorption analysis shows less than 10% $\text{NH}_4^+/\text{NH}_3$ was adsorbed at any ratio of Nafion- TiO_2 and plain TiO_2 . Another possible argument that can be explained higher $\text{NH}_4^+/\text{NH}_3$ removal using Nf- TiO_2 could be adsorption, followed by degradation, followed by desorption of reaction by products. Such a reaction dynamics may tend to cause faster $\text{NH}_4^+/\text{NH}_3$ PCD using Nf- TiO_2 , as noted 5.6 to 5.9.

Upon adding Nafion to the aqueous suspension, zeta potential becomes negative over the entire pH range and the negative shift in zeta potential of TiO_2 is larger at higher Nafion concentration [Park and Choi, 2005]. It was previously discussed that the point of zero potential (pH_{zpc}) of plain TiO_2 is 6.5 while that Nafion modified TiO_2 shows a negative value of zeta potential under both typical acidic or alkaline solution that means pH_{zpc} for Nafion modified TiO_2 is always negative [Lee et al., 2005]. Hence protons should be

more concentrated at the catalyst/water interface to counterbalance the negative surface charge.

Figure 5.10 shows that ratio of 1:1 i.e., 1 ml Nafion per gm of TiO₂ maximized the PCD of NH₄⁺/NH₃ which makes up approximately 70% removal efficiency after 6 hour illumination. It may be possible that the pH in Nafion internal channel is much lower than the pH in aqueous bulk phase. This may alter the micro dynamics of NH₄⁺/NH₃ and surface speciation causing enhanced ammonia removal at bulk pH of 12. However, a higher removal efficiency amounting near about 50% also found for least amount of Nafion (0.1 ml Nafion per gm of TiO₂) than plain TiO₂. A larger ratio of Nafion-TiO₂ (2ml Nafion per gm of TiO₂) was also investigated during this study and found to have less removal efficiency in comparison to the 1ml of Nafion per gm of TiO₂. In summary, Nf-TiO₂ modification resulted in a better increase in overall NH₄⁺/NH₃ removal, compared to plain TiO₂.

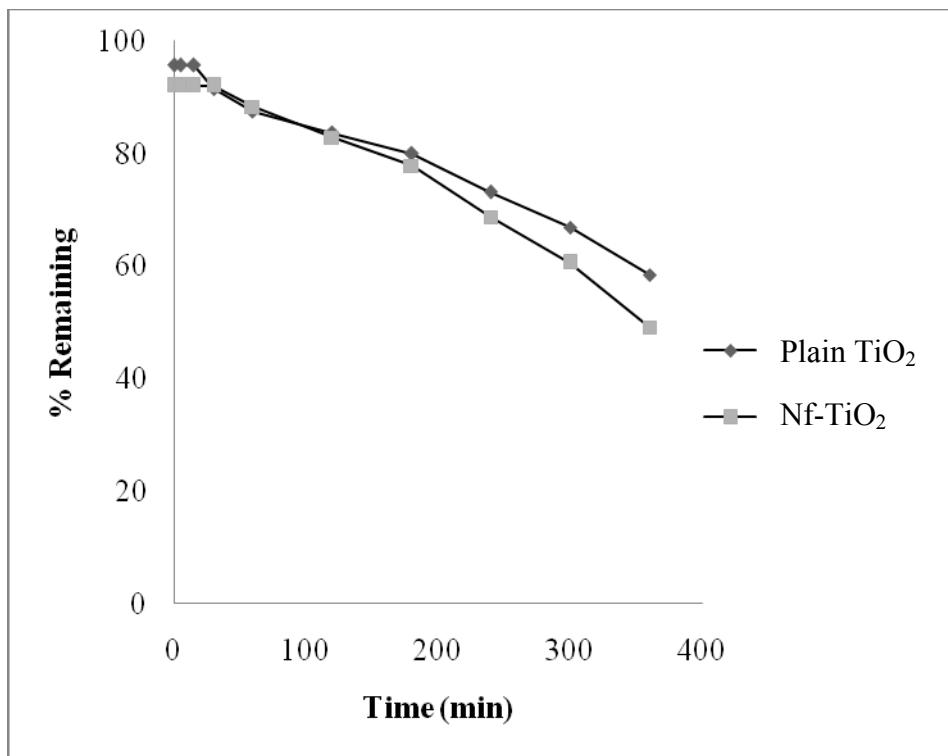


Figure 5.6: PCD of 10 ppm NH₄⁺/NH₃ using Plain and Nf-TiO₂ (0.1ml:1gm) at pH 12

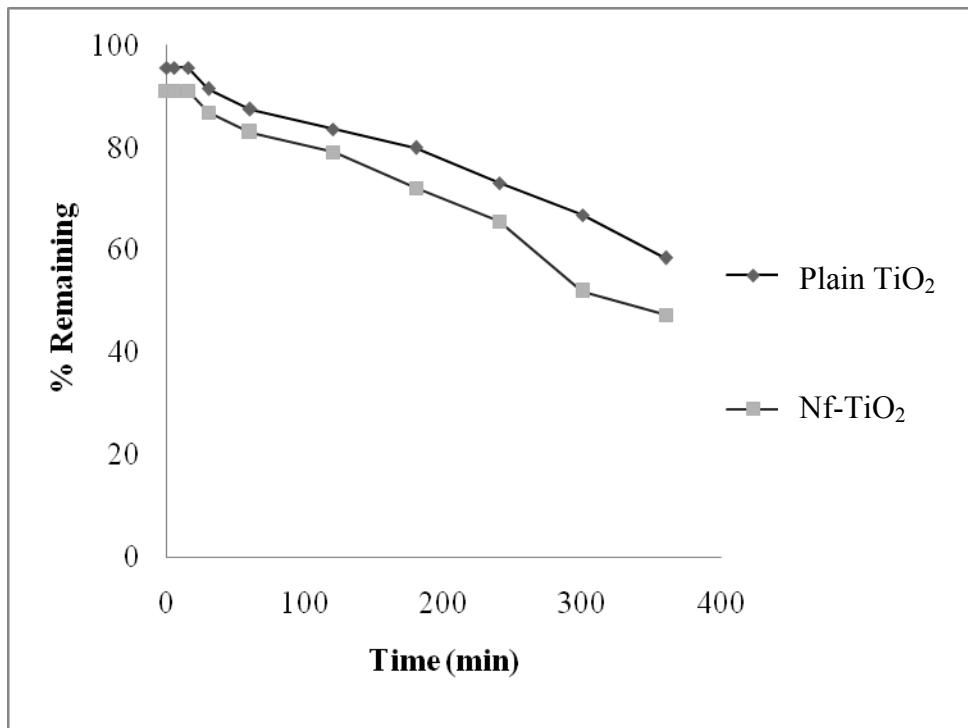


Figure 5.7: PCD of 10 ppm $\text{NH}_4^+/\text{NH}_3$ using Plain and Nf- TiO_2 (0.75ml:1gm) at pH 12

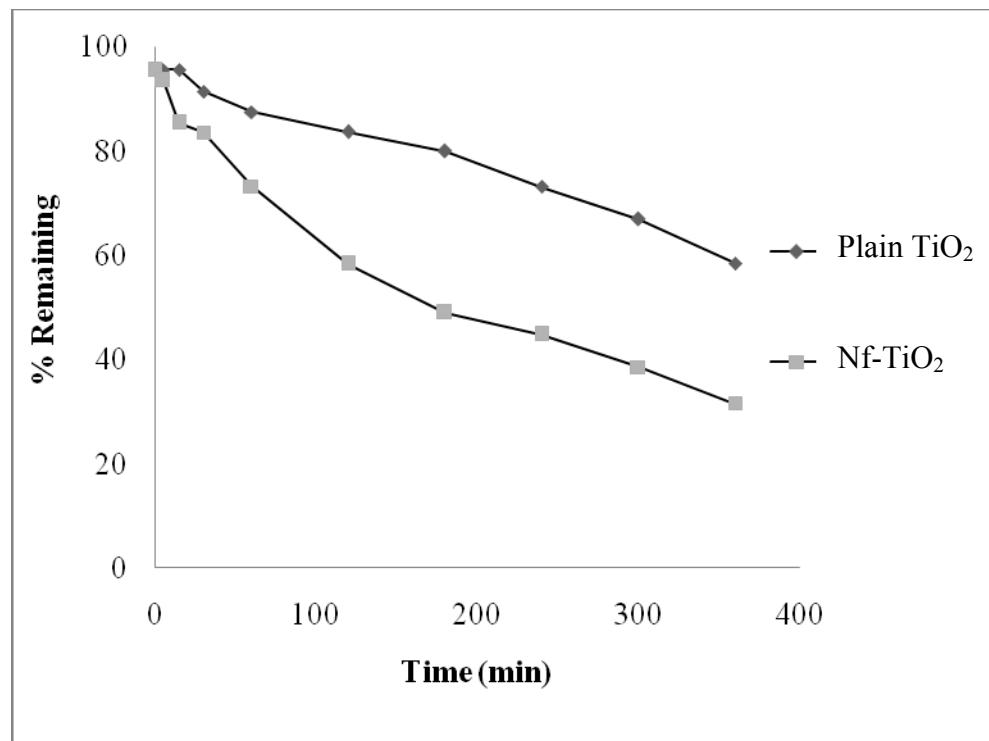


Figure 5.8: PCD of 10 ppm NH₄⁺/NH₃ using Plain and Nf-TiO₂ (1ml:1gm) at pH 12

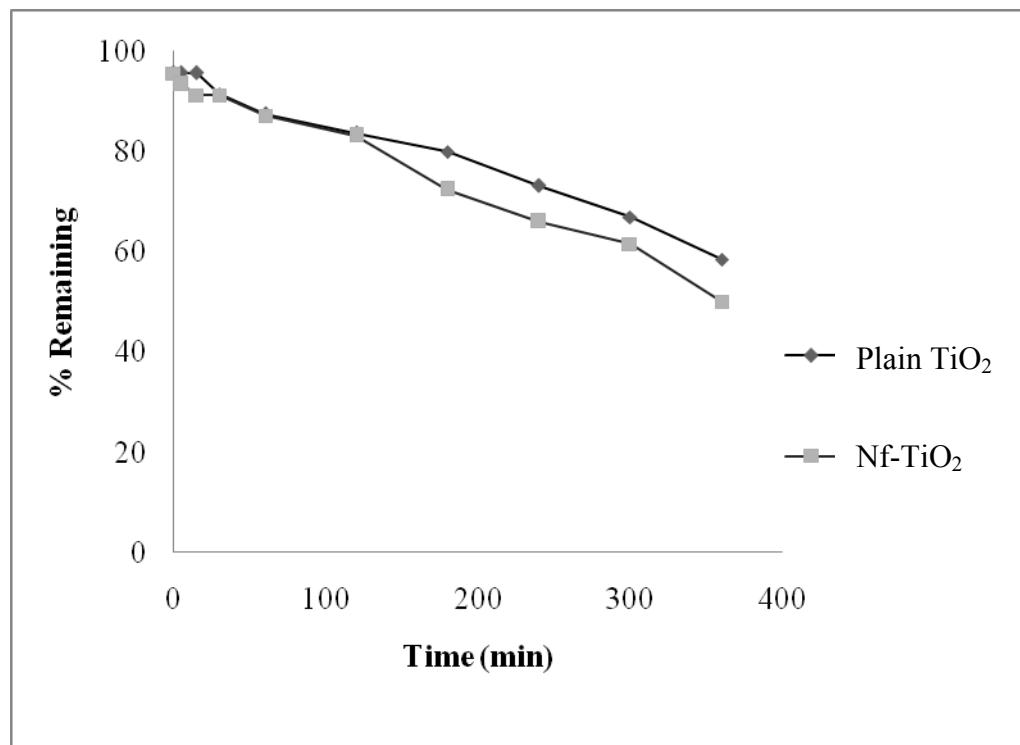


Figure 5.9: PCD of 10 ppm $\text{NH}_4^+/\text{NH}_3$ using Plain and Nf- TiO_2 (2ml:1gm) at pH 12

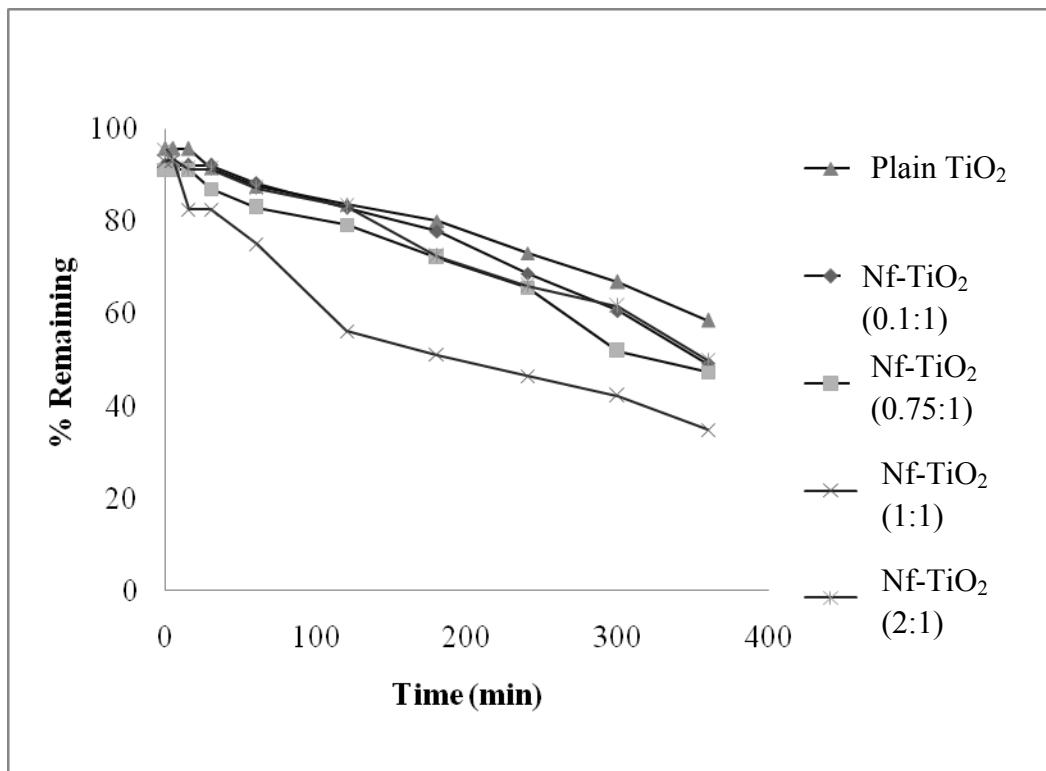


Figure 5.10: PCD of 10 ppm $\text{NH}_4^+/\text{NH}_3$ at pH 12: Effect of Nafion

5.3 PCD of $\text{NH}_4^+/\text{NH}_3$ using Silica modified TiO_2

The effect of silica coating on the overall $\text{NH}_4^+/\text{NH}_3$ degradation trend was also investigated to get the optimum ratio of silica- TiO_2 . The pertinent results are given in Figure 5.11 to 5.13. The results show that the silica content of 0.5 ml/g TiO_2 gives optimum $\text{NH}_4^+/\text{NH}_3$ degradation in comparison to the 0.25 ml and 1ml of silica per gm of TiO_2 though the difference is minimal. It has been suggested that silica modified TiO_2 enhances the charge separation efficiency by providing electron/hole trap sites to accelerate the mineralization rates which agrees with previous study [Ding et al., 2000]. The author also suggest that the addition of silica to titania prevented the agglomeration of nano-sized anatase particles while producing larger surface area and higher photoreactivity. However, the PCD trend after 6 hr for all Si- TiO_2 samples is almost the same. As previously discussed that SSA is an important characteristic for the increased rate of PCD; nevertheless increase in SSA reduces at higher silica contents, which probably consequences of possible particle agglomeration [Vohra et al., 2005]. Thus the degradation trends are stabilized at high silica content.

It is also found from the Figure 5.14 that initial percent removal of ammonia at time zero, is low for silica modified TiO_2 (0.25:1 and 1:1) as compared to 0.5:1 silica/ TiO_2 . A major portion of ammonia was adsorbed at zero minute amounting approximately 13% for the 0.5 ml silica content per gm of TiO_2 sample. It was discussed in literature section that the SSA increasing trend was found maximum at specific content of silica addition. Therefore it can be said 0.5 ml silica per gm of TiO_2 gives the more adsorption which lead better removal performance of $\text{NH}_4^+/\text{NH}_3$. The surface modification of TiO_2 by silica can also promote the adsorption of ammonia pollutants through changing the

surface charge characteristics of plain TiO₂ which in turn increases the initial adsorption (at zero minute illumination). These results suggest that the availability of enough surface adsorption sites at the Si-TiO₂ (0.5:1) results in faster substrate adsorption initiated uptake at time zero. However, it is important to note that in large scale system excess TiO₂ suspended in the aqueous solution could cause a shielding effect on the light. As most previous PCD investigations were conducted in a small-volume reactor, they did not encounter this problem [Fox and Dulay, 1993]. However this point should be considered while designing large scale systems.

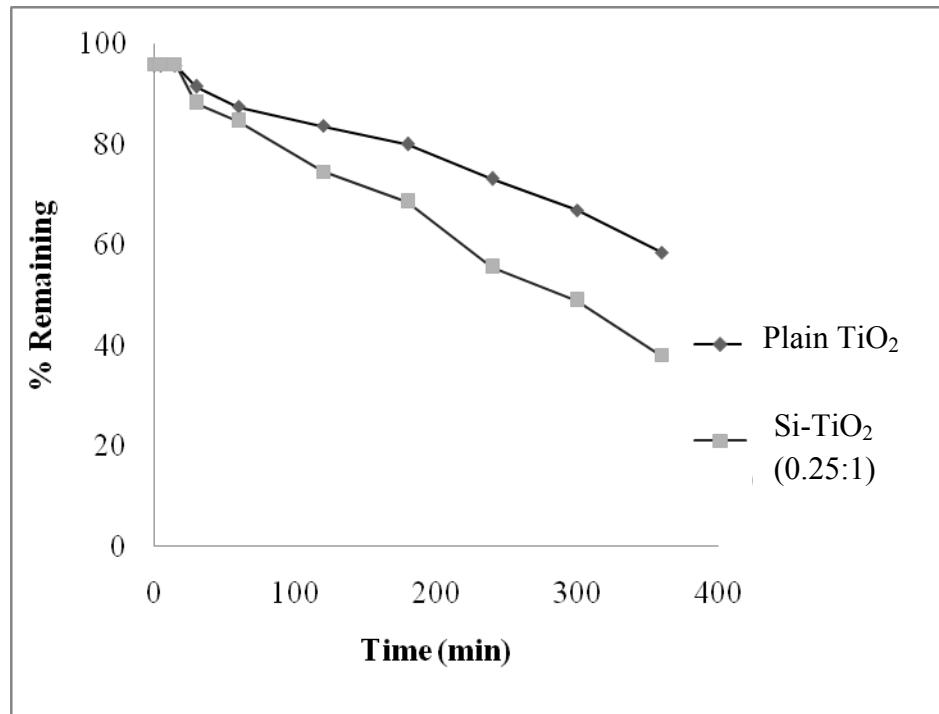


Figure 5.11: PCD of NH₄⁺/NH₃ using plain and Si-TiO₂ (0.25ml:1gm) at pH 12

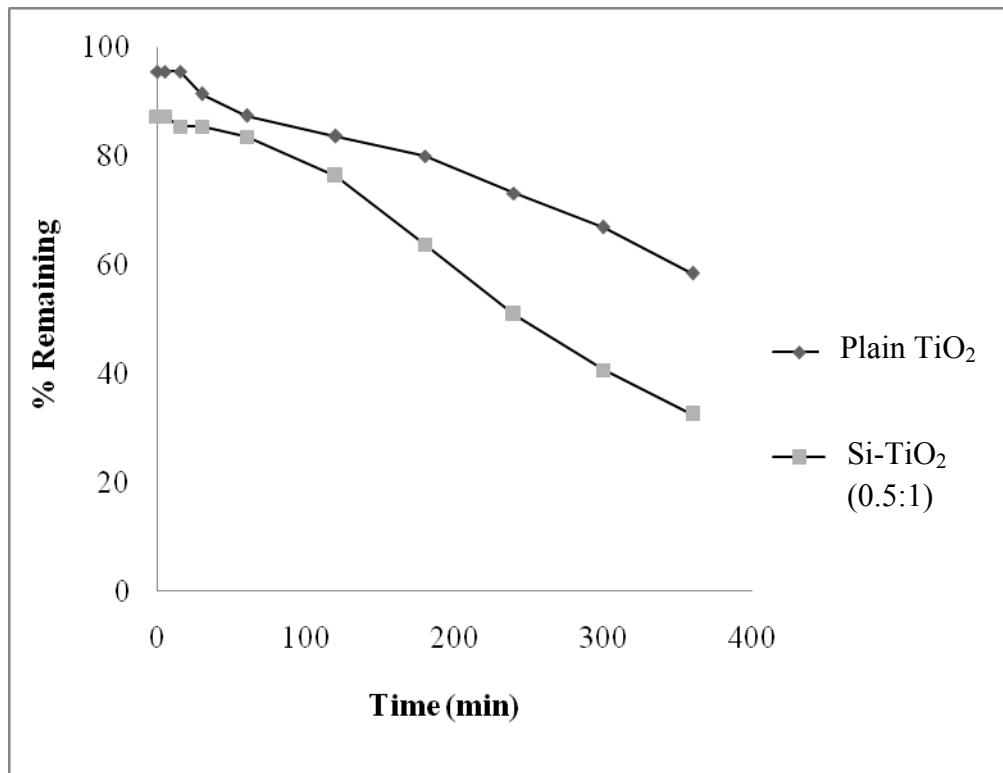


Figure 5.12: PCD of NH₄⁺/NH₃ using plain and Si-TiO₂ (0.5ml:1gm) at pH 12

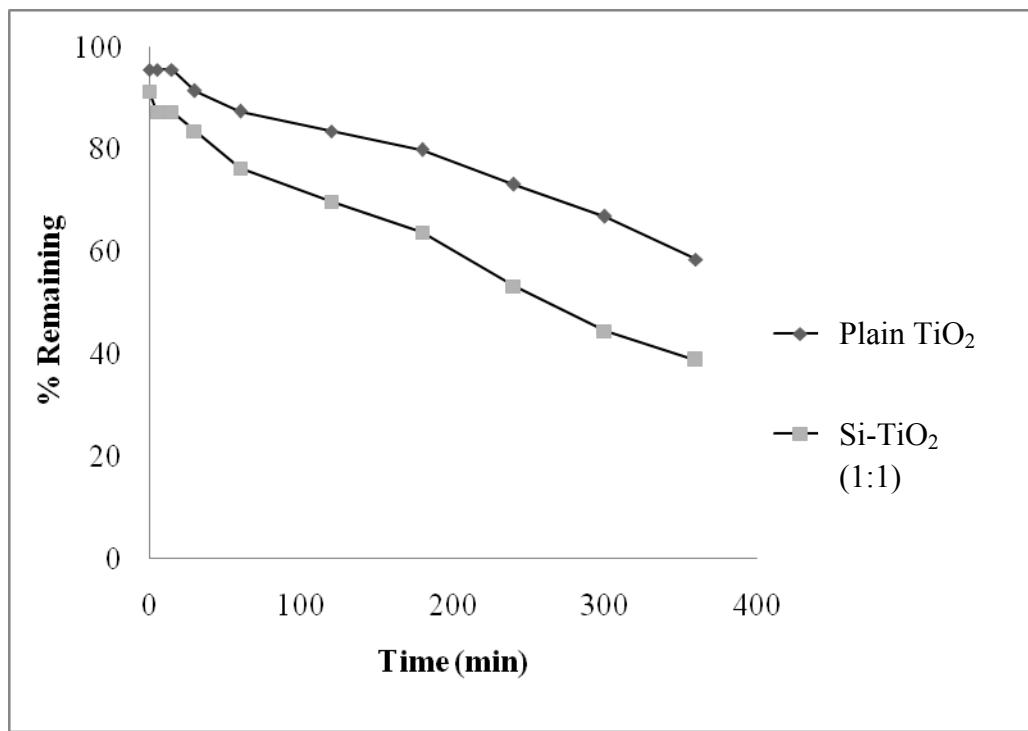


Figure 5.13: PCD of NH₄⁺/NH₃ using plain and Si-TiO₂ (1ml:1gm) at pH 12

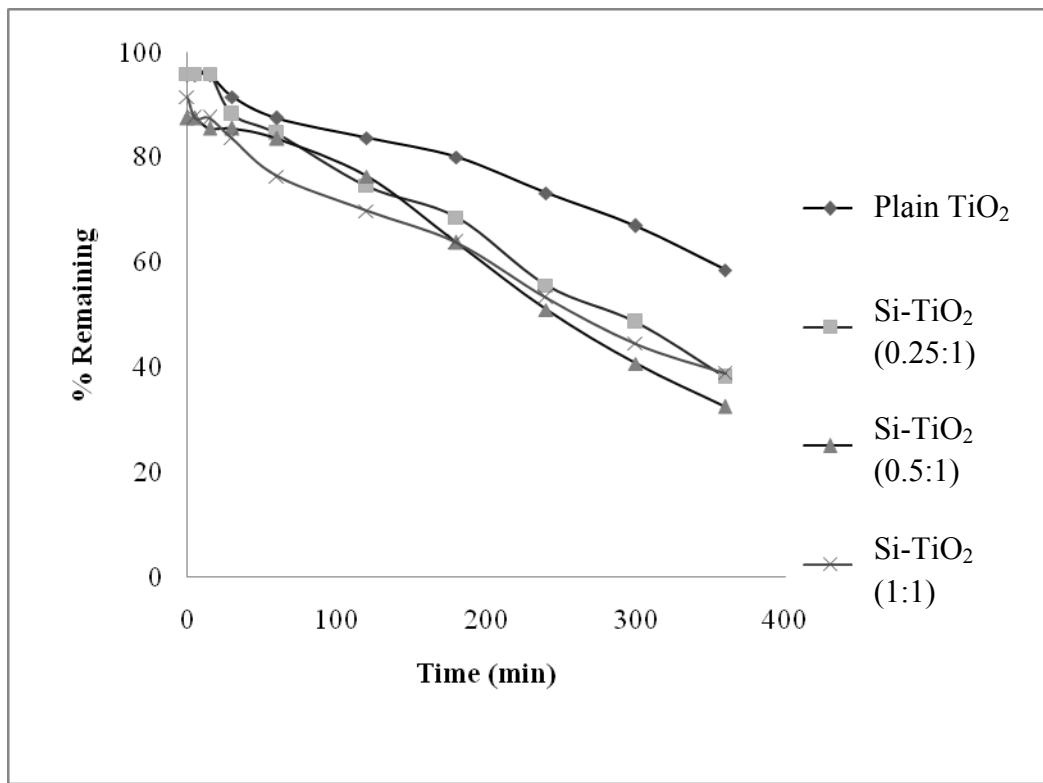


Figure 5.14: PCD of $\text{NH}_4^+/\text{NH}_3$ at pH 12: Effect of Silica

The results from plain TiO_2 , Nf- TiO_2 and Si- TiO_2 are summarized in Figure 5.15 that reports the PCD of 10 ppm $\text{NH}_4^+/\text{NH}_3$ under UV light using respective plain and surface modified TiO_2 photocatalysts. Comparing these three studies it is evident that the surface modification of TiO_2 markedly influences the substrate PCD rate. A significant amount of $\text{NH}_4^+/\text{NH}_3$ is removed using Nafion and silica modified TiO_2 . It has been reported that a higher SSA exhibits a higher PCD rate because more substrate-adsorption sites are available onto modified TiO_2 surface [Vohra et al., 2005]. Furthermore as mentioned earlier that surface modification of TiO_2 with Nafion shifts the zeta potential of TiO_2 to more negative values because the anionic sulfonate groups in the Nafion layer outnumber the positively charged surface groups on TiO_2 ($\text{Ti}^{iv} - \text{OH}_2^+$) [Wang and Ku, 2007]. On the Nafion-coated TiO_2 film, the side chains ($-\text{OCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2-\text{SO}_3^-$) of Nafion attached to the surface of TiO_2 via the hydrophobic backbone ($-(\text{CF}_2\text{CF}_2)_n-\text{CFCF}_2-$) with sulfonate group facing to the aqueous solution [Heitner-Wirquin, 1996]. This presents better adsorption condition for the cationic pollutants. On the other hand, an increase SSA of TiO_2 with silica enhances the substrate degradation because the surface of SiO_2 is more porous than the plain TiO_2 and hence capable of adsorbing more substrate moieties [Vohra and Tanaka, 2003]. In addition to this, changed surface charge characteristics also add to the enhanced substrate degradation. The experimental study also indicates that initial adsorption at zero minute is much high for silica modified TiO_2 in comparison to plain TiO_2 and Nafion TiO_2 . This observation is also suggestive of the fact that both surface charge properties and an increased SSA for Silica- TiO_2 yield a higher initial $\text{NH}_4^+/\text{NH}_3$ adsorption rather than Nf- TiO_2 . But as the PCD proceeds the excitation state of Si- TiO_2 takes longer time and thus the initial removal efficiency of $\text{NH}_4^+/\text{NH}_3$ is

somewhat less than Nf-TiO₂. Nevertheless, both modified TiO₂ samples show high PCD efficiency as compared to the plain TiO₂.

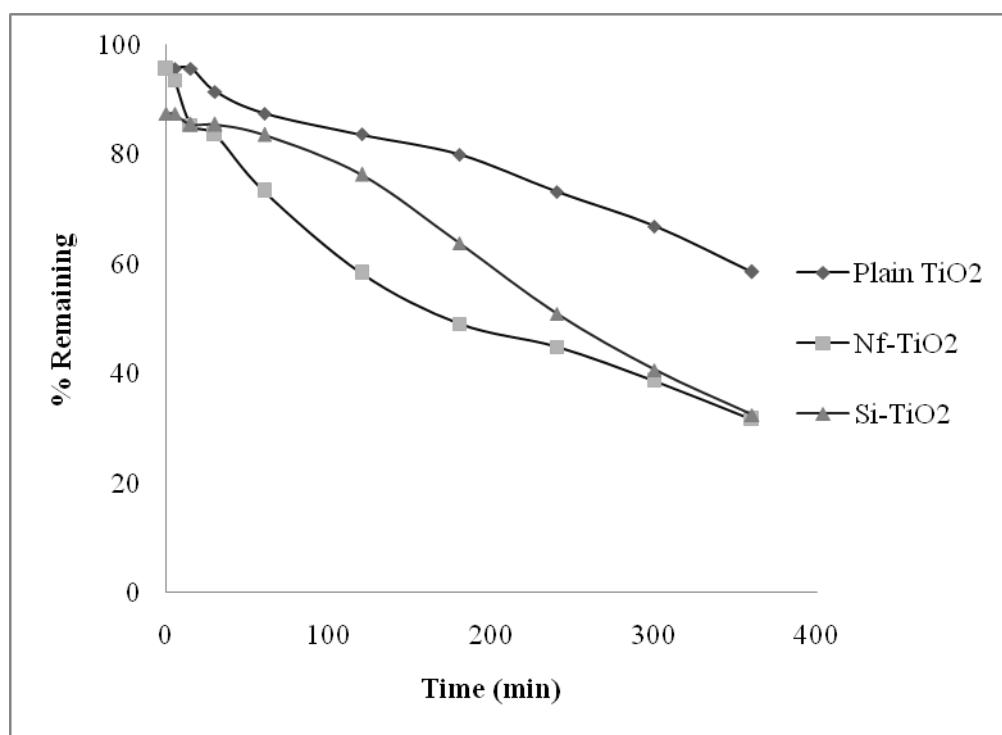


Figure 5.15: PCD of 10 ppm $\text{NH}_4^+/\text{NH}_3$ at pH 12: Effect of Surface Modification

5.4 Effect of $\text{NH}_4^+/\text{NH}_3$ concentration onto its PCD trend

To expand the previously mentioned high efficiency photocatalyst work, it was further investigated the effect of $\text{NH}_4^+/\text{NH}_3$ concentration onto its PCD. Figure 5.16 and 5.17 report the photocatalytic degradation of 50 ppm $\text{NH}_4^+/\text{NH}_3$ using plain and modified TiO_2 . Nafion modified TiO_2 shows the maximum $\text{NH}_4^+/\text{NH}_3$ removal efficiency up to 55% while Si-TiO_2 and plain TiO_2 indicates the removal efficiencies of 43% and 36% respectively. Hence, surface modification of TiO_2 shows better removal efficiency with Nf-TiO_2 showing 19% and Si-TiO_2 showing 7% more $\text{NH}_4^+/\text{NH}_3$ removal as compared of plain TiO_2 . Initial $\text{NH}_4^+/\text{NH}_3$ adsorption (at zero minute) of 6% is noted for Nf-TiO_2 rendering it to be more effective under UV light. Nevertheless, Si-TiO_2 that shows more initial substrate adsorption at zero minute but after 6 hr illumination it indicates lesser PCD compared to the Nf-TiO_2 . This difference between the initial adsorption and PCD trends is different and does not seem to follow a typical Langmuir-Hinshelwood type kinetics. It is suggested that when the pH increases, the active hydroxyl groups on the TiO_2 surface increase as well that cause a faster generation of OH^\bullet radicals accelerating the cationic species oxidation [Wei & Wan, 1991]. Such generation of OH^\bullet radicals may be higher in case of Nf-TiO_2 , specially within the interstitial surface bound polymer layer. This would possibly explain the noted high Nf-TiO_2 activity at 50 ppm $\text{NH}_4^+/\text{NH}_3$.

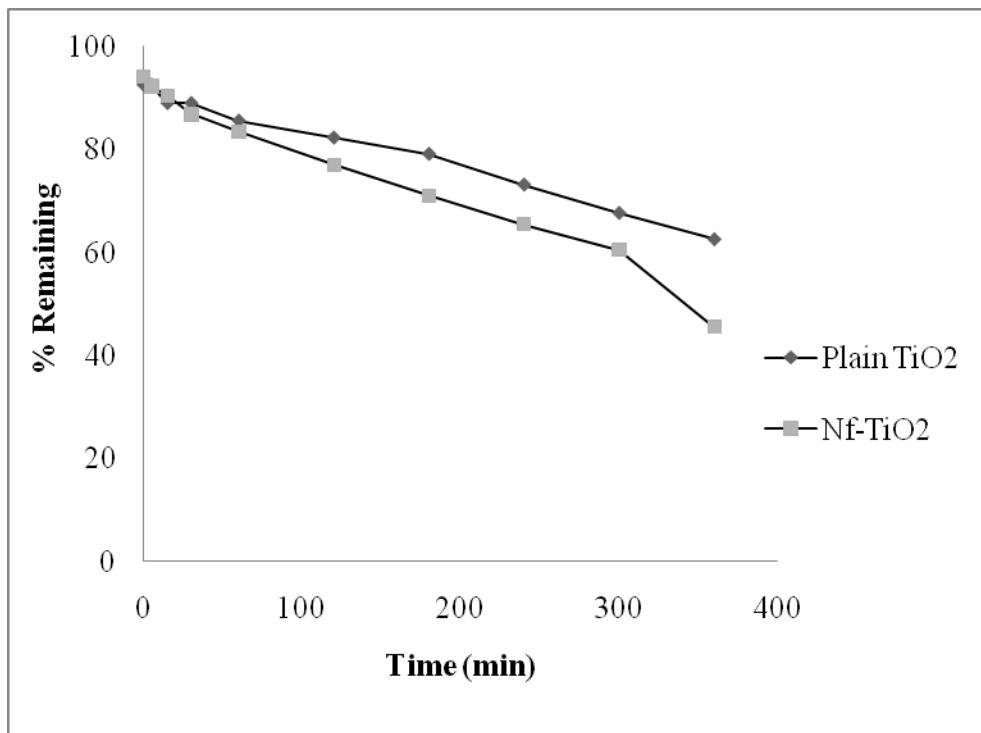


Figure 5.16: PCD of 50 ppm $\text{NH}_4^+/\text{NH}_3$ using plain and Nf-TiO₂ at pH 12

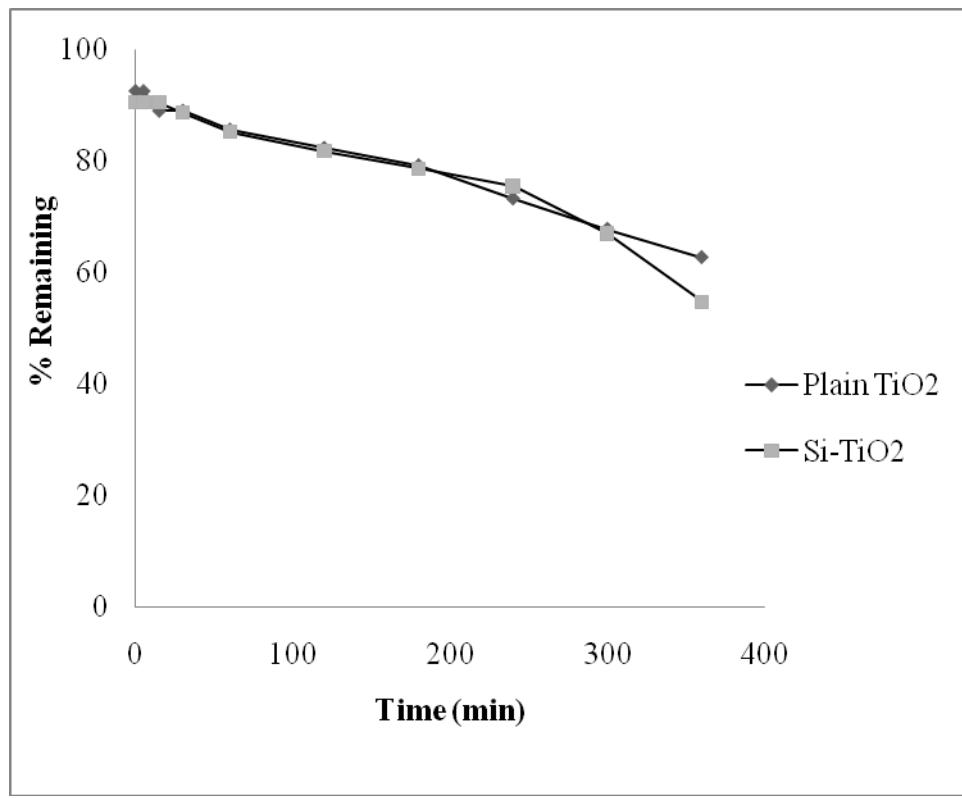


Figure 5.17: PCD of 50 ppm NH₄⁺/NH₃ using plain and Si-TiO₂ at pH 12

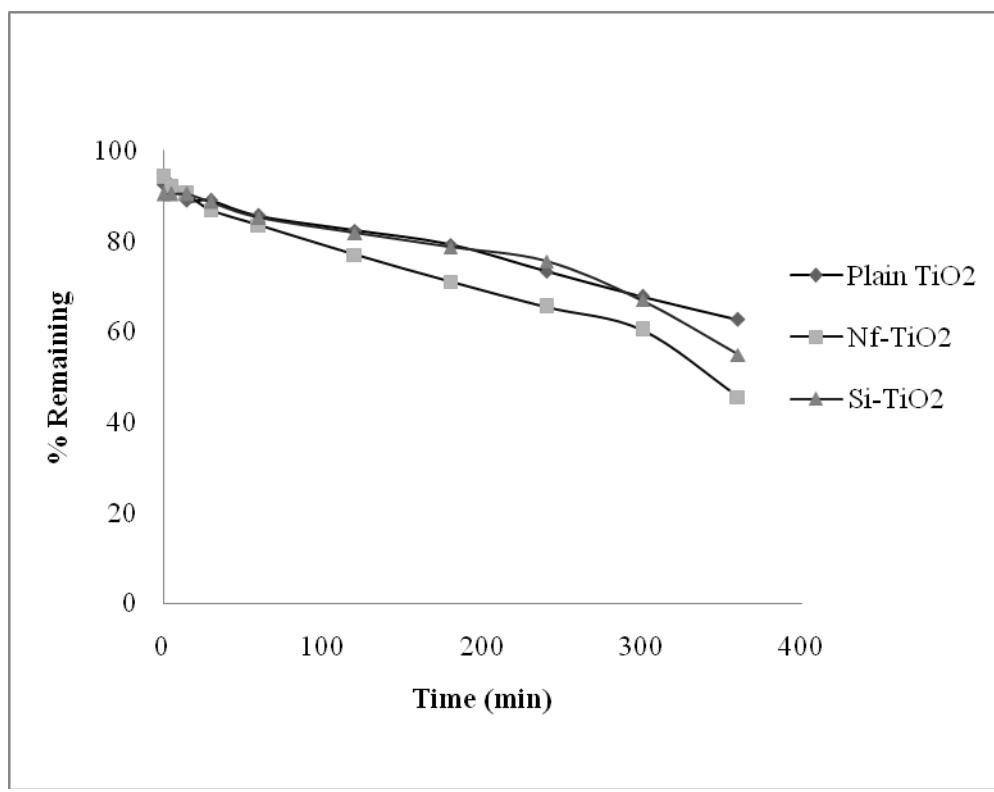


Figure 5.18: PCD of 50 ppm $\text{NH}_4^+/\text{NH}_3$ at pH 12: Effect of Surface Modification

The effect of $\text{NH}_4^+/\text{NH}_3$ concentration subject was further investigated by conducting another set of experiments at 100 ppm $\text{NH}_4^+/\text{NH}_3$ concentration. Figure 5.19 to 5.21 provide the respective $\text{NH}_4^+/\text{NH}_3$ degradation at pH 12. Compared to the previously given 10 and 50 ppm concentration of $\text{NH}_4^+/\text{NH}_3$, no significant change in ammonia removal efficiency is noted for 100 ppm $\text{NH}_4^+/\text{NH}_3$ concentration using surface modified TiO_2 . After 6 hr illumination, percent remaining concentraton was 68% for plain TiO_2 , 70% for Nf- TiO_2 , and 73% for Si- TiO_2 . The general method for the photocatalytic destruction of cationic species begins with its excitation by valence band photons, and continues through redox reactions initiated by the OH^\cdot radicals, formed on the photocatalyst surface. A sufficient ammount of photocatalyst may allow to initiate free OH^\cdot radical formation on the photocatalyst surface which would also increase electron transfer between donor molecule and acceptor molecule; this electron transfer should result in an ion pair of the donor cation and the acceptor cation [Linsebigler et al., 1995]. Therefore it can be said that the lack of sufficient photocatalyst surface sites reduce the overall PCD at high concentration of $\text{NH}_4^+/\text{NH}_3$. Comparing the respective data, indicates higher initial ammonia adsorption onto plain TiO_2 as compared to the modified TiO_2 samples. This shows that the concentration dependent initial adsorption that tends to reach an equilibrium at high ammonia concentration, renders the noted PCD behaviour i.e., both plain- TiO_2 and modified- TiO_2 samples yield similar ammonia removal efficiency.

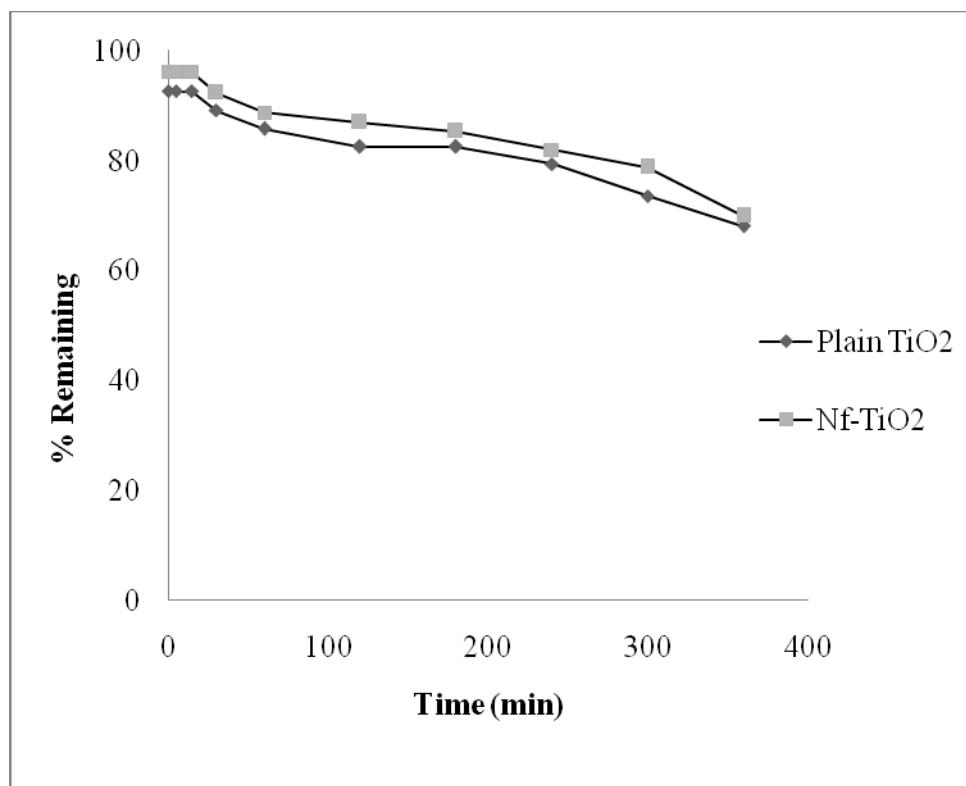


Figure 5.19: PCD of 100 ppm $\text{NH}_4^+/\text{NH}_3$ using plain TiO₂ and Nf-TiO₂ at pH 12

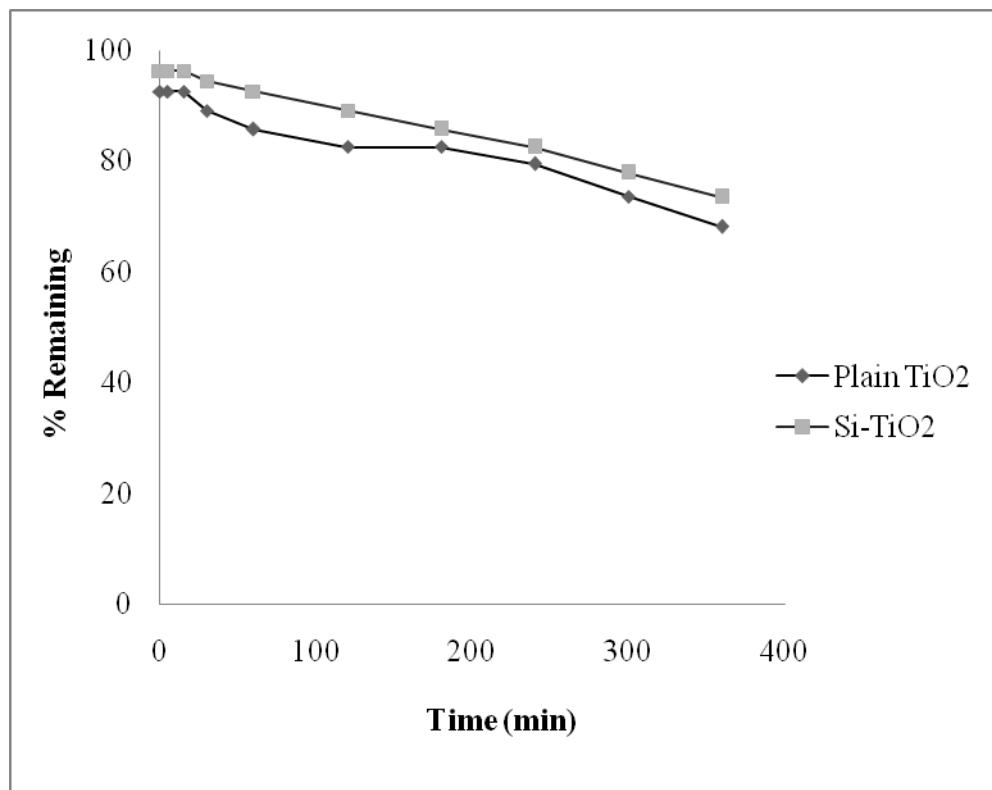


Figure 5.20: PCD of 100 ppm NH₄⁺/NH₃ using plain TiO₂ and Si-TiO₂ at pH 12

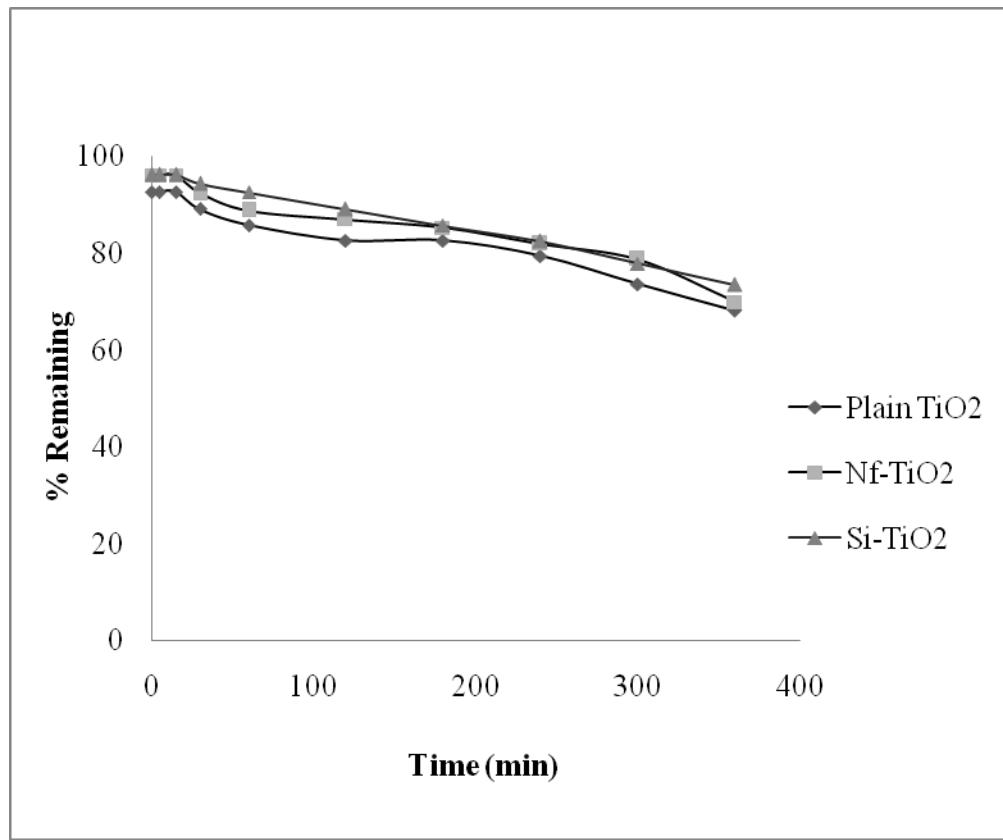


Figure 5.21: PCD of 100 ppm $\text{NH}_4^+/\text{NH}_3$ at pH 12: Effect of Surface Modification

Figure 5.22 compares the effect of substrate concentration during PCD using plain TiO₂ at pH 12. The overall NH₄⁺/NH₃ removal at 6 hr is noted to be the highest amounting to 42% for 10 ppm concentration of NH₄⁺/NH₃, whereas results for 50 ppm and 100 ppm ammonia show 37% and 32% removals respectively. The NH₄⁺/NH₃ PCD trend of 10 ppm and 50 ppm show more or less same trend whereas somewhat decreased removal transpires for 100 ppm NH₄⁺/NH₃. It is more interesting that the initial NH₄⁺/NH₃ adsorption at zero minute depicts an increased adsorption at higher concentration than the lower concentration. The interfacial mass transfer on the bulk solution will be high at higher concentration of NH₄⁺/NH₃. However increase in the NH₄⁺/NH₃ degradation at low concentration suggests that solution phase OH[·] radical attack is the favored mode of attack. Nevertheless according to the Fox and Dulay [1993], interfacial electron transfer is kinetically competitive only when the relevant donor or acceptor is preadsorbed before PCD. The above noted discrepancy between the initial substrate adsorption and its overall PCD, can be explained by looking into the mass removal trend for NH₄⁺/NH₃. For example, it is clear after comparing 10 and 100 ppm NH₄⁺/NH₃ results, though higher percent based NH₄⁺/NH₃ removal transpires at 10 ppm, however, the total NH₄⁺/NH₃ removal in term of mass is much higher at 100 ppm initial NH₄⁺/NH₃ concentration.

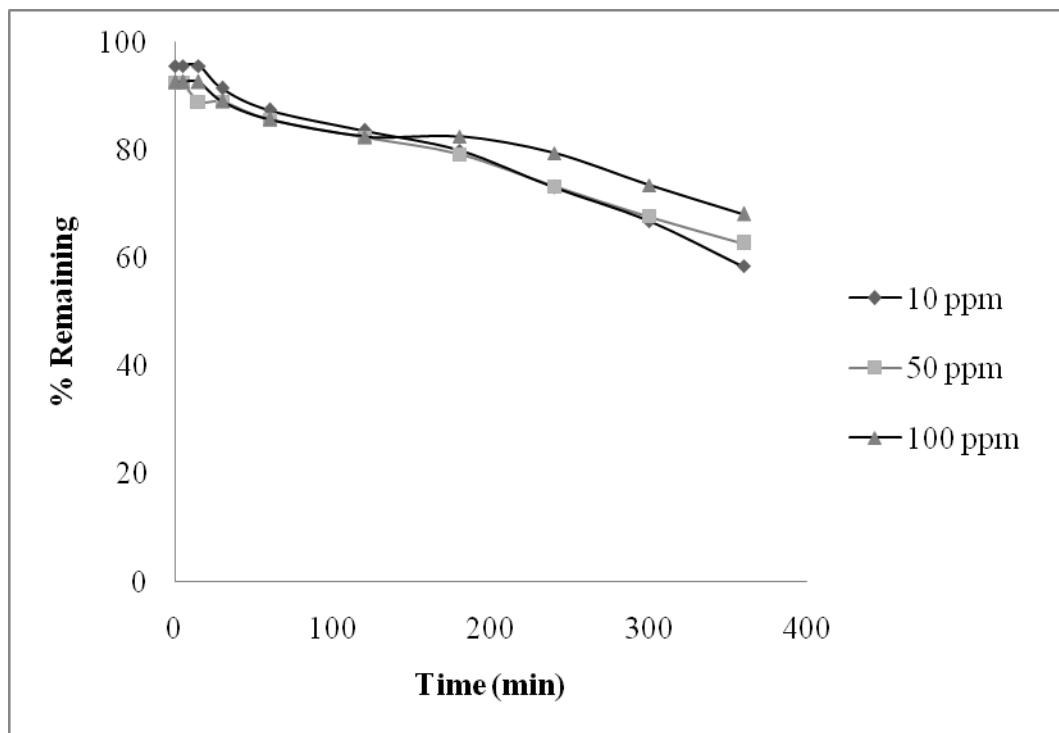


Figure 5.22: PCD of different concentration of $\text{NH}_4^+/\text{NH}_3$ with plain TiO_2 at pH 12:
Substrate concentration effect

Figure 5.23 summarizes the photocatalytic degradation at different concentration of $\text{NH}_4^+/\text{NH}_3$ using Nf-TiO₂ at pH 12. It is previously discussed that the pH_{zpc} of Nafion modified Degussa P25 TiO₂ is lower than 6.5 and thus it would mostly be present in the TiO⁻ form at typical pH values. Figure 5.23 also indicates initial $\text{NH}_4^+/\text{NH}_3$ adsorption for five different concentrations of $\text{NH}_4^+/\text{NH}_3$. These results indicate that the maximum degradation of $\text{NH}_4^+/\text{NH}_3$ after 6 hr period transpires for the 10 ppm study. It is also important to note that initial percent based $\text{NH}_4^+/\text{NH}_3$ adsorption (at time zero) on the TiO₂ surface is high for 10 ppm concentration. However, the overall $\text{NH}_4^+/\text{NH}_3$ removal gradually reduces with an increase in $\text{NH}_4^+/\text{NH}_3$ concentration. Moreover, it is important to note that the PCD rate of 5 ppm $\text{NH}_4^+/\text{NH}_3$ is poor in comparison to 10 ppm $\text{NH}_4^+/\text{NH}_3$. In other words, an increase in $\text{NH}_4^+/\text{NH}_3$ concentration though initially yield enhanced substrate removal, however, a further increase does not show the same trend. Nevertheless, it should be noted that overall $\text{NH}_4^+/\text{NH}_3$ removal in term of mass is still higher at 100 ppm $\text{NH}_4^+/\text{NH}_3$ compared to 10 ppm $\text{NH}_4^+/\text{NH}_3$. It proves the ratio of surface modification TiO₂ with Nafion is an important and gives optimum removal efficiency for a specific concentration of cationic species. It can happen due to specific adsorption on the respective TiO₂ sites.

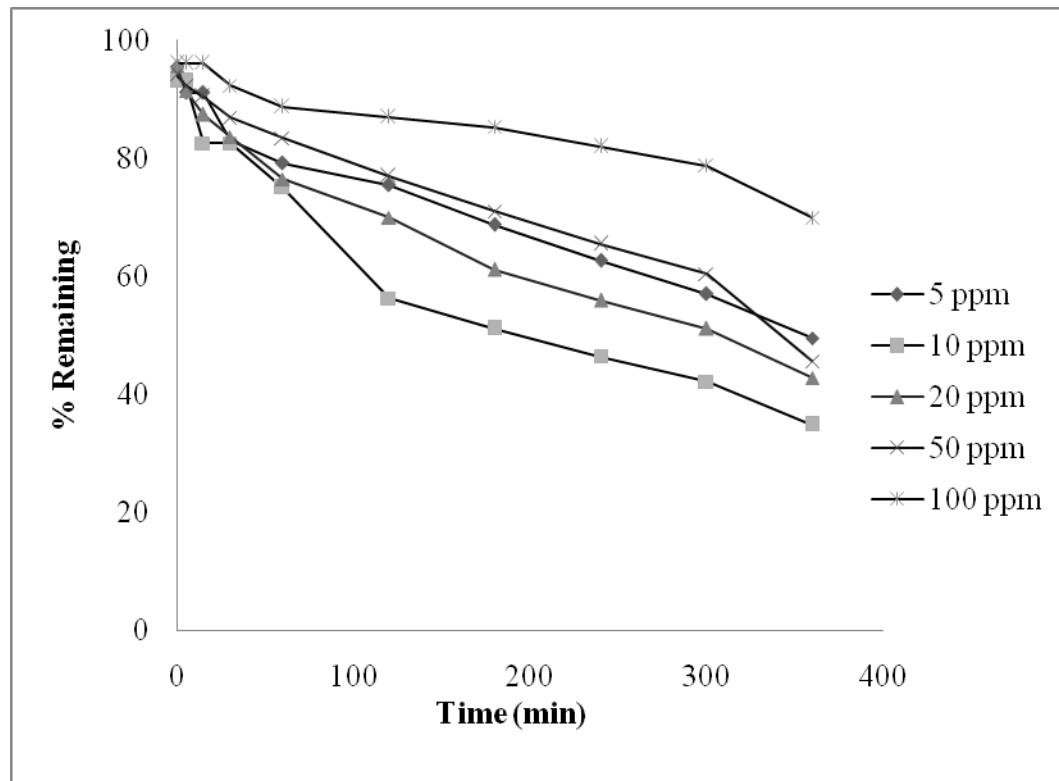


Figure 5.23: PCD of different concentration of $\text{NH}_4^+/\text{NH}_3$ using Nf-TiO₂ (1:1) at pH 12

Dependence of PCD initiated $\text{NH}_4^+/\text{NH}_3$ removal on its initial concentration for Si-TiO₂ is summarized in Figure 5.24. The results show that Si-TiO₂ has better adsorption at 10 and 50 ppm $\text{NH}_4^+/\text{NH}_3$ than 100 ppm $\text{NH}_4^+/\text{NH}_3$ PCD using plain TiO₂. Moreover, the percent based removal performance for Si-TiO₂ after 6 hr illumination is best for 10 ppm $\text{NH}_4^+/\text{NH}_3$ concentration. Hence high initial substrate adsorption, apparently, causes enhanced substrate degradation. It should also be noted this increment is not only percent based, but also mass based considering 5 fold higher concentration at 50 ppm. A decreased PCD is however seen as we move from 10 ppm to 100 ppm substrate concentration. This suggests that the availability of enough surface adsorption sites at the lower substrate amounts causes faster substrate degradation.

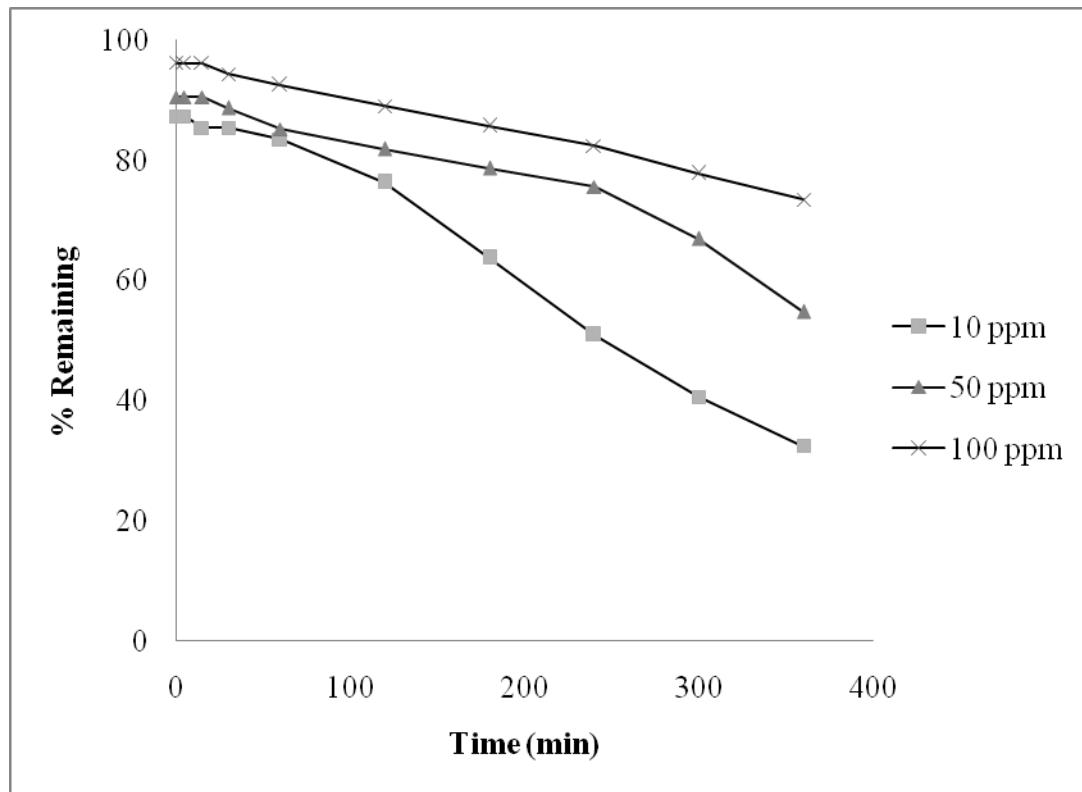


Figure 5.24: PCD of $\text{NH}_4^+/\text{NH}_3$ with silica modified TiO_2 at pH 12

Figure 5.25 reports the overall mass removal efficiency after 6 hr illumination for plain TiO₂ at pH 12. The overall mass removal at high concentration of NH₄⁺/NH₃ (100 ppm) is higher than at low concentration of NH₄⁺/NH₃ (10 ppm). Also the overall mass removal almost doubles with doubling of NH₄⁺/NH₃ from 50 to 100 ppm. Maximum NH₄⁺/NH₃ removal of 42% was noted for 10 ppm NH₄⁺/NH₃ case whereas the mass removal percentage for 100 ppm NH₄⁺/NH₃ is 32%. In principle, TiO₂ semiconductor with an appropriate magnitude of the bandgap and the position of band edges is able to initiate photoinduced redox reactions on its surface [Choi, 2006]. Though the overall percent mass removal efficiency for plain TiO₂ at pH 12 gradually decreases at high NH₄⁺/NH₃ concentration (Figure 5.25), nevertheless the overall mass removal at 100 ppm NH₄⁺/NH₃ approximately four times higher compared to 10 ppm NH₄⁺/NH₃. The overall mass removal almost doubles with doubling of NH₄⁺/NH₃ from 50 to 100 ppm. Therefore, though we do observe decreased percent based NH₄⁺/NH₃ removal with an increased in substrate concentration, however the overall results tends to be within a narrow window, which is different from the noted mass removal trends (Figure 5.25).

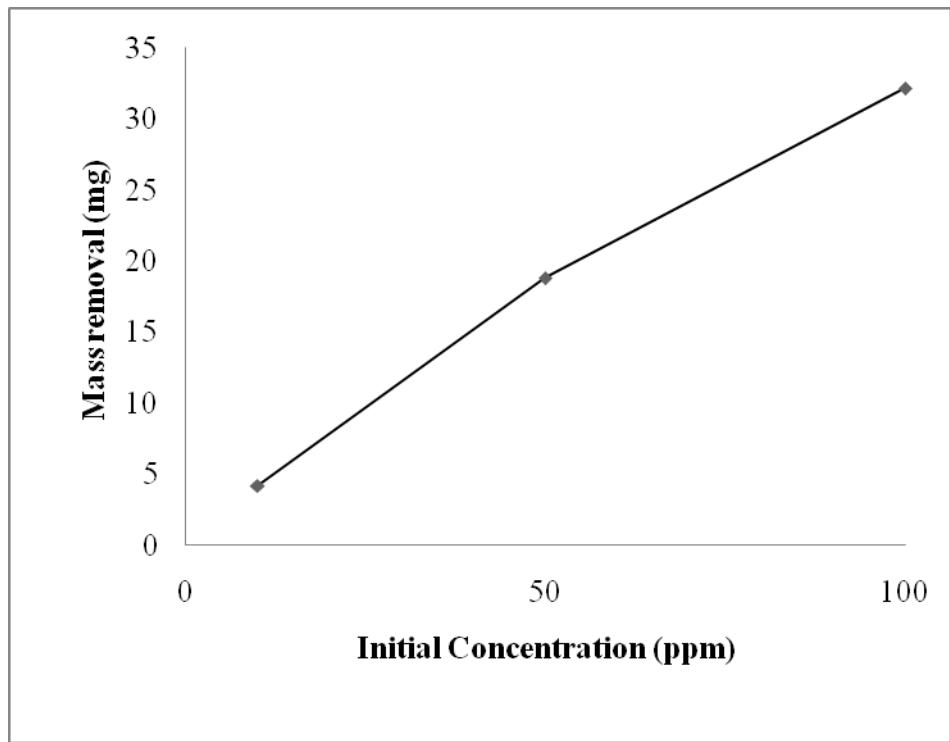


Figure 5.25: Mass removal curve for plain TiO_2

The percent based mass removal efficiencies for $\text{NH}_4^+/\text{NH}_3$ PCD using Nf-TiO₂ is shown in Figure 5.26. The best mg based mass removal performance is seen for 100 ppm $\text{NH}_4^+/\text{NH}_3$ concentration. However, considering the percent based results 100 ppm $\text{NH}_4^+/\text{NH}_3$ shows only 30% removal after 6 hr illumination while more than 65% of substrate concentration is successfully removed at 10 ppm $\text{NH}_4^+/\text{NH}_3$ using Nafion modified TiO₂ (Figure 5.26). It is also interesting to note that the mass removal of 5 ppm NH_4 is not as much effective as 10 ppm or even higher $\text{NH}_4^+/\text{NH}_3$ amounts. The mass based $\text{NH}_4^+/\text{NH}_3$ removal, (like plain TiO₂ results, as mentioned before) also showed an increased removal with an increase in initial $\text{NH}_4^+/\text{NH}_3$ amount. This trend follows almost a direct relationship up to 50 ppm $\text{NH}_4^+/\text{NH}_3$ after which a plateau seems to be reached at 100 ppm $\text{NH}_4^+/\text{NH}_3$. It was previously discussed that Nafion is an anionic perfluorinated polymer, consisting of a hydrophobic polytetrafluoroethylene backbone – $(\text{CF}_2\text{CF}_2)_n\text{CFCF}_2-$, and a hydrophilic acid group $\text{SO}_3^- \text{H}^+$ connected to the backbone via side chains of $-\text{OCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2-$ [Heitner-Wirquin, 1996, Wang and Ku, 2007]. Thus the availability of Nafion onto TiO₂ surface and subsequent $\text{NH}_4^+/\text{NH}_3$ capturing causes maximum mass removal performance under UV illumination.

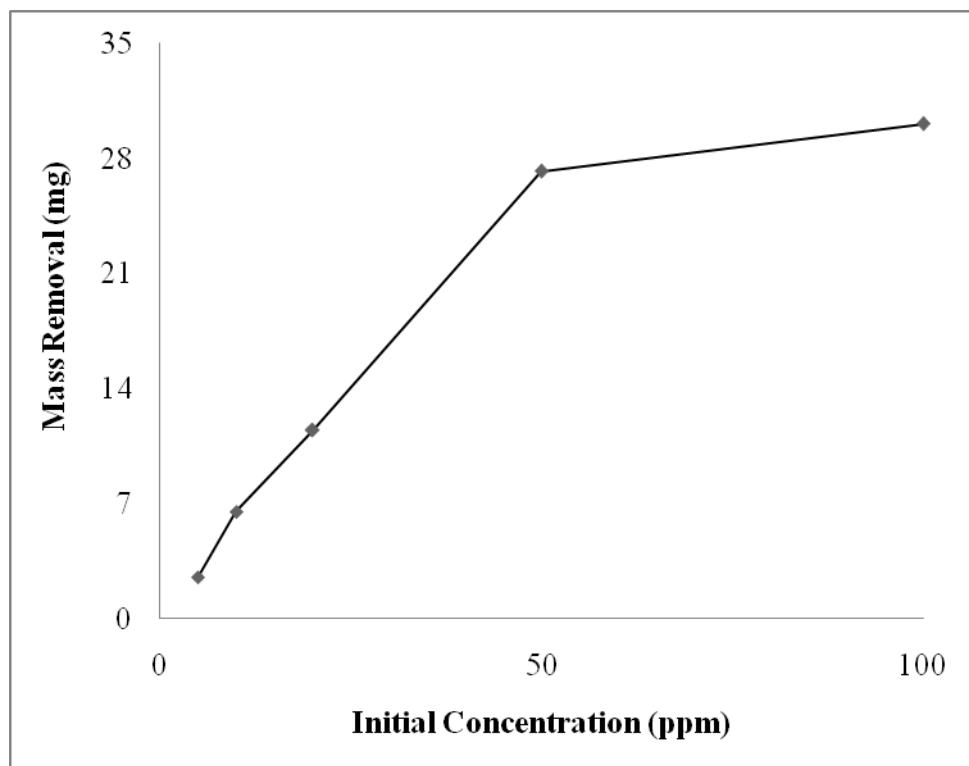


Figure 5.26: Mass removal analysis for Nf-TiO₂

The percent based $\text{NH}_4^+/\text{NH}_3$ mass removal findings for Si-TiO₂ are provided in Figure 5.27. Results show an increasing trend which is rapid from 10 ppm to 50 ppm $\text{NH}_4^+/\text{NH}_3$ for a fixed content of Si-TiO₂ photocatalyst. It is also seen that increasing trend readily slows down at higher concentration of $\text{NH}_4^+/\text{NH}_3$ i.e., from 50 ppm to 100 ppm $\text{NH}_4^+/\text{NH}_3$. The maximum amount of $\text{NH}_4^+/\text{NH}_3$ mass is removed at 100 ppm $\text{NH}_4^+/\text{NH}_3$, which makes up more than 26 ppm. Yet the percent based ammonia removal is low in comparison to 10 ppm $\text{NH}_4^+/\text{NH}_3$. The mass removal percentage is approximately 68% for 10 ppm $\text{NH}_4^+/\text{NH}_3$ while only 27% ammonia is removed for 100 ppm $\text{NH}_4^+/\text{NH}_3$. It was previously discussed that silica modified TiO₂ catalyst results in enhanced PCD of cationic species due to its increased surface area and introduction of Si-O⁻ groups, which leads a higher degradation rate of $\text{NH}_4^+/\text{NH}_3$ than plain TiO₂ [Vohra and Tanaka, 2003]. Vohra et al. [2005] in another study also found that the electrostatic attraction of cationic species tetramethylammonium (TMA) onto negatively charged Si-TiO₂ surface results in increased photoactivity of Si-TiO₂. This research work also shows that silica modified TiO₂ gives an enhanced PCD of $\text{NH}_4^+/\text{NH}_3$ and the overall mass removal (ppm based) also increases with an increase in initial $\text{NH}_4^+/\text{NH}_3$ concentration.

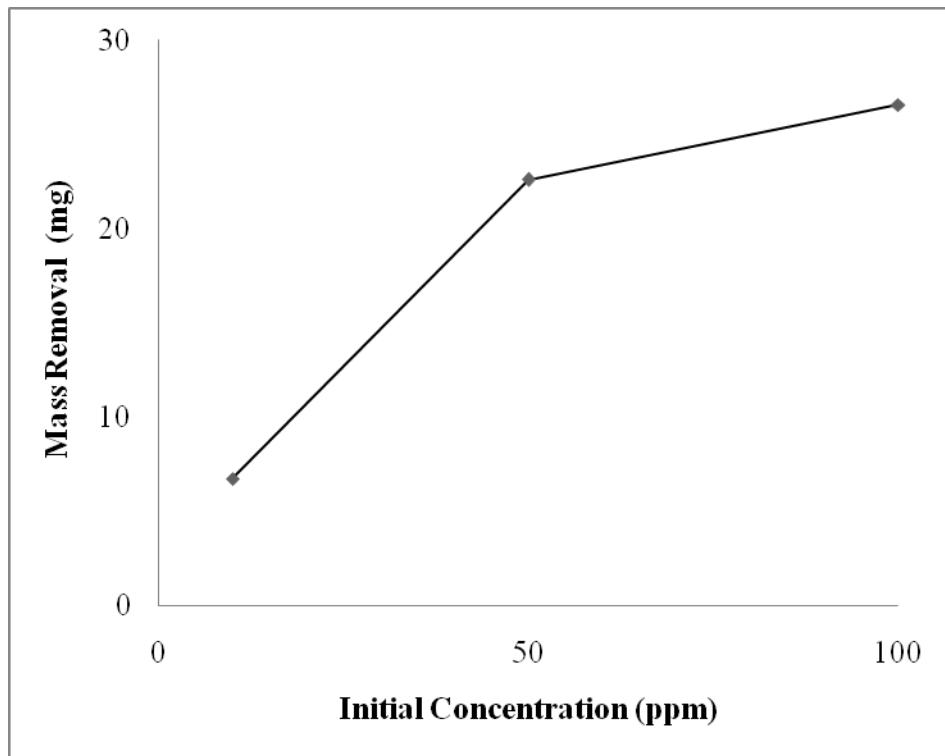


Figure 5.27: Mass removal analysis for Si-TiO₂

5.5 Photocatalytic Degradation of Methylene Blue (MB)

The removal of methylene blue by TiO₂ photocatalysis was also investigated at two different pH values (Figure 5.28). The pH value exhibits an increased PCD with an increase in pH in acidic solution. The photocatalytic activity of TiO₂ depends on several physic-chemical properties (e.g., crystal structure, specific surface area, surface hydroxyls, and particle size) and operating conditions (e.g., light intensity, oxygen, initial concentration of chemicals, amount of TiO₂, and pH value) [Xu et al., 1999]. It was previously discussed that Degussa P25 TiO₂ with a pH_{zpc} (pH at zero point charge) of approximately 6.5 would have increased Ti-O⁻ and Ti-OH sites at higher pH. Therefore increased photocatalytic degradation of MB with pH can be rationalized on the basis of the electrostatic adsorption model where cations are more readily accommodated at negative sites on TiO₂ [Lakshmi et al., 1995]. It was also reported by Lakshmi et al. [1995] that a rapid electron injection from methyl viologen radical cations (MV^{*+}) above the pH_{zpc} of the material, while the anionic species (ZV^{*-}) transferred electrons efficiently only at low pH. In present case, an increased initial adsorption (at zero min illumination) is seen at pH 6 in comparison to pH 3 which indicates the adsorption rate is high for TiO₂ at higher pH solution. However, no significant variance was seen for the final removal efficiency after 2 hr illuminations with 99% removal efficiency. Furthermore higher MB removal is noted at pH 6, till 1 hr reaction. It was previously observed by Lakshmi et al. [1995] that the rate increased with an increase in pH, exhibiting a maximum around pH 6.9-8.0 value. The above results illustrate that a detailed knowledge of the surface chemistry of TiO₂ particles is extremely important to predict and understand their photocatalytic activity.

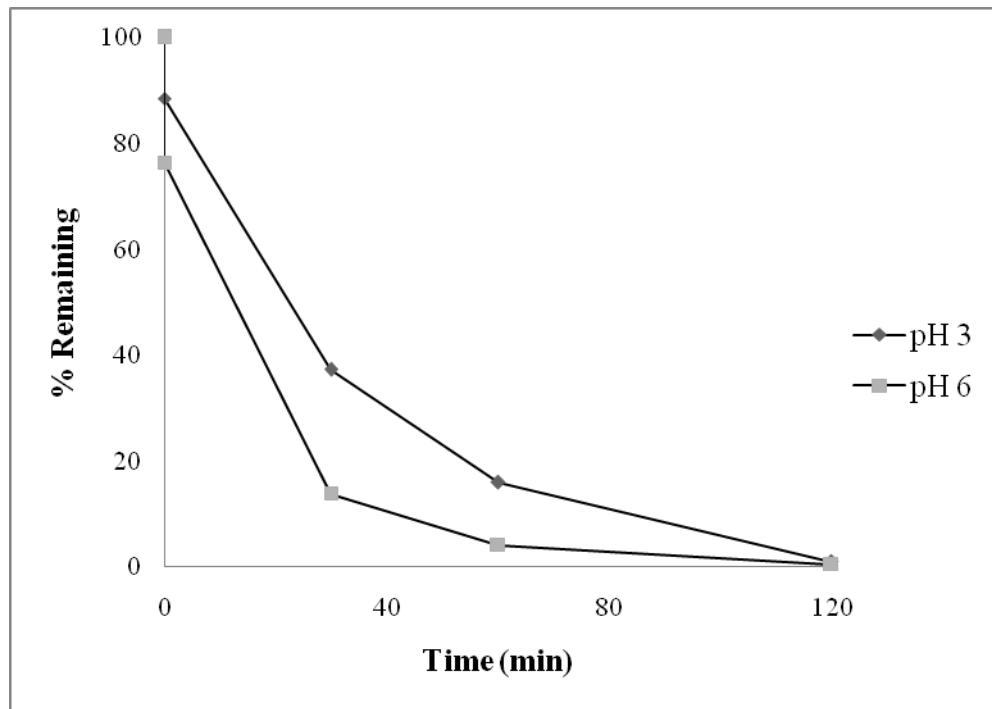


Figure 5.28: PCD of MB with plain TiO₂ (0.1gm/L): pH effect

Figure 5.29 provides the pH effect of Nf-TiO₂ during photocatalytic degradation of MB under UV illumination. A major amount of MB was degraded after 2 hr illumination at pH 3 which makes up 93%. Beside this, comparatively less portion of MB was degraded at pH 6 amounting near about 78% after 2 hrs. The adsorption of MB by Nf-TiO₂ suspension was found minimal at pH 3 possibly because of hydrophobic surface. Furthermore, it can be said that the enhanced adsorption at zero minute for Nf-TiO₂ at pH 6 indicates that negative shift of zeta potentials is larger at higher pH value, considering the previously discussed variation in zeta potential of suspended particles as function of pH [Park & Choi]. However, upon the addition of Nafion, zeta potential becomes more negative in the given pH range. Change of physical properties i.e., surface charge and surface area of photocatalyst with Nafion directly influence electrostatic attraction or repulsion between charged molecules and the catalyst surface. Furthermore, from the previous literature study, it was found that zeta potential at any pH value is negative and it becomes more negative at pH 6 in comparison to pH 3 [Choi, 2006]. Figure 5.29 reports that the adsorption at zero minute illumination is much higher at pH 6 which is near about 29% while Nf-TiO₂ adsorbed 14% of cationic species MB at pH 3. Therefore it can be said that electrostatic attraction between anionic photocatalyst and cationic substrate MB is more with negative shift of zeta potential at pH 6 for Nf-TiO₂. However such an increase in adsorption does not seem to influence the overall MB removal. Further investigation is needed to explore this point.

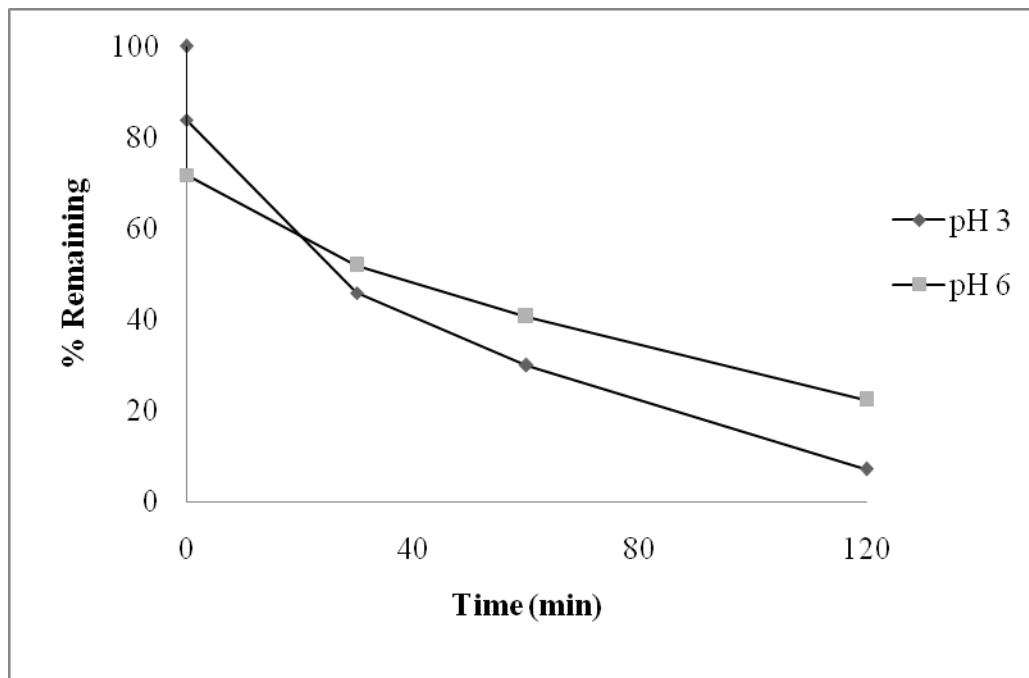


Figure 5.29: PCD of MB (10 ppm) with Nf-TiO₂: pH effect

The photocatalytic reactions of MB initiating on the plain and surface modified TiO₂ at pH 3 and 6 are reported in Figures 5.30 and 5.31. As is compared, Nf-TiO₂ depicts somewhat better adsorption (at zero minute illumination) for MB. However, it is not clear why Nafion modified TiO₂ results less removal efficiency in comparison to the plain TiO₂. The surface charge modification of TiO₂ with Nafion influences the photocatalytic reactivity of cationic substrate MB by altering the electrostatic attraction between Nf-TiO₂ and MB. Importance of MB adsorption is also evident from Figure 5.32, which shows gradual removal of MB from the TiO₂ surface between time 0 and 120 min. It was also discussed before that the surface charge of naked TiO₂ is positive at acidic condition ($\text{pH} \leq 5$) due to the presence of $\equiv \text{Ti}-\text{OH}_2^+$ groups, near neutral at pH 5–7, and negative at basic condition ($\text{pH} \geq 7$) owing to $\equiv \text{Ti}-\text{O}^-$ groups [Choi, 2006]. Park and Choi [2005] found MB was gradually degraded under visible-light-illuminated Nf-TiO₂. It is suggested that slower MB degradation using Nf-TiO₂ because of competitive adsorption of H⁺ and MB cations onto Nf-TiO₂, with H⁺ present in higher concentration having an edge. This will not only result in reduced MB degradation but also reduced OH[•] radical formation. This will be less significant for TiO₂ only considering its pH_{zpc} of 6.5, as compared to Nf-TiO₂.

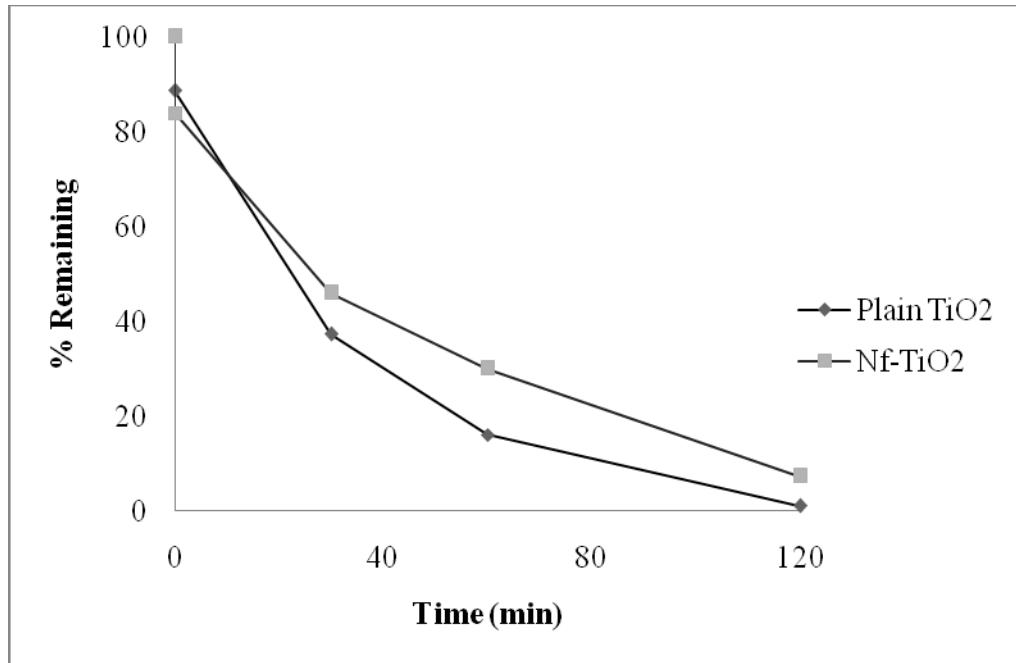


Figure 5.30: PCD of MB at pH 3 (0.1gm/L)

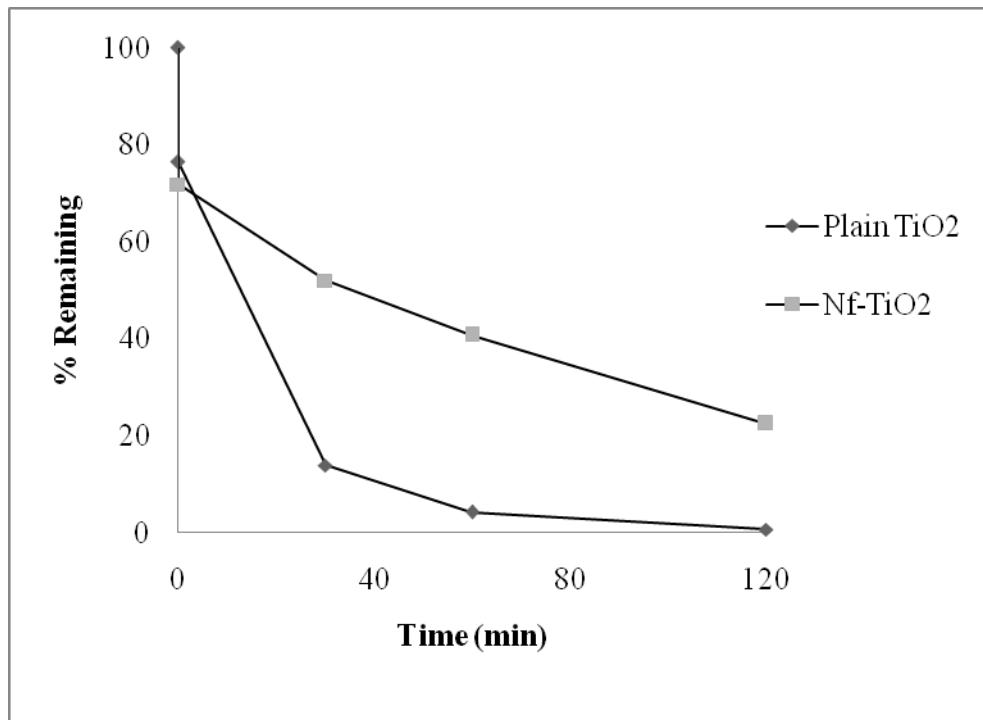


Figure 5.31: PCD of MB at pH 6 (0.1gm/L)

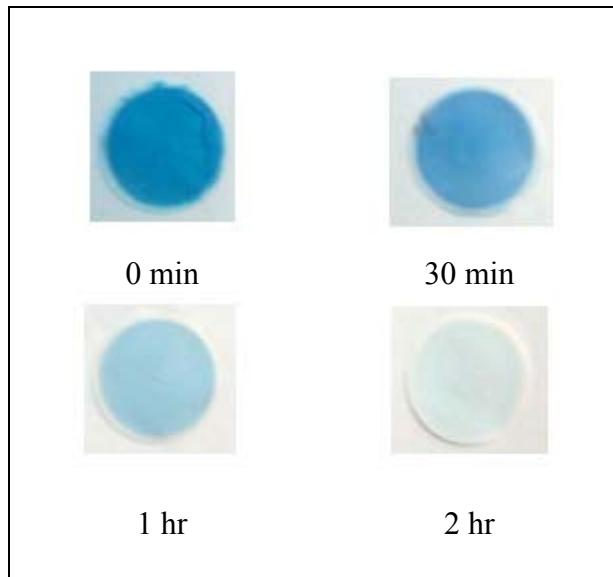


Figure 5.32: Photographical view of $0.2\mu\text{m}$ filter paper during PCD of methylene blue using Nafion TiO₂

5.6 PCD of $\text{NH}_4^+/\text{NH}_3$ in mixed system

The photocatalytic degradation of $\text{NH}_4^+/\text{NH}_3$ using surface modified TiO_2 , in presence of cyanide, was also evaluated. Figure 5.33 presents the PCD of $\text{NH}_4^+/\text{NH}_3$ and CN^- using Nf- TiO_2 . It is clear that cyanide removal under UV illumination is much higher (in comparison to ammonia) with 95% cyanide removal noted at 2 hr illumination. However, only 34% $\text{NH}_4^+/\text{NH}_3$ degradation is noted at 6 hr UV illumination. Yet, it is interesting to note that the initial CN^- adsorption onto TiO_2 is insignificant considering negative surface of Nf- TiO_2 that will inhibit. Figure 5.34 reports $\text{NH}_4^+/\text{NH}_3$ and cyanide degradation in mixed system using silica modified TiO_2 under UV light which shows similar trends. However, the photocatalytic degradation of $\text{NH}_4^+/\text{NH}_3$ and cyanide using Si- TiO_2 is faster in comparison to Nf- TiO_2 . In case of Nafion, the zeta potential is pushed to much lower pH value compared to Si- TiO_2 [Vohra et al., 2005; Park and Choi, 2005]. Therefore it can be concluded that more negative shifting of zeta potential in case of Nf- TiO_2 causes decreased NH_4 degradation in comparison to the silica modified TiO_2 in the mixed system.

Figure 5.35 compares the photocatalytic degradation of $\text{NH}_4^+/\text{NH}_3$ in the UV illuminated suspension of Nf- TiO_2 with different concentration of cyanide in mixed system. A decrease in the overall $\text{NH}_4^+/\text{NH}_3$ removal is noted as the cyanide concentration is increased. It is seen from Figure 5.33 that only 34% $\text{NH}_4^+/\text{NH}_3$ is removed in presence of 10 ppm cyanide and 56% of $\text{NH}_4^+/\text{NH}_3$ removed in presence of 5 ppm cyanide. On the other hand more than 66 % $\text{NH}_4^+/\text{NH}_3$ removed in absence of cyanide, using Nafion modified TiO_2 . Hence the presence of cyanide seems to reduce the overall $\text{NH}_4^+/\text{NH}_3$

removal efficiency, with higher cyanide concentration showing more negative effects. This possibly could result because of competitive cyanide PCD.

The surface modification of TiO₂ using silica shows comparatively higher substrate degradation in the presence of cyanide (in comparison to Nafion modified TiO₂ [Figure 5.38]). Using Si-TiO₂ causes better initial NH₄⁺/NH₃ adsorption in the absence of cyanide compared to presence of 5 ppm and 10 ppm cyanide. With PCD time up to 6 hr, 68% NH₄⁺/NH₃ is degraded in the absence of cyanide while in presence of 5 ppm and 10 ppm cyanide we note 64% and 52% NH₄⁺/NH₃ removal, respectively. Figure 5.34 and 5.35 also reports enhanced substrate degradation using Si-TiO₂ in presence of 5 ppm and 10 ppm compared to Nf-TiO₂.

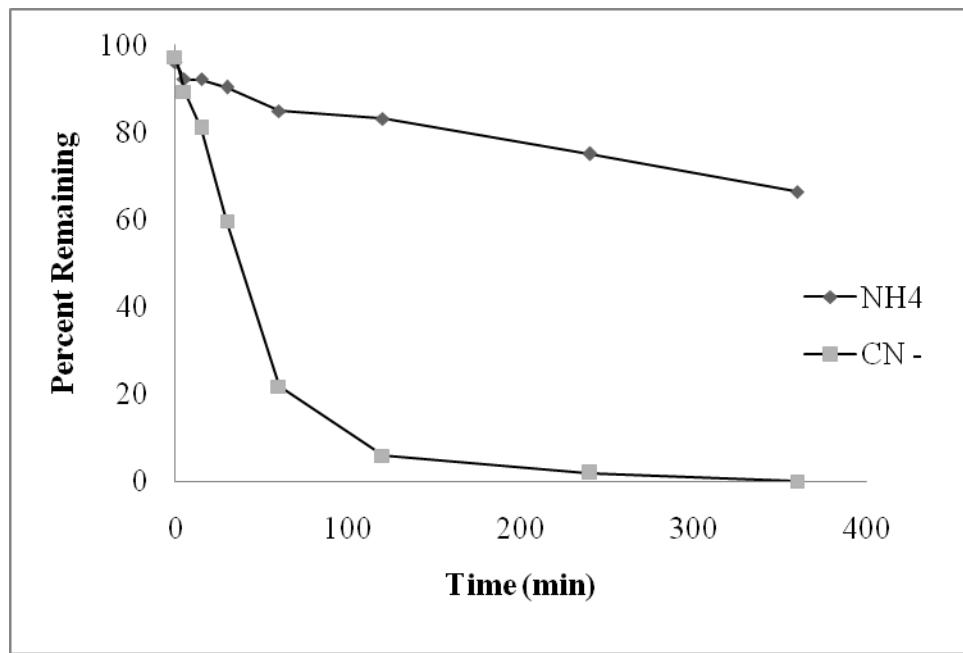


Figure 5.33: PCD of NH₄⁺/NH₃ and CN⁻ in mixed system with Nf-TiO₂ at pH 12

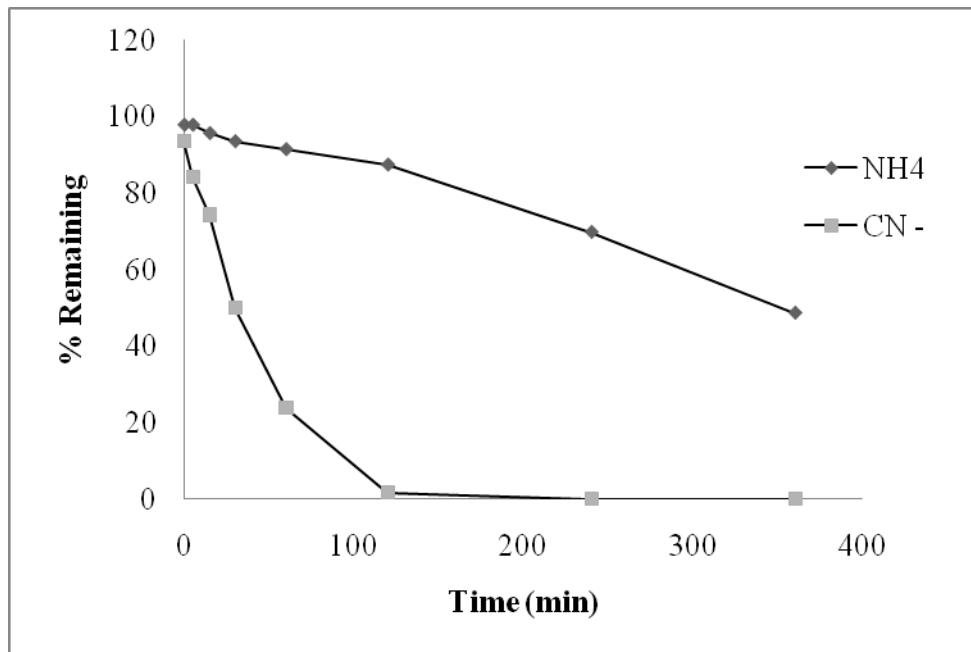


Figure 5.34: PCD of NH₄⁺/NH₃ and CN⁻ in mixed system with Si-TiO₂ at pH 12

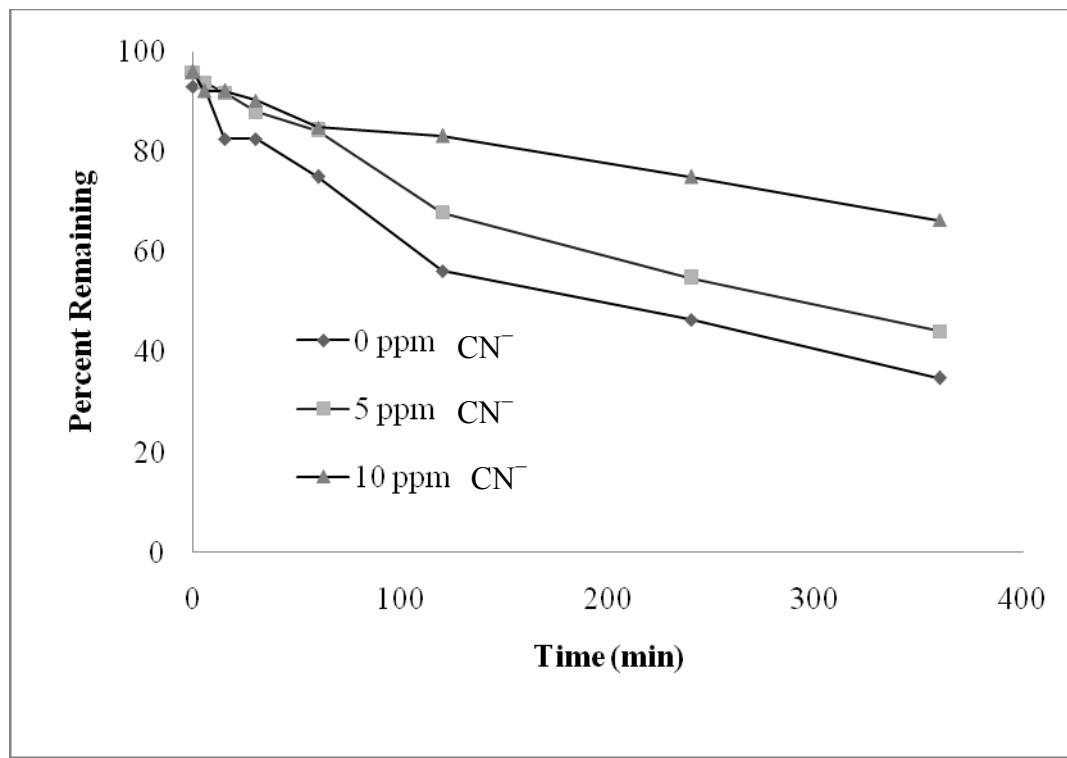


Figure 5.35: PCD of $\text{NH}_4^+/\text{NH}_3$ with Nf-TiO₂: Effect of CN⁻

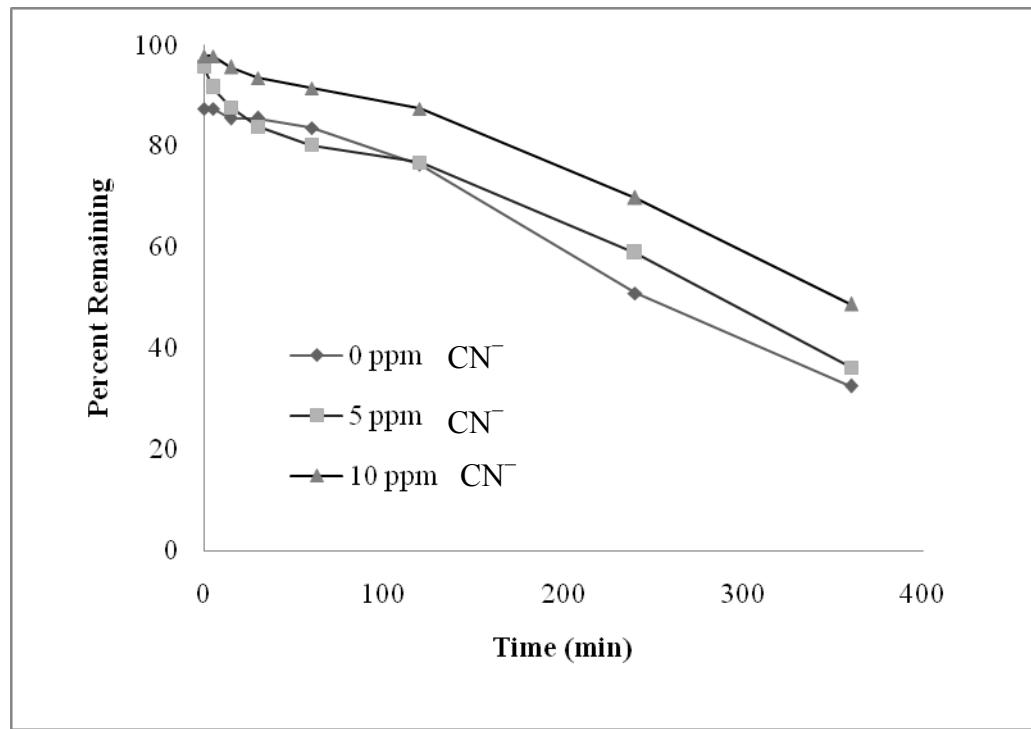


Figure 5.36: PCD of NH₄⁺/NH₃ with Si-TiO₂: Effect of CN⁻

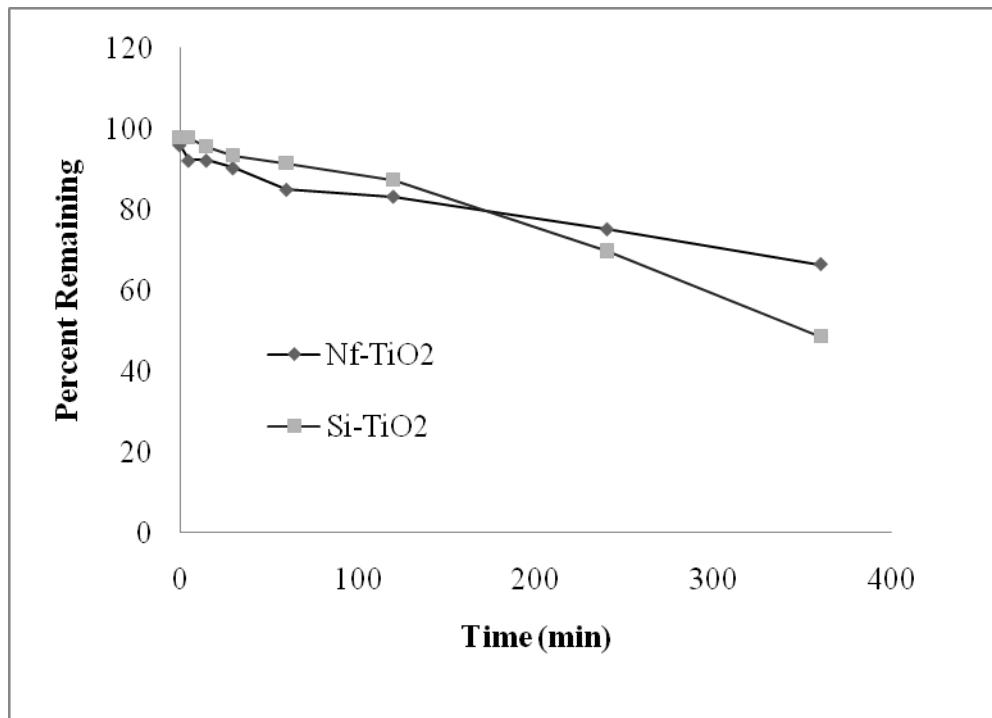


Figure 5.37: PCD of $\text{NH}_4^+/\text{NH}_3$ in mixed system (10 ppm CN^-)

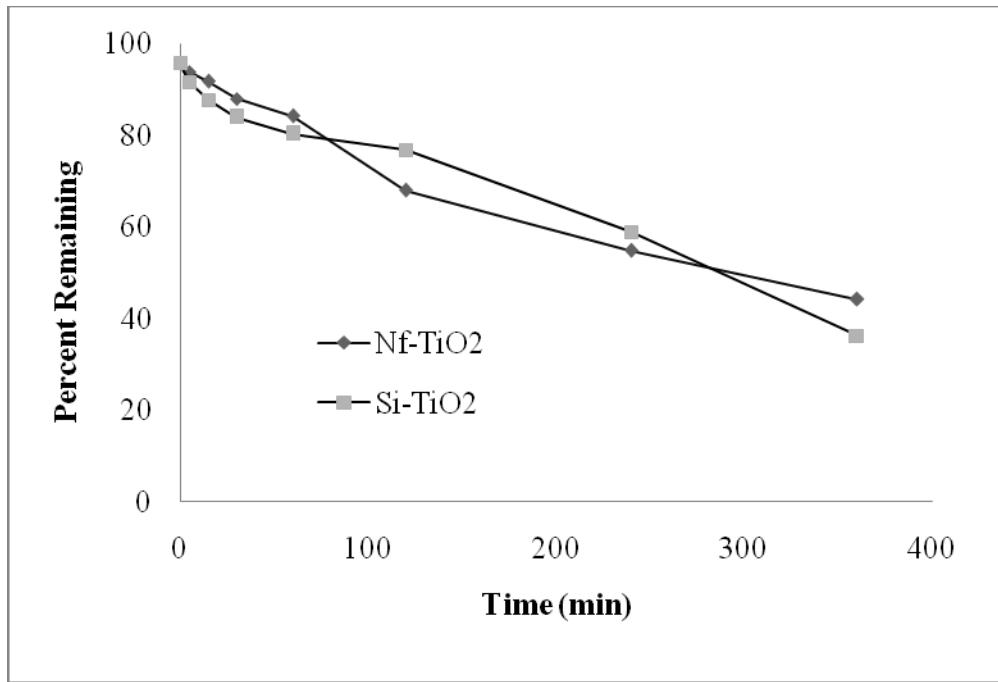


Figure 5.38: PCD of $\text{NH}_4^+/\text{NH}_3$ in mixed system (5 ppm CN^-)

5.7 PCD of cyanide in mixed system

Figure 5.39 compares the photocatalytic degradation of cyanide at two different amounts using Nafion modified TiO₂. A significant initial adsorption is seen at low concentration (5 ppm) of cyanide which makes up 33% removal in comparison to higher concentration of cyanide (10 ppm). However, the difference in term of removal is not significant, with the PCD after 2 hr illumination near about same for 5 ppm and 10 ppm cyanide concentrations. Therefore it can be concluded that Nafion modified TiO₂ becomes more active catalyst under UV light while it shows less adsorption for higher concentration cyanide at zero minute illumination. Aguado et al. [2002] also found that the amount of cyanide ions decreased with increasing irradiation time during photocatalytic degradation. However cyanide oxidation was not noted by Aguado et al. [2002] in the absence of either catalyst, or UV light thus indicating the photocatalytic nature of the studied process.

Figure 5.40 depicts the PCD of cyanide at two different concentrations using Si-TiO₂ as photocatalyst. It is seen from Figure 5.40 that the degradation trend is higher for low concentration (5 ppm) of cyanide up to 1 hr illumination. In later portion both 5 ppm and 10 ppm cyanide degradation show complete cyanide removal. Also the initial adsorption is insignificant for 5 ppm and 10 ppm concentration of cyanide. Barakat et al. [2004] have also found the same result, i.e., cyanide has low tendency for adsorption onto TiO₂ as at high pH value the surface of TiO₂ is negatively charged and the formation of surface-cyanide complexe is inhibited. It is previously discussed that zeta potential significantly shifts to negative range due to surface modification of TiO₂ which may lead to low cyanide adsorption at zero min illumination. The change in zeta potential therefore

confirms that the titanium dioxide surface only interacts and adsorbs cyanide slightly at higher pH value [Chiang et al., 2003]. Figure 5.41 shows more initial adsorption of 5 ppm cyanide for Nf-TiO₂ in comparison to the Si-TiO₂. Nevertheless enhanced degradation trend under UV illumination for Si-TiO₂ is seen compared to Nf-TiO₂ till 60 min illumination. Nevertheless after 120 min illumination the cyanide removal is almost 100% for both catalysts. However in case of higher cyanide concentration (10 ppm), there is no significant difference in initial cyanide adsorption between Nf-TiO₂ and Si-TiO₂ (Figure 5.42). It is also found from Figure 5.39 that the degradation trend of cyanide is same while almost 100% cyanide is removed after 2 hr illumination. These trends are somewhat different from the respective NH₄⁺/NH₃ removal results as reported in Figures 5.37 and 5.38. The differences in the modified-TiO₂ surface affinities for NH₄⁺/NH₃ and cyanide species, may explain these anomalies in the respective PCD trends.

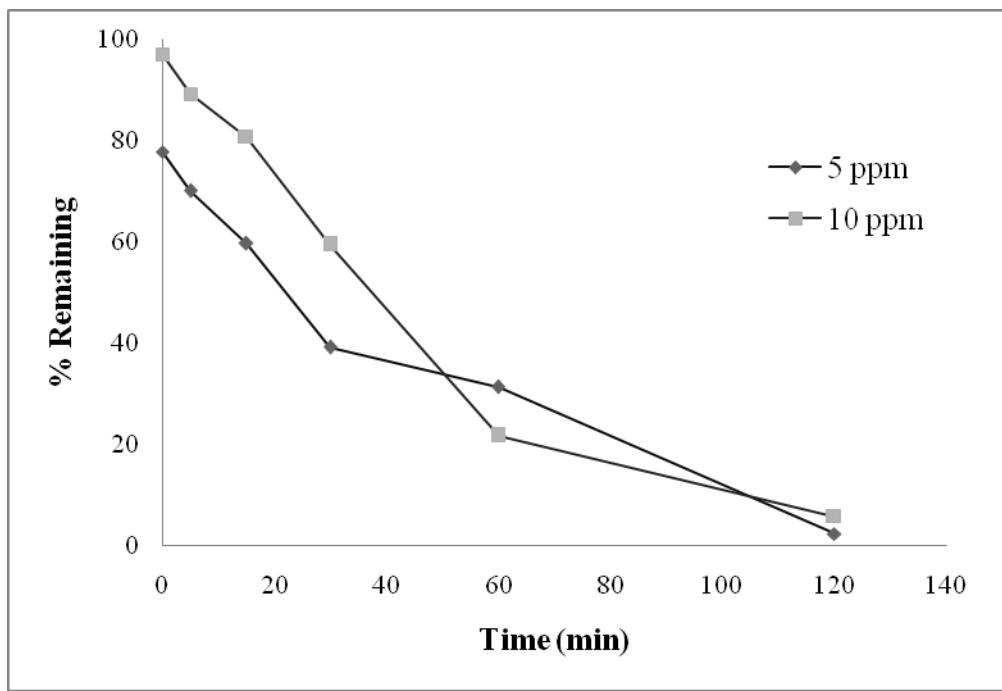


Figure 5.39: PCD of two different concentration of CN^- on Nf-TiO₂

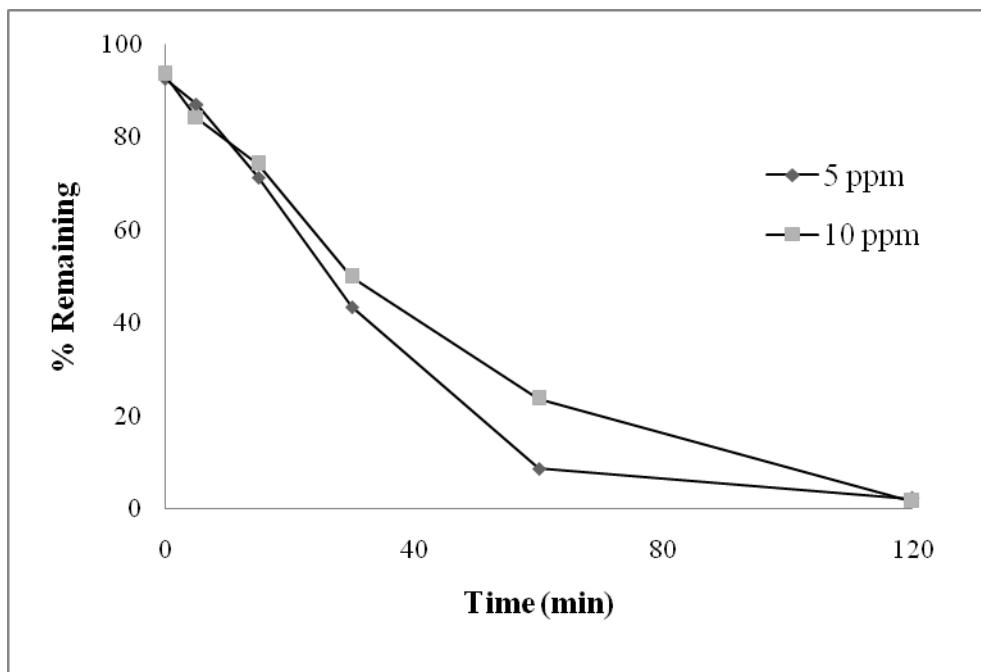


Figure 5.40: PCD of two different concentration of CN^- on Si-TiO_2

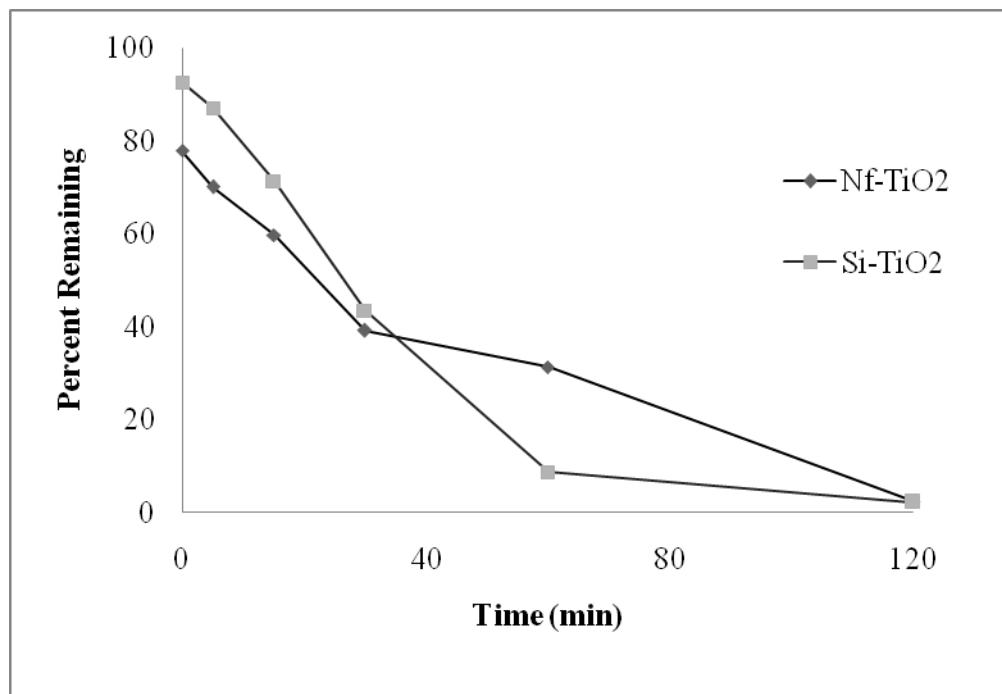


Figure 5.41: PCD of 5 ppm CN⁻ in mixed system on modified TiO₂

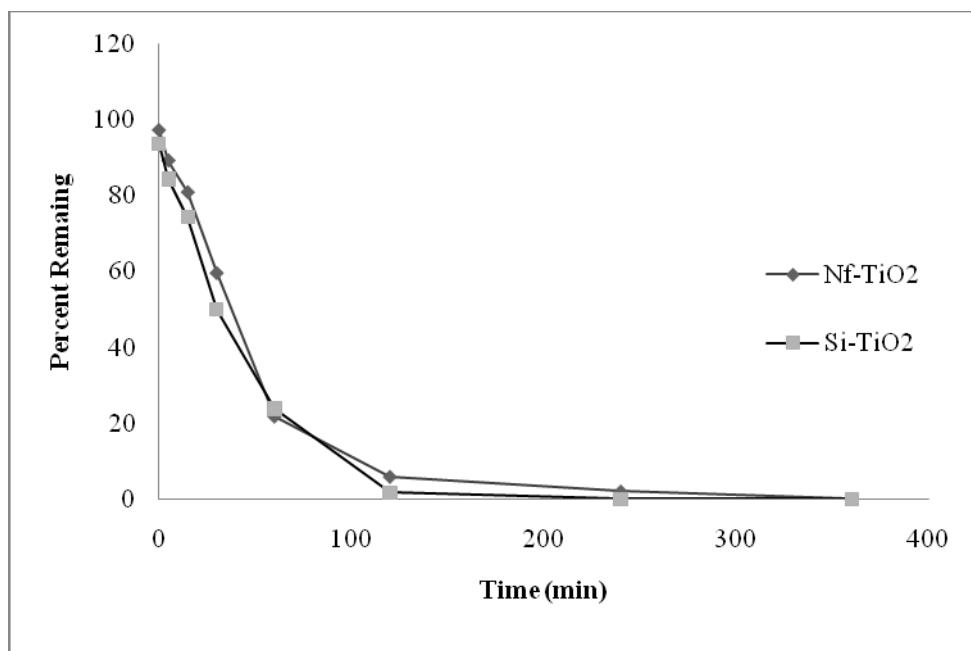


Figure 5.42: PCD of 10 ppm CN^- in mixed system on modified TiO_2

CHAPTER 6

6. Conclusions and Recommendations

6.1 Conclusions

Photocatalysis of aqueous phase pollutants was investigated using modified TiO₂ from diverse points of view. The use of Nafion modified TiO₂ and silica modified TiO₂ resulted in increased ammonia PCD compared to plain TiO₂. For both individual and mixed systems, the PCD trends were noted to be a function of pH. This was ascribed to the fact that changing the speciation of NH₄⁺/NH₃ and TiO₂ will also alter the electrostatic interaction between the two species and can explain enhanced NH₄⁺/NH₃ PCD at high pH. Nafion modified TiO₂ was found to be an efficient catalyst in comparison to plain TiO₂ with higher removal efficiency at pH 10 and pH 12. The ratio of 1:1 (1 ml Nafion per gm of TiO₂) maximized the PCD of NH₄⁺/NH₃ which makes up approximately 70% removal efficiency after 6 hour illumination. These results indicate that surface modification of photocatalyst TiO₂ with Nafion increases the PCD rate of substrate. A significant amount of MB was also degraded (93% removed) using Nf-TiO₂ after 2 hr illumination at pH 3. PCD of ammonia in presence of cyanide, indicated that Nafion-TiO₂ becomes more active catalyst under UV light while it shows less adsorption for higher concentration of cyanide at zero minute illumination. Silica modified TiO₂ also showed enhanced PCD of aqueous phase NH₄⁺/NH₃. The silica content of 0.5 ml/g TiO₂ yielded maximum NH₄⁺/NH₃ degradation in comparison to the 0.25 ml and 1ml of silica per gm of TiO₂. Furthermore the respective results also suggested that the availability of enough surface adsorption sites at the silica modified TiO₂ (0.5:1) results in faster substrate adsorption initiated uptake at time zero.

Surface modification of TiO₂ also showed better removal efficiency for 50 ppm NH₄⁺/NH₃, with Nf-TiO₂ showing 19% and Si-TiO₂ showing 7% more NH₄⁺/NH₃ removal, as compared to plain TiO₂. However, the overall percent based NH₄⁺/NH₃ removal gradually reduced with an increase in NH₄⁺/NH₃ concentration using plain or modified TiO₂ catalysts. It showed that even with the given surface modification TiO₂ with Nafion or silica, optimum removal efficiency is achieved only a specific concentration of substrate. For mixed systems, PCD were found to be comparatively faster for Si-TiO₂ when compared with Nf-TiO₂. Furthermore, approximately 99% of cyanide was also removed after 120 min. However, decrease in the overall NH₄⁺/NH₃ removal was noted as the cyanide concentration increased in the mixed systems.

6.2 Recommendations

Based on the result presented in this work, it is recommended that further research be conducted in the following area:

- Effect of modified TiO₂ amount, and UV-lamp power should be explored for enhanced ammonia removal at substrate concentration 100 ppm and above.
- Ammonia removal in the presence of cyanide should be further investigated, by optimizing the respective variables, to improve NH₄⁺/NH₃ removal efficiency in mixed systems.
- PCD of methylene blue should be further investigated to optimize its removal using modified TiO₂.

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