

Visible-Light Degradation of 2-Chlorophenol by TiO₂ doped with Neighboring Transition Metal Cerium via Various Approaches and Operation Parameters

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Research

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Abstract

TiO₂-related materials or processes for 2-chlorophenol (2-CP) degradation either under UV or visible light irradiations with key operational conditions was systematically reviewed in the beginning of this study. Cerium (Ce), which was neighboring transition metal elements of titanium (Ti), were individually doped with TiO₂ via various methods. Three synthetic parameters in the two approaches were examined their significance by using experimental designs. It was found that the 2-CP can be 100% removal within 4-h irradiation by visible light in the synthetic condition of 0.35 mol.% Ce, 0.15 vol.% nitric acid and calcined at 600°C. Moreover, effects of three operation parameters of the as-prepared catalysts were further investigated. The most efficient condition obtained was 3 g·L⁻¹ catalysts at initial pH and 2-CP concentration of 7 and 10 mg·L⁻¹, respectively. A critical parameter, pH_{pzc} of undoped and Ce-doped TiO₂, were also determined. In addition, surface area, pore volume and size of both TiO₂-based catalysts were found affected by the calcination temperatures and consequently degradation efficiency. The presenting results and mini-review were facilitated the development and applications of TiO₂ in the degradation of 2-CP under lower energy radiations.

1. Introduction

Chlorophenols (CPs) are listed as priority toxic chemicals [1] and considered to be carcinogenic, mutagenic, low biodegradable and difficult to remove by conventional wastewater treatment processes [2]. They are commonly used as precursor to chemical products such as pharmaceuticals, synthetic dyes, biocides, paints, textiles, leather products and wood preservatives [3]. Considering public health risks and ecological impacts, it may address the attentions as chlorophenols release from industrial wastes incineration, residual pesticides and petroleum refining effluents. Toxicological profiles of CPs and their derivatives were recently evaluated [3,4] as well as their environmental fates and transformations were addressed [5]. Di-chlorophenol (2-CP) is extensively used as precursors of the higher-substituted CPs or being generated as a by-product from plastic, papermaking, insecticidal and petrochemical industries. Due to its high solubility in water (28 g·L⁻¹) at room temperature, concentrations of 2-CP released in natural aquatic environment have been reported to be 103-164 ng·L⁻¹ in Lake Balaton, 31 ng·L⁻¹ in River Danube, Hungary [6], average of 82±20 ng·L⁻¹ in River Pearl, Guangzhou [7] and 6 ng·L⁻¹ in Taihu Lake, China [8]. Five types of phenols have been identified in effluents of five sewage treatment plants [2].

In addition, to reduce the presence of phenolic substances, specifically 2-CP, in the surface water [8], wastewater [2,9,10], and tap water [11], efficient and economical degradation of it is highly critical. Various processes such as heterogeneous photocatalysis [10], catalytic wet air oxidation [12], photosensitized oxidation [13], hydrodechlorination [14] and titanium dioxide adsorption [15, 16] have been initiated and proposed. Kinetics and mechanism of 2-CP via photodegradation in aquatic environment has been reviewed [17]. Juretic et al. [18] measured SUVA₂₅₄ and SUVA₂₈₀ of 2-CP, and obtained the corresponding values of three reference treatment periods utilizing UV-C/H₂O₂ process. TiO₂ can be used alone to decompose 2-CP by irradiated either under UV [19-21], concomitant UV [22], or with

applied external bias voltage [23]. Furthermore, the process intensifications and integration of TiO₂ photocatalytic system includes introduction of other semiconductor, enhance adsorption, enhanced UV light absorption via metal ion transition and application with H₂O₂/iron oxides [24-28].

In order to reduce energy cost, directly applying of lower energy demand such as the renewable (sun) or the visible lights as driving sources of photocatalysis were preferred instead of UV [29-30]. The band-gap of commercially available pristine TiO₂ is large and only small fraction of the solar spectrum can be utilized [31]. Consistent efforts to improve visible light activity (VLA) of TiO₂ were diligently worked out [32]. However, there is no detailed comparison of actual 2-CP degradation efficiency under diversified application of irradiations and conditions studied based in literatures. Various ion doping with TiO₂ using different methods of synthesis were the popular approach to enhance its VLA [32, 33]. Pristine commercial TiO₂ has been studied for its degradation efficiencies to 2-CP using a variety of parameters from early 1990s [19]. Since then various degradation conditions such as the initial 2-CP concentrations, types of substituted phenols, UV irradiation wavelengths, dissolved oxygen with/without applied external bias voltage, pH and presence of another semiconductor have been investigated [20-22,24]. Process integrations with TiO₂ photocatalysis and adsorption have been evaluated for 2-CP removal efficiency [25]. Adsorption of 2-CP by organo-clay combined with Degussa P25 under UV irradiations was also undertaken [26]. Moreover, biological process was also integrated with the commercial TiO₂ under the absence of light and natural sunlight irradiations, whereas the study of complete removal by the sole photocatalysis and by integrated process were achieved after 11 and 3 hours, respectively [11].

Apart from process integration with the commercial TiO₂ (Degussa P25), more researchers take approaches to enhance 2-CP degradation efficiencies and VLA of the most popular semiconductor by direct materials modification. Buzby et al., (2006) synthesized N-doped TiO₂ via plasma assisted chemical vapor deposition of gaseous ammonia and found higher N doping amounts resulting in higher efficiency of 2-CP degradation under visible light irradiation [34]. Ananpattarachai et al. (2006) compared N-doped TiO₂ synthesized from three nitrogen precursors in sol-gel method [35]. Mangrulkar et al. (2012) applied N-doped mesoporous titania to achieve 2-CP degradation of 98.62% under solar radiation [36]. Sharotri and Sud, (2016, 2015) synthesized N-doped and S-doped TiO₂ by green irradiation method for the degradation of 2-CP [37] [38]. There were studies that modified the surface of TiO₂ by doping with Co(III) while others tend to doped it with triple elements [39] [40]. Nanomaterials, such as reduced graphene oxide, carbon nanotube, In₂O₃ and InVO₄ were used to dope TiO₂ as well as Fe₃O₄/SiO₂/TiO₂ core-shell-shell nanoparticles for 2-CP removal [41-45]. A V₂O₅-doped TiO₂ catalyst prepared by impregnation method was used to convert two gaseous 2-CP isomers and obtained completely conversion to CO₂ at 270 °C [46]. Pt-doped TiO₂ prepared by immersed coating on Ti plate and Ag-doped TiO₂ nanofibers made by sol-gel and electrospinning was synthesized for the same purpose [47-48]. Ga, I-co-doped TiO₂ was also synthesized for the degradation of 2-CP in aqueous solution [49]. Elsalamony and Mahmoud, (2017) doped TiO₂ with ruthenium and yielded 98% degradation of 2-CP directly under UV

light irradiation [50]. Lin et al., (2018) applied CuSO₄-doped TiO₂ to degrade 2-CP and obtained 100% removal after 6h [51].

Apart from TiO₂, some nanocomposites also used as photocatalysts to degrade 2-CP. This includes Cu-nano zeolite was demonstrated excellent adsorption capability in 2-CP reduction in real wastewater (81.8%) with 150 min as well and efficient in the laboratory experiment with an optimized pH of 6 [52]. The study of Aslam et al., (2016) focused on sunlight induced surface defects of nanosized CeO₂ and revealed the role of superoxide anion radicals on the 2-CP oxidation [53]. On the other hand, Abou Taleb, (2014) synthesized Chitosan/ CoFe₂O₄ nanocomposite, while Rashid et al., (2014) ZrO₂-doped ZnCo₂O₄ nanoparticles obtained 91.7% removal of 2-CP under visible light irradiation [54-55]. ZnO nanoparticles as thin films without and with V doping can achieved complete degradation of 2-CP, eventually [56-57]. There were study on nanosized CeO₂ was examined its sunlight induced surface defects on photocatalytic degradation of phenol and its derivatives [58]. But other used Ce on TiO₂ synthesis for photocatalytic degradation of 4-CP [59]. An insight of Fe_(III)-porphyrin surface anchored TiO₂ for improving 4-nitrophenol photocatalytic decomposition under solar light irradiation was also studied [60].

Sidheswaran and Tavlarides, (2009) also evaluated the performance on visible light photocatalytic activity of Ce- and Fe-doped TiO₂ prepared by sol-gel method in oxidizing indoor VOCs [61]. Other researchers use Vanadium in doping titania for the photodegradation of phenol [62]. Ce- and V-doped TiO₂ were utilized for photocatalytic degradation of 3,4-dichloroaniline under visible light irradiation [63]. Thus, in this study, Ce-doped TiO₂ were synthesized and evaluated its performance via photocatalytic degradation of 2-CP. Moreover, three operational parameters were used to evaluate its photocatalytic degradation performance on 2-CP under simulated visible light irradiation. Part of the study is to determine and characterize the synthesized TiO₂ calcined at five temperatures including the pH_{pzc} of the pristine and Ce-doped TiO₂. Based on these experiments, utilizations of the doped TiO₂ could not only contribute to efficient photocatalytic degradation of 2-CP from materials modification aspects but also facilitated real applications in wastewater treatment processes.

2. Experimental

2.1. Chemicals and doping methods

In this study, Ce-doped TiO₂ catalysts were made by two methods, a sol-gel and a hydrothermal method. The first method is similar to the method but with modification reported by Tolosa et al. (2011b) where 10 mL of the Ti(OBu)₄ (98%, Alfa Aesar) was added to 40 mL ethanol (EtOH, 99.5%, Merck) and mixed at a constant stirring rate of 450 rpm for 5 min [64]. Two investigating amounts of HNO₃ (0.05 or 0.15 mol.%) was added into the mixture and continuously stirring for 10 min. Two investigating amounts (0.07 or 0.35 mol.%) of cerium (III) nitrate hexahydrate (99.5%, Sigma-Aldrich) with 5 mL of deionized water were added and mixed. The gels were aged for 24 h to complete hydrolysis, and then incubated in an autoclave at 121°C and 103.4 kPa. The samples were dried in an oven at 105°C. The produced xerogels

were pulverized and then calcined at various temperatures with a heating rate of 5°C/min. The second method as reported by Elsalamony and Mahmoud, (2017) was applied to synthesize pristine TiO₂ to compare with Ce-doped made by the first method [50]. The sample names were given named after individual calcination temperatures with digits after the doping elements thereafter.

2.2. Experimental designs, set-up and analytic methods

Design of experiments based on 2³ full factorial design (FFD) was utilized the same approach with previous study [51]. Two levels (-1 and +1) of three factors for Ce-doped TiO₂ were shown in **Table 1**. The responses (Y) obtained by individual photocatalytic degradation experiments were calculated based on below equation:

$$Y = (C_0 - C_t) / C_0 \times 100$$

(1)

where C₀ and C_t represent initial and residual concentrations of 2-CP (mg·L⁻¹) at the 4th h. The experimental set-up, sampling procedure, analyzed instruments and method of pH_{pzc} measurements were the same as previously reported [51].

3. Results And Discussion

3.1. Effects of experimental factors for Ce-doped TiO₂ on 2-CP degradations

Effects of three factors, such as (a) calcination temperature, (b) amount of dopant, and (c) amount of nitric acid added on Ce-doped TiO₂ for the degradation of 2-CP under visible light irradiation were shown in **Fig. 1**. For the Ce-doped TiO₂ photocatalysts synthesized by hydrothermal method, cerium amount of 0.35 mol.%, nitric acid amount of 0.15 vol.% and calcined at 600°C, the optimum degradation of 99.1% was obtained (refer to **Table 1**). Although three factors all showed positive effects with their increasing levels in **Fig. 1**, it is more significant of the first two factors (A and B) for Ce-doped TiO₂ than the third (C). The preliminary investigations were helpful for material scientists to fabricate a more suitable photocatalyst to degrade hazardous materials, such as 2-CP, in this case.

3.2. Effects of synthesized Ce-doped TiO₂ and its operational parameters on 2-CP degradations

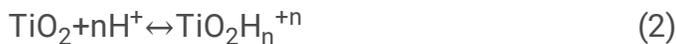
The Ce-doped TiO₂ made by hydrothermal method from previous optimized condition, was further compared to a commercial TiO₂ (P25) and undoped TiO₂ made by both methods. This is to assess the

contribution of cerium doping on the 2-CP degradation efficiency of TiO_2 under visible light irradiation. As shown in **Fig. 2a**, the P25 TiO_2 showed the lowest degradation ratio of 2-CP (38.0%) during the continuous monitoring up to 7 hours (420 min). The best fitting of 2-CP degradation by P25 was a polynomial quadratic equation with a R^2 of 0.9990 the blue light LED irradiation. The TiO_2 photocatalyst made by sol-gel method without doping by cerium had a better of 2-CP degradation at approximately 88.8% during the 7 hours irradiation. Similar trend of 2-CP degradation utilized by the undoped TiO_2 photocatalyst synthesized via hydrothermal method found to be more efficient on the degradation of 2-CP (93.1%) with the same time duration. Both undoped TiO_2 , synthesized by both methods fitted well with exponential decay double equations with five parameters, whereas respective R^2 were 0.9930 and 0.9992 for sol-gel and hydrothermal methods, respectively. The most promising degradation (99.1%) at 5 hours was exhibited by utilizing the Ce-doped TiO_2 (0.28 mol.%) made via hydrothermal method. An exponential decay double equation with three parameters was found to be interpreted the decay behavior well (R^2 of 0.9945). Therefore, the hydrothermal method was confirmed as the most feasible synthetic approach for Ce-doped TiO_2 and the same doping amount (0.28 mol.%) was applied in the subsequent studies.

Kosmulski and Tolosa et al. (2011) mentioned the pH-dependent surface charging and pH of point of zero charges (pH_{pzc}) [64, 65] can be a reference in searching of optimal pH either for homogeneous or heterogeneous photocatalysis systems. As the pH_{pzc} were critical in determining the operational pH in wastewater treatment, pH_{pzc} of the pristine (undoped) and Ce-doped TiO_2 (0.28 mol.%) was determined and shown in **Fig. 2b**. The former pH_{pzc} of the undoped TiO_2 (3.51) was consistent with previously study [40, 51]. Also, the latter pH_{pzc} of 2.83 for the Ce-doped TiO_2 measured in this study was close to TiO_2 doped with other dopants, e.g. CuSO_4 -doped TiO_2 ($\text{pH}_{\text{pzc}}=3.84$) [51] and $\text{KAl}(\text{SO}_4)_2$ -doped TiO_2 ($\text{pH}_{\text{pzc}}=1.90\sim 3.39$) [40].

As photocatalytic degradation efficiency of specific contaminants was affected by actual conditions of the wastewater streams, insights of the effects of operational parameters were examined intensively here. Detailed investigating ranges of three parameters (initial pH, catalyst dosages of Ce-doped TiO_2 and initial 2-CP concentrations) that utilizes the previous optimized Ce-doped TiO_2 (0.28 mol %, calcined at 600 °C) were listed in **Table 2**. The residual concentration of 2-CP under visible light irradiation at five initially conditioned pHs were all gradually decreased over time, as displayed in **Fig. 3a**. The solutions conditioned to neutral (pH 7) and slightly acidic (pH 5.5) performed better than the other three set pH. It can be shown that at initial pH of 5.5 and 7.0, the degradation of 2-CP at the end of 4-hour irradiation is approximately 100%. Highly acidic conditions with the pH of 3.0 and 2.0 have a good removal efficiency also during the 4-hour degradation of 2-CP which is about 83.9% and 85.8%, respectively. It can be seen in **Fig. 3a** that the degradation profiles with respect to time of pH 3.0 and 2.0 were quite close to each other. Moreover, the solution conditioned to basic (pH 9.0) yielded the lowest degradation efficiency of 2-CP. Aggregation of TiO_2 particles occur as the conditioned pH approaches to pH_{pzc} , while it tends to stabilize at both higher and lower pH conditions [64, 65].

For positively charged surface, $\text{pH} < \text{pH}_{\text{pzc}}$:



For negatively charged surface, $\text{pH} > \text{pH}_{\text{pzc}}$:



From previously determined pH_{pzc} of the Ce-doped TiO_2 at 2.83, the surface charge of the Ce-doped TiO_2 in the extreme low acidic condition (pH 2.0) was positive. But applying the photocatalyst at pH 3.0 that is very close to its pH_{pzc} , the charge effects may not be significant. As a result, the degradation profiles of pH 3.0 and 2.0 were overlapping, as displayed in **Fig. 3a**. The best 2-CP degradations in aqueous solutions conditioned to neutral may contributed to the surface charge of Ce-doped TiO_2 which became negative and the pK_a of 2-CP is 8.56. Similar results of pH-dependent in the degradation of 4-CP were observed by Silva et al. [58] whereas they found main deactivation mechanism of Ce-doped TiO_2 is ceria loss from the catalyst surface during reaction.

The effects various dosages of the Ce-doped TiO_2 catalyst that utilized for 2-CP degradations under visible light as shown in **Fig. 3b** were also investigated. Increasing the photocatalyst dosage from 1 to 3 $\text{g}\cdot\text{L}^{-1}$ increased the number of active sites available for surface adsorption and reaction. This results to more OH and $\cdot\text{O}_2^-$ radicals generated to facilitate photocatalytic activity that gives final removal in 4-hour duration of 66.7%, 85.2% and 99.9% shown in **Fig. 3b**. However, further increasing the Ce-doped TiO_2 dosage from 4 to 5 $\text{g}\cdot\text{L}^{-1}$, decreases the 2-CP degradation efficiency of 97.0 % and 70.4%, respectively. This phenomenon can be associated with the overcrowding catalysts that could block the light absorption on the catalyst surfaces [40]. The same trends were also found in our previous studies for CuSO_4 -doped TiO_2 catalysts [51]. Effects of initial 2-CP concentration on the degradation performance were also carried out from 10 to 50 $\text{mg}\cdot\text{L}^{-1}$ shown in **Fig. 3c**. Unsurprisingly, higher initial 2-CP concentration yielded lower degradations. This result is obvious since this can be associated with the pore blocking and multi-layer adsorption in the catalysts surface which will limit the release of the OH and O_2^- radicals [40]. In summary, optimal degradation of 2-CP was achieved at the dosage of Ce-doped TiO_2 catalysts, initial pH and initial 2-CP concentration of 33g, 7.0 and 10 $\cdot\text{mg}\cdot\text{L}^{-1}$, respectively. Such results would be helpful in practical operation of this system in wastewater treatment facility.

3.3. Characterizations of Ce-doped TiO_2 synthesized at various calcination temperatures and doping amounts

As catalysts calcined at various temperatures possess various properties and may affects their photocatalytic degradation efficiencies under visible light irradiation. Characterizations of the Ce-doped TiO_2 photocatalyst were conducted by Brunauer–Emmett–Teller (BET), Langmuir, t-plot external and

single point methods to measure its surface area, pore volume and pore size. As shown in **Table 3**, it can be observed no matter which methods analyzed, surface area of the Ce-doped TiO₂ photocatalyst generally decreased with the increasing calcination temperatures from 200 to 500 °C. However, there is a different trend in the result observed in 600 °C calcination temperature where the surface area increases. The occurrence is also evident with the pore volume and pore size measurements of the Ce-doped TiO₂ photocatalyst. As all surface areas characterized by various methods consistently showed that the Ce-doped TiO₂ calcined at 600 °C were higher than that calcined at 200 °C, we can concluded that structures of the Ce-doped TiO₂ was not the sole factor affecting the photocatalytic degradation of 2-CP. Instead, the cerium doping amount played a certain role as shown in the previous data in the Section 3.1 and these characterizations obtained here. Tong et al. [59] have prepared Ce–TiO₂ catalysts by controlled hydrolysis of titanium alkoxide based on esterification reaction followed by hydrothermal treatment. They doped various cerium amounts (0.1, 0.2, 0.4, 0.6 and 1.0 wt.%) into TiO₂ by the controlled hydrolysis and calcined at 460°C (733 K) can be a reference as well. As shown in **Table 3**, the Ce-doped TiO₂ calcined at 400 °C registered the highest pore volume of 0.2208 cm³/g among the five (5) calcination temperatures. Although there is no clear relationships between calcination temperatures and pore volumes, it was noted that there is significant correlation between small particle size, large surface area and pore volume. Consequently, calcined at either middle temperatures (e.g. 300, 400 °C or in between) can be a feasible option for future large-scale production the Ce-doped TiO₂ catalysts.

Morphology of the undoped and the TiO₂ doped with low, medium and high amounts of cerium (from 0.07, 0.28 to 0.35 mol.%) can be observed by scanning electron micrographs (SEM) shown in **Fig. 4**. All SEM images were taken at magnitude of 1,000 times. A more uniform distribution of spherical particles was obtained in the undoped TiO₂ as shown in **Fig. 4a**, while irregular shapes of crystals were obtained in the Ce-doped TiO₂ (**Fig. 4b, 4c and 4d**) regardless of doping amounts added. Even the diverse distributions of the particles of Ce-doped TiO₂ revealed by the SEM images. It can also see that the presence of Cerium in the preparation of the catalysts modify the surface morphology of the TiO₂ which means that might affect the light absorption of the catalysts. The main effects on performance of 2-CP degradation were affected by their specific surface area.

4. Conclusion

In summary, the degradation efficiency of the synthesized TiO₂-based photocatalysts is successful in degrading aqueous 2-chlorophenol via photocatalytic oxidation process. The Ce-doped TiO₂ calcined between 300 °C and 400 °C which gives an ideal specific surface area, pore volume and pore size of 219.3 – 267.3 m².g⁻¹, 0.2052 – 0.2208 cm³.g⁻¹, and 30.7 – 40.3 Å, respectively. However, if we based the selection of photocatalyst in terms of pore volume, the Ce-doped TiO₂ calcined at 400 °C gives the highest result. In addition, based on the morphology of the synthesized photocatalysts using SEM shows the diverse distribution of particles of Cerium in TiO₂. Such that it shows an excellent surface modification

of the TiO₂. From the photocatalytic activity on varying Ce-doped TiO₂ concentration, the dosage of 3 g.L⁻¹.

A priority hazardous substance, 2-chlorophenol (2-CP), was carefully reviewed degradation efficiency by TiO₂-based photocatalysts under UV or visible light irradiation and compared diverse experimental conditions in the literatures. Two new photocatalysts synthesized in this study, either Ce-doped TiO₂ prepared by hydrothermal method or V-doped TiO₂ prepared by sol-gel method, were investigated effects of synthetic parameters on their visible-light activities via blue-LED irradiations. Furthermore, effects of three operation parameters of the as-prepared catalysts were investigated.

Declarations

Availability of data and materials

All data generated or analyzed during this study are available upon request to the corresponding author.

Competing interests

The authors declare they have no competing interests.

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Authors' contributions

AG, TJ and JCTL carries out the literature review and performed the design of the study. AG and TJ facilitate on the experimentation and data collection with the supervision of KS and MCL. JCTL and NCT participated in the data validation and drafting of the manuscript through the contribution of all authors. All authors read and approved the final manuscript.

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Tables

Table 1. Experimental designs of visible–light degradation of 2-CP by Ce-doped TiO₂.

Experiment No.	Parameter A:		Parameter B:		Parameter C:		Response Y: Degradation percentage [%]
	Calcination temperature [°C]		Amount of cerium [mol.% Ce/TiO ₂]		Amount of nitric acid [vol.% HNO ₃ /Ti(OBu) ₄]		
Cerium							
	(-1)*	(+1)*	(-1)*	(+1)*	(-1)*	(+1)*	
1	200	-	0.07	-	0.05	-	64.87
2	-	600	0.07	-	0.05	-	72.21
3	200	-	0.07	-	-	0.15	80.52
4	-	600	0.07	-	-	0.15	78.24
5	200	-	-	0.35	0.05	-	72.43
6	-	600	-	0.35	0.05	-	72.96
7	200	-	-	0.35	-	0.15	99.08
8	-	600	-	0.35	-	0.15	99.10

*(+1: upper level, -1: lower level)

Table 2. Operational parameters of Ce-doped TiO₂ and experimental ranges investigated in this study.

Operational parameters	Unit	Experimental ranges
Input pH	—	2.0, 3.0, 5.5, 7.0, 9.0
Photocatalysts dosage	g/L	1.0, 2.0, 3.0, 4.0, 5.0
Initial 2-chlorophenol concentration	ppm	10, 20, 30, 40, 50

Table 3. BET results of Ce-doped TiO₂ at calcination temperatures of 200-600°C

Sample name	Surface Area [unit: m ² /g]				Pore Volume	Pore Size
	BET	Langmuir	t-Plot External	Single point	[unit: cm ³ /g] Single point adsorption total pore volume of pores	[unit: Å] Adsorption average pore width (4V/A by BET)
Ce200	275.5	391.2	319.4	254.5	0.1882	27.3
Ce300	267.3	376.1	304.0	249.8	0.2052	30.7
Ce400	219.3	308.3	243.7	207.6	0.2208	40.3
Ce500	164.7	228.6	178.2	157.2	0.2105	51.1
Ce600	201.5	281.8	214.4	191.4	0.1705	33.9

Figures

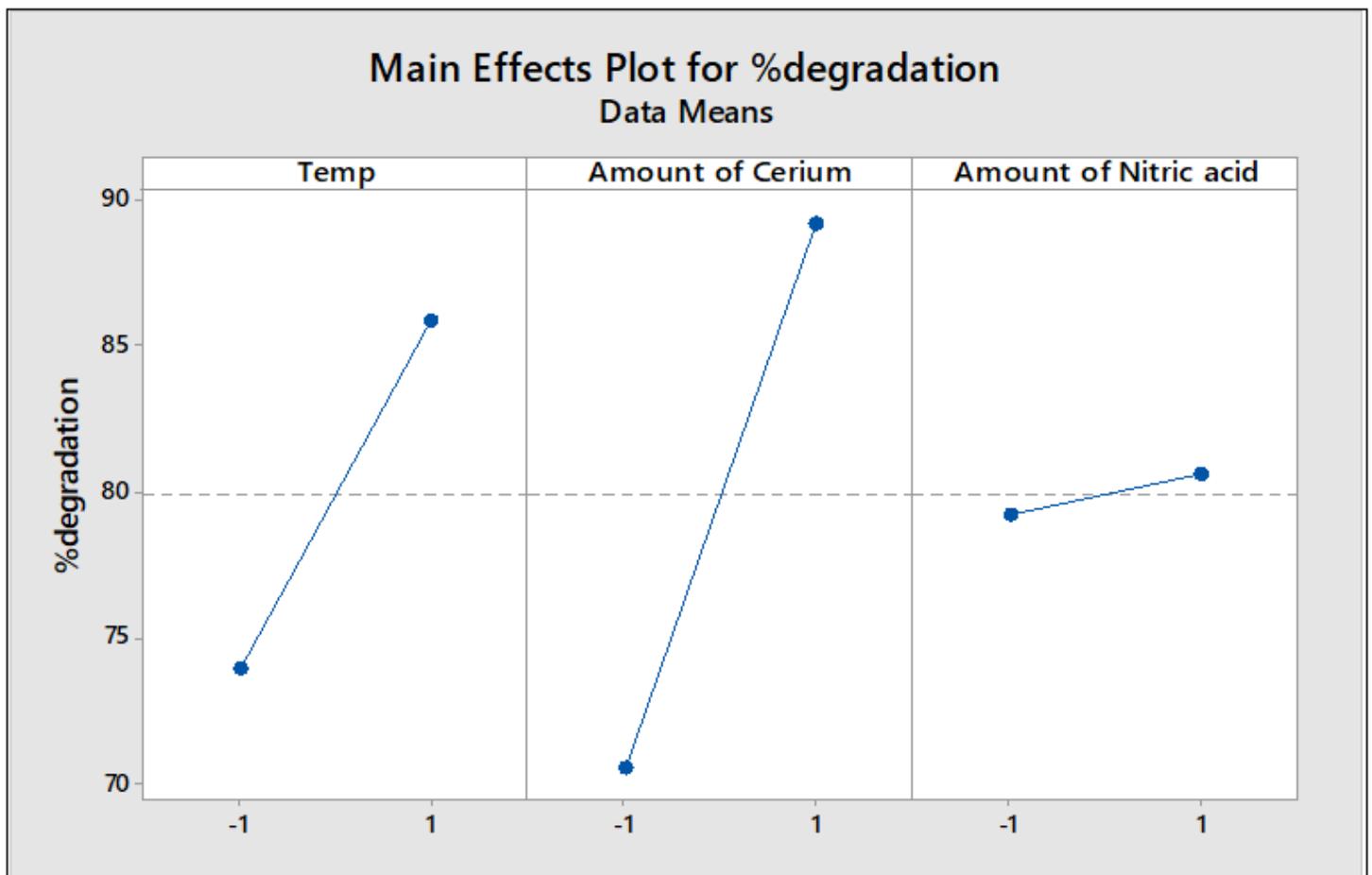


Figure 1

Main effect plot of three synthetic parameters on 2-CP degradation percentage by using Ce-doped TiO₂ under visible light irradiation.

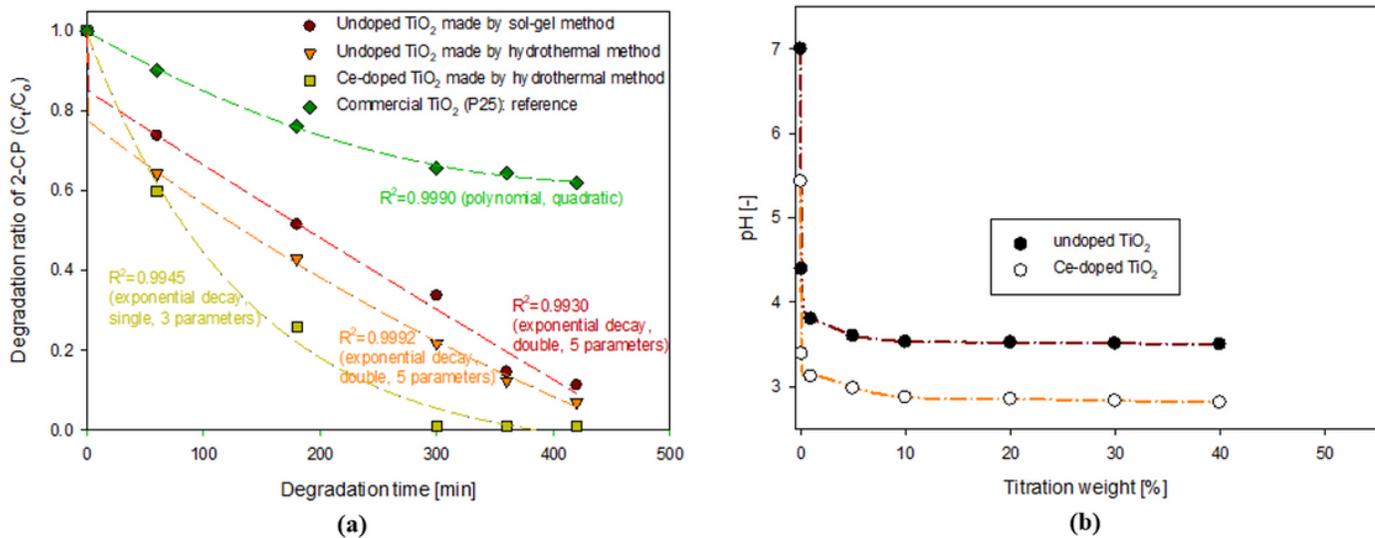
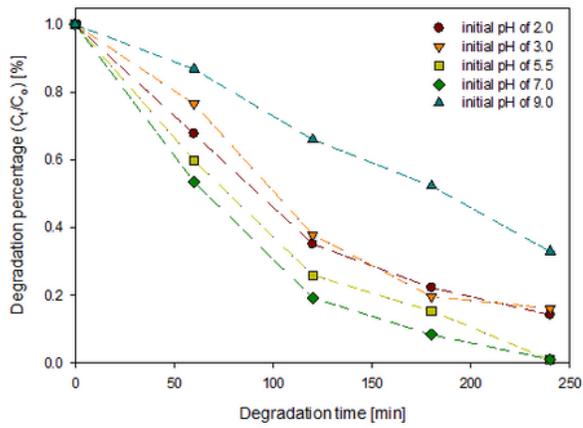
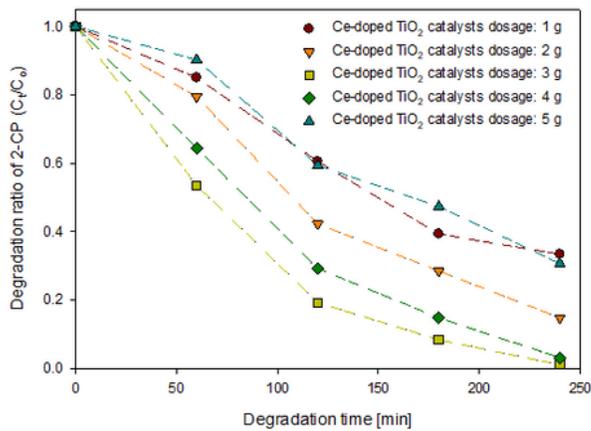


Figure 2

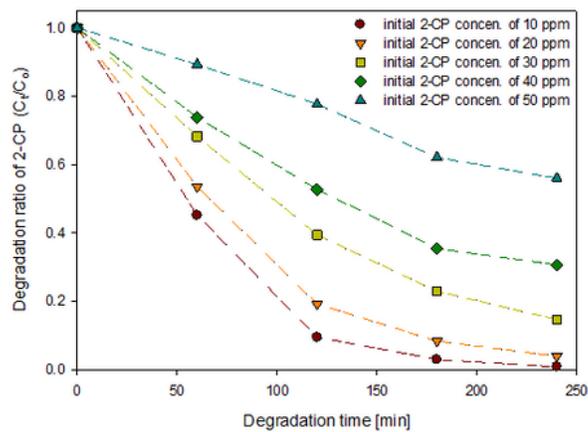
(a) Comparison of the degradation efficiencies of 2-CP by pristine TiO₂ made by sol-gel method, hydrothermal method, Ce-doped TiO₂ (0.28 mol.%) made by hydrothermal method and commercially available TiO₂ (P25). (b) Measurements pHzpc of undoped and Ce-doped TiO₂.



(a)



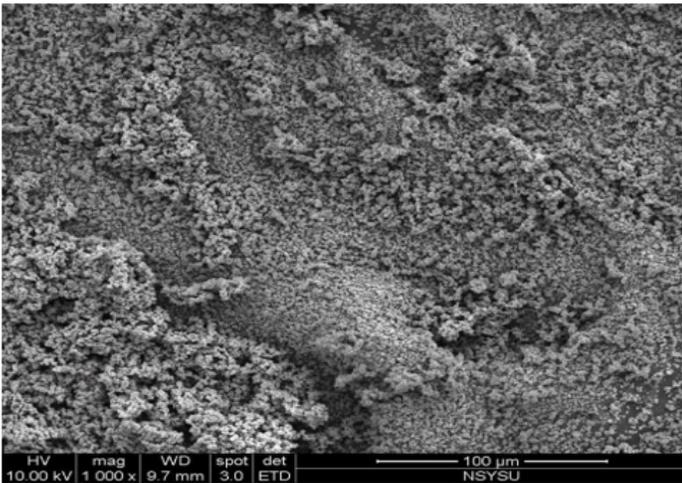
(b)



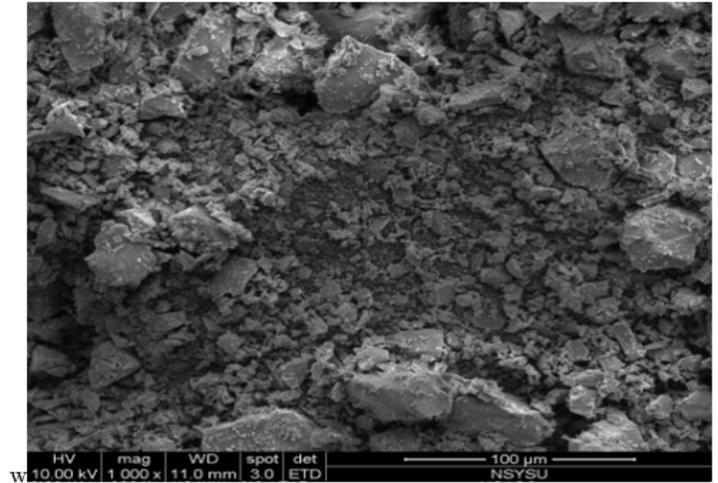
(c)

Figure 3

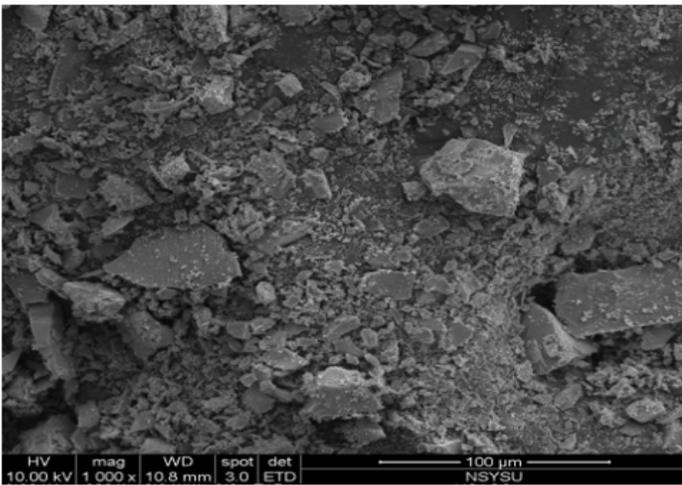
Effects of (a) initial pH, (b) catalyst dosages and (c) initial 2-CP concentrations on the degradations of 2-CP (concentrations of 20 mg·L⁻¹) with the Ce-doped TiO₂ (dosage of 3g/L) under visible light irradiation.



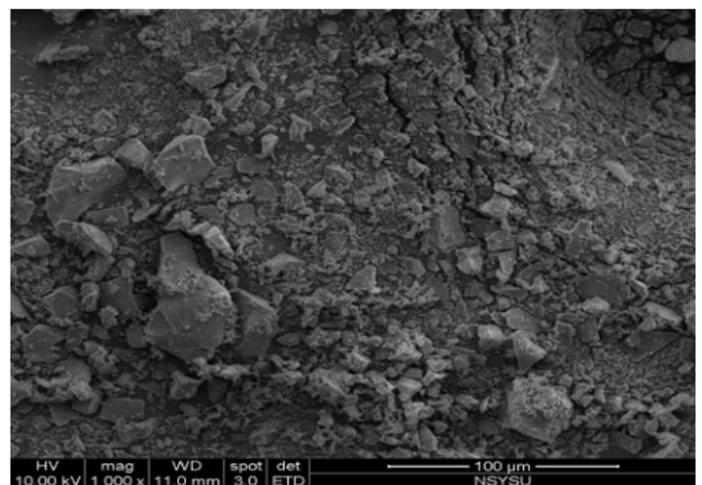
(a)



(c)



(b)



(d)

Figure 4

Scanning electron micrographs of (a) undoped TiO_2 , and Ce-doped TiO_2 doped with (b) 0.07 mol.%, (c) 0.28 mol.% and (d) 0.35 mol.% Cerium.