

# The Effect of Crystalline Phase on the Simultaneous Degradation of Phenol and Reduction of Chromium (VI) Using UV/TiO<sub>2</sub> Photocatalysis

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Chromium (IV) contamination in industrial wastewater has been on the rise due to increased anthropogenic activities. Similarly, typical industrial wastewater contains high levels of phenol as a result of the direct disposal on phenol into industrial effluent or as degradation products from phenolic compounds. Both these contaminants have adverse effects to human health and the environment and it is therefore necessary to develop technologies to remove them in a sustainable manner. Photocatalysis using TiO<sub>2</sub> catalyst activated by UV light is one such technology as it can either oxidize and mineralize organic pollutants or reduce heavy metals contaminants into a noble form. Degussa P25 TiO<sub>2</sub> is normally used in photocatalysis due its ability to reduce electron-hole recombination. It has been theorized that the addition of organic compounds as hole scavengers during the photocatalytic reduction of Cr(VI) aids in the reduction efficiency. This study investigated the use of anatase-form TiO<sub>2</sub> on the reduction of Cr(VI) in the presence of phenol and compared the results to similar work carried out by our group out Degussa P25 as catalyst. The anatase was shown to be an effective catalyst in the reduction of Cr(VI) with as much as 32 % reduction occurring at neutral pH with no phenol present. Adjusting the solution pH to 3 increased the percentage reduction to 40.7 % whilst addition of 100 ppm of phenol at pH 3 resulted in a 52.3 % Cr(VI) reduction. Comparison of the results obtained for anatase and Degussa P25 TiO<sub>2</sub> at the same pH revealed approximately the same Cr(VI) reduction efficiencies with the Degussa P25 having a slight edge. This suggests that the nature of the crystal phase of the two TiO<sub>2</sub> investigated does not significantly influence the reduction efficiency of Cr(VI) in the presence of phenol.

## 1. Introduction

Most municipal wastewater treatment plants receive influent from both domestic and industrial sources. This results in the water containing a wide range of pollutants with varying concentrations. Depending on the predominant industrial activities, the typical pollutants include aromatic-based organic pollutants such as pesticides, dyes and phenol or inorganic heavy metals such as chromium (Gupta and Balomajumder, 2015). In nature chromium is mostly found in the trivalent Cr (III) state, however, the more mobile Cr (VI) is discharged in wastewater from various anthropogenic activities such as mineral processing, electroplating, leather tanning and pigment production (Igboamalu and Chirwa, 2016). Cr (VI) is a non-biodegradable and persistent pollutant which has mutagenic and carcinogenic effects that are highly toxic to most living organisms even at concentrations as low as 0.05 ppm (Yang et al., 2013). Aromatic compounds such as phenol and its derivatives are widely used as raw materials in many industries such as petrochemicals, chemical and pharmaceutical. Effluent from these industries thus tends to contain high concentrations of phenol. Other sources of phenol in wastewater include the natural degradation products of insecticides and dyes, coking operations, as well as decomposition of plant matter. Phenol classified as a priority pollutant, which may result in serious health risks to humans, animals, and aquatic life if left untreated (Villegas et al., 2016). Besides the adverse health and environmental effects discussed, phenol also tends to give rise to the presence of offensive odours in water. These odours cause poor appetite for food, lowered water consumption, impaired respiration, nausea and

vomiting, and mental perturbation (Safoniuk, 2004). The WHO stipulates that the maximum permissible limit for Cr (VI) and phenol are 0.05 and 1 ppm respectively (Gupta and Balomajumder, 2015). In order to secure human health and environmental sustainability it imperative that these pollutants be removed from wastewater before it is discharged to natural water bodies. Conventional technologies which make use of phase separation techniques such as adsorption, reverse osmosis and liquid-liquid extraction (stripping) have been developed and are widely used in order to control this type of pollutants (Andreozzi et al., 1999). However, these techniques suffer in that the adsorbing medium or pollutant-rich stripping phase would still need to be disposed of. Advanced oxidation processes (AOP's) on the other hand make use of chemical oxidation and effectively mineralize the contaminants. In some cases, partial oxidation of these pollutant is sufficient to render specific compounds more amenable to subsequent biological treatment or to reduce their toxicity (Safoniuk, 2004).

Photocatalysis has been identified as one of the advanced oxidation technologies that can be used to treat these pollutants. This technology either oxidizes and effectively mineralizes organic pollutants or reduces heavy metals contaminants into a noble form or less mobile oxidation state. It is possible for both redox reactions to occur simultaneously, thus providing an opportunity for the removal of both classes of pollutants in the same reactor. Photocatalysis makes use of a semiconductor catalyst suspended in aqueous medium which is then illuminated with light producing photogenerated electrons and holes on the surface of the catalyst. These photogenerated sites then act as sites for the oxidation and reduction of organic and inorganic pollutants.

While a wide range of possible semi-conductors have been reported in literature, titanium dioxide is arguably the most well studied semi-conductor material in photocatalysis applications (Yang et al. 2013). This is due to a number of reasons which include high chemical stability, low cost and high reaction potential. Titanium oxide exists in 3 main phases, namely anatase, brookite and rutile. However, Degussa P25, a commercial mixture of rutile and anatase is the  $\text{TiO}_2$  of choice. This is because the interaction of these two phases in the particles enhances separation of the electron and hole which ultimately increases the quantum yield (Huang et al., 2012). While a number of studies have been reported on the photocatalytic removal of phenol and Cr(VI) separately from wastewater, limited studies have been reported on simultaneous pollutant removal. It has been suggested that the addition of organic compounds into solution during the photocatalytic reduction of Cr(VI) will increase the efficiency since charge separation is increased by the organic consuming the hole. However, in the case of Degussa P25, since charge separation is already efficient any further addition organic may not enhance separation. Therefore, Degussa P25  $\text{TiO}_2$  may not be the most suitable  $\text{TiO}_2$  phase in simultaneous Cr(VI) reduction, phenol degradation studies (Huang et al., 2012). A comparison between the effect of  $\text{TiO}_2$  crystal phase on the reduction efficiency of Cr(VI) in the presence of phenol has not been reported to the best of our knowledge. Therefore, the current study investigated the use of anatase form  $\text{TiO}_2$  as a photocatalyst in the simultaneous removal of Cr(VI) and phenol from wastewater. The results obtained were then compared to previous data reported by our group where Degussa P25  $\text{TiO}_2$  was used instead (Tshuto et al., 2017). While significant research has been conducted on the use of photocatalysis as a viable technology for pollutant removal, its uptake for commercial applications has been limited. This study forms part of a greater project where as pilot scale reactor is to be set up in an existing wastewater treatment plant that receives influent with high concentrations of phenol and Cr(VI) in South Africa. Materials and methods

## 2. Materials and methods

### 2.1 Materials

Anatase form  $\text{TiO}_2$  was purchased from Sigma Aldrich while the Degussa P25 was obtained from Nanoshel (USA). The simulated wastewater was prepared using potassium chromate ( $\text{K}_2\text{CrO}_4$ ) and phenol mixed in deionised water from a lab still. Methanol and 1.5-Diphenylcarbazide (DPC) were also purchased from Sigma Aldrich. High Performance Liquid Chromatography (HPLC) grade sulphuric acid ( $\text{H}_2\text{SO}_4$ ) (98 % purity) was purchased from Glassworld, South Africa. Other chemicals and reagents used in this study, such as sodium hydroxide pellets and acetone, were purchased from Merck Chemicals (SA).

### 2.2 Methods

The experimental setup that was used is illustrated in Figure 1. A magnetic stirrer was used to maintain homogeneity of the catalyst suspension throughout the experiment. Compressed air was continuously bubbled into the solution to aid in mixing together with providing oxygen which acts as a hole scavenger. The temperature of the solution was kept in the 24-26 °C range using water flowing through a water jacket. A lamp sleeve was submerged at the centre of the reactor, depending on the experiment, different light sources were placed in the sleeve. In order to prevent distortions from alternative light sources, the whole setup was contained in a box.

The first set of experiments involved control experiments which established the effect of catalyst adsorption in the absence of light (catalysis) and possible influence of the light source only in the absence of catalyst (photolysis). These tests were carried out at constant 0.02 g/L catalyst loading and varying Cr(VI) concentrations

(10 – 100 ppm). Finally, photocatalysis experiments were conducted under similar conditions using a 400 W UV light source. All the experiments were carried out for 2 h. Based on the results from the first set of experiments an optimum Cr(VI) concentration was identified and this was carried over to the next experiments where the concentration of the Cr(VI) solution was kept constant and the catalyst loading was varied from 0.005 to 0.08 g/L of anatase TiO<sub>2</sub>. The effect of pH on the reduction of Cr(VI) was determined by controlling the solution pH at 3, 7 or 9 using either sulphuric acid or sodium hydroxide. Finally the influence of the presence of phenol on the reduction of Cr(VI) was investigated under the following parameters: chromium solution concentration of 20 ppm, 0.02 g/L catalyst loading at controlled pH values of 3, 7 and 9 whilst varying the amount of phenol from 10 to 100 ppm.

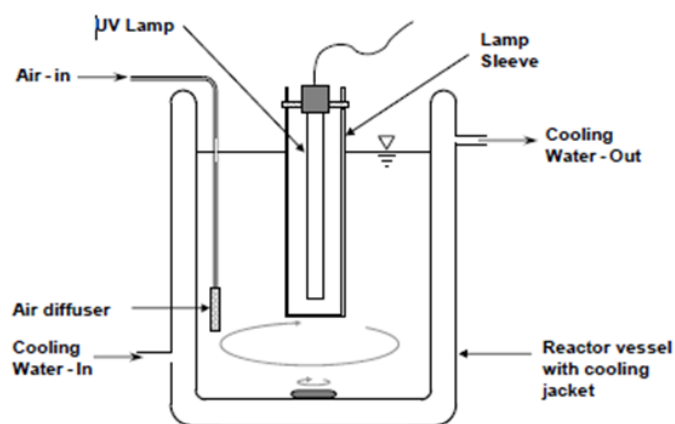


Figure 1: Photocatalysis reactor set-up

### 2.3 Characterization and analysis

The morphology and average particle size of the two catalysts under consideration was determined using a HR FEGSEM Zeiss Ultra Plus 55 ultrahigh resolution field emission scanning electron microscopy (SEM) and JEOL 2100F transmission electron microscopy (TEM). The purity and phases of the different TiO<sub>2</sub> powders was analysed using a Siemens D-501 automated diffractometer operated at 40 kV and 40 mA using CuK $\alpha$  radiation ( $\lambda = 1.5406\text{\AA}$ ). The chemical composition was confirmed using a Thermo Fisher ARL Perform'X Sequential XRF instrument with Uniquant software was used for analyses. Changes in Cr (VI) concentration were analysed using a standard method described by Federation and Association (2005). A sample volume of 0.1 mL is first acidified with 1 N H<sub>2</sub>SO<sub>4</sub> before reacting it with 1,5-diphenyl carbazide to produce a purple colour. The resultant samples were then analysed using a WPA, LIGHT Wave, Labotech UV-vis spectrophotometer at a 540 nm wavelength.

## 3. Results and discussion

### 3.1 Material characterization

X-ray diffraction analysis confirmed the anatase TiO<sub>2</sub> to be of high crystalline purity (Figure 1), while the Degussa P25 TiO<sub>2</sub> was confirmed to be a mixture of anatase (87.3 %) and rutile (12.7 %). Elemental analysis using X-ray fluorescence, however, established the presence of silica contamination in the anatase. While, the silica might interfere with the electron transitions upon light irradiation, SiO<sub>2</sub> is known to have good adsorption properties (Rosales-Landeros et al. 2013). A high loss on ignition value was recorded for Degussa P25 TiO<sub>2</sub> indicates the presence of an organic coating on the powder, possibly to minimize particle agglomeration.

Figure 2 shows the morphology of the different catalyst powders. The SEM pictures show that both powders are highly agglomerated, with the particles having a near spherical shape. TEM images were taken in order to determine the primary particle size. This was determined to be 30 nm for the anatase and 50 nm for the Degussa P25. This suggests that in order to maximize on the surface area advantages brought about by the nanomaterial, the catalyst/wastewater suspension has to be sonicated to breakdown the agglomerates.

### 3.2 Photocatalysis studies

Control experiments were initially carried out to establish the efficiency of the anatase catalyst as well as the suitability of the reactor set-up. Different initial concentrations of Cr(VI) were used and the influence of light only (photolysis) on the reduction of Cr(VI) was determined. The percentage removal due to UV light only was 8.4 %

at a concentration of 10 ppm Cr(VI) and less than 5 % for all the other concentrations tested. The slight reduction of Cr(VI) under these conditions has previously been reported (Kieber and Helz, 1992). The effect of the catalyst as an adsorbent was tested using 0.02 g/L of anatase under dark conditions. The catalyst had no effect on the Cr removal. Cr(VI) reduction under photocatalysis conditions was shown to be superior regardless of the initial concentration. The lower Cr(VI) concentration had a higher percentage reduction (31.5 %) compared the 100 ppm solution which had a 13 % reduction.

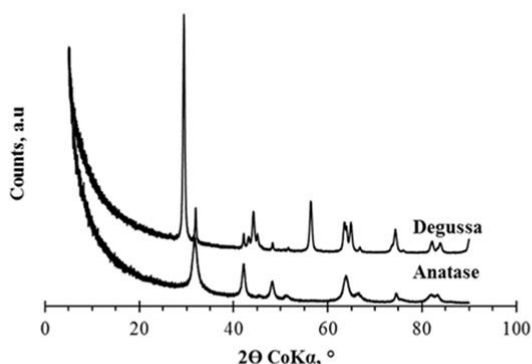


Figure 2: XRD scans of Anatase and Degussa titanium oxide

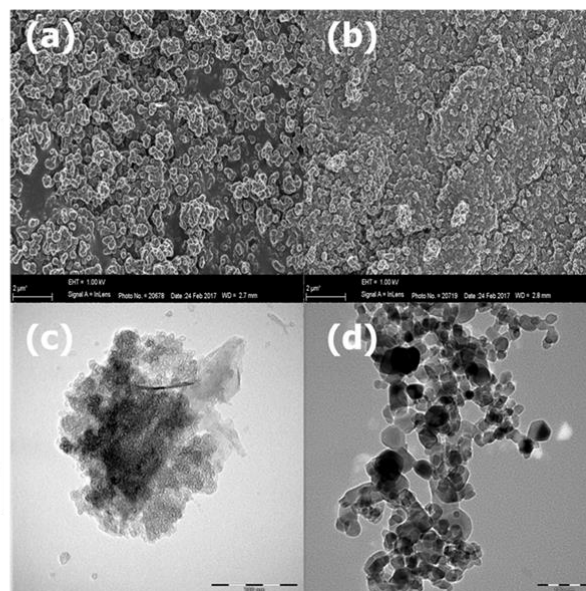


Figure 3: Scanning electron microscopy images of (a) Anatase  $\text{TiO}_2$  (b) Degussa P25  $\text{TiO}_2$  and Transmission electron microscopy images of (c) Anatase  $\text{TiO}_2$  (d) Degussa P25  $\text{TiO}_2$

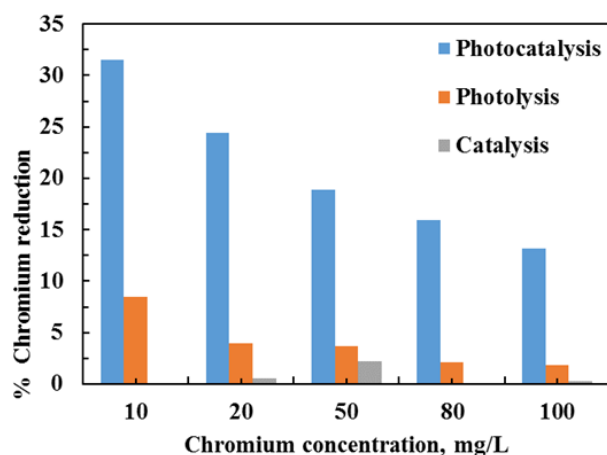


Figure 4: Percentage Cr(VI) reduction at different initial Cr(VI) concentrations under photolysis, catalysis and photocatalysis conditions

The highest chromium reduction occurred at an initial concentration of 10 ppm, therefore all further tests were conducted at this concentration. Figure 4 shows the effect of catalyst loading on the reduction of chromium. The maximum reduction occurred at 0.02 g/L catalyst loading. Any further increase resulted in decreased removal efficiency. This is likely due to shielding effects that might occur as the concentration of the particles increases in suspension. This results in a fraction of the catalyst particles not getting adequate irradiation to create the electro-hole pairs needed for the reaction to take place, thus reducing the quantum yield.

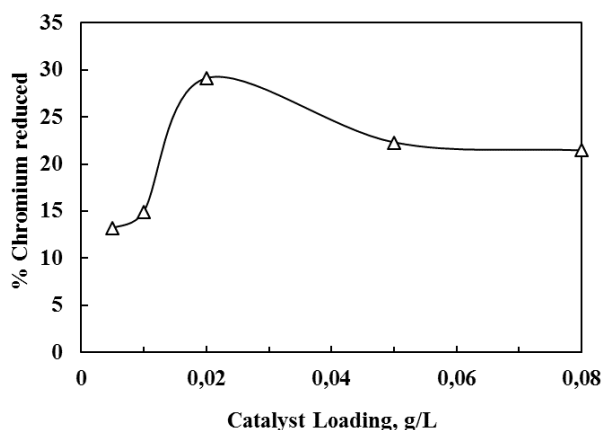


Figure 5: Effect of catalyst loading at a fixed 20 ppm Cr(VI) concentration

It has been shown that Cr(VI) exists as different species depending on the solution pH (Chamberlain and Day 1956). This influences the extent of Cr(VI) reduction that occurs during photocatalysis. In this study the effect of pH on the efficiency of Cr(VI) reduction by anatase photocatalysis was studied at pH of 3, 7 and 9. The highest reduction was obtained at a pH of 3 which showed a 40.7 % reduction Cr(VI) compared to 31.5 % at pH 7. The alkaline pH 9 solution had a slightly lower percentage reduction (26.4%). It has been reported that Cr(VI) reduction by the photogenerated electrons takes place under the following reactions shown in Scheme 1 depending on the solution pH (Ku and Jung, 2001). Based on the standard redox potentials of the two reactions, it is clear that reduction is favoured under acidic conditions where the  $\text{Cr}_2\text{O}_7^{2-}$  ion is a stronger oxidizing agent. Similar trends were observed by Wu et al. (2013).



**Scheme 1.** Reduction of Cr(VI) under acidic and basic conditions

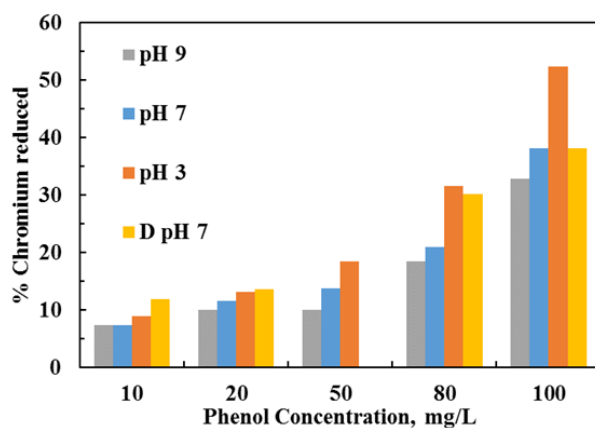
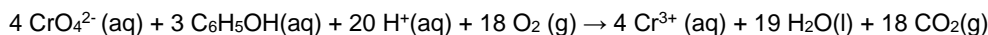


Figure 6: Cr(VI) reduction at different pH in the presence of varying concentrations of phenol. Results marked D pH7 represent previously reported values using Degussa  $\text{TiO}_2$

It has been shown that the accompanying hole created when a valence electron is promoted to the conduction band is capable of decomposing organic materials into  $\text{CO}_2$  and  $\text{H}_2\text{O}$  (Cheng et al. 2015). The effect of the presence of phenol on the Cr(VI) reduction is shown in Figure 5. As the amount of phenol is increased, a greater portion of the chromium is reduced. A similar trend was previously reported using Degussa P25  $\text{TiO}_2$  (Tshuto et al. 2017) at a pH of 7. The previous results have been labeled "D pH 7" in Figure 5. The Cr(VI) reduction efficiency was almost similar for both the Anatase and Degussa form of  $\text{TiO}_2$ , however, Degussa was slightly better. The influence of pH was comparable for at lower phenol concentrations, however, at higher phenol

concentrations pH 3 solutions were more superior. Increased Cr(VI) reduction efficiencies in the presence of phenol are attributed to the redox reaction shown in Scheme II (Tshuto et al. 2017).



**Scheme II.** Overall redox reaction between Cr(VI) and phenol in an acidic environment in the presence of photogenerated electrons

#### 4. Conclusions

Anatase form TiO<sub>2</sub> was shown to be an efficient photocatalyst for the reduction of Cr(VI). The optimum conditions for reduction were a Cr(VI) concentration of 10 ppm, with a 0.02 g/L catalyst loading and an acidic pH. The presence of phenol markedly increased the reduction efficiency as the organic compound reacted with the holes produced in the semiconductor catalyst thereby reducing the possibility of electron-hole recombination. Comparison of the Cr(VI) removal in the presence of phenol using Anatase and Degussa TiO<sub>2</sub> revealed comparable results although Degussa had a slight edge. Further experiments are being carried out to determine the degradation efficiency of the phenol under similar conditions.

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