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Simultaneous Degradation of Phenol and Reduction of Chromium (VI) Using UV/TiO_2 Photocatalysis

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Organic compounds can serve as electron donors when reducing metallic pollutants such as hexavalent chromium [Cr(VI)] during a photocatalytic reaction. However, simultaneous Cr(VI) reduction and degradation of phenol has not yet been studied under photolytic and photocatalytic processes. Both processes, reduction of Cr(VI) and phenol degradation, are desirable since both phenol and the hexavalent form of chromium are acutely toxic at high concentrations. Cr(VI) is also carcinogenic under low and subchronic conditions. An investigation was launched to devise an effective method of simultaneously degrading phenol and reducing Cr(VI) in a waste water sample using photocatalysis. TiO_2 was added to a solution of Cr(VI) and phenol in a laboratory cooling jacket reactor. This was studied under UV light for an hour and readings recorded. Controls were run under the same set up to determine the impact of the catalyst and UV light. In this study, it was noted that at higher concentrations of phenol while keeping Cr(VI) constant at 50 mg/L, a higher percentage reduction of Cr(VI) to Cr(III) was achieved. This was as a result of a high number of reaction sites available. However, at lower concentrations of phenol and Cr(VI) set at 50 mg/L, higher phenol degradation rates were observed. Photolysis degrades phenol to a much higher percentage (47.27 %) compared to photocatalysis (23.19 %) under the same conditions. A 30.03 % Cr(VI) reduction was achieved during photolysis, while for photocatalysis, only 13.69 % was obtained. It was therefore discovered that the presence of a catalyst inhibits the reaction, hence the effect of UV light is key in the photocatalytic experiment. A better understanding of the effectiveness of the photocatalytic process could be obtained by running the experiment using a different reactor set up.

1. Introduction

A wide range of organic pollutants like phenol and heavy metals such as chromium (Cr) are found in high concentrations in huge water sources as a result of discharge of waste water from industries (Chirwa and Wang, 2000). In nature chromium is mostly found in the trivalent [Cr(III)] state. Wastewater containing Cr(VI) is routinely discharged from mineral processing operations especially from the gold and platinum industries which is the main cause of chromium pollution (Patterson et al., 1997; Chirwa and Igboamalu, 2016). Phenol is produced from petroleum and is used to synthesise plastics. If exposed to humans, it causes critical damage to health and possible risk of carcinogenesis (Dieguez-Santana et al., 2016). Cr(VI) when exposed to humans in high concentrations, has drastic effects that include liver damage, internal haemorrhage and respiratory disorders (Tchounwou et al., 2014) and consequently this contaminants need to be removed from water sources before the water can be fit for human consumption (Federal Register, 2004).

Various research work and studies have proved that treatment of a water sample of the two contaminants can be done separately. This is evident by processes like degradation of phenol and selective reduction of Cr(VI) using photocatalysis (Zeng et al., 2015). However, performing the two treatments separately can be very costly and thus a need to develop a way to perform the process simultaneously has been long a topic under study. There has been no report that investigates the simultaneous degradation of phenol and reduction of chromium(VI) using UV/TiO_2 Photocatalysis. The problem lies in the fact that the two compounds cannot react spontaneously.

Since chromium does not react with phenol, photocatalysis was employed. Photocatalysis is the interaction between a semi-conductor and the UV radiation which produces electron-hole pairs in the surface of the

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semiconductor. These charged points react both with organic compounds and water. In the first case, the redox reactions are responsible for the destruction of the organic compound, whereas in the latter hydroxyl radicals are generated and these radicals react with the organic compound (Esplugas et al., 2002). The semiconductor used in the photocatalysis was Titanium dioxide (TiO_2). The photocatalytic property of TiO_2 is its super-hydrophilicity. This means that its surface is permanently changed by UV light in respect of the effect it has on water. When a TiO_2 surface is irradiated by light, the photocatalytic effect and hydrophilicity are activated together. Any organic chemical in contact with the surface will undergo decomposition to CO_2 and H_2O, a process which occurs at ambient temperatures (Fujishima et al., 2000). The nett redox reaction equation that occurs is shown below:

$$4\ CrO_4^{2-}{}_{(aq)} + 3\ C_6H_5OH_{(aq)} + 20\ H^+{}_{(aq)} + 18\ O_{2\,(g)} \rightarrow 4\ Cr^{3+}{}_{(aq)} + 19\ H_2O_{(l)} + 18\ CO_{2(g)} \tag{1}$$

The Gibbs free energy (ΔG°) of the reaction is negative, meaning that the reaction is thermodynamically feasible.

Two sets of experiments had to be conducted and a final set to confirm the effect of the catalyst on the photocatalytic process. For the first set the concentration of phenol was varied and that of chromium kept constant. The second set involved varying concentration of chromium and keeping that of phenol constant. The second set was done to verify the results from the first set. For the final set, Cr(VI) and phenol concentration were kept constant while the TiO_2 concentration was varied.

2. Materials and Methods

2.1 Experimental Setup

To break down the solid particles, a magnetic stirrer was used. A 1 L jacketed reactor was aerated using compressed air to ensure proper mixing as the experiment was taking place. A cold water bath was prepared in order to control the temperature of the solution as the experiment ran. The ratio of ice to water was 3 to 2. To ensure a continuous flow of cold water in and out of the jacketed reactor wall, a pump was used to deliver water from the cold water reservoir. A UV lamp inside a tube was carefully lowered into the mixture using a retort stand. The lamp had to be just submerged into the mixture. The whole setup was placed in a box as UV light is very dangerous. The box was covered, the lamp switched on and then the experiment ran for an hour.

2.2 Batch Studies

Two sets of experiments were ran with the concentration of the catalyst kept constant at 20 mg/L. Firstly, experiments were conducted at varying initial concentrations of phenol from 10-600 mg/L while Cr(VI) was kept constant at 50 mg/L. The second set of experiments were conducted at varying concentrations of Cr(VI) from 10-600 mg/L while phenol was kept constant at 20 mg/L. The solutions were then diluted to the calibration mark with distilled water. Each of the 5 samples were conditioned using a magnetic stirrer. 950 mL of each of the solutions was poured into a 1 L jacketed reactor and the experiment ran under UV light for an hour. The UV lamp was switched off after an hour and the temperature of the sample taken. The pump was switched off and the compressed air supply stopped as well. The sample had a brownish colour. 1 mL of each of the two samples (the remaining 50 mL and the 950 mL after photocatalysis) were centrifuged. 0.1 mL of each of the centrifuged samples was used for chromium analysis. The remaining 0.9 mL was then poured into vials ready for analysis using a Gas Chromatography Machine (GC). The first control experiment was run for an hour without a catalyst (photolysis) while the second one was run without light (catalysis).

2.3 Analytical Method

2.3.1 Chromium Analysis

A UV/VIS spectrophotometer (WPA, LIGHT Wave II, Labotech, South Africa) was used at a wavelength of 540 nm (10 mm light path) to measure the Cr(VI) concentration after acidification of 0.1 mL of the sample with 1 N H_2SO_4 and reaction with 1,5-diphenyl carbazide to produce a purple colour (APHA, 2005). Cr(III) was estimated as the difference between added Cr(VI) at time zero and residual Cr(VI) measured at any time (*t*).

2.3.2 Phenol Analysis

The phenol samples were analysed using a GC system comprising of a Clarus 600 GC, Clarus 600T mass spectrometer (MS), attached to a Turbomatrix 40 trap headspace sampler (PerkinElmer, South Africa division). The chemical separation component was the Elite 5MS GC system capillary column (30 m, 250 m) from PerkinElmer. Helium (He) carrier gas of 99.999 % purity and applied at a flow rate of 1 mL/min. MS interface comprised of an electron ioniser (EI) and a high performance mass analyser. This was used to measure the concentration of phenol before and after photocatalysis.

3. Results and discussion

3.1 Phenol degradation: Chromium set at 50 mg/L while varying Phenol concentrations

A standard curve for phenol was generated using the GC. The results obtained from the first set of experiments conducted under varying phenol concentrations from 10-600 mg/L showed that at low initial concentrations of 10 and 20 mg/L of phenol, a higher percentage phenol degradation of 40.99 % and 48.70 % respectively were obtained within an hour of photocatalysis as illustrated in Figure 1. Subsequently, the 20 mg/L initial phenol that resulted in the highest degradation was chosen to perform the control experiments to investigate the effect of UV light and the effect of TiO_2 in the presence of 50 mg/L Cr(VI). The results obtained showed that catalysis had no effect on phenol degradation as shown in Table 1, since no reaction took place. Photolysis on the other hand resulted in a higher percentage degradation as shown in Table 2, which was almost the same as the percentage degraded in the photocatalytic process. These results showed that photolytic degradation is almost as effective as photocatalysis.

Table 1. Phenol analysis control without UV light (catalysis)

Phenol prepared at t = 0 (mg/L)	Phenol at t = 0 as per GC (mg/L)	Phenol at t = 1 h as per GC (mg/L)	Amount of Phenol degraded (mg/L)	% Phenol degraded
20	18.06	18.68	0.00	0.00

Table 2. Phenol analysis control without TiO2 catalyst (photolysis)

Phenol prepared at t = 0 (mg/L)	Phenol at t = 0 as per GC (mg/L)	Phenol at t = 1 h as per GC (mg/L)	Amount of Phenol degraded (mg/L)	% Phenol degraded
20	16.55	10.06	6.49	39.23

3.2 Chromium reduction: Chromium set at 50 mg/L while varying Phenol concentrations

At different concentrations of chromium under photocatalytic, catalytic and photolytic processes the percentage reduction was also monitored. The latter two processes were used to perform the control experiments and results tabulated in Table 3 and Table 4. It was noted that as the phenol concentration increased the percentage reduction of chromium also increased .This direct proportionality is illustrated in Figure 3. A 13.69 % reduction of chromium was achieved during photocatalysis and only 2.18 % Cr(VI) reduction during catalysis. Photolysis had a strong impact compared to photocatalysis since 30.03 % Cr(VI) reduction was observed. These results show that the solid particles of the catalyst (TiO_2) block the light and thus inhibiting the rate of the reaction. In the absence of a catalyst the light penetrates easier and thus reduces chromium more.

Table 3: Chromium analysis control without UV light (catalysis)

Chromium prepared at t = 0 (mg/L)	Absorbance at t = 0 as per UV/VIS	Absorbance at t = 1 h as per UV/VIS	Calculated Chromium at t = 0 (mg/L)	Calculated Chromium at t = 1 h (mg/L)	% Chromium reduced
50	0.49	0.41	29.1	28.46	2.18

Table 4: Chromium analysis control without TiO2 catalyst (photolysis)

Chromium prepared at t = 0 (mg/L)	Absorbance at t = 0 as per UV/VIS	Absorbance at t = 1 h as per UV/VIS	Calculated Chromium at t = 0 (mg/L)	Calculated Chromium at t = 1 h (mg/L)	% Chromium reduced
50	0.44	0.31	30.72	21.49	30.03

3.3 Phenol degradation: Phenol set at 20 mg/L while varying Chromium concentrations

The second set of experiments were run, by keeping phenol concentration constant at 20 mg/L, to confirm the results that were obtained in the first set so as to be able to come to a firm conclusion. At the different concentrations of Cr(VI) the percentage degradation was monitored. It was noted that 20 mg/L phenol was among the most degraded as shown in Figure 2 and therefore this concentration was used to perform the controls at a constant Cr(VI) concentration of 50 mg/L as shown in Table 5 and Table 6. The results obtained when phenol was kept constant showed that a phenol degradation of 16.63 % was achieved for catalysis as compared to 23.19 % obtained during photocatalysis. In the second control performed (photolysis) a higher phenol degradation of 47.27 % was achieved as compared to photocatalysis. This proved the fact that photolysis was a more efficient method to degrade phenol and therefore titanium dioxide does not really have an adverse effect on the degradation of phenol.

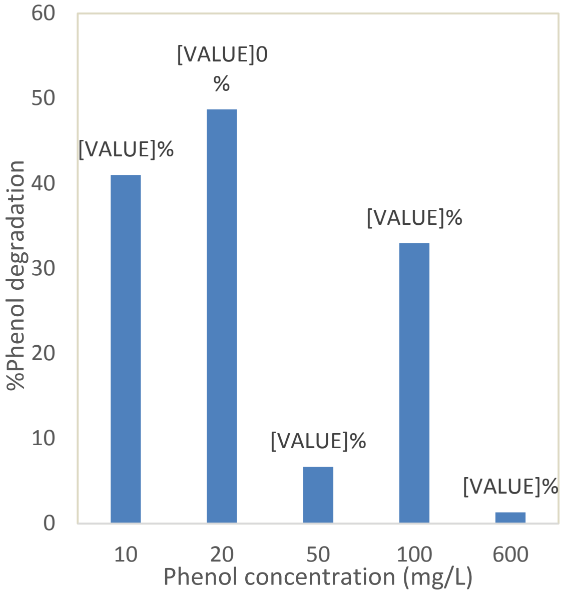

Figure 1: Graph showing percent phenol degradation at different phenol concentrations

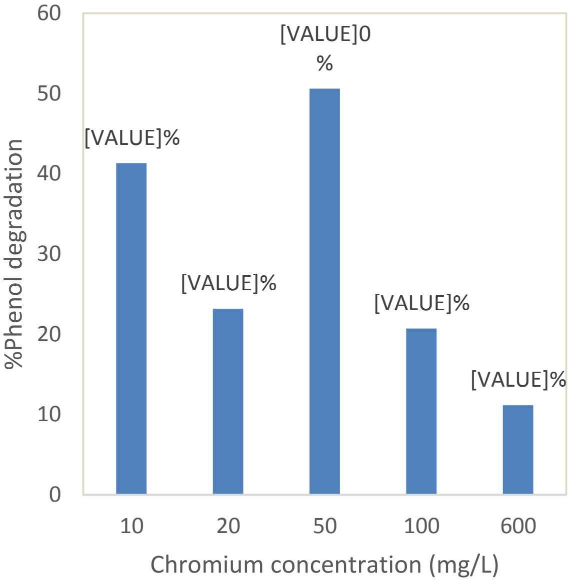

Figure 2: Graph showing percent phenol degradation at different Cr(VI) concentrations

Table 5: Phenol analysis control without UV light (catalysis)

Phenol prepared at t = 0 (mg/L)	Phenol at t = 0 as per GC (mg/L)	Phenol at t = 1 h as per GC (mg/L)	Amount of Phenol degraded (mg/L)	% Phenol degraded
20	18.82	15.69	3.13	16.63

Table 6: Phenol analysis control without TiO2 catalyst (photolysis)

Phenol prepared at t = 0 (mg/L)	Phenol at t = 0 as per GC (mg/L)	Phenol at t = 1 h as per GC (mg/L)	Amount of Phenol degraded (mg/L)	% Phenol degraded
20	21.14	11.14	9.99	47.27

3.4 Chromium reduction: Phenol set at 20 mg/L while varying Chromium concentrations

At different concentrations of chromium the percentage reduction of chromium was also monitored. It was noted that at a higher concentration of chromium a smaller percentage reduction of chromium was observed, due to the unavailability of reaction sites since only 20 mg/L of phenol was used. Figure 4 shows this inverse relationship. Similar control experiments were run to determine the effect of light and TiO_2. The results for the two controls are tabulated in Table 7 and Table 8. As expected a less percentage reduction of 0.22 % was observed during catalysis as compared to the value of 1.58 % obtained during photocatalysis. A high percent reduction of 7.78 % was observed for photolysis. This seals the fact that the catalyst does indeed inhibit Cr(VI) reduction.

Table 7: Chromium analysis control without UV light (catalysis)

Chromium prepared at t = 0 (mg/L)	Absorbance at t = 0 as per UV/VIS	Absorbance at t = 1 h as per UV/VIS	Calculated Chromium at t = 0 (mg/L)	Calculated Chromium at t = 1 h (mg/L)	% Chromium reduced
50	0.468	0.467	32.55	32.48	0.22

Table 8: *Phenol analysis control without TiO2 catalyst (Photolysis)*

Chromium prepared at t = 0 (mg/L)	Absorbance at t = 0 as per UV/VIS	Absorbance at t = 1 h as per UV/VIS	Calculated Chromium at t = 0 (mg/L)	Calculated Chromium at t = 1 h (mg/L)	% Chromium reduced
50	0.429	0.396	29.80	27.48	7.78

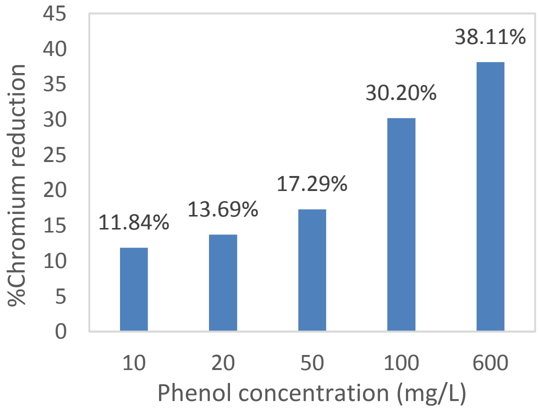

Figure 3: Graph showing percent chromium reduction at different phenol concentrations

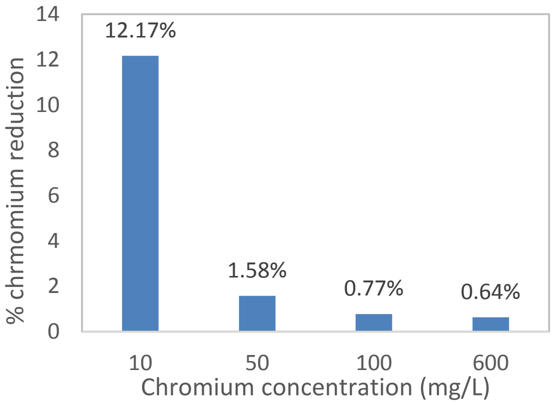

Figure 4: Graph showing percent chromium reduction at different Cr(VI) concentrations

3.5 Effect of the TiO_2

At different concentrations of TiO_2 while keeping chromium and phenol concentration constant, the effect of the catalyst on the degradation of phenol and reduction of chromium was monitored. This was done to determine at what concentrations of the catalyst other than 20mg/L would the process of simultaneous degradation of phenol and reduction of Cr(VI) by photocatalysis be most effective since at 20mg/L photolysis seemed to be more effective. It was observed that as the concentration of the catalyst was increased from 0-20 mg/L the percentage of Cr(VI) reduced decreased. On the other hand, phenol degradation was highest when there was no catalyst at all. However, upon increasing the concentration of the catalyst, degradation occurred but no particular trend was observed. Figure 5 and Figure 6 illustrate the results obtained during this set of experiment. From these figures it can be concluded that to simultaneously degrade phenol and reduce Cr(VI), photolysis is a more effective way of achieving the objective.

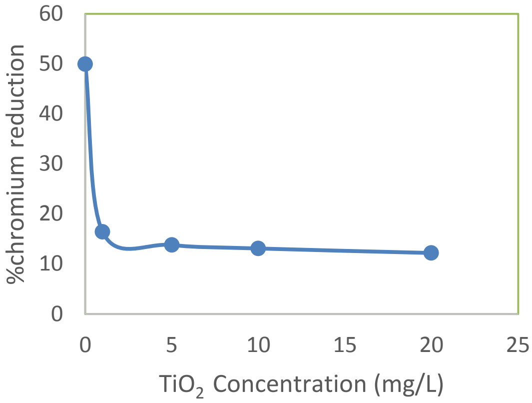

Figure 6: Graph showing percent chromium reduction at different concentrations of TiO$_2$

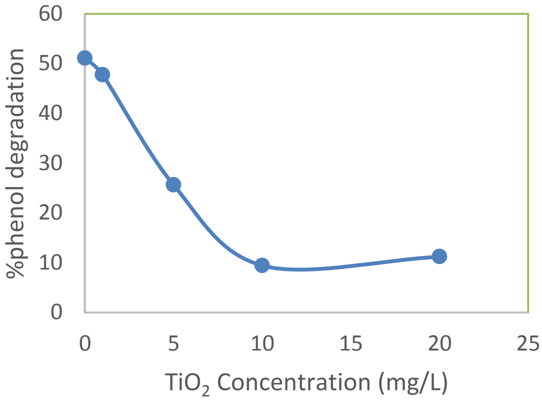

Figure 7: Graph showing percent phenol degradation at different concentrations of TiO$_2$

4. Conclusion

In this study photocatalysis has proved to be an efficient way to simultaneously degrade phenol and reduce Cr(VI). Therefore, a simultaneous degradation of phenol and reduction of Cr(VI) is feasible. However on performing the controls for both sets of experiments it was discovered that the presence of a catalyst inhibits the reaction. It was noted that at lower concentrations of TiO$_2$, a higher percentage reduction was observed for Cr(VI), while degradation of Phenol showed no obvious trend. The highest percentages for both reduction and degradation were observed when the experiment was run without a catalyst. It can be concluded that a catalyst acts as a barrier to the penetration of light. It is therefore, recommended that for a simultaneous analysis, a more efficient and cost effective process would be photolysis. More successful simultaneous Cr(VI) reduction and phenol degradation can be achieved by performing photolysis for a longer period of time. Running the experiment using a different reactor set up, in which the catalyst is not directly mixed in the solution could be used to improve the effectiveness of the photocatalytic process. In that way the catalyst will not act as a barrier to UV light and its presence might make the process more effective.

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