INTRODUCTION

There has been a recent interest in using photocatalytic degradation to treat dye wastewater. Photocatalytic degradation of dyes or photocatalysis is an advanced oxidation process (AOP) that typically uses a catalyst (typically a semiconductor) to form the necessary constituents to decolourize a dye species. This affirms the sentiment that the treatment of dye wastewater has evolved from using only conventional sanitary engineering processes to more technologically advanced techniques. Photocatalysis can be used to address the pollutants of concern such as high biological oxygen demand (BOD), chemical oxygen demand (COD) and total suspended solids (TSS), along with toxicity and colour. These pollutants can be created before, during, or after dyeing processes.

There are many other treatment methods available to treat dye wastewater. Some of these methods include aerobic and anaerobic treatment, advanced oxidation processes such as ozone and electrocoagulation. Aerobic and anaerobic treatment are capable of achieving comparable results, but these methods require long retention times [1-3]. Also, some microorganisms that thrive in aerobic environments are incapable of biodegrading because of the xenobiotic constituents present within the wastewater [4,5]. Advanced oxidation processes (AOP) such as ozone have high energy costs associated with the equipment necessary for ozone generation [6]. Finally, electrochemical methods such as electrocoagulation produce waste from spent electrodes. These electrodes must be either regenerated for reuse or sold as scrap metal. The accumulation of spent electrodes and the process of regenerating or scrapping can make electrocoagulation undesirable. Photocatalysis is the best option because it can completely decolourize dye wastewater quicker than many other wastewater treatment methods. It is not only capable of treating wastewater, but because of its regeneration potential, it is also capable of being a sustainable treatment technology for dye wastewater [7].

Titanium dioxide is one of the primary photocatalysts used in the degradation of dye wastewater [8-13]. While seeing an influx of research related to using this constituent, TiO$_2$ has been used as a semiconductor since inaugural research occurred in the 1960s at the University of Tokyo [14]. Titanium dioxide has many advantages—it is non-toxic, there are many methods of synthesis available to the researchers and it is versatile in photocatalysis applications [15,16]. Also, TiO$_2$ has been expressed as being the most useful in environmental applications [17]. However, throughout literature it has been discovered that one of the biggest issues with using titanium dioxide is the band gap energy, an estimated 3.2 eV [18-21].
This eliminates the opportunity for TiO₂ to be used with light sources less than the measured band gap energy of 385 nm. As a result, TiO₂ nanocatalysts are insufficient in being used in visible light [22]. Therefore, research has been conducted by combining TiO₂ with a transition metal in a process known as doping.

There are three advantages of using transition metals to augment TiO₂. First, transition metals increase a photoreaction by increasing the surface area. Second, doped TiO₂ nanocatalysts trap electrons within band gaps forming anions. Anion formation increases dye decolourization [23]. Third, the augmentation of TiO₂ with transition metals develops a sustainable treatment method making this a more cost effective treatment process. Instead of the high costs and safety hazards associated with using UV lamps, photo-oxidation can be performed under various light sources, such as simulated or actual solar light [24-26]. Finally, doped-TiO₂ also has the potential of being reused following purification [27,28].

The transition metal used for doping in this work is cobalt (Co³⁺). Cobalt is a transition metal with high reduction potential; its Co³⁺ ions trap conduction electrons. As a result, Co³⁺ ions are oxidized to Co²⁺. Cobalt ions can also initiate p-type conductivity at the surface of the TiO₂. This provides an easier pathway for holes to move from the valence band to the surface of the catalyst [29] enhancing the photocatalytic activity. When a Co-doped TiO₂ catalyst is excited, it will react with superoxide anions. This ultimately prevents the potential of electron-hole recombination. The prevention of recombination maintains high photocatalytic productivity [30].

The aim of this paper is to explore the effects of pollutant and catalyst concentrations on wastewater decolourization while using cobalt-doped titanium dioxide (Co-doped TiO₂). Research on wastewater treatment by Co-doped titanium dioxide has been well documented [21-37]. Yet, while the degradation of a pollutant using Co-doped TiO₂ is evident, these texts have been limited to only discussing the effects of varying both the concentration of waste-pollutant and photocatalyst concentrations. Therefore, this work will focus on varying both the concentration of wastewater and the photocatalyst loading on the decolourization of acid orange 7 dye. The calculation of acid orange 7 dye efficiency of decolourisation was determined by using the following equation:

\[
\text{Decolourisation} \% = \left(1 - \frac{(\text{AO7})_f}{(\text{AO7})_i}\right) \times 100
\]

where (AO7)ᵢ is the initial acid orange 7 concentration (mg/L); (AO7)ᵢ is the final acid orange 7 concentration (mg/L).

### RESULTS AND DISCUSSION

**Characterization of Co-doped TiO₂:** The XRD patterns of Co-doped TiO₂ powders calcined at 600 °C for 4 h in air are shown in Fig. 1. The pattern shows that the prepared Co-doped TiO₂ has diffraction patterns similar to JCPDS71-1166. This confirmed the successful preparation of anatase-phase TiO₂ with a minor rutile phase as listed in JCPDS 78-1508. In addition, Co⁺⁺ ions are inserted into the crystal lattice of TiO₂ and substituted for Ti⁺⁺ ions to form Co-O-Ti structures. This occurs because the ion radius of Co⁺⁺ (0.55 Å) is close to Ti⁺⁺ (0.68 Å) [39]. Based on the XRD results, we determined that even a tiny amount of doped Co⁺⁺ can transition TiO₂ from anatase to the rutile phase. Lattice parameters and unit cell volumes were calculated from the corresponding XRD patterns and are listed in Table-1.

The scanning electron microscopy (SEM) images and the energy dispersive spectroscopy (EDS) analysis results of Co-

| TABLE-1 | LATTICE PARAMETERS AND CELL VOLUMES OF 2 MOLE % CO-DOPED TiO₂ POWDERS |
|---------|---------------------------------------------------------------|
| a       | b                  | c                  |
| Co-doped| 3.7793             | 3.7793             | 9.4918             | 135.6 |
doped TiO\textsubscript{2} powders are provided in Fig. 2. It was revealed that the grain sizes of Co-doped TiO\textsubscript{2} were uniformly distributed in the range of 100-200 nm. The grains formed significant agglomeration. The results from the EDS indicate that the Co element composition of the Co-doped TiO\textsubscript{2} nanocatalyst is slightly higher than the expected stoichiometric composition.

The elemental compositions and chemical status of the surface of Co-doped TiO\textsubscript{2} powder was further analyzed by XPS. The full range survey of XPS spectra of 2 mol % Co-doped TiO\textsubscript{2} powder is shown in Fig. 3(a). The main peaks are C 1s, Ti 2p, O 1s and Co 2p, centered at 284.9, 458.6, 530.0 keV.

![Fig. 1. XRD pattern of 2 mole % Co-doped TiO\textsubscript{2} prepared by solid state reaction technique](image1)

![Fig. 2. SEM images and EDS results of 2 mole % Co-doped TiO\textsubscript{2} spectra of the 2 mole % Co-doped TiO\textsubscript{2}](image2)

![Fig. 3. XPS spectra of the 2 mole % Co-doped TiO\textsubscript{2}: (a) wide-survey spectrum; (b) Ti 2p core level spectrum; (c) O 1s core level spectrum; (d) Co 2p spectrum](image3)
and 780.1 eV, respectively. The carbon peak for C 1s located at 284.9 eV. This is due to the formation of adventitious carbon at the surface. Ti 2p core level spectrum obtained from the Co-doped TiO2 powder is shown in Fig. 3(b). As shown from the figure, the Ti 2p1/2 and Ti 2p3/2 spin-orbital splitting photo-electrons were found at 464.6 and 458.6 eV, respectively.

These results correspond to results found in literature for the presence of Ti4+ [40]. The XPS photopeak of O 1s was fitted by multiple Gaussians as shown in Fig. 3(c). The O 1s spectrum was asymmetric and the main peak of O 1s was found at 529.5 eV. This is because of the oxygen molecules in TiO2.

There were two peaks observed at binding energies of 529.5 and 531.2 eV. These were attributed to the Ti-O and C-O groups with corresponding ratios of 81.7 and 18.3 % [41,42]. The XPS signals of Co 2p were weak in Co-doped TiO2 as shown in Fig. 3(d). This was likely caused by low doping levels. The binding energies of 2p3/2 and 2p1/2 Co2+ were approximately 780.9 and 798.3 eV. These binding energies are very close to those in CoO (780.9 eV for 2p3/2) [43]. Overall, Co is in a trivalent form within the Co-doped TiO2 powder.

The N2 adsorption-desorption isotherms and pore diameter distributions of Co-doped TiO2 were further analyzed using N2 adsorption. As presented in Fig. 4(a), Fe-doped TiO2 adsorption-desorption isotherms are type IV with porous structures between 0.80 and 0.90, suggesting the presence of a well-defined mesoporosity in the samples. The BET surface area for Co-doped powder was 24.1 m²/g as shown in Table-2. The pore size distribution curves of for Co-doped TiO2 are shown in Fig. 4(b). The average pore diameter of Fe-doped TiO2 is 3.6 nm. There were two peaks to be found, one peak at 3.9 nm, while the second at 17.9 nm.

UV-visible absorption spectra of Co-doped TiO2 powders were presented in Fig. 5. The absorption wavelengths (413.3 nm) appeared with band gaps at 2.93 eV.

**Decolourization of acid orange 7**

**Effects of dye wastewater concentration:** Results from the decolourization of acid orange 7 have been presented in Fig. 6(a-c). It was first discovered that the efficiency of decolourizing acid orange 7 by Co-doped TiO2 is related to the initial dye concentration. In other words, as the initial concentration increases, the degradation of acid orange 7 decreases. Summarizing the results, at an initial concentration of 24 mg/L, the percent of dye decolourization observed was between 62.8 and 76.0 %. The range of decolourization decreased to 40.4-60.7 % at 34 mg/L. Finally, treatment dropped to 35.7-40.1 % when the initial concentration was 44 mg/L. This relationship has been confirmed in previous work by other authors degrading other pollutants [30,34,45,46].

There are two possible reasons for this trend. First, as the dye concentration increases, there is an increase in the equilibrium adsorption of dye on the surface of the catalyst. The increase of dye adsorption reduces the adsorption of OH−, thereby decreasing the formation of hydroxyl radicals, an important component in decolourizing the dye. Second, because the dye concentration has increased, photons could have been adsorbed at the dye surface and not on the catalyst thereby decreasing the efficiency of photocatalysis [11,12,45,46].

**Effects of photocatalyst loading:** When the photocatalyst loading increases the treatment efficiency decreases [12,30]. In the experiment, this held true at 24 mg/L (Co-TiO2 = 0.025 g, 76.0 %; Co-TiO2 = 0.05 g, 64.4 %; Co-TiO2 = 0.1 g, 62.8 %). However, as the dye concentration increased, the maximum treatment efficiency peaked when the photocatalyst loading was 0.05 g and then decreased at 0.1 g.

In principle, the increase of photocatalyst increases the overall number of active binding sites available thereby potentially producing more hydroxyl radical and superoxide anions. However, as the catalyst loading increases, binding sites can decrease. This is because the catalyst agglomerates and remains in suspension within the Pyrex glass vessel. As a
doped TiO_2 with different photocatalyst loadings in the range of 0.025 to 0.1 g/100 mL acid orange 7 and three different dye concentrations (24, 34 and 44 mg/L). These results can be found in Fig. 7a-c.

In summary, all the three graphs of \(-\ln(C/C_0)\) vs. time yield a good linear relationship for photocatalytic degradation of acid orange 7 using Co-doped TiO_2 as photocatalyst. The kinetics of photocatalytic degradation by Fe-doped TiO_2 obey the first-order kinetic rate. Asiltürk et al. [47] observed similar trends with the degradation of malachite green dye using Fe-doped TiO_2. The calculated results for experimental rate constants, \((k_{exp})\) and R squares are listed in Table-3.

In addition, having analyzed the corresponding data for each photocatalyst loading, as the dye wastewater concentration increases, the \((k_{exp})\) value peaks at a photocatalyst loading of 0.1 g/100 mL acid orange 7.
of 0.05 g with the exception of when the dye concentration was 24 mg/L. These results correspond with trends found when reviewing the decolorization of acid orange 7.

Conclusion

The effects of varying wastewater strength and photocatalyst loading on the photocatalytic degradation of acid orange 7 by Co-doped TiO$_2$ photocatalyst under UV irradiation have been studied. From the results, it was determined that as the dye wastewater concentration increased the photocatalytic degradation decreased. As the dye concentration increased, the most efficient photocatalytic loading observed was 0.05 g. Higher doses of photocatalyst were observed to be ineffective as the particles remained suspended within the vessel preventing light from penetrating through. These are important findings because they indicate that there exists a plateauing point at which the nanocatalyst concentrations swing from having positive removal effects, to hindering the removal process. This could help in reducing the cost of materials and the time and effort necessary to synthesize the catalysts and perform the treatment. This relationship is explained using first-order kinetics, which is consistent with previous studies of Co-doped TiO$_2$ dye wastewater decolorization.

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