



## Simultaneous degradation and adsorption of cyanide using modified fly Ash and TiO<sub>2</sub>/UV

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### Original Article

#### Abstract

Due to the present water shortage and environmental problems associated with industrial effluent, investigation of novel treatment technologies is an essential approach. Being a highly toxic chemical of asphyxiating characteristics, cyanide is seen as a major environmental pollutant in a wide range of industrial effluents. The present study aimed to address the adsorption and photocatalytic degradation of cyanide using activated fly ash and TiO<sub>2</sub>/UV. To investigate the removal efficiency of cyanide, two sets of experiments were designed. First, cyanide was absorbed by activated fly ash and degraded via a photocatalytic process, individually. Second, simultaneous adsorption and degradation was examined. The removal efficiency of cyanide by modified fly ash (MFA), TiO<sub>2</sub>/UV, and their combination (MFA-TiO<sub>2</sub>/UV) was 76.1%, 81%, and 86.6%, respectively. Optimal conditions for the combination of activated fly ash AFA-TiO<sub>2</sub>/UV were contact time of 6 hours, temperature of 100 °C, and AFA: TiO<sub>2</sub> ratio (w/w) of 1:1. Under these conditions, a maximum removal rate of 92.4% was obtained when 1.2 g of MFA/TiO<sub>2</sub> was used with a pH value of 3 in the presence of UV light. Based on the results of cyanide removal, it can be concluded that the combination of adsorption and photocatalytic degradation with MFA-TiO<sub>2</sub>/UV can be utilized to improve the removal of cyanide from wastewater.

**KEYWORDS:** Adsorption, MFA-TiO<sub>2</sub>/UV, Cyanide, Photocatalytic Degradation

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#### Introduction

As a result of the increasingly growing rate of pollutant discharge by industries into the environment and ecosystem many problems are emerging such as health concerns and contamination of water resources. As a strong asphyxiating chemical group, cyanides are

present in several industrial wastewaters including those of paint, oil refining, explosives, chemicals, plating, pesticides, synthetic fiber production, mining, electronics, and coking industries.<sup>1-3</sup> The health damages caused by high levels of cyanide exposure include headaches, dizziness, dermatitis, pruritus, weak and rapid pulse, nausea, and vomiting. Extreme levels of exposure may lead to brain damages, coma, and eventually death. A cyanide concentration of about 0.05 mg/dl

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can produce some toxins in the blood.<sup>4,5</sup> The lethal dose of cyanide for humans has been determined to be about 5 mg per kg of body weight.<sup>6,7</sup> Common processes of cyanide removal encompass physical, chemical, and biological techniques. Through physical techniques (such as membrane processes, ion exchange, and adsorption), the removal process is only completed by phase change. On the other hand, the toxicity of cyanide may limit the use of biological techniques to low concentrations, requiring a long duration of time to proceed. The most common chemical method for cyanide removal is alkaline chlorination, with its greatest limitation being the production of cyanogen chloride.<sup>8-10</sup> However, because of their incomplete cyanide removal and remarkably high cost, chemical methods are limited in application. Today, the use of the photocatalysis process as a strong and efficient yet green technology is growing in comparison to conventional methods.<sup>11,1</sup> Many researches have confirmed the efficiency of the photocatalysis process in cyanide removal.<sup>12,13</sup> Some researchers have suggested considerable improvements, provided the photocatalysis system is coupled with a primary adsorbent such as zeolite or activated carbon.<sup>14</sup> Adsorption is an important part of photocatalytic removal;<sup>16</sup> thus, an increase in adsorption capacity can improve photocatalytic characteristics.<sup>15</sup> Therefore, adding a high capacity adsorbent such as fly ash (FA) to a catalysis system such as TiO<sub>2</sub>, in the presence of UV light, can improve the photocatalytic performance. The main decomposition mechanisms by combined modified fly ash (MFA)/TiO<sub>2</sub> are defined in the three steps of chemical species adsorption on the surface of MFA/TiO<sub>2</sub>, optical dispersion over the surface, and desorption of final product from the surface of MFA/TiO<sub>2</sub>. Hence, when TiO<sub>2</sub> is loaded on FA, the adsorbed analytes on FA move to the catalyst, via diffusion process, where they are decomposed.<sup>17,18</sup> The present

study aimed not only to perform a simple modification process to enhance FA adsorption capacity, but also to mix MFA with TiO<sub>2</sub> nanoparticles in the presence of UV to achieve a higher removal efficiency for cyanide. To the best of our knowledge, no similar study has been reported.

## Materials and Methods

All material and chemical reagents were of analytical grade. The experimental study was conducted on both synthetic and real samples at the laboratory scale. Raw FA was collected from Zarand Thermal Power Plant (Kerman, Iran). Once prepared, FA was sieved to isolate particles of 100 to 200 mesh size. Then, FA was washed with distilled water at a liquid: solid ratio of about 10 for 48 hours, before being filtered and dried in an oven at 105 °C to obtain washed fly ash (WFA). The size and specific surface area of the used TiO<sub>2</sub> were 20 nm and 40 m<sup>2</sup>/g, respectively.

In order to determine the optimum conditions for obtaining an optimal FA, 4 consecutive stages were evaluated following a single-factor optimization approach. In the FA modification process, effective parameters such as acid concentration, time modification, acid/WFA ratio, and temperature modification were set to their optimal values. At the end, MFA/TiO<sub>2</sub> ratio was evaluated. In order to determine acid concentration, raw fly ash (RFA) was modified at different concentrations of sulfuric acid, including 0.01, 0.1, 1, 1.8, and 2 M/l, at boiling point under reflux for 3 hours. After filtration using Whatman filter (pore size ~ 0.45 μm), FA was washed several times with distilled water, and then, rinsed using ethanol to bring its pH value to 0 (neutral pH). Then, FA was dried at 105 to 120 °C and stored in a desiccator for further analysis. In the next step, WFA was modified using different acid/WFA ratios of about 3, 7, 9, 10, 11, and 13. Subsequently, WFA was modified using different times (i.e., 1, 3, 6, and 9 hours) and temperatures (i.e., 29, 70, 85, 100, and 120 °C).

The effect of MFA:TiO<sub>2</sub> ratio was evaluated at the ratios (in w/w) of 0:4, 3:1, 1.5:2.5, 1:1, 2.5:1.5, 1:3, and 4:0.

At all steps, optimal values of effective parameters in cyanide removal by MFA-TiO<sub>2</sub>/UV were selected as judging criteria.

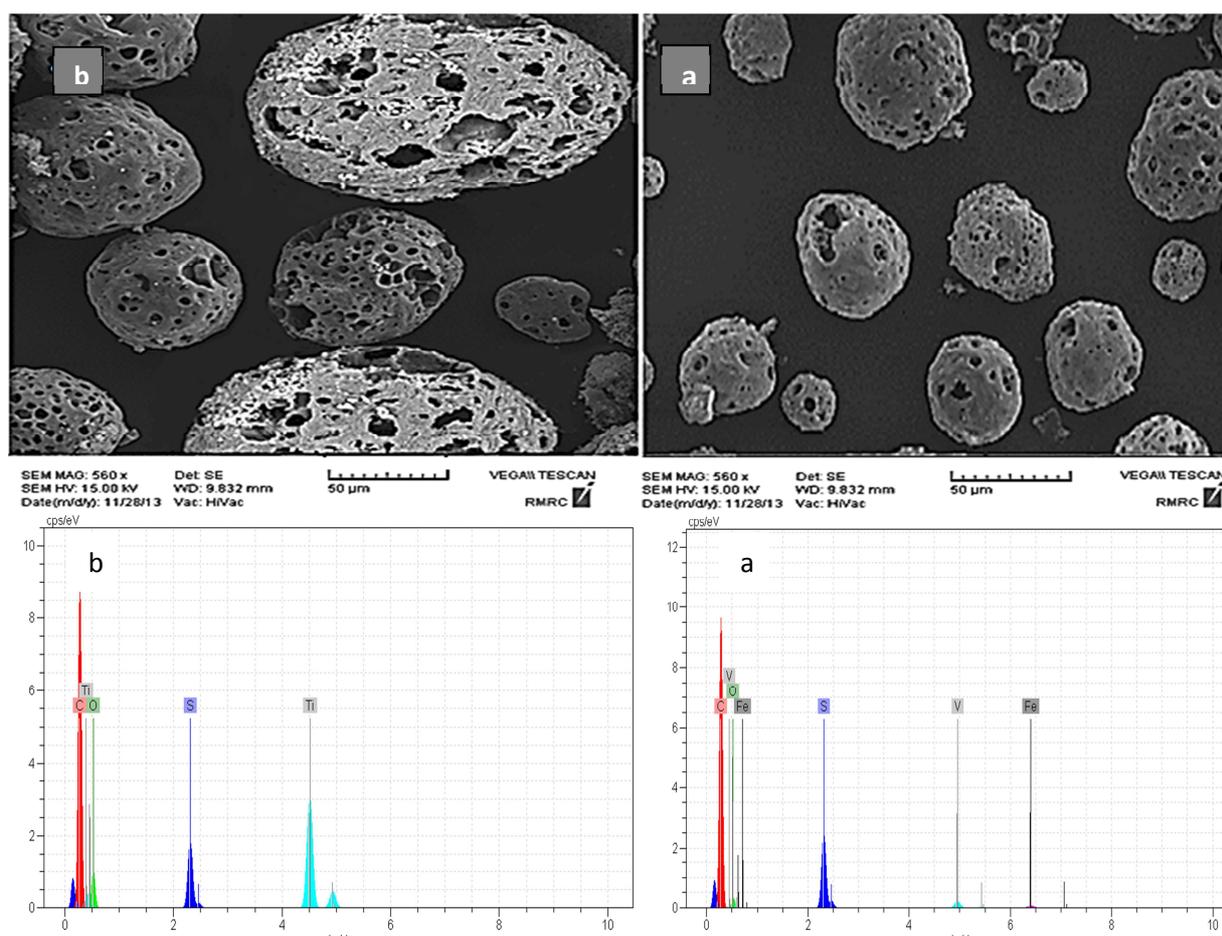
In this section, other parameters effective on photocatalytic degradation [e.g., initial pH (2-11) and substrate dose (0.3-1.5 g)] were studied. Moreover, different concentrations of cyanide (2.5 to 75 mg/l) were brought into contact with the MFA-TiO<sub>2</sub>/UV at optimum conditions. Degrees of oxidation reactions were also determined. To evaluate MFA-TiO<sub>2</sub>/UV under actual conditions, real samples were prepared from the electroplating industry and treated under optimum conditions using MFA-TiO<sub>2</sub>/UV.

All tests were analyzed at room temperature and conducted in duplicates to increase the accuracy of the results. Residual cyanide was determined using an atomic absorption spectrophotometer (Philips-PU 9100X) coupled with a mercury UV lamp (30 W, 338 mw/m<sup>2</sup>) as light source with maximum wavelength of 360 nm. To avoid light reflection, the entire system was wrapped in aluminum foil.

## Results and Discussion

### Scanning Electron Microscopy-Energy-dispersive X-ray Spectroscopy (SEM-EDS)

Figure 1 shows the growth of porosity and active sites on FA surface after modification. These micropores can be occupied by TiO<sub>2</sub> nanoparticles on the surface of the adsorbent.



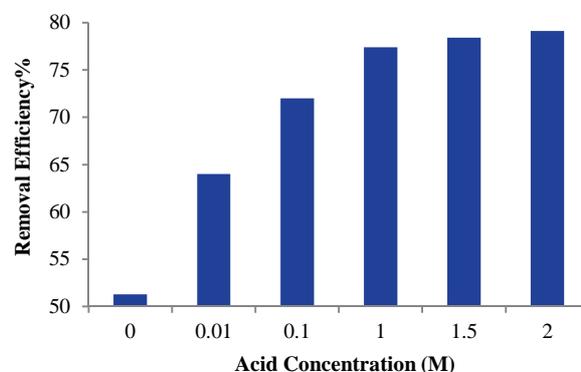
**Figure 1. Scanning Electron Microscopy-Energy-dispersive X-ray Spectroscopy (SEM-EDS) images of raw fly ash (a) modified fly ash (MFA)-TiO<sub>2</sub> (b)**

Simultaneous determination of electrical conductivity (EC) and total dissolved solids (TDS) after 48 hours of washing of FA indicated them to increase to about 2.3-4.07 mS/cm<sup>2</sup> and 80-1710 ppm, respectively. These results reveal that water-soluble compounds from FA had dissolved as a result of acidic treatment and the development of pores. EDS results demonstrate the weight percent (wt%) of different elements and metal oxides in FA, including carbon, sulfur, oxygen, CO<sub>2</sub>, SO<sub>3</sub>, iron, vanadium, V<sub>2</sub>O<sub>5</sub>, and Fe<sub>2</sub>O<sub>3</sub>. The weight percent of the abovementioned elements before FA modification were about 77.94, 7.73, 10.9, 91.97, 6.22, 1.32, 2.09, 1.2, and 0.61 wt%, respectively. After treatment, the values changed to 86.52, 6.8, 6.68, 92.94, 5.08, 0, 0, and 0% wt%, respectively, indicating an increase in carbon content after acidic treatment, which confirms the enhancement of adsorption capacity. The results were in agreement with those reported by Wang et al.<sup>19</sup>

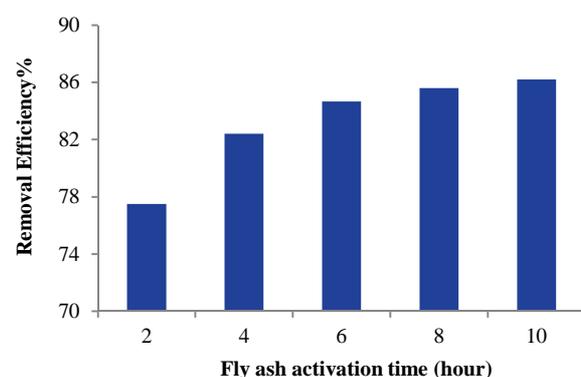
#### Effect of acid concentration and activation time

Figure 2 illustrates the photocatalytic removal of cyanide by MFA-TiO<sub>2</sub> under different acidic conditions. Under these conditions, the removal rate increased with acid dose. The removal efficiency was 51.3% when WFA/TiO<sub>2</sub> was used alone. With the increasing of acid concentration from 0.01 to 2 M, the removal rate increased from 64 to 79.11%. Accordingly, 1 M was considered as the optimum acid concentration for the following experiments. Statistical analysis indicated that acid concentration was not significantly correlated with cyanide removal efficiency ( $P \sim 0.256$ ). Figure 3 presents a demonstration of the effect of activation time. The results showed that the removal percentage was improved from 77.5 to 86.2% with the increasing of activation time from 2 to 10 hours. Through further evaluation of removal efficiency, the activation time of 6 hours was found to be the optimum value. In addition, a significant relationship was observed between

activation time and removal efficiency ( $P \sim 0.026$ ).



**Figure 2. Effect of acid concentration on cyanide removal [cyanide: 30 mg/l, unadjusted pH]**

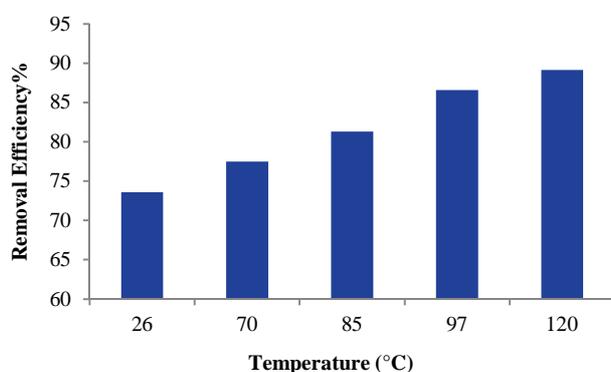


**Figure 3. Effect of activation time on cyanide removal [cyanide: 30 mg/l, unadjusted pH]**

#### Effect of temperature

Figure 4 shows cyanide removal efficiency when activation temperature changes from 26 (room temperature) to 120 °C. The figure indicates the significant effect of temperature on cyanide removal, where removal efficiency changes from 73.6 to 89.13% with the increasing of temperature. With regard to greater cyanide removal at 97 °C, boiling point of water was chosen as the optimum temperature for FA activation. Based on statistical analysis, there was a significant relationship between temperature and removal efficiency ( $P = 0.01$ ). Panitchakarn et al. reported an initial increase in the purity of FA with increasing acid concentration, followed by

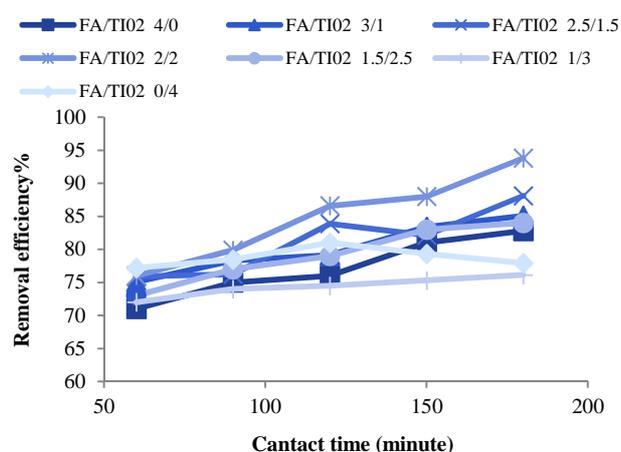
a relatively constant trend with further increase in the acid concentration.<sup>21</sup> The acid:FA ratio did not significantly contribute to the modification of fly ash. Porosity and surface area increased with the reduction in impurities due to longer activation time and higher treatment temperature.<sup>20-22</sup> According to the results, optimal acid/WFA ratio was found to be about 7 (data not reported). The removal of vanadium compounds by acid-treated adsorbent was confirmed in the studies by Kashiwakura et al.<sup>23</sup> and Kashiwakura et al.<sup>24</sup> in which dangerous substances such as arsenic and selenium were successfully removed.



**Figure 4. Effect of activation temperature on removal efficiency [cyanide: 30 mg/l, unadjusted pH]**

Figure 5 shows changes in removal efficiency with MFA to nanoparticles ratio for different contact times. The cyanide removal efficiency for MFA, TiO<sub>2</sub>/UV, and MFA-TiO<sub>2</sub>/UV were found to be 76.1, 81, and 86.6%, respectively. Accordingly, the removal efficiency of MFA-TiO<sub>2</sub>/UV was higher than that of either the adsorbent or the catalyst alone. The appropriate ratio of TiO<sub>2</sub> to MFA was 1. No statistically significant relationship was found between MFA:TiO<sub>2</sub> ratio and removal efficiency ( $P \sim 0.098$ ). By increasing the surface area, chemical species were provided with further area, which improved photocatalytic removal efficiency.<sup>25</sup> Optical dispersion rate of pollutants is affected by light absorption of the used catalyst and the active

sites. Evidently, the photocatalytic process is likely to proceed more efficiently with appropriate adsorption. When TiO<sub>2</sub> is introduced into fly ash pore space, due to the proximity of contaminants and the catalyst, a better removal condition is provided. This can be associated with FA serving as an adsorbent. In other words, depending on the type of fly ash, the removal efficiency changed, leading to a reformed process.<sup>26</sup> In mixture substrate (MFA/TiO<sub>2</sub>), a competition is established on active sites, with the located TiO<sub>2</sub> molecules on adsorbent surface behaving similar to its host. During this process, both substrates (MFA and TiO<sub>2</sub>) are engaged with pollutants, and the absorption process takes place before the photocatalytic process. Chemical and structural changes in FA lead to changes in surface morphology, ultimately leading to important changes in the substrate affinity toward pollution before and after the modification. Such a sharp change confirmed the increase in EC and TDS by the deposition and dissolution processes.<sup>27</sup> Through studying the effect of radiation time, it was found that the longer the radiation time, the more free electrons were likely to be generated in the conductor band, which resulted in the enhancing of removal efficiency.

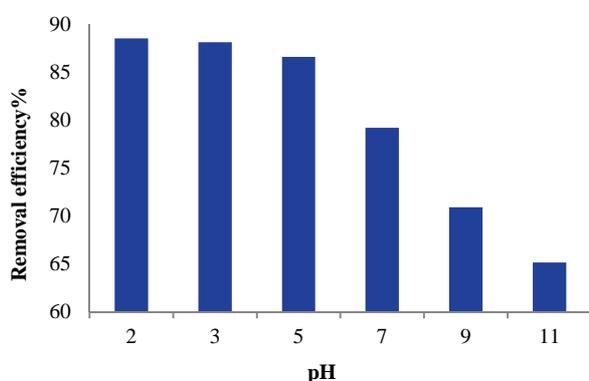


**Figure 5. Effect of different FA:TiO<sub>2</sub> ratios on removal efficiency [cyanide: 30 mg/l, unadjusted pH]**

Samarghandi et al. argued that increasing the radiation time from 15 minutes to 180 minutes may raise the efficiency of cyanide removal using UV/TiO<sub>2</sub> from 56.4% to 84.4%.<sup>28</sup> Moreover, the results of this research were consistent with those of the studies by Kim et al.<sup>29</sup> and Wahaab et al.<sup>30</sup>

### Effect of MFA/TiO<sub>2</sub> dosage and pH

Figure 6 shows cyanide removal efficiency for various pH values. Because the substrate surface contains more negative charges, the removal efficiency decreases with the increasing of pH,<sup>28,31</sup> so that higher cyanide removal efficiency was obtained for acidic pH values (herein ranging from 5 to 2). Accordingly, the acidic pH value of 3 was selected as the optimum pH value for further experiments. A statistically significant association was found between pH and removal efficiency ( $P = 0.001$ ).

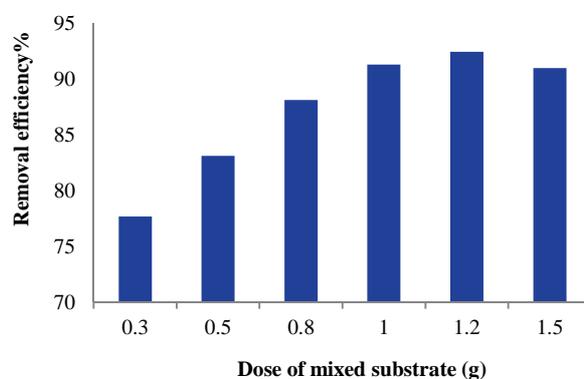


**Figure 6. Effect of pH on the removal efficiency of cyanide [cyanide: 30 mg/l, pH: 2-11]**

Figure 7 illustrates the effect of MFA/TiO<sub>2</sub> dosage. The presented results show that the removal rate increased with the increasing of composite dosage. However, further increasing of the MFA/TiO<sub>2</sub> ratio from 1.2 to 1.5 g showed a negative effect. Thus, 1.2 g was chosen as the optimum dose. The reduction of removal efficiency by increasing the substrate dose was possibly a result of increased solution turbidity which consequently disrupted the photons'

traveling path. In addition, some responses can be effective in this regard, including reduced UV light penetration and total excitation surface.<sup>32</sup> Some authors reported that such an increase can lead to the adhesion of contaminants to the solid photocatalyst surface, and thus, prevent photons from being stimulated.<sup>33</sup> Similar results were reported by Shirzad Syboni et al., who obtained a higher removal efficiency of about 92.45%.<sup>34</sup> In addition, a significant relationship was obtained between the mixed substrate (MFA/TiO<sub>2</sub>) dose and removal efficiency ( $P_v = 0.015$ ).

Under optimal conditions, the influence of initial cyanide concentration was investigated by changing the concentration from 2.5 to 75 mg/l (data not reported), which caused the efficiency to decrease from 98.1 to 64.14%. It is clear that, when the concentration is increased, TiO<sub>2</sub> surface is quickly occupied by cyanide molecules, further inhibiting an effective photon-excitation of the catalyst surfaces.



**Figure 7. Effect of mixed substrate dose on removal efficiency [cyanide: 30 mg/l, pH: 3]**

This may also be due to reduced light penetration due to increased pollutant concentration, as well as the reduced length of the incoming photons into the solution.<sup>33</sup>

High concentrations may degrade the pollutants and produce water-insoluble polymer compounds that attach to the catalyst surface and slow down the photocatalytic degradation.<sup>35</sup> The removal rate data was fitted to the second order kinetics equation and a high

correlation coefficient ( $R^2$ ) of about 0.999 was determined. The removal efficiency in the real sample (74.4%) was lower than that in the synthetic sample because of the presence of intervening compounds.

### Conclusion

In the present study, the adsorption and photocatalytic degradation of cyanide using activated fly ash (AFA) and  $\text{TiO}_2/\text{UV}$  was addressed. Based on the results, the removal efficiency of cyanide by MFA,  $\text{TiO}_2/\text{UV}$ , and their combination (MFA- $\text{TiO}_2/\text{UV}$ ) was about 76.1, 81, and 86.6%, respectively. Under optimum conditions, a maximum removal rate of about 92.4% was obtained. According to the results, it can be concluded that simultaneous adsorption and photocatalytic degradation using MFA- $\text{TiO}_2/\text{UV}$  can successfully remove cyanide from wastewater.

### Conflict of Interests

Authors have no conflict of interests.

### Acknowledgements

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