Green synthesis of Fe_2O_3/TiO_2 nanocomposite using orange peel extract for photocatalytic degradation of cyanide in wastewater.

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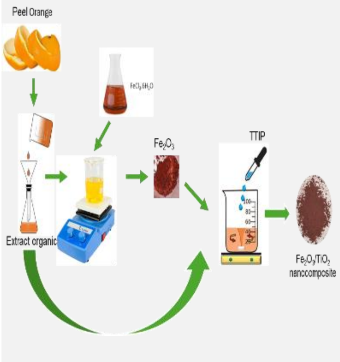
Graphical Abstract



A method for obtaining Fe_2O_3/TiO_2 nanocomposites by green synthesis using the organic extract of orange peel was studied. For this purpose, the extraction of secondary metabolites presents in orange peel that acted as reducing and stabilizing agent was carried out and the respective qualities such as XRD, Raman, FTIR, SEM and UV-Vis diffuse reflectance were performed demonstrating the stability of the heterojunction of the Fe_2O_3/TiO_2 nanocomposite compared to pristine Fe_2O_3 and TiO_2. The studies demonstrated that this method is crucial to form the Fe_2O_3/TiO_2 nanocomposite with highly crystalline structures and narrow size distributions, which enabled the heterojunction to improve photocatalytic performance with a higher efficiency of 95 % using in the visible region a 440 nm source at low concentrations in a time of 2 h for the degradation of cyanide.

Introduction

Peru is considered one of the main exporters of gold, silver, and other metals in the world. Due to the huge high value, one of the most used extraction procedures is the cyanidation process due to its high selectivity. This technique has caused quantities of cyanide waste to enter the water, endangering human health and the environment Many strategies were investigated for its eradication, which photocatalysis turned out to be the most practical, low cost and easy to implement.[1] Several semiconductors have been explored, with TiO_2 receiving the most attention due to its optical and electrical characteristics. However, due to its huge bandgap energy of 3,2 eV, it can only be activated by ultraviolet light irradiation [2]. This drawback can be overcome by adding with Fe_2O_3 NPs, which will reduce the electron/hole pair recombination and increase the number of active reaction sites, thus significantly improving the photocatalytic performance in the visible light spectrum [3]. Recently it has focused on promoting the best possible use of available natural resources. Green synthesis has attracted special attention because it uses organic extract which presents secondary metabolites that act as a reducing, stabilizing, and coating agent throughout the synthesis process. In addition, it produces less harmful waste and is more profitable, at the same time, respectful of the environment. Previous research has shown that the polyphenolic components of the organic extract function as reducing and stabilizing agents during the formation of nanoparticles with regulated morphology and structure [4]. For the analysis, numerous methods were used for the analysis such as FTIR, UV-Vis diffuse reflectance, Raman, XDR, and SEM They demonstrated excellent photocatalytic activity in the visible range in the decomposition of cyanide in water at low concentrations.

Material and Methods

All precursors of $FeCl_3.6H_2O$ and TTIP ($C_{12}H_{28}O_4Ti$ 97%) were used from Merck. The orange peel was washed with distilled water several times and cut into smaller pieces. The pieces were then placed on paper and dried at 40°C in the oven for 1 week and ground to a moderately fine powder. The Soxhlet equipment was assembled, and 20 g of the orange peel powder was weighed and placed in cartridges and placed in a 500 mL ball with 250 mL of isopropanol and allowed to heat at 90°C for 2 h. Finally, it was filtered with Whatman filter paper (N° 40) and refrigerated. The synthesis of the Fe_2O_3/TiO_2 nanocomposite was carried out by mixing the organic extract and $FeCl_3$. $6H_2O$ (0,5 mol L^{-1}) in a volume ratio of 1:2 at 70°C for 3 h until a reddish-brown solution is obtained due to reduction. 1 mol L^{-1} of NaOH was added with constant stirring for 1 h. The red precipitates were washed with ultrapure water and centrifuged at 8000 rpm for 10 min. It was dried at 95°C for 2 h and calcined at 550°C for 10 h. To obtain Fe_2O_3/TiO_2 nanocomposite, 0,4 g of the Fe_2O_3 nanoparticles was dispersed in 30 mL of the extract and 2 mL of TTIP was added to the Fe_2O_3 suspension. It was stirred for 2 hours. It was placed in a crucible and dried in an oven at 95°C for 3 h.

Finally, it was calcined in the muffle at 550°C for 10 h to obtain a milky red Fe_2O_3/TiO_2 powder.

Results and Discussion

As shown in figure 1, the composition and structure of the synthesized materials were identified by XRD spectra in the range of 20–80° of 2θ using Cu-Kα radiation of wavelength 1,540 Å. The presence of several diffraction peaks is observed: 25,3°; 37,7°; 48,0°; 55,0° and 62,6° , which would correspond to the crystalline planes (101), (004), (200),(211) and (204) respectively, and which would correspond to TiO_2 with an anatase crystalline phase and a tetragonal structure and the diffraction peaks at 24,1°; 33,1°; 35,6°; 40,8°; 49,4°and 62,4°,with crystal planes (012), (104), (110), (113), (024), (214) respectively, which corresponds to Fe_2O_3. Confirming this, Fe_2O_3 peaks of 33° (104), 36° (110) and 41° (113) were observed in the spectra of the Fe_2O_3/TiO_2 heterojunction [4-5]. For the cyanide degradation studies, a 440 nm lamp was used dispersing ~20 mg of photocatalyst in 50 mL of 3 ppm solution. The reaction mixture was subjected to vigorous stirring using a magnetic stirrer throughout the period of the experiment. The cyanide ISE was used to measure the amount of cyanide after incubating the sample for 2 h. As shown in figure 2, the Fe_2O_3/TiO_2 nanocomposite shows photodegradation results at low concentrations with an efficiency higher than 95 %. The presence of Fe_2O_3 would act as an electron scavenger by attracting the photogenerated electrons from TiO_2 that were not used to reduce oxygen, instead of recombination with holes. This electron transfer could avoid the charge recombination in TiO_2, so the cyanide oxidation could still occur in the VB of TiO_2 and enhances the photocatalytic degradation.[5]

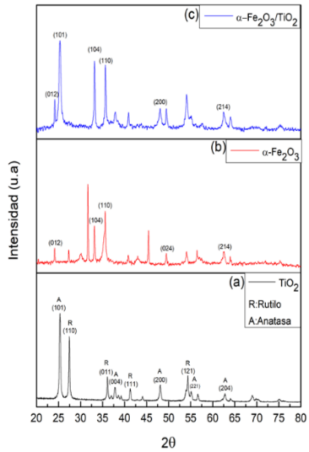


Figure 1. XRD pattern of TiO_2, Fe_2O_3 and Fe_2O_3/TiO_2 nanocomposites.

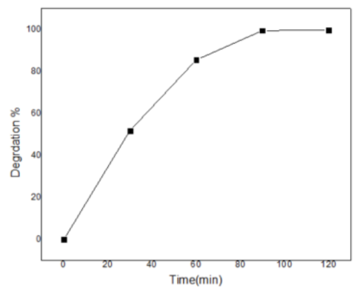


Figure 2. Photocatalytic degradation of cyanide under visible light by the Fe_2O_3/TiO_2 Nanocomposite.

Conclusions

In the present investigation, it was synthesized using the green synthesis method from orange peel extract. Thanks to the qualities, we were able to confirm the formation of Fe_2O_3/TiO_2 nanocomposite. Semiconductors can provide mutual characteristics that increase the activity of hybrid compounds compared to separate components. After two hours of exposure to a 440 nm light source, the photocatalytic activity was good, and the efficiency exceeded 95 %. This produced high photocatalytic activity during cyanide destruction, making it a potential candidate for wastewater treatment.

Acknowledgments

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