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Treatment of Petroleum Wastewater Using Fe-ZSM-5@TiO_2/Ag Nano Photocatalyst

Mohammad Delnavaz[1] Kiarash Eshaghi[2]

1- Introduction

Petroleum wastewater contains a wide range of hard biodegradable pollutants that are not treated by conventional treatment methods. Recently, plenty of research focus on assessing different ways of industrial discharge treatment. This attention is largely due to the huge water consumption of the majority of industrial factories as well as generating more complex wastewater than domestic one. Among industries, petrochemical wastewater largely contains different kind of organic persistent matter like hydrocarbons, various aromatic compounds and phenol. The criteria of these compounds categorize them as a non-biodegradable and toxic for receiving aquatic ecosystem. Harmful effects of these pollutants on the environment require the use of high-efficiency and low-cost processes.

Photocatalytic process is one of the advanced oxidation processes (AOP) that is used to decompose stable organic matter in petrochemical wastewater. In order to become practical in large scale, it should be enabled to adsorb extending wavelength light such as sun light. To overcome this issue, plenty of strategies have been examined and published in research papers. Photocatalytic performance of specific nanomaterial relies on the grain size, morphology, optical property and so on. The huge efforts have been made to either reduce recombination rate of e^-/h^+ or increase visible region efficiency of TiO_2. For this purpose, modifying the surface of nanoparticles with other semiconductors such as graphene and ZnO is recommended to improve electron transfer. Nevertheless, literatures suggest that the contact of noble metals like Au, Pt, Pd and Ag as a doping materials with semiconductors could obviously promote decontamination rate of numerous pollutants from aqueous solution. Noble metal deposition on the surface of TiO_2 increase the available active sites for adsorption properties improvement and charge transfer to increase electron-hole generation for much effective interaction with organic matters. Among noble metals, silver is relatively cheaper and stable than the rest of noble metal mentioned, above.

Catalyst Immobilization on the particular media has been growing. This trend is largely owing to that in the slurry method, the separation of suspended catalyst in the aqueous solution is just possible through either filtration or taking time to be settled. These drawbacks make researchers to consider fixing catalyst on the particular media. In this way, a huge number of researches have been focused on either moving media such as glass plate, or immobilized media like concrete surface.

In this study, the photocatalytic degradation of organic pollutants in the petroleum wastewater were investigated using Fe-ZSM-5@TiO_2/Ag synthetic nano-photocatalyst.

2. Material and Methods

The real wastewater was withdrawn from the petrochemical treatment plant located in the west of Iran. The wastewater was immediately transported to the lab and then, kept in refrigerator to maintain its temperature at 4℃ to prevent further biological decomposition. The raw petrochemical wastewater analysis was conducted and the results are reported in table 1.

Table 1 Characteristics of petroleum wastewater.

Parameter	Value
pH	7
COD	4150 mg/L
TBOD	3725 mg/L
TS	2216 mg/L
TDS	2101 mg/L
TSS	115 mg/L
FSS	87 mg/L
VSS	28 mg/L
Density	0.832
Turbidity	110 NTU

The reactor of the photocatalytic process consists of two UV-A lamps provided in the outside of the reactor. An aeration pump with the power of 2 l/min placed in the bottom of the reactor. The aluminum foil was used for covering the entire reactor to ensure UV emitted to the sample and safety considerations. Before the required volume of the wastewater injected into the reactor, the wastewater barrel was shaken to feed the reactor with homogenous wastewater. Then, after the pH adjustment, the UV-A lamps switch on and at the specific time intervals the COD measurement was conducted. The rate of organic matter photo degradation at the outlet of the reactor was monitored through COD test according to colorimetric method (5220-D). In addition, the pH value was also recorded by HACH portable probe. All required chemicals containing TiO_2, silver nitrate, sodium hydroxide, hydrochloric acid, dichromate potassium, silver sulfate, for pH adjustment, COD measurement and catalyst synthesis were prepared from Merck.

Synthesis of nano photocatalyst was done by immobilizing iron on zeolite to improve ZSM-5 structure and then TiO_2 and Ag coated to reduce the band gap energy. Physical and chemical properties of the materials determined by XRD, SEM, FT-IR and BET analyzes. TiO_2 in the anatase phase was shown using XRD analysis. The uniformity of the nanoparticles was also revealed in the SEM images, which showed that the TiO_2 and Ag particles were well located on the surface of Fe-

[1] Corresponding author. Associate professor, Faculty of Engineering, Civil Engineering Department, Kharazmi University.
Email: delnavaz@khu.ac.ir
[2] MSc student in environmental engineering, Faculty of Engineering, Civil Engineering Department, Kharazmi University.

ZSM-5. Experimental procedure was done using experimental method by response surface method (RSM).

3. Results and discussion

To better understanding of photo catalyst features, number of analytical experiments conducted on the synthesized composite. The morphology and elemental composition investigation of the ZSM-5/TiO_2-Ag was done using SEM – EDX (Quanta 200 FEI America). Results showed the existence of both silver and titanium in Ag/TiO_2 nanocomposite.

Figure (1) shows the X-ray diffraction patterns of Fe-ZSM-5/TiO_2-Ag recorded on the Philips, PW1730 (Netherland) diffraction system with Cu Kα radiation source at 40 kV and 40 mA. The peaks at 25.09- 37.65- 48.02- 53.89- 55.07- 62.38- 68.07- 70.07-75 are in agreement with JCPDS (no. 21-1272). Additionally, the peaks located at 38.01- 44.26- 64.02- 77.36 belongs to the Ag/TiO_2 photo catalyst having conformity with JCPDS (no. 04-0783).

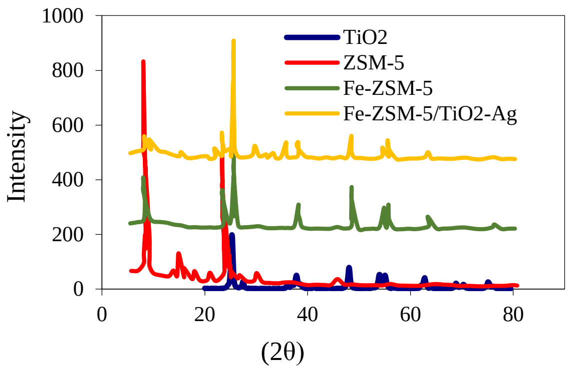
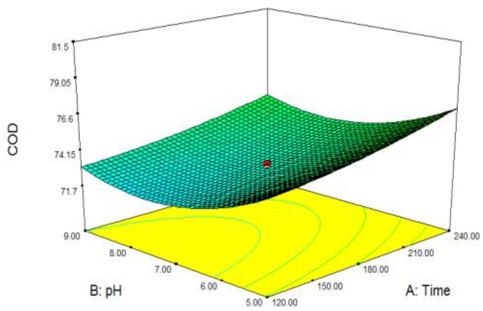
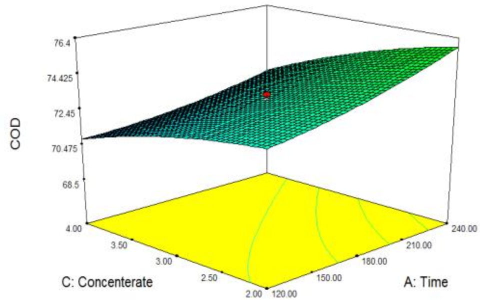


Figure 1. XRD spectrum of pure TiO_2 and ZSM-5/TiO_2-Ag

The pre-test experiments on pure TiO_2 and Fe-ZSM-5/TiO_2-Ag had shown that metal doped catalyst had higher photo catalytic activity than the pure TiO_2 to decontaminate wastewater. Then, the proposed experiments of software were conducted by adding 1 liter of the real petrochemical wastewater to the reactor and adjusting the primary operational treatment condition including the amount of photo catalyst dosage, pH of influent wastewater and contact time. The figures (2 a-c) are presented to show the photo reactor performance with respect to single and interactive variables effect.



a)



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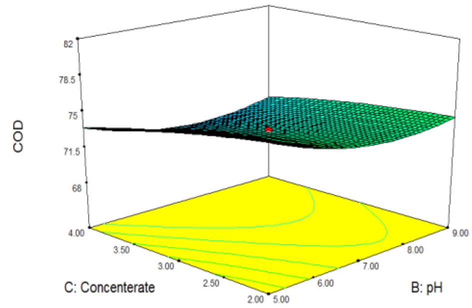

c)

Figure 2. a: interactive impact of pH & contact time, b: interactive impact of contact time and catalyst dosage, c: interactive impact of pH & catalyst dosage

4. Conclusion

In this study, the synthesis of Ag/TiO_2 catalyst was successfully conducted and immobilized on the zeolite. The effects of main parameters containing pollutant concentration, photocatalyst concentration, pH, reaction time, radiation wavelength and different photocatalysts were performed in a batch pilot. The uniformity of the nanoparticles was also revealed in the SEM images, showing that the Ti and silver particles were well on the surface of the Fe-ZSM-5 zeolite. The results show that at pH=5 and the photocatalyst dosage of Fe-ZSM-5@TiO_2-Ag equal to 2 g/L under UV-A irradiation at 54 watts and 240 min contact time the best COD removal performance equal to 83% were achieved. The immobilization of Fe-ZSM-5 zeolite increases the removal efficiency of organic matter in aqueous medium. The synthetic photocatalyst can be used up to 5 times without reducing performance.