



Assessment of Hydrogen Sulfide Gas in Petroleum Company and Photocatalytic Degradation Using mesoporous TiO₂ Nanostructured Thin Films



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Abstract

The search applied the evaluation and risk assessment of H₂S gas at Suez Oil Processing Company (Coker complex units). Different samples were measured for the Hazard H₂S in many places around the Coker units in 2012. TiO₂ was prepared by hydrothermal approach in presence of oleic acid. TiO₂ was characterized by XRD and SEM. Treatment of the produced H₂S was carried out by photocatalysis using (TiO₂) photocatalyst and UV light source. The removing efficiency of H₂S reaches 98% using UV lamp. The stability and the capacity of the removing were also studied. The degradation reaches 97% 96% after catalyst poisoning through three cycles.

Keywords: TiO₂; Photocatalysis; H₂S, Coker complex units.

1-Introduction

The waste gases emission contains toxic substances, including sulfur-containing compounds, is a harmful environmental crisis of different industries (Cheremisina et al. 2020). H₂S emissions are a growing concern for oil & gas companies. There is a relentless growth of global oil and gas exploration. As a result, many mature fields containing high concentrations of hydrogen sulfide (H₂S) are essential to develop, called sour fields. At a concentration of around 0.5 ppb, H₂S has a corrosive, poisonous gas and a rotten egg odor (Canela et al. 1998, Kataoka et al. 2005) and has developed many applications for the treatment of pollutants using photochemical phenomena from the animal recycling waste industry (Anet et al. 2013, Defoer et al. 2002), waste treatment (Tsang et al. 2008), paper processing (Rappert & Müller 2005) and meat industries (Boyjoo et al. 2017) many applications for pollutant treatment by using photochemical phenomenon (Alonso-Tellez et al. 2012, Boraphech & Thiravetyan 2015, Demeestere et al. 2005, Fu et al. 1997, Guillard et al. 2007, Kako et al. 2005, Kataoka et al. 2005, Kato et al. 2005, Rochetto & Tomaz 2015, Sopyan 2007).

TiO₂ photodegradation for other compounds (not only H₂S) like dimethyl sulfide (Cantau et al. 2007, Einaga

et al. 2015, Nishikawa & Takahara 2001, Turki et al. 2015), phenol [21] and others. The most strongly bounded TiO₂ thin film to substrate glass or ceramic (Allen et al. 2008, Kataoka et al. 2005, Saleiro et al. 2010). paints use TiO₂ depending on certain characterizes can present photocatalytic properties (Auvinen & Wirtanen 2008, Maggos et al. 2007, Marolt et al. 2011) differing according to paint type most type used are acrylic (Auvinen & Wirtanen 2008, Martinez et al. 2011, Monteiro et al. 2014) Vinyl-based paint (Águia et al. 2010, Ângelo et al. 2014, Costa et al. 2012) and suspension liquid type (Ramírez et al. 2011).

Our work represents assessment study of hydrogen sulfide produced in Suez Oil Processing Company. A simple continuous design for photocatalytic degradation of hydrogen sulfide produced from the Coker unit was constructed. A modified TiO₂ thin film was prepared by hydrothermal approach and characterized by different techniques as XRD and SEM.

2- Experimental

2.1 Materials and chemicals

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Receive Date: 17 March 2021, Revise Date: 16 May 2021, Accept Date: 24 May 2021

DOI: 10.21608/EJCHEM.2021.68185.3486

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Tetrabutyltitanate and oleic acid was provided from Aldrich. The physical properties of the produced hydrogen sulfide were shown in Table 1.

Table 1: physical properties of hydrogen sulfide (U.S. EPA, 2003)

Molecular formula	H ₂ S
Molecular weight	34.08 g
Vapor pressure	15,600 mm Hg at 25°C
Density	1.5392 g/L at 0°C, 760 mm Hg
Boiling point	-60.33°C
Water solubility	3980 mg/L at 20°C
Dissociation constants	pKa1 = 7.04; pKa2 = 11.96
Conversion factor	1 ppm = 1.39 mg/m ³

2.2. Synthesis of mesoporous TiO₂

70 ml of oleic acid was dissolved in 20 mL of ethanol in a standard method of synthesis. Then 170 ml of tetrabutyltitanate was applied, stirring at room temperature, to the solution. After 15 min, 5 mL of pure water with medium agitation at room temperature was applied to the mixed solution. The mixture was eventually allowed to react at room temperature for 30 min. The solution was transferred to Teflon reactor with a lid and placed in a 300 mL Teflon-lined

autoclave before being heated for 12 hours to obtain mesoporous TiO₂ at a temperature of 150 °C. The Teflon reactor was cooled down to ambient temperature in the air following the completion of the reaction. The resulting products were collected at 60 °C overnight after separation by centrifuge and dried in the air.

2.3. Characterization technique

X-ray diffraction patterns were registered with a Pan Analytical Model X' Pert Pro system, which was equipped with Cu-K α radiation ($\lambda = 0.1542$ nm).

Field emission scanning electron microscopy (FESEM) investigation was performed on JEOL, JEM 3500electron microscope.

2.4. Photocatalytic degradation of H₂S

Treatment of H₂S was carried out in a glass box with the dimension of 50 x 25 x 50 cm. The catalyst was spread on a glass substrate by doctor blend method with the size 16 x15cm. The glass box was connected to balloon filled with H₂S gas. The box was provided with a UV lamp of the length 30 cm. The gas was purged to the box

The experimental apparatus consists of the following parts :(1) balloon container with H₂S gas;(2) H₂S gas analyzer monitor ;(3) valve, (4) photocatalyst , (5) UV lamp (6) photocatalytic reactor body (glass box).

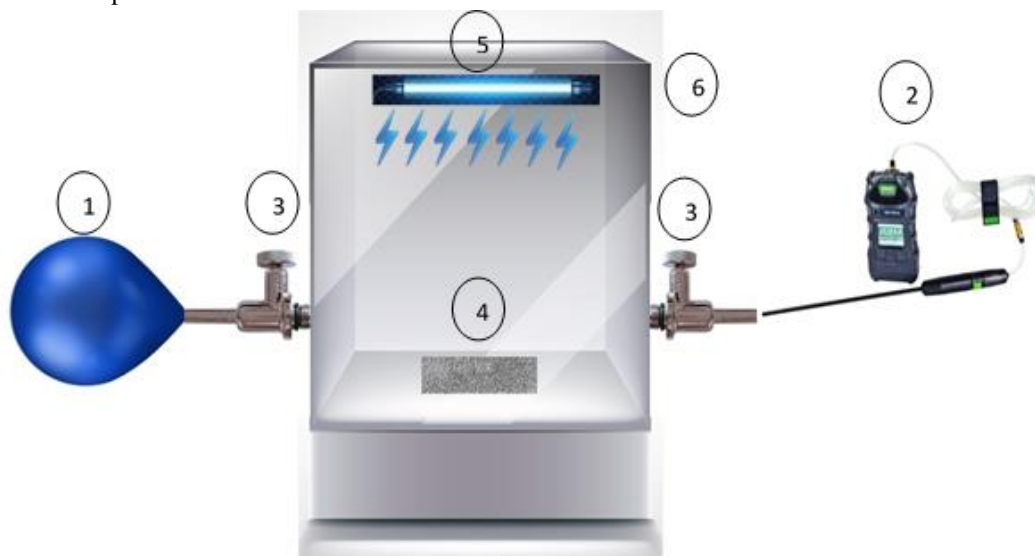


Figure 1: The photoreactor of H₂S gas

A known concentration of H₂S was purged in the glass box. After complete occupation of the gas the on stream concentration of the gas was recorded then the lamp was switched on. At the outlet piston the gas was measured using an analyzer quipped for H₂S gas detector model VENTIS MX4 sensor and the amount of H₂S degraded fromthe gas-phase was evaluated using the Equation (1):

$$\text{Degradation efficiency (\%)} = \frac{[\text{H}_2\text{S}]_{\text{in}} - [\text{H}_2\text{S}]_{\text{out}}}{[\text{H}_2\text{S}]_{\text{in}}} \times 100$$

Where [H₂S]_{in} and [H₂S]_{out} are the concentrations (ppm) of H₂S at the inlet and outlet of the reactor, respectively.

3. Results and Discussion

3.1. Crystal structure and phase identification

XRD analysis shows that TiO₂ NPs exhibit the anatase structure (Figure 2), and the average crystallite size calculated from the broadening of the (101) was in the size of 6.6 nm using Scherrer's equation. XRD and in general diffraction peaks appears relatively sharp with low intensity.

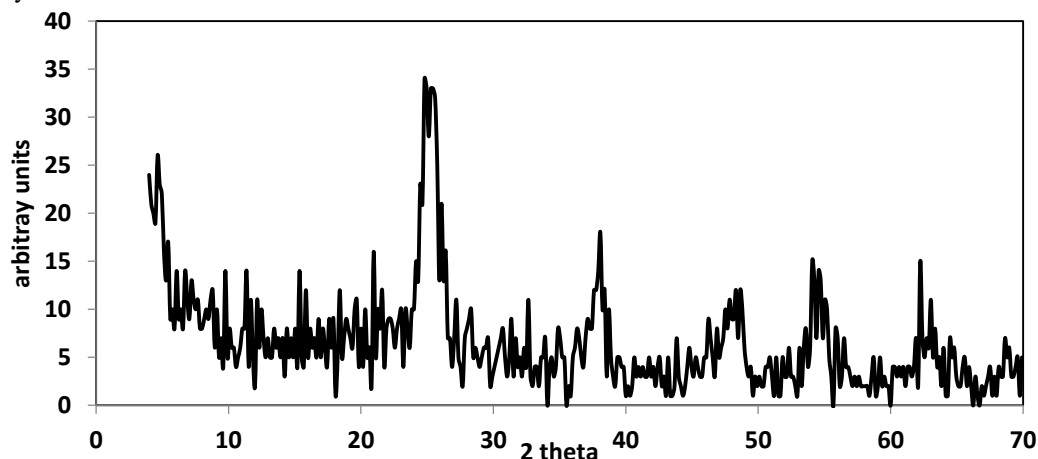


Figure 2: X-ray diffraction of anatase TiO₂ NPs

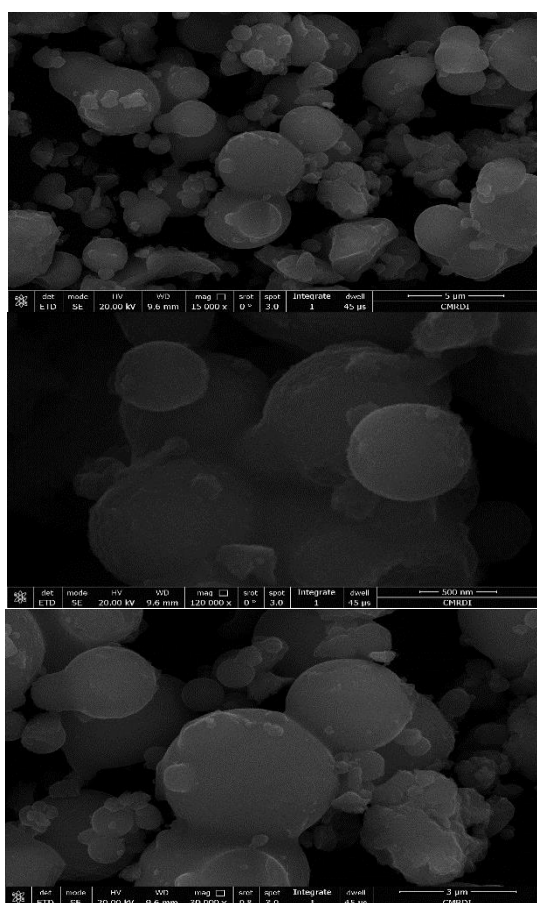


Figure 3: SEM of TiO₂ NP at different magnification

3.2. SEM

Figure 3 shows the SEM of TiO₂ NPs at different magnifications with diameter size ranged from 0.89 to 4.45 μm. TiO₂ shows spherical shaped with unsmooth surface, the spherical mesoporous TiO₂ arises from the assembly of ultrafine particles. The organic oleic acid prevents the distortion of the spherical.

3.2. Assessment & photodegradation

At concentrations between 500 and 1000 ppm or higher, exposure to hydrogen sulphide can be acutely lethal and the maximum permitted daily exposure without appreciable risk of deleterious effects over a lifetime is 1.4 ppb (U.S. EPA, 2003), while OSHA regulations provide for extended exposure concentrations of up to 10 ppm. Mechanical and electrical equipment used for process control, energy generation, and heat recovery may be seriously affected by hydrogen sulphide. The finery and processes of petroleum in Suez oil process company specially in cracking(coking) plants which product about half of Egypt production and on third of reserve medium distillate (gas oil). Coker plants contain three sectors; the first sector, consist of two processes. The first re-distillation under air pressure and 2nd distillate under vacuum by heating in furnaces and distillate by two towers to get (gas oil) and the residue is the feed of the second unit which called the main Coker sector. It is about thermal cracking process. The feed of the first unit residue meet preheating process by heat exchanger and inters furnace to heating feed into 500°C so the petroleum or hydrocarbon chains convert into coke .so steam was introduced to spread the flow speed to delay the coking process into drum. The main Coker contains three parts every part contains furnace and two drums one drum filled with coke and open mid valve between two drums in continuous feeding so this process called batch continuous system. The fuel vapors transfer into the main Coker tower and residue is coke drums so product of the Coker tower is the feed of third sector. It contains two main units; unit 10 is

treatment unit which treats the feed unit's reactor with Co, Mo, Ni and Mo. Catalysts to saturate hydrocarbon chains by injection hydrogen to convert olefins into saturated chain, spread H_2S gas, and transfer into unit 13. It is containing four compressors to press or compress the gas into 15 unit to convert the gas into sulfur raw material So, the main hazard, main highly effect of H_2S gas at 13,14 unit according to main concentration of H_2S , also this unit was built (constructed) since 1960 so it is very old unit which have metal corrosion, leakage hazard. So H_2S leakage take place into different concentrations due to

corrosion, negatively human or workers acts. So my sample research work depend on getting samples from the second and third unit which represent as evaluation of this unit, economic evaluation of gas percentage mixed with H_2S gas which was burned in flare with no use (waste gas), take special samples (safety samples) through maintenance processes or for work permits to measure concentration of H_2S gas in workers environment Samples through shut downing and operation of coking units, special for the third unit work permits.

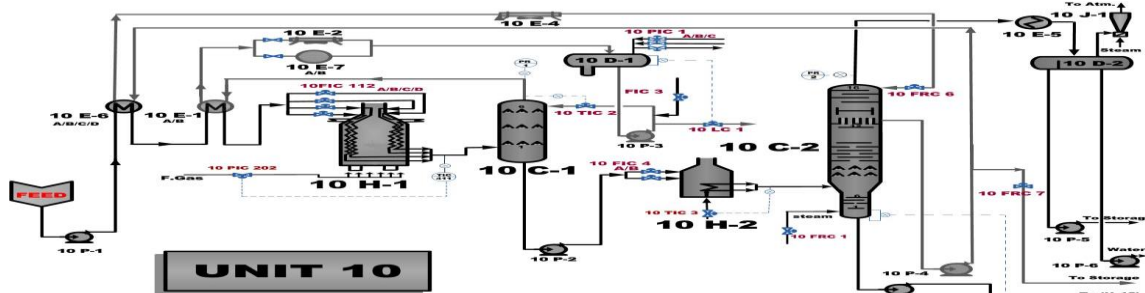


Figure 4: Unit 10 Coker complex in the Suez Company

There are many methods to remedy H_2S like bio-filtration (Grandclerc et al. 2017, Luo & Lindsey 2006, Sheridan et al. 2003), adsorption (Boraphech & Thiravetyan 2015, Ma et al. 2016, Mochizuki et al. 2016) or chemical washing (40,41) but these methods need chemicals and high energy consumption (Kato et al. 2005, Rappert & Müller 2005). Hydrogen sulfide, a major source of malodors emitted from wastewater remediation facilities or industrial plants and high harm to human's health, is one of the most targeted sulfur compounds that need to be degraded.

During the past decades, some progress has been made in photocatalytic degradation of H_2S (Allen et al. 2008, Einaga et al. 2015, Saleiro et al. 2010), but it is far from enough, studies on decomposition of H_2S using

visible light-active photocatalysts are scarce, and the achieved conversion efficiencies are relatively low.

3.3. Evaluations the hazard gas around the Coker unit

Through the measurement of the concentration around the treatment unite for outlet Coker at different day time. Figure 5 shows the variation of the H_2S concentration with the time from 4-10pm. The concentration increases from 36 to 44 ppm due to the decrease in temperature at night. It was noticed that all the obtained values was higher than the permissible limits.

Figure 6 shows the variation of H_2S concentrations around the Coker unite at 8 am-2 pm. The concentrations varied from 46-37 ppm indicate that the concentration decrease as the temperature increase.

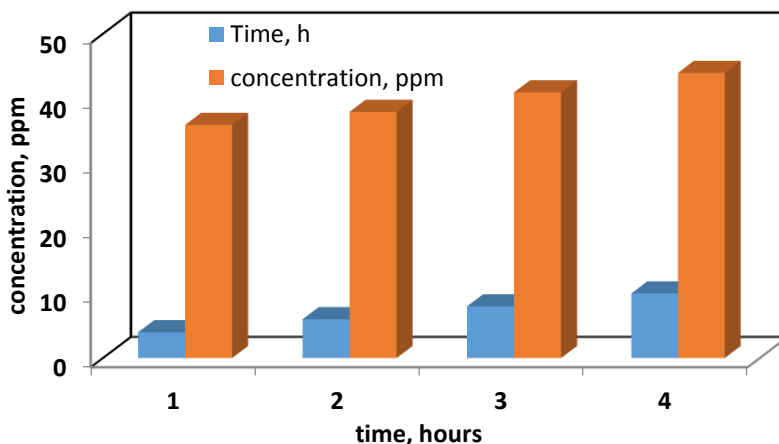


Figure 5: Variation of H_2S concentration with time (4-10 pm)

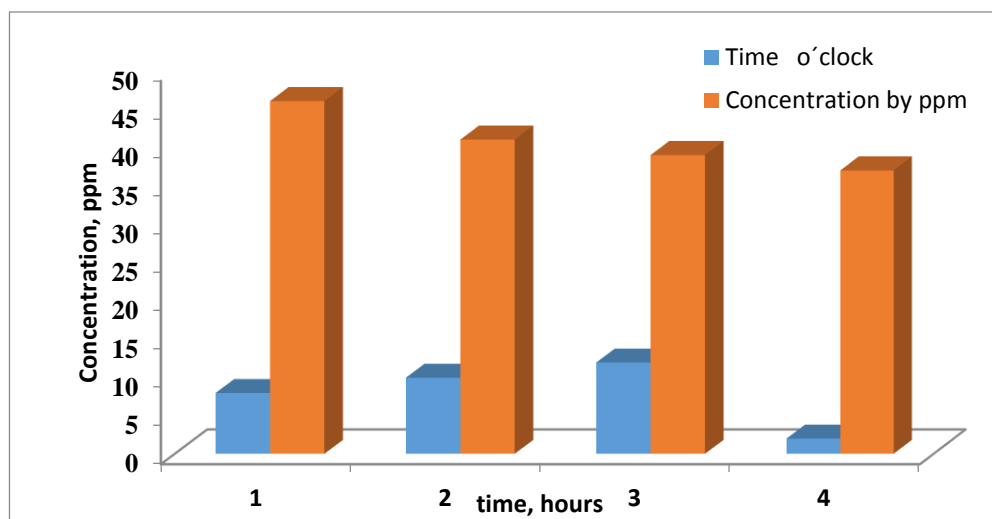


Figure 6: Variation of H₂S concentration with time (8 am-2 pm)

Figure 7 shows the assessment of H₂S gas on January 2012 during the day from 8 am-2 pm during the drain of the unit. The concentration ranged from 500-360 ppm.

Figure 8 shows the concentration of H₂S concentration during night on winter (February) at 8 pm-2 am. The Figure shows that the concentration ranged from 200 to 160 ppm.

3.4. The treatment of H₂S in the gas-phase

Figure 9 shows the photocatalytic degradation of hydrogen sulphide using TiO₂. As seen

in the Figure the concentrations of H₂S sharply decreased with time after irradiation with 'UV. This behaviour suggests the significant degradation of H₂S by the photo catalysis reaction. The removal percent attained 98.37% within 25 min. The stability of the catalyst was studied through the cycling of TiO₂ photocatalyst. The results show a slight decrease in the efficiency of the catalyst with cycling. The removal % of H₂S gas reaches 97.42 and 96.04 upon second and third cycling, respectively.

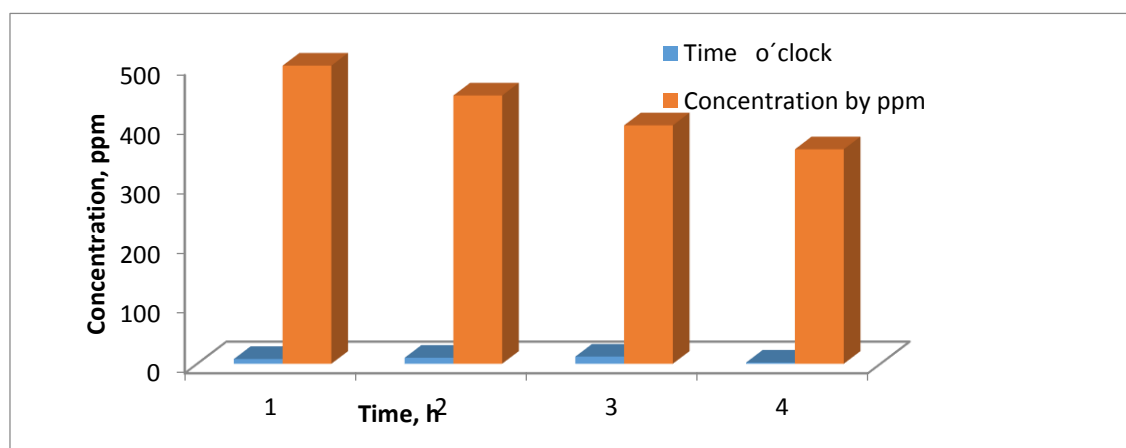


Figure 7: The concentration of H₂S on the drain

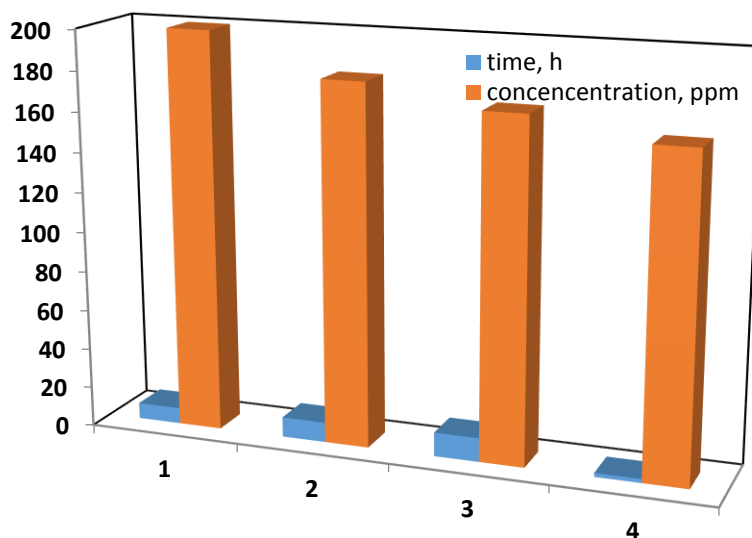


Figure 8: Variation of H₂S gas with time at night

The assessment results show that the concentration of gas ranged from 36 - 500 ppm and that represent high risk for workers and equipment.

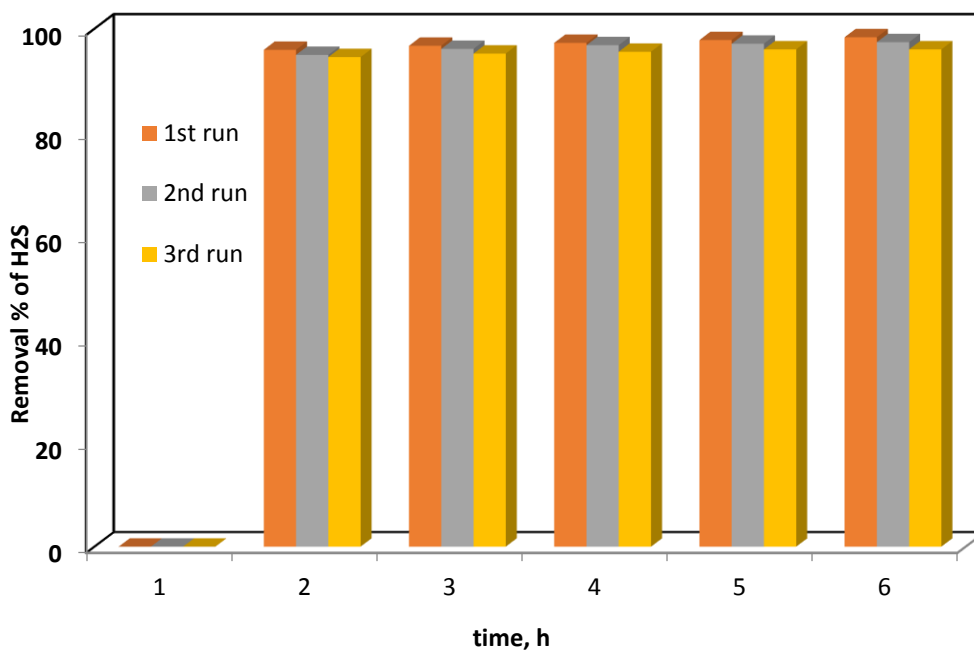


Figure 9: Removal percent and the stability of the catalyst across three runs

Conclusions

1- In the assessment study more than 66 samples of the gas was used to measure the H₂S gas concentrations (the whereabouts of the workers, around the units and the control rooms) and different times during operation and maintenance processes. The concentration of the gas was

ranged between 17:20 ppm to 500 ppm and of course these measurements exceed the permissible limits it has a negative impact on the human health and the surrounding environment (where the minimum allowable of H₂S concentration is 10 ppm per 8 hours per day).

- 2- The study showed that there is an effect of some factors on the gas concentration, such as temperature, wind speed, and volume. It was found that
- The higher the temperature, the lower the gas concentration and vice versa.
 - The higher the wind speed, the lower the gas concentration and vice versa.
- 3- The study showed that there is a decrease in the concentration of H₂S in the middle of the day shift and an increase in the concentration at night time and especially before dawn.
- 4- A direct relationship was observed between humidity and H₂S concentration
- The higher the humidity, the higher concentration of the gas.
- 5- A treatment of H₂S gas was carried out in the gaseous phase with a concentration of 368 ppm inside a glass reactor with a dimension (50 x 25 X 50) containing an ultraviolet lamp that passes the gas parallel or tangential to the catalyst TiO₂ Nanostructure thin film until it reached a concentration of 6 ppm within 25 minutes with a degradation rate 98.37%.
- 6- A treatment of H₂S gas was carried out in the gaseous case with a concentration of 696 ppm inside a glass reactor with a dimension (50 x 25 X 50) containing an ultraviolet lamp the gas passes parallel or tangential to the TiO₂ Nanostructure thin film catalyst after being poisoned from the previous treatment stage to know the efficiency/stability of the catalyst for the treatment process. It was found that the remaining gas concentration was 18 ppm within 25 minutes with a degradation rate of 97, 41%.
- 10- The treatment of H₂S gas was carried out in the gaseous phase with a concentration of 1740 ppm inside a glass reactor with a dimension (50 x 25 X 50) containing an ultraviolet lamp so that the gas passes parallel or tangential to the TiO₂ Nanostructure thin film catalyst after being poisoned from the previous treatment stages to evaluate the reuse of the catalyst for the treatment process. The remained concentration attained 69 ppm within 25 minutes with a 96.03% degradation rate.

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