WASTEWATER TREATMENT BY ELECTRO-OXIDATION PROCESS WITH TiO_2

Q.J., Rasheed[1], F., Ghanim[2] and T.A., Abdullah[3]

[1]Production Engineering & Metallurgy Department,
[2, 3]Applied Science Department,
University of Technology, Baghdad, Iraq.

Email: *2fanar_ganem@yahoo.com

ABSTRACT: The environment of wastewater containing toxic organic compounds by the industrial community has the environment of wastewater containing toxic organic compounds by the industrial community has increased significantly in the recent past. So, the treatment of such wastes generated from the industries is considered necessary. Untreated wastewater, if allowed to accumulate will result in the decomposition of organic material that leads to the production of toxic gases. For wastewater, the objective is to remove or reduce the concentration of organic and inorganic compounds. Some of the constituents and compounds present in wastewater lead to serious problem to the environment. This study presents the treatment of petroleum wastewater using nano scale TiO_2 in the presence of electro-oxidation process. TiO_2 physio-chemical characterization of sol-gel method analyzed using Ultraviolet light (which is an electromagnetic radiation), Scanning Electron Microgram (SEM), Fourier Transform Infrared Spectroscopy (FTIR) and X-ray Diffraction (XRD). The influence of TiO_2 dosage and initial pH on % COD reduction was studied. The results indicated that using TiO_2 in combination with electrocoagulation at a dosage of 0.15 g/l and a pH 10 in Current Density (CD) respectively is an efficient method for the treatment of petroleum wastewater

KEYWORDS: *TiO_2, nano, electrocoagulation, petroleum refinery effluent; COD reduction*

1.0 INTRODUCTION

Petroleum effluent contains free hydrocarbons, suspended solids, phenol, benzene, sulphides, ammonia, heavy metals, cyanide, mercaptans, solvents, inorganic elements having high concentration of salts, and organic carbon [1]. The current regulation of discharge limits for petroleum effluents prior to discharge into water bodies is in accordance with the Presidency of Meteorology and Environment (PME). The most toxic compounds present in petroleum effluent, according to the cooperative survey by the Environmental Protection Agency (EPA) and the American Petroleum Institute (API), are: methylene chloride, benzene, carbon tetrachloride, trichloroethane,

phenol, toluene, chloroform, trichloroethylene, ethyl benzene, pyrene, di-n-butyl phthalate, and bis (2- ethylhexyl) phthalate. These compounds cause major environmental impacts such as oxygen depletion and toxic effects on aquatic life tainting the water, and making it unsuitable for human use. Also, many studies have shown that oily effluents often have an impact on the fauna, fish, crustaceans, plankton, and algae, especially in the areas around the outfalls.

Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) values are in the range of 150-200 ppm and 300-600 ppm [1]. Typical cyanide, oil, phenols, benzene, sulfide, ammonia and heavy metals can be found in refinery effluents. Dependent of the source (surface water, ground water, re-used water) the make-up water will need a specific treatment such as sand filtration, iron removal, and (partial) softening. In addition, chemicals are dosed to control corrosion and biofouling. For boiler feed water the water is desalinated (reverse osmosis, ion exchange).

Nanoparticles are materials having a size in the range of 1–100 nm. Iron oxide, titanium dioxide, fullerenes and carbon nanotubes have been made into nanoparticles [2]. Titanium dioxide is an effective reducing agent and catalyst for various applications in environmental remediation [3]. The heterogeneous reaction using TiO_2 involves five steps: (i) mass transfer of the reactant to the TiO_2 surface from the bulk solution; (ii) adsorption of the reactant on the TiO_2 surface; (iii) chemical reaction at the TiO_2 surface; (iv) desorption of the reaction product from the TiO_2 surface; and (v) mass transfer of the product into the bulk solution [4]. Treatment of wastewater using nano-scale iron particles represents a new generation of environmental remediation and this provides cost-effective solutions to some important environmental problems [5]. The scope of the present study is the treatment of petroleum refinery wastewater sonochemically in the presence of TiO_2. TiO_2 particles were synthesized from ferrous sulfate, and were characterized using Ultraviolet light is electromagnetic radiation (UV), scanning electron microgram (SEM), Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD). According to their finding, the removal observed with venturi was higher than with the orifice plate in combination with Fenton chemistry.

The degradation experiments on p-chlorophenol using both electrocoagulation and hypervalent iron and concluded that the electroassisted ferrate degradation method was more effective than the simple ferrate method [6]. Afzal et al [7] studied the combined action of sonochemical and UV irradiation for the treatment of carbaryl

(Carcinogenic compound). The sample was treated in an electrocoagulation reactor with three different current densities. The highest degradation of carbaryl was achieved at 130 KHz compared to 35 KHz. The combination of ultrasound and UV irradiation was considerably more effective than when UV or electrocoagulation was operated individually. Based on the sonochemical degradation of Congo red, the results showed that the initial dye concentration and pH of the dye solution influenced the decolorization and low initial values resulted in high decolorization [8]. Basiri [9] reported on the reduction of nitrite by electrocoagulation dispersed nanoscale TiO_2 and showed that TiO_2 could be an efficient reductant. Ther using of TiO_2 is to reduce nitrobenzene in aqueous solutions [10].

The scope of the present study is to treat petroleum refinery wastewater sonochemically in the presence of TiO_2. TiO_2 particles were synthesized from ferrous sulfate, and were characterized using scanning electron microgram (SEM) and X-ray diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIER).

2.0 METHOD

2.1 Apparatus

The electro-oxidation process was carried out in a batch electrochemical reactor. Iron was used as anode and ruthenium oxide coating titanium as cathode with surface area of 45cm^2, working volume of 500 milliliter and sonication time of 10 min.

Chemical oxygen demand measurements were performed using COD digester (Open reflux method). All pH measurements were made using a digital pH meter.

2.2 Wastewater characteristics

The petroleum effluent was collected from a professional automobile service station in Baghdad, Iraq. Oily effluent is considered as one of the most serious polluting sources, as it contains toxic substances such as phenols, petroleum hydrocarbons, oil and grease, high biological oxygen demand (BOD) and chemical oxygen demand (COD) loads. This type of effluent comes from different sources, such as water produced from crude oil production, petroleum refinery, petrochemical, metal processing and car washing. The professional automobile service stations include all services like automobile maintenance, washing, and change of engine oil.

Petroleum wastewater from an automobile service station is caused by mixing of automotive oil, such as lubricant oil with emulsifiers and wash water. The initial characteristics of the petroleum effluent are as shown in Table 1.

Table 1: Characteristics of the Petroleum Effluent

S. No.	Parameters	Values
1	pH	7
2	Oil and grease	570mg/L
3	Total solids (TS)	1750mg/L
4	Total dissolved solids (TDS)	1610mg/L
5	Total suspended solids (TSS)	110mg/L
6	Chemical oxygen demand (COD)	3000mg/L
7	Biological oxygen Demand	370mg/L

2.3 Preparation of TiO2

The material used is a special grade reagents Titanium (IV) isopropoxide (Aldrich Chemicals Ltd., USA), Glacial acetic acid. All chemicals were reagent grade and used without further purification. Ultra pure deionized water was used in all the preparations.

The typical synthesis procedure for the preparation of TiO_2 nanoparticles by sol-gel method is as follows. Initially, 18.6 ml of Titanium (IV) isopropoxide was hydrolyzed by 35.8 ml glacial acetic acid at 0 ºC in which 395 ml of water was added drop wise to this solution under vigorous stirring for 1 h and the stirring was continued for a further 5 h. The prepared solution was kept in the dark for 24 h for nucleation process. After the period, the solution was placed in an oven at 70 °C for 12 h for gelation and aging process. The gel was then dried at 100 °C and subsequently the product was crushed into fine powder.

During the sol-gel synthesis of TiO_2 nanoparticles, high water ratio was kept to enhance the nucleophilic attack of water on titanium (IV) isopropoxide and to suppress the fast condensation of titanium (IV) isopropoxide species to yield TiO_2 nanocrystals.

2.4 Degradation experiments

Degradation experiments were performed in an electro oxidation reactor. Anode used was rhenium oxide coated titanium and cathode used was iron, while the area of the anode was 45cm^2. About 2000 ml

of the wastewater sample was placed in a beaker that was covered by a water bath to maintain constant temperature during Electro oxidation. To the beaker was added about 0.05 g of TiO_2, and Electro-oxidation was performed for 120 min. 1 ml samples were withdrawn at 5 min intervals and centrifuged for 10 min at 6000 rpm. The supernatant was subjected to COD determination. The pH optimization studies were performed under various initial pH conditions, including pH = 4, 6, 7, 8 and 10. At the optimum pH, nanoparticle dosage was then varied 0.05 g/L, 0.1 g/L and 0.15 g/L.

2.5 Analytical methods

Chemical oxygen demand (COD) was determined by the Open Reflux method.

3.0 RESULTS & DISCUSSION

3.1 Apparatus

The %COD remaining with respect to time of exposure to Effect of Oxidation time is shown in Fig.1. The results show clearly that the % degradation of wastewater increases with an increase in time and almost 60% of degradation was achieved in 120 min.

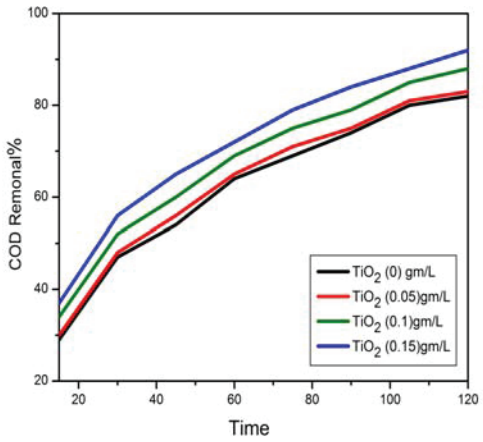


Figure1: Effect of Oxidation time on % COD removal

Generally, prolonged exposure of wastewater to electro-oxidation may enhance the generation of oxidative species in water. This is initiated by the hemolytic cleavage of water molecules by pyrolytic reactions, which may be represented as follows:

$$H_2O \longrightarrow OH + H \quad (1)$$

$$2\,OH + 2H \longrightarrow H_2O_2 + H_2 \quad (2)$$

The OH and $H2O_2$ are strong oxidizing agents, and the production rate of such oxidants depends on the final temperature and pressure at the time of bubble collapse. These oxidizing agents are responsible for the degradation of organic substances present in the wastewater.

3.2 Characterization of TiO2

Fig.2 shows the absorption spectra of TiO_2 nanocomposites taken at room temperature. The sample possess an absorption edge around 370-430 nm.

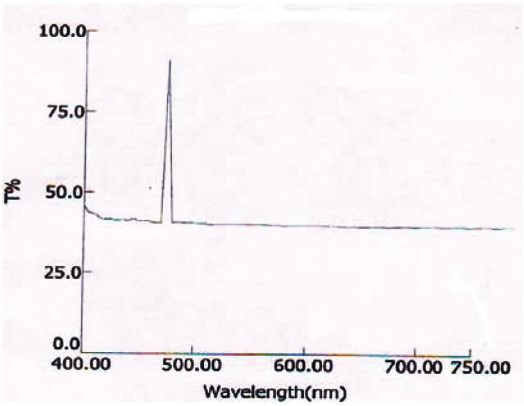


Figure 2: UV–vis spectrum for TiO_2 nanoparticles.

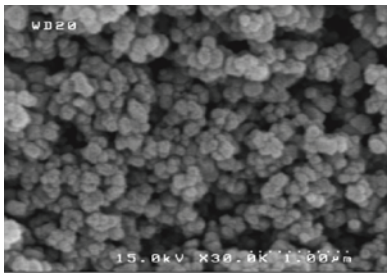
The scanning electron microscopy (SEM with EDX) image of synthesized TiO_2 particles were shown in Fig 3. The results indicate that the synthesized TiO_2 particles are almost spherical. Fig. 3(a) shows evenly distributed spherical particles approximately 1μm in size, and Fig. 3(b), under higher magnification, confirms the spherical shape and the size range of each particle. Fig.3 (b). These structures increased the available surface area of reaction. Fig.3 (c) shows the wt% for TiO_2 as 70.9 for Ti and 29.1 for O. Fig.4 shows the X-ray diffraction pattern of the TiO_2 sample annealed at 300°C in air for 1 h. The spectrum shows two major diffraction intensity peaks at 2θ = 36.08° and 41.01°. The peaks were identified to originate from the (1 1 0), (1 1 1), (2 1 1), (2 2 0),

(0 2 2), (3 1 0) and (3 0 1) planes of FeO respectively (JCPDS no: 772355). The X – ray could be indexed to the $Fm^{-}3m$ (225) face group (Face – centered) cubic structure, with cell parameter a = 4.309 Å.

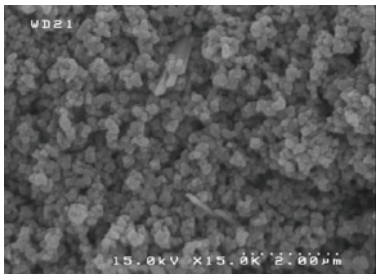
The information on the particle size was obtained from the full width at half maximum (FWHM) of the diffracted beam using scherrer formula: The crystalline size was calculated using Debye-Scherrer formula.

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (3)$$

a : magnification at 20 lm/200



b: Magnification at 10 lm/1000



c: EDX of TiO_2

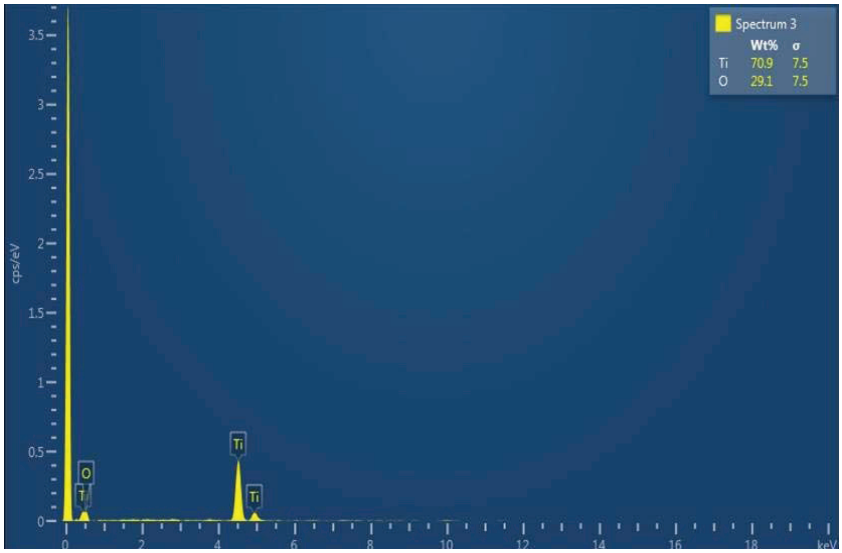


Figure 3: SEM –EDX images of TiO_2

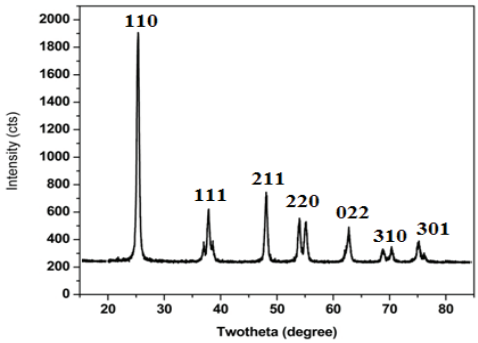


Figure 4: X-ray diffraction analysis of TiO_2 samples

The sample has an average crystalline size 226 of 3l.l nm +0.5.

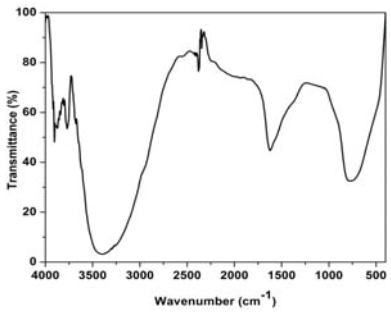


Figure 5: FTIR spectrum of TiO_2.

Fig.5 shows the absorption peak at 3457cm-1 as representation of the O-H stretching vibration of free water and its corresponding O-H bending vibration occurred at 1636 cm-1 due to the chemically adsorbed water.

3.3 Effect of current density

TiO_2 assisted Electro oxidation degradation was carried out and the %COD removal with respect to time is shown in Fig.6. During the first 5 min of the reaction, the reduction was much higher. This is due to the initial reaction of TiO_2 with the organic pollutants that are highly susceptible to oxidization. Later, due to the effect of oxidization, the COD continued to decrease to a considerable level, but became constant after a certain time. This may either be attributed to the presence of nondegradable organics in the effluent or to the exhaustion of TiO_2 particles.

The destruction may be improved by increasing the amount of TiO_2. In this kind of reaction, there are two ways in which the organic pollutants are degraded, namely, through pyrolysis and reduction on TiO_2 surface.

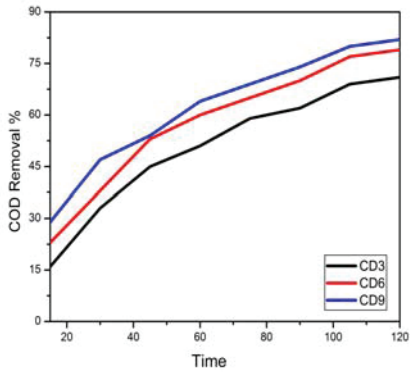


Figure 6: Effect of current density on COD with treatment time of 120 mins at pH=7.

3.4 Effect of pH

The effect of pH on the %COD removal after 120 min of processing is shown in Fig.7. From the results suggested by the figure, it could be noted that at pH 4, pH 6, pH 7, pH 8 and pH 10 the %COD removal value was much lower and hence the effective reduction took place at this pH. However, when the pH was adjusted to 6, a poorer effect on COD reduction was noted. This may be due to the reduced activity of TiO_2 under pH conditions.

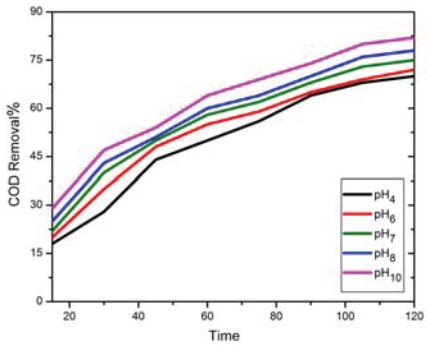


Figure 7: Effect of pH on % COD removal at treatment time of 120 min

3.5 Effect of TiO2 Dosage

The changes due to % COD under various TiO_2 dosage conditions are shown in Fig.8. The results show that an increase in TiO_2 dosage increased the reduction in COD, as the %COD removal decreased. This can be attributed to an increase in the surface area of TiO_2 accessible for the organic pollutants.

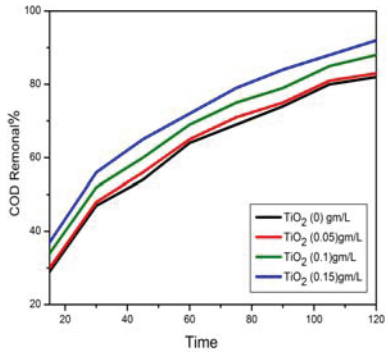


Figure 8: Effect of TiO_2 on % COD removal at treatment time of 120 min

4.0 CONCLUSSION

TiO_2 nanoparticles prepared through a liquid-phase reduction method are almost spherical and exhibit higher surface area available for reactions. The absorption spectrum of TiO_2 at 400 nm is due to the charge-transfer from the valence band (mainly formed by 2p orbitals of the oxide anions) to the conduction band (mainly formed by 3d t2g orbitals of the Ti4+ cations). The broad intense absorption edge of the spectrum is the result of formation of nanoparticles. The SEM find on the spherical particles where there were thread-like or tube-like structures clearly visible in these structures due to increased the available surface area of reaction. The sample annealed at 300°C/1h has an average crystalline size of 31.1 nm ±0.5. As the annealing time or temperature increases, the crystalline size increases. The band at 2432 cm-1 is assigned to C-H vibrations. The C-H could be attributed to the organic residues, which remained in TiO_2 even after calcinations. The broad intense band below 1200 cm-1 is due to Ti-OTi vibrations. Reduction test results indicated that oxidization can accelerate the reduction of organic pollutants present in wastewater when used with TiO_2. The degradation of organic pollutants present in wastewater with TiO_2 under Electro oxidation. Experiments carried out under various CD, pH levels revealed and dosage of TiO_2. The electro oxidation experiments

for the treatment of petroleum wastewater using ruthenium oxide coated titanium as the anode and iron as the cathode. were conducted in batch reactor. The optimized conditions was absorbed at current density of 9 mA/cm^2, pH of 10, catalyst additional of TiO_2 0.15 g/L, and treatment time of 120 min. Under these conditions, the COD removal efficiency of 92 %, were estimated. The electrochemical techniques are viable processes for the treatment of oily wastewater. The degradation strongly depended on pH 10 while efficient degradation occurred in acid media. TiO_2 serves as a substantial part that can be added to the reaction to reach desirable results.

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