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Combined electrocoagulation and photocatalytic for oily wastewater treatment using TiO_2 nano-catalysts

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Abstract

Photocatalytic process, as an environmental application aspect is a relatively novel subject with tremendous potential in the upcoming future. This oxidation process with light and semiconductors have gained an unusual research attention as a functioning water and wastewater cleansing procedure due to its high efficiency in disintegrating and mineralizing various dangerous contaminants as well as the prospect of exploiting the UV-Vis. spectrum of the sun. On the other hand, electrocoagulation has been proven to be an effective procedure to remove wide range of pollutants. In the current study, a photocatalytic and electrochemical combined treatment using synthetic oily wastewater with TiO_2 suspensions were tested. Turbidity was used to monitor the pollutants degradation. A number of parameters have been evaluated such as pH, applied voltage, and temperature. Both photocatalytic and electrochemical processes were applied to carry out comparative studies to treat the waste. The idea of doing this work was the modification of the electrochemical system for combination with the oxidation process for oily wastewater treatment approach in order to reduce the organic content of COD and treat the color. Our study here exhibited a noticeable enhancement in treatment efficiency of water quality in terms of turbidity, color, and COD under optimal conditions. The contribution to COD removal from EC process and EC-PC combined processes revealed that EC alone resulted in COD removal of 58%, while EC-PC contributed with 70% of COD removal. Both processes were effective in reducing oils 98%, color 99.5%, turbidity 99.9%, COD 80%, BOD 60%, Phenols 95% and Sulphides.

Keyword: Electrocoagulation, photocatalytic, Oily Wastewater, TiO_2, nanoparticles

1. Introduction

Water has been enormously consumed in all aspect of our life such as in farming, domestic, manufacturing, recreational and many other activities. It is true that the Earth's surface is almost covered with water, however, most of that water is not suitable enough for human use. Nowadays, millions of people all over the world do not have enough water for their basic needs. Industrial procedures consume substantial amounts of water that required treatment before discharging to environment or to be used again. The naturally available water is extremely used and polluted by the effluents from these activities. Wastewater treatment is a vital part of industrial work in the production process which is regularly contaminated with diversity constituents. A suitable treatment is prerequisite to discharge it to water bodies to reduce its effect on the environment and human life [1].

Oily wastewater is taken as a foremost pollution found in water resources in the oil industry because of the existence of organic contents and other pollutants. The majority of this discharged waste is coming from petrochemical processes, which are well-thought-out as the most common causes of environmental pollutants. The high level of COD in oil refinery waste is largely owing to the existence of aromatic, aliphatic, ammonia and organic constituents. The discharge of this oil wastewater harmfully influences water bodies, by tumbling the growth of algae, lessening the DO concentration, that is as a result of the oxidation of organic contents by bacteria, and altering the color, the taste and smell of water [2]. The treatment may comprise some procedures such as adsorption, filtration, reverse osmosis, membrane, electro-dialysis, ozonation, radiation, oxidation, photocatalytic disintegration and bio-treatment. For

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each method, it advises a diverse and special style and maybe brings certain benefits over others for a specific condition. However, when big quantities of water having toxic structures are to be treated, it would be a boundless gainful to have a cost effective system [3].

Thus, a countless struggle has been taken to create new tools leading the treatment of determined materials in the environment such as electrochemical, photocatalytic techniques and photo-electrochemical processes. Electrocoagulation (EC) adopts the basics and advantages of flotation, coagulation, and electro-chemistry mechanisms. Each of these principal techniques has been very significant in the environmental practice and extensively considered discretely. Though, the interaction mechanism between these techniques used in an EC procedure must still be elucidated. Photocatalytic processes (PC) for wastewater treatment are frequently investigated up to now. It proposals some advantages that may include: high surface area, high deprivation rate, limitless mass transfer, and simple reactor design. The efficiency of degradation is affected by several factors, ie. the type of the catalyst (i.e. TiO_2/ZnO semiconductors), radiance time, illumination intensity, light source, contaminant concentration, acidity and temperature [4,5].

The uniqueness of the current study was in the modification of the EC process to be integrated with the oxidation processes such as PC for wastewater remediation in order to eliminate/reduce the organic contents, while offering effective treatment outcomes. In this study, EC with Al electrodes and PC deprivation have been adopted to handle raw oily wastewater. The behavior of each and combined processes was evaluated. Yet, the outcomes propose that none of proposed individual processes would be applied for the effective remediation of oily wastewater. Conversely, a combined EC-PC degradation system suggested high removal efficiency of organic contents.

2. Background

2.1. Electrocoagulation Process

The electrolysis process can be defined as a method in which both reactions (oxidation and reduction) happening when passing current through an aqueous solution. EC process depends upon dissolution of the anode electrode (sacrificial anode) which provides ions acting as coagulant mediators in the solution in situ. Briefly, the EC system involves two electrodes (an anode and a cathode) made of inexpensive metal, where both sunken in the treated wastewater solution. The EC electrodes are generally made of cheap metals such as Al or Fe and readily obtainable, recognized as effective metals, and has no toxicity. Therefore, they have been approved as the core electrode applied in the EC processes. The design of EC systems differs which may have monopolar or a bipolar connection mode and may comprise either one or multiple anode/cathode pairs. Throughout EC procedure, there are countless reactions that may occurred at the electrodes to produce various ions (ie. Al^{+3} / or Fe^{+2}) besides gases such as O_2 and H_2. Fe^{+2} can be oxidized to Fe^{+3} by atmospheric oxygen or anode oxidation. Moreover, when chloride is found with high anode potential, forming energetic chlorine constituents (ie. Cl_2, HClO, OCl^-) that would improve the acting of the EC process over the oxidation reactions. Generated metal cations would react spontaneously forming various monomeric species and polymeric species that may transformed into $Al(OH)_3$ according to a intricate mechanism. Generated Ferric ions may create monomeric ions, ferric hydroxo complexes with OH^- ions, and polymeric species. These produced species further interact to create $Fe(OH)_3$. The founding of these complexes depends strongly on the value of pH where believed that above (9), would give $Al(OH)^{-4}$ and $Fe(OH)^{-4}$ [6-8].

The hydrolysis products of Al and Fe then destabilize various pollutants found in the aqueous solution. This allows agglomeration and additional departure from the solution by deposition and flotation processes. This is accomplished generally by ways of two distinct procedures; neutralization of colloids (negative charge) by cationic hydrolysis products and "sweep flocculation", where contaminates are surrounded and detached in the amorphous hydroxide precipitate produced.

The key features influencing the EC efficiency are the type of the electrode materials, applied voltage, operating time, initial pH and the constituents of the treated solution. Other parameters such as temperature, added salt, and distance between electrodes have also an influence on the removal efficiency of pollutants and economic durability of a given EC application [9].

The advantages of EC process over the typical coagulation procedure contain economic sides, lower capacity of produced sludge, better sludge quality, better efficiency, no chemical addition, modest equipment and compactness of EC reactor, greater practical pH range and neutralization influence, and the occurrence of electro-flotation [10].

2.2. Photocatalytic Oxidation Process

Generally, the photo reaction in the photocatalytic system (FC) takes place on the photo-catalyst surface. The mechanism is ruled by the creation of electron/hole pairs into the semiconductor and its moving to react with the organic pollutants found in the solution. Frank et al. first inspected the prospect of applying a TiO_2 nanocatalyst for the disintegration of cyanide pollutants [11]. Others widely considered the

potential use of FC for organic removal [12]. Semiconductor FC mainly absorb diverse color light reliant on their bandgap energy, thus it is applied as photocatalysts due to their charge carrier transport property, motivating electronic configurations, light absorption ability, and lifetimes of the excited-state. Figure (1) presents the basic mechanism of a semiconductor photocatalyst. When a semiconductorsis exposed to iradiation of energy that is identical to or larger than the bandgap energy of the semiconductor, which generates a holes in the valance band and electrons in the conduction band by stimulating the electrons in the valance band to the conduction band [13].

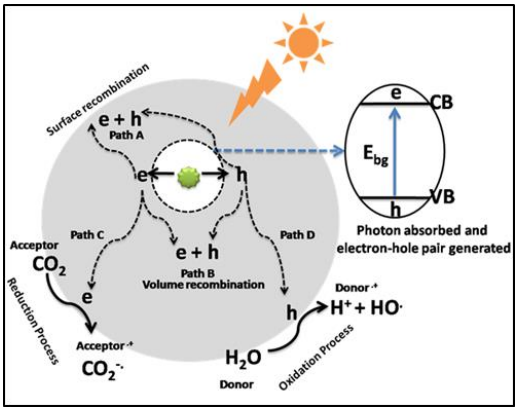

Fig. 1. Schematic diagram of the basic reaction mechanism of a semiconductor photocatalyst.

The mechanism of photocatalytic reaction can be described in the following:

$$Photocatalysts\ (TiO_2) + h\upsilon \rightarrow e^- + h^+ \quad (1)$$
$$h^+ + H_2O \rightarrow H^+ + OH^- \quad (2)$$
$$h^+ + OH \rightarrow OH^+ \quad (3)$$
$$e^- + O_2 \rightarrow O_2^- \quad (4)$$
$$2e^- + O_2 + 2H^+ \rightarrow H_2O_2 \quad (5)$$
$$e^- + H_2O \rightarrow OH^* + OH^- \quad (6)$$
$$Organic + OH^* + O_2 \rightarrow CO_2 + H_2O + other\ products \quad (7)$$

The electron conduction band reduces oxygen into O_2^- according to equation (4) adsorbed on the surface of TiO_2, whereas the hole with positive charge oxidizes organic contents by water according to equation (2) to generate OH free radicals. In this process, the oxidation of contaminants and the reduction process of O_2 do not happen alongside, it appears there is a buildup of electrons in the conduction band of the photocatalyst, hence serving a recombination of electrons with the positively charged holes. Consequently, the efficient consumption of electrons is needed to inspire photocatalytic process [12].

The photocatalytic oxidation relies on creation and combining the electrons and holes on the semiconductor surface. Adsorbed O_2 on the surface performs as an electron captor. This would govern the recombination of photo induced electron-hole interaction. The catalysts in nano have greater efficiency in comparison to the normal bulk photocatalyst materials. One of the direct effects occurs if the catalysis size turns out to be in nanometer rang. This would give rises to what is called “quantum size effect”, that is due to the quarantine of the e-movement. This leads to that both the valence and conduction bands of the semiconductor would modify into distinct energy levels, meaning that the electrical potential of valence band adjusts more positive; then the conduction band electric potential becoms more negative. Thus, the oxidation-reduction potential of the electrons and holes is enlarged, and enhancing the oxidation activity of TiO_2 photocatalyst.

Finding more atoms on the surface, it may improve the adsorption ability of the photocatalysts towards organic contents. The photocatalysis activity is related with the reaction time needed by the electrons and holes to reach the surface of the catalysis. When the TiO2 photcatalysis are in the nano-range, their diameter turn out to be very miniature, and direct for the charge carriers to move from the inside to the surface of the catalysis, starting the reduction-oxidation reaction. This means, higher the surface to volume ratio, lesser the particle diameter and thus reducing the time that may be used by the charge carriers that spreading to the surface from inside. This would offer minor recombination probability of electron and hole, hence, greater activity. Consequently, the nano TiO_2 have better efficiency than the common (bulk) titanium in photocatalysis [13].

2.3. EC-PC Previous Studies

The EC/PC combined processes have not been widely investigated, however, some wastewater have been remediated under this system, giving greater removal efficiency of organic contents. Table (1) shows a summary review of the research papers between 2007 to 2021.

Table 1. Summary Review of Previous Works

Ref.	Research Focus	Research Finding
Neelavannan et al. [14] (2007)	They reported the EC-PC procedure for the textile wastewater treatment where they considered the outcome of several experimental factors (pH, conc. of electrolyte, applied current and catalyst conc.) on the removal efficiency of the discharge procion blue dye solution.	COD reduction and color removal were found to be 96 and 100%. The dye Photo-degradation efficiency was high when photocatalysis was done with 40 mg/l of TiO_2. From the inhibitive consequence of dye, it was established that OH radicals were the main reactive constituents involving the positive holes in the reaction.
Rodrigues et al. [15] (2008)	They examined the combined treatment of post-bleaching effluent from a cellulose and paper industry using coagulation–flocculation followed by heterogeneous PC.	They exhibited that the combined method reduced the organic and the inorganic pollutant constituents in the effluent with about 86% COD removal.
Parga et al. [16] (2009)	They developed an EC combined with PC procedure for cyanide removal from mining wastewaters using TiO_2 nano-catalysis.	Data showed that photo-elimination of cyanide is 93 % in 30 min time using a 450 W halogen lamp. This system has the likelihood to assist as a dependable and economical process as sunlight can be used effectively as the power source.
Boroski et al. [17] (2009)	Work was done on wastewater treatment using EC–flotation process followed by PC. The authors used UV/TiO2/H2O2 hybrid PC system .	EC procedure was able of eliminating COD at 46%, whereas EC-Fenton was efficient in removing 54% when treating tannery wastewater using Fe electrodes for cyanide removal from mining wastewaters.
Modirshahla et al. [18] (2013)	They carried out decolourization of tartrazine in aqueous solutions by coupling EC and PC methods. Decolorization was improved by the utilization of UV after the EC treatment.	This paper revealed that joining EC with UV/ZnO may bring a Fenton or Fenton-like reaction and quicken decolourization.
Sala et al. [19] (2014)	They described the effectiveness of a PC-EC system to eradicate color in textile dyeing effluents containing a bi-functional reactive dye.	Dye decolorization was improved by the utilization of UV after the EC treatment.
Santos et al. [20] (2015)	They assessed the combination between EC system going on in the dark, and TiO_2/PC system for dye elimination, using the azo dye tartrazine as a model of oxidizable substrate.	It was determined that the PC and EC coupling could be utilized as an substitute for the treatment of this kind of waste and possibly containing other azo dyes.
Akyol et al. [21] (2015)	They focused on improving the purging of non-biodegradable pollutants through EC and PC for the removal of hydroquinone (HQ) from the treated solution.	The removal efficiency depended on the HQ conc., current density, UV intensity, oxygen supply and the exposure time.
Suárez-Escobar et al. [22] (2015)	They made an optimization of TOC elimination for the remediation of lithographic wastewater by EC then followed by TiO_2/FC process.	A TOC removal of 74.43% was gotten for the combined processes in 20 min of EC and 45 min of PC. It was also found that the upgrading of the optical features of the water was essential for the achievement of the PC treatment.
Gadad et al. [23] (2016)	The PC process followed by EC was carried out to study the color and COD removal of distillery spent wash as a possible source of water contamination with high organic contents and volatile constituents.	Maximum efficiency was obtained by combining the two processes (PC and EC).
Qing et al. [24] (2016)	They developed a new remediation technique using an EC device combined technologies of electrolyzing and PC to deal with the stimulated ship sewage. Titanium and coated anode of the electrolysis unit was adopted for the treatment of organic contents in the treated water.	They suggested that UV irradiation method can be a substitute technique for the conventional de-Chlorine methods.
Ates et al. [25] (2017)	They tested EC and PC reactors to comprehend the act of the combined EC and PC deprivation of olive washing wastewater.	It was reported that EC as a individual treatment system provided a COD reduction of 62.5%, color elimination of 98.1%, and total phenol degradation of 87%. The combined system confirmed the removal efficiency of 88.0% COD, 100% total phenol and color at optimal conditions.
Nazari and Ayati [26] (2019)	They evaluated sodium dodecyl benzene sulfonate elimination using EC/flotation and FC nano-catalyst of TiO_2 slurry schemes.	They found that in the case of hybrid system, COD removal efficiency reached 96.27% in comparison to 90% with EC alone.
Keramati and Ayati [27] (2019)	They evaluated COD removal rate using EC procedure along with a PC method with nano-catalyst of ZnO, also the combined treatment was also implemented.	The COD removal efficiency was attained at 95.8% for the combined system and that the petroleum compounds were significantly removed. Also combining the two processes reached energy savings and higher performance.

Khorram and Fallah [28] (2020)	They investigated a comparison of energy consumption related to EC and PC process for the industrial dyeing wastewater treatment.	They found that COD elimination was better in PC system and the energy consumption in EC was lower than in PC. Outcomes presented that decolorization same, while COD removal efficiency was 32.52% in PC system more than in EC system due to the finding of soluble organic contents.
Maher et al. [29] (2020)	They investigated the energy reduction when doing EC procedure followed by electro-oxidation (EO) system directing preliminary removal of (DOC) during EC and following the exclusion of estrogenic compounds in EO.	They recommended that this procedure could be more effective than some other oxidation processes including EC alone, EO alone, ozonization, TiO_2 /PC, and UV photolysis. They used EC as a pretreatment procedure to lessen the consumed energy.
Pelawi et al [30] (2020)	They reported combining EC and PC methods to monitor the outcome of adding CuO dopant into TiO_2-Nanotubes to decolorize the dye waste and concurrently yield H_2 in a reactor made of acrylic which is fortified with a power supply and UV lamps.	This system can increase the concentration of H_2 by 44% and depleted tartrazine solution to 10.5%, which was better than using pure TiO_2 Nanotubes.
Çalışkan et al. [31] (2020)	They reported using UVA-assisted EC as a hybrid process for the treatment of Greywater reusability.	They showed that UVA irradiation has not effectively contributed for the removal of COD and turbidity whereas BOD was rapidly and effectively decreased to regulated standards for reclaimed water given by regulations.

3. Materials and Methods

Wastewater primarily from the petroleum refinery process was collected from local refinery factory (Nasryiah Oil Refinery in Dhi Qar province in south of Iraq) with concentrations of more than 1000ppm. The foremost constituents of this water according to the materials used for this step of the process are essentially organic materials, oil, and water.

TiO_2 was obtained from Sigma-Aldrich (USA). Powder of TiO_2, of crystalline structure anatase > 99%, that has nano-size range of 5-10 nm, with a specific surface (SBET) of around 320 $m^2\ g^{-1}$. Other chemicals were obtained from a commercial supplier. All chemicals were used without any further treatment.

A commercial DC power supplier of (0-15 V/0-2 A) and a magnetic stirrer (BOECO Magnetic Stirrer-model MSH-300N, 50-1250 RPM), circular-plates anode and cathode were adopted, Electrodes dimension of circular (Ø95mm x 1mm). The electrodes (Al) were positioned in the bottom of a Pyrex glass with the gap distance of 10 mm between anode and cathode, Figure (2a). In most experiments, the net volume of the EC reactor was 1000 ml, and the net reaction volume was 800 ml. In each experiment, the 800ml of the solution was treated and in 5 min process intervals, the DC power supply was switched off to let settling for 5 min. Then, the acquired solution was analyzed by resources of some tools to determine COD/BOD and Turbidity. In order to uphold the solution conductivity and its ionic strength modification, salt was added in all progressions (approximately 0.5-1 gm).

Optimization procedure for EC process has been already detailed elsewhere [7].

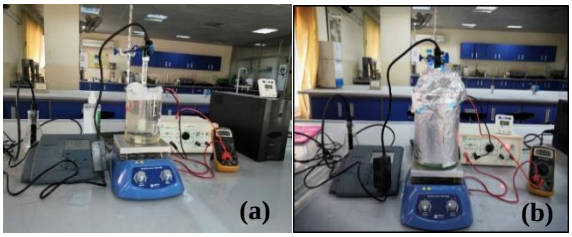

Fig. 2. Images of the EC - PC experimental setup.

All combined experiments were performed in a batch photocatalysis-reactor. The irradiation source was a commercial UV lamp (30 W, UV-C, λ_{max} = 254 nm) which was located direct above the Pyrex reactor. During irradiation experiment, the Pyrex beaker positioned on a magnetic stirrer to preserve the suspension homogenous and at 15 min reaction intervals, 5 cm^3 of the sample was removed and analyzed. The reactor was wrapped with aluminum foil to maximize the efficiency of the irradiation. The TiO_2 catalyst was added to the aqueous solution and then the electrodes were immersed in the reactor. The total flooded surface area of each electrode was 18 cm^2. Then, the electrodes were wired to the DC power supplier. In each experiment, 1000 cm^3 of the treated water was poured into the EC cell and in 5 min process intervals, the DC power and UV lamp were switched off to let settling for 5 min. Then, the achieved solution was analyzed. The COD of the treated water was tested following standard methods for the examination of wastewater.

Whenever required, NaOH 0.1 M or HCl 0.1 M was used to alter the pH value of the treated solution and the electrodes were cleaned with nitric acid before each experiment. The treated wastewater was stirred at all experiments (around 900 rpm) with an average

operating time of 20 min which was adopted according to preceding data obtained in the literature [6-8]. After finishing the procedure, a precipitation period of 30 min was secured, and then a collected sample of the treated water was reserved for analytical measurements.

Figure (2b) illustrates the EC/PC combined reactor setup batch where PC reactions were done in a Pyrex glass photo-reactor with working volume of 800 ml and the net treated volume of 750 ml. The exposure time to the UV irradiation was 45-60 min. A number of experimental processes was carried out to optimize both EC and PC systems. The effecting factors for the EC experiments were found to be the current density and the initial pH. Catalyst concentration was taken as a fixed value and chosen to be about 0.5 gm for the PC process. Turbidity was measured and evaluated using Hanna HI 93703 Turbidity- meter. The pH readings were taken with a Metrohm 780 pH -meter and the conductivity figures were taken with a Hanna HI8730 conductivity-meter. Throughout the experiments, the removal measurements of the organic contents and phenol contents were calculated with COD and phenol analyses (Curried out in the Environmental Centre at University of Technology). The EC and PC removal efficiencies were monitored by measuring the COD, phenol content, and color.

4. Results and Discussion

Experiments were performed to remediate oily effluent by EC system using Al for both the anode and the cathode electrodes. All initial EC experiments were carried out on petroleum refinery effluents using Turbidity measurements. Typically, the experiment was done in a parallel hole-plated of total volume of 150 ml. The parameters used in the EC procedure were chosen as follow: operating time, mixing effect, initial concentration, applied voltage and temperature. Initial concentration and other properties of oily wastewater are shown in table (2).

Table 2.

Pollutant present in Petroleum Refinery Wastewater

Pollutants/ ppm	Crude Wastewater
pH	9.5
Suspended Solids	698
Oil	2180
BOD	< 258
COD	710
Phenols	< 3.7
Sulphides	< 68

Figure (3) demonstrates the variation of Turbidity with running time at various mixing speeds (0-1250 RPM). Results demonstrate that a moderate speed of 1012 RPM is the optimum choice for the turbidity removal especially around 10 min time and initial concentration of 350 FTU. Similar behavior was obtained with TDS removal as a function of operating time, as presented in figure (4).

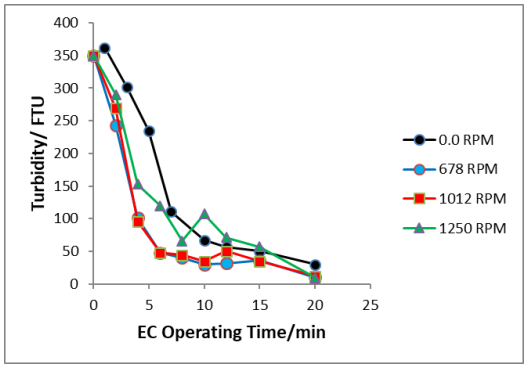

Fig. 3. Relation between time and Turbidity

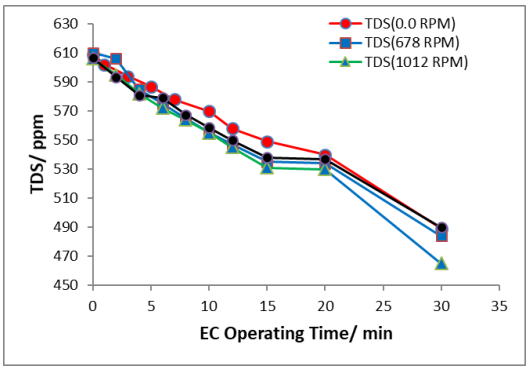

Fig. 4. Relation between time and TDS

Figure (5) describes the outcome of running time on the oil removal. It was found that, by varying the time from 0 to 50 min the removal efficiency increases from 0 to 60%. In this practice, EC comprises of two steps: destabilization and aggregation. The starting period is generally short, while the later period is fairly extended. The dissolved ions, as destabilization species, are furnished at the anode over electrochemical reactions. This resulted in a small charge loading when the running time is reduced, as a result of which the dissolved ion quantity was found to be inadequate to destabilize all colloidal. Accordingly, the oil removal efficiency was not high enough. Data illustrate that all-out efficiency of the EC system found at a running time of 40 min, and a additional upsurge in running time did not give any noteworthy enhancement in the efficiency of the studied parameter.

Figure (6) displays that the applied voltage has changed mildly with running time during the EC system and with using different agitating speeds. During the EC process the anodic dissolution for Al begins which in turn, makes (hydroxo-cationic) complexes, resulting in improving turbidity removal. More, the applied voltage may control the rate of coagulants (ie. flocs formation) and bubble creation

(H_2 and O_2 gases), which may inspire the process efficiency. An upsurge in the gas bubble density with a reduction in their size boosts the upward instability, ensuing higher pollutant deprivation and rise flotation of the sludge.

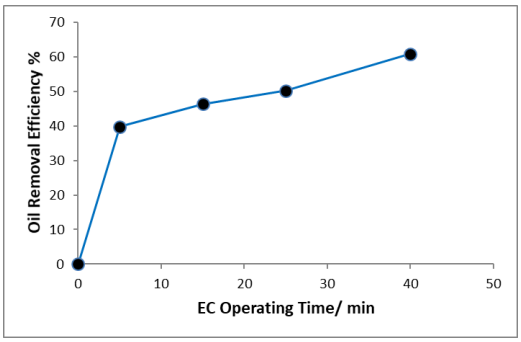

Fig. 5. Relation between time and oil removal

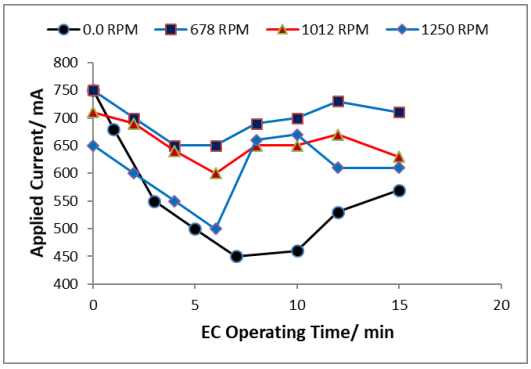

Fig. 6. Relation between time and applied current

The temperature outcome on the removal of oily water treatment through EC system was also investigated here. The effect of three different temperatures of 30 ºC, 50 ºC and 70 ºC was considered for the removal efficiency of oily wastewater as shown in Figure (7) at time interval 0-15 min, initial conc. of 1000 mg/L, initial pH of 8 and NaCl conc. of 1 g/l. The records indicates that the efficiency decreased with growing temperatures due to the volume of colloid $M(OH)_3$ solution would decrease and pore production on the metal anode well be closed. Previous results showed similar behavior [7].

Some researchers have specified that pH is a key factor inducing the performance of the EC system [3-5]. In general, the acidity of the treated wastewater changes during the operating course and this depends on the type of metal electrode and the initial pH. Instead, the EC system displays some buffering bulk, especially in alkaline environment, which averts large variations in the pH and diminutions the contaminant removal efficiency. The result of changing the initial pH on output turbidity is accessible in Figure (8).

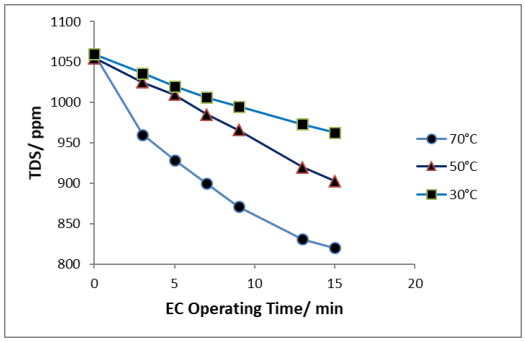

Fig. 7. Relation between time and TDS at different T

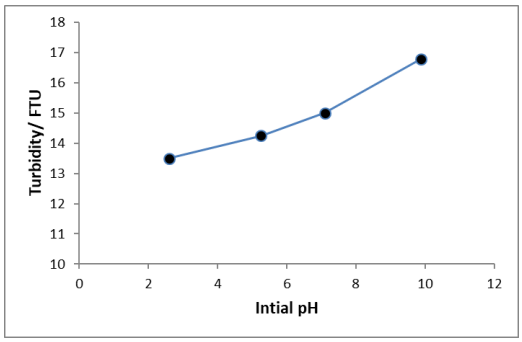

Fig. 8. Relation between initial pH and output Turbidity

Samples collected right after the EC procedure was adopted for photocatalytic (PC) experiments after concluding all the analytical measurements. The physical and chemical characteristics of the treated wastewater using both EC process and EC-PC process are shown in the Table 3. It was found that utmost of the turbidity was detached after the EC treatment with efficiency of 99%. Optimally, samples were left overnight to reach a required turbidity of 0.5 NTU for most of the prepared samples. Besides the wastewater was color-less, however, having a high quantity of organic content near to 20% of the original value of the wastewater. As soon as performing the PC experiments, the values of final TOC were attained after the process.

Table 3.

Pollutant present in Petroleum Refinery Wastewater after treatment

Pollutants/ ppm	Crude Wastewater	After EC Treatment	After EC-PC
pH	9.5	7.8	7.6
Suspended Solids	698	< 140	108
Oil	2180	< 92	43
BOD	< 258	< 127	< 120
COD	710	< 296	<214
Phenols	< 3.7	< 0.8	< 0.2
Sulphides	< 68	< 2.2	< 0.9

The experimental data confirmed a positive impact of nano-TiO_2 conc. on the depleting rate, owing to the surge in the oil molecules that were absorbed by the TiO_2. An optimal TiO_2 dosage in the (EC-PC)

combined system achieved was 0.5 g/l. Previous results showed that TiO_2 dosage greater than 0.5 g/l may have a undesirable effect on this system since the extra quantity of TiO_2 may rise the turbidity of the treated water that would diminution the light penetration into the aqueous solution, follow-on in a lessening in production of OH radicals at the TiO_2 surface available to deplete the organic contents in the oily water. These interpretations were also cited by several papers [17].

The effect of EC combined PC on the COD/BOD is shown clearly in Table.3. oil level, COD and color removal upsurges rather with time for all applied voltages, with higher voltage displaying proportionally higher reductions. With a applied voltage of 10V and 60 min of treatment, EC-PC reduced the COD and color of the electrocoagulation effluent by 60% and 70%, respectively. The suggested mechanism for organic contents oxidation with the concomitant, oxygen growth taking place on the surface of the electrode through construction of OH radicals.

The contribution to COD removal from EC process and EC-PC combined processes revealed that EC alone resulted in COD removal of 58%, while EC-PC contributed with 70% of COD removal. Both processes were effective in reducing oils 98%, color 99.5%, turbidity 99.9%, COD 80%, BOD 60%, Phenols 95% and Sulphides.

Our results greed well with the outputs of Mahdieh Keramati et al. [27] who published data on petroleum wastewater using a combination of EC-PC process with immobilized ZnO nanocatalysts. The authors obtained a COD removal efficiency of 95.8% for the combined system.

5. Conclusions

This paper reports the purging of organic contents in oily wastewater using a combined of EC-PC system. EC is a comparatively fast procedure (30 min), which is very operative in eradicating colloidal particles, as has been seen in variations in the turbidity and color of the treated water. However, it is moderately unsuccessful in destroying stable organic contents—in this work, only 50% of the COD was removed from oily wastewater. EC-PC combined system is very functioning in breaking down organic species through oxidation as reflected in the abolition of COD, BOD, but needs more time that it has limited practicality, especially when excessive colloidal are existing. In the combined EC/PC technique, starting EC quickly coagulates and removes the colloidal, suspended particles, and charged species, then the PC oxidizes the remaining organic contents. Petroleum refinery wastewater comprises a high load of organic contents signified in a 2180 ppm oil, COD of 710 ppm and a TOC of 698 ppm, a total amount of solids of 5.1 g/L with a turbidity of >1000 NTU. The main conclusions obtained from experimental results disclosed that EC-PC is effective at reducing organics. The contribution to COD removal from EC and EC-PC showed that EC alone resulted in COD removal of 58%, while EC-PC contributed with 70% of COD removal. Both processes were very effective in reducing oils 98%, color 99.5%, turbidity 99.9%, COD 80%, BOD 60%, Phenols 95% and Sulphides 99%.

For future work, detailed study will be conducted on the EC-PS optimization, this includes investigating the effect of important parameters such as; the concentration of TiO_2, UV intensity, running time, pH value and Temperature.

5. Conflict of Interest

The authors declare no conflicts of interest.

6. Acknowledgments

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