Decontamination of oilfield produced water containing petroleum hydrocarbons by high flow rate bioelectrocoagualtionsystem.

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Abstract

It is of critical importance in case of oilfield produced water (PW) treatment designing what the composition of constituents of target water and how the degradation should be observed as efficiently as possible. Total petroleum hydrocarbons (TPH) and other pollutants, such as heavy metals, and dissolved/suspended solids are generally occurring in PW. This study presents the hybrid system to stimulate the suitable conditions withhigh flow rate electrocoagulationbiodegradation ofPW.The efficiency of a bioelectrocoagualtion (BEC)system for the continuous removal of TPH and sulfur compounds from PW has many problems. Treatment conditions were changed to overcome the formation of hydrogen sulfide as a reduced form of sulfate. This study observed the results of lab scale hybrid system setup with electrocoagulation and biodegradation. The initial removal rate of TPH was partially enhanced at detention time, current densities and electrolytes modifications and the same trend for sulfide formation rate.Collectively, the results of this study confirmed that sulfate converted to sulfide taking place within the electrochemical zone. The maximum TPH, sulfate and COD removal efficiency was achieved 75%, 25.3% and 22.3, respectively when the detention time was about 5L/hour. Also, the results indicated that the flow rate is very important to keep the balance between current density and more TPH removalof high saline water in the hybrid system.

Key words: oilfield produced water, Bioelectrocoagualtion, total petroleum hydrocarbon, sulfate and sulfide.

1. Introduction

In oil and gas production activities, additional water is injected into the reservoir to

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sustain the pressure and achieve greater recovery levels. Both formation water and injected water are produced along with hydrocarbon mixture. At the surface, processes are used to separate hydrocarbons from the produced water (PW). Then, PW is considered to be one of the largest waste streams in the petroleum, oil, and gas industry. Effects of PW components on the environment are as follows: (i) increase in the salinity, (ii) dispersed and soluble oil contribution in marine ecosystems, (iii) inclusion of other compounds from treating chemicals,(iv) higherconcentration of heavy metals than in seawater, and (v) the presence of radio nuclides **(Veil *et al*. 2004, Abdelwahab, *et al*., 2009; Fakhrul-Razi*et al*., 2009).**The amount of PW generated varies during oil production: a new field produces 5–15 vol%, while at the end of its lifetime; it reaches 75–90 vol**% (Gomes de Lima, *et al*., 2009).**

Regarding the significant matter of environmental concern, many countries have implemented more stringent regulatory standards for discharging PW. On the other hand, because large volumes of PW are being generated, many countries with oilfields, which are also generally water-stressed countries, are increasingly focusing on efforts to find efficient and cost-effective treatment methods to remove pollutants as a way to supplement their limited freshwater resources **(Dos Santos *et al*., 20**14). Therefore, considering the extent and volume of produced water, employing biodegradation as a removal method of petroleum hydrocarbons from contaminated aquifers requires extremely large treatment facilities**(Doggett and Rascoe, 2009**). Advanced oxidation processes are the most efficient in the degradation of organic contaminants, but they are very expensive and complex to design and operate. These disadvantages have motivated researchers to explore the capabilities of other techniques for the removal of petroleum hydrocarbons from produced waters **(Marcilly, 2003).**

Electrocoagulation (EC) promotes the production of coagulating agents using a current to dissolve Al sacrificial anodes immersed in the polluted water, giving rise to the corresponding metal ions that yield different Al(III) species with hydroxide ion depending on the medium pH **(Holt *et al*. 2002).** In general, the EC have important advantages and disadvantages **(Martinez-Huitle and Brillas2009).**BECis a variant of the conventional coagulation process in which coagulant agents are generated in situ through the dissolution of a sacrificial anode by applying current between the anode–cathode electrodes **(Erick*et al*., 2011).** The BEC has several advantages that make it attractive for treating various contaminated streams. It has been shown

that Bio electrochemical is an efficient and promising process in treating various wastewater contaminants, such as reactive dyes, azo dyes, oily bilge water, industrial wastewater, petroleum refinery waste water, fluoride, pulp and paper mill wastewater, and phosphate and zinc **(Nazih*et al*., 2010).**

In order to meet the needs of a regulations and sustainable development, upgrade of oilfield infrastructure is required. In offshore platforms, because of space constraints, compact physical and chemical systems are used. However, major research efforts are being developed with innovative technologies for treating PW in order to comply with discharge limits and reuse. Among them, PEC technologies have been proposed as a promising alternative for the treatment of this kind of wastewaters. Accordingly, the main purpose of this study was first to investigate the effects of the primary operational factors on the efficacy of the BEC cell in treating petroleum produced water. These factors were examined by performing batch experiments and included water pH, current density, and reaction time. In this paper, in order to apply the BEC process in the crude oil production, related parameters havebeen analyzed in detail. Many parameters such as current densities flow rates and pH of the influent could influence this hybrid system, including TPH removal, sulfate modification, even biofilm contents.With utilizing aluminum electrodes to generate reaction zonewith coagulation features followed by biofilterfor TPH degradationin aqueous solution were investigated.

2.Materials and Methods

All chemicals used in this study were analytical grade. Quantification of total petroleum hydrocarbons (TPH) in the PW was performed by test kit that was purchased from HACH Company. TPH were determined colorimetrically by DR -890 according to immunoassay method (TPH pocket colorimeter TM II test kit, HACHCompany, USA).Deionized water (18.2 MV cm) obtained from a Veolia water system was used in all the experiments. DR 890 colorimeter and DR200 reactor from HCH Company were used for direct detections.

2.1 Produced water samples

PW samples were supplied byScimitar Egypt(Issran oil field, RasGhareb; Egypt). PW samples analyses were carried out by Egyptian petroleum research institute. Total dissolved solids (TDS) was determined experimentally according to ASTM D-1888. Conductivity and resistivity were d 3301 according to ASTM D-1125. pH was determined experimentally according to ASTM D-1293. Salinity value was calculated upon chloride content value. Cations and anions were determined experimentally according to ASTM D-4327 using Dionex IC model DX 1100 equipped with high capacity columns. Alkaline species (CO_3, OH, and HCO_3) were determined experimentally according to ASTM D-3875. BOD_5 was determined after incubation for 5 days in tightly stoppered bottles in the dark at 20^0C and determining the oxygen consumed. Conductivities were measured at 25^0C directly in mS/cm using a digital conductivity meter (APHA, 2005).

The real PW that collected for used as plant influent has characterswere dismantled and then a daily sample was collected until the final of the experiments. Water sampling was also done at the beginning for homogenized caliche and at the end for the residues of each column, when they. Table 1 details the chemical composition of soluble species of PW.

Table 1: Composition of PW was used inBEC experiments.

Parameters		Unite	Value
General indicators	TDS	mg/l	10131
	pH		7.3
	Hardness	mg/l	4799
	TPH	mg/l	670
	COD	mg/l	1331
Cations	Li	mg/l	0.72
	Na	mg/l	1121
	K	mg/l	577
	Mg	mg/l	705
	Ca	mg/l	758
	Fe	mg/l	0.5
	St	mg/l	8.9
	Ba	mg/l	0.62
Anions	SO_4	mg/l	3173
	Cl	mg/l	2730

	HCO_3	mg/l	902
	Fl	mg/l	22.7

2.2 Experimental procedure

The aluminum electrodes and biological filter were used to enhance electrochemical degradation of TPH in flow unit (Figure 1). The BEC experiments have been carried out in a bench-scale plant.Bioelectrochemical oxidation-reduction unit was manufactured cooperation with technicians of Civil and Environmental Engineering Department, Northeastern University, Boston, MA, USA. Aluminum electrodes with dimensions of 3.6 X 5.2 X 0.5 (WXLXT) cm were used as electrode materials in all experiments. Prewashedgravels with water and hydrochloric acids were used as biofilter media. These media were maintained in PW to build natural selection of their biofilm. An average flow velocity was maintained by gravity through 200 L storage tank. Before application of current, the whole system was washed for an hour by PW. A constant volt during treatments was applied by DC power supply (NBC labs electronics).

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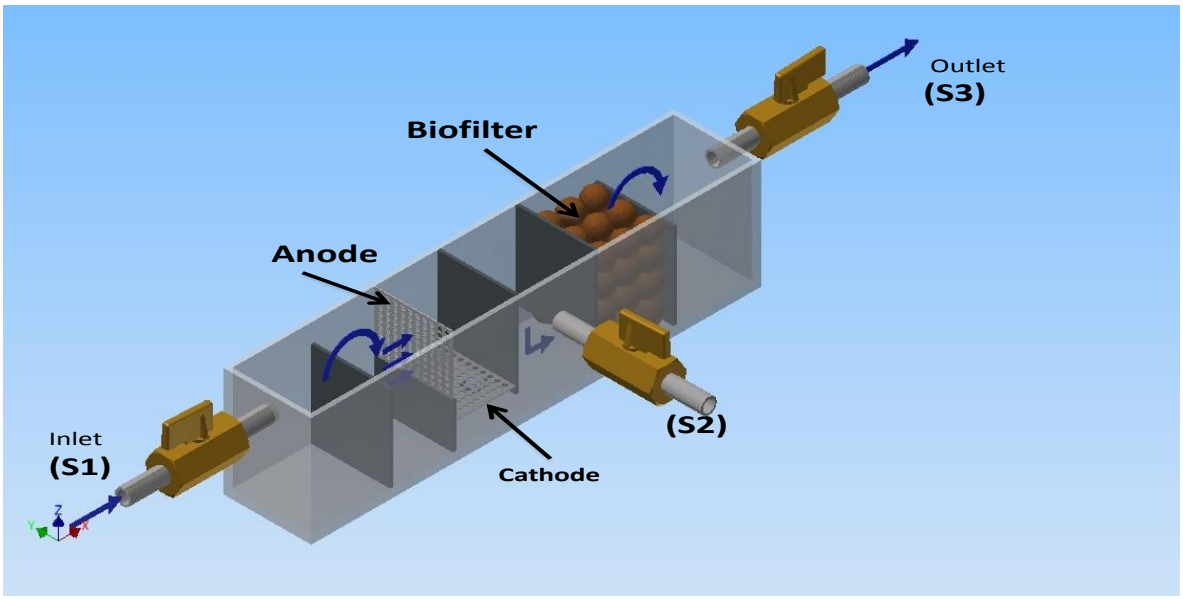


Fig. 1. A schematic of the BEC flow-through reactor,S1, S2, and S3 are sampling ports.

It is important to be able to predict the rate at which contaminants are removed in order to design the full scale application of the technology (Rajic*et al*., 2016). TPH removal was calculated by the following equation:

$$\%\text{removal} = \frac{C0-Ct}{C0} * 100 \quad (1)$$

Where Co is the initial TPH concentration (mg/L) and Ct is TPH concentration at a defined time during treatment (mg/L).

2.3 Microbiological analysis.

Water samples were collected in glass bottles that have been cleansed and rinsed carefully, given a final rinse with distilled water, and sterilized by autoclave at 121 ° C for 15 min. Analysis was initiated as soon as possible after collection to minimize changes in bacterial population. The enumeration of total bacterial count (TBC) in water samples (S1, S2 and S3) was done using the spreading plate technique over plate count as tryptone glucose yeast agar medium (Oxoid, Basingstoke, Hampshire, England). Additional blanks were prepared to determine contamination of plates, pipets, and room air. Sterility of medium and dilution water blanks was checked by pouring control plates for each series of samples. Additional controls were prepared to determine contamination of plates, pipets, and room air **(APHA, 2005).**

3. Results and Discussion:

3.1. Effect of using electrobioremediation on TPH removal:

The electrochemicaland biological treatment of PW have been performed with aluminum electrodes at average flow rates 20L/h,under a current of 20 volt that corresponds to potentials of oxidations-reduction in the region of free radicals evolution [Yuan *et al*., 2013].The results presentedin Figure 2 and Table 1 showed that the concentration of TPH removalwas strongly influenced existence of neutral electrolytes.At this electrochemical region, a maximum depletion of organic pollutants was achieved as a function of pH. In particular, maximumremoval was obtained by neutral medium, thus indicating the effect of time on the TPH of the PW by using BEC flow cell at room temperature.It was found thatthe removal needed to 30 min to reach the optimum as shown in Figure 3.

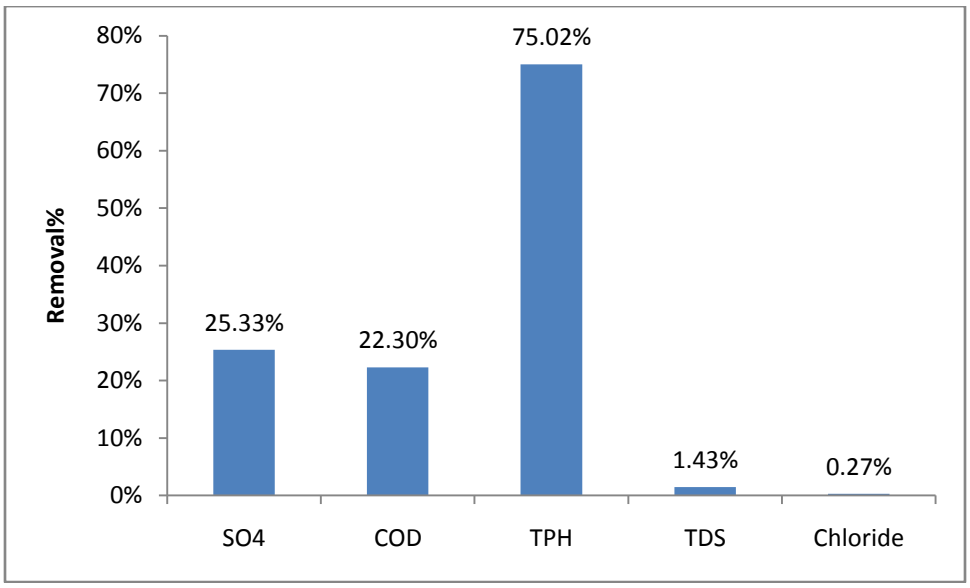
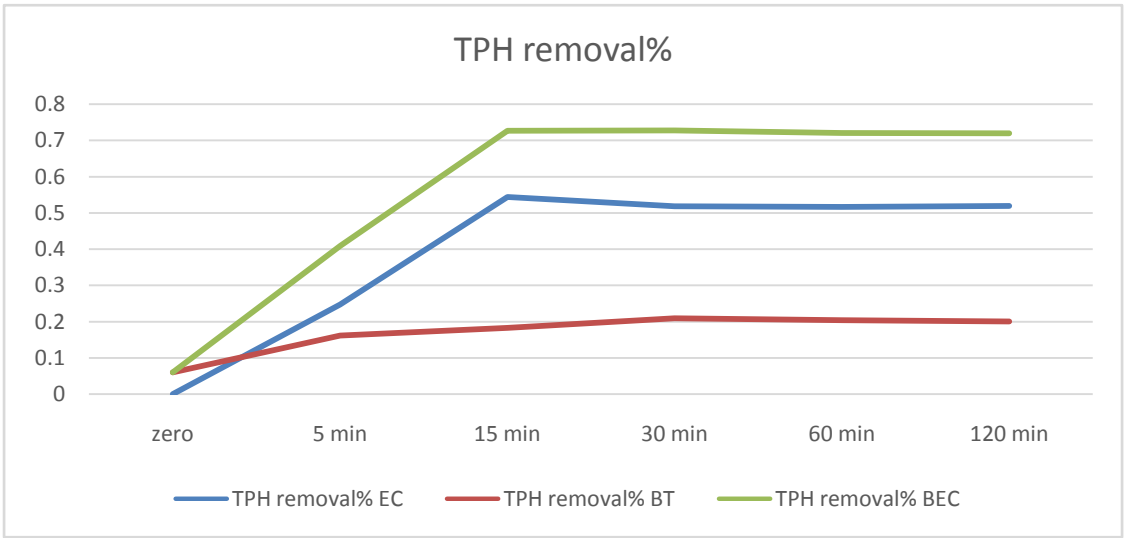


Figure (2): effect of total BEC processes for different pollutants under treatment conditions.

The performances of the tested BEC were totally in the order of EC and BT in both the acidic and basic oilfield PW. The TPH removal was the highest at a current density of about 890mA and pH 7 over which it decreased, because the decomposition of TPH at the electrode surface was transformed by the hydroxyl ions. The CODchange yield increased with the concentration of the hydroxyl free radical in the solution. However, the increment rate became much slower over 60 minutes of the reaction time. The aluminum electrodes among the tested system generated the most OH radicals which could oxidize the TPH at pH 7.



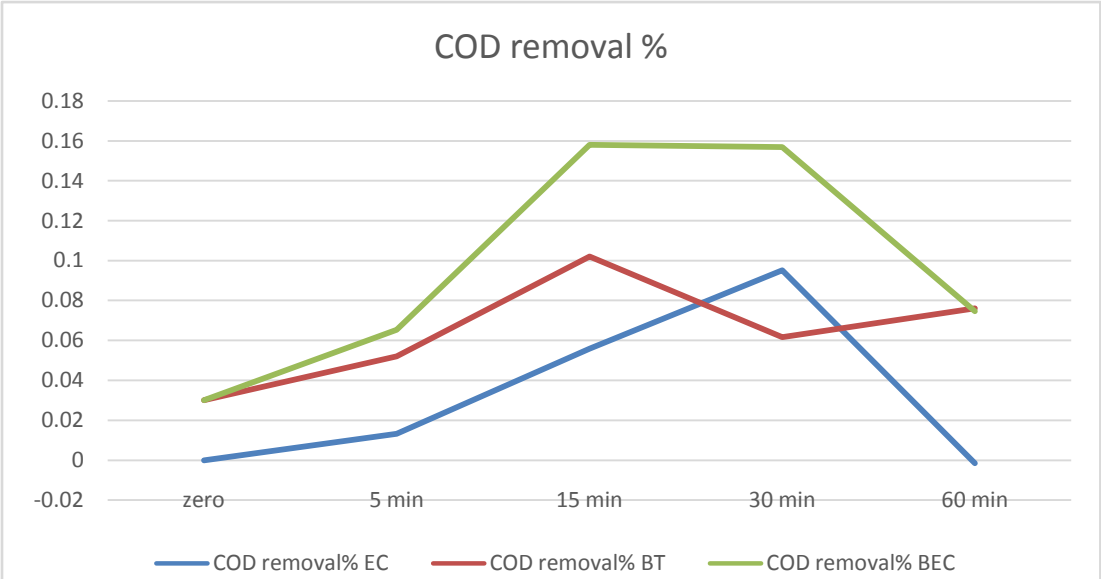


Figure (3): Removal averages of TPH with time through electrobiochemical unit.

3.2. Effect of current application on TPH removal%:

Produced water is co-produced during oil and gas production and represents one of the most dangerous sources of oily wastewaters. Therefore, treatment of this produced water may improve the environment, economic viability and lead to a new source of water for beneficial use. The results of using the bioelectrical unit in the produced water treatment are shown in figure 4.The bioelectrocoagulationtreatment of PW has been performed with aluminumelectrodes.For application of different volts (16 – 22 volt) high constituent'selectrolytes of PW that has important condition to electrochemical processes.The results show 20 volt that corresponds with 890 mA has the optimum removal% for different pollutant indicators (COD and BOD_5).

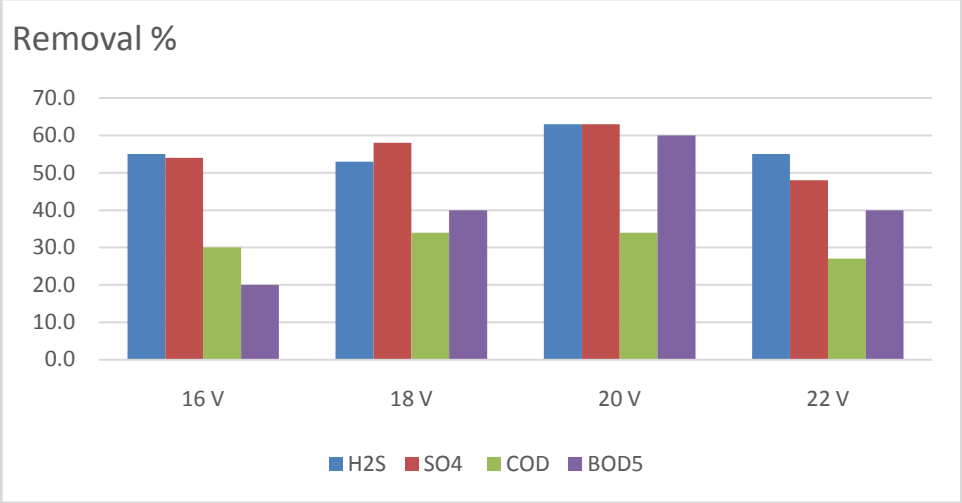


Fig. 4: Removal% of pollutants corresponding to different volts.

3.3. Effect of pH throughbioelectrochemical unit:

The pH value, like temperature, affects mostly indirect oxidation processes. However, a review of previous publications does not allow a conclusion to be reached on whether increasing or decreasing pH favours pollutant removal in electrochemical treatment of waste-waters (Jonnalagadda and Mhere, 2001).Figure 5 shows that the sulfides of synthetic water samples are oxidized and removed by bioelectrical electrode at all pH but the highest removal occurs at pH 7.

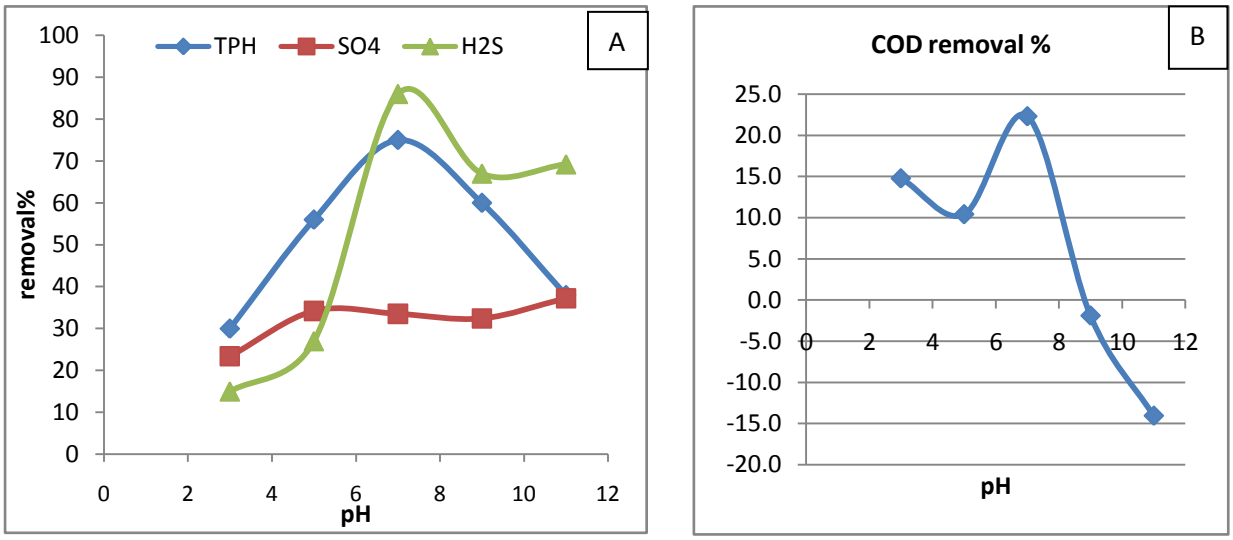


Figure (5) Removal% averages (A) of sulfide (H_2S) Sulfate (SO_4) total petroleum hydrocarbon(TPH) and COD(B) with different pH through BEC unit.

The organic pollutant removal performance and the system effluent characteristics of a biofilter, employing a high current and lowdetention time, for the treatment of saline PW were considered. Total bacterial count occurred in the treated water at all pH is shown in Figure 6, but biodegradation was identified as the major organic removal mechanism. With increasing pH, initially increase in TBCand later formation of oil/biomass bodies took place but due to the presence of the high salts occur. The mixed liquor was pseudoplastic and the apparent viscosity and flow behavior index generally increased with salt concentration.

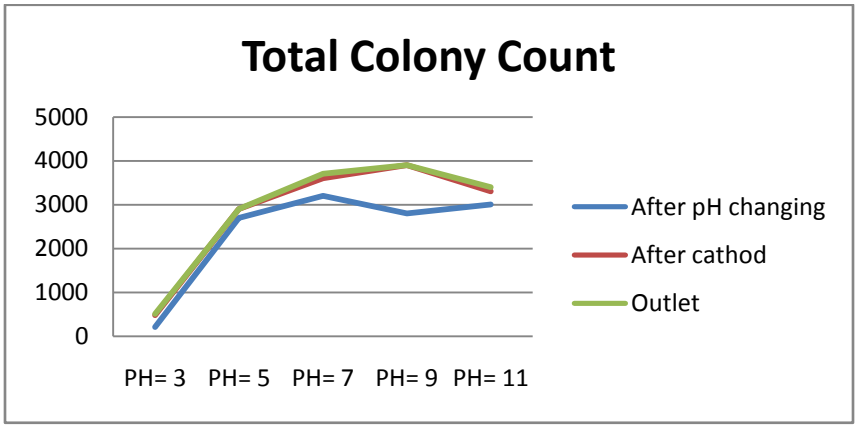


Figure 6: Total count of water at application of BEC flow cell with different pH conditions

3.4. Distribution of biological content on TPH removal:

From Fig. 6that shows the total bacterial colonyincreased obviously with the PW path through BEC unit.For example, the colony forming unit (CFU/ml) in the influent was only 3200when the pH was7.2, which increased by 23.3% of that at room temperature after electrochemical zone. There were no significant relationship between bacteriological load of treated water after electrochemical zone and biofilter. The mainreason was that the high saline PW did not get suitable condition for bacterial growth, which indicated less removal %.

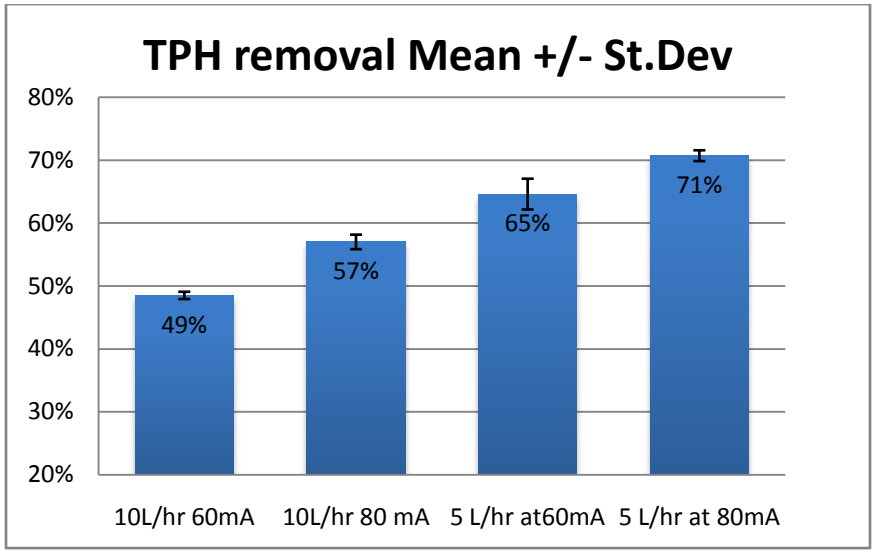


Figure 7: TPH removal% at application of BEC flow cell with different flow rates and applied currents conditions

It can also been seen from Fig. 7 that the TPH increased obviously with the density of current application through EC unit but decreased with increasing of flow rate. There were significant relationship between quality of treated water with both flow rates and current density. The main reason was that the low detention time allowed for treatment, which indicated less removal %of TPH.

4.Conclusion

The bioelectrolytic cell showed a betterdecomposition yield of TPHwith or without the biofilter in the cases of the high TDS solutionswith chloride and sulfate ions.The COD and TPH removal efficiencies in the range 25.3 and 75.3% respectively but increase the effluent sulfide were achieved. There was no pronounced filter fouling at any applied current. Because thebiofilter prohibited the many intermediate species generated at the electrolysis chamber, utilizing biological filter for the removal of electrocoagulation by-productsis a phase change technique. BEC requires the maintenance the biofilm on the filter media, which is sensitive and a complex operation. Although biofilters are efficient for the degradation of oil and organic compounds, the critical drawback to their utility in full-scale operations is high TDS water

content and pH.Further research efforts are needed to clarify factors and conditions affecting the electrocoagulation biodegradation processes.

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الملخص باللغة العربية

ازالة الملوثات الهيدروكربونية من المياه المنتجة من حقول انتاج الزيت الخام بواسطة التخثر الكهربائي البيولوجي.

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قسم البوتكنولوجيا البيئية- معهد الهندسة الوراثية والتكنولوجيا الحيوية-جامعة مدينة السادات

في مجال إنتاج النفط والغاز يتم حقن كميات كبيرة من الماء في الخزان للحفاظ على الضغط ورفع مستوي الزيت الخام لسهولة انتاجه وزيادة معدلات الانتاج.ثم يتم إنتاج كل من الماء المتكون طبيعيا داخل طبقة الخزان بالاضافة للماء الذي تم حقنه مع خليط النفط والغاز.

تستخدم عمليات معالجة كميائية وميكانيكية لفصل المياه من الزيت الخام وبالتالي تشكل المياه المستخلصة من عمليات المعالجة واحدا من أكبر النفايات في مجال انتاج النفط وصناعة الغاز

آثار المياه المنتجة من ابار النفط والغاز على البيئة هي على النحو التالي: (أ) زيادة في الملوحة، (ب) تسرب وانتشار المواد النفطية وايضا بعض المواد الهيدروكربونية القابلة للذوبان الي النظم الإيكولوجية البحرية (ج) تسرب بعض المواد الكميائية والتي تستخدم في عمليات المعالجة (د)زيادة تركيز المعادن الثقيلة في مياه البحر.

ولما كان الحفاظ علي النظام البيئي ذو اهمية كبيرة ، وضعت العديد من الدول معايير تنظيمية أكثر صرامة تحرم صرف هذه المياه الي مياه البحر وضرورة التخلص من الملوثات بداخلها ومعالجتها معالجة تسمح باعادة استخدامها او صرفها الي مياه البحر. وظهرت طرق عديدة للمعالجة مثل التحلل البيولوجي وعمليات الاكسدة المتقدمة لمعالجة المواد الهيدروكربونية وازالتها من المياه المنتجة.

عمليات الاكسدة الكهربية والتي تسبب تخثر للمواد الهيدروكربونية الذائبة وترسيبها ثم فصلها تعتبر واحدة من الطرق المتقدمة والفعالة في عمليات معالجة المياه بالاضافة لعمليات المعالجة البيلوجية والكيموفيزيقية وتتم عن طريق مرور المياه خلال قطب موجب وهو الانود وقطب سالب وهو الكاثود يتم خلالهما عمليات اكسدة للمواد العضوية.

تم استخدام نموذج تجريبي لوحدة معالجة يتضمن وحدة داخلية بها الانود والكاثود واللذان يتم توصيلهما بتيار كهربي وتغيير مستوي شدة التيار للوصول لانسب قيم. أيضا تتضمن غرفة بها بايوفيلم مناسب لنمو الميكروبات والتي قد يكون لها تاثير في المعالجة.

تم قياس مجموعة من المعملات الدالة علي الملوثات قبل وبعد المعالجة ومقارنتها ببعضها احصائيا للوصول الي نتيجة المعالجة بشكل جيد.

اظهرت النتائج زيادة في ازالة المواد الهيدروكربونية الكلية وايضا في محتوي الاكسجين الكميائي والذي يعبر عن حجم الملوثات الموجودة في المياه وذلك قد تم عند درجاة حموضة وقاعدية مختلفة وايضا قدررات كهربية مختلفة الا ان النتائج اثبتت ان انسب الظروف هو الوسط المتعادل وايضا استخدام تيار قدرته 20 فولت.

اثبتت النتائج ايضا وجود تاثير ايجابي علي ازالة الملوثات العضوية باستخدام التحلل البيولوجي ولكنه ضئيل اذا ما قورن بالاكسدة الكهربية ويرجع ذلك للملوحة العالية جدا والتي تحول دون نمو الميكروبات.

أظهرت خلية التحليل الكهربائي الحيوي افضل نتائج تحلل مع ايونات الكلوريدات والكبريتات والهيدروكربونات النفطية.كفاءة ازالة المواد الهيدروكربونية مستوي الاكسجين الكميائي الذائب وصلت الي 75.3 و 25.3 علي التوالي.