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Mechanisms of Plant-Correlation Phytoremediation of Al-Daura Iraqi Refinery Wastewater Using Wetland Plant from Tigris River

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ABSTRACT

In developing countries, conventional physico-chemical methods are commonly used for removing contaminants. These methods are not efficient and very costly. However, new in site strategy with high treatment efficiency and low operation cost named constructed wetland (CW) has been set. In this study, *Phragmites australis* was used with free surface batch system to estimate its ability to remediate total petroleum hydrocarbons (TPH) and chemical oxygen demand (COD) from Al-Daura refinery wastewater. The system operated in semi-batch, thus, new wastewater was weekly added to the plant for 42 days. The results showed high removal percentages (98%) of TPH and (62.3%) for COD. Additionally, *Phragmites australis* biomass increased significantly during experiment period with 60% increasing in wet weight. These results proved the ability of *Phragmites australis* to tolerance in contaminant environment and enhanced biodegradation of TPH. Two kinetic models were used, and pseudo-second order was fitted to data with R^2 of 0.999.

Kay words: Phragmites australis, Total Petroleum Hydrocarbon, free surface batch system, phytotoxicity

آليات النبات في المعالجة النباتية لمياه مصفى الدورة الملوثة بأستخدام نبات الاراضي الرطبة من نـهر دجلة

الخلاصة

في البلدان النامية ، تستخدم الطرق الفيزيائية الكيميائية التقليدية عادة لإزالة الملوثات. هذه الأساليب ليست فعالة ومكلفة للغاية. تم وضع استراتيجية جديدة موقعية ذات كفاءة معالجة عالية وتكلفة تشغيل منخفضة تسمى الأراضي الرطبة المبنية (CW). في هذه الدراسة ، تم استخدام نبات Phragmites australis مع نظام السطح الحر لتقدير قدرته على معالجة إجمالي الهيدروكربونات النفطية (TPH) والطلب على الأوكسجين الكيميائي (COD) من المياه الملوثة لمصفى الدورة. يعمل النظام في شبه دُفعة ، وبالتالي ، تمت إضافة مياه ملوثة جديدة أسبوعيًا إلى النبات لمدة 42 يومًا. وقد أظهرت النتائج ارتفاع نسب الإزالة (98 ٪) من TPH و (62.3 ٪) لـ COD. بالإضافة إلى ذلك ، زادت الكتلة الحيوية لنبات Phragmites australis بشكل ملحوظ خلال فترة التجربة مع زيادة 60 ٪ في الوزن الرطب. هذه النتائج تثبت قدرة Phragmites australis على

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التحمل في بيئة الملوثات وتعزيز التحلل البيولوجي لـ TPH. كذلك، تم استخدام معادلتين حركيتين، ومعادلة حركيات الدرجة الثانية الزائفة (PSO) كانت اكثرملائمة مع R^2 يساوي 0.999.

الكلمات الرئيسية: نبات القيصوب، اجمالي الهيدروكاربونات النفطية، نظام السطح الحر، اختبار السمية النباتية

1. INTRODUCTION

In petroleum refineries huge amount of water used in cooling towers, steam engines and vacuum distillation. Refinery effluents contain more aromatic hydrocarbons than crude oil which is more toxic and with the potential of carcinogenic and teratogenic effects in human and aquatics animals **Wake, 2005**. Also, phenol presents abundantly in refineries wastewater and it is one of the most toxic and hazard organic compound in wastewater to plants and bacteria even at low concentration **Stefanakis, et al., 2016**. In growing countries, conventional physical and chemical methods are commonly used for removing contaminants. These methods are very costly, produce other contaminants, and as well as the conventional methods may destroy **the** ecosystem at the site **Peng, et al., 2009**. However, novel remediation techniques with high removal efficiency and low cost should be initiated. A new technique in remediation of pollutants is Phytoremediation which is defined as the use of plants and their associated bacteria to remove pollutants from the environment. This technique has many advantages over traditional techniques include: 1) cost-effective strategy (costs10-20% of mechanical treatment); 2) able to treat large areas of contamination; 3) involves biological systems (plants and microbes) that can provide strong tools for the management of environmental risks connects with contaminated sites **Sobariu, et al., 2017**; 4) offers a sustainable alternative for the repair of contaminated areas; 5. in situ technique, which minimize environmental disturbance **Haritash and Kaushik, 2009**.

Constructed wetlands (CWs) are engineered strategies used to apply phytoremediation technique for treating wastewater **Al-Baldawi, et al., 2013; Sung, et al., 2013**. Thus, CWs are a promising alternative to conventional treatment systems for wastewater **Wu, et al., 2015** because of low costs and energy consumption **Liu, et al., 2018**, easy operation and maintenance **Wu, et al., 2015** as well as higher efficiency. The Processes involved phytoremediation using constructed wetlands are sorption, volatilization, evapotranspiration, precipitation, plant uptake as well as microbial degradation **de la Varga, et al., 2017**. In CWs, a plant used to enhance removal and degradation of contaminants by improving microbial activity **Mustapha, et al., 2018;Khandare, et al., 2013**. Perennial plants such as *Phragmites australis* are commonly used in constructed wetlands due to their worldwide distribution, high biomass, tolerance to various environmental hardships and resistance to pollutants **Tam, et al., 2009**. Constructed wetlands can be classified basically according to the water flow system (free-surface flow, sub-surface flow, and hybrid systems).

In this study, free surface flow (FSF) system with *Phragmites australis* as vegetation was used to investigate the removal efficiency of TPH and COD from refinery wastewater. The removal mechanisms in FWS are physical such as sedimentation and filtration **Vymazal, 2014**, chemical such as precipitation and adsorption **Vymazal, 2011**, and biological degradation **de la Varga, et al., 2017**. Emergent plants promote pollutant removal in FSF wetlands by (a) enhancing sedimentation of suspended solids and provide a surface for microorganisms growth **Vymazal, 2013**; (b) providing oxic condition in the root zone **Kadlec, Martin, and Tsao, 2012**. FSF systems have a number of characteristics include: 1. low-cost systems and simple to operate; 2. require large surface areas; 3. have the ability to deal with water level changes; **de la Varga, et al., 2017 and Wu, et al., 2015**. FSF constructed wetlands are effective in the removal of suspended solids by sedimentation and filtration, organics matter by either filtration or microbial degradation **Vymazal, 2014**, nitrogen by nitrification in water column and denitrification in media layer **Vymazal, 2010**, and ammonia which is highly removed in FWS systems **Buhmann and Papenbrock, 2013** through nitrification in aerobic zones and followed by denitrification in anaerobic zones **Vymazal, 2011.**

2. MATERIAL AND METHODS

2.1 Experiment set up*:*

The phytotoxicity study was done in Al-Khwarizmi College of Engineering, University of Baghdad. In this study, 4 aquariums made of glass with (50cm L× 30cm W× 30cm D) were used. As shown in **Fig. 1**, two aquariums (A1 and A2) were applied as replicate for wastewater treatment with the plant (*Phragmites australis*), while the aquariums PC and CC were used as plant control without contaminants and contaminants control without the plant, respectively. Each aquarium, as shown in **Fig. 2**, was filled with sand up to 12 cm and topped up to 6 cm with real refinery wastewater. The wastewater used in this study was taken from wastewater treatment unit in Al-Daura refinery before the physicochemical stage. The concentrations of TPH, COD, and BOD_5 in mg/L of wastewater were measured and were between 65 to 70, 250 to 350, and 100 to 120 mg/L, respectively. The study was continued for 42 days, and 7 liters of wastewater was added every week to simulate the semi-batch system.

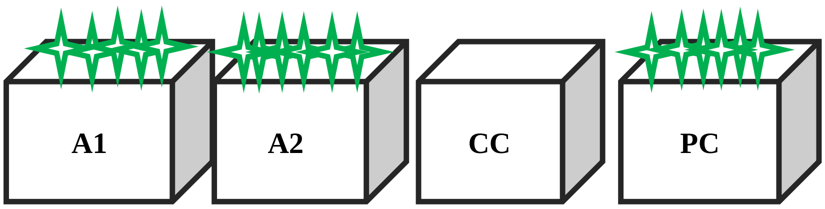


Figure 1. Aquariums set up for phytotoxicity study.

2.2 Monitoring of physicochemical parameters

Water samples were collected from each aquarium at 0, 7, 14, 21, 28, 35, and 42 days within the experiment period. Then, physicochemical parameters of temperature (T), pH, dissolved oxygen (DO), oxidation-reduction potential (ORP), and chemical oxygen demined (COD) were measured to observe the physicochemical changes in water. The temperature and pH were recorded using WTW probe (3110- Germany), ORP and DO were recorded using probes HACH (MTC 101, USA) and HACH (HQ430d, USA), respectively. While, COD was measured using COD digestion vial, rang (0-1500 ppm) (HACH, USA).

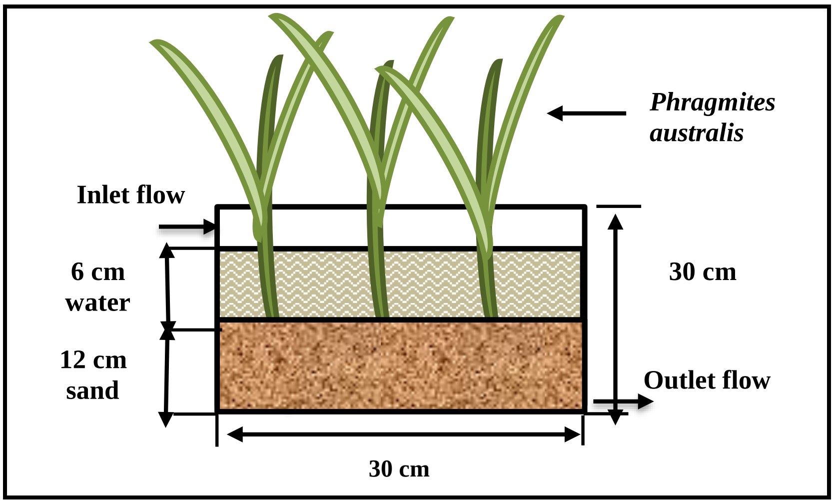


Figure 2. Diagram of free surface system aquarium for the phytotoxicity test.

Furthermore, Total petroleum hydrocarbons were extracted on each sampling day by Tetrachloromethane (CCL_4) (Merck, Germany) using a liquid-liquid extraction method as mentioned by EPA **USEPA, 1996**. The concentration of TPH in water was analyzed using oil content analyzer (Horiba, Ocma-350, USA), and the removal percentage of TPH was determined according to:

$$\%Removal = \frac{TPH0 - TPHe}{TPH0} \times 100 \qquad (1)$$

Where TPH0= total petroleum hydrocarbon at 0 day
TPHe= total petroleum hydrocarbon on each sampling day

2.3 Observation of plant growth

The response of *Phragmites australis* to contaminants was monitoring for 42 days. On each sampling day, one plant was taken from A1, A2, and PC aquariums in order to estimate wet weight and dry weight. The plant first washed with tap water and then wet weight record. Dry weight was recorded after plant sample was dried at 70°C for 24 h in an oven **Al-Baldawi, et al., 2013**.

2.4 Statistical analysis

In this study, IBM SPSS Statistics version 19 was used to analyze the removal of TPH and COD statistically. The concentration as (dependent variables) according to day, system and treatment (independent factors) were analyzed using the general linear model test with Duncan's multiple range tests to separate means. Statistical significance was defined as $p < 0.05$ **Al-Baldawi, et al., 2013.**

2.5 Kinetic of TPH biosorption by plant

There are numerous studies about the ability of plant tissues (root, stem, and leaves) to uptake organic contaminants. **Chu, et al., 2006** studies the accumulation and

transformation of polychlorinated biphenyl (PCB) by *Phragmites australis* which was very effective in removing PCBs from the solution. The amount of hydrocarbons that uptake by the plant is a function of plant species, microbial population and initial concentration **Watts, et al., 2006**.
In this study, the TPH uptake by *Phragmites australis* tissues was calculated using the following equation:

$$q_e = \frac{V\,(Ci - Ce)}{X} \quad (2)$$

Where, qe is the TPH removal (mg TPH/g biomass), V is the volume of the wastewater (L), Ci is the initial concentration of TPH in the refinery wastewater (mg TPH/L), Ce is the final concentration of TPH in the wastewater (mg TPH /L), and X is the dry weight of the biomass (g).
The kinetic of TPH removal was described based on initial concentration. Two commonly used kinetic model was applied, Lagergren first-order model which mentioned by **Lin and Wang, 2009** as following:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (3)$$

Where q_e and q_t are the TPH uptake by biosorbent at equilibrium and at any time (mg TPH/g biomass), k_1 is the rate constant of Lagergren first-order biosorption (d^{-1}).
And pseudo-second-order of **Y. S. Ho and McKay, 1999** which is used to describe the sorption of heavy metals, hydrocarbons, and dyes by activated carbon, microorganisms, plant and biomass **Yuh Shan Ho, 2006**. The model was expressed as in the following **Lin and Wang, 2009**:

$$\frac{t}{q_t} = \frac{1}{k_2\, qe^2} + \left(\frac{1}{q_e}\right) t \quad (4)$$

Where, k_2 is the rate constant of second-order biosorption (mg TPH/g biomass d).

3. RESULTS AND DISCUSSION

3.1 physicochemical parameters of wastewater

During 42 days of phytotoxicity test, the selected physicochemical parameter was measured with plant, without plant, and plant control (PC) **(Fig. 3)**. Generally, temperature increased in the test period depending on weather, and varied from 23-30^{o}C for all treatments. The optimum temperature for plants growth and degradation of hydrocarbons has been ranged between 20 and 30^{o}C According to **Kivaisi, 2001** and **Al-Baldawi, et al., 2013**. The pH for aquarium without plant was between 7.3 and 9 and between 7.4 and 8.5 for an aquarium with plants. According to Hambrick, Delaune, and Patrick (1980), highest mineralization rate of hydrocarbons occurred at pH 8. The oxygen rate is one of the most important parameters in wastewater treatment biologically, since a high rate of oxygen (aerobic condition) record high degradation efficiency **Meng, et al., 2017**. The indication between aerobic and anaerobic condition was made by measuring DO and ORP. The DO was between 5.8 and 7.78 mg/L for treatment with and without plants and ORP was between 137 and 251mV. Therefore, the treatment environment was at aerobic conditions.

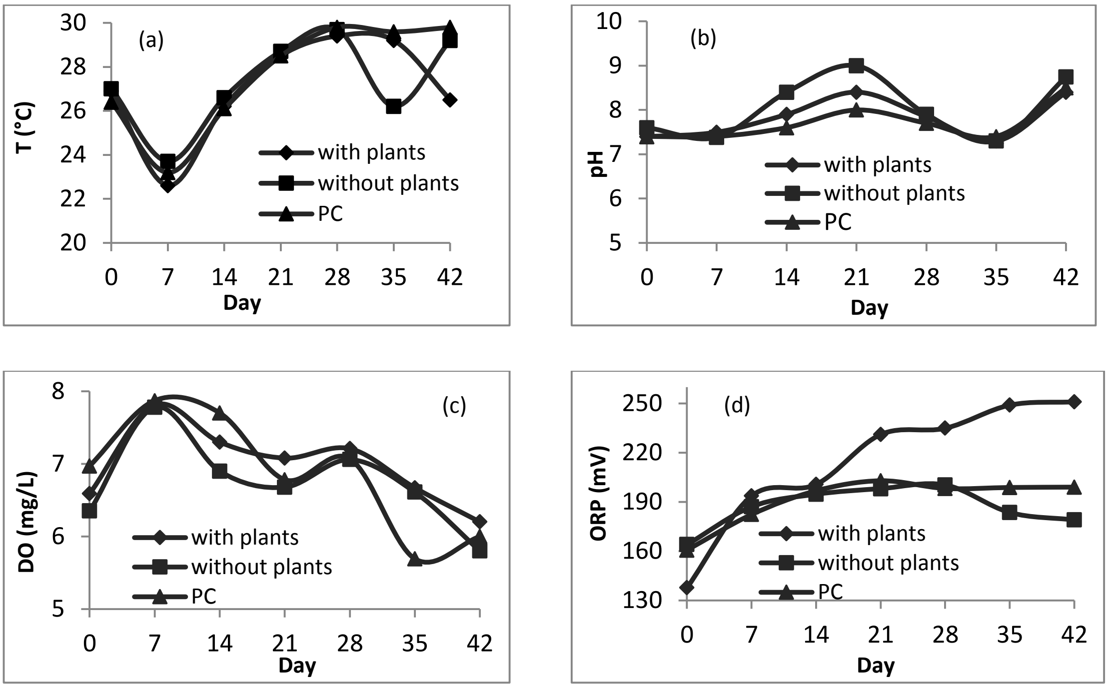


Figure 3. Variation of physical parameter along the phytotoxicity test in FSF system: (a) temperature, (b) pH, (c) dissolve oxygen, (d) redox potential.

The results show that COD values were below the quality requirements in Iraq which is 100 mg/L **KAZ Oil Terminal Project, 2014**. In this study, COD were between 93 to 60mg/L for aquaria with plants and between 129 to 70 mg/L without plants which ranged below and above the quality requirements in Iraq respectively, as shown in **Fig. 4**. The result was statistically significant ($p < 0.05$) between FSF system with plant and system without plant (paired sample t-test), which shows that vegetation gives a positive impact on COD removal by substrate filtration and plant sorption **Ji, et al., 2007**.

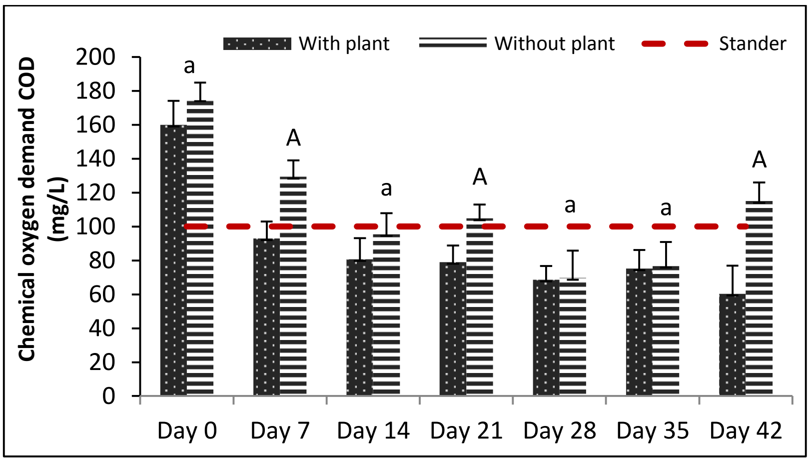


Figure 4. COD concentration 42 days in FSF system with plant and without the plant. Bars indicate the standard error of two replicates (n = 2). A: significant difference at $p < 0.05$ between treatments (with and without plants); a: no significant difference between treatments (with and without plants)

3.2 Degradation of TPH

The concentrations of TPH in treatment with plant and without plant during experiment period are shown in **Fig.5**. The decreased in TPH concentration was due to several reasons: 1) phytoremediation mechanisms (phytodegradation, phytoextraction, phytostabilization **Chirakkara and Reddy, 2015**, rhizodegradation **Hussain, et al., 2018**; 2) plant enzymes such as peroxidase, lacasse and dehalogenase **Meggo and Schnoor, 2013**; 3) microorganisms (bacteria and fungi) **Pant, et al., 2016**; 4) physical mechanisms (adsorption, volatilization) **Al-Baldawi 2018**. The removal percentage of TPH for every week within the experiment period in treatment with plant and without plant is shown in **Fig. 6**. The result show that TPH removal by *Phragmites australis* was statistically significant ($P < 0.05$) for all weeks compared with treatment without plant (paired samples t-test). The removal percentage of TPH by the plant was between 95 and 98% while the removal percentage in the corresponding contaminated control without plant was between 78 and 87%.

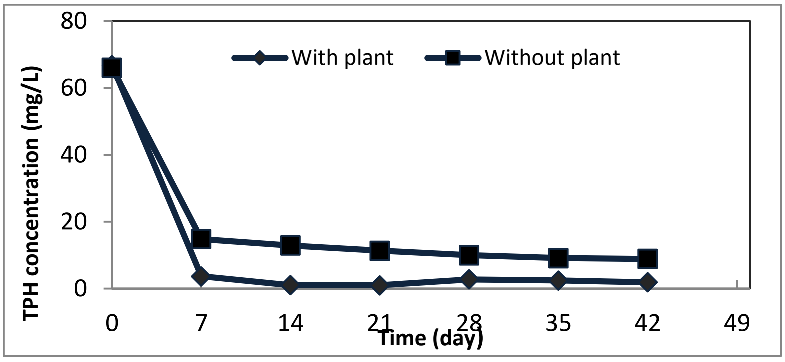


Figure 5. TPH concentrations through 42 days in FSF.

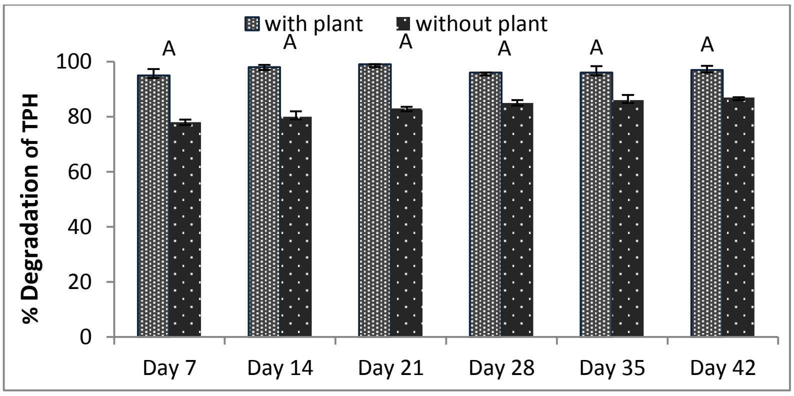


Figure 6. TPH degradation by *Phragmites australis*. A: significant difference at ($p < 0.05$) between treatments (with and without plants)

These results declare the capability of *Phragmites australis* to improve and accelerate the removal of petroleum contaminant from water. In a previous study mentioned by **Yasseen, 2014**, *Phragmites australis* was used to test petroleum contaminant phytoremediation and the result prove that *Phragmites australis* was excellent in breaking down petroleum compounds.

3.3 Plant growth

The growth of *Phragmites australis* during the study period (42 days) was observed to understand the physical changes in the plant due to exposure to refinery wastewater, as shown in **Fig. 7**. Growth of plant was low at the first week of experiment, but Week after week growth of plant was in increasing especially that exposed to wastewater and that may be as a result of plant adaptation to environmental conditions and as explained by **Megharaj, et al., 2011,** that low concentrations of TPH act as a growth enhancer. Also, in previous study of **Judy, et al., 2014**, *Phragmites australis* showed high tolerance to wethered Macondo oil (the largest oil spill in the united state). Wet weight and dry weight of *Phragmites australis* were measured for 42 days and the results shown in **Fig.8**.

Observation time

Day 0 | Day 28 | Day 42

FSF

FSFcontrol

Figure 7. Phytotoxicity test of *Phragmites australis* with the free surface flow system

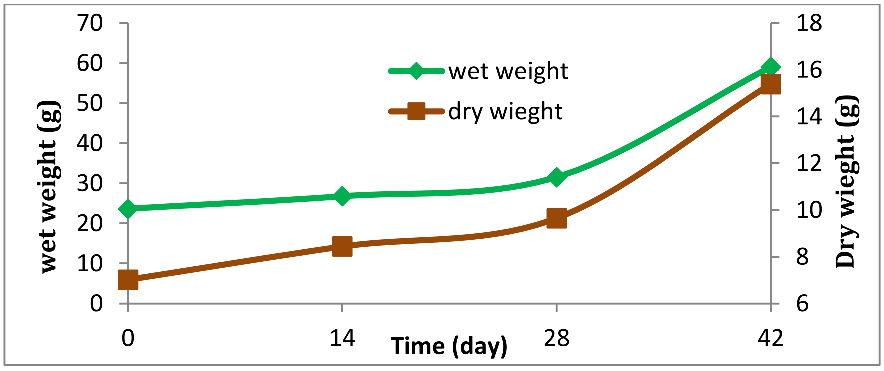
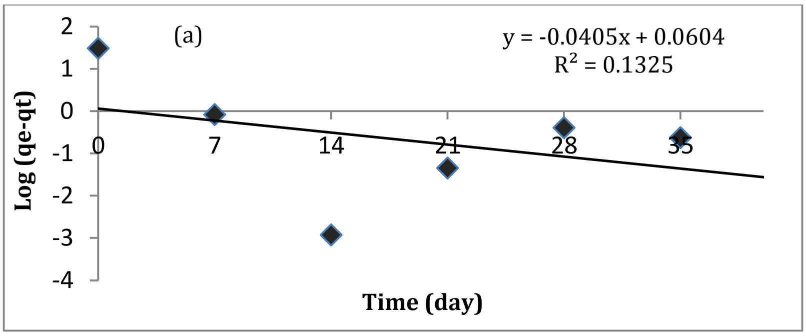


Figure 8. Wet and dry weight (g) of *Phragmites australis* over the phytotoxicity test.

3.4 Kinetics of Phragmites australis to Remove TPH from Refinery Wastewater

The two models, pseudo-first-order and pseudo- second order were applied to estimate the reaction order of phytoextraction process based on initial concentration. According to equation (2) with Ci of 66.8 mg/L, Ce of 1.9 mg/L, V of 7 liters, and X of 14.8 g, the amount of TPH that uptake by plant tissues was 30.69 mg TPH/g biomass. Moreover, the intercept (q_e) and slope (k_1) of Lagergren first-order model (equation 3) were 1.1492 TPH/g biomass and 0.093 d^{-1}, respectively. The slope (q_e) and intercept (k_2) that were obtained from pseudo-second order model (equation 4) were 30.487 mg TPH/g biomass and 5.379 mg TPH/g biomass d, respectively. Thus, pseudo- second order **(Fig. 9b)** was closer to experimental data with R^2 of 0.999, than Lagergren first-order **(Fig.9a)** with R^2 of 0.1325. the result indicates that the reaction is more inclined towards chemisorption, also according to study of **Azizian, 2004,** when the initial concentration Ci is not high, the sorption process is fit to pseudo-second order kinetics.



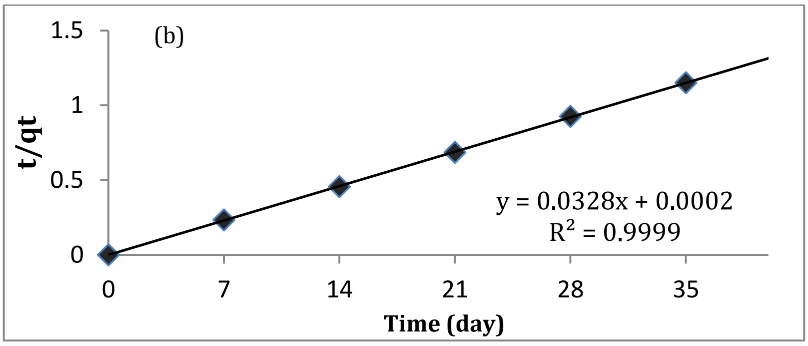


Figure 9. Plot of biosorption kinetic of TPH on *Phragmites australis* (a) pseudo-first-order, (b) pseudo-second order.

4. CONCLUSIONS

During 42 days of study, *Phragmites australis* was weekly watered with real refinery wastewater in free surface system in order to remove TPH and COD, and the results showed that 98% and 62.3% of TPH and COD were removed, respectively. Also, the growth parameters indicate the ability of *Phragmites australis* to tolerate and grow in the contaminant environment with petroleum hydrocarbons, where 60% of the wet weight of plant increased within 42 days of exposure to refinery wastewater. Thus, free surface system with *Phragmites australis* prove be used super capability in removing hydrocarbons and other organic pollutants and can use as a good strategy in refinery wastewater treatment instead of conventional methods.

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