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BIOREMEDIATION OF HEAVILY CONTAMINATED SOIL IN WASHEINDUSTRIAL AREA USING BIO-COMPOSTING TECHNIQUE WITH SHEEP AND CHICKEN MANURE IN KURDISTAN REGION, IRAQ

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ABSTRACT

Their derivatives were taken (195.5-200) m downward the private refinery factories in kwashê industrial area in the west of Duhok city about 35 km. bioremediation of the contaminated soil were done by bio-composting with sheep and chicken manure and were affected some soil physical, chemical and biological properties. The rise of the composting heaps pH reached its peak at the 3 months for the both sheep and chicken manure but even greater than the control (zero time).Statistical analysis of electrical conductivity changed within time and manure treatments showed a decline in electrical conductivity value through the whole time of experiment and in both manure kinds. Although, the heights decline of EC value were noticed after 3 months of composting process (3.6 ± 0.1) as a result of, interaction time and manure kinds. The boosts of both organic matter and hydrocarbon degradation occurred after 1 month to 3 months, and sheep, then was recorded high percentage 14.1% organic matter remained and 31.49% organic matter, then was remained in chicken manure. In the first month of bio composting the rate of oil biodegradation reached 32.88% with sheep manure and 27.88% with chicken manure. The rate of highest degradation of oil were obtained in the case of sheep manure after 3 and 5 months and recorded 50% and 86.912% respectively comparing with 36.24% and66.44% in the case of chicken manure in the same time respectively.

KEYWORDS: Contamination; Soil Environment; Hydrocarbons; Bioremediation; TPH; Composting.

1. INTRODUCTION

Two centuries of industrialization created severe soil contamination to become one of the common problems all over the Europe. Generally specialists, businessman, decision maker persons, and natives agreed on and comprehend that water contamination, and air pollution can have adverse effects on human beings health, although the impact of such soil pollution on our body had an enough minor figure, though are not too better understood (Huber and Prokop, 2012).Nowadays, contamination of soil ecosystem by hydrocarbons (especially petroleum hydrocarbons) is turning into widespread issues all over the world. This is likely to happen because of excessive rely on crude oil as a main origin of power across the globe, manufacturing development, increasing community, and the entire neglecting for the surroundings health, The quantity of the everyday oil leaking was determined to be 600,000 metric tons per year with a domain of unsure of 200,000 metric tons per year (Kvenvolden and Cooper, 2003).It has been realized that the environmental contamination with crude oil, hydrocarbons, and petrochemical derivatives as an important and real problem (Alexander, 1995, 2000).The revolution of oil industry in Iraqi Kurdistan region and their transport by tankers and wide spread of electrical generators that depend in petroleum in our region lead to huge seepage and leakage of various petroleum products in to the soil ecosystem is behind this study, and because of availability of both sheep and chicken manure in sufficient. Quantity in our region, Iraq increased production by 200,000 bbls /day in 2010, and boosted yield by an extra 400,000 bbls/day in 2011.

The whole aims of this current study are isolation and detection of microbial population size especially total aerobic heterotrophs and oil-degrading bacteria during bio composting, determination of some important soil chemical characteristics that will improve during remediation process and to compare between sheep and chicken manure by bio-composting mechanisms efficiency with using bioremediation of petroleum products.

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2. MATERIAL AND METHODS

2.1. Sample location

This research started in (March) 2017 by investigating of the Kwashê Industrial area, Duhok City, Kurdistan region, Iraq aiming that the Bioremediation of heavily contaminated soil by petroleum products through bio-composting technique, Petroleum contaminated area is located between latitude, and longitude 36º59'30.2" and, 42 º 48' 05.7" respectively, and the distance between samples location and oil refineries were approximately (195.5 – 200) m. The study was implemented in March 2017. Soil samples (1 - 30 cm) depth were taken from polluted site by heavy crude oil and their derivatives (195.5-200) m downward the private refinery factories in kwashê industrial area in the east of Duhok city about 35 km, (figure1).

Fig. (1): Location of the study samples.

2.2. Sample collection

Samples were taken and then spread over nylon sheet at College of Agriculture, in the open yard, through two composting heaps technique (about 150 kg each) of oil polluted soil, then treated by (sheep and chicken manure) for each (3) kg of oil contaminated soil added (1.5) kg of sheep, chicken manure and wood cheeps as layers until complementation of the heaps.

2.3. Laboratory analysis

During each period of 1, 3, 5 months of bioremediation some of the following soil physical, chemical and biological properties were measured: The soil pH of extracts (1:2) was determined utilizing a model (HI 9023) pH meter as described by Jackson(1958).The electrical conductivity of the studied soil was implemented through soil extracts of (1:2.5) utilizing EC meter of a model (Microprocessor Conductivity/TDS meter HANNA-HI-9635) as performed by Rowell (1996). The soil organic mattercontent was implemented during this scientific research by Walkly and Black technique using K2CR2O7 (1N) according to Allison (1965).by using below equation:

The quantity of petroleum decomposed in the studied soil was measured by the weight loss method of Bossert and Bartha (1984).This work was done through using 10 gm of contaminated soil in 20 ml of Dichloromethane(DCM) in a conical flask of known weight and shaken gently for soil extraction. The solvent- oil mixture was at room for a period 24 hours to allow the solvent evaporate completely. The new weight of the conical flask involving the residual petroleum was taken and the percentage of petroleum decomposed calculated by the equation described by Ijah and Ukpe (1992).

$$\text{Oil degraded\%} = \frac{\text{originaloilconcentration} - \text{finaloilconce.}}{\text{originaloilconcentration}} * 100$$

2.4. Statistical analysis

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The measured values of analyzed parameters, pressed by SPSS software (SPSS, 2013), in order to analyzing it. The repeated measuring procedure (within- subject effects), was applied for all studied parameters according to the following model:

$$Y_{ijk} = \mu + g_i + \delta_{ij} + t_k + (g*t)_{ik} + e_{ijk}$$

Where: Y_{ijk} = parameter $_{ijk}$
μ = over all mean,
gi = the effect of group(treatment).
tk= the effect of period $_k$ (time).
δij= randomeffect of subject (replication) within group (treatment).
(g*t)ik = effect of interaction between group $_i$and period $_k$. **eijk** = random error (experimental error).

3. RESULTS AND DISCUSSION

Effect of Bioremediation on Chemical Parameters such as Compost pH has a great effect on the soil pH because it directly influence on the availability of nutrients to plants. optimumrange of pH of compost is from 6.9-8.3 as recommends by Bord (2003) and efforts must be made to decrease the compost pH if this value exceeds over 8.3.Declining the pH will also decline the volatility of NH_3 and decrease odors by Woods End Research Laboratory (1998). Table (1) shows that the statistical analysis of bio-composting heaps for pH is apparent 7.2 ± 0.1 at zero time (control sample) then increased to about (7.7) in the case of sheep manure and to (8.3) in the case of chicken manure after 1 month of bioremediation technique this is due to a variety of alkaline substances released from both organic amendments and hydrocarbons in the soil. The best pH value for microorganism growth is 5.5 and 8.5 as indicated by Shilev*et al*., (2007).

Table (1): Effect of group manures type and timeon the pH values.

Group	Time				Over all mean	P (sig.)		
	Before treatment	After 1month	After 3month	After 5month		G	T	G * T
Sheep manure	7.2 ± 0.1	7.7 ± 0.05	7.6 ± 0.08	7.6± 0.01	7.53± 0.02 b	0.000**	0.000**	0.011*
Chicken manure	7.2 ± 0.1	8.3 ± 0.05	8.5± 0.08	8.1± 0.01	8.05± 0.02 a			
Over all mean	7.1 ± 0.07c	8.01± 0.04ab	8.08± 0.06a	7.8± 0.01ab				

Within treatment means or their interaction, values followed by similar alphabetical letters are not significantly different according to Duncan, test (1955) at 5% level of significant.G = Group, T = Time, ns = non significant, * = significant (P<0.05), **= highly significant (P<0.01).

This rise of the composting heaps pH reached its peak at the 3 month for sheep and chicken manure during remediation process then declined after 5 month for both sheep and chicken manure but even greater than the control (zero time) of bioremediation operation as indicated from the figure (2). However the increase of compost pH is greater in the case of chicken manure utilizing (8.3, 8.5, and 8.1) respectively after 1, 3, and 5 month of bioremediation. It may be due to high amount of alkaline nutrients such as (Ca, Mg, N, P and K) in chicken manure rather than sheep manureor may be due to the cleavage of alkaline hydrocarbon by the action of microbial community in the compost addition to the high buffer capacity of alkaline calcareous soils. Same results are stated by Feinstein *et al*., (1986); Kubota and Nakasaki, (1991); Marin *et al*., (2006) as a recommended ranges of pH for composting. From the below table, it could be noticed that the interaction between group and time is significant (P< 0.01), and this result reflect the interaction between chicken manure and period of 3 months after treatments because it resulted in the highest value of pH (8.5).

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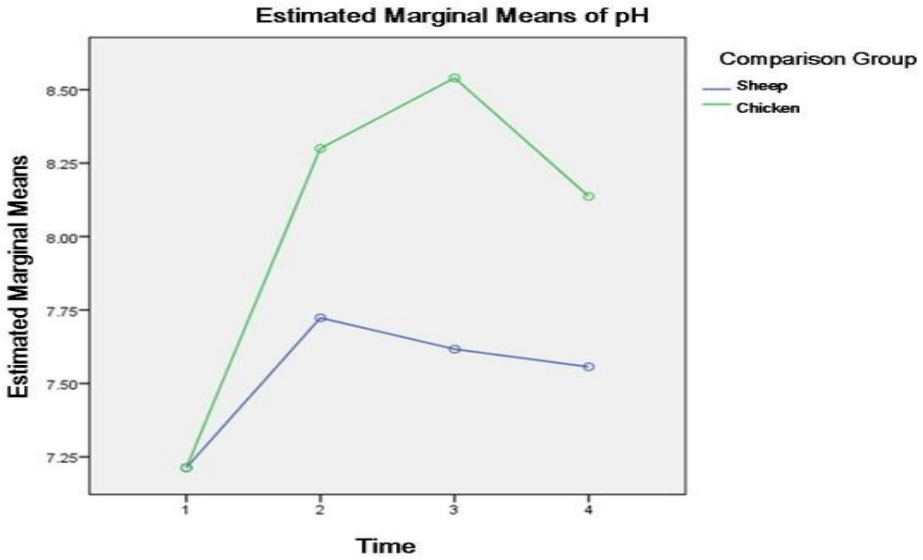

Fig. (2): Effect of manure types with time on the pH.

During compost periods 40, 50 and 60 days, pH values were found to be larger than the natural range which indicates that the declines in pH during various degradation stages were showed from 10 to 60 days which can be related to organic acid, CO_2, and nitrogen loss byLugtenberg andKamilova(2009). As shown in figure (3) the crude oil and their derivatives pollution of soil has increased the amount of O.M in the soil from (2.2%) to 11.6 % in polluted soil. This reflects the organic matter of crude oil with high organic carbon but associated with poisoning of all life sorts in the soil which make it intensive organic pollutants. The boosts of both O.M and hydrocarbon degradation occurred after 1 month to 3 months, and sheep manure recorded high amount of degradation 14.1% O.M remained and 31.49% O.M remained in chicken manure. The percentage of O.M decreases with the bio-composting process as a result of microbial degradation of O.M. The sheep manure gives on optimum condition for both total heterotrophic and petroleum degrading bacteria. Another research also showed a similar result of decreasing organic carbon (Mondini*et al*., 2003).

The composting heaps reached their stability in decomposition rate of O.M in the compost heaps and recorded a slight increase between sheep and chicken 10.54%, 11.84%, respectively and composting heaps become odorless from ammonia and hydrocarbon gasses which indicate the final stage of degradation similar results were obtained by Cabrera *et al*., 2005; Fang *et al*., 2001; andNakasaki*et al*., (1985). The content of O.M as indicated from figure (3) increased the amount of organic carbon and organic matter after one month of bio-composting from 11.6% O.M to 57.7% with manure and 33.4% with chicken manure, this result reflect the efficiency of chicken manure over sheep manure to increase microbial efficiency to degrade O.M in compost heap, this high value of O.M in first month also shows the little growth and activity of microorganisms during one month of degradation as a result of high hydrocarbon amount in the compost heaps which rendered microorganisms to slow adaption to new environment.

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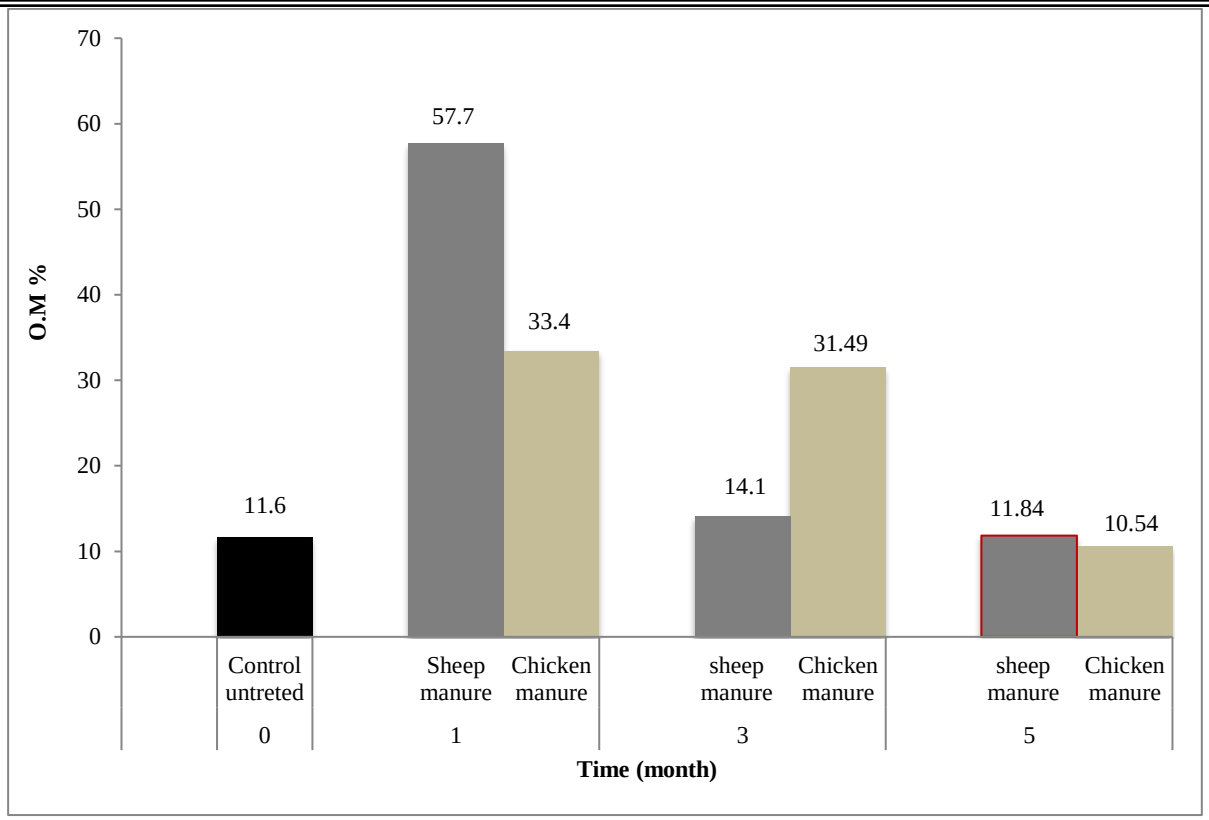

Fig. (3): Variation in O.M content during composting periods of polluted soil by crude oil.

The loss of carbon during the composting process accounted for the initial total carbon; also the microbial biomass assimilated a part and the other part of C in the decomposing residues developed in the form of CO_2 as reported by Fares.,*et al*(2005);Shyamala and Belagali, (2012).

From table (2) the statistical analysis of electrical conductivity changes with time and manure treatment shows a decline in electrical conductivity value throughout the whole time of experiment and in both kinds of manure. Although, the heights decline of EC value were noticed after 3 month of composting process (3.6 ± 0.1) as interaction of time and manure type. The electrical conductivity of
compost is due to the existence of Na, Cl, K, NO3, SO4-2 and NH3 salts (Brinton, 2003).Sheep manure is less affected than chicken manure during the composting time(4.5 ± 0.05) comparing with (5.1 ± 0.05) of chicken manure, and this attributed to the less decomposition of TPH in chicken manure compared with high degradation of total petroleum hydrocarbons in sheep manure which increases the EC by increasing soluble ions both from petroleum products and sheep manure.
As noticed the treatments of polluted soil with crude oil by manures reduced the value of EC because the continuous compost watering at 70% water holding capacity continuously dissolved cations as Na, K, and Cl. Bio-composting of TPH enhanced the improvement of EC from higher range 6.1±0.09 in control sample to acceptable ranges lower than 4 ds/m-1 as recommended standards for composting (Shilev*et al*., 2007).
Over all mean of time is progressively till the end of composting as shown in the figure (4).Bio-composting is aimed to degraded anxious compounds like petroleum hydrocarbon by aerobic microorganisms which proliferate by adding nonhazardous organic manure, thermophilic microorganisms gradually increase the temperature of composting heaps leading to the formation of stable compost that can be used as soil organic amendment.

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Table (2): Effect of manure types and time on the EC.

Group	Time				Over all mean	P (sig.)		
						G	T	G * T
	Before treatment	After 1month	After 3month	After 5month				
Sheep manure	6.1± 0.09	4.5± 0.1	3.6 ± 0.1	3.8± 0.09	4.5± 0.05 b	0.002**	0.000**	0.007**
Chickenmanure	6.1± 0.09	5.2± 0.1	4.8± 0.1	4.1± 0.09	5.1± 0.05 a			
Over all mean	6.1± 0.07 a	4.9± 0.010 b	4.2± 0.09 bc	3.9± 0.06c				

Within treatment means or their interaction, values followed by similar alphabetical letters are not significantly different according to Duncan, test (1955) at 5% level of significant.G = Group, T = Time, ns = non significant, * = significant (P<0.05),**= highly significant(P<0.01).

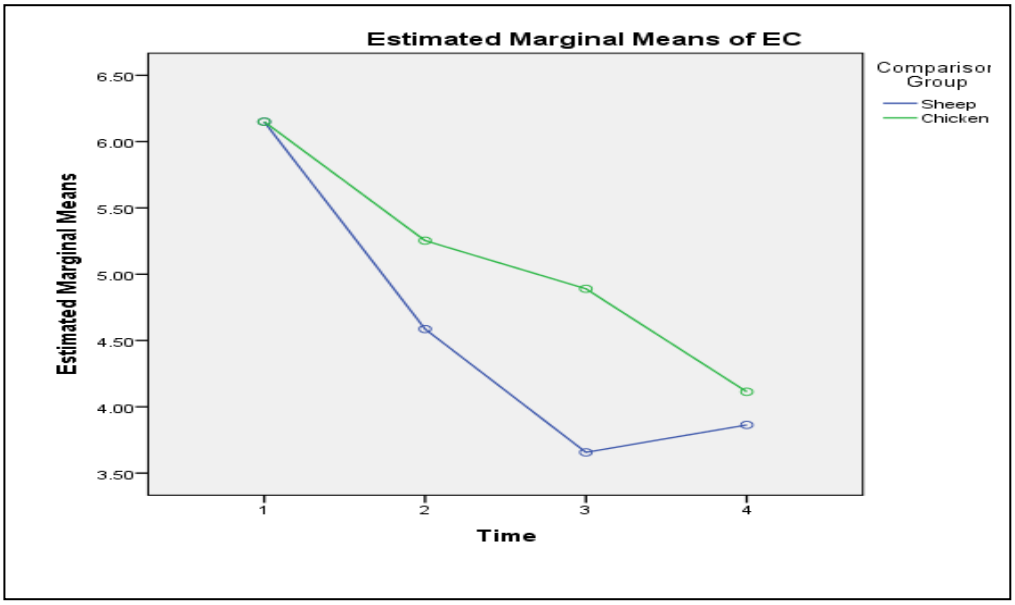

Fig. (4): EC changes during bio-composting periods (Estimated marginal means of EC).

As indicated from table (3) the efficiency of organic manure is tremendous in reducing the amount of total petroleum hydrocarbons. Although in the first month of bio composting the rate of biodegradation reached 32.88% with sheep manure and 27.88% with chicken manure. The rate of highest degradation were obtained in the case of sheep manure after 3 and 5 months and recorded 50% and 86.91% respectively comparing with 36.24% and66.44% in the case of chicken manure in the same time respectively.The supreme of sheep manure over chicken manure may attributed to faster decomposition of chicken manure during the first month of composting in which oil degrading bacteria still well not adapted and increased. Also the clayey nature of contaminated soil may prevented the lighter density chicken manure than sheep manure to mix well with the matrix of contaminated soil.

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Table (3): Monthly reduction of petroleum hydrocarbons in sheep manure and chicken manure.

Months	Oil reduction by % (Sheep manure)	Oil reduction by % (Chicken manure)
1	32.88	27.88
3	50	36.24
5	86.912	66.44

4. CONCLUSION

The sheep manure is supreme over chicken manure in reducing the percentage of oil in contaminated soil during bio-composting process. The available and free sheep manure in our region which withdrawal in most cases and cause serious environmental and health issues can be utilized as super bio remediating agents for soil contaminated with petroleum hydrocarbons. Which increased in last years as a result of oil industry flourish in Iraqi-Kurdistan Region?Bio- composting is simple and eco-friendly techniques to degraded anxious compounds like petroleum hydrocarbon by aerobic microorganisms which proliferate by adding nonhazardous organic manure, leading to the formation of stable compost that can be used as soil amendments and increases their fertility.

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چارەسەریا زیندەیی بو ئاخێن دژوار پیسبوی ب پترولا خاڤ و ژچێکەرێن وێ ب تەکنیکا تێکەلێ زیندەیی ل ناوچا پیشەسازی کواشێ, قەزا سێمێل , باژێرێ دهوکێ , هەرێما کوردستانا عێراقێ

پوختە

میناکێن ئاخا دژوار پیس بوی ب پترولا خاڤ و چێکەرێن وێ نێزیکی (195.5-200م) ل بن ناوچا پیشەسازی (کواشێ) ئە وا کارگەهێن نافخویی یێن پاقژکرنا گازێ لێ زێدەدبن ل روژهەلاتا پارێزگەها دهوکێ ب 35کم . چارەسەریا زیندەیی بو ئاخێن پیسبوی ب تەکنیکا تێکەلێ زیندەیی ب بەرمایکێن ئاژەلی و پەلەوەران ,و ڤەکولین ل سەر هندەك ساخلەتێن کیمیایی و فیزیایی و یێن زیندەیی هاتنە کرن.زێدەهی د پلا ترشاتیا تێکەلێ زیندەیی دا pH یا دیاربو پشتی 3 مەها ژ پروسێسا حەلیانێ و چارەسەریێ و لدویڤ دا کێم بو پشتی 5 مەها د هەردو کومێن بەرمایکێن ئاژەلی و یێ پەلەوەران ل سەرهندێرا زێدەتربو ژ میناکا کنترولی یا نە چارەسەر ل دەمێ سفر.شیکارکرنا ئاماری یا گەهاندنا کارەبێ و گوهورینا وێ دگەل دەمی و جورێ بەرمایکێن چارەسەریی و کێم بون دیاربو د بهایێن گەهاندنا کارەبێ د هەردەمەکێ چارەسەریێ و بو هەردو جورێن بەرمایکا.و بلندترین کێم بون یا گەهاندنا کارەبێ هاتە تومارکرن پشتی 3 مەها ژ چارەسەریێ (0.1 ±3.6) وەك تێکەل بون دناڤ بەرا دەمی و بەرمایکێن پەلەوەران.

پەقین د پروسێسا حەلاندنێ و چارەسەریێ بو هەر ئێك ژ مادێ ئەندامی و هایدروکاربوناتا چێبو پشتی مەهەکێ ژ پروسێسا چێبونا کومپوستی بو سێ مەها.و بەرمایکێن ئاژەلی بلندترین چەندی تومارکر د حەلاندنا مادێ ئەندامی دا و بتنێ 14.1% و 31.49% ژ مادێ ئەندامی د دوخێ بەرمایکێن پەلەوەران د مەها ئێکێ دا ژ پروسێسا کومپوستێ زیندی کو تێکرایا داخوران و حەلاندنێ یا پەترولێ نێزیکی 32.28% د دوخێ بەرمایکێن ئاژەلی و و هاتە تومارکرن 50% و 86.91% ل دویڤ ئێك و وەکهەڤی دگەل 36.24%و 66.44% د دوخێ بەرمایکێن پەلەوەران دهەمان دەمدا ل دویڤ ئێك

المعالجة الحيوية للترب الشديدة التلوث بالنفط الخام و مشتقاتها بتقنية الكومبوست الحيوي بمخلفات الاغنام و بقايا الدواجن من المنطقة الصناعية في كواشى ، قضاء سيميل ، اقليم كردستان العراق

الخلاصة

اخذت عينات تربة شديدة التلوث بالنفط الخام ومشتقاتها بحوالي (195.5-200) م اسفل المنطقة الصناعية التي تكثر فيها مصافي النفط الاهلية في شرق محافظة دهوك بحوالي 35 كم . المعالجة الحيوية للترب الملوثة تمت بتقنية الكومبوست الحيوي بمخلفات الاغنام والدواجن وتم دراسة بعض الصفات الكمياوية والفيزياوية والحيوية . الزيادة في درجة حموضة الكومبوست PH وصلت ذروتها بعد 3 اشهر من عملية التحلل والمعالجة ومن ثم تناقصت بعد 5 اشهر في كلا كومتي مخلفات الاغنام والدواجن ولكنها ظلت اكبر من عينة الاسيطرة غيرالمعالجة عند زمن صفر . التحليل الاحصائى الايصالية الكهربائية وتغيرها مع الزمن ونوعية المخلفات المعالجة ، اثبت تناقصا في قيم اللايصالية الكهربائية خلال كل فترة المعالجة ولكلا نوعي المخالفات . واكبر تناقص الايصالية الكهربائية سجلت بعد 3 اشهر من المعالجة 3.6 ± 0.1 كتداخل بين الزمن ومخلفات الدواجن .

الانفجار في عملية التحلل والمعالجة لكل من المادة العضوية والهيدروكاربونات حدثت بعد شهر من عملية تكوين الكومبوست الي ثلاثة اشهر. ومخلفات الاغنام سجلت اكبر كمية من تحلل المادة العضوية وبقي فقط 14.1 % و 31.49% من المادة العضوية بقيت في حالة مخلفات الدواجن في الشهر الاول من عملية الكومبوست الحيوي كان معدل تأكل وتحلل النفط بلفت 32.88% في حالت مخلفات الاغنام و 27.88% مع مخلفات الدواجن . واكبر عملية تحلل اللنفط سجلت بعد 5،3اشهر في حالت المخلفات الاغنام وسجلت و50% و 86.91% على توالي مقارنتا 36.24 % و 66.44% في حالت مخلفات الدواجن ولنفس الفترة على التوالي.