Bioremediation of Crude Oil Contaminated Soils Using Agricultural Wastes

Ham Petrolle Kirlenmiş Toprakların Tarımsal Atıklar Kullanarak İyileştirilmesi

Sakine Ugurlu Karaağaç[1*], Omar Alaa Khaleel Al-Shathr[1]

[1]Karabuk University, Engineering Faculty, Department of Environmental Engineering, 78050 Karabuk, Türkiye.

** Corresponding author: sakineugurlu@karabuk.edu.tr*

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ABSTRACT

Soil pollution is defined as the accumulation of persistent toxic compounds, chemicals, salts, radioactive substances or disease-causing substances in the soil that have adverse effects on plant growth and animal health. Soil polluting resources can be divided into two groups as agricultural resources and non-agricultural resources. Petroleum pollution endanger the living life in the environment, causes extinction of some species, pollution of underground and surface resources, can cause fire hazard with the evaporation of the volatile components in its structure, thus disrupting the ecological balance of nature. Therefore, it is important to clean the contaminated areas. This study was undertaken with the aim of rehabilitating soils contaminated with crude oil by using agricultural wastes for various purposes. For this purpose, crude oil pollution in the soil was created artificially in the laboratory by mixing soil and crude oil at a ratio of 10:1. In the studies, trials were established by using chicken manure, rice husk, barn manure and sawdust from agricultural wastes in order to eliminate crude oil pollution. For identification of total petroleum hydrocarbons (TPH) and trace of heavy metals namely (Zn, Cd and Co) in the crude oil contaminated samples. Each samples was mixed with sawdust (30g), chicken manure + wood sawdust (22.5 g +22.5g), chicken manure (30g), barn manure (30 g) and rice husk (30g) the results indicated that rice husk ultimately removed more petroleum hydrocarbons compared to chicken manure and their combinations. It was also found that the combination of rice husk and chicken manure reduced 75.5% of C_O concentration, reduced 75.5% of Zn concentration, and reduced 75.5% of Cd concentration.

Keywords: Crude oil, soil pollution, agricultural waste, remedition methods, remediation methods.

ÖZET

Toprak kirliliği, bitki büyümesi ve hayvan sağlığı üzerinde olumsuz etkileri olan kalıcı toksik bileşikler, kimyasallar, tuzlar, radyoaktif maddeler veya hastalığa neden olan maddelerin toprakta birikmesi olarak tanımlanır. Toprağı kirleten kaynaklar tarımsal kaynaklar ve tarım dışı kaynaklar olmak üzere iki gruba ayrılabilir. Petrol kirliliği ortamdaki canlı hayatının tehlikeye girmesine, bazı türlerin yok olmasına, yer altı ve yer üstü kaynaklarının kirlenmesine neden olmakta, yapısında bulunan uçucu komponentlerin buharlaşması ile yangın tehlikesine yol açabilmekte ve böylece doğanın ekolojik dengesini bozmaktadır. Bu nedenle bulaştığı alanların temizlenmesi önem kazanmaktadır. Bu çalışma, çeşitli nedenlerle ham petrolle kirlenmiş toprakların tarımsal atıklar kullanılarak iyileştirilmesi amacıyla ele alınmıştır. Bu amaçla, toprakta ham petrol kirliliği laboratuvarda yapay olarak 10:1 oranında toprak ve ham petrol karıştırılarak oluşturulmuştur. Çalışmalarda ham petrol kirliliğinin giderilmesi amacıyla tarımsal atıklardan tavuk gübresi, pirinç kabuğu, ahır gübresi ve odun talaşı kullanılarak denemeler kurulmuştur. Denemelerin 0. Günü ve denemelerden 45 gün sonra ham petrol kirliliğinin göstergesi olan toplam petrol hidrokarbonlarının (TPH) % ayrışma miktarları ve bazı ağır metallerin (Zn, Cd ve Co) miktarı belirlenmiştir. Yapılan analizler sonucunda Toplam Petrol Hidrokarbonlarında (TPH) % ayrışma sağlayan tarımsal atıklar ve miktarları sırasıyla odun talaşı (30g), Tavuk Gübresi + Odun Talaşı (22,5 g +22,5g), tavuk gübresi (30g), ahır gübresi (30g) ve pirinç kabuğu (30g) olarak sıralanmaktadır. Ağır metallerdeki azalma en fazla çinko miktarında tespit edilmiştir. Bu çalışma ile tarımsal atıkların daha verimli bir şekilde kullanımları sağlanırken, diğer taraftan petrol hidrokarbonlarının parçalanmasında kullanılan fiziksel ve kimyasal yöntemler gibi pahalı uygulamalara alternatif olacak yöntemler araştırılmıştır. Aynı zamanda, ham petrolle kirlenerek tarımsal açıdan uygun olmayan toprakların tarıma elverişli hale getirilmesi hedeflenmiştir. Çalışmalar, Karabük Üniversitesi Mühendislik Fakültesi, Çevre Mühendisliği laboratuvarında yürütülmüştür.

Anahtar Kelimeler: Ham petrol, toprak kirliligi, tarımsal atıklar, bioremediasyon, arıtım yöntemleri.

1. INTRODUCTION

Many petroleum products play an important role in modern society. The amount of crude oil and petroleum products used today is more dangerous than other chemicals for ecological and health importance. The increasing global use of oil and its products has caused severe soil and groundwater pollution (Lim et al., 2016). Gasoline, diesel or petroleum products including lubricants can be released into the environment as unwanted by-products of industrial, commercial or private activities through accidents, controlled spills. Environmental pollution can occur due to the large number of businesses and various activities that affect human health, water resources, ecosystems and other receptors. Understanding and managing soil contaminated by hydrocarbons requires an appropriate risk assessment, enabling us to develop an appropriate risk assessment program. Oil spills cause adverse effects on the environment, economy and society (Park and Park, 2011; Petroleum et al., 1998; Pinedo et al., 2013; Todd et al., 1999).

Hydrocarbons are referred to as the most common primary energy and fuel sources in the world. Human activities during accidental exploration and distribution often result in an accidental discharge or spill. Therefore, hydrocarbon is an important pollutant for soil and water (Abbasian and Lockington, 2015). Hydrocarbon-contaminated soils harm local ecosystems, as pollutants can accumulate in animal and plant tissues, causing death or mutation of generations. The toxic components of petroleum turn arable land into poor soils and cause soil pollution.

In order to ensure the sustainable development of our society, it is necessary to remove pollutants and wastes from the environment (Varjani, 2015). Remediation techniques must be used to recover polluted areas due to oil-induced environmental pollution. Many of these techniques are not applicable due to the magnitude of the contamination. Different remediation technologies for oiled soil can be classified as biological, chemical, thermal and physicochemical methods.

Bioremediation technology is used to remove toxic and dangerous substances from the environment. Bioremediation is a technology for environmental pollutants that restores and prevents further pollution in the initial natural environment (Zhao et al., 2017). Bioremediation has been defined as the cost-effective and ecology-friendly treatment of oiled areas using microorganisms (Rizzo et al., 2010). Single or many groups of microorganisms are responsible for the degradation of pollutants. Today, molecular techniques are often used to confirm the presence of microflora that helps in removing pollution in any given area. However, they are affected by various physicochemical and ecological parameters such as degradation by microorganisms, nutrients, electron acceptors or donors, pH and temperature (Khudur et al., 2015). Among other remedial alternatives such as physical and chemical treatments for the remediation of soil contaminated with crude oil, the advantages of bioremediation are important in terms of its low cost, environmental friendliness and ease of use of the processes.

The aim of this study is to invesigate the performance efficency of different agricultural waste includes chicken manure (CM), barn manure (BM), rice husk (RH) and sawdust (SD) in removing total petrol hydrocarbons from soils.

2. MATERIALS AND METHODS

2.1. Materials

Crude oil used in this study was obtained from TÜPRAŞ Turkish Petroleum Refineries Inc. in Ankara Branch. Chicken manure (CM) and barn manure (BM) were obtained from farms near the Karabuk. Rice husk (RH) was obtained from rice producer in Edirne where rice mills are located. .Sawdust (SD) were obtained from an industrial forest products company. Chemicals used in the experiments were obtained from ISOLAB chemical company in Ankara. The soils to be used in the experiments were obtained from the clean areas around Karabuk University from a depth of 30 cm.

Sieve cups of 1 mm size were used to confirm the soil texture. Borosilicate glass jars and plastic boxes were used as the simulation medium. Precision balance was used to control the weight of the soil samples, and a pH meter was used to measure the acidity level of the soil.

During the mechanical agitation extraction method, 180 ml of acetone were used as the solvent to extract the oil from the soil. Other instruments and equipment used are conical flasks and beakers, GC-MS, IR Spectroscopy and AA Spectroscopy.

2.2 Soil Preparation

For the first trials, 500 g of soil was contaminated with 50 ml of crude oil at a weight ratio of about 10:1., to this mixture, 30 g CM, BM, RH and SD were added. The trials were set up by adding distilled water to provide humidity. In the trials, a 10:1 ratio of soil and crude oiled soil was used as a control (Manufacturing et al., 2017; Ron and Rosenberg, 2014). A trial set to form the first day samples from the established trials was reserved for analysis.

For the second trials, 500 g of soil was contaminated with 50 ml of crude oil at a weight ratio of about 10:1., to this mixture, different dosage of CM and SD were added. A three duplicated of the polluted samples were treated separately using 10, 15g, 30g and 45g of CM, and 10, 15 g, 30 g, 45 g of SD and mixture of different dosage of CM and SD at the same time. Similar to first, the trials were set up by adding distilled water to provide humidity. In the trials, a 10:1 ratio of soil and crude oiled soil was used as a control (Manufacturing et al., 2017; Ron and Rosenberg, 2014). A trial set to form the fist day samples from the established trials was reserved for analysis.

The soil and crude oil mixture and other mixtures were monitored in terms of pH and moisture and kept at 20-25 °C under laboratory conditions for 6 weeks. At the end of this period, the soils were analyzed and the decomposition percentage of TPH was calculated with the following formula:

$$\%TPH = (TPH \text{ on day } 1 - TPH \text{ on day } 45) / (TPH \text{ on day } 0) \times 100\ \%$$

2.3 Statistical Analysis

Results were expressed as the means ± standart deviation (SD). Between groups data comparison was performed using one-way analysisi of variance (ANOVA). $P < 0.05$ was considered to be significant between groups using Duncan's multiple range tests (DMRT).

3. RESULTS AND DISCUSSION

According to the first trial results, using 30 grams of CM, BM, RH ve SD, percentage of Total Petrolium Hydrocarbon (TPH) removal was obtained 34 %, 28%, 14% ve 65 % , respectively. The highest TPH removal was obtained with the use of SD (65%) and CM (34%) , respectively.

Chicken manure (CM), and Sawdust (SD) were used in this study, in which the usability of agricultural wastes was investigated for the improvement of soils contaminated with crude oil. The Total Petroleum Hydrocarbon (TPH) removal throughout the interval time from after in 1^{st} to 45^{th} days with five days interval, which were tested by adding 10,15, 30, 45 grams of CM and SD to the soil and crude oil mixture sample, as shown in Figue 1,2.

Figure 1,2 shows TPH removal efficency within the period from 1^{st} to 45 th days of the experments by adding 10,15,30,45 grams of CM and SD to the soil and crude oil mixture sample.

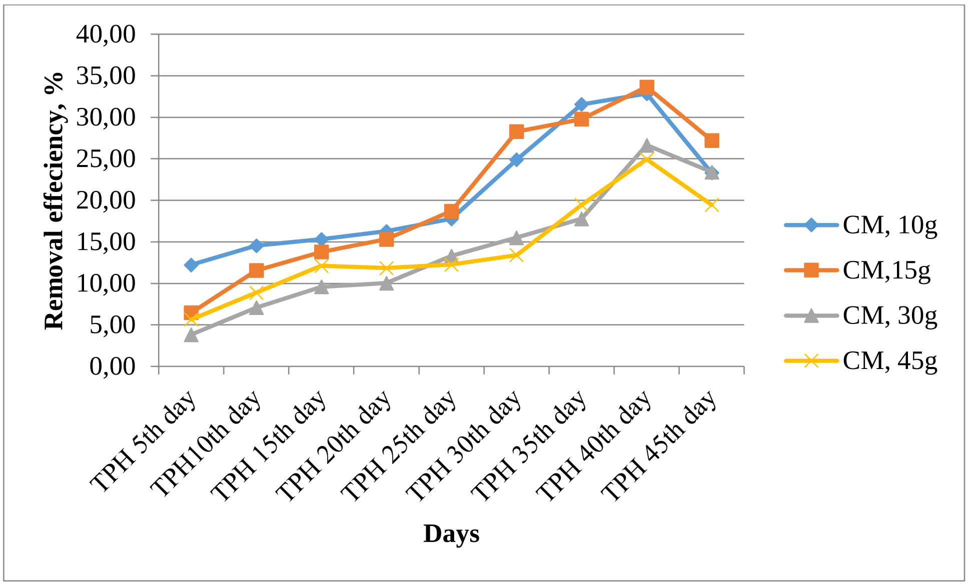


Figure 1. Effects of CM in removal of TPH at differents dosages, with respects to days intervals

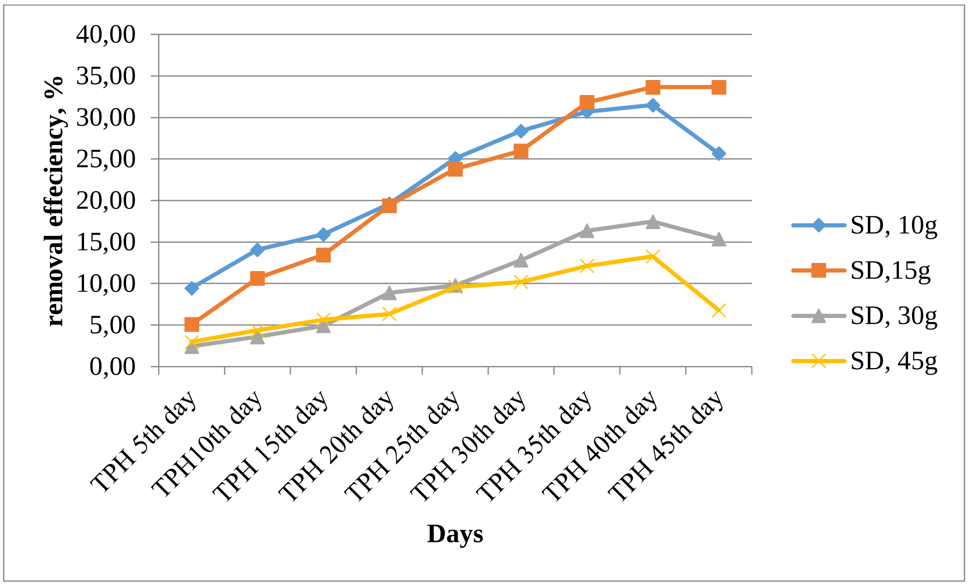


Figure 2. Effects of SD in removal of TPH at differents dosages, with respects to days intervals

As illustrated in Figure.1,2, an increase in removal effiency of TPH increased with time increase to day 40th. The decrease on TPH removal take place, this is due to the overcrowding of adsorpent, because when the adsorpent was added, there was more availability of adsorption mechanisms to take place and a corresponding increase in removal occurs, at 15g/500 g of the sample at day 40th with maximum removal efficieny of 33.66%. While with more dosage and time there was no more adsorption process taking place, and this refer to adsorption equilibrium such that additional dose can have no effect on removal (Hamoudi-Belarbi et al., 2018; Manufacturing et al., 2017).

Table 1 shows the analysis of variance (ANOVA) of the regression parameters of the predicted response surface quadratic models and other statistical parameters for the removal of TPH. The data presented in this table show that all models are significant at the 5% confidence level, given that the P values are less than 0.05. The coefficient of determination ($R^2 = 0.99$) obtained for TPH removal in this study was higher than 0.80. For a good model fit, the coefficient of determination should be at least 0.80. A high R^2 value close to 1 indicates good agreement between the calculated and predicted results over the experimental range, and a desirable and reasonable agreement with the adjusted R^2 (Hamoudi-belarbi et al., 2018; Schmidt and Shaver, 2004).

The Model's Sufficient Sensitivity (AP) ratio is 1877, which is a sufficient signal for the model. AP values greater than 4 are desirable and confirm that the predicted patterns can be used to navigate the CCD defined area. The coefficient of variance C.V. It is 0.23. A C.V value of less than 10 is desirable.

Table 1. Statistical analysis results applied to the data obtained from the experiments with chicken manure and sawdust mixed in different ratios.

Source	**Sum of squares**	**DF**	**Mean**	**F Value**	**Probability > F ***	
Model	9434.71	7	1347.82	4.436E+005	< 0.0001	significant
A	0.34	1	0.34	111.90	< 0.0001	significant
B	0.18	1	0.18	58.18	< 0.0001	significant
C	0.13	1	0.13	43.73	< 0.0001	significant
D	0.10	1	0.10	33.55	< 0.0001	significant
E	0.70	1	0.70	229.35	< 0.0001	significant
F	0.14	1	0.14	47.55	< 0.0001	significant
G	0.40	1	0.40	130.56	< 0.0001	significant
Residual	0.039	13	3.038E-003			
Standart Dev.:0.055		R^2: 0.99				
Avarage : 24.01		Corrected R^2: 0.987				
C.V.:0.23		Expected R^2: 0.986				
PRESS: 0.27		Coefficient of Conformity: 1877.231				

* If p <0.0001, the result was found to be significant.

As a result of the analysis, the differences were found to be significant. Normal probability plots of learned residuals and diagnostics are provided by the Design Expert 6.0.7 software to verify whether the selected model provides an adequate approximation for the real system. Normal probability plots helped us decide the models. Figure 2.A shows the normal probability plots of student-allocated residues for TPH removal. A normal probability plot shows that if the residuals follow a normal distribution as shown in Figure 2.A., the points will follow a straight line for each case. However, some scattering is expected even in normal data. Accordingly, the data could possibly be considered normally distributed in the responses of certain models. Figure 2. B shows that the estimated values of the TPH removal efficiency obtained from the model are in good agreement with the actual experimental data.

Final Equation in Terms of Coded Factors:

TPH removal (%) = +179.53+35.90 A +25.89 B +22.47 C +19.68 D +51.55 E+23.38 F +38.79 G

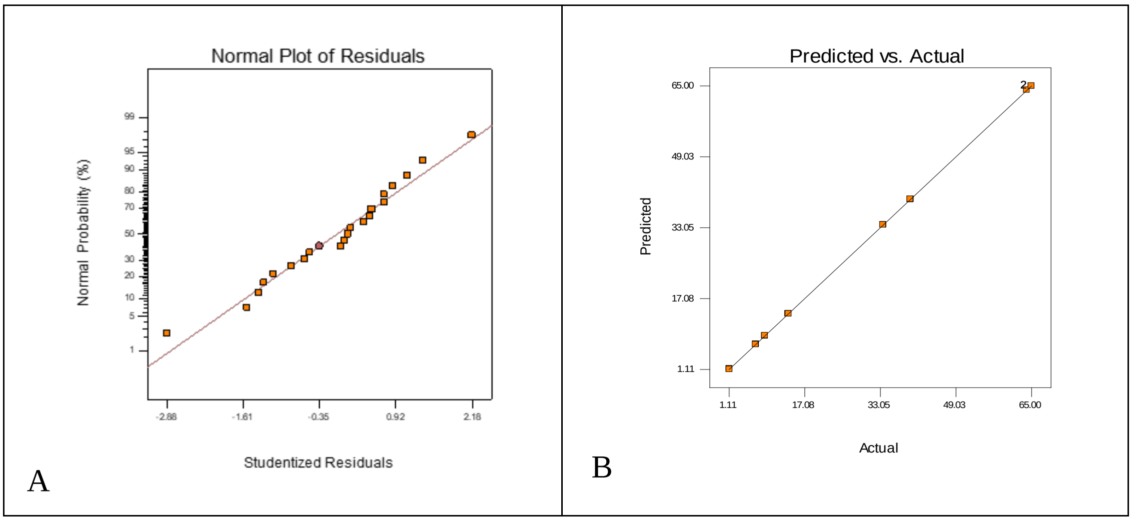
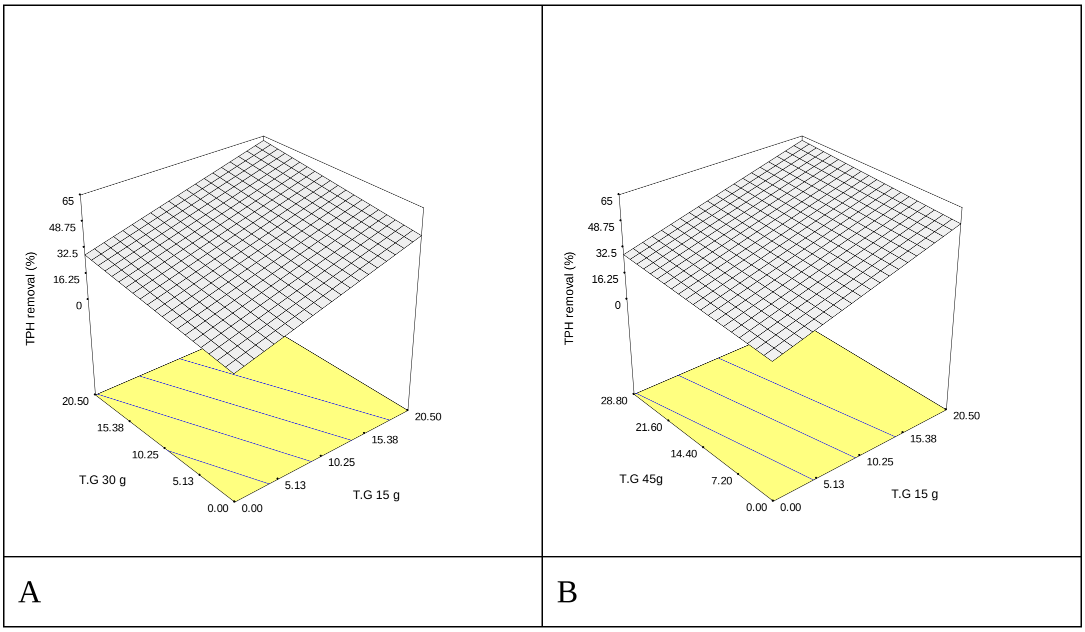
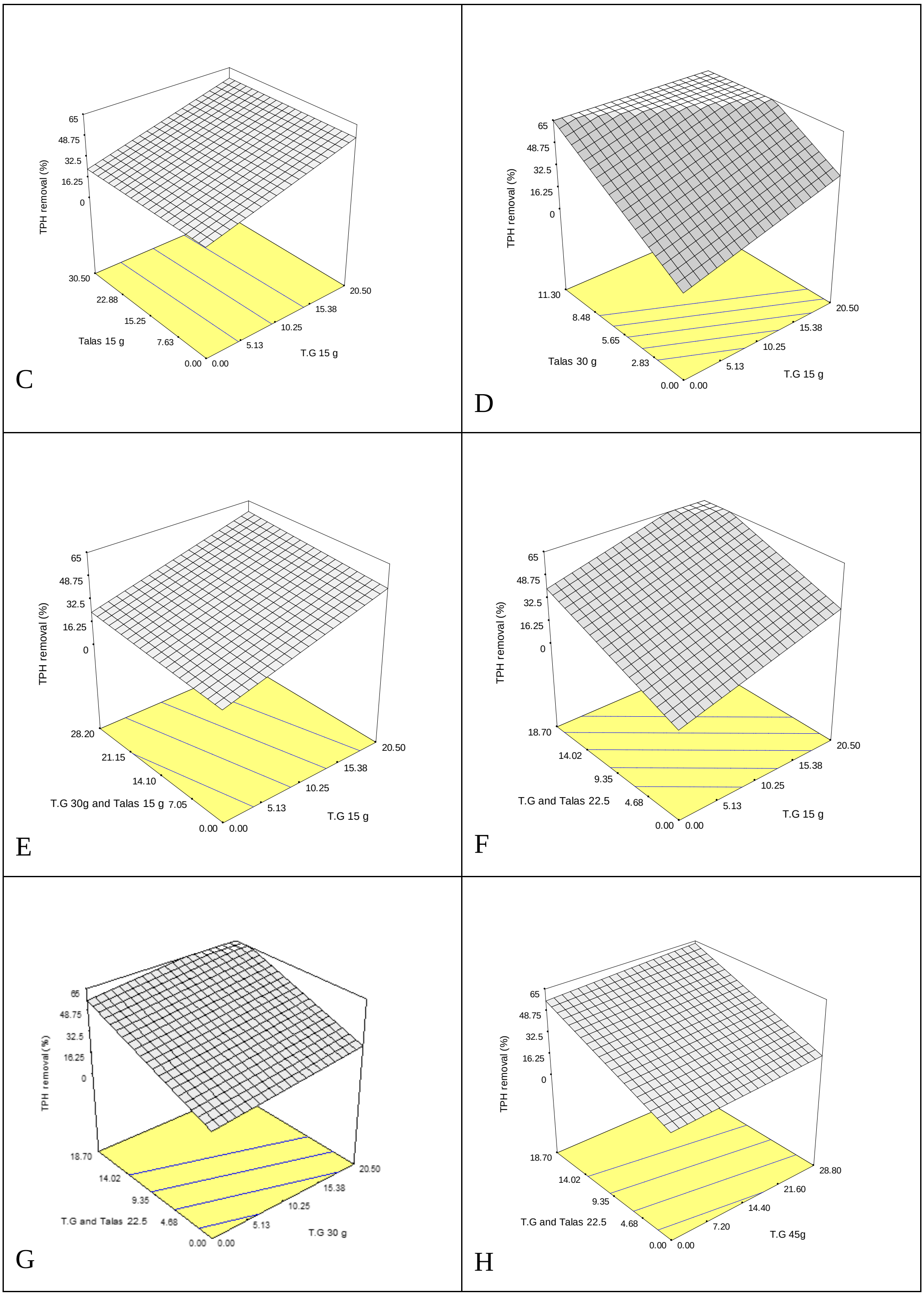


Figure 2. Normal probability plots (a), estimated and actual removal values for TPH (b)




C
TPH removal (%)
65
48.75
32.5
16.25
0
30.50
22.88
15.25
7.63
0.00
Talas 15 g
0.00
5.13
10.25
15.38
20.50
T.G 15 g
D
TPH removal (%)
65
48.75
32.5
16.25
0
11.30
8.48
5.65
2.83
0.00
Talas 30 g
0.00
5.13
10.25
15.38
20.50
T.G 15 g
E
TPH removal (%)
65
48.75
32.5
16.25
0
28.20
21.15
14.10
7.05
0.00
T.G 30g and Talas 15 g
0.00
5.13
10.25
15.38
20.50
T.G 15 g
F
TPH removal (%)
65
48.75
32.5
16.25
0
18.70
14.02
9.35
4.68
0.00
T.G and Talas 22.5
0.00
5.13
10.25
15.38
20.50
T.G 15 g
G
TPH removal (%)
65
48.75
32.5
16.25
0
18.70
14.02
9.35
4.68
0.00
T.G and Talas 22.5
0.00
5.13
10.25
15.38
20.50
T.G 30 g
H
TPH removal (%)
65
48.75
32.5
16.25
0
18.70
14.02
9.35
4.68
0.00
T.G and Talas 22.5
0.00
7.20
14.40
21.60
28.80
T.G 45g

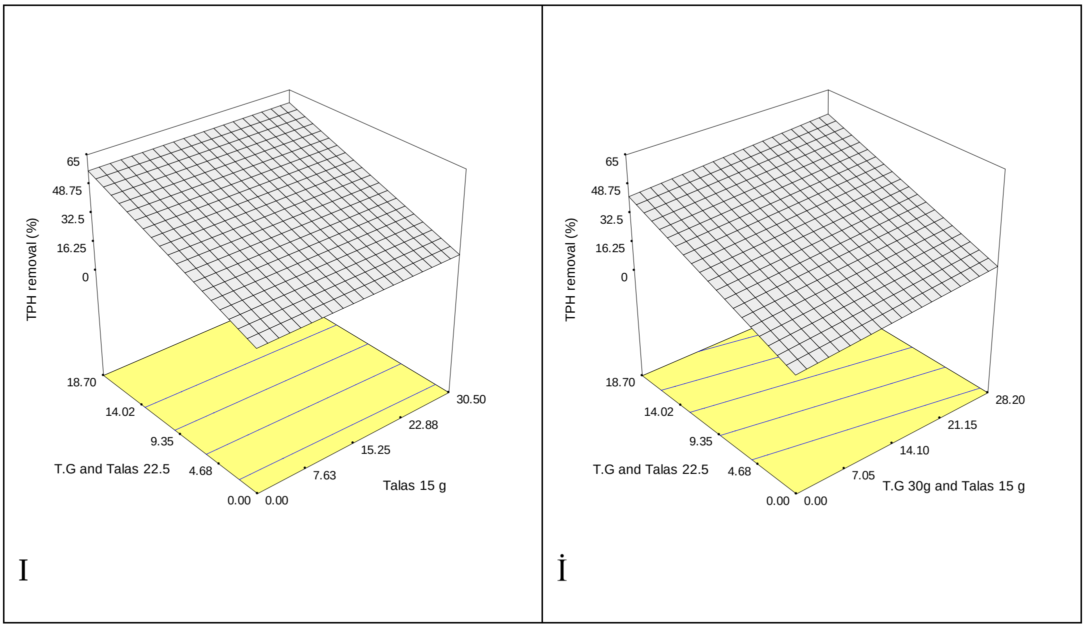


Figure 3. Surface Response Charts for various factors used in TPH removal

The heavy metal amounts determined after the 1th and 45th days of the trials by adding 30 grams of chicken manure, rice husk, barn manure and wood sawdust to the soil and crude oil mixture are given in Table 2.

Table 2. The heavy metal amounts determined after the 0th and 45th days of the trials made by adding 30 grams of chicken manure, rice husk, barn manure and wood sawdust to the soil and crude oil mixture.

Trials	Heavy metals (mg/kg)	1th Day (mg/kg)	45th Days (mg/kg)
Control	Zinc (Zn)	65,4	44,1
	Cadmium (Cd)	<0,25	0,3
	Cobalt (Co)	27,5	3,0
Chicken manure	Zinc (Zn)	109,0	70,3
	Cadmium (Cd)	< 0,25	0,3
	Cobalt (Co)	3,6	3,2
Rice husk	Zinc (Zn)	71,7	51
	Cadmium (Cd)	< 0,25	0,3
	Cobalt (Co)	4,2	3,4
Cow dung	Zinc (Zn)	65,3	53,8
	Cadmium (Cd)	< 0,25	<0,24
	Cobalt (Co)	4,5	4,0
Saw dust	Zinc (Zn)	65,3	55,4
	Cadmium (Cd)	< 0,25	0,50
	Cobalt (Co)	4,5	3,63

4. CONCLUSION

In this study, while agricultural wastes such as chicken manure, barn manure, rice husk and sawdust, which do not have enough area of use and do not pose a risk to the environment and human health when used appropriately, find an area of use, on the other hand, it is an economical solution to the areas polluted with crude oil, where agricultural production cannot be made due to pollution, will be cleaned accordingly. While agricultural wastes will be used more efficiently, alternative methods such as physical and chemical methods used in the breakdown of petroleum hydrocarbons will be introduced. It was also found that the combination of rice husk and chicken manure reduced 75.5% of Co concentration, reduced 75.5% of Zn concentration, and reduced 75.5% of Cd concentration. At the same time, soils that are not suitable for agriculture by being polluted will be made suitable for agriculture.

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REFERENCES

Abbasian, F., Lockington, R., 2015. A Comprehensive Review of Aliphatic Hydrocarbon Biodegradation by Bacteria. Appl. Biochem. Biotechnol. 3, 670–699. https://doi.org/10.1007/s12010-015-1603-5

Hamoudi-belarbi, L., Hamoudi, S., Belkacemi, K., Nouri, L.H., 2018. Bioremediation of Polluted Soil Sites with Crude Oil Hydrocarbons Using Carrot Peel Waste. Environments 5, 124. https://doi.org/10.3390/environments5110124

Khudur, L.S., Shahsavari, E., Miranda, A.F., Morrison, P.D., Nugegoda, D., Ball, A.S., 2015. Evaluating the efficacy of bioremediating a diesel-contaminated soil using ecotoxicological and bacterial community indices. Environ. Sci. Pollutıon Res. 22, 14809–14819. https://doi.org/10.1007/s11356-015-4624-2

Lim, M.W., Lau, E. Von, Poh, P.E., 2016. A comprehensive guide of remediation technologies for oil contaminated soil — Present works and future directions. Mar. Pollut. Bull. 109, 14–45. https://doi.org/10.1016/j.marpolbul.2016.04.023

Manufacturing, P., This, E.B. V, By-nc-nd, C.C., This, E.B. V, By-nc-nd, C.C., 2017. Bioremediation of Crude Oil Contaminated Soil Using Agricultural Wastes. Procedia Manuf. 7, 459–464. https://doi.org/10.1016/j.promfg.2016.12.037

Park, I., Park, J., 2011. Determination of a risk management primer at petroleum-contaminated sites : Developing new human health risk assessment strategy. J. Hazard. Mater. 185, 1374–1380. https://doi.org/10.1016/j.jhazmat.2010.10.058

Petroleum, T., Criteria, H., Group, W., 1998. Analysis of Petroleum Hydrocarbons in Environmental Media Analysis of Petroleum Hydrocarbons in Environmental Media.

Pinedo, J., Ibáñez, R., Lijzen, J.P.A., Irabien, Á., 2013. Assessment of soil pollution based on total petroleum hydrocarbons and individual oil substances. J. Environ. Manage. 130, 72–79. https://doi.org/10.1016/j.jenvman.2013.08.048

Rizzo, A.C.D.L., Ronaldo, L.C., Soriano, A.U., Cunha, D., Rosado, A.S., Luis, G., Sobral, S., Leite, S.G.F., 2010. Petroleum-contaminated soil remediation in a new solid phase bioreactor. J. Chem. Technol. Biotechnol. 85, 1260–1267. https://doi.org/10.1002/jctb.2425

Ron, E.Z., Rosenberg, E., 2014. ScienceDirect Enhanced bioremediation of oil spills in the sea. Curr. Opin. Biotechnol. 27, 191–194. https://doi.org/10.1016/j.copbio.2014.02.004

Schmidt, I.K., Shaver, G.R., 2004. NITROGEN UPTAKE BY ARCTIC SOIL MICROBES AND PLANTS IN. Ecol. Soc. Am. 85, 955–962.

Todd, G.D., Chessin, R.L., Colman, J., 1999. TOXICOLOGICAL PROFILE FOR TOTAL

PETROLEUM HYDROCARBONS (TPH).

Varjani, S.J., 2015. Microbial degradation of petroleum hydrocarbons. Bioresour. Technol. 223, 277–286. https://doi.org/10.1016/j.biortech.2016.10.037

Zhao, J., Gui, L., Wang, Q., Liu, Y., Wang, D., Ni, B., 2017. Aged refuse enhances anaerobic digestion of waste activated sludge. Water Res. 123, 724–733. https://doi.org/10.1016/j.watres.2017.07.026