Investigating Natural Physical Adsorption of Oil Content by Mangroves, A field-scale study

Partani, S.1*, Ghiassi, R.1, Khodadadi Darban, A.2 and Saeedi, M.3

¹School of Civil Engineering, College of Engineering, University of Tehran, Iran Enghelab St., PO box 43516-66456, Tehran,Iran ²Faculty of Engineering, Tarbiat Modares University, Tehran,Iran ³Faculty School of Civil Engineering, Iran University of Science and Technology, Tehran, Iran

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ABSTRACT: Mangroves are one of the main important species which have critical function in ecological processes in the coastal habitats. Recent studies have focused on long term effects such as biological and chemical responses and reactions of ecosystems. In this research, short term response of *Avicennia marina*'s pneumatophores as one of substantial parts of mangroves has been considered while facing the oil slick in tidal waves. Factorial experimental design was conducted considering three factors, each one in two levels in both spring and winter seasons, separately. Experiments were carried out in the north coastline of the Persian Gulf where one of the mentioned species habitat in the Nayband Natural National Park of Iran is located. Experimental evidences on the studied blocks were investigated by experimental analysis, accurately. Results revealed the main effective factors which can raise the damages of oil spill in the mangroves habitat through oil adsorption on the pneumatophores. Investigations showed the concentration level of the main significant factors that can affect the adsorption process. The second significant factor on physical adsorption is retention time, also known as contact time. Tests results indicated that adsorption in winter is generally more than that in spring. No significant effect of day or night time on the physical oil adsorption by pneumatophores was traced.

Key words: Physical adsorption, Oil content, Mangrove, Oil spill, Pneumatophore

INTRODUCTION

Coastlines in subtropical areas are especially coastal habitats are subjected to oil pollution due to several oil industrial and transportation accidents effects. In the past forty years there has been a significant increase in the oil accidents (Song et al. 2011), industrialization and urbanization, and oil pollution beside of all other environmental crisis(Lee and Yi 1999). This is related to this fact that oil pollution and hydrocarbons are dangerous factors that threat the ecosystems seriously. Coastlines as the interface of terrestrial and aquatic ecosystems have been subjected to the serious threats of oil pollution. In this areas, Mangroves' habitats are exposed to oil (Duke et al. 2000) spill (Duke and Watkinson 2002) contamination (Nansingh and Jurawan 1999) in intertidal long waves regions in tropical and subtropical zones (Tam et al. 2005). Mangroves and their wetlands are known as one of the renewable resources and productive ecosystems in the world (Kjerfve 1990). Also mangrove's swamps are considered as an important factor to prevention of

al. 2012). Previous studies on oil contamination in mangroves were mostly focused on large scale crude oil spills as these were often perceived to be major threats on the Bio-chemical and geo-biological (Berthe-corti and Hopner 2005) response of mangroves, sediments (Gao and Chen 2008; Esteves et al. 2006) and ambient(Abilio Soares-Gomes et al. 2010; Proffitt et al. 1995a; Duke and Watkinson 2002). A lot of researches have studied the long-term oil pollution (Janeiro et al. 2014; Duke et al. 2000; McGuinness 1990; Nansingh and Jurawan 1999) and oil adsorption in different species of mangroves communities (Proffitt et al. 1995b; Lewis et al. 2011). Also oil residues in mangroves swamp especially in sediment (Ohowa 2009) can affected on mangroves trees (Burns et al. 1994; Levings and Garrity, 1997). Field trials were designed to fill a gap between surveys of real spill incidents (Duke et al., 1997) and instant physical oil adsorption. Burns et al. (2000) used mangroves for bioremediation field study to apply for treatment of oil

coastline erosion and coastal conservation (Duc et

*Corresponding author E-mail: s_partani@ut.ac.ir

spill in coastal zones(Burns *et al.* 2000). Naidoo G. *et al.* (2010) tried to find out the response of *Avicennia marina* and *Bruguiera gymnorrhiza* to oil spill in greenhouse experimental pots and natural physical pots (Naidoo *et al.* 2010). They revealed that some tissues of *A. marina* have more resistance than others and can show adaptive response. Debarked and normal *A. marina* and *B. gymnorrhiza* were subjected to oil pollution in a long term. Results showed that the leaves of both were damaged, while the stems seemed to be more resistant (Naidoo *et al.* 2010). In These kinds of researches, field study and experimental measurements were done for long term periods but physical adsorption by each tissue has not been considered.

Some studies have focused on polycyclic aromatic hydrocarbons (PAHs) (e.g. Abílio Soares-Gomes et al. 2010; Tam et al. 2001) during long-term period and sediment media of mangroves' habitat (Tam et al. 2005). The main concern of this research is to evaluate the physical short-term oil contamination through biota species focusing on mangroves as one of important intertidal plants in different perspectives. The new approach is short-term adsorption of mangroves facing to oil slick which can be the basis of long-term contamination effects. Hence the first stage of oil affects is physical attachments on the mangroves' tissues, the amount of primary oil content which can attach and cover the breathing feeder roots (Tam et al. 2005) is very important. There is not any field and natural study or records on physical short-term adsorption of oil slick with mangroves even in the actual oil spill disasters. Pneumatophores as one of exposed roots of A. marina is very important in gas exchange in plant structure and may avoid forming the anaerobic soil (Purnobasuki and Suzuki 2005).

The study has aimed to consider a physical approach to short-term oil slick adsorption by mangroves due to intertidal water surface fluctuation. In this research some field trials were conducted as natural oil spill physical models at the northern coastline of Persian Gulf's mangroves' pneumatophores to Fig. out the physical adsorption amount of crude oil by mangroves. Experiments and sampling were designed according to an offshore oil spill accident and tidal behavior of coastal zones in the *Avicennia marina* habitats and sampling carried out before starting any kind of chemical and biological adsorption.

MATERIALS & METHODS

Iran has the wide area of natural mangrove forest as 43rd country in area ranks in the world and 10th in Asia (FAO, 2007). Nayband Natural National Park as one of most important mangroves' habitat dominated by Avicennia marina, has been known locally as the "Hara" or "Harra" trees (Ghasemi and ;Mohamed Zakaria; Ebil Yusof; Afshin Danehkar 2010). it islocated close to the most important gas and oil resources, refinery, storages and transfer facilities in the middle east that authorizing under Pars Special Energy Economic Zone (PSEEZ) administration (Fig. 1). The study and experiment were conducted in Nayband Natural National Park (Nayband Bay) at the south-east coast of Bushehr province,north of Persian Gulf (as illustrated in Fig. 1) due to high oil contamination risk there. The average daily maximum (summer) and minimum (winter) temperatures for this area are 12 °C and 42 °C, respectively(Taghizadeh and Eftekhari 2014).

Since the preparation of an oil spill disaster is desirable which described before, the export fresh crude oil of Iran were provided for treatments of experiments. In the separate tank the crude oil should be mixed preweathered in seawater about 24 hours before application. In preparation time it is better for tank to be exposed to stirring calmly and monsoon or local winds and settlement can be allowed just one hour before application (Duke N. C. et al. 2000); since the plant would be exposed to natural off shore oil accident and the natural physical model for oil spill simulation of actual situation as possible was desired. Weathered crude oil could simulate the oil accidents which may happen due to offshore structures crashes like DWH2010 etc. So the Iran (Iranian Heavy) crude was selected for oil spill simulation (Taghizadeh and Eftekhari 2014). It had special gravity of 0.8592 gr/cm³ at 15.6 degree of Celsius and 51 kPa RVP.



Fig.1. Study area and experiments location

Factors	Number of Levels	Number of Blocks	Number of Samples
Day/Night	$L_1 = 2$	2	2
Spring/Winter	$L_2 = 2$	2	2
LH^1/LL^2	$L_3 = 2$	2	2
CL ³ /CH ⁴	$L_4 = 2$	2	2
Number of Experiments	$L_1 * L_2 * L_3 * L_4 = 2 * 2 * 2$	2*2=16, two Replication v	via two Blocks for each = 32

Table 1.	Experimental	design	parameters
			See entre e e lo

¹Tidal situation, water surface level fluctuating during test, Low tidal level to High tidal level, half wave length

 2 Tidal situation, water surface level fluctuating during test, Low tidal level to Low tidal level, compelled wave length

³Low Concentration of oil release(1:8 relation of weathered oil: water volume in block)

⁴High Concentration of oil release(1:4 relation of weathered oil: water volume in block)



Fig.2. Some of blocks carried out on the experiment field; (a) Winter daytime test for complete tide wave length retention time (LL) for high concentration (LH); (b) Winter daytime test for half tide wave length retention time (LH) for low concentration (LC); (c) spring daytime test for complete tide wave length retention time (LL) for low concentration (LC); (d) spring daytime test for half tide wave length retention time (LH) for high concentration (LH)

Pneumatophores (i.e., aerial roots) of Avicennia marina species were selected as treatment objects (Hovenden and Allaway 1994) since they are one of the entrance gates of nutrients and contamination load and act as the indicator of environmental condition (Nath et al. 2014). Hence treatments were designed as following table in two concentrations and three retention times at day and night, each in two blocks. Treatments were assigned within blocks, each treatment once per block. The number of blocks is the number of replications. Two different concentrations in two different retention times represented treatments. Therefore there were 2 blocks for each of three treatments in this research for each sunlight situation (day and night separately were investigated). Since different quality of seawater and sediment may change (Tam et al. 2001) the reaction of pneumatophores, tests were done in high tide and low tide along the tidal long wave lengths.

In Randomized Block Designs (RBD) trial runs of experiments estimated for 4 factors as following levels.

According to Table 1, 32 blocks (Fig.2) laid down overall. Blocks' position was selected randomly and the experiments were carried out 23 to 30 January 2014 for winter tests and 10 to 16 May 2013 for spring tests. Experiments location is an area around 30 Ha with center coordination of 665819 mE., 3037218 mN. Two samples were taken randomly from each block. Oil release (treatments) and sampling was base on low tide and high tide duration (Fig.5 illustrates the day sampling) and the times were according to season and tidal wave prediction obtaining from buoy records which had established in the nearest harbor, Nakhl-e-Taghi authorizing by Ports and Maritime Organization of Iran. QC/QA process has been defined in laboratory measurements and field sampling. QA plan reviewed before field studies reducing anticipated problems dur-



Fig.3. (a) Soxhlet extraction device scheme; (b) Employed Soxhlet extraction device (c)Vitreous container pipe that sample is located and extracted there. (d) Residual extracted oil balloon



Fig.4. Extracted oil content in different extraction solvents in different extraction times



Fig.5. Day sampling retention times (LLandLH)

ing tests according QA guidelines including study and design consideration and field activities stages under the sampling standards avoiding the contaminating samples, clean sample collection equipment regularly, check equipment cleanliness and performance by running blanks and reference samples where appropriate (Keith, L.H. 1991). Time and collection before laboratory measurements, appropriate time of transfer in standard sample box, duplicating and replicating of sampling and measurements (mentioned in Table 1 and Table 2) are considered in field study. Each block subjected to duplicate sampling. So four samples and for laboratory measurements were carried out and couple of results which were closer to average of them was selected for paper tables. For satisfying accuracy and precision if the variation coefficient (STEDV by mean)



Fig.6. Main stages of experimental evidence analysis process

was more than 18%, (GBC, 1998) outlier data eliminated. Effective parameters and variables were selected based on natural oil spill simulation. Time retention, which is referred as contact time sometimes, in mangroves ambient is one of the most important factors which lead researchers to talk about reaction types of oil and environment in mangroves swamps (Tovalop, 1986).

Since bio-chemical degradation starts about 6 hours after oil spill (Carmo J. A. et al 2010), the experiments went on the time retention on the tide wave pattern time (between 6 and 12 hours). The oil content in sampling units (pneumatophores) was considered for treatment variables as oil adsorption index. laboratory measurements was done through the Soxhlet extraction method (Straccia, M. C., 2012, EPA method SW-846 #3541). In a Soxhlet extractor (Fig.3), the solvent is heated in a boiler; the pure vapor rises up through a vitreous container pipe hole and pass from the top part of the Soxhlet container where the sample to extract is contained to the condenser. In the condenser, the vapor is condensed and drip into the sample-containing thimble. Then in the certain temperature sample would be submerged through the boiling solvent for optimum extraction time and the liquid containing the extracted material is dropped back into the boiler. This kind of Soxhlet extraction is a continuous procedure instead of a batch system with repeated extractions.

To find the suitable solvent and optimum circulation time, three grams of weathered crude oil were weighted out and then injected on the Pneumatophores which were subjected to seawater for at least two days in field. Then weighted and folded in a weighted with certain weight filter paper circles (125mm, Cat No. F2042-125 produced by CHMLAB Group) was placed in the extraction thimble and then Soxhlet extracted for different times from 1 to 9 hours using 150 ml solvent at 50-70 C). After extraction, the solvent was evaporated and the extract was dried to remove residual solvent, cooled for 30 minutes in desiccators, and weighed. This procedure was repeated until a constant extract weight was obtained. For water resistance, sealing and lubricating performance, chemical stability and lower volatility, silicon grease vacuum (Distributed by MM TECH, UK)

So the circulation duration time was considered in determined control concentration samples finding the optimum extraction time and solvent. Three kinds of solvent were examined in nine circulation times. Solvents selected according to Soxhlet extraction method 3540, 3541 and 3550. The maximum detection of oil content was observed after 5 hours continues extraction process and Carbon Tetrachloride could solve maximum oil content (Fig.4). So minimum of 5 hours is considered necessary to complete the extraction via Carbon tetrachloride.

		Massive Percentage of Crude Oil									
Treatments	Season Climate		Spr	ing			Winter				
	Sun Radiation Effect	Da	iy	Ni	ght	D	ay	Night			
Treatments	water Surface Rising	Retentio	on Time	Retentio	on Time	Retention Time		Retention	Гime		
	Tidal Condition	L to H	L to L	L to H	L to L	L to H	L to L	L to H	L to L		
	B1 sample#1	3.934	7.237	4.723	6.992	6.179	5.943	6.518	9.052		
	B1 sample#2	4.96	6.154	4.728	7.19	7.663	4.88	6.194	8.325		
	B2 sample#1	4.131	6.734	4.936	6.344	5.091	8.211	5.963	8.68		
Concentration A	B2 sample#2	3.899	7.195	4.694	7.473	5.936	7.937	5.883	7.896		
	Mean	4.231	6.830	4.770	7.000	6.217	6.743	6.140	8.488		
	Varariance	0.247	0.255	0.012	0.230	1.146	2.564	0.081	0.244		
	Variation Co.	0.117	0.074	0.023	0.069	0.172	0.237	0.046	0.058		
	B1 sample#1	6.135	10.549	7.191	9.527	11.261	7.977	10.709	15.810		
	B1 sample#2	6.870	11.427	8.076	12.043	12.195	6.642	8.196	11.315		
	B2 sample#1	7.496	12.612	8.440	9.567	8.857	14.417	10.915	12.308		
Concentration B	B2 sample#2	6.652	11.260	6.224	11.496	11.166	13.743	9.249	12.435		
	Mean	6.788	11.462	7.483	10.659	10.870	10.695	9.767	12.967		
	Varariance	0.318	0.733	0.980	1.697	2.016	15.652	1.648	3.843		
	Variation. Co.	0.083	0.075	0.132	0.122	0.131	0.370	0.131	0.151		

Table 2. Measurements results of laboratory extraction for 64 samples in 32 blocks



Fig. 7. Box plots for experiments

Pneumatophores were cut with the length of (oil slick fluctuation on the) water surface which had contact by it. Pneumatophores are a part of shoot which transpiration and uptake (Hodson and Acuff 2006) and respiration (Davis 1968) are implemented there. Furthermore to find the probable influx amount of oil content, measurements were carried out on the epidermis separately. For experiments evidence investigation 8stage analytical method (Barrentine 1938) was carried out for experimental analysis separately for winter and spring with two sampling replication in two blocks as shown in Fig. 6. Main effects have been estimated as difference between mean responses (actual physical adsorption) in high and low levels of factors. So each level of factors has been appeared in + or – symbols as introduces in the Table 3 for winter tests and in the Table 4 for spring tests.

RESULTS & DISCUSSION

Mangroves' density was counted for each block. Mean density of mangroves was equal to 340 per square meter. The height of them was 13.40 cm averagely with maximum of 39.5cm and minimum of 4.5cm. For minimizing the errors two samples were taken from each block and two blocks were carried out for each treatment level (factor's level). Therefore 4 samples were taken in each treatment for each level of factors. According to Table 2, 64 samples were analysis in laboratory for oil content extraction. Experimental analysis was implemented for each season. Experiments showed that nights' conditions cause to more adsorption. Obviously the high concentration release leads the circumstances to increase in oil adsorption. Retention time also affects on further adsorption. More than 70 percent of oil content attaches to epidermis on pneu-

Test	Dox/Night	Concentration.	Retention Time	Day/Night-	Day/Night	Concentration	A 11	maan V	Vorionaa
1050	Day/Ingin	CH/CL	LL/LH	Concentration	-Time	-Time	AII	mean 1	v al lance.
1	+	+	+	+	+	+	-	10.695	15.652
2	-	+	+	-	-	+	+	12.967	3.843
3	+	-	+	-	+	-	+	6.743	2.564
4	-	-	+	+	-	-	-	8.488	0.244
5	+	+	-	+	-	-	+	10.870	2.016
6	-	+	-	-	+	-	-	9.767	1.648
7	+	-	-	-	-	+	-	6.217	1.146
8	-	-	-	+	+	+	+	6.140	0.081
Sum y+	34.524	44.298	38.893	36.192	33.344	36.018	37.697	Level	Symbols
Sum y-	37.362	27.588	32.993	35.694	38.542	35.868	34.189	Day	+
Mean y+	8.631	11.075	9.723	9.048	8.336	9.005	9.424	Night	-
Mean y-	9.341	6.897	8.248	8.924	9.636	8.967	8.547	High	+
Effects	-0.710	4.178	1.475	0.125	-1.300	0.038	0.877	Low	-
Effect Abs.	0.710	4.178	1.475	0.125	1.300	0.038	0.877	LL	+
Dec.Limit	1.343	1.343	1.343	1.343	1.343	1.343	1.343	LH	-

Table 3. Winter experimental analysis on effects consideration for three factors in 3 levels and its Interactions

Table 4. Spring experimental analysis on effects consideration for three factors in 3 levels and its Interactions

Test	Day/Night	Concentration.	Retention Time	Day/Night-	Day/Night	Concentration-	All	mean Y	Variance.
				Concenti ation	-Time	1 шис		11.460	0.722
1	+	+	+	+	+	+	-	11.462	0.733
2	-	+	+	-	-	+	+	10.659	1.697
3	+	-	+	-	+	-	+	6.830	0.255
4	-	-	+	+	-	-	-	7.000	0.230
5	+	+	-	+	-	-	+	6.788	0.318
6	-	+	-	-	+	-	-	7.483	0.980
7	+	-	-	-	-	+	-	4.231	0.247
8	-	-	-	+	+	+	+	4.770	0.012
Sum y+	29.311	36.391	35.950	30.020	30.545	31.121	30.175	Level	Symbols
Sum y-	29.911	22.831	23.272	29.202	28.677	28.101	29.047	Day	+
Mean y+	7.328	9.098	8.987	7.505	7.636	7.780	7.544	Night	-
Mean y-	7.478	5.708	5.818	7.301	7.169	7.025	7.262	High	+
Effects	-0.150	3.390	3.169	0.204	0.467	0.755	0.282	Low	-
Effect Abs.	0.150	3.390	3.169	0.204	0.467	0.755	0.282	LL	+
Dec.Limit	0.544	0.544	0.544	0.544	0.544	0.544	0.544	LH	-

matophores while water surface rising in high tide process weather at night or day. Winter in lower temperature and lower radiation angle may cause further attachment. Laboratory results revealed that overall physical adsorption of crude oil in nighttime is more than daytimes and in the winter condition is more than spring condition. High concentration also caused greater adsorption. According to latest related researches at days, sun radiation may affect on evaporation rate (Fingas 1994) and should have increased the evaporation rate (Azevedo et al. 2014) and viscosity (Taghizadeh and Eftekhari 2014) and oil attachment but high humidity (Guo and Wang 2009) decreases the evaporation rate (James 2002). At nights the morning breeze and monsoons sometimes cause more evaporation (Fingas 1994) specially in volatile light hydrocarbons (Ahmed T., 2010). So it seems low temperature and more evaporation may increase the viscosity and lead to more adsorption. According to Box plot graph (Fig.7), spring tests on LL retention time have more adsorption while generally those have less scatter in measurements of oil content. It may be due to climate condition and less variation in temperature and wind. However, small amount of adsorption appears in low concentration (CL) of oil releases. General trend of adsorption amounts decreasing due to low concentration (CL) and increasing in LL retention time as the greater contact time. Data Table including average and variance is presented in Table 2. Table 3 and Table 4 show the winter experimental analysis and effects consideration for three factors in two levels and its Interactions. Effects estimation as the first stage of experimental analysis is presented in these two tables. Y represents the oil adsorption in samples. The absolute effects of each combination of factors for each season have been calculated in the following tables. Regarding to data numbers decision limit which can express the significant effects for winter and spring tests estimated as 1.343 and 0.544 respectively. In winter just concentration and retention time are found as the significant factors while daytime and nighttime factor also are close to a significant factor. It can confirm



Fig.8. Effects Pareto graphs for each season; absolute effects graph for winter tests (left), absolute effects graph for spring tests (right)

Exp. Anls. Parameters	Winter Tests	Spring Tests
Treatments (in different levels)	8	8
Replication No.(samples*Blocks) for each treatment	4	4
Observations	32	32
S _e	1.8437	0.7476
S _{eff}	0.6519	0.2643
Degree of Freedom (Replication No1)* Treatments	24	24
t	2.0600	2.0600
Decision Limit (DL) = $t^* S_{eff}$	1.3428	0.5445
Number of Significant Effects	2	3

Table 5. Experimental analysis parameters

mentioned statement about more adsorption at nighttime in winter. In the spring again concentration and retention time are found as the significant factors.

Effects Pareto graphs for each season support that retention time and concentration have main effects as significant factors. The absolute amounts of effects in concentration and retention time are 3.196 and 3.390 respectively which are greater than 0.544 as the decision limit for effective factors. Therefore they can be considered as main effective factors (Fig.8).

Following table shows the stages 3 to 6 of experimental analysis process which is shown in Fig.8. Daytimes and nighttimes are unexpectedly less effective factors.

Results led the Retention time and concentration to be considered as main significant factors which the interaction graphs are shown in Fig.9. Trends from LL to LH and high concentration to low concentration lead to descending trends in oil adsorption. Trends are parallel generally with negative slope. Different between effects line for concentration is almost same in winter and spring but for retention time isn't same.

In the case of this range of factors level the effects modeling has been calculated in table. Obtained equations can predict the response of experiments between studied levels of significant factors.

Main Eq.

$$Y = y + 0.5 [E(A)^*A + E(B)^*B + E(AB)^*AB]$$
(1)

Winter Model Equation

Y = 8.986 + 0.7374A + 2.0888B + 0.0188AB(2)

Spring Model Equation

$$Y = 7.403 + 1.5847A + 1.6949B + 0.3776AB$$
(3)

A:Retention Time Levels (maximum level=+1 and minimum Level=-1)

B: Concentration Levels (maximum level = +1 and minimum Level=-1)



Fig.9. Significant factors and interaction graphs

		combination of treatments for different factors									ıal Y	Predic	ted Y	Resi D	duals iff.
														Modela	ndA ctual
	Tes	ts	Day/Night	CH/CL	LL/LH	Day/Night Conc.	Day/Night Time	Conc. Time	All	Spring	Winter	Spring	Winter	Spring	Winter
÷	1		+	+	+	+	+	+	-	11.462	10.695	11.0602	11.831	0.402	-1.136
S 0	2		-	+	+	-	-	+	+	10.659	12.967	11.0602	11.831	-0.402	1.136
s sel	3		+	-	+	-	+	-	+	6.830	6.743	6.9152	7.6158	-0.085	-0.873
Le	4		-	-	+	+	-	-	-	7.000	8.488	6.9152	7.6158	0.085	0.872
act	5		+	+	-	+	-	-	+	6.788	10.870	7.1356	10.3186	-0.348	0.551
fere F	6		-	+	-	-	+	-	-	7.483	9.767	7.1356	10.3186	0.347	-0.551
ĴĤ	7		+	-	-	-	-	+	-	4.231	6.217	4.501	6.1786	-0.270	0.039
П	8		-	-	-	+	+	+	+	4.770	6.140	4.501	6.1786	0.269	-0.039
Spring	F		1.0011	3.5283	1.1474	1.0003	1.0013	1.8303	1.0014	Division	of greate	er varian	ce of re	esiduals	by minor
Winter	F		1.0001	2.0896	6.7236	1.0003	1.0002	1.2131	1.0003	one (whi factors se	ile varian eparately)	ces calc	ulate for	r + or –	levels of
DF=(No. _{Resi}	_{iduals} -1)		3	3	3	3	3	3	3	Degree denomina	of freed ator are s	dom (D upposed	F) for to be the	numera e same	ator and
F (α=0.05)			9.28	9.28	9.28	9.28	9.28	9.28	9.28	The risk	is 10%				
F (α=0.10)			5.39	5.39	5.39	5.39	5.39	5.39	5.39	The risk	is 20%				

Table 6. Variance Analysis and residual resolution at 10% and 20% risk

AB: Combination of AandB Levels (multiply of A by B)

- y: Average of Effects
- E(): Effects of Factors Levels

Y: Predicted Functional Response

In this part the experiments variances trends and factors variation is considered to Fig. out if their fluctuations in studied amounts range affect on the results' variations. It should investigate that both significant factors and their interaction weather have any influence on the variation or not. This process shall conduct through the variance analysis (Peruchi *et al.* 2014). When actual results are better than expected results given variance is described as favorable variance. In common use favorable variance is denoted by the letter F. Variance analysis is usually associated with explaining the difference (or variance) between actual responses (oil adsorption) and the predicted responses via experiments models equations (Eq. 1 and 2) allowed for the good output. Variance of mentioned difference is calculated for each combination of treatments for each season while levels of factors were + or -, the Variance of results while factors are in + levels - levels appeared respectively. *F* test statistic is calculated dividing the greater variance to less variance of each

combination of treatments for certain levels (+ or -). According to the variance analysis which is presented in Table 6, all considered factors have no effects on variations at 10% risk but retention time at 20% risk affects the results variations in winter tests (6.7236 in winter row is greater than 5.39 in the last row). Moreover concentration in spring tests affects on the variation at 20% risk potentially.

CONCLUSIONS

As outlined above, studies of short term oil adsorption via pneumatophores in three experimental design factors at the twin replication blocks with randomized sampling showed the effects of season and weather conditions and retention time or contact time in different tidal situations and concentration levels at night and day. Results represented the significant factors in physical oil adsorption, while coming up of an oil slick toward the mangroves' habitat, due to tidal long waves. Physical adsorption was measured from 3.9% to more than 12% of pneumatophores mass, in two seasons and several factors. Experimental analysis may differentiate with the raw data; however, it can lead the research to reveal the factors affecting the less effective data, in reality. It supported the idea that daytimes or nighttimes may have negligible effects on oil adsorption rate, while concentration has significant effects. This approach demonstrated that the major portion of oil contamination would happen in the full tidal wave, while sea level rises from low tide to high tide. Retention time or contact time, which represents tidal waves period and its interactions with concentration level are two main factors with the most significant effects of oil slick on mangroves at night or day or in spring or winter. Observations illustrated a remarkable mass ratio percentage of crude oil content in the pneumatophores, which can lead to further serious hazards in mangroves' habitats. It means the short term physical adsorption is important, due to its biological and chemical damages on mangroves, in a long term after every oil spill.

The damages of oil contents on the mangroves have been estimated by some field studies carried out on oil pollution in mangroves (Duke *et al.* 2000, Duke and Watkinson 2002). Naidoo (2010) has considered oil contamination on the same species, revealed the long term effects on leaves. However, investigation of damages in a short term contact has not been considered, while it can be of significant importance.

Regarding the trends of the almost constant climate variables, in this research for the first time, some assumptions were considered on the ambient variables as constant trends. Therefore, the responses of investigated factors revealed that their interaction with other factors may change the adsorption amount. Further investigation in mangroves' morphology of epidermal is suggested to find out the physical adsorption mechanism and its persistence to conduct the results toward the appropriate cleanup process in oil spill disasters in the mangroves' habitats.

This research provides an overview of the role of mangroves in oil adsorption due to an oil slick threatening a coastline ecosystem. Results can be applied in off shore oil spill management, where the oil spill arrives at coastline and coastal vegetation. So the portion of oil adsorption into the valuable coastal plants such as mangroves can be estimated.

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