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RESEARCH ARTICLE

PREDICTIVE MODEL TO MONITOR THE SPREAD OF CRUDE OIL IN WATER SURFACE ENVIRONMENT

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ABSTRACT

Predictive model to monitor the spreading rate of crude oil in surface water environment was developed in this paper, this model were generated through an experiment performed, The experiments were performed to examine the rate of crude oil spread in surface water, This experiment yield allots of results, some of the results were applied to examine the rate of spread through graphs that were plotted, The generated model equation from the graph were resolved, the resolved equation yielded theoretical values, this values were compared to other measured values from different locations, both parameters generated the following model equations  $y = 1.909x + 20.24$  with  $R^2 = 0.999$ ,  $y = 9.968x - 1.951$   $R^2 = 0.995$ ,  $y = -1.988x + 13.55$   $R^2 = 0.998$ ,  $y = 9.977x - 4.528$   $R^2 = 0.999$ ,  $y = -1.777x + 9.166$   $R^2 = 0.991$ , and  $y = 3.635x + 1.257$   $R^2 = 0.987$ . This model if applied will predict the rate of spread of crude oil in surface water environment. The rate of marine habitats degradation in most rivers and lake is of serious concern, especially in developing nations where the level of environmental pollution of oil spill is very high, this model will go a long way in predicting the rate of pollution, and reduce the threat of life in the study area.

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INTRODUCTION

Continuous advances in knowledge have enlarged the demand of crude oil. More so crude oil and other petroleum products are transported across the world's oceans; the tendency of oil spill incident is always (Jenkins et al., 1991). In addition, pipeline blowouts, tanker loading and unloading, and other offshore industrial operations can also generate oil spills (Jenkins et al., 1991). Incidents like the Exxon Valdez and Torrey Canyon have heightened the public and government concern about environmental damages due to oil spills. People now expect oil industries to be well prepared and responsive to such emergencies (Jenkins et al., 1991). When crude oil spills on the surface of seawater, it undergoes various biological, physical, and chemical processes, collectively known as the weathering of the oil (Shweta, 2007). The weathering process includes spreading, evaporation, dissolution, dispersion, photochemical oxidation, emulsification, sinking, biodegradation, adsorption to suspended matter, and deposition on to the seafloor (Ezra et al., 2000; Mackay, 1987). Among these, the three dominant processes that change the physical characteristics are spreading, evaporation, and emulsification (Wei et al., 2003). Spreading is the most immediate and obvious process

undergone by the released crude oil (Cormack, 1999, Buschmann 2006). Consideration of oil spillage definitely integrate their interact between the composition and behavior of the oil with respect to time since it is essential to determine an effective oil spill response. The evaluation of past investigate has shown more focus on the laboratory methods and computerized modeling schemes to approximation the structure and contravention of emulsions after an oil spill. However, comparatively less effort has gone into the study of emulsions corresponding to actual field conditions. This study aims to simulate an oil spill at sea by generating a new method to make water in oil emulsions, without troubling the marine wildlife. Further, this investigation also attempts to analyze the viscosities of water in oil emulsions and determine appropriate emulsion breakers for different crude oil emulsions. The overall test design for the research includes a test apparatus for spreading and evaporation, three different crude oils, a mixing chamber to form the emulsion, and emulsion breakers. Experiments in this study attempt to gain a better understanding of the processes that occur after oil spills at sea. In particular, the rate of evaporation of different crude oils and the formation of crude oil emulsions on the sea surface have been investigated. It was observed that different crude oils behave differently when subjected to the same weathering (Shweta, 2007). After spreading, the brightness volatile mechanism of the crude oil starts evaporating. The

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rate of evaporation depends upon the vapor pressure and the volatile components current in the crude oil (Cormack, 1999, Bowden 2005). Further, the residual concentrated fraction of crude oil mixes with the surface seawater under the pressure of wind and wave action to form an emulsion (Wei et al., 2003). The emulsion formed can be either water in oil (w/o) or oil in water (o/w) emulsion (Shweta, 2007). The spreading of water droplets into the external phase of oil is called as water in oil (w/o) emulsion, while the dispersion of oil droplets in the aqueous medium/water is called oil in water (o/w) emulsion (Cormack, 1999). Water in oil emulsions may be tremendously stable because the water droplets (1-10  $\mu\text{m}$  diameter range) are held in a rigid structure by the components like asphaltenes, waxes, and resins (Cormack, 1999). On the other hand, oil in water emulsions is less stable because the inner droplet distance is comparatively very large and the oil droplets are relatively free to migrate (Cormack, 1999, Shweta, 2007). One way that oil enters in seaways is through natural seeps, accidental spills, pipeline leakage, urban runoff, wastewater discharge, industrial emissions, and other operations (Mackay and McAuliffe, 1988). Substantial effort has gone into documenting and considerate spill incidents and estimating the adverse effects of such discharge (Mackay and McAuliffe, 1988). The basic objective of the response system is to reduce the presence of surface slicks and to avoid beach pollution (Cormack, 1999). New technologies such as boom technology, skimmers, use of surfactants to disperse the oil into small droplets, and other various systems have emerged for controlling and treating the discharged oil (Mackay and McAuliffe, 1988). Nevertheless, due to the complexities of the weathering processes and slick movement, it is hard to predict the most proficient response technology (Daling, 1996). Crude oil is a mixture of a large amount of hydrocarbons, varying amount of waxes and low content of asphaltenes (Johansen et al., 1988). The carbon content normally is in the range of 83-87%, and the hydrogen content ranges from 10-14% (Sjöblom et al., 2002). In addition, small amounts of nitrogen, sulfur, oxygen, nickel and vanadium may be found in the crude oils (Sjöblom et al., 2002). Crude oils from different regions have different properties (Elsharkawy et al., 1995). The physical properties that mainly affect the behavior and persistence of crude oil spilled at sea are described in the following subsections. Disastrous oil spills often occur in near shore regions, upsetting coastal ecosystems (Bartha and Atlas, 1977). According to a 1987 U.S. Coast Guard report (USCG, 1987), ports and harbors, river channels, and open protected waters receive the vast bulk of oil spills, in difference to offshore areas. Texas has 2360 miles of shoreline and two of the country's top 10 ports, Houston and Corpus Christi. Most of this handles 50% of the nation's crude oil import, while 80% of Corpus Christi's business is gasoline related. As a result, Texas coasts are particularly susceptible to catastrophic spills. After crude oil enters the marine system, the mixing circumstances in the natural water impact both the size sharing and chemical composition of entrained oil droplets. Various chemical composition as a function of droplet size will be reflected as a difference in bioavailability (Shaw and Reidy, 1979). Colloidal oil droplets that can be taken up as food by sieve feeders and small grazers, at the same time as dissolved oil constituents could enter the circulatory system through the gills of all animals. In fish, hydrocarbons taken up in the course of the gut from food that are deposited in the liver, whereas hydrocarbons engrossed from water preferentially

accumulates in muscle tissue. Consequently, it is achievable that differences in the structure of entrained oil may result in kinds of oil exposures with markedly different biochemical and physiological consequences. One fraction of this study investigates the effects of integration shear and preliminary slick thickness on crude oil entrainment pace and droplet bulk allocation. A laboratory study was conducted in which the chemical composition and droplet size distributions of the oil-water dispersions were analyzed at different levels of mean shear rates and initial oil loadings. Because of the controlled nature of the examination, insights on the relationship between subsurface generated shear and oil entrainment were gained. In addition, a model describing oil constituent partitioning at these circumstances can be applied for toxicity or chemical partitioning studies in laboratory apparatuses. To counter potential environmental damages resulting from crude oil spills, chemical dispersants are being investigated for near shore marine oil spill response. Besides a lower cost of implementation than most perfunctory responses, other potential benefits include improved biodegradation due to higher bioavailability and greater dispersion in water, protective shoreline deposition (Page et al., 2000b). However, near shore environments can vary considerably in mixing energy and salinity, two parameters that are likely to impact dispersed oil droplet coalescence and perpendicular transport. To study the potential impacts of the near shore environment on dispersant efficiency, a laboratory study was conducted to determine the effects of salinity and mixing energy on dispersed crude oil coalescence. Size allocation of dispersed oil droplets in water has been noted as a significant measure of dispersant efficiency. Mackay et al. (1986) applied their model concept of a critical oil droplet diameter, exceeding most oil resurface and below which most oil remains dispersed (NRC, 1989). The superior the mixing energy, the larger this critical droplet diameter will be (NRC, 1989). However, Mackay's model does not detail mechanisms of droplet interactions or predict likely droplet size distributions as required for preserved mass based models in an exterior spill, oil first forms a slick that is then broken into smaller droplets and entrained in the water column. This entrainment can result from primarily physical factors such as wind, currents, and wave action, or from chemical factors such as the addition of surfactant based chemical agents. Once entrained, oil can be truly dissolved, or form particles in the form of emulsions, or can associate with organic or inorganic materials (Neff, 1979). For this study, oil compounds existing in the water column on a molecular level are defined as "dissolved". Alternatively, larger oil droplets with radii of tens to hundreds of microns are defined in this study as "colloidal". The organisms that reside in the water column are vulnerable to chemical uptake in some or all of these forms that oil can assume. Understanding the dissolution of PAHs is critical for estimating exposure, uptake, and bioaccumulation by affected organisms (Neff, 1979, Baude 2005). Due to their non polar, hydrophobic nature, PAH solubility's are comparatively low. PAHs are usually less soluble in aqueous salt solutions such as seawater than in pure water (Xie et al., 1997). The solubility behavior of a compound in a complex mixture such as crude oil may not correspond to that predicted from pure component data (Banerjee, 1987). The aqueous solubility of individual PAHs decreases when they are part of a mixture because the pure component has a stronger affinity for the non-polar oil phase than the water (Shiu et al., 1990). Lee et al. (1992 a, b)

described the partitioning of PAHs into water from diesel fuel and coal tars using a Raoult's law convention for solute activity coefficients and assuming ideal behavior. Page *et al.* (2000a) applied the same modeling paradigm in describing partitioning of PAHs into water from crude oil.

## MATERIALS AND METHODS

The sample of Bonny light weighted crude oil was collected from the Nigerian Agip Oil Company, while dispersant (isopropylene alcohol) was collected from NNPC Port Harcourt laboratory. Container and instruments were obtained from the department of chemical/petrochemical engineering laboratory in Rivers State University of Science and Technology, and the research work involves the laboratory analysis to determine the effect of dispersant (isopropyl alcohol) on the spreading rate of oil spill on calm water environment, and to determine the effect of the spreading rate of crude oil on calm water environment. Standard materials were applied to measure the corresponding variables, responsible for the spreading rate of crude oil in water, following the experimental process, some of the constants in this study were; amount of oil used (50ml per trail) Size of container (50cm × 41cm × 13cm), Shape of container (Rectangular), Amount of water used (14 litres). Number of repeated trails (3), type of water (tap water), temperature used (room temperature – 21<sup>0</sup>C), type of oil (medium weight crude oil). Size of pixel glasses (50cm × 80cm). Rate at which the oil is spilled into water, Rate at which dispersant is spilled on crude oil, pixel glass height above water (7cm) and Syringe height above water (1cm).

### Experimental set- up procedure

The experimental setup is to investigate the spreading rate of crude oil sample in surface water environment was carried out using the following materials and method and reagents, crude oil and dispersant (Isopropyl alcohol) on calm water inside application rectangular container were used to explain the responding variable on the oil as well as the spreading rate. In carrying out this experiment the following procedures was applied such as, ensuring that pixel glass was contained, after reviewing the diameter of oil drop on water, north, south, west and east as well as the average diameter of oil droplet on water. The experiments were prepared fills one container with 14 litres of water and allow water in the container settle and at room temperature (21<sup>0</sup>C). Place the pixel glass grid on top of the container, setting the initial radius of spill to be 5cm. The diameter of the hole in the centre of the pixel glass is measured and considered the spill diameter. The spreading rate of crude oil in calm water without application of dispersants as well as fill the syringe with 50ml of crude oil and then squeeze the syringe gently and ensure that all the crude oil in it is disposed into the pixel glass, wait until the oil has stopped spreading and has taken the spill diameter of the pixel glasses. Remove the pixel glass gently, start the stop watch and then watch the spreading length on the ruler on the body of the transparent container. Record the spreading rate in cm/s and dispose oil and clean up. Start by recovering the oil with isopropylene pads and take the pads and put them in a doubled up trash bag and repeat the experiment for three trails and record your results. The effect of the spreading rate of crude oil on calm water on application of dispersants, using

the same experimental preparations repeating the same experimental preparations until the third step in, fill the syringe up to 20ml of the dispersant (isopropyl alcohol) and then squeeze the syringe gently and ensure there is no spill, allowing all the dispersants to spread on the oil surface as well as allow the oil to settle then remove the pixel glass, start the stop watch immediately, watch and record the spreading length on the ruler on the body of the transparent container and record the spreading rate in cm/s. Dispose the oil and clean up, start by recovering the oil with isopropylene pads. Take the pads and put them in a doubled up trash bag as well as repeat the experiment for three trails and record your results at time 30 seconds. This experiment generated numerous results; some of the results were applied to monitor the rate of spread applying oil dispersant, the results were plotted developing some equations that were resolved, leading to theoretical values, the theoretical values are compared with other result from other locations in the study area.

## RESULTS AND DISCUSSION

The predictive model results obtained from this investigation are presented in Tables and Figure as shown below.

**Table 1. Comparison of theoretical and measured at various stock**

Stock	Theoretical values of oil equivalent at various stocks	Measured values of oil equivalent at various stocks
1	18.45	18.55
1.5	17.47	17.33
2	16.5	16.44
2.5	15.52	15.56
3	14.55	14.60
3.5	13.57	13.45
4	12.6	12.57
4.5	11.68	11.68
5	10.65	10.72

**Table 2. Comparison of theoretical and measured values of oil equivalent at various stocks**

Stock	Theoretical Result of oil equivalent values	Measured Result of oil equivalent values
1	9.3	8.9
1.5	14	13.8
2	18.77	18.04
2.5	23.46	21.1
3	28.1	27.6
3.5	32.85	32
4	37.54	37.71
4.5	42.24	43.88
5	46.93	48.54

**Table 3. Comparison of theoretical and measured values of oil equivalent at various stocks**

Stock	Theoretical Result of Transmittance	Measured Result of Transmittance
1	11.41	11.63
1.5	10.45	10.55
2	9.49	9.66
2.5	8.53	8.39
3	7.62	7.68
3.5	6.6	6.58
4	5.64	5.6
4.5	4.68	4.44
5	3.72	3.78

**Table 4. Comparison of theoretical and measured values of oil equivalent at various stocks**

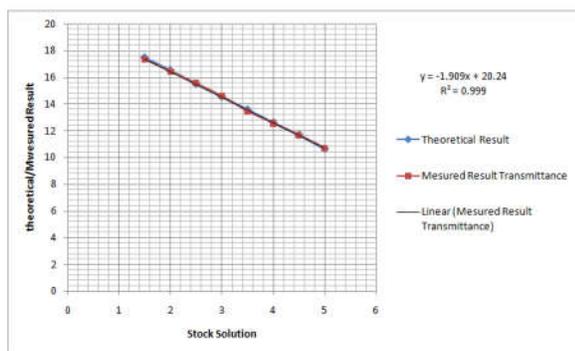
Stock	Theoretical values of oil equivalent	Measured values of oil equivalent
1	5.04	5
1.5	10.54	10.15
2	15.1	15.25
2.5	20.14	21.11
3	25.17	25.45
3.5	30.21	30.19
4	35.24	35.33
4.5	40.2	40.48
5	45.32	45.22

**Table 5. Comparison of theoretical and measured of transmittance values at various stock**

Stock	Theoretical Result of Transmittance	Measured Result of Transmittance
1	7.36	7.44
1.5	6.47	6.66
2	5.57	5.59
2.5	4.67	4.82
3	3.37	3.68
3.5	2.88	2.75
4	1.9	1.83
4.5	1	0.98
5	0.18	0.77

**Table 6. Comparison of theoretical and measured values of oil equivalent at various stocks**

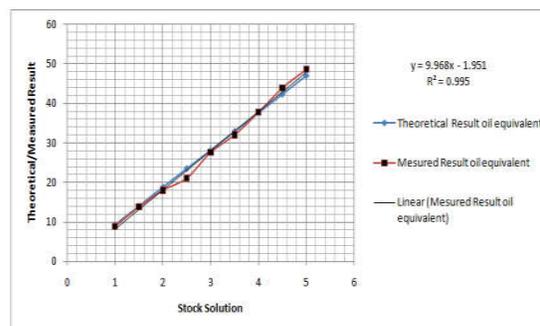
Stock	Theoretical value of oil equivalent	Measured values of oil equivalent
1	4.89	3.93
1.5	6.68	7.3
2	8.47	9.39
2.5	10.26	10.47
3	12.05	11.97
3.5	13.84	13.53
4	15.64	15.58
4.5	17.99	17.99
5	19.22	19.32



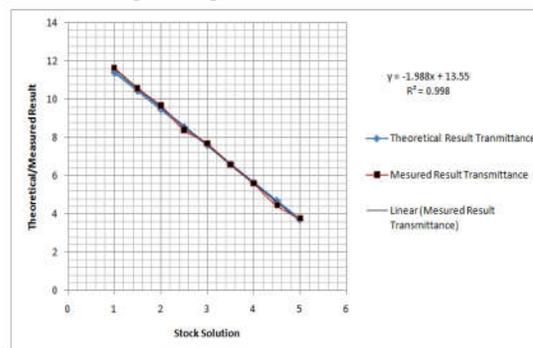
**Fig. 1. Comparison of theoretical and measured values of spreading rate of transmittance at various stocks**

Figure I shows that the theoretical and measured values displayed its spread rate of the crude in were found decreasing down in a linear form, this condition explain the effect of dispersants that has influenced the degradation of the crude. The results displayed  $y = -909x + 20.24$  and  $R^2 = 0.999$ . Figure 2 the theoretical and measured values displayed its rate of spread in a linear form, but the measured developed some slight fluctuation, both parameters were found to be

increasing in its spread rate, this condition can be attributed to the rate of velocity of flow. This may not be that the concentration has not reduced, because the theory of diffusion may have take place including the application of dispersants, both parameters displayed best fit equation of  $y = 9.968x - 1.951$  and  $R^2 = 0.995$ . From figure 3 the theoretical and measured values were found decreasing, its rate of spread showing that the initial concentration of the crude were found to degrade with respect to time and the influence including dispersants application in the river, the condition can be attributed to the level variation of time, and other constituents that is deposited on the surface water. Both parameters displayed its best fit equation of  $y = -1.988x + 13.55$  and  $R^2 = 0.998$ . Figure 4 shows that theoretical and measured values displayed its rate of spread in linearly form increasing due to variation in length and other deposited physiochemical parameters that have influence the increase of spread in the surface water, the parameters developed its beat fit equation as  $y = 9.977x - 4.528$  and  $R^2 = 0.999$ , In figure 5 theoretical and measured values level of spread were found decreasing with increase in stock solution showing that the dispersant applied to clean up the spill were found to active as presented from the figure, other influence may be from the level velocity that include tidal effect on the surface water that may have contributed to rapid decrease in concentration with respect to length and stock solution. The parameters generated its best fit line equation as  $y = 1.777x + 9.166$  and  $R^2 = 0.991$  Finally Figure 6, Illustrate the theoretical and measured value and the results obtained were found in similar condition like that of Figure 4 they increased with time base on the variation of tidal effect on the surface water including the variation from the stock solution influenced by the length of spread, the application of dispersant that develop to stock may be influenced by the rate of velocity both parameters displayed the best fit line equation as  $y = 3.635x + 1.257$  with  $R^2 = 0.987$ .



**Fig. 2. Comparisons of theoretical and measured values of spreading rate at various stocks**



**Fig. 3. Comparison of theoretical and measured of transmittance values at various stock**

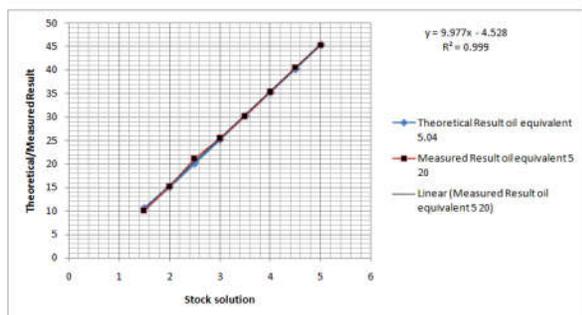


Fig. 4. Comparison of theoretical and measured of oil equivalent values at various stock

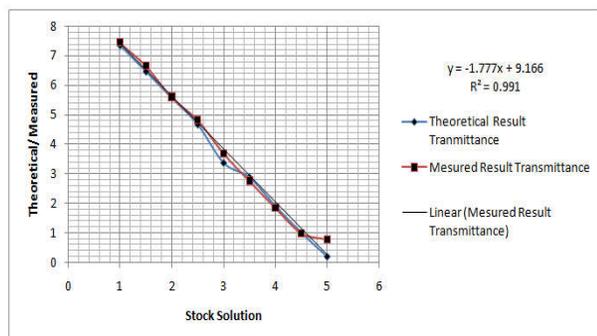


Fig. 5. Comparison of theoretical and measured of transmittance values at various stock solution

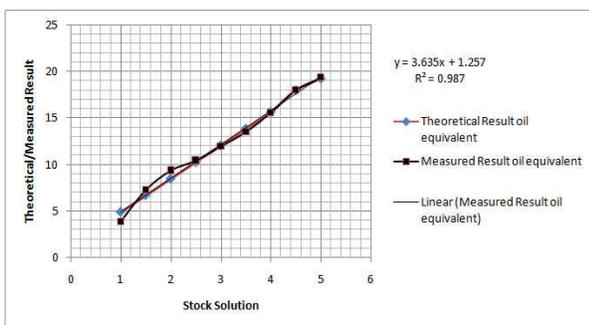


Fig. 6. Comparison of theoretical and measured of oil equivalent values at various stock

### Conclusion

Predictive model to monitor the spread rate of oil spill in surface water environment were developed. The level of oil spillage in water surface is a serious concern and there is need to pay a serious attention to this type water pollution. This type of contaminant degrade the quality of our rivers lakes and ocean, all the aquatic habitats are dying every time from this type of water pollution, therefore there is need for preventive model to be established. The developed model for water surface environment can be applied to monitor the spread rate of oil spill in surface water. The theoretical model compared favourably well with the measured values from other station in the study area, this model takes care of the lake and rivers that are calm, this implies that the rate of tides may not be compared to that of ocean and therefore the water from calm environment velocity and other physiochemical parameters will vary. The level of degradation of every aquatic habitats may vary from Atlantic ocean where the velocity are very high, most river, lake in developing nation are source of drinking water. Finally the cost treating water from river and lakes for those areas that treat surface water for drinking or

industrial use will be very high. Therefore this model will be useful to prevent this type of life.

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