FULL FACTORIAL ANALYSIS OF PARAMETERS USED FOR CRUDE OIL CLEANUP FROM CONTAMINATED SOIL USING ZNCL$_2$ BASED DEEP EUTECTIC SOLVENT (DES) AS SOLVENT

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ABSTRACT

A new strategy of crude oil cleanup from contaminated soil using synthesized DES based on zinc chloride/acetamide was studied. The ability for cleaning up crude oil from soil was investigated under different condition and was optimized using full factorial design of experiment. Physiochemical analysis of synthesized DES showed viscosity to be 26.0cp at 28 °C, pH was found to be 5.4, density was 1.32 g/cm^3 and the flammability test confirmed the solvent to be non-flammable. Factors considered for the optimization of cleanup include solvent volume, temperature and contact time. Experiment was carried out in duplicates generating 16 runs giving percentage yields of 40%,54%,58%, 56%, 44%, 56%, 28%, 78%, 41%, 54%, 58%, 54% 48%, 60%, 32% and 81% from standard run order of 1- 16 respectively. From the results, run 16 gave the best yield of 81% with optimal conditions (A+ B+ C+) at 25 mL solvent volume, 120°C temperature and 30 min contact time. Run 7 gave the least yield of 28%. Results were subjected to various analyses using Minitab 18.0 to find significant factors, effect of factors and interactions. Analysis of variance (ANOVA) showed that at SV and T were significant factors at p = 0.05. However, CT was statistically not significant at the same confidence level. Perato chart ranked the order of factor and interaction effect as: SV > SV*T*CT > SV*CT > T > SV*T > T*CT > CT with SV being the most effective factor and CT being the least effective at P = 0.05. Main effect analysis showed that SV is the most significant factor with individual effect of 61% yield followed by T with individual yield of 56% and CT is the least with yield of 53%. Model Summary for the optimization of cleanup parameters showed the predicted R-Squared value of 0.972 which is in reasonable agreement with the R-Squared adjusted value of 0.9897. From the results, the application of the DES as solvent for crude oil cleanup was found to be effective with optimal cleanup at run 16.

Keywords: Deep eutectic solvent, ionic liquids, cleanup, Total petroleum hydrocarbon

INTRODUCTION

Oil spillage is the discharge of crude oil into either soil or water a result of activities such as accidental spillage or intentional spillage. Oil-spill pollution is hazardous and problematic worldwide (Okereke *et al.*, 2007). Oil sands are combination of crude oil, sand and water which is bound together (Fekete, 2009). These can be treated and be converted into gasoline, diesel fuels and other

useful products. Problems associated with crude oil pollution have been present since the beginning of petroleum exploration in Nigeria (Okoh *et al.,* 2001). Contaminated soil damages body system due to the accumulation of pollutants in tissues of animals and plant which may result to mutations and possibly death on the long run. Spillage of crude oil has the tendency to cause serious health implications to organisms in the sea and those close to the shore (Rodríguez-Martínez, 2006).

In Niger Delta, large amount of harmful chemicals entering the environment are on the increase (Eregha & Irughe, 2009; Linden & Palsson, 2013). These harmful chemicals get into the environment through various ways such as leaching and seepage, extraction, transportation, distribution, storage and refining (UNEP, 2011). Human activities which contaminate the environment can be controlled to reduce crude oil spillages by monitoring of oil infrastructure with state-of-the-act technology (Zabbey, 2016). Crude oil spillage cannot be controlled until proper policies and improved technologies for detection are implemented. Other ways in which spillage can be prevented from getting into the environment is by controlling leakages from wellhead, pipelines, overflow and stop dumping of contaminated soil (Kadafa, 2012; Nwilo & Badejo, 2006).

Deep Eutectic Solvents (DESs) are combination of two compounds that has the lowest melting point and depression of freezing point related to the strength of interaction between the two components (Abbott *et al.,* 2003). They are liquids at ambient temperature and have properties that are very similar to ionic liquids (ILs). DES and ILs are more environmentally friendly than traditional volatile organic solvents because of their near-zero volatility, suggesting that these are attractive alternatives for solvents use in chemistry. Deep Eutectic Solvents (DESs) are possible green replacements for organic solvents for chemical reactions, extractions and biotransformation. They are not volatile, stable to heat and their solvation properties vary by altering the cation or anion. (More *et al.,* 2014). These types of solvents have high capacity to make new technologies which have more potential applicability.

Solvent extraction is a widely used technology for soil remediation, in which contaminants are removed from soil using a single or mixture of solvents (Gan *et al*., 2009). Soil contaminated with crude oil can be cleaned using reagent and solvent which are capable of removing the contaminants from the soil (Lim *et al*., 2016 ; Yao *et al*., 2012).

The aim of this paper is to carry out full factorial analysis of cleanup parameters used in crude oil cleanup from contaminated soil using $ZnCl_2$ based Deep eutectic solvent (DES) as solvent.

MATERIALS AND METHODS

Synthesis of deep eutectic solvent (DES)

Zinc chloride/Acetamide DES was prepared by heating $ZnCl_2$: (acetamide) CH_3CONH_2 in a 1:4 molar ratio. $ZnCl_2$ (0.125 mol = 17.0393 g) and acetamide (0.5 mol = 29.5350 g) were

weighed and then transferred to a beaker (Kumari *et al.,* 2016). The beaker was placed on a magnetic stirrer at 80 °C and stirred at 300 rpm until a homogenous liquid formed.

Sample collection

The contaminated soil was collected within Warri Refining and Petrochemical Company Limited (WRPC), a Subsidiary of Nigerian National Petroleum Corporation (NNPC) Delta state, Nigeria. Six samples were taken within the depth of 0 to 10 cm each around pump house A and used to form a composite sample. Soil samples were poured inside sterile labeled polyethylene bags which were carried to the laboratory. Clean uncontaminated soil was collected within the same location and poured inside sterile labeled polyethylene bags too. Samples were prepared through hand picking of dirt, stone, irons etc., air dried and filtered using 2 mm sieves.

Optimization

The soil extraction conditions were optimized using full factorial design of experiment (FFD). In this study, the factors adopted were solvent volume, temperature and contact time. Table 1 illustrates the coded and actual operating conditions of the factors to be optimized.

Table 1: Parameters for the full factorial design of experiment for crude oil cleanup from contaminated soil using DES based on $ZnCl_2/CH_3CONH_2$

Factors	symbols	Low level (-)	High level (+)	unit
Solvent volume	SV	15	25	mL
Temperature	T	100	120	˚C
Contact time	CT	15	30	Mins

RESULTS

Results for the physiochemical properties of synthesize DES is presented in Table 2. The parameters analysed for the DES include- pH, viscosity, density and flammability test.

Table 2: Physiochemical Properties of DES

Parameter	Values
pH	4.3
Viscosity	26.0 cP (28°C)
Density	1.32 g/cm^3
Flammability	Not flammable

Table 3: Results for full factorial design of experiment for crude oil cleanup from contaminated soil using DES based on $ZnCl_2/CH_3CONH_2$

Runs	SV	T	CT	%Yield
1	-	-	-	40
2	+	-	-	54
3	-	+	-	58
4	+	+	-	56
5	-	-	+	44
6	+	-	+	56
7	-	+	+	28
8	+	+	+	78
9	-	-	-	41
10	+	-	-	54
11	-	+	-	58
12	+	+	-	54
13	-	-	+	48
14	+	-	+	60
15	-	+	+	32
16	+	+	+	81

key: +high-level and - low level

Table 4: Analysis of Variance (ANOVA) for the optimization of cleanup parameters of soil contaminated with crude oil using type IV DES based on $ZnCl_2/CH_3CONH_2$

	Source	DF	MS	F-Value	P- Value
Model		7	425.82	109.89	0.000
Linear	SV	7	1296.00	334.45	0.000
	T	1	144.00	37.16	0.003
	CT	1	9.00	2.32	0.061
2 way interaction	SV*T	1	110.25	28.45	0.001
	SV*CT	1	650.25	167.81	0.000
	T*CT	1	42.25	10.90	0.011
3 way interaction	SV*T*CT	1	729.00	188.13	0.004
Error			2.06		

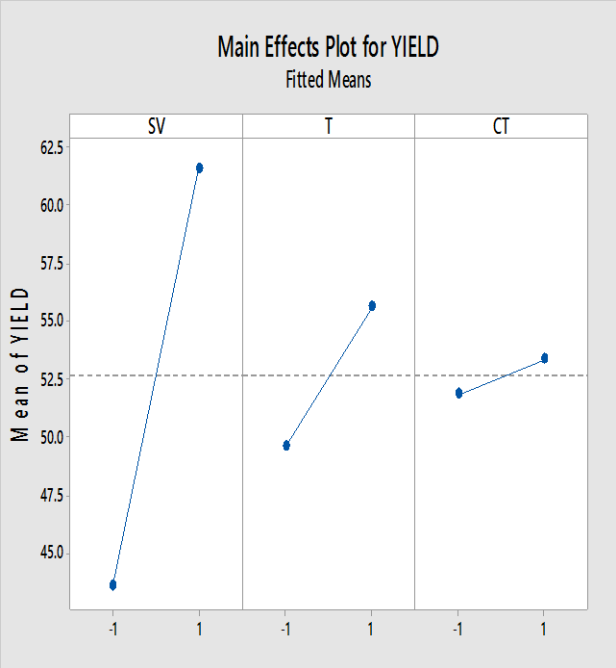

Figure 1: main effect plots for yield for the optimization of cleanup parameters of soil contaminated with crude oil.

SV=solvent volume, + = high level
T= temperature, - = low level
CT= contact time

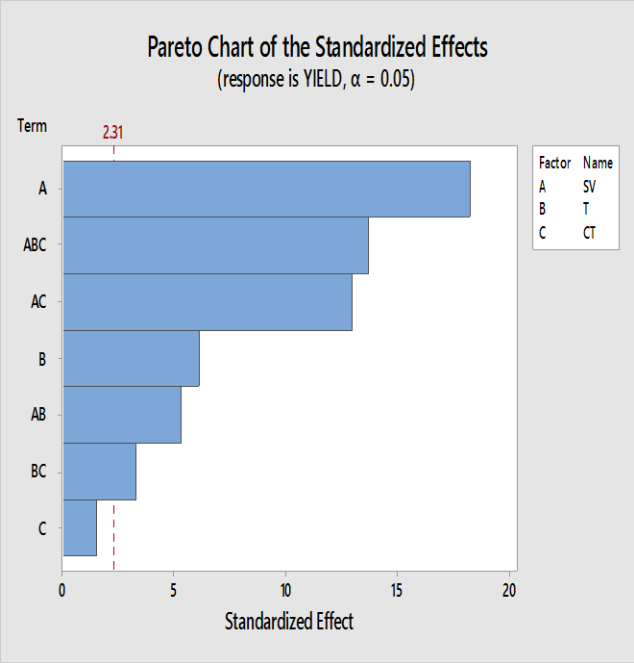

Figure 2: Pareto chart of standardized effects for the optimization of cleanup parameters of soil contaminated with crude oil.

A=solvent volume B= temperature C= contact time

AC, AB, BC, ABC= factors interaction

DISCUSSION

Optimization of cleanup parameters

The result of the optimization parameters for the cleanup of crude oil from contaminated soil using type IV DES based on $ZnCl_2/CH_3CONH_2$ using full factorial design of experiment (FFD) is shown in Table 3. The experiment is carried out in duplicate which produce 16 runs with their corresponding percentage yields. The result shows run 16 has the best yield of 81% while run 7 gave the lowest yield of 28%.

Analysis of variance (ANOVA)

ANOVA results for the optimization of cleanup parameters of crude oil from contaminated soil using the synthesized DES is presented in Table 4. The Table indicates that in both the linear parameters SV and T, the effects are significant on removal of crude oil from the contaminated soil at p = 0.05. Similarly, the response levels of the interactions of independent variables SV*T, SV*CT, T*CT are all significant at p = 0.05. However the independent variable CT is statistically not significant at p = 0.05. Likewise F-values of all parameters and interactions were above critical values which implies they are all significant at p = 0.05 except the F- value of CT which is 2.31 and hence not a significant factor. The Predicted R-Squared value (R^2 = 0.9721) and the adjusted R^2 value (0.9807) indicate that the model was well correlated.

Main effect analysis

The main effects plot shows how each of the analyzed responses changes within the boundaries of the stated upper and lower limit factor values. Fig. 1 shows that the increase in values for SV, T and CT stimulated the raise in the cleanup efficiency. Solvent volume SV has the highest increase (61%) when the values change from low to high (15 to 25 mL) cleanup was significantly enhanced. This shows that increase in solvent volume promotes extraction of the crude from soil as the interaction between the oil contaminants and solvent is enhanced. Crude oil desorption from the soil surface is favored at higher volumes. This result is in agreement with a study by Li *et al*, (2012) and another study by Islam *et al*., (2012) which shows that higher solvent volume favors higher removal efficiency of oil contaminants from soil.

Effect of increase in temperature shows increase in cleanup efficiency of 56%. As the temperature values changes from low to high, viscosity reduces; this invariably will enhance the removal of oil from soil. The reduction in viscosity will lead to the mobilization of oil, which creates an avenue for its separation from soil (Alomair *et al*, 2014; Urum *et al*, 2005).

The response observed for the change in values from low to high of contact time CT (53%) is not very steep as seen in the graph. This means that there is no much increase in cleanup efficiency when values change from low to high values. A study by Taki *et al.*, (2018) gave similar results which showed

that crude oil removal increased little as run time is increased.

Pareto analysis

The analysis of the Pareto chart of standardize effect of crude oil cleanup using DES as solvent (Fig. 2) ranks the order of effective variables on crude oil cleanup is SV > SV*T*CT > SV*CT > T > SV*T > T*CT. the factor CT falls below the red line which means it has a negative effect on the cleanup of crude oil from contaminated soil using the synthesized DES. The pareto chart of standardize effect indicates that cleanup efficiency is not directly influenced by contact time, the effect of which is only significant in terms of interactions. This is in agreement with a study by Tejowulan and Hendershot (1998) which reported that clean up efficiency is not dependent on contact time.

CONCLUSION

Full factorial design (FFD) was used to optimize crude oil cleanup from soil using DES based on $ZnCl_2/CH_3CONH_2$. Factors that were employed in the optimization includes solvent volume, temperature and contact time. Analysis of the results showed that the solvent volume and temperature are crucial factors for cleanup. The optimum conditions for cleanup were found to be (A+ B+ C+) at 25 mL solvent volume, 120°C temperature and 30 min contact time according to the quadratic model in run 16. Under these experimental conditions (A+ B+ C+), crude oil removal was 81%. This infers that the model used was adequate and can be applied in crude oil cleanup from contaminated soil.

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