Single and Mixed Surfactants-aided Removal of Mixed Toxic Metals and Petroleum Hydrocarbons in Contaminated Soil: Batch and Column Studies

Audu P[1,2]*, Wuana RA[1], Eneji IS[1] and Itodo AU[1]

[1]*Department of Chemistry, College of Sciences, Federal University of Agriculture, Makurdi, Nigeria*

[2]*Environment Health and Safety Department, OVH Energy Limited, Onne Terminal, Nigeria*

*Corresponding author: Audu P, Department of Chemistry, College of Sciences, Federal University of Agriculture, Makurdi, Nigeria, Tel: +2348111753334; E-mail: pius.audu@yahoo.com

Abstract

Indiscriminate disposal of different kinds of wastes on soil at auto-repair sites in Makurdi, Nigeria is becoming an environmental issue and the restoration of impacted soil is a challenge. The potential of single surfactants and their binary blends to remove mixed contaminants were evaluated via bench scale soil washing experiments. Impacted soil samples from auto-repair site, located in Makurdi Nigeria was assayed for Cd, Cu, Ni, Pb, Zn and total petroleum hydrocarbon (TPH) concentrations. Batch and column soil washing experiments were designed to assess the effectiveness of the single surfactants (sodium dodecyl sulphate (SDS) and Triton x-100 or their binary blends to remove the mixed contaminants with the view to optimizing operating conditions such as surfactant initial concentration (10-150 mM), surfactant initial pH (3-12), soil/liquid ratio (1:50-1:1 g/mL), washing time (30-240 min) and % w/w of surfactant in blend. Prior to soil washing, the critical micelle concentration (CMC) of the surfactants were measured to be: SDS (8.50 mM) and Triton x-100 (0.25 mM. Results of batch soil washing experiments for the two surfactants showed that % contaminants removal increases as the initial surfactants concentration increases, decreases as pH increases, increases as S/L ratio decreases and increases as washing time increases. Results of column experiment showed that % contaminants removal decreases with time. Synergism parameter showed more synergistic effects in the binary blend and hence was more effective than the individual surfactants. Reasons for these behaviors have been suggested.

Keywords: Soil; Contaminants; Concentration; Surfactants; Washing; Auto-mechanic

Introduction

In Makurdi, Nigeria, several portions of agricultural lands have been contaminated through unregulated human activities such as the several auto-mechanic sites across the metropolis [1,2]. The net result is large scale contamination of the receiving soils and subsequent leaching of some of the contaminants into the groundwater, which may act as a source of water supply for domestic use of inhabitants of the localities. The Auto-mechanic village in Apir, Makurdi Nigeria has been in operation for over 25 years now and still counting. Several researchers have carried out determination of potentially toxic metals (PTM) and total petroleum hydrocarbons (TPH) in the soil under this land use, but effort towards remediating the soil is still sketchy.

Remediation of soil contaminated with mixed contaminants is usually difficult and compounded due to the adsorption on the soil matrix and the low solubility of these contaminants, among others. It has been shown that the contaminants which are more insoluble in water remain longer in the soil matrix [3]. Furthermore, in Makurdi, enforcement of environmental protection regulations is weak, and this encourages indiscriminate contamination of soils in many parts of the state. In many cases, inhabitants of contaminated area may want to remediate the soil but have little or no idea of any cost effective and easy to apply techniques that would be efficient [4]. Several techniques have been tested in mixed contaminants removal from soils. However, surfactant-aided soil washing has shown to be highly cost effective [5]. Hence the need for this study.

A surfactant is a material that, when present at low concentration in a system, has the property of adsorbing onto the surfaces or interfaces of the system and altering to a large extent the surface or interfacial free energies of the surfaces (or interfaces) [6]. Two mechanisms are distinctly involved in surfactant aided soil washing: one mechanism takes place below the critical micelle concentration (known as mobilization or contaminants rollup mechanism) and the other takes place above the critical micelle concentration (referred to as solubilization mechanism) [7]. This work employs surfactant-aided washing of mixed contaminants in the soil being used for auto-mechanic activities and aims to provide a cost effective method of remediating impacted soil around the auto-repair sites.

Materials and Methods

Chemicals that were used in this work included: sodium dodecyl sulfate (SDS) (99.0% GC), Triton X-100 (98%) for soil washing; Nickel (II) nitrate hexahydrate (98 w/w%); copper (II) nitrate trihydrate (99.0 w/w%); zinc nitrate hexahydrate (99.0 w/w%); cadmium nitrate tetrahydrate (99.0%) and lead nitrate (99.0 w/w%) was used to spike soil sub-samples to simulate artificial contamination with Ni, Cu, Zn, Cd and Pb, respectively. All reagents were analytical grades and were used as received without further purification.

Surface soil (0-20 cm) composite samples were collected from Apir auto-mechanic village Makurdi Nigeria and assayed for Cd, Ni, Pb, Zn, Cu and TPH. The concentrations of the metals were built up by spiking the soil with calculated amount of nitrate salts of the various metals.

The critical micelles concentrations of the two surfactants were determined using dilution principle described by Oremusova and Lengyel [8].

Batch soil washing experiment was performed using the method described by Peng et al. [9]. The washing solutions for both surfactants were prepared using 10 mM, 50 mM, 100 mM and 150 mM. pH was varied from 3, 5, 7, 9 and 12. Soil/liquid ratio was varied from 1:1, 1:10, 1:20 and 1:50. Washing time was varied from 30 min, 60 min, 90 min, 120 min, 150 min, 180 min, 210 min and 240 min. Column washing experiments were carried out using the procedure described by Yang et al. [10] with some modification. An optimization model was used to establish the optimum surfactant concentration, soil/liquid ratio, initial surfactant pH and washing time generated in the batch soil washing experiments, and this optimum condition were used to conduct the column studies.

Results and Discussion

Soil spiking

The soil sample was deliberately contaminated (spiked) with a calculated amount of the nitrate salts of each metal which was expected to increase the concentration to 1000 mg/kg, so as to obtain a rather homogeneous sample, with consistent PTMs concentration, speciation, and contamination process and period. The concentrations of PTMs in the soil sample after spiking were as shown in Table 1.

Metal	Conc. in Neat sample (mg/kg)	Conc. in spiked sample (mg/kg)	Recovery (%)
Cd	1.0 ± 0.1	1,138.00 ± 1.02	114
Pb	82.78 ± 0.03	999.07 ± 0.5	92
Ni	16.25 ± 0.05	1,048.13 ± 1.01	103
Zn	75.46 ± 0.06	1,057.80 ± 1.04	98
Cu	28.74 ± 0.02	851.35 ± 0.2	82
TPH	355.10 ± 0.04	N/A	N/A

Table 1: Mean Concentration of Toxic Metals and TPH in the Soil Sample Before and After Spiking with Nitrate Salts of the Metals.

Concentration of Cd increased from 1.0 mg/kg to 1,138.0 mg/kg implying a percentage recovery of 114%. Pb concentration increased after spiking from 82.78 mg/kg to 999.07 mg/kg with a percentage recovery of 92%. Ni concentration increased from 16.25 mg/kg to 1,048.13 mg/kg having a percentage recovery of 103%. Zn concentration increased after spiking from 75.46 mg/kg to 1,057.80 mg/kg indicating a percentage recovery of 98%. Cu concentration increased from 28.74 mg/kg to 851.35 mg/kg with a percentage recovery of 82%. The percentage recovery is calculated using the equation:

$$\% \text{ Recovery} = \frac{\text{Observed - Neat}}{\text{Expected}} \times 100 \qquad (1)$$

Where 'Observed' is the spiked sample value, 'Neat' is unspiked sample value and 'Expected' is the amount spiked into sample. USEPA recommended that controlled spike should have a percentage recovery value within 80-120% [11]. The percentage recovery values shown in Table 1 were within the recommended range, indicating that the spiking was carried out in a controlled process.

Determination of surfactant CMC

The contaminant removal experiment was carried out with the aid of two surfactants, viz-an anionic surfactant SDS and a nonionic surfactant Triton x-100. It is necessary to determine the CMC of the surfactants before the washing process so as to be guided on the concentration of washing solution to be prepared. Using dilution principle, Figure 1a shows a plot of experimental data of concentration verses conductivity for determination of CMC of SDS. The plot shows a linear behavior with two different slopes, the concentration at the point of intersection of the two straight lines (0.0085 mol/dm^3 or 8.5

mM) gives the CMC of the surfactant at 25°C. Figure 1b shows a plot of experimental data of concentration verses kinematic viscosity at 40°C for determination of CMC of Triton x-100. Again, the plot shows linear behavior with two different slops, the concentration at the point of intersection of the two straight lines (0.25 mM) gives the CMC of Triton x-100. These values compare favourably with the values 8.0 mM to 8.6 mM and 0.22 mM to 0.24 mM reported in literature respectively for SDS and Triton x-100 [12-14]. In Figure 1a, at concentrations above the CMC, conductivity was decreasing slowly with decreasing concentration (dilution) due to the availability of micelles, and after the CMC, conductivity started decreasing sharply with decreasing concentration. In Figure 1b, viscosity was decreasing sharply as concentration decreases before the CMC, after the CMC, viscosity was somewhat steady with further dilution indicating that CMC of Triton x-100 is very low.
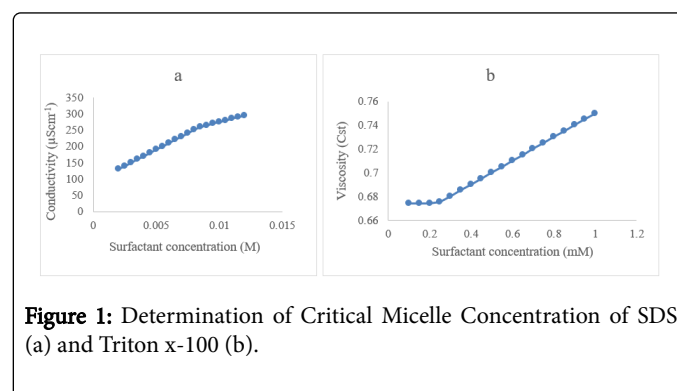
Figure 1: Determination of Critical Micelle Concentration of SDS (a) and Triton x-100 (b).

Batch washing experiment

Effect of initial surfactant concentration: Figure 2 shows removal of mixed contaminants from the spiked soil sample at varying SDS and Triton x-100 concentrations at pH 3. Using SDS, the highest amount of Cd (115.70 mg/kg) was removed at surfactant concentration of 150 mM and the lowest (102.89 mg/kg) was removed at surfactant concentration of 10 mM representing 10.17% and 9.03% of Cd concentration in the sample respectively. Ni removal was highest (64.70 mg/kg) at 150 mM and lowest (58.99 mg/kg) at 10 mM representing 6.17% and 5.63% respectively. The trend is not different with Pb. However, the amount of Pb removed was higher in all the experimental concentrations as 334.73 mg/kg was the lowest and 490.92 mg/kg was the highest representing 33.50% and 49.14%, respectively. Zn removal did not show remarkable variation with changes in surfactant concentration in this experiment as the amount of Zn removed remained between 15.16 mg/kg and 15.61 mg/kg as the surfactant concentration varied from 10 mM to 150 mM, respectively, representing 1.43% and 1.48%, respectively. However similar trend is still discernible. Cu removal at surfactant concentration of 10 mM was 86.44 mg/kg, and at 150 mM it was 95.29 mg/kg representing 10.15% and 11.19%, respectively. This result was higher than those obtained by Khalil et al. [15], when SDS alone was used to remove Cu from contaminated soil. TPH removal were 0.41 mg/kg, at 10 mM and 5.33 mg/kg at 150 mM representing 0.12%, and 1.50% removal, respectively. In this batch, the removal efficiency follows the trend Pb>Cd>Cu>Ni>Zn>TPH. However, for each contaminant, the amount removed increases with increasing concentration which compares favorably with results obtained by Mansour et al. [16].
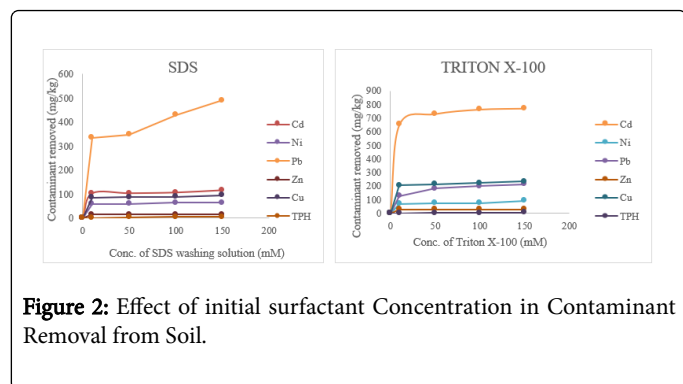
Figure 2: Effect of initial surfactant Concentration in Contaminant Removal from Soil.

The percentage of contaminant removed was determined using the following equation:

$$\text{Percent contaminant removed}(\%) = \frac{C_1 V_1}{C_s M_s} X100 \quad (2)$$

Where C_1 is concentration (mg/L) of contaminant in supernatant, C_s is concentration (mg/kg) of contaminant in soil, V_1 is volume (L) of supernatant and M_s is dry mass (kg) of soil.

When Triton x-100 was used, the lowest amount of Cd (653.92 mg/kg) and the highest (771.51 mg/kg) were removed at 10 mM and 150 mM respectively from the spiked soil sample. This result showed Triton x-100 is more effective in removing Cd from the soil sample than SDS. However, the amount of Cd removed increases as the concentration of surfactant increases in both cases. Ni removal at 10 mM, and 150 mM were 67.64 mg/kg, and 91.66 mg/kg, respectively, these represent 6.65% and 8.75%, respectively. The amount of Pb

removed at 10 mM and 150 mM were 127.84 mg/kg and 212.54 mg/kg, respectively which represent 12.80% and 21.27%, respectively. The amount of Zn removed from the spiked soil sample using Triton x-100 at 10 mM and 150 mM were 27.97 mg/kg and 29.91 mg/kg, respectively, which represent 2.64% and 2.83%, respectively. 205.20 mg/kg and 233.11 mg/kg representing 24.10% and 27.38%, respectively of Cu were removed using Triton x-100 at concentrations of 10 mM and 150 mM, respectively, TPH removal were 0.15 mg/kg and 6.5 mg/kg at Triton x-100 concentration of 10 mM and 150 mM, respectively, these represent 0.04% and 1.83%, respectively. In general, Triton x-100 was more efficient in this experiment than SDS. This observation is in variance with the reports shown by Qi et al. [17] who conducted their own experiment using SDS and another nonionic surfactant (Tween 80) and found out that removal efficiency was higher using SDS than Tween 80 for all experimented concentrations. Though, both nonionic surfactants have polyethylene hydrophilic groups, Triton x-100 has aromatic ring in its lipophilic moiety while tween 80 has oleic acid in its lipophilic moiety. This structural difference may have played a role in the removal efficiency of the surfactants. Furthermore, the CMC of Tween 80 (0.012 mM) is lower than that of Triton x-100 (0.25 mM), this implies that there is higher tendency of Tween 80 to form micelles and precipitate contaminants. It has been reported that at higher concentrations when micelles are formed, contaminants trapped in the micelles and precipitated will not be expected to be in the supernatant which would be analyzed for contaminants concentrations [18]. However, the percentage removal increases with increasing surfactant concentration in both surfactants, which agrees with the trend obtained in this work. At all experimented Triton x-100 concentration, the number of contaminants removed is in the order Cd>Cu>Pb>Ni>Zn>TPH. Furthermore, the number of contaminants removed increases as surfactant concentration increases for both SDS and Triton x-100. This may be due to the fact that surfactants enhance apparent solubility of contaminants by partitioning the contaminants into micelles, and this occurs only if the surfactant concentration in the aqueous phase is above its CMC [19]. At concentrations lower than CMC, the surfactants appear in the medium as soluble macromolecules and cannot interact with contaminants. At higher surfactant concentrations, the solution has more micelles and lower surface tension which assist in solubilizing the contaminants more effectively. This agrees with the trend reported by Tang et al. [20] who used a nonionic surfactant saponin in a similar experiment. The trend also compares favorably with those reported by other researchers [18,16,21].

A t-test was applied to the percentage removal of each contaminants by SDS and Triton x-100 with change in initial surfactant concentration. The results demonstrated that the surfactant pairs (SDS-Tx) for each contaminant Cd (2.20E-07), Ni (0.01), Pb (8.48E-04), Zn (4.95E-08), Cu (4.80E-07) and TPH (0.31) had significantly negative variance except for Pb and TPH where SDS performed better at p<0.05 significant level. Consequently, it can be inferred that Triton x-100 performed better than SDS when initial concentration was varied.

Effect of soil/liquid ratio

Soil/liquid ratio is an important factor in surfactant soil washing experiment. Lower solid/liquid ratio indicates greater ability for solubilization [9]. Figure 3 shows plots of how SDS and Triton x-100 solutions at pH 3 removed mixed contaminants from the spiked soil with changes in soil/liquid ratio. At a soil/liquid ratio 1:1 SDS removed 492.14 mg/kg (43.25%) of Cd and Triton x-100 removed 25.91 mg/kg

(2.28%) and at ratio 1:50 895.15 mg/kg (78.66%) was removed by SDS while Triton x-100 removed 976.38 mg/k (85.80%). At soil/liquid ratio 1:10 and 1:50, the amount of Ni removed by SDS were 57.03 mg/kg (5.44%) and 381.96 mg/kg (36.44%), respectively, while Triton x-100 removed 23.60 mg/kg (2.25%) and 35.17 mg/kg (3.36%), respectively. The amount of Pb removed at ratio 1:1 and 1:50 by SDS were 199.80 mg/kg (20.00%) and 465.02 mg/kg (46.55%), respectively, and Triton x-100 was only able to remove 42.66 mg/kg (4.27%) and 229.29 mg/kg (22.95%), respectively. Zn removal by SDS at ratio 1:1 and 1:50 were 31.01 mg/kg (2.93% and 521.95 mg/kg (49.34%), respectively, while it was 15.24 mg/kg (1.44%) and 26.82 mg/kg (2.54%) by Triton x-100, respectively. The amount of Cu removed by SDS at ratio 1:1 and 1:50 were 216.36 mg/kg (25.41%) and 533.92 mg/kg (62.71%), respectively, while the amount removed by Triton x-100 were 37.83 mg/kg (4.44%) and 171.79 mg/kg (20.18%), respectively. At ratio 1:1 and 1:50 SDS removed 4.59 mg/kg (1.29%) and 62.22 mg/kg (17.52%) of TPH, respectively, while Triton x-100 removed 0.66 mg/kg (0.19%) and 10.15 mg/kg (2.86%), respectively. The experiment with SDS showed that at soil/liquid ratio 1:1, the amount of contaminants removed is in the order Cd>Cu>Pb>Ni>Zn>TPH; at ratio 1:10, the amount of contaminants removed is in the order Cd>Cu>Ni>Pb>Zn>TPH; at ratio 1:20, it Cd>Ni>Zn>Cu>Pb>TPH; and at 1:50, the order was Cd>Cu>Zn>Pb>Ni>TPH. The experiment with Triton x-100 showed that at ratio 1:1, amount of contaminants removal were in the order Pb>Cu>Cd>Ni>Zn>TPH; at ratio 1:10, amount of contaminants removal followed the order Cu>Pb>Cd>Ni>Zn>TPH; at ratio 1:20, the order of contaminant removal was Cd>Cu>Pb>Ni>Zn>TPH; while at ratio 1:50, the trend of contaminant removal was Cd>Pb>Cu>Ni>Zn>TPH. In all cases, the percentage removal was increasing with decreasing soil/liquid ratio.
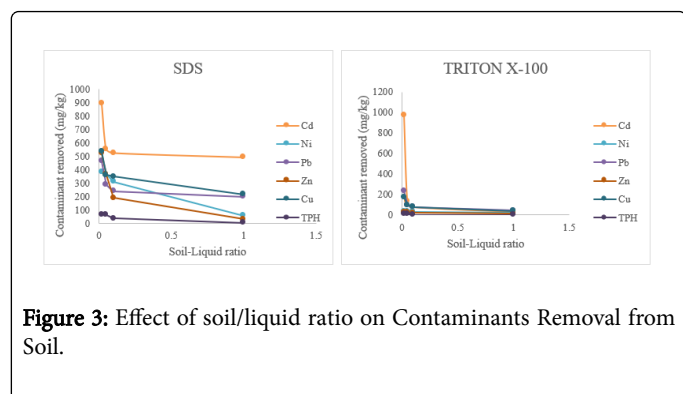

Figure 3: Effect of soil/liquid ratio on Contaminants Removal from Soil.

Other researchers have reported that at higher soil/liquid ratio, there is insufficient mixing between the contaminants and the surfactant which would obviously affect the removal efficiency [20]. This was evidently shown in this experiment as less percentage of contaminants were removed at higher soil/liquid ratio. Except at ratio 1:50 where Triton x-100 removed 85.80% of Cd, SDS showed to be more effective in contaminant removal in all the ratios experimented. Triton x-100 is nonionic and SDS is anionic and therefore ion exchange mechanism may have favoured SDS efficiency in this process. However, the trend which shows increasing percentage removal with decreasing soil/liquid ratio is similar.

Test of significance showed that SDS performed better with positive variance ($p<0.05$) for all the contaminants except for Cd ($p=0.12$) when soil/liquid ratio was varied.

Effect of initial surfactant pH

In soil washing, the washing solution pH is another critical factor determining the efficiency of contaminants removal from soil due to its influence in retention of contaminants by adsorption onto soil surfaces. Figure 4 shows the behavior of contaminants removal with variation in pH from 3 to 12 using SDS and Triton x-100. At pH 3 and 12, the amount of Cd removed from the soil sample by SDS were 134.87 mg/kg (11.85%) and 131.17 mg/kg (11.53%), respectively, and the amount of Cd removed by Triton x-100 were 1,097.59 mg/kg (96.45%) and 4.01 mg/kg (0.35%), respectively. At pH 3 and 12, Ni removed by SDS were 110.24 mg/kg (10.52%) and 89.84 mg/kg (8.58%), respectively, while Triton x-100 removed 67.24 mg/kg (6.41%) and 4.91 mg/kg (0.47%), respectively. Pb removal by SDS at pH 3 and 12 were 172.56 mg/kg (17.27%) and 19.97 mg/kg (2.00%), respectively, and by Triton x-100 were 165.3 mg/kg (16.55%) and 0.72 mg/kg (0.075), respectively. Zn removal by SDS at pH 3 and 12 were 27.50 mg/kg (2.60%) and 24.00 mg/kg (2.27%), respectively, while Triton x-100 removed 27.03 mg/kg (2.56%) and 4.34 mg/kg (0.41%), respectively.
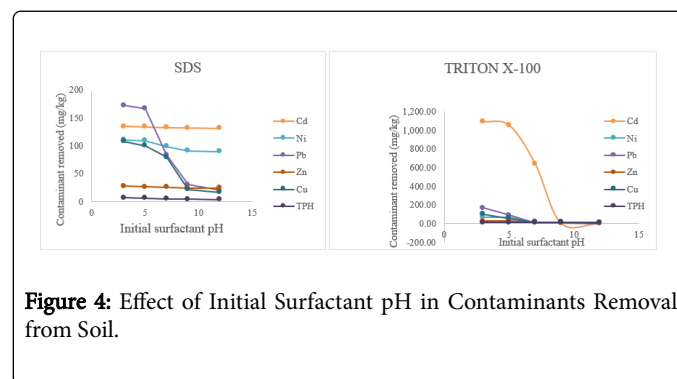

Figure 4: Effect of Initial Surfactant pH in Contaminants Removal from Soil.

The amount of Cu removed by SDS at pH 3 and 12 were respectively 107.84 mg/kg (12.67 5) and 16.35 mg/kg (1.92%), and that removed by triton x-100 were 101.80 mg/kg (11.96%) and 9.31 mg/kg (1.09%), respectively. TPH removal at pH 3 and 12 showed that SDS removed 6.52 mg/kg (1.84%) and 3.32 mg/kg (0.94%), respectively, while Triton x-100 removed 11.66 mg/kg (3.28%) and 7.28 mg/kg (2.05%), respectively. In the experiment with SDS, at pH 3 and 5, amount of the contaminants removed followed the order Pb>Cd>Ni>Cu>Zn>TPH; the amount of contaminants removed at pH 7 is in the order Cd>Ni>Pb>Cu>Zn>TPH; at pH 9, contaminant removal followed the order Cd>Ni>Pb>Zn>Cu>TPH; while at pH 12, the order was Cd>Ni>Zn>Pb>Cu>TPH. In the experiment with Triton x-100, at pH 3, the amount of contaminants removal was in the order Cd>Pb>Cu>Ni>Zn>TPH; at pH 5, the amount of contaminants removal followed the order Cd>Pb>Ni>Cu>Zn>TPH; at pH 7, the amount of contaminants removal was in the order Cd>Zn>Ni>Cu>TPH>Pb; at pH 9, the trend was Zn>Cu>TPH>Ni>Pb>Cd; while at pH 12, the contaminants removal was in the order Cu>TPH>Ni>Zn>Cd>Pb. In general, for all the contaminants, the amount removed decreases as the pH increases from acidic region to alkaline region. This may be due to the fact that at lower pH, there is higher concentration of H^+ ions which compete with the contaminants for adsorption sites on the soil. This competition may lead to displacement of more contaminants from the soil, hence increasing the contaminants solubility and surfactant-contaminants complexes formation. This trend agrees favorably with those reported by other researchers [16,20,22]

Test of significance in the performance of the two surfactants suggested that SDS has positive variance with Ni, Pb, Zn and Cu while it has negative variance with Cd and TPH at $p < 0.05$.

Effect of washing time

Figure 5 gives plots of contaminants removal with washing time using SDS and Triton x-100 at pH 3. The results showed that at 30 min and 240 min, Cd removal by SDS were 252.99 mg/kg (22.23%) and 505.60 mg/kg (44.43%), respectively, while that by Triton x-100 were 765.43 mg/kg (76.26%) and 1,015.11 mg/kg (89.20%), respectively. Ni removal by SDS were 68.27 mg/kg (6.51%) and 72.25 mg/kg (6.89%), respectively, while that by Triton x-100 were 49.05 mg/kg (4.68%) and 54.72 mg/kg (5.22%), respectively. Pb removal by SDS were 39.00 mg/kg (3.90%) and 103.78 mg/kg (10.39%), respectively, while that by Triton x-100 were 99.70 mg/kg (9.98 5) and 116.38 mg/kg (11.68%), respectively. Zn removal by SDS were 21.65 mg/kg (2.04%) and 24.39 mg/kg (2.31%), respectively, while that by Triton x-100 were 27.28 mg/kg (2.58%) and 29.93 mg/kg (2.83%), respectively. Cu removal by SDS were 12.65 mg/kg (1.49%) and 39.40 mg/kg (4.63%), respectively, while the removal by Triton x-100 were 51.48 mg/kg (6.05%) and 65.17 mg/kg (7.65%), respectively.

TPH removal by SDS were 5.87 mg/kg (1.65%) and 7.45 mg/kg (2.10%), respectively, while TPH removal by Triton x-100 were 2.95 mg/kg (0.83%) and 8.87 mg/kg (2.50%), respectively. In the experiment using SDS, at washing times of 30 min to 150 min, the number of contaminants removed from the spiked soil sample followed the order Cd>Ni>Pb>Zn>Cu>TPH. At washing time of 180 min the order was Cd>Ni>Pb>Cu>Zn>TPH. While at washing time of 210 and 240 min, contaminants removal followed the order Cd>Pb>Ni>Cu>Zn>TPH. In all the experimented washing time using Triton x-100 solution, the amount of contaminants removed followed same order Cd>Pb>Cu>Ni>Zn>TPH.
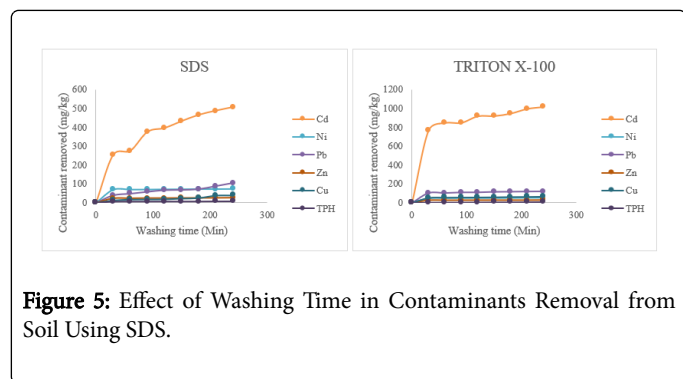

Figure 5: Effect of Washing Time in Contaminants Removal from Soil Using SDS.

The general trend that is discernible in all cases is that although the experiment continued for 240 min, equilibrium was attained within 60 min, there exist a slight plateau region after which desorption increased again and get stabilized. As the washing time increases, the contact time between the surfactant and the contaminants increases and this implies increasing period of effective collision and interaction between the surfactant molecule and the contaminants which helps in stripping off the adsorbed contaminants from the soil. This trend obtained compares to a large extend with the trend reported in similar studies [15,20,22].

Test of significance for the performance of the two surfactants during change in washing time demonstrated that SDS had a positive variance at $p < 0.05$ with Ni and TPH while it had a negative variance with Cd, Pb, Zn and Cu.

Column studies

Figure 6 shows plots of contaminants removal verses time (h) in the column experiment on the spiked soil sample using SDS, Triton x-100 and their binary blend at pH 3. The column experiment showed that maximum number of contaminants were removed from the soil at 4 h using the surfactants individually and using their binary blend. Cd gave 84.43 mg/kg (7.42%) with SDS, 14.66 mg/kg (1.29%) with Triton x-100 and 437.89 mg/kg (38.48%) with the blend. Ni removed was 51.27 mg/kg (4.89%) with SDS, 37.85 mg/kg (3.61%) with Triton x-100 and 36.80 mg/kg (3.51%) with the blend. Pb removed was 12.79 mg/kg (1.28%) with SDS, 92.85 mg/kg (2.29%) with Triton x-100 and 27.30 mg/kg (2.73%) with the blend. Zn gave 15.88 mg/kg (1.50%) with SDS, 16.78 mg/kg (1.59%) with Triton x-100 and 21.88 mg/kg (2.07%) with the blend. Cu removed was 43.68 mg/kg (5.13%) with SDS, 26.36 mg/kg (3.10%) with Triton x-100 and 13.50 mg/kg (1.59%) with the blend. TPH gave 5.64 mg/kg (1.59%) with SDS, 8.31 mg/kg (2.34%) with Triton x-100 and 9.80 mg/kg (2.76%) with the blend. Analysis of the column experiment using SDS showed that at 4 h and 8 h, the amount of contaminants removed is in the order TPH<Pb<Zn<Cu<Ni<Cd; while at 12 h and 24 h the following order prevailed TPH<Pb<Zn<Cd<Ni<Cu. Analysis of the column experiment using Triton x-100 showed that at 4 h, the amount of contaminants removed followed the order Pb>Ni>Cu>Zn>Cd>TPH; at 8 h, the order was Ni>Zn>Cd>TPH>Pb>Cu; and at 12 h and 24 h the order were Ni>Zn>Cd>TPH>Cu>Pb. In the column experiment using the binary blend the plots further indicated that at time interval of 4 h, the amount of contaminants removed were in the order Cd>Ni>Pb>Zn>Cu>TPH; at time interval of 8 h the order was Cd>Ni>Zn>Cu>Pb>TPH; while at 12 h interval, the order was Ni>Cd>Zn>TPH>Pb>Cu; and at interval of 24 h, the order was Ni>Zn>Cd>TPH>Pb>Cu.
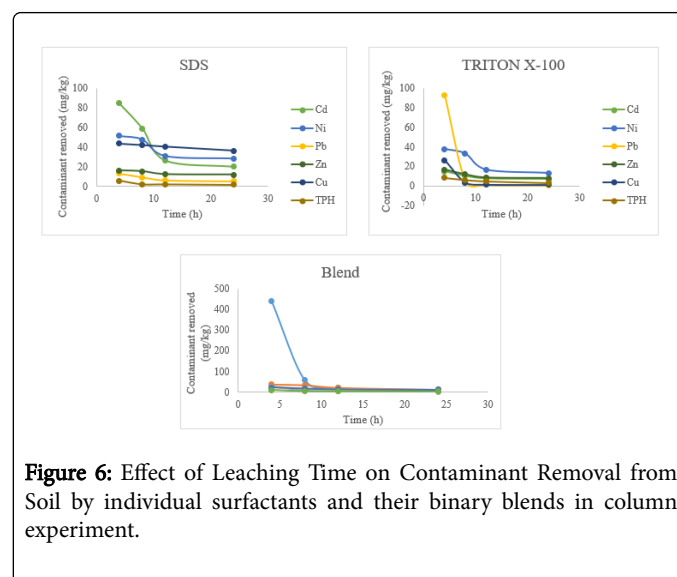

Figure 6: Effect of Leaching Time on Contaminant Removal from Soil by individual surfactants and their binary blends in column experiment.

In general, the number of contaminants removed decreases as the time interval increases. This may be due to the fact that as the leaching progresses on the fixed mass of the soil, the amount of the contaminants remaining in the soil inside the column decreases, and therefore concentration of the contaminants that can be leached

continue to decrease. Test of significance applied on the column experiment showed that at $p < 0.05$, SDS recorded a positive variance with Cd, Ni, Zn and Cu while it recorded negative variance with Pb and TPH.

Contaminant	Leaching Time (h)	Percent Contaminant Removed (%)				Synergism Parameter (S1)	Relationship
		I_1	I_2	I_{1+2}	$I^!_{1+2}$		
Cd	4	7.42	1.29	8.71	38.48	0.21	Antagonistic
	8	5.18	0.87	6.05	5.01	1.26	Synergistic
	12	2.31	0.65	2.96	1.7	2.82	Synergistic
	24	1.75	0.6	2.35	0.85	-9.28	Antagonistic
Ni	4	4.89	3.61	8.5	3.51	2.99	Synergistic
	8	4.55	3.16	7.71	3.21	3.04	Synergistic
	12	2.92	1.59	4.51	1.99	3.54	Synergistic
	24	2.67	1.26	3.93	1.11	27.91	Synergistic
Pb	4	1.28	9.29	10.57	2.73	5.53	Synergistic
	8	0.92	0.51	1.43	0.7	-1.44	Antagonistic
	12	0.61	0.13	0.73	0.41	0.45	Antagonistic
	24	0.51	0.08	0.6	0.2	0.5	Antagonistic
Zn	4	1.5	1.59	3.09	2.07	1.95	Synergistic
	8	1.43	1.1	2.54	1.54	2.87	Synergistic
	12	1.15	0.79	1.94	1.24	3.94	Synergistic
	24	1.12	0.74	1.86	1.05	15.96	Synergistic
Cu	4	5.13	3.1	8.23	1.59	12.35	Synergistic
	8	4.95	0.43	5.38	0.84	-27.82	Antagonistic
	12	4.75	0.18	4.93	0.37	-6.25	Antagonistic
	24	4.22	0.15	4.37	0.2	-4.23	Antagonistic
TPH	4	1.59	2.34	3.93	2.76	1.66	Synergistic
	8	0.56	1.76	2.32	1.46	2.86	Synergistic
	12	0.56	1.39	1.94	1.29	3.21	Synergistic
	24	0.41	0.91	1.32	1.09	3.72	Synergistic

Table 2: Synergism Parameters for the Relationship Between SDS, Triton x-100, and their Binary Blends.

Table 2 shows that "I1 and I2 are the % contaminant removed from soil by SDS and Triton x-100 respectively, I!1+2 is the % contaminant removed from soil by the blend, S1 is the synergistic parameter, S1<1 is antagonistic, S1>1 is synergistic".

Results of the column experiments with the surfactant blend and those of the individual surfactants were subjected to synergism parameters to establish the relationship between SDS, Triton x-100, and their binary blends. The results demonstrated that out of the 24 runs, there were 16 synergistic relationship and 8 antagonistic relationship. Consequently, it can be inferred that the performance of the binary blend of SDS-Triton-100 in contaminants removal from soil was better than that of the individual surfactants.

Furthermore, the auto mechanic soil which was used in this experiment has clay content of 11.84%. Clay has net negative charge even at low pH values and therefore has higher capacity to adsorb positive ions [23]. Mechanisms such as ion-exchange, counter-ion binding and dissolution precipitation advance the removal of PTMs from soil by surfactants. One of these procedures is dominant depending on the nature of surfactant and the PTM ion involved [18]. In the removal of Cd, Ni, Pb, Zn and Cu using SDS (which is anionic), counter-ion binding and precipitation could play an influential role. Since nonionic surfactants do not carry charges, they do not participate in counter-ion binding and ion-exchange processes and are expected to have less capability in removing PTMs from soil in

comparison with anionic surfactants [18]. However, the results in this experiment indicated that Triton x-100 compares favorably with SDS in removal efficiency. This may be related to precipitate formation of the PTM ions from soil solution at concentrations above CMC. This behavior was also reported by Ramamurthy and Schalchian [18].

In most of the experiments, both SDS and Triton x-100 show higher efficiency in Cd removal than the other contaminants. Cd is highly mobile in soils and remains in aqueous medium as Cd^{2+} up to about pH 8, and in the presence of competitive ions such as Cu^{2+}, Pb^{2+}, Zn^{2+} and Ni^{2+}, adsorption of Cd^{2+} is inhibited [23]. This may be attributed to the relatively low electronegativity value of Cd. PTMs which existed in reducible and exchangeable fractions are easily removed from soil into the surfactant solution [20]. The higher removal efficiency of some of the PTMs from soil may be attributed to these two mobile chemical fractions. However, the efficiency of Triton x-100 in PTM removal may be based on the affinity of Triton x-100 ligands for PTM ions.

The extent to which these complexes are formed between Triton x-100 ligands and PTM ions mainly depends on the competition between the metal-binding functional groups from the soil structure and the Triton x-100 for the PTM. Some PTMs form more stable complexes with Triton x-100 than with the soil particles functional groups [20]. The higher removal efficiency of Cd might be attributed to its strong complexing tendency with Triton x-100. While Zn seemed to form more stable complexes with the soil functional groups than Triton x-100.

The lower TPH removal in most cases could be attributed to the presence of different kinds of organic compounds involving aliphatic and aromatic hydrocarbons in petroleum fractions, each of these compounds has a specific behavior at different experimental conditions. Therefore, it is very difficult to attain specific conditions to remove all the compounds. At lower pH 3 for example, high (>5 aromatic rings) molecular weight compounds are favored than low (<5 aromatic rings) molecular weights [16]. However, interactions between water, particles, metals and hydrophobic particles could be contributing factors to the lower TPH removal by the surfactants. In general, the more the initial soil TPH concentration, the higher the efficiency of removal by surfactants [24]. This may also have influenced the percentage removal.

Distilled water which was used as a blank washing solution removed 7.32 mg/kg Cd, 12.16 mg/kg Ni, 18.69 mg/kg Pb, 7.60 mg/kg Zn, 15.4 mg/kg Cu and 0.14 mg/kg TPH representing 0.86%, 1.16%, 1.87%, 0.67%, 1.46% and 0.04% of Cd, Ni, Pb, Zn, Cu and TPH, respectively. Evidently, the surfactants have performed better than distilled water.

Conclusion

Two surfactants (SDS and Triton x-100) were selected for the soil washing experiment. The batch experiment showed the removal of contaminants generally increases as the initial surfactant concentration increases. Variation in pH indicated that the lower the pH, the higher the contaminants removal efficiency. The lower the soil/liquid ratio, the more the efficiency of contaminant removal and percentage of contaminants removed increases as washing time increases. In the column experiment, removal of contaminants was seen to decrease with time interval. Statistical test of significance (t-Test at p<0.05) demonstrated that these inferences are significant. The two surfactants were blended at different percentages and washing experiment conducted with each blend. The result showed that the surfactant blend performed better than when the surfactants were used individually and

the blend with 90% Triton x-100 and 10% SDS gave the optimum result. Test of Synergism parameters on the blend performance indicated there are more synergistic conditions than antagonistic phenomenon.

References

1. Leke L, Akaahan TJ, Attah S (2011) Heavy metals in soils of auto-mechanic shops and refuse dumpsites in Makurdi Nigeria. Journal of Applied Science and Environmental Management 16: 207-210.

2. Beetseh CI, Ocheje A (2013) Analysis of Lead, Zinc, Chromium, and Iron in the major dumpsite on North Bank Mechanic Village in Makurdi Metropolis Benue State. Chemistry and Materials Research 3: 001-007.

3. Montserrat ZS, Mabel V, Miguel AF, Erick RB, Luis GT (2013) Surfactant-enhanced washing of soils contaminated with wasted-automotive oils and the quality of the produced wastewater. Journal of Environmental Protection 4: 1495-1501.

4. Odoh R, Agbaji EB, Dauda MS, Oko OJ (2014) Assessment of Soils in the vicinity of Rice Mill industry, Otukpo, Benue State for potential heavy metal contaminations. International Journal of Modern Analytical and Separation Sciences 3: 1-12.

5. Khodadadi A, Ganjidoust H, Seyed RSN (2012) Treatment of crude-oil contaminated soil using biosurfactants. Journal of Petroleum and Gas Engineering 3: 92-98.

6. Rosen MJ, Kunjappu JT (2012) Surfactants and interfacial phenomena. 4th edn. John Wiley and Sons Inc, New York, pp: 300-305.

7. Paria S (2008) Surfactant enhanced remediation of organic contaminated soil and water. Advances in Clloid and Interface Science 138: 24-58.

8. Oremusova J, Lengyel A (2009) Exercise 9 critical micelle concentration of ionic surfactants. CMC by Dilution Principle.

9. Peng S, Wu W, Chen J (2011) Removal of PAHs with surfactant-enhanced soil washing: Influencing factors and removal effectiveness. Chemosphere 82: 1173-1177.

10. Yang Z, Zhang S, Liao Y, Li Q, Wu B, et al. (2012) Remediation of heavy metal contamination in calcareous soil by washing with reagents: A column washing. Procedia Environmental Sciences 16: 778-785.

11. USEPA (2011) Contract laboratory program. National functional guidelines for inorganic data reviews. US Department of Energy. USEPA-540-R-10-011, pp: 392-400.

12. Domínguez A, Fernández A, González N, Iglesias E, Montenegro L (1997) Determination of Critical Micelle Concentration of Some Surfactants by Three Techniques. Journal of Chemical Education 74: 1227-1231.

13. Shah SS, Khan AM (2008) Determination of CMC of SDS and the effect of low concentration of pyrene on its CMC using Origin software. Journal of Chemical Society of Pakistan 30: 186-191.

14. Sigma (2018) Product information Triton x-100. Sigma-Aldrich, Inc. Sigma-Aldrich.com. Saint Louis, Missouri 63103, USA.

15. Khalil AH, Alquzweeni SS, Modhloom HM (2015) Removal of Copper Ions from Contaminated Soil by Enhanced Soil Washing. International Journal of Environmental Research 9: 1141-1146.

16. Mansour B, MohamMad RM, Ali A, Mehran MF, MohamMad M, et al. (2014) Efficiency of non-ionic surfactants - EDTA for treating TPH and heavy metals from contaminated soil. Journal of Environmental Health Science and Engineering 12: 1-10.

17. Qi X, Xu X, Zhong C, Jiang T, Wei W, et al. (2018) Removal of Cadmium and Lead from Contaminated Soils Using Sophorolipids from Fermentation Culture of Starmerella bombicola CGMCC 1576 Fermentation. International Journal of Environmental Research and Public Health 15: 2334.

18. Ramamurthy A, Schalchian H (2013) Surfactant assisted removal of Cu(II), Cd(II) And Pb(II) from contaminated soils. Environment Protection Engineering 39: 87-99.

19. Zhu H, Aitken MD (2010) Surfactant-Enhanced Desorption and Biodegradation of Polycyclic Aromatic Hydrocarbons in Contaminated Soil. Environmental Sciences and Technology 44: 7260-7265.

20. Tang J, He J, Liu T, Xin X (2017) Removal of heavy metals with sequential sludge washing techniques using saponin: optimization conditions, kinetics, removal effectiveness, binding intensity, mobility and mechanism. Royal Society of Chemistry 7: 33385-33401.

21. Gitipour S, Narenjkar N, Farvash ES, Asghari H (2014) Soil flushing of cresols contaminated soil: application of nonionic and ionic surfactants under different pH and concentrations. Journal of Environmental Health Science and Engineering 12: 47.

22. Mukhopadhyay S, Mukherjee S, Hashim MA, Sahu JN, Villegas NM (2018) Zinc Removal from Soil by Washing with Saponin Obtained from Sapindus mukorossi. Journal of Environmental Analytical Chemistry 5: 249.

23. Lukman S, Essa MH, Nuhu DM, Bukhari A, Basheer C (2013) Adsorption and desorption of heavy metals onto natural clay materials: influence of material pH. Journal of Environmental Sciences and Technology 6: 1-5.

24. Iturbe R, Torres LG, Flores CR, Chávez C, Bautista G (2003) Remediation of TPH/PAHs contaminated soil using soil washing. In Tenth Annual Int. Petroleum Environmental Conf, Integrated Petroleum Environmental Consortium (IPEC), The Univ. of Tulsa, Tulsa, Okla.