Cleaning of heavy metals from Spent Lubrication Oil (SLO) by adsorption process using acid modified clay

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Abstract
In this study, spent lubrication oil (SLO) was treated with naturally sourced clay materials modified with three different mineral acids. 1.0 M of nitric, sulphuric and phosphoric acids was used to modify the natural clay after beneficiation. Analysis of the SLO showed the presence of Pb, Zn, Fe, Cu, Cr, Mn and Ni. Fe and Zn had the highest concentration of 73.4 and 24.1 mg/L while copper has the lowest amount of 0.02 mg/L. The adsorbent materials (sulphuric acid modified clay, nitric acid modified clay and phosphoric acid modified clay namely, SAMC, NAMC and PAMC respectively) were contacted with the SLO in a batch adsorption technique to adsorb the heavy metals. The results of the adsorption capacity showed higher percentage removal of the metals by SAMC with over 80% followed by PAMC and NAMC. The percentage removal of these heavy metals was shown to depend on the degree of adsorbent modification.

Key Word: Adsorption, Heavy metals, spent lubrication oil (SLO), adsorbent modification and adsorption capacity.

1.0 INTRODUCTION
Improper management of waste is one of the main causes of environmental pollution and degradation in many cities, especially in the developing countries like Nigeria. Many of these cities lack waste regulation and proper disposal facilities, including for harmful waste. Such waste may be infectious, toxic or radioactive [1-3]. This situation becomes more difficult when hazardous wastes (waste containing heavy metals) are involved for example; the management of spent lubricating oil. Petroleum based products like lubrication oil (commonly called engine oil) contains no or little amount of heavy metals through the blending process as reported by Irwin [4]. As the lubrication oil circulate through the engine, it picks up heavy metals (arsenic, lead, cadmium, copper, zinc, chromium, manganese) deposited in the engine from the action of wear and tear alongside other contaminants thereby contaminating spent lubricating oil with toxic metals which are considered as potential pollutants in the environment according to the U.S environmental protection agency [5, 6].

In Nigeria, it has been reported that about 20 million gallons of spent lubrication oil are generated annually from mechanic workshop, industrial areas and domestic’s places and dispose improperly into the environmental media [7]. Unfortunately, these spent lubrication oil end up directly in the environment therefore enriches the soil with heavy metals which can drain into both surface waterways and ground water [6-8]. Since it’s very difficult to prevent spent lubrication oil getting into our environmental media with the available disposal practices, the best option is to treat this oil for recycling or safe disposal by cleaning up the heavy metal component of the spent lubrication oil. Nabil, M. A et al. [9] carried out an investigation on the removal of heavy metals from spent lubrication oil using different adsorbents. The studies reviewed that adsorption of heavy metals from SLO was greater in acid activated bentonite than all the other adsorbent used. Similar result was also reported by Udonne [10] in his research used lube oil was treated by different methods among which, acid/clay treatment gave the highest adsorption capacity of the metals.
2.0 MATERIALS AND METHODS
2.1 Adsorbent collection and pre-treatment
2.0 kg of clay sample from the Benue valley were collected by
digging a pit in the clay deposit along the University of
Agriculture Makurdi - Gbajimba Road in Makurdi Local
Government area of Benue State (N07° 45’11.3” and E008°
57’12.2”) at a depth of 30 cm using a stainless steel digger
and stainless steel shovel similar to the sampling method
reported by Osabor [11].

2.2 Lubrication oil
Eight (8) liters of unused lubricating oil of Total brand with
a commercial grade labeling of 10W-30 were obtained from
Total filling station in Port Harcourt City of Rivers
State. Four (4) liters of the oil were introduced into the
automobile engine of Nissan Pathfinder car and allowed to
operate a period of three months. After which, the
lubrication oil from the engine was evacuated and labeled as
Spent Lubricating Oil (SLO) after pretreatment by
filtration.

2.3 Adsorbent preparation
The beneficiated clay was air-dried for two weeks
thereafter; 20 g of the air-dried clay was packed into
polyethylene bags and labeled as unmodified clay (UMC)
while 100 g of the air-dried clay (size 0.2 mm) was
equilibrated with 150 mL each of 1.0 M phosphoric acid,
Nitric acid and sulphuric acid in a 500 mL Teflon beaker,
stirred with a glass rod for 30 minutes and shaken for 1
hour with rotary shaker. The mixture was oven dried for 6
hours at a temperature of 80°C using a Paste-like material
was formed and allowed to cool, washed severally with
distilled water until a neutral pH was reached. The
modified clay were then air-dried, sieved and labeled as
PAMC, NAMC and SAMC for Phosphoric Acid, Nitric
Acid and Sulphuric Acid modified clay respectively.

2.4 Clay characterization
Adsorbent materials were characterized for Moisture
content using the method reported by Buurman, P. B et al
[12]. Bulk density was determined using the method
recommended by American soil scientist [12]. Attraction
coefficient was determined as reported by Adejo, S. O. et al
while pH and CEC were determined using ASTM D 2867
and the method used by Gillman, G. P. and Sumpter, E. A.

2.5 Characterization of used engine oil
SLO was ashed at a temperature of 600°C for 6 hours,
digested with 10 mL of 0.02 M Nitric acid and analyzed for
heavy metal (lead, zinc, copper, chromium, iron,
manganese and Nickel) concentrations using Flame atomic
absorption Spectrophotometer Phoenix-986

2.6 Batch adsorption process
0.5 g each of the modified and unmodified clay was mixed
with 50 mL of the SLO in a 100 mL Erlenmeyer bottle and
the mixture was shaken thoroughly using electrical shaker
SF1 Stuat for 3 hours and heated in a thermostatic water
bath at a temperature of 28°C for a period of 12 hours. The
slurry was centrifuged using D800 centrifuge at a speed of
4.000 rpm for 20 min, decanted and filtered using a plastics
funnel and glass wool. The filtrate (treated spent lubricating
oil) was ashed in a muffle furnace at 600°C for 4 hours and
digested with 10 mL 0.02 M Nitric acid and analyzed for
the presence of heavy metals using the flame atomic
absorption Spectrophotometer Phoenix-986. The removal
efficiency of the clay for all the metal ions was calculated
as adsorption percentages using equation 3.5.

\[ \text{Adsorption (\%)} = \frac{C_i - C_e \times 100}{C_i} \] [3.5]

Where, \( C_i \) and \( C_e \) are the initial and final metal ion
concentration respectively.

The equilibrium capacity of adsorption was calculated
respectively using the formula described by Mohammed et

\[ q_e = \frac{(C_o - C_e) \times V}{M} \] [3.6]

Where \( q_e \) (mg/g) is the equilibrium adsorption capacity, \( C_o \)
(mg/L) and \( C_e \) (mg/L) is the initial and equilibrium metal
concentration, respectively, \( V \) is the volume (L) and \( M \) is
the amount of the adsorbent (g) and the values tabulated.

3.0 RESULTS AND DISCUSSION
The physico-chemical parameters of the adsorbent
materials determined in this study affects adsorption
capacity of adsorbent [15]. The results in table 1.1 showed
that the physico-chemical parameters changes with acid
modification. The extend of modifications of these
adsorbent materials was revealed in the increased value of
CEC and porosity of the adsorbent while bulk density,
attrition coefficient, pH and moisture content decreases.
The cation exchange capacity of the adsorbent materials
used in the adsorption process ranged from 23.09 - 25.25
meq/100 kg with SAMC bearing the highest value of 25.25
deq/100 kg.

From the result (table 1.1) it is evident that SAMC can be
kept for a longer period of time without the fear of
becoming substrate for microbial activity owing by the fact
that it has little water content of 7.0±1.27% compared to
the values of the other adsorbent materials [16 - 17]

3.1 Adsorption capacity
In this study, the removal of heavy metals from SLO by 0.5
g UMC at 28°C for 12 hours indicate that of Zn ion was
favouredly adsorbed with the removal efficiency of
69.08%. Generally, more than half of the amount of metal
ion were removed from the SLO using UMC with the
removal percentages range from 50.2 - 69.08%.

Generally, more than half of the amount of metal
ion were removed from the SLO using UMC with the
removal percentages range from 50.2 - 69.08% in the order:
Zn> Ni> Cr> Fe> Cu> Mn.

However, the modified adsorbent materials showed a
better adsorption capacity for all the metal ions under
study. As recorded by Adediran, modification of clay either
by physical or chemical means opens up more binding and
exchanging sites of the materials hence better adsorptive
capacities. The physico-chemical properties improves on
moldification with SAMC having the best properties as
regards adsorptive potentials.
PAMC removal percentage for the metals ranged fro 70 -
87% with Cu and Pb ions bearing highest and lowest
removal percentage respectively. The removal percentage followed the order of Cu>Mn>Zn>Ni>Cr>Fe>Pb. While the increasing order for removal percentages of metal ions using NAMC was found to be Pb>Ni>Cu>Zn>Cr>Mn>Fe. Table 1.1: physico-chemical characterization of the Unmodified Clay (UMC) and acid modified Clay

<table>
<thead>
<tr>
<th>parameters</th>
<th>UMC</th>
<th>PAMC</th>
<th>NAMC</th>
<th>SAMC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk Density (g/cm³)</td>
<td>1.42±0.01</td>
<td>1.40±0.02</td>
<td>1.29±0.04</td>
<td>1.27±0.02</td>
</tr>
<tr>
<td>pH</td>
<td>6.02±0.25</td>
<td>5.91±0.42</td>
<td>5.71±1.78</td>
<td>5.27±0.07</td>
</tr>
<tr>
<td>Attrition Coefficient (%)</td>
<td>21.15±0.35</td>
<td>16.8±0.14</td>
<td>20.0±1.83</td>
<td>14.0±0.28</td>
</tr>
<tr>
<td>Moisture content (%)</td>
<td>21.25±0.21</td>
<td>9.9±0.56</td>
<td>13.4±0.70</td>
<td>7.0±1.27</td>
</tr>
<tr>
<td>Porosity</td>
<td>0.42±0.02</td>
<td>0.49±0.02</td>
<td>0.44±0.01</td>
<td>0.52±0.09</td>
</tr>
<tr>
<td>CEC (meq/100 kg)</td>
<td>23.09±1.30</td>
<td>24.55±1.06</td>
<td>25.21±0.09</td>
<td>25.25±4.03</td>
</tr>
</tbody>
</table>

Table 1.2: Result of Equilibrium Adsorption of Heavy metals by unmodified clay (UMC), phosphoric acid modified clay (PAMC), sulphuric acid modified clay (SAMC) and nitric acid modified clay (NAMC) using 0.5g of the adsorbent at 28°C for 12h

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Initial conc. C₀ (mg/L)</th>
<th>Equilibrium conc. Cₑ (mg/L)</th>
<th>Amount adsorbed (mg/L)</th>
<th>Equilibrium capacity qₑ (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>0.25</td>
<td>0.12</td>
<td>0.13</td>
<td>0.013</td>
</tr>
<tr>
<td>Zn</td>
<td>73.11</td>
<td>22.6</td>
<td>50.51</td>
<td>5.051</td>
</tr>
<tr>
<td>Cr</td>
<td>0.23</td>
<td>0.09</td>
<td>0.14</td>
<td>0.014</td>
</tr>
<tr>
<td>Fe</td>
<td>10.51</td>
<td>4.51</td>
<td>6.00</td>
<td>0.600</td>
</tr>
<tr>
<td>Mn</td>
<td>0.12</td>
<td>0.12</td>
<td>0.00</td>
<td>0.001</td>
</tr>
<tr>
<td>Ni</td>
<td>24.14</td>
<td>8.59</td>
<td>15.55</td>
<td>1.555</td>
</tr>
</tbody>
</table>

The order of removal percentages of these metal ions from SLO using the different acid modified clays materials did not follow a definite pattern, however, similar order of removal percentage was noticed between the NACM and SAMC contrast to the removal percentage order observed for using PAMC.

Comparing the removal percentages of all the heavy metal among the three acid modified clay adsorbent, it was also observed that SAMC removes greater percentages of all the heavy metals detected in the SLO with the least removal efficiency of 95% from the results it is imperative to point that Lead and Nickel are more favourably adsorbed by SAMC and NAMC than PAMC.

Metal ions

Figure 1.1: Removal percentage of heavy metals by the various adsorbents
SAMC and NAMC closely followed by Copper and Zinc while Chromium recorded the least removal percentage of 60.86% unto NAMC at the set experimental conditions. Comparing the adsorption capacities of these adsorbent materials showed that SAMC adsorbed more metal ions at the set experimental conditions followed by PAMC while NAMC showed the least adsorption capacities. The inconsistent pattern observed in the adsorption of these metals on the different adsorbent materials (unit adsorption) could be linked with the dynamics associated with adsorption processes as well as the ease to access the adsorption sites by the adsorbates [18, 19]. The higher adsorptive capacities of the acid modified clay over the unmodified clay can be attributed to the increase in adsorptive sites on the adsorbent surface due to removal of dissolved and excess salts located in the adsorptive sites of the natural clay on addition of the acid [20]. The adsorption capacities of these adsorbent materials used in this study correlates with the physico-chemical properties of the various adsorbents such as CEC, bulk density and porosity. In the case of CEC of the adsorbent, CEC of SAMC correlates positively (0.9596) with the percentage removal of metals. Bulk density values of these adsorbents also correlates negatively (-0.977) with the adsorption capacities of the adsorbent as increase in bulk density of the adsorbant decreases its adsorption capacity [20].

Over 80% removal percentages of lead, nickel and chromium by adsorption process was also reported by Yabe Santos and Oliveira [20] by studying heavy metals removal in industrial effluents by sequential adsorbent treatment. Phosphoric acid moldified earth worm cast soil adsorbed about 99% and 89% of lead and chromium respectively from aqueous solution as experimented by Adediran et al. [22]. A comparative study of recycling used lubrication oil using distillation acid and activated charcoal with clay methods as done by Udonne [10], revealed that, the composition of heavy metals in the used lubrication oil were lowest (minimal) with improved properties when treated with clay which indicate that used lubrication oil can be treated/reycled using clay as adsorbent material.

4.0 CONCLUSION

From the result of this study, the following conclusions are made:

- Modification of the clay materials changes the physico-chemical characteristic of the adsorbent materials hence making them better adsorption materials for heavy metal.
- Among the adsorbent materials used in the study, SAMC proved to be the best adsorbent material followed by PAMC while NAMC has the least adsorption capacity for Fe, Zn, Pb, Ni, Cu, Cr and Mn ions.
- Pb ions are more favorably adsorbed by SAMC and NAMC while PAMC has less adsorptive affinity to Pb.

REFERENCES


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