Washing of Coastal Sediment from Mboppi River (Douala, Cameroon) Polluted by Polycyclic Aromatic Hydrocarbons (PAHs) using Sodium Dodecyl Sulfate (SDS)

Philemon Ze Bilo’o, Christelle Solange Jessie Ekoka, Raïssa Kom Regonne, and Martin Benoit Ngassoum

Abstract — Because of their hydrophobic nature, polycyclic aromatic hydrocarbons (PAHs) have low solubility in an aqueous medium and strong adsorption on soils and sediments, resulting in their persistence in the environment. This work was undertaken with the goal of having enough data to set up a stirred reactor, which will be used in the treatment of soils and sediments polluted by hydrocarbons while preserving the environment. To this end, sediment samples from the Mboppi were taken successively during the rainy season and the dry season. Gas chromatography coupled with a flame ionization detector (CPG/FID) was used to carry out a preliminary analysis of the samples. Then, chemical washing treatment tests using sodium dodecyl sulfate (SDS) were carried out on the most polluted sediment sample using a complete factorial plan with three factors (temperature, speed, and duration of agitation) to determine the parameters that influence depollution yields. It appears that the temperature (80 °C), the speed (1000 rpm), and the stirring time (40 min) give a better desorption yield (85.79%). The results show that SDS can effectively and significantly reduce the content of PAHs in sediments. The reduction of HMW-PAHs was observed, with the highest percentage (82.69%) obtained for 6 ring PAH under the same conditions. The environmental health risk assessment was reduced from 74.34 to 24.41, thus showing how far the washing with SDS is satisfactory.

Keywords — PAHs, SDS, Sediment, Washing, Risk assessment.

I. INTRODUCTION

The preliminary study carried out by Jessie et al. [1] on the source and distribution of polycyclic aromatic hydrocarbons (PAHs) in water from the Mboppi River, located in the Mboppi industrial zone, showed that it is polluted by hydrocarbons as a whole and, in particular, polycyclic aromatic hydrocarbons. Ze et al. (2022) studied the pollution evaluation and risk assessment of PAHs in coastal sediment of two rivers among which the Mboppi River in four sampling points. It came out that coastal sediment from the Mboppi River was the most polluted, with the highest total concentration of 1,639.03 µg of PAHs/g of sediment. Because of its high value, this obtained total concentration drew our attention.

Furthermore, many studies conducted around the world present total concentrations that are not so high. The following presents some of these total concentrations of PAHs in marine and river coastal sediments. In Cameroon, sediments from Mboppi and Ngoua rivers had 513.27–1,639.03 µg.g⁻¹ and 48.89–333.49 µg.g⁻¹ respectively [2]. Some studies conducted on sediments in China bought values such as 89.52–208.02 µg.g⁻¹ for Yangtze River Estuary [3], 533.15–1,422.83 ng.g⁻¹ for Middle Reach of Huai River [4], 221–3,205 ng.g⁻¹ for Urban Districts of Chongqing City [5], 4–3,700 ng.g⁻¹ for Marginal seas along China Mainland [6], 638–1,620 ng.g⁻¹ for Lanzhou Reach of the Yellow River [7], 79.93–159.09 ng.g⁻¹ for Tail-reaches of the Yellow River Estuary [8], 11.78–129.21 ng.g⁻¹ for Shilaoren Bay [9], and 103.9–620.6 ng.g⁻¹ (dry season), 60.9–330.7 ng.g⁻¹ (wet season) for Estuarine sediments [10]. The content of 4.6–146 ng.g⁻¹ for Marine area of Mayo [11] and 58.4–445 ng.g⁻¹ for Arctowski station [12] in King George Island could be determined. In other countries such as Iran (Hoor Al-Azim wetland with 15.78–410.2 µKg) [13] and Indonesia (Mahakam River with 54.7–2,256.15 ng.g⁻¹) [14], PAHs content could be assessed. The Edremit Bay (0.65–175 ng.g⁻¹) of the Aegean Sea was also studied by Darilmaz et al. [15].

The persistence of PAHs in the sediments led to the development of techniques for depollution, washing, or cleaning of polluted sediments. To achieve this, many chemicals can be used, such as anionic and ionic surfactants [16], nonionic and anionic surfactants [17], Sodium Dodecyl Sulfate (SDS) and Tween 80 [18], other surfactants [19], surfactants and co-solvents [21], a combination of surfactant enhanced soil washing and iron-activated persulfate oxidation [22], and aqueous extracts of waterleaf [23]. The use of physical methods such as immobilization, stabilization, and solidification [24], thermal desorption, and incineration [25].

DOI: http://dx.doi.org/10.24018/ejen2022.7.2.2768

R. Kom Regonne, Laboratory of Industrial Chemistry and Bioresources (LICB), National School of Agro-Industrial Sciences (ENSAI), The University of Ngaoundere, Cameroon,
(e-mail: rkregonne@yahoo.fr).

M. B. Ngassoum, Laboratory of Industrial Chemistry and Bioresources (LICB), National School of Agro-Industrial Sciences (ENSAI), The University of Ngaoundere, Cameroon,
(e-mail: ngassoum@yahoo.fr).

Submitted on April 22, 2022.
Published on May 18, 2022.
P. Ze Bilo’o, National Advance School of Mines and Petroleum Industries (ENSMIP), The University of Maroua, Cameroon.
(e-mail: zebiloop@yahoo.fr).
C. S. Jessie Ekoka, Laboratory of Industrial Chemistry and Bioresources (LICB), National School of Agro-Industrial Sciences (ENSAI), The University of Ngaoundere, Cameroon.
(e-mail: jessieekoka2020@gmail.com).
Based on the availability of financial, material, and chemical means, the SDS was used to find out if the polluted coastal sediment from the Mboppi River can be washed efficiently. The treatment tests were carried out with the most polluted coastal sediment sample from the Mboppi (1.639.03 μg.g⁻¹). The aim of this experiment was to determine the factors which have an influence on the percentage of desorption even though the primary selection of factors to appreciate the effect was guided by the literature [26].

II. MATERIAL AND METHODS

A. Material

Coastal sediment from the Mboppi River has a total PAH concentration of 1,639.03 μg.g⁻¹ of which 669.34 μg.g⁻¹ represented low molecular weight (LMW) PAHs and 969.69 μg.g⁻¹ for heavy molecular weight (HMW) PAHs was used in this study. The concentrations of individual PAH are given later in the results. The exact sampling point at Mboppi market [2] has the following GPS coordinates: 4°02'44.945''N and 9°42'56.516''E.

The chemical used for washing is sodium dodecyl sulfate (SDS), which is a surfactant with a critical micellar concentration of 1.586 g.L⁻¹, while the concentration used in the study was 1 g.L⁻¹ [27].

B. Methods

The use of the complete factorial experimental design (as described in Table I) served to observe the effectiveness of the surfactant through its desorption efficiency. The yield expressed as a percentage is determined according to the equation:

\[ R(\%) = \frac{H_t - H_r}{H_t} \times 100 \]  

where

\( H_t \): Total concentration of PAHs before washing;
\( H_r \): Total residual concentration of PAHs after washing;
\( R \): Desorption yield.

The retained factors from the literature [26] are temperature (°C), stirring speed (rpm), and stirring time (min).

The washing tests are carried out on a rotary magnetic stirrer with 1 g of sediment to which 20 mL of a surfactant solution at a concentration of 1 g.L⁻¹ is added. The experimental conditions are then applied according to the experimental design as illustrated in Table II.

After washing with SDS, the sediments were air-dried and the concentration of PAHs remaining in the sediments was determined by the method described by Ze et al. [2]. The surface response model denoted by \( Y \) represents the effectiveness of the surfactant based on the residual amount of PAHs in the washed sediment.

\[ Y = y_0 + a_1X_1 + a_2X_2 + a_3X_3 + a_{12}X_1X_2 + a_{13}X_1X_3 + a_{23}X_2X_3 + a_{123}X_1X_2X_3 \]  

where \( y \) is the residual amount of PAHs.

### Table I: Experimental Domain of Studied Factors

<table>
<thead>
<tr>
<th>Factor Xi</th>
<th>Coded values (Xi)</th>
<th>Real values</th>
<th>Coded values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>X₁</td>
<td>20</td>
<td>-1</td>
</tr>
<tr>
<td>Stirring speed (rpm)</td>
<td>X₂</td>
<td>500</td>
<td>-1</td>
</tr>
<tr>
<td>Stirring time (min)</td>
<td>X₃</td>
<td>20</td>
<td>-1</td>
</tr>
</tbody>
</table>

The different coefficients are estimated as follows:

\[ y_0 = (y_1 + y_2 + y_3 + y_4 + y_5 + y_6 + y_7 + y_8)/b \]  

\[ a_1 = (-y_1 + y_2 - y_3 + y_4 - y_5 - y_6 - y_7 + y_8)/b \]  

\[ a_2 = (-y_1 - y_2 + y_3 - y_4 + y_5 + y_6 + y_7 + y_8)/b \]  

\[ a_3 = (-y_1 - y_2 - y_3 + y_4 + y_5 + y_6 - y_7 + y_8)/b \]  

\[ a_{12} = (y_1 - y_2 + y_3 - y_4 + y_5 - y_6 - y_7 + y_8)/b \]  

\[ a_{13} = (y_1 - y_2 + y_3 - y_4 - y_5 - y_6 - y_7 + y_8)/b \]  

\[ a_{23} = (y_1 + y_2 - y_3 - y_4 - y_5 + y_6 + y_7 + y_8)/b \]  

\[ a_{123} = (-y_1 + y_2 + y_3 - y_4 + y_5 - y_6 + y_7 + y_8)/b \]

### Table II: Design of Experimental Conditions

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>X₁ (°C)</th>
<th>X₂ (rpm)</th>
<th>X₃ (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20</td>
<td>500</td>
<td>20</td>
</tr>
<tr>
<td>2</td>
<td>80</td>
<td>500</td>
<td>20</td>
</tr>
<tr>
<td>3</td>
<td>20</td>
<td>1000</td>
<td>20</td>
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<tr>
<td>4</td>
<td>80</td>
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</tr>
<tr>
<td>8</td>
<td>80</td>
<td>1000</td>
<td>40</td>
</tr>
</tbody>
</table>

X₁ (Temperature); X₂ (Stirring speed); X₃ (Stirring time).

The analysis carried out on washed sediments allowed the qualitative and quantitative determination of 15 of the standard PAHs. The sums of LMH and HMW, the total concentrations of PAHs, and the concentrations of the individual PAHs in the original sample (Sample 0) and the washed samples are presented in Table III.

Statistical exploitation of results after chromatographic analysis giving the residual concentrations of PAHs brought out the effect of washing parameters on the PAHs (LMW, HMW, and total concentration) removal.

The following Fig. 1 illustrates the percentage reduction of PAHs for each experiment. It can be observed that the highest reduction of LMW PAHs is obtained under the 5th experiment (92.67%), while 81.92% is the yield for HMW PAHs under the 8th experiment. However, the eighth experiment results in the greatest reduction in total PAHs (85.79%).

DOI: http://dx.doi.org/10.24018/eje.2022.7.2.2768
Furthermore, detailed exploitation of results requires consideration of the number of rings of individual PAH. The following Fig. 2 illustrates the graphical representation of the concentration of PAHs related to the number of rings. In all experiments, it appears that 4 ring PAHs are the most abundant (42.78–66.81%) even after washing, followed by 3 ring PAHs (11.35–27.07%). This pushed us to investigate the percentage reduction of PAHs in washed sediment in comparison with fresh sediment content related to the number of rings.

The study of the percentage of reduction of PAHs related to the number of rings, as illustrated in Fig. 3 below, brought up the fact that 2 ring PAHs are the most removed PAHs in almost all the experiments. The observation made is that, in almost all experiments, the percentage of reduction of PAHs based on the number of rings reduces as the number of rings increases. This can be justified through the influence of the oil/water distribution coefficient, which reduces as the number of rings in PAHs increases. This is why two-ring PAHs are the most extracted from coastal sediment, with a percentage that reaches 100% in three (03) experiments. The highest percentage of six-ring PAH reduction (82.69%), however, was obtained under experimental conditions of 80 °C, 1 000 rpm stirring rate, and 40 min stirring time.

![Fig. 1. Reduction percentages of LMW, HMW, and total PAHs.](image)

![Fig. 2. Concentration reduction of PAHs related to the number of rings.](image)
The percentage of reduction of PAHs related to the number of rings.

**B. Influence of Parameters on the Yield and Mathematical Modeling**

The selected parameters based on literature [26] illustrated a direct positive influence on the yield. This is shown by the Pareto chart (Fig. 4), which represents the effect of parameters on the yield, including their interactions. From Figure 4, it appears that the temperature, the speed of agitation, and the duration of agitation are the most significant parameters having a positive effect on the yield. This confirms the assumption that these three parameters influence the efficiency of PAH desorption by SDS. The interactions between the studied parameters are having negative effects on the yield, with the most significant interaction observed between stirring time and stirring speed, as illustrated in Fig. 4.

The percentage of reduction of PAHs after washing using the complete factorial experimental design is the yield of the experiment. The results obtained and represented in the above Fig. 1 allowed the deduction of a mathematical model following (11).

The first-degree mathematical model with interactions representing the effectiveness of the surfactant tested (Y) is as follows:

\[
Y = 59.06 + 3.71X_1 + 12.31X_2 + 22.76X_3 + 0.25X_1X_2 - 3.71X_1X_3 - 9.80X_2X_3 + 18.37X_1X_2X_3 \tag{11}
\]

The following significant effects emerge from the above equation: There was a significant positive effect (+22.76) of the variable \(X_3\), which corresponds to the stirring time. The duration of agitation increases the desorption efficiency. Indeed, a high contact time allows the fixation of the hydrocarbons on the micelles formed from the surfactant solution. There is a positive effect (+12.31) of the variable \(X_2\), which corresponds to the stirring speed. The agitation speed, therefore, increases the efficiency of desorption by facilitating the dislodging of hydrocarbons from contaminated sediments. A positive effect (+3.71) of the variable \(X_1\) corresponds to the temperature. Indeed, the increase in temperature facilitates the formation of micelles, which will mobilize the hydrocarbons. A significant negative effect (-9.80) of the \(X_3X_3\) interaction, which corresponds to the stirring speed and duration, and -3.71 for the \(X_1X_3\) interaction, which corresponds to temperature and stirring time, was also observed. There was a significant positive effect (+18.37) of the interaction between the studied parameters \(X_1X_2\). \(X_2X_3\) interactions had a negligible effect (+0.25). There are interactions between temperature and stirring speed.

The above results demonstrate that SDS can be used in the treatment of sediments polluted by hydrocarbons in general and PAHs in particular. However, the treatment test did not allow us to reach the threshold value (44.48 µg/g) in the sediments. For this, it would be wise to optimize these
parameters to know the optimal treatment conditions, or to test other parameters (surfactant concentration, ionic strength, etc.) which allow us to reach the threshold value of the sediment guides.

C. Impact of Washing on the Ecological Toxicity

The environmental health risk assessment of PAHs on Mboppi’s sediments was realized as described by Ze et al. [2]. The TEQ was calculated following the equation below [28,29], where the factors affecting the concentration of individual PAHs are called Toxic Equivalent Factors (TEF):

\[
TEQ = C_{Bap} + C_{Baha} + 0.1C_{Baa} + 0.1C_{Bfp} + 0.1C_{cdP} + 0.1C_{Bde} + 0.01C_{ghiP} + 0.01C_{Chr} + 0.01C_{Ant} + 0.001C_{Nap} + 0.001C_{ACY} + 0.001C_{Ace} + 0.001C_{flu} + 0.001C_{phe} + 0.001C_{Fla} + 0.001C_{pyr}
\]

(12)

The Mboppi’s sediments using the Toxicity Equivalent (TEQ) as shown in Fig. 5 below confirmed that the sediments from the Mboppi River are risky environmentally speaking. The assessment realized on washed sediments (Fig. 5) indicates that the use of the SDS also reduces the toxicity equivalent and consequently reduces the ecological risk. Based on the observations of the TEQ analysis, HMW-PAHs are the principal risk culprits in Mboppi’s sediment.

IV. Conclusion

The purpose of this work was to test the effectiveness of SDS under certain parameters in the treatment of PAHs in polluted sediments from the Mboppi River. The results show that the temperature, stirring speed, and duration give good performances. At 80 °C, 1000 rpm, and 40 minutes, depollution of up to 85.79% could be achieved. The reduction of HMW-PAHs was observed, with the highest percentage (82.69%) obtained for 6 ring PAH at the same conditions. The environmental health risk assessment was reduced from 74.34 to 24.41, thus showing how far the washing with SDS gives satisfaction. Since our work has significant environmental implications, it would be interesting to first optimize the treatment process to accurately determine the values for which we have an optimum. Secondly, the study of other parameters (presence of salts, particle size, the effect of organic matter, the nature of the sediments, etc.) in the treatment process can help in washing PAH-polluted sediments.

ACKNOWLEDGMENT

The authors would like to thank the Laboratory of Industrial Chemistry and Bioresources (LICB) of the National School of Agro-Industrial Sciences (ENSAl) which provided the necessary devices and equipment.

CONFLICT OF INTEREST

The authors declare that they do not have any conflict of interest.

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DOI: http://dx.doi.org/10.24018/ejeeng.2022.7.2.2768


