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Preliminary studies on the sorption of dibenzothiophene from synthetic fuels using fruit wastes

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ABSTRACT

The massive combustion of coal and fossil fuels during the first and second industrial revolutions started the emissions of organosulfur compounds. The concerns associated with the presence these compounds have heightened with the increasing greenhouse gas emissions into the atmosphere and exacerbated the problem of acid rain. This preliminary study proposes the bioremoval of dibenzothiophene (DBT) from synthetic gasoline and diesel fuels using dead biomass such as fruit peels. The peels of orange (OG), pineapple (PN), and lime (LM) were investigated in continuous-flow and batch experiments to determine their adsorption capacities as a function of initial concentration of DBT, type of adsorbent and adsorbent dosage. DBT adsorption follows the trend LM (12.3%) > PN (8.8%) > OG (6.9%) in gasoline with 50 mg, 125 mg, and 50 mg, respectively and LM (14.6%) > OG (4.2%) > PN (3.5%) in diesel with 50 mg, 75 mg, and 75 mg, respectively. Instrumental analysis suggests a polar adsorption mechanism between the carboxyl and hydroxyl groups that are present on the adsorbents and the sulfur-oxygen bonds present in DBT. Additionally, these fruit wastes display appropriate thermal and mechanical properties according to the thermogravimetric analyses. Adsorption dynamics experiments demonstrate the potential applications of these adsorbents in continuous-flow systems for the remediation and treatment of larger volumes of fuel. These preliminary results suggest that fruit peel wastes are a sustainable, low cost and eco-friendly alternative to removal of harmful organosulfur compounds from fuels.

KEYWORDS: fruit peels, sorption, dibenzothiophene, acid rain, synthetic fuels.

INTRODUCTION

Acid rain has been a worldwide problem even before the expansion of the manufacturing and transportation industries. Constant gas emissions from volcanos and other natural sources have resulted in the generation of rainfall with high acidity, contributing to the deterioration of crops, soils, and infrastructures. Acid rain is defined as the precipitation of atmospheric moisture that is more acidic than usual [1]. The United States of America and its Northeast region in particular, do not escape from this issue. As described by the US Geology Survey Water Science School [1, 2] the rainfall in the Northeast region of the US included a substantially high amount of acidic rainfall (pH value of 4.3) than the rest of the country in 1992. This acid rain mostly affected the states of New York, Pennsylvania, Ohio, and Connecticut. Although the rainfall acidity decreased in 2018 (reaching pH values of 4.8), however in 2018, the acid rain affected a larger number of states, covering not only the 4 states mentioned above, but the entire East, South and Mid-East regions of the country as indicated by the wet acidic depositions [2].

These reports [1, 2] indicate that the affected regions in the US have the densest populations,

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*Corresponding author: anavarro@bmcc.cuny.edu larger number of cities, and a higher concentration of power and industrial plants. Then, what does really cause acid rain? It is mainly caused by the emission of SO_x and NO_x gases into the atmosphere [1-4] that mix with the atmospheric water, yield sulfuric and nitric acids, and then, precipitate as acid rain. Sulfur-containing compounds are present in coal and fossil fuels and their combustion releases these acidic sulfur and nitrogen oxides into the atmosphere [3]. Organosulfur compounds are the most important pollutants in fuels and the most latent problem of oil refineries [4, 5]. Unfortunately, this problem will not get any better in the future. According to Mearns [3], coal, natural gas and petroleum are the top primary energy sources, and the most aggressive producers of acid rain gases. This trend is expected to increase with the population growth and the construction of more industrial and power plants. Developed countries strongly depend on gasoline, diesel and fossil fuels for their manufacturing factories and large amounts of organosulfur compounds are expected to be released into the air.

The elimination of organosulfur from fuels is one of the top priorities of oil refineries and an area of active research over the last 20 years. Most organosulfur compounds that are present in fossil fuels include aromatic compounds such as thiophenes, benzothiophenes and dibenzothiophenes, which are highly concentrated in the heavier crude fractions and are partially converted during the refining process. The awareness of these organosulfur compounds increased due to the promulgation of more restrictive environmental rules. The maximum allowable sulfur content in highway diesel fuel was reduced to less than 15 ppmw in 2006 in the US from the previous maximum of 500 ppmw [5]. The risk of organosulfur compounds derives from the production of sulfur oxides such as SO_2 and SO_3 during their combustion, which are important contributors to acid rain [6]. Likewise, sulfur is a known poison for catalysts that ruins catalytic converters in cars, causing extra expenses for the automobile industry [5, 6].

The conventional methods for deep desulfurization of liquid hydrocarbon fuels can be divided into catalytic hydrodesulfurization, chemical oxidation, adsorption, extractive desulfurization, and bacterial desulfurization [7, 8]. Among them, selective adsorption seems to be one of the most promising techniques for the removal of sulfur from fuels due to its low price and realistic operational conditions at room temperature and atmospheric pressure.

The most common adsorption techniques are based on the use of activated carbon, which is well-known for its adsorption properties towards other pollutants including phenolic compounds, dyes, metals, and organic molecules in general. Therefore, its application for the elimination of sulfured compounds has been subject of research in the past [9-11]. Unfortunately, the production of activated carbon involves the burning of wood and other vegetal materials, which also produces the known greenhouse gas, carbon dioxide. On the other hand, bioremediation using naturally occurring materials such as hydrogels [12, 13], marine algae [14], and spent tea leaves [15-17] has emerged as a field of biotechnology to address the problem of pollution by inorganic and organic substances. These studies indicate that the high affinity between these non-living biological materials and the pollutants depends on physico-chemical interactions of the functional groups of the adsorbents. These functional groups are part of the structure of these materials (mainly as part of the cellulose structure): carboxyl, amine, hydroxyl, amide, thiol, phosphate, and sulfonyl. Previous results demonstrate that heavy metals can be efficiently removed from wastewaters by using spent tea leaves in continuous-flow experiments [18-20]. The success of these materials can be taken to medium-scale processes for the treatment of larger volumes of contaminated solutions. Another advantage of these materials is that they are highly selective, meaning that, even in the presence of other substances like salts and surfactants, they can still eliminate pollutants [16, 17]. Extensive research has been done in the elimination of pollutants from aqueous systems by using these biological materials, but the treatment of fuels and liquid hydrocarbons has been left aside. For example, a quick search on the database Entrez PubMed shows <200 publications on adsorption of thiophenes by using activated carbon, special oxides, doped materials and special polymers [21-23]. However, the research on eco-friendly materials for the uptake of thiophenes is limited.

For this study, we have used fruit peels as a biological adsorbent for the elimination of dibenzothiophene (DBT) from synthetic fuels. Canned fruits, especially pineapple, orange and lime are commercially available and are in high demand. What do they do with their peels? Perhaps they are used in scent industries, or in the production of fruit zests, or end up as landfills. Regardless of the end of those peel wastes, we propose an alternative use of these waste by-products for the decontamination of fuels. A long-term project includes the collaboration with Goya, Dole, and Libby's to obtain their fruit peels to make filters with these renewable materials for the treatment of fossil fuels in continuous systems.

The objective of this study is to investigate equilibrium parameters that maximize the uptake of DBT from synthetic diesel and gasoline. Batch adsorption experiments and column experiments were carried out to compare the strength of the peels of orange (OG), and pineapple (PN) as potential adsorbents. We expect that these positive results can be transmitted to the scientific community to further investigate the viability of these "clean" adsorbents on the removal of pollutants from non-polar solutions such as gasoline and diesel.

MATERIALS AND METHODS

Preparation of the adsorbents

Fresh orange, pineapple and lime fruits were purchased from a local supermarket. All fruits were ripe, with no signs of spoiling. In the lab, fruits were peeled, and excess fruit was scrapped off with a spoon. Then, the peels were vigorously rinsed with tap water to remove any impurities and placed in the oven for at least 2 days at a temperature not higher than 60 °C to prevent organic decomposition. Upon drying, the peels were cut in pieces, ground and sieved to a particle size not larger than 100 um. Upon grinding, the peels were soaked in and rinsed with distilled water. Final separation was accomplished by vacuum filtration in a cheese cloth. Final rinses were done with deionized water to eliminate residual impurities. Then, the adsorbents were placed in the oven for drying at 60 °C. Adsorbents were placed in Erlenmeyer flasks and stored at room temperature until their use in adsorption experiments. No signs of spoiling were observed during the storage for more than one year. Adsorbents lost their characteristic smells, confirming that only structural polysaccharides were present. The prepared materials were labeled as orange (OG), pineapple (PN) and lime (LM).

Synthetic fuels and solutions

Synthetic gasoline and diesel were prepared based on their major components, according to the literature [9-11]. Hexadecane was chosen as synthetic gasoline and a 1:1 mixture of decane and hexadecane was used for diesel. All the solvents were of a purity of 99% or higher (Acros Organic, USA). DBT-containing solutions were freshly made prior to every single experiment, to avoid changes in concentrations due to spontaneous evaporation of the fuels. DBT was purchased from Aldrich, USA (Reagent grade) and used without further purification.

Batch adsorption experiments

Batch experiments were carried out in duplicate at room temperature in amber glass vials to prevent photo-degradation of DBT and the vials were tightly sealed to avoid evaporation and changes in the pollutant concentration. Adsorption samples were made by combining variable masses of the fruit peels with 20 mL of a DBT solution of the two synthetic fuels with orbital agitation at 200 rpm for 24 h. The adsorption time was determined by preliminary experiments. Thereafter, the suspensions were centrifuged and the remaining concentration of DBT was determined through UV spectrophotometry at a wavelength of 330 nm using a microplate reader (Biotek, Synergy4). This quantitative analysis was performed right after the end of the experiment to avoid changes in the concentration of DBT due to evaporation. Some spectrophotometric interference was noticed from the fruit peels. This problem was circumvented by running control experiments where the adsorbents were soaked in the same volume of the fuels as the regular adsorption samples, but in the absence of DBT. These control samples were also measured by UV to determine the absorbance of the substances that are discharged by the adsorbents. This absorbance was subtracted from the UV absorbance after the adsorption of DBT.

Continuous-flow experiments (column tests)

Column experiments take the batch results to a scaled-up process and provide more valuable information for industrial applications. We envision the preparation of biodegradable filters made of these fruit peels and their use in continuous systems. Continuous-flow experiments were conducted in glass columns with dimensions 15 cm length and internal radius of 0.5 cm. The DBT-solution was run against gravity at a flow rate of 1 ml/min and had a DBT concentration of 50 ppm. A control run was not carried out, since the column was washed out with the pure fuels at low flow rate for 4-hour prior pumping DBT into the column. Samples were taken every minute with a programmed fraction collector. Samples were spectrophotometrically quantified right after collection to prevent changes in the concentration.

Characterization of the adsorbents

All the adsorbents were characterized by instrumental analyses. Fourier-transformed infrared (FTIR) spectroscopy elucidated the presence of important functional groups that could be responsible for the adsorption of DBT. This analysis was carried out with PN before and after the adsorption of DBT to determine changes in the spectra due to the presence of DBT. A Frontier (Perkin Elmer) spectrometer with an ATR accessory was utilized.

Thermal analyses were also carried out to study the thermal, mechanical, and physical resistance of the materials. This test provides further insights into the use of fruit peels as adsorbents. Although these adsorbents will not be used at high temperature, heat stability can be used as an indicator of the resistance of these materials. A simultaneous thermal analyser (STA 6000, Perkin Elmer) was used for this experiment. Runs were conducted under nitrogen gas at a heat rate of 5 °C/min covering a temperature range from 30 to 500 °C.

Data analysis

The amount of the DBT adsorbed on the adsorbents was expressed as adsorption percentage (%ADS) and calculated as shown in equation (1):

$$\%ADS = \frac{c_i - c_f}{c_i} x100 \qquad (1)$$

where C_i and C_f are the initial and final concentrations of DBT expressed in mg/L (ppm) in the solution. Graphs and calculations were done with Origin v8 software. Errors were calculated and fell between 2.8-3.9%.

RESULTS AND DISCUSSION

Characterization of the adsorbent

New applications of existing materials require a deep characterization of their chemical and physical properties. The FTIR spectra of the adsorbent before and after the DBT adsorption are shown in Figure 1. As expected, the three adsorbents display similar FTIR profiles, characteristic of the high cellulose and polysaccharide composition (Figure 1A). Infrared peaks at wavenumbers 3300 cm^{-1}, 2950 cm^{-1}, 1740 cm^{-1} and 1620 cm^{-1} can be observed, which are associated with the presence of hydroxyl, alkane, carboxylic carbonyl, and carbonyl groups, respectively. Therefore, the presence of carboxylic acids, alcohol and aldehyde/ketones can be confirmed as potential adsorptive sites for the uptake of DBT. An important feature to highlight is the hydroxyl absorption band for the adsorbents, which are similar in intensity and wavenumber for LM and OG; however, it is surprisingly a more intense and blue-shifted peak. This could be interpreted as a higher content of polysaccharides when compared to LM and OG, or (and most likely) the higher composition in lignin. Both species have shown adsorption properties towards pollutants [24, 25]; therefore their presence in these adsorbents should have a positive effect. The structure of DBT is shown in Figure 2, displaying the plausible groups that might be interacting with the surface of the adsorbents. For example, the sulfur atom is able to form strong dipole-dipole interactions with the alcohol, and carboxyl groups of the adsorbents. The dominance in the DBT adsorption of LM could be attributed to the tridimensional arrangement of these polysaccharides in lime peels that allow a better interaction or contact between the pollutant and the adsorption sites. As any cellulosic material, fruit peels also contain lignin, a cross-linked polyphenol in a percentage between 10-15% weight. Polyphenols could also interact with the aromatic rings of DBT, by using π stacking-like interaction between aromatic rings. Therefore, it could be proposed that dipole and π stacking are responsible for the affinity between DBT and fruit peel adsorbents. More tests are still needed to elucidate this mechanism. Future work includes the use of lignin-free materials to test the relevance of π stacking on the adsorption of DBT onto fruit peels.

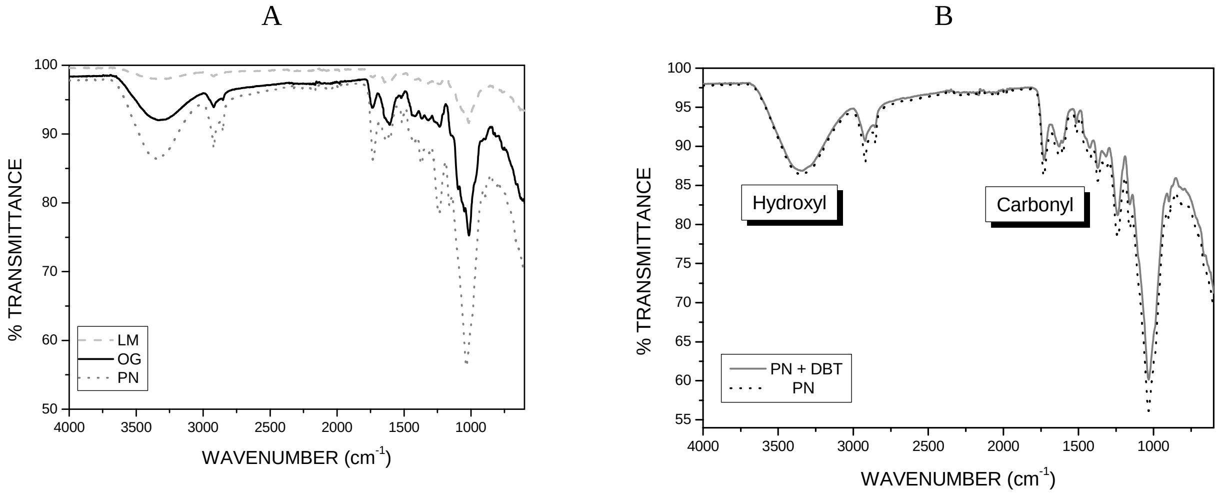

Figure 1. (A) FTIR spectra of the adsorbents used in this project and (B) FTIR spectra of PN before and after the adsorption of DBT.

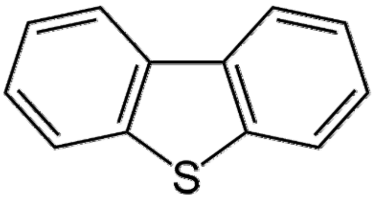

Figure 2. Chemical structure of dibenzothiophene (DBT).

In addition to the FTIR characterization of the adsorbents, a second FTIR test was conducted before and after the adsorption of DBT and is displayed in Figure 1B. According to the results, small changes in the FTIR signals are observed at 3300 cm^{-1}, 1740 cm^{-1} and 1620 cm^{-1} wavenumbers. These signal shifts suggest that these functional groups could be associated with the uptake of DBT. Shifts in hydroxyl and carboxylic carbonyl confirm that strong dipole forces are being formed between DBT and PN. It is expected that in a hydrophobic environment (decane and hexadecane as solvent), polar interactions are maximized to hide the polarity from the adverse solvent environment. Unfortunately, the aromatic bands of the lignin of PN are not visible in the spectrum, which could elucidate the contribution of the π stacking forces in the adsorption. Once again, more tests are needed to determine how the binding occurs between the fruit peels and DBT.

Finally, the adsorbents were also studied by thermal analysis to determine the mechanical, thermal, and physical resistance. The results are shown in Figure 3, where the graphs indicates that PN is the strongest adsorbent, since it starts decomposing at 250 °C. Conversely, OG displays a weaker resistance to heat, showing decomposition at 220 °C. Although PN and OG are the strongest and weakest adsorbents, respectively; PN loses more matter at high temperatures. Therefore, it could be concluded that PN has less cellulose (degrades between 200-300 °C) than OG and LM. As expected, LM and OG have similar thermal curves, due to their vegetal similarities. It is important to highlight that all curves show two thermal transitions. The first one between 250-260 °C and the second one between 320-330 °C. The phenomena could be attributed to the presence of different types of carbohydrates (cellulose, hemicellulose, and pectin) and lignin in the samples. Different structures will have different decomposition temperatures.

Batch experiments

Any potential adsorbent for the elimination of pollutant should not only have a high adsorption percentage but should also minimize the amount of adsorbent. The effect of the mass on the adsorption of DBT was studied in synthetic gasoline and diesel. The results are shown in Figure 4. According to the data, higher adsorption removals are observed in gasoline. Surprisingly, LM showed a higher adsorption than OG and PN, although they share similar chemical compositions. At this moment,

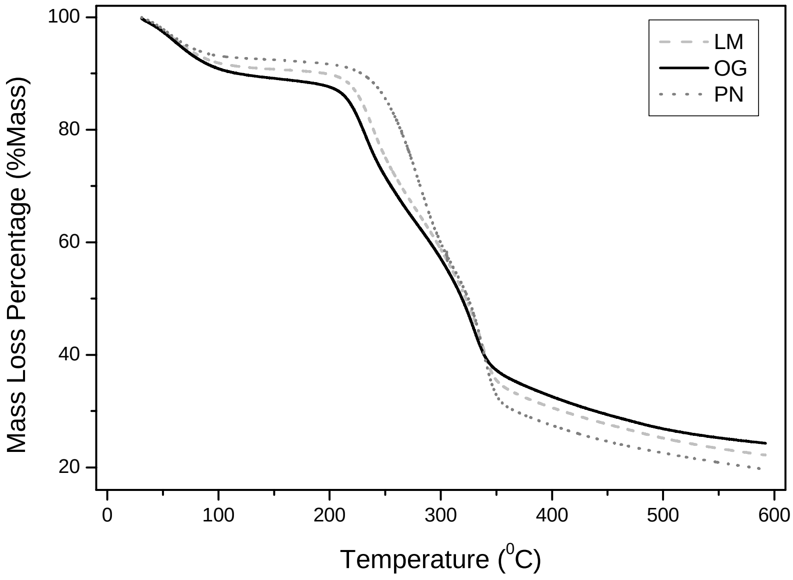

Figure 3. TGA plots of the adsorbents used in the removal of DBT.

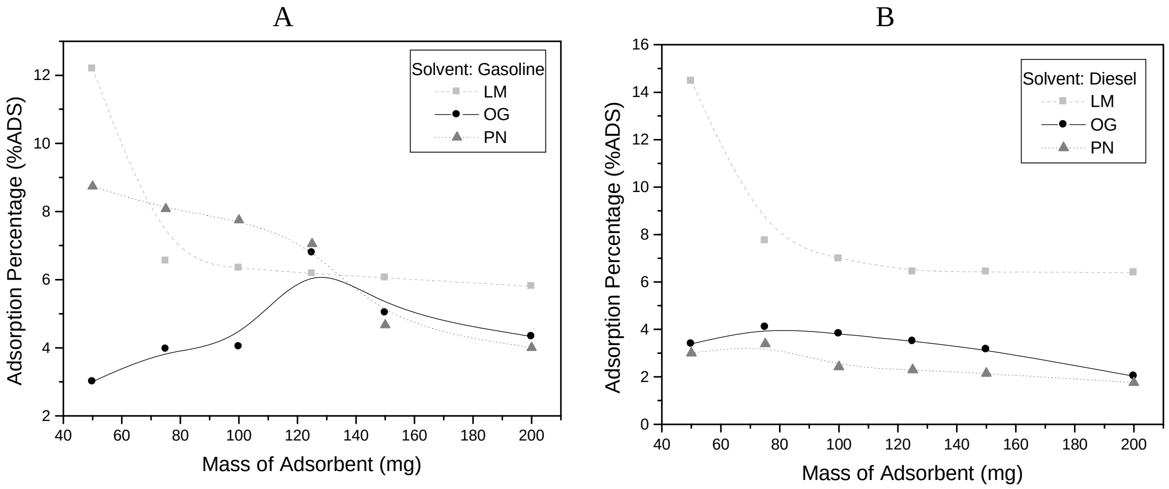

Figure 4. Effect of the mass of adsorbent on the adsorption of DBT in gasoline (A) and diesel (B) fuels.

more experiments are centered around LM, since it shows a better efficiency. Although LM reports a higher DBT adsorption in both, diesel, and gasoline, nevertheless its preparation as an adsorbent is more time consuming and less biomass can be obtained per fruit. PN produces most of the mass of adsorbent per fruit and is easier to purify (rinsing and filtering).

According to Figure 4 the trend of DBT adsorption in gasoline is: LM (12.3%) > PN (8.8%) > OG (6.9%) with 50 mg, 125 mg, and 50 mg, respectively. On the other hand, the adsorption of DBT in diesel followed the trend: LM (14.6%) > OG (4.2%) > PN (3.5%) with 50 mg, 75 mg, and 75 mg, respectively. It is important to highlight that PN shows a better affinity towards DBT in gasoline, whereas OG and PN have similar affinities in diesel. The differences in adsorption in diesel and gasoline is unclear but could be attributed to the density and viscosity of the fuels that prevent or facilitate the accessibility of DBT to the adsorption sites. Synthetic gasoline is only composed of hexadecane, whereas diesel is a 1:1 mixture of decane and hexadecane. Both hydrocarbons are linear molecules with identical intermolecular interactions.

The effect of the initial DBT concentration was also studied in the concentration range between 10 and 125 ppm for OG and PN in both fuels. This study did not include LM as an adsorbent since these adsorption assays are currently being conducted. A more detailed report with LM will be published later this year and further insights into the adsorption kinetics and mechanism will be provided. For this concentration effect study, the optimal masses from the previous mass effect were used. The results are shown in Figure 5, corroborating that DBT can be more efficiently removed from gasoline rather than diesel (by a factor of 4 in the case of OG). Surprisingly, the adsorption in diesel is strongly affected at increasing DBT concentrations. Adsorption of DBT is almost negligible at high DBT concentrations. Apparently, all adsorbents reach saturation very rapidly and are not suitable at high DBT concentrations. Although high adsorption efficiencies are expected for a broad range of pollutant concentration, nevertheless for real conditions, the US-EPA and other major environmental institutions have regulated the levels of organosulfur compounds to a maximum level of 10-15 ppm (depending on the country) and according to our results, PN and OG can remove up to 28% and 21% of DBT from gasoline and diesel, respectively at that range of concentration. As previously mentioned, LM was not tested as an adsorbent for this report but has a higher affinity towards DBT (approximately 50-65% removal).

Column experiments

A real application of this adsorption technique for the elimination of organosulfur compounds from fuels involves the automation in continuous-flow systems. These materials can be used as filtering devices to reduce solid wastes of fruit-related industries and to reduce the amount of organosulfur compounds from fuels. A continuous system is needed to decontaminate larger volumes of fuels and to make it more attractive to oil refineries that circulate their fuels for commercialization.

For this test, columns of OG and PN were prepared and tested in synthetic gasoline and diesel, respectively. Breakthrough curves were plotted and are displayed in Figure 6. The *x*-axis represents the volume of fuels that passed through the column and the *y*-axis represents the fraction of DBT (initial concentration of 50 ppm) that remains in the column effluent. Upon reaching the exhausting point of the column (plateau in the curve that reaches a constant DBT fraction of 1) clean fuel is flushed through the column to confirm that the DBT is tightly bound to the adsorbents and does not discharge back into the clean fuel. A steeper drop in this last stage represents a better adsorption, since no residual DBT can be desorbed from the column with fresh fuels. This is observed in both columns (OG and PN), where both columns need

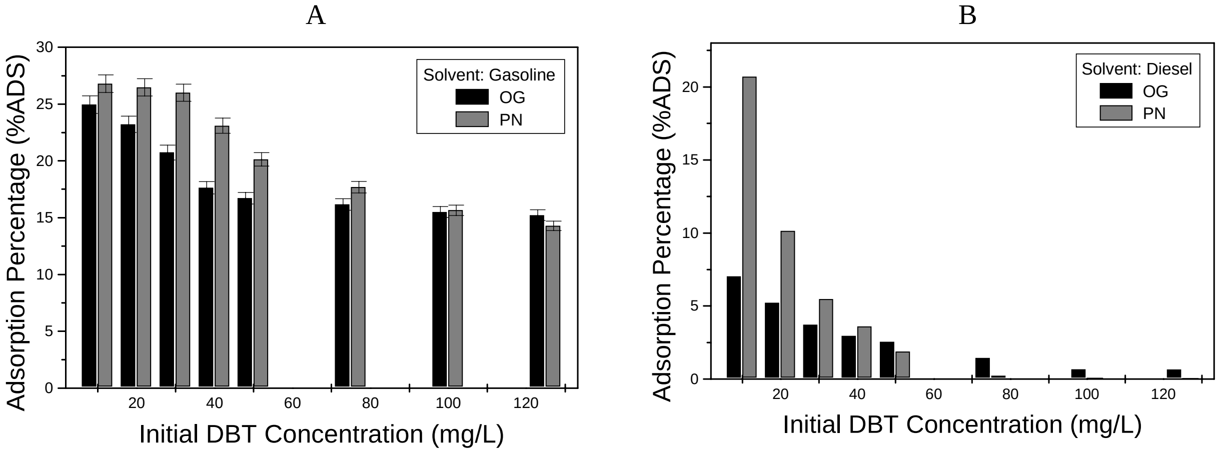

Figure 5. Effect of the initial DBT concentration on the adsorption of DBT in gasoline (A) and diesel (B) fuels.

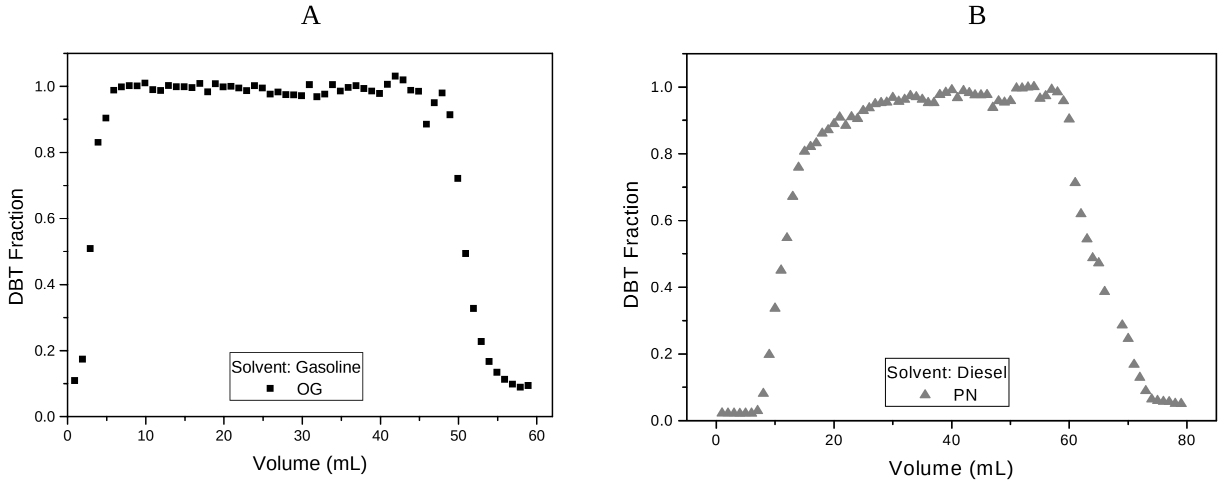

Figure 6. Continuous-flow experiments for the removal of DBT with OG in gasoline (A) and PN in diesel (B).

about 6 mL of clean fuel to eliminate any unbound DBT from the columns.

Figure 6 also confirms that PN is a better adsorbent than OG under these working conditions: PN (1.1 g) can fully clean up to 10 mL (break point) of diesel containing 50 ppm of DBT. Upon saturation at 10 mL, the column continues with the uptake of DBT from the fuel until the exhaustion point at 22 mL. In the case of OG in gasoline, this adsorbent is a weak candidate since it reaches the break point at 2 mL of DBT solution and achieves the exhaustion point at 9 mL. Further studies are still needed in this system at different flow rates and column dimensions that could maximize the residence time and allow for a more efficient interaction between DBT and the fruit peels and allow a better transport phenomenon of the pollutant from the bulk solution to the surface of the adsorbent.

The use of these new adsorbents in the removal of DBT can be compared to recently published reports [21-27]. Moosavi *et al.* have used copper and nickel-doped activated carbons achieving 14 mg S per gram of adsorbent [26]. Yu *et al.* [27] have utilized acid-treated activated carbon, obtaining adsorption removals of 60% of DBT. Although our fruit peels do not have adsorption capacities as high as these other materials, LM, PN and OG are low-cost and do not require any additional doping, acid-treatment or chemical reaction that might create new contaminants. The proposed fruit peels use solid industrial waste from fruit-related industries and their residues for the preparation of eco-friendly materials. This approach will not only benefit the industries that produce fruit peel waste, but also contribute to the decrease of acid rain levels in the planet. This will not only benefit the Northeast U.S. but can be used as a model for any region facing similar or worse acidic rainfall problems.

CONCLUSIONS

This project demonstrates that solid industrial wastes such as fruit peels of pineapple (PN), lime (LM) and orange (OG) can be potentially utilized as adsorbents for removal of dibenzothiophene (DBT) from synthetic fuels (diesel and gasoline) at room temperature. Batch experiments demonstrate that LM has a higher affinity towards DBT in both fuels. DBT adsorption follows the trend LM (12.3%) > PN (8.8%) > OG (6.9%) in gasoline with 50 mg, 125 mg, and 50 mg, respectively. On the other hand, the adsorption of DBT in diesel followed the trend: LM (14.6%) > OG (4.2%) > PN (3.5%) with 50 mg, 75 mg, and 75 mg, respectively. These results align with the chemical composition of the adsorbents (mainly lignin and polysaccharides) as demonstrated by FTIR studies. Initial DBT concentration was also explored that demonstrated that these adsorbents maximize their adsorption at low DBT concentrations, matching the maximum permissible levels of organosulfur compounds in fuels (15 ppm). Instrumental characterization of the adsorbents before and after the adsorption was also carried out to determine the potential adsorption mechanism and properties of the materials. The results suggest that the uptake of DBT is mainly driven by polar interactions between carboxyl and hydroxyl groups of the adsorbent and the sulfur atom of DBT. Thermal analysis confirmed that PN is a more resistant material (surviving temperatures as high as 250 °C) and all adsorbents have two thermal transitions, elucidating the presence of two main components in their structures (lignin and cellulosic materials). Finally, continuous-flow experiments with columns indicate the potential of these adsorbents as filtration devices for continuous systems in industrial applications. Further studies are needed, especially with LM but these preliminary results are very promising. Overall, this project constitutes a major contribution to the field of biotechnology for the development of cost-efficient adsorbents for the removal of pollutants in general. The versatility of biowastes such as fruit peels as adsorbents of organosulfur compounds opens the door for their extensive use in new techniques for fuel purification at low cost.

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CONFLICT OF INTEREST STATEMENT

The authors declare that they have no conflict of interest.

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