

Article

On the Removal and Desorption of Sulfur Compounds from Model Fuels with Modified Clays

Jeong W. Ha, Tenzing Japhe, Tesfamichael Demeke, Bertin Moreno and Abel E. Navarro *

Science Department, Borough of Manhattan Community College, The City University of New York, New York, NY 10007, USA; jeongwooha@gmail.com (J.W.H.); Tenzing.Japhe71@myhunter.cuny.edu (T.J.); tesfademeke@hotmail.com (T.D.); bertmoreno2014@gmail.com (B.M.)

* Correspondence: anavarro@bmcc.cuny.edu; Tel.: +1-212-220-8000

Received: 25 May 2018; Accepted: 27 June 2018; Published: 10 July 2018



Abstract: The presence of sulfur compounds in fossil fuels has been an important concern in recent decades as an environmental risk due to the increase of greenhouse gases in the atmosphere and accentuation of acid rain. This study evaluates modified clays as low-cost and efficient adsorbents for the removal of dibenzothiophene (BT) and 4,6-dibenzothiophene (DBT). Adsorption was investigated in a batch system with synthetic fuels (gasoline and diesel) as a function of type of clay modification, adsorbent dosage, initial concentration of the pollutants, desorption, and isotherm modeling. Maximum adsorption was observed with clays modified with benzyltrimethylammonium ion (BM), achieving a maximum adsorption capacity (q_{max}) of BT of 11.3 mg/g in gasoline and 31.3 mg/g in diesel. The formation of Van der Waals interaction as well as aromatic forces as the main mechanism is proposed based on the results. A 40% desorption was accomplished in 0.1 N HCl. Adsorbents were characterized by scanning electron microscopy (SEM) and Fourier transform-infrared spectroscopy (FT-IR), indicating their optimum properties as adsorbents in fuels. This work highlights the potential use of reverse polarity clays in the elimination of sulfur compounds from model fuels as a low-cost and environmentally friendly purification technique.

Keywords: benzothiophenes; adsorption; modified clays; quaternary ammonium salt; isotherm

1. Introduction

The abatement of the presence of sulfur in fuels is one of the most important priorities for oil refineries and has been the subject of active research in the last 20 years. This has been propelled by the production and use of more environmentally friendly transportation fuels that attract the attention of many countries. The majority of sulfur-containing compounds present in these fuels include thiophenes, benzothiophenes and dibenzothiophenes (BTs), which are highly concentrated in the heaviest crude fractions and are partially reduced during the refining process. The removal of these compounds is becoming more relevant due to the creation of more restrictive environmental rules. The maximum allowable sulfur content in highway diesel fuel was reduced to less than 15 ppmw in the US from the maximum of 500 ppmw early in this century [1]. The potential risk of these sulfur-containing compounds during any combustion process resides in their transformation into sulfur oxides such as SO_2 and SO_3 which are important contributors to acid rain [2]. Likewise, the presence of sulfur promotes the poisoning of catalysts that are used in the treatment of gases from automobiles.

In general, methods for deep desulfurization of liquid hydrocarbon fuels can be classified into catalytic hydrodesulfurization with improved new catalysts, chemical oxidation, adsorption, extractive desulfurization, and biodesulfurization by using special bacteria [3,4]. Amongst 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.

Nowadays, the most common adsorption techniques are based on the use of activated carbon. Activated carbon is well known for its adsorption properties, including phenolic compounds, dyes, metals and organic molecules in general. Therefore, its application to the elimination of sulfured compounds has been subject of research in the past [5–7]. Unfortunately, the next question this raises is: is activated carbon not prepared by burning organic materials? Is this process not also by-producing carbon dioxide and other greenhouse gases? Perhaps, one of the most important tasks that need to be studied is the recycling of the activated carbon or to improve the experimental conditions to isolate the pollutant and reuse the same adsorbent in sequential cycles.

Conversely, natural clays are naturally occurring resources whose extraction does not require sophisticated equipment and does not produce environmentally toxic substances. Clays are molecularly composed of up to two silica tetrahedral sheets with a central octahedral sheet. The main structure of clays is negatively charged and electrically balanced by the presence of exchangeable cations (Na, K, Ca, etc.). The presence of these ions imparts a high surface polarity that is not chemically friendly to non-polar environments like gasoline and diesel. Unfortunately, the target pollutants (benzothiophenes) are highly hydrophobic. For this reason, a modification is needed to improve the hydrophobic affinity of natural clay to aim these apolar molecules. This is done by taking advantage of the exchangeable ions that reside on the porous surface of clays. Non-polar quaternary ammonium ions have been used in the past to improve the adsorption of phenolic compounds on bentonite [8,9]. Positive results showed reversal of polarity on the surface and enhancement of affinity towards non-polar substrates.

The objective of this research is to investigate the most important equilibrium parameters on the adsorption of 2,4-dimethyldibenzothiophene (DBT) and BT as model sulfur compounds present in transportation fuels. Batch adsorption experiments in room conditions were carried out in synthetic gasoline and diesel fuels to compare the strength of modified clays in different types of fuels. It is expected that these important results will promote more studies on the viability of these “clean” adsorbents for the removal of pollutants from apolar solutions such as gasoline and diesel.

2. Experiments

2.1. Conditioning of the Adsorbents

Bentonite is a type of clay from the montmorillonite group and smectite mineral family. Bentonite was purchased as a raw mineral (Sigma-Aldrich, Allentown, PA, USA) and then modified with three different ammonium salts: benzyltrimethylammonium chloride (BM), tetramethylammonium chloride (TM), and with hexadecyltrimethylammonium chloride (HM). These quaternary ammonium ions have demonstrated high affinity towards organic compounds [8,9] to enhance their adsorption capacity. The exchange procedure was as follows: 20 g of clay was suspended in 2 L of distilled water and combined with two equivalents of its cation exchange capacity (CEC) of the ammonium salts (99% Sigma Aldrich, USA). The final suspension was stirred at 250 rpm during 24 h at room temperature. The modified clays were decanted, vacuum filtered and vigorously rinsed with distilled water to eliminate the excess of ammonium salts, dried at 60 °C in an oven for 48h and stored until their use. The clays were identified according to the ammonium salt used in their modification. The CEC of the clay (0.06 mmol/g) was determined using the methylene blue standard method (ASTM C-837-81) and corroborated with the manufacturer. Prior results also demonstrate that the bentonite used in this experiment is mainly composed of montmorillonite with impurities of cristobalite, quartz and muscovite [10].

2.2. Synthetic Fuels and Solutions

Synthetic gasoline and diesel were prepared based on their major components, according to the literature [5–7]. Hexadecane was chosen as synthetic gasoline and a 1:1 volume mixture of decane and hexadecane was used for diesel. All the solvents were of a purity of 99% or higher (Acros Organic, Pittsburgh, PA, USA). DBT- and BT-containing solutions were freshly made prior to every single experiment, to avoid changes in concentrations due to spontaneous evaporation of the fuels. DBT and BT were purchased from Aldrich, USA (Reagent grade) and used without further purification.

2.3. Adsorption Experiments

Batch experiments were carried out in triplicate at room temperature combining variable masses of the clays with 20 mL of a solution of the fuels under orbital agitation at 200 rpm for 24 h in amber vials with septum caps. The adsorption time was determined by preliminary experiments. Thereafter, the suspensions were centrifuged and the remaining concentrations of DBT and BT were determined through ultraviolet (UV) spectrophotometry using a microplate reader (Biotek, Synergy4, Winooski, VT, USA) at a wavelength of 330 nm [5]. The BT and DBT solutions showed no degradation for at least 2 days, according to preliminary results. UV-transparent microplates were utilized for the measurements. This quantitative analysis was performed right after the end of the experiment to avoid changes in the concentration of the pollutants due to evaporation. No spectrometric interference was noticed from other substances, improving the resolution of the spectra.

2.3.1. Best Modified Clay

Three different modified clays were prepared as mentioned in Section 2.1. However, the best clay was chosen based on an experiment in which all the clays, including the non-modified clay (NC), were exposed to DBT and BT. The purpose of this experiment was to discover any chemical or physical differences in clay samples. This assay was conducted with an initial concentration of 25 ppm of the sulfur compound and a mass of 25 mg of adsorbent.

2.3.2. Adsorption Isotherms and Effect of Adsorbent Dosage

Solutions of DBT and BT were prepared at different concentrations ranging from 20 to 300 ppm. Then, a variable mass, between 25 and 200 mg of the best clay was added. Experimental data was fitted to adsorption isotherms theories and their equation to obtain a mathematical equilibrium parameters and constants.

2.4. Desorption Experiments

Batch experiment with the optimized parameters of best clay, adsorbent dose and concentration of pollutant was carried out with both fuels. The adsorbents were centrifuged, carefully rinsed with the same fuel to eliminate any residual DBT or BT from the adsorbents, and air-dried till dryness. Then, 25 mg of the dry pollutant-loaded adsorbents were put in contact with co-solvents during 2 h to identify the best eluting solution. The co-solvents included solutions of methanol, acetone, toluene, NaOH (0.1 N), and HCl (0.1 N). Finally, the samples were centrifuged and the supernatant was taken for quantification of residual amounts of DBT and BT by UV spectrophotometry. Although the spectra showed no interference from the presence of clays and fuels, nevertheless for the desorption experiment, some adjustments were needed where some of the co-solvents showed UV-light absorbance at the worked wavelength such as acetone.

2.5. Data Analysis

The amount of the DBT and BT adsorbed on the clays were expressed as Adsorption Capacity (q , mg/g) and calculated as shown in Equation (1):

$$q = \frac{(C_i - C_{eq}) \times V}{m} \quad (1)$$

where m is the mass of the adsorbent expressed in g, V is the volume of the solution in L and C_i and C_{eq} are the initial and at the equilibrium concentrations of DBT and BT expressed in mg/L, respectively.

A different, commonly used, quantitative indication of the adsorption is expressed as percentage. In this research, (%DES) was used to quantify the amount of pollutant that was recovered during the desorption experiment, and was determined according to Equation (2):

$$\%DES = \frac{C_d}{C_l} \times 100 \quad (2)$$

where C_d represents the concentration of DBT or BT present in the eluting solution and C_l is the concentration of the pollutant that was loaded in the adsorbent after the adsorption experiment.

2.6. Physical and Chemical Characterization of the Adsorbents

Instrumental analyses included scanning electron microscopy (SEM), using a TableTop Microscope (TM3000, Hitachi, Tarrytown, NY, USA). Samples were directly observed in the microscopy without any conductive gold film. Clay samples were also characterized by Fourier transform-infrared spectroscopy (FT-IR) by attenuated total reflectance (ATR). This technique determines the chemical functional groups and vibrational response of polar bonds that are present on the surface of the adsorbents. A FT-IR Spectrum 100 (Perkin Elmer, Shelton, CT, USA) was attached to a crystal diamond ATR device. Scans were collected from 400 to 4000 cm^{-1} wavenumbers.

3. Results

3.1. Best Modified Clay

Three different types of quaternary ammonium salts were compared to natural clay to determine the improvement in the adsorption due to the reversal of surface polarity. The structures of the three different ammonium ions are shown in Figure 1. As observed, we can categorize these three ions according to the dimensions of the chain as: short chain (TM), bulky chain (BM) and long chain (HM). We expected substantial changes in adsorption with chain size due to the specific and selective hydrophobic interaction.

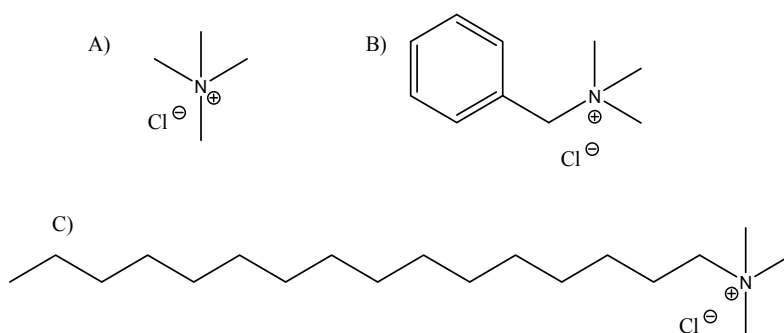


Figure 1. Chemical structure of the quaternary ammonium ions: (A) tetramethylammonium chloride (TM); (B) benzyltrimethylammonium chloride (BM); and (C) hexadecyltrimethylammonium chloride (HM).

The chemical modification involved the replacement of some positively charged ions such as Na and Ca with these ammonium cations. The positive charge located on nitrogen tightly binds to the clay surface, while the hydrophobic side chain interacts with non-polar substances such as DBT and BT.

The adsorption results on gasoline and diesel are shown in Figure 2. From the results, we chose BM as the most efficient ammonium salts for the adsorption of DBT and BT in both fuels. It seems like both pollutants preferentially bind to bulky chains. On the other hand, diesel also shows a better environment for the adsorption of both benzothiophenes. With the exception of BT on BM in gasoline, most of the adsorption capacities are in the range 2–4 mg/g, whereas diesel presents adsorptions in the range 6–7 mg/g. Moreover, HM shows the smallest affinity towards DBT and BT in both fuels. As expected, the non-treated clay (NC) presented an almost negligible adsorption due to the high polarity of its surface. To summarize, we could describe the side chain dependence as follows: $BM > TM > HM > NC$. Therefore, BM clay was chosen for the next experiments.

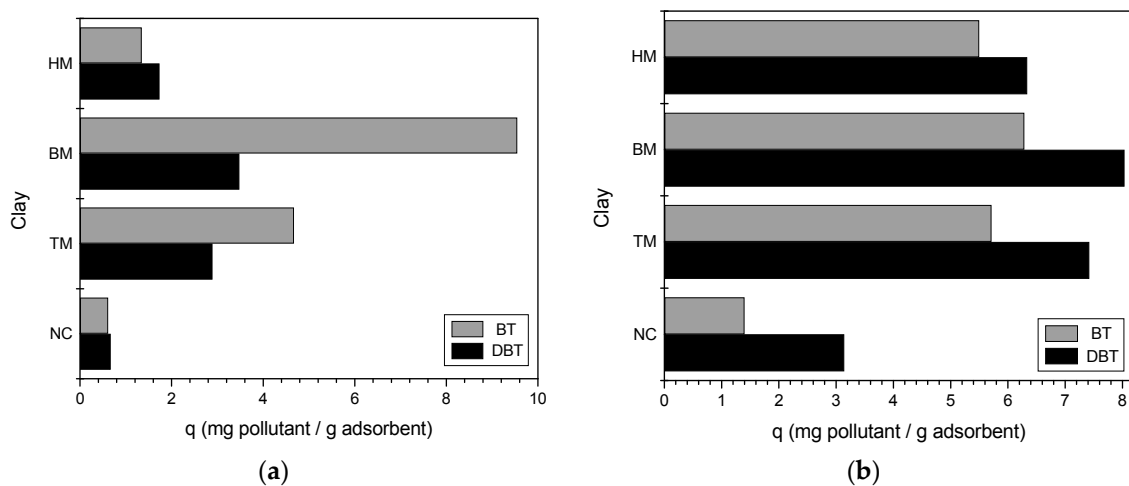


Figure 2. Determination of the best adsorbent for 4,6-dibenzothiophene (DBT) and dibenzothiophene (BT) in (a) gasoline; and (b) diesel.

3.2. Effect of Adsorbent Dosage

The minimum amount of adsorbent is crucial for scaled-up processes. Minimized costs attract investors and compete with other, perhaps, more efficient adsorbents. Adsorbent dosage effect was tried to optimize the mass of BM clay used to adsorb DBT and BT. Results are shown in Figure 3. Negligible adsorption changes are observed at adsorbent masses higher than 75 mg. However, the higher adsorption was obtained with 25 mg, being this value taken as the optimal mass dosage for the future experiments.

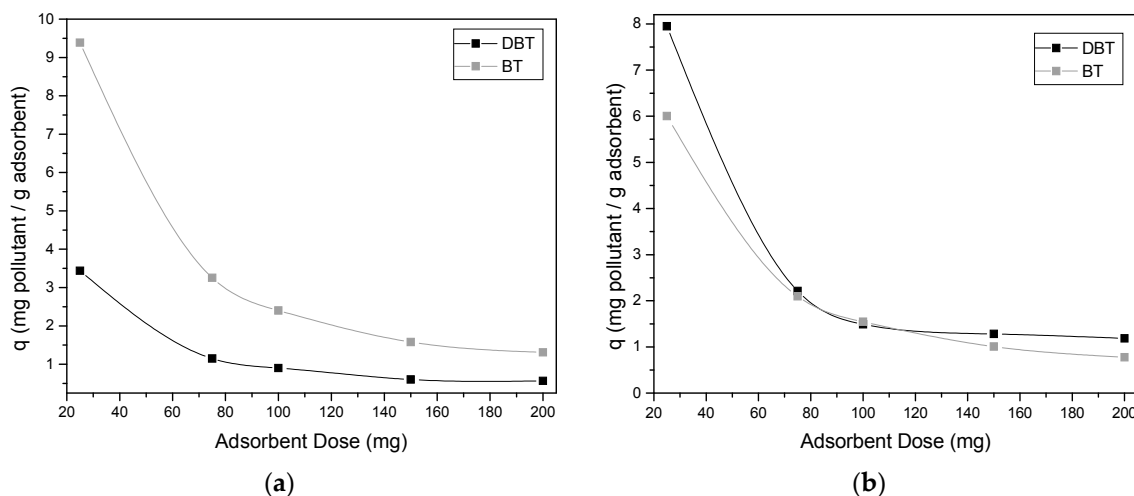


Figure 3. Adsorbent Dosage effect for DBT and BT in (a) gasoline and (b) diesel.

3.3. Effect of the Concentration of Pollutant—Adsorption Isotherms

The range of concentration at which the adsorption is optimum is important to determine the saturation of the clays. There is a maximum amount of pollutant the adsorbent can handle and where no more DBT or BT will be adsorbed. This effect was explored and the isotherms shown in Figure 4. From the results, we can conclude that most of the adsorbent reached a plateau meaning that all the active sites were occupied by the pollutant.

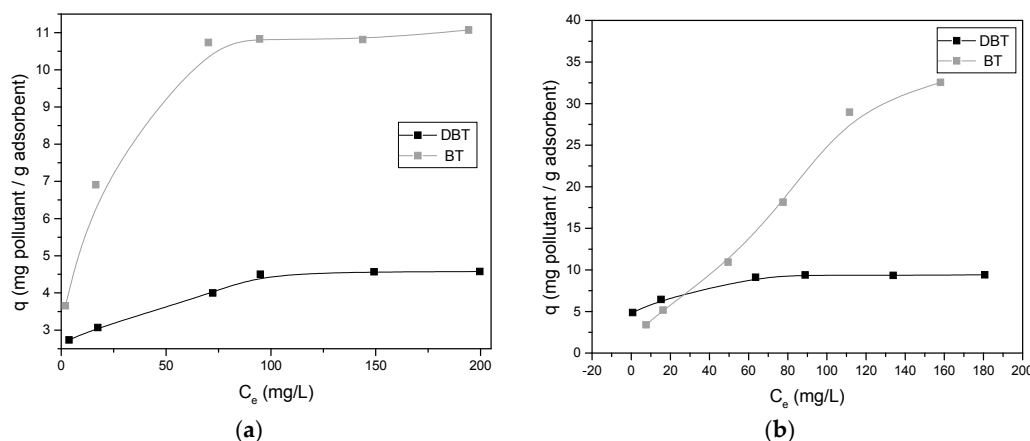


Figure 4. Adsorption isotherms for DBT and BT in (a) gasoline; and (b) diesel at room temperature.

Concentration effect experiments also allow us to determine important parameters that explain and predict thermodynamics and equilibrium behavior of the interactions between adsorbent and adsorbate. Different theories have been developed to explain the physical and chemical forces in heterogeneous and homogenous mixtures that attract an adsorbate to an adsorbent.

All these isotherms can be mathematically described and their constants can be determined [8,11–13]. These theories and their equations are:

Langmuir model:

$$\frac{1}{q} = \frac{1}{q_{max}} + \left(\frac{1}{q_{max} \times b} \right) \times \frac{1}{C_{eq}} \quad (3)$$

where q_{max} is the maximum adsorption capacity under these working conditions, b is a constant related to the affinity between adsorbent and the pollutant.

Freundlich model:

$$\ln q = \ln k_F + \frac{1}{n} \times \ln C_{eq} \quad (4)$$

where k_F and n are the Freundlich constants related to the adsorption capacity and the adsorption intensity, respectively.

Dubinin–Radushkevich (D-R) model:

$$\ln q = \ln q_{max} - KR^2T^2 \times \ln \left(1 + \frac{1}{C_{eq}} \right)^2 \quad (5)$$

where K is the activity coefficient related to the mean adsorption energy (mol^2/J^2). R is the universal gas constant in $\text{J}/\text{K} \times \text{mole}$, and T the temperature in the Kelvin scale. The mean adsorption energy, E (kJ/mol) can be calculated with the equation: $E = (2 \times K)^{-1/2}$. Finally:

Temkin model:

$$q = \frac{R \times T}{b_t} \ln a_t + \frac{R \times T}{b_t} \times \ln C_{eq} \quad (6)$$

in which R is the gas constant, T is absolute temperature in Kelvin, b_t is a constant related to the heat of adsorption, and a_t is the Temkin isotherm constant.

The mathematical models produced equilibrium constants that are summarized in Table 1. The coefficient of correlation is also shown as an indication of how appropriate is the fitting of that theory to the experimental data.

Table 1. Parameters and constants for the adsorption isotherms of DBT and BT in gasoline and diesel.

Isotherm Model and Parameters	Gasoline		Diesel	
	DBT	BT	DBT	BT
Langmuir Model				
q_{max} (mg/g)	4.74	11.311	9.404	31.32
b (L/mg)	0.103	0.245	1.407	0.015
R^2	0.979	0.999	0.998	0.964
Freundlich Model				
k_F (L/g)	2.222	3.242	4.928	0.631
n	7.465	4.041	7.562	1.286
R^2	0.966	0.979	0.954	0.982
D-R Model				
q_{max} (mg/g)	4.582	10.867	9.317	34.834
K	2.18×10^{-5}	1.07×10^{-6}	1.56×10^{-7}	5.08×10^{-4}
E (J/mole)	151.41	684.02	1789.68	31.362
R^2	0.999	0.999	0.998	0.955
Temkin Model				
a_t	44.9	4.237	220.145	0.072
b_t	4857.62	1433.57	2715.39	195.736
R^2	0.955	0.985	0.936	0.891

3.4. Desorption Experiments

The success of any adsorbent resides on the capability of adsorbent recovery for its potential use in repetitive cycles. The transfer of the pollutant from the exposure to humans and environment to a safe place where the levels of concentration can be controlled gives the adsorption process a great advantage compared to other techniques. This difficult task was accomplished by treating pollutant-loaded BM clays with several solvents. These solvents were chosen based on their chemical properties such as acid/base behavior, and polarity. The low solubility of DBT and BT predicted little or no desorption with aqueous solutions. However, as observed in Figure 5, a 0.1 M solution of HCl, provides the desorbing conditions that maximize the release of DBT and BT. Conversely, the low polarity solvents like ethanol and acetone, expected to be powerful eluting solutions, and did not present enough strength to liberate the pollutants.

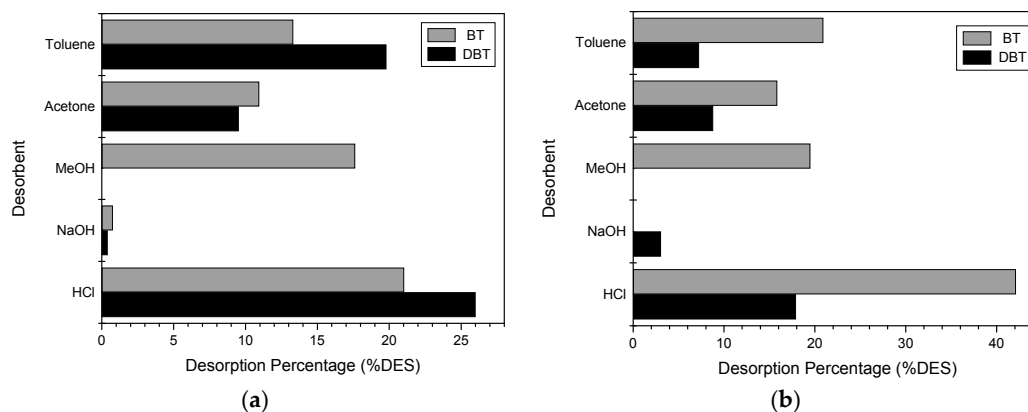


Figure 5. Desorption properties of cosolvents for DBT and BT in adsorbent pollutant-loaded in (a) gasoline; and (b) diesel.

3.5. Physical and Chemical Characterization of the Adsorbents

FT-IR spectra were taken for all the clay samples and displayed in Figure 6. As observed in the figure, all the samples possess the same functional composition as a product of the predominance of silicate and aluminate groups. For example the Si–O and Al–O peaks that show up around 1050 cm^{-1} . The most important difference between NC and all the modified clays is observed between wavenumbers $1470\text{--}1490\text{ cm}^{-1}$, where NC shows no signal at all. These peaks are associated with C–H bend, corresponding to the addition of hydrocarbon chains to the modified clays. In addition to these peaks, HM also shows an intense peak at 2900 cm^{-1} , associated with the C–H sp^3 signal. This is expected since HM was modified with 16-carbon chain. On the other hand, BM also displays a small sharp peak at 1485 cm^{-1} , indicating the presence of C=C aromatic bonds. Unfortunately potential C–N bond signals overlap with silicate and aluminate signals that are predominant in the clay structure.

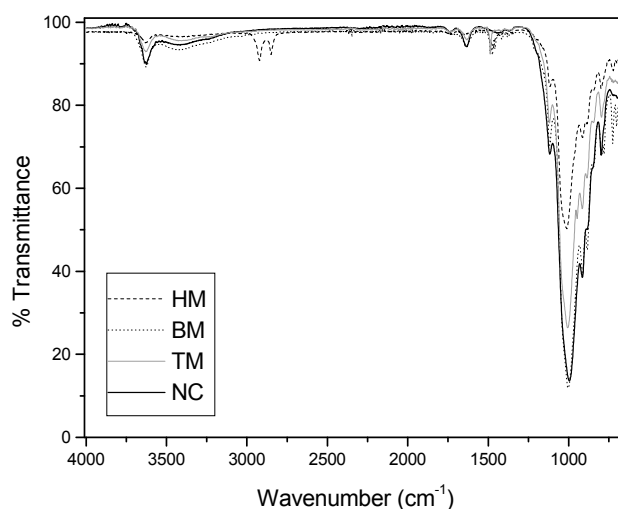


Figure 6. Fourier transform-infrared (FT-IR) spectra of the clay adsorbents.

Electron micrographs were also taken for all the adsorbents and are shown in Figure 7. The images reveal the formation of small conglomerates of particles on the surface of modified clays. All the surfaces show heterogeneity and a high porosity, which makes them suitable as adsorbents in the liquid phase. It is important to highlight that even though all the modified clays display aggregation on their surfaces (when compared to NC), TM has a more defined surface, due to the small size of the ammonium cation of the modification. BM and HM show a more diffuse surface due to the presence of bulky aromatic rings and long aliphatic chains, respectively.

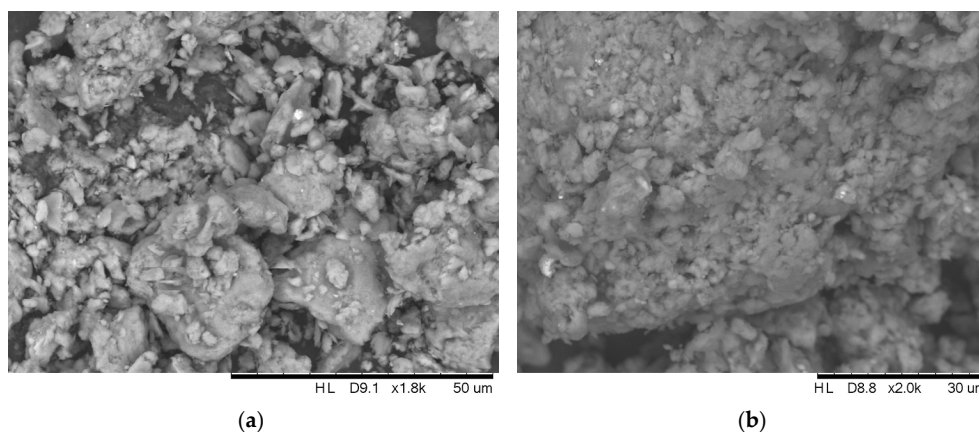


Figure 7. Cont.

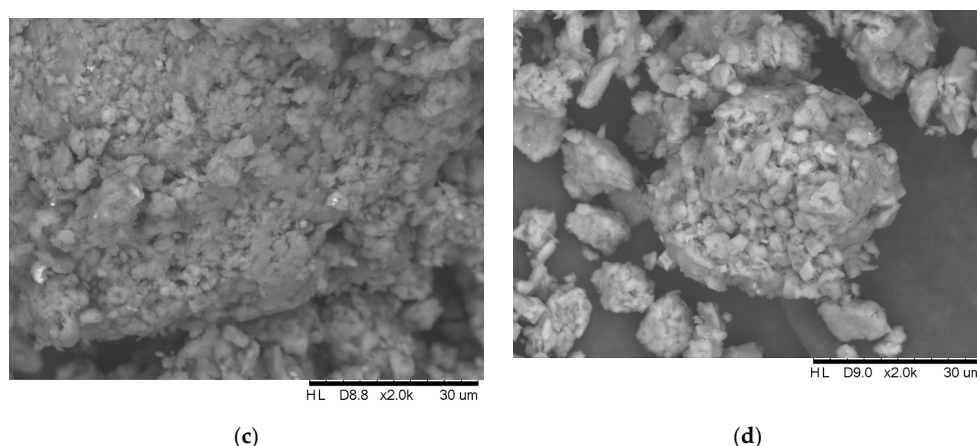


Figure 7. Scanning electron microscopy (SEM) analysis of the clay adsorbents: (a) Non-modified clay (NC); (b) BM; (c) HM; and (d) TM.

4. Discussion

4.1. Best Modified Clay

Although TM, BM and HM are highly hydrophobic compared to the natural clay (NC) nevertheless; DBT and BT show preference to bulky side chain, like BM in both fuels. The observed ranking in both fuels and for both pollutants can be described as: BM > TM > HM > NC. Natural clay was expected to display the lowest affinity due to its high polarity. This polarity is the product of electrostatic interactions due to the presence of numerous ions on the clay surface. A plausible explanation to the differences observed with the 3 modified clays is not only attributed to the size of the side chain, but also to the type of interaction they can offer to DBT and BT. The structures of these two pollutants are shown in Figure 8.

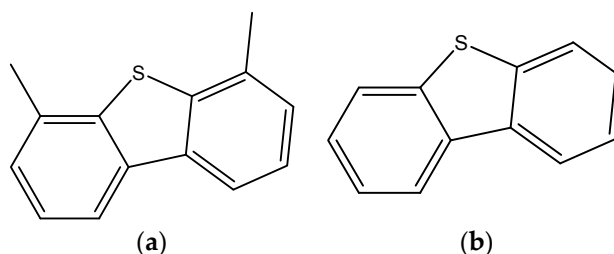


Figure 8. Chemical structures of (a) DBT; and (b) BT, adsorption targets in this work.

The structure of both pollutants are very similar with the exception of the extra two methyls observed in DBT, which would slightly increase the hydrophobicity. The relatively low adsorption capacity of HM could be attributed to the poor affinity towards DBT and BT. Even though they are both hydrophobic, Van der Waals interactions are among all the intermolecular forces the weakest and the least contributing to molecular interactions. Moreover, the crowding that occurs in the passages and pores of the clay bends and coils the long hydrophobic chain of HM and decreases the effective molecular surface that this side chain has. It might look more like a twine instead of a straight chain of carbons. Therefore the adsorbent–adsorbate interaction is decreased. TM shows a medium adsorption in gasoline and diesel; the small side chains create enough hydrophobicity to retain some molecules of DBT and BT, but not enough to cover the majority of its surface. The short distance between the polar walls of the clays and the pollutant might be affecting the interactions and repelling divergent polarities. Conversely, BM is a medium-sized side chain, and in addition to this property, it presents an

aromatic ring, which looks like the rings present in DBT and BT (conjugated double bonds in a ring). For this particular base, aromatic interactions would be playing a more preponderant role [14].

4.2. Effect of Adsorbent Dosage

The results shown in Figure 3 demonstrate that there is a saturation of adsorbent in the system. Therefore, the addition of more adsorbent does not change the overall adsorption. This could be understood as the saturation of the adsorbent surface under these experimental conditions. Rubin et al. [11] studied the adsorption of phenols, observing that 500 mg of marine seaweed leveled off the adsorption percentage. They consider that the plateau observed in the adsorption at high biomass concentration is a consequence of partial aggregation of the adsorbent in solution that reduces the number of available adsorption sites. The fact that the adsorbents are immersed in 20 mL of solution, the higher number of particles in the same solution volume promotes the aggregation of adsorbent preventing the pollutants from occupying the active centers. Moreover, clays coated with hydrophobic substances have a tendency to aggregate.

4.3. Adsorption Isotherms

From the equilibrium results, BT is strongly adsorbed on BM clay and reports the highest adsorption capacity ($q_{max} = 11.3$ and 31.3 mg/g in gasoline and diesel, respectively). DBT was also decently adsorbed in both fuels with q_{max} values of 4.7 and 9.4 mg/g in gasoline and diesel, respectively. Both pollutants in both fuels adjusted to all the adsorption theories of Langmuir, DR, Temkin and Freundlich, suggesting a mixed adsorptive mechanism. From the Langmuir isotherm, the constant b predicts a high affinity, reporting the adsorption of DBT in diesel, as the better and faster. According to the Freundlich theory, n values larger than 1 reflect positive adsorbate–adsorbent contacts. As observed in Table 1, all the adsorbents presented n larger than 1. Other adsorption studies of DBT and BT with activated carbon [5–7] show lower adsorption capacities than the ones reported in this work, with q values around 25 mg/g at low pollutant concentration [5] and 12.16 mg of sulfur per gram of pristine activated carbon [6].

The non-linearity of the isotherms confirms the competitive adsorption of the pollutants for the adsorption sites of the clay [12]. This is understandable due to the mixed nature of clays, with a polar skeleton that is coated with a non-polar molecule. In this case, DBT and BT will run away from the polar walls of the clay looking for a non-polar substrate to bind.

The D-R and Temkin isotherms are commonly used to determine the energetic factor in the adsorption process. According to the results, DBT in diesel has the most exothermic energy (1.8 kJ/mol) and, therefore, the most favorable interaction with the adsorbent from the thermodynamic point of view. The value of these levels of energy might seem relatively low (ranging between 0.2 and 1.8 kJ/mole), but it is necessary to remember that we are dealing with hydrophobic interactions and this type of force does not release as much energy as the polar or ionic interaction, mostly due to dehydration/hydration phenomena. Finally, q_{max} obtained with the D-R model completely agrees with the values observed with the Langmuir theory, confirming the combined adsorption mechanism with the adsorbents [14].

4.4. Desorption Experiments

Desorption expectations were highly placed in toluene as an aromatic solvent and, therefore, with a higher affinity towards aromatic molecules (DBT and BT). However, HCl showed the highest desorption properties with both pollutants and fuels. A possible explanation to this observed “contradiction” could be related to the acidity of HCl. DBT and BT have a sulfur atom with two electron pairs that can be protonated easily under acidic conditions, making DBT and BT charged and, therefore, water-soluble. This hypothesis is corroborated by the fact that NaOH has zero desorption, due to the basic environment. An alternative explanation is due to the usually underestimated cation- π interaction that exists between an aromatic compound (like DBT and BT) and positively charged ions like H^+ . This affinity could override the weak hydrophobic interaction on the clay surface and release

the pollutants to the solution. This desorption is able to recover up to 40% of BT in diesel and 25% of DBT in gasoline. Toluene also shows some desorption properties, and these could be understood as an aromatic interaction or “like dissolves like” with the pollutants. The medium low capacity of acetone and methanol could be explained due to their amphipathicity which is not friendly with the non-polar character of DBT and BT [15].

4.5. Insights into the Adsorption Mechanism

According to Figure 2, the exchange of metal ions from the clays with ammonium salts greatly increased the adsorption of DBT and BT. However, BM clays display higher adsorption when compared to HM and TM clays. This could be explained by structural similarities between BM ammonium salt and the sulfur compounds DBT and BT, having the aromatic interactions playing an important role in the affinity. This behavior has been previously observed in the adsorption of phenol, which also has an aromatic ring [10]. On the other hand, the desorption studies (Figure 5) show that 0.1 M solution of HCl is the best desorbing solution, followed by toluene. Acidic conditions could potentially form a stronger cation- π in aqueous solutions (polar environment). The efficiency of toluene could be explained due to the rupture of aromatic interactions between the BM adsorbent and the pollutants to form entropically favorable aromatic interactions with a less crowded toluene. This is confirmed by the low desorption by more polar solvents such as acetone and methanol, indicating that DBT and BT prefer to interact with aromatic-like compounds in non-polar environments. Likewise, gasoline and diesel did not desorb the pollutants, showing that dispersion forces with long hydrocarbons are not enough to break the BM clay-pollutant interaction. Therefore, these results suggest that DBT and BT could potentially be interacting with BM clays by aromatic interactions that are strong in the presence of water, polar solvents and hydrocarbons, but are weaker in the presence of acidic conditions or aromatic solvents due to the formation of stronger intermolecular forces.

5. Conclusions

This work demonstrates that exchanged bentonite clay can potentially be utilized as an adsorbent of dimethyldibenzothiophene (DBT) and dimethyldibenzothiophene (BT) from synthetic fuels at room temperature. Batch experiments exhibit a strong adsorption of ammonium salt as chemical exchanger, reporting a maximum adsorption capacity of around 11.3 mg/g and 31.3 mg/g of BT in gasoline and diesel, respectively. A smaller adsorption was observed for DBT, with q_{max} values of 4.7 mg/g and 9.4 mg/g for DBT in gasoline and diesel, respectively. The effect of the adsorbent dosage was studied as well, showing a decreasing adsorption at increasing masses of adsorbent (due to the formation of adsorbent aggregates). Moreover, the mathematical models of Freundlich, Dubinin–Radushkevich, Temkin and Langmuir demonstrate a mixed mechanism. The calculated parameters from the isotherms demonstrate a high affinity between adsorbate and adsorbent when compared to those reported in literature and the equilibrium experiments suggest that aromatic interactions might be responsible for the adsorption. Finally, the use of 0.1 N HCl as an eluting solvent, removed about 40% of BT and 25% of DBT from diesel and gasoline, respectively. This advantage will allow the re-use of adsorbents in consecutive cycles. Overall, this project constitutes a major contribution towards the development of cost-efficient adsorbents for the removal of pollutants in general.

Author Contributions: Jeong W. Ha prepared the modified clays and conducted the first adsorption experiments. Tenzing Japhe and Bertin Moreno conducted the adsorption and desorption experiments, Tesfamichael Demeke conducted the adsorbent characterization and contributed to the writing of the manuscript. Abel E. Navarro supervised the work, structured the research and wrote the manuscript.

Funding: This research was funded by a PSC-CUNY grant to AEN. The authors would also like to thank the financial support from the Science Department, CSTEP and CRSP programs at BMCC and CUNY.

Acknowledgments: A special acknowledgement to Jeong H. Ha for the preliminary studies in adsorbent preparation and adsorption experiments. Alvaro Sponza is thanked for the FT-IR analysis and Chiu Hong Lee for her technical support.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Brock, W.A.; Taylor, M.S. *Economic Growth and the Environment: A Review of Theory and Empirics*; En NBER Working Paper 10854; National Bureau of Economic Research: Cambridge, MA, USA, 2004.
2. Stern, D.I. Beyond the environmental Kuznets curve: Diffusion of emissions reducing technology. *J. Environ. Dev.* **2005**, *14*, 101–124. [[CrossRef](#)]
3. Dharaskar, S.; Sillanpaa, M.; Tadi, K.K. Sulfur extraction from liquid fuels using trihexyl(tetradecyl)phosphonium tetrafluoroborate: As a promising solvent. *Environ. Sci. Pollut. Res. Int.* **2018**, *25*, 17156–17167. [[CrossRef](#)] [[PubMed](#)]
4. Saleh, T.A.; Al-Hammadi, S.A.; Tanimu, A.; Alooshani, K. Ultra-deep adsorptive desulfurization of fuels on cobalt and molybdenum nanoparticles loaded on activated carbon derived from waste rubber. *J. Colloid Interface Sci.* **2018**, *513*, 779–787. [[CrossRef](#)] [[PubMed](#)]
5. Shah, S.; Ahmad, I.; Ahmad, W. Adsorptive Desulphurization study of liquid fuels using Tin (Sn) impregnated charcoal. *J. Hazard. Mater.* **2016**, *304*, 205–213. [[CrossRef](#)] [[PubMed](#)]
6. Ho, H.P.; Kasinathan, P.; Kim, J.; Lee, D.; Woo, H.C. Deep desulfurization of fuel gas by adsorption on Cu-impregnated activated carbons in practical conditions. *Korean J. Chem. Eng.* **2016**, *33*, 1908–1916. [[CrossRef](#)]
7. Baltzopoulou, P.; Kallis, K.; Karagiannakis, G.; Konstandopoulos, A. Diesel fuel desulfurization via adsorption with the aid of activated carbon: Laboratory- and Pilot-scale studies. *Energy Fuels* **2015**, *29*, 5640–5648. [[CrossRef](#)]
8. Navarro, A.E.; Cuizano, N.; Lazo, J.; Sun-Kou, M.; Llanos, B.P. Comparative study of the removal of phenolic compounds by biological and non-biological adsorbents. *J. Hazard. Mater.* **2009**, *164*, 1439–1446. [[CrossRef](#)] [[PubMed](#)]
9. Navarro, A.E.; Lazo, J.; Cuizano, N.; Sun-Kou, M.; Llanos, B.P. Insights into the removal of phenol from aqueous solutions by low cost adsorbents: Clays versus algae. *Sep. Sci. Technol.* **2009**, *44*, 2491–2509. [[CrossRef](#)]
10. Lazo, J.C.; Navarro, A.E.; Sun-Kou, M.R.; Llanos, B.P. Synthesis and characterization of organophilic clays and their use as adsorbents for phenol. *Rev. Soc. Quím. Perú* **2008**, *74*, 3–19.
11. Rubin, E.; Rodriguez, P.; Herrero, R.; Sastre de Vicente, M. Biosorption of phenolic compounds by the Brown algae *Sargassum muticum*. *J. Chem. Technol. Biotechnol.* **2006**, *81*, 1093–1099. [[CrossRef](#)]
12. Navarro, A.E.; Portales, R.; Sun-Kou, R.; Llanos, B.P. Effect of pH on phenol biosorption by marine seaweeds. *J. Hazard. Mater.* **2008**, *156*, 405–411. [[CrossRef](#)] [[PubMed](#)]
13. Liu, Y.; Wang, J. *Fundamentals and Applications of Biosorption Isotherms and Kinetics and Thermodynamics*; Nova Science Publishers, Inc.: New York, NY, USA, 2009.
14. Volesky, B. *Sorption and Biosorption*; BV Sorbex, Inc.: Quebec, QC, Canada, 2003.
15. Chojnacka, K. *Biosorption and Bioaccumulation in Practice*; Nova Science Publishers, Inc.: New York, NY, USA, 2009.



© 2018 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).