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Article

## Comparative Sorption of Methylene Blue onto Hydrophobic Clays

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**Abstract:** Chemical modifications of clay to remove methylene blue (MB) from aqueous solutions at room temperature were compared. Natural bentonite (NC) was modified by cation exchange with hexadecyltrimethylammonium chloride (HC), benzyltriethylammonium chloride (BC), and tetramethylammonium chloride (TC) to reverse the surface polarity of the hydrophilic bentonite. The adsorption of MB was studied and fitted by the adsorption theories of Langmuir, Freundlich, Dubinin-Radushkevich, and Temkin. Equilibrium parameters were calculated, indicating that chemical modification did not improve the adsorption, due to the electrostatic adsorption mechanism. Specific surface area was determined, reporting the following trend: NC > TC > BC > HC. Isotherms show that TC is the best modified clay for the adsorption of MB with a capacity of 217 mg/g. Adsorbents were characterized by SEM and the determination of their point zero charge, indicating a charge reversal at pH 9.5 and a heterogeneous surface that is optimum for the adsorption of molecules and ions onto their surfaces.

**Keywords:** adsorption; isotherm; methylene blue; modified clay; point zero charge

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## 1. Introduction

Different types of substances are commonly used to color a high variety of materials. Artificial dyes can be divided into two groups: the water-soluble colorants and pigments that are water-insoluble [1]. Colorants can be defined as substances that have the capacity of attributing color to fibers without being affected by factors like light, water, and surfactants. These compounds, even at very low concentrations, produce very visible and undesired contamination [2,3]. Textile industry is the industry most responsible for the generation of colored effluents, where 700,000 tons and around 10,000 colorants are annually produced across the world [2,4,5]. In addition to this, some toxic, mutagenic, and carcinogenic characteristics have been established for some of them [6].

Colored wastewaters are treated with diverse physico-chemical methods, such as flocculation, chemical oxidation, activated sludge reactors, photo-degradation, ozonolysis, filtration, ionic exchange, and others [1,6–8]. Although these are very efficient techniques, most of them present several drawbacks like high cost, incomplete elimination of the contaminants, and generation of sludge or by-products [7,9,10]. Biological methods have also been evaluated for this type of effluents; however, the scaling of this process represents a big obstacle for their industrial applications [11].

Adsorption is perhaps one of the most convenient techniques for the elimination of organic and inorganic pollutants [10,11]. Activated carbon has the reputation of being a good adsorbent due to the large surface area that serves as adsorption sites for the trapping of these contaminants [10]. However, activated carbon has a low regeneration capacity and cannot be used in consecutive adsorption cycles [9,10]. Therefore, an alternative adsorbent with similar surface characteristics has always been wanted. Studies have been recently conducted for the removal of colorants [5,8], and they agree in their special characteristics. Dyes are usually amphipathic, and as such they need adsorbents that are not totally hydrophobic or hydrophilic [7]. For this purpose, clays are good candidates as dyes adsorbents. They are naturally-occurring minerals with low-cost and mechanical and physically resistant. They are normally highly hydrophilic, but that polarity can be modulated by a simple chemical modification [12,13]. These modified clays have already been used in the removal of organic pollutants such as phenol and derivatives [14–16].

On the other hand, methylene blue (MB) is a colorant that is commonly used in the industry for coloring cotton, silk, and wood [5]. MB is not toxic, but its exposure during prolonged periods can potentially cause negative effects in humans and animals [17]. For example, inhalation of MB can cause respiratory disorders, and its ingestion causes nausea, vomiting, mental confusion, and other symptoms [5].

The objective of this study was to evaluate the potential use of different chemically-modified clays on the removal of methylene blue from solutions as an alternative technique for the treatment of dye-containing wastewater. The study of methylene blue as adsorbate also provides further insight into the surface properties of the adsorbents as a standard for the determination of specific surface area.

## 2. Experimental Section

### 2.1. Chemical Reagents and Solutions

Bentonite (raw mineral), Methylene Blue (analytical grade) and benzyltriethylammonium chloride (BE), tetramethylammonium chloride (TM) hexadecyltrimethylammonium (HM) chloride salts

(reagent grade) were purchased from Sigma Aldrich (Milwaukee, WI, USA) and used without further purification. Stock solutions of methylene blue were prepared in deionized water. All working solutions for the adsorption experiments were prepared by diluting the stock solution with deionized water to the needed concentrations.

## 2.2. Cationic Exchange of Bentonite with Ammonium Salts

Exchange of ions such as  $\text{Na}^+$  and  $\text{K}^+$  with quaternary ammonium salts was carried out following a procedure detailed elsewhere [14,15]. 20 g of raw bentonite (NC) was suspended in 2 L of distilled water and combined with two equivalents of its cation exchange capacity (CEC) of each of the ammonium salts. The suspension was stirred at 250 rpm overnight at room temperature. The resulting bentonites were vacuum filtered and vigorously rinsed with distilled water to eliminate residues of the ammonium salts. Then, modified bentonites were oven dried at 60 °C for 48 h and stored in plastic containers until their use. Modified bentonites were identified according to the exchanged ammonium salt as follows: benzyltriethylammonium (BC), tetramethylammonium (TC) and hexadecyltrimethylammonium (HC). According to previous studies [14,15], TC has the higher loading degree due to the lower molecular mass of the quaternary ammonium ion, followed by BC and HC. The loading degree was determined by calculating the Nitrogen percentages in the samples, indicating a proportionality of 25:10:1 for TC, BC and HC, respectively.

## 2.3. Adsorption Tests

Batch experiments were conducted at room temperature in triplicates by putting in contact an accurately weighed amount of the natural or modified bentonites (50 mg) to reach equilibrium with 50 mL of MB solutions of different concentrations, ranging from 20 to 200 mg/L. Prior to mixing, the initial solution pH was adjusted to 10 by adding aliquots of HCl and NaOH solutions. Samples and blanks were shaken at 250 rpm for 24 h to assure the completeness of the adsorption. At the end of the equilibrium the samples and blanks were filtered and subsequently analyzed for residual MB concentration by UV-vis spectrophotometry using a microplate reader (Synergy4, BioTek, Winooksi, VT, USA) at a wavelength of 663 nm.

## 2.4. Characterization of the Adsorbents

Surface texture and morphological properties of all the adsorbents were explored by scanning electron microscopy using a Tabletop microscope (TM3000, HITACHI). Samples were directly observed without gold coating. Surface comparisons were conducted under equal conditions and zoom. The point zero charge ( $\text{pH}_{\text{pzc}}$ ) of the four adsorbents were determined by a method described elsewhere [18]. In brief, the pH of 0.01 M NaCl solutions were adjusted to different values between 2 and 13 by the addition of aliquots of 0.1 M HCl or NaOH solutions. Then, these solutions were mixed with the adsorbents and the final pH values were recorded after 48 h of orbital shaking.

## 2.5. Data Analysis

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

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

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 MB, expressed in mg/L, respectively. Plots and linear regression were carried out using the statistical software Origin v8.0. Linear regression reported data includes  $R^2$  correlation coefficient values, and p-value defined as the significance relevance of the modeling that is associated with the possibility of an observed result that a null hypothesis is true.

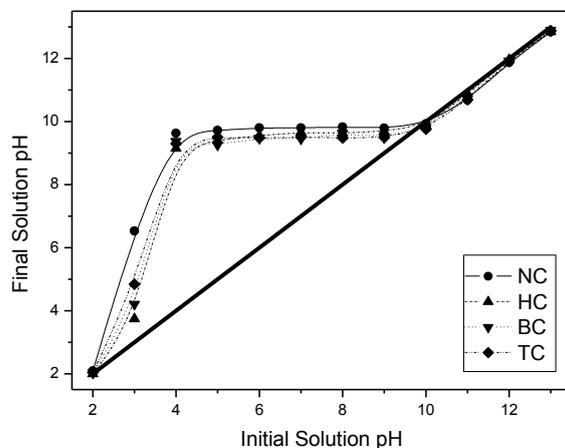
## 3. Results and Discussion

### 3.1. Characterization of the Adsorbents

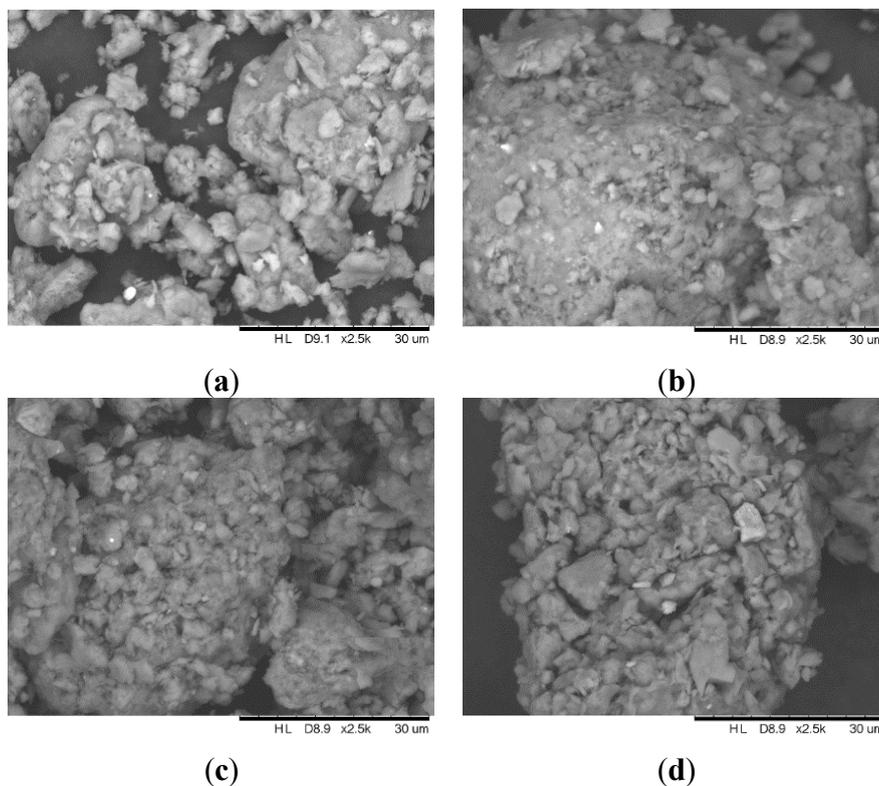
The point zero charge. PZC, is defined as the pH value at which the  $pH_{\text{final}}$  curve versus  $pH_{\text{initial}}$  intersects the straight line corresponding to  $pH_{\text{initial}} = pH_{\text{final}}$ . This physical parameter is extremely crucial in adsorption, as it translates the pH value where the surface charge is reversed. MB is a cationic dye and therefore will display a higher affinity towards negatively charged adsorbents. Figure 1 shows the PZC curves for the natural and modified clays. The results indicate that regardless their modification, all the adsorbents have a PZC of 9.5. Therefore all the clays are positively charged at pH values below 9.5 and negatively charged at higher values. Other results on bentonites report PZC value of 8 under similar conditions [19]. This high PZC can be explained by the presence of negatively charge groups on the clays, such as silicates and aluminates [19]. In the case of HC, BC and TC, there is no substantial change in PZC, when compared to the unmodified clay, NC. This might be due to the nature of the chemical modification, where only adsorbed cations are exchanged, leaving the negative groups of the surface intact for its interaction with different pH values. These are actually very positive results, as our goal with the chemical modification was the change in polarity of the adsorbent surface. The inclusion of quaternary ammonium ions only exchange the adsorbed sodium and potassium ions that are present in clays and attribute a more hydrophobic environment [14]. This exchange is not meant to cause chemical changes on the surface. Based on these results, the adsorption experiments were conducted at pH 10 to assure that the adsorbents are negatively charged and can potentially adsorb the maximum amount of MB due to electrostatic affinity.

The selection of the three quaternary ammonium salts for the modification of the clays was done based on the bulkiness and hydrophilicity of their ions. HC clays resemble the long aliphatic chain; BC represents the bulky and aromatic chain, and TC, the short chain. As indicated by the PZC experiment, there is no difference in charge surface with these ions. However, physical differences were explored by scanning electron microscopy to study the morphology and texture of the clays with different modifications. Figure 2 shows the micrographs of the four clays. The images reveal the formation of small conglomerates of particles on the surfaces of the modified clays. This can be explained by the hydrophobic attractions. Since the natural clay is modified in aqueous phase, aggregates are expected to be observed. NC displays a cleaner surface with well-defined layers and more separated particles.

On the other hand, all the surfaces show heterogeneity, which is beneficial for any adsorbent. The presence of valleys, protrusions, and pockets are expected to house and trap the adsorbates and enhances the intermolecular forces with the adsorbent. Lastly, the SEM images also indicate an important difference amongst the three modified clays. Although, they have a heterogeneous surface, TC shows the highest surface randomness, followed by BC and then HC. Therefore, we could predict a similar trend in their adsorption capacities from the morphological point of view.



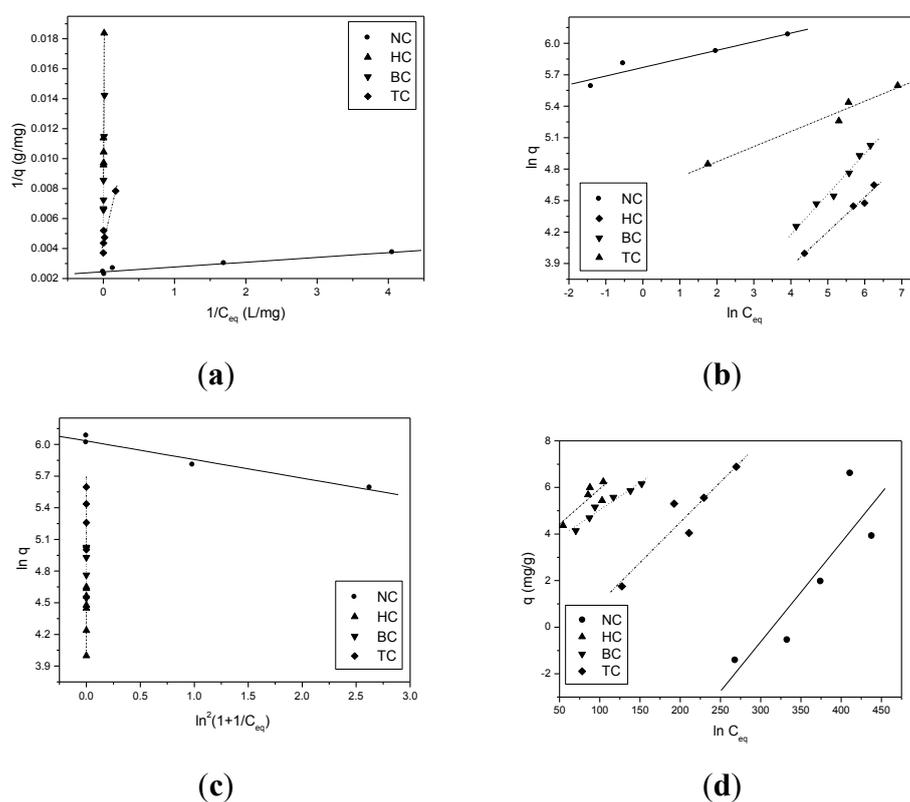
**Figure 1.** Determination of the Point Zero Charge of the natural and modified clays.



**Figure 2.** Scanning Electron Micrographs of the adsorbents: NC (a); HC (b); BC (c) and TC (d).

3.2. Adsorption Tests

A comparison of the adsorptive properties of the four adsorbents was studied and modeled by different mathematical theories. These theories are purely empirical, derived from adsorption models and originally developed for different systems on the basis of assumptions that are quite simplistic for biological cases. These models have been widely applied since they are simple; give a good description of experimental data in a large range of fixed operating conditions, and are characterized by a limited number of adjustable parameters. These parameters have a physical meaning and predict the adsorption in ideal and equilibrium conditions. Another advantage of these models is the simple mathematical treatment to process the data with the linearization of the equations. The isotherms for the four adsorbents at room temperature in their linearized form are shown in Figure 3. The Langmuir, Freundlich, Dubinin-Radushkevich, and Temkin theories were chosen as they are the most representative for the adsorption of pollutants [12].



**Figure 3.** Linearization of the Isotherms for sorption of MB onto the adsorbents: Langmuir (a); Freundlich (b); Dubinin-Radushkevich (c); and Temkin (d).

Langmuir theory assumes uniform adsorption energy on the surface of the adsorbents, where the interactions of the adsorbed particles are restricted. The linearized equation of the Langmuir isotherm is calculated as follows (Equation (2)):

$$\frac{1}{q} = \frac{1}{q_{max}} + \frac{1}{b q_{max}} \times \frac{1}{C_{eq}} \tag{2}$$

where  $q_{max}$  (mg/g) and  $b$  (L/mg) are the Langmuir constants related to the maximum adsorption capacity and the adsorption energy, respectively. The constant  $q_{max}$  represents the total number of available adsorption sites for an adsorbent. For instance, a high  $q_{max}$  indicates the maximum adsorption that can be attained by a given adsorbent. The constant  $b$  is crucial for the comparison of adsorption efficiency between two different adsorbents under the same experimental conditions. The higher the constant  $b$ , the faster the equilibrium is reached by an adsorbent. This implies a high adsorbent/MB affinity and therefore more efficiency. An ideal adsorbent should have the combination of a high  $q_{max}$  and a high  $b$  value. The corresponding calculated Langmuir constants are shown in Table 1. Our results indicate maximum adsorption capacities of 408, 153, 167, and 217 mg MB/g of adsorbent for NC, HC, BC, and TC, respectively. It is important to notice that the adsorption capacity of the clay decreases with the chemical modification.

**Table 1.** Equilibrium constants and parameters for the Adsorption of MB onto the adsorbents.

Adsorption Isotherm	Parameter	NC	HC	BC	TC
Langmuir	$q_{max}$ (mg/g)	408	153	167	217
	$b$ (L/mg)	7.65	0.0074	0.011	0.248
	$p$ -value	0.004	0.038	<0.0001	0.026
	$R^2$	0.953	0.925	0.978	0.948
Freundlich	$k_F$ (mg/g) (L/mg) <sup>1/n</sup>	320.3	12.88	13.92	90.55
	$n$	12.24	3.04	2.59	6.54
	$p$ -value	0.042	0.009	<0.0001	0.011
	$R^2$	0.916	0.981	0.978	0.911
Dubinin-Radushkevich	$q_{DR}$ (mg/g)	404.06	99.96	155.41	287.3
	$B$ (mol <sup>2</sup> ·J <sup>2</sup> )	$2.64 \times 10^{-8}$	$6.05 \times 10^{-4}$	$2.57 \times 10^{-3}$	$3.14 \times 10^{-3}$
	$E$ (J/mol)	4.35	0.03	0.014	0.012
	$p$ -value	0.011	0.009	0.003	0.053
	$R^2$	0.91	0.848	0.959	0.898
Temkin	$a_T$	$9.5 \times 10^7$	0.165	0.077	31.04
	$b_T$ (J/mol)	139.28	106.6	60.79	97.94
	$p$ -value	0.055	0.075	0.001	0.019
	$R^2$	0.757	0.704	0.948	0.874

However, there are important differences with the chemical modifications. For example, the most negative effect is observed on HC, followed by BC, and then TC. We can conclude that MB prefers less hydrophobic environments (short chain in TC), and is greatly affected by long hydrophobic chains (HC). The aromatic properties in BC also decreased adsorption in a similar manner. These results were certainly expected as MB is a positively charged molecule and therefore will have a better interaction with more hydrophilic surfaces, such as NC. The selectivity of these adsorbents is also corroborated by the  $b$  values.

The  $q_{max}$  values of the modified clays also agree with their respective  $b$  values, showing the same trend. Although the adsorption capacity of these hydrophobic clays is lower than the unmodified clay, the removal of MB is still significant and even higher than other recently studied adsorbents like corn cob (111 mg/g), and agave bagasse waste (156 mg/g) [20]. Castile nutshells (141 mg/g) [1], grape

stalks, and corn barks with 106 and 31 mg/g, respectively have also been studied for the elimination of MB and display a lower adsorption [21].

The Langmuir isotherm has also been used in the determination of the specific surface area of biological and inorganic materials [22,23]. Since the Langmuir theory assumes monolayer coverage of the adsorbent's surface, the area can be calculated using physical constants [23]. The specific surface area was calculated by the following Equation (3) [24]:

$$S_{MB} = \frac{q_{max} \times a_{MB} \times N \times 10^{-20}}{M} \quad (3)$$

where  $S_{MB}$  is the specific surface area in  $m^2/g$ ;  $q_{max}$  is the maximum adsorption capacity in  $mg/g$  (calculated from the Langmuir isotherm);  $a_{MB}$  is the occupied surface area of one molecule of methylene blue =  $197.2 \text{ \AA}^2$  [25].  $N$  is the Avogadro's number,  $6.02 \times 10^{23}$ ; and  $M$  is the molecular weight of methylene blue,  $373.9 \text{ g/mol}$ . The specific surface areas of the four adsorbents were calculated and are shown in Table 2. According to the results, NC has the largest specific surface area ( $1295 \text{ m}^2/g$ ), followed by TC, BC, and HC. These results are in agreement with previously reported data [23], where a Colombian bentonite displays a  $S_{MB}$  of  $1288 \text{ m}^2/g$ . Biological materials have also been investigated and cotton fiber shows a  $S_{MB}$  of  $32,000 \text{ m}^2/g$ . This bentonite-cotton difference should not be surprising, since cotton fibers have much lower density than bentonites.

**Table 2.** Specific Surface Areas determined by the methylene blue method adsorption for all the adsorbents.

Adsorbent	Specific Surface Area ( $m^2/g$ )
NC	1295
HC	486
BC	530
TC	689

Adsorption of MB was also fitted with the Freundlich equation, expressed in Equation (4):

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

where  $k_F$  and  $1/n$  are the Freundlich constants related to the adsorption capacity and the adsorption intensity, respectively. The calculated Freundlich constants are also shown in Table 1. The  $k_F$  values indicate the more favorable adsorption capacity for NC, followed by TC, BC, and HC. These results agree with the tendency observed by the Langmuir theory. Similar results have been observed with pecan nutshells, which report a  $k_F$  value of 3.14 [1].

Dubinin-Radushkevich (D-R) isotherm is also used in the adsorption modeling [12]. The importance of this model resides on the determination of the Energy of Adsorption ( $E$ ). The D-R parameters were determined using the linearized Equation (5):

$$\ln q = \ln q_{DR} - B R^2 T^2 \ln^2 \left( 1 + \frac{1}{C_{eq}} \right) \quad (5)$$

where  $B$  ( $mol^2/J^2$ ) is the activity coefficient related to the Mean Adsorption Energy.  $R$  is the Universal Gas Constant in  $J/mol.K$ , and  $T$  is the temperature in the Kelvin scale. The Mean Adsorption Energy,  $E$  ( $J/mol$ ) can be calculated with the equation:  $E = (2B)^{1/2}$ . The four studied adsorbents report low

adsorption energy ( $E$ ) as observed in Table 1. These energies are associated with weak attraction forces, such as Van der Waals. This is understandable, since the modified clays were exchanged with hydrophobic ions. NC has the highest adsorption energy, as an indication of its higher affinity towards MB. From these values, we can conclude that the adsorption is mainly driven by molecular (Van der Waals) and not electrostatic forces [7,26].

Lastly, the experimental data was also modeled according to the Temkin isotherm [7,12,26]. This theory takes into account indirect adsorbate-adsorbent interactions. The linearized Temkin equation is expressed in Equation (6):

$$q = \frac{RT}{b_T} \ln a_T + \frac{RT}{b_T} \ln C_{eq} \quad (6)$$

$R$  is the Universal gas constant,  $T$  is the absolute temperature,  $b_T$  is a constant related to the heat of adsorption and  $a_T$  is the Temkin isotherm constant. As observed in Table 1, NC shows a higher heat of adsorption, followed by the modified clays. The heat of adsorption trend differs from the D-R isotherm, because of the poor fitting to this model (as indicated by the  $R^2$  values). However, both models agree in the more exothermic character of the MB adsorption by NC. The Temkin isotherm constant corroborates the highest and lowest affinities with NC and modified clays, respectively.

#### 4. Conclusions

The modification of natural clay (NC) was carried out using quaternary ammonium salts to produce HC, BC, and TC clays. The use of these materials as potential adsorbents of methylene blue (MB) as a model dye was evaluated. A comparative adsorption in batch conditions at room temperature was conducted and the Langmuir, Freundlich, Dubinin-Radushkevich, and Temkin models were fitted to the experimental results. Langmuir theory indicates that NC has a higher adsorption capacity (408 mg/g) and affinity when compared to the modified clays. Amongst the modified clays, the adsorption efficiency follows the trend: TC > BC > HC with adsorption capacities of 217, 167, 153 mg/g, respectively. Results indicate that hydrophobicity plays a negative role in the adsorption of MB and adsorption is mainly driven by Van der Waals forces. Equilibrium experiments were also used to determine the specific surface area, indicating that NC has the largest area with 1295 m<sup>2</sup>/g. Finally, the adsorbents were characterized by the Point Zero Charge determination and Scanning Electron Microscopy. The results indicate that all the adsorbents have a zero charge at pH 9.5 and micrographs show that chemical modification increases the surface randomness when compared to NC. This study proposes the chemical modification of naturally-occurring clays as an environment-friendly adsorbent for the removal of dyes from solutions. Future research envisions other modifications that enhance the adsorption of MB, or the removal of more hydrophobic pollutants.

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## Author Contributions

David Yang and Karla A. Ortiz prepared and characterized the adsorbents and contributed with the data analysis. Alvaro D. Sponza and Natalia J. Fernandez performed the adsorption experiments and data analysis. Abel E. Navarro designed the research and edited the manuscript. All authors read and approved the final manuscript.

## Conflicts of Interest

The authors declare no conflict of interest.

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