Methomyl removal from synthetic water using natural and modified bentonite clays

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Abstract. The removal of methomyl from synthetic aqueous solutions by using Ecuadorian bentonite clays was studied. A natural clay was purified (P-C) and modified by three methods: thermal activation at 200°C for 2 h, acid activation with a 3N sulfuric acid solution for 1 h, and saline activation with hexadecyltrimethyl ammonium bromide (HDTMA) for 12 h. Clays were characterized by X-ray diffraction, Fourier transform infrared spectroscopy and the BET method. The removal was performed with the natural and modified bentonites considering three particle size ranges and three operating temperatures (20, 30 and 40°C). For this purpose, 0.5 g of clay were added to 50 mL of a 100 µg L⁻¹ synthetic methomyl wastewater. Pesticide removal was quantified using ultraperformance liquid chromatography - tandem mass spectrometry. It was found that the adsorption process can be relatively efficient, particularly with thermally activated clays being used at 40°C. In this case, removal efficiencies between 66 and 76% were achieved. The highest efficiency was observed for a relatively large particle size (106-150 µm). The adsorption curves obtained were fitted to the Langmuir model. The analysis of variance for the removal of methomyl showed a significant effect for the temperature x clay x particle size interaction with a confidence level of 95% (p = 0.004).

1. Introduction
Agriculture is the activity that uses the most pesticides, whose main purpose is the management of pests and diseases that could reduce crop yields. Without pesticides, yields could not be increased, the quality of the products could not be maintained, nor could agricultural productivity be improved, or the shelf life maximized. However, only a small portion of the pesticides applied affect the organisms that were intended to be eliminated. Another portion could go to the environment and contaminate it. Methomyl (S-methyl N-(methylcarbamoyloxy) thioacetiminate) is a carbamate with insecticidal activity. It was introduced in the 1960s as an insecticide and affects several species. It is effective in target insects in two ways: (a) as a contact insecticide, killing on direct contact; and (b) as a “systemic insecticide”, causing general poisoning after being absorbed and transported through pests that feed on treated plants. Methomyl was classified by the World Health Organization, the US Environmental Protection Agency and the European Environment Agency as a toxic and dangerous pesticide [1]. Methomyl is highly soluble in water (57.9 g L⁻¹ at 20 °C), has low sorption affinity to soils, and therefore can easily cause groundwater contamination in agricultural areas [2]. In the United States, methomyl was present in groundwater in concentration of 9.0 and 1.2 µg L⁻¹. The maximum
concentration permitted of the pesticide in surface waters is 0.02 µg L⁻¹ in liquid discharges in Sweden and 0.02 µg L⁻¹ in the Netherlands [3]. Because of the problems associated to methomyl in different ecosystems, there is an interest to eliminate it. However, treatments of wastewater contaminated with pesticides and other emerging contaminants such as pharmaceutical and personal care products, surfactants, plasticizers, among others, using conventional methods are not efficient.

Physicochemical treatments can be used to eliminate pesticides and other emerging contaminants. In the case of methomyl, adsorption, chlorination, chemical coagulation, ion exchange, reverse osmosis, among others, are used. Several studies agree that the removal of emerging contaminants using oxidation and adsorption treatments is efficient, reaching removals greater than 90% [4]. In fact, hybrid treatments could be the best alternative in cases in which the compounds to remove are difficult to deal with. However, these processes are very costly. For this reason, different alternatives have been explored, such as the use of adsorption. This is one of the most widely used methods for wastewater treatment, generally considering materials with high ion exchange capacity or activated carbon.

Considering the relatively high cost of conventional adsorbents, such as activated carbon, there is an interest for finding materials that can be locally available, that are of natural origin or that are synthesized using environmentally friendly procedures. The use of clays becomes attractive since they are abundant in many parts of the world and can be obtained at low costs. Additionally, they can be modified by heat treatments or chemical activation methods.

Among the clays, bentonites have expansive and plastic characteristics. Depending on their exchangeable ion, they are divided into those with Na, Ca or Mg content. This content affects their adsorption capacity, which is determined by the specific surface and the porosity. The dehydrated Na bentonites show a specific surface between 25 and 50 m² g⁻¹. When they are hydrated, their surface increases 6 to 12 times, while for Ca bentonites increases 8 to 10 times [5]. El-Geundi et al. (2012) studied the adsorption of methomyl by montmorillonite natural clays at 25, 40 and 60 °C. It was found that the removal efficiency ranges between 27.6 and 32.9 % for initial concentrations of methomyl between 43.71 mg L⁻¹ and 19.99, respectively [6]. Another study analyzed the adsorption of carbamates using bentonite modified with Coscinium fenestratum obtaining a removal up to 80% [7].

The purpose of this work was to study the removal of methomyl from synthetic water, using an Ecuadorian bentonite clay as adsorbent. First the clay was purified and then it was thermally and chemically modified. Then the natural and modified clays were used in removal tests in which three particle sizes and three temperatures were considered.

2. Materials and methods

2.1. Clay purification

Natural bentonite clay (N-C) was obtained from a mine located at the commune of Villingota, Chanduy parish, municipality of Santa Elena, Ecuador. For the initial impurity removal, the N-C was mixed with water, stirred manually for 30 min, allowed to sit for 1 h and the supernatant was removed. This procedure was repeated 3 times, then the suspension was set to stand for 24 h. Subsequently, the supernatant was removed, and the clay was dried at 110 °C for 24 h. For the organic matter removal, a suspension was prepared with the washed clay, using for this purpose 10.7 mL of deionized water per gram of clay. 6 mL of a 50% w/w solution of H₂O₂ (technical grade) was added per gram of clay. The temperature was maintained at 65 °C with stirring at 100 rpm until the effervescence caused by the reaction of organic matter disappeared. It was then dried at 110 °C and stored in a desiccator.

The clay without organic matter just obtained was used to prepare a suspension by adding 10 mL of deionized water per gram of clay. The suspension was stirred at 100 rpm. Simultaneously, a 2M hydrochloric acid solution was added drop by drop, keeping a pH value close to 4.5 [8]. The product obtained clay was designated as purified clay (P-C).

2.2. Thermal and chemical activation

The P-C was manually crushed and sieved in a ROTAP Rx-29 equipment. Three ranges of particle sizes were obtained: 106-150 µm (passed sieve #100), 75-106 µm (passed sieve #140), and <75 µm
(passed sieve #200). The crushed and sieved P-C was placed in a muffle at 200 °C for 2 h[9]. The product obtained was designated as thermally activated clay (TA-C). The P-C was placed in a beaker. Sulfuric acid 3N was slowly added and constantly stirred for 1 h at room temperature. Subsequently it was vacuum filtered and dried at 40 °C until it was completely dehydrated. The dried activated clay was crushed and sieved to obtain the same three particle sizes as for the TA-C. The product obtained was designated as acid activated clay (AA-C).

The P-C was placed in deionized water with constant stirring for 2 h and hexadecyltrimethylammonium bromide (HDTMA) was added. The cation exchange process was carried out for 12 h at room temperature. Subsequently it was vacuum filtered and repeatedly washed with deionized water to remove the excess of halide ions. The clay was filtered again, and the resulting solid was dried for 48 h at 60 °C. The activated clay was crushed and sieved to obtain the above mentioned three particle sizes. The product obtained was designated as salt activated clay (SA-C).

The ion-exchange capacity was determined using the BaCl₂ method, as performed by[10].

2.3. Characterization

The natural and activated clays were characterized by X-ray diffraction, FT-IR spectroscopy and the Brunauer, Emmet & Teller method using a Panalytical XpertPro diffractometer, a Perkin Elmer Spectrum 100/Spotlight spectrometer and a Quantachrome Novatouch LX1 equipment, respectively.

For determining the clay swelling power, 2 g of dry natural bentonite was added in 2 min intervals divided into 20 equal portions to a solution of 10 g of sodium lauryl sulphate in 100 mL of deionized water. The solution was set to rest for 2 h. The data obtained after 1, 16 and 24 h were recorded. The same procedure was performed with the clay in water. The tests were carried out in duplicate.

The synthetic water used for adsorption testing was obtained from a 1 g L⁻¹ solution of methomyl in water. This synthetic water had a concentration of 100 µg L⁻¹. 0.5 g of each type of clay studied was added to 50 mL of the synthetic water solution at a given temperature (20, 30 and 40°C). The resulting suspension was stirred at 120 rpm, 20 °C for a 3 h contact time. The adsorbent clay was removed by using a Hermle Z 366 centrifuge rotating at 2800 rpm for 10 min, and qualitative filter paper. Ultraperformance liquid chromatography-tandem mass spectrometry (UPLC-MS/MS) was used to quantify the amount of methomyl present in the treated synthetic water. For this purpose, an ACQUITY UPLC coupled to a XEVO TQ-S MS/MS from Waters Corporation were used. A BEH C18 chromatography column, hypergrade LiCrosolv methanol for LC-MS and ultrapure water were used for the analysis. The tests were carried in duplicate.

The adsorption data obtained was fitted to the Freundlich and Langmuir isotherm models, using the corresponding linearized equations (1) and (2). The adsorption model that best described experimental data was selected based on the highest coefficient of determination, R².

\[
\log(q_e) = \left(\frac{1}{n}\right)\log(C_e) + \log(k_F),
\]

(1)

where \(q_e\) is the amount of solute adsorbed per unit weight of adsorbent material (µg g⁻¹), \(C_e\) is the equilibrium concentration for the analyzed solution (µg L⁻¹), \(k_F\) is the constant of the Freundlich equation (µg g⁻¹) and \(1/n\) is the coefficient of the Freundlich equation.

\[
\frac{C_e}{C_s} = \left(\frac{1}{Q* b}\right) + \left(\frac{1}{Q}\right)C_e,
\]

(2)

where \(C_s\) is the amount of solute adsorbed per unit weight of adsorbent material (µg g⁻¹), \(C_e\) is the equilibrium concentration for the analyzed solution (µg L⁻¹), \(Q\) is the amount of solute needed to form a monolayer per unit weight of adsorbent (µg g⁻¹) and \(b\) is the Langmuir equation constant (L µg⁻¹).

2.4. Statistical analysis

For the examination of the results obtained, an analysis of variance (ANOVA) was performed for a completely randomized design in a split-plot (3 x 5 x 2) with two replications, using general and mixed linear models. INFOSTAT 2019 was used to perform the analyses.
3. Results and discussion

3.1. XRD and FTIR characterization

Figure 1 shows the diffraction patterns for the natural clay, P-C, TA-C, AA-C and SA-C. As can be observed, in every sample there is a peak that would correspond to the plane (0 0 1) in montmorillonite, between 5° and 7.5°. We can also observe that the impurities present in the modified clays are not altered by the activation treatments. The N-C basal plane \( d_{(001)} \) is 15.4 Å \( (2\Theta = 5.7^\circ) \), it is closed to the P-C plane located in the 15.2 Å \( (2\Theta = 5.8^\circ) \), but they present difference intensity. In both cases, the basal plane is greater in thermal and acid activation than in saline activation. The values decrease from 15.4 Å \( (N-C) \) to 12.4 Å \( (2\Theta = 7.1^\circ) \) and 12.2 Å \( (2\Theta = 7.2^\circ) \) for TA-C and AA-C, respectively. The decrease was produced due to the changes in the bentonite thermal activation (the solvation water is eliminated) and acid activation (the clay structure delamination is produced) [9, 11], respectively. On the other hand, the basal plane increases in SA-C from 15.4 Å to 17.7 Å \( (2\Theta = 5^\circ) \) because there is an organic cation intercalation in the space between the mineral layers [12].

The principal phases present in the natural clay, and the activated clays studied correspond to quartz, stellerite and montmorillonite.

![Figure 1: X-ray diffraction patterns for the natural (blue), purified (green), thermally activated (red), acid activated (black) and salt activated (light blue) clays.](image)

Figure 2.a shows the spectrum of the N-C. The signal in bands at 3702 and 3575 cm\(^{-1}\) corresponds to the stretching of the O-H bond of the hydroxyl group that is between the tetrahedral and octahedral sheets [13]. The 3660 cm\(^{-1}\) band is due to stretching of O-H bonds at structural (Al-Al-OH) sites, which provides information on the nature of the cations present in the octahedral layer and is typical of montmorillonite with a high content of Al. The bands at 3262 cm\(^{-1}\) and 1620 cm\(^{-1}\) are due to adsorbed water, and the signal at 2312 cm\(^{-1}\) corresponds to the presence of traces of CO\(_2\). A great stretch can also be observed in the 1034 cm\(^{-1}\) band due to vibrations of Si-O-Si, characteristic of smectites [14]. Furthermore, the signal in the 901 cm\(^{-1}\) band is associated with the deformation vibrations of the Al-Fe-OH group. Bands at 761 and 520 cm\(^{-1}\) are also observed, indicating the presence of Al-O-Si groups, characteristic of the Si-O stretch in the quartz structure [15]. In figure 2.b the IR spectrum of the P-C is presented, maintaining the characteristic signals of the montmorillonite. Thus, the signals corresponding to the stretches of the O-H bond of the hydroxyl group were located at 3778 and 3569 cm\(^{-1}\). The 3660 cm\(^{-1}\) band, typical of smectites with a high Al content, remains the same. The signals in the bands at 3262 cm\(^{-1}\) and 1620 cm\(^{-1}\) (adsorbed water) and the signal at 2305 cm\(^{-1}\) (traces of CO\(_2\)) were identical in both N-C and P-C. It can also be seen that the stretch in the 948 cm\(^{-1}\) band due to vibrations of Si-O-Si weakens but maintains the typical characteristic of smectites. Furthermore, the band that is associated with the deformation vibrations of the Al-Fe-OH group is accentuated at 915 cm\(^{-1}\) and finally it is observed that the characteristic bands of the quartz structure are located at 716 cm\(^{-1}\) and 531 cm\(^{-1}\).
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In figure 2.c the IR spectrum of the TA-C is observed, which maintains the characteristic bands of montmorillonite. The signals that are due to the absorbed water, at 3248 and 1620 cm\(^{-1}\), weaken and almost disappear. This is because the clay was subjected to an activation temperature of 200 °C for 2 h. Figure 2.d corresponds to the IR spectrum of the AA-C, and does not show relevant changes on the structure of the montmorillonite. However, clear signs of the intensity ratio of the vibrations between Al-Al-OH, OH-Mg-Al and Si-OH-Al are observed. In 2.e the IR spectrum of the SA-C is observed, in which important changes are presented. Stretching vibrations are observed due to the interaction between the methyl and methylene groups present in the amine chains, according to the signal 2850 cm\(^{-1}\), characteristic in organ-bentonites [16]. In addition, the 1243 cm\(^{-1}\) signal caused by the flexing vibrations of the quaternary ammonium cation is presented [17]. In figure 2.f we observe the comparison of the spectra obtained. The purified clay (P-C) maintains the characteristic signs of montmorillonite more accentuated by the removal of impurities from the clay. With the thermal activation process, the crystalline structure was maintained, although the signals or peaks present due to the water adsorbed in the N-C were weakened, by exposing the A-AT to a temperature of 200 °C for 2 h during the activation. In contrast, in acid-activated clay (AA-C) increases the stretching vibrations of the Si-OH-Al group. Salt-activated clay (SA-C) shows an increase in the intensity of flexing vibrations.

3.2. BET analysis
Figure 3 shows the adsorption isotherms of the N-C and the activated (TA-C, AA-C and SA-C) clays studied, in the three size ranges considered. The isotherms show higher nitrogen adsorption volumes for the N-C and TA-C than in the chemically activated clays AA-C and SA-C, evidencing an increase in specific surface and porosity in the thermally activated clay. In chemically activated clays (with sulfuric acid and HTDMA), porosity decreased respect to the natural clay. All isotherms are classified.
as type IV, according to the IUPAC, with the hysteresis and solids-mesopore loop being typical. Furthermore, the desorption branch of the isotherms forms H₂ hysteresis, which indicates the presence of pore agglomerates with non-uniform sizes.

**Figure 3.** Adsorption and desorption isotherms for natural and activated clays with different particle size ranges: (a) 106-150 μm, (b) 75-106 μm, (c) <75 μm.

The specific surface areas calculated for the N-C were 52.5 m² g⁻¹, 45.9 m² g⁻¹, 47.4 m² g⁻¹ for the 106-150 μm, 75-106 μm, <75 μm particles, respectively. In the natural state, montmorillonite-type clay minerals have BET surface areas between 20 and 100 m² g⁻¹. Therefore, the values obtained are in the expected range, as can be observed when compared with the values calculated by Kaufhold et al. (2010) for a group of 36 different bentonites samples [18]. Thermal activation of bentonite clay causes the BET surface area to increase to 53.2 m² g⁻¹, 46.3 m² g⁻¹ and 41.7 m² g⁻¹ for the 106-150 μm, 75-106 μm, <75 μm particles, respectively. Maqueda et al. (2013) reported that montmorillonite sample surfaces increased slightly from 47.20 m² g⁻¹ to 49.22 m² g⁻¹ after heating to 500 °C. On the other hand, the acid activation reduces the surface area to 10.9 m² g⁻¹ and 11.2 m² g⁻¹ for the 106-150 μm and 75-106 μm particles, respectively. [19]. This could be mainly because microporosity decreases with the acid attack. Finally, the BET surface area and the pore volume were substantially reduced when the bentonite was modified with HTDMA. The values determined for the specific surface were 1.2 m² g⁻¹, 1.7 m² g⁻¹ and 1.7 m² g⁻¹, for the 106-150 μm, 75-106 μm, <75 μm particles, respectively. This indicates that the textural properties of bentonite were affected by the surfactant. Furthermore, it suggests that the pores of the bentonite were occupied by the surfactant molecules interspersed in the interlamellar space. In addition, Te & Yossapil (2015) reported reductions in the BET surface area and pore volume of a modified clay with FeSO₄ and FeCl₃ for arsenate adsorption [20].

Regarding the swelling power, it was observed that the natural clay studied did not show a relevant expansion. The clay corresponds to a low-swelling bentonite clay.

### 3.3. Methomyl adsorption

Table 1 shows the average methomyl removal efficiency for the natural and activated clays, as a function of temperature and particle size range. As can be observed, the more efficient treatments were the ones performed using the thermally activated clays. Operating at 40 °C and with a particle size between 106 and 150 μm, the removal efficiency was close to 76%. This was the best treatment. At the same temperature (40 °C), these clays achieved an efficiency of approximately 67% when the particle size was <75 μm. Operating at 30 °C and with a particle size <75 μm, the same clays reached a 68% removal efficiency. The HTDMA activated clays operating at 30 °C were deficient since they were not able to remove the pesticide from the synthetic water prepared. At 20 °C, the purified clays were the most efficient for the removal of methomyl (49 and 52%). The analysis of variance for the removal of methomyl showed a significant effect for the temperature x clay x particle size interaction with a confidence level of 95% (p = 0.004).

Methomyl adsorption curves were prepared for the clays that resulted in the best removal efficiency; that is, the TA-C. The adsorption curves were fitted to the Langmuir and Freundlich models. The best fit (R²= 0.58) corresponds to the Langmuir monolayer model (Q= 5000 μg g⁻¹).
Table 1. Average methomyl removal efficiency using natural and activated clays, as a function of temperature and particle size range.

| Clay | Temperature (°C) | Size range (μm) | Average removal efficiency (%) |
|------|------------------|-----------------|-------------------------------|
| N-C  | 106-150          | 15.7            |
|      | 75-106           | 17.4            |
|      | <75              | 29.2            |
|      | 106-150          | 49.3            |
|      | 75-106           | 52.0            |
|      | <75              | 51.8            |
|      | 106-150          | 32.7            |
|      | 75-106           | 34.5            |
|      | <75              | 43.3            |
|      | 106-150          | 12.2            |
|      | 75-106           | 38.0            |
|      | <75              | 30.4            |
|      | 106-150          | 15.0            |
|      | 75-106           | 4.9             |
|      | <75              | 22.7            |
|      | 106-150          | 7.9             |
|      | 75-106           | 19.9            |
|      | <75              | 6.8             |
|      | 106-150          | 52.0            |
|      | 75-106           | 57.1            |
|      | <75              | 60.8            |
|      | 106-150          | 58.8            |
|      | 75-106           | 31.4            |
|      | <75              | 67.5            |
|      | 106-150          | 0.2             |
|      | 75-106           | 9.2             |
|      | <75              | 25.1            |
|      | 106-150          | 0.0             |
|      | 75-106           | 2.9             |
|      | <75              | 0.0             |
|      | 106-150          | 14.6            |
|      | 75-106           | 25.3            |
|      | <75              | 19.8            |
|      | 106-150          | 14.9            |
|      | 75-106           | 59.5            |
|      | <75              | 56.4            |
|      | 106-150          | 75.8            |
|      | 75-106           | 66.2            |
|      | <75              | 67.0            |
|      | 106-150          | 48.2            |
|      | 75-106           | 40.1            |
|      | <75              | 37.1            |
|      | 106-150          | 31.5            |
|      | 75-106           | 42.6            |
|      | <75              | 44.2            |

4. Conclusion
The removal of methomyl from synthetic aqueous solutions can be carried out using natural and modified bentonite clays. The adsorption process can be relatively efficient, particularly with
thermally activated clays being used at 40 °C. In this case, removal efficiencies between 66 and 76% can be achieved. The highest efficiency was observed when working with a relatively large particle size (106-150 µm). On the other hand, purified clays showed efficiencies between 49 and 52% when used at 20 °C. These purified clays allow, in general, to achieve better efficiencies than the acid and the salt (HDTMA) activated clays for the three particles sizes considered in this work (106-150, 75-106 and <75 µm). Finally, it was observed that the methomyl adsorption processes fits the Langmuir model and that, according to the statistical analysis performed, there is a significant effect for the temperature × clay × diameter interaction with a confidence level of 95% (p = 0.004).

5. References
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