A comparative adsorption study of benzophenone-3 onto synthesized lipophilic organosilicate, Laponite and montmorillonite

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Graphical abstract:
In this study, the adsorption of a hydrophobic molecule, benzophenone-3 (BZ-3) was investigated onto three adsorbents: synthesized lipophilic organosilicate (OSL), Laponite (Lap) and montmorillonite (Mt). A comparative study for all adsorbents with batch adsorption experiments was achieved to determine the optimal conditions. The effects of the main experimental parameters were determined such as solvent, pH, temperature, initial concentration of BZ-3 and contact time. The adsorption capacity was evaluated by means of HPLC analysis equipped with UV detection and the adsorbent - BZ-3 complexes were characterized by means of Dynamic Light Scattering (DLS) analysis and Attenuated Total Reflectance - Fourier Transform InfraRed (ATR - FTIR) spectroscopy. Finally, the adsorption isotherm equilibrium was described according to Langmuir, Freundlich and Temkin models. The results showed that optimal value of the adsorbed BZ-3 for all adsorbents was found at pH 10, at 38 °C, with BZ-3 concentration of 2.5 g/L during 24 h of contact time. The results obtained showed a promising capacity of the OSL to adsorb BZ-3 (340 mg of BZ-3/g of adsorbent) compared to Lap (137 mg/g) and Mt (192.3 mg/g). Langmuir model fitted the best with OSL and Mt adsorption while Freundlich model fitted the best with Lap adsorption.

1. Introduction

Clays and clay minerals have been described as efficient adsorbents for several bioorganic molecules, most importantly for environmental (Ngulube et al., 2017) and pharmaceutical applications (Moraes et al., 2017). Their attractive properties were correlated with their natural abundance, swelling capacity, presence of electrical charge on their surfaces and ion exchange capacity (Li et al., 2017). Furthermore, their interesting colloidal properties explain their widespread use as emulsifying, gelling and thickening agents in pharmaceutical formulation (López-Galindo et al., 2007). Clays can adsorb bioorganic molecules by: hydrogen bonding, ion exchange, dispersion forces and by donation of π electrons (Ngulube et al., 2017).

Natural clays extracted from quarries present severe contamination by microorganisms, heavy metals and also variations in their composition according to the geographic site of extraction (López-Galindo et al., 2007). Among the smectite group, Montmorillonite (Mt) is a natural clay mineral composed of silica tetrahedral sheets layered between an alumina octahedral sheet (Murray, 2006). Mt has been widely used as an adsorbent
for several metal contaminants such as antimony (Zhao et al., 2010) and bioorganic molecules such as ciprofloxacin (Wu et al., 2010).

Synthetic clays can overcome the clays limitations with a guarantee of a reproducible composition, better adsorption qualities along with an improved specific surface as well as reduced toxicity. We were interested in the study of Laponite (Lap) for its adsorption properties. Xu et al. described Lap as a synthetic layered silicate with a disk-like structure with a thickness of 1 nm and a diameter of about 25 nm (Xu et al., 2010).

More interestingly, this synthetic clay has been used as adsorbent for several antifungal drugs such as itraconazole (Jung et al., 2008) and antibiotics such as tetracycline (Ghadiri et al., 2013).

Clays and clay minerals can be modified by different ways (Lv et al., 2017) such as inserting organic side chains into their layered structure, leading to hybrids called organoclays. Hexadecyltrimethylammonium (HDTMA) was intercalated into Mt by cation exchange process and adsorption isotherm of an acidic dye. Wang et al. found that the adsorption capacity of modified Mt was higher than that of raw Mt. The increased adsorption capacity could be related to a higher interlayer space between the tetrahedral sheets of Mt and hydrophobic interactions between HDTMA and the acidic dye (Wang et al., 2004). Fukushima and Tani (Fukushima and Tani, 1995) described a sol-gel process to obtain new organoclay-like materials with a phyllosilicate structure. Hence, such organoclays had accurate homogeneity, purity and controlled porosity when compared to natural clays (Dey et al., 2010).

In the purpose of finding new adsorbents, many reports have shown the adsorption equilibrium of compounds such as drugs or heavy metals onto natural clays (Li et al., 2017), synthetic clays (Badshah and Airoldi, 2013), and one pot sol-gel synthesized phyllosilicates (Oubagaranadin and Murthy, 2010).

In previous works, aluminium/calcium organosilicate (OS) was synthesized (Lhéritier et al., 2017) (Lorentz et al., 2014). As a reminder, the described sol-gel process used a fixed molar ratio of alkoxy silanes: tetraethoxysilane (34.0%), octyltriethoxysilane (49.5%) and [hydroxy(polyethyleneoxy)propyl]trimethoxysilane (16.5%) mixed with calcium chloride (CaCl₂) and aluminium chloride (AlCl₃) under basic catalysis. Such obtained organosilicate was lipophilic (OS₄) mainly due to the predominant octyl side chain and could stabilize concentrated water-in-silicone (W/Si) Pickering emulsions (Lorentz et al., 2014). Attenuated Total Reflectance - Fourier Transform InfraRed (ATR - FTIR)
spectroscopy analysis confirmed the presence of inorganic (Si-O-Si) and metal-organic frameworks of OS_{L}.

Analyses of OS_{L} by Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM) confirmed the presence of lamellar sheets and a semi-crystalline structure, respectively. X-Ray Diffraction (XRD) showed that the interlayer space was 21.97 Å. Dynamic Light Scattering (DLS) analysis showed a unimodal sub-micron distribution centered on 650 nm (Lorentz et al., 2014).

The purpose of this study is to investigate for the first time the adsorption capacity of OS_{L} in comparison with the adsorption capacity of Mt and Lap in ethanol. For this purpose, the adsorption mechanism was investigated according to the Langmuir (Langmuir, 1918), Freundlich (Freundlich, 1906) and Temkin (Temkin and Levich, 1946) isotherm models. As a proof of concept, the hydrophobic benzophenone-3 (BZ-3, LogP = 3.79) was chosen as a reference compound (Kim and Choi, 2014).

2. Materials and Methods

2.1. Chemicals and reagents

The lipophilic organosilicate OS_{L} was synthesized according to the process described by Lorentz et al. (Lorentz et al., 2014). The experimental elemental analysis of the OS_{L} (wt.%), is: Si (13.69%), Al (3.02%), Ca (3.46%), C (27.79%), H (5.78%), Na (3.00%) (Lorentz et al., 2014). A synthetic hectorite-like clay mineral Laponite® XLG (Lap) with cation exchange capacity (CEC) of 100 meq/100 g (Kim et al., 2018) was purchased from Rockwood Additives Ltd (United Kingdom). The mineralogical composition of Laponite (wt.%) is: silicium oxide (SiO_{2}) 59.5%; magnesium oxide (MgO) 27.5%; lithium oxide (Li_{2}O) 0.8%; sodium oxide (NaO) 2.8%. A natural white-pinkish montmorillonite CosWHITE™ (Mt) was kindly provided by Argile du Velay®-ARVEL (France, CEC not described by the manufacturer). The mineralogical composition of montmorillonite (wt.%) is: SiO_{2} 53.18%, aluminum oxide (Al_{2}O_{3}) 26.43%, iron oxide III (Fe_{2}O_{3}) 5.06%, potassium oxide (K_{2}O) 0.44%, MgO 5.57%, calcium oxide (CaO) 3.11%, NaO 5.21%, titanium oxide (TiO_{2}) 0.41%, phosphorus oxide (P_{2}O_{5}) 0.28%, manganese oxide (MnO) 0.10%. Sodium hydroxide (NaOH) and hydrochloric acid (HCl) were purchased from Carlo Erba (Italia). BZ-3 was purchased from Merck KGaA (Germany) under the commercial denomination Eusolex® 4360. HPLC Grade solvents such as ethanol...
(>99.9%), methanol, water, acetic acid and acetonitrile were purchased from Fisher Chemicals (USA). Milli-Q water (Millipore Corp.) with a specific resistivity of 18.2 MΩ.cm at 25 °C was used in this study.

2.2. Adsorption experiments

2.2.1. Parameters controlled during batch adsorption experiments

For batch adsorption experiments, a preliminary study was conducted to find the most appropriate solvent for the couple adsorbent-BZ-3. Theoretical solubility tests were performed with HSPiP 3.1 software (Version 3.1) (Image Metrology, Lyngby, Denmark), involving BZ-3 and a panel of solvents (Fig. S1 in the Supplementary Information file). The BZ-3 adsorption capacity of OSL, Lap and Mt was evaluated by typical batch adsorption experiments (Arellano-Cárdenas et al., 2013). These batch experiments were conducted to determine the optimal solvent for BZ-3, pH, temperature, initial concentration and contact time on the adsorption of the BZ-3.

2.2.2. Batch adsorption experiments

Several batch experiments were carried out in order to obtain information about the effect of pH, temperature, initial BZ-3 concentration and contact time. For each batch adsorption experiment, 25 mL of BZ-3 solution was added to 50 mL conical tube containing 0.5 g (weighted per duplicate) of OSL, Lap or Mt and protected from light. This mixture was stirred with a constant speed of 150 rpm. At the end of each experiment, samples were withdrawn, and centrifugated (5000 rpm, 5 min) and an aliquot of the corresponding supernatants was analyzed for BZ-3 concentration. Blanks without adsorbent were run to rule out possible BZ-3 losses due to degradation, volatilization, or adsorption on tube walls. The pH effect on BZ-3 adsorption was studied at pH 5.5, 7 and 10. Each pH value was measured using a specific ethanolic solution electrode (EtOH-Trode, inner and bridge electrolyte KCl = 3 mol/L, Metrohm, Ionenstrasse, Switzerland). The initial pH of the solution was adjusted by addition of either aqueous solution of HCl (1 M) or NaOH (1 M). Temperature effect was studied at 5, 20 and 38 °C using controlled-temperature water-bath. The adsorption experiment was performed with different initial concentrations of BZ-3 at 0.01, 0.05, 0.1, 0.5, 1, 1.5, 2 and 2.5 g/L. Contact time effect was studied by analyzing the adsorbed amount of BZ-3 from solution at different time intervals (0 - 24 h). For all
experiments in this study, 20 g/L was used as adsorbent dosage. Adsorption isotherms were determined by the analysis of the residual BZ-3 concentration from solution at increasing concentration. For this aim, solution of different BZ-3 concentrations (0.01 - 2.5 g/L) was evaluated. The samples were treated as described above. The amount (%) of BZ-3 was calculated using the following relationship (Arellano-Cárdenas et al., 2013) as given via Eq. 1:

\[
\% \text{ of Adsorbed BZ-3} = \left( \frac{C_0 - C_t}{C_0} \right) \times 100
\]  

(1)

where \( C_0 \) (mg/L) is the initial BZ-3 concentration and \( C_t \) (mg/L) is the concentration at time t. The amounts adsorbed were calculated from the following relationship (Arellano-Cárdenas et al., 2013) via Eq. 2:

\[
q_e = (C_0 - C_e) \frac{v}{w}
\]  

(2)

where \( q_e \) (mg/g) is the adsorbed amount of adsorbate at equilibrium, \( C_0 \) and \( C_e \) (mg/L) are the concentrations of BZ-3 at initial time and at equilibrium, respectively, \( v \) (L) is the volume of solution and \( w \) (g) is the mass of adsorbent.

2.3. Determination of adsorbed amount of BZ-3 by HPLC

Samples were analyzed for BZ-3 residual concentration by High-Performance Liquid Chromatography (HPLC) using an alliance e2695 (Waters, Milford, MA, USA) equipped with a UV detector and a Supelco column nucleosil C18 (250 mm × 4.6 mm, 5 µm,) (Merck KGaA, St. Louis, MI, USA). The mobile phase, which was degassed and filtered before analysis, consisted of acetonitrile (A) and methanol (B) and water with 0.1% acetic acid (C). The eluent flow rate was 1.0 mL/min. The elution conditions applied included the following: 30% A, 30% B and 40% C. UV measurements were carried out at 288 nm. Data were collected and processed using Empower 2 software for HPLC system. Calibration was performed by triplicate injection of standard solution between 0.1 and 10 mg/L (R²=0.999) with these conditions, the retention time (RT) of BZ-3 was 8.3 min.
2.4. Assay precision and accuracy

Using common analytical method based on signal to noise (S/N) ratio (Kasichayanula et al., 2005), the limit of detection (LOD) was calculated as three times greater than the baseline noise and the limit of quantification (LOQ) was calculated as ten times greater than the baseline noise. Under chromatographic conditions in this study, LOD and LOQ values were 0.002 g/L and 0.01 g/L, respectively (Fig. S2 in the Supplementary Information file).

2.5. Adsorbent - BZ-3 complexes characterization

2.5.1. Particles size

OSL, Lap and Mt particles size were measured using a laser diffraction granulometer (Malvern Mastersizer 2000, Malvern, UK), equipped with a small volume Hydro 2000S sample dispersion unit. The measurements were performed using the following parameters: refractive index of the particles 1.55, refractive index of water 1.33 and particle absorption coefficient 0.1. The data obtained was averaged by the Mastersizer 2000® Software (Version 5.54). The mean diameter of particles in suspension was measured according to the median number diameter $d_{(0.5)}$ defined as the diameter, where 50% of the distribution was above the indicated value. Control samples (without BZ-3) were prepared ahead from the analysis by putting each adsorbent in the medium (ethanol) for the same contacting time (24 h).

2.5.2. Specific surface measurements

The specific surface area of all adsorbents was measured through nitrogen adsorption using the Brunauer–Emmett–Teller (BET) method, carried out in a GeminiVII apparatus (Micromeritics Instrument Corp. Norcross, GA, USA). The samples were previously treated at 110 °C under stream of N$_2$ for 2 h.

2.5.3. Infra-Red spectroscopy measurements

Powder samples were directly used for the Infra-Red spectroscopy analysis using ATR - FTIR spectroscopy (IRAffinity-1 FT-IR Spectrophotometer, Shimadzu Corporation, Kyoto, Japan) with a single horizontal
reflection ATR accessory (PIKE instruments, Madison WI, USA). All the spectra were recorded in a dry atmosphere at room temperature (20 ± 2 °C) within a range of 4500 - 600 cm\(^{-1}\) by averaging 45 scans, with a wave number resolution of 4 cm\(^{-1}\). The ATR effect as well as the atmospheric contributions from carbon dioxide and water vapor were corrected by the IRSolution\(^{®}\) Software (currently Labsolution\(^{®}\)).

2.5.4. Thermal analysis

The thermal analysis was performed with the Seiko Thermogravimetry (TG) and Differential Thermal Analyzer (DTA) Model 220 (Seiko Instruments Inc., Chiba, Japan). Samples were heated from 20 °C to 800 °C with heating rate of 10 °C/min, under high-purity nitrogen atmosphere with a gas flow rate of 80 mL/min.

2.6. Reproducibility and Statistical data analysis

All adsorption experiments were performed in triplicate assays for each condition and repeated at least twice. The coefficient of determination (R\(^2\)) as well as isotherm constants were calculated using statistical functions of Microsoft Excel 2017 (version Office XP, Microsoft Corporation, USA). Statistical analysis was performed with software R (version 3.1.2). Data were analyzed using single-factor analysis of variance (ANOVA) and presented as mean values ± standard error of the mean (SEM) from at least six independent measurements. The comparison among groups was performed by the independent sample Student’s t-test. The difference between variants was considered significant if \( p \) value < 0.05. A Chi-square test (\( \chi^2 \)) was performed to analyze error for fitting data with isotherm models. The Chi-square test statistic is basically the sum of the squares of the differences between experimental data and data obtained by calculation from models, with each squared difference divided by the corresponding data obtained by calculation from models. The equivalent mathematical statement as given via Eq. 3:

\[
\chi^2 = \sum (q_{e,\ exp} - q_{e,\ calc})^2/q_{e,\ calc}
\]

where \( q_{e,\ exp} \) is the experimental data of the equilibrium capacity (mg/g), \( q_{e,\ calc} \) is the equilibrium capacity obtained by calculating from the model (mg/g) (Mouni et al., 2018). If the data from the model were found like the experimental data, \( \chi^2 \) would be a small number and if data were different, \( \chi^2 \) would be a large number.
3. Results and Discussion

3.1. pH effect

The pH effect on adsorption of BZ-3 was studied for OSL, Lap and Mt in 2.5 g/L BZ-3 solution at 20 °C for 24 h at three pH values: 5.5, 7 and 10 (Fig. 1). This parameter is important to check the adsorption capacity of the three adsorbents regarding BZ-3.

Insertion of Figure 1

In the case of OSL, the results showed a stronger hydrophobic attraction with BZ-3 and greater adsorption capacity. OSL is a layered organosilicate functionalized with both hydrophobic octyl side chains and hydrophilic poly (ethylene oxide) chains (PEO) and hydrophobic CH₂-CH₂ groups. It was reported in the literature that PEO may interact with guest molecules by means of hydrogen bonding (Mathur and Moudgil, 1997). Moreover, the same authors explained that the adsorption could be related to the interaction between the ether oxygen of PEO (a Lewis base) and strong Bronsted acid sites on the surface. While, the interactions at the Si-O-Si, the Al-O-Si and hydroxyl groups of the Ca-OH are important to maintain the structure at pH between 5.5 and 10. BZ-3 adsorption onto OSL showed the highest level at pH 10 which can be explained by i) increased external surface interactions and ii) larger interlayer space with the existence of octyl and PEO side chains (Moscofian et al., 2008). In several cases, Park et al. also reported that the increased adsorption capacity of organoclays could be either related to their hydrophobic behavior or to the difference in the interlayer space when compared to raw clays (Park et al., 2011).

Laponite particles are considered hydrophilic due to the difference in the charges between the negatively charged faces (top and bottom) and the positively charged borders of Lap (Xu et al., 2010). Laponite® XLG is a gel forming grade which contains low levels of heavy metals with minimal toxic effects and a pH 10 - 11 (Tomás et al., 2017) and is used as a vehicle in drug delivery. The batch adsorption experiments occurred in ethanol. The manufacturer reported that at concentrations of 2% or greater in water, highly thixotropic gels are obtained (Technical Information B-RI 21., 2018). Xu et al. (Xu et al., 2010) reported the surface hydrophilicity and charge influenced the adsorption of Lap in solution. The obtained results showed that
significant effect of pH was observed on the adsorption of BZ-3 on Lap at pH 5.5 and 10. Tomás et al. (Tomás et al., 2017) have reported that Lap may interact with charged species, polar and non-polar compounds.

In recent studies, Castro et al. have reported that pKₐ_w in water (with 20% ethanol) was 9.6 (Castro et al., 2000). This could be explained by the resonant forms of BZ-3 (participation of the C=O function, electron-donating effect of OCH₃, increased intramolecular hydrogen bonds) that could influence the acid-base properties of the hydroxyl group (Castro et al., 2000). This pKa increases in ethanolic solutions, further modeling studies by the Castro et al. showed difference in pKa values between pure aqueous and ethanolic solutions, at 29% w/w water/ethanol, pKₐ_w-ol was 10.7 (Castro et al., 2003). In the presented study, the % of ethanol is more than 30% which could explain that BZ-3 in ethanol was in its neutral form and had interactions with the negatively charged Mt and Lap. A slight variation on pH values was observed after the adsorption of BZ-3 on each adsorbent. pH was not affected by BZ-3 adsorption which can indicate that adsorption can be attributed to interaction other than electrostatics interactions (hydrogen bond with silanol group of adsorbents, hydrophobic interactions with organic moieties of OSₜ particles) (Fig. S3 in the Supplementary Information file).

The decrease of adsorption capacity occurred probably because low pH could increase the electrostatic interactions between the Lap negatively charged faces and its positively charged borders which may explain the encapsulation of BZ-3 inside the inter-crystal species defined by the “House-of-cards” structure or self-assembling gel.

A significant effect of pH on the adsorption was found only between the adsorption values measured at pH 5.5 and 10. According to the analysis carried out on the BZ-3 adsorption data for Mt, the pH seemed to have no significant effect on adsorption if the pH is increased from 5.5 to 7. When increasing the pH, Altin et al. (Altin et al., 1999) found that the micropore and mesopore surface increased, which could explain the highest percentage of adsorbed BZ-3 at pH 10. Moreover, the authors reported that above pH 5.5, increasing the pH contributed to the cross linking by edge to face associated particles, leading to the formation of gels. At pH 10 the percentage of adsorbed BZ-3 by OSₜ was higher than those achieved by Lap and Mt. These results have been proven by the analysis of variance (ANOVA) which showed a significant higher percentage of adsorbed BZ-3 on OSₜ compared to those obtained with Lap and Mt. These observed results were consistent
with the described increased percentage of the adsorbed dye onto Mt which increased with pH of the solution until it reached a maximum adsorption at pH 10 (Almeida et al., 2009). For the following studies, batch adsorption experiments will be carried out at the optimal pH 10 (Fig. S3 in the Supplementary Information file).

3.2. Temperature effect

Batch experiments were carried out at the optimal pH 10 and the temperature effect was studied at three different temperatures (5, 20 and 38 °C) to evaluate the BZ-3 adsorption capacity of OS₅L, Lap and Mt (Fig. 2).

Insertion of Figure 2

In the case of OS₅L, the increase of % BZ-3 adsorbed in each temperature value was significant which proved the positive effect of temperature on BZ-3 adsorption onto OS₅L. The ANOVA test allowed to conclude that, for the OS₅L, at the three-studied temperature values, a significant increase was observed in the percentage of adsorbed BZ-3 from 5% at 5 °C to 30% at 20 °C until it reached 43% at 38 °C. Increasing the temperature is known to increase the rate of diffusion of the BZ-3 within: i) the external boundary layer of the adsorbents and ii) the internal pores correlated with the decreased viscosity of the ethanol at high temperature (Doğan et al., 2004). Likewise, De Oliveira et al. reported that temperature could explain the increase in the mobility of BZ-3 and improve the adsorption capacity as well as BZ-3 surface interaction (De Oliveira et al., 2017). Another mechanism could also happen through reducing the energy of activation which corresponds to physisorption (De Oliveira et al., 2017). This assumption is not sufficient alone to understand the adsorption mechanism of the OS₅L adsorption and further investigations and evaluation of thermodynamic parameters (e.g enthalpy and entropy changes were evaluated). At 38 °C, BZ-3 adsorption seems to be improved with higher mobility of the octyl side chains.

In the case of Lap, only a difference between 5 °C (17%) and 38 °C (28%) was observed, the adsorption effect was not investigated beyond 38 °C. Liu and Thomas reported that heating Lap solution to more than 100 °C allowed a complete adsorption most likely due to the dehydration of Lap, a coordination with Na⁺ as well as the creation of new adsorption sites after dehydroxylation (Liu and Thomas, 1991).
In the case of Mt, the influence of temperature on adsorption of BZ-3 was only noticeable between 20 °C (19%) and 38 °C (39%). This was consistent with the described high rate adsorption of dyes on Mt with increased temperature. Almeida et al. explained that the temperature effect on Mt could be related to the release of hydrated inorganic cations from the Mt causing an overall increase in entropy (Almeida et al., 2009). Analogous or structural changes could be a result of interactions of BZ-3 with active groups in the Mt surface. All these results showed that between 5 °C and 38 °C; % of adsorbed BZ-3 increased with rising temperature which reveals an endothermic adsorption process (Arellano-Cárdenas et al., 2013). Compared to the other adsorbents, OS_L have shown the highest adsorption percentage of BZ-3 at the experiment conditions (pH 10, temperature 38 °C). The comparison of BZ-3 adsorption (%) was significantly higher for OS_L than Lap at 38 °C (ANOVA test) and not different from Mt (ANOVA test). OS_L, Lap and Mt have shown the highest adsorption capacity at 38 °C. For the following studies, batch adsorption experiments will be carried out at the optimal pH 10 and the optimal temperature of 38 °C.

3.3. Effect of initial BZ-3 concentration

The effect of initial concentration of BZ-3 on the adsorption of BZ-3 onto OS_L, Lap and Mt was studied at pH 10 at 38 °C with a concentration varying from 0.01 to 2.5 g/L. Results are depicted in Fig. 3.

Insertion of Figure 3

The amount of BZ-3 removal is expressed in mg/g of adsorbent for BZ-3 initial concentration of 0.01, 0.05, 0.1, 0.5, 1, 1.5, 2 or 2.5 g/L. For all the adsorbents, an increase in the adsorbed amount of BZ-3 was observed at higher concentrations. Fig. 3 showed that a change in the equilibrium could be related to a chemisorption process for all adsorbents taking place at the surface of the adsorbents at low concentrations. Almeida et al. explained in their study on methylene blue (MB) dye that this process could be followed by a second layer of adsorbed compound. This could explain the decrease in the mass transfer resistance between the BZ-3 ethanolic solution and the adsorbents (Almeida et al., 2009). The occupation of the adsorbent available binding sites when the concentration increased could generate the dependence of adsorption process to the initial concentration of BZ-3. At higher concentration, the competition between BZ-3 and available binding sites increased. Adsorption reached a plateau when initial BZ-3 concentration exceeded 1.5 g/L. However, plateau
was reached for Lap and Mt at 2 g/L but with large standard error of the mean (SEM). For this study, the choice of the concentration of 2.5 g/L was the most adequate for a comparative study between the three adsorbents.

In the case of OSL, an increase in the amount of adsorbed BZ-3 linked to the increase of the initial concentration was observed. Only with Mt and Lap at high concentrations, a slight decrease in the adsorption capacity was observed at 2.5 g/L. The OSL showed a higher adsorption capacity at all ranges of initial BZ-3 concentration values, which revealed that OSL could be more efficient for BZ-3 adsorption when compared to Mt and Lap (according to the ANOVA test). For the following studies, batch adsorption experiments will be carried out at the optimal pH 10 and the optimal temperature 38 °C and initial BZ-3 concentration of 2.5 g/L.

3.4. Effect of contact time

The required optimal contact time was evaluated for adsorption equilibrium of BZ-3 onto OSL, Mt and Lap particles. As previously mentioned, the adsorption experiments were carried out at pH 10, 38 °C and with initial BZ-3 concentration of 2.5 g/L and the equilibrium concentrations were measured at defined contact time. Effect of contact time for the BZ-3 adsorption by the three adsorbents is shown in Fig. 4.

Insertion of Figure 4

It is noteworthy to mention that a rapid initial uptake for all three adsorbents occurred within the first 200 min. At this period, the adsorption process of OSL was faster than Mt and Lap (315 min) and the adsorption rate reached 300 mg/g for OSL against 200 mg/g for Mt and 150 mg/g for Lap. This could be explained by BZ-3 transfer at higher concentration, the resistance to BZ-3 uptake diminished as the mass driving force increased. In the first phase, the adsorption rate is controlled by the availability of the surface sites of adsorbent. The difference in the amount adsorbed may be related to the interactions between the OSL and BZ-3 where molecular (π-π) interactions could explain the observed enhancement of BZ-3 adsorption (De Oliveira et al., 2017). The equilibrium optimal contact time for the adsorption of BZ-3 onto the three adsorbents was found to be 24 h.
3.5. Adsorption isotherm experiments

Adsorption experiments of BZ-3 onto OS_L, Lap and Mt were conducted at pH 10, 38 °C and equilibrium reached within 24 h. The isotherm for the adsorption of BZ-3 on OS_L, Lap and Mt showed in Fig. 5 exhibited a L-shaped (Langmuir) type isotherm and more precisely L2 according to Giles classification (Giles et al., 1960).

Insertion of Figure 5

Based on the adsorption data for the three adsorbents, the adsorption amount of BZ-3 was higher for OS_L than for Lap and Mt, probably because of structural differences between the adsorption particles. The purpose of this study is to better understand the adsorption capacities of the OS_L and compare it to Lap and Mt adsorption capacities. Langmuir (Epstein et al., 2015), Freundlich (Araújo et al., 2018), and Temkin (Abdelnaeim et al., 2016) models were used, equations and isotherm constant parameters were calculated to better predict adsorption capacities. For all the adsorbents, the same experiments were carried out at the same conditions.

3.5.1. Langmuir adsorption isotherm model

The Langmuir adsorption isotherm model is mainly related to chemisorption occurring at energy-equivalent adsorption sites without considering surface coverage and interactions between BZ-3 molecules (Vinati et al., 2015). In another words, an equilibrium saturation point is reached when all adsorption sites are occupied (Foo and Hameed, 2010). where K_L (L/mg) and a_L (L/mmol) are the Langmuir equilibrium constants. q_max is the theoretical monolayer capacity (mg/g), it is numerically equal to (K_L/a_L). The linearized form of the Langmuir model can be given via Eq. 4 (Abbass et al., 2017):

\[
\frac{C_e}{q_e} = \frac{1}{q_{max}K_L} + \frac{C_e}{q_{max}}
\]  

All experimental data were plotted in terms of C_e/q_e vs C_e whereas K_L and q_max can be calculated from intercept and slope of linear plot. The linearized forms of Langmuir adsorption isotherm model for the adsorption of BZ-3 onto OS_L, Lap and Mt particles are shown in Fig. 6 (a).

Insertion of Figure 6
The Langmuir isotherm model can be expressed in other forms which are based on a dimensionless separation factor \( R_L \) (Nafees and Waseem, 2014) defined by Weber and Chakravorti (Weber and Chakravorti, 1974). The separation factor \( R_L \) is given via Eq. 5:

\[
R_L = \frac{1}{1 + aLC_0}
\]  

(5)

where \( R_L \) is a dimensionless separation factor or equilibrium parameter, \( a_L \) is the Langmuir isotherm constant and \( C_0 \) (mg/L) is the initial concentration of BZ-3. This latest form is interesting since the value of \( R_L \) is arranged as \( R_L = 0 \) (irreversible process), \( 0 < R_L < 1 \) (favorable process) and \( R_L > 1 \) (unfavorable process). Thus, the determination of \( R_L \) provided a good theoretical proof whether the adsorption was favorable or not.

Based on this study, it seemed that the adsorbed amount of BZ-3 was higher onto OS\(_L\) (340 mg/g) than onto Mt (192.3 mg/g) and Lap (137 mg/g) (Table 1). The adsorption properties of all adsorbents could be linked to the chemical nature of BZ-3 (De Oliveira et al., 2017), the two aromatic rings could interact through donation of \( \pi \) electrons (Ngulube et al., 2017).

**Insertion of Table 1**

For BZ-3 adsorption, all adsorbents described a successful adsorption with the Langmuir model according to the calculated coefficient of linearity \( R^2 = 0.983 - 0.997 \). \( R_L \) for all adsorbents (0.98 - 0.21) would suggest a favorable process.

### 2.6. Thermodynamic analysis

The thermodynamic constants, Gibbs free energy change \( \Delta G^\circ \), enthalpy change \( \Delta H^\circ \), and entropy change \( \Delta S^\circ \) were calculated to evaluate the thermodynamic feasibility and the spontaneous nature of the adsorption process of BZ-3 on the three adsorbents. These thermodynamic constants as given in Eq. 6:

\[
\Delta G^0 = -RT \ln K^0_L
\]

(6)

where \( \Delta G^\circ \) (kJ/mol), \( R \) is the universal gas constant (8.314 J/mol/K), \( K^0_L \) the thermodynamic equilibrium constant (L/mg) and \( T \) is the absolute temperature (K). Values of \( K^0_L \) may be calculated from isotherm data as (Mouni et al., 2018). All concentrations have been changed to molar form considering the standard state \( C^\circ = 1 \) mol/L (Salvestrini et al., 2014) as given via Eq. 7:
\[ K_0^L = K_L \times 1000 \text{ (mg/g)} \times M_{BZ-3} \text{ (g/mol)} \times C^0 \text{ (mol/L)} \]  

(7)

where \( M_{BZ-3} = 228 \text{ g/mol} \) is the BZ-3 molar mass, and the factor 1000 allows converting g to mg.

The enthalpy (\( \Delta H^0 \)) (KJ/mol) and entropy (\( \Delta S^0 \)) (J/mol K) parameters were estimated from classical relationship as given via Eq. 8 and 9:

\[ \ln K^0 = (\Delta S^0/R) - (\Delta H^0/RT) \]  

(8)

\[ \Delta G^0 = \Delta H^0 - T\Delta S^0 \]  

(9)

\( \Delta H^0 \) and \( \Delta S^0 \) can be obtained from the slope and intercept of Van’t Hoff plot of \( \ln K^0 \) vs. \( 1/T \) (Fig. S5 in the Supplementary Information file).

The values of \( \Delta G^0 \) were calculated from \( \Delta H^0 \) and \( \Delta S^0 \) (Table 2). The observed positive values of \( \Delta H^0 \) for all adsorbents further confirmed the endothermic nature of the adsorption process which was consistent with the previously described increased amount of adsorbed BZ-3 at 38 °C. The negative values of \( \Delta S^0 \) confirmed, for all adsorbents, the decreased randomness at the solid–liquid interface and suggested that the internal structure of the adsorbents remained unchanged during adsorption. The negative \( \Delta G^0 \) values confirmed the spontaneous nature and feasibility of the adsorption process (Mouni et al., 2018).

**Insertion of Table 2**

3.6.2. Freundlich adsorption isotherm model

Freundlich isotherm model might be used to describe the sorption of heterogeneous surface and multilayer sorption formation (Vinati and Mahanty, 2015). According to such model, BZ-3 would be first linked to the strongest binding until adsorption equilibrium and then the energy exponentially would decrease at the end of the adsorption process (Foo and Hameed, 2010). The expression of the Freundlich model is given via Eq. 10:

\[ q_e = K_F C_e^{1/n} \]  

(10)

and the linearized equation is presented via Eq. 11:

\[ \log q_e = \log K_F + \frac{1}{n} \log C_e \]  

(11)
where \( \frac{1}{n} \) and \( K_F \) (\( mg^{(1-1/n)} L^{1/n}/g \)) are the rate constant related to the adsorption intensity and capacity, respectively. The plot of \( \log q_e \) vs \( \log C_e \) should give a right curve. Values of \( n \) and \( K_F \) can be both obtained from slope and intercept, respectively. The value of \( n \) reflects the adsorbent-adsorbate interaction (Gereli et al., 2006) The linearized form of Freundlich adsorption isotherm model for the adsorption of BZ-3 onto \( O_{SL} \), Lap and Mt is shown in Fig. 6 (b). Value of \( \frac{1}{n} \) can reveal favorable or unfavorable adsorption conditions (Koyuncu et al., 2011). For BZ-3 adsorption, all adsorbents described a successful adsorption with the Freundlich model (\( R^2 \) value 0.983-0.991) since value of \( \frac{1}{n} \) was found to lie between zero and one in the case of \( O_{SL} \), Lap and Mt (Table 1) indicating that BZ-3 is favorably desorbed by these adsorbents. In addition, Lap adsorption seemed to slightly better fit with the Freundlich model.

3.6.3. Temkin adsorption isotherm model

Temkin isotherm model was first reported in the adsorption of hydrogen onto platinum electrodes in acidic solutions, this model reflects the adsorbent–adsorbate interactions. Although Temkin equation is usually not appropriate to the liquid-phase adsorption isotherm models to be represented (Foo and Hameed., 2010), the results showed that \( O_{SL} \) adsorption fitted as well with this model. Temkin isotherm equation is given via Eq. 12:

\[
q_e = B_1 \ln K_T + B_1 \ln(C_e)
\]

where \( B_1 \) and \( K_T \) (L/mg) are the Temkin constant and the equilibrium binding constant, respectively (Melo et al., 2018). The linearized forms of Temkin adsorption isotherm model for the adsorption of BZ-3 on \( O_{SL} \), Lap and Mt are shown in Fig. 6 (c).

For BZ-3 adsorption, all adsorbents described a good adsorption with the Temkin model with \( R^2 \) value of 0.932 - 0.958, with a slightly less fit with the data than for Langmuir and Freundlich isotherm models, according to the \( R^2 \) value (Table 1).

In this study, the adsorption isotherm for BZ-3 onto \( O_{SL} \) and Mt were shown to best fit the Langmuir model (\( R^2 \) values 0.982 and 0.996, respectively), the degree of affinity between BZ-3 and both \( O_{SL} \) and Mt seemed to be the same (De Oliveira et al., 2017). The adsorption of BZ-3 onto Lap has shown to best fit the Freundlich model (\( R^2 \) value 0.990) (Table 1).
3.7. Particles Size distribution measurements

Our purpose is to seek to understand the adsorption mechanism of OSL that has not yet been described as adsorbing agent. The adsorption may be related to the chemical nature of the starting silanes and therefore to the final structural organization of the organosilicate (Guégan et al., 2015). An increase in the particle’s size was observed when comparing the adsorbent - BZ-3 complex to the particle size analysis of the adsorbent (Fig. S6 in the Supplementary Information file).

This observation may be correlated with the agglomeration of particles after the adsorption and further investigation related to SEM and XRD (d_{001} -value) as well as the study of the porosity may explain this difference. The analysis of the size distribution showed that OSL - BZ-3, Lap - BZ-3 and Mt - BZ-3 had a unimodal distribution with average size of 1.5 µm, 0.6 µm and 0.2 µm, respectively.

3.8. Specific surface area (SSA) determination

The SSA determination by the Brunauer-Emmett-Teller (BET) method (S_{BET}) method is based on the adsorption-desorption of N\(_2\) molecule on the surface of the dry adsorbent particles (Liu et al., 2014). The results (Table S1 in the Supplementary Information file) was compared to previous described results (Herrera et al., 2005, and Macht et al., 2011). Lap had the highest SSA value (364.7 m\(^2\)/g) when compared to Mt (75.2 m\(^2\)/g) and OSL (6.8 m\(^2\)/g). The penetration of nitrogen can be correlated to the regularity of the gallery structure of the particles (Hegyesi et al., 2017). OSL have organic moieties (PEO chains) and hydrophobic tailored side chains (octyl) which can explain the decrease in the SSA measured for these particles (De Oliveira et al., 2017). This suggested that BZ-3 adsorption capacity can be correlated to the monolayer coverage as well as the contribution of other complexation processes. The presence of organic moiety within the inorganic structure of organoclays helped improving the efficiency of the adsorption of numerous chemicals, especially hydrophobic molecules (Melo et al., 2018). It is noteworthy to mention that other parameters could also affect the SSA value such as the interlayer micropores availability and the microporosity characteristics (Deng et al., 2017).
3.9. Infra-Red spectroscopy measurements

The absorption bands from ATR-FTIR spectrum of BZ-3 as shown in Fig. 7 (a) were assigned as follows: 3434 cm\(^{-1}\) for O-H; 1591 cm\(^{-1}\) for C=O; 1599 cm\(^{-1}\), 1572 cm\(^{-1}\), 1506 cm\(^{-1}\), and 1443 cm\(^{-1}\) for the C=C aromatic of BZ-3; 1259 cm\(^{-1}\) for C-O of the CH\(_3\)-O group; 1204 cm\(^{-1}\) for C-O of the phenol group; and 820 cm\(^{-1}\), 700 cm\(^{-1}\), and 597 cm\(^{-1}\) for C-H (Li et al., 2014).

Insertion of Figure 7

The ATR-FTIR spectrum of OS\(_L\) and OS\(_L\)-BZ-3 complex in Fig. 7 (b), showed typical features characteristics of the organic moieties with four distinct peaks in the high-frequency region at 2955 and 2920 cm\(^{-1}\) assigned to -CH\(_3\) and -CH\(_2\) asymmetric stretching, and at 2872 and 2853 cm\(^{-1}\) assigned to -CH\(_3\) and -CH\(_2\) symmetric stretching, respectively. In addition, the sharp peak observed around 1200 cm\(^{-1}\) for both samples and assigned to Si-C asymmetric scissoring confirmed the covalent binding of alkyl chains in the samples. All these results agree with the assumption of the effective contribution of the alkyl organic moiety in the interlayer space of the materials. The obtained results highlight the low frequency of the (Si-O-Si) stretching band at 982 cm\(^{-1}\) which is usually obtained in silicate tetrahedral (Lorentz et al., 2014). Lap - BZ-3 complex and Lap ATR-FTIR spectrum shown in Fig. 7 (c) presented the characteristic bands at 1010 and 655 cm\(^{-1}\) due to the stretching of Mg-O and Si-O, respectively (González et al., 2017). In the case of Lap - BZ-3 spectra, intense bands attributed to BZ-3 were observed. For both Mt and Lap, the characteristic bands of BZ-3 (1591 cm\(^{-1}\) for C=O and 1259 cm\(^{-1}\) for C-O of the CH\(_3\)-O group) were found after the adsorption but with lower intensity of the OH band which could be related to the difference in the adsorption capacity. Mt and Mt - BZ-3 complex ATR-FTIR spectra as shown in Fig. 7 (d) revealed the characteristic peaks at 1115 and 1035 cm\(^{-1}\) which may be due to Si-O stretching (out-of-plane) and Si-O stretching (on-plane) vibration for layered silicate, respectively (Meng et al., 2009). Bands at 915, 875 and 836 cm\(^{-1}\) are attributed to Al-Al-OH, Al-Fe-OH and Al-Mg-OH bending vibration, respectively (Patel et al., 2007).
2.5. Thermal analysis

The TGA thermograms of OS\textsubscript{L}, BZ-3 and OS\textsubscript{L}-BZ3 prepared at pH 10 and 38 °C are shown in Fig. 8. Two peaks were obtained in differential thermogravimetry (DTG) of OS\textsubscript{L}: the first one occurred before 100 °C and can be due to the evaporation of adsorbed water whereas the second at 470°C corresponded to the decomposition of organic moieties. Maximum mass loss of BZ-3 occurred at about 300 °C, as indicated by DTG curve Fig. 8 (b). This loss can be attributed to the decomposition of BZ-3. Similar, DTG curve of OS\textsubscript{L}-BZ3 complex revealed that besides dehydration and organic decomposition peaks there was a mass loss reached at about 340 °C corresponding to decomposition of BZ-3 in OS\textsubscript{L}, which was higher than that of free BZ-3. The result can be attributed to the protective effect of OS\textsubscript{L} network structure and confirmed that BZ-3 was intercalated within OS\textsubscript{L} interlayer space, which consequently made it more thermally stable than free BZ-3.

4. Conclusion

In this study, batch adsorption experiments were carried out to study the BZ-3 adsorption onto synthesized lipophilic organosilicate (OS\textsubscript{L}), Laponite (Lap) and montmorillonite (Mt). The adsorption characteristics were studied at different pH values, temperature, initial BZ-3 concentration and contact time. Thus, the results obtained can be summarized as follows: the optimal pH is 10 and the temperature is 38 °C to obtain the highest adsorption capacity of adsorbents. The amount of adsorbed BZ-3 increased with increasing BZ-3 initial concentration, the optimum initial BZ-3 concentration is 2.5 g/L. The optimum contacting time for BZ-3 adsorption onto the three adsorbents is 24 h. At optimal conditions of pH, temperature, initial BZ-3 concentration and contacting time, the adsorbed amounts of BZ-3 were 340 mg/g, 137 mg/g and 192.3 mg/g for OS\textsubscript{L}, Lap and Mt, respectively. BZ-3 isotherm adsorption experiments showed that OS\textsubscript{L} and Mt fitted the best with Langmuir isotherm model. BZ-3 adsorption onto Lap fitted the best with the Freundlich isotherm model. OS\textsubscript{L} showed promising adsorption efficiency versus Mt and Lap, which could be due to presence of pendent lipophilic organic moiety on OS\textsubscript{L} structure. However, further investigations would better elucidate the interaction mechanism of BZ-3 and OS\textsubscript{L} as potentially new adsorbents by X ray diffraction patterns.
(XRDP) analysis ($d_{001}$-value) and the study of the OS$_L$ porosity. Preliminary studies have been currently given that showed a macroporosity between 5 and 10 µm which could be assigned to the interparticular porosity, these results are conducted to further examination. These methods would better explain the observed difference in the adsorption capacity of OS$_L$. Thus, studies of the adsorption kinetics and modeling are currently studied followed by desorption experiments to have an overview of the potential reversible release of bioactive molecules within defined limits of LogP.

Conflict of interest
The authors declare that they have no competing interest.

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References


Fig. 1. Effect of the pH on BZ-3 adsorption onto OS₄, Lap and Mt (temperature 20 °C, BZ-3 concentration 2.5 g/L, contact time 24 h). The data are presented as mean ± SEM (Standard Error of the Mean) value (n=6) (**), p<0.05, (***), p<0.01.

Fig. 2. Effect of temperature on the adsorption amount of BZ-3 onto OS₄, Lap and Mt (pH 10, BZ-3 concentration 2.5 g/L, contact time 24 h). The data are presented as mean ± SEM (Standard Error of the Mean) value (n=6) (**), p<0.05, (***), p<0.01.
Fig. 3. Amount of adsorbed BZ-3 onto OS₅, Lap and Mt as function of initial BZ-3 concentration (pH 10, 38 °C and contact time 24 h).

Fig. 4. Effect of contact time on BZ-3 adsorption onto OS₅, Lap and Mt (pH 10, temperature 38 °C, BZ-3 concentration 2.5 g/L and contact time 24 h).
**Fig. 5.** Adsorption isotherm profiles of BZ-3 onto OSL, Lap and Mt (pH 10, temperature 38 °C, BZ-3 concentration 2.5 g/L and contact time 24 h). Where \( q_e \) (mg/g) is the adsorbed amount of adsorbate at equilibrium (mg/g) and \( C_e \) (mg/g) is the concentration of BZ-3 at equilibrium.

**Fig. 6.** Linearized form of (a) Langmuir, (b) Freundlich and (c) Temkin adsorption isotherm model for the adsorption of BZ-3 on OSL, Lap and Mt (pH 10, temperature 38 °C, adsorbents at 20 g/L, contact time 24 h).
**Fig. 7.** ATR-FTIR Spectra of (a) BZ-3, (b) OS₅ and OS₅-BZ-3 complex, (c) Lap and Lap - BZ-3 complex, and (d) Mt and Mt - BZ-3 complex.

**Fig. 8.** TGA thermograms of (a) TGA of OS₅, BZ-3, OS₅-BZ3, (b) DTG of OS₅, BZ-3 and OS₅-BZ3.
Table 1. Langmuir, Freundlich and Temkin isotherm parameters for adsorption of BZ-3 onto OS\textsubscript{L}, Lap and Mt.

<table>
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<th>OS\textsubscript{L}</th>
<th>Lap</th>
<th>Mt</th>
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<td>$q_m$ (mg/g)</td>
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Table 2. Thermodynamic parameters for BZ-3 adsorption onto OS₅, Lap and Mt.

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