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Caffeine Adsorption onto Bentonite Clay in Suspension and Immobilized

Giane Gonçalves Lenzi[1*]
https://orcid.org/0000-0003-2065-9622

Maria Eduarda Kounaris Fuziki[1]
https://orcid.org/0000-0003-3871-6365

Michel Zampieri Fidelis[1]
https://orcid.org/0000-0003-0169-0843

Yuri Barros Fávaro[1]
https://orcid.org/0000-0001-6737-9332

Mauricio Aparecido Ribeiro[1]
https://orcid.org/0000-0001-7314-0723

Eduardo Sidinei Chaves[2]
https://orcid.org/0000-0003-0982-3698

Ervin Kaminski Lenzi[3]
https://orcid.org/0000-0003-3853-1790

[1]Federal University of Technology, Department of Chemical Engineering, Ponta Grossa, Paraná, Brazil, [2]Federal University of Santa Catarina, Department of Chemistry, Florianópolis, Santa Catarina, Brazil; [3]State University of Ponta Grossa, Department of Physics, Ponta Grossa, Paraná, Brazil.

*Correspondence: gianeg@utfpr.edu.br, Tel.: +55 (42) 3220-4800 (G.G.L.)

HIGHLIGHTS

- Adsorption process to remove contaminant of emerging concern – Caffeine.

- Bentonite clay has shown to be an efficient adsorbent in the caffeine removal.

- The adsorption process on immobilized bentonite is slower than in suspension.

Abstract: This study describes the use of bentonite in suspension for the caffeine adsorption (pollutant of emerging concern) by taking different conditions of the pH, adsorbent mass, adsorbent calcination temperature and interferents into account. The results were compared with those obtained using bentonite immobilized in alginate beads. The acid medium has a greater efficiency for the caffeine adsorption and the adsorbent calcination temperature exerts, due to structural changes. Caffeine removal higher than 90% was obtained at optimized conditions. The Langmuir model indicated a better fit of the data and the adsorption capacity of caffeine onto bentonite. The bentonite immobilized led to a slower adsorption process in relation to the suspended.

INTRODUCTION

The growing industrialization and urbanization over all the planet have produced a large amount of chemical and biological substances discarded that end up reaching watercourses [1,2] with direct implications on the water quality, which is one of the most discussed and researched subjects. In this scenario, the so-called emerging contaminants or organic micropollutants such as pharmaceuticals, hygiene and beauty products, pesticides, hormones are known as endocrine disruptors (ED), and even at very low concentrations can case undesirable effects to the exposed organisms [3]. The presence of these compounds in analyses

carried out in sewage treatment plants (STP) and water treatment plants (WTP) indicates that the current methods of treatment are not completely efficient in their removal. Bolong and coauthors showed that many EDs can produce harmful effects to aquatic biota, including changes in sex ratios of fish and changes in invertebrates habits [4,5].

Caffeine is widely find in coffees, teas, nuts, cocoa, analgesics and stimulants; it acts in the organism as a stimulant of the central nervous system and in plants as a pesticide [6,7]. Consequently, due to the high consumption of caffeine and quantities dumped into water bodies, is indicated as a chemical marker to measure pollution in ground and surface water. It presents high solubility in water ($K_s > 10,000$ mg L^{-1}), low accumulation rate (log $K_{ow} < 0.5$) and high removal rates in wastewater treatment plants (approximately 80%). However, when metabolized by the human body, it becomes theophylline, theobromine, and paraxanthine, stable metabolites that are not efficiently removed in conventional plants of water treatment [8]. Thus, efficient alternatives of water treatment are necessary to improve the removal of these contaminants in the aquatic biota [9]. Several mechanisms were developed aiming at the caffeine removal in treatment plants, such as oxidative advanced processes [10], ozonation [11], membrane separation [12,13].

Among the treatment processes, the adsorption is one of the most efficient and economical methods for removal of contaminants with low concentrations. The most widely used adsorbent is activated carbon, due to its high surface area, surface reactivity and porosity. Nevertheless, it presents serious disadvantages such as relatively high price and adsorbent loss in the regeneration with chemicals [14,15]. Searching for highly efficient and economical adsorbents, Jiang and Ashekuzzaman [14] indicated that the treatment of micropollutants with clay minerals can be considered as a good alternative to activated carbon. These clays can be found on a large scale in most continents, they have low cost, high surface area and high porosity. Various types of clays have those characteristics, such as bentonite, kaolinite and vermiculite [16].

The bentonite clay is formed by raw clay minerals of the smectite group, and, in geological terms, is formed by montmorillonite, a material of volcanic origin, which after the devitrification process becomes fine particles, with high surface charge, cation exchange capacity, surface area and porosity [17]. The world bentonite production, in 2014, reached 12.2 million t, with the United States (38.6%) leading the production, followed by Turkey (9.1%), Greece (8.3%), Mexico (5.1%) and Brazil (3.4%) [18]. In this sense, this work proposes the use of bentonite in suspension and immobilized forms for the caffeine adsorption (pollutant of emerging concern) by taking different conditions of the pH, adsorbent mass and adsorbent calcination temperature. Moreover, the influence of interferents (Ba^{2+} and Pb^{2+}) were evaluated.

MATERIAL AND METHODS

Reagents and Instrumentation

The reagents used in experiments were: caffeine ($C_8H_{10}N_4O_2$), supplied by Química Fina LTDA; Bentonite clay, supplied by Perquim; nitric acid (HNO_3), supplied by Merck; sodium alginate, supplied by Sigma–Aldrich; calcium chloride ($CaCl_2.2H_2O$), supplied by BIOTEC; lead nitrate (Pb ($NO_3)_2$), supplied by BIOTEC and (barium nitrate ($Ba(NO_3)_2$), supplied by Perquim. The caffeine removal was monitored at 267.0 nm in a UV-Vis FEMTO Spectrophotometer

Adsorbent

The bentonite was the adsorbent used, with no heat treatment and calcined at 500, 700 and 900°C, for 5 h under static air atmosphere. Besides being used in suspension, tests were performed with bentonite immobilized on calcium alginate beads. Immobilization was performed as described previously for biosorbent [19] and photocatalyst [20]. For bentonite immobilization, 4.0 g of sodium alginate and 8.0 g of bentonite were added to 200 mL of ultrapure water. The mixture was agitated and trickled in 2% (m/v) $CaCl_2$ solution. When in contact with the solution, calcium alginate immobilized bentonite beads were formed, by replacing Na^+ ions with Ca^{2+}. The beads were immersed into the solution overnight and then well washed and stored in ultrapure water for later testing.

Adsorbent Characterization

Thermogravimetric analysis (TGA) of the non-calcined bentonite clay sample was performed using the SHIMADZU-Thermo-Model TGA-50 equipment. Approximately 10 mg was subjected to a heating rate of 10°C min^{-1}, from room temperature to 1273K, while an inert gas (N_2) passed through the samples at a 20 mL

min^{-1} flow rate. The analysis of infrared spectroscopy (FTIR) were performed in an infrared spectrometer equipment (Varian 7000) with Fourier transform.

Estimation of the immobilized bentonite mass in the beads

The estimate mass of the bentonite, immobilized on the alginate beads, was obtained by the mass difference, before and after the calcination. Calcination was conducted on muffle, under static air atmosphere and subjected to a heating pad, from room temperature up to 773 K, for 2 h. The analysis was performed at least in triplicate.

Kinetic study

To assess the caffeine adsorption kinetics on bentonite, experiments were carried out in different conditions of pH, adsorbent calcination temperature and mass. In all experiments, 500 mL of caffeine solution, with a concentration of 20 mg L^{-1} were placed in contact with the adsorbent under agitation for 24h. The temperature was maintained at 298K and the agitation was approximately 200 rpm. Variation of pH occurred between 2 and 6.5 and the adjustment was accomplished by the addition of diluted solution of nitric acid.

For the equilibrium study, the adsorbent mass used in the tests varied between 0.250 g and 0.600 g (temperature at 298K). During the experiments, aliquots of the samples were collected at regular time intervals. The aliquots were centrifuged and then filtered with an inert millipore filter of 22 μm of pore. The concentration of samples was then determined by Spectrometry in the UV region, at wavelength 267. nm. The optimum conditions found (pH, calcination temperature and adsorbent mass) have been selected for experiments with the immobilized bentonite.

Influence of Interferents

Experiments were carried out to assess the effects the competition between ions (Pb^{2+} and Ba^{2+}) have on the kinetics of caffeine adsorption. These tests followed a methodology similar to that described previously, with optimized conditions of pH, calcination temperature and adsorbent mass. For the tests involving heavy metals, three solutions were prepared: Solution 1: caffeine with Pb^{2+} (25 mg L^{-1}); Solution 2: caffeine with Ba^{2+} (25 mg L^{-1}) and Solution 3: caffeine and the two metals (Pb^{2+} and Ba^{2+}), both at concentration of 25 mg L^{-1}. The solutions were prepared from the salts $Pb(NO_3)_2$ and $Ba(NO_3)_2$. In the three solutions, the concentration of caffeine was the same (20 mg L^{-1}).

RESULTS

Characterization

The TGA/DTGA result of bentonite clay is shown in Figure 1. The FTIR spectra of bentonite clay, before and after, the process of caffeine adsorption are showed in Figure 2.
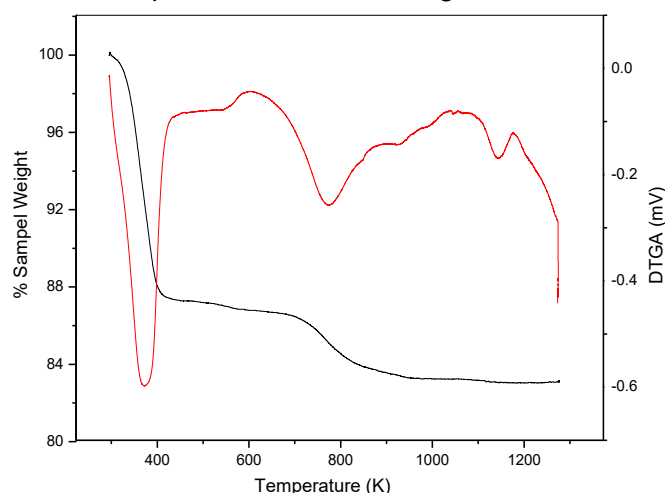

Figure 1. TGA/DTGA data for Bentonite sample (non-calcined).
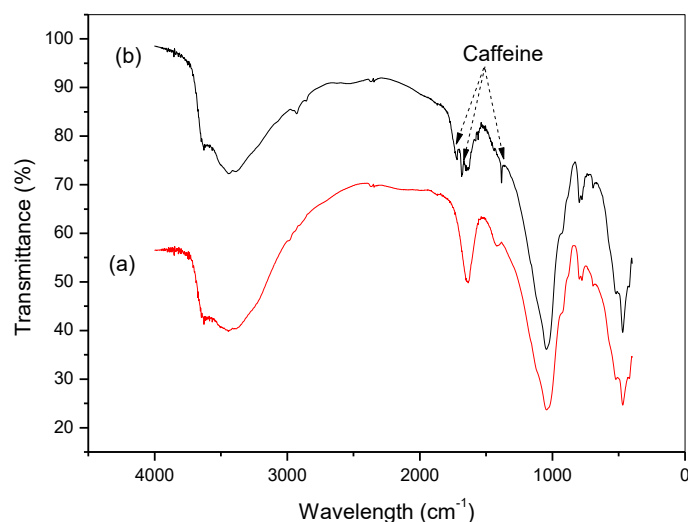
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Figure 2. FTIR spectrum (a) before and (b) after caffeine adsorption (Bentonite powder).

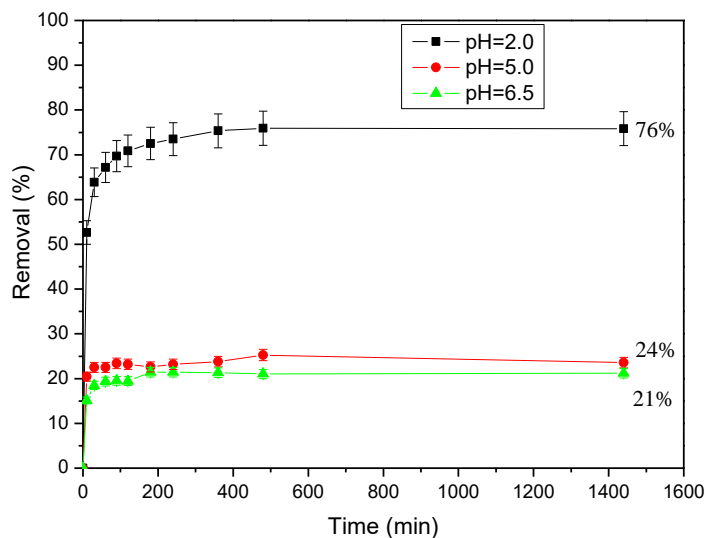The results pH and thermal treatment effect are presented in the Figure 3 and 4, respectively.

Figure 3. Effect of pH on kinetics of caffeine removal. Caffeine concentration 20 mg L^{-1} and 0.5 g L^{-1} of bentonite calcined at 773K. The error bars represent the standard deviation of 3 measurements.
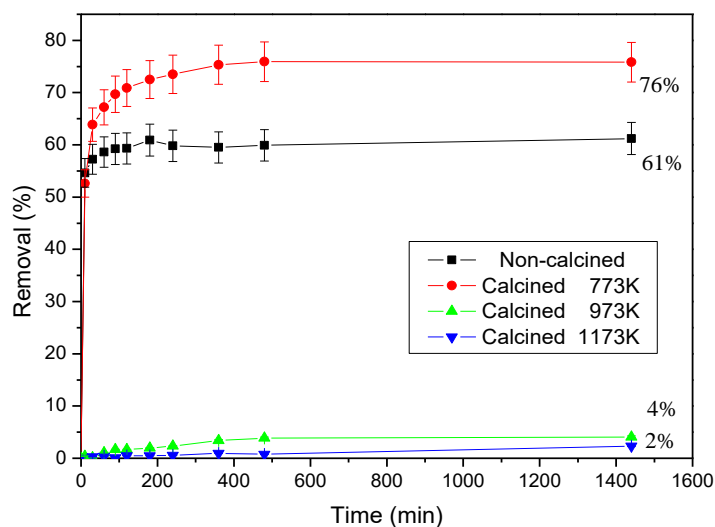

Figure 4. Effect of bentonite calcination temperature. Caffeine concentration 20 mg L^{-1}, pH=2,0 and 0.5 g L^{-1} of bentonite.

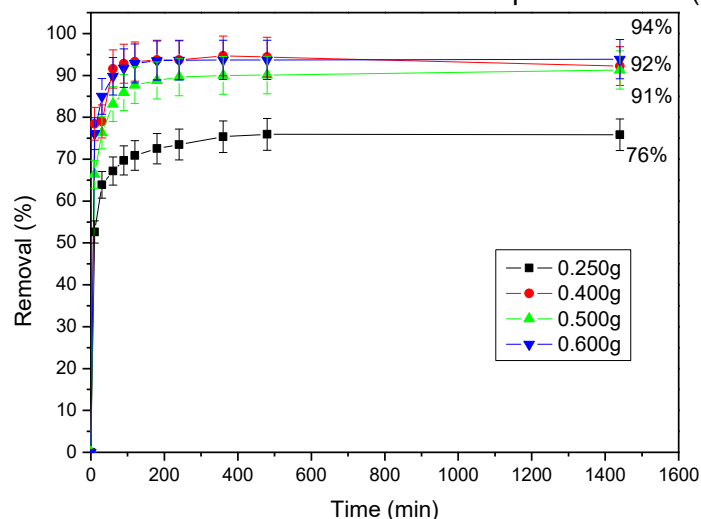The results of adsorbent mass influence on the caffeine adsorption kinetics (Figure 5).

Figure 5. Effect of adsorbent mass variation on caffeine removal (Caffeine concentration 20 mg L^{-1}, T calcination = 500°C, pH = 2,0). The error bars represents the standard deviation of 3 measurements.

The Table 1 present the parameters of the Langmuir and Freundlich isotherm.

Table 1. Parameters of the isotherm models for caffeine adsorption by bentonite powder.

Langmuir Model				Freundlich Model		
K_L(L mg^{-1})	q_{max}(mg g^{-1})	R_L	R^2	K_F(mg g^{-1})	n	R^2
0.7186	41.667	0.0651	0.9671	18.5097	2.8050	0.7928

Tests performed with Ba^{2+} and Pb^{2+} interferent are shown in Figure 6A (Pb and Ba) and Figure 6B (Caffeine).
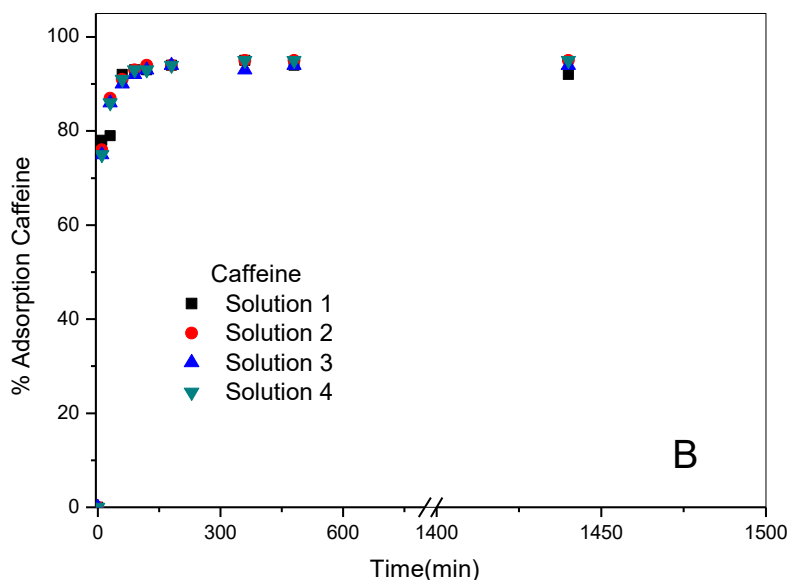
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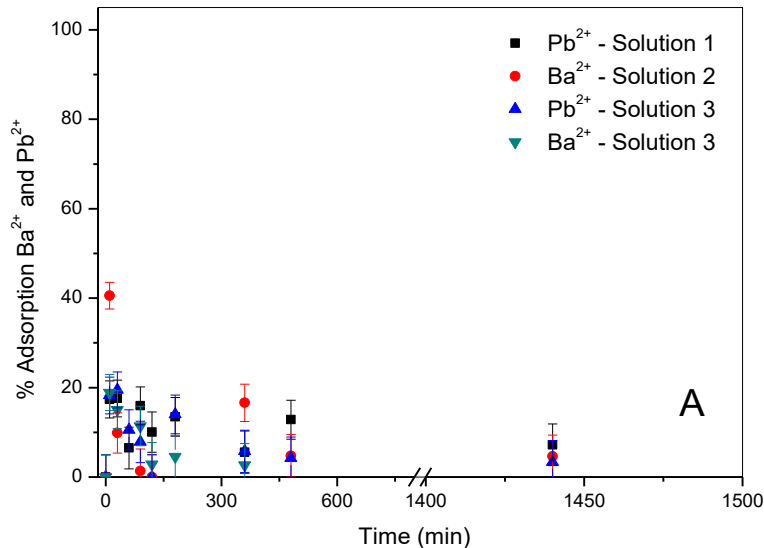
Figure 6. Effect of Interferents on Caffeine adsorption (T calcination = 773K; pH = 2.0 0.8 g L^{-1}, Ba^{2+} and Pb^{2+} 25 mg L^{-1}) A) Interferents Results and B) Caffeine results. (Solution 1: Solution Pb^{2+} (25 mg L^{-1}) + Caffeine; Solution 2: Ba^{2+} (25 mg L^{-1}) + Caffeine; Solution3: Ba^{2+} (25 mg L^{-1}) + Pb^{2+} (25 mg L^{-1}) + Caffeine).

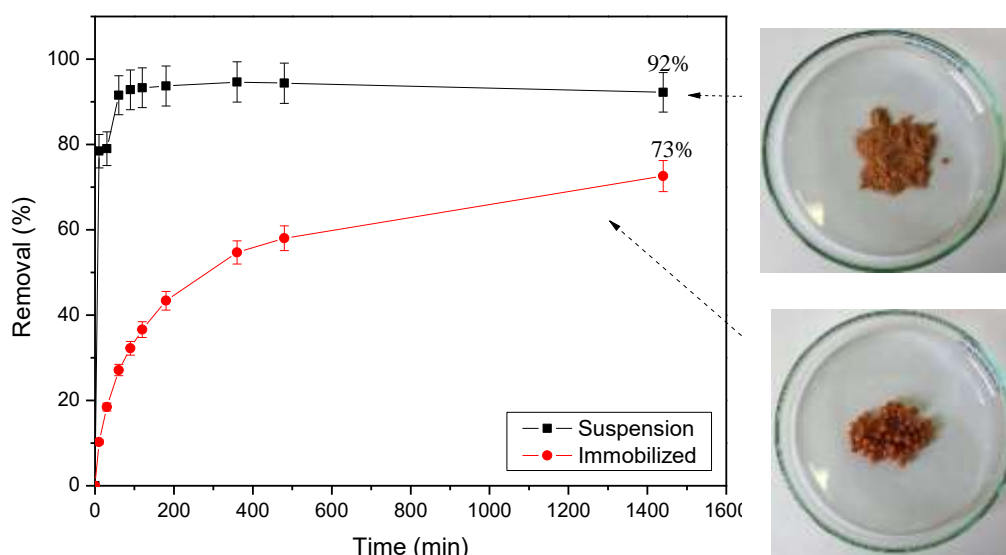The results on immobilization Influence are shows in the Figure 7.

Figure 7. Caffeine adsorption by Bentonite clay in suspension and immobilized. pH = 2.0; Adsorbent: Bentonite calcined at 773K in suspension and immobilized.

DISCUSSION

The TGA/DTGA result of bentonite clay, without prior thermal treatment, presented a profile basically divided into two regions of mass loss, as shown in Figure 1.

These regions are in the following temperature ranges: 298 K to 416 K and 416 to 973K, with maximum temperatures at 347 and 723K, respectively. The mass loss observed in the low temperature region (room temperature up to 416K) are assigned to adsorbed water on the surface of the clay [21].

The FTIR spectra of bentonite clay before and after the process of caffeine adsorption are showed in Figure 2. The spectra indicate the presence of different functional groups, highlighting the complex nature of the adsorbent. The FTIR spectrum before adsorption has a wide band at 3623 and 3463 cm^{-1}, indicating the presence of the isomorphic substitution of octahedral cations Al^{3+} by Fe^{2+} or Mg, and of lengthening of OH group, respectively. The band at 470 cm^{-1}, is attributed to band enlargement of Si-O-Si [22]. The FTIR

spectrum for bentonite after the adsorption process showed a significant difference in the bands, indicating the presence of adsorbed caffeine, more intensely in the region 1700 to 1300 cm^{-1} [23].

pH influence

The results, presented in Figure 3, show the pH influence in the caffeine adsorption on bentonite. This result indicated that adsorption is favored at low pH values. For solution pH equal to 2.0, the removal after 24 hours was much higher than the removal for pH 5.0 and 6.5. Couto Jr and coauthors [24] studied caffeine adsorption on activated carbon; the highest caffeine removal at acidic pH (3.0 and 4.9) and lower removal at basic pH (10.0) were observed. According to the author, the adsorption process studied is strongly influenced by the pH, since this parameter is directly related to the pH$_{PZC}$ of the surface and to the pKa of caffeine. Then, the following experiments were performed at pH=2.0

Thermal treatment Influence

The Thermal treatment (calcination) conducted in bentonite had a strong impact on the adsorption capacity, as shown in Figure 4. The bentonite calcined at 773K presented the best result, in comparison with the other adsorbents used in the tests. However, the adsorbents that were submitted to thermal treatment at temperatures higher than 973K showed a reduced adsorption capacity, possibly due to the modification of the adsorbent structure.

This is described by Yamamoto and coauthors [25] at calcination temperatures greater than 573K. The calcination of montmorillonite, a major component of bentonite, at temperatures above 573K definitively changes the structure of the material, making the dehydration process irreversible and decreasing the distance between the layers of the montmorillonite structure.

Mass adsorbent influence

The adsorbent mass used in the process affects the kinetics of caffeine adsorption (Fig. 5). The results obtained in the equilibrium study indicated that for a bentonite mass (powder) of 0.250 g the adsorption in 24 hours was approximately 76%. However, from a mass of 0.400 g the influence was not so significant (0.400-0.600 g), being the adsorption in 24h around 91 to 94%. However, was observed that in the initial minutes adsorption kinetics was rapid for all bentonite masses studied. In approximately 90 minutes, the adsorption obtained was final practically (24 hours).

Langmuir and Freundlich Models

The Langmuir and Freundlich isotherm models were applied to describe the caffeine adsorption by bentonite (Table 1). The Langmuir isotherm model was applied to analyze the data obtained in the equilibrium study, according to the equation (1),

$$\frac{C_e}{q_e} = \frac{1}{q_{max}}C_e + \frac{1}{K_L q_{max}}, \tag{1}$$

Where, q$_{max}$ is the maximum capacity of adsorption (mg g^{-1}) and K$_L$ is the Langmuir constant (L mg^{-1}) related to adsorption energy. The linear plot of C$_e$/q$_e$ versus C$_e$ is used for q$_{max}$ and K$_L$ calculation.

The obtained maximum adsorption capacity (q$_{max}$) in this study was 41.667 mg·g^{-1} and this value is comparable to adsorption capacity obtained at the literature. For example, the adsorption capacity of caffeine on Grape Stalk was 68.633 mg·g^{-1} [26].

The essential characteristics of the Langmuir isotherm can be expressed by means of a dimensionless constant separation factor (R$_L$), defined as equation 2:

$$R_L = \frac{1}{1 + K_L C_0}, \tag{2}$$

The R$_L$ value indicates whether the isotherm adsorption is favorable (0 < R$_L$ < 1), unfavorable (R$_L$ > 1), linear (R$_L$ = 1) or irreversible (R$_L$ = 0) [27]. The R$_L$ value obtained for the caffeine adsorption by bentonite in suspension was 0.0651, indicating that the adsorption process is favorable.

The Freundlich isotherm model was also applied to the data obtained, according to the equation 3:

$$log q_e = log(K_F) + \frac{1}{n} log C_e, \tag{3}$$

where K_F and n are Freundlich constants that are respectively defined as the adsorption capacity and intensity. The parameters and their respective correlation coefficients (R_2) obtained for the isotherms models applied are shown in Table 1.

Influence of Interferents

In tests conducted with interferent, Ba^{2+} and Pb^{2+}, (Figure 6) indicated a low adsorption of metals (Figure 6-A). The pH condition used in the test may be responsible for the low adsorption of metals, since, according to Ijagbemi and coauthors [28] on adsorption of Cu^{2+} and Ni^{2+} in montmorillonite, low pH values lead to higher concentration of H^+ ions on the adsorbent surface, which compete with the metals ions. Other processes such as photocatalysis, which has adsorption on the solid surface as one of the steps, also indicate that an acidic pH is not favorable for Barium removal [29].

On the other hand, the metals presence did not affect the caffeine removal (Figure 6-B), demonstrating that there was no competition between caffeine and the metals for the bentonite adsorption. Even the presence of the two metals in solution, simultaneously, did not reduce the capacity of caffeine removal by adsorption. We need to consider that the NO_3^- ions present in the medium did not interfere in the adsorption process.

In a study on caffeine adsorption in activated carbons, Couto Jr and coauthors [24] evaluated the effect of water hardness on caffeine removal. The results indicated that the presence of Ca^{2+} and Mg^{2+} ions reduce caffeine removal by adsorption, probably by increasing its solubility caused by the presence of ions in solution.

Immobilization- Influence

Based on the results of bentonite concentration in the bead (0.072g bentonite/g bead), for comparison, approximately the same mass used in suspension was estimated for the tests. The results of adsorption kinetics of bentonite, calcined at 500 °C, in suspension and immobilized in calcium alginate are shown in Figure 7. We can observe that the immobilization of the adsorbent significantly affected the adsorption process, making the caffeine removal rate slower.

Zarzar and coauthors [30] investigated the caffeine adsorption on alginate and chitosan beads in different conditions. In the case of alginate beads, the maximum removal obtained in the tests was less than 6%. The study about the effect of pH showed that the alginate beads had better removal at pH 6, and the adsorption capacity decreased considerably in lower pH values [28].

Nevertheless, the results indicate that the removal observed in the tests with immobilized bentonite is mostly due to the caffeine adsorption in the clay, and not in the alginate. The decrease in the removal speed occurs because the caffeine is not directly in touch with bentonite since the beginning of the process. The diffusion of caffeine inside the bead is possibly a limiting step for the adsorption process, making the removal slower. In addition, alginate beads can release calcium, which affects the adsorption of caffeine.

CONCLUSION

Bentonite clay has shown to be an efficient adsorbent in the caffeine removal, due to its low cost and the possibility of immobilization. Optimization of the parameters indicated that the pH 2.0 is best suited for the process of caffeine adsorption and the adsorbent mass influences significantly on this process. With the thermal treatment (calcination) a change occurred in the structure of adsorbent, affecting the process. The immobilization of bentonite in calcium alginate slowed down the process, and in 1440 min the caffeine adsorption on immobilized bentonite decreased 19% compared to bentonite in suspension. The Langmuir model presented a better fit for the data obtained and the adsorption capacity of caffeine onto bentonite was 41.667 mg g^{-1}.

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