

Banana Peel for Acetylsalicylic Acid Retention

Araceli Veronica F. N. Ribeiro¹, André Romero da Silva², Tiago Pereira da Cunha¹,
Rowenna Tonani L. dos Santos¹, Jairo Pinto de Oliveira³, Evaldo Vitor Pereira³,
Marcus Vinicius V. J. Licinio³, Madson de Godoi Pereira⁴, Arnaud Victor dos Santos⁴,
Joselito Nardy Ribeiro^{3*}

¹Instituto Federal do Espírito Santo, Campus de Vila Velha, Brazil

²Instituto Federal do Espírito Santo, Campus de Aracruz, Brazil

³Centro de Ciências da Saúde, Universidade Federal do Espírito Santo, Vitória, Brazil

⁴Departamento de Ciências Exatas e da Terra, Universidade do Estado da Bahia, Salvador, Brazil

Email: *rinajokrauser@gmail.com

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Abstract

A method for adsorption involving banana peel (BP) was studied to remove the pollutant acetylsalicylic acid (ASA) in aqueous medium. The results show that bioadsorbent has satisfactory maximum adsorption capacity (2.29 mg/g) for removing this analgesic and anti-inflammatory drug in aqueous solution (pH 7.0) using the Langmuir mathematical model. The tested concentrations of this pollutant were higher than the levels commonly found in the aquatic environment. This and other results suggest the BP as an alternative to ASA removal in water contaminated with pharmaceuticals pollutants.

Keywords

Adsorption, Banana Peel, Acetylsalicylic Acid

1. Introduction

These pharmaceuticals pollutants are consistently detected in different aquatic environmental samples [1] [2]. The concentrations are usually detected in the order of $\mu\text{g}\cdot\text{L}^{-1}$ and $\text{ng}\cdot\text{L}^{-1}$ [3]. The main sources of contamination are the hospitals [4] and domestic sewage effluents [1]. These drugs and their metabolites may contaminate groundwater, rivers, lakes, and wastewater treatment plants [5] [6]. Montagner and Jardim [7] detected the presence of drugs pollutants in the Atibaia River, Sao Paulo State, Brazil. Among the pharmaceuticals investigated were detected acetylsalicylic acid, acetaminophen, diclofenac and others. The presence of these residues in the environment induces undesirable biological responses in various types of organisms and may

be dangerous to human health [8]. Therefore, the development of efficient and economical techniques to remove these pollutants pharmaceuticals in the aqueous medium is very important [9]. Among the techniques studied, the adsorption, using natural adsorbents, is one of the most important. The chemical and physical adsorption by natural adsorbents stands out as an efficient and economical alternative for removing pharmaceuticals and other pollutants present in aqueous medium [9] [10] [11] [12]. Among these adsorbents include sugar cane bagasse for removal of textile dyes [10], paracetamol [11] and tetracycline [13], green coconut mesocarp for removal of tetracycline and paracetamol [9], vermicompost for removal of metallic ions, synthetic dyes [14] and paracetamol [15], vegetable sponge for removal of paracetamol [11], goethite for the removal of tetracycline [8] and finally banana peel for removal of phenol [16] and metals [17]. In this work we evaluated the banana peel (BP) for the removal of acetylsalicylic acid (ASA) in aqueous medium. Furthermore, this study aimed to provide a new alternative for the reuse of banana peel, which is abundant in the Brazil.

2. Material and Methods

2.1. Materials

The bioadsorbent banana peel (BP) was obtained from the banana silver fruit in fairs fruit of Vitoria city, Espírito Santo State, Brazil. The banana silver is the most commonly eaten variety in Brazil. The reactants of analytical degree and deionised water ($18.2 \text{ M}\Omega\text{-cm}^{-1}$) were used to prepare all of the solutions. Acetylsalicylic acid (ASA) was obtained from Sigma-Aldrich Company (St Louis, MO, USA), hydrochloric acid was purchased from Vetec (Duque de Caxias-RJ, Brazil) and sodium hydroxide from Dinâmica (Diadema-SP, Brazil). The following equipment was used: an analytical balance (Shimadzu AY 220 model), UV/Vis spectrophotometer (Biospectro SP-220 model), infrared (Perkin-Elmer Spectrum-100 model), pH meter (PHTEK), magnetic stirrer (Nova Ética and Biomixer), laboratory oven (Quimis Q-317 B model), industrial blender (FAET), ultrasonic device (Ultracleaner 1400), scanning electron microscope (SHIMADZU, SSX 550 model), sputter coater (SHIMADZU, IC-50 Ion Coarter model), specific particle size sieves (Granutest), peristaltic pump (Instrutherm, BP 1000), Microtrac (Model Zetratac NPA152).

2.2. Methods

2.2.1. Adsorbent Preparation and Physical Chemistry Analysis

The adsorbent preparations and physical chemistry analysis of scanning electron microscopy and spectroscopy infrared were performed as previously described by our laboratory in [13]. The BP was washed with hydrochloric acid 0.2 M, water (pH 7.0) and then dried in a laboratory oven (60°C) for 15 hrs. In the next step, the BP was triturated in an industrial blender with posterior sieving to obtain particle sizes between 1.19 mm and 4.76 mm. In the scanning electron microscopy the BP particles samples were covered with a thin layer of gold using the sputter coater, and then analyzed using the scanning electron microscope. An electron beam of 10 kV was used, which allowed

for obtaining micrographs of the physical structure of the BP particles surface. Finally in the spectroscopy infrared analysis the organic functional groups were characterized by Fourier transform IR spectroscopy using KBr discs to prepare the BP samples. The spectral range varied from 4000 to 500 cm^{-1} .

2.2.2. Zeta Potential

The zeta potential of the particulate material was measured using a particle size analyzer from Microtrac Model Zetatrac NPA152. Typically, aqueous suspension (2 ml) of mashed BP, pretreated at different pH, were added to a Teflon cuvette containing a pair of palladium electrodes for measuring the zeta potential which is determined via electrophoretic mobility of the particles at room temperature (25 °C on average).

2.2.3. Evaluation of pH

The solutions containing 250 ml of 100 $\text{mg}\cdot\text{l}^{-1}$ ASA and 3.0 g of triturated BP were magnetically stirred (800 rpm at 10 minutes) at different pH values (from 3.0 to 10.0). After vacuum filtration, the supernatants were analyzed in an UV/Vis spectrophotometer at maximum absorbance of ASA (275 nm).

2.2.4. Evaluation of Stir Time

At this stage we evaluated the influence of contact time between ASA and BP in the adsorptive process. Therefore, solutions containing 250 ml of 100 $\text{mg}\cdot\text{l}^{-1}$ ASA (pH 7.0) were magnetically stirred (800 rpm) at different times (from 0 to 25 minutes) in contact with 3.0 g of triturated BP. After vacuum filtration, the supernatants were analyzed in an UV/Vis spectrophotometer at maximum absorbance of ASA (275 nm).

2.2.5. Evaluation of Mass

The solutions containing 250 ml of 100 $\text{mg}\cdot\text{l}^{-1}$ ASA (pH 7.0) were magnetically stirred (800 rpm at 15 minutes) at different mass values of triturated BP (from 0.5 to 5.0 g). After vacuum filtration, the supernatants were analyzed in an UV/Vis spectrophotometer at maximum absorbance of ASA (275 nm).

2.2.6. Obtaining the Maximum Adsorption Capacity

At this stage we evaluated the maximum adsorption capacity (MAC) of BP for ASA at 25 °C \pm 1 °C. Adsorption isotherms were built for estimating the MAC value. This value represents the amount of ASA which can be adsorbed by 1 g of triturated BP. For this purpose, 100 ml of ASA solutions at different concentrations (from 10 to 60 $\text{mg}\cdot\text{l}^{-1}$) were stirred in the conditions previously established: pH 7.0, 3.0 g of triturated BP and 15 minutes for stir time. The data obtained in this step were important for obtaining the adsorption isotherm using the mathematical model described by Equation (1) [18]:

$$q = a \times b \times Ceq \times (1 + a \times Ceq)^{-1} \quad (1)$$

where q represents the quantity of ASA (mg) adsorbed in triturated BP (g) ($\text{mg}\cdot\text{g}^{-1}$), a represents the constant related to adsorption energy ($\text{l}\cdot\text{mg}^{-1}$), b is the maximum ASA adsorption capacity of the BP ($\text{mg}\cdot\text{g}^{-1}$), and Ceq is the equilibrium ASA concentration ($\text{mg}\cdot\text{l}^{-1}$). The linearizing of this equation permits the obtaining of Equation (2):

$$C_{eq}/q = (a \times b)^{-1} + (b)^{-1} \times C_{eq} \quad (2)$$

which permits calculation of MAC value.

3. Results and Discussion

3.1. Scanning Electron Microscopy and Spectroscopy Infrared Analysis

The scanning electron microscopy revealed that the BP adsorbent an irregular morphology characterized by the presence of concavities of different sizes (**Figure 1**).

Furthermore, the data obtained through the spectroscopy infrared analysis (**Figure 2**)

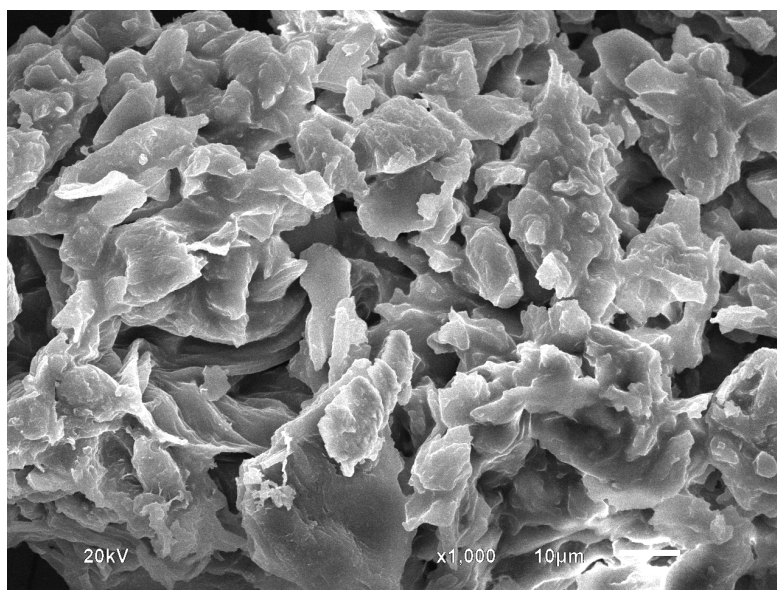


Figure 1. Scanning electron microscopy of banana peel with magnifications of 1000x.

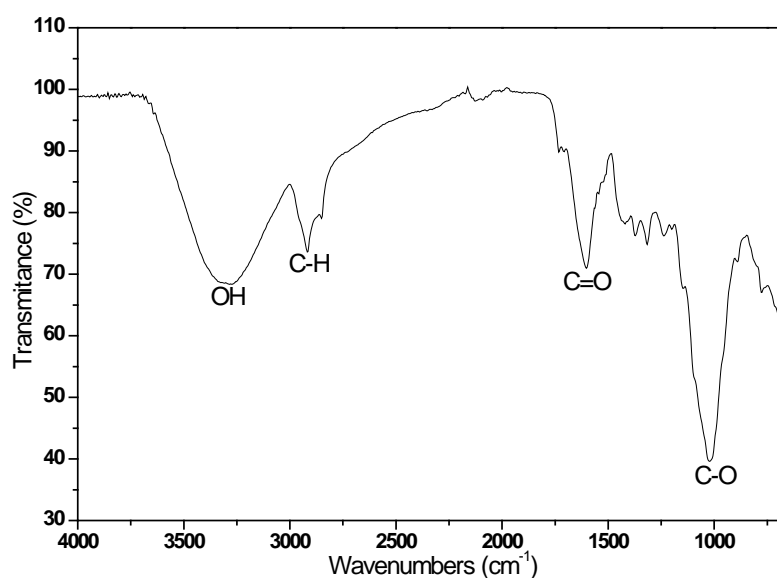


Figure 2. Spectroscopy infrared analysis of banana peel.

of BP revealed the presence of important chemical groups, for interaction with ASA structure (Figure 3). The following groups were found on BP: O-H group ($3500 - 3400 \text{ cm}^{-1}$) probably from the alcohols, C-H sp^3 carbon in approximately 2920 cm^{-1} , C=O in approximately at 1666 cm^{-1} and, finally the presence of the band at 1000 cm^{-1} may indicate the presence of the carbon group C-O [19]. The presence of these chemical groups is mainly due to the occurrence of biomolecules such as cellulose, hemicellulose and lignin [9].

Finally, the superficial morphology and presence these chemical groups in BP suggests that this natural adsorbent has important characteristics for interaction with ASA.

3.2. Zeta Potential

The zeta potential analysis of triturated BP, present in aqueous suspension (2 ml) at different pH, revealed that surface charge of this natural adsorbent becomes more negative in increase of pH (Figure 4). Probably this increase of negative charge occurred because of deprotonation of O-H, -COOH, and other chemical groups from various biomolecules of BP constituents. Duran and Flores [20] observed this same behavior when performing the zeta potential analysis of vermicompost natural adsorbent.

3.3. Evaluation of pH

The adsorption tests at different pH of ASA solutions showed that adsorption percentage

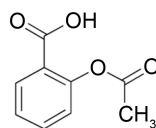


Figure 3. Acetylsalicylic Acid structure.

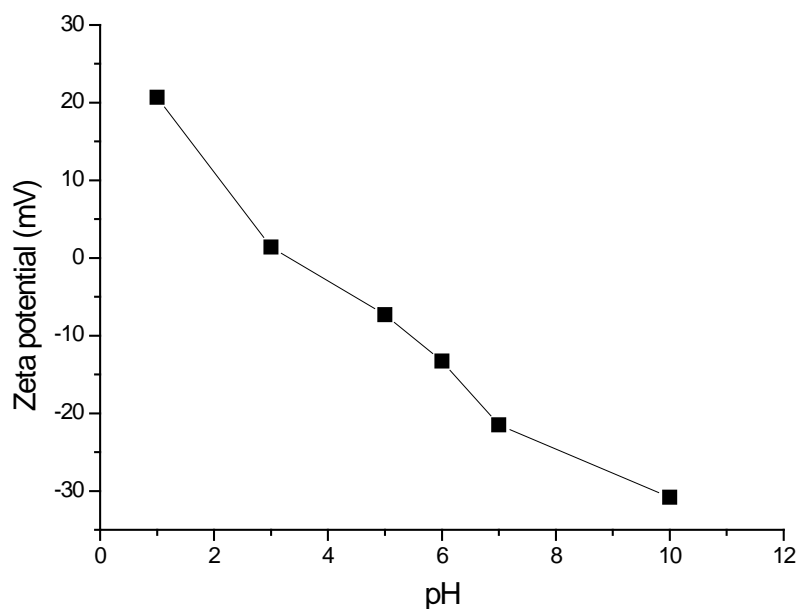


Figure 4. Zeta potential analysis of triturated BP at different pH.

of ASA decreases by increasing the pH of the aqueous solution (**Figure 5**). Possibly, this result is due to the increase of negative charges of the adsorbate (pK_a 3.50) (**Figure 6**) and adsorbent at higher pH, causing repulsion between ASA and BP. This result is in agreement with **Figure 5** that showed an increase in the negative surface charge BP at higher pH than 3.0. Duran and Flores [20] observed that vermicompost adsorbent acquires a negative charge at high pH which makes an efficient adsorbent for the removal of the positive lead (Pb^{2+}) adsorbate in an aqueous medium. Despite the pH 3.0 is considered to be more efficient in removing the ASA from aqueous medium, it was decided to use the pH 7.0 due to its use in water treatment plants in Brazil.

3.4. Evaluation of Stir Time

Figure 7 showed that the satisfactory percentage adsorption of the drug occurred at 15 minutes of stirring and after this time observed a decrease in the drug adsorption. Probably, this decrease is related to the desorption of ASA from the BP, due to the system's constant stirring and weak interactions between the drug and the banana peel [10].

3.5. Evaluation of Mass

Figure 8 shows the influence of the BP adsorbent mass on percentage of ASA adsorption. The better retention of the drug occurred with use of 1.5 g of adsorbent. The

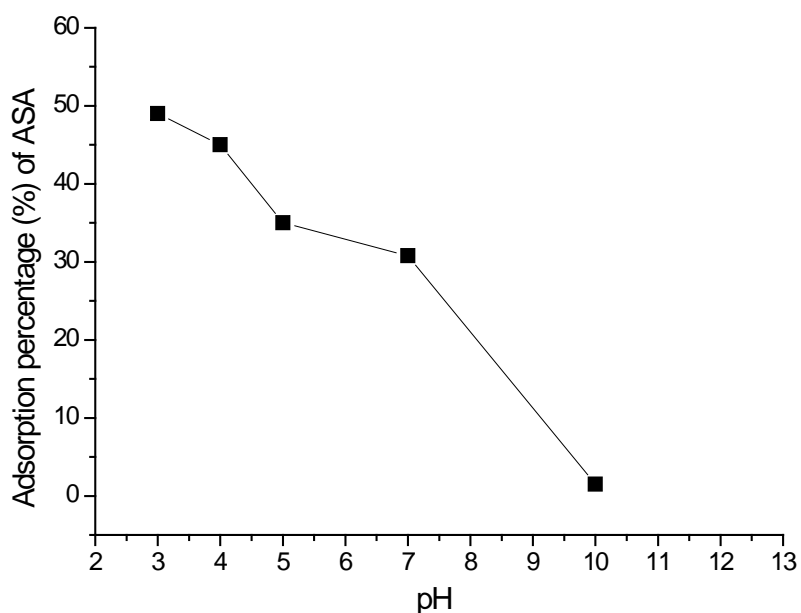


Figure 5. Influence of pH in the percentage adsorption of ASA by BP.

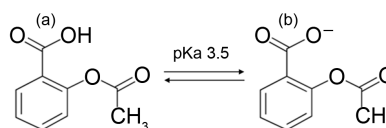


Figure 6. Protonated (a) and unprotonated (b) ASA structure.

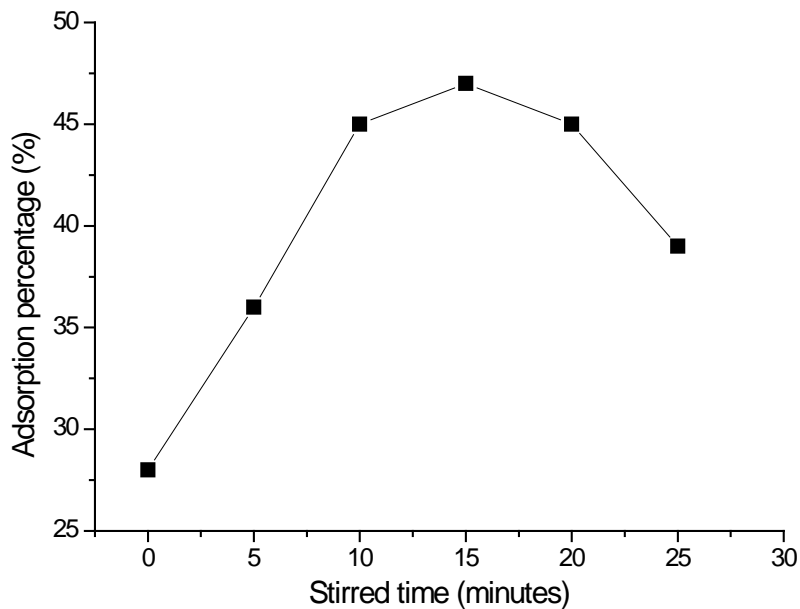


Figure 7. Influence of the stir time in the percentage of ASA adsorption by BP.

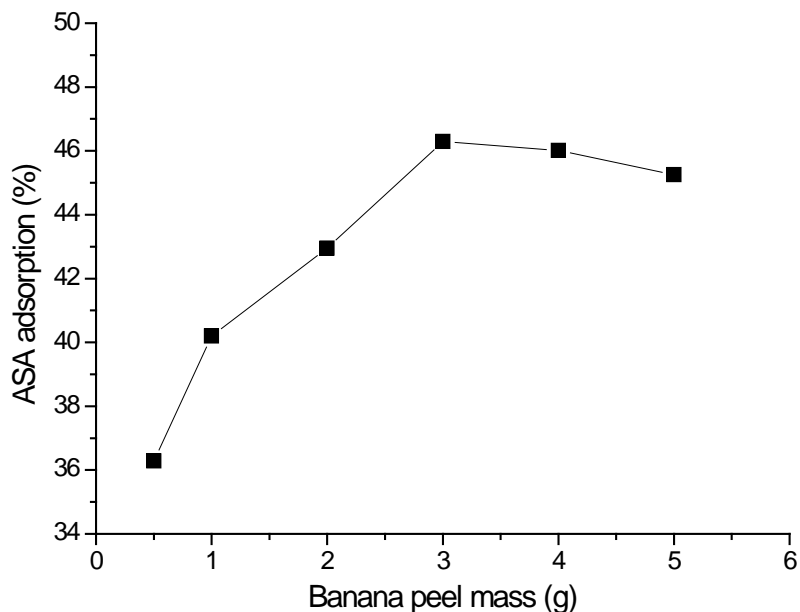


Figure 8. Influence of the banana peel mass in the percentage of ASA adsorption.

quantity of adsorbent to be used is very important; not only to have a good retention of the pollutant, but also to project the area required to stock the adsorbent resulting from the treatment [10].

3.6. Maximum Adsorption Capacity (MAC)

To determine the MAC of BP adsorbent to ASA, adsorption isotherm (Figure 9) was obtained from different ASA concentrations. Then the isotherm was linearized (Figure 10) according to the Langmuir Mathematical Model [18]. The MAC value 2.29 mg/g

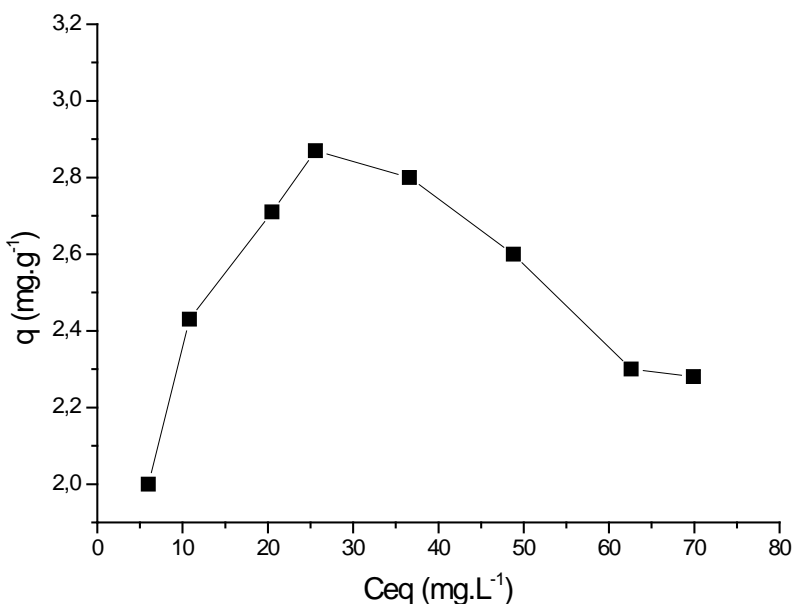


Figure 9. Isotherm adsorption.

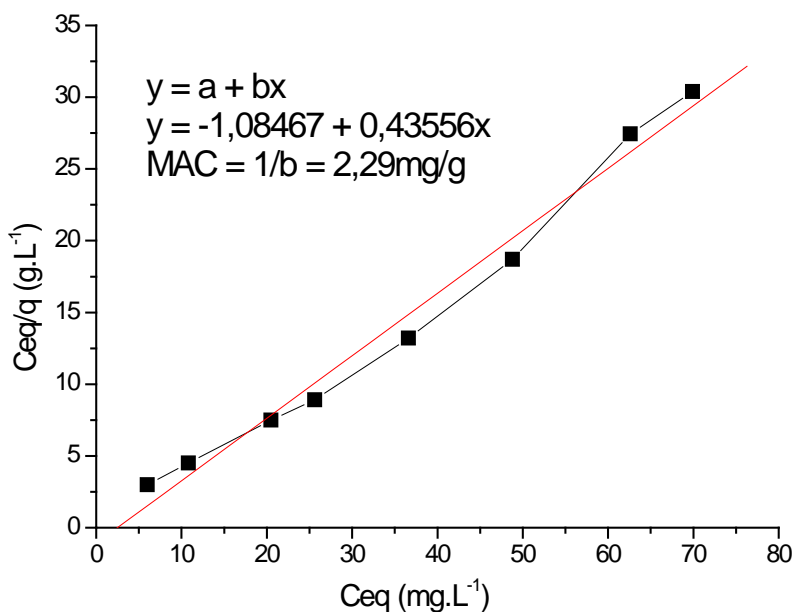


Figure 10. Isotherm linearized adsorption.

obtained for ASA adsorption by BP can be considered satisfactory, because drugs are commonly found in aquatic environmental at $\mu\text{g/L}$ or ng/L [3] [4]. In previous studies [9] and [13] also found satisfactory MAC values for paracetamol and tetracycline utilizing the natural adsorbents green coconut mesocarp and sugar cane bagasse respectively. Ribeiro *et al.* [11] found interesting results for the removal of paracetamol using sugar cane bagasse and vegetable sponge as natural adsorbents. Finally was verified that several authors studied diverse types of natural adsorbents for retention of several chemical pollutants from water in stirring system and columns. These studies obtained

satisfactory MAC values [21].

4. Conclusion

The results suggest that BP has characteristics that qualify it as a possible natural adsorbent for water treatment containing ASA pollutant. This material showed satisfactory maximum adsorption capacity. Finally, the results encourage more detailed studies, including the retention of other pollutants and economic viability.

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