Evaluation of the rubber seed shell (hevea brasiliensis) as an adsorbent: kinetic study

Avaliação da casca da semente de borracha (hevea brasiliensis) como adsorvente: estudo cinético

ABSTRACT

This study consisted in a technical evaluation of the adsorption process as a treatment for effluents contaminated by dyes. Due to that, a methyl orange solution was used in order to simulate a textile effluent, and the rubber seed shell was used as an adsorbent. It was evaluated an untreated seed shell (CS), the calcinated seed shell (CCS) and the calcinated shell that was also submitted to a chemical treatment using a solution of HNO3 15% (CCS-T). The experiments were performed in a batch mode to evaluate the individual efficiency of each treatment. The adsorbent’s mass and the initial concentration of the solutions used were remained constant at 0.15 g and 100 mg/L, respectively. The absorbance analysis was done for all the samples obtained during 6 h of operational time. The results indicated that the CCS-T provided the best efficiency in the removal of methyl orange dye, reducing its concentration to 55.98 mg/L, whereas the use of the CCS achieved a value of only 75.53 mg/L. It was not observed adsorption using CS. The maximum adsorption capacity of methyl orange was 7.59...
mg/g, through the CCS-T adsorbent. Two kinetic models were used to model the experimental data obtained with the CCS-T adsorbent, with the pseudo-first order model providing the best correlation with the experimental data.

**Keywords**: Adsorption; Kinetic study; Effluents.

**RESUMO**

Este estudo consistiu em uma avaliação técnica do processo de adsorção como tratamento de efluentes contaminados por corantes. Por isso, foi utilizada uma solução de laranja de metila para simular um efluente têxtil, e a casca de semente de borracha foi utilizada como adsorvente. Foram avaliadas uma casca de semente não tratada (CS), a casca de semente calcinada (CCS) e a casca calcinada que também foi submetida a um tratamento químico utilizando uma solução de HNO3 a 15% (CCS-T). As experiências foram realizadas em lote para avaliar a eficiência individual de cada tratamento. A massa do adsorvente e a concentração inicial das soluções utilizadas permaneceram constantes em 0,15 g e 100 mg/L, respectivamente. A análise de absorvância foi realizada para todas as amostras obtidas durante 6 h de tempo operacional. Os resultados indicaram que o CCS-T proporcionou a melhor eficiência na remoção do corante laranja de metila, reduzindo sua concentração para 55,98 mg/L, enquanto o uso do CCS alcançou um valor de apenas 75,53 mg/L. Não foi observada adsorção usando CS. A capacidade máxima de adsorção da laranja de metila foi de 7,59 mg/g, através do adsorvente CCS-T. Dois modelos cinéticos foram utilizados para modelar os dados experimentais obtidos com o adsorvente CCS-T, com o modelo de pseudo-primeira ordem fornecendo a melhor correlação com os dados experimentais.

**Palavras-chave**: Adsorção; Estudo cinético; Efluentes.

**1. INTRODUCTION**

Dyes are commonly used in textile, leader and paper industries, and are seen as one of the main responsible for water contamination through their untreated effluents, as well as being damaging to human health, causing headaches, allergies and skin rashes (ZHAI et al., 2014). Their impact in the environment is equally serious, blocking part of the sun light, preventing photosynthesis, which reduces the concentration of available oxygen, causing the death of hydric bodies’ habitants (YAGUB et al., 2014). Furthermore, the waste of water is another predominant factor in such industries, consuming approximately 150 m3 of water per ton of textile processing, being considered the most polluting industry of clean water after agriculture (HUSSAIN & WAHAB, 2018). As they are organic molecules resistant to aerobic digestion, and are stable to light, heat and oxidizing agents, the treatment of the effluents is complex and difficult (RANGABHASHIYAM, ANU & SELVARAJU, 2013).

There have been studied many technologies for this kind of treatment, as coagulation and flocculation, reverse osmosis, chemical oxidation, biological treatments, photo degradation and adsorption (KUMAR et al., 2010). According to Sumanilog et al. (2017), the adsorption process is the most simple, having low cost and producing high quality effluents, with a high efficiency (RANGABHASHIYAM et al., 2013). In this point of view, many
agricultural wastes and different biomasses have been applied as adsorbents, evaluating the performance of the adsorption process as coffee powder (RATTANAPAN et al., 2017), eggshells (ALJEBOREE et al., 2017), and limestone peel (SARTAPE et al., 2017).

In this work, the rubber tree seed shell was chosen to be used as an adsorbent. This motivation relies on the fact that the rubber tree has a fundamental economic role, being responsible for the latex production that is the main raw material for the fabrication of natural rubber. The seed shells were considered wastes, although they can be utilized for the production of biodiesel and manure, avoiding the discard and future environmental problems (BORHAN et al., 2016). Because of that, the adsorbent’s efficiency was evaluated comparing the process using the seed shell in three different ways: untreated, calcinated and calcinated with acid treatment.

2. MATERIALS AND METHODS

2.1 MATERIALS

The rubber tree seeds were collected in the state of Maranhão in February of 2018 and forwarded to the Universidade Federal Rural do Rio de Janeiro. The material was then shattered with a hammer in order to separate the shells from the seeds. The methyl orange P.A. and the nitric acid 65% were acquired from Vetec Química Fina (RJ, Brazil).

2.2 SOLUTION PREPARATION

The preparation started with the weighing of 0.1 g of methyl orange using analytical scales. The material was then transferred, and diluted in a volumetric flask of 1 L, being agitated for complete homogenization.

2.3 ADSORBENT PREPARATION

The shells were initially washed to remove impurities, and dried in a stove (DeLeo A35E) at 80 °C for 12 h. The material was milled in a knife mill and then sifted in order to obtain the desired granulometry (-24+80 mesh). The dried material was called CS. The CCS was prepared promoting a calcination in a muffle stove at 400 °C for 90 min, which was then washed with distilled water, filtered, and placed in a stove at 105 °C for 12 h. Then, a part of the calcinated material was treated with nitric acid, adding a solution of HNO3 15% in a 1:1 proportion. The material stayed in a stove muffle at 500 °C for 20 min for activation, washed with distilled water from 5 to 7 times to remove impurities, and dried in stove at 105 °C for 12 h, obtaining the CCS-T.
2.4 ANALYSIS OF THE SAMPLES

The methyl orange solution’s concentration was determined through a calibration curve made in a spectrophotometer (Bel UV-M51 UV-VISÍVEL), using the wavelength of 465 nm. The curve was obtained through the linear adjustment of concentration versus absorbance data. The absorbance readings in the spectrophotometer were made using solutions of known concentrations (0-35 mg/L).

2.5 EXPERIMENTAL PROCEDURE

The experimental trials were performed in a batch mode. In an erleymeyer it was added 0.15 g of adsorbent and 25 mL of solution with initial concentration of 100 mg/L. The erleymeyers were distributed in an agitating table (LM-7550), and the experiment was performed at 180 rpm at controlled temperature (25 ºC) for 360 min. The samples were analyzed at each interval of 60 min. Each sample was filtered using quantitative-white band filter paper to remove the adsorbent from the solution, thus stopping the adsorption process. The solution’s concentration was determined through the calibration curve. The experiment was performed in triplicate, for each of the three adsorbents studied: the untreated seed shell (CS), the calcinated (CCS) and the chemically treated (CCS-T).

2.6 CALCULATION OD ADSORBED AMOUNT

The calculation of the adsorbed amount (qe, mg/g) indicates the quantity of adsorbent that was adsorbed in function of the mass of adsorbent. It was calculated through Equation 1 (LI et al., 2018):

\[ q_e = \frac{V(C_0 - C_e)}{m} \]  

\[ (1) \]

with C0 and Ce as the initial and equilibrium concentrations (mg/L), respectively, V as the volume of the solution (L) and m as the adsorbent mass (g).

2.7 KINETIC MODELING

The kinetic adsorption models of pseudo-first and pseudo-second order were used to adjust the experimental data, and evaluate the mecanism of the adsorption process. The pseudo-first order model, Equation 2, in its linearized form, is based on the principle that the adsorption removal velocity in function of time is directly proportional to the difference
between the saturation concentration and the number of active sites in the solid (LAGERGREN, 1898). On the other hand, the pseudo-second order model, Equation 3, in its linearized form, indicates that the process is controlled by chemical adsorption and is based on the solid adsorption capacity (MCKAY and HO, 1999).

\[
\ln(q_e - q_t) = \ln (q_e) - k_1 t
\]  
(2)

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}
\]  
(3)

with \(q_e\) and \(q_t\) as the quantities of adsorbed adsorbates in equilibrium and through time, \(k_1\) as the pseudo-first order adsorption rate’s constant (min\(^{-1}\)) and \(k_2\) as the pseudo-second order adsorption rate’s constant (g/mg.min). The \(q_{e,cal}\), \(k_1\) and \(k_2\) can be obtained through the linear adjustment of the experimental data.

3. RESULTS AND DISCUSSION
3.1 EVALUATION OF THE INFLUENCE OF THE CONTACT TIME IN THE ADSORPTION PROCESS

The concentration variation of the methyl orange in solution in relation of the contact time can be seen in Figure 1, where it is possible to observe that the increase of the contact time did not favor the adsorption process, using CS. During the first 60 min, the adsorption process occurred in the same manner for both the CCS and CCS-T adsorbents. From that point forward, the removal, using CCS-T, proved to be more efficient, reaching a concentration of 55.98 mg/L, whereas the minimal concentration achieved by CCS was of 75.53 mg/L.

Figure 1 – Concentration variation in function of the operational time. 
The kinetic modeling was performed using the adsorption experimental data using the CCS-T as adsorbent, since it was the one that proved to be the most efficient for the treatment of the solutions.

3.2 KINETIC MODELING

The values obtained for the kinetic constants, calculated adsorbed amounts and correlation coefficients are shown in Table 1.

Table 1 – Kinetic constants of the adsorption process using CCS-T as adsorbent of the methyl orange.

| Initial Concentration | Pseudo-first order | Pseudo-second order |
|-----------------------|--------------------|--------------------|
| 100 mg/L              | k₁=0.0113 min⁻¹  | k₂=7.15.10⁻⁵ g/mg.min |
|                       | qₑ,cal=7.60 mg/g  | qₑ,cal=10.70 mg/g |
|                       | R²=0.9794         | R²=0.9520         |

The model that best adjusted the experimental data was the pseudo-first order model, as can be seen due to the proximity between the qₑ,cal value and the experimental one of 7.59 mg/g. It is possible to conclude through the kinetic study that the determinant step of the adsorption process is the particle diffusion, which was also shown in the study conducted by Gupta et al. (2011).

4. CONCLUSIONS

It was proved that the rubber seed shells could be reutilized as adsorbents of dyes present in effluents. According to the experimental results obtained, the difference in efficiency between the adsorbents used for the removal of the methyl orange solution could be observed, with the chemically treated rubber seed shell reaching the lowest values of concentration with time, and thus obtaining the highest adsorption rate among all the adsorbents tested. The kinetic model that best correlated the experimental data was the pseudo-first order model.

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