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Removal of Methylene Blue Using Cassava Bark Residue

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Dyes are used in several industrial sectors; the methylene blue, specifically, is often used in manufacture of paper and other materials such as nylons and polyesters. Given this, many researches related to the treatment of these effluents frequently appear. A process widely used in the treatment of industrial wastewater involving dyes is the adsorption. It presents high efficiency and does not require high initial investments. In order to reduce the costs of the adsorption process, biomasses can be used as adsorbent materials. Cassava is a crop of easy adaptation, being cultivated in all states of Brazil. In this research the ability of cassava bark residue (CBR) to remove methylene blue from aqueous solution was evaluated. Its physical characteristics were studied by scanning electron microscope (SEM) and potential zeta analysis. Methylene blue biosorption studies were performed in batch experiments, isothermally at 25 ºC. The contact time was determined by the study of kinetics of the process. It was also performed an acid and alkaline treatment to improve methylene blue removal in aqueous solution. Biosorption of methylene blue using CBR with alkaline modification presented 97.99% removal after 24 h. The use of the CBR was confirmed as a good biosorbent for methylene blue removal, and could be considered as a new alternative for the treatment of wastewater, presenting an application for the destination of residue of manioc bark.

1. Introduction

In Brazil, agroindustries produce several basic products and, consequently, solid wastes. The cassava industry is no exception. Solid wastes are generated in the processing of cassava roots. Most of the residues are used for animal feed and production of biofertilizers. Cassava peel compose approximately 3 to 5% of the total mass of roots and about 1 million tons of cassava peels is annually produced in Brazil and 11 million tons worldwide (Schwantes et al., 2015). Cassava is a crop of easy adaptation, being cultivated globally, with great production and an enormous increasing potential. More than 100 countries produce cassava, with Brazil accounting for 10% of world production, being the second largest producer in the World (EMBRAPA, 2006).
Another issue that also refers to human activities and that cause, directly or indirectly, contamination of the environment, is water contamination by dyes. Dyes in wastewaters, if not removed, cause disturbance to the ecological systems of the receiving waters. From the environmental point of view, the removal of color of the effluents is one of the greatest problems faced by the textile sector. The high biological stability of dyes makes their degradation difficult by the conventional treatment systems employed by the textile industries. The contamination of rivers and lakes with these compounds causes, besides visual pollution, serious damages to fauna and flora of these places. With their intense colorations, dyes restrict the passage of solar radiation, reducing the natural photosynthetic activity, causing changes in the aquatic biota and causing acute and chronic toxicity for organisms of these ecosystems (Dallago et al., 2005).
Methylene blue dye is an organic dye belonging to the phenothiazine family. It is mainly used for coloring bast, paper, leather, cotton, silk, and wool. Due to its large application for coloring different industrial materials, there is a constant interest in removing it from aqueous solutions (Royer et al., 2009).

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There are numerous methods that are used for treating wastewaters containing dyes, such as, coagulation and flocculation, degradation, photocatalytic ozonation, photocatalytic oxidation (Sima and Hasal, 2013), Fenton process, catalytic wet air oxidation, electrochemical degradation, biological treatment. However, all these processes lead to the production of other byproducts that require continuous monitoring and identification, besides most of them are expensive for treatment on a large scale (Forgacs et al., 2004).

A process widely used in the treatment of industrial effluents involving dyes is the adsorption procedure. It presents high efficiency and does not require high initial investments. In this process dyes are withdrawn from the aqueous phase and transferred to a solid phase, which in this case is the adsorbent material, decreasing remarkably its concentration in water effluent. In this way, the decontaminated effluent could then be released to the environment or the water could be reutilized in the industrial process (Cardoso et al., 2011).

Therefore, there is a growing interest in finding alternative low cost adsorbents for wastewater treatment. The search for alternative adsorbents, mainly from natural resources, was pioneered by Tsezos and Volesky in the early 1980s. Several studies have been conducted, most focused on finding unconventional adsorbents. Since many studies have been devoted to the biosorption of different pollutants it is still prevalent and necessary the research of biosorbents, due to the following reasons: different types of biomass contain different types of functional groups so that the pollutant binding mechanism; biomass materials are heterogeneous and their chemical compositions are different; they are abundantly available; biosorbent use has not been extended and applied for the removal of contaminants in the industry (Kosasih et al., 2010).

In this research methylene blue removal from aqueous solution was evaluated using crude CBR, and CBR modified with H_2SO_4 and NaOH with the objective of obtaining a new alternative for the treatment of wastewater and water containing dyes, and to present a new application for the cassava bark, considering its abundance, low cost, aiming at the preservation of the environment with efficient treatment of effluents containing dyes and the reuse of cassava residues.

2. Materials and methods

2.1 CBR preparation

Firstly, CBR was washed with tap water repeatedly to eliminate surface dirt. It was subsequently dried in oven at 100 °C for 24h. Biomass size was then reduced using a knife mill model SP-030 N Series 99/09 - Splabor and further sieved to obtain desirable particle size. It was used granulometries of 20, 28, 35 and 42 mesh, corresponding to 850 μm, 600 μm, 425 μm and 355 μm. Only 20 to 28 (sample 20), 28 to 35 (sample 30) and 35 to 42 (sample 40) mesh were used, discarding granulometry larger than 20 mesh or greater than 42 mesh. Final products were later stored in plastic containers for further experimental use.

2.2 CBR modification

CBR was modificated in order to evaluate its results. For alkaline modification, 20 g of CBR 20 mesh were treated in 400 mL of 0.1 mol L^{-1} NaOH solution, and for acid modification 20 g of CBR 20 mesh was treated in 400 mL of 0.1 mol L^{-1} H_2SO_4 solution, in a 500 mL Erlenmeyer flask at a temperature of 25 °C. The flasks were shacked using shaker incubator, at 150 rpm for 24 hours, after which the solutions were washed to constant pH, resulting in samples 20 basic and 20 acid, respectively.

2.3 CBR characterization

The surface morphology of the CBR was characterized by scanning electron microscopy using a Shimadzu SS-550 microscope. The zeta potential analyses were realized by electrophoretic laser Doppler anemometry at different pH values for samples 20, 20 acid and 20 basic using a Delsa NanoTM C Beckman Coulter.

2.4 Adsorption studies

The adsorption studies were performed in batch, using 50 mg of CBR samples in 50 mL of 10 mg L^{-1} of methylene blue solution in a 125 mL Erlenmeyer flask at a temperature of 25 °C, using a Shaker incubator model Luca-223, at 150 rpm for 24 h. The amount of dye adsorbed on the CBR (q_e) was calculated by Eq. (1):

$$q = \frac{(C_i - C_f)}{M} \times V \tag{1}$$

where Ci (mg L^{-1}) is the initial concentration of dye in the aqueous solution, Cf (mg L^{-1}) is the concentration of dye in remaining solution after the contact with CBR, V (L) is the volume of solution, m (g) is the mass of the adsorbent material (DOTTO et al., 2011). The quantification of C_f was performed by spectrophotometry in the visible region, using a Hach spectrophotometer model DR 5000 UV-Vis, with a wavelength of 664 nm. All the adsorption experiments were performed in duplicate.

2.5 Kinetic studies

For the kinetic study 50 mg of CBR sample 20 basic was added to 50 mL of a 10 mg L^{-1} methylene blue solution. The mixtures were shaken in the shaker incubator for different times (15 min, 45 min, 1 hour, 1h15min, 2 hours, 3 hours, 4 hours, 6 hours, 8 hours and 24 hours), the temperature was controlled at 25 °C, and all assays were performed in duplicate.
After the contact time the blends were vacuum-filtered and the remaining methylene blue concentrations were determined spectrophotometrically.

Results and discussion

2.6 CBR characterization

Characterization of the CBR was performed to determine its surface morphology, characterized by means of scanning electron microscopy and zeta potential analysis. Scanning electron microscopy image of CBR is presented in Figure 1.

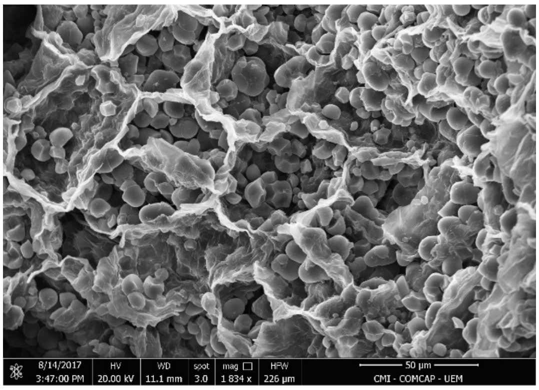

Figure 1: Scanning Electron Microscopy (SEM) analysis of CBR.

The image (Figure 1) clearly demonstrated the presence of starch granules and fibers. The starch granules are the rounded structures, while the fibers (peptidic and cellulosic material), are the structures encompassing the granules. The granules were mostly polygonal, globular, with a smooth surface and slightly flattened at one end. It was also verified that the surfaces of some granules presented depressions in the surface, giving an aspect and irregular shape. These findings agreed with the findings of Versino et al. (2015) and Leite (2017), who investigated the by-products of cassava starch processing.
It is known that measuring the zeta potential of adsorbents as a function of pH, the acidity or basicity of surfaces and isoelectric point (IEP) can be determined (Yamaguchi et al., 2016). Figure 2 presents results from zeta-pontential analysis.

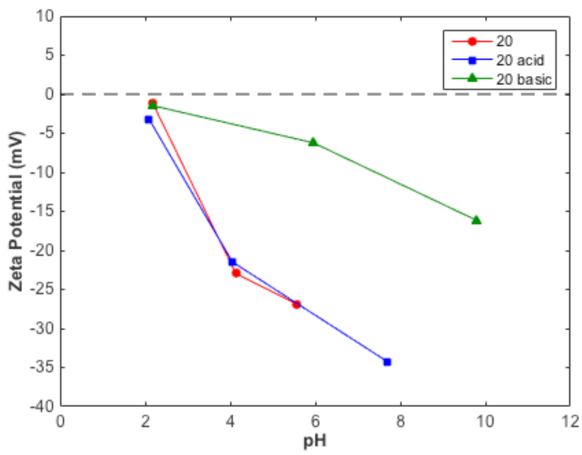

Figure 2: pH dependent zeta-potential plots of CBR samples 20, 20 acid, 20 basic.

It was observed that the acid modification did not alter CBR global charge in acid sample. However, a great change with the alkaline modification was noticed. CBR 20 basic sample turned to be less negative, however maintained a negative global charge being able to promote biosorption of pollutants positivelly charged. These results are in agreement with data previously published by Schantes et al. (2016).
In a previous work developed by Schwantes et al. (2016) it was shown that the concentration of K, Ca, Mg, Cu, Zn, and Pb in the composition of modified adsorbents was effectively reduced and demonstrated that the modifying solutions (H_2SO_4 and NaOH) worked as extracting solutions, predigesting the biomass, and extracting certain chemical elements of its structure. The obtained results may be related to the change in CBR composition.

2.7 Adsorption studies

2.7.1 Effect of particle size and modification

The methylene blue removals can be observed in Figure 3, according to the CBR granulometries and modifications used.

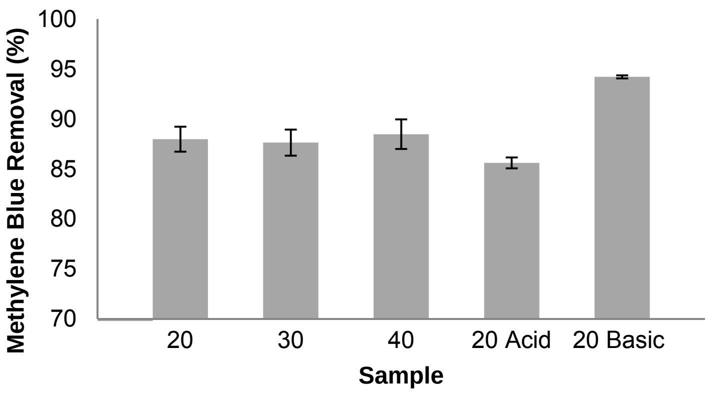

Figure 3: Effect of CBR granulometry size and modifications on methylene blue removal.

It was observed that the different granulometries did not significantly influence the methylene blue adsorption 20 (88.0%), 30 (87.7%), 40 (88.5%). However, the acidification of CBR caused a slight decrease in methylene blue removal (85.6%) and it is clear that the alkalinization caused a considerable improvement, showing 94.2% of methylene blue removal.
Cassava peel is principally made up of lignin and cellulose. Therefore, carboxyl and hydroxyl groups are present in abundance in its structure. These groups may function as proton donors; hence, deprononated hydroxyl and carboxyl groups become negatively charged (Mohd-Asharuddin et al., 2017). An improved adsorption process occurs due electrostatic attraction, since methylene blue has positive charge due to the amine group present. This explains why all samples showed high removal of methylene blue.
Another research on the feasibility of CBR to remove Cu(II) and Ni(II) indicated that the presence of hydroxyl, carboxyl and carboxylate group contributed to the removal of the metals up to 90% (Awokoya et al., 2016). The inclusion of hydroxyl group in CBR on metal binding was also reported by Kokasih et. al (2010). Jorgetto et. al (2013) suggested that the oxygen on each hydroxyl group acted as a strong Lewis base because of the presence of its vacant double electrons, and this hydroxyl group undergoes a complex coordination with metal Cu(II) which is electron deficient. The increase in hydroxyl groups in basic CBR surface has also improved methylene blue adsorption, and may be attributed to a mechanism by electrostatic attraction.

2.7.2 Kinetics studies

Adsorbents have different equilibrium times depending on the adsorbent and the compound to be adsorbed. The equilibrium time is a very important factor in the adsorption studies, being fundamental to determine how long the adsorbent takes to reach its maximum adsorption capacity. Figure 4 shows the results obtained in the kinetic study for the adsorption of methylene blue using CBR 20 basic varying the contact time from 15 minutes to 24 hours.

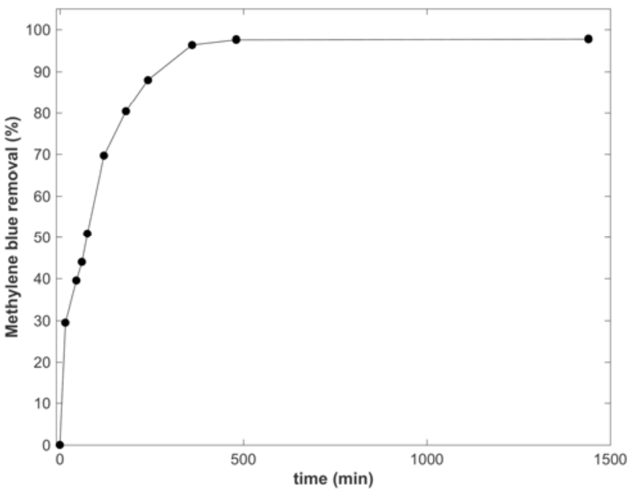

Figure 4: Methylene blue biosorption kinetics by CBR 20 basic at 25 °C.

According to the kinetic results obtained, it was observed that the removal speed was higher at the beginning due to the greater adsorbent surface area available. A two-phase adsorption is a possible phenomenon, predominantly by a relatively fast phase and a following slow phase. This can be attributed to the fact that available sites tend to become progressively saturated by methylene blue with time and, therefore, resulting in a slow adsorption of the solute ions on a major part of the adsorbent. The rapid adsorption at the initial contact time, and due to the availability of negatively charged active sites on the CBR surface for methylene blue interaction and decrease in adsorption over time, is due to the electrostatic impediment between adsorbed species loaded positively (Herath et al., 2016). After 6 h of contact, it can be said that the system entered into equilibrium, and the methylene blue biosorption stagnated.

3. Conclusions

CBR is an inexpensive and readily available biomass, with potential use for dyes removal from contaminated waters. It can be concluded that CBR has considerable potential as a biosorbent for the removal of methylene blue from aqueous solution. It was also countered that methylene blue removal by CBR can be enhanced by alkaline treatment. The use of solid waste is a relevant alternative for disposal of this waste and even enables added value to waste which is normally disposed. This process will be environmentally friendly and will reduce the huge amount of CBR from the several cassava processing zones in Brazil. It may also provide an affordable technology for small and medium-scale industry in Brazil and enhanced local entrepreneurship.

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