ACTIVATED CARBON-ALGİNATE BEADS FOR EFFICIENT REMOVAL OF CATIONIC AND ANIONIC ORGANIC DYES FROM AQUEOUS SOLUTION

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RESUMO – This study presents activated carbon-alginate (AC-alginate) utilized as adsorbent to remove a cationic and anionic dyes: methylene blue (MB) and tartrazine (TZ), from aqueous solution. The adsorbent, AC-alginate beads, were synthesized by ionotropic gelation. The textural characterization was performed by using N₂ adsorption–desorption and the morphology was analyzed by SEM microscopy with EDX analysis. Batch experiments were conducted on two temperatures (30 and 50°C), different initial concentrations (20–100 mg.L⁻¹), fixed volume of adsorbate (20 mL) and fixed amount of adsorbent (4 g.L⁻¹) at pH 7.0 for MB and 3.0 for TZ. Equilibrium adsorption isotherms and kinetics were investigated. The equilibrium experimental data were analyzed by the Langmuir and Freundlich models. The best results were achieved with the Langmuir isotherm equilibrium model. The kinetic data obtained were better fitted by a pseudo-second order. The AC-alginate beads were found to be very effective low-cost adsorbent for MB and TZ from aqueous solutions.

1. INTRODUCTION

Adsorption process is widely used to treat water and wastewater, removing certain classes of pollutants, especially those which are not easily biodegradable as the organic dyes. This technique has been receiving great attention from researches, mainly on the way to the development of low-cost adsorbents. Materials of natural occurrence on the nature, agricultural and industrial wastes can be utilized as low-cost adsorbent.

Alginate is a carbohydrate polymer of natural occurrence obtained from brown algae and has the ability to remove toxic pollutants. One of the important properties of alginate is the ability to form hydrogels by a process called “ionotropic gelation”. An aqueous solution of alginate is readily transformed into a hydrogel (egg box structure) in the addition of metal divalent cations, such as Ca²⁺. This biopolymer is widely used to create different adsorbents to remove residues such as dyes, pigments and metals from aqueous solutions. Alginate also has several desirable properties, such as non-toxicity, biodegradability, biocompatibility and low cost.

Methylene blue (MB), cationic dye, and yellow tartrazine (TZ), anionic dye, were
selected as model compounds to evaluate the capacity of activated carbon immobilized on alginate for their removal from aqueous solutions in batch mode.

2. MATERIALS AND METHODS

The AC-alginate beads were prepared based on ionotropic gelation method [1]. A solution of sodium alginate (3% w/w) was stirred for 2h and sonicated for 40 min. 5 g of activated carbon was added per 100 g of solution. The mixture was stirred for 30 min and then sonicated for 20 min. The resulting solution was dropped through a micropipette tip (200µL) into a 2% (w/w) CaCl₂ solution. The beads were stirred for 1h to improve the mechanical strength. Then, they were washed several times with distilled water to remove the unbounded CaCl₂ from the surface, and subsequently dried at 60°C for 24h. SEM was used to investigate the surface morphology. Energy dispersive X-ray analysis (EDXA) was performed to determine the elemental composition. BET (Brunauer, Emmet and Teller) was used to obtain the specific surface area (S_BET).

The adsorption capacity of the prepared adsorbent was evaluated by cationic (methylene blue-MB) and anionic (tartrazine-TZ) dyes models. The experiments were carried out in 125 mL Erlenmeyer flasks, each one, containing 20 mL of dye solution with initial concentration ranging from 10 to 100mg.L⁻¹ and 0.08 g of AC-alginate beads (4.0 g.L⁻¹). The flasks were covered and then placed in a water bath orbital shaker/100 rpm (Solab, Brazil). The equilibrium adsorption was carried out for 24h. The remaining dye concentration in the solution in each flask was measured by UV-vis spectrophotometry. The adsorbed amount (q) was calculated using the following equation:

\[ q = \left( C_0 - C \right) \frac{V}{M} \]  

Where \( C_0 \) is the initial concentration of MB and TZ (mg.g⁻¹), \( C \) can be the equilibrium concentration (\( C_e \))(mg.g⁻¹) for the adsorbed amount on equilibrium (\( q_e \)) and the concentration at time \( t \) (\( C_t \)) for the adsorbed amount on time \( t \) (\( q_t \)). \( V \) is the volume of adsorbate and \( M \) is the mass of AC-alginate beads (adsorbent). The kinetic experimental data were adjusted to kinetic models: pseudo-first and pseudo-second order. The experimental data of adsorption equilibrium were correlated to the mathematical models of Langmuir and Freundlich. The applicability of Langmuir and Freundlich models, as well the kinetic models were evaluated by \( R^2 \) and RMSE function values.

3. RESULTS

The AC-alginate beads were spherical in shape with average diameter of 2.3 mm (Figure 1-a). At least 10 beads were randomly selected for the average diameter determination and presented variation of 6,7% between the measures. The SEM imagens taken under different magnifications showed rough surface and irregular pores. The EDX spectra shows the presence of calcium on AC-alginate beads surface.
Figure 1- SEM of AC-alginate beads (a) 100x and (b) 1000x; (b) EDX analysis.

The BET surface area ($s_{BET}$) and cumulative pore volume for AC-alginate obtained were: 246.596 m².g⁻¹ and 3.42954 cm³.g⁻¹, respectively. Figure 2 shows a type IV isotherm for the adsorbent with a hysteresis loop which indicates the mesoporous nature [2]. Previously, was observed that the maximum adsorption of MB and TZ at 30 and 50°C on AC-alginate beads was obtained for pH 7.0 and 3.0, respectively. So, the experiments of equilibrium adsorption and the kinetic study were done at these pH values. The adsorption of dyes was found to be endothermic, which means that adsorption capacities increase as temperature do in the experimental range studied (30 and 50°C).

Figure 2- BET isotherm and pore size distribution of AC-alginate beads.

The adsorption isotherms of MB and TZ (data not shown) on AC-alginate were obtained by plotting the amount of dye adsorbed, $q_e$ vs. the equilibrium concentration of dye in liquid-phase, $C_e$ for eight initial concentrations, $C_0 = 20, 30, 50, 100, 150, 200, 250, 300$ mg L⁻¹. Langmuir equation fitting describes better the experimental system once it presents higher $R^2$ and lower RMSE values. Such that adsorption equilibrium is well described by a monolayer Langmuir type isotherm for both dyes (Table 1).

The kinetic modelling of the MB and TZ adsorption on the AC-alginate beads indicates that adsorption process is pseudo-second order with high correlation coefficients for both dyes ($R^2$ above 0.989 and RMSE less than 1.82). This model is more likely to predict the behavior over the whole adsorption experimental range of adsorption than pseudo-first order model. Pseudo-second order kinetic model was also observed to present better fitted for adsorption of other dyes onto alginate beads [3].
Table 1 – Langmuir and Freundlich isotherm parameters for the adsorption of MB and TZ on AC-alginate Beads

| Mathematical Model | Parameter | MB 30°C | MB 50°C | TZ 30°C | TZ 50°C |
|--------------------|-----------|---------|---------|---------|---------|
| Langmuir           | $q_m$ (mg.g$^{-1}$) | 128.2   | 263.5   | 93.4    | 121.9   |
|                    | $K_a$ (L.mg$^{-1}$) | 0.0025  | 0.0026  | 0.491   | 0.0423  |
|                    | $R^2$ | 0.9989  | 0.9992  | 0.9858  | 0.9906  |
|                    | RMSE  | 0.4032  | 0.4837  | 2.659   | 2.297   |
| Freundlich         | $K_f$ (mg.g$^{-1}$)(L.mg$^{-1}$)$^{1/n}$ | 0.113   | 0.205   | 1.735   | 1.938   |
|                    | $n$      | 0.897   | 0.840   | 0.783   | 0.9358  |
|                    | $R^2$ | 0.6737  | 0.8027  | 0.611   | 0.6179  |
|                    | RMSE  | 8.623   | 13.385  | 13.469  | 10.919  |

Figure 3 - Pseudo-second order kinetic plot for the adsorption of MB and TZ at 30°C

5. CONCLUSION

The mesoporous AC-alginate beads were successfully synthesized by ionotropic gelation and were efficient for removal of MB and TZ from aqueous solution. At the studied conditions, the maximum adsorption capacities were 263 mg.g$^{-1}$ and 121.95 mg.g$^{-1}$ at 50°C for MB and TZ, respectively. Langmuir isotherm model best fitted the experimental data on the equilibrium. Kinetic of pseudo-second order also better explained the experimental data.

6. REFERENCES

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