Evaluation of dyes adsorption properties of TiO$_2$-alginate biohybrid material.

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Abstract. In this study a TiO$_2$-alginate biohybrid material was obtained by the sol gel method and its adsorption properties were compared to those of its precursors using eosin B (anionic) as model dye. The results showed that the TiO$_2$ and biohybrid have a greater affinity for eosine B than alginate. The maximum adsorption capacity for the eosin B was obtained at pH = 10. Kinetic studies showed that the biohybrid has greater rate and adsorption capacity than its precursors. Kinetic data were fitted to a pseudo-second order kinetic model. The experimental isotherms were fitted to the Langmuir model.

1. Introduction
Effluents contaminated with dyes generated from various industrial operations are important because they contain several toxic compounds that affect aquatic life because of their high biological and chemical oxygen demand. Today the removal of this kind of pollutants requires more precise and effective techniques, such as adsorption, which has a high capacity for the purification of effluents [1].

In recent years there has been a growing interest in the development of new hybrid materials and their potential application as adsorbents for the removal of different types of pollutants. In this sense, polymethacrylic acid (PMAA) was grafted onto the surface of silica gel particles (PMAA/SiO$_2$) for the adsorption of phenol [2].

Some authors have investigated the feasibility of using TiO$_2$ based materials as new adsorbents for solid phase extraction (SPE) of organic compounds, like DDT and its metabolites, and metals in water [3-6]. TiO$_2$ has different selectivity for a variety of analytes when compared to a silica matrix. Therefore, the use of TiO$_2$ as inorganic phase instead of silica, could serve to improve the selectivity of the adsorption processes [4]. In other work, TiO$_2$ particles coated with polyacrylonitrile, was used for the extraction of metals, with recovery rates from 60 to 95% [7].

On the other hand, chitosan-silica hybrid materials obtained as microparticles had been prepared by the sol-gel method using TEOS or oligomers in the presence of the biopolymer. These materials may be used as stationary phase in HPLC [8]. The hybrid particles, based on algal polysaccharides such as alginate and carrageenan, appear to be a good candidate for the formation of silica-based bio-composites. Alginate is a copolymer of L-guluronic and D-mannuronic acid that can be reversibly gelled by the addition of divalent metal, like calcium [9]. Chuang et al. [10] used bamboo and modified bamboo on its surface with TiO$_2$ nanoparticles for the removal of benzene and toluene, obtaining good results.
In these examples, the interaction of the biological and inorganic components have synergistic effects that lead to hybrid materials with improved mechanical strength, higher thermal and chemical stability, and in some cases, functional properties.

In this study TiO$_2$-alginate biohybrid material was obtained using the sol gel method and the adsorption properties were compared to their predecessors using an anionic dye model: eosin B (EB). The effect of pH, contact time and initial concentration of dye on the adsorption capacity of different materials were studied. The kinetic parameters were also calculated to determine rate constants. The equilibrium experimental data were fitted to Langmuir model.

2. Materials and Methods

2.1. Synthesis of adsorbents

TiO$_2$ was synthesized by mixing Titanium Isoproxide (TIPO), ethanol and distilled water in a beaker with slow stirring. 1 M HCl was added to the mixture until pH 2 and allowed to stir for 30 minutes. 0.1 M NaOH was added until pH 7 and then continued with stirring to obtain a gel. The gel obtained was allowed to grow for 24 h, and then washed with water. Subsequently, the product was dried at 85 °C in air oven to constant weight.

Calcium alginate powders were obtained by spraying 600 mL of 2% sodium alginate solution on 500 mL of 0.05 M CaCl$_2$ solution. The formed calcium alginate particles were allowed to mature for 24 h. After that, they were filtered, washed with distilled water and dried at 50 °C in air oven for 24 h. After drying, the particles were maintained in a desiccator.

Biohybrid sorbent was synthesized by mixing TIPO, ethanol and distilled water in a beaker with slow stirring. The ratio TIPO/H$_2$O was kept constant and equal to 1. Then 1 M HCl was added to the mixture until pH 2 and allowed to stir for 30 minutes. The above mixture was added dropwise to 500 mL of a solution of 2% sodium alginate with rapid stirring until total homogenization of the two solutions. After completed addition, agitation was reduced and continued to obtain a gel. Subsequently, the gel was dried in vacuum oven at 85 °C and washed with distilled water, then dried again at 85 °C in air oven to constant weight. All materials were characterized by BET technique using a Quantachrome ASiQwin analyzer.

2.2. Effect of initial pH

30 mL of dye solution of 50 mg/L initial concentration different pH values (1 to 11) were put in contact with 0.1 g of sorbent and agitated for 24 h. The resultant solutions were filtered before analyses. Initial and equilibrium dye concentrations were determined by spectrophotometry using UV-VIS spectrophotometer (Thermo Scientific, LR 162800). Absorbance measurements were made at the maximum wavelength of EB ($\lambda$= 517 nm). The amount of adsorbed EB, $q_e$ (mg/g), was calculated from mass balance using equation (1):

$$ q_e = \frac{(C_0-C_e)V}{m} \quad (1) $$

where $C_0$ and $C_e$ are the initial and equilibrium concentrations of dye solution (mg/L), respectively, $V$ is the volume of dye solution (L) and $m$ is the mass (g) of the sorbent used.

2.3. Sorption kinetics

150 mL of EB solution ($C_0$= 50 mg/L) at the pH of maximum adsorption, which was previously determined, was put in contact with 0.5 g of sorbent and placed under stirring for 10 h. Samples were taken at predetermined time intervals and analyzed as described before. Kinetic data were analyzed with a pseudo-second-order model (equation (2)) [11].

$$ \frac{t}{q_t} = \frac{1}{K_2q_e^2} + \frac{1}{q_e}t \quad (2) $$
where \( q_e \) is the adsorption capacity at equilibrium (mg g\(^{-1}\)), \( q_t \) is the adsorbed amount of sorbate at time \( t \) (mg g\(^{-1}\)), and \( K_2 \) is the pseudo-second order rate constant (g mg\(^{-1}\) min\(^{-1}\)).

2.4. Adsorption isotherms

0.1 g of sorbent was added to a bottle containing 30 mL of EB aqueous solution of desired concentration (10-100 mg/L) at the pH of maximum adsorption, previously determined. The bottles were subsequently capped and placed on a mechanical shaker at a speed of 200 rpm at (20±2) °C for 24 h. Initial and equilibrium dye concentrations were determinate as describe above. Experimental data were fitted to the isotherm model of Langmuir (equation (3)) [10].

\[
q_e = \frac{q_{\text{max}}K_LC_e}{1 + K_LC_e}
\]

where \( C_e \) is the supernatant concentration at the equilibrium (mg L\(^{-1}\)), \( K_L \) is the Langmuir affinity constant (L mg\(^{-1}\)), and \( q_{\text{max}} \) is the maximum adsorption capacity of the sorbent (mg g\(^{-1}\)) assuming a monolayer coverage of the sorbent.

3. Results and discussions

3.1. pH Influence

Figure 1 shows the influence of pH on the sorption of eosin B onto on TiO\(_2\), TiO\(_2\)/Alginate biohybrid, and alginate. It can be see that both TiO\(_2\) materials have great affinity for EB. As expected, alginate has a very low sorption capacity, due to his negative surface charge, that repels the anionic EB. This results shows that the biohybrid keeps the adsorption properties of TiO\(_2\).

3.2. Sorption kinetics

Figure 2 shows that the rate of sorption of the biohybrid is greater than that of the TiO\(_2\). That seems to indicate that the alginate increases the porosity of the adsorbent, making the active sites of the biohybrid more accessible for the molecules of EB. BET analysis shows that the biohybrid has a half pore width of 16.6 Å, while for the TiO\(_2\) it is 8 Å. Experimental data fitted well to the pseudo-second order model \((R^2 > 0.99)\). The values of \( K_2 \) for the biohybrid and TiO\(_2\) were 0.009 and 0.00085 respectively, which agree with the experimental observations.

3.3. Sorption isotherms

Sorption isotherms for the biohybrid and TiO\(_2\) are depicted in figure 3. It can be see that the both...
experimental isotherms fit well with the Langmuir model. The values of $q_{\text{max}}$ were 263.7 mg/g for the biohybrid and 398.3 mg/g for the TiO$_2$. Although the TiO$_2$ seems to have a higher adsorption capacity that the biohybrid, it must be pointed out that the biohybrid has only half the mass of TiO$_2$, and that the alginate contributes little to the total capacity of the biohybrid, so his adsorption capacity is higher than that of the TiO$_2$.

![Figure 3. Sorption isotherms of eosin B on TiO$_2$/Alginate biohybrid and TiO$_2$](image)

4. Conclusions
A new TiO$_2$/alginate biohybrid was synthesized by sol-gel method and his dye adsorption properties evaluated and compared to that of his precursors using an anionic eosin B, as model dye. The results show that pH has a great influence on the dye sorption onto the different studied adsorbents. Maximum dye adsorption capacity for the biohybrid was obtained a pH = 10. Kinetic and equilibrium data shows that the biohybrid has higher rate and adsorption capacity than his precursors. Kinetic data were well described by the pseudo-second order kinetic model, while equilibrium data fitted well to the Langmuir model. The improved rate and adsorption capacity of biohybrid shows a synergistic effect of the two components; from titanium oxide the biohybrid acquired the property of adsorbing anionic molecules, while the alginate yielded a more porous structure.

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