Adsorption of cationic dye on a biohybrid SiO$_2$-alginate

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Abstract. In this work, a biohybrid material based on SiO$_2$-alginate was obtained and its properties of adsorption evaluated using methylene blue as a model dye. The experimental results showed that the biohybrid SiO$_2$-alginate has a higher adsorption ability compared to their base compounds (SiO$_2$ and alginate). Methylene blue adsorption is pH dependent, resulting in a maximum adsorption at pH = 8. The sorption kinetics rate is similar to SiO$_2$. Kinetic data were fitted to a model of pseudosecond order. The experimental isotherms fit well the Langmuir model.

1. Introduction

With the rapid development of large industries and the increasing growth of urban areas, the discharge of effluents contaminated with dyes represents a serious risk to health and the environment. Various technologies have been developed and tested in colored industrial effluent treatment systems. In this reference framework, the activated carbon adsorption has proven to be the most promising strategy, but its high cost restricts its large scale implementation. Hence, the exploration of alternative materials with similar properties, natural origin, easy acquisition, minimal economic value and environmentally friendly is imperative. 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 [1, 2]

Researchers have reported studies on compounds derived from silica, which have been successfully applied as adsorbents in the removal of pollutants such as aromatic compounds and some heavy metals. An et al. [3, 4] developed a new adsorbent material PAM/SiO$_2$ for removal of 2,4,6-trinitrotoluene (TNT) and aniline. The material produced had a strong adsorption ability and reusability for the removal of both, TNT and aniline.

On the other hand, chitosan-silica hybrid materials obtained as microparticles, have been prepared by the sol-gel method using TEOS or oligomers in the presence of the polymer polyethoxysiloxanes. These materials may be used as stationary phase in HPLC [5]. The hybrid particles, based on algal polysaccharides such as alginate and carrageenan, appear to be a good candidate for the formation of silica-based biocomposites. Especially, alginate is a copolymer of L-guluronic and D-mannuronic acid. It can be reversibly gelled by the addition of divalent metal, like calcium [6, 7].

The biopolymer/silica composites are suitable for the design of membranes and coatings used in drug detection systems [6], as sorbent materials for some metals such as copper [7], and for the encapsulation of bioactive molecules such as enzymes, antibodies, yeast and plant cells and even...
bacteria, resulting in biomaterials for various biotechnological applications [8]. In these examples, the interaction of the biological and inorganic components has synergistic effects that lead to hybrid materials with improved mechanical strength, higher thermal and chemical stability and, in some cases, functional properties.

In this paper, a biohybrid material based on SiO$_2$-alginate was obtained and its properties of adsorption evaluated using a cationic dye, namely Methylene Blue (MB) as a model dye. The effects of pH, contact time and initial dye concentration on the dye removal were investigated. The kinetic parameters were also calculated to determine rate constants. The equilibrium experimental data were fitted to the Langmuir model.

2. Materials and Methods

2.1. Synthesis of adsorbents

SiO$_2$ was synthesized by mixing Tetraethyl Orthosilicate (TEOS), 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 in a beaker with slow stirring, TEOS, ethanol and distilled water. The ratio TEOS/H$_2$O was kept constant and equal to 1. 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 2% sodium alginate solution of under rapid stirring until total homogenization of the two solutions. After complete 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.

2.2. pH Influence

0.1 g of sorbent were put in contact with 30 mL of 50 mg/L initial dye concentration solution, at different pH values (1 to 11) 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 MB ($\lambda$ = 668 nm). The adsorbed amount of MB at any time, $q_e$ (mg/g), was calculated from mass balance using equation (1):

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

where $C_0$ and $C_e$ are the initial and equilibrium dye concentrations (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 MB dye solution ($C_e$ = 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 on a mechanical shaker 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)) [9].

$$\frac{t}{q_t} = \frac{1}{Kq_e^2} + \frac{1}{q_e} t$$
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 experiments

0.1 g of sorbent was added to a bottle containing 30 mL of BM aqueous solution of desired concentrations (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 3 h. 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 initial pH on the adsorption of MB onto SiO$_2$/alginate biohybrid, SiO$_2$ and alginate. It can be seen that in the case of the basis compounds the adsorption is pH dependent, however, this effect is less important in the case of the biohybrid, probably as a result of a synergic effect of SiO$_2$ and alginate. This phenomenon allows the use of biohybrid in a wider range of pH conditions with good yields. The maximum adsorption capacity was obtained a pH = 8.

#### 3.2. Sorption kinetics

Sorption kinetics for the three sorbents studied is depicted in figure 2. This figure shows that the biohybrid has sorption kinetics similar to SiO$_2$, but with a slightly better sorption equilibrium capacity. Experimental data fit well to the pseudo-second order model ($R^2 > 0.99$). The values of $K_2$ for the biohybrid, SiO$_2$ and alginate were 0.0027, 0.0045 and 0.0067 respectively, which indicate that the sorbents have similar kinetic sorption rates.
3.3. Sorption isotherms

Figure 3 shows the sorption isotherms for SiO\textsubscript{2}/Alginate biohybrid, SiO\textsubscript{2} and alginate. Experimental data and the parameters of the Langmuir equation show that the biohybrid has a far better maximum adsorption capacity (241.1 mg/g) than SiO\textsubscript{2} (33.5 mg/g). The experimental sorption isotherm of calcium alginate has an unusual form and could not be modeled with the Langmuir equation.

![Figure 3. Sorption isotherms of MB on SiO\textsubscript{2}/Alginate biohybrid, SiO\textsubscript{2} and alginate](image)

4. Conclusions

The dye sorption capacity of a new SiO\textsubscript{2}/alginate biohybrid was evaluated using methylene blue as model dye. Results show that the biohybrid is less affected by the pH than his basis compounds. Maximum dye adsorption capacity for the biohybrid was obtained a pH = 8. Sorption kinetics shows that the biohybrid has similar sorption rate than SiO\textsubscript{2} and alginate. The sorption isotherms demonstrate that the new biohybrid has a better sorption capacity than his basis compounds. Kinetic data were well described by the pseudo-second order kinetic model, while equilibrium data fitted well to the Langmuir model. The biohybrid SiO\textsubscript{2}-alginate proved to have excellent adsorptive properties and can be an alternative for the treatment of water contaminated with dyes.

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References

[1] Cestari AR, Vieira EFS, Vieira GS., da Costa LP, Tavares AMG, Loh W and Airoldi C 2009 J. Hazard. Mater. 161 307;
[2] Anbia M, Hariri SA and Ashrazadeh SN 2010 Appl. Surf. Sci. 256 3228
[3] An F, Feng X and Gao B 2009 J. Hazard. Mater. 168 352; An F, Feng X, and Gao B 2009 Chem. Eng. J. 151 183;
[4] An F, Gao B and Feng X 2009 Chem. Eng. J. 153 108
[5] Rashidova S, Shakarova D, Ruzimuradov O, Satubaldieva D, Zalyalieva S, Shpigun O 2004 J. Chromatogr. 800 49
[6] Xu B, Bartley J P and Johnson, R A 2003 Appl. Polym. Sci. 90 747
[7] Veglio F, Esposito A and Reverberi A 2002 Hydrometallurgy 65 43
[8] Coradin T, Allouche J, Boissière M and Livage J 2006 Curr. Nanosci. 2 219
[9] Ho YS, McKay G 1998 Chem. Eng. J. 70, 115-124
[10] Wong YC, Szeto YS, Cheung WH, McKay G 2003 Langmuir 19, 7888-7894