

ADSORPTION CAPACITY OF BIOLOGICAL POWDERED ACTIVATED CARBON IN A HYBRID MEMBRANE PROCESS FOR DRINKING WATER TREATMENT

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Abstract.- Hybrid membrane process integrates low-pressure driven membrane filtration to activated carbon (AC) adsorption. One of their main features is the possibility of operating either in adsorption or in biological mode, which can be accomplished by shifting the AC residence time (*i.e.*, sludge age) within the reactor. The purpose of this work was to evaluate the adsorption capacity of PAC maintained in a hybrid process operated in biological mode (at 10 and 60 days of sludge age) and to compare it with that of the same virgin (*i.e.* uncolonized) material. For that purpose, kinetic tests were carried out using methylene blue as the adsorbate (10^{-5} M). A pseudo second order model was fitted to the kinetic data with good compliance. The results showed an inverse relationship between q_e and the initial PAC dose. Although both biological PAC lead to lower adsorption rates than the uncolonized material, our results indicate that the adsorption mechanism plays a role in hybrid processes even though they are operated at high sludge ages.

Introduction

The hybrid membrane process is an alternative technology for the reliable treatment of drinking water. In this process, low-pressure driven membrane filtration is coupled to an activated carbon (AC) contactor. The performance of membranes is thus enhanced by the adsorption of dissolved compounds by AC (*i.e.* natural organic matter, synthetic organic chemicals, cyanotoxins and compounds responsible for taste, odor and color such as geosmin and methylisoborneol). Since AC is a good support for microorganisms, hybrid membrane technology also allows biodegradation and nitrification to occur.

The versatility of the hybrid process lies in the possibility of (i) using granular (GAC) or powdered activated carbon (PAC) and (ii) operating either in an adsorption or in a biological mode. This objective is accomplished by shifting the AC residence time (*i.e.*, sludge age) within the reactor [1]. For further microbial activity (mainly targeting the removal of natural organic matter and ammonia), high sludge ages are reached by reducing the volume of purged AC. Although there is not a clearly established threshold, the dominance of biological mechanisms over adsorption is expected at sludge ages higher than 30 days. However, the relative contribution of adsorption and biological processes in hybrid systems is still unknown.

The purpose of this work was to evaluate the residual adsorption capacity of PAC from a hybrid process operated in biological mode at two sludge ages (10 and 60 days). In order to do that, batch tests with methylene blue as adsorbate were carried out. This compound was selected for the assays as the amount of methylene blue adsorbed is considered as a measure of the adsorption capacity towards high molecular weight solutes such as natural organic matter [2].

Materials and methods

Biological PAC. Two pilot-scale units (171.7 L of working volume) with immersed-type membranes were studied. Hollow fiber membranes (PES) with nominal pore size of 0.05 μm were used. In the contactors, the AC-biomass slurry was agitated by aeration (50 L min^{-1}). The reactors were filled initially with uncolonized 25- μm PAC (PicaHydro® LP39). This wood-based PAC has a mean diameter of 24.0 μm and is microporous and macroporous [1]. In the 10 day-age reactor the PAC content was of about 5 g L^{-1} , whilst a PAC content of 10 g L^{-1} and a sludge age of 60 days were maintained in the other reactor. The influent to both contactors was settled river water (Rivière des Mille-Îles, Laval, Canada). The main water characteristics are 2.9 mg COD L^{-1} , 0.23 mg CODB L^{-1} and 154 μg N-NH₃ L^{-1} [3].

Activated carbon preparation. For uncolonized PAC, a slurry was prepared by mixing overnight 1 g of the material with 200 mL of Milli-Q water. The pH of the slurry (about 3) was raised to 7.0 by adding 1N NaOH. Samples of PAC slurries to be used in adsorption assays were recovered by filtering through a Whatman filter (8 μm of pore size). The water content of all the filtered PAC (uncolonized and biological) was measured to obtain the actual weight of PAC introduced to the adsorption tests.

Dynamic adsorption tests. A solution of methylene blue at a concentration of 10^{-5} M was prepared in Milli-Q water. As the pH value modifies the adsorption of methylene blue [4], the pH of the solution was set to 7.0 with 1 M phosphate buffer. Adsorption tests were performed in 500-mL jars containing 200 mL of the methylene blue solution. In each jar, a different amount of uncolonized or biological PAC was added. The content of the flasks was mixed at 150 rpm with a magnetic bar using a multi-stirrer system, and samples were collected at increasing intervals. The solution was separated from the activated carbon by centrifugation at 10,000 rpm for 10 min. Then, the methylene blue concentration was measured by spectrophotometry at 655 nm using a calibration curve.

Theoretical model

A pseudo second-order model (Eq. 1) was used to describe the kinetics of adsorption [5]:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \quad (\text{Eq. 1})$$

where q_t is the adsorption capacity (in mg methylene blue $\text{g}_{\text{PAC}}^{-1}$), q_e is the adsorption capacity at the equilibrium and k (in $\text{g}_{\text{PAC}} \text{mg}^{-1} \text{h}^{-1}$) is the pseudo second-order rate constant. Integrating Eq. (1) with the following boundary conditions: $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, gives:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + kt \quad (\text{Eq. 2})$$

Eq. (2) can be linearized as follows:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t \quad (\text{Eq. 3})$$

Thus, the parameters k and q_e can be obtained from the intercept and slope of the plot of (t/q_t) against t [5].

Results and discussion

The kinetics of methylene blue adsorption was studied in batch dynamic tests with three types of activated carbon (uncolonized, 10 day- and 60 day-aged PAC). Different adsorbent amounts were employed, varying from 0.0014 to 0.0067 g dry PAC (corresponding to 7.0-33.5 mg dry PAC L⁻¹). For each sample the mass of methylene blue adsorbed per mass of adsorbent (*i.e.*, q_t) was calculated. The results are shown in Figure 1.

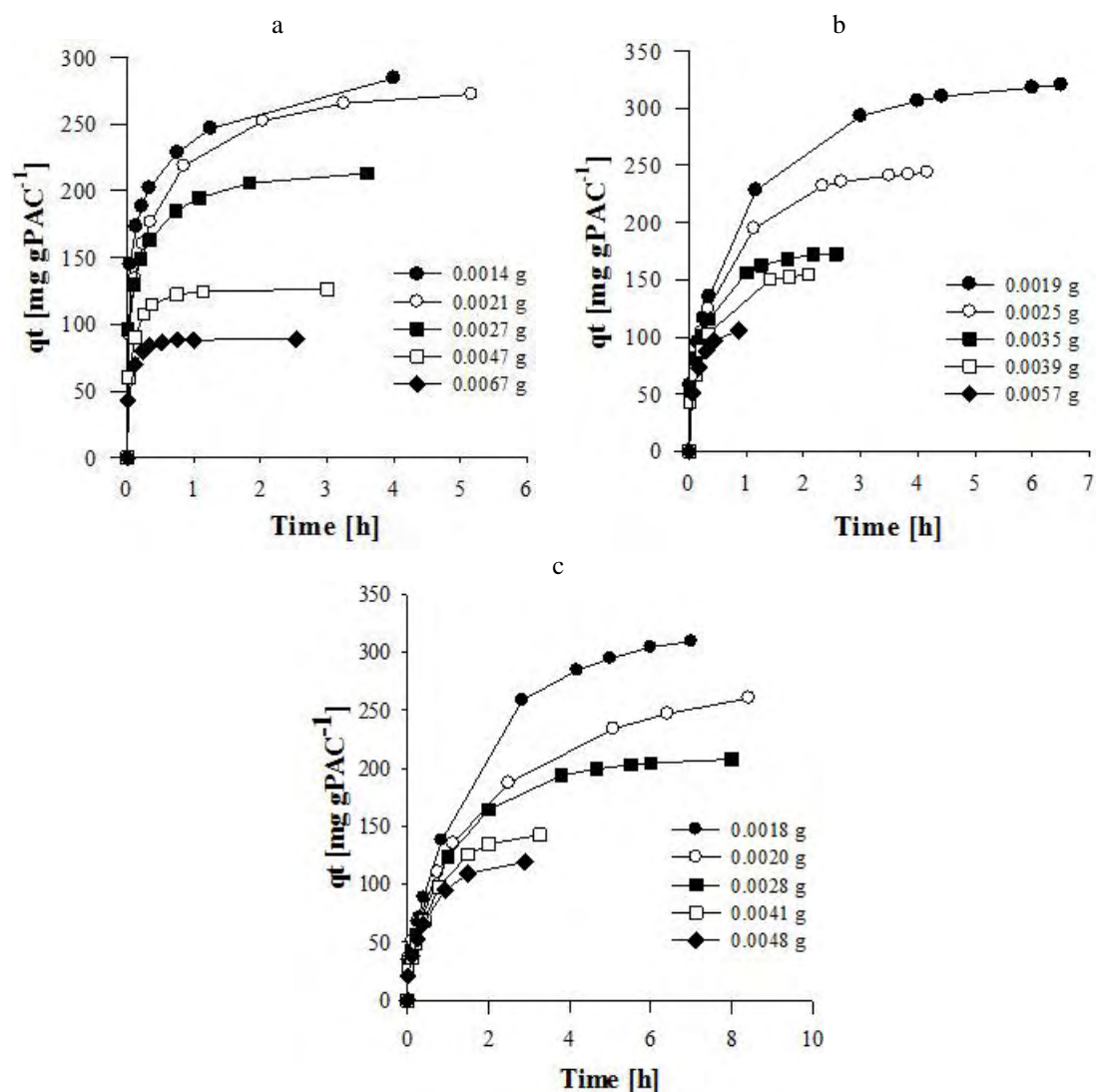


Figure 1. Adsorption of methylene blue on different amounts of a) uncolonized (virgin); b) 10 day-aged and c) 60 day-aged PAC.

As depicted in Fig. 1, the adsorption capacity (q_t) increases with time until a plateau appears, due to the decrease in the concentration driving force [5]. Both the plateau level and the initial rate of q_t depend on the mass of adsorbent used for the test. Consequently, the kinetics of adsorption on different PAC can only be compared if similar amounts of adsorbent were used. For instance, in the assays carried out with the lowest dosages of biological PAC (0.0019 and 0.0018 g of 10 day- and 60 day-aged PAC, respectively), the time required to reach the plateau was similar (of about

6 h) but inferior than that required by the lowest amount of uncolonized PAC (of about 4 h).

The kinetic data obtained from batch adsorption tests were analyzed by using the pseudo second-order model. Fig. 2 shows the linearized plots of the results. The data demonstrate a good compliance with the pseudo second-order equation, as the regression coefficients for the linear plots were higher than 0.985 for all the conditions tested.

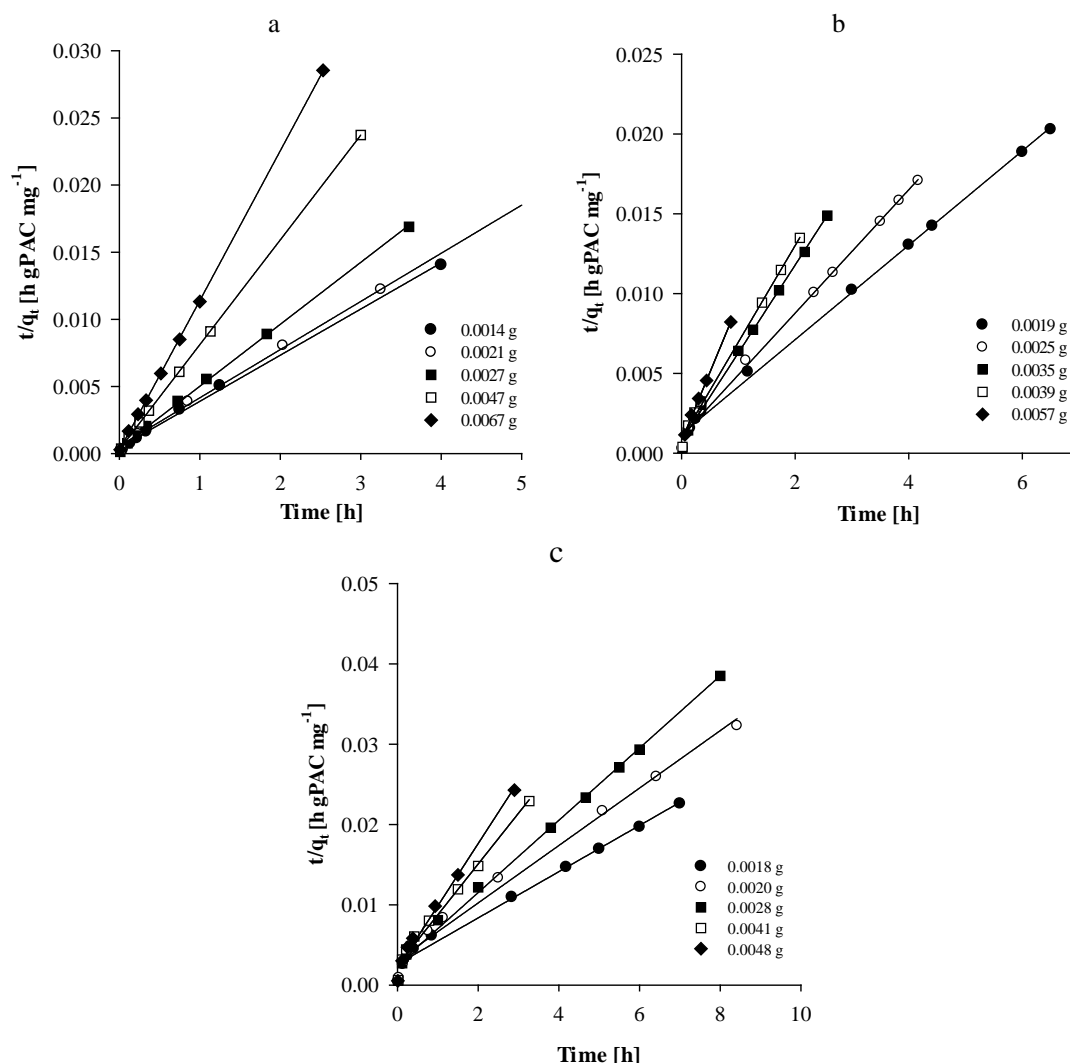


Figure 2. Pseudo second-order adsorption kinetics of methylene blue on different amounts of a) uncolonized; b) 10 day-aged and c) 60 day-aged PAC.

Figures 3a and 3b show the relationship between the values of q_e and k , respectively, and the amount of PAC used in the dynamic tests. Although the adsorption capacity of a material (q_e) is rather evaluated from isotherms obtained by equilibrium studies, some conclusions can be drawn from this kinetic dataset. First, as reported previously [6], the theoretical amount of methylene blue adsorbed per gram of PAC decreases with the augmentation of the adsorbent mass. Second, the q_e values measured for both biological PAC do not seem to be significantly different from those measured for the uncolonized PAC (Fig. 3a). However, this should be confirmed by the corresponding isotherms obtained from equilibrium tests. Third, the maximal q_e value obtained for

uncolonized PAC (i.e., 294 mg g⁻¹) corresponds to the range of values reported for a GAC from equilibrium studies (260-319 mg g⁻¹) [7]. In another study made in equilibrium conditions [8], a q_e of 184 mg g⁻¹ was estimated for PAC.

Dynamic adsorption studies provide data concerning the rate of removal of solutes. The values of k indicate that higher adsorption rates result from the use of higher amounts of PAC (Fig. 3b). By comparison between the k values measured for the lowest quantities of each PAC (0.0014, 0.0019 and 0.0018 for uncolonized, 10 day-aged and 60 day-aged PAC, respectively), the effect of microbial colonization on the adsorption rate of the activated carbon is evident. For comparable amounts of adsorbent material, the 10 day-PAC led always to higher adsorption rates than 60 day-PAC. In fact, the biofilm formed diminishes both the porosity of the material and the number of adsorption sites [9], which can explain the lower adsorption rates.

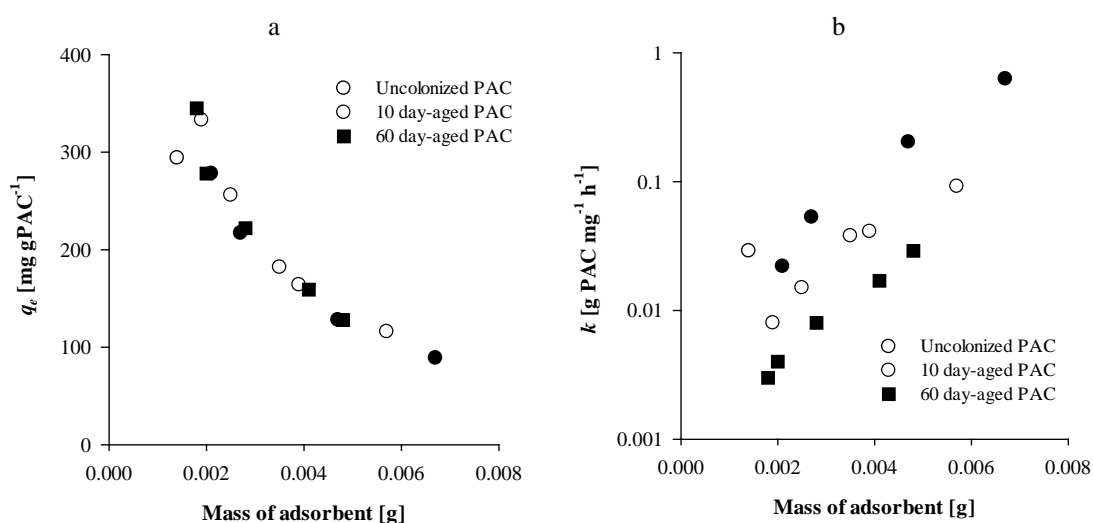


Figure 3. Relationship between the values of the kinetic parameters and the amount of PAC used in the tests. a) q_e (adsorption capacity at the equilibrium) and b) k (pseudo second-order rate constant)

Conclusions

PAC with various sludge ages was studied in terms of adsorption capacity and adsorption rate of methylene blue in dynamic batch tests. A pseudo second-order model allowed to describe the adsorption kinetics. The rate constants demonstrate the effect of the biofilm in the adsorption kinetics, as lower rates were observed for 10 day- and 60 day-aged PAC than for uncolonized PAC. Finally, our results demonstrate that the adsorption mechanism plays a role in the hybrid process even though it is operated at high sludge ages (60 d).

Acknowledgements

The authors owe special thanks to the technical staff of the NSERC Industrial Chair on Drinking Water of the École Polytechnique de Montréal for assistance with laboratory work and sample collection.

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