Hes·so
Haute Ecole Spécialisée de Suisse occidentale
Fachhochschule Westschweiz
University of Applied Sciences and Arts Western Switzerland

Master of Science HES-SO in Life Sciences

Design and characterization of a biosorption process

Mathischan Maheswaran

Applied Bioscience

HES-SO Valais

Advisor: Dr. Simon Crelier / Additional advisor: Dr. Gilles Evéquoz / Expert: Dr. Lucie Rivail

CONTEXT

Treatment of wastewater is becoming an increasing concern since environmental issues have become more and more significant. Pollution of water by industries have several adverse effects on plants, animals and microbes which have raised a considerable concern in the scientific community as well as in the public. The heterogeneity of pollutants (dyes, metals, antibiotics, drugs,…) make wastewater treatment very difficult. Conventional treatment technologies exists since many decade, but those methods are expensive and difficult to eliminate after use. Biosorption seems to be an alternative treatment technology. But further understanding of the adsorption steps are needed. Therefore, a focus in the development of a numerical approach was made in this thesis.

OBJECTIVES

The aim of this thesis was to characterize an adsorbent/adsorbate system useful for the design of a numerical approach which will help the determination of external and internal diffusion coefficient.

Using Matlab software and the finite element method, it was possible to solve some partial differential equations (PDEs) composing the homogeneous surface diffusion model (HSDM). HSDM is one of the few diffusion model permitting to determine the limiting step of diffusion.

METHODS

For the characterization of the sorbent/sorbate system (charcoal/tartrazine) isotherm and kinetic studies were conducted. The kinetic studies were done in batch reactor, differential column batch reactor and fixed bed. The obtained results permit to estimated the Freundlich isotherm constants and the film mass transfer coefficient k_f with Worch approach. With the k_f coefficient it was possible to calculate the surface diffusion coefficient Ds using a numerical approach.

The numerical approach was designed in Matlab using the finite element method (FEM). This method was developed to solve the partial differential equations of the selected diffusion model, the homogeneous surface diffusion model. Those equations describe the intraparticle diffusion but also the mass balance equation and the average adsorption amount.

Intraparticle diffusion: $\frac{\partial q}{\partial t} = \frac{D_s}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial q}{dr}\right)$ mass balance: $q_t = \frac{V}{m_A}\left(C_o - C(t)\right)$

Average adsorption amount: $\frac{3}{{R_p}^3}\int_0^{R_p} r^2 q dr$

The FEM gives an approximate solution to the PDEs which means that the application of this approach will five an approximate representation of the experimental curve.

The first stage of FEM consists in the conversion of the PDEs into ordinary differential equations and the transformation of the auxiliary conditions (boundary condition(s) and initial condition(s)) into a discrete system of algebraic equations. Usually, this step is called discretization.

And the second stage implicate the resolution of the algebraic equations system to obtain an approximate solution to the original partial differential equation.

RESULTS

The film mass transfer $\mathbf{k_f}$ was obtained with two different approaches both presented in *adsorption technology in water treatment* by Eckhard Worch. Here are the values for the GAC fraction 6 for different flow rates:

C_0 [kg/m³]	Q [ml/min]	Q [m³/s]	dq_t/dt [(kg/kg)/s]	ρ_p[kg/m³]	r_p [m]	k_f [m/s]
0.053	4.5	7.50E-08	1.18E-05	1166	1.04E-04	1.20E-05
0.051	11.5	1.92E-07	1.19E-05	1166	1.04E-04	1.53E-05
0.052	42	7.00E-07	1.44E-05	1166	1.04E-04	1.87E-05
0.052	90	1.50E-06	1.76E-05	1166	1.04E-04	2.03E-05

After validation of the finite element method algorithm in Matlab, it was possible to determine the surface diffusion coefficient $\mathbf{D_s}$. Here are the values obtained for the GAC fraction 6 for different flow rates:

Flow rate [ml/min]	4.5 ml/min	11.5 ml/min	42 ml/min	90 ml/min
k_f [m/s]	1.20e-5	1.53e-5	1.87e-5	2.03e-5
D_s [m²/s]	1.28e-14	1.43e-14	1.74e-14	2.02e-14

The surface diffusion coefficient was obtained by comparing the experiment values with the values obtained by the algorithm. Statistical technique, sum of squares was used to determine the closest numerical value for $\mathbf{D_s}$. Here a graphic illustrating the experimental points and the simulated curve:

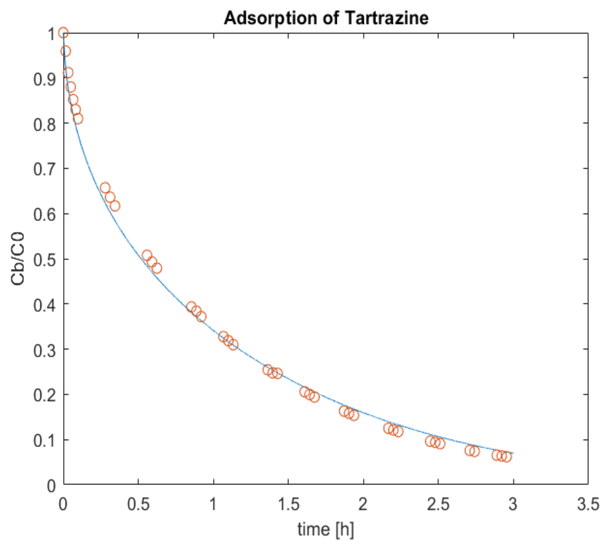

Figure 2: Comparison of Matlab modelization with experimental value – rp = 1.03e-4 m, k_f = 2.03e-5, D_s=2.02e-14, V=0.100 L, m = 163.46 mg, C0=51.725 mg/L, rhop = 1166 g/L, n = 7.26, K_F = 53.52 K_F [(mg/g_{GAC})*(g/L)$^{-1/n}$], Q = 90 ml/min

The obtain values for k_f and D_s can be compared with existing value with a similar sorbent/sorbate system. Choy et al.

Coefficient	Acid Yellow 117	Acid Blue 80	Acid Red 114
k_f [m/s]	5.043e-6	2.972e-6	2.524e-6
D_s [m²/s]	8.02e-15	4.68e-15	4.72e-15

Worch has explained that the typical range of surface diffusion coefficients for GAC was situated between 10^{-11} m²/s for small molecules and 10^{-15} m²/s for larger molecules. Both experimental value and choy et al. value were in between the range.

CONCLUSION

The data acquired through batch reactor, DCBR and fixed bed have allowed to understand the sorbent/sorbate model and to use it on the numerical development. It has permitted to design a numerical method which allowed to determine the surface diffusion coefficient Ds and to have a deeper understanding of the different diffusion steps in model system. It was decided to use the homogeneous surface diffusion model (HSDM) for the numerical approach since many papers working with GAC and similar size molecule sorbate were already working with this model. But alternatively, the pore volume diffusion model (PVDM) can be a greater model for smaller size molecule sorbate.
The finite element method (FEM) algorithm was used for lab scale experiment and it was validated with lab scale experiment. Pearl, a French company working with wastewater and adsorption was contacted to obtain some lab scale and industrial scale data to compare both information with the simulation obtained by the algorithm, but no answer was obtained. Ideally a comparison with the simulated data and the real industrial data could help determine the specificity of the algorithm.
The simulation software can be improved by solving the partial differential equations for a fixed bed which will help design adsorption curve for fixed bed. And it can be interesting to conduct supplementary experimentation in fixed bed setting for different column height to observe a longer breakthrough point.