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Modeling and Simulation of Organic Compounds Adsorption Process in Brazilian Oil Shale

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Abstract

The high cost of commercial active carbon has motivated the study of new adsorbents materials with the aim to reduce costs of the residuary waters treatment by means of adsorption process. Among then, the pyrolyzed oil shale has demonstrated adsorbents characteristic and has been studied as adsorbent material for organic and inorganic pollutants. In oil refineries, before deciding for the implantation of a new alternative, it must be assured which will be the operational limits of the proposal technology. In this context, the present work proposes the modeling and simulation of organic composites adsorption process in Brazilian oil shale with HSDM model by considering the adsorbent systems hydraulic behavior. The results indicate that is possible to use the oil shale adsorbent in the wastewater treatment containing composed organic and the accomplished simulation had good adherence to the real data.

Keywords: HSDM Model, Modeling and Simulation, Brazilian Oil Shale.

1. Introduction

The research for new adsorbent materials has contributed for the new uses of residues, potentially polluting agents, aggregating value to these residues and reducing the cost of adsorbent used in the industrial wastewaters treatment. Among then, the oil shale has demonstrated adsorbents characteristic and has

been studied as adsorbent material for organic and inorganic pollutants [1,2]. A similar residue is the by-product of oil shale generated in the pyrolysis of oil shale, known commercially as SIX/PETROBRAS process. This residue has been also investigated as organic substances adsorbent [3].

2. Problem Statement Background

The planning, project, adaptation and operation of wastewater treatment systems involve time and considerable financial resources. In oil refineries, before deciding for the implantation of a new alternative of wastewater treatment, it must be assured which will be the operational limits (real pollutants reduction) of the proposal technology.
In these conditions, this work studies the use of low cost adsorbent materials, in substitution to the commercial active carbon. For that, a mathematical model (HSDM Homogeneous Surface Diffusion Model) is developed to simulate the organic compositions adsorption process considering the hydraulic behavior of the system. This behavior is based on the Continuous-Stirred Tank Reactor Equations (CSTR).

3. Paper approach

3.1. Methodology

Equilibrium and kinetic modeling of adsorption: The design of continuous adsorbent process requires proper mathematical representation of the target contaminant adsorbed on the adsorbent at equilibrium. The Freundlich model (Eq.1) was used to describe the equilibrium relationship between aqueous and surface concentration of an adsorbate on adsorbents.

$$q = KC^{\frac{1}{n}} \tag{1}$$

in which C is the liquid-phase concentration of the target contaminant, q is the target contaminant solid-phase concentration in equilibrium. K and n are the system Freundlich constants. These constants also indicate the system adsorption capacity and intensity, respectively.
The description of the adsorption process is given by a Homogeneous Surface Diffusion Model (HSDM). The originally HSDM was developed for the granular active carbon adsorption process simulation, and later it was adapted to use with powdered active carbon [4,5].
The HSDM consists of a tree-step-process: (i) the adsorbate diffuses through a stagmant liquid film layer surrounding the adsorbent particle; (ii) the adsorbate adsorbs from the liquid phase onto the other surface of the adsorbent particle. In this process, instantaneous equilibrium is assumed between the adsorbate

liquid-phase concentration at the interface C and its solid phase concentration at the interface q; (iii) the adsorbate diffuses along the inner surface of the adsorbent particles until it reaches its adsorption sites. In this work, we consider that the adsorption process was not affected by the film diffusion [6]. So the HSDM with no film diffusion is used in the CSTR model, Eq.2, which is numerically solved using the following initial and boundary conditions (Eq.3-5).

$$\frac{\partial q}{\partial t} = D_s\left(\frac{\partial^2 q}{\partial r^2} + \frac{2}{r}\frac{\partial q}{\partial r}\right) \quad (2) \qquad t = 0,\ 0 \le r \le R,\ q = 0 \quad (3)$$

$$r = 0,\ t \ge 0,\ \frac{\partial q}{\partial r} = 0 \quad (4) \qquad r = R, q = K = C_{ef}^{\frac{1}{n}} \quad (5)$$

Eq.2 describes the change rate of surface concentration q with time t at any distance r from the center of adsorbent particle during adsorption [7]. The surface diffusion coefficient D_s represents the diffusion rate of the target compound along the adsorbent surface.

Continuous-Stirred Tank Reactor model: Crank e Skelland [7] solved Eq.2 for a constant boundary condition and developed a nonlinear equation for the total mass of adsorbate present on the surface of a unit weight of adsorbent q_t for a specific contact time t. With no film diffusion limitation, this nonlinear equation can be generalized into a nondimensional equation (Eq.6)[8].

$$\gamma = \frac{q_t}{q_{\inf}} = 1 - \frac{6}{\pi^2}\sum_{i=1}^{\infty}\left\{\frac{1}{i^2(1+\pi^2 i^2 \lambda)}\right\} \quad (6)$$

in which q_{inf} is the mass adsorbed per mass of adsorbent in contact with that concentration solution long enough for equilibrium to be reached. $\lambda = tDs / R^2$ is a nondimensional parameter. The nondimensional Eq.6 can be used to describe the steady-state performance of a CSTR for any combination of physical parameters (q_t and R), equilibrium parameters (K and n) and kinetic surface diffusion coefficient D_s. The Freundlich equation (Eq.1) can be used to calculate the value of q_{inf} ($q_{inf} = q$). The plots of γ versus λ allow evaluating the adsorbent efficiency in continuous process. For a constant diffusion coefficient and adsorbent particle size, λ is a parameter representing the contact time in treatment process. The value of γ represents the efficient of the process considering the full capacity of the adsorbent that is an important variable for the simulation.

The infinite series in Eq.6 converge rapidly within the first three to five terms to a finite value [5]. A more complex procedure is commonly involved in estimating the value of D_s. This approach uses a numerical optimization technique to determine the value of diffusion coefficient that minimizes the error between measured data (from laboratorial test) and calculated data (using

the HSDM solution). In this study, the Eq.6 expansion is limited to 10 terms as given by Eq. 7.

$$\gamma = \frac{q_t}{q_\infty} = 1 - \frac{6}{\pi^2}\left[\left\{\frac{1}{1^2(1+\pi^2 1^2 \lambda)}\right\} + \left\{\frac{1}{2^2(1+\pi^2 2^2 \lambda)}\right\} + \ldots + \left\{\frac{1}{10^2(1+\pi^2 10^2 \lambda)}\right\}\right] \qquad (7)$$

For each point in the data batch, all parameter values are known except D_s. So for each adsorbent material, an interactive procedure is accomplished for D_s computation. The optimization algorithm was implemented in the LINGO® (2001) software running on a Pentium 4, 2.4 GHz, 1GB RAM personal computer.

3.2. Experimental arrangement

Adsorbent material: The adsorbents used in this study were obtained from SIX/PETROBRAS: (OS) Oil Shale; (POS) Pyrolyzed Oil Shale (by-product of SIX process); (TOS) pyrolyzed Oil Shale with Tire dosage (about 5%) and PAC (Powdered Activated Carbon).

Synthetic Wastewater: The synthetics wastewater used in this study are prepared by diluting with stock solution of analytical reagent grade. The organic adsorbate are: (MB) Methylene Blue dye, (RB) Reactive Blue 5G dye e (Ph) Phenol. The adsorbates size is similar to the organic composites size found in oil refineries. For the adsorption tests the ranges of concentrations prepared from stock solution varied between the values: MB = 2-60mg/L; RB= 2-30mg/L; Ph = 2-30mg/L.

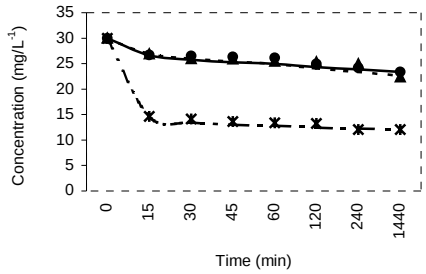
Adsorption equilibrium and Kinetics: Adsorption equilibrium experiments were conducted using 50 mL of synthetic wastewater in flasks. The adsorbent concentration varied from 0 to 1 g/L. The flasks are shaken continuously for 24 h at 125.64×10^{-1} rad/s (120 rpm) at 25 ºC. The measurement of concentration had been made in a Shimadzu UV – Visible spectrophotometer UV-Cary50. The adsorption kinetics batch experiments were carried out using 1L of synthetic wastewater at 25 ºC. The adsorbent doses varied from 0 to 10 g/L. The stirring speed was maintained at 125.64x10-1 rad/s (120 rpm). The samples were mixed with adsorbent and the amount of adsorption was determined for different contact times.

3.3. Results and discussions

Adsorption equilibrium and Kinetic: The constants K and n of the Freundlich model (Eq.1) are shown in table 1. The determined Diffusion coefficient (Eq.7) obtained from adsorption kinetics batch experiments for CSTR are listen in table 1. The simulation results of CSTR reactor are show in figure 1.

Table 1 – Constants adsorption equilibrium and kinetics results

(Adsorbate)Adsorbent	Freundlich Model		D_s 10^{-7} ($cm^2.min^{-1}$)
	K $(mg/g)(L/mg)^n$	n	
(MB)OS	24.90	6.98	2.266
(MB)POS	5.82	4.41	0.095
(MB)TOS	5.89	5.36	0.624
(MB)PAC	24.01	1.91	0.892
(RB)POS	0.63	2.49	1.560
(RB)TOS	0.58	3.44	0.764
(RB)PAC	10.08	3.15	0.054
(Ph)POS	0.13	2.11	1.648
(Ph)TOS	0.10	1.72	1.533
(Ph)PAC	36.96	3.05	1.232



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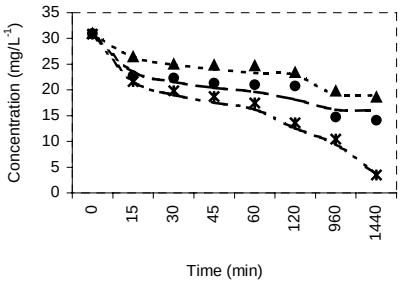

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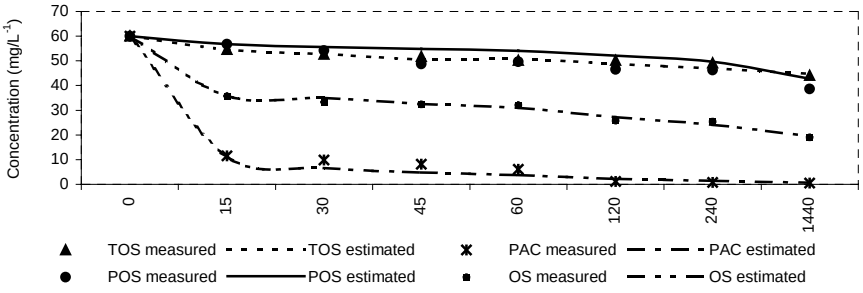

(c)

Figure 1 – Validation of the HSDM: (a) Reactive Blue Dye; (b) Phenol; (c) Methylene Blue Dye

The table 1 shows that the oil shale adsorbents (OS, POS, TOS) have a good adsorption capacity. The OS material doesn't present important adsorption for RB and Ph. In many real adsorption systems is necessary a short contact time due to need the processing of great wastewater volumes. The diffusion (D_s) coefficient presents important information about the necessary time to remove the adsorbate from the aqueous solution. It can be verified in the table 1 that the

oil shale adsorbents (OS, POS, TOS) had excellent performance, resulting sometimes in better diffusion coefficients than PAC. The figure 1 presents simulated and real data, demonstrating the good quality of the model. The simulation depends on D_s that were obtained with the optimization algorithm.

4. Conclusions

The adsorption and kinetic results validate the use of these materials adsorbents in the wastewater treatment with pollutant organic. The mathematical model combining a HSDM model with the hydraulic behavior based on CSTR model has been presented good properties when compared with the experimental data. Simulation software is under development based on this mathematical model. This tool can support the implantation of wastewater treatment units in oil refineries. Specially, those use the oil shale as adsorbent material in the adsorption process. Other alternatives models are under investigated and can be improve the simulation software.

5. Acknowledgements

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6. References

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