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2-D Simulation of the Catalytic Dechlorination of P-Chlorophenol in a Magnetically Stabilized Fluidized Bed

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2-D SIMULATION OF THE CATALYTIC DECHLORINATION OF *P*-CHLOROPHENOL IN A MAGNETICALLY STABILIZED FLUIDIZED BED

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ABSTRACT

This study adopted the fundamentals of the catalytic dechlorination of *p*-chlorophenol in a MSFB column, technology developed by Graham (3). A CFD-DPM approach is used to simulate the catalytic process (7). The code is validated by comparison with the experimental results, considering the *p*-chlorophenol removal and the particle catalyst deactivation.

INTRODUCTION

The rate at which we are increasing pollution is greater than the rate of recovery. The actual world is responsible for cleaning up polluted waters and soils of the past while preventing further pollution and environmental deterioration. Chlorinated organics in the form of pesticides, pharmaceutics, solvents, and dielectric fluids have been released from industrial, commercial, and agricultural activities. Unfortunately, most of them end up in soils and underground waters that we use for crops and as drinking water, (5).

This research, start with the basic study at lab scale, of the clean up of a *p*-chlorophenol contaminated soil using a Magnetically Stabilized Fluidization Bed (MSFB) as a catalytic reactor. An illustration of the reaction mechanism proposed for this process is shown in Figure 1. On the catalyst surface, chlorine is replaced by hydrogen, producing two products phenol and chlorine, (3)

Figure 2 shows a schematic representation of the experimental apparatus used at laboratory scale. Experimental data from a MSFB reactor, were obtained under the following conditions: ferromagnetic particles (nominal diameter: ~2 [mm]) were composite particles prepared with sodium alginate and Pd/Fe catalyst powder. In average, the alginate beads consist of 88% alginate (1.5% algin, 98.5% dionized water) and 12% catalyst with 0.188 Pd/Fe [w/w%]. Magnetic susceptibility: 0.2548. Particle average density: 1.173 [kg/m^3]. Minimum fluidization velocity: 0.0104 [m/s]. The experimental samples were collected from the slurry phase and analyzed in a

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HPLC, (3).

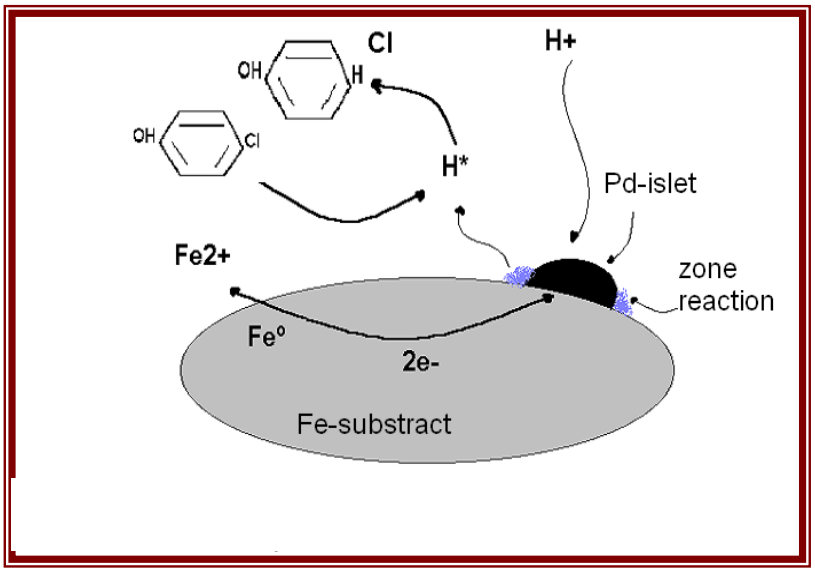

Figure 1. Multistep Dechlorination Reaction on the Pd/Fe Catalyst Surface

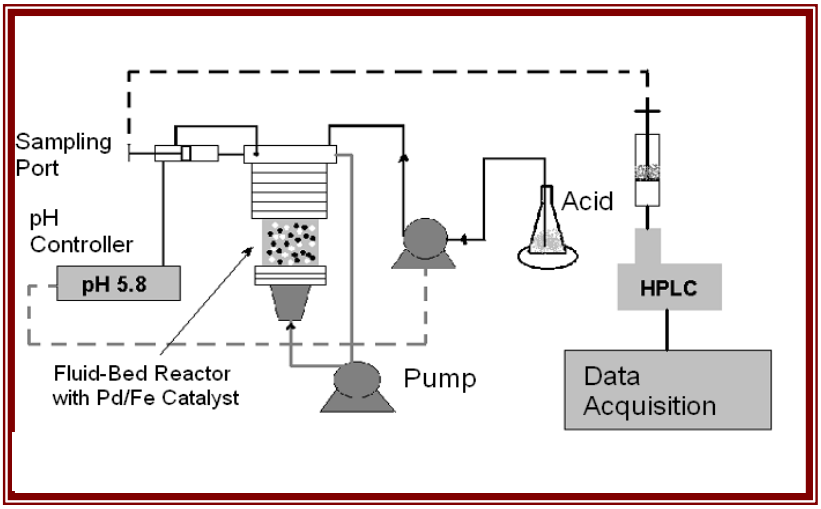

Figure 2. MSFB Experimental Apparatus

METHODOLOGY

To perform the dechlorination simulation, it is necessary to modify the AZTECA® code, (7),(2),(6). Besides of the Navier-Stokes equations and Newton second law of motion, which describes momentum of fluid and particles respectively, the heterogeneous catalytic reaction should be considered as follows, (5):

The pseudo-first order rate with respect to the chlorinated hydrocarbon (*p*-

chlorophenol) concentration was found to be the most appropriate kinetic model; these equations describe the mass transfer phenomena of the process, (1).

$$-\frac{d(VC_A)}{dt} = (kW)C_A a = k^* C_A a \tag{1}$$

$$-\frac{da}{dt} = k_d a^n \tag{2}$$

To account for the passivation effects on the Pd/Fe surface, an activity term, a, is integrated into the reaction kinetics as shown above. This term accounts for the decrease in catalyst activity caused by the loss of active sites. Numerical solution of the partial differential equations for *p*-chlorophenol diffusion trough alginate beads with entrapped Pd/Fe catalyst and the respective boundary conditions implemented are described below, (3).

$$\frac{\partial C_l(r,t)}{\partial t} = D_e\left(\frac{\partial^2 C_l(r,t)}{\partial r^2} + \frac{2}{r}\frac{\partial C_l(r,t)}{\partial r}\right) - \frac{k^*}{V}C_l(r,t)(a)^n \tag{3}$$

$$\varepsilon V\frac{dC_b(t)}{dt} = -\varepsilon V k_l a\left[C_b(t) - \frac{C_l(R,t)}{K_b}\right] \tag{4}$$

Initial conditions:

$$C_l(r, t=0) = C_{l,0} \tag{5}$$

$$C_b(t=0) = C_{b.0} \tag{6}$$

Boundary conditions:

$$\left.\frac{\partial C_l(r,t)}{\partial r}\right|_{r=0} = 0 \tag{7}$$

$$D_e\left.\frac{\partial C_l(r,t)}{\partial r}\right|_{r=R} = k_l\left[C_b(t) - \frac{C_l(r,t)}{K_b}\right]_{r=R} \tag{8}$$

Calculation of *p*-chlorophenol aqueous diffusivity will be made by an approximation considering a D_{AB} of a known compound with molecular weight of similar structure; this approximation is represented by Schwarzenbach *et al* (8).

$$\frac{D_{AB,\text{p-chlorophenol}}}{D_{AB,\text{Phenol}}} = \left(\frac{molecular\_weight_{\text{Phenol}}}{molecular\_weight_{\text{p-chlorophenol}}}\right)^{0.5} \tag{9}$$

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RESULTS

In Figure 3, it is shown the magnetic field applied to the MSFB reactor used during the dechlorination process, (4).

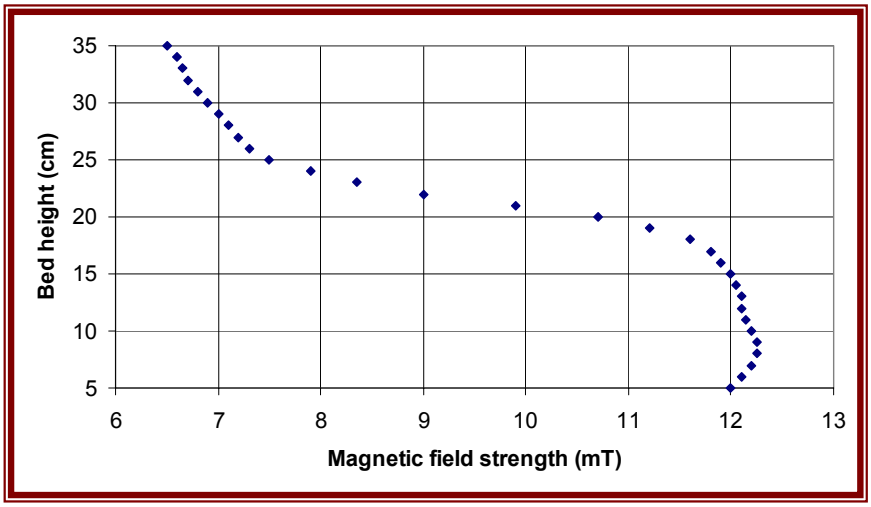

Figure 3. Magnetic Field Applied to MSFB dechlorination process

Table 1 shows a comparison of experimental and simulated constants used in dechlorination process. Such constants were evaluated at similar conditions used during the experimental run, (3).

Table 1. Comparison of determined constants

Constants	Experimental data	Calculated data
De [m²/s]	10.876E-10	8.2E-10
k [m³/s-kg(catalyst)]	0.021	0.021
kd [1/s]	2.292E-04	2.3E-04
*k** [m³/s]	1.386E-04	1.386E-04
Kd [moles/kg(soil)/ moles/L(solution)]	1.08792	1.12
kl [m/s]	1.215475E-04	1.3E-05

In Figure 4, the simulated results are compared with the experimental. Quantitatively, the simulated result shows an excellent agreement with the experimental ones. The *p*-Chorophenol concentration drops approximately 58 %, in the experimental data and about 50 % with simulation; which is a reasonable approximation.

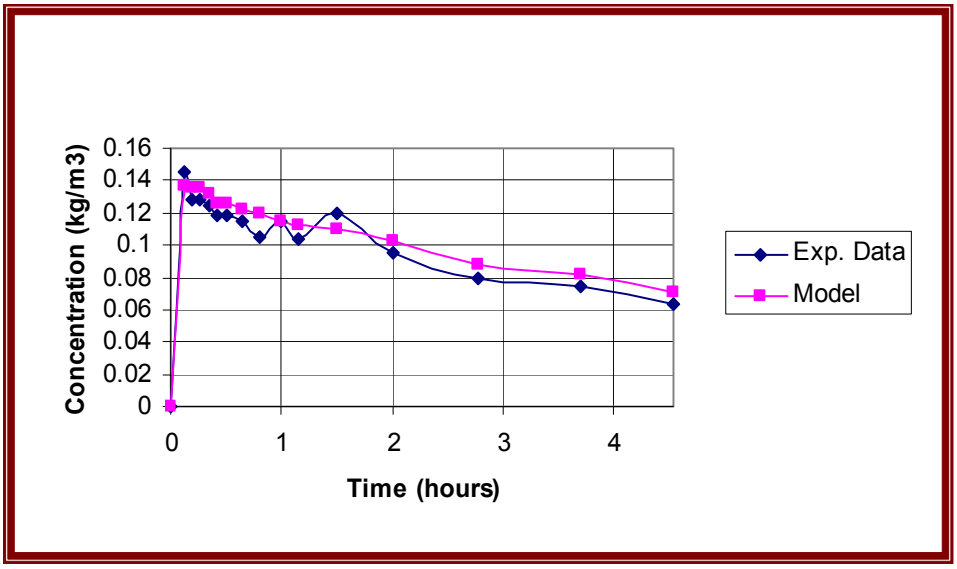

Figure 4. *p*-Chlorophenol dechlorination in a MSFB reactor

The modified AZTECA® code allows tracking the *p*-chlorophenol consumption, the average fluid velocity, particle position, particle activity decaying, average voidage and column pressure drop. The simulated data is storages in a binary file and then opened using a Visual Basic interface code named BOLITAS®, (7). The AZTECA® code was developed following the SAFIRE code procedure in a 2-D environment, (6).

CONCLUSIONS

The software has been validated by comparing the simulated data with the experimental ones, as shown in Table 1 and Figure 4. The only significant discrepancy found is in the mass transfer coefficient, *kl*, however it was due to a printing error, (3). The experimental results have proven that the dechlorination process has a promising future. Although, there is not enough experimental data, more evidences will be collected using this software at different operative conditions. The magnetic field generated enhanced a better column stabilization which allows working at higher flow rate without catalyst dragging. Some experiments are on the way, at simulation level, to determine more evidences about the magnetic field contribution in a MSFB reactor on the dechlorination process.

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NOTATION

ε	Reactor voidage in magnetically stabilized fluidized bed (H≠0), [-]
a	Catalyst activity [-]
C_A	Concentration of *p*-chlorophenol, mol/m^3
C_b	Bulk concentration, mol/m^3
C_l	Alginate bead liquid concentration, mol/m^3
D_e	Effective diffusion coefficient for p-chlorophenol in alginate beads, m^2/s
k	Reaction rate coefficient for p-chlorophenol dechlorination, m^3/kg$_{catalyst}$s
k^*	Reaction rate coefficient for *p*-chlorophenol dechlorination, m^3/s
K_b	Gel solid-water distribution ratio, mol/kg bead/(mol/L H_2O)
k_d	Deactivation rate coefficient for H_2 (g) passivation, 1/s
k_l	Liquid-solid mass transfer coefficient in MSFB (H≠0),m/s
n	Deactivation order
r	Bead radius, m
t	Time, s
V	Volume of reactor liquid, m^3
W	Weight of catalyst Pd, kg

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