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Dechlorination of Polychlorinated Phenols on Bimetallic Pd/Fe Catalyst in a Magnetically Stabilized Fluidized Bed

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Abstract

Dechlorination of 2,4,6-trichlorophenol was performed within a magnetically stabilized fluidized bed (MSFB), containing a palladized iron (Pd/Fe) catalyst entrapped within alginate beads. Kinetic parameters of this multistep reaction yielding phenol as a final product were preliminarily defined in a batch system using four different intermediates as substrates for Pd/Fe catalyzed dechlorination. Further work using the fluidized bed reactor provided the basis for mathematical description of the full dechlorination process both with and without the assistance of an applied magnetic field. The resulting model includes convective mass transfer in the bulk media, diffusion within the alginate beads and reaction kinetics, including catalyst deactivation caused by passivation. Very good agreement was observed between experimental data and predictions of the model. These results confirmed the benefit of using MSFB reactors for more efficient dechlorination of toxic polychlorinated phenols, as compared to fluidized bed reactors without magnetic field stabilization.

Keywords: catalytic dechlorination, Pd/Fe catalyst, magnetic field, fluidized bed, polychlorophenol

1. Introduction

Chlorinated phenols (CPs) are commonly used in industry, mainly as chemical intermediates in chemical and pharmaceutical production, in dyes, as biocides, insecticides, herbicides, and wood preservatives. They have been detected in water, soil, and air resulting from misuse, accidental spillage, and improper disposal [1]. The effect of these compounds on the environment is of great concern because of their resistance to degradation, as well as due to genotoxicity, mutagenicity, carcinogenicity, and histopathological alterations in humans and animals [2]. Several chlorinated phenols are included in the U.S. Environmental Protection Agency Toxic and Priority Pollutants List [3, 4], as well as in the EU list of dangerous substances [2]. Furthermore, they were classified as priority 3 among carcinogenic and/or genotoxic food environmental contaminants in Belgium [5].

Several technologies have been proposed for elimination of chlorinated phenols from water and soil, including conventional processes such as adsorption, ion exchange, liquid-liquid extraction, and more novel methods such as thermal photocatalysis, degradation. advanced chemical oxidations. well as as biodegradations by various microorganisms [6-8 and refs. therein]. However, reductive methods have emerged as advantageous for remediation of polychlorinated biphenyls and chlorinated phenols due to lower energy consumption, minimized formation of noxious byproducts, and better remediation efficiency [8-10 and refs. therein]. In recent years, hydrodechlorination methods, both catalytic and electrocatalytic involving various metal catalysts, have received attention as very promising technologies innovative [8-11 and refs. therein]. Catalytic hydrodechlorination with H₂ and Fe-based reductive dechlorination were found effective for remediation of a wide range of compounds, including chlorinated organics [10 and refs. therein]. A Pd/Fe catalytic system, where Pd effectively dissociates zero valent iron-generated H₂ for dechlorination, has gained much attention since it is highly reactive and because it can be implemented in a number of ways, including palladized iron wire, Pd impregnated iron particles including nanoparticles, microparticles, alginate-entrapped catalyst, and palladized iron plates [10,12-17]. Recently, magnetically recoverable PdCoB bimetallic catalyst was employed in the dechlorination of 4-chlorophenol (4-CP), 2,4-dichlorophenol (2,4-DCP) and 2,4,6-trichlorophenol (2,4,6-TCP) [8].

A general mechanism of multi-step dechlorination of CPs by corrosion of a Pd/Fe catalyst in the presence of water is shown in Fig. 1 and is summarized in the overall dechlorination reaction process as [14-17]:

$$Fe^{0} + R-CI + H^{+} \rightarrow R-H + Fe^{2+} + CI^{-}$$



Fig. 1. a) Dechlorination reaction mechanism on the Pd/Fe catalyst and mechanisms

involved in catalyst deactivation by b) the formation of an $Fe(OH)_2$ layer and c) H_2 bubble formation.

Three types of chemical reactions are involved in the dechlorination reaction process on the surface of the Pd/Fe catalyst [14-17]. The first type comprises various surface reactions which include the dissolution of iron from the zero-valent state and the consumption of hydrogen ion on both the iron and palladium surfaces as represented by Eqs. 2 - 4. The second type are solution phase ionization reactions as described by Eqs. 5 and 6. The abundance of hydrogen ion, H^+ , is controlled by the balance between its formation in solution and its consumption by Fe⁰ to form H₂(g) or by Pd to form the intermediate reactive hydrogen, H*. Hydrodechlorination is the third type of reaction resulting in chlorine removal from the phenolic substrate, (Eq. 7), which presumably involves several consecutive reaction steps. The electrons freed in the iron dissolution reaction are used at the palladium surface to form the highly reactive intermediate, H*, which is consumed in the dechlorination reaction. Similar reactions have been described for 2,4,6-TCP dechlorination using Pd/Fe catalyst in the form of nanoparticles [9].

Surface Reactions:

| $Fe^0 \rightarrow Fe^{2+} + 2e^{-}$ | 2 |
|-------------------------------------|---|
|-------------------------------------|---|

 $2H^{+} + 2e^{-} \xrightarrow{Fe} H_{2}(g)$ 3

 $H^+ + e^- \xrightarrow{P_d} H^*$ 4

Solution Reactions:

$$H_2O \rightarrow H^+ + OH^-$$
 5

$$HCI \rightarrow H^+ + CI^-$$
 6

Dechlorination Reaction:

$$2H^{2} + R-CI \rightarrow R-H + HCI$$
 7

Several other reactions can take place simultaneously in the reaction volume. Of particular interest is the formation of insoluble $Fe(OH)_2$ from Fe^{2+} and OH^- at pH higher than 6, while the formation of $Fe(OH)_3$ can take place at even lower pH if oxygen is present in the system. Deposition of $Fe(OH)_2$, $Fe(OH)_3$, and formation of hydrogen bubbles (Eq. 3) occur on the surface of the catalyst during the dechlorination reaction. These products passivate the Pd/Fe interface where the dechlorination reaction takes place, thus effectively deactivating the Pd/Fe catalyst as shown in Fig. 1b and 1c. The deactivation mechanism is dependent on pH of the reaction mixture and dissolved O₂ concentration and can be controlled by adjusting pH in a deoxygenated reaction mixture [14-17].

While first reports on Pd/Fe catalyst-promoted hydrodehalogenation of CPs considered mono-chlorophenols [12,14,16,17], dechlorination of polychlorophenols over this bimetallic catalyst has been gaining recent attention. Kinetic studies of the dechlorination of 4-chlorophenol (4-CP), 2,4-dichlorophenol (2,4-DCP), and 2,4,6-trichlorophenol (2,4,6-TCP) with Pd/Fe nanoparticles [8, 9] and with PdCoB nanoparticles [8] have been published.

Most studies on dechlorination processes consider batch processing. As a promising alternative, a continuously operated microreactor system made of two

parallel palladized iron plates was reported for 4-CP dechlorination which enabled very efficient treatment of aqueous solutions [17]. On the other hand, for continuous treatment of contaminated soil or sludge slurries containing solid particles, employment of a magnetically stabilized fluidized bed (MSFB) reactor containing alginate beads with Pd/Fe catalyst was suggested [14,16]. MSFB reactors employ magnetic field gradients to augment gravity via the imposition of a supplementary body force on magnetically susceptible fluidized particles (beads), thus allowing higher fluid velocities to be achieved for a given degree of fluidization.

The interaction between gradient magnetic field and magnetically susceptible particles, and the interactions among magnetized fluidized particles can produce several benefits in the operation of the MSFB. It can improve homogeneity of the fluidized bed by stabilizing and extending the range of particulate fluidization versus less efficient bubbling bed fluidization. The presence of the magnetic field gradient in the fluidized bed reactor results in an increased convective mass transfer due to higher relative velocities between sludge and catalyst beads. It also prevents elutriation of beads, which are often close to neutral buoyancy, thus enabling the use of smaller beads and/or higher fluidization in the reactor. Deployment of smaller beads is reducing diffusion limitations within the beads containing catalyst powder [14,16]. In the studies of 4-CP removal from soil, the MSFB reactor was demonstrated as an excellent engineering solution which can be implemented in a variety of catalytic and non-catalytic liquid-solid reaction processes [14,16]. Magnetic-field assistance was recently reported to be beneficial also for agglomerate bubbling fluidization of various nanoparticles where decreased minimum fluidization velocity and increased bed expansion together with improved homogeneity of mixing were obtained in an MSFB as compared with a traditional fluidized bed without magnetic field application [18].

In the present study, a freshly prepared Pd/Fe catalyst was entrapped in Ca²⁺ crosslinked Na-alginate beads and used within the MSFB reactor, enabling a continuous 2,4,6-TCP dechlorination process. The kinetics of Pd/Fe catalyst-promoted 4-CP, 2,4-DCP, 2,6-DCP and 2,4,6-TCP dechlorination processes was preliminarily studied in a batch system in order to obtain kinetic parameters for each individual reaction step. Subsequent experiments were conducted to examine 2,4,6-TCP dechlorination reactions within an MSFB using alginate beads with entrapped Pd/Fe catalyst. The resulting data were employed to evaluate a detailed mathematical model of the MSFB-assisted dechlorination process, by accounting for mass transfer in the bulk solution (convection), transport within the alginate beads with the catalyst (diffusion), and hydrodehalogenation reaction kinetics including catalyst deactivation.

2. Mathematical Model

2.1 Determination of Reaction Rate Constants in Dechlorination of 2,4,6-TCP

The rate of chlorinated hydrocarbon (denoted as A) dechlorination on powder Pd/Fe catalyst is related to the concentration of A, C_A , concentration of H*, C_{H^*} , and reaction rate coefficient, k', which is proportional to the amount of catalyst, W, as indicated in the mass balance shown in Eq. 8 [14-17]. At constant pH, the production of H* at the surface of the palladium catalyst, as indicated by the surface reaction (Eq. 4), was assumed to be constant. With this assumption one can consolidate C_{H^*} with k' to obtain the reaction rate constant expressed per amount of catalyst, k, which combined with W yields the overall reaction rate constant k''.

$$-\frac{d(VC_A)}{dt} = k'WC_AC_{H^*} = kWC_A = k''C_A$$

Since iron dissolution byproducts $Fe(OH)_2$, $Fe(OH)_3$, and hydrogen bubbles formed on the surface of Pd/Fe catalyst may increase the resistance to the overall dechlorination reaction process, an activity term, *a*, was incorporated into Eq.8 to account for the deactivation process (Eq.9). This term describes the decrease in catalyst activity by loss of dechlorination sites [14,16,17]

$$-\frac{d(VC_A)}{dt} = k''C_A a$$

The activity of the Pd/Fe catalyst may be described as an nth order expression (Eq.10) [19].

$$-\frac{da}{dt} = k_d a^n$$
 10

A second-order deactivation process was reported for 4-CP dechlorination with Pd/Fe catalyst on the surface of a microchannel system [17], while first order catalyst deactivation described 4-CP dechlorination within Pd/Fe entrapped alginate beads [14-16].

The proposed reaction scheme for 2,4,6-TCP (designated as species 1 in mathematical descriptions) dechlorination on the Pd/Fe catalyst is schematically represented in Fig. 2 as a multistep reaction where phenol is the final product [8, 9, 15]. Intermediates such as 2,4-DCP, 2,6-DCP, 4-CP, and 2-CP and final product phenol, denominated as species 2, 3, 4, 5, and 6, respectively, are formed and subsequently dechlorinated at catalyst sites.



Fig. 2. Schematic illustration of the multi-step dechlorination of 2,4,6-TCP on Pd/Fe catalyst.

The kinetic form shown in Eq. 9 can represent dechlorination rate equations of all above-mentioned compounds in this multiple reaction scheme. Therefore, mass balance equations for each component in a batch process are

$$-\frac{d(VC_1)}{dt} = (k_1" + k_2") C_1 a$$
 11

$$-\frac{d(VC_2)}{dt} = (k_3" + k_4")C_2 a - k_1"C_1 a$$
12

$$-\frac{d(VC_3)}{dt} = k_5 " C_3 a - k_2 " C_1 a$$
 13

$$-\frac{d(VC_4)}{dt} = k_6 "C_4 a - k_3 "C_2 a$$
 14

$$-\frac{d(VC_5)}{dt} = k_7 " C_5 a - k_4 " C_2 a - k_5 " C_3 a$$
15

$$-\frac{d(VC_6)}{dt} = -k_6 " C_4 a - k_7 " C_5 a$$
 16

where initial conditions for differential equations (11-16) are:

$$C_1(0) = C_{1,0}$$
 and $C_2(0) = C_3(0) = C_4(0) = C_5(0) = C_6(0) = 0$ 17

Simultaneous solution of differential equations (Eqs. 11 through 16) with the appropriate boundary conditions (Eq. 17) considering also catalyst deactivation (Eq. 9, 10) was performed numerically using Mathematica[®] software, while the reaction rate constants ($k_1 - k_7$) and the deactivation rate constant k_d were derived by least squares analysis of data from batch experiments.

2.2 Modeling of 2,4,6-TCP Dechlorination in Alginate Beads with Entrapped Pd/Fe Catalyst

Modeling of the dechlorination process within the catalyst bead was developed based on consideration of transport phenomena in the bulk liquid (convective mass transport) and within the porous beads where diffusion takes place, as well as considering reaction kinetics at catalytic sites within beads [14-16].

A differential mass balance within the liquid phase in the alginate bead is given by:

$$\frac{\partial C_{I}(r,t)}{\partial t} = D_{e} \left(\frac{\partial^{2} C_{I}(r,t)}{\partial r^{2}} + \frac{2}{r} \frac{\partial C_{I}(r,t)}{\partial r} \right) - \frac{k \omega}{V_{bd}'(1-\phi)} C_{I}(r,t) a^{n}$$
18

The initial concentrations in the bead $(C_{l,0})$ and in the bulk liquid $(C_{b,0})$ are

$$C_{l}(r,0) = C_{l,0}$$
 and $C_{b}(0) = C_{b,0}$ 19

The boundary condition at the center of the bead (r=0) is

$$\frac{\partial C_{I}(0,t)}{\partial r} = 0 ; t \ge 0$$

while at the surface of the bead (r = R) the boundary condition is

$$D_{e}(1-\phi)\frac{\partial C_{l}(R,t)}{\partial r} = k_{l}[C_{b}(t) - C_{l}(R,t)]; t \ge 0.$$
²¹

The accumulation of chlorinated compounds in the bulk liquid $(C_b(t))$ depends on the convective mass transfer between the bulk liquid and the surface of particles

$$\frac{dC_{b}(t)}{dt} = -k_{l}\frac{3}{R}\eta \frac{(1-\varepsilon)}{\varepsilon} [C_{b}(t) - C_{l}(R,t)]$$
²²

where η is the *enhancement coefficient*. The enhancement coefficient reflects the efficiency of fluid-bead contacting pattern, which depends on the quality of fluidization attainable in the fluidized bed, with and without an applied magnetic field. At the surface of the alginate beads chlorinated compounds are acted upon by the diffusion mass transfer mechanism (Eq. 21) and carried further into the interior of the bead (Eq. 18).

3. Materials and methods

3.1 Materials

2,4,6-TCP (98%) and 2,6-DCP (99%) were obtained from Alfa Aesar (Ward Hill, MA, USA). 2,4-DCP (99%), 2-CP (\geq 99%) and phenol (98.5%) were purchased from Sigma Aldrich (Saint Louis, MO, USA), while 4-CP (\geq 99%) was obtained from Acros Organics (Geel, Belgium). All of these chlorophenols are solid at room temperature, except 2-CP, which is a liquid.

Iron powder in the size range of 5-8 μ m, hexachloropalladate (K₂PdCl₆), CaCl₂, concentrated HCI solution, HPLC grade acetic acid and HPLC grade methanol were obtained from Sigma Aldrich (Saint Louis, MO, USA). Sodium alginate (Algin, Keltone HV) was donated by Kelco Company (San Diego, CA, USA). Witconol SN70 non-ionic surfactant, a linear alcohol ethoxylate ([CH₃(CH₂)_x(OCH₂CH₂)₅OH], where x ranges from 10 to 14, with average molecular weight 392 g/mol and specific gravity 0.98 kg/m³), was obtained from Witco (Houston, TX, USA).

3.2 Catalyst preparation

The iron powder was pretreated with 6 M HCl for 5 min, rinsed with deionized water and added to an aqueous solution of hexachloropalladate (K_2PdCl_6) to obtain Pd coverage from 0.17 - 0.75% (w/w), vigorously mixed for 15 min and further rinsed with 50 mL of deionized water according as previously described [14-16].

For the preparation of alginate beads with Pd/Fe catalyst, a 1.5% (w/w) of sodium alginate was mixed with distilled water at room temperature until a homogeneous solution was achieved. The solution was then combined with powdered Pd/Fe catalyst with 0.188% (w/w) Pd, prepared as described above, to give a final catalyst concentration of 17.35% (w/w). The solution was poured into a pressurized vessel and extruded into a 1 M CaCl₂ aqueous solution to form the Ca²⁺ cross-linked gel.

Manipulation of the flow rate of air supplied to the tip of the nozzle and the degree of pressurization of the vessel effectively allowed for control of the bead size. Beads of the nominal diameter of 2.4 mm were used for the experiments described herein.

3.3 Dechlorination Processes in a Batch Reactor System with Pd/Fe Particles

6 g of a micron size Pd/Fe catalyst was suspended in the reaction mixture and vigorously mixed at room temperature. A 200 mL solution of known initial concentration of selected chlorophenol (typically 3.7·10⁻³ M) was added into the batch reactor and vigorously mixed at 300 min⁻¹. This intensity of mixing was sufficient to eliminate the influence of convective mass transfer from the bulk of the reaction mixture to the surface of the catalyst carrier.

To avoid the effect of the formation of iron hydroxide at the catalyst surface, all experiments were run under deoxygenated conditions and at a controlled pH of 5.7. Two supply lines, providing HCl and N₂, were applied to control the pH and maintain a thoroughly deoxygenated environment. Samples were collected at suitable time intervals and centrifuged to separate all microscopic solid particles. Thus, the sample solution was separated from the catalyst particles to prevent further reaction in the sample test tube prior to chemical analysis [15].

3.4. Dechlorination in the MSFB Reactor System with Pd/Fe Particles Entrapped in Alginate Beads

To illustrate the applicability of the MSFB reactor for the dechlorination reaction processes, dechlorination of 2,4,6-TCP was also performed in the fluidized bed reactor both with and without an external magnetic field. An aqueous solution with an initial concentration of $3.7 \cdot 10^{-3}$ M 2,4,6-TCP was recycled through the fluidized bed

reactor system containing 145 g of alginate beads containing 17.35% [w/w] Pd/Fe catalyst. The beads were fluidized in the fluidization column at appropriate liquid flow rates to enable retention of beads within the reactor. The MSFB equipment used in this investigation is schematically shown in Fig. 3. The reactor column was 45 cm high and 3.8 cm wide. Three Helmholtz coils wrapped around the fluidization column generated the gradient magnetic field. Each coil contained three layers of copper wire ($d_{wire} = 1 \text{ mm}$) concentrically wrapped to varying heights providing flexibility in axial magnetic flux densities and magnetic field strengths, which ranged between 0.006 – 0.012 T, and 5,000 – 10,000 A/m, respectively. A Masterflex peristaltic pump with Tygon tubing provided a recirculating flow of the liquid through the fluidized bed. An overflow box facilitated the insertion of the pH probe to control the addition of acid, and flow lines were attached to facilitate pH control and the extraction of samples during experiments. All liquids were initially deoxygenated by N₂, which was also supplied into the holding tank. This effectively prevented air from reaching the recirculating fluid thereby ensuring deoxygenated conditions during the course of each MSFB reactor run [14-16].



Fig. 3. Schematic presentation of the MSFB reactor with Pd/Fe catalyst entrapped in alginate beads.

3.5. Analytical methods

3.5.1 Analysis of Pd/Fe Catalyst

BET surface area of the prepared Pd/Fe particles was measured using a Coulter SA 3100 surface area analyzer. Scanning electron microscope (SEM) images of the acid treated iron particles were taken prior and after palladization using AmRay 3300 Field Emission Scanning Electron Microscope (Amray Inc., Bedford, MA, USA).

3.5.2 Analysis of Aqueous Chlorophenol Solutions

Concentrations of 2,4,6-TCP, 2,4-DCP, 2,6-DCP, 4-CP, 2-CP and phenol in aqueous solutions were determined by isocratic reverse phase High Pressure Liquid Chromatography (HPLC) with a 5-µm reverse-phase LC-8 column (Supelco, Bellefonte, PA, USA) with a mobile phase consisting of 70 vol% acetic acid/methanol solution (1:99 vol%) and 30 vol% acetic acid/deionized water solution (1:99 vol%) at a flow rate of 1.0 mL/min. Absorbance was measured at 254 nm using a UV/VIS detector (Gilson Inc., Middleton, WI, USA) and the concentrations were determined from calibration curves obtained with standard solutions [15].

4. Results and Discussion

4.1. Pd/Fe Catalyst preparation and analysis

The relatively uniform palladization of iron particles is evident from the SEM micrograph of powder catalyst shown in Fig. 4, where nano-size palladium islets rising from the iron support can be easily identified. Previous findings indicated that coverage with 0.188% (w/w) Pd provided good catalytic activity without restricting access of the reactants to the zero-valent iron surface [14, 16]. This catalyst composition was used throughout the dechlorination experiments reported herein.

Based on the analysis of several consecutively prepared samples, BET specific surface area of the Pd/Fe powder catalyst with 0.188% Pd was estimated to be 4.56 m²/g with a relative standard deviation below 18%. This is close to the 5 m²/g value reported for a metallic palladium catalyst used for hydrodehalogenation of 1- to 3- carbon halogenated organic compounds [20]. On the other hand, the specific surface area of Pd/Fe sponge-like particles containing 0.02% Pd prepared for *p*-dichlorobenzene dechlorination was only 0.62 m²/g [21]. Furthermore, Pd/Fe

nanoparticles with 0.03% (w/w) Pd [8] and 0.5% (w/w) Pd [9], which were used for polychlorinated phenol dechlorination, had BET specific surface areas of 13 m²/g [8] and 26 m²/g [9], respectively. This was primarily a consequence of variations in the size of synthesized particles, as well as in Pd loadings which were also confirmed to significantly affect the specific surface area of palladized iron particles [8,12].



Fig. 4. SEM image of Fe particles after HCl treatment and palladization with K₂PdCl₆.

4.2. Dechlorination Processes in the Batch Reactor with Powdered Pd/Fe Catalyst

Initial dechlorination experiments were run in a batch reactor with powdered Pd/Fe catalyst at room temperature (24°C) and at constant pH of 5.7. This pH was shown to be beneficial as compared to lower pH values where the mass transfer resistance due to $H_2(g)$ formation and consequent surface coverage with gas bubbles resulted in catalyst passivation which effectively represent a loss of catalyst activity

[14,16,17]. Due to the addition of HCI solution for pH regulation, as well as sample removal for monitoring of concentrations of all species in the solution, changes of the reaction volume within 3% were observed [15]. In order to increase the relatively low solubility of 2,4,6-TCP and chlorinated intermediates in water, various surfactants were tested in a preliminary study [15], resulting in the use of a 1% (w/w) Witconol SN70 aqueous solution throughout the present work.

The time course of 2,4,6-TCP dechlorination reactions catalyzed by the Pd/Fe powder catalyst shown in Fig. 5 reveals that concentrations of the intermediate compounds, namely 2,4-DCP, 2,6-DCP, 4-CP, and 2-CP, are significantly lower than the concentration of parent 2,4,6-TCP and/or final product phenol for much of the reaction time.



Fig. 5. Time course of 2,4,6-TCP dechlorination performed with Pd/Fe powder catalyst in a batch process. Solid lines represent model simulations based on Eqs. 8-17 with optimized parameters specified in Table 1.

In order to obtain more resolute information for the determination of individual reaction rate constants, separate processes of 2,4-DCP, 2,6-DCP, and 4-CP dechlorination were performed sequentially in the batch reactor under the same conditions. Fig. 6a-c show experimental data together with model simulations using Eqs. 8-17 for each of these batch processes.





Fig. 6. Time course of experimental data and model simulations for batch Pd/Fecatalyzed dechlorination of a) 2,4-DCP, b) 2,6-DCP, and c) 4-CP. Solid lines represent model simulations based on Eqs. 8-17 with optimized parameters specified in Table 1.

As evident from time courses of all dechlorination processes shown in Fig. 5 and Fig. 6 a-c, the kinetics curves derived from model simulations show good agreement with experimental data for both primary substrate and reaction intermediates. The reaction rate constants k_1 through k_7 , and the deactivation rate constant, k_d , were determined by least-squares minimization of the differences between experimental data and predictions resulting from simultaneous solution of model equations relevant for the specific reactions (Eqs. 8-17). All experimental data available were used in this optimization process. A summary of the rate constants obtained by numerical solutions and compared with available literature data is presented in Table 1.

| | | | | | Reference | Refe- |
|-------------------------|----------------------------|-----------------------|---|-------------------------|---|-------|
| | k" | | k | k | k | Tence |
| Constant | (L/min) | Constant | (m ³ /kg _{cat} s) | (L/g _{Pd} min) | (L/g _{Pd} min) | |
| <i>k</i> ₁ " | 0.0137 | <i>k</i> ₁ | 3.81·10 ⁻⁵ | 1.21 | 2.07 | [9] |
| k ₂ " | 0.0095 | k ₂ | 2.64·10 ⁻⁵ | 0.84 | 0 | [9] |
| k ₃ " | 0.015 | k ₃ | 4.17·10 ⁻⁵ | 1.33 | 1.144 | [9] |
| <i>k</i> ₄ " | 0.018 | <i>k</i> 4 | 5.00·10 ⁻⁵ | 1.60 | 1.796 | [9] |
| k ₅ " | 0.0505 | k ₅ | 1.40·10 ⁻⁴ | 4.48 | 0 | [9] |
| k ₆ " | 0.05 | <i>k</i> ₆ | 1.39·10 ⁻⁴ | 4.43 | 9.24 | [9] |
| k ₇ " | 0.0445 | <i>k</i> ₇ | 1.24·10 ⁻⁴ | 3.95 | 4.468 | [9] |
| | | | | | | |
| | k_d (min ⁻¹) | | <i>k_d</i> (s ⁻¹) | | <i>k_d</i> (s ⁻¹) | |
| k _d | 0.0349 | | 5.81·10 ⁻⁴ | | 1.14·10 ⁻⁵ | [17] |

Table 1: Optimized values of rate constants and the deactivation rate constant.

The values of rate constants for dechlorination of 2,6-DCP (k_5), 4-CP (k_6) and 2-CP (k_7) are significantly higher than those for conversion of 2,4,6-TCP (k_1+k_2) and 2,4-DCP (k_3+k_4) which is consistent with the results of 2,4,6-TCP dechlorination with Pd/Fe and various PdCoB nanoparticles, where the order of CPs degradability was 2,4,6-TCP<2,4-DCP<4-CP [8, 9]. The comparison of kinetic constants k_1 with k_2 , as well as k_5 with the sum of k_3 and k_4 indicates that dechlorination at the *ortho* position is faster than at the *para* position of the benzene ring. Hence, the conversion of 2,4,6-TCP to 2,4-DCP is the preferred pathway over the reaction yielding 2,6-DCP. This is in agreement with other studies on 2,4,6-TCP dechlorination using Pd/Fe nanoparticles, where no 2,6-DCP was detected [8, 9]. Comparison of kinetic rate constants of the study of Zhou et al. [9], expressed per amount of Pd catalyst, with parameters obtained within this study (Table 1) indicates very similar results for k_3 , k_4 and k_7 , as well as for the kinetic rate constant of 2,4,6-TCP dechlorination (k_1+k_2), despite the 5.7 times larger specific surface area of the nanoparticles. On the other hand, k_2 , k_5 and k_6 were quite distinct between the two studies. This discrepancy arises because 2,6-DCP was not detected as an intermediate in the 2,4,6-TCP dechlorination processes catalyzed by Pd/Fe nanoparticles [9], while in our study it was present in all consecutive 2,4,6-dechlorination reactions, as evident from Fig. 5. It should be noted that in the study by Zhou et al. [9], significantly different values for a given kinetic rate constant were reported for dechlorination reactions using different starting intermediates. For example, the 4-CP dechlorination rate constant, k_6 , obtained for dechlorination of 2,4,6-TCP, 2,4-DCP and 4-CP as starting reactants yielded values of 1.70, 7.716, and 9.24 L/g_{Pd} min, respectively. In contrast, for the present study the kinetic parameters were uniformly consistent throughout the experiments with all tested chlorinated compounds, as indicated from Fig. 5 and 6 ac, where all simulations were done with the parameters listed in Table 1.

According to previous studies, catalyst deactivation should also be accounted for, since appreciable loss in activity has been observed after extended use of Pd/Fe catalysts [14-17]. The deactivation which results from the loss of catalyst base (i.e., dissolution of Fe into the liquid phase), iron hydroxide precipitation (Fig. 1b), and extensive hydrogen gas bubble formation (Fig. 1c), was introduced into our reaction kinetics model by an activity term (Eqs. 9,10). First and second order rate equations were tested and the latter one, where $a=1/(1+k_dt)$ was found to better fit experimental data. This was also the case in our previous study considering dehalogenation of 4-CP with Pd/Fe catalyst in the microreactor, although the value of deactivation constant k_d obtained in the current study is an order of magnitude higher

than that obtained for palladized iron plates forming a micro-scale reactor [17].

4.3. Dechlorination of 2,4,6-TCP in MSFB Reactor with Pd/Fe Catalyst Entrapped in Alginate Beads

Ambient temperature dechlorination of 2,4,6-TCP was performed using Pd/Fe catalyst entrapped in alginate beads within the fluidized bed reactor, which is schematically shown in Fig. 3. To estimate the influence of the MSFB on process efficiency, dechlorination was performed both with and without energizing the magnetic field. In a conventional fluidized bed (with given fluid and particles), the only available mechanism to increase mass transfer between particles and fluid is to increase fluid velocity. However, the bed readily expands due to the increased fluid velocity, thus causing the bed voidage to increase. As a result, the fluid interstitial velocity, u_{int} , which is the relative velocity between fluidized particles and fluid, does not change appreciably. Bed voidage and fluid velocity essentially unchanged despite the increase in overall fluid throughput. As a consequence, the mass transfer coefficient, k_{l} , which depends strongly on interstitial velocity, will not change appreciably either.

In the MSFB configuration, however, applying an external gradient magnetic field on particles containing ferromagnetic material generates additional forces. The ferromagnetic particles are magnetized whenever the magnetic field is present. The magnetization of particles results in two types of forces acting on fluidized solids; an interparticle (bead-to-bead) magnetic force and an external (field-to-bead) magnetic force. The induced interparticle forces tend to rearrange particle distribution in the bed, and generally reduce the average distance among particles, which results in a decrease of the bed voidage. The application of a non-uniform external magnetic field (gradient magnetic field) generates external magnetic force, which points in the positive direction of the field gradient. Thus, if the field gradient is oriented towards the bottom of the fluidized bed (in the same direction as gravity) the fluid-bead drag force (which is oriented in opposite direction) must be increased to compensate this new macroscopic force, which acts on ferromagnetic particles only [22-24]. Hence, the fluid velocity through the bed must be increased to compensate this new force, if one wants to preserve similar quality of fluidization and the same bed height. Consequently, in the MSFB one can increase the fluid velocity without changing the bed height or voidage, which results in increased interstitial velocity as well as the mass transfer coefficient. Therefore, the application of magnetic field enables substantially higher fluid flow rates while maintaining an equivalent bed expansion and results in more homogeneous distribution of beads within the fluidization column. Interstitial velocities of 0.107 m/s and 0.158 m/s were achieved for the operation of classical fluidized bed and MSFB, respectively; while maintaining the same average bed height (ie. voidage).

Another important collateral benefit from the application of the magnetic field related to interparticle (bead-to-bead) forces is more uniform distribution of beads within the MSFB. In conventional fluidized beds the bypassing between fluid and fluidized particles is a common phenomenon, even in liquid-solid fluidization [25, 26]. The interparticle, bead-to-bead, magnetic forces, which are attractive in the direction of magnetic field lines and repulsive in the orthogonal direction to field lines, tend to destruct the usual architecture of the conventional fluidized beds consisting of regions of higher and lower particle concentration, often referred to as emulsion and fluid bubble phases. The induced bead-to-bead magnetic forces must be *moderate* in

strength (compared to collision forces arising from the kinetic energy of particles) to still allow for random motion of particles and macroscopic homogenous particle distribution in the MSFB. It is well known that very strong magnetic forces can create particle chaining, which ultimately can collapse fluidization regime in MSFB and create a packed bed operation [25-27]. Therefore in a moderately strong magnetic field the contacting pattern between beads and fluid can be enhanced if compared to classic fluidization operation in which agglomeration of particles and bubbling naturally occur. We capture this positive effect of the magnetic field in MSFB by introducing enhancement coefficient, η .

Fig. 7 shows experimental data for 2,4,6,-TCP dechlorinations in the fluidized bed reactor with and without gradient magnetic field application. The benefit of using MSFB to improve reactor efficiency is clearly evident. Model simulations based on Eqs. 18-22 and presented in Fig. 7 show good agreement with experimental data for both processes. The kinetic rate constant *k* employed in the simulations was the sum of k_1 and k_2 as defined in preliminary experiments and stated in Table 1. Values of V'_{bd} , ε , and Φ were determined to equal $1.1 \cdot 10^{-4}$ m³, 0.95 and 0.0341, respectively. Based on previous studies considering MSFB dechlorination reactions [14-16] at various interstitial velocities, the liquid-solid mass transfer coefficient, k_i , was estimated as $1.7 \cdot 10^{-5}$ m/s and $3.4 \cdot 10^{-5}$ m/s for the classical fluidized bed operated at lower flow rates and the MSFB operated at higher flow rates, respectively.



Fig. 7. Experimental data (circles) and model simulations (curves) based on Eqs. 18-22 for fluidized bed dehalogenation of 2,4,6-TCP with or without magnetic field stabilization.

Based on model simulations, the effective diffusivity (D_e) of 2,4,6-TCP within the alginate catalyst carrier was estimated to equal 1.3·10⁻¹¹ m²/s, which is almost 50-times smaller than the value reported for the diffusion coefficient of 2,4,6-TCP in pure water (6.25·10⁻¹⁰ m²/s) [28]. A plausible explanation for the relatively small value of the D_e is the presence of the ethoxylated surfactant employed to facilitate aqueous phase solubility of the substrate at reaction pH. Surfactants in aqueous solution aggregate to form micelles with hydrophobic interiors and hydrophilic exteriors. The affinity of 2,4,6-TCP for the hydrophobic interior of micelles increases the solubility in water, but the diffusivity is reduced because of the large molecular size of the micelle. To the best of our knowledge, no experimental data or correlations have been reported that estimate or predict the diffusion coefficient for this or similar systems.

It should be noted that the mathematical model, which describes the chemical reaction process in the fluidized bed reactor, assumes ideal mixed batch reactor with porous catalyst (Eq. 22). This is somewhat counterintuitive to the construction of the experimental set-up, which consists of a fluidized bed reactor with a total volume of 0.51 L, connected with a stirred tank holding reactor containing more than 75 vol% of the liquid. The analysis of characteristic times, pertinent to all major steps (convection, diffusion, reaction) in this chemical reaction process, was done in order to verify adequateness of this assumption. Comparison of i) the mean residence time, $\tau_L = (V - V'_{bd})/F$, which is 14 or 21 s for the reactor with or without an external magnetic field, respectively, with ii) the characteristic reaction time. $\tau_k = V'_{bd}(1 - \Phi)/(k_1 + k_2)$, which is 266 s, and iii) the *characteristic diffusion time* in the bead, $\tau_D = r^2 / D_e$, which is $1.1 \cdot 10^5$ s, clearly shows that the overall reaction process is limited by diffusional mass transfer inside the beads. Long diffusion time and very short mean residence time within the recirculated system justify the assumption of a batch reactor.

Although the liquid-solid mass transfer coefficient k_l , increased in the MSFB when compared to fluidized bed operation without the magnetic field, the model simulation could not adequately describe the difference in experimental data. However, the introduction of the enhancement factor, η , accounting for the efficiency of fluid-bead contacting in MSFB, resulted in good agreement between mathematical description and the data, as evident from Fig. 7. The value of η derived by least squares analysis of data for MSFB with Eq. 22 using previously stated parameters was 22% higher than for the non-magnetized fluidized bed, confirming better fluid-bead contacting in MSFB.

5. Conclusions

Fluidized bed dechlorination of 2,4,6-trichlorophenol using a palladized zerovalent iron (Pd/Fe) catalyst entrapped within a calcium cross-linked alginate beads has been successfully demonstrated. Comparisons were made between reactor operation with and without augmentation by gradient magnetic field induced forces acting on the ferromagnetic catalyst. The MSFB reactor configuration was found to be beneficial as compared to the process using a fluidized bed without magnetic field assistance. Improved dehalogenation performance within the MSFB is attributed to enhanced mass transfer rates, more efficient fluid-bead contacting and reduced heterogeneity of catalyst carrier particle distributions within the fluidized bed.

Rate constants for dechlorination of 2,4,6-trichlorophenol and reaction intermediates were derived in initial batch reactor experiments. These were incorporated into a numerical model of fluidized bed operation describing mass transfer within the bulk phase (convection), pore diffusion within the catalyst carrier, dehalogenation kinetics, and catalyst deactivation by passivation of the catalytic surfaces. Simulations using the resulting model provided good agreement with experimental results from both MSFB and non-magnetic fluidized bed operations.

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Nomenclature

| а | Catalyst activity [/] |
|-------------------------|--|
| C ₁ | Concentration of 2,4,6-TCP, mol/m ³ |
| C ₂ | Concentration of 2,4-DCP, mol/m ³ |
| C ₃ | Concentration of 2,6-DCP, mol/m ³ |
| C ₄ | Concentration of 4-CP, mol/m ³ |
| C_5 | Concentration of 2-CP, mol/m ³ |
| C_6 | Concentration of phenol, mol/m ³ |
| C _A | Concentration of compound A, mol/m ³ |
| C _{A,0} | Initial concentration of compound A , mol/m ³ |
| C _b | Bulk concentration of 2,4,6-TCP, mol/m ³ |
| C _{b,0} | Initial bulk concentration of 2,4,6-TCP, mol/m ³ |
| C_l | Alginate bead liquid concentration of 2,4,6-TCP, mol/m ³ |
| C _H | Concentration of H^+ in solution, mol/m ³ |
| $C_{H^{\star}}$ | Concentration of H^* (reactive intermediate) in solution, mol/m ³ |
| D _{AB} | Diffusivity of a solute, A, in water, B, m ² /s |
| De | Effective diffusivity for 2,4,6-TCP in alginate beads, m ² /s |
| d_b | Diameter of alginate bead, m |
| k _l | Liquid-solid mass transfer coefficient, m/s |
| k | Dechlorination reaction rate constant based on amount of catalyst, |
| | m ³ /kg _{catalyst} s (L(g _{cat} min) |
| k' | Dechlorination reaction rate constant based on amount of catalyst and |
| | H [*] concentration, m ⁶ /mol kg _{catalyst} s |

Dechlorination reaction rate constant coupled with amount of catalyst, k" m³/s (L/min)

| <i>k</i> ₁ " | Reaction rate constant for dechlorination of 2,4,6-TCP to 2,4-DCP, m^3/s |
|-------------------------|--|
| k ₂ " | Reaction rate constant for dechlorination of 2,4,6-TCP to 2,6-DCP, m^3/s |
| k ₃ " | Reaction rate constant for dechlorination of 2,4DCP to 4-CP, m ³ /s |
| <i>k</i> ₄ " | Reaction rate constant for dechlorination of 2,4-DCP to 2-CP, m^3/s |
| k ₅ " | Reaction rate constant for dechlorination of 2,6-DCP to 2-CP, m^3/s |
| <i>k</i> ₆ " | Reaction rate constant for dechlorination of 4-CP to phenol, m ³ /s |
| <i>k</i> ₇ " | Reaction rate constant for dechlorination of 2-CP to phenol, m ³ /s |
| k _d | Deactivation rate constant, s ⁻¹ |
| n | Deactivation rate order |
| r | Bead radius, m |
| t | Time, s |
| и | Linear fluid velocity, m/s |
| U _{int} | Interstitial velocity, m/s |
| V | Volume of reactor liquid, m ³ |
| V ₀ | Initial volume of reactor liquid, m ³ |
| V' _{bd} | Total volume of alginate beads in a reactor, m ³ |
| W | Weight of a Pd/Fe catalyst, g |
| | |

Greek symbols

| Е | Reactor voidage in a fluidized bed [/] |
|-----------|--|
| Φ | Fraction of gel solid within the alginate bead [/] |
| η | Enhancement factor accounting for better fluid-bead contacting in MSFB |
| | [/] |
| $	au_{D}$ | Diffusion time, s |
| τ_k | Reaction time, s |

 τ_L Mean residence time, s

Abbreviations

| 2-CP | 2-chorophenol (o-chlorophenol) |
|-----------|--------------------------------|
| 4-CP | 4-chorophenol (p-chlorophenol) |
| 2,4-DCP | 2,4-dichlorophenol |
| 2,6-DCP | 2,6-dichlorophenol |
| 2,4,6-TCP | 2,4,6-trichlorophenol |
| CP | chlorophenol |
| | |

MSFB magnetically stabilized fluidized bed

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