



Modeling the effects of methanol on iron dechlorination of a complex chlorinated NAPL

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ABSTRACT

Research was conducted to examine the effects of various fractions of cosolvent solutions on dechlorination of toxaphene by zero-valent iron (Fe^0). Experimental results showed that toxaphene degradation in solution was found to be the result of dechlorination at the Fe^0 surface. The rate of toxaphene dechlorination was also found to reduce with the increase of cosolvent in solution, as the cosolvent presence caused a reduction in toxaphene adsorption to Fe^0 surfaces. Toxaphene sorption to Fe^0 was found to correspond to a Freundlich nonlinear sorption equation and indicated that the linearity of this isotherm in the presence of cosolvent was related to the saturation of solution, which was the ratio of aqueous concentration to the solubility (C_a/S_c). When $C_a/S_c > 0.2$, the sorption isotherm was almost linear and the concept of cosolvency power can be applied mathematically to describe this process. A mathematical model detailing the sorption and dechlorination of toxaphene by Fe^0 was developed, and showed that experimental data agreed with the theoretically derived data. Overall, results indicated that dechlorination of complex chlorinated substances, such as toxaphene, by Fe^0 can be greatly dependent upon adsorption to the iron surface.

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1. Introduction

Cosolvent flushing utilizing chemicals such as methanol and ethanol has been shown to provide rapid mass removal of various chlorinated contaminants by dissolution and/or mobilization from their contaminated zone [1–4]. Once extracted, management of the highly concentrated chlorinated contaminants becomes a concern. Iron treatment has been used widely in the reductive dechlorination of many chlorinated contaminants [5,6]. Many studies have utilized iron treatment as field scale test with permeable reactive barriers (PRB) or with pump-and-treat technologies, and have shown its effectiveness in treating chlorinated contaminant waste [5].

The present research was conducted to examine potential combination of these two technologies: cosolvent flushing, to provide rapid mass removal by solubilization of toxaphene, a chlorinated DNAPL pesticide; and iron treatment, for effective treatment of the chlorinated waste solution by dechlorination post-flushing. Simultaneously, however, the ability of DNAPLs to be adsorbed to iron surfaces will likely be reduced by presence of cosolvents [6], which should cause a decrease in the degradation rate [6,7]. Therefore, the levels to which cosolvent fractions will affect not only the sorp-

tion of toxaphene to the iron surface, but also, its degradation by the iron requires further exploration, including modeling of the system. Reports on the kinetic modeling of the process involving sorption and dechlorination were limited, however, Burris et al. [8] developed a sorption and reduction kinetics modeling approach for dechlorination of trichloroethylene (TCE) and tetrachloroethylene (PCE) with zero-valent iron. In reality, though, most complex chlorinated chemicals present as hazardous waste contain thousands of possible structures, such as toxaphene, DDD or DDT. Therefore, it is necessary to develop a kinetics modeling approach to better explain the combined sorption and dechlorination process with respect to complex chlorinated chemicals.

Overall, this research examined: (1) the sorption isotherm of toxaphene onto zero-valent iron surfaces; (2) the variability of toxaphene sorption to iron as a function of cosolvent presence in solution; and (3) the development and testing of a kinetic model which described the process involving both sorption and dechlorination.

2. Materials and methods

2.1. Chemicals and materials

The once widely used pesticide named toxaphene has been found to be harmful if contacted with skin, toxic if swallowed, and irritating to the respiratory system if inhaled [9]. A complex

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mixture comprised of at least 2300 closely related polychlorinated compounds, toxaphene has shown the potential to cause long-term adverse effects in the aquatic environment and related food chain [10], including a hydrolytic half-life of 10 years in water with pH ranging from 5 to 8 [9]. Further, toxaphene can persist at anywhere from 1 to 14 years [9] when released into soil.

Technical grade pure toxaphene was obtained from Ultra-Scientific Inc., Lot# 302-1258 (North Kingstown, RI, US). Reagent-grade chemicals used including DI water, *n*-hexane, and methanol (MeOH) were obtained from Fisher Scientific Co. (Pittsburgh, PA, US) at purity >99%. Zero-valent iron (Fe⁰) metal powder was also obtained from Fisher Scientific Co. (Pittsburgh, PA, US).

2.2. Solubility

Solubility of toxaphene in methanol solution was analyzed by placing 5 mg of pure toxaphene into 5 mL empty vials with Teflon-coated, septum-lined caps. Various methanol fractions from 0% to 25%, in triplicate, were added to the vials leaving no headspace. Methanol and water were measured separately and combined to avoid volume change due to volume shrinkage during mixing. The solutions were placed on a rotator for 48 h at room temperature because preliminary tests showed that this time was sufficient for equilibrium to be reached in the batch systems [4]. Preliminary analysis also showed that volatilization was negligible. For analysis, the samples were extracted with hexane and, subsequently, >95% of the toxaphene was found to partition into the hexane extracted phase.

2.3. Dechlorination experimentation

Individually sealed batch reactor experiments were performed over 1-week intervals to evaluate dechlorination efficiency of toxaphene in aqueous solutions contacted with zero-valent iron (Fe⁰). Each batch reactor was prepared in a 5 mL glass vial fitted with a Teflon-lined septa screw-top cap. Initially, the empty vials were weighed, and following addition of iron substrates, the vials were reweighed. The vials were then filled with aqueous toxaphene solutions, allowing no headspace, and reweighed. A mass of 1.25 g of Fe⁰ was added to each of 5 mL vials for a 4:1 volume to mass ratio used in previous work [5,11]. Methanol at various volume fractions from 10% to 100%, and varied initial toxaphene concentrations from 2 to 100 µg/mL were added to the vials. All samples were run in triplicate. The vials were rotated (40 rpm) for various times up to a week and individual sample sets were removed at set intervals.

Toxaphene mass in the vials was evaluated into two parts, concentration in aqueous phase, C_a (mg/(L mL)⁻¹), and the concentration adsorbed by iron, C_s (mg/kg). Aqueous solution was separated from iron and extracted by hexane for GC analysis to obtain the value of C_a . Methanol was added to the batch reactor vials for 12 h to desorb residual toxaphene from the iron. In preliminary experimentation, this time was shown to permit only negligible toxaphene dechlorination on the iron surface while sufficient enough time to desorb toxaphene from the iron in the presence of methanol. The contents representing the sorbed phase concentration were then transferred to 0.5 mL vial insert for analysis.

2.4. Sample analysis

Two surrogates (decachlorobiphenyl and tetrachloro-*m*-xylene) were added to all samples prior to extraction by hexane, including the calibration standards, the QC samples, and the samples. The aqueous phase samples were analyzed by a GC-17A Shimadzu (Columbia, MD, US) gas chromatograph with an electron capture

detector (GC-ECD). Toxaphene's complexity produces a wide GC spectral area output indicative of a complex elution output, therefore, a total area approach which integrates output peak over the entire elution time was used for measuring the toxaphene in solution, similar to previous research [12–14]. Operating condition for the GC-ECD included a DB-5 column with 30 m length and 0.32 mm i.d. and the carrier gas was H₂. Injector temperature was set at 220 °C and detector temperature at 300 °C.

Chloride ion presence was analyzed in the batch systems before and after contact with the various substrates. The presence of chloride ions in the aqueous system was used as evidence of dechlorination of toxaphene in a solution. This analysis was conducted with a high-performance liquid chromatograph (HPLC) equipped with an IonPac AS4A-SC analytical column, utilizing an eluent 1.8 mM Na₂CO₃/1.7 mM NaHCO₃ solution at 2.0 mL/min, and a regenerant solution of 50 mN H₂SO₄ solution at 5 mL/min.

3. Results and discussion

3.1. Cosolvent effect on solubility

Analysis of the surrogates indicated the recoveries of the toxaphene were higher than 92% by GC-ECD analyses. Experimental results displayed a log-linear relationship for solubility of toxaphene in a methanol-water system, similar to what was described by Li and Yalkowsky [15]:

$$\log(S_{s,m}) = \log(S_{s,w}) + \beta\sigma f_c \quad (1)$$

where $S_{s,m}$ and $S_{s,w}$ represented the solubility of toxaphene in cosolvent solution and water (mg/L), respectively, and f_c represented the volume fraction of methanol. Previous research indicated that the slope of this log-linear relationship, or product of β and σ , was 3.43; in which β depicted the solvent-water interaction and σ represented the cosolvency power [3,4]. Addition of methanol increased the solubility of toxaphene in water, which mirrored results gathered from experimental methods and estimated from theoretical log-linear and extended log-linear equations seen in the literature [3,4]. This slope was dominated by the cosolvency power of methanol related to toxaphene since β values were ≈ 1 , and validated the assumption that solvent-water interaction is negligible for the methanol-water system.

3.2. Cosolvent effect on sorption

Due to the complexity of toxaphene's chemical structure, a non-linear Freundlich sorption equation was applied to study toxaphene sorption isotherm to Fe⁰:

$$C_s = K_f C_a^n \quad (2)$$

where n represented the linearity power, K_f is the Freundlich coefficient, and C_s and C_a are toxaphene concentrations in the solid and aqueous phases (mg/L), respectively. Fig. 1 shows the instance of 50% methanol cosolvent solution with 15 ppm toxaphene concentration.

Bouchard [16] suggested that linearity of sorption isotherm is related to the saturation of solution (C_a/S_c), in which S_c represented solubility of toxaphene in solution (mg/L) for this research. Results indicated that when the value of C_a/S_c was higher than 0.2, the linearity power was nearly 1 (Fig. 2), which was consistent with observations in previous research [17]. Based on having the same initial concentration of toxaphene in solution, the linearity of sorption isotherm was noted to reduce with increase of cosolvent fraction. The nonlinearity of the toxaphene absorption to the Fe⁰ surface in the presence of higher cosolvent fractions can

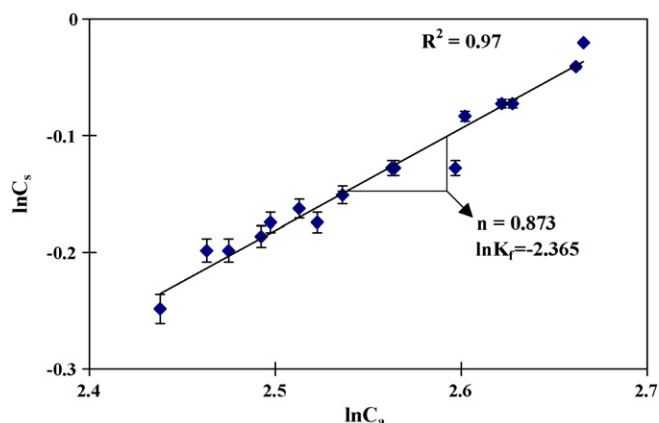


Fig. 1. Sorption isotherm of 50% methanol with 15 ppm initial toxaphene concentration.

be attributed to the decrease in marginal adsorption energy with increasing related surface concentration saturation [16].

Results also showed that the presence of cosolvent increased the toxaphene aqueous solubility as it concurrently reduced its sorption to the iron surface, similar to previous research [5,6]. With K_f values displaying values of $n \approx 1$, the concept of cosolvency power [18] was applied mathematically to describe the effect of cosolvents on toxaphene adsorption to the Fe^0 surface:

$$\log K_f = -\beta \delta f_c + \log K_{f,0} \quad (3)$$

where $K_{f,0}$ represented the value of Freundlich coefficient of toxaphene on iron surface in water. Analysis of various methanol fractions in aqueous solution resulted in a cosolvent power for toxaphene of 3.45, which was consistent with the value of 3.43 gathered from solubility testing; furthermore, $K_{f,0}$ was found to be 0.58 from extrapolation. These results indicated, as expected, that increased methanol fractions increase aqueous solubility of toxaphene while hindering its adsorption to Fe^0 .

3.3. Cosolvent effects on dechlorination (Model I)

In the study of toxaphene dechlorination when contacted with Fe^0 , Clark et al. [11] reported the following relationship, which will be referred to as Model I:

$$\frac{C_T}{C_{T0}} = t^{-k_1} \quad (4)$$

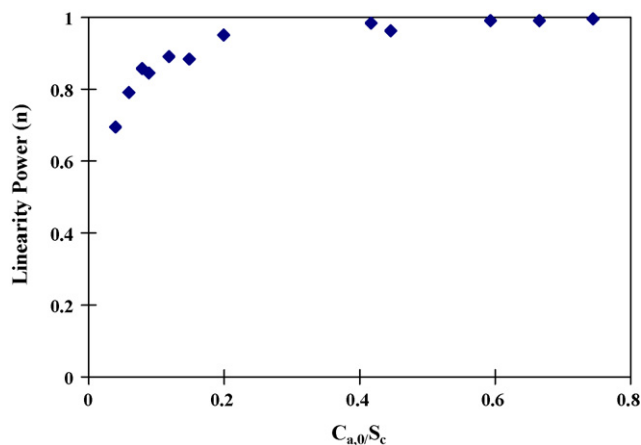


Fig. 2. Linearity of sorption isotherm to the C_a/S_c , which is changed with initial concentration of toxaphene and cosolvent fraction in solution.

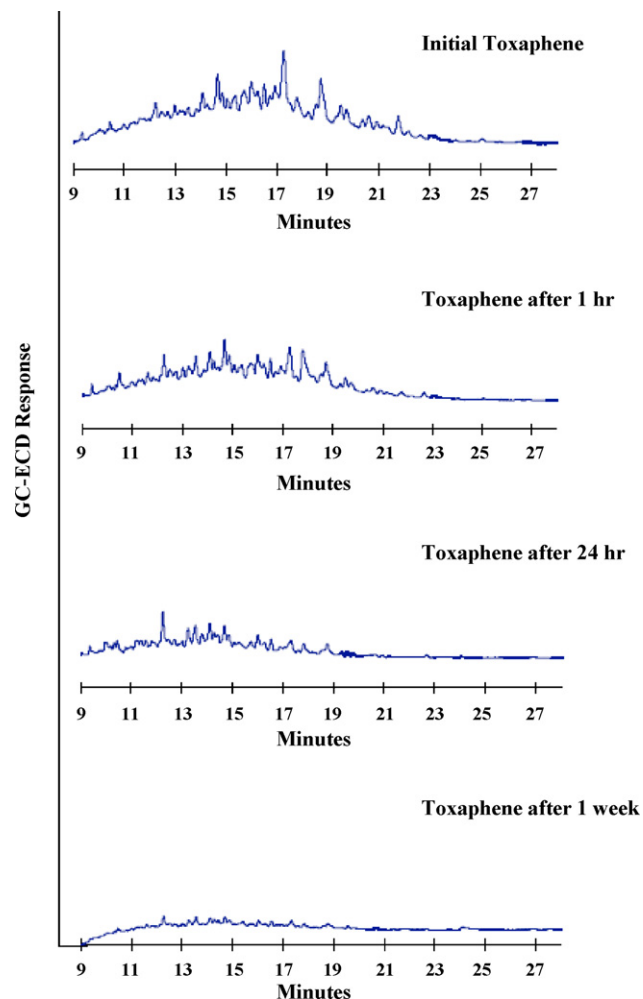


Fig. 3. GC-ECD chromatograms of toxaphene dechlorination by zero-valent iron with different time periods.

where C_T/C_{T0} represented toxaphene relative concentration over time (t), as a function of the dechlorination reaction rate (k_1). Change in the GC-ECD chromatograms' peak distribution indicated that as toxaphene contact time with Fe^0 increased, overall peak area of toxaphene decreased while later eluting peaks decreased or disappeared (Fig. 3). Work by Howdeshell and Hites [19] suggested that this phenomenon occurred because the higher molecular weight components of toxaphene dechlorinated into lower weight components over time. To determine if dechlorination occurred, further analyses were conducted and the presence of chloride in the aqueous solution was found to increase over experimental run time until equilibrium was reached (Fig. 4). The increase of chloride ion in solution as contact time increased indicated that it was being produced as the overall amount of toxaphene was decreased in solution.

Based on the experimentally derived degradation rates (k_1), half-lives for toxaphene in batch tests were calculated to be from 7 h to 120 days. These half-lives showed a vast acceleration in toxaphene degradation compared with the aerobic degradation of toxaphene in soil, half-life up to 14 years [20] and anaerobic biodegradation technology with half-lives between 1 and several months [12].

In Model I, toxaphene dechlorination rate, k_1 , was found to have an overall linear relationship with methanol fraction in solution (Fig. 5) and the existence of the cosolvent reduced the rate

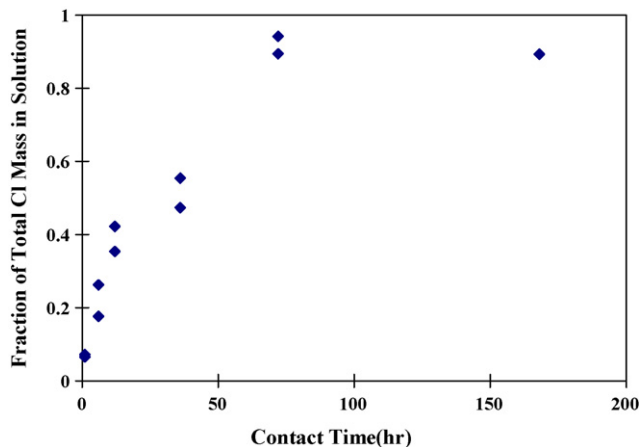


Fig. 4. Presence of total Cl mass found in aqueous solution as a function of toxaphene contact time with Fe⁰.

of dechlorination. The suppressed adsorption led to a decrease in toxaphene dechlorination rates for various initial toxaphene concentrations in solution (Fig. 5). This phenomenon suggested that sorption to Fe⁰ surface is the controlling factor for toxaphene dechlorination, which was also observed in previous research with many other smaller chlorinated contaminants, TCE and PCE, in the presence of cosolvents [6,7].

3.4. Cosolvent effects on adsorption and dechlorination (Model II)

Model I was an empirical equation, and, therefore, can only obtain values of toxaphene concentration in the total system. To study the change of toxaphene concentration in aqueous phase, a second model (Model II) was evaluated based on the reaction and sorption equations instituted in this research. Complexity of the reaction mechanisms involved in toxaphene dechlorination with Fe⁰ and the nonlinearity of experimental data describing toxaphene degradation was found to be best described using the following equation from Burris et al. [8]:

$$\frac{dC_T}{dt} = -k_T C_T^{N_T} \tag{5}$$

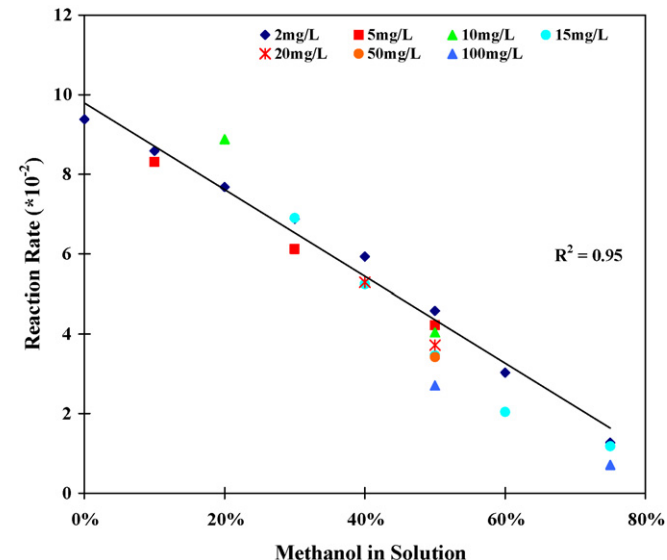


Fig. 5. Toxaphene degradation rate as functions of methanol fraction under different initial toxaphene concentration C₀.

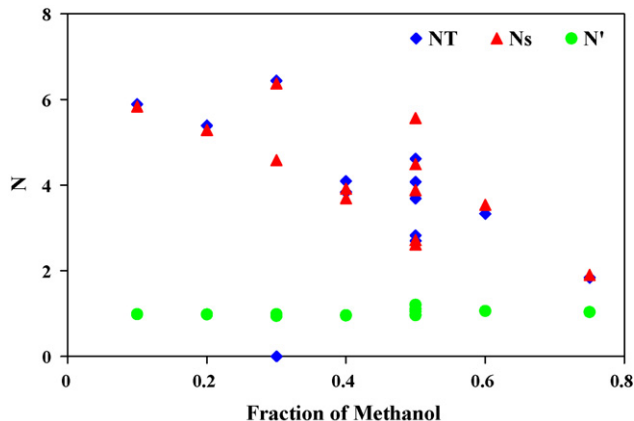


Fig. 6. Exponents of the equations as function of methanol in solution.

where C_T represented the toxaphene concentration in total system, k_T, its reaction rate constant, and N_T, the reaction order. Burris et al. [8] used this relationship to analyze PCE and TCE degradation rate with iron treatment. When N_T equals 1, the reaction is a pseudo first-order reaction, which was observed in the dechlorination reaction of PCE [11]. Integrating Eq. (5) and employing initial total toxaphene concentration (C_{T0}) yielded the following relationship:

$$C_T = C_{T0} \exp(-k_T t) \text{ for } N_T = 1 \tag{6}$$

$$C_T = (at + C_{T0}^{1/b})^b \text{ for } N_T \neq 1 \tag{7}$$

where, a = (N_T - 1)k_T and b = 1/(1 - N_T). Results indicated that the N_T, or reaction order, was higher than 1 (Fig. 6) as a function of the complexity of the toxaphene dechlorination reaction on iron surface. This complexity may be mostly attributed to the varying mixtures that constitute toxaphene and the removal of chlorides from various positions within its bicyclic, polychlorinated configuration.

It was assumed that solid phase dechlorination dominated the overall toxaphene dechlorination, as stipulated by previous research [6]. To take into account the change of solid phase concentration C_s, the following equation was applied to include losses of concentration due to degradation, sorption, and desorption:

$$\frac{dC_s}{dt} = -k_s C_s^{N_s} - \alpha_1 C_s + \alpha_2 C_a \tag{8}$$

where k_s was the reaction rate constant, N_s represented the reaction order, and α₁ and α₂ represented the sorption and desorption rate coefficients, respectively. In addition, the change in concentration in the aqueous phase was a function of toxaphene transport to the solid surface:

$$\frac{dC_a}{dt} = \alpha_1 C_s - \alpha_2 C_a \tag{9}$$

Combining Eqs. (8) and (9) resulted in the following relationship:

$$\frac{dC_s}{dt} = -k_s C_s^{N_s} - \frac{dC_a}{dt} \tag{10}$$

Since the overall mass balance for toxaphene in the batch reactors can be expressed by the equation:

$$C_T = C_a + C_s \tag{11}$$

Eq. (10) can be expressed as

$$\frac{dC_T}{dt} = -k_s C_s^{N_s} \tag{12}$$

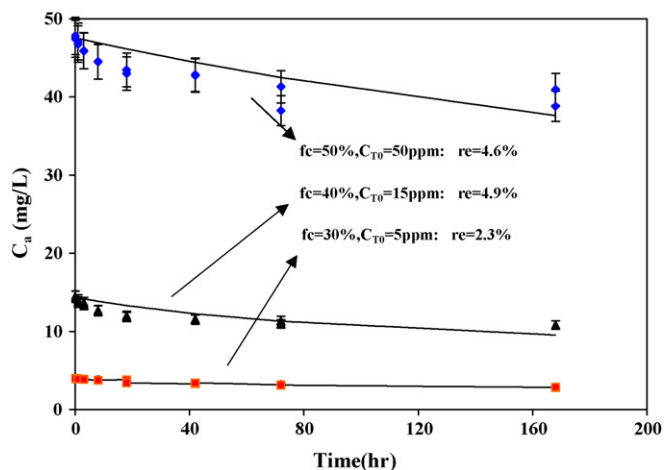


Fig. 7. Comparison of experimental data and Model II kinetic results (average relative error <5%).

Relating Eqs. (5) and (12), provides the following relationship:

$$\frac{dC_T}{dt} = -k_T C_T^{N_T} = -k_S C_S^{N_S} \quad (13)$$

which can be transformed to

$$C_S = k' C_T^{N'} \quad (14)$$

where k' and N' are defined as the reaction rate and order on the solid phase which represented $k' = (k_T/k_S)^{1/N_S}$ and $N' = N_T/N_S$. The values of k' and N' were derived from the linearized form of Eq. (14):

$$\ln(C_S) = N' \ln C_T + \ln(k') \quad (15)$$

which allowed for the value of N_S to be derived. Combining Eqs. (7) and (14), the sorption isotherm equation with coefficients derived from kinetic data can be expressed as (Model II):

$$C_S = k'(at + C_{T0}^{1/b})^{bN'} \quad (16)$$

$$C_a = (at + C_{T0}^{1/b})^b - k'(at + C_{T0}^{1/b})^{bN'} \quad (17)$$

The discrepancy between the Model II data predictions and the experimentally derived data was evaluated using the relative root mean squared error, rRMSE, which weights relative errors in predictions equally throughout the range of observed values:

$$rRMSE = \left[\frac{1}{n} \sum_{l=1}^n \left(\frac{p_l - \hat{p}_l}{p_l} \right)^2 \right]^{1/2} \quad (18)$$

A comparison of C_a derived from Model II with the experimental data indicated that the average relative errors were <4.9%, and the average relative errors for C_T were <5.2%. Fig. 7 displays the correspondence of the toxaphene experimental data to the data gathered from Model II analysis of the toxaphene degradation. The agreement between the experimental and modeled data in Fig. 7 supports the validity of the assumption that the sorption of toxaphene to the Fe⁰ surface was the crucial determining factor in toxaphene degradation.

Fig. 6 shows the comparison the power values of N_S , N_T , and N' with different methanol fractions. The results indicated that both N_S and N_T reduced with the increase of methanol fraction, which can be attributed to the fact that the addition of methanol reduced the adsorption of toxaphene to the surface of iron and, therefore, increased the linearity of the reaction of toxaphene on the iron surface. Therefore, the toxaphene that did adsorb to the iron surface was readily dechlorinated without competition for adsorption

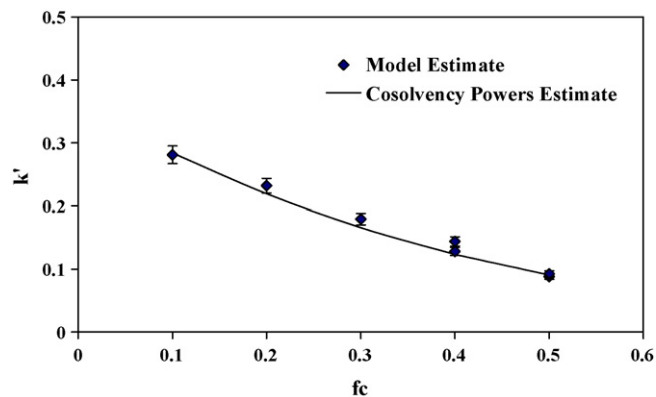


Fig. 8. Comparison of k' value obtained from Model II and from cosolvency power.

sites, which would have affected the reaction rates. The value of N' remained nearly 1 throughout the process, which resulted in Eq. (14) being linear. Comparing the linear sorption of toxaphene onto iron surface, when the value of $C_a/S_c > 0.2$, the value of both N' and n are 1, and the value of k' can be transformed to K_f by combining Eqs. (2) and (14). Since K_f can be obtained from cosolvency power (Eq. (4)), Model II can be reduced to only two unknown parameters a and b for the case of linear absorption:

$$C_a = (1 - k')(at + C_{T0}^{1/b})^b \quad \text{for} \quad \frac{C_{T0}}{S} \geq 0.2 \quad (19)$$

where

$$k' = \frac{K_f}{1 + K_f} = \frac{1}{1 + K_{f0} 10^{\beta \delta f_c}}$$

Fig. 8 shows the comparison of k' , which represents the reaction rate on the solid phase, obtained from Eq. (19) and derived from Model II. These model results compared well with the prediction of k' from cosolvency power, which, again, validated the assumption that the majority of the toxaphene degradation occurred on the solid surface of the Fe⁰.

4. Conclusions

Research was conducted to examine the effects of various types and fractions of cosolvent solutions on dechlorination of toxaphene by zero-valent iron. Experimental results showed that rate of toxaphene dechlorination reduced with increase of methanol fraction in solution. This was expected as increased cosolvent fraction was also noted to reduce toxaphene adsorption to Fe⁰ surfaces.

In addition, a nonlinear Freundlich sorption equation indicated that the linearity of the Freundlich sorption isotherm was related to the saturation of solution, which was the ratio of aqueous concentration to the solubility (C_a/S_c). When $C_a/S_c > 0.2$, the sorption isotherm was almost linear and the concept of cosolvency power can be applied mathematically to describe this process. Furthermore, a mathematical model (Model II) detailing the sorption and dechlorination of toxaphene by Fe⁰ was developed. This model showed that experimentally gathered data regarding toxaphene dechlorination paralleled the theoretically derived data.

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