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Kinetic analysis of data obtained from studies on microbial degradation of cement waste forms, using shrinking core models

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Abstract

Model equations based on analytical solutions of two shrinking core models (acid dissolution or shrinking unreacted core (SUC) model, and bulk diffusion model), were used to analyze the kinetics of microbial degradation of cement waste forms. Two current approaches of waste form microbial stability evaluation (Nuclear Regulatory Commission (NRC) method and refined biofilm formation) were used to generate the data. Good linear correlations with $R^2 > 0.95$ were obtained for the leaching data from both the NRC and biofilm approaches, using the model equation based on the bulk diffusion concept. Analyses using the model equation based on the acid dissolution model generally gave poor correlations except when data obtained from biofilm formation method was normalized.

Keywords: Shrinking core models; Nuclear Regulatory Commission method; Refined biofilm formation method

1. Introduction

Chemical stabilization/solidification (S/S) process is a widely used technology for the treatment and disposal of hazardous wastes [1]. Stabilization refers to the process whereby hazardous wastes are treated in ways to reduce their toxicity, and to prevent dissolution and release of the toxic components into the environment [2]. Solidification on the other hand refers to the conversion of waste into a solid state with advantages of improved handling

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characteristics, reduced surface, and lower permeability [3]. The most commonly used binder for waste stabilization/solidification is the ordinary Portland cement (OPC).

The major goal of S/S is the long-term storage of hazardous wastes in the field without leakage to the environment. To achieve this goal, it is important that extensive performance assessment of the waste forms be carried out before disposal. The relatively short period of existence of S/S technology in comparison to the projected storage life span of thousands of years for the waste forms means that performance assessment has to be based mainly on laboratory protocols and derived models [4,5].

The development of laboratory protocols and models for microbial degradation processes has been slow in comparison to physical and chemical processes. This is largely due to the initial treatment of waste form degradation as a physico-chemical phenomenon. The involvement of microbes in degradative processes was considered insignificant relative to abiological processes [6]. Only after microbial activities were detected in areas containing both low and high level wastes [7–10] that the idea of possible involvement of microbes in waste form degradation started to be given serious consideration. Thus, initial performance protocols were tailored mainly towards evaluation of physical and chemical stability, with no consideration given to microbial stability assessment of waste forms. It was only in 1996 that the first comprehensive package for evaluation of microbial stability of waste forms was put together for the Nuclear Regulatory Commission (NRC) by researchers at Idaho National Engineering and Environmental Laboratory (INEEL) [11].

The early treatment of waste form degradation as a physico-chemical phenomenon ensured that the bulk of accumulated data are based on chemical stability protocols. Thus, models developed for both predictive and quantitative comparative evaluations are based mainly on the chemical concept of waste form degradation. However, it is now well established that microorganisms contribute significantly to waste form degradation even though details of mechanisms are still sketchy. As far back as 1945, Parker [12] reported the isolation of sulfur oxidizing bacterium from the surface of a corroding concrete sewer pipe and postulated that the bacterium (*Thiobacillus concretivorus*) converted hydrogen sulfide to sulfuric acid and that this biogenic acid reacted with the cementitious material of the concrete. Many other bacteria have since been isolated and shown to play a role in the degradation of cement-based materials [13–15]. So far, existing evidences point to indirect involvement of microbes in waste form degradation via production of biogenic acids. However, there are speculations of a more direct involvement of microorganisms in the leaching of metals through interactions between the microbes and the metals within the monolith. The few microbial degradation models available are actually based on concrete corrosion, and not exactly on waste form degradation. A typical example of such models is the one developed for USEPA by Pomeroy [16], which is basically a chemical-based model, since it has acid production (sulfuric acid) as the most important component of the degradation process. The absence therefore, of any analytical model equation based on theoretical and experimental evaluation of microorganisms-related degradation of stabilized waste specimens, is the primary motivation by this study to attempt the application of existing chemical-based model equations to the analysis of experimental data obtained using various microbial degradation approaches involving *Thiobacillus thiooxidans*. This organism is recognized as the most dominant microorganism among a consortium implicated in the degradation of cement-based materials, and is found commonly at many landfill sites.

The secondary motivation of this study has to do with the understanding that production of mineral acids is a major component of degradative activities of microbes as part of their respiratory cycle. Thus, it is our thinking that if non-acidic contribution to microbial activity is not substantial, then the chemical-based model equations should be adequate to approximate the overall kinetics of microbial degradation.

2. Materials and methods

2.1. Microorganism

T. thiooxidans was the microorganism used in this study, it was obtained from Idaho National Engineering and Environmental Laboratory. The composition of the *T. thiooxidans* growth media is as follows (g/l): $MgSO_4 \cdot 6H_2O$ (0.4), $(NH_4)_2SO_4$ (0.5), $CaCl_2$ (0.1), $FeSO_4$ (0.01), potassium tetrathionate (3.0), and potassium phosphate monobasic (3.0). To avoid precipitation, the potassium phosphate monobasic was prepared, autoclaved separately, and mixed with the rest of the components prior to use. The ferrous sulfate was added to the other components using sterile disposable membrane filters to avoid oxidation to ferric during autoclaving.

2.2. Waste formulation

Two different waste formulations were used in this study, 21% cobalt chloride/79% cement, and 4% chromium chloride/80% cement. The 21% cobalt chloride/79% cement was formulated by mixing 1 part cobalt chloride with 3.76 parts Portland type 1 cement and 2.76 parts water. The 4% chromium nitrate/80% cement waste form on the other hand was formulated by mixing 1 part chromium nitrate with 21 parts cement, 15 parts water, and 1 part each manganese(II) chloride, lead nitrate, cobalt chloride, nickel sulfate. The mixes were allowed to set in 5 ml plastic vials serving as moulds. All the waste forms were cylindrically shaped after setting, and had the following dimensions: 2.0 cm height $\times$ 1.5 cm diameter.

2.3. Waste form stability evaluation

Evaluations of waste form stability to microbially induced degradation (MID) were carried out using the NRC approach of Rogers et al. [11] and the refined biofilm formation method of Idachaba et al. [17]. The NRC approach involved intermittent immersion of experimental waste forms in *T. thiooxidans* broth (pH 2.00), and of control waste forms in a sterile growth medium for *T. thiooxidans* (pH 4.00). The *T. thiooxidans* broth was pumped from a continuously operated bioreactor over experimental waste forms contained in soxhlet tubes, while the sterile growth medium was pumped from a reservoir over control waste forms contained in soxhlet tubes. The refined biofilm formation approach is a substantially modified version of the NRC approach; it consists of a two-stage process. The first stage involves the pumping of sterile medium for *T. thiooxidans* (pH pre-adjusted to 1.9 using sulfuric acid) over control samples, and the pumping of fermenter broth of *T. thiooxidans*

(pH 1.9) from a continuously operated bioreactor over experimental waste forms, for a 24 h period. This stage of the process, which is meant for colonization of the experimental waste forms by *T. thiooxidans*, ends with the shutting off of supply of *T. thiooxidans* to the experimental waste forms, and the supply of sterile medium of pH 1.9 to the control waste forms. The second stage of the refined biofilm formation process begins and continues to termination, with the supply of a fresh normal medium for *T. thiooxidans* (pH about 4.00) to both control and experimental waste forms. Effluents obtained using both methods were collected in vessels and removed periodically for analysis. For the refined biofilm formation approach, formation of biofilm on experimental samples was confirmed from changes in pH and sulfate concentration.

2.4. Metal analysis

Analysis of the metals in the media, fermenter broth, and the effluents were carried out using inductively coupled plasma (ICP) Optima 3300 DV (Perkin-Elmer) spectrophotometer. The sulfate concentration of the media and effluents was estimated by the Turbidimetric method, based on the standard methods for the examination of water and wastewater [18]. This method involved adding a quantity of barium chloride crystals to a buffered amount of the sample and measuring the absorbance of the barium sulfate formed at 420 nm using the HacH 2010 DR spectrophotometer. The sulfate concentration was calculated using a standard calibration curve. The pH of the media, fermenter broth and effluents was determined using a corning pH meter 345.

2.5. Analysis of the kinetics

The most widely referenced chemical-based models for predictive and quantitative evaluations of waste form degradation are those based on the shrinking core concept. Two model equations based on two shrinking core models were used comparatively to analyze the kinetics of microbial degradation as determined using the NRC and refined biofilm formation approaches. The two model equations are:

$$\tfrac{2}{3}a - (1-a)^{2/3} = K_{\mathrm{D}}t \quad \text{(bulk diffusion model)} \tag{1}$$

$$1 - (1-a)^{1/3} = K_{\mathrm{A}}t \quad \text{(acid dissolution model)} \tag{2}$$

Where a represents the fraction of metal leached at time t, and K_{D} and K_{A} the overall rate constants for the leaching process.

The bulk diffusion model assumes that contaminant release is a result of the concentration gradient between the leachant and the bulk concentration within the monolith [1], and that the interaction between solid and fluid was non-catalytic [19]. The model is based on Fickian diffusion; it was originally developed according to the following equation [1]:

$$\frac{\mathrm{d}C}{\mathrm{d}t} = \frac{D_{\mathrm{e}}d^2C}{\mathrm{d}x^2} \tag{3}$$

D_{e} is effective diffusion coefficient, corrected for porosity and tortuosity ($\mathrm{cm^2\,s^{-1}}$); C is concentration of the contaminant ($\mathrm{g\,cm^{-3}}$); t is time (s); x is the distance traveled by the

inward moving leachant (cm). The bulk diffusion model is limited by its inability to account for the leachant pH and the observed matrix dissolution in cement during exposure to an acidic environment [1,20,21]. These limitations led Hinsenveld and Bishop to develop a shrinking unreacted core (SUC) model to describe leaching mechanisms from solidified/stabilized specimens [1,20,22]. The basic premise of the SUC model is that contaminant release is directly related to the conversion, or acid penetration depth [1]:

$$M''(t) = l_s C_m f_{mo} \tag{4}$$

where $M''(t)$ is the contaminant release per unit surface, C_m the solid contaminant concentration (mol cm^{-3}), f_{mo} the leachable fraction (dimensionless), and l_s the thickness of the leached shell (cm). Many analytical solutions of the two models have been reported. However, the frequently cited [23,24] model equations for quantitative analysis of kinetic data are Eqs. (1) and (2) above.

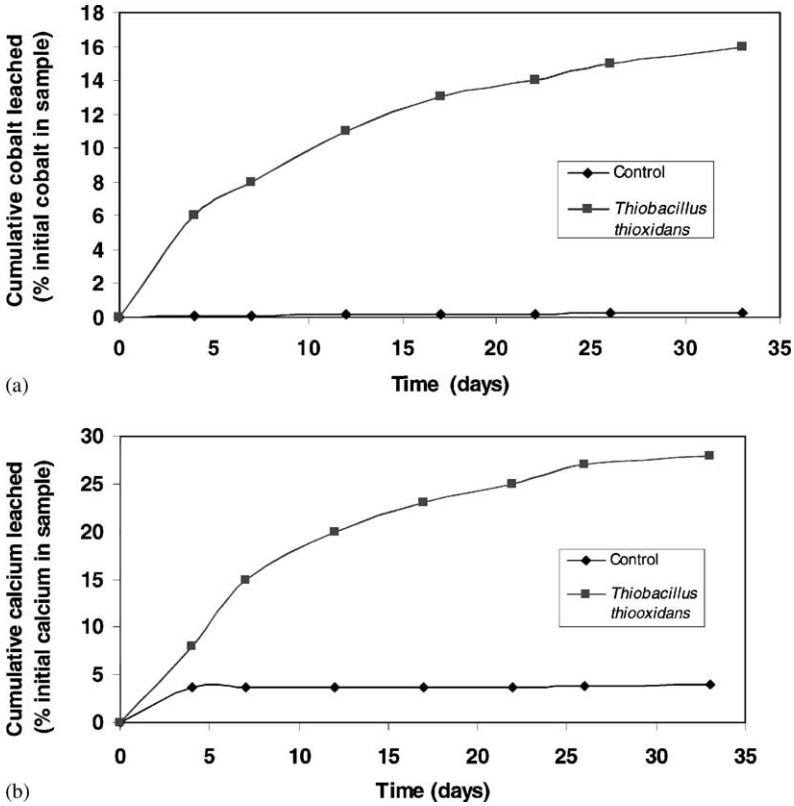

Fig. 1. The leaching profiles of cobalt (a) and calcium (b) from cement/cobalt chloride waste forms using the NRC method of microbial stability evaluation.

3. Results

Typical results on microbial degradation evaluations using the NRC approach are presented in Fig. 1. Results from the figure show that substantially higher levels of both cobalt and calcium were leached from the experimental samples at the beginning of the evaluation (i.e. the first 7 days) than at later periods. The total calcium leached from the experimental sample within 30 days of evaluation was about 28% of the initial calcium; approximately half of this amount was leached within the first 7 days alone. Similarly, the total cobalt leached from the experimental sample within 30 days of evaluation was about 16% of the initial cobalt, with half of this amount also leached within the first 7 days of evaluation. The amount of cobalt and calcium leached from the controls were substantially lower than those from the experimental samples.

Typical results on microbial degradation evaluations using the refined biofilm formation method are presented in Fig. 2. The results indicate that the levels of calcium leached from both experimental and control samples were similar within the first 3 days of evaluation after which the levels of calcium leached from the experimental sample became substantially higher that those from the control. No chromium was detected in the effluents from the

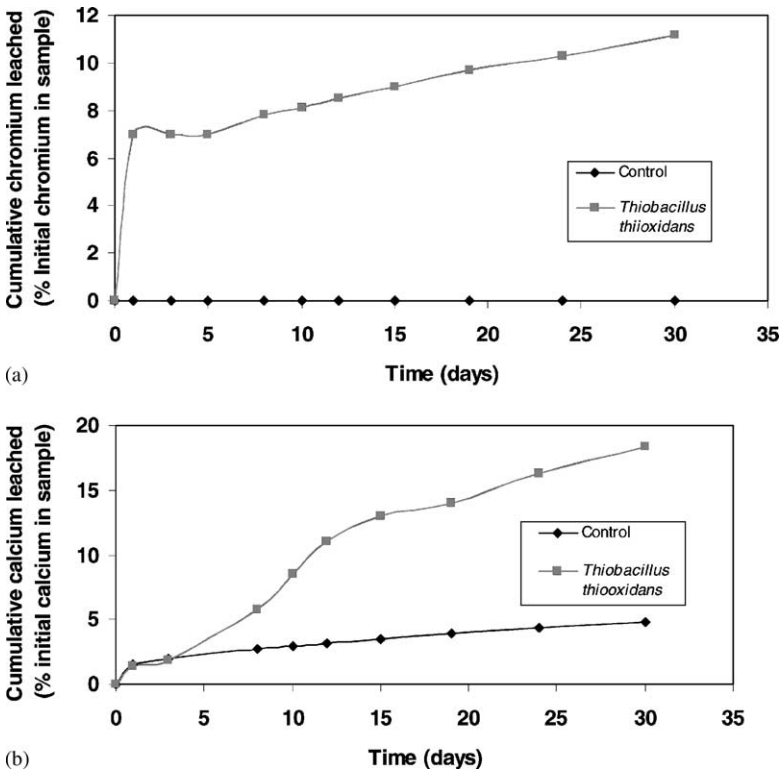

Fig. 2. The leaching profiles of chromium (a) and calcium (b) from cement/chromium nitrate waste forms using the refined biofilm formation approach of microbial stability evaluation.

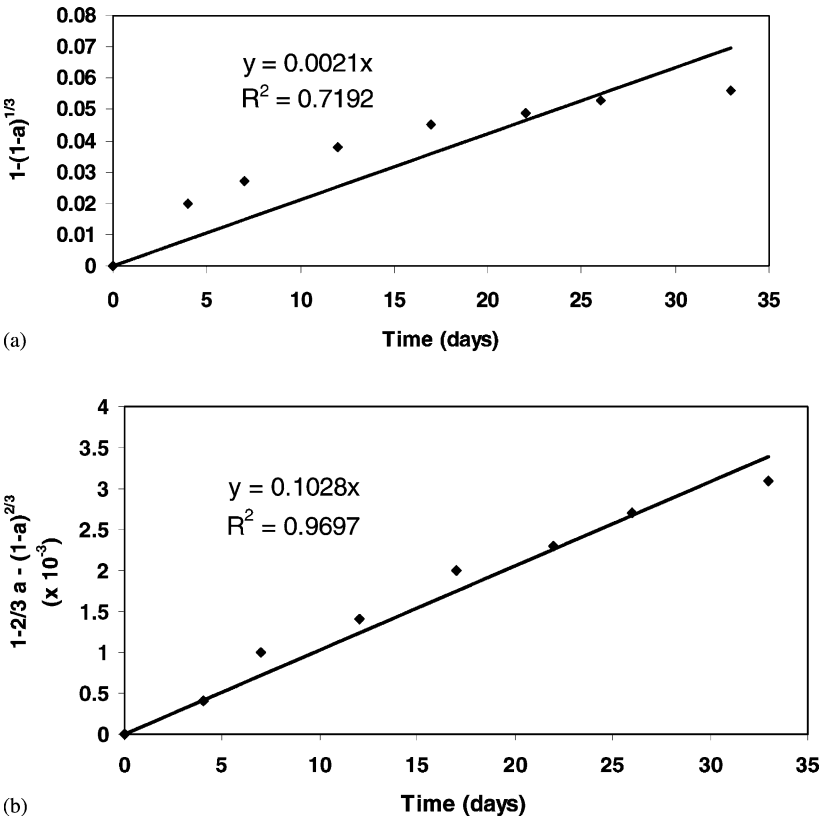

Fig. 3. Comparison of the use of the acid dissolution (a) and bulk diffusion (b) models for kinetic analysis of cobalt leaching data generated using the NRC method of microbial stability evaluation.

control sample, while about half of the total chromium leached from the experimental sample was leached within the first 24 h of evaluation (i.e. the first stage).

Results of comparative kinetic analysis of cobalt leaching data from the NRC approach, using acid dissolution and bulk diffusion kinetic model equations are presented in Fig. 3. It is evident from the figure that analysis of the data using the bulk diffusion model (Fig. 3b) gives a better linear correlation than analysis using the acid dissolution approach (Fig. 3a). While a straight line going through the origin with R^2 of about 0.97 and a rate constant K of 0.1028×10^{-3} can be obtained using the bulk diffusion model, the distribution of the data points using the acid dissolution approach does not allow for the drawing of any statistically reasonable straight line. The best straight line through the data points gives a substantially low R^2 of 0.7192.

Results of comparative kinetic analysis of calcium leaching data from the NRC approach, using acid dissolution and bulk diffusion kinetic model equations are presented in Fig. 4. As in the results for cobalt in Fig. 3, a good correlation was obtained using the bulk diffusion approach with an R^2 of 0.9773 and K value of 0.3502×10^{-3}. Analysis using the acid dissolution approach gave a poor correlation with an R^2 of 0.7912.

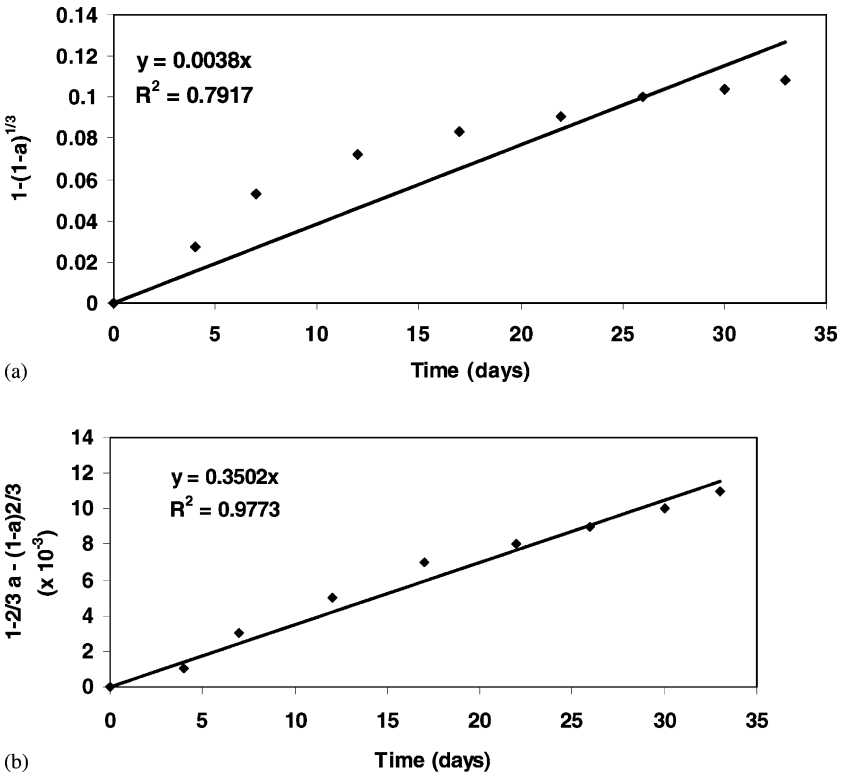

Fig. 4. Comparison of the use of the acid dissolution (a) and bulk diffusion (b) models for kinetic analysis of calcium leaching data generated using the NRC method of microbial stability evaluation.

Results of comparative kinetic analysis of calcium leaching data from the refined biofilm formation approach, using acid dissolution and bulk diffusion kinetic model equations are presented in Fig. 5. A good linear correlation with an R^2 of 0.9633 and K value of 1.2492×10^{-4} was obtained using the bulk diffusion approach, while analysis using the acid dissolution approach gave a poor correlation with an R^2 of 0.9312 and a K value of 2.4×10^{-3}. Normalization of the data obtained for the bulk diffusion approach (Fig. 6b) resulted in an improvement in the correlation from 0.9633 to 0.9704 and a minor change in the K from 1.2492×10^{-4} (without normalization) to 1.303×10^{-4} (with normalization). Similarly, normalization of the data obtained for the acid dissolution approach (Fig. 6a) also resulted in an improvement in the correlation from 0.9312 to 0.9858 and a slight change in the K value from 2.4×10^{-3} (without normalization) to 2.24×10^{-3} (with normalization). Normalization was carried out to account for degradation occurring only in the second stage of the biofilm formation method, when the actual contribution of microbes to waste form degradation is measured.

Results of comparative kinetic analysis of chromium leaching data from the refined biofilm formation approach, using acid dissolution and bulk diffusion kinetic model equations are presented in Fig. 7. The results indicate that none of the two models gave good

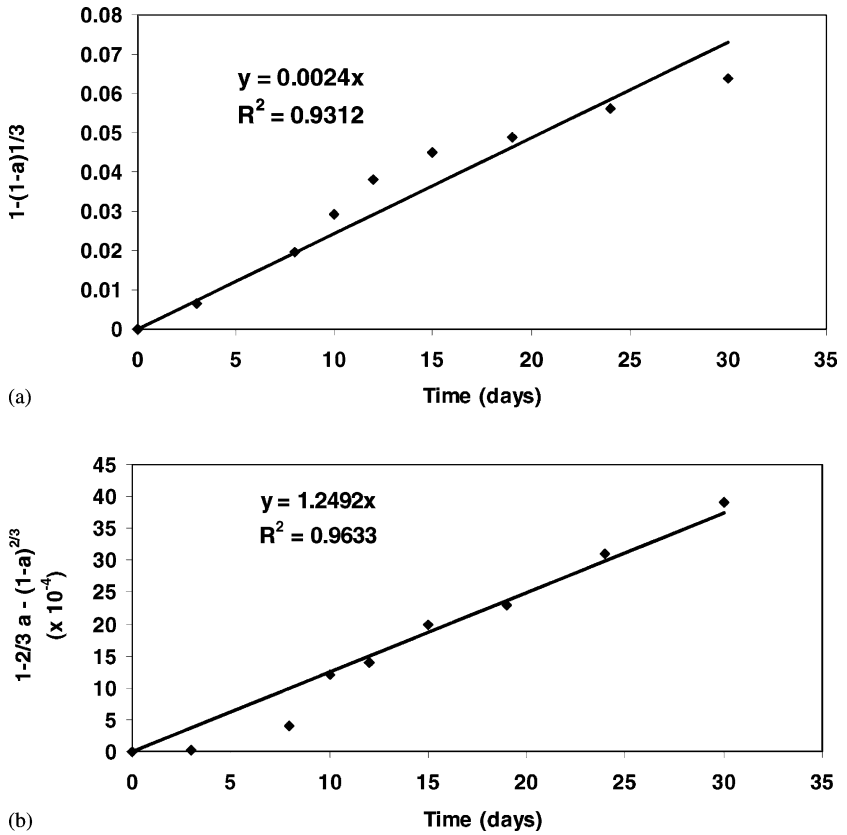

Fig. 5. Comparison of the use of the acid dissolution (a) and bulk diffusion (b) models for kinetic analysis of calcium leaching data generated using the biofilm formation method of microbial stability evaluation.

correlation with R^2 values (0.7394 for bulk diffusion, 0.087 for acid dissolution) that are substantially lower than 0.95. After normalization of the data to reflect only degradation taking place during the second stage of the biofilm formation approach, analysis using both the acid dissolution model and the bulk diffusion approach resulted in good correlations with substantially high R^2 values of 0.9972 (for acid dissolution) and 0.9947 (for bulk diffusion). The K values obtained using the two approaches are 0.3363×10^{-4} (for bulk diffusion) and 0.562×10^{-3} (for acid dissolution) (Fig. 8).

4. Discussion

The good linear correlation obtained when the bulk diffusion approach was applied to the analysis of virtually all the data from both the NRC and biofilm formation methods of waste form microbial stability evaluation, suggests that microbial degradation follows

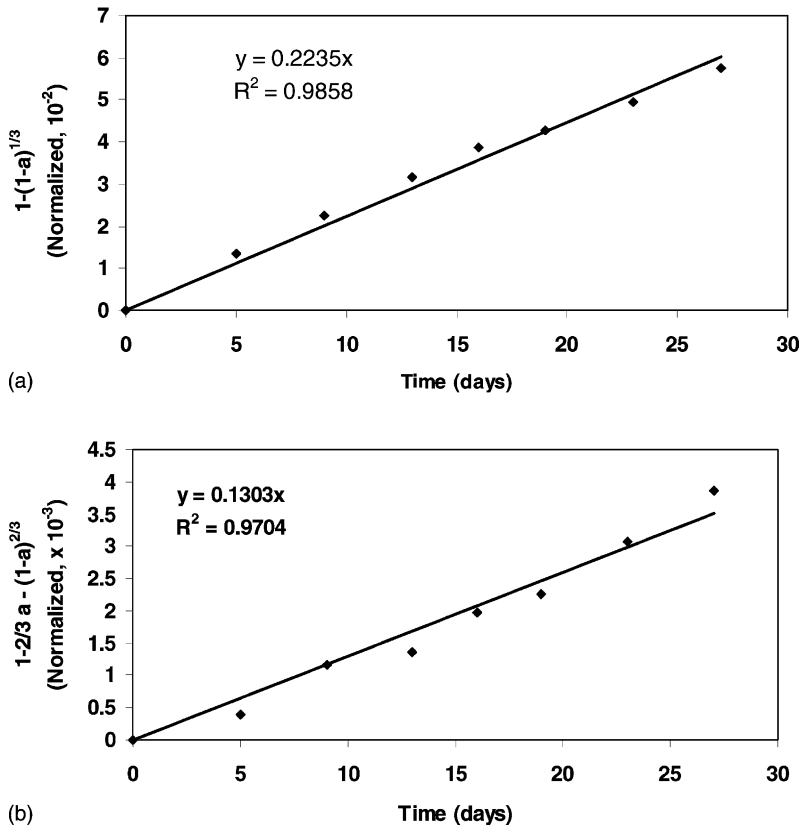

Fig. 6. Normalization of calcium leaching data generated using the biofilm formation method of microbial stability evaluation and improvement in the linear correlation for kinetic analysis based on both acid dissolution model (a) and the bulk diffusion model (b).

closely the bulk diffusion mechanism of waste form degradation. Thus, the kinetic model equation based on the bulk diffusion approach can be used for quantitative kinetic analysis of data obtained from microbial degradation experiments.

The occurrence of a good correlation in the application of a chemically based model to evaluate the kinetics of microbial degradation using the NRC approach is not surprising. This is because it has been demonstrated previously that degradation taking place using the NRC approach is basically due to the presence of pre-existing acid in the fermenter broth, and not as a result of microbial activities, since the arrangement of the procedure ensures substrate limitation [5,17].

The good correlation observed between a chemical-based model such as the bulk diffusion model, and microbial degradation using the biofilm formation method, is partly surprising. This is because recent studies by our group, suggests that microbial degradation of waste forms may involve additional mechanisms than mere production of acids [25]. It was expected therefore that models derived basically from observations made in a complete

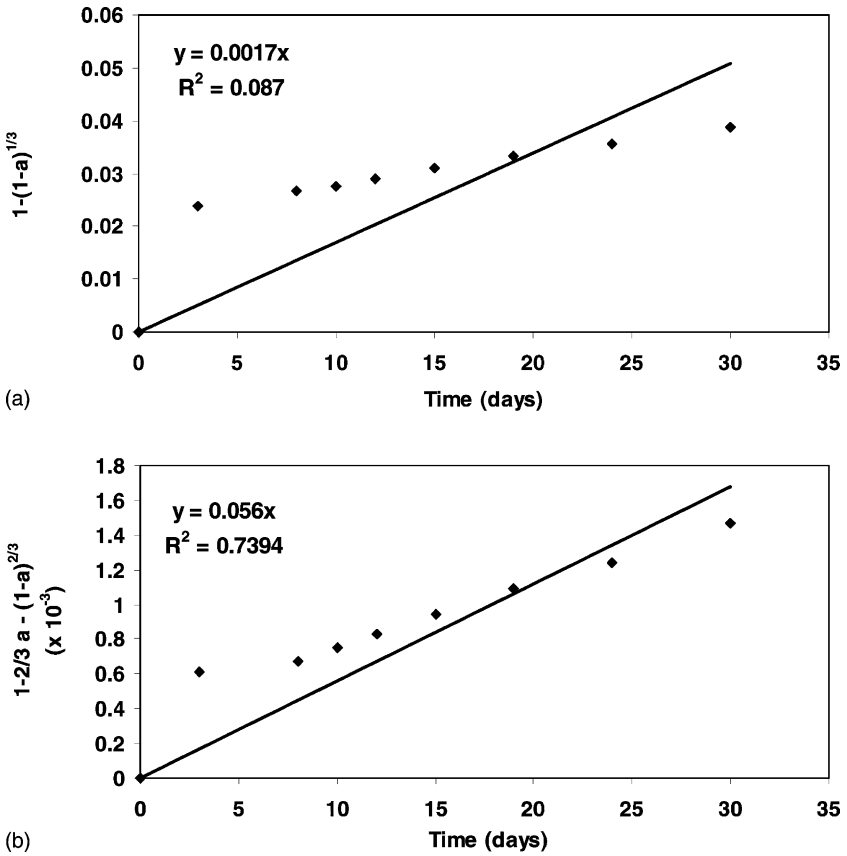

Fig. 7. Comparison of the use of the acid dissolution (a) and bulk diffusion (b) models for kinetic analysis of chromium leaching data generated using the biofilm formation method of microbial stability evaluation.

acid environment might have to be modified to include constants for non-acid contribution to microbial degradation, if those models are to be used in evaluating microbial degradation in a global context. The good correlation obtained therefore suggests that the production of acid by microbes and its contribution to microbial degradation is substantially higher than previously thought. Microbes such as *T. thiooxidans* are known to produce mineral acids such as sulfuric acid as part of their growth process, with attendant lowering of environmental pH to as low as 1.5. The effect of such a pH depression may be overwhelming such that the impact of non-acid sources to the overall microbial degradation profile is not noticeable.

The fact that a good correlation was obtained for the acid dissolution model when the data was normalized to account for degradation taking place only in the second stage of the biofilm formation method, suggests that acid dissolution model could be used for kinetic evaluation of microbial degradation under certain conditions. Given that acid production is considered the dominant factor for degradation in the second stage of the biofilm formation

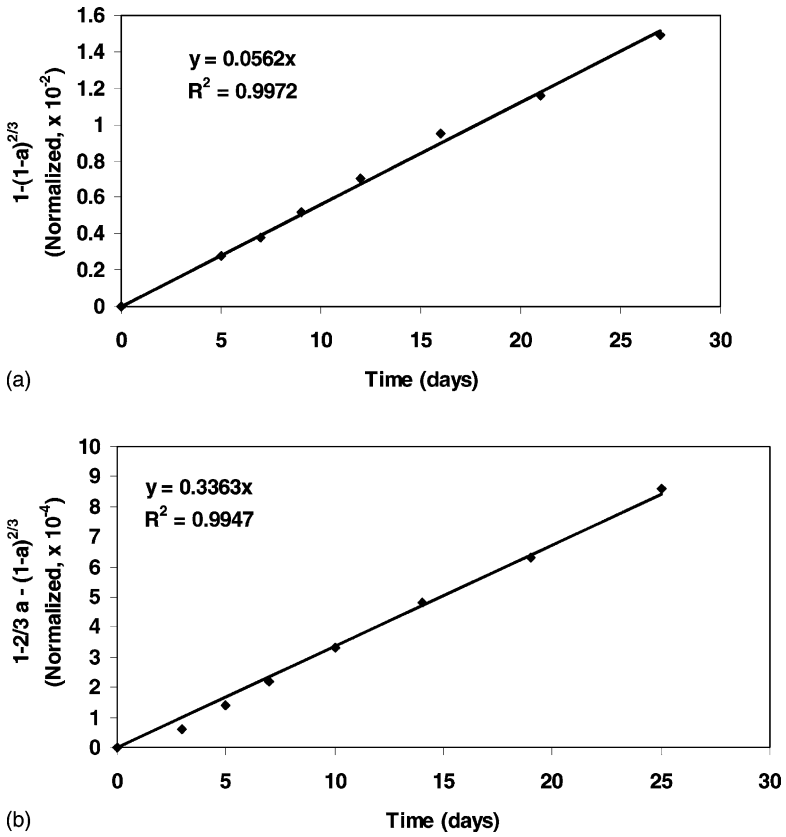

Fig. 8. Normalization of chromium leaching data generated using the biofilm formation method of microbial stability evaluation and improvement in the linear correlations for kinetic analysis based on both acid dissolution model (a) and the bulk diffusion model (b).

process, it appears logical to conclude that the conditions under which acid dissolution model are most likely to be useful for kinetic evaluation of microbial degradation are those in which contributions of non-acid factors to degradation are negligible. Since bulk diffusion model gave an equally good correlation after normalization, it appears the bulk diffusion model is more universal in application for analysis of the kinetics of microbial degradation.

5. Conclusions

Model equations based on the bulk diffusion model are more universal in their applications for quantitative analysis of the overall kinetics of microbial degradation processes than the acid dissolution model. The major driving force therefore in the leaching of metals from waste forms during microbial degradation appears to be bulk diffusion as a result of concentration gradient rather than acidity. Non-acid contribution to microbial degradation

even if present may be too small in magnitude to have any noticeable impact on the overall degradation profile.

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