

STABILIZED HYDROGEN PEROXIDE DECOMPOSITION DYNAMICS
IN ONE-DIMENSIONAL COLUMNS

By

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A thesis submitted in partial fulfillment of the
requirements for the degree of

MASTER OF SCIENCE IN ENVIRONMENTAL ENGINEERING

WASHINGTON STATE UNIVERSITY
Department of Civil and Environmental Engineering


MAY 2006

To the Faculty of Washington State University:

The members of the Committee appointed to examine the thesis of
JEREMY T. SCHMIDT find it satisfactory and recommend that it be accepted.


Chair





ACKNOWLEDGEMENT

I would like to sincerely thank my committee chair Dr. Richard Watts for his support and guidance in this project and for hiring me as a lab technician during my undergraduate years. I would also like to thank Dr. Balasingam Muhunthan and Dr. Marc Beutel for being part of my committee. In addition, I would like to extend my gratitude to Dr. Dennis Finn for being an integral part of my graduate studies.

I would also like to extend my thanks to all of the staff and faculty in the Department of Civil and Environmental Engineering. Their hard work, professionalism, and cordial personalities are what make this happen.

Finally, I would like to thank my parents, Tim and Camille Schmidt and my brother and sister-in-law, Andy and Michelle Schmidt, for their support. A very special thanks to my fiancé, Lynn Cutler, for her assistance with hundreds of experiments and her steady support for the past 4 years.

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Abstract

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May 2006

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Catalyzed hydrogen peroxide propagation (CHP) is the most effective *in situ* chemical oxidation (ISCO) process for contaminant destruction, but its use for groundwater remediation is limited by its short lifetime in the subsurface and subsequent low potential for transport away from injection wells. Hydrogen peroxide decomposition with and without the presence of organic acid stabilizers was investigated in one-dimensional columns containing manganese coated sand (MCS) and iron coated sand (ICS). In addition, destruction of the sorbed contaminant Hexachlorobenzene (HCB) was evaluated in the column with and without stabilization. Citrate and phytate effectively stabilized hydrogen peroxide in MCS columns and phytate was effective in stabilizing hydrogen peroxide in ICS columns. The use of these stabilizers resulted in increased hydrogen peroxide lifetimes of two to five or more orders of magnitude. Destruction of the sorbed contaminant HCB was as effective in the stabilized systems as in the columns in which the pH was maintained at pH 3 – the condition that has previously been shown to be the most effective for hydrogen peroxide stability and contaminant destruction. Only phytate-stabilized MCS columns were inefficient in HCB destruction. The results of this research demonstrates that hydrogen peroxide can be effectively stabilized in

dynamic systems using citrate or phytate, which should provide more effective treatment of contaminated groundwater systems by CHP *in situ* chemical oxidation.

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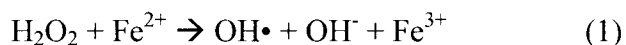
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Introduction

In situ chemical oxidation (ISCO) is an increasingly popular technology for the treatment of contaminated soils and groundwater. The most common ISCO processes include permanganate, catalyzed hydrogen peroxide propagations (CHP-modified Fenton's reagent), persulfate, and ozone (Watts and Teel 2006). *In situ* chemical oxidation with CHP is a widely used process that is based on Fenton's reagent:



Hydroxyl radical (OH \cdot) has traditionally been considered the primary reactant in CHP systems; it is a strong, nonspecific oxidant that reacts rapidly with most contaminants of concern (Haag and Yao 1992). The relatively high hydrogen peroxide concentrations used in CHP processes promote propagation reactions that generate several other reactive oxygen species, including perhydroxyl radical (HO $_2\cdot$), superoxide anion (O $_2\cdot^-$), and hydroperoxyl anion (HO $_2^-$). The generation of this suite of oxidants provides CHP with the highest potential of all the ISCO technologies for the rapid treatment of biorefractory compounds, sorbed contaminants (Corbin et al 2006), and dense non-aqueous phase liquids (DNAPLs) (Smith et al 2006).

Catalyzed hydrogen peroxide propagation process conditions differ substantially from traditional Fenton reagent. For example, hydrogen peroxide concentrations are generally much higher (8-15%); furthermore, a wide range of catalysts has been used to initiate the decomposition of hydrogen peroxide. Typical CHP catalysts include soluble iron,

chelated iron, and iron minerals (Watts and Teel 2005). The advantage of using chelated iron is the potential for conducting CHP at neutral pH (Sun and Pignatello 1992; Pignatello and Baehr 1994). Conversely, iron minerals have been used at acidic pH regimes to reduce the rate of hydrogen peroxide decomposition and increase the hydrogen peroxide decomposition stoichiometry, providing the highest production of reactive oxygen species per mole of hydrogen peroxide consumed (Tyre et al 1991, Ravikumar and Gurol 1994, Miller and Valentine 1995).

Regardless of the initiator used for CHP, hydrogen peroxide is rapidly consumed in the subsurface. Lifetimes of hydrogen peroxide are typically a few hours to two-three days in groundwater systems. Even though CHP provides the most wide-ranging treatment chemistry of the various ISCO processes, the rapid decomposition of hydrogen peroxide minimizes its contact with contaminants, vastly reducing the effectiveness of CHP (Watts and Teel 2006). For this technology to be more successful in large scale applications, the process chemistry must be improved to minimize the rate of hydrogen peroxide decomposition.

Recent findings have shown that the rate of hydrogen peroxide decomposition can be minimized by the addition of salts of low molecular weight organic acids to hydrogen peroxide-mineral slurries. Phytate and citrate have been shown to minimize the rate of hydrogen peroxide decomposition in slurries of iron and manganese oxide minerals and several natural soils (Watts et al 2006). However, hydrogen peroxide stability has not been evaluated in flow-through systems that provide a better model of dynamic

groundwater flow. The purpose of this research was to evaluate hydrogen peroxide stability in one-dimensional sand columns with the addition of citrate and phytate to stabilize hydrogen peroxide.

Materials and Methods

Materials

Manganese (II) chloride (99.4%), iron(III) nitrate (98%), hexachlorobenzene (99%), sodium citrate (99%), and sodium phytate were purchased from Sigma-Aldrich (Milwaukee, WI). Toluene was obtained from J.T. Baker (Phillipsburg, NJ). Sand was purchased from Lane Mountain Company (Valley, WA) in 0.74 and 0.225 mm grain sizes. Double deionized water (>18 m⁻¹cm) was purified using a Barnstead Nanopure II deionizing system. Hydrogen peroxide was provided *gratis* by Solvay Interlox (Deer Park, TX.).

Probe Compound

Hexachlorobenzene (HCB) was used as a probe because it is readily oxidized by hydroxyl radicals ($k_{OH\cdot} = 3.7 \times 10^9$) (Haag and Yao 1992) and degraded by superoxide (Bielski et al 1991); HCB is also highly hydrophobic ($\log K_{ow} = 5.65$), and therefore provides a measure of local degradation by CHP reactions. HCB is also characterized by low volatility ($H=0.0017 \text{ atm}\cdot\text{m}^3/\text{mole}$). Based on the linear range of analysis, the initial concentration sorbed onto the mineral coated sand was 10 mg HCB/kg sand.

Mineral Coated Sand Preparation

Prior to coating with minerals, the sand was acid washed for 24 hours in 30% nitric acid and then continuously rinsed with deionized water until there was no change in pH between the influent and the effluent wash water. The rinsed sand was then oven dried at 93° C. After drying, iron-coated sand (ICS) was prepared by adding 3 L of 30 g/L aqueous ferric nitrate to 5500 ml of acid washed sand. The sand was then stirred until evenly coated and placed in an oven at 93° C until dry (Stenkamp and Benjamin 1994). Manganese coated sand (MCS) was prepared by combining 585 ml of 1 mM manganese chloride, 1.5 ml 5.5 M sodium hydroxide, and 726 ml of deionized water. After the compounds dissolved, the solution was added to 3.75 kg of acid washed sand. The sand was then stirred until evenly coated and placed in an oven at 40° C until the water evaporated (Stahl and James 1991). HCB coated sand was prepared by dissolving HCB in toluene and adding to ICS or MCS to a concentration of 10 mg HCB/kg sand. The toluene was allowed to evaporate, leaving the HCB sorbed to the sand.

Modified Fenton's Reactions in Batch Systems

Initial experiments were conducted in batch systems to determine 1) the lowest concentration of stabilizer required to maintain extended hydrogen peroxide lifetimes and 2) the amount of iron and manganese used to coat the sand to provide similar decomposition rates of unstabilized hydrogen peroxide for the two coated sands.

Batch reactions were conducted with 100 g of ICS or MCS with sorbed HCB in 250 ml Erlenmeyer flasks and 60 ml hydrogen peroxide-stabilizer solution. The pH was

adjusted to 7.0 with 1.0 N sulfuric acid or 1.0 N sodium hydroxide. Control reactions were evaluated in parallel with no stabilizer addition and with a stabilizer but no hydrogen peroxide. The reactions were conducted over six hr., and aliquots were collected at 0, 1, 2, 3, 4, and 6 hr. Sand samples were collected at the beginning and at the end of each reaction, extracted with toluene, and analyzed by gas chromatography to determine the initial and final concentrations of HCB on the sand. The batch experiments were conducted in triplicate and the optimum results from the batch reactions were applied to the one-dimensional columns.

CHP Stabilization in One-Dimensional Columns

The most effective process conditions determined in the batch reactors were used in the one-dimensional columns in order to evaluate hydrogen peroxide decomposition dynamics and potential for contaminant destruction in a dynamic environment. ICS or MCS was loaded into a plexiglass column 125 cm high x 7.5 cm in diameter fitted with ports at 12.7 cm intervals. The bottom 6.4 cm of the column was filled with 0.74 mm mesh size sand to promote drainage; as a result, the total depth of experimental sand in the column was 102 cm. The column was filled with the HCB-sorbed sand, double deionized water was then applied using a peristaltic pump and a head of 6.4-7.5 cm was maintained above the sand in the column for the duration of the experiments. After the column reached steady state (i.e., the influent flow rate was equal to the effluent flow rate), a pulse of hydrogen peroxide-stabilizer mix was applied. The volume of the pulse was equal to one-half the pore space of the sand in the column (1.95 L). The pulse consisted of 5.0% hydrogen peroxide and 25 mM stabilizer at pH 7.0. Following dosing

with the hydrogen peroxide and stabilizer, double deionized water was added to the column until the hydrogen peroxide concentration in the lowest port (port 8) was below the level of detection. Sand samples were collected from each port using a syringe, weighed, and analyzed for residual HCB concentration.

Liquid samples were taken from each port every 10 minutes and were analyzed for hydrogen peroxide and stabilizer concentrations. The experiments were terminated when the concentration of hydrogen peroxide in the effluent of the lowest port fell below the level of detection.

Analysis

HCB extracts were analyzed using a Hewlett-Packard 5890A gas chromatograph with a 30 mm (i.d.) x 0.53 mm DB-5 capillary column and electron capture detector. The injector port and detector port temperatures were 300° C and 325° C, respectively. The initial temperature was 40° C and the program rate was 30° C min⁻¹. Sodium citrate concentrations were measured by UV spectrophotometry after color development by lyophilizate, glycylglycine buffer, L-malate dehydrogenase, L-lactate dehydrogenase, NADH, and lyophilizate citrate lyase (Möllering and Gruber 1966). Sodium phytate concentrations were measured by UV spectrophotometry after color development by Wade's Reagent (Vaintraub and Lapteva 1988). Hydrogen peroxide concentrations were determined by iodometric titration using 0.1 N sodium thiosulfate (Schumb et al 1995).

Results and Discussion

Batch Studies

CHP reactions were first conducted in batch systems at pH 7 to investigate the effectiveness of each stabilizer at a range of concentrations. The effect of different stabilizer concentrations on hydrogen peroxide decomposition in ICS systems is shown in Figure 1. The only effective stabilizer in ICS systems was sodium phytate; its lowest effective concentration in extending the lifetime of hydrogen peroxide in an ICS system was 25 mM. These results demonstrate that phytate can dramatically reduce the rate of hydrogen peroxide decomposition in ICS batch systems at a neutral pH. To be consistent, the citrate and phytate concentrations were maintained at 25 mM when applied to the one-dimensional columns. The effectiveness of different stabilizer concentrations in MCS systems are shown in Figure 2. Phytate and citrate were both effective stabilizing hydrogen peroxide in MCS systems at concentrations < 100 mM. These results demonstrate that both 25mM sodium citrate and 25mM sodium phytate were effective in stabilizing hydrogen peroxide in MCS systems, and each of the stabilizers were applied to one-dimensional columns at concentrations of 25 mM.

Hydrogen Peroxide Stabilization in One-Dimensional Columns

To investigate the effectiveness of stabilizing reagents in lowering the rate of hydrogen peroxide decomposition in one-dimensional saturated columns, reactions were conducted at pH 7 in the ICS and MCS systems using 25 mM citrate or phytate. Hydrogen peroxide concentrations in each of the eight ports as a function of time for

unstabilized hydrogen peroxide in the ICS column are shown in Figure 3. Hydrogen peroxide residuals were detected in Port 1, but decreased dramatically in Ports 2 and 3, with no detectable hydrogen peroxide concentration reaching Port 4. These results are similar to hydrogen peroxide decomposition rates found in the subsurface with high concentrations of iron or manganese oxides, which would result in a lifetime of hydrogen peroxide < 1 hr. The hydrogen peroxide concentrations at different column depths in a parallel system with the addition of 25 mM phytate are shown in Figure 4. The hydrogen peroxide concentration at Port 8 reached a maximum of 3.3% in the stabilized experiment, demonstrating a significant increase in stabilization relative to the unstabilized hydrogen peroxide. These results show that phytate is effective in stabilizing the decomposition rate of hydrogen peroxide in ICS. In addition, the columns with phytate addition showed minimal decrease in flow rates compared to the systems in which unstabilized hydrogen peroxide was applied.

Hydrogen peroxide concentrations in each of the eight ports as a function of time for unstabilized hydrogen peroxide applied to the column containing MCS are shown in Figure 5. The maximum hydrogen peroxide concentration at Port 1 was 4.75% and the hydrogen peroxide concentration decreased slightly in each of the ports, but maintained a concentration of 3.8% in Port 8. However, in the column stabilized with 25 mM phytate, the maximum hydrogen peroxide concentration showed no significant decrease from Port 1 to Port 8 (Figure 6). In the column stabilized with 25 mM citrate (Figure 7), the maximum hydrogen peroxide concentration decreased from 4.8% in Port 1 to 4.4% in

Port 8. These results demonstrate that both citrate and phytate were effective in stabilizing hydrogen peroxide in MCS.

Treatment of a Sorbed Contaminant

To investigate the potential for phytate and citrate stabilized hydrogen peroxide to treat contaminants in the subsurface, HCB was sorbed to ICS and MCS before treatment in one-dimensional columns. The overall degradation of HCB in ICS and MCS column experiments are shown in Figures 8 and 9, respectively. The results of Figure 8 demonstrate that 18.5% of the initial HCB was destroyed in an ICS column at pH 3 with unstabilized hydrogen peroxide. However, more contaminant destruction occurred with unstabilized hydrogen peroxide in the ICS column at pH 7; in this experiment, 39% of the HCB was destroyed. The contaminant destruction is likely due to the generation of a high proportion of superoxide as well as the generation of hydroxyl radicals. In contrast to the ICS column results, HCB destruction in the MCS column with unstabilized hydrogen peroxide at pH 3 was minimal (Figure 9). Unlike iron oxide CHP reactions, manganese oxide-mediated hydrogen peroxide decomposition generates superoxide but no hydroxyl radicals (Watts et al 2005). However, at pH 3 superoxide is protonated, and the perhydroxyl radical from is predominant:



$\text{HO}_2\cdot$ is a weak oxidant and likely has minimal potential for HCB destruction, which is supported by the data of Figure 9. In this experiment, HCB destruction was conducted in the MCS system at pH 3, resulting in minimal HCB destruction. At pH 7, which is well above the pKa of 4.8 for Equation 2, MnO_2 -mediated hydrogen peroxide decomposition

generates superoxide, which likely desorbs and degrades HCB. This concept is supported by the results of Figure 9, where 45.7% of the HCB was destroyed in the MCS system at pH 7. The destruction of HCB in the citrate-stabilized MCS column is also shown in Figure 9. These results show that HCB was degraded even when the hydrogen peroxide was stabilized with citrate, providing more efficient stoichiometry than HCB degradation with unstabilized hydrogen peroxide.

The concentration of citrate in each port as a function of time can be found in Figure 10, which shows that citrate is not degraded by the CHP reactions as the solution moves through the column. In an MCS column stabilized with phytate, no detectable HCB destruction occurred (Figure 9). Although the phytate was not retarded in the column and did not degrade (Figure 11), the phytate may have stabilized the hydrogen peroxide so effectively that superoxide and hydroxyl radicals were not being produced. However, in an ICS column stabilized with phytate, 18.5% of the HCB was destroyed (Figure 9). Similar to the data in Figure 11, the phytate moved readily through the column and did not degrade (Figure 12). The flow rates of column experiments are shown in Figure 13. These results show that the flow rates in the stabilized column systems do not decline as much as in unstabilized column systems. Plugging can be a significant problem in the application of CHP in the field, often through the gases produced by CHP reactions. The results of this research demonstrate that stabilization of hydrogen peroxide using citrate and phytate lower the rate of hydrogen peroxide decomposition in model subsurface systems, provides contaminant destruction comparable to unstabilized systems, and potentially minimizes plugging of the subsurface.

Summary

The stabilization of hydrogen peroxide using citrate and phytate was studied in one-dimensional columns containing iron oxide and manganese oxide coated sand. Hydrogen peroxide at an initial concentration of 5% was applied to the columns without stabilization and with stabilization by sodium citrate and sodium phytate at neutral pH. Citrate and phytate were effective hydrogen peroxide stabilizers, increasing hydrogen peroxide residuals by 70% over unstabilized hydrogen peroxide. Although they provided much lower hydrogen peroxide decomposition rates, the stabilized CHP systems provided effective contaminant destruction. Because of the increased lifetime of stabilized hydrogen peroxide, the treatment efficiency and depth of treatment in the subsurface may potentially increase by at least an order of magnitude. Citrate and phytate stabilization appears to be mineral specific; therefore a matrix of treatability studies using native materials will need to be conducted to determine the most effective stabilizer and its concentration

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Figure Legends

Figure 1: Rate of H_2O_2 decomposition in ICS for unstabilized H_2O_2 and H_2O_2 stabilized with 25 or 50 mM phytate or 100 mM citrate.

Figure 2: Rate of H_2O_2 decomposition in MCS for unstabilized H_2O_2 and H_2O_2 stabilized with 25 mM citrate or phytate.

Figure 3: H_2O_2 decomposition of unstabilized H_2O_2 within an ICS column for CHP reactions at pH 7.

Figure 4: Decomposition of H_2O_2 stabilized with 25 mM phytate in CHP reactions at pH 7 in an ICS column.

Figure 5: H_2O_2 decomposition of unstabilized H_2O_2 within an MCS column for CHP reactions at pH 7.

Figure 6: Decomposition of H_2O_2 stabilized with 25 mM phytate in CHP reactions at pH 7 in an MCS column.

Figure 7: Decomposition of H_2O_2 stabilized with 25 mM citrate in CHP reactions at pH 7 in an MCS column.

Figure 8: Degradation of HCB in ICS for unstabilized columns at pH 3 or pH 7 or a column stabilized with 25 mM phytate at pH 7.

Figure 9: Degradation of HCB in MCS for unstabilized columns at pH 3 or pH 7 or columns stabilized with 25 mM citrate or 25 mM phytate at pH 7.

Figure 10: Concentration of citrate at each port with time in a column experiment with HCB coated MCS at pH 7.

Figure 11: Concentration of phytate at each port with time in a column experiment with HCB coated MCS at pH 7.

Figure 12: Concentration of phytate at each port with time in a column experiment with HCB coated ICS at pH 7.

Figure 13: Flow rate with time for unstabilized or stabilized (25 mM phytate) ICS or unstabilized or stabilized (25 mM phytate or 25 mM citrate) MCS column experiments.

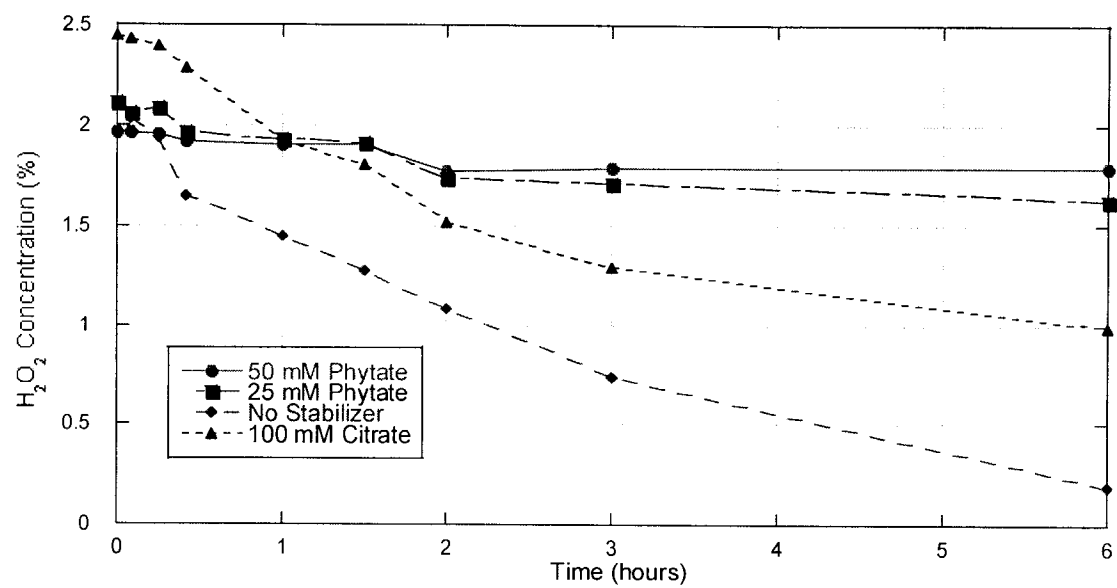


Figure 1

Rate of H_2O_2 decomposition in ICS for unstabilized H_2O_2 and H_2O_2 stabilized with 25 or 50 mM phytate or 100 mM citrate.

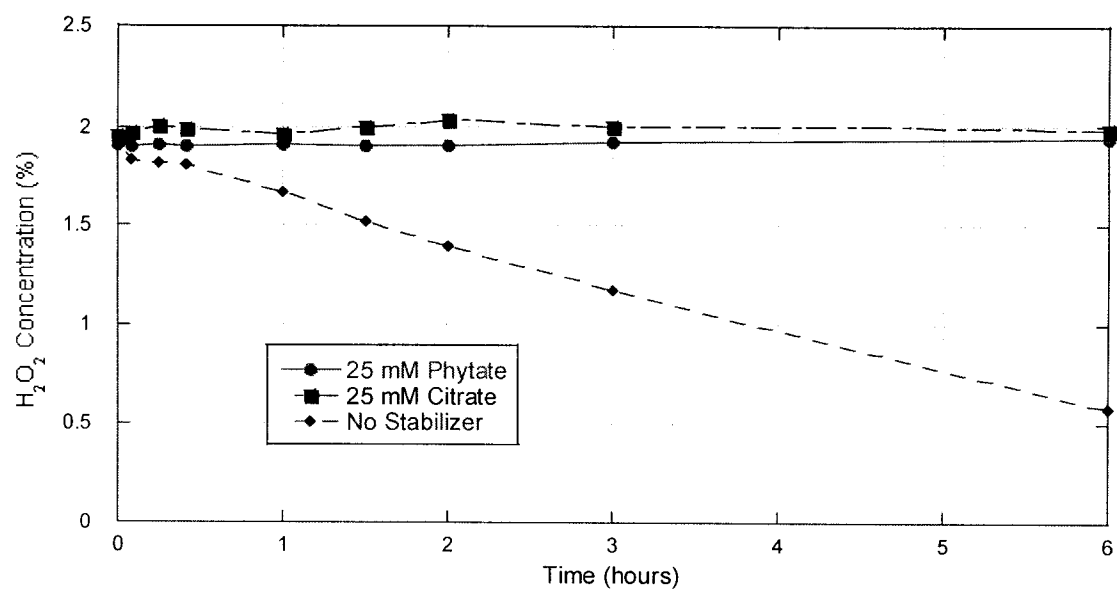


Figure 2

Rate of H₂O₂ decomposition in MCS for unstabilized H₂O₂ and H₂O₂ stabilized with 25 mM citrate or phytate.

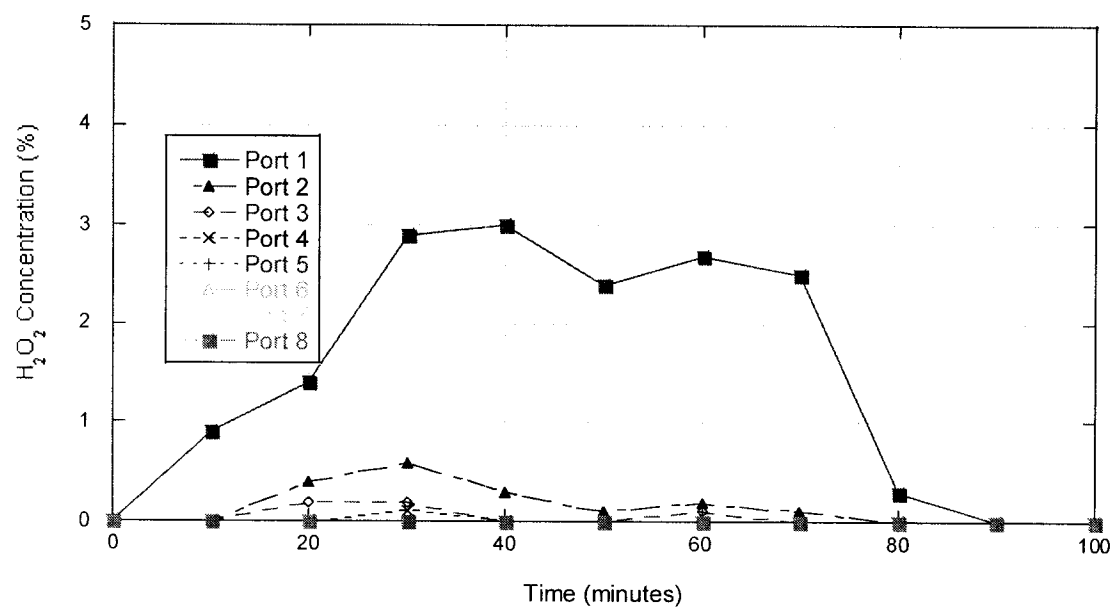


Figure 3

H₂O₂ decomposition of unstabilized H₂O₂ within an ICS column for CHP reactions at pH

7.

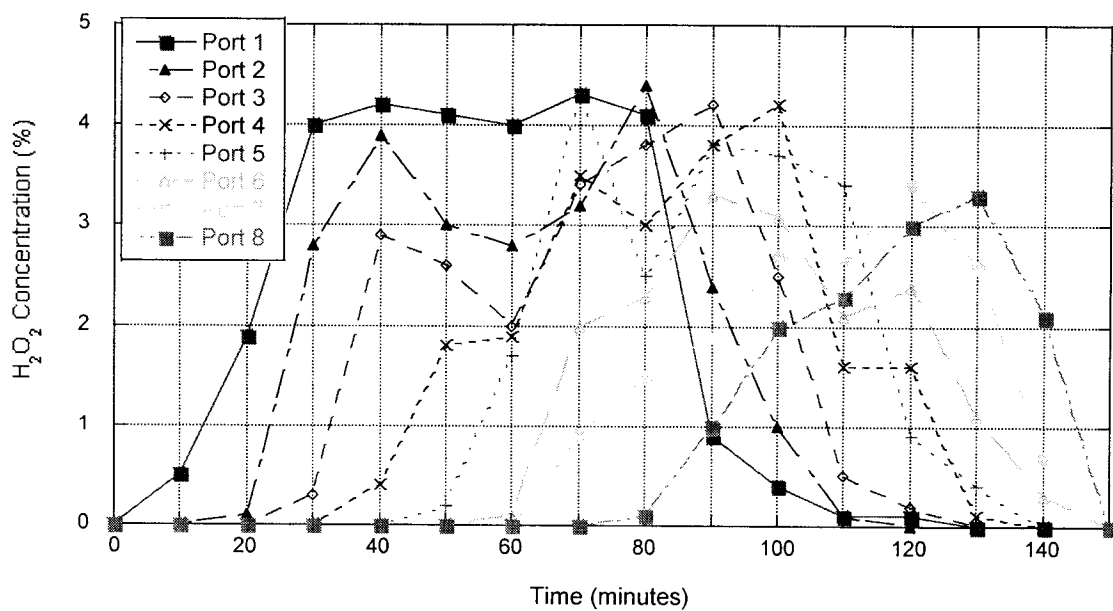


Figure 4

Decomposition of H₂O₂ stabilized with 25 mM phytate in CHP reactions at pH 7 in an ICS column.

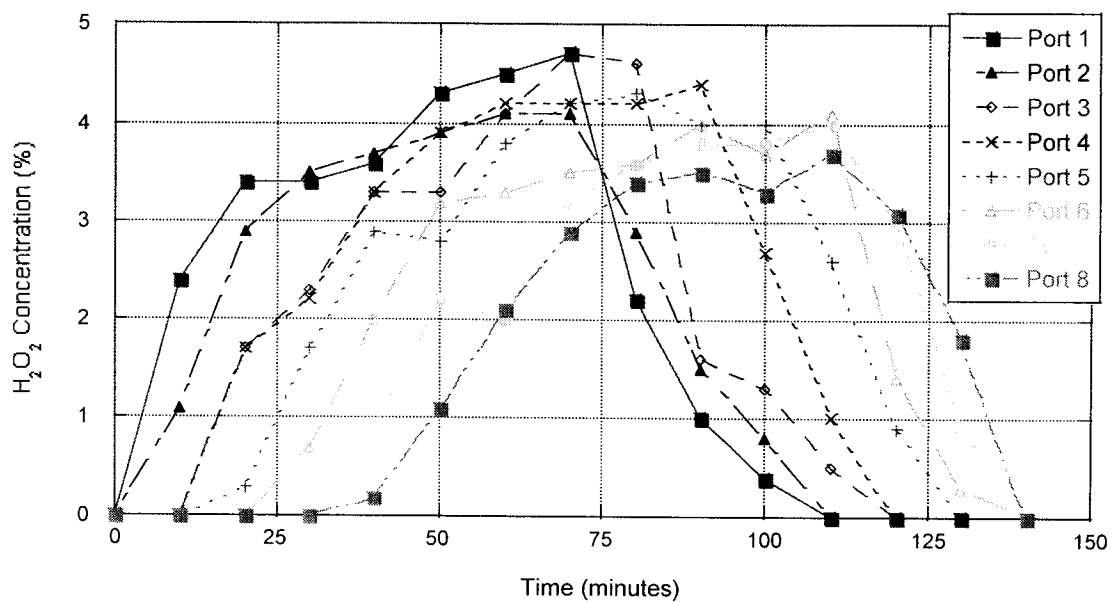


Figure 5

H₂O₂ decomposition of unstabilized H₂O₂ within an MCS column for CHP reactions at pH 7.

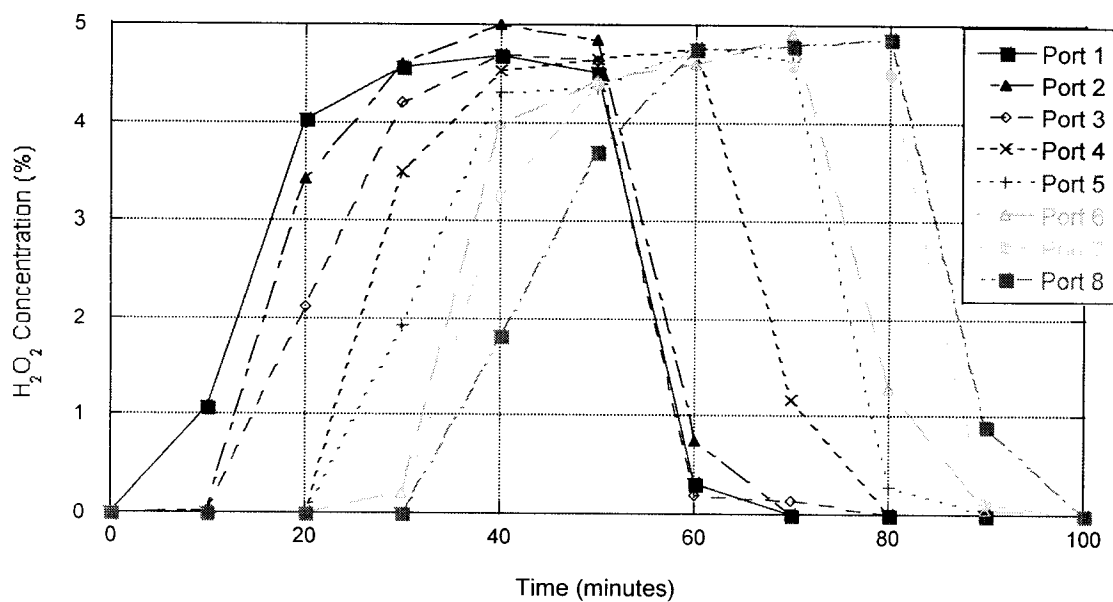


Figure 6

Decomposition of H_2O_2 stabilized with 25 mM phytate in CHP reactions at pH 7 in an MCS column.

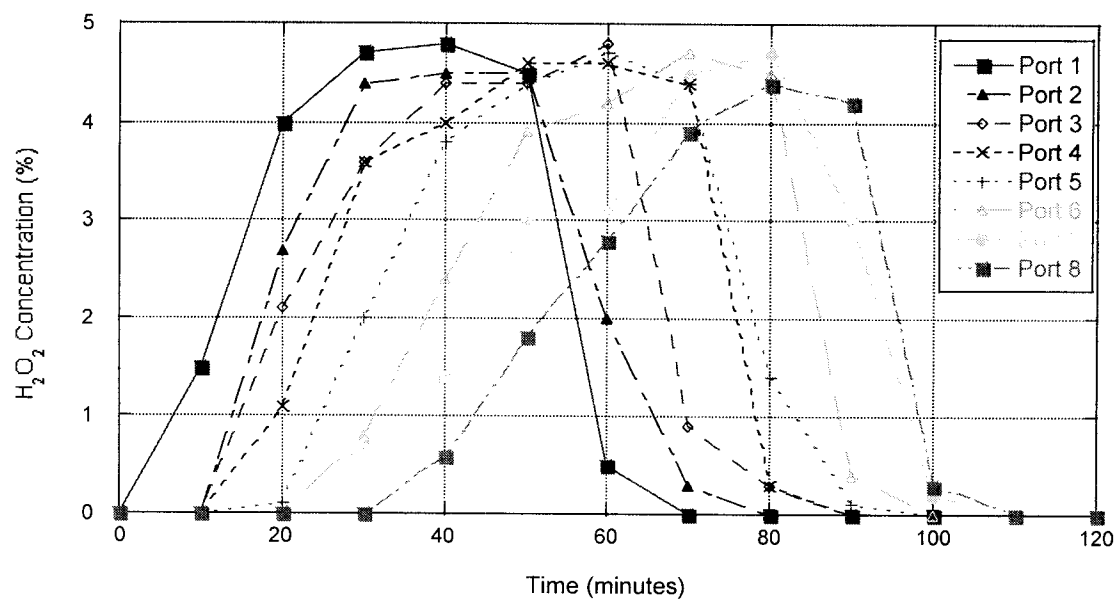


Figure 7

Decomposition of H₂O₂ stabilized with 25 mM citrate in CHP reactions at pH 7 in an MCS column.

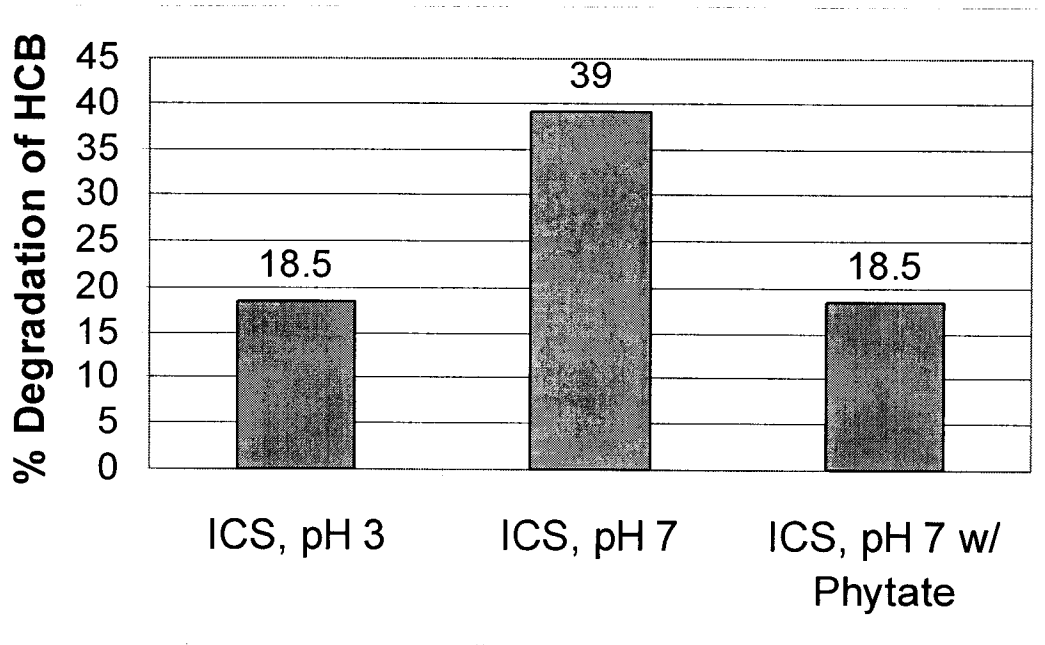


Figure 8

Degradation of HCB in ICS for unstabilized columns at pH 3 or pH 7 or a column stabilized with 25 mM phytate at pH 7.

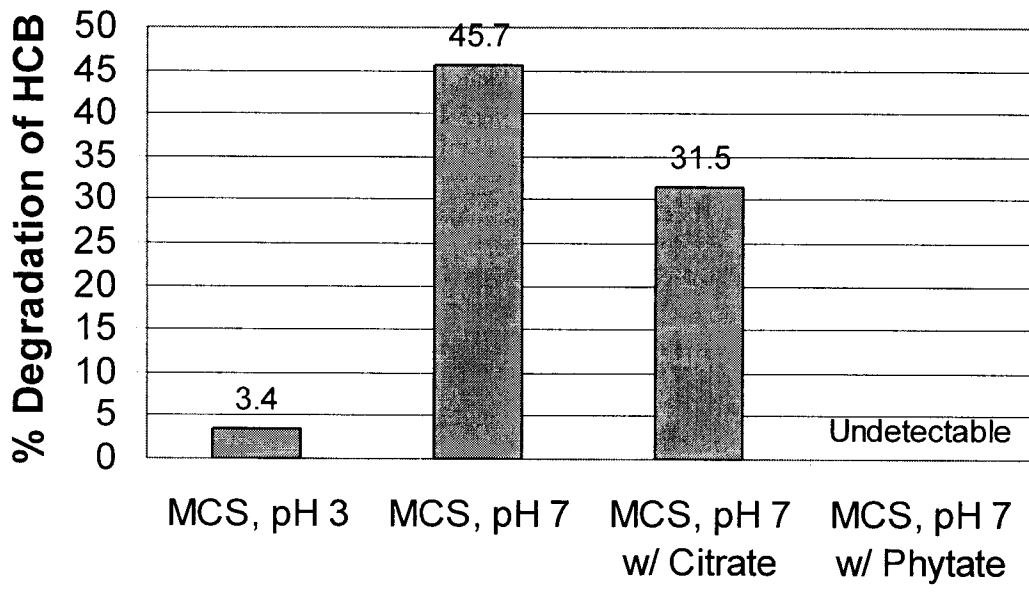


Figure 9

Degradation of HCB in MCS for unstabilized columns at pH 3 or pH 7 or columns stabilized with 25 mM citrate or 25 mM phytate at pH 7.

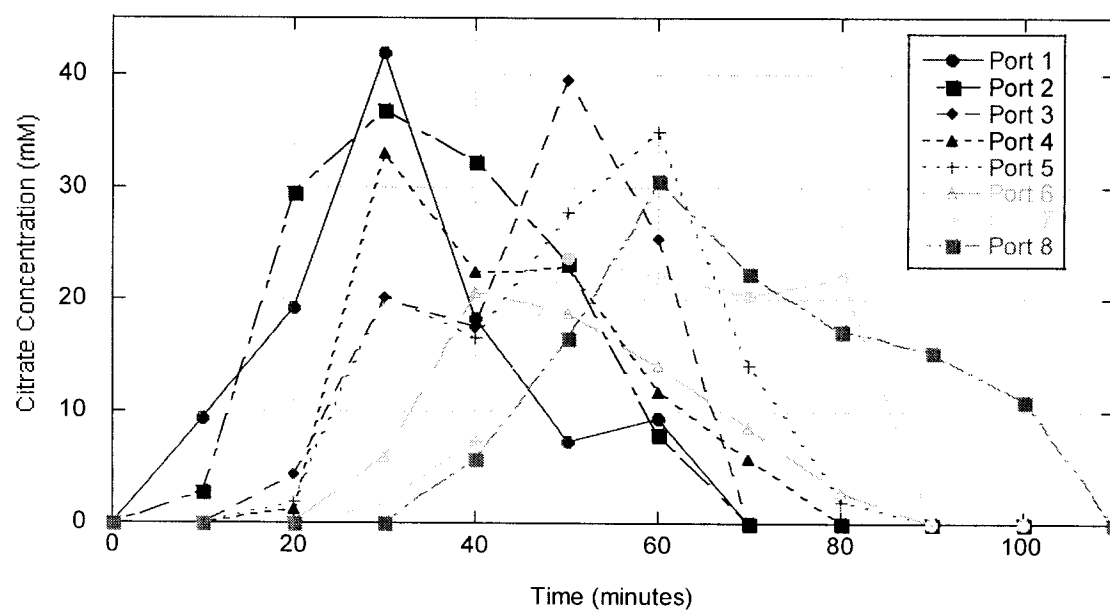


Figure 10

Concentration of citrate at each port with time in a column experiment with HCB coated MCS at pH 7.

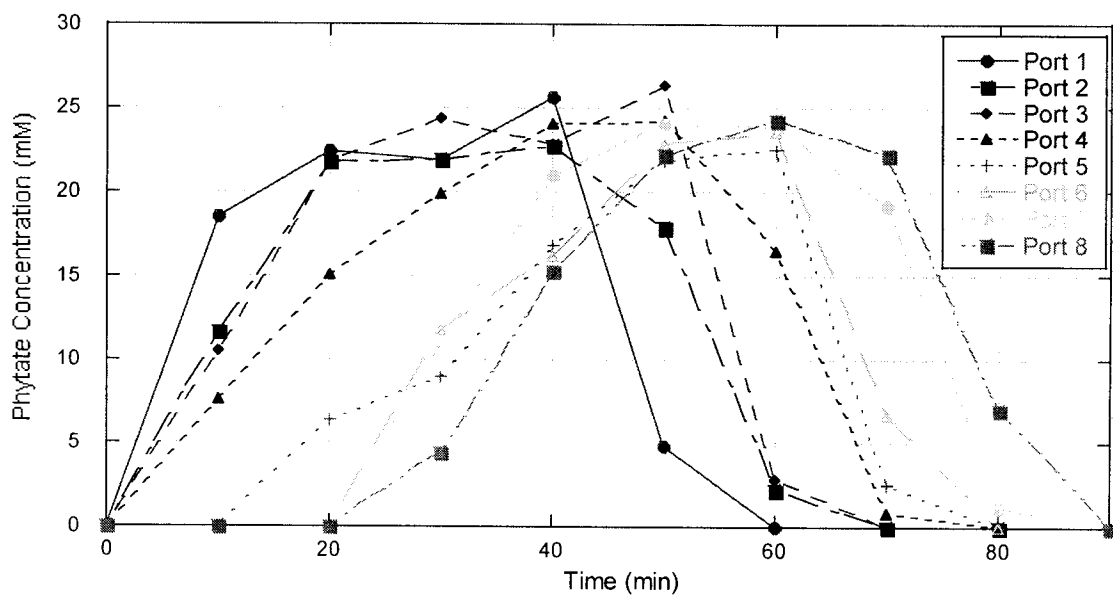


Figure 11

Concentration of phytate at each port with time in a column experiment with HCB coated

MCS at pH 7.

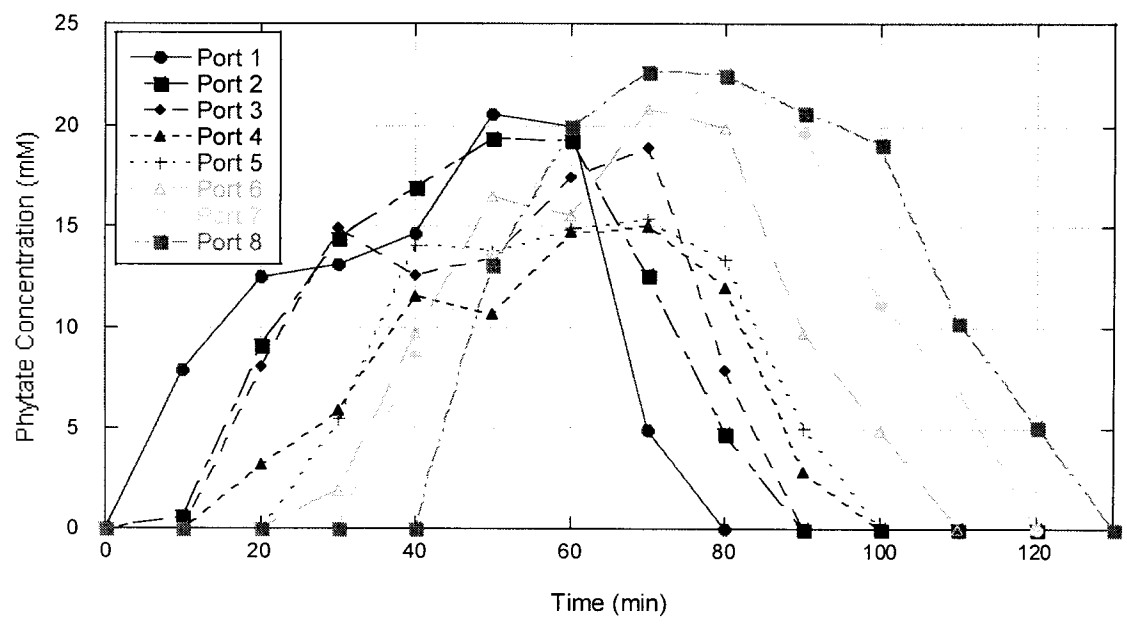


Figure 12

Concentration of phytate at each port with time in a column experiment with HCB coated ICS at pH 7.

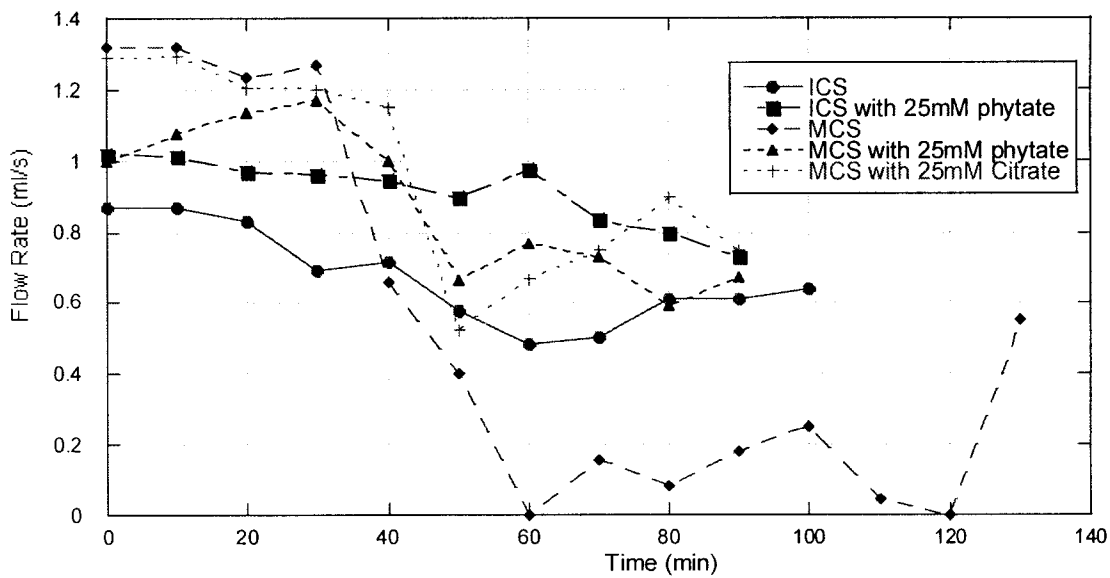


Figure 13

Flow rate with time for unstabilized or stabilized (25 mM phytate) ICS or unstabilized or stabilized (25 mM phytate or 25 mM citrate) MCS column experiments.