Remediación in situ de agua contaminada con diesel
por oxidación con peróxido de hidrógeno

In situ remediation of water contaminated with diesel
using oxidation with hydrogen peroxide

Recibido para evaluación: 23 de Marzo de 2010
Aceptación: 04 de Noviembre de 2010
Recibido versión final: 15 de Diciembre de 2010

Santiago Alonso Cardona Gallo[1]

RESUMEN

Las grandes cantidades de hidrocarburos que se manejan en el mundo y en México, generan derrames de crudo y sus derivados, deteriorando en gran medida el medioambiente y especialmente las fuentes de suministro de agua subterránea. En México, el 27% del agua potable proviene de los acuíferos. Lo anterior permite plantear la necesidad de desarrollar sistemas de tratamiento viables que pueden reducir la contaminación rápida y económicamente de los acuíferos. Este trabajo presenta la oxidación del diesel combustible en solución con un agente oxidante, peróxido de hidrógeno; grado industrial al 50%. Se utilizó el H2O2, porque es un agente oxidante fuerte muy conocido, de fácil manejo, de bajo costo y una solubilidad mayor en el agua que el oxígeno molecular. Se tuvo una concentración inicial de diesel en solución de 45.000 mg/L, bajo agitación horizontal continua en un sistema en serie durante 114 horas. Las muestras fueron tomadas periódicamente. Al final de las 114 horas, la concentración del hidrocarburo descendió hasta 24.000 mg/L, obteniendo una velocidad de la reacción de 0,0047 h-1 (0,1128 d-1). El estudio fue llevado a cabo sin catalizador. El efluente presentó un intervalo de pH entre 6,5 y 7,5. Con los resultados previos fueron diseñadas las columnas y operadas intermitentemente, y se comparó con columnas sin adición de peróxido de hidrógeno. La eficiencia del sistema y el bajo costo pueden ser aplicados en diferentes sistemas para el tratamiento de diesel en barreras reactivas permeables, zonas reactivas o aguas subterráneas.

Palabras Clave: Diesel combustible, oxidación, peróxido de hidrogeno, barreras reactivas permeables, zonas reactivas, remediación de aguas subterráneas.

ABSTRACT

The large quantities of hydrocarbons that are handled in the world and specialty in Mexico have caused spills of raw and their derivatives, this can pollution or deteriorating the environment and particularly the sources of supply of groundwater. In Mexico 27% of the drinkable water comes from underground. This has led to the necessity of obtaining treatment systems that are able to reduce contamination rapidly and economically. This paper presents the oxidation of diesel fuel in solution with an oxidant agent like hydrogen peroxide from industrial grade to 50%. Was used H2O2, a well- known stronger oxidizer. H2O2 is easy handling, low cost and a greater solubility in water than the molecular oxygen. Be had an initial concentration of diesel of 45,000 mg/L in solution in continuous horizontal agitation in a batch system for 114 hours. Periodic samples were taken. At the end of the 114 hours, the concentration of the hydrocarbon had declined to 24,000 mg/L, obtaining a velocity of reaction of 0.0047 h-1 (0.1128 d-1). The study was carried out without catalyst. The effluents presented a pH interval between 6.5 and 7.5. With the previous results the columns were designed and operated by batches, and compared with columns without hydrogen peroxide addition. The method for efficient and low cost can be applied in different systems of treatment of diesel, in permeable reactivate barriers, reactive zones or groundwater.

Key Words: Fuel diesel, oxidation, hydrogen peroxide, permeable reactive barriers, reactive zones, groundwater remediation.

---

[1] Profesor Escuela de Geociencias y Medio Ambiente, Facultad de Minas, Universidad Nacional de Colombia, Sede Medellín

scardona@unal.edu.co, sancardonagallo@gmail.com

1. INTRODUCTION

Many societies have developed and thrived at the expense of inefficient and unsustainable exploitation of the environment. In the twentieth century, the tension that existed between civilization and nature grew disproportionately. About 39- 50% of the land surface of our planet was modified due to human activities such as agriculture and urbanization, and the atmospheric CO_2 concentration increased by 40% over the past 140 years (mainly due to hydrocarbon combustion and deforestation). This raises serious concerns about global warming (Intergovernmental Panel on Climate Change, 2001). Biodiversity has also been significantly impacted, and more than 20% of bird species have become extinct in the last 200 years (Wilson, 2002).

Many natural resources show some degree of anthropogenic impact, including the widespread contamination of groundwater aquifers by hazardous wastes. This is particularly significant because groundwater represent about 98% of the available fresh water on the planet. It provides some statistic on the magnitude of the environmental contamination problem in the United States, and the main sources of groundwater contamination. The fact that we are already using about 50% of readily available fresh water makes groundwater protection and cleanup of paramount importance (Alvarez and Illman, 2006).

The magnitude of the hazardous waste contamination problem in the United States: United States generates 100 million tons of hazardous wastes per year. In 1987, 4 million tons of toxic chemicals were released to streams, 0.87 million tons were discharged to wastewater treatment plants, 1.2 million tons were disposed in landfills, 1.5 million tons were injected into deep wells for disposal. There are 300,000–400,000 sites in the United States that are highly contaminated by toxic chemicals and require remedial action. As of 1997, cleanup activities had not begun at 217,000 of these sites. Forty million U.S. citizens live within 4 miles of a Superfund site (there are thousands of Superfund sites). About 440,000 out of 2 million underground tanks storing gasoline in the United States have leaked (11 million gallons of gasoline leaked every year in the U.S., and BTEX account for 60% of soluble components). 50% of the U.S. population drinks groundwater, and 1- 2% of readily available groundwater is contaminated (1.2 trillion gal of contaminated groundwater infiltrates every day). According to a 1982 EPA survey, 20% of drinking water wells showed contamination by synthetic organic chemicals. Approximately 30% of 48,000 public drinking water systems serving populations in excess of 10,000 were contaminated, and 3% of these systems had groundwater contamination in excess of EPA standards. The estimated cost of environmental cleanup and management for the United States is of the order of $1 trillion (LaGrega et al., 1994; and NRC, 1994, 1997).

The principal sources of groundwater contaminations in the United States are: Leaking underground storage tanks (450,000). Municipal solids and hazardous waste landfills (93,000). Hazardous waste management sites (18,000). Unlined pits, ponds, and lagoons (180,000). Household septic systems (20 million). Pesticide application areas ($75x10^6$) tons/yr in Iowa). Abandoned petroleum wells. Saltwater intrusion along the U.S. coastline. Surface spills (LaGrega et al., 1994; and NRC, 1994, 1997).

Remediation costs for sites contaminated with hazardous wastes in Europe are expected to exceed $1.5 trillion in the near future (ENTEC, 1993). In the United States, the Office of Technological Assessment (OTA) of the U.S. Congress estimates that the cost of cleaning up more than 300,000 highly contaminated sites will exceed $500 billion (National Research Council (NRC) 1994). This does not include costs associated with about 440,000 sites impacted by gasoline releases from leaking underground storage tanks (U.S. Environmental Protection Agency (USEPA) 2003) or about 19,000 landfill sites used for disposal of municipal and industrial wastes (USEPA 1989). Thus, there is an urgent need for cost-effective treatment approaches (Alvarez and Illman, 2006).

In situ chemical oxidation (ISCO) is one of several innovative technologies that show promise in destroying or degrading an extensive variety of hazardous wastes in ground water, sediment, and soil. The oxidants used are readily available, and treatment time is usually measured in months rather than years, making the process economically feasible (EPAb, 1998). Enrichment with dissolved oxygen has been shown to stimulate *in situ* biological processes, but also is used in at least one site to oxidize other chemicals. Hydrogen peroxide and potassium permanganate are stable and easily handled oxidants in both solid and solution form. Hydrogen peroxide can be very cheap. Nevertheless, the shorter process may save on labor and operating costs (EPA, 1998b). ISCO can be applied in conjunction with other treatments such as pump-and-treat and soil vapor extraction to break down remaining compounds. It is less costly and disruptive than other traditional soil treatments such as excavation and incineration. ISCO may be used in applications where the effectiveness of bioremediation is limited by the range of contaminants and/or climate conditions (EPA, 1998b).

During the last decade, chemical oxidation has been developed and has been shown to be a useful technology to clean contaminated places. While during the chemical oxidation of an organic compound this compound is modified by an agent to final simpler products, having high oxygen content or a low hydrogen content than the original compound.

ISCO is based on the delivery of chemical oxidants to contaminated media in order to destroy the contaminants by converting them to innocuous compounds commonly found in nature. The oxidative agents which are used in different circumstances include chlorine dioxide (ClO_2) sodium hypochlorite (NaOCl) or calcium hypochlorite ($Ca(OCl)_2$), hydrogen peroxide (H_2O_2), air, ozone (O_3), phenton reaction, sodium permanganate ($NaMnO_4$), solid redox reactions (ORC, oxygen release compound as RegenOx™), and recently the potassium permanganate ($KMnO_4$) which is considered a strong chemical oxidative to chlorinated organic compounds (Suthersan, 1997; Siegrist, 2000 y 2001, Regenesis, 2007).

Several studies have been carried out where dibenzotiofeno has been oxidized using H_2O_2 (Collins et al., 1997), phenol (Ince y Apikyan, 2000), phenol y chlorophenols (Grigoropoulou y Philippopoulos, 1997), diesel (Tae Lee y Woong Kim, 2002), chlorinated hydrocarbons, solvents, oil hydrocarbons y volatile organic compounds (Yin y Allen, 1999).

The most common field applications thus far have been based on Fenton's Reagent whereby hydrogen peroxide is applied with an iron catalyst creating a hydroxyl free radical. This hydroxyl free radical is capable of oxidizing complex organic compounds. Residual hydrogen peroxide decomposes into water and oxygen in the subsurface and any remaining iron precipitates out. This process has a history of application in waste treatment fields (EPA, 1998b).

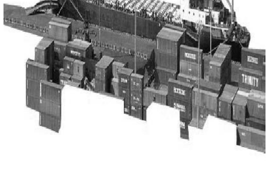
The volume and chemical composition of individual treatments are based on the contaminant levels and volume, subsurface characteristics, and pre- application laboratory test results. The methods for delivery of the chemical may vary. The oxidant can be injected through a well or injector head directly into the subsurface, mixed with a catalyst and injected, or combined with an extract from the site and then injected and recirculated (EPA, 1998b).

ISCO is used for ground water, sediment, and soil remediation. It can be applied to a variety of soil types and sizes (silt and clay). It is used to treat volatile organic chemicals (VOCs) including dichloroethene (DCE), trichloroethene (TCE), tetrachloroethene (PCE), and benzene, toluene, ethylbenzene, and xylene (BTEX) as well as semi-volatile organic chemicals (SVOCs) including pesticides, polycyclic aromatic hydrocarbons (PAHs), and polychlorinated biphenyls (PCBs) EPA (1998b).

Chemical oxidation mechanisms, involves the breaking of chemical bonds and the removal of electrons. The electrons are transferred from the contaminant to the oxidant. The contaminant is in turn oxidized and the oxidant, the electron acceptor, is reduced. All reactions are always paired in this way- hence the term oxidation- reduction reaction (Regenesis, 2007).

Oxidant agent reactions in order to completely oxidize (mineralize) contaminants to carbon dioxide and water, all chemical oxidants must either supply oxygen from the oxidant itself or from reactions involving water. In addition to the oxygen provided by its oxidant, oxidative specie is capable of promoting the propagation reactions that yield a mixture of free radicals. A free radical is a highly reactive molecule having an unpaired electron. Free radicals are generated by the decomposition of peroxide in the presence of metal salts such as a ferrous salt. The free radicals that are formed by oxidative specie include (Regenesis, 2007):

Perhydroxyl radical $HO_2\cdot$: (oxyhydroxyl or protonated superoxide). The perhydroxyl radical is a species formed by a base catalyzed free radical mechanism. In the oxidative system, the perhydroxyl radical is one of the predominant radical intermediates formed.



$H_2O_2 + OH\cdot \rightarrow HO_2\cdot + H_2O$

$Fe^{+3} + H_2O_2 \rightarrow HO_2\cdot + H^+ + Fe^{+2}$

In addition, the hydroperoxide anion HO_2^-, is the conjugate base of H_2O_2, will form. The hydroperoxide anion is a reductant.

$HO_2\bullet + O_2\bullet^- \rightarrow HO_2^- + O_2$

$HO_2\bullet + Fe^{+2} \rightarrow HO_2- + Fe^{+3}$

Hydroxyl radical OH·. The reaction of ferrous iron and hydrogen peroxide generates hydroxyl radicals. The hydroxyl radical can react with almost any hydrocarbon or chlorinated hydrocarbon. However, because of the alkaline conditions promoted by the oxidative specie catalyst hydroxyl radicals have only a minor role in the active mechanisms of this oxidative system.

$H_2O_2 + Fe^{+2} \rightarrow OH\cdot + OH^- + Fe^{+3}$

Superoxide radical O2·⁻, is also a reductant which can break down highly oxidized compounds such as carbon tetrachloride and chloroform.

$HO_2\cdot \rightarrow H^+ + O_2\cdot^-$

Oxidation potentials of chemical oxidants are often ranked in terms of their electropotential. The electropotential is the electromotive force in units of volts (V) based on half-cell reactions. Theoretically, larger values indicate a greater potential for the half reaction to proceed.

Relative electropotentials: (ITRC 2005)

Hydroxyl Radical	2.8 V
Ozone (Gas)	2.1 V
Sodium Persulfate	2.0 V
Sodium Percarbonate	1.8 V
Hydrogen Peroxide	1.8 V
Permanganate	1.7 V
Superoxide Ion	-2.4 V

Oxidation potentials (half-cell reactions) for oxidants, however, do not tell the whole story. They rate oxidants only against hydrogen and do not account for the chemistry needed to provide the oxygen for the oxidation reactions, provide the cation for the chloride, account for all electrons transferred, and provide the needed components for completely balanced equations (the contaminant side of a half-cell). Further, oxidation potentials tell us nothing about the speed of reactions. To understand the complete image, one must evaluate the oxygen content of the oxidant, the thermodynamics and kinetics of the reaction (Regenesis, 2007).

Relative Oxygen Equivalence (Active Oxygen) says that having more oxygen in the oxidizer does not necessarily mean more oxygen will be used. To better understand each oxidant's provision of oxygen to oxidize, it can gauge the relative weight fraction of oxygen in each oxidant that can contribute to chemical oxidation. This is known as % active oxygen (A.O.), is have:

Hydrogen Peroxide	47% active oxygen
RegenOx™ Oxidizer Complex	15.3%
Potassium Permanganate	15.2%
Sodium Persulfate	6.7%

Thus on an Active Oxygen basis, oxidative specie has 1/3 the electron equivalence of H_2O_2, approximately the same as permanganate, and over 100% more than sodium persulfate.

Thermodynamics tells us the likelihood or potential that a reaction will take place as well as to what extent the reversible reaction has proceeded when equilibrium is reached. Interpreting completely balanced equations in terms of the Gibb's Free Energy is a more valid approach for comparing reactions than that based on half-cell reactions alone. The Gibb's Free Energy (ΔG) is a measure of the amount of energy that is available from some process operating at constant pressure and is directly connected to voltage. The Gibb's Free Energy function is a convenient way to determine which way a reaction will go. If $\Delta G < 0$, that reaction will.

The voltage for the complete oxidation-reduction reaction (ε) is equivalent to the chemical change in Gibb's Free Energy (ΔG) divided by the number of electrons transferred (n) and a constant of nature termed Faraday's Constant (F).

$\varepsilon = -\Delta G / nF$ (2- 2)

The lower the free energy (the more negative), the higher the voltage and the more likely the reaction will occur. The peroxide mediated reactions are the strongest based on the most negative ΔG. The calculations show the energetic of peroxide under basic conditions, as is done with oxidative specie, are more favorable than for permanganate and persulfate under their use conditions.

When treating chlorinated contaminants, chloride is a terminal product of the oxidation and it would prefer it not form a problematic chlorine species such as an oxide. By operating peroxide reactions under basic conditions, as is done with oxidative specie, more benign chloride salts are formed. The Formation of ClO_2 from the Peroxidation of PCE under Acidic Conditions show than:

$C_2Cl4 + 12H_2O_2 \rightarrow 2CO_2 + 4ClO_2 + 12H_2O$

RegenOx™ has ΔG = -338 kcal/mol, for $C_2Cl_4 + 2H_2O_2 + 4NaOH \rightarrow 2CO2 + 4NaCl + 4H_2O$.

Potassium Permanganate has ΔG = -329 kcal/mol, for $C_2Cl_4 + 4KMnO_4 \rightarrow 2CO_2 + 4MnO_2 + 4KCl + 2O_2$.

Potassium Persulfate has ΔG= -271 kcal/mol, for $C_2Cl_4 + 2K_2S_2O_8 + 4H_2O \rightarrow 2CO_2 + 4KCl + 4H_2SO_4$.

Hydrogen Peroxide has ΔG = -261 kcal/mol, for $C_2Cl_4 + {}_2H_2O_2 \rightarrow 2CO_2 + 4HCl$.

The fact which is self-evident is that these reactions have been observed in practice, thus the required Energy of Activation is manifested.

If kinetics of the reaction is thermodynamically favored, it is still governed by kinetics. In essence, thermodynamics addresses the probability of the reaction and kinetics tells us how fast the reaction will happen. If the reaction is fast, equilibrium calculations will predict the results of the reaction. If the reaction is not fast, then the only way to follow the course of the reaction is to measure the chemical composition as a function of time (Robinson, 1987).

The rate of reaction that describes the destruction of the compound of interest over time as a function of the concentrations of the various species participating in the reaction. For chemical oxidation, the rate of reaction (with respect to the contaminant) for a contaminant A reacting with an oxidant B can be written as a function of both the concentrations of A and B with k as the rate constant, as per equation: $-r_A = k (C_A / C_{Ao}) * (C_B / C_{Bo})$, where C_A is the final concentration of A and C_{Ao} is the concentration of A at time = 0, and C_B is the final concentration of B and C_{Bo} is the concentration of B at time = 0.

When the concentration of oxidant B is greatly in excess the concentration of contaminant A so that the concentration of oxidant B does not change much during the course of the reaction, then $C_B = C_{B0}$. The rate equation would then reduce to

$-r_A = k (C_A / C_{A0})$, and after integration $C_A = C_{A0} e^{-kt}$.

This equation would define a pseudo-first order reaction. A plot of the natural logarithm (ln) of C_A / C_{A0} versus time should yield a straight line.

Half- life is used as a measure of rate for first-order reactions. Half-life is the time required for the concentration of contaminant to reduce in half.

Thus at time $t_{½}$ when $C_A = ½C_{A0}$, then $t_{½} = \ln 2/k = 0.693/k$ (Levenspiel 1972). The reaction rates will tend to be slower. However, practically speaking, the only way chemical oxidation is affordable is if the rate of the oxidation of the contaminant is faster than the rate of the interaction of the oxidant with the background oxidant demand of the aquifer (Regenesis, 2007).

2. MATERIALS AND METHODS

Obtaining the order of the Reaction

A numerical equation for the intrinsic velocity was applied in the design of the process. It was necessary to know the form of the function of the concentration. From this information the expression which accorded with the available data was determined. From this information was determined the expression that better agree with the available data. This procedure was of trial and error, comparing diverse equations of proposed velocity with the dates. Various procedures laboratory exist to detect the course of an equation. It was considered that the reactions are homogeneous by batches to constant volumes. The kinetic obtained experimental was compared with the equations proposed velocity and with the methods of integration and differential.

Integral method

The data analysis integration method consists of comparing the concentrations observed and obtained over a period of time. This experimental always provides a kinetic equation. This equation was integrated, and the data calculates were compared C against t. If the adjustment is not satisfactory is suggested and practices another kinetic equation (Smith, 1999; Levenspiel, 1998).

Differential method

The differential method requires a differentiation of the experimental dates of Ci in function of t, to obtain an experimental velocity. The velocity is compared with that obtained in base to the equation of proposed velocity. This method using directly the differential equation trailed. All the terms of the equation were evaluated, including the differential dCi/dt, and the fit of the adjustment of the equation with the experimental dates (Smith, 1999; Levenspiel, 1998).

Batch

The kinetics oxidation of diesel was determined by means of the hydrogen peroxide in order to obtain its velocity of transformation during 114 hours. The oxidation test was made in triplicate with a concentration in each vial of 40,000 mg/L diesel. 25 mL of synthetic contaminated solution were added. Afterward, 6.1 mL of H_2O_2 were applied according to the stoichiometrical equation. The vials were placed under horizontal agitation for 48 hours at 50 revolutions per minute. Finally, the residual diesel in liquid phase was analyzed. The vials had 40 mL. The kinetics of transformation works by the first order reaction (Crittenden, et al. 1999, Suthersan, 1997, Jenkins, 1997, Siegrist et al., 2000). The diesel equation proposed by Jackson (1990) $C_{15}H_{30}$, was applied to the stiochiometry oxidation of diesel by means of the hydrogen peroxide.

$C_{15}H_{30} + 45H_2O_2 \rightarrow 60H_2O + 15CO_2 + C_{15}H_{30}$. Be requires 4 kg of O_2 = 7.29 kg of H_2O_2 for kg of diesel.

The rate equation applied was first-order (Smith, 1986) $-r_A = k\ (C_A / C_{A0})$, integration $C_A = C_{A0} e^{-kt}$.

A plot of the natural logarithm (ln) of C_A / C_{A0} versus time should yield a straight line. To measure the rate of first order reactions with half-life the equation, $t_{½}$, where $C_A = ½C_{A0}$, then $t_{½} = \ln 2/k = 0.693/k$ (Levenspiel 1972).

Columns

For the design of the oxidative phase in the continuous column, was applied the order first kinetic.

$A \Rightarrow P$ Ec. 1

(Diesel) (Product)

Where

A= Contaminant

P= Oxidation of the product

$$\frac{dC_A}{dt} = -kC_A \qquad \text{Ec. 2}$$

$$\frac{dC_A}{C_A} = -kdt \qquad \text{Ec. 3}$$

Integrating from 0 to t and of C_0 to C

$C=C_0e^{-kt}$ Ec. 4

Figure 1 shows the plan of the process of the oxidation phase of the diesel inside the column and from which the equations that shape its operation were determined as time of residence, volume of the column and thickness of the half a reagent.

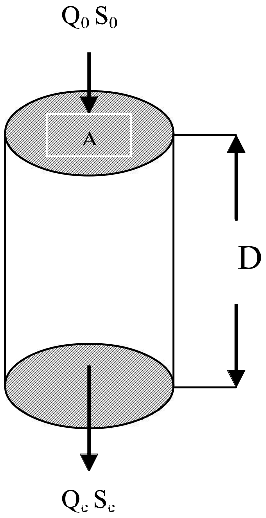


Figure 1. Model conceptual oxidative by flow piston.
Figura 1. Modelo conceptual oxidativo para flujo pistón.

Retention time, t_h (d)

$$t_h = \frac{1}{k(\ln\frac{C}{C_o})} = \frac{v}{Q} = \frac{v}{Fv_T}(d) \qquad \text{Ec. 5}$$

In the next equation is obtained: the t_h, where the constant kinetic k was determined experimentally:

Where F is the composed flow fed (mols/s), is the volume of feed (L/mol), Q discharge and $Fv_T=Q$.

Volume of the reactor of oxidation, (m3, L)

$V = t_hQ$ (m3,L) Ec.6

Thickness of the half oxidative of the reactor, D.

$$b = \frac{Q}{Ak(\ln\frac{S_o}{S_e})} = vt_h \qquad \text{Ec. 7}$$

Where

v = velocity of the flow, m/s

Thickness of the half a reagent (b), retention time (t_h), diameter of the column (d), velocity of the flow (v) and volume of the reactor (V)

$$b = Lt_h = \frac{Q_0}{A}t_h(m) \qquad \text{Ec. 8}$$

$$t_h = \frac{1}{k}\ln\frac{S_0}{S_e} = \frac{V}{Q_0}(h^{-1}) \qquad \text{Ec. 9}$$

$$d = \left(\frac{4A}{\pi}\right)^{\frac{1}{2}}(m) \qquad \text{Ec. 10}$$

$$v = \frac{Q_0}{A}(m/s) \qquad \text{Ec. 11}$$

$$V = AD = \frac{Q_0}{K}\ln\frac{S_0}{S_e}(m^3) \qquad \text{Ec. 12}$$

The hydraulics load was calculated at a depth and a percentage of specific removal.

$$L = \left(\frac{kD}{\ln\left(\frac{S_e}{S_o}\right)}\right)^{\frac{1}{n}} \quad (m^3/m^2s) \qquad \text{Ec. 13}$$

The cross area required for the reactor is:

$$A = \frac{Q_0}{L}(m^2) = \frac{Q_0}{KD}\ln\frac{S_0}{S_e}(m^2) \qquad \text{Ec. 14}$$

They were daily fed by its upper part with a volume of 300 mL and a concentration of 10, 000 mg/L of diesel completely mixed. Every day the samples of all the columns were collected; from each column 300 mL were taken. Every six days the corresponding sample was analyzed in the gases chromatograph with a Hewlett Packcard mass selector 5890 serie II with technique 8015 EPA for 78 days. The mix of diesel and distillate water was carried out in a precipitate vessel of 500 mL with a continuous agitation the solution was homogenized. The columns were built in transparent acrylic from 20 cm the long and 10.7 cm in diameter. The gasket was silica sand.

3. RESULTS AND DISCUSION

Batch

To start with, the kinetic first order reaction to diesel fuel was obtained and the results of the characterization of the applied SS as a reactive medium are presented. Secondly the obtaining of the coefficient of partition is presented (K_d) (the diesel on the silica sand) and the factor of retardation (R) was obtained; third the kinetic degradation of the diesel and the adsorption capacity of the SS, and finally the design and working of the columns.

Obtaining order of the Reaction

Table 1. Obtained order of the kinetic reaction for the oxidation with the differential and integral method.

Tabla 1. Determinación orden de la cinética para la oxidación con el método integral y diferencial.

Time (h)	-lnC/Co	**1/C**	**1/C-1/Co**	C	logC	log r=(log(C=x(Co))/t)	2logC
0	0.01198	2.238E-05	-2.70E-07	44682.7	4.65	3.088	9.30
1	0.02775	2.301E-05	3.601E-07	43459.6	4.64	3.076	9.28
2	0.07509	2.413E-05	1.475E-06	41450.4	4.62	3.055	9.24
3	0.07864	2.421E-05	1.563E-06	41303.4	4.62	3.054	9.23
4	0.12753	2.542E-05	2.774E-06	39332.7	4.59	3.033	9.19
8	0.17259	2.660E-05	3.946E-06	37599.8	4.58	3.013	9.15
12	0.23476	2.830E-05	5.652E-06	35333.4	4.55	2.986	9.10
24	0.26836	2.927E-05	6.619E-06	34165.7	4.53	2.971	9.07
28	0.30652	3.041E-05	7.758E-06	32886.6	4.52	2.955	9.03
32	0.38778	3.298E-05	1.033E-05	30320.0	4.48	2.919	8.96
49	0.25428	2.886E-05	6.210E-06	23100.3	4.36	2.801	8.78
54	0.42793	3.433E-05	1.168E-05	19417.7	4.29	2.726	8.58
78	0.43678	3.464E-05	1.199E-05	19246.7	4.28	2.722	8.57
114	0.59633	4.063E-05	1.798E-05	16408.4	4.22	2.653	8.43

$1/C_o = 2.265 \times 10^{-5}$.

Integral method

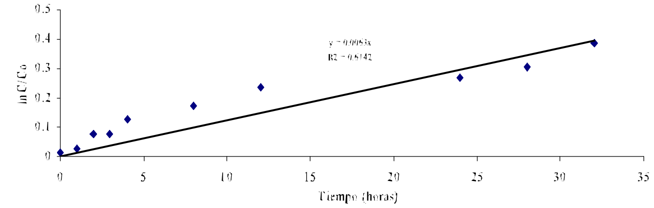


Figure 2. Graphic of the results of the integration method for the reaction of diesel with a first order kinetic.

Figura 2. Gráfica de los resultados del método de integración para la reacción del diesel con una cinética de primer orden.

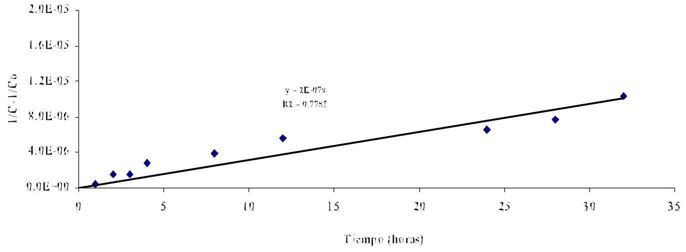


Figure 3. Graphic of the results of the integration method for the reaction of diesel with a second order kinetic.

Figura 3. Gráfica de los resultados del método de integración para la reacción del diesel con una cinética de segundo orden.

The method show two graphics of dispersion that does not illustrate any particular tendency, to conclusion the adjustment is not acceptable with the precision required for the lineal relation. At last was the differential method trail (Smith, 1999, Levenspiel, 1998).

Differential method

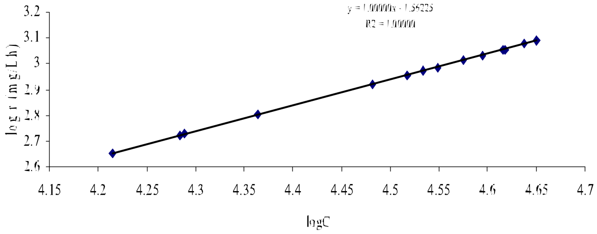


Figure 4. Graphic of velocity in function of the concentration of diesel for a slope of 1 and first order kinetic.
Figura 4. Gráfica de velocidad en función de la concentración de diesel para una pendiente de 1 y primer orden.

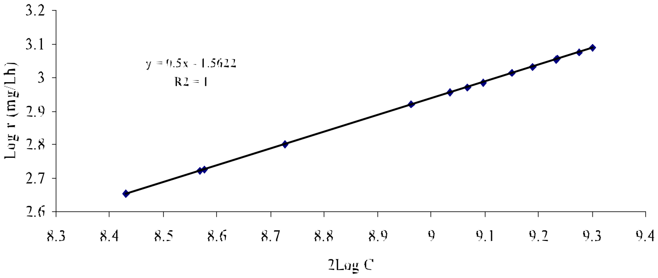


Figure 5. Graphic of velocity in function of the concentration of diesel for a slope of 1 and second order.
Figura 5. Gráfica de velocidad en función de la concentración de diesel para una pendiente de 1 y segundo orden.

The results drawn by the differential method demonstrated an adequate adjustment of the two equations. For the first order kinetic a slope of 1 in the straight line was expected (figure 4), and was obtained; and a slope of 2 for the second order kinetic (figure 5) and was not obtained. Figure 4 presented a slope of 1 and figure 5 a slope of 0,5; which permitted the conclusion that the experimental dates of the oxidation of diesel by H_2O_2, and continues a first order kinetic reaction (Smith, 1999, Levenspiel, 1998).

Characterization of silica sand

Table No. 2 presents the characterization of the silica sand that served as backup of the half a reagent for oxidation of the diesel fuel. High porosity and adsorptive capacity to diesel was obtained. The test did not detection of organic matter in silica sand, guaranteed only the oxidation of the hydrocarbon.

Table 2. Characterization of silica sand.
Tabla 2. Caracterización de la arena sílice.

Parameter	Obtained value
Porosity	37.88%
Real density	2.64 g/mL
Apparent density	1.64 g/mL
hydraulic conductivity	$9.52X10^{-3}$ cm/s
Organic Carbon, f_{oc} (%)	0.00
Diameter	0.60-0.84mm (mesh 20-30)

Table No. 3 and figure No. 6 present the adsorption capacity and the distribution coefficient (K_d) of the diesel in the silica sand, to identify the hydrocarbons that were remain and available. The retardation factor of the diesel was determinate in silica sand in against with water.

Cs (mg/g)	Cw (mg/L)
0.00	0.00
1.059	4,613
3.209	7,717
7.819	12,385
11.108	18,753

Table 3. Results of adsorption of diesel in the silica sand.
Tabla 3. Resultados de adsorción en la arena sílice.

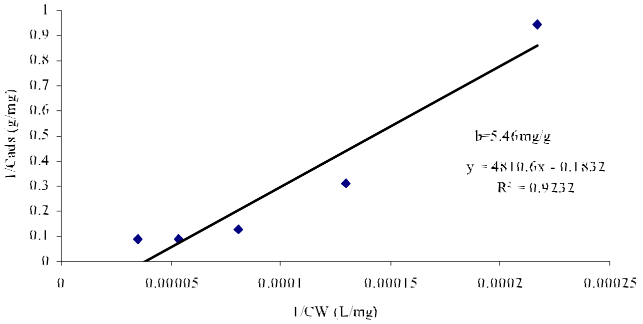


Figure 6. Obtained of Kd for the silica sand.
Figura 6. K_d obtenido para la arena sílice.

The silica sand obtained a Kd of 0.45mL/g, and was compared with a Kd of an agricultural soil of 0.80mL/g (Cardona, 2007) table No. 4. The two materials presented percentages of similar porosity, 44% for the agricultural soil and 38% for the silica sand, but its coefficient of distribution is not similar and the Kd of the agricultural soil duplicates the coefficient of distribution of the diesel in the SS. The greater distribution (K_d) of the diesel on the agricultural soil may be caused by the content of, The silica sand did not present organic matter (Schwarzenbach, 1993). The previous K_d is consistent with it reported by other authors where they showed that the greater content of organic matter in the soil (f_{oc}=1.49% for the agricultural soil and 0.00% for the silica sand) had greater distribution of the organic compound (Schwarzenbach et al., 1993).

Material	Parameter	
	K_d (mL/g)	R
Agricultural soil	0.76	3.69
Silica sand	0.45	2.73

Table 4. Determination of the coefficients of partition for the silica sand and the agricultural soil.
Tabla 4. Determinación de los coeficientes de distribución para la arena sílice y suelo agrícola.

K_d: Coefficient of distribution. R: factor of retardation for diesel in the silica sand of 2.73 and of 3.69 for the agricultural soil. The silica sand is 2.73 times slower than the groundwater.

The factor of retardation was determined with the proposed equation by Freeze and Cherry (1979) $R = 1 + \frac{\rho}{\eta} K_d$, which relates the coefficient distribution with the porosity (h) of the soil and its density (r). As the R for the silica sand was expected (2.73) is smaller than for the agricultural soil (3.69). This factor is greater in organic matter that in the agricultural soil and can be attributed as was shown above, the contained in agricultural soil present organic matter (as was observed, the silica sand did not present f_{oc}). The before permits the inference that can be the content of organic matter that the flow of the diesel can will be retarded more in a soil with organic matter that without her. In the silica sand the retardation was due to the porosity and to the surface of the sand (Schwarzenbach, 1993).

Volatilization

The volatilization trial of diesel was carried out in open vials and closed for eight days. The volatilization of the diesel in the trials carried out was of zero, which is similar to that reported in other studies (Márquez-Rocha et al., 2001) that were smaller that 5% approximately of the initial concentration. The results of the volatilization of the diesel showed a few loss of this. Which it can concludes that the hydrocarbon was not volatilized inside the reactors by batches and was transformed for oxidation or itself adsorbed in the SS. The concentration of volatilization with closed vials was of 50,000 mg/L and with open vials was of 15,000 mg/L of diesel. They applied two different concentrations to observe the influence of the concentration in the volatilization. The run was carried out for triplicate. Figure No. 7 and table No. 5 present the oxidation of diesel with a kinetic the first order.

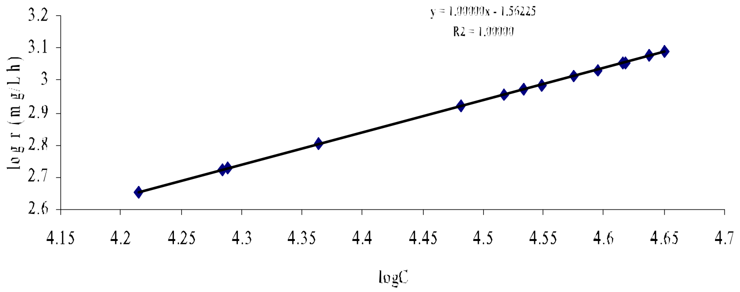


Figure 7. Graphic of velocity in function of the concentration of diesel for a slope of 1 and first order.
Figura 7. Gráfica de la velocidad en función de la concentración de diesel para una pendiente de 1 y una cinética de primer orden.

Table 5. Results of oxidation of diesel by hydrogen peroxide.
Tabla 5. Resultados de oxidación del diesel con peroxide de hidrógeno.

Time (h)	C_1 (mg/L)	C_2 (mg/L)	C_3 (mg/L)	C (mg/L) average	lnC/Co
Time (h)	C_1 (mg/L)	C_2 (mg/L)	C_3 (mg/L)	C (mg/L) average	lnC/Co
0	43,472	45,505	45,336	44,682	0.01198103
1	40,738	43,368	44,136	43,459	0.02775405
2	37,408	42,631	43,575	41,450	0.07508807
3	38,272	42,297	43,007	41,303	0.07864127
4	34,212	41,694	41,489	39,332	0.12752837
8	29,320	39,760	41,785	37,599	0.17258637
12	28,298	35,002	37,942	35,333	0.23475612
24	34,186	32,380	33,309	34,165	0.26836287
28	31,921	31,746	34,359	32,886	0.3065199
32	28,581	34,942	30,633	30,320	0.38777728
49	30,150	29,863	34,359	34,650	0.2542763
54	28,850	30,061	28,390	29,126	0.42793395
78	25,930	24,990	27,679	28,870	0.43678038

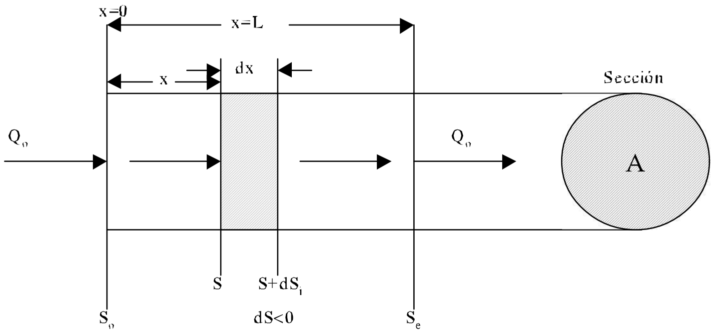
Columns: The columns for intermittent operation and the conceptual model of piston flow were designed with the velocity of oxidation obtained.

With the velocity of oxidation obtained and the conceptual model of piston flow were designed the columns for operation intermittent (Cardona, 2004). Kinetic leading was determined by:

$$\frac{dC_A}{dt} = -kC_A \qquad \text{Ec. 1}$$

Where A is the diesel concentration.

The model mathematic applied to determine the volume and thickness of the columns is present below (Cardona, 2004).



$$\int_{x=0}^{x=l} \frac{Adx}{Q_o} = \int_{S_o}^{S_e} \frac{dS}{kS} \Rightarrow \frac{A}{Q_o} L = \frac{1}{k} \ln \frac{S_o}{S_e}$$ Ec. 2

Y AL=V (volume of reactor) Þ

$$\frac{V}{Q_o} = t_h \Rightarrow t_h = \frac{1}{k} \ln \frac{S_o}{S_e}$$ Ec. 3

$$t_h = \frac{1}{k(\ln \frac{C}{C_o})} = \frac{v}{Q} = \frac{v}{Fv_T}(d)$$ Ec. 4

The previous equation presents the time of residence to determine as much as time will remain in the column the water contaminated for reach a concentration desired. Where F is the composed flow feed (moles/s), n_T is the volume of feed (L/mol), Q flow y Fn_T=Q.

Volume of the reactor of oxidation (m^3, L)

V= t_hQ (m^3,L)
Thickness of the half an oxidative of the reactor, b is:

$$b = \frac{Q}{Ak(\ln \frac{S_o}{S_e})} = vt_h$$ Ec. 4

Where the thickness of reactive medium (b), time of residence (t_h), diameter of the column (d), velocity of flow, m/s (v), load hydraulic (*L*) and volume of reactor (V).

$$b = Lt_h = \frac{Q_0}{A} t_h (m)$$ Ec. 5

$$t_h = \frac{1}{k} \ln \frac{S_0}{S_e} = \frac{V}{Q_0}(h^{-1})$$ Ec. 6

$$d = \left(\frac{4A}{\pi}\right)^{\frac{1}{2}} (m)$$ Ec. 7

$$v = \frac{Q_0}{A}(m/s)$$ Ec. 8

$$V = AD = \frac{Q_0}{K} \ln \frac{S_0}{S_e}(m^3)$$ Ec. 9

The load hydraulic considering is calculated a depth and a percentage of specific removal.

$$L = \left(\frac{kb}{\ln\left(\frac{S_e}{S_o}\right)}\right)^{\frac{1}{n}}$$ (m^3/m^2s) Ec. 10

The cross area required for the reactor is:

$$A = \frac{Q_0}{L}(m^2) = \frac{Q_0}{Kb}\ln\frac{S_0}{S_e}(m^2) \qquad \text{Ec. 11}$$

Table No. 6 presents the dimensions of the column utilized in the study.

Table 6. Parameters of design by columns.
Tabla 6. Parámetros de diseño para las columnas.

Parameter	Value
v	0.83cm/d
t_h	5.3d
b	4.4-10cm
V	395.65cm^3
A	89.92cm^2
L	3.34cm^3/cm^{2}d
ϕ	10.7cm
Q	300cm^3/d
Adsorption (Langmuir)	5.46mg/g

The column then operated for 78 days. Four columns packed with silica sand were installed. Columns 1 and 2 were operated with diesel plus hydrogen peroxide adding, and the 3 y 4 diesel fuel only. Table No. 7 present of average of oxidation diesel in columns. Figure No. 8 present of conceptual model used the columns.

Tabla 7. Resultados medios de la oxidación del diesel.
Table 7. Average results of oxidation diesel in columns

Time (days)	Columns 1-2 (mg/L)	Columns 3-4 (mg/L)
	Diesel + H_2O_2	Diesel
6	552	698
12	571	718
18	708	838
24	638	867
30	1091	1043
36	1505	3862
42	1581	3684
48	2086	3362
54	3835	9818
60	1515	5334
66	763	7333
72	2618	6508
78	1217	6130

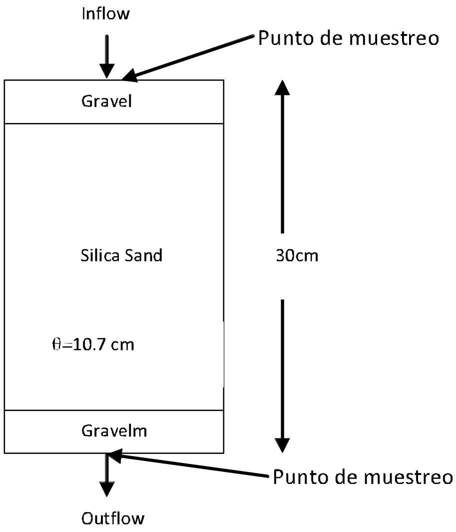


Figure 8. Columns designed
Figura 8. Columna diseñada

5. CONCLUSIONS

The kinetics of diesel oxidation with hydrogen peroxide could be obtained with a first order equation. The results obtained in batches and in columns allow the conclusion that diesel can be oxidized with H_20_2. The speed of reaction can permit the application of the oxidant agent to the remediation projects of contaminated soils and aquifers. The diesel volatilization test was made where it gave less than 1 mg/L of lost diesel. The data achieved conclude that hydrogen peroxide due to its low cost, major dissolution in water and oxidative strength makes it a good candidate for use in cleaning systems.

ACKNOWLEDGMENTS

This work was supported by the Reseacher Rosario Iturbe Argüelles of Engineering Institute the National Autonomous University of Mexico.

REFERENCES

Alvarez, P. and Illman, W., 2006. Bioremediation and natural attenuation : process fundamentals and mathematical models. John Wiley & Sons. New Jersey.

Cardona, S., 2004. Tratamiento de hidrocarburos con un sistema de barrera reactiva permeable. Universidad Nacional Autónoma de México. México, D.F.

Cardona, S., 2009. Biodegradation of diesel fuel in water by microbial consortium. Submitted to Journal of Bioremediation.

Collins, F., Lucy, A. and Sharp, Ch., 1997. Oxidative desulphuration of oils via hydrogen peroxide and heteropolyanion catalysis. J. of Molecular catalysis. 117: pp. 397- 403.

Choi, H., Lim, H-N., Kim, J., Hwang, T-M. and Kang, J-W. , 2002. Transport characteristics of gas phase ozone in unsaturated porous media for in-situ chemical oxidation. J. Contaminant Hydrology. Vol. 57, pp. 81- 98.

ENTEC. Directory of Environmental Technology, 2006. Earthscan Publications and Lewis Publishers/CRC Press, Ann Arbor, MI. 1993. In Alvarez, P. and Illman, W. Bioremediation and natural attenuation: process fundamentals and mathematical models. John Wiley & Sons. New Jersey.

Grigoropoulou, H. and Philippopoulos, C., 1997. Homogeneous oxidation of phenols in aqueous solution with hydrogen peroxide and ferric ions. Water Science Technology. Vol. 36, N° 2- 3, pp. 151- 154.

Ince, N. and Apikyan., 2000. Combination of activated carbon adsorption with light- enhanced chemical oxidation via hydrogen peroxide. Water Research. Vol. 34, N° 17, pp. 4169- 4176.

Kong, Sung-Ho, Watts, R. and Choi, Jin- Ho., 1998. Treatment of petroleum- contaminated soils using iron mineral catalyzed hydrogen peroxide. Chemosphere. Vol. 37, N° 8, pp. 1473- 1482. Ozonation of diesel fuel in unsaturated porous media. Applied Geochemistry. Vol. 17, pp. 1165- 1170.

Levenspiel, O., 1972. Chemical Reaction Engineering, Second Edition. John Wiley & Sons, New York.

National Research Council, 1994. Alternatives for Ground Water Cleanup. National Academy Press, Washington, DC.

National Research Council, 2006. Innovations in Ground Water and Soil Cleanup: From Concept to Commercialization. National Academy Press, Washington, DC. 1997. In Alvarez, P. and

Illman, W. Bioremediation and natural attenuation : process fundamentals and mathematical models. John Wiley & Sons. New Jersey

La Grega, M., P. Buckingham, and J. Evans., 2006. Hazardous Waste Management. McGraw Hill, New York. 1994. In Alvarez, P. and Illman, W. Bioremediation and natural attenuation : process fundamentals and mathematical models. John Wiley & Sons. New Jersey.

Lee, Byung-Tae and Kim, Kyoung, 2002.

National Research Council, 2006. Natural Attenuation for Ground Water Remediation. National Academy Press, Washington, DC. 2002. In Alvarez, P. and Illman, W. Bioremediation and natural attenuation : process fundamentals and mathematical models. John Wiley & Sons. New Jersey.

Regenesis, 2007. Principles of Chemical Oxidation Technology for the Remediation of Groundwater and Soil. Design and Application Manual. San Clemente, California.

Robinson, R., s.a. Chemical Engineering Reference Manual, Fourth Edition. Professional Publications.

Siegrist, R., 1987. In situ chemical oxidation. Technology features & applications. Advances in innovation ground water remediation technologies. GWRTAC and EPA-TIO. Boston.

Siegrist, R., Urynowicz, M., West, O., Crimi, M. and Lowe, K., 2001. Principles and practices of in situ chemical oxidation using permanganate. Battelle Press. Columbus, Ohio, USA.

Suthersan, S. S., 1997. Remediation Engineering. CRC Lewis Publisher. Boca Raton, Florida. USA.

U.S. Environmental Protection Agency, 2006. Toxic Release Inventory. Magnetic Tape Number P.B. 89- 186- 118, NTIS or TRI Data Base, National Library of Medicine, Bethesda, MD. 1989. In Alvarez, P. and Illman, W. Bioremediation and natural attenuation : process fundamentals and mathematical models. John Wiley & Sons. New Jersey.

U.S. Environmental Protection Agency. Washington, DC, 2006. (www.epa.gov/swerust1/pubs/ustfacts.pdf.). 2003. In Alvarez, P. and Illman, W. Bioremediation and natural attenuation: process fundamentals and mathematical models. John Wiley & Sons. New Jersey.

Wilson, E.O., 2006. The Future of Life. Little Brown & Company, Warner Books, Lebanon, IN. 2002. In Alvarez, P. and Illman, W. Bioremediation and natural attenuation : process fundamentals and mathematical models. John Wiley & Sons. New Jersey.

Yin, Yujun and Allen, Herbert E, 1999. In situ chemical treatment. Groud- Water Remediation Technologies Analysis Center, GWRTAC. Technology evaluation report. Series TE- 99- 01.