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Solar Detoxification
Treatment of Contaminated Groundwater

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Abstract

Recently a solar-based AOP technology (known as the Solaqua® process) was developed by a group of Canadian researchers. This solar detoxification process offers the potential for significant energy savings in the treatment of groundwater. This new technology could contribute to the reduction of environmental footprint and at the same time demonstrate an innovative approach in alternate energy source application.

Research was conducted to develop the Solaqua® technology further through bench-scale work. Bench-scale test results showed excellent destruction of BTEX, MTBE and MMT contaminants using the Solaqua® technology. This is consistent with our earlier experience in BTEX and MTBE destruction using conventional AOP systems. A performance model was developed to predict solar detoxification technology performance based on the Solaqua® technology. Very often, confidence in performance estimation is the central issue in the adaptation of solar-based technologies.

A number of areas for future work have been identified. Some of this work may be included in the next phase of this project where performance prediction model could be tested and validate using field test results. It was demonstrated by the results of this phase of the project that the Solaqua® technology (based on a renewable energy source) could be an effective tool in the treatment of contaminated groundwater.

Introduction

Contamination from organic compounds such as benzene, toluene, ethylbenzene and xylenes (BTEX) represent a common issue in the oil and gas industry. A number of technologies have been developed and demonstrated for the treatment of groundwater contaminated with these compounds. Some of these technologies include advanced oxidation process (AOP), steam stripping, air stripping and more recently, monitored natural attenuation. Each technology has its own set of advantages and limitations. As an example, the AOP technology gained some popularity in the 1990s as a remediation technology for treating trace concentrations of organic contaminants; however, power consumption of AOP treatment plants is relatively high. This energy consumption constitutes the majority of the plant operating cost and adds to the general demand on electricity.

Recently a solar-based AOP technology was developed by a group of Canadian researchers. This solar detoxification process offers the potential for significant energy

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savings in the treatment of groundwater. This new technology could contribute to the reduction of the environmental footprint from oil and gas production and at the same time demonstrate an innovative approach in alternate energy source application.

Photo-oxidation involves the use of ultraviolet (UV) light plus an oxidant to generate hydroxyl radicals. The hydroxyl radicals then attack the organic compounds to initiate oxidation. There are two major oxidants that act as a source of hydroxyl radicals: hydrogen peroxide and ozone. Photochemical degradation is based on the oxidative reaction that is generated by the photolysis of the oxidant, hydrogen peroxide, in this case.

In a conventional AOP system, the oxidant absorbs UV in the 200-300 nm range and initiates the degradation process of organic contaminants. However, the solar energy that reaches earth's surface is mainly at wavelength above 300 nm due to atmospheric absorption. Since hydrogen peroxide and ozone do not absorb significantly beyond 300nm, the solar source is not suitable for these absorbers. An alternative is the injection of ferrioxalate that absorbs in the region of 250-480 nm (Safarzadeh, Bolton & Cater, 1996). Photolysis of ferrioxalate generates iron(II) which then reacts with hydrogen peroxide to produce hydroxyl radical. As in conventional AOP, hydroxyl radicals then degrade organic contaminants in the treated medium. As hydroxyl radicals are generated, iron (II) is oxidized to iron(III). Iron (III) chelates then repeats the generation of iron (II) under irradiation. Previous research had demonstrated that photolysis of the ferrioxalate in the presence of hydrogen peroxide provides a continuous source of radicals. When conditions are correct, iron (III) chelates act as a catalyst in this process. At higher pH, ferric iron precipitates as ferric hydroxide. From previous studies, workable pH range for this process is between 4 and 5. The efficiency of the process decreases dramatically as pH goes above 5. The use of ferrioxalate enables the utilisation of approximately 18% of the incident solar radiation energy.

This technology was developed by Dr. Bolton, Dr. Safarzadeh and Dr. Cater in the early 1990s (Bolton, Safrazadeh and Cater, 1993). It is generally referred to as the Solaqua® process. The Solaqua® technology has been tried and found effective on a number of contaminants at the laboratory scale. However, additional work is required to expand the knowledge on this process to a bench and pilot-scale levels. This step would be important in the potential commercialisation of this innovative treatment technology.

Analytical Method

The analysis of samples collected during the bench-scale tests was carried out in the accredited SAIC Canada Analytical Laboratory. Following CAEAL accredited quality program, QA/QC samples were included in all analytical runs.

The samples were analyzed for pH and hydrogen peroxide upon sampling. The pH was measured in-line using a digital pH meter. The hydrogen peroxide was measured using peroxide stick. This hydrogen peroxide measurement technique was semi quantitative, and only served to ensure that the hydrogen peroxide was present in excess of a certain minimum concentration. Purge and trap, gas chromatography with flame ionization detection was used to analyzed the samples for volatile organics. The method used was a modified version of USEPA method 624.

A number of target contaminants were selected for the purposed of this bench-scale study. The analysis of target contaminants included benzene, toluene, ethylbenzene, xylenes (BTEX), and methyl-t-butyl ether (MTBE) using purge and trap GC-FID, and methyl cyclopentadienyl manganese tricarbonyl (MMT) using GC-MS.

For the quantitation of BTEX, SAIC Canada has been accredited for conducting these tests. The MTBE has been under extensive studies in the past using a validated method. The MMT test method was recently developed in-house and validated through intensive testing and calibration processes.

Research Approach

An in-house bench-scale advanced oxidation process (AOP) unit was available to demonstrate contaminant destruction. Contaminant destruction testing would be conducted safely in a close-loop environment. An overall test plan was developed to cover the desired range of contaminant concentrations and water characteristics. Throughout the destruction tests, the identification of appropriate sampling times and ensuring discharge from the process met regulatory limits were the only two challenges encountered. Both were easily managed.

One important aspect of this work was the development of a performance prediction model on the solar detoxification technology. Often it is desirable to perform bench-scale tests in the laboratory before conducting fieldwork or implementing a full-scale system. Therefore, it was deemed useful to have a model that could provide some indication on performance for the field system based on bench-scale testing. To this end, a process for performance prediction was developed. First, a model (called the lamp-reactor model) was developed to simulate the contaminant destruction process in the effluent stream in the bench-scale equipment. Using a number of known effluent characteristics and process parameters, bench-scale test results could then be simulated by the model. Then a second model (called the solar model) was developed to include these characteristics and variations in the solar input to the destruction process in the field. Using this solar model and the same process parameters and effluent characteristics as the bench-scale test, performance of the field system could then be estimated.

To provide an opportunity for validating the performance modelling process, pilot-size equipment was tested at the National Solar Testing Facility (NSTF) following the initial bench-scale test. NSTF has a simulated solar lamp with known energy outputs. This allowed validation runs to be performed under controlled environmental conditions. Irradiance received by the pilot equipment was also monitored and recorded.

Test System (Bench- and Pilot-scale)

Bench-scale testing was performed at SAIC Canada’s Environmental Technology Laboratory in Ottawa, Ontario. This facility is a state-of-the-art laboratory with a comprehensive health and safety policy. The pilot scale testing was carried out at

National Solar Testing Facility (NSTF) in Mississauga, Ontario. This is also a state of the art facility with stringent heath and safety protocols.

An advanced oxidation reactor (AOP) unit was used for the bench scale tests. The unit is designed to use ultraviolet light from a mercury vapour lamp. The light passes through a quartz sleeve, which is transparent to the ultraviolet light, into the reactor. The light generated by the lamp differs from natural sunlight in its intensity especially in the ultraviolet spectrum. In order to mimic natural sunlight in the reactor, the quartz sleeve was replaced with a Pyrex (glass) sleeve. This new Pyrex sleeve filters UV light that enters the reactor, more closely simulating the natural effect of sunlight passing through the atmosphere to the surface of the earth. The unit also houses a pH controller, sampling ports, recirculation pumps, and a heat exchanger.

The catalyst used was a solution of approximately 2% ferrioxalate (FeOx). The reagent used was a solution of hydrogen peroxide (H_2O_2) at 30 %.

The NSTF located in Mississauga, Ontario is operated by Bodycote Ortech on behalf of Natural Resources Canada. At NSTF, tests can be performed in the environmentally controlled chamber at different light intensities, temperatures and wind velocities. In fact, tests can be performed under a specific light or pre-programmed variation by the 150 kW Vortek solar simulator which intensity ranges from 150 to 1120 watts per square meter. The variation in angle of illumination in the chamber is 0 to 30 degrees above the horizontal due to the mirrors located 12 to 16 feet above the floor. The temperature can also be controlled within 1 °C from – 20 to 50 °C. To better simulate other outdoor environment conditions, a close loop wind generator provides wind velocities from 0.5 to 3.5 meters per second.

The equipment was first set up and tested at SAIC Canada's ETP facility before being dismantled and re-assembled in the environmental chamber at NSTF. An overview of the equipment set-up and use is given below.

The 100 L holding tank was filled with water. The water flowed through the diaphragm pump, which was supplied with compressed air from the NSTF building. The water was pumped to the polypropylene solar panel. Once the liquid had flowed through the solar panel, it exited through the drain directly into the holding tank. All of the tubing needed was made with _ inch breaded propylene.

Before testing begins, the solar panel is horizontally placed 3 to 4 feet above the floor in the large black environmental chamber. The solar simulator is located outside the environmental chamber on an elevator platform and can be turned on and off as required.

Experimental Procedures

Experimental procedures were produced for all bench- and pilot-scale experiments performed. As the testing proceeded, many new concepts were developed in order to optimise the mechanical processes of the runs. The procedures were also revised in order to take into account the results of the analysis from previous runs. Experimental procedures for the bench- and field-scale tests performed are summarised below. Details and complete test data were documented in a recent PERD report (Wong, Obenauf, Robichaud, Cathum and Valicogna, 2002).

The reagents used were purchased from chemical supply companies, except for the ferrioxalate solution, which was prepared in house. The reagents consisted of Hydrogen Peroxide (ACS Grade, Fisher Scientific), Sulphuric acid (Reagent Grade, Caledon Laboratories), Sodium Hydroxide (Reagent Grade, Caledon Laboratories), Ferric Sulphate (hydrated) (Reagent Grade, Caledon Laboratories), and Oxalic Acid dihydrate (ASC Grade, Fluka Chemicals).The preparation of the Ferrioxalate solution is as follows. This preparation will result in a ferrioxalate solution containing 2% ferric ion (Fe^{3+}).

1. Add about 1 ml of concentrated sulphuric acid to about 800 ml of deionized water.
2. Add 97g of ferric sulphate and stir for 30 minutes.
3. Add 150 g of oxalic acid and stir until solids are dissolved. Do this in the absence of light.
4. Bring the volume up to 1000 ml with deionized water. The solution can be heated (to 50°C) to aid in the dissolution of materials. If solids are still present, the solution should be filtered.
5. Maintain the solution above 15°C at all times to prevent crystallization.

The tests were performed on a modified bench scale SolarChem advanced oxidation unit. The modification performed was the replacement of the quartz sleeve with a pyrex sleeve. This modification changed the spectrum of transmitted light to better mimic sunlight. Most tests were performed using 12 L of solution. The procedure used to perform the tests was as follows:

1. Turn on cooling water to condenser.
2. Fill the reactor to 6 litres with tap water.
3. Add the spike solution to achieve the desired concentration of contaminant into the feed line.
4. Continue filling the reactor to 12 litres
5. Add the desired amount of Ferrioxalate and hydrogen peroxide.
6. Plug in the pH metering pumps and recirculate the fluid during pH adjustment.
7. Let circulate for two minutes.
8. Turn on lamp while taking the time 0 sample (initial).
9. Take samples and readings as per the predetermined sampling schedule.
10. When the run is completed, turn off the lamp and metering pumps. Let the system recirculate for two minutes.
11. Turn off pump, and clean the unit.

The pilot-scale system consists of a solar panel, recirculation pump, and associated plumbing. The holding tank contains 100 L of feed water. At a flow rate of approximately 10 L per minute, and a depth of approximately 2.5 cm, hold up in the system was estimated at 75L. The procedure followed for NSTF testing (using simulated sun light that can be switched on and off):

1. Fill reservoir with 100 L of test fluid.
2. Set up pump to recirculate the fluid back into the tank, bypassing the panel, and start the pump.
3. Adjust pH to 5 with the addition of sulphuric acid and mixing.
4. Add Peroxide and FeOx.
5. Adjust pH to 4.
6. Add spike solution.
7. Recirculate fluid for two minutes.
8. Stop the pump and connect the panel.
9. Start the pump and adjust flows to attain a 2.5 cm depth in the panel.
10. Turn on lights and take the time zero (initial) sample at the exit of the panel.
11. Sample and record data as per the sampling table.
12. Monitor pH and peroxide and adjust as necessary.
13. Once sampling is complete, turn off lamps and pumps.
14. Let system drain of fluid, and rinse precipitate out.

In order to minimise the quantity of wastewater generated from testing at NSTF, the water was reused for some experiments. In these cases, the excess iron produced from photochemical reaction of FeOx had to be removed from the system. This was done by filtering the process water using 75 µm and 1 µm hydrex dead-end filters between runs.

Test Results

Bench-scale Tests

Two system check runs were completed using BTEX spiked tap water. The conditions of the run were the same in both: 25 ppm of FeOx, 350 ppm H_2O_2, and a pH of 4 (approximately) in 12 L of tap water. These two check runs lasted for over 30 minutes. The degradation of BTEX observed in both runs indicated that no leaks or contamination within the system.

Since both MTBE and BTEX were analysed using the same analytical method, they were combined in a spiking solution and run together through the reactor without reagents as a baseline. For this 30 minute run, there was no FeOx nor H_2O_2 added. The analysis also showed that there was no significant amount of contaminant loss due to volatilisation in the system.

A number of test runs were made with varying reagent concentrations in order to determine optimal process parameter. A typical BTEX degradation curve is shown in Figure 1. For MTBE, similar degradation trends were observed. It was found that the most desirable process parameters for the tested effluent were: 25 ppm FeOx, 350 ppm H_2O_2, and pH 4.

The analytical data supported the degradation of both BTEX and MTBE within 15 minutes of exposing the solution to ultraviolet (UV) light. One test run was performed with a lower concentration of hydrogen peroxide (100 ppm) but chemically still in excess. As long as there was excess peroxide, it appeared that the degradation rate would remain fast (less than 15 minutes).

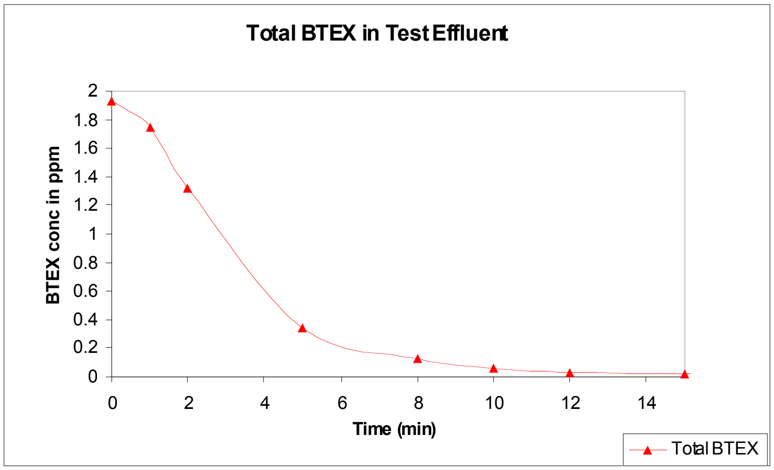
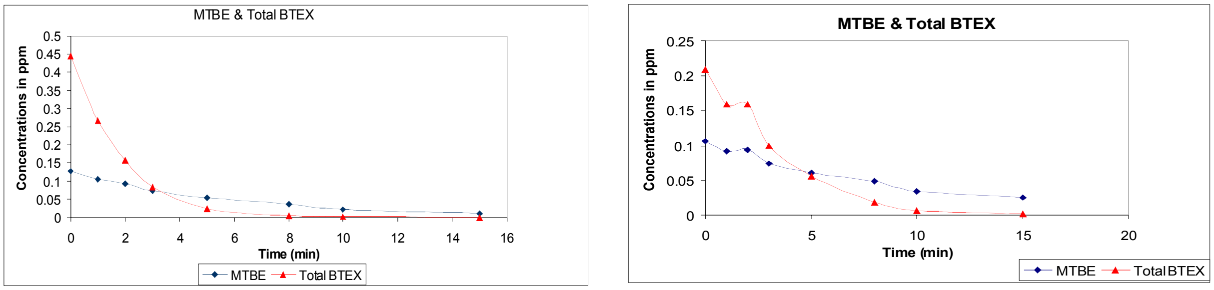


Figure 1 Typical BTEX Degradation Curve

In one test, the concentration of FeOx was reduced to approximately 16.6 ppm although the H_2O_2 concentration remained at 350 ppm. This reduction in FeOx caused a slower reaction (slowed the degradation rate for both contaminants). Figure 2 illustrates the difference in the degradation of both BTEX and MTBE. In the case of 25 ppm FeOx, the 90 % removal time for BTEX was approximately 4 minutes. At 16.6 ppm FeOx, 90% removal time was approximately 9 minutes. The reaction therefore was dependent on the amount of FeOx available.



FeOx at 25 ppm

FeOx at 16.6 ppm

Figure 2 Degradation Rates with Different Catalyst Concentrations

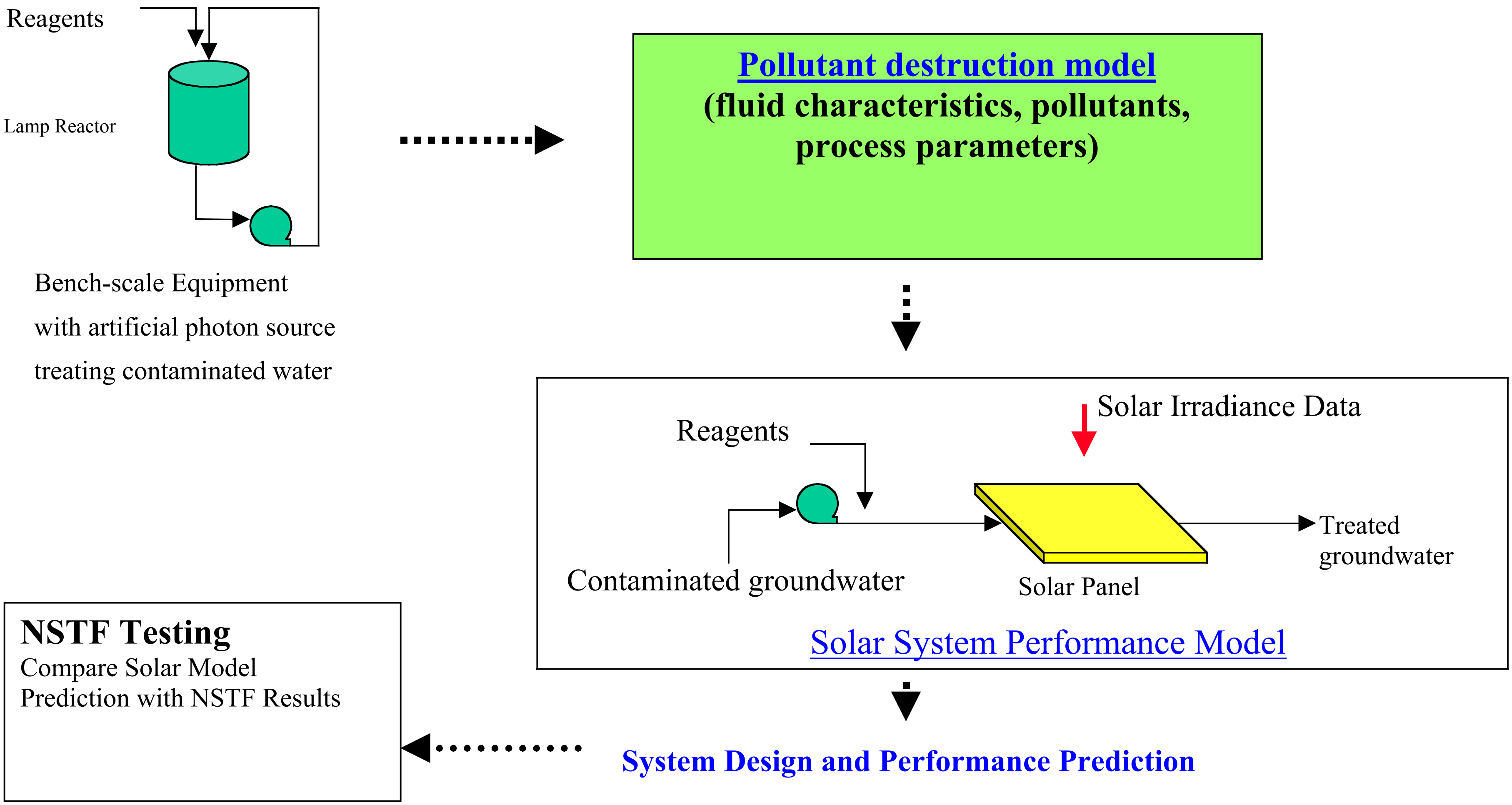
A final control run was carried out at the end of the bench-scale study. This final control run was a test on spiked BTEX tap water with no FeOx, however UV and hydrogen peroxide were present. The same experimental procedures as in all earlier bench-scale test runs were followed. As expected, BTEX concentrations dropped slightly over time as hydrogen peroxide reacted with organic contaminants and results indicated a very stable BTEX concentration. This final test confirmed that no significant volatilisation was taking place for runs made using the bench-scale equipment.

NSTF and Performance Model Tests

Two Microsoft Excel spreadsheet process models were written during this project. The first was a process model to predict the rate of reaction in the UV lamp reactor used for the bench scale work (Lamp Model). The second was a model to predict the rate of reaction in the solar flat-plate reactor (Solar Model).

The main use of the process models was to predict relative changes in the rate of reaction as certain parameters (ferrioxalate concentration, UV absorbance of the water, etc.) were changed and for scale-up. The model also served to predict the rate of treatment in the solar reactor from tests in the bench reactor. In this case, all the water parameters were constant so only the rate and wavelength dependence of photon flux on the reactor were changed. It was anticipated that this use of the model should yield reasonable agreement to practice. Ultimately, the solar reactor model can be used to predict treatment rates for a given water at various locations throughout North America and at various times of the year as the appropriate sunlight data had been entered in the model. The overall process of performance prediction model validation is shown schematically in Figure 3.

Figure 3 Solar Detoxification Model Validation



The first step in model validation was to perform contaminant destruction tests to provide bench-scale data for the Lamp Model. This gave us a general understanding of the Soalqua process and knowledge on the degradation characteristics for the target contaminants. The Lamp Model was then used to simulate bench-scale destruction performance.

The second step was to use the solar model to estimate destruction rate in a flat plate solar panel subjected to solar energy or simulated sunlight. The same process conditions and effluent characteristics were entered into the solar model. This model gave us an estimated field scale system performance (degradation rate) and the design data for required system size.

Finally, using a pilot-scale solar panel, the degradation rate of contaminants under actual solar irradiation or simulated sun light was measured. This test had to be conducted under the same process conditions and effluent characteristics. The results from the solar model prediction and the actual tests would be compared to evaluate how accurate the model was in predicting field-scale equipment performance. Gaps observed in this comparison would present opportunities to enhance or improve the model.

This validation process would need to be repeated a number of times for a variety of different treatment scenarios to build accuracy in the performance model. For the current work only a few cases were studied due to time constraints. And field tests were done using the solar simulation lamp at the National Solar Test facility (NSTF). However, the approach and principle behind this validation process is now established and proven.

In the test runs made at NSTF, results showed that all contaminants degraded quickly as expected. Throughout each run, pH was adjusted manually by the addition of sulphuric acid. Hydrogen peroxide was added when the hydrogen peroxide test strips indicated that it was below a minimum level. In addition to the flow rate measurement taken when time permitted, a close eye was kept on the level of the liquid in the panel. The goal was to maintain a depth of 1” liquid in the panel by adjusting the flow.

Test runs were made using pre-determined process conditions. Following the model validation process discussed earlier, the lamp model was adjusted to simulate the bench-scale contaminant degradation. This was done by finding the right value (“best-fit”) for a “Pollutant Factor” (an user input in the lamp model) to match the bench-scale data with the lamp model output. This "Pollutant factor" and other process conditions were then entered into the solar model to predict pilot-scale system performance based on solar irradiance. Bench-scale and NSTF test results were summarized in Table 1.

For Test # 1, we saw an excellent prediction for the simulated field performance (NSTF measured results), as solar model matched closely with the measured NSTF degradation rate (23% vs. 21%). For Test # 2, the predicted degradation rate was also very close to the actual NSTF value. The third case, Test # 3, involved the testing using dilute leachate from a municipal landfill site. This case was interesting in that it provided a good opportunity to challenge the model. Although the predicted degradation rate is different from the measured value, it was considered very promising given the circumstances. From our previous work on treating landfill leachate, we learned that pH changed rapidly as FeOx reaction took place (Volchek and Obenauf, 2001). As the process got underway at NSTF, it was possible that the pH of the effluent (dilute leachate) drifted out of the desired range, especially in the later portion of the solar panel. This pH drift combined with the high organic content of the leachate could explain the difference between the solar model and the measured results. The composition of the leachate is much more complex and the current model does not capture any of the competing reactions occurring in this effluent.

NSTF Test #	Bench-scale degradation rates	Lamp model degradation rates	Pollutant Factor	Predicted solar model degradation rates	Measured NSTF degradation rates
1	20%	21%	0.0002	25%	21%
2	10%	10%	0.0004	13%	10%
3	20%	21%	0.0035	27%	10%

Table 1 Performance Model Prediction vs. Actual NSTF Results

NSTF Test # 1 and Test # 2 produced very promising results in support of using this model to predict field equipment performance. For greater confidence in this model, additional test for different scenarios need to be done.

Conclusions and Recommendations

Bench-scale test results showed excellent destruction of BTEX, MTBE and MMT contaminants using the Solaqua® technology. Degradation was achieved in minutes in the bench-scale tests. This was consistent with our earlier experience in BTEX and MTBE destruction using conventional AOP systems.

One challenge encountered during this work related to the modelling of field equipment performance. In general, photochemical reactions were complex processes to model. This was especially the case when dealing with a catalyst and when a number of intermediary products and competing species were involved. A more thorough study is required to model each of the target contaminants in a specific groundwater condition. For the purpose of the current study, a simplified model with a higher (but acceptable) uncertainty in its calculations was developed and used for performance prediction.

The lamp reactor model and the solar model were developed and tried. Once this model becomes fully validated, it would be a useful tool in the commercialisation of this technology. Very often, confidence in performance estimation is the central issue in the adaptation of solar-based technologies. This model would aid in the design of the full-scale system and predict performance of the system. The model performed well for two test cases conducted using pilot-scale equipment.

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One factor that affected the validation was the pH of the effluent in the solar panel during the field test. As photochemical reaction took place in the solar panel, catalyst, reagents and contaminants react and cause pH changes. In turn, these changes in pH levels could hinder FeOx reactions. For the test conducted at NSTF, the flow rate was relatively low and residence time in the solar panel was considered long (in relation to the residence time in the holding tank where pH measurement and adjustment took place). This long residence time in the solar panel made it difficult to monitor and adjust pH of the effluent in the system. For future validation runs or full-scale system implementation, flow rate through each solar panel should be increased. In addition, it may be beneficial to include inter-panel mixing tanks to monitor and adjust pH before effluent is moved to the next solar panel. This would allow for an optimal pH to be maintained in each solar panel.

Overall, the project objectives were met through the reported work. A number of areas for future work have been identified. Some of this work may be included in the next phase of this project where model performance could be tested and validated using field test results. It was demonstrated through the results of this phase of the project that the Solaqua® technology (based on a renewable energy source) could be an effective tool in the treatment of groundwater contaminated with trace organics contaminants.

Acknowledgement

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