Decontaminate Passaic River Sediments using Ultrasound with Ozone Nano Bubbles

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ABSTRACT: Passaic River facilitated and played a key role in the industrialization of Newark and North East New Jersey. The Passaic River was identified as the second most polluted river in the United States in 1984. The contaminants in the river included PAHs, PCDD/F, PCBs, DDT and other pesticides and their byproducts and heavy metals including Hg, Cr, Pb and many other. Due to the severity of the contamination USEPA has proposed a remediation plan under the national superfund program, which includes dredging, dewatering and offsite disposal of the lower 12.88 kilometers of the river. Scrutiny of the EPA proposed plan indicated the need to find an alternative method that will decontaminate the soil. This study investigates the development of an in-situ remediation technology using nano ozone bubbles and ultrasound to decontaminate river sediments. The preliminary experimental results showed reasonable PAHs removal efficiencies of contaminated sediments. The data obtained from the laboratory experiments will be used to develop a pilot scale study for possible field application.

RÉSUMÉ: Passaic River a facilité et joué un rôle clé dans l'industrialisation de Newark et du nord-est du New Jersey. Le fleuve Passaic a été identifié comme la deuxième rivière la plus polluée aux États-Unis en 1984. Les contaminants dans la rivière comprenaient des PAH, des PCDD / F, des PCB, du DDT et d’autres pesticides et leurs sous-produits et métaux lourds dont Hg, Cr, Pb et plusieurs autres. En raison de la gravité de la contamination, USEPA a proposé un plan d'assainissement dans le cadre du programme national de superfundage, qui comprend le dragage, l'assèchement et l'élimination hors site des 12,88 kilomètres de la rivière. L'examen du plan proposé par l'ÉPA indiquait la nécessité de trouver une autre méthode qui permettrait de décontaminer le sol. Cette étude étudie le développement d'une technologie d'assainissement in situ utilisant des bulles d'oxyde de carbone nano et des ultrasons pour décontaminer les sédiments fluviaux. Les résultats expérimentaux préliminaires ont montré des rendements d'élimination des PAHs raisonnables. Les données obtenues à partir des expériences en laboratoire serviront à élaborer une étude pilote pour une éventuelle application sur le terrain.

KEYWORDS: Contaminated Sediments, Ultrasound, Ozone Nano Bubbles

1. INTRODUCTION

The Passaic River formed as a result of drainage from a massive proglacial lake that formed in the North New Jersey at the end of the last ice age. The Passaic River watershed approximates 130 kilometers and starts near Mendham, NJ. Its river basin drains almost 2422 square kilometers in northeastern New Jersey and southeastern New York.

The mid-1940s marked the beginning of the manufacturing operations in the lower 12.88 kilometers of the Passaic River, including the production of dichlorodiphenyltrichloroethane (DDT) and phenoxy herbicides, which lasted until 1983. Between 1951 to 1969, the Diamond Alkali Company operated a chemical plant and manufactured the herbicides 2,4-dichlorophenoxyacetic acid (2,4-D), and 2,4,5 trichlorophenoxy - acetic acid (2,4,5-T). The compound 2,3,7,8 tetrachlorodibenzo - p-dioxin (TCDD), was produced as a by-product of the herbicide production, which the United States Environmental Protection Agency (USEPA) categorizes as a likely carcinogen. In addition over 100 other industrial facilities have been identified as potentially responsible for discharging contaminants into the river.

Due to the heavy contamination, USEPA included the lower 12.88 kilometers of the Passaic River to the national priority list, which makes eligible for the remediation funds under the federal superfund program. The proposed remediation action by USEPA is estimated at 1.7 billion dollars, where the project include bank to bank dredging of the sediments and capping. Sediments are dredged up to 0.76 meters, except 3.22 kilometers from the Newark bay where the river is dredged to allow navigation through the river.

The current remediation plan is extremely expensive and poses a risk of contaminant resuspension. In addition the impact on the society due to the current plan include closing bridges to traffic to move the dredge sediments, reduction in the use of river for recreational activities such as rowing, boating and fishing. Dredging also results in damage of the river sediment bed impacting the ecosystem. Dredging is often associated with high cost, limiting application in remediating contaminated sediments (Mora et al. 2005). Also, contaminated sediment remediation by dredging has a high probability of re-suspension (Cassidy et al. 2002). Hence the advantages from in-situ remediation far outweighs the benefits of the current remediation plan.

There are multiple in-situ remediation technologies such as solvent extraction, bio remediation and surfactant treatment are available to remediate soils contaminated with PAHs, and PCBs. However, given the site conditions none of the above systems are not viable for Passaic River. Hence, an in-situ remediation technology based on oxidizing contaminants using a highly reactive oxidant that will convert the contaminants to a harmless product or a product that can be extracted should be a much preferable.

Use of ultrasound to remediate contaminated soil has been proven to be a successful method (Meegoda et al. 1995, Meegoda et al. 1996, Meegoda et al. 2001, & Morra et al. 1992). This study attempts the use of ultrasound enhanced with oxidation by using ultrasound with ozone nano bubbles at lower cost and risk.

2. USE OF ULTRASOUND IN SOIL REMEDIATION

Ultrasound is generated using piezoelectric crystals that has frequencies ranging from 20 kHz to 100MHz. The lower frequency of 20 kHz is used in cleaning of metal and glass surfaces and for materials with higher bonding strengths a frequency of 40-44 kHz is used to desorb contaminants. Studies carried out by Meegoda, and Perera, (2001) and Meegoda, and Veerawat, (2002) showed the feasibility of decontamination of sediments using ultrasound and vacuum pressure.
In soil decontamination application, the contaminants (organics and inorganics) are usually attached to clay and silt fractions. The application of ultrasound energy results in generating localized high shear forces to separate and desorb organic and inorganic compounds and heavy metals from sediments or soils, thereby, increasing the mobility of contaminants in the soil water suspension. Increasing the mobility of contaminants will allow the remediation by direct oxidation or removal of the contaminants using surfactants. The use of ultrasound in large scale soil washing provided promising results (Mason et al. 2004). Ultrasound and surfactants were used to remove the Polycyclic Aromatic Hydrocarbons (PAHs) in heavily coal tar contaminated soil achieving more than 90% contaminant removal efficiency (Meegoda et al., 1995 and 1996). Similarly, ultrasound enhanced soil washing with different surfactants indicated significant improvements in removing diesel fuel from contaminated soil (Kim et al. 2013). Acoustic cavitation due to ultrasound energy coupled with vacuum pressure was used to remove of chromium (Meegoda and Perera 2001) and PAHs (Meegoda and Veerawat, 2002) from contaminated sediments. The removal efficiency of heavy metal in soil increased with the use of ultrasound in soil washing (Chung and Kamon 2005).

3. OZONE AS AN OXIDIZING AGENT

Use of chemical oxidation as an in-situ remediation technology is a very common and a successful method used by numerous industries. Oxidizing organic compounds using ozone will create harmless byproducts, where the main two byproducts of PAHs being CO₂ and H₂O.

Many common oxidizing agents with high oxidizing potentials are readily available in the industry. Among the most common oxidizers: hydrogen peroxide (H₂O₂); potassium permanganate (KMnO₄); ozone (O₃) and fluorine (F₂) are the most extensively used. Using KMnO₄ and F₂ in in-situ remediation will leave numerous byproduct that can be hard to control and harmful. Hence the best oxidizing agents that can be used in an in-situ remediation is O₃ and H₂O₂ that do not leave toxic byproducts. However, out of O₃ and H₂O₂, H₂O₂ require special storage facilities and costlier to manufacture, whereas O₃ can be generated on site with inexpensive methods.

Interest in using ozone to remediate contaminated soils has been rising over years, especially the application for non-volatile organic compounds that are not removed by conventional soil venting (OMahoney, Dobson, Barnes, and Singleton (2006)). Ozone can be utilized in both gaseous and aqueous forms (Choi et al. (2001)). Ozone is also reported to be suitable in degradation of PAHs in soils (Choi et al. 2001; Masten and Davies 1997). Microorganisms are only capable of degrading PAHs that are dissolved in the aqueous phase and bio-graftation of PAHs absorb onto soils has limited application (Bosma et al. 1996; Luthy et al. 1994). Intermediates of oxidation products of PAHs are extra soluble would therefore be available to microbes for biodegradation. Hence ozone is used to degrade PAHs into intermediates that are more soluble in the aqueous phase (Kornmüller and Wiesmann (2003)). Ozone also, oxidizes heavy metals to their higher oxidation state making them water soluble and easy to separate by filtration (McBride 1989).

The radicals (OH·) formed during the decomposition of ozone are highly unstable with a very short life span. Due to the high instability of the radicals, it possess strongest oxidation capabilities. The reaction of ozone occurs is two different forms in an aqueous solution; direct oxidation or formation of oxidation with free radical intermediates (Siegrist and Crimi, 2011). The direct reaction of ozone is often selective towards specific compounds and functional groups. The dipolar structure of ozone gives rise to cyclo-

addition to unsaturated bonds, Criegee mechanism, forming ozone radicals (Wadt and Goddard, 1975). Ozone is also a strong electrophile and reacts quickly with both organic and inorganic compounds by an oxygen-atom transfer reaction.

Considering the short half-life of ozone and its high solubility compared to oxygen, it is necessary to identify an optimum delivery method and to ensure the availability of ozone during remediation. Keeping undissolved ozone in the water will allow the water saturated with ozone to react with pollutants. Hence we propose the use of nano-bubbles to deliver ozone and planning to significantly reduce the cost of treatment by utilizing all the supplied ozone for oxidation of contaminants.

4. NANO BUBBLES IN WATER

Nano-bubbles are nano-scopic gaseous (typically air) cavities in aqueous solutions that have the ability to change the normal characteristics of water. Ordinary bubbles have a diameter which range from 1 µm and larger and in equilibrium due to capillary and buoyant forces (Hu et al. 2013, 2014). If not in equilibrium these quickly rise to the surface of a liquid and collapse, whereas nano-bubbles remains in water for months and do not burst (Takahashi 2007). Nano-bubbles which are <100 nm in diameter can remain in liquids for an extended period of time.

The stability of nano-bubbles is supported by the electrically charged liquid-gas interface, which creates repulsive forces that prevent bubble coalescence, and by the high dissolved gas concentration in the water, which keeps a small concentration gradient between the interface and the bulk liquid (Ushikubo et al. 2010). The measured zeta potential of water after the introduction of macro and nano oxygen bubbles was in the range from –45 mV to –34 mV and from –20 mV to –17 mV in water bubbled with air, indicating the presence of stable electrical charge on the surface (Ushikubo et al. 2010). Some of the advantages of the micro- and nano-bubbles are their high specific area (surface area per volume) and the high stagnation time in the liquid phase, which increase the gas dissolution.

Since the rate of movement of electrolyte ions in water is not sufficiently high to counteract the increasing rate of shrinkage of the micro bubbles, it is possible for some excess ions to be accumulated at the gas–water interface during the final stage of the collapse which accounts for accelerated increase in the ionic potential (Takahashi et al. 2007). The micro ozone bubbles can be applied to various water treatment processes, since the Ozone micro bubbles have high solubility and improved disinfection ability due to the generation of OH radical and/or pressure waves (Sumikura et al. 2007). The introduction of ozone nano-bubbles to aqueous systems will provide assistance towards the bioremediation of the system. Considering the Passaic River system, once the treatment is performed, the remaining dissolved ozone will break into oxygen and will help to remediate the river water and revitalize the ecosystem.

5. PROPOSED FIELD APPLICATION

The experimental study will explore the possibility of using ultrasound and ozone nano bubbles to decontaminate the heavily contaminated Passaic river sediments. The results from the laboratory experiments will be used to develop a fully functioning in-situ treatment method to be applied to treat the contaminated sediments in the Passaic River.

A containment chamber will be designed to house ultrasound probes, which will include an ozone delivery system and a water extraction system that will incorporate a nano filtration unit to remove dissolved pollutants. A preliminary illustration of the system is presented in figure 1.
6. LABORATORY EXPERIMENTS

The Passaic River and Newark bay sediments were tested to analyze the particle size distribution, field moisture content, organic content and pollutant concentrations. To mitigate possible health risks of using Passaic river sediments during the initial stage of the laboratory experiments, a synthetic soil was developed simulating the particle size distribution and consistency limits of the river sediments.

The synthetic soil was contaminated with p-Terphenyl. p-Terphenyl is a diphenylbenzene in aromatic hydrocarbon with a boiling point of 383°C. Acetone was used to dissolve terphenyl. To produce contaminated sediments, 0.15g of p-Terphenyl was dissolved in 60ml of acetone and mixed with 80g sample of synthetic soil. The sediment with organic solution was thoroughly mixed using a mechanical mixer for 2 hours to ensure that p-Terphenyl is dispersed evenly in the sediments to produce a contaminated sediment with 1875 PPM p-Terphenyl.

The EP A method 3550B (Ultrasonic Extraction) (USEPA 1996) was employed to extract p-Terphenyl from the treated sediments. The samples were concentrated using Kuderna-Danish (K-D) method. A 1.0mL of concentrated solution from extraction was used to analyze the concentration of p-Terphenyl in sediments using a gas chromatograph with mass spectrometry (GC/MS).

7. EQUIPMENT USED

7.1 Ultrasound

A 1500 Watts (Blue Wave Ultrasonics Inc., Model IM-1620, 240 Volts, Max Power 1500 Watts, Frequency 20 KHz) probe type ultrasonic transducer was used. It consists of a signal generator, high voltage amplifier (to increase the voltage supplied by the signal generator to a level to excite piezo-electric crystals), piezo-electric crystals and a stainless steel housing for the crystals.

7.2 Ozone generator

Ozone was produced by passing air through ozonator (Model T Series, Welsbach Ozone System Corporation, USA). Ozone is extremely hazardous to human and hence all experiments are conducted inside a fume hood.

7.3 Nano-bubble generator

Nano-bubbles were generated with micro-nano bubble nozzle (Model BT-50FR, Riverforest Corporation, USA), and the ozone gas was introduced to the inlet of the nozzle pump (Model 3YU50A, Dayton, USA) to produce the ozone nano-bubbles.

8. RESULTS

The study was conducted to examine the feasibility of in-situ decontamination of sediments using ultrasonic energy coupled with nano ozone bubbles and to optimize process for potential field application. All experiments were carried out in the batch mode.

The laboratory experiment started with the use of ultrasound and ozone where, the ozone was bubbled into the beaker containing contaminated soil and water. The soil/water ratio was kept at 4%. The temperature, ozone concentration and sonication time were taken as the key variables. It was observed that, the interaction between ultrasound and water generated heat raising the temperature. The initial trials indicated low removal efficiencies as shown in Table 1.

Table 1. Initial trials with high water temperatures at the end of the experiment.

<table>
<thead>
<tr>
<th>Sonication (Freq. 20 kHz)</th>
<th>Temp. (°C)</th>
<th>Efficiency (%)</th>
</tr>
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<tbody>
<tr>
<td>Ultrasound time (min.)</td>
<td>Ultrasound Power (W)</td>
<td>Pre</td>
</tr>
<tr>
<td>5</td>
<td>600</td>
<td>21.2</td>
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<tr>
<td>10</td>
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<td>600</td>
<td>22.7</td>
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<tr>
<td>10</td>
<td>750</td>
<td>24.2</td>
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<td>10</td>
<td>600</td>
<td>22.1</td>
</tr>
</tbody>
</table>

High temperatures resulted in low removal efficiencies. Hence, the ultrasound application was broken in to sessions of 2 minutes periods and the temperature in the water is brought down to lower initial temperatures. Table 2 indicate the results obtained from the trials carried out after the modifications to the experiments.

Table 2. Initial trials with lower water temperatures at the end of the experiment.

<table>
<thead>
<tr>
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<tr>
<td>Ultrasound</td>
<td>Ultrasound Power (W)</td>
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<tr>
<td>10</td>
<td>750</td>
<td>8</td>
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<tr>
<td>10</td>
<td>900</td>
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<td>10</td>
<td>900</td>
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<td>6.1</td>
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<tr>
<td>10</td>
<td>900</td>
<td>6.8</td>
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The above results shows that the process is successful with operating temperatures. The application of sonic power in discrete intervals allowed the system to saturate and ready for the next sonication.

The nano bubbles were tested to analyze the size distribution and the zeta potential using Zetasizer Nano ZS90. Instrument coupled to a capillary cuvette cell (gold plated Beryllium Copper electrodes) measured both the size and the zeta potential of the bubbles. The sample of water was tested at a temperature of 25°C. The size distribution is presented in figure 2.
Record 1 from the test indicated a peak of the nano bubbles at 70nm where the Record 2 and Record 3 indicated peaks at 100nm and 102nm respectively. The size distribution indicate that the system is generating stable nano-bubbles (Hu et al 2014). The average zeta potential of the ozone bubbles were -15.67mV, Najafi (2007), indicate the range of zeta potential in nano bubbles to be from +2mV to -30mV in 0.01 mol/L of NaCl and 2.2-2.4 pH.

With the successful generation of nano ozone bubbles, the experimental stage was moved to use nano ozone bubbles to treat the contaminated sediments where the generated nano ozone bubbles were fed into the beaker and the ultrasound was applied in discrete segments. The segments were divided in to 3 minutes of ultrasound followed by 45 minutes of rest for the soil to settle in. Then the water was drained out of the beaker and a new batch of nano ozone bubble saturated water was added. Table 3 shows that the higher intensities of ultrasound power and lower water temperatures produced higher removal efficiencies of PAH contaminated sediments. The highest removal efficiency was obtained at 1050W power output. The lower the water temperatures found to be much effective with or without the use of nano ozone bubbles.

Table 3. Initial trials with lower water temperatures at the end of the experiment.

<table>
<thead>
<tr>
<th>Ultrasound (Freg. 20 KHz)</th>
<th>Temp. (°C)</th>
<th>Efficiency</th>
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<tr>
<td>Sonication time (min)</td>
<td>Ultrasound Power (W) Pre Post (%)</td>
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<td>10</td>
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<td>15</td>
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<td>16.4 22 52.07</td>
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<td>24</td>
<td>900</td>
<td>12 16.8 90.02</td>
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<td>24</td>
<td>900</td>
<td>15.3 24.3 55.87</td>
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<tr>
<td>36</td>
<td>1050</td>
<td>13.2 17 92.99</td>
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9. SUMMARY AND CONCLUSIONS

Over 100 industrial facilities have discharged chemicals into the Passaic River, making it a superfund site. The contaminants in the river included PAHs, PCDD/F, PCBs, DDT, pesticides and their byproducts, and heavy metals including Hg, Cr, and Pb. Due to the severity of the contamination, the USEPA has proposed a remediation plan, which included dredging, dewatering and offsite disposal of sediments from the lower 12.44 kilometers of the river. However, the proposed EPA plan has many drawbacks. Hence a new in-situ remediation technology was proposed using ultrasound and nano ozone bubbles. An extensive experimental program is underway to validate the above technology. The preliminary results of this study indicated promising data of using nano ozone bubbles and ultrasound to remove PAH from the sediments. The preliminary research also showed high removal efficiencies of PAH from the contaminated sediments at lower temperatures and high ultrasound power levels. With the encouraging preliminary results the proposed technology can be used in the winter months when the river is minimally used for recreation purposes. This study will be continued to identify and optimize parameters that will influence the removal efficiency of the contaminated sediments.

10. ACKNOWLEDGEMENTS

This research was sponsored by the US National Science Foundation Award # 1634857 entitled “Remediation of Contaminated Sediments with Ultrasound and Ozone Nano-bubbles”. The contents of this paper reflect views of authors, who are responsible for the facts and the accuracy of the information presented herein. The contents do not necessarily reflect views or policies of NJIT or NSF. This paper does not constitute a standard, specification or regulation. Authors wish to acknowledge the efforts NSF project manager Dr. Richard J. Fragaszy.

11. REFERENCES


