

**STUDIES ON ZERO VALENT IRON LOADED BIODEGRADABLE
POLYMERIC PARTICLES FOR GROUNDWATER REMEDIATION**

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**STUDIES ON ZERO VALENT IRON LOADED BIODEGRADABLE
POLYMERIC PARTICLES FOR GROUNDWATER REMEDIATION**

by

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Submitted

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to the



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Dedicated to my family.

CERTIFICATE

This is to certify that the thesis entitled, “Studies on zero valent iron loaded biodegradable polymeric particles for groundwater remediation” being submitted by Ms. Kalpana Pandey to Indian Institute of Technology Delhi for the award of degree of Doctor of Philosophy is a record of bonafide research work carried out by her. Ms. Kalpana Pandey has worked under my guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard. The results contained in this thesis are original and have not been submitted, in part or full, to any other University or Institute for the award of any other degree or diploma.

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KALPANA

ABSTRACT

Surface modified Zerovalent iron nanoparticles (ZVINPs) are one of the most sought-after metal nanoparticles for groundwater remediation. In the area of water research, modified ZVI nanoparticles gain popularity because of their high efficiency in deactivating hazardous contaminants (both organic and inorganic), prolonged stability, recyclability, enhanced surface area and environmental friendliness. However, they suffer from rapid oxidation and agglomeration due to large surface area. To circumvent the issues, a significant progress in modifying ZVI nanoparticles using various techniques have been made in recent years. So far, Control Release Materials (CRMs) are mostly preferred techniques for application of these modified ZVI nanoparticles in groundwater remediation, since slowly released ZVINPs from a polymeric wrapper may retain their activity for prolonged period of time without undergoing significant agglomeration. In our work, we have developed ZVINPs encapsulated biodegradable polymer particles that may release iron nanoparticles in controlled fashion for *in-situ* groundwater remediation. Lab scale studies (both batch and sand column) simulating the ground conditions, and their various challenges such as transport of ZVI nanoparticles towards groundwater are discussed and demonstrated. Ultimately, ZVINPs encapsulated polymer particles exhibited slow-release technology for *in situ* groundwater remediation of both hydrophilic (methyl orange dye) and hydrophobic (trichloroethylene) water contaminants.

To begin with, in the second chapter, electrospraying technique was used to fabricate microparticles comprised of biodegradable PLA (polylactic acid) and ZVINPs at a ratio of 10:1. Around 8 wt% ZVINPs was slowly released from the composite microparticles after 60 hrs and 32 hrs of incubation in water, to fully remediate methyl orange (25 mg/L) and trichloroethylene (0.2 vol%) from water, respectively. The results from the sand column study show that released ZVINPs from composite particles could effectively remediate water contaminated with methyl orange solution (25 mg/L) completely over 1.5 months. The usefulness of the slow release remediator was also verified by monitoring the pH and conductivity of the effluents collected from the sand column. The storage stability of encapsulated ZVINPs was vastly improved (>1 month in open air) as compared to bare ZVINPs (1 hr in the open air), and recyclability of the particles was also evaluated (reused up to 4 cycles). These PLA based

microparticles fabricated in a single step, can potentially act as slow-release reservoir to remediate groundwater contaminants irrespective of their hydrophilicity.

In the third chapter, the study aims at improving the hydrophilic property of the polymer particles to facilitate their dispersibility in water. In order to accomplish the goal, three simple steps were adopted such as: 1) electrojetting of PLA (polylactic acid) with FeCl_3 (~17 wt%) to yield ~700 nm sized monodisperse spherical particles (PLA_ FeCl_3) 2) surface modification of PLA_ FeCl_3 particles using oxygen plasma to enhance surface hydrophilicity and porosity (~ 75%) 3) reduction of plasma treated PLA_ FeCl_3 particles in presence of NaBH_4 to produce ZVI (size: 20-50 nm) entrapped PLA particles (PLA_ZVI) with high encapsulation efficiency of iron (~85%). The plasma treated semi-porous PLA_ZVI particles exhibited slow and sustain release of iron (~90% in ~100 hrs) that were further employed to completely decontaminate both methyl orange (hydrophilic dye) and trichloroethylene (hydrophobic waste). Interestingly, the plasma treated particles were recyclable up to fourth batch, whereas the non-plasma treated one hardly show any recyclability due to burst release of surface entrapped iron from the latter. Moreover, the plasma treated hydrophilic particles provided stable dispersion (96 hrs) and prolonged reactivity (~10 days in sand column) in water as opposed to non-plasma treated particles displaying 1 min dispersion stability in water. As a result, the plasma treated particles displayed smooth transportability through sand column (>80%) with negligible attachment efficiency (α)=1.1 onto sand particles. These attributes make them a potential alternative to bare ZVI (transportability <20%) for targeting hazardous pollutants by injecting them in groundwater.

In the fourth chapter, the aim of the study was to encapsulate the ZVINPs (50 nm) in amphiphilic bicompartamental Janus particles (711 ± 11 nm) fabricated by EHDC (electrohydrodynamic co-jetting) to further improve water dispersibility and transportability of the polymer particles. The dual compartments were composed of PLA (polylactic acid) and a blend of PLA, PE (poly (hexamethylene 2,3-O-isopropylidene tartarate) and PAG (photo acid generator). Upon UV irradiation, PAG releases acid to unmask hydroxyl groups present in PE to make only PE compartment hydrophilic. The entrapped ZVI nanoparticles (20 w/w%; ~99 % encapsulation efficiency) were observed to degrade both hydrophilic (methyl orange dye) and hydrophobic (trichloro ethylene) contaminants. UV treated Janus particles provided stable dispersion (dispersed up to 3 weeks in water), prolonged reactivity (~24 days in contaminated water), and recyclability

(recyclable up to 9 times) as compared to non-treated ones. In addition, the amphiphilic Janus particles demonstrated high transportability (>95%) through porous media (sand column) with very low $\alpha = 0.07$, making them a promising candidate to target contaminants at NAPL/water interface prevailed in groundwater.

In the last chapter, transportability of these three types of ZVINPs entrapped polymer particles (as described in chapters 2, 3 and 4) through sand column were investigated in details to compare their performances. Aim of this study was to determine the effect of transportability (through porous media of varying porosity (31-35%) of different types of polymer particles encapsulating zero valent iron including monophasic PLA-ZVINPs (P1, chapter 2), plasma modified PLA_ZVINPs (P2, chapter 3) fabricated using electro spraying technique, and amphiphilic Janus particles, i.e., PLA_ZVINPs/PLA_PE_ZVINPs (P3, chapter 4) fabricated using electrohydrodynamic co-jetting technique. These particles displayed high reactivity towards water contaminants and marginal to high stability in aqueous media with varying ionic strength. The transport behavior of these particles in a diverse array of natural porous media was evaluated in a series of lab experiments. Among the three, the amphiphilic Janus P3 particles exhibited best transportability through the sand column of varying porosity under various ionic strength conditions. For example, sand with low porosity (31%) resulted in increasing the C/C_0 (normalized concentration of effluent, i.e., ratio of amount of iron passed through the porous media over amount of iron in the feed particles) value for P3 polymer particles (best performer) at 1.5-2 pore volume whereas in case of high porosity (35%) sand, the C/C_0 values started to rise at 1-1.5 pore volume. The impact of different types of ions such as monovalent (Na^+ , K^+), divalent (Ca^{2+} and Mg^{2+}) and trivalent (Al^{3+}) on these particles during their transport through sand column filled with contaminated water was also explored. Interestingly, Al^{3+} showed highest impact in lowering down the stability of polymer particles while passing through the sand column. In addition, α (attachment efficiency) value of these particles on sand surface in presence of various salts was also found to be increased from 0.09 (Na^+), 1.09 (Ca^{2+}) to 2.1 (Al^{3+}) for P3 particles (best performer) showing maximum reduction of particle transportability in presence of trivalent ions at highest salt concentration of 200 mM. Overall, it can be stated that among the three, amphiphilic Janus P3 particles hold a great promise to be considered for groundwater remediation *in situ*. In future, a real field application of P3 particles will be considered.

सार

सतह संशोधित ज़ीरोवैलेंट आयरन नैनोपार्टिकल्स (ZVINPs) भूजल उपचार के लिए सबसे अधिक मांग वाले धातु नैनोकणों में से एक हैं। जल अनुसंधान के क्षेत्र में, संशोधित ZVI नैनोपार्टिकल्स खतरनाक प्रदूषकों (जैविक और अकार्बनिक दोनों), लंबे समय तक स्थिरता, पुनर्चक्रण, उन्नत सतह क्षेत्र और पर्यावरण मित्रता को निष्क्रिय करने में उनकी उच्च दक्षता के कारण लोकप्रियता प्राप्त करते हैं। हालांकि, वे बड़े सतह क्षेत्र के कारण तेजी से ऑक्सीकरण और ढेर से ग्रस्त हैं। मुद्दों को दरकिनार करने के लिए, हाल के वर्षों में विभिन्न तकनीकों का उपयोग करके ZVI नैनोकणों को संशोधित करने में महत्वपूर्ण प्रगति हुई है। अब तक, भूजल उपचार में इन संशोधित ZVI नैनोकणों के अनुप्रयोग के लिए नियंत्रण रिलीज सामग्री (CRMs) ज्यादातर पसंदीदा तकनीकें हैं, क्योंकि धीरे-धीरे एक बहुलक आवरण से ZVINPs जारी किए बिना महत्वपूर्ण ढेर के बिना लंबे समय तक अपनी गतिविधि बनाए रख सकते हैं। अपने काम में, हमने बायोडिग्रेडेबल पॉलीमर कणों को घेरने वाले ZVINPs विकसित किए हैं जो इन-सीटू भूजल उपचार के लिए नियंत्रित तरीके से आयरन नैनोकणों को छोड़ सकते हैं। प्रयोगशाला पैमाने पर अध्ययन (बैच और रेत स्तंभ दोनों) जमीनी परिस्थितियों का अनुकरण करते हैं, और उनकी विभिन्न चुनौतियाँ जैसे कि भूजल की ओर ZVI नैनोकणों के परिवहन पर चर्चा और प्रदर्शन किया जाता है। अंततः, ZVINPs ने हाइड्रोफिलिक (मिथाइल ऑरेंज डाई) और हाइड्रोफोबिक (ट्राइक्लोरोइथाइलीन) जल संदूषकों के सीटू भूजल उपचार के लिए धीमी गति से रिलीज होने वाली तकनीक का प्रदर्शन किया।

शुरू करने के लिए, दूसरे अध्याय में, बायोडिग्रेडेबल PLA (पॉलीलैक्टिक एसिड) और ZVINPs को 10:1 के अनुपात में माइक्रोपार्टिकल्स बनाने के लिए इलेक्ट्रोस्प्रेडिंग तकनीक का उपयोग किया गया था। लगभग 8wt% ZVINPs को पानी में 60 घंटे और 32 घंटे के ऊष्मायन के बाद धीरे-धीरे समग्र माइक्रोपार्टिकल्स से मुक्त किया गया, ताकि पानी से क्रमशः मिथाइल ऑरेंज (25mg/L) और ट्राइक्लोरोएथिलीन (0.2vol%) को पूरी तरह से ठीक किया जा सके। सैंड कॉलम अध्ययन के नतीजे बताते हैं कि संयुक्त कणों से जारी ZVINPs मिथाइल ऑरेंज सॉल्यूशन (25mg/L) से दूषित पानी को 1.5 महीने में पूरी तरह से ठीक कर सकते हैं। रेत स्तंभ से एकत्र किए गए बहिस्त्राव की पीएच और चालकता की निगरानी करके धीमी गति से रिलीज रेमेडिएटर की उपयोगिता को भी सत्यापित किया गया था। नंगे ZVINPs (खुली हवा में 1hr) की तुलना में एन्कैप्सुलेटेड ZVINPs की भंडारण स्थिरता में काफी सुधार हुआ (> खुली हवा में 1 महीने), और कणों की पुनर्चक्रण क्षमता का भी मूल्यांकन किया गया (4 चक्रों तक पुनः उपयोग किया गया)। ये पीएलए

आधारित माइक्रोपार्टिकल्स एक ही चरण में गढ़े गए हैं, जो संभावित रूप से धीमी गति से रिलीज जलाशय के रूप में कार्य कर सकते हैं, जो भूजल प्रदूषकों को उनकी हाइड्रोफिलिसिटी के बावजूद दूर कर सकते हैं।

तीसरे अध्याय में, अध्ययन का उद्देश्य बहुलक कणों की हाइड्रोफिलिक संपत्ति में सुधार करना है ताकि पानी में उनके फैलाव को सुविधाजनक बनाया जा सके। लक्ष्य को पूरा करने के लिए, तीन सरल कदम अपनाए गए जैसे: 1) FeCl_3 (~17 wt%) के साथ PLA (पॉलीलैक्टिक एसिड) की इलेक्ट्रोजेटिंग ~ 700 एनएम आकार के मोनोडिस्पर्स गोलाकार कण (PLA- FeCl_3) प्राप्त करने के लिए 2) की सतह संशोधन PLA- FeCl_3 कण सतह की हाइड्रोफिलिसिटी और सरंधता (~ 75%) बढ़ाने के लिए ऑक्सीजन प्लाज्मा का उपयोग कर रहे हैं 3) NaBH_4 की उपस्थिति में प्लाज्मा उपचारित PLA- FeCl_3 कणों की कमी ZVI (आकार: 20-50 nm) फंसे हुए PLA कणों (PLA-ZVI) को उच्च एनकैप्सुलेशन के साथ उत्पन्न करने के लिए लोहे की दक्षता (~ 85%)। प्लाज्मा उपचारित अर्ध-झरझरा PLA-ZVI कणों ने लोहे की धीमी और निरंतर रिलीज (~ 90% ~ 100 घंटे में) का प्रदर्शन किया जो कि मिथाइल ऑरेंज (हाइड्रोफिलिक डाई) और ट्राइक्लोरोएथिलीन (हाइड्रोफोबिक अपशिष्ट) दोनों को पूरी तरह से कीटाणुरहित करने के लिए आगे नियोजित किया गया था। दिलचस्प बात यह है कि प्लाज्मा उपचारित कण चौथे बैच तक पुनर्चक्रण योग्य थे, जबकि गैर-प्लाज्मा उपचारित कण बाद वाले से सतह में फंसे लोहे के फटने के कारण शायद ही कोई पुनर्चक्रण दिखाते हैं। इसके अलावा, प्लाज्मा उपचारित हाइड्रोफिलिक कण पानी में स्थिर फैलाव (96 घंटे) और लंबे समय तक प्रतिक्रियाशीलता (रेत स्तंभ में ~ 10 दिन) प्रदान करते हैं, जो पानी में 1 मिनट फैलाव स्थिरता प्रदर्शित करने वाले गैर-प्लाज्मा उपचारित कणों के विपरीत है। नतीजतन, प्लाज्मा उपचारित कणों ने रेत के कणों पर नगण्य लगाव दक्षता (α) = 1.1 के साथ रेत स्तंभ (> 80%) के माध्यम से चिकनी परिवहन क्षमता प्रदर्शित की। ये विशेषताएँ उन्हें भूजल में इंजेक्ट करके खतरनाक प्रदूषकों को लक्षित करने के लिए नंगे ZVI (परिवहन क्षमता <20%) के लिए एक संभावित विकल्प बनाती हैं।

चौथे अध्याय में, अध्ययन का उद्देश्य EHDC (इलेक्ट्रोहाइड्रोडायनामिक को-जेटिंग) द्वारा निर्मित एम्फीफिलिक बायोकोम्पार्टमेंटल जेनस पार्टिकल्स (711 ± 11 एनएम) में ZVINPs (50 एनएम) को एनकैप्सुलेट करना था, ताकि पानी के फैलाव और बहुलक कणों की परिवहन क्षमता में और सुधार हो सके। दोहरे डिब्बे PLA (पॉलीलैक्टिक एसिड) और PLA, PE (पॉली (हेक्सामेथिलीन 2,3-*O*-आइसोप्रोपाइलिडेनेटरेट) और PAG (फोटो एसिड जनरेटर) के मिश्रण से बने थे। यूवी विकिरण पर, PAG मौजूद हाइड्रॉक्सिल समूहों को अनमास्क करने के लिए एसिड जारी करता है। PE में केवल PE कम्पार्टमेंट

हाइड्रोफिलिक बनाने के लिए। फंसे हुए ZVI नैनोकणों (20 w/w%; ~ 99% एनकैप्सुलेशन दक्षता) को हाइड्रोफिलिक (मिथाइल ऑरेंज डाई) और हाइड्रोफोबिक (ट्राइक्लोरो एथिलीन) संदूषक दोनों को नीचा दिखाने के लिए देखा गया। यूवी उपचारित जानूस कण प्रदान किए गए गैर-उपचारित लोगों की तुलना में स्थिर फैलाव (पानी में 3 सप्ताह तक फैला हुआ), लंबे समय तक प्रतिक्रियात्मकता (~ दूषित पानी में 24 दिन), और पुनर्चक्रण (9 गुना तक पुनर्चक्रण)। इसके अलावा, एम्फीफिलिक जानूस कणों ने उच्च परिवहन क्षमता का प्रदर्शन किया (>95%) झरझरा मीडिया (रेत स्तंभ) के माध्यम से बहुत कम $\alpha = 0.07$ के साथ, उन्हें भूजल में प्रचलित NAPL/वाटर इंटरफेस में दूषित पदार्थों को लक्षित करने के लिए एक आशाजनक उम्मीदवार बनाता है।

अंतिम अध्याय में रेत स्तंभ के माध्यम से इन तीन प्रकार के ZVINPs फंसे हुए बहुलक कणों (जैसा कि अध्याय 2, 3 और 4 में वर्णित है) की परिवहन क्षमता को उनके प्रदर्शन की तुलना करने के लिए विवरण में जांच की गई थी। इस अध्ययन का उद्देश्य मोनोफैसिक पीएलए-जेडवीएनपी (पी1, अध्याय 2), प्लाज्मा संशोधित पीएलए-जेडवीएनपी (पी1, अध्याय 2) सहित जीरो वैलेंट आयरन को समाहित करने वाले विभिन्न प्रकार के पॉलीमर कणों के अलग-अलग सरंध्रता (31-35%) के झरझरा मीडिया के माध्यम से परिवहन क्षमता के प्रभाव को निर्धारित करना था। P2, अध्याय 3) इलेक्ट्रो स्प्रेडिंग तकनीक का उपयोग करके निर्मित, और एम्फीफिलिक जानूस कण, यानी, PLA_ZVINPs/PLA_PE_ZVINPs (P3, अध्याय 4) इलेक्ट्रोहाइड्रोडायनामिक सह-जेटिंग तकनीक का उपयोग करके निर्मित। इन कणों ने पानी के दूषित पदार्थों के प्रति उच्च प्रतिक्रिया प्रदर्शित की और जलीय में सीमांत से उच्च स्थिरता प्रदर्शित की। अलग-अलग आयनिक ताकत के साथ मीडिया। प्राकृतिक झरझरा मीडिया के एक विविध सरणी में इन कणों के परिवहन व्यवहार का मूल्यांकन प्रयोगशाला प्रयोगों की एक श्रृंखला में किया गया था। तीनों में, एम्फीफिलिक जानूस पी3 कणों ने विभिन्न प्रकार के तहत अलग-अलग सरंध्रता के रेत स्तंभ के माध्यम से सर्वोत्तम परिवहन क्षमता का प्रदर्शन किया। आयनिक शक्ति की स्थिति। उदाहरण के लिए, कम सरंध्रता (31%) वाली रेत के परिणामस्वरूप C/C₀ (सामान्यीकृत सान्द्रता) में वृद्धि हुई। प्रवाह का प्रवेश, यानी फ्रीड कणों में लोहे की मात्रा से अधिक झरझरा मीडिया के माध्यम से पारित लोहे की मात्रा का अनुपात) P3 बहुलक कणों के लिए मूल्य (सर्वश्रेष्ठ प्रदर्शन) 1.5-2 पोर वोल पर जबकि उच्च छिद्र (35%) के मामले में रेत, C/C₀ मान 1-1.5 ताकना मात्रा में बढ़ने लगे। दूषित पानी से भरे रेत के स्तंभ के माध्यम से इन कणों के परिवहन के दौरान विभिन्न प्रकार के आयनों जैसे मोनोवैलेंट (Na⁺, K⁺), डाइवैलेंट (Ca²⁺ और Mg²⁺) और ट्रिवैलेंट (Al³⁺) के प्रभाव का भी पता लगाया गया। दिलचस्प बात यह है कि एएल³⁺ ने रेत स्तंभ से गुजरते समय बहुलक

कणों की स्थिरता को कम करने में उच्चतम प्रभाव दिखाया। इसके अलावा, विभिन्न लवणों की उपस्थिति में रेत की सतह पर इन कणों का α (अटैचमेंट एफिशिएंसी) मान भी 0.09 (Na⁺), 1.09 (Ca²⁺) से बढ़कर P3 कणों (सर्वश्रेष्ठ प्रदर्शन) के लिए 2.1 (Al³⁺) पाया गया। 200 मिमी के उच्चतम नमक एकाग्रता पर त्रिकोणीय आयनों की उपस्थिति में कण परिवहन क्षमता में कमी। कुल मिलाकर, यह कहा जा सकता है कि तीनों में से, एम्फीफिलिक जानूस पी3 कणों में भूजल उपचार के लिए सीटू में विचार किए जाने का एक बड़ा वादा है। भविष्य में, P3 कणों के वास्तविक क्षेत्र अनुप्रयोग पर विचार किया जाएगा।

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LIST OF ABBREVIATIONS

ZVINPs- Zero Valent Iron nanoparticles

TCE-Trichloroethylene

PLA- Polylactic Acid

PVA- Polyvinyl Alcohol

PEG-Polyglycolic Acid

PCE-Perchloroethylene

PCP- polychlorinated biphenyl

VOCs- volatile organic compounds

NAPL- Non aqueous phase liquid

MWCNT - Multi-Walled Carbon Nanotubes

CNT- Carbon Nanotubes

ZVI-Gn- ZVI-Graphene

CMC- Carboxyl Methyl Cellulose

S/ZVI/ZVI/AC- Sulfidated-ZVI/Activated Carbon

ICP-OES- Inductively Coupled Plasma

Fe/Cu-GO- Fe/Cu-Graphene Oxide

TCS-Tetracyclines

PAA-Polyacrylic Acid

PAAm- Polyacrylamide

PVP-Polyvinylpyrrolidone

PSM-Polyethylene Sorbitan Monolaurate

PV3A- Polyvinyl alcohol-co-vinyl acetate-co-itaconic acid

DBDE-Decarbomminated Diphenyl Ether

DLVO- Derhaguin, Landau, Verwey And Overbeek

CS@ZVI- Chitosan Impregnated ZVI Nanoparticles

CC-ZVI-Cotton Cloth Supported ZVI Nanoparticles

CC-CH-Cotton Cloth Coated Chitosan

Poly(Gg-Aam/ZVI)- ZVI Immobilized Gum-Ghatti-G-Acrylamide

KPS-Potassium Persulfate

ABC-Ascorbic Acid

MBA-N'-N'-Methyl Bis-Acrylamide

PET-Polyethylene Terephthalate

PAN/MA/IA- Polyacrylonitrile-Co-(Methyl Acrylate)-Co-(Itanoic Acid)

PAN-Polyacrylonitrile

PVDF-Polyvinylidene Fluoride

EDTA- Ethylenediaminetetraacetic

EDA- Ethylenediamine

PSF-Polysulfones

PA-Polyamide

IS-RPB- Impinging Steam Rotation Packed Bed

PTFE- Polytetrafluroethylene

CMC-Carboxyl Methyl Cellulose Coated Sulfidated ZVI

PEI-Polyethylene Imide

SM-ZVI-Surface Modified ZVI

HIPES-High Internal Phase Emulsion

EHDC-Electrohydrodynamic Co Jetting

BTC- Breakthrough Curve

DMF- Dimethyl Formaldehyde

MFC- Mass Flow Controller

RF-Radio Frequency

FESEM-Field Emission Scanning Electron Microscopy

BET- Brunauer-Emmett-Teller

FITC-BSA-Albumin-fluorescein isothiocyanate conjugate

EDC-Ethylene dichloride

NHS-n-Hydroxyl succinimide

MO- Methyl Orange

TCE- Trichloroethylene

DCM- Dichloromethane

TEM- Transmission Electron Microscopy

CLSM-Confocal Laser Scanning Microscope

ATR-FTIR- Attenuated Total Reflectance-Fourier Transform Infrared

DNAPL-Dense Non-Aqueous Phase Liquid

PAG-photoacid generator (2-(4'-methoxystyryl)-4,6-bis(trichloromethyl)-1,3,5-triazine))

PE- Poly (hexamethylene 2,3-O-isopropylidenetartarate)