RESEARCH PAPER

Fe–Ni Nanoparticles supported on carbon nanotube-co-cyclodextrin polyurethanes for the removal of trichloroethylene in water

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Abstract Nanoscale bimetallic particles of nickel on iron were supported on carbon nanotubes and then co-polymerized with β-cyclodextrin (CNTs/CD) and the resulting polymers applied to the degradation of pollutants in water. The bimetallic nanoparticles (BMNPs) were first embedded on functionalized carbon nanotubes (f-CNTs) before being copolymerized with beta cyclodextrin (β-CD) and hexamethylene diisocyanate (HMDI) forming a water-insoluble polyurethane. The particle size and distribution of BMNPs were determined by Transmission Electron Microscopy (TEM), and the surface area was determined by using the Brunauer–Emmett–Teller (BET) method. Energy dispersive X-ray spectroscopy (EDXS) was used to confirm the formation of the BMNPs. Degradation of trichloroethylene (TCE) as a model pollutant was studied and more than 98% reduction in TCE was achieved by the polymers. Polymers with the BMNPs maintained their efficiency in degrading TCE after several cycles compared to metal-free polymers. The degradation was monitored by using gas chromatography-mass spectrometry (GC-MS), while the production of chlorides was verified by using ion chromatography (IC). Atomic absorption spectroscopy (AAS) was employed to determine the possible leaching of the BMNPs from the polymer, and confirmed to be extremely low.

Introduction

Synthetic organic compounds such as trichloroethylene (TCE), tetrachlorophenol (TCP), and dichloroethane (DCE) are released either intentionally or unintentionally into ground water, surface water, and the soil (Schrick et al. 2002; Zhang et al. 1998). Even at concentrations of only a few parts per million (ppm), these compounds are suspected to be possible carcinogens (Bull et al. 1995). Zero-valent metals such as iron, tin, and zinc (Zhang et al. 1998; Xu et al. 2005) have been shown to convert some of these pollutants to benign compounds such as hydrocarbons and chloride ions as illustrated by the general reaction:

$$C_xH_yCl_z + zH^+ + zFe^0 \rightarrow C_xH_{y+z} + zFe^{2+} + Cl^-$$
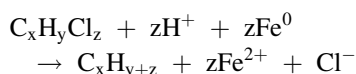
However, many challenges still exist with the use of zero-valent metals, including slow and incomplete degradation resulting in the production of chlorinated intermediates and by-products that are potentially

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more harmful than the parent compound (Su and Puls 1999; Roberts et al. 1996). Further efforts to overcome the drawbacks of these techniques have led to the use of bimetallic nanoparticles (BMNPs) such as Ni/Fe, Pd/Fe, Ni/Zn, Pt/Fe, and Cu/Fe to de-chlorinate organic compounds (Zhang et al. 1998). BMNPs have generated interest amongst researchers because of their outstanding electronic, optical, and catalytic properties (Ghosh et al. 2004; Hostetler et al. 1998). The properties of bimetallic particles are generally superior to those of single-metal zero-valent nanoparticles in terms of activity, selectivity, physical, and chemical stability and resistance to poisoning (Rousset et al. 2000). In the bimetallic nanoparticle systems one metal (Fe or Zn) acts as a reducing agent and the other metal i.e. Pd, Pt, Ag, or Ni behaves as a catalyst to facilitate electron-transfer processes (Zhang et al. 1998). The presence of a catalyst reduces the activation energy, while increasing the rate of de-chlorination, and also inhibits the production of chlorinated byproducts (Xu et al. 2005). Concerns over the release of these nanoparticles into the environment led to this study where bimetallic nanoparticles of nickel and iron were supported on carbon nanotubes (CNTs) in order to immobilize and reduce their environmental mobility. Nanotubes and nanofibers are ideal templates for immobilizing nanoparticles, and have recently been reviewed for various applications (Wildgoose et al. 2006). In our case, the added benefit is that suitable functionalisation also allows us to include nanotubes in the construction of advanced polymer systems for water treatment. Once the BMNPs were successfully supported on CNTs they were copolymerized with cyclodextrin (CD) moieties. This was done to increase the residence time of the pollutants at the polymer surface and "mop-up" any organic byproducts from the incomplete degradation of TCE, as previous experiments in our lab have demonstrated that cyclodextrin polymers are capable of removing TCE from water (Salipira et al. 2008).

Cyclodextrins (CDs) are cyclic oligomers formed from glucose units linked via α-1,4 linkages (Croft and Bartsch 1983). Although numerous CDs are known, three types are used almost exclusively, namely alpha-CD (α-CD), beta-CD (β-CD), and gamma-CD (γ-CD) (Easton and Lincoln 1999). CD based water-insoluble polymers have demonstrated the capacity to remove organic species from water at concentration levels as low as parts per trillion (Li and Ma 1999). However, the structural integrity of the polymers are somewhat compromised after prolonged recycling. Carbon nanotubes (CNTs) consist of graphitic tubular materials with various properties depending on the size and structure (Tasis et al. 2006; Mohlala et al. 2006). CNTs display an interesting range of electronic, optical, and mechanical properties including extremely high strength to weight ratios (Kim et al. 2008). When CNTs (1–5% m/m) were co-polymerized with cyclodextrin polymers the recyclability increased dramatically, losing only 10% of the polymer mass over 25 cycles, compared to 50% loss over 9 cycles for the native cyclodextrin polymers (Mhlanga et al. 2007). In addition, these composite polymers showed a removal efficiency of 99% for 10 mg/l *para*-nitrophenol when compared to 58% for the native CD polyurethanes.

Experimental

Preparation of bimetallic nanoparticles (BMNPs)

Bimetallic nanoparticles were first to be immobilized on carbon nanotubes (CNTs) before being co-polymerized with cyclodextrins and the diisocyanate linker. However, due to the lack of reactivity of pristine CNTs and poor solubility in organic or aqueous solvents, surface chemical modification of CNTs was performed by acid oxidation following now standard literature methods (Mhlanga et al. 2007).

Solutions of ferric nitrate (1 g) and nickel nitrate (1 g) (Riedel-deHaën) were prepared by dissolving each metal salt in 5 cm^3 of de-ionized water in separate containers. The two solutions were mixed together with the functionalized carbon nanotubes (f-CNTs) previously sonicated in de-ionized water. The mixture was stirred constantly for 24 h at room temperature. The solution was filtered, washed, and dried at 60 °C for 24 h. Conversion of the metal nitrate to the metal oxides was achieved by heating the sample in argon at 450 °C for 5 h at 5 °C/min at an argon flow rate of 60 cm^3/min. The metal oxides were then reduced to their zero-valent state by 10%H$_2$/Ar at 450 °C for 24 h at 5 °C/min at a flow rate of 60 cm^3/min (Chen et al. 1997). When the reaction was complete, the reaction chamber was

allowed to cool to ambient temperature at the same flow rate under the same conditions to minimize re-oxidation. These supported nanoparticles (BMNPs/CNT) were characterized using microscopy and spectroscopy. Separate nanoparticles (BMNPs) as well as nanoparticles supported on silica were also synthesized by the same procedure. These BMNPs were also characterized by electron microscopy and spectroscopy, and used as a base-line for comparing their catalytic activity.

Polymerization

Beta cyclodextrin (2.0 g) was dried and dissolved in *N,N*-dimethylformamide (DMF) (18 cm^3) with constant stirring. To this solution, 0.5% (m/m) metal-immobilized f-CNTs (BMNPs/CNT) (previously suspended in DMF (2 cm^3) by sonication for 15 min) were added. The mixture of the β-CD and BMNPs/CNT was heated to 70 °C followed by drop-wise addition of bi-functional linker, HMDI (2 cm^3). This mixture was stirred constantly at the same temperature under an inert atmosphere for 24 h. The formed polymer was precipitated and washed with acetone and then dried under vacuum at ambient temperature before characterization (Mhlanga et al. 2007).

Analytical methods

A water sample spiked with TCE (Riedel-deHaën) (30 cm^3, 10 mg L^{-1}) was percolated through 0.3 g of either the polymers containing BMNPs or those without BMNPs in a small column, roughly 1 cm^3 in diameter. The residual TCE was extracted from the eluent with 2 cm^3 hexane. Hexane extract (1 μL) was analyzed using GC-MS (Varian CP–380/Saturn 2000

GC-MS) to determine the residual TCE and any potential by-products. The GC column used was a DB 5 fused silica capillary column 30 m × 0.25 mm dimension, 0.25 μm film thicknesses. The initial GC temperature was 35 °C and was increased to 350 °C with a ramping rate of 6°C/min. Ultra high pure helium was used as a carrier gas with a flow rate of 1 cm^3/min. The mass spectrometry (MS) was operated in EI mode with a scan range from $m/z = 35$ to 460 at 0.6 s/scan. The production of the chloride ion in an aqueous solution was determined by ion chromatography (IC) (Dionex-100) while atomic absorption spectroscopy (AAS, Varian Spectra AA – 10) was used to monitor the metal ion concentration leaching out from the polymers.

Results and discussion

Characterization of nanoparticles

The synthesized bimetallic nanoparticles were characterized by microscopic techniques as to confirm their formation and determine their size and distribution. Similarly, the BMNPs supported on functionalized nanotubes were also characterized. Scanning Electron Microscopy (a: SEM) and Transmission Electron Microscopy (b: TEM) with an energy dispersive X-ray (EDX) spectrum Fig. 1 were used to confirm the composition and location of the synthesized BMNPs. In general the BMNPs synthesized in the absence of nanotubes were considerably larger (average 25–40 nm) than those supported on nanotubes or nanofibers.

The EDX spectra show iron and nickel peaks from the reduced metal precursors and spectral lines of Fe
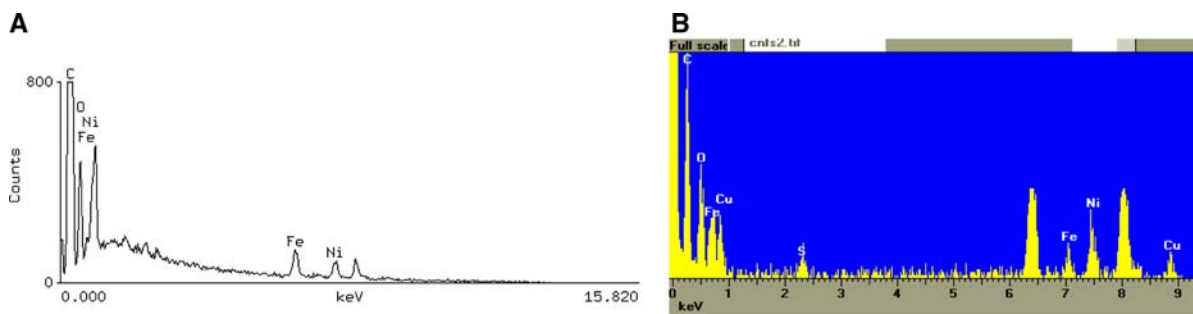

Fig. 1 EDX spectra (**a** SEM) (**b** TEM) displaying nickel and iron supported on CNTs

L_β (0.72 keV) and Ni L_α (0.85 keV) can clearly be seen. Further K lines confirm qualitatively the elemental Fe and Ni at 6.4 keV (K_α) and 8.3 keV (K_β), respectively in the BMNPs. The oxygen peak (at 0.3 keV) may result from the presence of the oxygen bearing functional groups that were attached during the surface chemical modification of CNTs or a surface re-oxidation of the metal oxides. The carbon peak K_α originates from the carbon nanotubes. Copper peaks are from the copper TEM grids (Robinson et al. 2005). It should be noted that while no conclusive proof exists for bimetallic particles, as opposed to collections of separate Ni and Fe particles supported on the CNTs, the BMNPs synthesized in the absence of CNTs also show characteristic EDX spectral lines for Ni and Fe. Planned high-resolution electron energy loss spectra (EELS) of these materials may answer this question.

The particles were evenly distributed along the surface of the nanotubes as illustrated by the TEM image Fig. 2.

The diameter distribution of BMNPs was calculated with an average diameter of 16 nm. About 40% of BMNPs were found in the 11–15 nm range as shown by the bar chart Fig. 3.

Characterization of polymers

Polymers were characterized and compared with metal-free polymers containing only CNTs. Surface morphology was examined using scanning electron microscopy (SEM) and pore volume and surface area determined by BET was utilized.

All SEM micrographs were captured using secondary electron imaging (SEI) and the polymers were carbon coated for better imagery. The surfaces
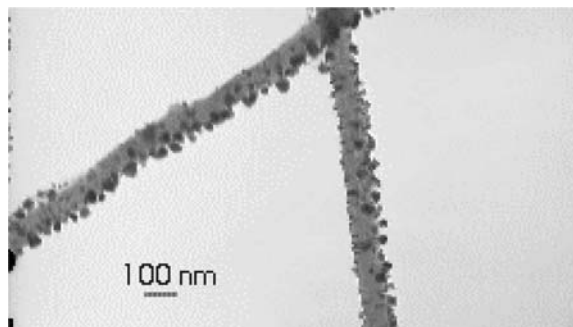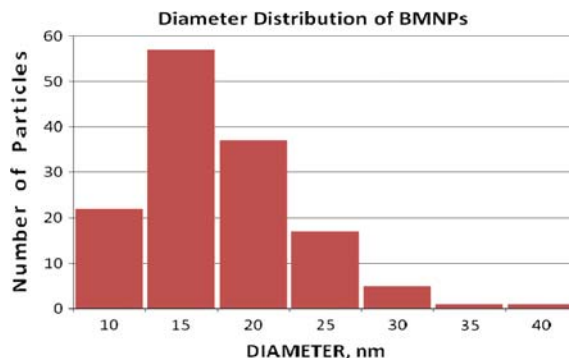

Fig. 2 TEM image showing CNTs with BMNPs

Fig. 3 Diameter distribution of BMNPs embedded on CNTs

(Fig. 4) of all polymers were rough and spongy. The roughness of the polymers is often an indication of their absorption capability, which is advantageous when trapping pollutants during water treatment applications. The meso- and micro-porous nature of the polymers should also allow efficient percolation of water through the polymer particles thereby negating the need for very fine particles which are difficult to handle and difficult to use in adsorptive water treatment.

BET analyses indicate that the presence of BMNPs on polymers result in a slight increase on the surface area and pore volume when compared to the polymers with no metal nanoparticles. For example, the surface area and pore volume measurements for CNTs/CD polymers were 6.78 m^2/g and 0.021 cm^3/g, respectively, while these measurements were 7.13 m^2/g and 0.021 cm^3/g for BMNP(Ni/Fe)/CNTs/CD polymers. This increase in surface area should play an important role in water treatment since it provides more absorption sites for the pollutant but is in contrast to another study in our laboratory with silver nanoparticles (Lukhele 2008).

Degradation and removal of TCE

The degradation and removal of TCE was studied for two reasons. The first was because this model organic pollutant was well known and the second was because of an industrial enquiry about possible decontamination methods if there were a spill. The characteristic mass-spectral peaks (e.g. parent ion $m/z = 98$) was detected in all standards and was confirmed by NIST (Version 2) reference libraries. The GC-MS chromatogram of the TCE spiked water

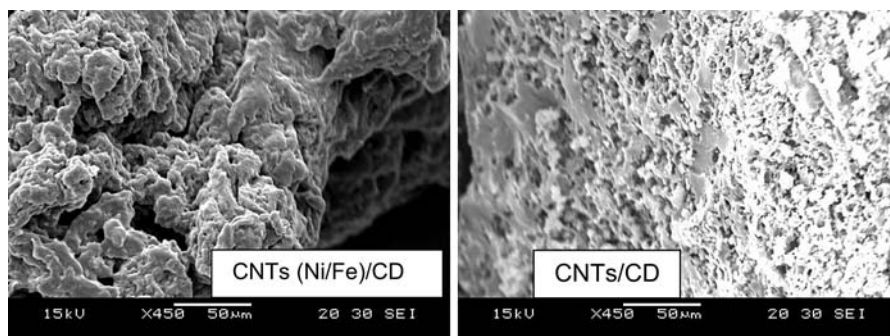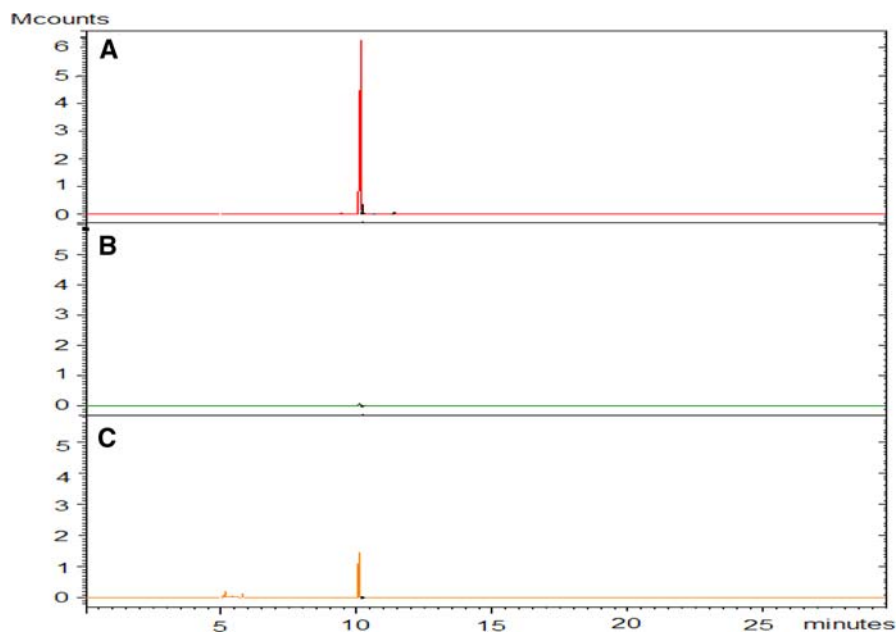**Fig. 4** SEM images of polymers with BMNPs [CNTs (Ni/Fe)/CD] and without (CNTs/CD)

Fig. 5 GC-MS chromatograms of TCE before (**a**) being passed through polymers, (**b**) after being passed through polymers with BMNPs (**c**) polymers without BMNPs

sample (10 mg L^{-1}) before being passed through polymers is shown in Fig. 5a. While this concentration is significantly higher than levels commonly found in drinking water, it is not unusual to find these and higher concentrations around industrial sites. Figure 5b and c show chromatographs after the spiked sample is passed through polymers with BMNPs and those without BMNPs, respectively. It can be observed that polymers with BMNPs completely removed TCE (Fig. 5b) while those without BMNPs had measurable residual TCE. It is difficult to quantify how much of the TCE is simply adsorbed and how much is destroyed, but we offer the following estimation: the polymers with no BMNPs were able to reduce TCE concentration by around 70% initially and 40% after several cycles. In a separate experiment, isolated BMNPs (3 mg) were allowed to react with the TCE-contaminated water in

an attempt to determine the products of the catalytic destruction. The mass of BMNPs was chosen to represent an amount of metal similar to what is available in the polymers. In this case the metal nanoparticles destroy nearly 90% of the TCE. Although only chloride ions were detected, and the organic products are unknown at this stage this is a satisfactory result. In the polymers, however, we believe access to the metal nanoparticles will be restricted through partial encapsulation by the polymer chains, and hence we can not accurately predict the how much of the pollutant is simply removed and how much is destroyed.

The polymers were then tested for their recycleability, that is, the ability to regenerate the polymers after use. Both polymers were subjected to at least eight cycles of treatment with the pollutant and the results are graphically represented in Fig. 6.
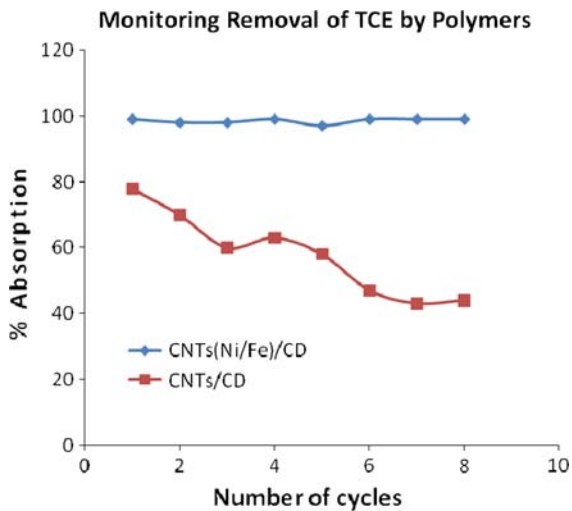
Monitoring Removal of TCE by Polymers

Fig. 6 Comparing the recylability of polymers with and without BMNPs on their efficiency in removing and degrading TCE

The saturation point of the polymers was determined using a crude break-through analysis from a 10 mg L^{-1} TCE solution. Approximately 30 cm^3 of solution was needed for complete break-through, which represents about 10 bed-volumes using a contact time of 2–3 min. The polymers were then repeatedly subjected to this pollutant load, followed by the draining of excess liquid and washing with ethanol.

Polymers with BMNPs maintained their efficiency with an average of 99% removal of TCE, while polymers without BMNPs plunged from a 78% to 44% removal. Polymers without BMNPs were able to degrade some TCE because of the presence of trace

iron impurities in CNTs. However, the iron loses its reactivity as the number of cycles increases. The reactivity decreases due to the formation of hydroxides on the surface of the metal; hence it becomes inert and loses its reactivity to degrade TCE (Schrick et al. 2002; Zhang et al. 1998). The removal of TCE reaches a plateau at about 40%, which is the amount of TCE we suspect is removed by the polymer alone.

A proposed mechanism of TCE degradation by BMNPs involves the oxidation of iron and the adsorption of hydrogen to the nickel. As iron corrodes, protons of water are reduced to hydrogen atoms then to molecular hydrogen. The formed hydrogen is adsorbed on the catalytic nickel surface. TCE is then adsorbed on the surface of Ni–Fe particles, leading to the breaking of C–Cl bond. The chlorine atom is then replaced by hydrogen (Fig. 7) (Schrick et al. 2002).

One of the by-products formed during the degradation of TCE is the chloride ion. The chloride ion production was monitored by IC and quantitatively determined by plotting the peak area of the standards against their corresponding concentration. The average chloride ion concentration for polymers with BMNPs was 22.8 ppm, while for polymers with only CNTs and no nanoparticles it was 9.8 ppm. Their standard deviations were 0.399 ppm and 0.673 ppm respectively. Periodically, the chloride production for polymers without BMNPs decreased to near zero, indicating the declining efficacy of the trace iron in the polymer (Fig. 8).

Immobilization of the bimetallic nanoparticles on carbon nanotubes was imperative as leaching of the

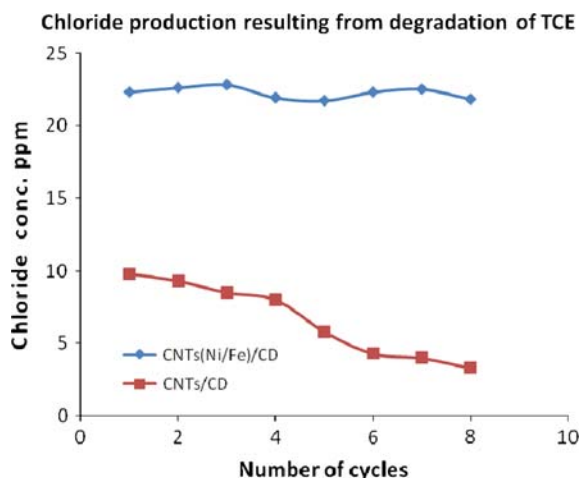**Fig. 7** Proposed mechanism for the degradation of TCE by BMNPs of Ni–Fe

Chloride production resulting from degradation of TCE
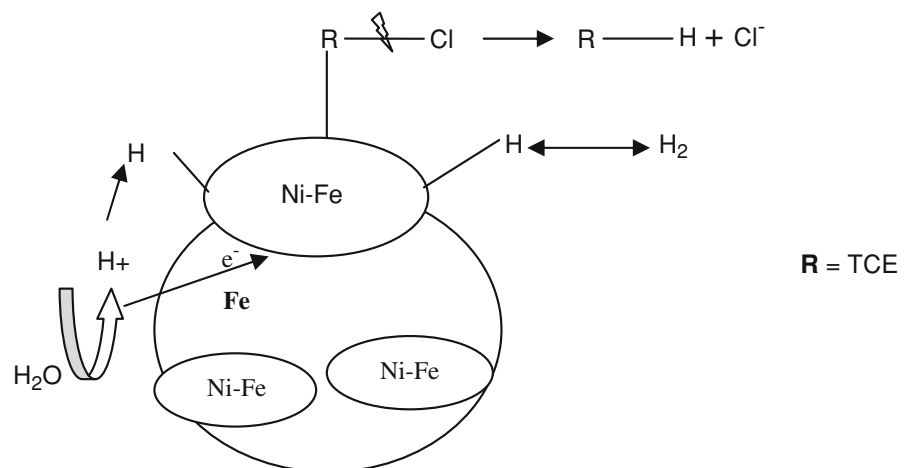
Fig. 8 The effect of recyclability on chloride ion production during the degradation of TCE

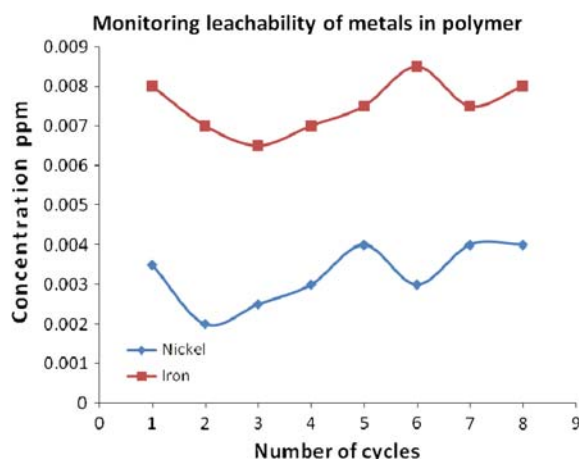## Monitoring leachability of metals in polymer

Fig. 9 Assesment of BMNPs leaching in the polymer as the polymer is recycled

particles would be another environmental concern. Thus leaching of iron and nickel was monitored after each cycle (Fig. 9).

From the results in Fig. 9 it can be observed that leaching was negligible for as low as 0.008 ppm Fe and 0.004 ppm Ni were detected with a standard deviation of 0.00065 ppm and 0.00076 ppm, respectively. The limit of detection of the method was found to be <0.09 ppb and the limit of quantification 0.9 ppb calculated at 95% confidence level. According to Environmental Protection Agency (EPA) the maximum acceptable level of iron and nickel in water should be 0.1 to 0.5 ppm (USEPA 2008). Thus the

detected concentration of the metals in solution was certainly negligible. What is also noteworthy from the results is the slow rate at which nickel was "spent" compared to iron. This may be the cathodic protection of nickel by iron; hence it is used up ahead of the nickel.

Conclusion

Bimetallic nanoparticles of nickel and iron were successfully synthesized, immobilized on carbon nanotubes, and copolymerized with β-CD. The polymer with BMNPs was at least 98% efficient in degrading and removing trichloroethylene (10 mg L^{-1}), even when subjected to several cycles. Negligible leaching of BMNPs is of great interest because of the undesirable environmental fate of metals in water. While these materials are far from direct application in water treatment, they may be useful in treating industrial spills, or water that is contaminated with chlorinated organics. Further tests are underway to determine which by-produced are formed during this process and whether or not these materials are also active at very low pollutant concentration levels (μg/L).

References

Bull RJ, Brinbaum LS, Cantor KP, Rose JB, Butterworth BE, Pegram R, Tuomisto J (1995) Water chlorination: essential process or cancer hazard? Fundam Appl Toxicol 28:155–156

Chen YK, Chu A, Cook J, Green MLH, Harris PJF, Heesom R, Humphries M, Sloan J, Tsang SC, Turner JFC (1997) Synthesis of carbon nanotubes containing metal oxides and metals of the d-block and f-block transition metals and related studies. J Mater Chem 7:545–549

Croft AP, Bartsch R (1983) Synthesis of chemically modified cyclodextrins. Tetrahedron 39:1417–1474

Easton CJ, Lincoln SF (1999) Modified cyclodextrins: scaffolds and templates for supramolecular chemistry. Imperial College Press. ISBN 1-86094-1443

Ghosh SK, Mandal M, Kundu S, Nath S, Pal T (2004) Bimetallic Pt-Ni nanoparticles can catalyze reduction of aromatic nitro compounds by sodium borohydride in aqueous solution. Appl Catal A Gen 268(1–2):61–66

Hostetler MJ, Zhong CJ, Yen BKH, Anderegg J, Gross SM, Evans ND, Porter M, Murray RW (1998) Stable, monolayer-protected metal alloy clusters. J Am Chem Soc 120(36):9396–9397

Kim j-Y, Kim HK, Kim KB (2008) Fabrication and electrochemical properties of carbon nanotube/polypyrrole composite film electrodes with controlled pore size. J Power Sources 176(1):396–402

Li DQ, Ma M (1999) Nanosponges from inclusion chemistry to water purification technology. Chemtech 35:31–37

Lukhele L.P (2008) M.Sc. Dissertation, University of Johannesburg

Mhlanga SD, Mamba BB, Krause RW, Malefetse TJ (2007) Removal of organic contaminants from water using nanosponges cyclodextrin polyurethanes. Chem Technol Biotechnol 82:382–388

Mohlala MS, Liu XY, Coville NJ (2006) Synthesis of multi-walled carbon nanotubes catalyzed by substituted ferrocenes. J Organometal Chem 691:4768–4772

Roberts AL, Totten LA, Arnold WA, Cattenot M, Pellarin M, Stievanno L, Renouprez A (1996) Environ Sci Technol 32:3017

Robinson JW, Frame EMS, Frame GM (2005) Undergraduate instrumental analysis. Marcel Dekker, New York, p 175

Rousset JL, Aires F, Bornette F, Cattenot M, Pellarin M, Stievanno L, Renouprez A (2000) Characterization and reactivity of Pd–Pt bimetallic supported catalysts obtained by laser vaporization of bulk alloy. Appl Surf Sci 164:163–168

Salipira KL, Krause RW, Mamba BB, Malefetse TJ, Cele LM, Durbach SH (2008) Cyclodextrin polyurethanes polymerized with multi-walled carbon nanotubes: synthesis and characterization. Mat Chem Phys 111:218–224

Schrick B, Blough JL, Jones AD, Mallouk TE (2002) Hydrodechlorination of trichloroethylene to hydrocarbons using bimetallic nickel-iron nanoscales. Chem Mater 14(12):5140–5147

Su C, Puls RW (1999) Kinetics of trichloroethene reduction by zero-valent iron and tin: pretreatment effect, apparent activation energy, and intermediate products. Environ Sci Technol 33:163–168

Tasis D, Tagmatarchis N, Bianco A, Prato M (2006) Chemistry of carbon nanotubes. Chem Rev 106:1105–1136

USEPA Methods (2008) http://www.epa.gov/ogwd/consumer/2ndstandards.html Accessed 8/11/08

Wildgoose GG, Banks CE, Compton RG (2006) Metal nanoparticles and related materials supported on carbon nanotubes: methods and applications. Small 2:182–193

Xu J, Dozier A, Bhattacharyya D (2005) Synthesis of nanoscale bimetallic particles in polyelectrolyte membrane matrix for reductive transformation of halogenated organic compounds. J Nanopart Res 7:449–467

Zhang WX, Wang CB, Lien HL (1998) Treatment of chlorinated organic contaminants with nanoscale bimetallic particles. Catal Today 40(4):387–395