P29: PREPARATION OF ENVIRONEMNTALLY BENIGN ZERO VALENT IRON NANOPARTICLES FOR REMOVING SOIL CONATMINANTS

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Abstract – In this paper we present a comparative evaluation of green and semi-green synthesis methods. The former utilized coffee, green tea and Virginia creeper leave extracts, the latters were based on sodium dithionite and sodium borohydride. nZVI synthesis was done in untreated tap water at room temperature to reduce the environmental footprint of the process. nZVI performance was assessed on the basis of time-dependent oxidation/reduction potential measurements and by the reductive dehalogenation of volatile chlorinated organics.

Keywords: up to five

1. INTRODUCTION

Nanotechnology in environmental remediation is enhancing due to its capacity to reduce costs and to facilitate the efficiency of the remediation process. Nanoremediation means the utilization of highly reactive nanoscale materials for the elimination and purification of pollutants through chemical reduction or catalytic process. For the production of nZVI particles numerous methods can be used. Green synthesis is a cost effective, environmental friendly alternative. Components as polyphenols from coffee and tea, protein, vitamins and wine polyphenols are available. These components have come into view as replacements for established chemical synthesis of metallic iron particles. In addition these components are extracted from natural sources that are non-toxic, biodegradable and the green material acts as both a dispersive and capping agent, helping to minimize agglomeration and oxidation of the nanoparticles. Sodium-dithionite can be used to reduce Fe(II) and produce nZVI under of high pH and in the presence of oxygen. The synthesis method that used dithionite as a reductant for nZVI production has been reported. The efficiency of trichloroethylene degradation is similar to if not slightly better than that of the more conventional borohydride procedure. In addition in the case of dithionite method are that: it uses a less expensive and available reducing agent; there is no explosive hydrogen gas production.

2. EXPERIMENTAL

Green synthesis of iron nanoparticles: Virginia creeper (VC-Fe) extract was prepared by boiling 5 g dry PQ leaves in 100 mL deionized water at 80 °C for 80 minutes, thereafter the extracts were vacuum-filtered and stored at 4 °C for further use. A similar process was employed for the green tea (GT-Fe) and coffee (C-Fe) extracts except that the purchased dry tea leaves and coffee were boiled directly without any pretreatment. VC-Fe, C-Fe and GT-Fe labelled "green" nZVI.

Half-green synthesis of iron nanoparticles: Reagents were prepared using normal drinking water. The reactions of nZVI were studied in pH-buffered solutions with NaOH. The sodium-hydroxide was added to the iron salt solution and mixed for 10 minutes. After that sodium-borohydride or sodium-dithionite was added and stirred until the solution became completely black. nZVI samples made from $FeCl_2$ by using $Na_2S_2O_4$ or $NaBH_4$ and labelled HG1-Fe and HG2-Fe, respectively. HG3-Fe was a reference sample made by reducing $FeCl_3$ with $NaBH_4$ and HG4-Fe was the product of reducing $FeSO_4$ with $Na_2S_2O_4$.

3. RESULTS AND DISCUSSION

We compared the reductive dehalogenation efficiency of zero valent iron nanoparticles in removing volatile chlorinated organic compounds (VOCls) from groundwater samples obtained from a real remediation target site.

Iron nanoparticles produced by using plant extracts featured ORP values in the -100 mV to -250 mV range immediately after synthesis, then their reduction potential decreased as a linear function of time. The ORP values of nZVI sols of semi-green origin were lower than those of the green ones and also increased with time. The best initial ORP results were measured for HG2-Fe and HG3-Fe. However, these were also the samples that lost their reduction potential at the fastest rate in the long run. Sample HG4-Fe offered a balanced performance, combining the third best initial ORP value with a linear loss of reduction potential.

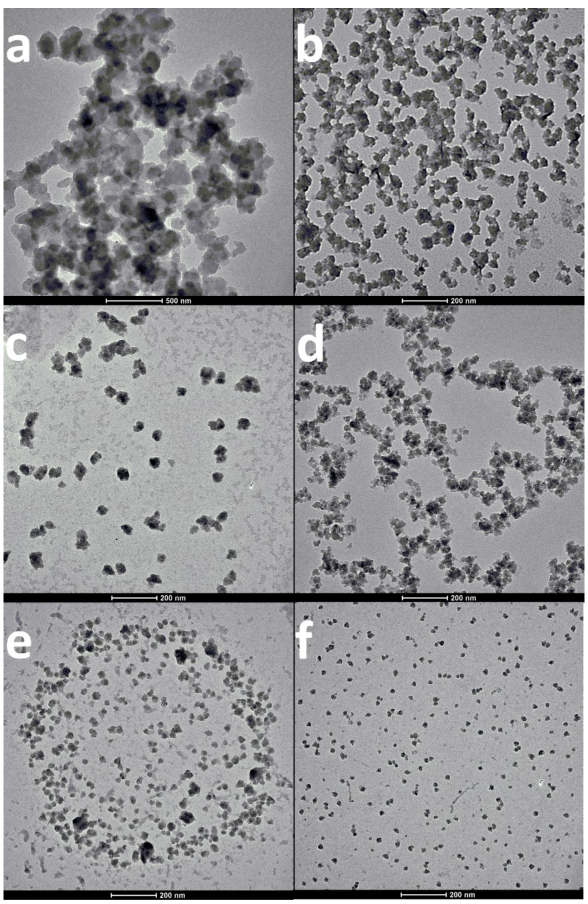

Figure 1. TEM images of nZVI samples: a) GT-Fe, b) VC-Fe, c) HG1-Fe, d) HG2-Fe, e) HG3-Fe, f) HG4-Fe. The TEM image of C-Fe was indistinguishable from that of GT-Fe, therefore, it is not shown here.

TEM images were taken from samples are seen on Fig.1/a-b. C-Fe and GT-Fe nanoparticles are morphologically very similar with average size of 100-200 nm. The VC-Fe particles have smaller average size, below 100 nm (40-70 nm). The half-green method's TEM images are seen on Fig.1/c-f. HG1-Fe sample has the biggest average size in diameter. The other three HG samples have less than half the size.

Half-green samples efficiency against VOCl degradation was identified by GC-MS measurement. nZVI suspensions were applied in one, twice and triple the proportion of VOCl, in three different concentrations (2500, 5000 and 10000 mg/dm^3).

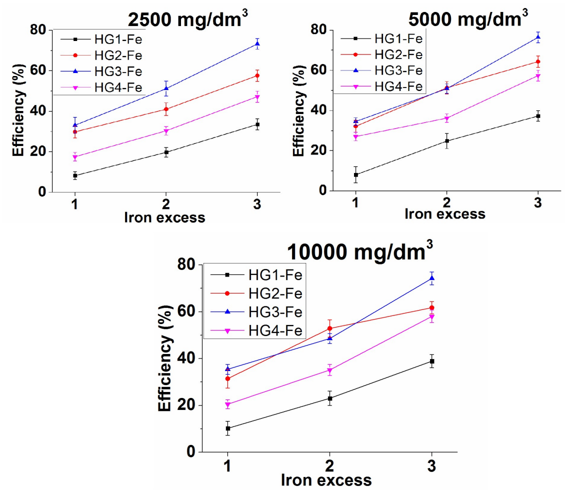

Figure 2. Efficiency of semi-green nZVI sols applied in three different concentrations for the reductive dehalogenation of VOCl-containing groundwater.

Increasing the nZVI excess is beneficial for VOCl removal: regardless of the sol concentration and the synthesis method, triplicating the iron to VOCl ratio roughly doubles the dehalogenation efficiency. Performance is also significantly affected by the iron nanoparticle synthesis method: the best HG3-Fe material outperformed the worst HG1-Fe by a factor of three under identical conditions. In agreement with literature reports, $NaBH_4$ reduced samples work slightly better than $Na_2S_2O_4$ derived ones. Interestingly, increasing the iron concentration from 2500 to 5000 mg/dm^3 causes only a marginal efficiency improvement and increasing it further to 10000 mg/dm^3 can even reduce the efficiency. A possible explanation for the

5000 mg/dm^3 optimum is that nZVI-consuming side reactions are relatively more important at low iron concentration, whereas at high iron concentration the probability of particle agglomeration increases.

4. CONCLUSIONS

Completely green synthesis methods utilized plant extracts (green tea, coffee, Virginia creeper) as iron salt reducing and nanoparticle capping agents, semi-green methods utilized industrial chemicals but all reactions were carried out at ambient conditions in untreated tap water instead of resource-hungry deoxygenated solvents. Although semi-green methods yielded iron nanoparticles with smaller average diameter and better reducing abilities than green ones, the latter performed acceptably as well. The applicability of Virginia creeper extract in nZVI synthesis was reported here for the first time.

Iron nanoparticles prepared using $NaBH_4$ outperformed those made with $Na_2S_2O_4$ in ORP and VOCl deterioration tests. However, sodium borohydride is more expensive and more toxic than sodium dithionite and yields toxic boron compounds that should not be allowed into the environment. Therefore, the sustainable optimum nZVI material identified by this study was HG4-Fe, which was prepared from $FeSO_4$ and $Na_2S_2O_4$. This material was tested under field conditions at a contaminated site and was found to degrade VOCls with appreciable efficiency.

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