AC 2007-365: INTRODUCING NANOTECHNOLOGY INTO ENVIRONMENTAL ENGINEERING CURRICULUM

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Introducing Nanotechnology into Environmental Engineering Curriculum

Background

As a result of the National Nanotechnology Initiative [1], substantial advances have been made in using nanotechnology to generate nanomaterials with novel properties [2]. These materials and processes have or will produce products ranging from coatings for stain resistant fabrics to smaller and faster computer chips. Recent studies have also suggested that nanotechnology can be employed in pollution prevention, treatment, and remediation [2-3].

The use of commercially available zero-valent-metal powders for the degradation of halogenated aliphatics is well documented [4]. Nancoscle Fe^0 has a much smaller grain size than commercially available powdered iron, making it much more reactive. Nanoiron and nanoscale bimetallic particles have been shown to be extremely effective for the reductive dehalogenation of common soil and ground water contaminants such as: chlorinated methanes [5], chlorinated ethanes [6] and chlorinated ethenes [7, 8] and essentially eliminate all the undesirable byproducts [9].

Lead is among the most toxic elements and has widespread presence in the environment [10, 11]. Common treatment technologies for lead removal include chemical precipitation and adsorption. However, precipitation becomes less effective and more expensive at high metal concentrations [12] and successful adsorption depends on finding low-cost, high-capacity sorbents [12-23] or microorganisms that accumulate toxic metals [24-26]. Innovative nanospheres have shown promise for lead complexation.

Despite the research progress that has been made, there is very little effort to introduce nanotechnology into undergraduate environmental engineering curriculum. The objective of this project was to introduce nanotechnology experiences into undergraduate environmental curriculum so that students will be exposed to cutting-edge advances in nanotechnology and their impact on the environment.

Overview of Modules

Three research-based environmental nanotechnology modules have been designed and implemented. Modules 1 and 3 have been incorporated into an undergraduate level environmental engineering course, and Modules 1 and 2 have been successfully incorporated into a senior-level chemistry course. For these modules, we selected two nanomaterials (nanoscale bimetallic iron particles and engineered nanospheres) that may provide solutions to challenging environmental pollution problems [3]. Table 1 shows a summary of each module and its learning objective(s).

Table 1. Overview of modules

Module	Objective
Module 1: Synthesis of Palladized Nanoscale Iron Particles	To understand chemical synthesis for environmental remediation
Module 2: TCE Degradation with Palladized Nanoscale Iron Particles	To apply nanotechnology for groundwater remediation
Module 3: Use of Engineered Nanospheres for Lead Complexation Lab	To determine the effectiveness of novel nanospheres for lead complexation

Module Creation and Description

Module 1: Synthesis of nanoscale bimetallic iron particles. The module has been created according to existing literature. Nanoscale iron particles are synthesized by mixing $NaBH_4$ (0.25 M) and $FeCl_3 \cdot 6H_2O$ (0.045 M) solutions (1: 1 volume ratio) [8]. The reaction is as follows:

$$4\ Fe^{3+} + 3\ BH_4^- + 9\ H_2O \rightarrow 4\ Fe^0 \downarrow + 3\ H_2BO_3^- + 12\ H^+ + 6H_2 \uparrow$$

The freshly prepared nanoiron particles are then coated with palladium acetate to form Pd/Fe bimetallic particles [8].

Module 2: Using nanoscale bimetallic iron particles for groundwater remediation. This module has been created according to existing literature. Trichloroethylene (TCE), one of the most ubiquitous soil and groundwater contaminants from groundwater, is used as a sample contaminant. The reductive dehalogenation of TCE via zero-valent nano iron particles can be described by the following equation [27]:

$$3Fe^o + C_2HCl_3 + 3H_2O \rightarrow C_2H_4 + 3\ Fe^{2+} + 3Cl^- + 3OH^-$$

However, the reaction of using palladized iron particles is not clear. TCE degradation by Pd/Fe nano-particles is assumed to follow pseudo-first-order kinetics. The pseudo-first-order decay coefficient and half life ($t_{1/2}$) can be determined after plotting experimental data.

Module 3: Using engineered nanospheres for lead removal. This module has been created in conjunction with ongoing research. This module evaluates the potential of using nanospheres functionalized with carboxyl groups for lead complexation from aqueous solutions. Bench-scale experiments are conducted to observe Pb^{2+} complexation after mixing carboxyl functionalized nanospheres with various concentrations of Pb^{2+} solution (6-30 mg/L) for 30 minutes. Residual free lead ion concentration is quantified by a Lead Ion Selective Probe. The average molecular weight of the carboxyl functionalized nanospheres is 12,000 g.

Course Description

- Junior-level "Environmental Engineering" and **"**Environmental Engineering Laboratory**"** are core courses for Civil & Environmental Engineering students. This course and laboratory focus on the physical, chemical, and biological principles of water and wastewater treatment, the design of wastewater treatment facilities (WWTFs), and hazardous waste site remediation. The current experiments concentrate on measures for performance of WWTFs, such as pH, biochemical oxygen demand, chemical oxygen demand, suspended solids, etc. The addition of Modules 1 and 3 (Module 2 was not ready to be implemented in Spring 2006) to the laboratory greatly expanded the existing curriculum that exposed the students to the aspects of using novel technology to solve environmental problems.
- Senior-level "Advanced Inorganic Chemistry" is a core course for the Chemistry students. In this course, students study the reactions of ions in aqueous solutions and carry out inorganic syntheses and characterizations. The addition of Modules 1 and 2 (implemented in Fall 2006) to the course greatly enhanced the existing curriculum that allowed the students to see the application of the products (nanoscale iron particles) synthesized through a simple inorganic reaction.

Module Implementation

For each module implementation, a brief power point presentation was delivered by the instructor on the overall background of nanotechnology and the specifics of the module. Students were given a lab handout containing detailed background information and the laboratory procedure. Upon completion of each module experiment, each student wrote a laboratory report analyzing the data generated by the whole class, answered several questions related to each lab and provided a discussion of the experimental results.

- During Spring 2006, Modules 1 and 3 were incorporated into "Environmental Engineering" and **"**Environmental Engineering Laboratory**"** as part of the curriculum in the Department of Civil & Environmental Engineering (CEE).

  In Module 1, students were given the appropriate chemical solutions and they followed detailed procedures to synthesize Pd/Fe nanoiron particles.

  In Module 3, students were divided into four groups and each group was given the same amount of carboxyl functionalized nanospheres to complex varying initial concentrations of free lead ion (each group used a different initial Pb^{2+} concentration). Lead complexation efficiency was determined by the students using an ion selective probe. The class plotted the following graph (shown in Figure 1) using the molar ratio between the carboxyl functionalized nanospheres to initial free lead concentration vs. lead complexation efficiency. The students were asked to evaluate the impact of the amount of nanospheres used on lead complexation based on the results obtained from the class.

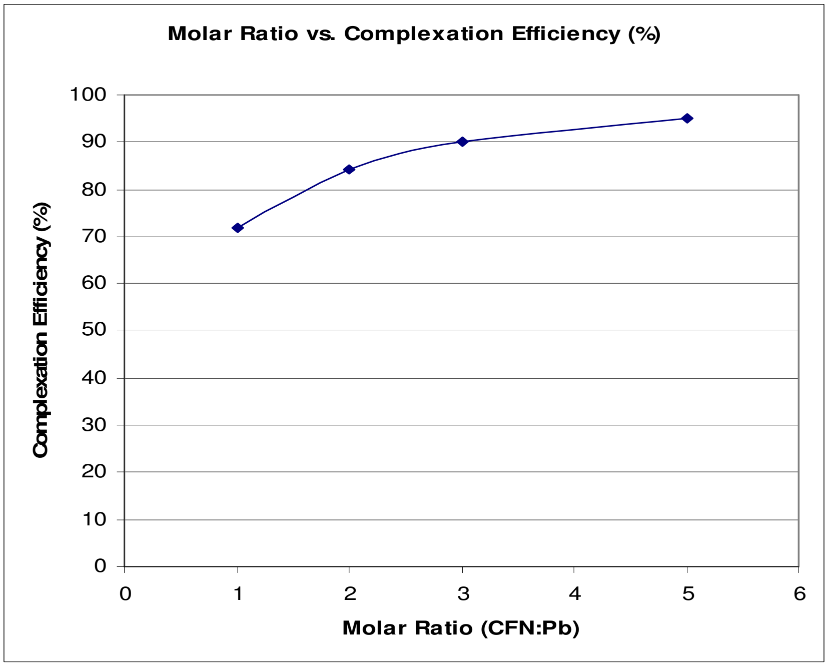

Figure 1. Lead complexation with carboxyl functionalized nanospheres.

In Fall 2006, Modules 1 and 2 were implemented in a senior-level "Advanced Inorganic Chemistry." In Module 2, students monitored the removal of TCE using the Pd/Fe made in Module 1. TCE was measured by a gas chromatograph. The students obtained the following plot shown in Figure 2 and determined the kinetic constant for TCE degradation to be 0.0393 min^{-1} with a half life of 17.6 minutes.

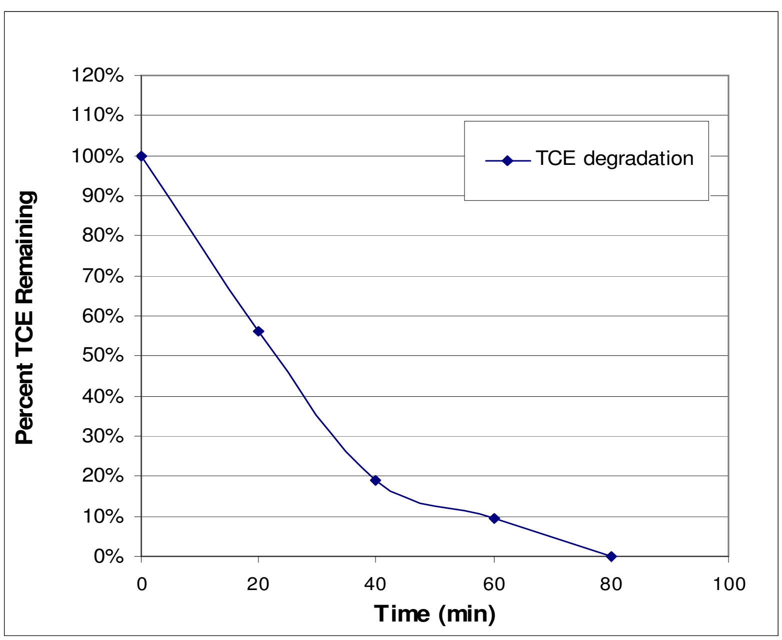

Figure 2. TCE dechlorination by nanoscale Pd/Fe.

Assessment

Modules were evaluated by the University of Massachusetts Donahue Institute (UMDI). Two survey instruments were used, namely feedback surveys (Appendix A) and multiple choice pre-post-tests (see Appendixes B, C, and D for specific pre- post- test questions for each module). They were distributed to students during class time. Table 2 includes a summary of the number of students who completed each of the evaluation tools in the courses listed below.
11% of the participating students were female, and all were enrolled in courses as part of an educational requirement.

Table 2. Survey distribution and response rate

	Module	Course Name	Feedback Survey	Pre-test	Post-test
Spring 2006	Modules 1 & 3	Environmental Engineering Lab	30	29	29
Fall 2006	Modules 1 & 2	Advanced Inorganic Chemistry	8	8	8

The quality of the modules has been documented through student feedback surveys. Students reported:
(1) a greater level of understanding related to nanotechnology after participating in courses (88%);
(2) expressed an interest in experiencing nanotechnology modules in other courses (60%);
(3) an increased interest in science and/or engineering after completing courses (55%);
(4) they would enroll in other courses containing nanotechnology modules (47%).

Assessment 1. Environmental Engineering Lab (Spring 2006, Modules 1 and 3)

Student learning was assessed through the use of multiple-choice pre- and post-tests. For both modules, student scores on post-test questions were significantly higher after implementation of the module, providing evidence that student learning increased as a result of the implementation of the modules.

Figures 3 and 4 provide an analysis of the pre- and post-test results for Modules 1 and 3, respectively. For Module 1, changes from pre- to post-test scores in this group were statistically significant for question 3 ($p<0.001$), question 4 ($p=0.002$), and question 6 ($p<0.001$). For Module 3, statistically significant differences between pre- and post-test scores were found for question 1 ($p=0.011$), question 2 ($p<0.001$), and question 6 ($p=0.008$).

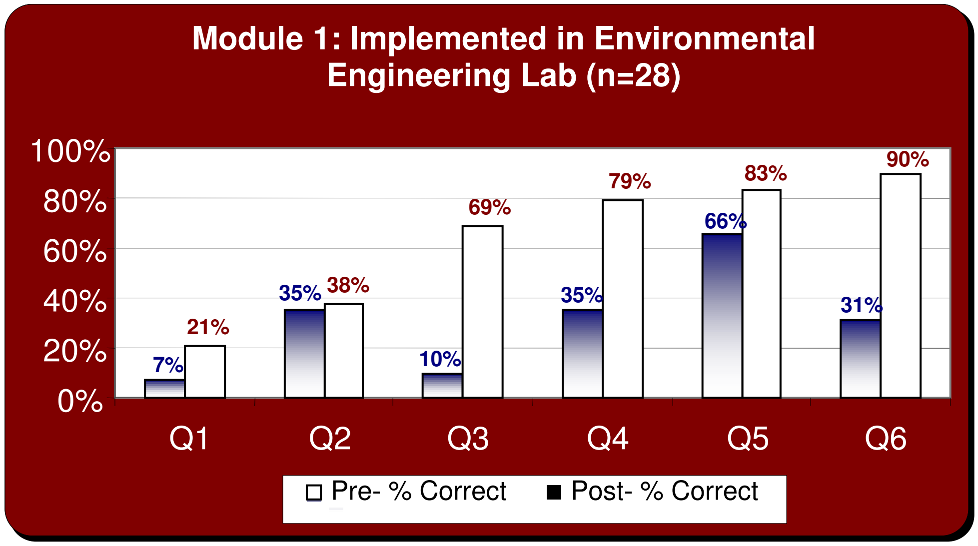

Figure 3. Pre- and post-test results for Module 1.

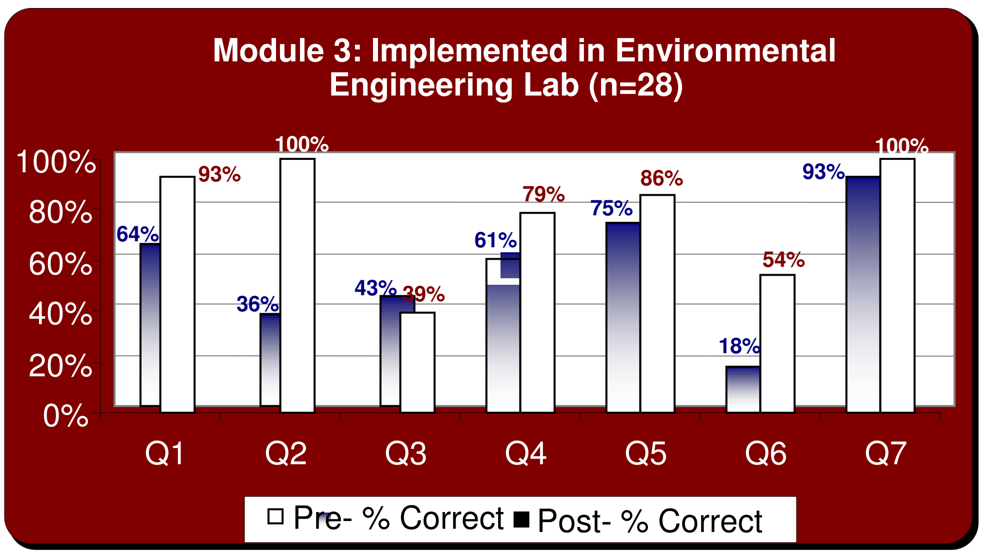

Figure 4. Pre- and post-test results for Module 3.

Students' responses to the open-ended questions that were asked on the feedback survey (after implementing Modules 1 and 3).

(1) What did you like about this module? (n=27)

- new understanding of nanotechnology
- excited to learn about a new technology
- interesting
- many were particularly interested in the focus on lead.

(2) What was most challenging about this module? (n=23)

- the precise measurement, stirring, and waiting
- understanding the theory, how the material can be used, the chemical background, and the terminology
- setting up the concentration probe (n=1)
- discovering the best way to remove the nanospheres from the aqueous solution (n=1)
- the module was not challenging (n=3)

(3) Any other comments or suggestions that would improve the quality of this module and/or your learning experience? (n=5)

- not having to pour 25 mL
- start the 30 minute stirring then do the intro talk
- can be shorter

Assessment 2. Advanced Inorganic Chemistry (Fall 2006, Modules 1 and 2)

Student learning was also evaluated for the students participated in the implementation of Modules 1 and 2 in Advanced Inorganic Chemistry course during Fall 2006. Figures 5 and 6 reflect the mean (average) number of correct responses to pre- post- test questions for Module 1 and 2. The number of correct responses on the post-test was much higher than on the pretest. These results were statistically significant ($p < .01$).

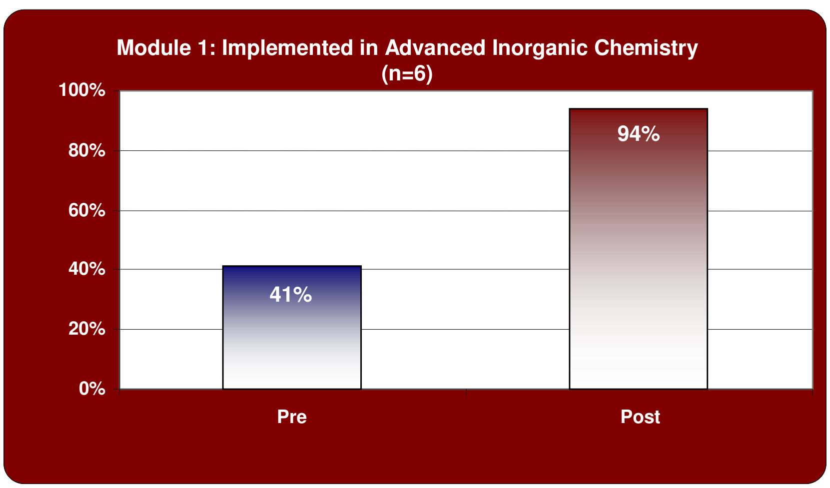

Figure 5. Pre- and post-test results for Module 1 implemented in Fall 2006.
(no individual question comparison)

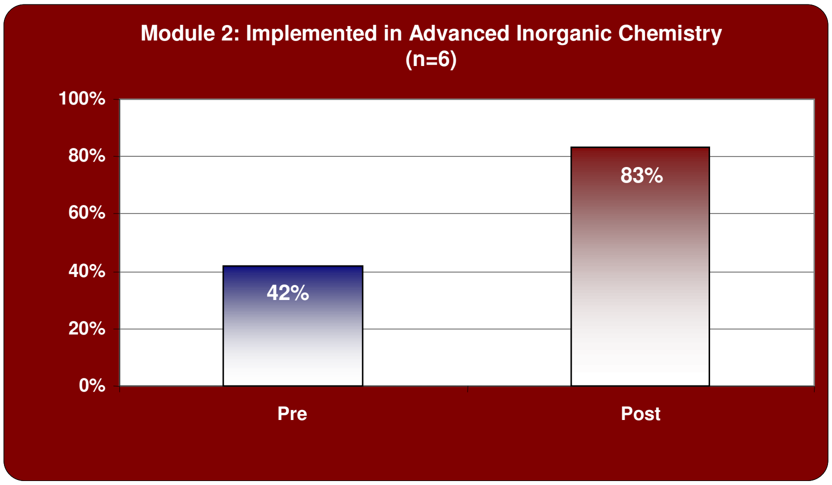

Figure 6. Pre- and post-test results for Module 2 implemented in Fall 2006 (n=6).
(no individual question comparison)

Students' responses to the open-ended questions that were asked on the feedback survey (after implementing Modules 1 and 2)

(1) What did you like about this module? (n=6)

- I learned how easy it can be to solve environmental problems with a little ingenuity.
- The concept of using nanotechnology for clean ground water.
- Well explained, practical application, great instructor.
- Working on new technology. Also, using acquired lab experience to research something new.
- Well organized, very information, good time use, good safety skills, interesting, fun.

(2) What was most challenging about this module? (n=6)

- The writing.
- Making nano Fe.
- The laboratory is kind of hot.
- Time constraints working with a group.
- Waiting between segments.

Conclusions

This paper reported our efforts to introduce three laboratory modules into two undergraduate-level courses (Environmental Engineering Lab and Advanced Inorganic Chemistry) so that students will be exposed to cutting-edge advances in nanotechnology and their impact on the environment.

All modules were fully evaluated with two survey instruments, feedback surveys and multiple choice pre-post-tests. Overall students had positive exposure to nanotechnology and such experience increased their interest in science and/or engineering. Modules 1 and 2 are portable and can be easily implemented in other institutions.

Appendix A:

Evaluation of Nanotechnology Modules Feedback Survey - Fall 2005

Please answer the following questions to help us learn more about the students who are enrolled in this course and to evaluate and improve the quality of modules taught in this course. All responses will remain strictly confidential.

Course Name:

Module Name:

Why did you enroll in this course? O Requirement O Elective

Year in School: O Freshman O Sophomore O Junior O Senior O Other

Gender: O Female O Male

Please respond to each of the following statements by filling in the bubble that best reflects your opinion.

	Strongly Disagree	Disagree	Neither Agree nor Disagree	Agree	Strongly Agree
I have a better understanding of nanotechnology after completing this course.	O	O	O	O	O
I would like to experience additional nanotechnology modules in other courses.	O	O	O	O	O
My interest in science (and/or engineering) has increased as a result of this course.	O	O	O	O	O
I will enroll in other courses that have nanotechnology modules in them.	O	O	O	O	O

Please answer the following questions. If you need additional space, please use the back of this survey.

1. What did you like about this module?

2. What was most challenging about this module?

3. Any other comments or suggestions that would improve the quality of this module and/or your learning experience?

THANK YOU FOR COMPLETING THIS SURVEY!

Appendix B: Module 1 Pre- Post-Test

Synthesis of Palladized Nanoscale Iron Particles*
Multiple Choice Questions

1) What role does nano-sized iron play in groundwater treatment?
   a) It kills bacteria
   b) It dechlorinates organic material
   c) It precipitates out contaminants
   d) All of the above

2) What are the byproducts of ground water treatment with nano irons?
   a) Hydrocarbons and elemental chlorine
   b) Hydrocarbons and elemental hydrogen
   c) Hydrocarbons and chloride ions
   d) Hydrocarbons and HCl

3) In the synthesis of nano irons, iron is reduced from iron (III) to elemental iron. What is used as the reducing agent?
   a) Elemental hydrogen
   b) Chloride ion
   c) Hydride ion
   d) Borohydride ion

4) What gas is evolved during the synthesis of nano irons?
   a) Hydrogen
   b) Chlorine
   c) Oxygen
   d) None of the above

5) What reaction conditions are used to grow uniform nano-sized particles?
   a) A large excess of reducing agent
   b) Vigorous stirring
   c) Slow addition of reagents
   d) All of the above

6) Why are the nano iron particles stored, wet, under nitrogen, rather than filtered?
   a) The particles will oxidize in air
   b) The particles are toxic when dry
   c) The particles, if dried, will absorb moisture from the air
   d) All of the above

*These questions have been modified in Spring 2007.

Appendix C: Module 2 Pre- Post-Test

TCE Degradation with Palladized Nanoscale Iron Particles

Multiple Choice Questions

1) Which of the following statements are true with respect to first-order reactions?
    a. The rate constant (k) is independent of the remaining contaminant concentration
    b. The rate of contaminant decay (mass/time) does depend on the concentration of contaminant remaining
    c. The time required for a given fraction of a contaminant to decompose is independent of the initial concentration
    d. All of the above

2) Why do we use pseudo first-order kinetics to characterize the reaction of TCE and Pd/Fe bimetallic particles?
    a. It is a well documented first-order reaction
    b. It is used as a first approximation when variables are not well understood
    c. Zero-order analysis requires extensive analysis and does not improve fit
    d. All of the above

3) What are the byproducts of <u>TCE contaminated ground water treatment</u> with nano irons?
    a. Hydrocarbons and elemental chlorine
    b. Hydrocarbons and elemental hydrogen
    c. Hydrocarbons and chloride ions
    d. Hydrocarbons and carbon dioxide

4) Why do we add pentane to the reaction bottle at the end of the kinetic experiment?
    a. To serve as a reaction catalyst
    b. To inhibit by-product formation
    c. To extract TCE for GC measurement
    d. To minimize the risk of TCE exposure

5) If the rate constant (k) is known, which of the following statements are true?
    a. It is possible to predict the composition of the degradation byproducts.
    b. The contaminant half-life can be predicted
    c. The original contaminant concentration can be calculated
    d. All of the above

6) Kinetic analysis to determine a first-order rate constant requires which of the following?
    a. Statistical analysis of data
    b. Use of the quadratic equation
    c. Use of geometry
    d. Graphical analysis of data

Appendix D: Module 3 Pre- Post-Test

Use of Engineered Nanospheres for Lead Complexation Lab*

Multiple Choice Questions

1) What are the main effects of Lead in drinking water?
   a) mental retardation
   b) anemia
   c) cancer and accumulative poisoning
   d) all of the above

2) What is the EPA limit for lead concentration in drinking water?
   a) 1 mg/L
   b) 100 ppb
   c) 15 ppb in more than 10% of the samples from a particular source
   d) no limit

3) What is the role of functionalized nanospheres in lead absorption process?
   a) removal of lead from aqueous solutions
   b) lead reacts with functional groups
   c) lead is absorbed by the functionalized nanospheres
   d) all of the above

4) What is the function of the Ion Selective Electrode used in this lab?
   a) detect nanosphere concentration
   b) detect the concentration of free lead ions in aqueous solutions
   c) detect ions other than lead in solution
   d) detect the concentration of nanospheres and lead solution mixture

5) How is lead removal efficiency calculated?
   a) initial concentration – final concentration
   b) final concentration/initial concentration
   c) (initial concentration – final concentration)/100
   d) (initial concentration – final concentration)/ initial concentration*100

6) What could be done in order to increase the adsorption capacity of the nanospheres used?
   a) Increase the number of functional groups
   b) Decrease the number of functional groups
   c) Increase surface area
   d) Decrease surface area

7) What models can be applied to calculate the adsorption capability of the functionalized nanospheres used?
   a) Freundlich isotherm
   b) Langmuir isotherm
   c) Both Freundlich and Langmuir
   d) Newton's Law

*These questions have been modified in Spring 2007.

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