Redox Reactions and Groundwater Remediation

Introduction

Scientists and engineers have developed many innovative methods to remove contaminants from soil, surface water, and groundwater. Permeable reactive barriers (PRBs) are a good example of new technology that was created to solve environmental problems. A PRB is a wall built below ground to remove pollutants from contaminated groundwater. The walls are permeable, so water will flow through, but are made of reactive materials that will trap or detoxify pollutants. PRBs made of metallic iron are used to remove chlorinated organic solvents and heavy metals from groundwater. The chemical principle is simple—iron is a good reducing agent. It reduces toxic organic compounds and converts them to less harmful substances. The reaction of iron powder with organic redox indicators (dyes) in this activity demonstrates the "potential" of this method to reduce organic compounds.

Concepts

- Groundwater remediation
- Oxidation–reduction
- Permeable reactive barrier
- Chlorinated organic solvents

Materials

Indigo carmine dye, 0.25 g
Iron powder, 8 g
Methylene blue solution, 1%, 1 mL
Water, distilled or deionized
Beral-type pipets, 2
Bottles, square-cut, clear plastic, with caps, 60- or 125-mL, 2
Erlenmeyer flasks, 500-mL, 2
Spatula
Stirring rods, 2
Weighing dishes, 2

Safety Precautions

Iron powder and other metals in fine-powder form represent a possible fire and explosion risk. Keep away from flames, sparks, and other sources of ignition. Avoid breathing fine metal dust. Wear safety glasses or chemical splash goggles whenever working with chemicals, heat or glassware in the laboratory. Please review current Safety Data Sheets for additional safety, handling, and disposal information.

Preparation

1. Prepare 20 ppm methylene blue solution: Add 1 mL of 1% methylene blue indicator solution to 500 mL of distilled or deionized water in an Erlenmeyer flask or beaker. Stir the solution with a stirring rod to obtain a uniform concentration.
2. Prepare 20 ppm indigo carmine solution: Dissolve 0.25 g of indigo carmine in 100 mL of distilled or deionized water. Dilute 4 mL of this 0.25% solution to 500 mL with water to obtain a 20 ppm solution. For best results, prepare this solution fresh the day of use.

Procedure

1. Weigh approximately 2 g of iron powder into a small weighing dish. Using a funnel or weighing paper, transfer the iron into a clear plastic or glass bottle.
2. Pour the 20 ppm methylene blue solution into the bottle containing iron powder until the liquid is just about overflowing (try not to leave any air space or air bubbles in the liquid).
3. Cap the bottle and shake vigorously for 3–5 minutes. The bright blue dye solution will gradually fade and decolorize, and the resulting gray mixture will settle on standing to reveal a clear and colorless liquid and a bottom layer of iron.
4. The dye solution will remain colorless on standing for about 15 minutes before the blue color slowly begins to return

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due to air oxidation.

5. Follow a similar procedure to treat the 20 ppm indigo carmine solution using about 5 g of iron powder.
6. The indigo carmine solution will gradually change from its initial blue color to green and then to yellow. The mixture will settle on standing to give a clear yellow solution and a bottom layer of iron.
7. The dye solution will remain yellow for about 15 minutes before gradually turning green and then blue again. The first traces of green (oxidized color) appear near the cap, where air can enter, and then slowly diffuse throughout the liquid.

Disposal

Please consult your current *Flinn Scientific Catalog/Reference Manual* for general guidelines and specific procedures, and review all federal, state and local regulations that may apply, before proceeding. The heterogeneous reaction mixtures generated in this activity should be filtered to separate the iron powder. The waste iron may be packaged for solid waste disposal according to Flinn Suggested Disposal Method #26a. The remaining aqueous dye solutions may be disposed down the drain with plenty of excess water according to Flinn Suggested Disposal Method #26b.

Connecting to the National Standards

This laboratory activity relates to the following National Science Education Standards (1996):

Unifying Concepts and Processes: Grades K–12
Evidence, models, and explanation
Form and function

Content Standards: Grades 9–12
Content Standard A: Science as Inquiry
Content Standard B: Physical Science, structure of atoms, structure and properties of matter, chemical reactions, motions and forces, conservation of energy and increase in disorder, interactions of energy and matter
Content Standard F: Science in Personal and Social Perspectives, personal and community health, population growth, natural resources, environmental quality, natural and human-induced hazards, science and technology in local, national, and global challenges
Content Standard G: History and Nature of Science, science as a human endeavor, nature of scientific knowledge, historical perspectives

Tips

- Permeable reactive barriers are a passive technology, relying on the natural flow of water underground to clean the groundwater. To illustrate the passive nature of PRBs, set up a series of capped test tubes containing methylene blue or indigo carmine solution. Add iron to the first test tube, and then add the same amount of iron to the next test tube in the series every day after that for five days. At the end of the week there will be a visible color gradient "from the ground up" in each test tube.
- Methylene blue and indigo carmine are used in classic demonstrations, the blue-bottle reaction and the "stop-and-go" light, respectively, to illustrate reversible oxidation–reduction reactions. Other redox indicators that give interesting color changes include resazurin and dichloroindophenol. The original (oxidized) colors of the dyes are restored upon standing (steps 4 and 7) because of reaction with oxygen in air.

Discussion

Permeable reactive barriers have been installed at more than 40 hazardous waste sites in the United States and Canada since 1980. PRBs are installed underground, beneath the water table, to clean up contaminated groundwater (see Figure 1). A barrier is built by digging a long, narrow trench and installing the reactive material in the natural flow path of the polluted groundwater. PRBs do not require pumps or other expensive machinery, there are no energy costs to operate the barriers, and the process does not generate additional waste that would need to be disposed of in a landfill or by incineration.

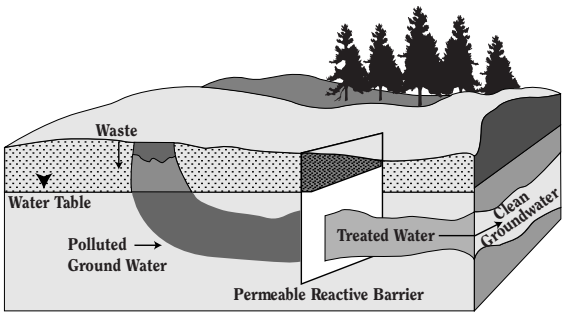
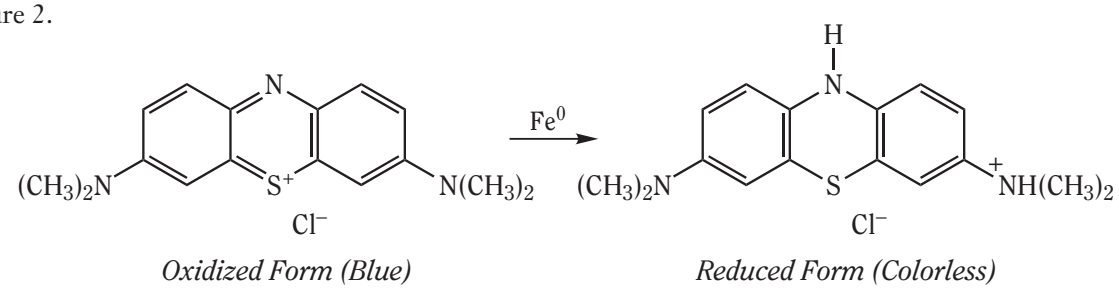


Figure 1. Installation and Design of a Permanent Reactive Barrier.

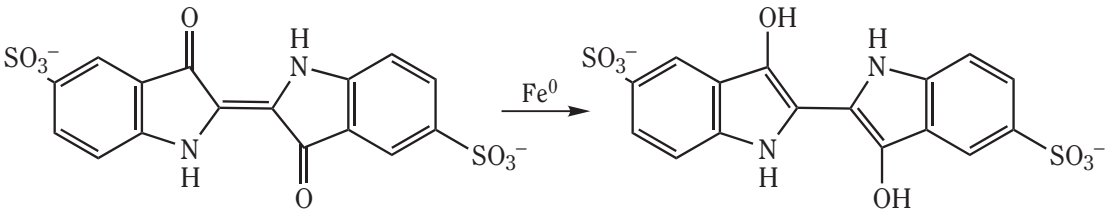
There are three major classes of PRBs. Barriers are designed to (1) trap pollutant chemicals by adsorption, using charcoal; (2) precipitate dissolved ionic pollutants using limestone; or (3) react with toxic chemicals and convert them into less harmful substances. Metallic (zerovalent) iron is the most important reactive chemical used in the third class of PRBs. Iron is inexpensive, readily available, and a good reducing agent, capable of reducing a wide range of organic and inorganic compounds in high oxidation states. So-called "iron walls" are commonly used to remediate groundwater contaminated with chlorinated organic solvents, such as trichloroethylene and perchloroethylene (dry-cleaning solvents), and are also effective for removing pesticides, nitrates, and chromates from water.

This demonstration illustrates the reduction of organic compounds using metallic iron. The substrates are organic redox indicators that exist in two oxidation states having different colors. The structures of the oxidized and reduced forms of the dyes are shown in Figure 2.



Oxidized Form (Blue) *Reduced Form (Colorless)*

Methylene Blue



Oxidized Form (Blue) *Reduced Form (Yellow)*

Indigo Carmine

Figure 2. Structures of Organic Redox Indicators

Materials for *Redox Reactions and Groundwater Remediation* are available from Flinn Scientific, Inc.

Catalog No.	Description
M0074	Methylene Blue Solution, 1% Aqueous, 100 mL
I0047	Indigo Carmine, 5 g
I0013	Iron Powder, 100 g

Consult your *Flinn Scientific Catalog/Reference Manual* for current prices.