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AUTHOR Boeschen, John; Randall, John M.
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ABSTRACT

This publication is the fifth in a series of seven supplementary investigative materials for use in secondary science classes providing up-to-date research-related investigations. This unit is structured for grade levels 9 through 12. It is concerned with the removal of heavy divalent metals from water with the use of tannin-containing agricultural by-products. The first part of this guide provides the teacher with information about: (1) materials needed; (2) supplementary information; (3) preparation of peanut skins for use in the investigation; and (4) suggested readings. The second part provides students with background information and two investigations: (1) discovering an ion-exchange medium, and (2) scavenging heavy metals from solution. Each investigation consists of: (1) materials needed for a four-student team; (2) procedures; (3) questions for thought; (4) extending the investigation; and (5) suggested readings. (HM)

science study aids

5

tannin: nature's filter

Developed by John Boeschen, a graduate student in Science Curriculum and Instruction at U. C. Berkeley. Mr. Boeschen prepared the manuscript in cooperation with Dr. John M. Randall, scientist, of the Agricultural Research Service, U. S. Department of Agriculture, at the Western Regional Research Center (WRRC), Berkeley, California.

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TO THE TEACHER

This Science Study Aid (SSA) is based upon work of the U. S. Department of Agriculture's Agricultural Research Service (ARS) conducted at the Western Regional Research Center in Berkeley, California. It is concerned with the removal of heavy divalent metals from water with the use of agricultural by-products. The SSA provides students with background information to help them understand the advantages of this technique as well as the principal of its working. There are two Investigations for the students. In this section, suggestions to facilitate classroom use are provided for each of the Investigations.

Tannin: Nature's Filter is structured for grade levels 9-12. It is designed to stimulate creative thinking and to act as a focal point for class and group discussion. This SSA is an appropriate supplement to general science courses. Also, it is readily adaptable to chemistry and conservation courses.

SELECTING A COLUMN FOR INVESTIGATIONS 1 & 2

Columns can be made of glass or plastic. They should be approximately 15 to 20 cm long. They should have inside diameters (I.D.) of not less than 1 cm if ion-bands are to form. If glass columns are not available, clear plastic soda straws or clear plastic rigid cigar tubes may be substituted. The cigar tubes are preferred because ion-band formation can be clearly observed whereas the smaller I.D. of soda straws precludes formation of distinct bands. The bands, trapped CU^{++} ions, are formed as the $CuSO_4$ solution percolates through the ion-exchange medium in the columns.

PREPARE FRESH COLUMNS FOR EACH INVESTIGATION.

MATERIALS LIST

For your convenience, we have listed below the materials needed to perform all the Investigations contained in this Science Study Aid. The following list gives the quantities needed for a team of three students:

STUDENT MATERIALS

(Appropriate size household glasses, baby food jars, etc., can be used instead of laboratory beakers.)

6 columns
3 medicine droppers
4 150 ml beakers
6 one-inch strips of cellophane tape
24 small glass or ceramic beads
2 nine cm sections of cotton (1 cm thick)
300 ml tap water
300 ml $CuSO_4$ solution
100 ml 0.IN HCl
150 ml NaCl solution
sawdust
peanut skins

TEACHER MATERIALS

1. one-litre beaker
oven.
0.IN HCl
$CuSO_4$
NaCl

PREPARATION OF PEANUT SKINS

All peanut skins used in Investigations 1 & 2 should be unsalted. The skins contain a natural dye which should be removed before column use according to the following directions:

1. If the peanut skins can't be easily removed from the peanuts, they can be loosened by blanching. To blanch: place the peanuts on a cookie sheet or in a shallow pan, then bake them at 250°F. long enough for the skins to be easily slipped off by hand.
2. Once the skins have been removed, soak them in hot (120°F.) water 15 minutes. Then rinse them in a large beaker of warm water until no, or very little, dye leaches out.
3. Drain the water and dry the skins. To speed up the process, you may dry them in a 200°F. oven. Watch them carefully to prevent any burning or scorching.

Ions are most efficiently removed from solution when the ratio of peanut skin particle size to column I.D. is 1 to 8. The peanut skins can be pulverized by rubbing between your fingers. If the particles are too large, the solutions will channel around various portions of the column. This channelling prevents the solution from coming into contact with all of the skins.

You can easily observe channelling when wetting the column with tap water. If the water is channelling, dry areas of peanut skins next to the plastic surface of the column will be noticed. If these areas do not wet within five minutes, this is an indication that the particles in your column need to be ground finer.

Fill the columns with peanut skins or sawdust to a height no greater than 5/8's of the column's height. This allows room for a liquid head to form which will force the different solutions through the column.

A soda straw column requires approximately 0.5 grams of treated peanut skins. Thus, 20 to 30 peanuts will provide you with enough material for 1 soda straw column. If your columns are larger, adjust accordingly. Larger columns also will require glass or ceramic beads. The beads are placed on top of the column's ion-exchange medium to prevent the peanut skins and sawdust from floating to the surface as solution is poured in. The smaller soda straw columns do not need these beads.

INVESTIGATION 1

Students will determine which of two agricultural by-products, peanut skins or sawdust, removes copper ions from solution. The sawdust requires no special treatment before classroom use. The method for packing it in the columns is the same as that for peanut skins. Remind students that both materials must be packed loosely. If they are packed tightly, percolation through the columns will be extremely slow. A one-litre container loosely filled with sawdust will be sufficient for 50 or more soda straw columns.

In step #4, students are asked to note any color changes. As the Cu^{++} ions are trapped, the peanut skins turn a dark color. Because sawdust does not attract and hold the ions, it will not change color. The absence of a color change shows that sawdust is not an effective ion-exchange medium.

In step #5, a dilution of hydrochloric acid (HCl) is used. It is 0.1N. Prepare it by adding 1 ml of concentrated HCl to 100 ml tap water. This will be enough for two student teams. Multiply the formula according to the number of teams in your class.

The concentration of $CuSO_4$ in solution is 100 parts per million (100) ppm). Prepare it by making the following serial dilutions:

1. Add 1 gm of $CuSO_4 \cdot 5H_2O$ to one litre of water.

2. To 1 ml of the above solution, add one litre of water. This will be enough for six student teams.

In step #5, the percolation of HCl through the column will restore the peanut skins' original color. This happens as the Cu^{++} ions are removed from the peanut skins. The addition of HCl will not cause any observable change in the sawdust column.

INVESTIGATION 2

Because sodium (Na) is not divalent, it will not be removed from solution by the peanut skins. There will be no corresponding color change.

The concentration of NaCl in solution is 100 ppm. Prepare it by making the following serial dilutions:

1. Add 1 gm of NaCl to one litre of water.
2. To 1 ml of the above solution, add one litre of water. This will be enough solution for six students teams.

If your students wish to determine whether a column can be re-used after it is rinsed free of Cu^{++} ions with HCl, they must rinse the HCl out of the column. They may use fresh tap water to do this. Use Fishers test paper to determine when the liquid passing through the column is no longer acid. A pH of 7 is most acceptable.

SUGGESTED READING

<u>Ion Exchange Resins</u>, Kunin, Robert, and Myers, Robert J.; John Wiley and Sons, Inc., New York, N.Y., 1950. The short section on industrial water pollution (p. 155) is quite interesting because it is based on a hypothesis that has been borne out by time.

<u>Ion Exchange Separations in Analytical Chemistry</u>, Samuelson, Olof, John Wiley and Sons, Inc., New York, N.Y., 1963. Pages 97-132 deal with the dynamics of an ion exchange column in operation. Very technical. Not recommended for student reading.

TO THE STUDENT

When was the last time you turned on the TV, picked up a newspaper, or opened a magazine and were immediately confronted with the problems of pollution? It seems to be everywhere: in the air we breathe, in the food we eat, and even in the clothes we wear. Perhaps most noticeable of all is the pollution of our water resources.

The presence of heavy divalent metals (those with two valence electrons) are among the chief offenders. These metals include copper, lead, cadmium, chromium, and mercury. How do they get in our water? How can we remove them?

In order to answer these questions, the sources must first be identified. Many of these metals are cast off as waste from industrial and mining operations. They may enter our rivers and streams directly or they may leach into our underground water tables.

Many mining and manufacturing operations may have to shut down unless they are able to meet federal and local standards. These standards regulate the amount of pollutants a plant may release into streams and lakes. Even small quantities of toxic metals can kill and contaminate fish and can make water unfit for human use.

There are several methods which help reduce the concentration of heavy metal ions in water. Precipitation of copper and lead ions as hydroxides often is used industrially, but it is seldom efficient enough to meet water quality regulations. Bacteriologically-produced sulfide has been used to precipitate heavy metal ions. Again, this method has not consistently met the strict water quality limits for waste discharge. Ion exchange, on the other hand, can be efficient. Until recently, however, it has not always been economically possible. Synthetic ion-exchange resins are relatively expensive.

Recently, researchers at the Agricultural Research Service (ARS) of the U.S. Department of Agriculture discovered an inexpensive and effective method of scavenging these metals from waste streams. The method they developed works on the ion-exchange principle. It does not, however, use expensive synthetic resins.

Researchers at the Western Regional Research Center (WRRC), Berkeley, California, discovered that certain agricultural wastes effectively remove heavy metals from dilute solutions. These by-products include coconut husks, walnut expeller meal, and various tree barks. All these waste products contain a substance known as tannin. Tannic acid, used in tanning hides, is made from tannin, for example.

Imagine that copper, a heavy divalent metal, is in solution as copper sulfate ($CuSO_4$). ARS scientists believe that as the $CuSO_4$ molecule passes over the tannin, the Cu^{++} ion is trapped by the tannin. In other words, the tannin removes it from solution.

The ARS-developed process has the advantage of being more efficient and economical than other methods used for cleaning heavy-metal-polluted waters. Many of the tannin-containing agricultural by-products can be obtained cheaply. Waste bark, for example, is inexpensive. Also, it is available throughout the country in quantities that would make it an ideal material for ion-exchange columns. Further, many of the metals can be reduced to below 0.1 ppm —well below safety requirements. An added benefit is the easy recovery of these metals for reuse. They can be flushed from the column with a weak acid, such as hydrochloric acid. This flushing causes them to flow out through the system in a highly concentrated solution.

In this SSA, you will assemble your own ion-exchange column using an agricultural by-product. Then you will investigate the properties of the column using techniques similar to those used at the ARS research center in Berkeley, California.

SUGGESTED READING

By-Products Scavenge Metal Pollutants, Agricultural Research, United States Government Printing Office, Public Documents Dept., Washington, D.C. 20402, July 1975. A brief, concise description of the ARS technique. Recommended for all classes.

Ion Exchange Resins, Kitchener, J. A., John Wiley and Sons, Inc., New York, N. Y., 1957. The first chapter of the book gives a quick history of the discovery of the ion exchange process and shows the significant role it plays in the soil and in other biological processes. Recommended reading for all classes.

INVESTIGATION 1: DISCOVERING AN ION-EXCHANGE MEDIUM

Both sawdust and peanut skins are agricultural by-products. Only one of them, however, will remove copper ions from solution. In this Investigation, you will determine which one.

MATERIALS

4 columns
3 medicine droppers
4 150 ml beakers
4 one-inch strips of cellophane tape
16 small glass or ceramic beads
1 nine cm^2 section of cotton (1 cm thick)
150 ml tap water
100 ml $CuSO_4$ solution
50 ml 0.1N HCl
peanut skins
sawdust

PRELIMINARY PROCEDURE

1. Tape thin sections of cotton over the bottom of each column.

2. Loosely fill the columns with peanut skins. DO NOT PACK THE SKINS DOWN. As you are filling the columns, occasionally tap the outside of the columns with your fingers to help the peanut skins settle into place. Fill 5/8 of the column's height with peanut skins.

3. Place four beads on top of the peanut skins in each column. These beads will prevent the skins from rising to the surface as the columns are filled with solution. (Fig. 1)

4. Repeat steps #1-3 in the remaining two columns using sawdust instead of peanut skins.

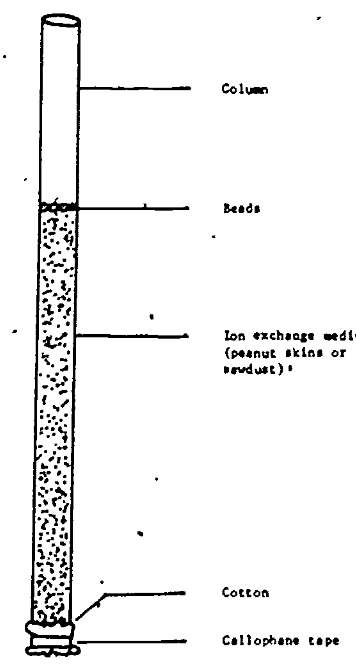

FIG. 1

PROCEDURE

1. Wet the material in each of your four columns with tap water. Use one of your medicine droppers to fill the columns. Then collect the water in one of the 150 ml beakers. Continue to add water until all the material in each of the columns is thoroughly wetted.

2. Add the $CuSO_4$ solution to one column of sawdust and to one column of peanut skins. Do this before the tap water drops below the top level of either the peanut skins or the sawdust. NEVER LET THE LEVEL OF ANY SOLUTION GO BELOW THE TOP LEVEL OF THE PEANUT SKINS OR THE SAWDUST.

3. While you are adding $CuSO_4$ solution to these two columns, continue to pour tap water through the two remaining columns. These two columns will serve as your controls. Try to keep each solution level as close to the top of the column as possible. This will help force the liquids through the columns. Continue to collect each column's solution in a separate 150 ml beaker.

4. Note the color of the four columns at two-minute intervals. If there is a color change, record it in your notebook. What might account for any color changes?

5. After 20 to 30 minutes, pour HCl through each of the four columns. Use one of your clean medicine droppers. Remember to add the HCl before the previous solution drops below the top level of the material already in the column. Record any changes you observe. What do you think is happening?

6. Clean your [illegible] area.

QUESTIONS FOR THOUGHT

1. Was there any color change in the sawdust columns? What happened to the peanut skin columns? How could you explain the differences?

2. Imagine that you are the manager of a copper mine. One of your biggest problems is controlling the amount of copper that is flushed out with the drainage water. Which of the agricultural by-products in this Investigation would you use to control the amount of copper in your drainage water?

3. In step #5, you poured HCl through the columns. The acid removed the Cu^{++} ions from the peanut skins and flushed the ions out of the column. In what ways would the recovery of this "waste" copper benefit the mining operation.

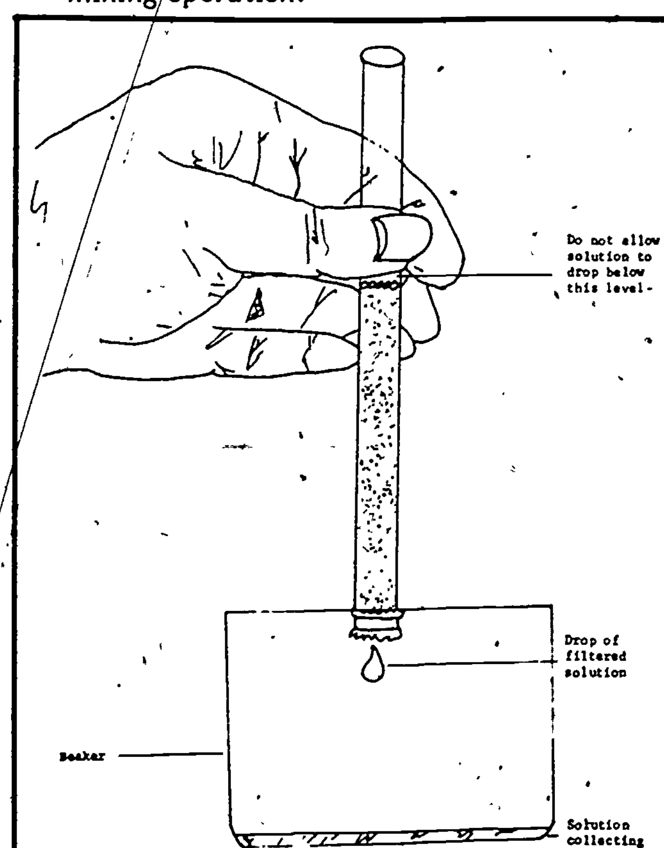

FIG. 2

4. What are some of the advantages gained by using agricultural by-products to help reduce pollutants in our water? Can you think of ways in which both energy and money can be saved? Who will benefit from these savings?

EXTENDING THE INVESTIGATION

1. What other materials could you use as an ion-exchange medium? Are they as effective as peanut skins? Investigate these materials to find out.
2. Design an investigation to determine the effect of the column's inside diameter (I.D.) on the removal of Cu^{++} ions from solution.
3. Investigate the effect of different substrate particle sizes on ion removal from solution. Can you determine the most efficient ratio of particle size to column I.D. for removing ions from solution?
4. Design an investigation to determine the greatest concentration of Cu^{++} ions that can be removed from solution by your ion-exchange column.

SUGGESTED READING

Removal and Recycling of Heavy Metal Ions from Mining and Industrial Waste Streams with Agricultural By-Products, Randall, J. M., Hautala, E., Waiss, A.C., Jr., a paper in the Proceedings of the Fourth Mineral Waste Utilization Symposium, jointly sponsored by the U. S. Bureau of Mines and IIT Research Institute, Held in Chicago, Ill., on May 7-8, 1974. A technical description of the process developed by ARS researchers. Describes other agricultural by-products which have been used to remove divalent metal ions from solution. Recommended for teachers and advanced classes.

INVESTIGATION 2: SCAVENGING HEAVY METALS FROM SOLUTION

Will tannin-containing substances trap and remove monovalent metals from solution? In this Investigation, you will determine if peanut skins will remove sodium, a monovalent metal, from solution.

MATERIALS

2 columns
3 medicine droppers
2 150 ml beakers
1 nine cm^2 section of cotton
2 one-inch strips of cellophane tape
150 ml $CuSO_4$ solution
150 ml NaCl solution
50 ml 0.1N HCl
8 glass or ceramic beads
peanut skins

PRELIMINARY PROCEDURE

1. Prepare two peanut skin columns. Follow steps 1-3 of the Preliminary procedure for Investigation 1.

PROCEDURE

1. Wet the peanut skins in each column with tap water. Use one of your medicine droppers. Collect the water in a 150 ml beaker.
2. Using a clean medicine dropper, add the $CuSO_4$ solution to one of the columns. Do this before the tap water drops below the top level of the skins.
3. Add the NACl solution to the second column with another clean medicine dropper. Be careful that the solution never drops below the top of the peanut skins.

4. At two-minute intervals, note the color of the two columns. If there is a change in the column's color, record it in your notebook.

5. When 20-30 minutes have elapsed, use a clean medicine dropper to pour HCl through the two columns. Record any changes you observe.

6. Clean up your lab area.

QUESTIONS FOR THOUGHT

1. People who process olives often have a problem disposing of used salt solutions. An excessive amount of the salt in their plant's drainage water can pollute the surrounding area. Can tannin-containing by-products help them reduce the amount of waste they produce?

2. Recovering heavy metals from drainage water often requires a lot of energy. Energy is needed to produce the necessary materials and equipment. Energy also is needed to run the machinery. In what ways does the process developed by ARS researchers require less energy?

EXTENDING THE INVESTIGATION

1. In Investigation 2, you observed that peanut skins do not effectively remove nondivalent metallic ions from solution. Sodium (Na) is an example. It would appear that only divalent metallic ions are removed. Design an investigation to determine what other divalent metallic ions can be removed from solution.

2. You have observed that a weak acid, dilute HCl, removes trapped Cu^{++} ions from peanut skins. Design an investigation to determine if an ion-exchange column can be reused after the acid rinse. Will it continue to remove ions from solution?

SUGGESTED READING

<u>Use of Bark to Remove Heavy Metal Ions from Waste Solutions</u>, Randall, J. M., Garrett, V., Bermann, R. L., Waiss, A.C., Jr., Forest Products Journal, Vol. 24, No. 9. Page 83 describes the process whereby the ion exchange medium can be regenerated. Recommended for advanced classes.

<u>Ion Exchange Technology</u>, edited by Nachod, F. G., and Shubert, Jack, Academic Press, Inc., New York, N.Y., 1956. Chapter 10, "Ion Exchange Technology in Water Treatment," gives a thorough overview of removing ions from water. Recommended for teachers and advanced classes.

science study aids

are a series of supplementary investigative materials for use in secondary science classes, grades 7 - 12. The materials are based on federal and private research programs. They are written by secondary science teachers working with scientists at research facilities throughout the country. Before being published, they are tested in the laboratory and in classrooms of cooperating teachers.

Several times during the year, new SSA's are developed. If you want to be notified of their availability, request that your name be added to Wordwork's mailing list. Because we cannot provide enough copies for students, we have designed SSA's so that teachers can easily reproduce the student portion for their classes.

We hope that you find the Science Study Aid Series a valuable supplement to your science curriculum. We welcome you comments on the SSA's that you receive.

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Wordworks
P. O. Box 5106
Richmond, CA 94805