

Selected Summaries of

WATER RESEARCH

Research and Development

Cincinnati Water Research Laboratory, Cincinnati, Ohio

May 1967

ELECTRODIALYSIS IN ADVANCED WASTE TREATMENT

A bench-scale experimental study was made to determine the practicality of partially demineralizing municipal wastewater by electrodialysis. Using filtration alone and filtration followed by carbon adsorption as pretreatments, long-term runs were made with a municipal secondary effluent to determine scaling and fouling effects of the water upon the electrodialysis membranes. During these runs a study was made to determine how high a ratio of product rate to concentrate rate could be obtained without forming scale on the membranes. Some fouling of anion membranes occurred with filtration and carbon adsorption pretreatment; without carbon adsorption, fouling was much worse. Scale formation was not a problem at product to concentrate ratios less than ten. At times much higher ratios were obtained without difficulty. The results of these runs indicated that the total operating cost for a 10-mgd electrodialysis treatment plant might be less than 10¢ per 1,000 gal.

Information is presented on the relative selectivity of the membranes for the common ions in wastewater. Included are data on the long-term runs in which actual wastewater was used, and some data on laboratory prepared solutions. A theoretical discussion of selectivity is included.

Smith, J. D. and Eisenmann, J. L., *Electrodialysis in Advanced Waste Treatment*, FWPCA Publication WP-20-AWTR-18, 1966, 219 pp.

SOIL CHEMICAL CHANGES UNDER SEWAGE SPREADING

Laboratory and field lysimeters were used to investigate the site and nature of soil-pore clogging under sewage spreading. The site of clogging was located by determining with a seepage meter the impedance profile at 0.5-cm depth intervals. Soil samples were analyzed for sulfide, iron, phosphate, total organic matter, polysaccharide, and polyuronide to evaluate possible causative relationships. The infiltration rate loss exhibited three phases: phase I, a slow reduction under aerobic conditions; phase II, a rapid reduction under anaerobic conditions; and phase III, a further gradual decline under anaerobic conditions. The primary site of clogging was the 0- to 1-cm depth of soil. Although sulfide

was an indicator of anaerobic conditions, it was not a primary cause of clogging. Accumulations of the other five measured constituents may contribute to clogging in both phase I and phase II. Organic matter was the only probable clogging agent to decline as the infiltration rate was partially recovered in a rest cycle.

Thomas, R. E., Schwartz, W. A., and Bendixen, T. W., "Soil Chemical Changes and Infiltration Rate Reduction Under Sewage Spreading," *Soil Science Society of America Proceedings*, 30:5, 641-646, September-October 1966.

AUTOMATED ANALYSIS FOR NITRATE

An automated procedure for the simultaneous determinations of nitrate and nitrite in water is presented. Nitrite initially present in the sample is determined by a conventional diazotization-coupling reaction. Nitrate is another portion of sample is quantitatively reduced with hydrazine sulfate to nitrite which is then determined by the same diazotization-coupling reaction. Subtracting the nitrite initially present in the sample from that after reduction yields nitrite equivalent to nitrate initially in the sample. The rate of analysis is 20 samples/hour. Applicable range of the described method is 0.05 to 10 mg/l nitrite or nitrate nitrogen; however, increased sensitivity can be obtained by suitable modifications.

Kamphake, L. J., Hannah, S. A., and Cohen, J. M., "Automated Analysis for Nitrate by Hydrazine Reduction," *Water Research* 1:205-216, 1967.

CARBONACEOUS ANALYZER AS WATER POLLUTION RESEARCH TOOL

The Carbonaceous Analyzer provides the water chemist with a unique tool for the measurement of organic material in water and wastewaters. The principle employed is the direct injection and subsequent evaporation and combustion of a microsample of water in a stream of oxygen in a heated tube, followed by measurement of the carbon dioxide resulting from oxidation of the organic matter present. The instrument is now being used as a

monitor for various processes involved in the renovation of wastewaters and various other research studies connected with water pollution.

Various techniques, operating procedures, and the instrument's sensitivity, accuracy and reproducibility are discussed.

Williams, R. T., "Water Pollution Instrumentation-Analyzer Looks for Organic Carbon," *Instrumentation Technology*, 14, 63-66, February 1967.

OREGON'S COASTAL AND ESTUARINE WATERS - BIBLIOGRAPHY

This bibliography brings together in one volume references to be published and readily accessible unpublished literature pertaining to research and engineering on the natural phenomena of Oregon's coastal and estuarine waters and their adjacent land masses. It is believed that the bibliography will serve future investigators by allowing them to learn of previous research without undertaking extensive literature surveys of their own.

A brief description of the content of each entry is given and notations indicate if data are presented in charts, graphs, or tables.

All located references dealing specifically with the Oregon coast are included. Many investigators, however, dealt with the entire Pacific Coast. In general these references have been included if the paper devotes several paragraphs to phenomena of the Oregon coast. However, those papers which deal only casually with the coastal area are not included.

References included in the bibliography were located by systematically searching the publications listed below:

American Fisheries Society Transactions; Deep Sea Research; Ecology; Ecological Monographs; Journal of Marine Research; Limnology and Oceanography; Monthly Weather Review; Northwest Science; Oregon Fish Commission: Research Briefs, Contributions; Oregon State University Monographs; Theses: Oregon State University, University of Oregon; U.S. Army Corps of Engineers, Senate, and House of Representatives documents pertaining to River and Harbor Projects in Oregon; U.S. Department of Interior, Fish and Wildlife Service Special Scientific Reports; and Weatherwise.

Ditsworth, G. R., *Environmental Factors in Coastal and Estuarine Waters Bibliographic Series-Volume 1 Coast of Oregon*, FWPCA Publication No. WP-20-2, 1966, 62 pp.

WATER SUPPLY WITH REFERENCE TO ALGAE

Algae frequently implicated in causing serious problems in water treatment in Virginia are the flagel-

lates *Dinobryon*, *Glenodinium*, and *Synura*; the diatoms *Asterionella* and *Synedra*; the desmid *Staurastrum*; the blue-green algae *Anabaena* and *Anacystis*; and the green alga *Spirogyra*. More than 250 genera of algae have been reported for the State. Tastes and odors are caused by algae throughout the State, and activated carbon and aeration are used extensively as treatment. Other algal problems in Virginia include filter clogging, attached growths in settling and aeration basins and open-storage reservoirs, and blooms in the many impoundments now being used for storage of raw water. Sixty-five references are cited.

Palmer, C. M., "Biological Aspects of Water Supply and Treatment in Virginia with Particular Reference to Algae", *Virginia Journal of Science*, 18, New Series, No. 1, 6-12, January 1967.

OXYGENATION IN FLOWING STREAMS

It is the intent of this communication to present a method which can be used to separate and measure the components of reaeration in flowing waters. Plastic boxes are used to separate the effects of photosynthesis, diffusion, and respiration on the oxygen balance of a stream's regimen and further separate these parameters according to the benthos and organisms which are free-floating.

Stay, F. S. Jr., Duffer, W. R., DePrater, B. L., and Keeley, J. W. *The Components of Oxygenation in Flowing Streams*, Research Report, Robert S. Kerr Water Research Center, Ada, Oklahoma, 1966.

EXTRACTION OF INSECTICIDES

Three separate extraction procedures for DDT and endrin-contaminated soils were compared for reproducibility, as well as sample size and equipment needed. Two of the methods were developed by the authors, the third came from the Shell Development Manual of Method. The Immerex extractor is recommended because of its reproducibility, rugged equipment and capability of handling large samples.

Teasley, J. I. and Cox, W. S., "Methods for Extracting Insecticides from Soil," *Journal of Agricultural and Food Chemistry*, 14, 519-520, September-October 1966.

ARTIFICIAL RECHARGE OF GROUND WATER

Chemical reactions between recharge water and aquifer water may alter the chemical quality of the water in the zone of reaction, cause fouling of pumping and distribution facilities in pumping wells near

the recharge point, and perhaps lead to permeability reduction in the ground-water aquifer. Existing laboratory and field data suggest, however, that the danger of permeability reduction may not be very great.

Precipitates of calcium and perhaps magnesium carbonate and various iron compounds are thought to be the most likely reaction products. Theoretical analysis suggests that calcium carbonate could be precipitated from mixtures of two waters both initially stable with respect to dissolved calcium carbonate. Dissolved ferrous iron in native ground water could be precipitated as ferric oxide or hydroxide as a result of mixing with oxygen-bearing recharge water. This reaction is a time-dependent one.

Mathematical models that describe the amount of chemical remaining in solution when chemical reaction occurs between recharge and aquifer water can be formulated from the basic dispersion equations if it is assumed that reaction does not alter the dispersion process. The models that have been obtained show the distribution of chemicals in some selected cases.

Reaction between recharge water and aquifer water can be prevented by continuous pretreatment to make recharge water nonreactive. A possible alternative method of preventing reaction in some cases is injecting a buffer-zone of nonreactive water between recharge water and aquifer water.

Warner, D. L. and Doty, L. F., "Chemical Reaction Between Recharge Water and Aquifer Water," *International Assoc. Scientific Hydrology, Symposium of Haifa, Artificial Recharge and Management of Aquifers*, Haifa, Israel, March 19-26, 1967, Publication No. 72, Belgium, 1967, pp. 278-288.

IMPOUNDMENT DESTRATIFICATION

Mechanical pumping was used to break up thermal stratification in four lakes in southern Ohio during the summer of 1964. The lake volumes were 98, 100, 120, and 1260 acre-ft. Each impoundment was thermally and chemically stratified before pumping began. The equipment was a pontoon-mounted, axial-flow pump, 13 acre-ft. per day capacity, driven by a gasoline engine. The pump drew water from the bottom and discharged it at the surface. Profiles of temperature, pH, and concentrations of dissolved oxygen and carbon dioxide were taken before and after pumping. Data presented show that this method was effective in destratifying these lakes. In addition, the data show that water quality was improved by artificial destratification and that an entire impoundment could be mixed with the pump location at a single position. Some data are presented on total work requirements, but these were found to be dependent on the efficiency of the mechanical equipment and the percentage of cold water in the impoundment before pumping.

Irwin, W. H., Symons, J. M., and Robeck, G. G., "Impoundment Destratification by Mechanical Pumping," *Journal of the Sanitary Engineering Division, ASCE*, 92, No. SA6, Proc. Paper 5032, 21-40, December 1966.

SILVEX AND ITS ESTERS

Silvex acid and its propylene glycol butyl ether ester (PGBE ester) can be determined in soil and water by electron capture gas chromatography.

Extraction of the water and soil, using organic solvents, is made by liquid-liquid and percolation, respectively.

Recoveries from fortified water samples range from 65.3 to 94.0% of dosage levels of 1.0 to 1000.0 parts per billion (ppb). The recoveries from fortified soils range from 0 to 115.6% of dosage levels of 10 to 500 ppb.

Silvex acid is esterified with 10% boron trifluoride in methanol before being chromatographed as the methyl ester.

Pope, J. D., Jr., Cox, W. S. III, and Grzenda, A. R., "The Determination of Silvex and its Low-volatile Esters in Water and Muds," *Advances in Chemistry Series*, No. 60, "Organic Pesticides in the Environment," American Chemical Society, Washington, D. C., 1966, pp. 200-206.

ATTACHED STREAM BACTERIA

The growth rate of slime bacteria is limited when the attaching surface becomes completely covered with one layer of cells. At this point, the increase in mass of organisms shifts from logarithmic to linear with respect to time. A second growth-limiting factor occurs when the thickness of the slime mass exceeds the limiting thickness for the diffusion of oxygen. From this point on, the rate of oxygen consumption will remain constant with respect to time. The maximum rate of nutrient removal from the substrate will occur when the slime thickness equals the limiting thickness for the diffusion of oxygen.

Sanders, W. M. III, "The Growth and Development of Attached Stream Bacteria Part I. Theoretical Growth Kinetics of Attached Stream Bacteria," *Water Resources Research*, 3:1, 81-87, 1967.

MARKET PROJECTIONS FOR AWT

Full conventional waste-water treatment will usually be applied before advanced treatment methods are required. To assess the present status of waste-water treatment, the type of treatment now in use and the amount of waste water discharged were determined for the major streams in the country. About 4% of 100-mile river basins now have full secondary treatment. A study was made to determine the percentage of municipal waste water present in surface supplies of 155 cities of populations of 25,000 or more. The maximum was 18%, and median was 3.5%.

Consideration was given in this study to the possibility of logistical imbalances that might occur if

advanced waste treatment were applied to nearly all waste waters. If a distillation-adsorption system were used, less than 6% of the Nation's annual fuel consumption would be used and less than 0.5% of the total power generation would be required. Activated-carbon needs, however, would double. If electrodialysis were applied, 4% of the national power would be required. Membrane production would have to increase several thousandfold. Ultimate disposal of concentrates by injection, incineration, pipelining, etc., would create no imbalances.

Koenig, L., *Studies Relating to Market Projections for Advanced Waste Treatment*, FWPCA Publication No. WP-20-AWTR-17, 1966, 72 pp.

CHLORINATED PESTICIDE RESIDUES

The isolation and identification of "trace" amounts of chlorinated hydrocarbon insecticides in complex substrates is usually difficult. The combination of column and thin-layer chromatography provides an effective technique for the isolation of many of these insecticides for identification by micro-infrared spectroscopy.

In addition to the method, an example of a very complex sample is given to further illustrate the effectiveness of this technique.

Payne, W. R., Jr. and Cox, W. S., "Micro-Infrared Analysis of Dieldrin, Endrin, and Other Chlorinated Pesticide Residues in Complex Substrates," *Journal of the Association of Official Analytical Chemists*, 49:5, 989-995, October 1966.

DETECTING CADMIUM POISONING IN FISH

Subacute exposures of bluegills (*Lepomis macrochirus*) to cadmium sulfate dissolved in water were made at sublethal concentrations for periods up to 90 days. Acute exposures of bluegills and brown bullheads (*Ictalurus nebulosus*) were made at lethal concentrations. In living fish the accumulation of cadmium never exceeded 130 ug/g of gill tissue based on dry weight, but in fish that died of acute cadmium poisoning, the accumulation of cadmium was a minimum of 150 ug/g of gill tissue. The data suggest that acute cadmium poisoning can be detected by measuring cadmium in the gill tissue.

Mount, D. I. and Stephan, C. E., "A Method for Detecting Cadmium Poisoning in Fish," *Journal of Wildlife Management*, 31, 168-172, January 1967.

ACETYLCHOLINESTERASE LEVELS IN FISH

Distressed menhaden collected from the Ashley River, South Carolina, were found to have 46.8% less acetylcholinesterase (AChE) activity in brain

homogenates as compared to menhaden collected from offshore waters. Menhaden and croakers also taken from the Ashley River, but not in a distressed condition, were found to be 16.5 and 35.8% inhibited, respectively. AChE-inhibiting materials were found in three of twelve waste-water samples collected from the vicinity of the Ashley River.

Williams A. K. and Sova, C. R., "Acetylcholinesterase Levels in Brains of Fishes from Polluted Waters," *Bulletin of Environmental Contamination & Toxicology*, 1:5, 198-204, 1966.

TRANSLOCATION OF PESTICIDES

There is increasing evidence that pesticides have contaminated extensive areas of the world not directly treated with pesticides. In many instances, the translocation can be attributed to food or water as the transmission vehicle. Another medium of dispersal of pesticides is the atmosphere. Analyses of rainwater and dust have revealed the presence of chloro-organic substances in all samples examined. Identification of specific pesticides has demonstrated that at least some of the chloro-organic compounds are pesticidal in origin. An analysis of dust, whose distant origin was documented by meteorological evidence, proved that pesticide-laden dust can be transported over great distances via the atmosphere and can be deposited over the land surfaces remote from the point of application.

Cohen, J. M. and Pinkerton, C., "Widespread Translocation of Pesticides by Air Transport and Rainout," *Advances in Chemistry Series*, No. 60, "Organic Pesticides in the Environment," American Chemical Society, Washington, D.C., 1966, pp. 163-176.

COLLOIDS IN WASTE WATER

Electron micrographs of the colloidal fraction in the effluent from an activated sludge waste water-treatment plant show fragments of bacterial cell walls as the dominant material. Viruses, phage, flagella, and other cellular debris are present to a lesser degree. The cell wall fragments appear to have a thickness near 100A. and a width from 500 to 5000 A. (0.05 to 0.5 micron). The fragments are loosely clumped together in preparations which have been freeze-dried at -75° C. but are flattened out and almost invisible in preparations dried near room temperature. Clarification by membrane filtration, or by flocculation with lime or ferric chloride, removes most of the colloidal material of cellular origin.

Dean, R. B., Claesson, S., Gellerstedt, N., and Boman, N., "An Electron Microscope Study of Colloids in Waste Water," *Environmental Science & Technology*, 1, 147-150, February 1967.

LACTATE DEHYDROGENASE ACTIVITY

The effect of chlorinated hydrocarbon insecticides upon rabbit-muscle lactate dehydrogenase was determined by both the direct determination of diphosphopyridine nucleotide reduction and a tetrazolium salt reduction method. Comparison of the two assay procedures revealed that the pronounced stimulation of lactate dehydrogenase LDH activity was noted with the tetrazolium salt method but could not be detected with a direct photometric determination method. Incubation of lactate dehydrogenase with DDT or heptachlor prior to the addition of either diphosphopyridine nucleotide or substrate resulted in a complete inhibition of enzyme activity. The inclusion of either diphosphopyridine nucleotide or substrate in the prior incubation mixtures afforded no protection to the enzyme.

Sova, C. R., "Lactate Dehydrogenase Activity: Effect in vitro of Some Pesticidal Chemicals," *Science*, 154, No. 3757, 1661-1662, December 30, 1966.

DIFFUSION COEFFICIENTS OF TIDAL WATERS - TABULATION

Diffusion coefficients presented in this tabulation have been computed for a velocity range from 0.01 knots to 5.00 knots at an interval of 0.01 knot. The equations employed in these computations were derived from the four-thirds law and the random process analogy equations. A difference function and mean value function are also tabulated.

Bunce, R. E., *A Discussion and Tabulation of Diffusion Coefficients for Tidal Waters Computed as a Function of Velocity*, CB-SRBP Technical Paper No. 9, FWPCA, 1967.

DIFFUSION COEFFICIENTS OF TIDAL WATERS

Both the four-thirds law and random process analogy formulas yield effective diffusion coefficients in the proper order of magnitude for the brackish portion of the Potomac Estuary. Either of these formulas should provide useful approximations for other estuaries where good information on salinity variations is not readily available. These formulas should be used with caution in the fresh-water portion of tidal rivers, in view of the possible important influence of salinity gradient induced density currents on diffusion. Prototype tracer studies in such locations appear to be necessary to provide reliable estimates of the appropriate diffusion coefficient.

Hetling, L. J. and O'Connell, R. L., *Estimating Diffusion Characteristics of Tidal Waters*, CB-SRBP Technical Paper No. 4, FWPCA, 1967.

BENTHAL OXYGEN DEMAND MEASUREMENT SYSTEM

In attempting to describe the oxygen balance of natural waters, it is essential that all significant sources and sinks of oxygen be considered. Oxygen uptake by the bottom muds found in rivers, lakes, and estuaries is such a sink and, in some situations, a most significant one. The magnitude, however, is usually difficult to evaluate with the desired degree of confidence. Most methods of evaluation in current use require removal of the muds from their natural environment for oxygen uptake measurements in the laboratory. However, it is extremely difficult to reconstruct the natural layering of solids in a laboratory flask, which could appear to be a necessary condition for obtaining realistic results. In addition, the interstitial water in bottom sludges is likely to contain soluble constituents having a high oxygen demand, and these materials may be lost or diluted in collecting the sludge sample. The quality of water overlying the sludges may also influence oxygen uptake rates in the natural environment. For these reasons a benthic respirometer capable of measuring the oxygen uptake rates of bottom muds in-situ is highly desirable. Such a device has been developed and is described in this paper.

O'Connell, R. L. and Weeks, J. D., *An In-Situ Benthic Respirometer*, CB-SRBP Technical Paper No. 6, FWPCA, 1967.

ACTIVATED CARBON TREATMENT

Columns of granular activated carbon remove essentially all the organic content of biologically oxidized effluents from secondary treatment plants if colloidal material is removed first by clarification. Less than 1 mg/l of organic matter as C may remain. Approximately half the turbidity is removed by 11 ft (3.35 m) of 10/30-mesh carbon. Powdered carbon can reduce the organic content of clarified effluents to less than 2 mg/l. The ability of a powdered carbon to remove total organic matter is not related to the surface area or phenol number.

Bishop, D. F., et al., "Studies on Activated Carbon Treatment," *Journal Water Pollution Control Federation*, 39, 188-203, February 1967.

BIODEGRADABILITY TEST

New wastes continually appearing create a need for knowledge about their biodegradability and whether or not they can be assimilated efficiently by existing waste-water treatment plants. There is a lack of a universally accepted method for gauging biodegradability of various compounds. The Cincinnati Water Research Laboratory (Robert A. Taft

Sanitary Engineering Center) of the Federal Water Pollution Control Administration has developed a test thought to be reliable for organic compounds. In addition to determining if a compound is degraded during the test period it also provides an indication of the time required for adaptation.

Bunch, R. L. and Chambers, C. W., "A Biodegradability Test for Organic Compounds," *Journal Water Pollution Control Federation*, 39, 181-187, February 1967.

INFRARED IDENTIFICATION

A method for identifying chlorinated insecticide residues in fish tissue is described. Whereas electron capture gas chromatography guides the isolation

procedures and provides tentative identification and quantitative estimation, positive identification is made on the basis of the infrared spectrum of isolated insecticides. The procedure consists of hexane extraction of fish tissue, partition between hexane and acetonitrile, column adsorption and thin layer chromatography cleanup, and micro-infrared analysis in a potassium bromide disc. The practical limit of sensitivity needed to provide excellent infrared spectra of a number of the more common chlorinated insecticides is about 1 ppm in the fish tissue; concentrations as low as 0.25 ppm have given informative infrared spectra.

Boyle, H. W., Burttschell, R. H., and Rosen, A. A., "Infrared Identification of Chlorinated Insecticides in Tissues of Poisoned Fish," *Advances in Chemistry Series*, No. 60, "Organic Pesticides in the Environment," American Chemical Society, Washington, D. C., 1966, pp. 207-218.

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