

LITERATURE CITED

- Eltekov, Yu. A., and V. V. Khopina, "Effect of Preadsorbed Water on the Adsorption of Toluene by NaX Zeolite from n-Heptane Solutions," *Proc. Third Intern. Conf. on Molecular Sieves*, p. 304, J. B. Uytterhoeven, (ed.), Leuven Univ. Press (1973).
- Hayhurst, D. T., "The Effect of NaY Zeolite Pretreatment on Sorption Equilibria," M.S. thesis, M.I.T., Cambridge, Mass. (1973).
- Satterfield, C. N., and C. S. Cheng, "Liquid Sorption Equilibria of Selected Binary Hydrocarbon Systems in Type Y Zeolites," *AIChE J.*, **18**, 720 (1972a).
- , "Liquid Counterdiffusion of Selected Aromatic and Naphthenic Hydrocarbons in Type Y Zeolites," *ibid.*, 724 (1972b).
- Manuscript received June 14, 1974; revision received and accepted July 2, 1974.

Equilibrium Data for Various Compounds between Water and Mud

E. J. GRESKOVICH

Department of Chemical Engineering
Bucknell University, Lewisburg, Pennsylvania 17837

A great deal of time and money has been/is being spent in the area of water pollution control in search of an economical total recycle system for pollutants. In most of these real life situations, a specific undesirable substance has been discharged into the water for extended periods of time rendering the stream, river, etc. polluted. Once the health hazard is discovered and pollutant no longer discharged, the water is proclaimed clean and healthy. However, just because the pollutant faucet was turned off, the health state of the stream bed is not so quickly advanced as the water itself. This certainly is the case today, for example, with mercury-methyl mercury effects. The purpose of this study is to evaluate the polluted stream bed by carefully studying the equilibria of various pollutants such as phenols, sulfates, and detergents between the water and soils comprising the muds, especially in the concentration range 5 to 10,000 ppm. The results from this study can be used not only to project how long it would take for a polluted stream bed to be revived but also to dramatize the total effect of water pollution to prospective polluters.

BACKGROUND

Once the flow of an undesirable pollutant is cut-off to a polluted body of water a natural period for both stream and bed reclamation is required. The water itself is cleansed much more rapidly than the bed no matter if the water is in the form of a flowing stream, river, lake, pond, etc. Therefore, the major objective of our work was to determine and consequently be able to predict the time lapse between the point at which the pollutant faucet was turned off and the point where the stream bed is healthy enough for human and animal recreation, sport, and various other uses. The term *healthy* refers to standards and specifications set by local, state, and Federal agencies for chemical and biological activity within the water. In order to evaluate this diffusion process, the degree of adsorption of pollutants in muds must first be determined. For the naturally flowing stream, the extraction of pollutants from a stream bed by rejuvenated water not only depends on local concentrations but also on the flow characteristics of the bed, that is, slope of ground rocks, bends, etc.

RELATED STUDIES

The number of articles written on the subject of water pollution has skyrocketed in the past few years. Although these articles describe current research in this area, few articles have appeared concerning a systematic method for evaluating stream bed reclamation. A most recent review of the 1969 literature published in the Water Pollution Control Federation Journal (1970) and a summary of advanced wastewater treatment processes being developed in the U.S. by Stephan and Schaffer (1970) support this statement. The studies that have been reported or funded by Federal agencies are summarized in the Water Resources Research Catalog and the Water Quality Resources Abstracts (1970). It is unfortunate that most of these studies involve the use of benthos and fishes to evaluate stream bed conditions while rarely (if at all) discussing basic chemical/engineering criteria that might be more general in nature to the overall rejuvenation process.

RESULTS AND DISCUSSION

In order to evaluate the rejuvenation of a polluted stream bed, the affinity of muds for various chemical species must be studied. This affinity is measured by contacting the pollutant species with soils in aqueous solutions until equilibrium is reached. These data are appropriately called *equilibrium* data. The first step in the collection of equilibrium data was to determine the degree of adsorption of various pollutants on muds to see if the process is purely physical or, if not, to what degree chemical interaction exists. Since the range of pollution in a typical stream might vary between high and low concentrations, two systems were chosen to cover as extended a range as possible. In the acid-mine pollution problem areas, waters are contaminated with the sulfate ion in forms such as sulfuric acid and ferric sulfate. Therefore, our initial equilibrium studies involved the sulfate system over a concentration range of 50 to 10,000 ppm by weight. Various aqueous solutions were prepared and contacted with a typical Central Pennsylvania soil until equilibrium was established. The soil consisted of particle sizes less than 0.198 mm dry-sieved with 40% less than 0.006 mm determined by

hydrometer studies. This soil can be appropriately called a clayey-silt since all particle sizes fell within this range.

The analytical procedure involved precipitating the sulfate with barium chloride at room temperature and determining concentrations via colorimetry according to Fisher (1925). In all the studies reported here, the solution-to-soil ratio was approximately 2 with the adsorbate initially placed in the water. The soil-water mixture was stirred for approximately one hour after which samples of the settled phases were analyzed. Additional stirring did not significantly change these results. The equilibrium data are reported as equilibrium concentration of sulfate in the water versus the concentration of sulfate in the soil slurry (mud) on a soil-free basis, Figure 1. It can be noted that the soil did exhibit a slight adsorptive-absorptive capacity for sulfate between approximately 150 and 1000 ppm. However, above and below this range there appears to be little, if any, adsorption. Past experience based on Gardner (1972) with sulfates in waters leads to the same conclusion.

The second specie studied was phenol. The equilibrium data were collected in a similar fashion as those for the sulfate system. Various aqueous solutions containing 5 to 100 ppm phenol were contacted with soil, and the equilibrium concentrations were measured colorimetrically. The equilibrium data are reported on a soil-free basis in Figure 2. Little or no adsorption of phenol on the soil was noted for the concentration range evaluated in these studies.

The third specie evaluated in our laboratories was the sodium salt of a synthetic linear alkylate sulfonate (LAS). A colorimetric analytical procedure was also used to measure concentrations. Limited results indicate that higher concentrations of LAS adsorbed on the soil than sulfate or phenol; however, we feel that there exist a strong interference from the soluble organic salts in the soil on the colorimetric procedure used. Results from two runs indicate approximately 4 to 7 times as much LAS in the mud phase as in the water phase (4.5 ppm vs. 15.6 ppm; 23.5 ppm vs. 170 ppm) confirming various prior literature data.

CONCLUSIONS

The equilibrium data or perhaps the lack of strong adsorption for sulfate and phenols between water and the Central Pennsylvania clayey-silt indicate that the rejuvena-

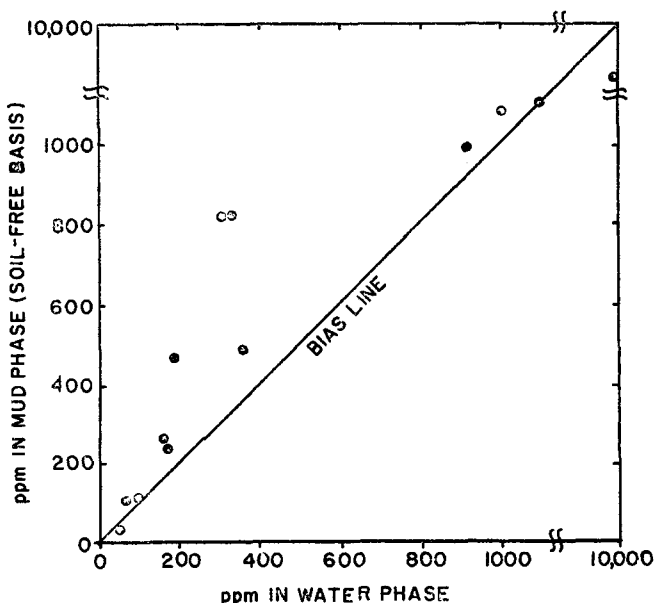


Fig. 1. Equilibrium data for sodium sulfate between the soil and water at 77°F.

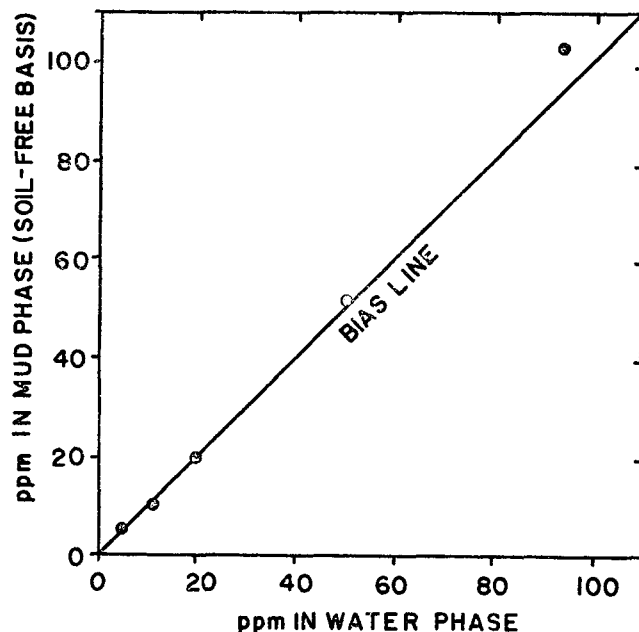


Fig. 2. Equilibrium data for phenol between the soil and water at 77°F.

tion process in the turbulent core of a stream will be fast. Even for detergents, which might be more highly adsorbed on muds than phenols or sulfates, the rejuvenation process would be relatively fast. It should be noted that the chemical makeup of muds are extremely important with regard to the adsorption of pollutants. The soil that was used in this study can best be called *typical*; however, it would be nearsighted to assume the equilibrium data presented in Figures 1 and 2 are applicable to all soils. If the limited results presented can be used to make a generalization, it can be stated that the rate of rejuvenation of a polluted stream bed will depend on the desorption of the pollutants from the muds below the slow-moving or stagnant waters, much more so than in the turbulent core. Hence, the controlling factor will be the diffusivities of the chemical pollutants through the muds. In this case, the equilibrium data reported here are a necessity in modeling the transfer process.

ACKNOWLEDGMENT

This work is being supported by the National Science Foundation Grant GK-32871. Computations were performed at the Bucknell University Computing Center. Additionally, thanks are to Messers Harold Black, Tom Pecsényak, and Dave Zeile for carrying out the experimental studies and computations.

LITERATURE CITED

- Fisher, R. J., "Turbidimetry and Nephelometry," in *Standard Methods of Chemical Analysis* (1925).
- Gardner, R. A., Private communication, Bucknell University, Lewisburg, Pa. (1972).
- J. Water Pollut. Control Fed., "A Review of the Literature on Wastewater and Water Pollution Control," 42, 861 (1970).
- Stephen, O. G., and R. B. Schaffer, "Wastewater Treatment and Renovation Status of Process Development," *J. Water Pollut. Control Fed.*, 42, 399 (1970).
- Water Resources Research Catalog, 6, No. 1 Item 6.0565 (1970).
- , *ibid.*, index—part 2 pp 2-559 (1970).
- Water Quality Resources Abstracts, 3 (18), 39 (1970).

Manuscript received December 4, 1973; revision received May 14 and accepted May 15, 1974.