

Methods for Removing Detergents from Waste Waters

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Abstract

A number of processes have been investigated or are being investigated for removal of alkylbenzene sulfonate (ABS) from waste waters. These can be divided into processes applicable to launderette wastes and processes applicable to municipal waste water although there is overlap. Launderette waste treating methods include, flocculation, flotation, adsorption on activated carbon or ion exchange materials and filtration. In municipal waste water treatment any ABS removal method must be very inexpensive. Two methods that have been used to remove most of the residual ABS after conventional sewage treatment are foaming and adding of cationic detergents. Both methods are capable of removing ABS down to levels of 0.5 ppm or less. A number of other treatment methods that will remove organics, including ABS, from municipal wastes are being studied. Their costs are, in general, too high to make them applicable for ABS removal alone. Processes under study include adsorption, chemical oxidation, ion exchange, electrochemical degradation and even distillation.

Introduction

THE USE OF DIFFICULTLY degradable or "hard" synthetic detergents, especially the anionic type, has created a number of water quality problems. The most obvious, as far as the public is concerned, is the aesthetic problem of foam formation on waterways and in ground water as a result of waste-water pollution. Foaming is also a problem at many municipal waste-water treatment plants.

Until rather recently there was little positive evidence that more readily degradable detergent materials would be developed. The chief solution to the problem of detergent foaming appeared to be treatment processes that remove detergents from waste waters. A number of process development studies were undertaken in this area. It now appears, however, that "softer" or more degradable detergents will be available and will be widely used in this country. While this will no doubt greatly alleviate the detergent pollution problem, most probably it will not solve it completely. Detergent removal methods may very likely still be necessary at some locations.

Detergent Pollution in Waste Water

Two waste water sources that have been sufficiently important contributors to detergent pollution for removal studies to have been undertaken are municipal waste treatment plants and launderettes. On a nationwide basis, the volume of launderette waste is insignificant in comparison to the volume of municipal waste, but there are locations such as Suffolk County, N.Y., where launderette waste causes intensive local pollution problems by mixing with the ground water used as the source of drinking water.

The ABS concn (as determined by the methylene blue analysis) of municipal waste water is often ca. 5 mg/liter and is seldom much above 10 mg/liter.

Launderette wastes, on the other hand, often have ABS concn of 50 mg/liter and several hundred mg/liter is not uncommon. In addition, launderette wastes contain concn of phosphate and of suspended matter that are as high as several hundred mg/liter. Because of differences in the over-all composition and the volume of the two waters, different treatment methods have been suggested for each.

Industrial wastes are another source of detergent pollution, especially nonionics. These wastes are extremely variable in nature. In many cases their behavior with respect to detergent removal is similar to that of municipal waste water.

Methods for Treating Launderette Wastes

A number of private companies have designed launderette waste-treatment equipment (1). Because it is desirable for this equipment to remove phosphate and suspended matter in addition to ABS, a number of operations usually are required. These include flocculation, adsorption or absorption, ion exchange, filtration and flotation. An excellent discussion of a number of systems is given by Flynn and Andres (2). The most efficient of these for ABS removal is capable of reducing the ABS concn to less than 3 mg/liter.

The total cost of treatment including amortization of equipment, operating costs and waste concn or residue disposal is likely to be somewhat more than \$1.00/1000 gal. In some cases, chemical costs alone are more than \$1.00/1000 gal. It might appear that treatment for only ABS removal would be considerably cheaper. This is not necessarily true, however, because processes would still be required that would allow the waste residue containing the removed ABS to be concd to a small volume. Small-scale processes that accomplish this are costly.

Methods of Treating Municipal Waste Water for ABS Removal

Since the amt of ABS in completely treated municipal waste water is often less than 1% of the total contaminants and less than 10% of the organic contaminants, any removal method for ABS alone must be very inexpensive in contrast to launderette waste treatment. Costs of a few cents or less/thousand gal are all that might be tolerated. Only a few methods at present can be considered. These include addition of cationic detergents, biodegradation of the ABS on soils and foaming.

The use of cationic detergents for removal of ABS has been studied by Samples (3). Materials such as an alkyl dimethyl benzyl ammonium chloride react with ABS to produce a precipitate. Removal of the precipitate by alum flocculation followed by filtration or even by filtration alone results in ABS concn of ca. 1 mg/liter or less. For the particular secondary effluent studied it was found that, in addition to ABS, one-half or more of the total organic pollution as measured by chemical oxygen demand (COD) also was removed.

Based upon present prices, the cost of cationic detergent for this process is ca. \$0.006/1000 gal for each mg of ABS/liter of waste water. For most municipal wastes, this represents a min chemical cost of ca.

TABLE I
Foaming of Secondary Effluent

Volume of air/mass of ABS in feed (liter/mg)	ABS concn of product water (mg/liter)
1.0	0.57
2.0	0.36
3.0	0.29

\$0.03/1000 gal. The total operating cost of the treatment method apparently would be barely within the range of acceptability. The price of the cationic detergent might decrease significantly, however, if the material were widely used. The process would then be more attractive.

The use of soils to remove organics from waste water has been known and practiced for some time. Robeck et al. (4), recently made a detailed lysimeter study of the ability of sandy soils to remove ABS and other organic contaminants from domestic waste water. By applying the water intermittently so as to maintain aerobic conditions in the soil, they found that ABS could be biologically degraded to a 0.5 mg/liter level even when the ABS concn had been artificially increased to levels higher than usually found in waste effluents. Radioactive tracer tests with S^{35} tagged ABS indicated that much of the ABS degraded far enough to produce sulfate ion. Most of the total organic material fed was actually removed. Although this treatment method is technically promising, it has the disadvantage of requiring large infiltration areas. Based on the lysimeter surface area used, the rate of application was, at most, 3.5 gpd/ft². At this rate ca. 600 level acres of suitable soil might be required for the waste water of a city of 500,000 population.

The cost of ABS removal by spreading the waste water on soil would certainly depend upon the cost of land. In addition, there would be cost for bed preparation and maintenance of the spreading and possibly any underdrain system required. The total cost is difficult to estimate at present, but might be reasonable in some areas.

Foaming of municipal waste water for ABS removal has been investigated and is presently being used in several treatment plants as a supplementary process after secondary or biological treatment. The success of the method results from adsorption of surfactants to the water-air interface. When bubbles of air are blown through the water a large amt of interface is produced, which is conveniently removed as foam. Table I shows average results from continuous laboratory runs in which secondary effluent samples from one treatment plant were used (5). Product water with the ABS concn almost as low has been obtained with pilot scale equipment at a different waste treatment plant. Organics in addition to ABS are removed from both primary and secondary effluent. Under proper conditions, 40% of the amt in the feed can be removed.

Total operating costs are estimated to be \$0.02/1000 gal, or less, for plants treating as little as 1 mgd. The disposal of ABS-rich collapsed foam could cause added expense. It may, however, be possible to recycle this coned solution back through the biological treatment step to give a longer residence time for the resistant types of ABS molecules. This foam recycle scheme has been found successful on a laboratory scale (6).

Other Processes Capable of Removing ABS from Municipal Waste

Other processes for more complete removal of contaminants from waste water than is possible with the

present conventional treatment methods are under study by the Advanced Waste Treatment Research Program of the U.S. Public Health Service. Although most of these processes will remove ABS, the gross removal of organics, inorganics or both, is their primary function. Those that remove ABS include adsorption on activated carbon, chemical oxidation, distillation, reverse osmosis and solvent extraction with secondary amines. These treatment methods are, in general, too expensive to be considered for ABS removal alone.

Adsorption, which is very promising for removal of many organics, can be carried out with granular or powdered carbon. Ca. 0.75 lb of granular carbon/1000 gal is required. The exhausted carbon must be reactivated for economical operation. The total cost for treatment of secondary effluent to produce water having a maximum ABS concn of 0.5 mg/liter might be less than \$0.10/1000 gal for plants treating 10 mgd.

Chemical oxidation with hydrogen peroxide or ozone can also be employed for removal of organic materials. In the process, ABS appears to be oxidized preferentially; concn of less than 0.5 mg/liter are achieved. The cost of the process appears to be greater than the cost of carbon adsorption, however.

Distillation removes nearly all the contaminants from waste water. With care to prevent foam carry-over, ABS can be reduced to negligible levels at costs probably comparable with those for sea water conversion.

Reverse osmosis is a relatively new treatment method that effects removals comparable to those of distillation. In the process, water is freed from impurities by being forced through a special type of membrane under high pressure. For waste-water treatment, preliminary results suggest that operating costs may be competitive with those for distillation.

Like distillation and reverse osmosis, the solvent extraction process referred to here is capable of separating both organic and inorganic materials from waste water. Water molecules form a loose complex with certain amines. By raising the temp of the complex, the water can be separated and recovered. Purity of the product water is not as high as in distillation. ABS removal down to ca. 1 mg/liter is all that is usually obtained. Operating costs can not yet be predicted with any degree of accuracy.

Future of Advanced Waste Treatment Processes After Use of Degradable Detergents Becomes Widespread

Municipal waste water that has been given conventional primary and secondary treatment contains an average of ca. 300 mg/liter more dissolved organic and inorganic material than does the water supplied to the city. The waste water from a laundrette contains, besides ABS and certain other materials, large amt of various forms of sodium phosphate. In addition, both waste waters contain suspended matter. Obviously this total amount of material added during use, not just the ABS, would have to be removed if man-made pollution were to be eliminated. In a closed system with continued reuse of the water for an indefinite period, complete removal of the contaminants added during each use would be necessary. Even with the degree of reuse presently practiced, removal of at least a fraction of the added contaminants is desirable. Any process, therefore, that removes a significant amt of organic or inorganic material could be of value now and should be of greater value in the future when increased reuse will be necessary.

All the processes discussed here remove significant amount of impurities other than ABS. They might, therefore, be used whether or not ABS were present. Most of the processes would, in fact, operate more efficiently if ABS were not present. Foaming is a possible exception. The synergistic action between small amount of ABS and other organic materials in waste water is, in many instances, very effective in producing stable foam. How strong the foaming tendency of waste water might be in the absence of the presently used ABS is not well known. A reduction in foamability would certainly be expected. This might be overcome partly by changes in the design of foaming equipment. It might also be possible to add small amount of foaming agents to produce a more stable foam.

Products and environmental patterns change with time. We cannot expect to tailor waste treatment for each new problem compound that comes along. Water reuse considerations will demand that only a very

low level of many contaminants be allowed to remain in water. We need an arsenal of highly efficient treatment methods to cope with all types of contaminants. There is no question that our technology can develop such methods. We must provide the treatment means if the clean water needed and demanded by the public is to be available.

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Performance of Straight-Chain Alkylbenzene Sulfonates (LAS) in Heavy-Duty Detergents

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Abstract

The foamability (dishwashing and washing machine) and detergency of LAS in heavy-duty detergents is directly compared with polypropylene ABS (PPABS) at various mol wt, conen, water hardnesses and temp. In every case a peak in performance is obtained in the C₁₁ to C₁₇ side chain range. The peak is shifted to lower mol wt as water hardness is increased, especially at low detergent conen. LAS opt performance is generally equal to PPABS, except in dishwashing foam in soft water. The LAS peaks, however, are shifted to ca. one carbon lower mol wt than the PPABS. Therefore, best over-all performance is obtained for LAS whose average mol wt corresponds to a 12.5 carbon side chain, whereas PPABS is best with an average 13.5 carbon side chain.

Dishwashing foamability is markedly different for the different isomers contained in LAS. When the phenyl group is attached to the middle of the alkyl chain, surprisingly high results are obtained. This dishwashing difference is great enough to be noticeable when the isomer distribution changes in whole products made using different alkylation catalysts. Detergency and washing machine foam are not affected enough to see differences between whole alkylates.

LAS solubility is greater than PPABS and is influenced by isomer distribution.

Introduction

THERE HAVE BEEN many reports on various aspects of the performance of detergents containing tetrapropylene ABS since it has been the most widely used synthetic anionic surfactant for many years. In the last few years the performance of some of the commercial polypropylene alkylates has been improved by

raising the average mol wt to equal about a 13.5 carbon side chain (1).

There have not been many reports on performance of LAS. Gray et al. (2,3) prepared several pure compounds and obtained wetting time, detergency and foam data. Baumgartner (4) prepared and tested a number of dodecylbenzene isomers. Koelbel and coworkers (5) reviewed the literature on the effect of structure on properties of a number of straight-chain and branched-chain alkylbenzene sulfonates and other anionics. Most of the data are on physical properties, such as surface tension and critical micelle concentration (CMC). Recently, Stanberry et al. (6) presented some data on performance of LAS vs. mol wt, but the LAS source was not specified and no direct comparison with polypropylene products was given.

Therefore, the question of how LAS performs in heavy-duty formulas in "practical-type" tests in direct comparison with PPABS has not previously been answered. The present report comes to bear on this question and on whether there is an opportunity to tailor straight-chain alkylbenzene sulfonates to obtain the superior properties of the higher mol wt polypropylene products. The dishwashing foam test is of particular interest because it was found to be a sensitive test for showing the improvement as mol wt was increased in the polypropylene case.

Unfortunately, polypropylene alkylbenzene sulfonate has become generally known simply as "ABS." Therefore, to avoid any confusion between materials and to emphasize the considerable difference between polypropylene and straight-chain products, we will refer to the latter as LAS, standing for linear alkylate sulfonate. The polypropylene product will be called PPABS.

Experimental

Preparation of Materials. The alkylbenzenes used in this work originated from several sources as summarized in Table I. They were batch sulfonated with

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