WASTEWATER

Emphasis Shifting to Toxicity Reduction

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Granular activated carbon is a proven method of removing organic materials that cause toxicity in a wastewater discharge.

By Steven L. Butterworth and John D. Sember

Under the Clean Water Act the U.S. Environmental Protection Agency (EPA) established the National Pollutant Discharge Elimination System (NPDES) permitting program as a means of controlling the discharge of waste water to national surface water supplies. The NPDES program is used within the CWA to help prevent the discharge of "toxic materials in toxic amounts" to the nation's waterways.

Historically, NPDES permits have contained discharge water quality limits based on specific parameters such as pH, chemical oxygen demand (COD), biological oxygen demand (BOD), and the priority pollutants. These parameters can be measured using standard laboratory equipment and procedures. Protocols and quality assurance procedures have long been established for quantifying these parameters. Thus, compliance or non-compliance was established easily by performing a chemical analysis of the wastewater and comparing the results to the discharge limits.

Permit writers, consulting-engineering firms, and dischargers have become familiar with how the chemical-specific permitting system works and know what to expect. Engineering practices have developed around this chemical-specific approach to the point that specific technologies can be recommended to bring a facility into compliance.

However, discharge limits based strictly on specific chemicals do not ensure that a discharge is non-toxic to the aquatic life in a receiving body. Many materials not in the priority pollutant list can produce toxic effects in a receiving water. Therefore, newer test methods have been developed to assess the toxicity of the components of wastewater in a receiving system. The methods fall into a broad category known as toxicity testing, or biomonitoring.

Testing to ensure a discharge is free from toxicity is accomplished by exposing various organisms to the wastewater and monitoring the response of the organisms. Since this type of test is usually much more sensitive than conventional analytical methods, wastewater treatment techniques have been challenged to demonstrate superior performance.

What is toxicity?

A working definition of toxicity is any adverse biological response. Toxicity for water quality monitoring purposes is categorized as either acute or chronic in nature. Acute toxicity means the adverse response measured is the death of an organism. The averse effect reported for chronic toxicity can be reduced growth, reduced reproduction, immobility or inhibition of any other normal growth function.

Toxicity testing increasingly is being introduced to NPDES permits as a method of establishing compliance with the CWA. The purpose of toxicity testing is to ensure that the wastewater being discharged does not introduce contaminants that adversely impact the receiving stream.

From a regulatory viewpoint, the coupling of chemical-specific limitations and toxicity-based limitations provides a strong combination for achieving the goal of no toxic discharges in toxic amounts. The addition of biomonitoring provides a direct measure of the potential biological effect a discharge may have on a receiving stream. From an engineering or permit writer's standpoint, however, toxicity measurement and elimination are relatively new areas containing more uncertainty than is customary with chemical specific limits.

Toxicity as a permit criteria

Toxicity testing could be required when complex wastewater matrices are involved or a known toxic chemical is present in a discharge. The type of toxicity test required of a discharger, acute or chronic, is generally a function of the discharge volume and the dilution is provided by the receiving body. If a high level of dilution is provided by the receiving body, an acute test most likely will be stipulated. As the dilution available in the receiving body decreases, chronic tests may become the preferred biomonitoring procedure. If a known toxicant is present, the test again may be based on flow and dilution or a specific test may be required automatically for certain toxicants.

When a discharger applies for a new permit, the permitting authority may require the permittee to screen its discharge for toxicity on a pass/fail basis. Once screening in complete, the permitting authority will decide weather a toxicity limit should become part of a permit or weather more testing in needed. In those cases where a discharge clearly seen as toxic, the discharger will be required to complete a Toxicity Reduction Evaluation (TRE) to bring the effluent into compliance with permit limits.

If a discharger currently is meeting an acute toxicity criterion in a permit, the permitting authority may change the criterion to include a more sensitive test organism or a more sensitive toxicity test (such as chronic tests) when the permit is renewed. Unfortunately, a good track record with acute testing under an old permit does not guarantee the same success with the new permit under these new conditions. In these cases, a TRE or treatibility-based toxicity reduction study may be necessary.

Once a discharger has determined it may have difficulty complying with a toxicity limit, a TRE is initiated (formally or informally). The goal of the TRE is to determine the source or cause of the wastewater toxicity and a means of controlling that toxicity. Many times it is impossible or impractical to identify a specific chemical or chemicals as causative agents in complex wastewaters; however, in those cases where changes in operating practices, raw materials, or housekeeping procedures do not resolve the toxicity problem, a properly conducted TRE will identify the chemical class of the contaminant(s) responsible for toxicity in an effluent. The toxicant's chemical class (metallic, neutral organic, oxidant, etc.) provides essential information from which to design treatability studies.

If the TRE indicates that organic compounds may be contributing to the toxicity detected, physical adsorption on granular activated carbon (GAC) is one potential treatment technology. Where specific chemicals or classes of chemicals can be identified as materials of concern, GAC has been shown to effectively remove phenolics, polyaromatic hydrocarbons (PHAs), volatile organic compounds (VOCs), synthetic organic chemicals (SOCs), certain low-level metals, and BTEX. In addition, oxidants, such as chlorine (HOCl), hydrogen peroxide (H_2O_2) and ozone (O_3) are eliminated by GAC.

Granular activated carbon is a highly porous material possessing an extensive internal surface area. The pore structure is composed of a disordered array of graphite crystallites, or plates, that are produced via a thermal activation process. It is the crystallites that give GAC its adsorptive power for many organic materials.

GAC removes contaminants from solutions in wastewaters by the process of adsorption. The adsorption phenomenon results from intermolecular forces called London Dispersion Forces. These forces cause the proper orientation and alignment between adsorbate molecules and the crystallites so an attraction and retention of the adsorbate can result.

Evaluating GAC for an application

Evaluating GAC for toxicity reduction requires the use of proper techniques to generate meaningful and accurate data. The first method that can be used to screen GAC is isotherm testing. Here, specific weights of pulverized GAC are added to specific volumes of effluent. The mixture is agitated for an extended amount of time (at least 24 hours) to allow the contaminants in a solution to achieve their equilibrium loading of the carbon. The residuals in the solution are measured and a loading on the GAC is determined by mass balance or toxicity balance. From this data, the potential performance of GAC can be estimated. If this performance estimate is within reason, a dynamic test is warranted.

The second and subsequent method of screening GAC is the dynamic test. The scale of this test should be determined by the volumes of water needed for toxicity testing and the results from the isotherm work. If the isotherm indicates the contaminant(s) of concern is extremely well adsorbed, a laboratory-scale pilot test or a large-scale pilot test may be used to develop design data.

For the laboratory-scale test, equipment composed of toxicologically inert material is needed. The columns containing the GAC must have diameters at least 15 to 20 times that of the mean particle diameter of the GAC being tested, and the GAC bed depth/system flow rate must be such that the toxicity mass transfer zone is contained in the GAC bed. The advantage offered by this scale of testing is that work can be conducted off-site, if the toxicity has shown to be persistent, or on-site if the toxicity is non-persistent. (Persistent toxicity does not change significantly over time, while non-persistent toxicity changes over time.) Results from this type of study can provide design parameters for a full-scale system or they can be used to design a large-scale, pilot-scale study for developing system design information.

The large-scale pilot test uses small commercial or semi-commercial equipment. A study of this size will address issues that may have developed in a smaller scale test, such as the impact of solids, fluctuations in wastewater quality over time, upset episodes, etc. The test typically will run for a longer time than the laboratory test and so will generate the data needed to design a full-scale system.

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GAC can be tested quickly to determine its applicability to a toxicity problem.

Here's How it Works

An oil refinery had a acute toxicity limit introduced to its NPDES permit that required 100 percent survival of stickelback fish in the plant's wastewater discharge. A flow-through test condition was specified. Assessment of the plant's wastewater facility showed that the system could not achieve this limit. The wastewater treatment system included biological contractors, aerators, API separators and equalization basins. The facility assessment determined that organics, possibly organic acids, in the wastewater were the cause of the effluent toxicity. As a result, GAC was screened via the protocols outlined in this article. GAC was shown to produce an effluent that resulted in 100 percent survival of the stickleback and, therefore, was installed at this facility.

Later, this facility's permit was renewed to include a more sensitive test organism, rainbow trout. The limit was again 100 percent survival. With the more sensitive organism, the GAC usage rate increased dramatically. An optimization study was conducted to determine if adjustments in the operating conditions would reduce the GAC use rate. Laboratory-scale pilot test equipment was used to evaluate the impact of a reduced flow rate on GAC performance. The results indicated that halving the flow rate improved system performance. These results justified the installation of additional adsorption equipment to improve utilization of the GAC's adsorption capacity.

A second industrial facility, a specialty organic chemicals plant, was faced with the introduction of a toxicity limit in its wastewater discharge permit. Previously, this facility had criteria based on BOD, solids, specific chemicals, and pH.

It had to prepare for new limits that included the addition of acute toxicity limits of 2.5 TUa. The limit was based on the more sensitive of two species, fathead minnows or Daphinia pulex (water flea), in a 48 hour static test. Its wastewater treatment system included equalization, pH adjustment, activated sludge, and final clarification. A preliminary evaluation of the wastewater treatment system indicated that the 2.5 TUa limit could not be achieved consistently. It also showed that organics were a major source of the effluent toxicity. Source controls were evaluated for reducing toxicity but were found to be unfeasible. Therefore, GAC treatment of the whole effluent was evaluated and rigorously screened. Following a laboratory-scale pilot test, a large-scale pilot test was conducted to develop system design data.

The benefits of a full-scale pilot study became apparent at this facility. The wastewater treatment system was prone to solids upsets and dissolved solids (salt) spikes. These were discovered and evaluated over the course of the longer duration full-scale pilot system. Thus, it was determined that prefiltration of the system effluent improved the GAC operation, not only in terms of use rate but also in terms of routine maintenance. In addition, the GAC handled the organic load of the effluent, but did not have appreciable capacity for the salt spikes. Since freshwater organisms were stipulated in the new permit's toxicity testing requirements, these salt spikes were shown to induce toxic effects to levels exceeding 2.5 TUa. Because the salts could be isolated as the problem, the chemical plant was able to petition the state for inclusion of a diffuser on its discharge pipe with a mixing zone in the receiving stream to resolve that aspect of the problem.

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Summary

A number of technologies are available for treating wastewater. As the parameters describing wastewater quality change from strictly chemical-specific to include toxicity based limits, more time and effort will be required to study and test solutions to these wastewater problems. From a screening standpoint, GAC can be tested quickly to determine its applicability where a wastewater's characteristics are of an uncertain nature. In cases where organics removal is required for toxicity reduction/ elimination, granular activated carbon adsorption is one technology that can be used to achieve discharge quality compliance.

Table 1
GAC Use Rates Toxicity Reduction

Facility	Toxicity Test	Use Rate
Oil Refinery	96 hr., FT - Stickleback	1lb./1,000 gallons
Oil Refinery	96 hr., FT - Trout	1.5 lb./1,000 gallons
Chemical Plant	48 hr., ST - Water Flea	1.5 lb./1,000 gallons
Chemical Plant	48 hr., ST - Flathead Minnow	1.5 lb./1,000 gallons

FT - Flow Through
ST - Static

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