EDC eliminating

Design experiment optimizes method for removing endocrine disrupters in treatment plants

By Hubert Cabana & Peter Jones

An endocrine disrupting chemical (EDC) is a synthetic chemical that when absorbed into the body either mimics or blocks hormones and disrupts the body's normal functions. EDCs can pass through wastewater treatment systems that currently are not designed to remove them.

A team of researchers recently performed a designed experiment to evaluate potential methods for removing three common endocrine disrupters in treatment plants. The researchers treated solutions containing the EDCs nonlyphenol (NP), bisphenol A (BPA) and triclosan (TCS) with an enzyme preparation from the white rot fungus *Coriolopsis polyzona*. "We used a designed experiment to optimize the temperature and pH at which the removal levels were the highest," said J. Peter Jones, professor for the Department of Chemical Engineering, University of Sherbrooke, Sherbrooke, Quebec, Canada. "The optimized conditions that we developed with the designed experiment removed 100% of the NP and BPA and 65% of the TCS in four hours."

Potential Risks

NP, BPA and TCS are EDCs that are frequently detected in waters downstream of wastewater treatment plants. NP comes from biodegradation in sewage treatment plants of nonlyphenol ethoxylates, which are mainly used as non-ionic surfactants in domestic and industrial applications. BPA is used as a raw material for the production of polycarbonates and epoxy resins. TCS is an antimicrobial agent that has been incorporated into personal care products such as toothpaste, deodorant sticks and soaps. Research has demonstrated that NP and BPA can bind to estrogen receptors, interfering with the action of estrogen, while TCS can interact with thyroid hormones.

Recently, there has been a considerable amount of interest in white rot fungi as a means of removing EDCs from the wastewater stream. White rot fungus produces oxidative enzymes such as laccase, lignin and manganese peroxidase, which are relatively nonspecific biocatalysts. However, no studies prior to the current one have addressed the potential mechanism of elimination, and there has been no precise determination of the byproducts formed during enzymatic treatment.

Removal Methods Study

The two goals of this study were to evaluate the effectiveness of the removal of NP, BPA and TCS with white rot fungi enzymes and to assess the transformation mechanisms by identifying the metabolites produced. The researchers also wanted to be sure that the elimination of the EDCs did not produce metabolites with estrogenic activity.

The conventional approach to optimizing the factors would be to run a series of experiments while varying a single factor. The problem with this approach is that it does not detect interactions between factors or second-order effects. As a result, the researchers decided to use the design of experiments (DOE) method that varies the values of all variables in parallel; it uncovers not just the main effects of each variable but also the interactions between the variables. This approach makes it possible to identify the optimal values for all variables in combination. It also requires far fewer experimental runs than the one-factor-at-a-time approach.

"Designing experiments and analyzing the results using DOE can be time-consuming and error-prone when manual methods are used," Jones said. "General purpose statistical tools can do the job but tend to be unintuitive and limited in their choice of experimental designs and results analysis techniques. We used Design-Expert DOE software from Stat-Ease, Inc., Minneapolis because it is very easy to use yet provides very powerful capabilities, including a wide range of experimental designs and powerful statistical methods to analyze the results."

The researchers decided to look at the following factors: temperature (20°C vs. 40°C vs. 50°C) and pH (3 vs. 4 vs. 5). Design-Expert software generated a full-factorial experiment with nine runs for each substance to be removed. Each combination was replicated three times in a randomized run plan.

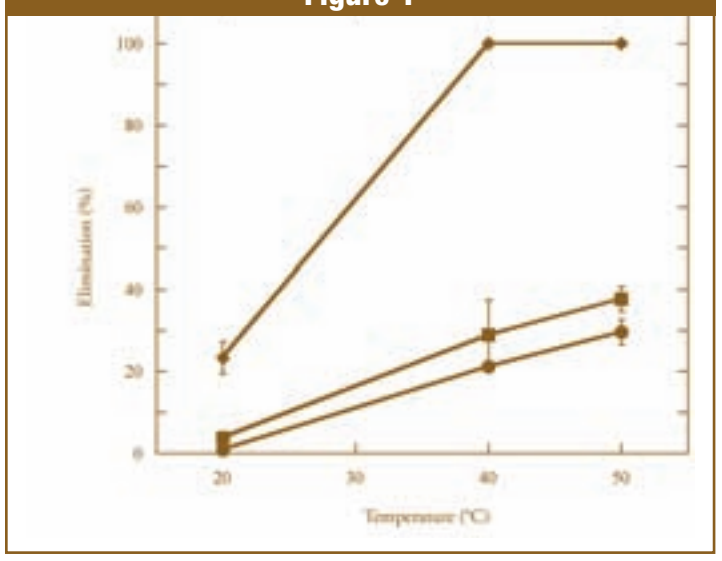
Optimal Removal Results

A statistical analysis of variance of the model highlights the significant impact of temperature and pH on the enzymatic transformation of NP, BPA and TCS. This analysis was used to determine the best conditions for enzymatic transformation of the three EDCs.

The results showed that 50°C was the best temperature for the removal of NP and TCS, while the results for 40°C and 50°C were not significantly different in the case of BPA. A pH of 5 gave the best results for all three compounds studied. These results can be explained by the higher stability produced by a higher pH and the higher catalytic activity resulting from a higher temperature.

The coefficient of determination (R^2) value provides a measure of how much variability in the observed response values can be attributed to the experimental factors and their interactions. The R^2 values of 0.995 for NP, 0.996 for BPA and 0.994 for TCS suggest that the fitted linear-plus interactions models can explain 99.5%, 99.6% and 99.4% of the total variation, respectively. The F-values were 426 for NP, 622.5 for BPA and 361.3 for TCS. Those values together with a *p* value of less than 0.001 for all eliminations indicated that the present models are statistically significant and can predict the experimental results well.

Figure 1



Effect of temperature and pH 3 (●), 4 (■) and 5 (◆) on the degradation of BPA after a four-hour treatment with 10 U/l of *laccase* of *C. polyzona*.

The above results are in agreement with a combination of stability produced by a higher pH and catalytic activity resulting from a higher temperature. Figure 1 shows the impact of the parameters on the laccase-catalyzed elimination of BPA as a function of pH and temperature after a 4-hour batch treatment.

The half life of laccase activity was estimated to be 4 hours, 6 hours and 16 hours at a pH of 3, 4 and 5, respectively, and a temperature of 40°C. The elimination of NP and BPA was directly associated with the disappearance of estrogen activity. Mass spectrometry analysis showed that the enzymatic treatment produced high molecular weight metabolites through a radical polymerization mechanism of NP, BPA and TCS.

"DOE played a critical role in this study by exploring the entire design space and helping researchers identify the optimal conditions for removal of the EDCs," Jones said. "This work may, in the future, lead to industrial-scale methods for the removal of EDCs as part of the wastewater treatment process." WWD

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