

## Pulp and paper wastewaters

# Radical steps in kraft effluent cleaning

Raising the percentage of chlorine dioxide in wood bleaching is an increasingly popular method of reducing AOX and colour in mill effluent. But it also changes wastewater chemistry, affecting linked treatment systems.

To get a better understanding of this interaction, engineers at the University of Arizona, USA, investigated how kraft bioeffluent was affected by different levels of  $\text{ClO}_2$  substitution.

They also looked at the effects of treating extraction stage (E-stage) wastewater with heterogeneous photocatalysis (HP) following ultra-filtration membrane processing.

Such work is becoming more important as environmental legislation continues to drive mill owners to replace elemental chlorine with  $\text{ClO}_2$  substitution in wood bleaching.

Already, several US states have proposed rules aimed at limiting AOX or total organic chlorine (TOCl) in wastewaters. And while the US Environmental Protection Agency is now focusing on dioxin, it may redirect its concern to AOX in the near future.

For treatment of E-stage wastewater, the Arizona engineers applied HP and membrane to the treatment of extraction stage (E-stage) wastewater produced with a 10% and 50%  $\text{ClO}_2$  substitution for chlorine.

They investigated both membrane and HP because of the processes' complementary characteristics. Membrane applied to E-stage wastewaters

is known to reduce COD by 45-85%, colour by 67-92% and TOCl by 56-90%. But membrane surfaces tend to become fouled.

HP oxidation can reduce this fouling. However, highly coloured solutions absorb the ultraviolet (UV) light necessary to activate titanium dioxide ( $\text{TiO}_2$ ) in the HP process, reducing oxidation efficiencies. Positioning membrane treatment prior to HP, overcomes this disadvantage.

### What are the effects on kraft effluent quality of chlorine dioxide substitution and treatment by illuminated titanium and membrane filtration?

Also, HP cuts the toxicity of wastewaters. The process involves beaming sunlight, or synthetic ultraviolet radiation from a lamp, onto  $\text{TiO}_2$ . Radiation stimulates valence band electrons in the  $\text{TiO}_2$ , suspended in contaminated wastewater. Excited electrons jump to the conduction band leaving holes in the valence band.

Holes are thought to react with water and hydroxyl ions to produce hydroxyl radicals ( $\text{OH}\cdot$ ). These radicals can completely oxidize organics, including halogenated organics, to water, carbon dioxide and mineral acids. Also, electrons can react with dissolved oxygen to form super oxide anions ( $\text{O}_2^-$ ) that can continue to

produce radicals.

Electrons may also react with metals, causing their precipitation on the anatase surface. Adding oxidants, such as ozone, is believed to enhance production of radicals, which would be reflected by increased destruction of organics. Finally, the probability of electron/hole pair recombination is increased by radical scavengers, such as bicarbonate and carbonate ions.

In the investigation, measured effluent parameters included TOC, COD, colour, AOX and toxicity, pointing to the following conclusions:

- Increasing  $\text{ClO}_2$  substitution from 10% to 50% in bleaching softwood produced a more readily biodegradable waste and an improved bioeffluent quality, especially in terms of toxicity and AOX;
- All the membrane/HP treatments yielded significant improvements to all measured parameters in aerobic bioeffluent;
- Biological treatment following any membrane/HP treatment of E-stage wastewater continued to remove equal or greater masses of all measured pollutants;
- Membrane/HP treatment of E-stage wastewater from 50%  $\text{ClO}_2$  substitution resulted in significant improvement in aerobic bioeffluent in terms of TOC, COD and colour and toxicity but no substantial reduction in AOX.

*This article is based on a paper by Raymond A Sierka and Curtis W Bryant, both of the Department of Civil Engineering and Engineering Mechanics, University of Arizona.*

containing a modular fixed film growth medium. The activated sludge plant had a 2.5m<sup>3</sup> aerated tank.

**L3:** Was an ordinary one-stage activated sludge plant. Wastewater entered a 4.5m<sup>3</sup> aerated tank equipped with 10 compressed air diffusers at the bottom, equally spaced along a ring 0.25m from the wall.

Air and defoamer were added as in the aerobic parts of L1 and L2. The final settler had a surface area of 0.75m<sup>2</sup>.

A total hydraulic retention time of 12 hours was used in all the three systems. Influent temperature was kept at 37-38°C, and biomass concentrations were 1.5-4kg TSS/m<sup>3</sup> in aerobic sections. The concentration

of fixed biomass in the anaerobic reactors after the experiments was estimated to be 10-20kg/m<sup>3</sup>.

During the first part of the experiments, approximately 75% chlorine dioxide substitution was used in the first bleaching stage, resulting in a sequence of (D75+C25)(EOP)DED. Chlorine dioxide substitution became total later, with a bleaching sequence of D(EOP)DED.

The change of bleaching conditions more than halved the discharge of AOX and increased the biological treatability of the bleach plant effluent. As the transformation of organic and chloro-organic material increased, a more stable operation could be obtained and the quality of the sludge improved.

No major differences in treatment efficiency between the three systems emerged, except for chlorate. Anaerobic pretreatment resulted in higher AOX removal and better tolerance to shock loads, especially with chlorine used in bleaching.

Membrane filtration of the E-stage effluent contributed significantly to the overall treatment with 75% chlorine dioxide (D) in the first bleaching stage. But its contribution was only marginal with 100% D.

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