Voltammetric Measurement of Lignin in Pulp and Paper Samples: An Electron Transfer Catalytic Approach with Mediators

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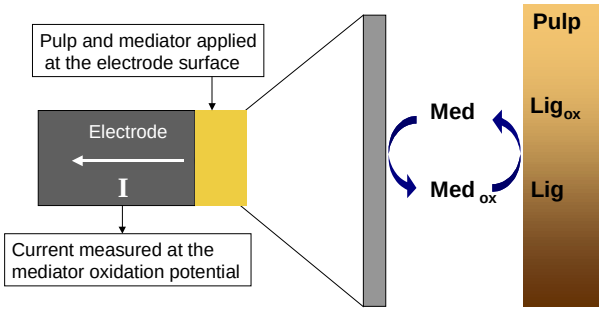
Rapid and accurate measurement of residual lignin in pulp is of prime importance for efficient control of the chemical pulping and bleaching processes currently used in the pulp and paper industry. We describe a new approach to determine lignin content in pulp and paper samples based on the voltammetric measurement of catalytic reactions between lignin and soluble redox mediators. This electrochemical method consists of measuring the rate of regeneration of a lignin redox catalyst in the presence of pulp following its oxidation at a voltammetric electrode. During the voltammetric process, the oxidized mediator diffuses into the pulp fibre to react reversibly with lignin (Figure 1). The redox catalytic reaction with lignin regenerates the reduced mediator at the surface of the electrode, resulting in an increase of the current when compared to the mediator alone. Using a fixed concentration of mediator, the current measured at the peak potential of the mediator in the presence of pulp is proportional to the amount and reactivity of residual lignin in pulp.

The mediator 2,2'-azinobis(3-ethylbenzthiazoline-5-sulphonate) (ABTS) has two stable and reversible redox couples in the range of voltage potential required for lignin oxidation. The first anodic peak at 0.52V, corresponds to the oxidation of ABTS to its cation radical ($ABTS^{\bullet+}$). The second peak at 0.92V corresponds to the formation of the dication ($ABTS^{2+}$). Figure 2 shows cyclic voltammograms at a slow potential scan rate with ABTS alone and in the presence of kraft pulp. The increase in the anodic current peak intensities of ABTS in the presence of pulp (I_k, catalytic current) when compared to ABTS alone (I_d, diffusion current) reflects the extent of the reactions taking place between the two oxidized forms of ABTS and the residual lignin in kraft pulp. The intensity of the catalytic current at the peak potential of the mediator depends on the amount and reactivity of residual lignin in kraft pulp. Within pulp types (softwood, hardwood, or oxygen delignified) linear relationships were obtained between the intensities of the generated current and a range of kappa numbers (Figure 3).



$I \propto$ Reaction rate $\propto$ Reactivity and concentration of lignin

Figure1. Mediator couple voltammetric measurement of lignin in pulp sample

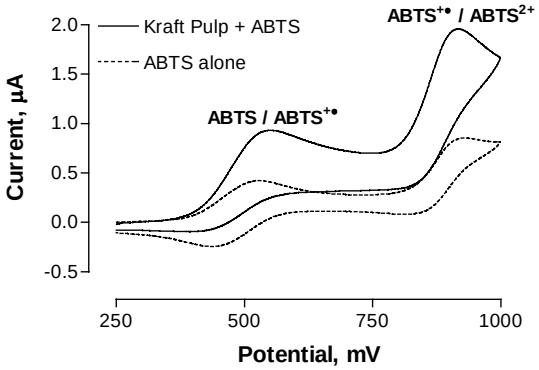


Figure 2. Cyclic voltammograms of ABTS in the presence of kraft pulp.

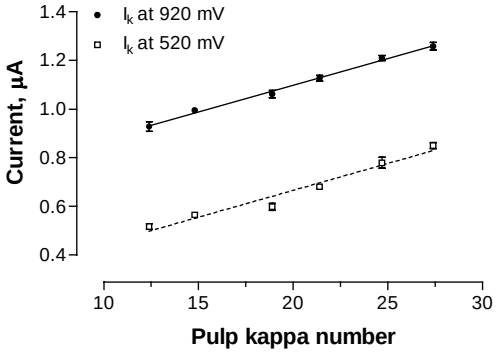


Figure 3. Relationship between lignin content (kappa number) of softwood oxygen-delignified pulp and catalytic peak current intensities of ABTS.