

Synthesis and redox properties of quinonoid-enriched humic substances prepared with a use of Fenton reaction

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Gas emissions from the landfills pose a threat to human health and provide a large source of greenhouse gases. Of particular concern is methane emission. The existing solutions to suppression of methane emission are costly and not efficient. New biocatalytic systems are needed. It has been reported in the literature that humic substances (HS) are capable of inhibiting methane synthesis by methanogenic bacteria. HS are natural polymolecular systems with numerous hydroxy- and carboxy-aromatic units. For enhancing inhibition ability of HS, it is necessary to increase their acceptor properties determined by the content of quinone units in the structure. Previously, we described a use of phenol formaldehyde condensation as the synthetic approach for preparing quinonoid-enriched HS [1]. In this work, we use Fenton oxidation for developing the green synthesis of quinonoid-enriched HS. Potassium humate from leonardite (CHP) and fulvic acids (FAP) were used for modification. Structure of the prepared products was studied using FTIR- and NMR- spectroscopy. Quinonoid centers used in this study are presented in Figure 1.

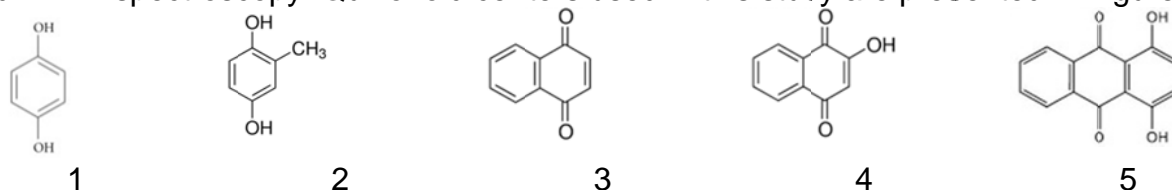


Figure 1. Quinonoid centers incorporated into the humic materials used in this study: hydroquinone (1), 2-methylhydroquinone (2), 1,4-naphthoquinone (3), 2-hydroxy-1,4-naphthoquinone (4), 1,4-dihydroxy-9,10-anthraquinone (5).

The redox capacity of all derivatives was determined as described in [2]. The method is based on reduction of $K_3Fe(CN)_6$ to $K_4Fe(CN)_6$. To get information on distribution of quinonoid-centers between molecular components of HS, we fractionated the CHP-HQ250 derivative on SPE PPL cartridge at pH 2 and 7.

According to the redox measurements, the reducing capacity of CHP was very low – 0.3 mmol/g, the values for its derivatives with anthraquinone (AQ) and naphthoquinone (NQ) were close to 0. Much higher reducing capacity (1.3 mmol/g) was obtained for hydroquinone derivative (CHP-HQ250). The fraction of this derivative isolated at pH 7 had the highest redox capacity of all the CHP-derivatives (1.8 mmol/g). The obtained results are indicative of high accepting properties of CHP and its NQ and anthraquinone derivatives, which are most suitable for suppressing methanogenic activity of microbial consortia. At the same time, fulvic acids and CHP-HQ possessed high donor capacity which is indicative of their substantial antioxidant properties. Our results show that directed modification is a promising tool for tailoring redox properties of HS.

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References

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