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## Stimulation of biogenic methane generation in coal samples following chemical treatment with potassium permanganate

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Biogenic coalbed methane is an underexploited source of clean energy that has attracted increased interest in recent decades. Most of the published studies have focused on biostimulation (the addition of nutrients) or bioaugumentation (the addition of nutrients and a nonindigenous consortium of bacteria). However, even with these amendments coal has proven to be a recalcitrant substrate for the microorganisms thereby limiting the bioconversion to methane. Our research effort has focused on a host of chemical treatments including acid, base and oxidants used to enhance the bioavailability as determined through bioassay. Acid (nitric acid) and base (sodium hydroxide) treatments have been shown to be more effective with respect to solubilizing the coal (i.e., the concentration of dissolved organic carbon). For example, as much as 14% of the coal was solubilized as a result of the nitric acid treatments as compared to 5.4% for permanganate. However, the biometer experiments revealed that there was not a direct correlation between solubility and bioavailability as the permanganate treatment which had much lower TOC produced more biogenic carbon dioxide. Consequently, permanganate was shown to be the most promising treatment agent and was utilized in subsequent experiments evaluating the potential for biogenic methane generation. For permanganate treated samples, 5.4% of the coal carbon was solubilized and 3.2% of the soluble carbon was converted to methane ($CH_4$) by a consortium of microorganisms derived from coal. The methane was rapidly generated and producing approximately 93.4 µmol $CH_4$/g coal (73.9 standard cubic feet (scf)/ton coal) as compared to estimates of 22-74 scf/ton within the PBR coalbeds. The results also showed that the most volatile fraction of the solubilized coal (as defined by sparging with $N_2$ gas) was the most readily used in the conversion to methane gas. The findings of this study provide the basis for a better understanding of the underlying processes involved in the rate-limiting step of coal solubilization; moreover, they provide evidence of the significant potential for the in situ enhancement of biogenic coal bed natural gas.

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