Steady-state fluorescence technique as a tool to evaluate residual antifouling concentration in oil and gas offshore.

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Keywords: *Fluorescence, antifouling, poly(4-styrenesulfonic acid-co-maleic acid) sodium salt.*

Introduction

Scale is a common problem in the oil industry. It is related to the formation of solid deposits that grow over time, blocking and hindering fluid flow through pipelines, valves and pumps, which significantly affect the production rates and equipment lifetime[1]. In order to prevent or retard the nucleation and/or crystal growth of inorganic scales (divalent metal cations - e.g. Ca^{2+}), different water-soluble antifouling have been designed and some of them are commercially available, mainly those based on carboxylates ($-COO^−$), phosphate ($-OPO_3H^-$) and sulfonate ($SO_3^−$) ions.[2]. According to the concentration of antifouling in the produced water the operator will know the exact moment when reinjection of chemical additives should be performed to keep its concentration above the MIC (minimum inhibitor concentration)[2-4]. The recent methodologies applied to quantify antifouling are based on lab techniques which are not available offshore,[2] thus there is the need to develop easy methodologies to be applied offshore. In this sense, the present work reports the preliminary evaluation of steady-state fluorescence technique as a tool to quantify a commercial antifouling in offshore (Figure 1).
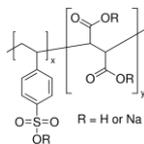

Figure 1. Chemical structure for poly(4-styrenesulfonic acid-co-maleic acid) sodium salt (NaPSS-co-MA).

Results and Discussion

It was evaluated from two channels via fluorescence technique (emission and excitation) the capacity to quantify NaPSS-co-MA. Steady-state fluorescence emission indicated only one emission peak at $\lambda_{em} = 286$ nm ($\lambda_{exc} = 260$ nm) which can be attributed to the rigid aromatic ring of the polymer structure. Six different concentrations of the polymer (1-40 mg.L^{-1}) were applied to build a standard curve for the quantification of residual antifouling. The corresponding linear equation was: $y = 17869x + 178983$ ($R^2 = 0,9986$). Validation analysis conducted with signals from different concentrations of NaPSS-co-MA confirmed the accuracy of the linear equation. The excitation spectrum for the commercial polymer showed two peaks: 231 and 262 nm, which corresponds to π-π^* and n-π^* transitions, respectively. The excitation spectrum presented bands close to those obtained via UV-visible technique, indicating that fluorescence emission at 286 nm is from NaPSS-co-MA and not from other possible fluorophore in the medium. The standard curve for the quantification of residual antifouling via excitation spectrum did not show good correlation, indicating that, in this case, the excitation channel can be used only for qualitative analysis.

In order to identify the main concentration method to quantify the commercial polymer, solid phase extraction (SPE) was conducted in synthetic medium, which can be mimetic to a real phase (presence of salt and oil residue). The best results were obtained at pH 7.5 using methanol and formic acid as eluent. The recuperation from SPE and quantification via emission fluorescence was more than 60% of NaPSS-co-MA.

Conclusion

From the obtained results, steady-state fluorescence channel can be applied as a possible tool to quantify fluorescence antifouling (e.g. NaPSS-co-MA) without the addition of a fluorescence developer. On the other hand, excitation channel did not show good correlation via quantitative analysis.

Acknowledgment

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