International Journal of Biological Macromolecules 108 (2018) 119–126

Contents lists available at ScienceDirect

International Journal of Biological Macromolecules

journal homepage: www.elsevier.com/locate/ijbiomac

Application of guar gum in brine clarification and oily water treatment

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ARTICLE INFO

Article history:
Received 27 June 2017
Received in revised form 18 October 2017
Accepted 26 November 2017

Keywords:
Guar gum
Gel
Salting-out effect
Oily water
Water treatment
Oil content

ABSTRACT

The increasing amount of oil wastewater is causing serious damage to the environment. Oily water is a worrisome by-product of the oil industry due to its growing volume in mature basins and complex chemical composition. Low-cost polymers are being used as alternative materials to treat oily waters after treatment by conventional methods, oil and grease (O&G) concentration being the primary parameter for final disposal. In this respect, guar gum can be used to treat petroleum-contaminated waters, with the advantage of being a low-cost, highly-hydrophilic natural polymer. In this study, guar gum, under specific conditions, shapes itself into three-dimensional structures with interesting physicochemical properties. The salting out effect occurs with reticulation of the polymeric chains by borate ions and in the presence of electrolytes, reducing the solubility of the polymeric network in the solution and leading to an electrolyte- and polymer-rich phase. When the guar gum gel was prepared *in situ* in the produced water, after the salting out effect, the oil was imprisoned in the interstices of the collapsed gel. The gelling guar gum was highly efficient in synthetic oily waters. In the case of initial O&G above 100 ppm, the oil removal percentage was above 90%.

1. Introduction

Most industrial processes produce sub products, which are considered sources of pollution and, as such, require treatment. The most important residue from oil extraction is oily water, due to the high volumes involved, particularly in mature oil fields. It is considered the main effluent produced by the petroleum industry [1,2].

Due to its toxic nature and effects on the environment, oily water management has become a serious public issue due to the improper disposal practices of many oil and gas companies [3].

In Brazil, the National Environment Council (CONAMA) established a limit of 20 mg/L of oil and grease in the oily water to be disposed of, according to Resolution 357/2005. Specifically for disposal on offshore platforms, CONAMA Resolution 393/2007, which establishes monthly mean O&G concentration of up to 29 mg/L, with a daily maximum of 42 mg/L, is applied [4].

The commonly used technologies to reduce O&G concentration are not usually able to achieve the necessary efficiency [5].

In recent years, new technologies developed for the treatment of oily waters and other effluents have awoken significant interest, due to the more stringent resolutions and laws enacted.

The literature reports a wide variety of processes to treat residual waters and other effluents. The following methods are commonly used by the oil industry to reduce O&G concentration in aqueous effluents: liquid–liquid extraction [6]; air flotation [7,8]; hydrocyclones [9,10]; gravitational separators [11,12]; and filtration, which uses different kinds of materials including sawdust [13,14], coal [15,16] and organoclay [17,18].

Processes that use polymers to treat oily water employ three main mechanisms: flocculation, adsorption and complexation [19].

Clarification by the addition of polymer flocculants has been extensively used for wastewater treatment [20]. It is a simple and efficient process [21,22]. Factors such as the type and dosage of flocculants, mixing speed, time, pH, temperature and retention time influence the efficiency of the wastewater clarification process. The optimization of these factors can considerably improve process efficiency [23].

Guar gum is a biopolymer used in several sectors of the industry, mainly due to its structural characteristics, which provide highly viscous solutions at low concentrations. It is non-toxic, biodegradable, easily obtained and inexpensive [24,25]. In the treatment of wastewaters from the food industry, for example, it acts as a flocculant, and a non-toxic alternative to synthetic polymers [26,27].

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https://doi.org/10.1016/j.ijbiomac.2017.11.166
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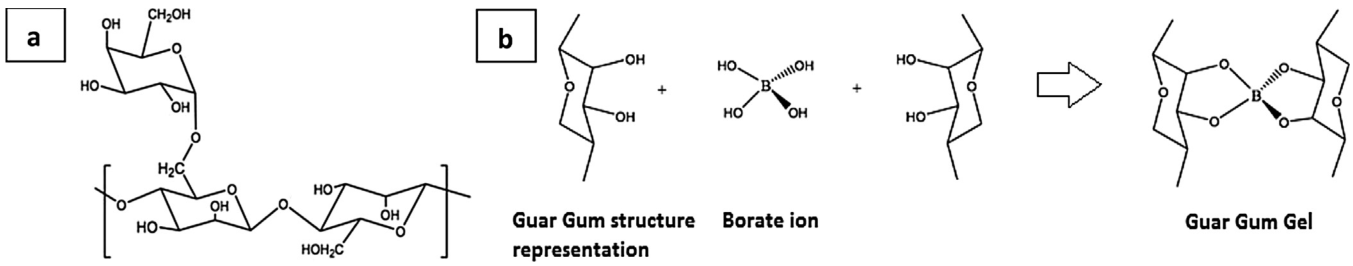

Fig. 1. (a) Basic structure of Guar gum. (b) Schematic representation of the cross-linking reaction in guar gum.

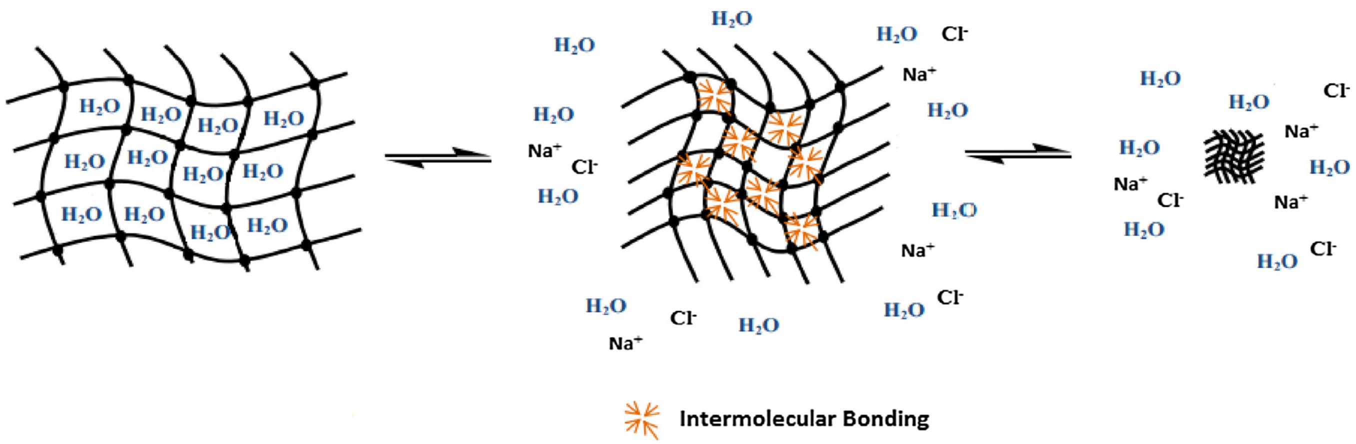

Fig. 2. Schematic representation of the salting-out effect in the gel structure.

Guar gum gels can be obtained by crosslinking with borate ions [28,29]. In an aqueous solution, boric acid coexists in equilibrium with borate ions, according to pH [30]. Borate ions have been shown to be an excellent crosslinking agent for polymers with hydroxyl groups, leading to the formation of a gel. The cis-diol groups present in the polymeric chains of the guar gum complex with borate ions, as shown in Fig. 1. Guar gum molecules can therefore be interconnected through borate ions, forming crosslinks between chains. The presence of several crosslinks imparts the gel properties [31]. In a recent work, borax cross-linked guar gum hydrogels were used as potential adsorbents to water purification [32].

In general, when electrolytes are added to colloidal aqueous dispersions, they provoke flocculation. Although hydrophilic colloids such as guar gum, are single-phase, thermodynamically stable systems, adding excess electrolytes may cause reversibility of polymer-induced flocculation. This effect is called salification or salting out [33]. For hydrophilic colloids, electrolyte flocculation capacity is associated with its power to dehydrate the colloid [34].

In guar gum gels, the salting-out effect causes a decrease in polymer solubility in aqueous medium and, in turn, shrinkage of the polymer network, as shown in Fig. 2.

In the present study, the efficiency of guar gum gels in reducing the O&G concentration of synthetic oily waters was evaluated, considering salinity and oil concentration.

2. Experimental

2.1. Materials

Guar gum was kindly supplied by PETROBRAS and was used as received. To structural characterization, the polymer was previously purified by solubilization in water, filtration through Millipore membranes and freeze-dried [35]. The intrinsic viscosity, $[\eta] = 5.79$ dL/g, was determined in distilled water at 25 °C using an Ostwald-Fenske viscometer. The viscosity average molecular weight, $M_v = 6.10 \times 10^5$, was obtained from Mark-Houwink-Sakurada Equation, using the constants $\mathbf{K} = 3.8 \times 10^{-4}$ and $\mathbf{a} = 0.723$ [35]. Besides this, the D-mannose to D-galactose ratio, M/G = 1.5, was determined by HPLC after total polysaccharide hydrolysis in 1 M H_2SO_4 under reflux for 16 h.

Boric acid was purchased from Alpha Galvano; sodium chloride from Norsal; and calcium chloride from Carboflex Chemicals. Hexane and sodium hydroxide were purchased from Labsynth Products. The crude oil was kindly donated by PETROBRAS.

2.2. Guar gum gel formation in brine

Initially, guar gum was solubilized in distilled water using a Hamilton Beach mixer at 16,000 rpm, for 20 min at room temperature (25 °C), at a polymer concentration of 3.6 g/L; 4.8 g/L; 6.0 g/L and 7.2 g/L. Next, salt (sodium chloride or calcium chloride) was added to reach concentrations of 20 g/L; 40 g/L and 60 g/L, as well as 3.0 g/L of boric acid and 8N NaOH aqueous solution to reach pH 12, the level required for boric acid conversion to borate ions.

2.3. Physicochemical properties of the supernatant after gel shrinkage

Viscosity and turbidity were measured in order to obtain information on the supernatant composition after gel formation and shrinkage.

Viscosity was measured using a *Haake Mars* rheometer coupled to a DG41 coaxial cylinder sensor. The viscosity of the supernatants was measured as a function of shear rate at 25 °C.

Supernatant turbidity was measured with a HACH 200AN turbidimeter. Before each measurement, samples were shaken and turbidity cells carefully wiped to remove dust particles and fingerprints. The turbidimeter was calibrated after each measurement using specific standards.