Journal of Environmental Chemical Engineering 2 (2014) 692–697

Contents lists available at ScienceDirect

Journal of Environmental Chemical Engineering

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

Bench-scale investigation of an integrated adsorption–coagulation–dissolved air flotation process for produced water treatment

Jessica M. Younker, Margaret E. Walsh *

Department of Civil and Resource Engineering, Dalhousie University, 1360 Barrington Street, Halifax, Nova Scotia B3H 4R2, Canada

ARTICLE INFO

Article history:
Received 20 September 2013
Accepted 9 November 2013

Keywords:
Adsorption
Coagulation
Dissolved air flotation
Organoclay
Produced water

ABSTRACT

In oil and gas extraction operations, water from the hydrocarbon reservoir is brought to the surface along with the oil or gas. This "produced water" contains organics which may be free, dispersed, or dissolved in the water. While certain dissolved compounds may contribute to environmental risk from produced water, current North American discharge regulations only address the dispersed fraction of oil and grease (29 mg/L in the US, 30 mg/L in Canada). The purpose of this research was to investigate, at bench scale, chemical coagulation with ferric chloride ($FeCl_3$) and adsorption with organoclay (OC) in a completely stirred tank reactor (CSTR) configuration as pre-treatment for dissolved air flotation (DAF) for the removal of dissolved and dispersed oils from produced water. The integrated process was evaluated and compared to the individual processes of coagulation-DAF, adsorption-DAF and DAF without pre-treatment for the removal of dispersed oil, naphthalene and phenol from synthetic produced water. Concentrations of dispersed oil in clarified water were reduced, from an initial concentration of 100 mg/L, to concentrations as low as 10 ± 1.6 mg/L after coagulation with $FeCl_3$ ($FeCl_3$-DAF), 15 ± 1.2 mg/L after adsorption with OC (OC-DAF), and 7 ± 1.4 mg/L after the integrated process (OC-$FeCl_3$-DAF). From an initial naphthalene concentration of 1 mg/L, both the adsorption (OC-DAF) and integrated process (OC-$FeCl_3$) achieved clarified naphthalene concentrations of 0.11 ± 0.01 mg/L, representing a significant improvement over the 0.53 ± 0.03 mg/L achieved by coagulation treatment ($FeCl_3$-DAF). However, none of the processes evaluated in this study were found to be effective for phenol removal.

Introduction

Produced water is the name given to the co-produced wastewater stream generated when water from underground reservoirs is brought to the surface during oil or gas extraction [1]. Offshore platforms often discharge this wastewater into the open ocean after treatment is applied to reduce total oil and grease concentrations. Oil and grease is limited to 30 mg/L as a monthly average in Canada [2] and North-East Atlantic Europe [3], while in the United States, this limit is 29 mg/L [1]. However, concentrations of dispersed oil and grease are not necessarily correlated to concentration of dissolved aromatics, which are considered to be the main contributors to produced water toxicity [4,5]. Recent changes to the Oslo–Paris Commission (OSPAR) discharge guidelines reflect these concerns by including BTEX concentrations in the calculations for oil and grease levels [6]. However, North American discharge regulations currently address only the free and dispersed fractions of oil and grease in produced water.

Alkylphenols and PAHs are specific classes of aromatic hydrocarbons which have been identified as endocrine disruptors [7]. These compounds may be highly soluble in water, partially soluble or may partition primarily into the dispersed oil phase, depending on molecular weight [7,8]. Substances which partition partially or primarily into the water phase are of particular concern as they are not removed with dispersed oils [4,8]. Alkylphenols and PAHs have been confirmed in produced water discharges [7] and within 2 km of discharge points [9]. While these concentrations are below acute harm levels for marine organisms, the chronic effects of these compounds are not well understood [9].

Flotation is a common technology for offshore produced water treatment, but is not considered to be an effective treatment for dissolved components, suggesting that pre-treatment processes may be necessary [10,11]. Organoclay is clay which has been modified with quaternary ammonium cations to be organophillic, and thus is able to sorb organic compounds from water. Organoclay adsorption in packed-bed adsorption columns has

---

* Corresponding author. Tel.: +1 902 494 8430; fax: +1 902 494 3105.
E-mail address: mwalsh2@dal.ca (M.E. Walsh).

2213-3437/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.jece.2013.11.009

been implemented as a treatment for produced water and gas plant wastewater [12,13]. This technology has been shown to achieve some removal of dissolved compounds from water, such as phenols and BTEX [12,14].

Organoclay adsorption is typically implemented in fixed-bed adsorption columns, although several studies have been conducted to evaluate the efficiency of this adsorbent in a completely stirred tank reactor (CSTR) design. Moazed and Viraraghavan [15] demonstrated up to 89% removal of oil from a produced water sample using batch adsorption with powdered organoclay. Organoclay adsorption in a CSTR with sedimentation as the clarification step was also investigated for oil refinery wastewater treatment, demonstrating that organoclays were amenable to removal by sedimentation after adsorption of oil had taken place [16]. Organoclay adsorption in a CSTR combined with alum coagulation and sedimentation was shown to simultaneously remove phosphate and phenanthrene from synthetic wastewater [17]. Similarly, combining chemical coagulation with powdered activated carbon (PAC) adsorption has been shown to improve both organics removal and subsequent clarification in synthetic wastewater containing humic acid and phenol [18]. However, no studies have investigated dissolved air flotation (DAF) as the clarification step for organoclay alone or in combination with a coagulant, or have evaluated an integrated coagulation–adsorption-DAF process for produced water treatment.

The overall purpose of this research was to investigate the efficacy of an integrated adsorption-coagulation CSTR process followed by DAF for produced water treatment. The treatment capacity of this integrated process was compared to the individual unit processes of $FeCl_3$ coagulation and organoclay adsorption followed by DAF.

Materials and methods

Synthetic produced water

Table 1 summarizes the characteristics of the synthetic produced water used in this study. A stock solution of synthetic produced water was generated by emulsifying crude oil into distilled (DI) water at a concentration of approximately 2 g/L by shearing the oil–water mixture in a blender for 3 min using 100 μL of Triton-X (Sigma–Aldrich) surfactant as an emulsifier. The emulsion was left to sit for 15 min to allow any residual free oil to float to the surface before the stable emulsion was recovered and synthetic produced water samples with 100 mg/L of oil and grease target concentration were prepared. As offshore produced water is typically saline [19], 32 g/L sea salt was added to synthetic produced water samples. Since the crude oil sample did not contain appreciable amounts of phenols or PAHs, 5 mg/L of phenol (Sigma–Aldrich) and 1 mg/L of naphthalene (Fisher Scientific) were added to the synthetic produced water which are within the concentration ranges reported for offshore produced water in other studies [4,20].

Table 1
Characteristics of synthetic produced water.

Parameter	Value	Unit
Oil and grease	100	mg/L
Phenol	5	mg/L
Naphthalene	1	mg/L
Salinity	32,000	ppm
pH	8	
Conductivity	46	mS/cm

Bench-scale experimental design

Three different treatments for produced water were tested: (1) ferric chloride coagulation-DAF ($FeCl_3$-DAF), (2) organoclay adsorption-DAF (OC-DAF) and (3) integrated adsorption-coagulation-DAF (OC-$FeCl_3$-DAF). Fig. 1 presents a process flow diagram of the integrated OC-$FeCl_3$-DAF process evaluated in this study. A control trial of DAF without pretreatment was also conducted. All tests were performed at bench-scale in a DAF batch jar test apparatus (EC Engineering, Edmonton, Canada). Raw water was adjusted from its natural pH of 8.3 to pH 8 by adding predetermined volumes of 0.5 M hydrochloric acid (HCl) or sodium hydroxide (NaOH) solution to achieve pH of minimum solubility for $FeCl_3$ coagulation. Coagulant was added in the form of 10 g/L ferric chloride ($FeCl_3$) solution. Granular organoclay (PM-199, Cetco, Hoffman Estates, Illinois) was pulverized and sieved through a 200 mesh filter to produce a powdered product which was added to the jar tester prior to the addition of $FeCl_3$ coagulant.

A factorial design was developed to investigate the impact of coagulant dose, adsorbent dose, flocculation mixing time and velocity gradients as outlined in Fig. 1. All tests were performed in triplicate, and conducted at room temperature. Table 2 summarizes mixing velocity gradients (G-values) and durations for each treatment type. Coagulation tests ($FeCl_3$-DAF) consisted of a 2 min rapid mix at 110 s^{-1}, followed by a 15 min slow mix at 20 s^{-1}. Adsorption tests (OC-DAF) consisted of an initial 1 min mix at 1000 s^{-1} to fully suspend the organoclay, followed by a 15 or 45 min mix at 110 s^{-1}. Integrated tests (OC-$FeCl_3$-DAF) in the low mixing time condition consisted of a 1 min rapid mix at 1000 s^{-1} to fully suspend the organoclay, followed by coagulant addition, a 2 min rapid mix at 110 s^{-1} and a 15 min slow mix at 20 s^{-1}. Integrated tests (OC-$FeCl_3$-DAF) in the high mixing time condition consisted of a 1 min rapid mix at 1000 s^{-1}, followed by a 30 min mix at 110 s^{-1}, coagulant addition, and a 15 min slow mix at 20 s^{-1}. After all treatments, particles were floated for 10 min after injecting dissolved air in DI water at a saturator pressure of 75 psi and recycle rate of 10%.

Analytical methods

Total oil and grease concentrations were determined by IR spectroscopy (Bruker Optics, Ettlingen, Germany) using Standard Method 5520C [21], with tetrachloroethylene substituted as the extraction solvent, as described by Farmaki et al. [22]. Phenols concentrations were analyzed by 4-aminoantipyrene indicator method and UV–vis spectroscopy (Hach Company, Loveland, USA) using Standard Method 5530 (APHA, AWWA, and WEF, 2005). Naphthalene concentration was determined by headspace analysis of a 0.8 mL sample by adsorption onto and desorption from solid phase micro extraction polydimethylsiloxane fibers using a 3800 Varian gas chromatograph (Agilent Technologies, Santa Clara, USA) with flame ionizing detection. Floc size was measured using a Malvern Mastersizer (Malvern Instruments, Worchestershire, UK). Statistical significance of treatment factors were determined using analysis of variance (ANOVA) with Minitab. Error bars and ± values throughout the manuscript represent one standard deviation.

Results and discussion

Dispersed oil and grease removal

Fig. 2 displays clarified water oil and grease concentrations after the control treatment of DAF with no pretreatment, as well as coagulation ($FeCl_3$-DAF), adsorption (OC-DAF), and integrated (OC-$FeCl_3$-DAF) treatments. DAF with no pretreatment (i.e., control treatment) produced a finished water oil and grease concentration