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Selective removal of photocatalytic non-degradable fluorosurfactants from reverse osmosis concentrate

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ABSTRACT

Recently photocatalytic treatment of municipal reverse osmosis concentrate (ROC) has drawn increasing attention due to its relatively high efficiency and low cost. However, photocatalytic reactions by commercially available TiO_2 are not able to degrade fluorosurfactants in the ROC sample due to the absence of photoreactive groups in these compounds. Here we investigated adsorption and coagulation methods and their efficiencies in removing fluorosurfactants. The analysis and characterization methods included mass spectrometry (LC-QToF), total organic carbon (TOC), fluorescence & UV–Visible spectra, SEM, IR, N_2 sorption, zeta potential, and elemental analysis. Ferric chloride (FER) coagulation was found to be quite efficient in removing fluorosurfactants, while powdered activated carbon (PAC) adsorption was inefficient. The FER pre-treatment process was found to perform better than the post-treatment process in removing the fluorosurfactants. FER selectively removed the bulky fluorosurfactants with long branches but not the slim ones with short or no branches. At a concentration of 10.60 mM, FER could efficiently remove 62.19% fluorosurfactants in total from the ROC sample. The applicability of Freundlich and Langmuir models for the adsorption processes was also investigated. FER was able to remove fluorosurfactant while PAC unable. While the PAC removal mechanism was adsorption, the FER coagulation mechanism was far more complicated.

1. Introduction

Reverse osmosis (RO) membrane technology has been widely applied in wastewater recovery processes. However, currently only 75–85% clean product water can be achieved by utilizing reverse osmosis for wastewater recovery. The remaining 15–25% (Westerhoff et al., 2009; Liu et al., 2012) RO concentrate (ROC) is brackish waste, potentially harmful to the environment due to its high organic content. Recent attention

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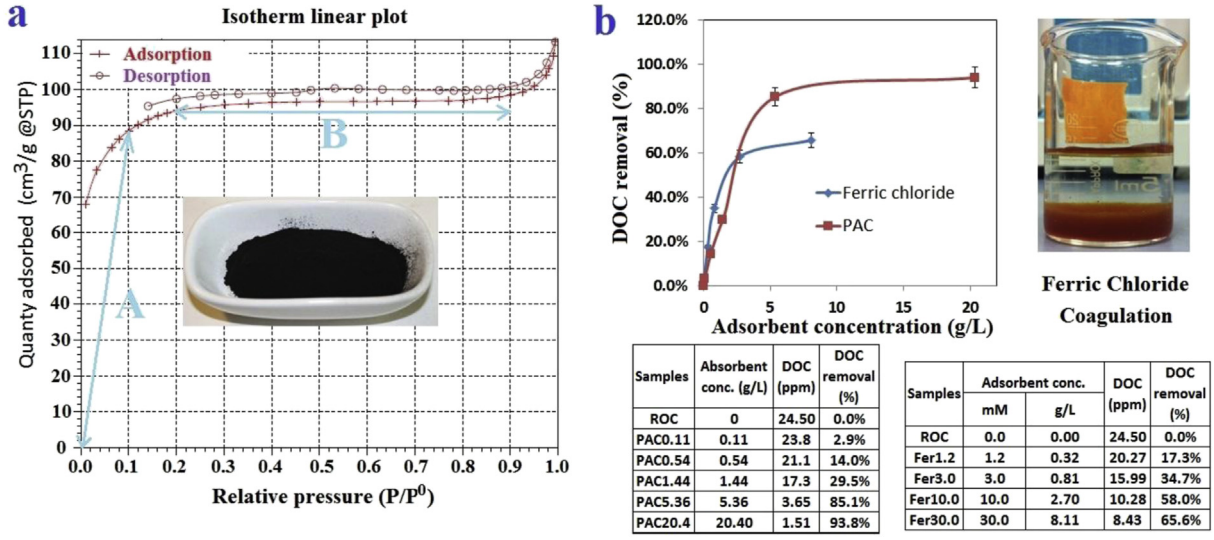

Samples	Absorbent conc. (g/L)	DOC (ppm)	DOC removal (%)
ROC	0	24.50	0.0%
PAC0.11	0.11	23.8	2.9%
PAC0.54	0.54	21.1	14.0%
PAC1.44	1.44	17.3	29.5%
PAC5.36	5.36	3.65	85.1%
PAC20.4	20.40	1.51	93.8%

Samples	Adsorbent conc.		DOC (ppm)	DOC removal (%)
	mM	g/L		
ROC	0.0	0.00	24.50	0.0%
Fer1.2	1.2	0.32	20.27	17.3%
Fer3.0	3.0	0.81	15.99	34.7%
Fer10.0	10.0	2.70	10.28	58.0%
Fer30.0	30.0	8.11	8.43	65.6%

Fig. 1 – (a) The N_2 adsorption/desorption isotherm linear plot of the PAC. Insert is the PAC image. (b) The DOC removal from the ROC sample by the FER coagulation and PAC adsorption methods with the pre-treatment process. The FER and PAC dosing quantities are listed. Insert is the image of FER coagulation with the ROC sample using the pre-treatment process.

on ROC focuses on the evaluation of various advanced organic processes (AOP) for ROC treatment: UV/TiO_2, UV/TiO_2/sand filter, $FeCl_3$/UV/TiO_2, UV/TiO_2/O_3, UV/H_2O_2, electrochemical treatment, sonolysis, etc. (Westerhoff et al., 2009; Liu et al., 2012; Zhou et al., 2011; Dialynas et al., 2008; Bagastyo et al., 2011a, 2011b; Benner et al., 2008; Perez-Gonzalez et al., 2012; Hermosilla et al., 2012; Huang et al., 2011). Organic contaminants in the ROC sample may include natural organic matter (NOM), refractory chemicals added by the public into wastewater (e.g., detergents, pesticides, personal care products, pharmaceutical products, and endocrine disruptors), residuals from the wastewater treatment processes (e.g., soluble microbial products, partially biodegraded organics, and anti-scaling chemicals), and biological materials (i.e., bacteria, viruses, oocysts, and cell fragments) (Westerhoff et al., 2009). Currently ROC is not classified as hazardous waste, and is usually be disposed to surface water, oceans, and underground water, thus posing potential risk to ecological systems (Pontius et al., 1996; Mickley and Int Water Supplyn, 1995). During wastewater treatment, researchers have found there are close relationships between chemical properties of wastewater constituents and their reactivity biologically or chemically. Some pharmaceuticals (such as carbamazepine and meprobamate) are photodegradable (while π electrons play an important role) by UV/TiO_2 through carboxylic intermediates (i.e. formate, acetate, etc.) and finally to CO_2 (Westerhoff et al., 2009). NOM could be removed with chlorine, bromine, O_3 or by wetland. Sedlak et al. (Agus and Sedlak, 2010) discovered the formation of n-nitrosodimethylamine from dimethylamine during chlorination and studied the transformation of odorants (Agus et al., 2011, 2012) by ozonation and UV/H_2O_2. Rosario-Ortiz et al. established the reactivity of effluent organic matter (EfOM) with OH• as a function of its MW, evaluated oxidation of pharmaceuticals by UV/H_2O_2 and the formation of DBPs during ozonation, and characterized the polarity of NOM (Gonzales et al., 2012). Although phenolic surfactants (Hidaka et al., 2001, 1990; Han et al., 2009; Xia et al., 2002; Hidaka et al., 1994; Hidaka and Zhao, 1992; Zhang et al., 2004), such as Nonylphenolics (NP), Octylphenolethoxylates (OPE), dodecylbenzenesulfonate (DBS), and benzenesulfonate (DS) could be photodegraded, the surfactants without aromatic ring and double bonds such as fluorosurfactants FC-143 (Huang and Hong, 2000) are stable under UV/TiO_2. Instead of being photocatalytically degraded, they were found to form micelles assisting the degradation of polychlorinated biphenyls (PCBs) and the pesticide permethrin (Hidaka et al., 1992). Our previous study reported the identification of 63 photocatalytic non-degradable fluorosurfactants in the ROC sample by liquid chromatography-quadrupole time-of-flight mass spectrometry (LC-QToF MS) and TiO_2 photocatalysis methods (Lin and Li, 2014). Since these fluorosurfactants are photocatalytic non-degradable, other methods instead of AOPs should be more suitable for their removal from the ROC before or after the UV/TiO_2 process. Possible methods include activated carbon (AC) adsorption, FER or alum coagulation, membrane filtration (microfiltration, MF or ultrafiltration, UF), and bio-filtration, etc. Bagastyo et al. (2011a) reported that alum preferred to remove large molecules rather than small molecules. Dialynas et al. (2008) found that AC adsorbed small molecules more efficiently than large ones. Zhou et al. (2011) concluded FER coagulation pre-treatment removed a wide range of molecules from small to large. Westerhoff et al. (2009) found that sand filter (bio-filter) post-treatment was efficient in removing the leftover organic contaminants after the UV/TiO_2 process. In this report we investigated the removal of fluorosurfactants from ROC by the coagulation method and the adsorption method, with both the pre-treatment and post-treatment processes. Freundlich and Langmuir models and selective removal of fluorosurfactants were also investigated. During