Photodesorption of Specific Organic Compounds from Titanium Dioxide Particles in Aqueous Media

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Abstract

This study investigates the photodesorption of organic compounds (beef extract, peptone, humic acid, tannic acid, sodium lignin sulphonate, sodium lauryl sulphate, arabic gum powder and arabic acid) from TiO_2 (1g/L in water, pH 7). After a period to reach adsorption equilibrium, photodesorption experiments were conducted in a recirculated reactor at a constant flow rate of 150 ml/min with a UV light intensity of 24 watts. Photodesorption was observed only for sodium lauryl sulphate (50%), sodium lignin sulphonate (43.47%), beef extract (20.35%) and tannic acid (10.5%) indicating that photodesorption is specific for some organic compounds but not all. Using liquid chromatography-organic carbon detection, untreated beef extract and sodium lignin sulphonate were found to contain significant amounts of humic substances (~1000 g/mole), which decreased in concentration after dark phase adsorption while a significant increase in low molecular weight (<350 g/mole) concentrations was observed after photodesorption. UV-treated sodium lauryl sulphate photodesorbed to give both higher molecular weight (HMW) and lower molecular weight (LMW) organics. Thus, the HMW fractions of organic compounds decomposed into smaller compounds after UV irradiation, which subsequently desorbed from TiO_2 surface. However, untreated tannic acid contained a larger proportion of LMW acids, which shows a high adsorption affinity to TiO_2 during adsorption and poorly desorb upon irradiation.

Keywords

Adsorption, dissolved organic carbon, organic compounds, photodesorption, titanium dioxide,

INTRODUCTION

Photo-induced desorption of dissolved organic carbon (DOC) from TiO_2 particles in aqueous media can be initiated by UV illumination of the suspension for a short period of time. This phenomenon has potential applications in water treatment as it significantly reduce process times and facilitate the regeneration of the adsorbent with low energy consumption. It has been proposed that photodesorption of DOC from TiO_2 in synthetic waste water (SWW)[1] involves a significantly reduced affinity between the photocatalyst and organic pollutants upon illumination leading to the detachment of adsorbed pollutants[2; 3; 4; 5]. The photodesorption effect strongly depends on the nature of organic compounds and their constituents. A recent study by El Saliby et al. [1] involved the photodesorption of dissolved organic carbon using SWW, which is a complex blend of several organic and inorganic compounds. The organic constituents are; beef extract (a mixture of peptides and amino acids, nucleotide fractions, organic acids, minerals and some vitamins[6]), peptone (an enzymatic digest of animal protein consisting of short polymers of amino acids linked by peptide bonds[7]), humic acid (a complex mixture of acids containing carboxyl and phenolated groups that behaves as a dibasic or occasionally a tribasic acid[8]), tannic acid (a polyphenolic compound containing hydroxyl groups that cross link to other compounds), sodium lauryl sulphate (an anionic orthosulfonate consisting of a 12-carbon chain attached to a sulfate group[9]), and gum arabic powder (a mixture of polysaccharides and glycoproteins[10; 11]).The organic compounds in SWW can be classified as polysaccharides (as found in beef extract, arabic acid and arabic gum powder), proteins and amino acids (as found in beef extract and peptone) and depending on the functional group attached, humic acid, tannic acid and sodium lignin sulphonate can be classified as carboxylic and phenolic hydrocarbons where as sodium lauryl sulphate represents an organosulphate compound. However, in previous studies using SWW, the contributions from each of the individual components to photodesorption were unclear. The purpose of the current work is to elucidate the contributions from each of individual components of SWW to photodesorption process and to investigate aspects such as variations in the physical transport and chemical reactivity of different organic pollutants. Therefore, in this study, the photodesorption behaviour of individual organic constituents of SWW (such as beef extract, humic acid, tannic acid, acacia gum powder and arabic acid) is reported. In particular, DOC data collected after adsorption and UV light illumination are presented and discussed.

EXPERIMENTAL

Materials

Titanium dioxide (Degussa P25) is a mixed phase nano-powder with anatase, rutile and amorphous structures. It has a surface area of 50m^2/g and an apparent density of 130 kg/m^3. Sodium hydroxide (97% w/w) was obtained from ChemSupply Pty Ltd and hydrochloric acid (37% v/v) from ScharlauChemie S.A. The properties of individual organic compounds used in the photodesorption experiments can be found elsewhere[1]. Distilled water was used to prepare solutions.

Photoreactor setup

A recirculating photoreactor setup (as reported elsewhere [1]) was used to study the photodesorption of specific organic compounds. The reactor was exposed to a luminous source composed of three 8 W germicidal lamps (G8T5, Sankyo Denki Co.). The dominant wavelength is 254 nm and light intensity is 3.6 mW/cm^2[12]. Suspensions of TiO_2 and organic solutions in a dark adsorption tank were continuously stirred at 400 rpm using a magnetic stirrer (IKA, C-MAG, MS7). Influent was pumped through three columns by an adjustable flow FMI lab pump (Fluid metering, INC, USA, Model QD) through connection tubes (Masterflex, precision pump tube 06508-17) at a flow rate of 150 ml/min.

Photodesorption of dissolved organic matter

The dissolved organic carbon (DOC) of SWW in previous studies was ~7 mg/L[1]. Hence, the photodesorption of individual organic compounds in the current work was studied by adjusting the DOC concentration to7 mg/L using the individual compounds. Experiments were conducted at pH 7 using 1 g/L of TiO_2 catalyst at flow rate of 150 ml/min and a light intensity of 24 watt. After the addition of TiO_2 to the organic solution, the slurry was mixed with a magnetic stirrer at 400 rpm for 30 min for dark adsorption. Then, the slurry was pumped to the photoreactor columns and UVC lamps were switched on. Photodesorption rapidly started after illuminating UV light to the suspension. Slurry samples were collected at fixed time intervals, filtered through 0.45 µm regenerated cellulose filters (Whatman, UNIFLO) and analysed using a Multi N/C 3100 (Analytik Jena) dissolved organic carbon analyser. Organic matter was identified and classified using liquid chromatography-organic carbon detection (LC-OCD) and associated software (Model 8, DOC-Labor, Germany). Three replicate experiments for each specific organic compound were conducted.

Calculation of adsorption and photodesorption

The adsorption and desorption percentages were calculated as follows:

$$Adsorption(\%) = \frac{[C_0 - C_{ads}]100}{C_0}$$

Where C_0 is the DOC in mg/L at t = 0, C_{ads} is the DOC at t = 30 min.

$$Photodesorption\ (\%) = \frac{[C_{des} - C_{ads}]100}{[C_0 - C_{ads}]}$$

Where C_{des} is the DOC in mg/L at t = 33 or 35 min (maximum photodesorption).

RESULTS AND DISCUSSION

Photodesorption of DOC

Beef extract, peptone, humic acid, tannic acid, sodium lignin sulphonate, sodium lauryl sulphate and arabic acid were studied individually by adjusting the DOC to 7 mg/L at pH 7 and with a catalyst loading of 1g/L (TiO_2). Three replicate experiments were conducted to obtain standard deviation and error obtained to be about 5%. As shown in Figure1, after allowing 30 minutes for dark phase adsorption, the DOC of tannic acid and beef extract was reduced by 97.25% and 42.79%, respectively, whereas the other organic compounds had adsorption ranging from 8 to 22%.

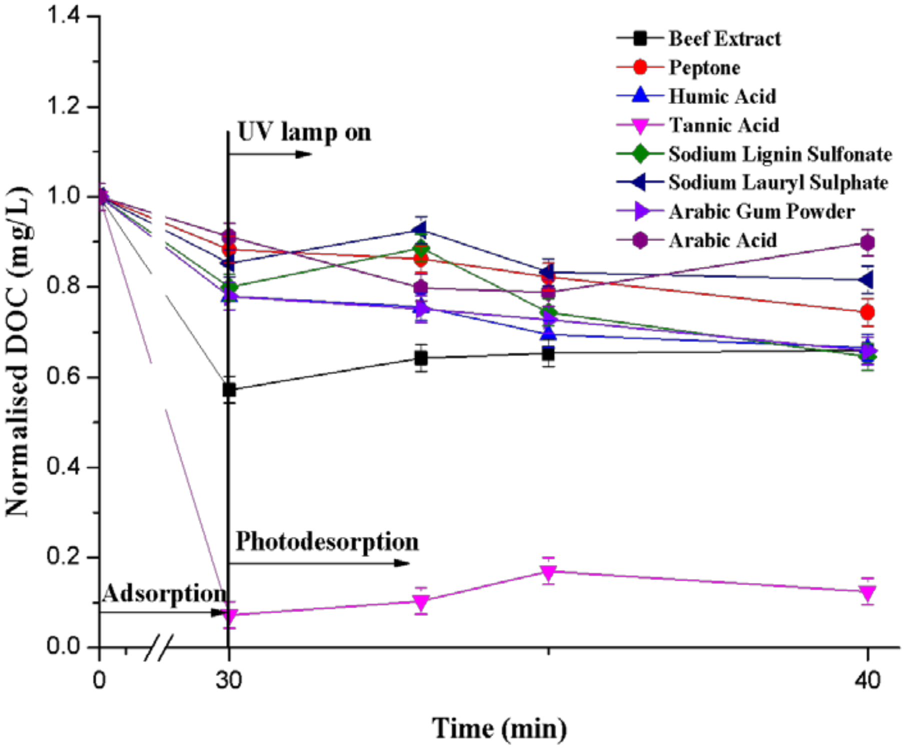


Figure 1. Normalised rate of adsorption and photodesorption of DOC of individual organic compounds.

After adsorption in the dark, the influent was pumped to a photoreactor and illuminated with UVC light. Figure 1 illustrates the detachment of sodium lauryl sulphate, sodium lignin sulphonate, beef extract and tannic acid from TiO_2 surfaces after UV light irradiation, indicated by an increase in DOC immediately after irradiation.

In particular (see Figure 2), photodesorption of sodium lauryl sulphate was 50% of the adsorbed fraction (14.73%), sodium lignin sulphonate (43.47% of adsorbed fraction), beef extract (20.35% of adsorbed fraction) and tannic acid (10.5% of adsorbed fraction). Arabic acid shows negligible photodesorption with extend UV exposure while desorption did not occur with peptone, humic acid and arabic gum powder.

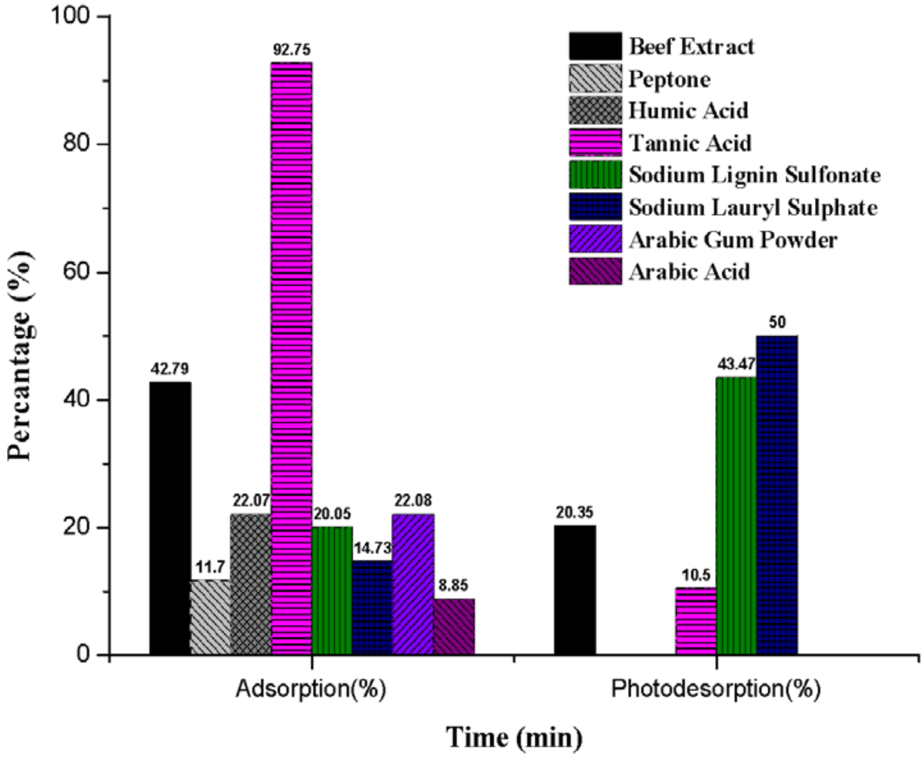
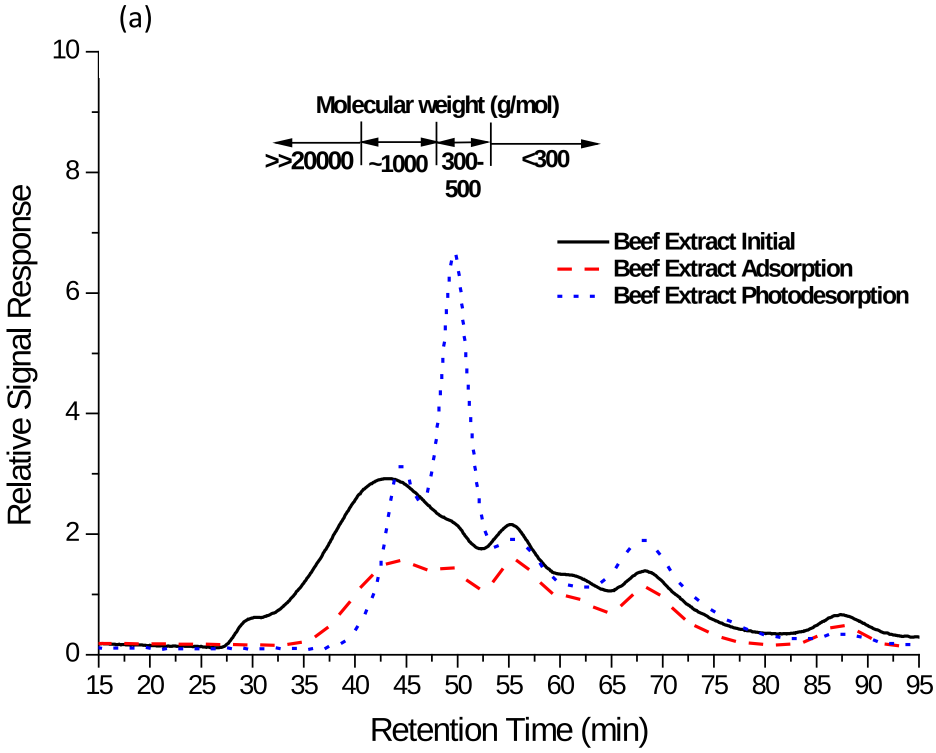
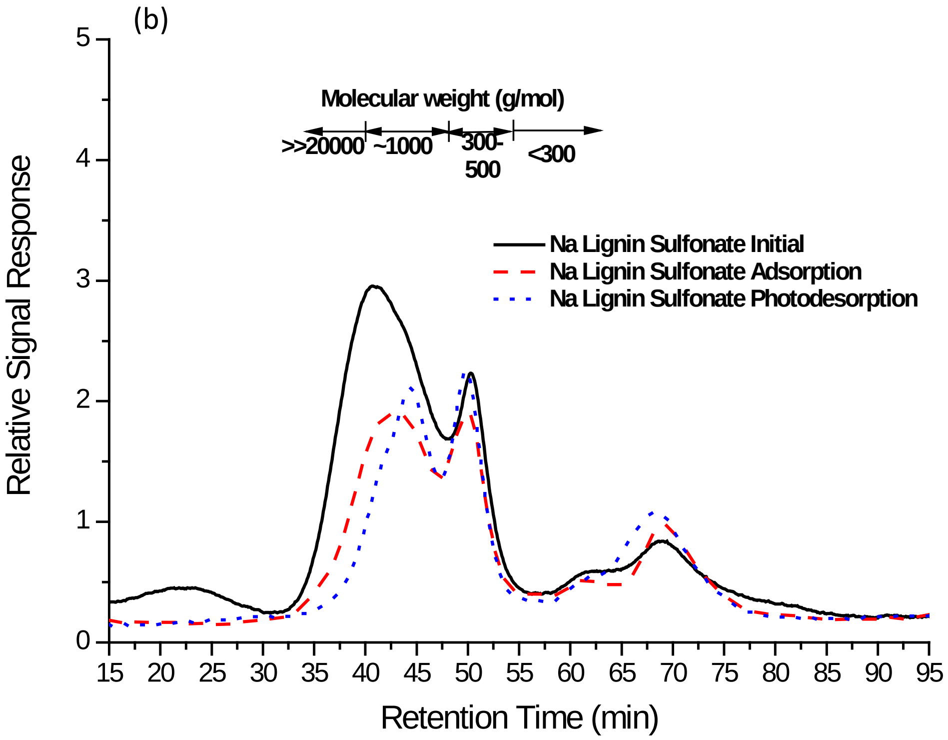


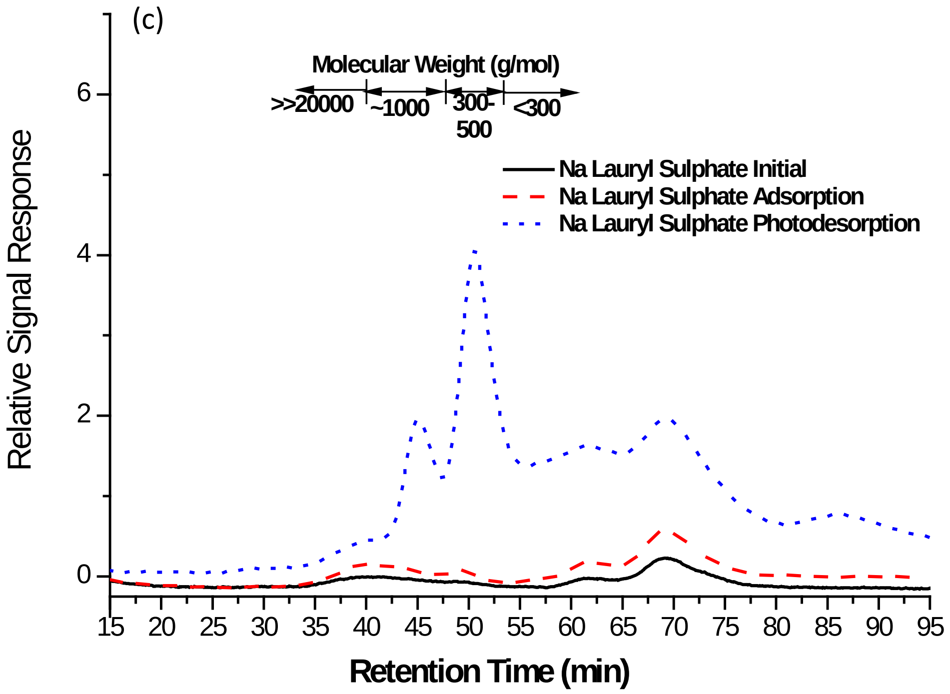
Figure 2.Percentage of adsorption and photodesorption of several organic compounds.

Molecular weight distribution of organic compounds

LC-OCD experiments was used to investigate the molecular fraction of untreated, adsorbed, and photodesorbed organic compounds[13].




(b)
Molecular weight (g/mol)
>>20000
~1000
300-500
<300
Na Lignin Sulfonate Initial
Na Lignin Sulfonate Adsorption
Na Lignin Sulfonate Photodesorption
Relative Signal Response
0
1
2
3
4
5
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
Retention Time (min)


(c)
Molecular Weight (g/mol)
>>20000
~1000
300-500
<300
Na Lauryl Sulphate Initial
Na Lauryl Sulphate Adsorption
Na Lauryl Sulphate Photodesorption
Relative Signal Response
0
2
4
6
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
Retention Time (min)

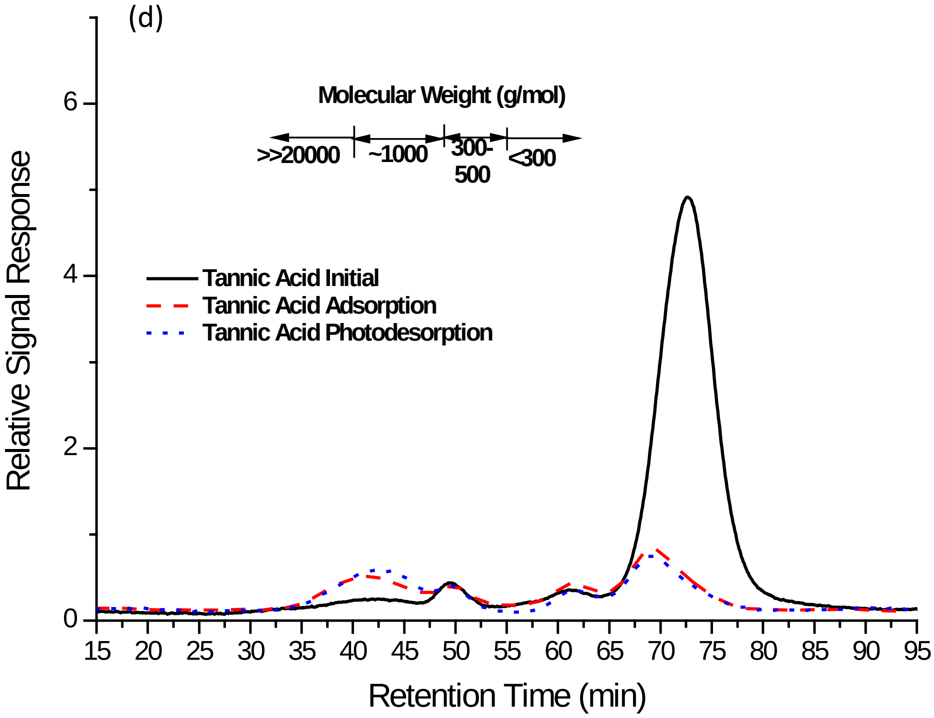


Figure:3. LC-OCD chromatograms of DOM before treatment (black line), after adsorption (red line) and after photodesorption (blue line) for (a) Beef extract. (b) Sodium lignin sulphonate. (c) Sodium lauryl sulphate. (d) Tannic acid.

Table 1: LC-OCD fractionation results of organic compounds, after adsorption and photodesorption

	DOC			Approximate molecular weight distribution (g/mol)				
		HOC	CDOC	>>20000	~1000	300-500	<350	<350
Sample	Dissolved	Hydrophobic	Hydrophilic	Biopolymer	Humic Substances	Building Blocks	LMW Neutrals	LMW Acids
Beef Extract Initial	100%	16.60%	83.40%	1.50%	34.40%	10.50%	36.80%	0.20%
Beef Extract Adsorption	100%	24.10%	75.90%	--	25.60%	7.50%	42.10%	0.70%
Beef Extract Photodesorption	100%	25.00%	75.00%	1.40%	17.90%	9.80%	35.60%	10.40%
Na Lignin Sulphonate Initial	100%	35.80%	64.20%	--	49.70%	--	8.20%	6.80%
Na Lignin Sulphonate Adsorption	100%	52.60%	47.40%	0.30%	25.30%	4.70%	12.10%	4.90%
Na Lignin Sulphonate Photodesorption	100%	33.40%	66.60%	5.70%	25.90%	2.20%	25.40%	7.30%
Na Lauryl Sulphate Initial	100%	97.40%	2.60%	--	0.70%	0.20%	1.70%	--
Na Lauryl Sulphate Adsorption	100%	95.70%	4.30%	--	1.00%	0.30%	2.90%	0.10%
Na Lauryl Sulphate Photodesorption	100%	63.40%	36.60%	1.10%	5.70%	6.70%	23.00%	0.10%
Tannic Acid Initial	100%	51.20%	48.80%	0.10%	1.90%	1.00%	45.00%	0.80%
Tannic Acid Adsorption	100%	51.70%	48.30%	--	16.10%	1.90%	28.60%	1.70%
Tannic Acid Photodesorption	100%	67.40%	32.60%	1.30%	12.50%	0.70%	16.50%	1.50%

LC-OCD chromatograms of water containing beef extract, tannic acid, sodium lauryl sulphate and sodium lignin sulphonate are shown in Figure 3.Table 1 shows the percentage of organic fractions of untreated, adsorbed and photodesorbed organic compounds as a function of the total DOC.The untreated beef extract and sodium lignin sulphonate solution (Figure 3a and 3b) contain significant amounts of humic substances (~1000 g/mole). After the dark adsorption phase, theamounts of high molecular weight (HMW i.e., ~1000 g/mole) species remained in solution decreases. After photodesorption, the beef extract shows a significant increase in low molecular weight (LMW i.e., <350g/mole). Therefore, the process of adsorption/desorption converted a reasonable proportion of HMW organics into LMW organic material. This process also occurred to a lesser extent in the sodium lignin sulphonate sample. Shon et al [3] reported similar finding after conducting a high performance size exclusion chromatography (HP-SEC) analysis on desorbed fractions. Desorption of LMW organics may be enhanced by accumulation of negative charge on the TiO_2 surface upon irradiation [14].

In contrast, the LC-OCD chromatogram of UV treated sodium lauryl sulphate (Figure 3c) reveals the photodesorption of a larger fraction of both HMW and LMW organics. Upon UV irradiation, fractions of hydrophobic constituents of sodium lauryl sulphate degrade into hydrophilic species [15] by oxidation of carbon-containing groups into carbonyl groups[16],which photodesorb (Table 1). However, the LC-OCD chromatograms of untreated tannic acid (Figure 3d) contained a larger proportion of LMW acids, which showed a high adsorption affinity to TiO_2 during dark phase adsorption and were found to poorly desorb upon irradiation. The photodesorption of HMW organic compounds such as beef extract, sodium lignin sulphonate and sodium lauryl sulphonate was observed to be higher than the LMW tannic acid. Thus, the HMW fractions of organic compounds decomposed into smaller compounds after UV irradiation, which was subsequently desorbed from TiO_2 surface.

CONCLUSIONS

The photodesorption of specific organic compounds with DOC of 7 mg/L was investigated at pH 7 with a flow rate 150ml/min and a TiO_2catalyst loading of 1g/L. Sodium lauryl sulphate, sodium lignin sulphonate and beef extract were found to be the major contributing organic compounds for photodesorptionin terms of adsorption of DOC and efficiency of photodesorption. LC-OCD fractionation of untreated and adsorbed organics reflects adsorption of HMW organic particulate matter onto TiO_2. The LC-OCD results after UV illumination indicate photodesorption of LMW organic, specifically <500 Da organic. Hence, the HMW organics were decomposed into smaller ones, which was subsequently desorb from TiO_2 surface.

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