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Behaviour of the X-ray contrast agent iopamidol during anaerobic treatment and effect on biogas production

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ABSTRACT

Among the iodinated contrast media, iopamidol (IOPA) has been frequently detected in effluents of wastewater treatment plants and surface waters at elevated concentrations due to their refractory nature and hence incomplete removal. The objective of this study was to investigate anaerobic treatability of aqueous IOPA and its effect on biogas production in lab-scale batch reactors treating synthetic sewage. Initial total COD (COD_{tot}) concentrations varied between 800–950 mg/L in the batch reactors having IOPA concentrations in the range of 0–100 mg/L. Findings of this study reflected that increased IOPA concentrations did not result in any significant decrease in anaerobic treatment performance as well as the biogas yield. Although the highest soluble COD (COD_{sol}) removal was observed in the bioreactor bearing no IOPA (i.e., 90% COD_{sol}); no meaningful change occurred at elevated IOPA concentrations up to 100 mg/L (i.e., 82% COD_{sol}). Results also indicated that IOPA could be removed from the supernatant at a rate of 33–44% at the end of a 32-day incubation period. Moreover, maximum cumulative biogas production was observed as 134 mL in the reactor with 75 mg/L IOPA compared to 111 mL in the control reactor.

Keywords: Anaerobic treatment; Biogas; Inhibition; Iopamidol; X-ray contrast agent

1. Introduction

The presence of high concentrations of pharmaceutical residuals in the aquatic environment, sludge, soils and sediments has gained considerable attention and concern in the recent past. Because of the presence of active biochemical structures in their molecules; pharmaceuticals, once released to aqueous environments, present potential hazardous effects on humans and aquatic ecosystems [1,2]. Pharmaceuticals are called "emerging pollutants" in the last decade, not only due to their potential ecotoxicological risks, but also to their continuous discharge to the environment [3–5]. These compounds are considered as emerging pollutants in waterbodies because they still remain unregulated or are currently undergoing a regularization process, although the directives and legal frameworks are not set-up yet [6]. For example, some persistent substances like diclofenac, sulfamethoxazole, trimethoprim, carbamazepine, have not been effectively transformed (<25%) by biological treatment [7]. Hence, they may threaten the aquatic life and in the worst case may re-enter the water cycle when discharged to surface waters [8].

Among the pharmaceuticals being frequently encountered in aquatic ecosystems, iodinated X-ray contrast media (ICM) are chemicals used to enhance the imaging of organs or blood vessels during diagnostic tests [9]. Iopamidol (IOPA; tradenames: Iopamiro, Isovue, Iopamiron, and Niopam) is a nonionic, low-osmolar ICM developed by Bracco Group [10]. IOPA is the most frequently used and commercially important ICM and concentrations up to 2.7, 15, 2.4, and 0.49 μg/L IOPA have been detected in raw water, treated

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sewage, groundwater, and rivers, respectively [11]. McArdell et al. [12] investigated 69 common pharmaceuticals that are expected in the effluent of medical facilities and it was reported that 52 of them were detected with IOPA being at the highest concentration in the mg/L range. Machek Jr. [13] also reported that the relatively inert ICM pharmaceuticals are found at high concentrations in clinical and domestic wastewater, surface waters, groundwater, back filtrate, soil leachates, and even drinking water supplies. On the other hand, concentrations in the hospital wastewater significantly correlate with the daily consumption in the hospital reaching up to 384 g/d for IOPA [14] whereas concentrations range from 0.072 to 78 μg/L in surface water.

Disinfection byproducts (DBPs) are always a concern when chlorine is used in water treatment facilities. ICM chemicals may also undergo transformation to halogenated DBPs in water treatment systems [15]. During chlorination and chloramination; hypochlorite (OCl^-) is considered as the primary reactive species with IOPA to form iodinated DBPs in the presence of natural organic matter [16]. Recently, iodinated DBPs originating from the discharge of ICM into water treatment facilities have drawn serious concern as they are potentially more cyto-genotoxic than brominated and chlorinated DBPs [16,17].

Considering its physicochemical properties that directly influence its fate and treatability in the environment; IOPA exhibits a low volatility, high polarity and inherent persistence to classical physicochemical and microbial degradation [18,19]. Conventional water and wastewater treatment plants (WWTPs) have only a limited elimination capacity for these organic micropollutants, as they are not specifically designed to remove complex chemicals such as pharmaceuticals from wastewater. Drewes [19] reported the primary removal mechanisms for ICM like pharmaceuticals in wastewater are adsorption onto suspended solids, aerobic, and anaerobic biodegradation, chemical (abiotic) degradation (via processes such as hydrolysis), and volatilization. Ternes and Hirsch [11] detected iopamidol, diatrizoate, iothalamic acid, ioxithalamic acid, iomeprol, and iopromide at almost the same levels in influents and effluents of municipal WWTPs. Seven WWTPs in Texas, Arizona, and California were monitored and organic iodine concentrations at these facilities varied between 5 to 40 μg/L [20].

Several processes have been investigated for ICM removal from wastewaters (i.e., hospital). Although biologically activated membranes were able to reduce pharmaceuticals to a concentration of 20% or less; ICM showed lower removal efficiencies (i.e., approximately 100% of the initial IOPA remained in solution after treatment) [12]. Results also showed that ionic ICM like diatrizoate was not susceptible to microbial transformation, but nonionic ICM like iohexol, iomeprol and IOPA were capable of being transformed by microbial degradation [21]. More recently, advanced oxidation processes such as UV photolysis, γ-irradiation, sonolysis, Fenton, Photo-Fenton, H_2O_2/UV-C, TiO_2/UV-A, O_3/H_2O_2 and zero-valent aluminum activated H_2O_2, and persulfate have been successfully used to remove ICM. However, these are energy-intensive processes and their full-scale applications are rather difficult [22–25]. Data on the occurrence and concentrations of ICM in effluents from WWTPs and surface waters gathered from the literature show that ICM concentrations in these sources fluctuate widely, most probably due to different dosages applied in various regions and inconsistent efficiency of treatment plants. Nevertheless, more information is required concerning the nature, variability, transport, and fate of these compounds in water/wastewater treatment facilities, because knowledge in this area is still limited.

Although according to our previous work, IOPA exhibits neither serious acute toxicity nor genotoxicity [25]; its inhibitory (toxic) effect in aerobic or anaerobic treatment systems has not been explored until now. Moreover, no exact information is available about the degree of biodegradation of IOPA during advanced treatment processes (e.g., A2O systems that involve anaerobic, anoxic, and aerobic reactors) at domestic/municipal WWTPs [19]. Hence, the main objective of this study was to investigate the biological treatability of the commercially important iodinated organic X-ray contrast agent IOPA and its effect on biogas production during anaerobic treatment of synthetic wastewater characterizing domestic sewage in lab-scale batch reactors. Effect of IOPA on anaerobic treatment was investigated by critical process variables including total and soluble chemical oxygen demand (COD), total and volatile solids concentrations as well as inhibition was monitored by biogas productions in batch reactors. Considering the gap in the scientific literature; in the present work the degradation of aqueous IOPA (25–100 mg/L) under anaerobic conditions at mesophilic temperature (35°C) was examined and compared with the results of the control sample bearing no IOPA in the reactor.

2. Materials and methods

IOPA (1,3-Benzenedicarboxamide, N,N′-bis[2-hydroxy-1-(hydroxymetyl)etyl]-5-[(2-hydroxy-1-oxopropyl) amino]-2,4,6-triiodo-, (S)-; $C_{17}H_{22}I_3N_3O_8$; 777 g/mol; CAS: 0060166-93-0; 0.263 mg TOC/mg IOPA) is a non-ionic radiographic contrast agent commercially available as "Pamiray 300/370" solution. Pamiray solution was purchased from BIEM Pharmaceutical Co. A.S. (Ankara, Turkey). According to the manufacturer, 1 mL Pamiray solution contains 612.4 mg IOPA equivalent to 300 mg iodine. The other ingredients are trometamole (tromethamine), disodium calcium edetate, diluted hydrochloric acide, and distilled water.

The high strength synthetic sewage was prepared according to the OECD guidelines [26] [i.e., in each liter of tap water; 3 fold of the following chemicals were dissolved: Peptone, 160 mg; meat extract, 110 mg; urea, 30 mg; anhydrous dipotassium hydrogen phosphate (K_2HPO_4), 28 mg; sodium chloride (NaCl), 7 mg; calcium chloride dihydrate ($CaCl_2{\cdot}2H_2O$), 4 mg; magnesium sulphate heptahydrate ($Mg_2SO_4{\cdot}7H_20$), 2 mg]. Accordingly, initial COD_{tot} concentration of the IOPA-free control reactor was about 800 mg/L.

Anaerobic treatment was conducted in N_2-flushed, 1 L glass flasks. Control reactors were run with the addition of only synthetic sewage (500 mL) and the seed sludge (150 mL). The inoculum was the flocculent sludge taken from a mesophilic anaerobic digester treating municipal sludge. Other reactors were started operation by the introduction of IOPA with the following concentrations; 25, 50, 75, 100 mg/L. Since during wastewater treatment, many contaminants partition onto solids as a consequence of their hydrophobic nature resulting in enrichment in biosolids at concentrations several orders of magnitude higher than in the raw wastewater [19];

such IOPA concentrations were selected in order to examine the extent and the time that biogas productions continued and inhibition was observed. Anaerobic treatment was conducted in parallel flasks that were stirred twice a day manually and a background reactor including only the seed was also operated at the same conditions. All the bioreactors were run in the batch-mode at 35°C constant temperature room (i.e., mesophilic) for 32 d until the changes in cumulative biogas productions were negligible.

Total COD (COD_{tot}), Soluble COD (COD_{sol}), Total Solids (TS), Volatile Solids (VS), Total Suspended Solids (TSS), Volatile Suspended Solids (VSS), pH, and alkalinity parameters were measured at the beginning and at the end of incubation period according to Standard Methods [27]. The change in IOPA concentrations was quantified on an Agilent 1100 Series HPLC equipped with a Diode-Array Detector (DAD; G1315A, Agilent Series) set at 242 nm. The C18 Symmetry (Waters, USA) column (3.9 mm × 150 mm) was utilized as a stationary phase, while the mobile phase was a mixture of acetonitrile/water in 10/90 (v/v) ratio. The flow rate was set at 1.0 mL/min and the temperature of the column was set at 25°C. The quantification limit of IOPA for an injection volume of 100 µL was calculated as 10 times of the signal-to-noise ratio (3.34 µg/L). Additionally, gas productions in bioreactors during anaerobic treatment were daily monitored using Lutron PM-9107 manometer before the produced biogas was released by an injection needle. The measured pressure was used to calculate the volume of biogas produced under the standard conditions.

3. Results and discussion

The effect of IOPA on biogas production during anaerobic treatment was investigated in lab-scale batch reactors treating synthetic domestic sewage. Experiments were conducted without (control sample) and with the presence of IOPA concentrations changing in the range of 25–100 mg/L. Findings of this study indicated that increasing IOPA did not result in any substantial decrease in anaerobic treatment performance based on COD removals and biogas production (Table 1). The initial pH and alkalinity values of the substrate were about 7.9 and 490 mg $CaCO_3$/L, respectively. At the end of the anaerobic treatment, the pH and alkalinity values of the bioreactors were observed in the ranges of 7.2–7.4 and 830–940 mg $CaCO_3$/L, respectively.

Initial TS and TSS concentrations were about 5000 and 3775 mg/L, respectively with a volatile content of ca. 50%. Final TS and VS concentrations in the bioreactors were in the range of 4400–4800 and 1915–2265 mg/L, respectively. Although the highest COD removals were observed in the control reactor (i.e., 77% COD_{tot} and 90% COD_{sol}); no meaningful change was observed at the investigated IOPA concentrations. According to Fig. 1a, COD_{tot} removals were in the range of 70–74% in the bioreactors at increasing IOPA concentrations.

Results also indicated that IOPA could be removed from the supernatant at a ratio of 33–44% at the end of a 32-d anaerobic treatment (Fig. 1b). Drewes et al. [20] reported that most pharmaceutical residues exhibited low K_d values in controlled batch experiments, indicating negligible sorption onto sewage sludge. These findings suggest that the removal of pharmaceutical residues observed in WWTPs is mainly the result of biodegradation. Martin et al. [28] reported that the highest degradation of the investigated pharmaceutical compounds was found under anaerobic digestion among different sludge treatment processes. Dimkic et al. [29] also reported that IOPA might undergo biodegradation under even anaerobic conditions. On the other hand, according to previous studies, the elimination of IOPA during anaerobic digestion might also due to sorption onto solid particles to

Table 1
Anaerobic treatment performance during mesophilic operating conditions (IOPA = 25–100 mg/L; T = 35°C; Incubation time = 32 d)

Parameter	Unit	Incubation time (d)	0 (Control)	IOPA (mg/L)			
				25	50	75	100
IOPA	mg/L	0	0	25	50	75	100
		32	–	16.25	28	50.25	67.50
		Removal (%)	–	35	44	33	33
COD_{sol}	mg/L	0	703	737	772	806	840
		32	74	89	117	138	154
		Removal (%)	90	88	85	83	82
COD_{tot}	mg/L	0	803	837	871	905	940
		32	184	230	228	273	263
		Removal (%)	77	73	74	70	72
Alkalinity	mg $CaCO_3$/L	0	487				
		32	940	917	880	887	900
pH	–	0	7.87				
		32	7.39	7.25	7.27	7.24	7.26

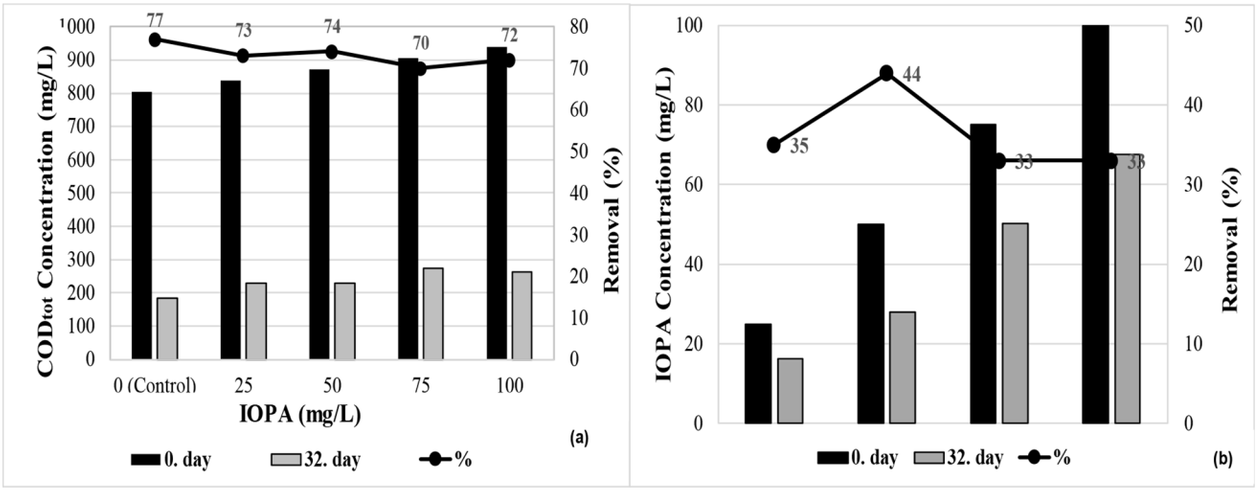

Fig. 1. Removals of (a) COD_{tot} and (b) IOPA during anaerobic treatment of synthetic sewage (IOPA = 25–100 mg/L; T = 35°C; Incubation time = 32 d).

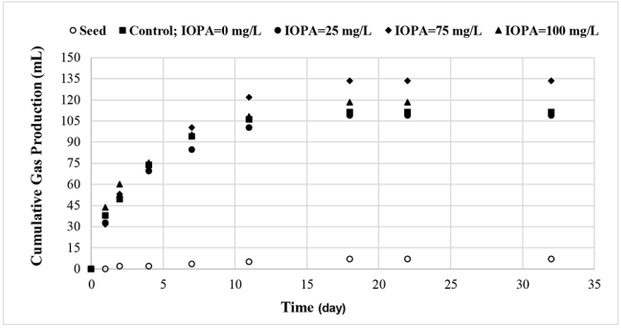

Fig. 2. Biogas productions at increasing IOPA in anaerobic bioreactors treating synthetic sewage (T = 35°C; Incubation time = 32 d; Initial COD_{tot} = 800–950 mg/L).

some extent because sewage sludge tends to concentrate potential contaminants from wastewater such as pesticides, metals, pharmaceutically active compounds and other organic chemical residues. Moreover, other ICM such as iopromide and diatrizoate were investigated in laboratory tests and it was reported that these highly hydrophilic compounds were bound to sludge solids at small percentages [30] as well as no adsorption of diatrizoate on the bacterial mass was detected [31]. Hence, although IOPA is known to be relatively polar and tends to dissolve in aqueous medium; for future studies, IOPA measurement in the sludge phase should be taken into account in order to evaluate whether its reduction in the supernatant was due to microbial removal or sorption onto solid particles or sediments as also recommended by Haiss and Kümmerer [31].

Results also showed that biogas production also continued as IOPA concentration in the batch systems increased up to 100 mg/L. Maximum cumulative biogas production was observed in the reactor having 75 mg/L IOPA concentration (i.e. 134 mL) compared to control system (i.e. 111 mL) as shown in Fig. 2 corresponding to 22% increase. However, biogas productions relative to the control sample were not substantially different when IOPA concentrations in synthetic sewage samples were 25 and 100 mg/L in the bioreactors.

4. Conclusions

In the present study, the effect of the index micropollutant and commercially important X-ray contrast agent IOPA on anaerobic performance in batch reactors treating synthetic sewage was examined. The following conclusions could be drawn from the experimental findings;

1. The investigated X-ray contrast agent IOPA (25–100 mg/L) could be removed from the supernatant of the synthetic sewage with a ratio of 33–44% by anaerobic treatment at the end of a 32-day operational period.
2. IOPA concentrations in the range of 25–100 mg/L did not result in any substantial decrease in the anaerobic treatment performance based on COD removal and biogas production.
3. COD_{tot} removals were in the range of 70–77% in the batch reactors without and with the presence of IOPA. Although the highest removal in terms of total and soluble COD was in the control reactor (i.e., 77% COD_{tot} and 90% COD_{sol}); no meaningful change in COD removals was observed at increasing IOPA concentrations (i.e., 70–74% COD_{tot} and 82–88% COD_{sol}).
4. Cumulative biogas productions in the bioreactors with IOPA concentrations up to 100 mg/L did not show substantial inhibition (99–134 mL) relative to the control (111 mL) reactor.

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