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DEGRADATION OF HEROIN, MORPHINE AND 6- MONOACETYLMORPHINE IN SEWAGE BATCH TESTS

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Abstract

The increasing global consumption of some narcotic drugs or drugs of abuse as reported by the United Nations Office of Drugs and Crime (UNODC) is a new source of emerging pollutants that is currently threatening the aquatic ecosystem due to associated toxicity levels. Apart from pharmaceuticals and personal care products, drugs such as heroin, morphine and 6- monoacetylmorphine have been found in the environment thereby worsening the already escalating situations. The persistence of pollutants in aquatic environment is due to their non – biodegradation owing to their hydrophilicity/lipophilicity properties. The pollutants principally reach the environment via Municipal Sewage Works or by direct dumping. Therefore, the degradation studies of drugs at different temperatures and times are apt and would improve removal approach using various sludge types. The analytical method used to determine their biodegradability involves initial characterization and after 3 hours equilibration, the removal rates were then measured for heroin (97.9%), morphine (99.7%) and 6-monoacetylmorphine (93.3%). The three substances have the partition coefficients (K_d) that ranged from 1.2 – 68.1 Kg L^{-1}. At 4 ± 0.5^o C, the degradation of compounds occurred slowly, but relatively greater at 19 ± 0.5^o C to between 5 and 10%. This paper therefore highlights the degradation studies of heroin and its principal metabolites and clearly demonstrated removal method at different laboratory conditions and times. The conceptual approach is aimed to achieve the best removal conditions to reduce the problems of chemical pollution due to persistence or non-degradation of these classes of drugs in the environment for the first time, a novel aspect of the work.

Keywords: *S*ewage, Biodegradation, Intracellular, Extracellular, Sewage treatment works

Introduction

Several studies in the literatures have reported the occurrence and removal of environmental pollutants from sources like pharmaceuticals, agricultural, personal care products, manufacturing and other sources [Olajire *et al*, 2005; Mustapha, 2013; Baena-Nogueras *etal*, 2017]. Recently, the annual report of the United Nations Office on Drugs and Crime (UNODC, 2017) have also shown the increasing global usage and consumption of some illicit substances or narcotic drugs but their persistence in aquatic environment have not been given sufficient attention and they exist in the environment as pollutants just like other chemicals. Insufficient information about the emerging pollutants in the environment made regulations on their 'safe levels' very difficult. Understanding the fate and behaviour of pollutants during sewage treatment will show the degradation possibility of compounds that are completely or partially degraded in aqueous and solid phases, sorbed to sludge solids or mineralised. In a study reported by Zhong *et al* (2017), organic contaminants are located within the fraction of large organic wastes (biomass) which are repository of living and dead micro-organisms required for degradation processes.

Investigations on the levels of removal of organic residues from a wastewater studies have shown toxicity correlation of wastewater pollution on aquatic organisms to determine the response levels with degree of contamination in many studies [Boruszko, 2017; Madikizela *et al*, 2017]. Biodegradability studies of organic priority pollutants and reduction in toxicity of these pollutants in wastewaters treatment processes have also been carried out [Tang *etal*, 2017; Gómez-Acata *etal*, 2017]. Difficult isolation of sludge samples arises also from non-uniformity of extraction procedures and variability in obtaining grab samples as a representative of all various genotoxins in the sludge matrix [Xu*et al*, 2016; Azaria *et al*, 2017; Ashfaq *et al*, 2017]. Different processes or techniques are often adopted for specific effluents depending on the origins of the contaminants. Generally factors often considered, though contaminants can be lost during treatments in a complex variety of ways are: 1) sorption/association with sewage solid surfaces 2) abiotic processes/hydrolysis involving chemical degradation 3) volatilisation and 4) biodegradation [Mustapha, 2017; Gómez-Acata *et al*, 2017].

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However, Lepik *et al* (2017) and Patrolecco *et al* (2015) have shown that degradation studies of pharmaceuticals have identified degradates of anti-inflammatory, analgesics and blood-lipid regulators. In batch studies of acetylsalicylic acid with suspended activated sludge, the decrease of about 70-99% in concentration after 6, 24 and 72 h was observed but no metabolites were detected using gas chromatograph as reported by Martín *et al* (2012). The degradation studies of anti-inflammatory and blood-lipid regulators such as bezafibrate, diclofenac, naproxen and ketoprofen in activated sludge were carried out, but only ketopofen biotransformed into [3-(hydroxyl-carboxy-methyl) hydratropic acid and [3-(keto-carboxyl-methyl) hydratropic acid [Ledjerietal, 2016; Xiang *et al*, 2017]. Biodegradation of trimethoprim showed resistance to degradation in a reactor filled with activated sludge, but its degradation in a nitrification process was completed in 3 days. In a similar study, Ashfaq *et al* (2016) investigated degradability of estrogens in aerobic batch reactors at two different concentrations using GCMS. The 17β-estradiol was oxidised to estrone without any detectable degradates. Also, 16α-hydoxy-estrone was similarly degraded without degradation products. In a subsequent work, the biodegradation studies of trimethoprim, anti-tumoralscisplatin, cyclophosphamide, cytarabine, X-ray contrast agents, iopromide and diatrizoate has been carried out but not all the details of metabolites identification were reported in the literature [Martín *et al*, 2012; Mendoza, 2015; Patrolecco, 2015].

Materials and Methods

Standard compounds of heroin, 6-acetylmorphine and morphine were purchased under license from both Sigma Aldrich (Gillingham Dorset, UK) and LGC standards (Teddington Middlesex, UK). 12.5 mg/250 mL of sample of each of the selected compounds was used for 3h duration for degradation studies. Batch experiments were conducted at two temperatures of 19 ± 0.5ºC and lower abiotic temperature of 4±0.5ºC. Sample were agitated using magnetic stirrer throughout to obtain homogenous sample of which 10 mL of batch sample was removed at every 15 min intervals. These subsamples were centrifuged (1500rpm for 5 min) and filtered using 0.45 µm cellulose acetate Whatmanand the aqueous phase was extracted by solid phase extraction using Oasis .HLB (500mg/6 mL) adsorbent (made up of a divinylbenzene/*N*-vinylpyrrolidone copolymer with both hydrophilic and hydrophilic properties).Gas chromatography mass spectrometry analyses were performed with an Agilent 6890 GC coupled to Agilent 5975 inert XL mass selector detector (MSD: 2564.7 eV). (Mustapha, 2013)

Results and Discussion

The sewage sludge characterizations

Due to variability in the overall composition of wastewaters as a result of continuous discharges and potential matrix effects on degradation studies, the sewage sludge characterizations for wastewaters and sewage samples were analysed for total suspended solids (TSS), organic carbon, ash and chemical oxygen demand (COD) and results are shown below in Table 1.

Table 1.Characterization Data for RAF MolesworthSamples

Molesworth STW Matrix	TSS (mg/L)	pH (Temp;ºC)	COD ($mgdm^{-3}O_2$)	Ash content (g)	Organic Carbon (g)
HS	36243.0	7.1 (14.2)	216.8	0.07	0.94
SAF-1	5.5	7.1 (14.6)	1.8	0.05	0.95
MSAF	77386.5	5.7 (14.4)	162.6	0.07	0.93
PS	8465.0	5.7 (14.4)	138.0	0.06	0.95
EffWW	70793.5	7.8 (18.7)	82.0		
InfWW	3563.5	8.5 (17.1)	52.4		

Note: PS = primary sludge;; HS = Humus sludge;SAF-1 = secondary aeration filter; MSAF = mixed SAF; EffWW = effluent wastewater; InfWW = influent wastewater;

Table 1 shows the mean results as presented and explained in the worked calculation above to illustrate the total COD, organic C and TSS contents achieved from different samples collected from the two different STWs. The highest effluent COD concentration from both STWs was 6.2 $mgdm^{-3}O_2$, and this was below the consent limit of 15 mg L^{-1} BOD as reported by Mustapha (2013), while the highest concentration of COD observed for influents were 216.8 $mgdm^{-3}O_2$(RAF Molesworth STW) and 48 $mgdm^{-3}O_2$ (Nottingham STW), indicating the nature of sewage and different treatment processes can influence the kinetics of degradation [Mustapha, 2013 and Tiwari, 2016]. The COD values obtained from the influent and effluent samples collected from Stoke Bardolph Nottingham and Molesworth STWs therefore compares well with the values reported for primary effluent (309 $mgdm^{-3}O_2$ COD), food processing sewage (7249 $mgdm^{-3}O_2$ COD), swine waste (67,444 $mgdm^{-3}O_2$ COD), secondary effluent (35 $mgdm^{-3}O_2$ COD), lagoon (27089 $mgdm^{-3}O_2$ COD) and effluent (71 $mgdm^{-3}O_2$ COD) in a study. This would indicate that the values produced in this work are in line with previous studies, ensuring sewage characteristics in the current batch studies can be assumed to be representative of most municipal sewage types [Mutapha,

2013; Paz, 2016; Song, 2016]. In this current work, the difference in influent and effluent results as reported may form a basis of empirical relationship between COD removal and the quality of treatment processes of sewage or wastewaters and these functions may be used to develop a gauge for sewage treatment to confirm adequate efficiency so that effluent quality is sufficiently good.

Treatment of organic matter in an activated sludge plant has also produced 22.7 – 253 mg L^{-1} TSS in a study, but in Nottingham and Molesworth STWs, the remaining suspended particulates after treatments represent the final effluent (TSS) concentrations found to be 5.5 mg L^{-1} (Molesworth STW) and 10.0 mg L^{-1} (Stoke Bardolph STW, Nottingham) compared to influent (TSS) concentrations of 797.9 mg L^{-1} (Stoke Bardolph, Nottingham) and 36243.0 mg L^{-1} (Molesworth STW) while 897.0 - 77386.5 mg L^{-1} of TSS were observed for sewage sludges from both STWs (Mustapha, *et al*, 2013). However, it is important to note the large difference in the levels of TSS from influent and effluent from the two STWs as quoted as this was evidence of extent of removals. Since domestic sewage differs in strength due to strong temporal variation, function controlling sludge characteristic can only be measured when effluent performance is compared to influent data and this was satisfactory with respect to our experimental results of TSS from both STWs. In addition, the TSS found in the effluents of the two STWs was significantly less than the 30 mg L^{-1} consent limit set by UK Environment Agency Compliance - Discharge Consent (USAFE OMTAP, 2007).

In our current work, the average concentration of organic carbon found in all the four sewage types collected from Molesworth STW was 0.94 g per 1.0 gram of sewage samples. The levels of organic carbon were expectedly higher in the sludge due to myriads of materials as they facilitate compound degradation and removal, since the extent of drug removal to particulates/solids depends on the amenability of drugs to degradation on association to biological solids and possible volatilisation.

Evaluation of degradation of drugs in primary and secondary sludge samples

A very rapid abiotic removal was observed in the first 15 min of cocaine degradation in primary sludge in batch studies. This observation was rather different from generally accepted positions from the literature that no significant degradation occurs in primary sedimentation (Mustapha, 2013). But over a period of 3h, the heroin showed decline in concentration with its uneven distribution between both solid and aqueous phases in a pattern that reflects their hydrophobic/hydrophilic nature. As compounds become lesser in concentration, the degradation products such as morphine and 6-acetylmophine were simultaneously identified and quantified. As degradation progressed the degradation products pattern could not be properly followed due to their diffuse nature of being further degraded as they are formed. The 6-acetylmorphine (a principal hydrolysis product) was detected possibly due to hydrolysis of heroin has been reported in pH = 2 at 25^{o}C for 5 days or low detection by Mustapha (2013). But also the presence of morphine and 6-acetylmophine (other bio-degradation products of heroin) were observed confirming the presence of bio-degradation processes in primary sludge. However, compound removal from aqueous phase in sewage may not indicate their complete degradation.

However, the partition fractions of each batch test with drug and their related metabolites were analysed and related to sludge types under the same condition. Similar degradation was observed in both sludge showing that biological aeration sludge in secondary treatment had little influence. The sorption behaviour of compounds was assessed by solid-water partition coefficient (K_d, L/Kg), as calculated by $C_{sorbed}/SS.C_{soluble}$ (where C_{sorbed} = chemical concentration in sorbed phase, $C_{soluble}$ is concentration in aqueous SS = suspended solids). The K_d values were calculated for each time period from batch studies data, the 2-3 HRT is the usual processing time in the Molesworth STW. The observed low solid-water partition coefficient for heroin (K_d< 14) in both sludge indicated low sorption as the removal mechanism but since recovery experiment for the solid could not completed, further experiment is needed for confirmation. From the results, the K_d values for heroin and other drugs ranged from 1.2 – 68.1 were however generally very much lower than the range of 12300 – 37700 L/Kg calculated for detected ten antibiotics in a municipal sewage treatment work (Ai, 2012).

Over 98% removal of heroin was achieved in 3h. The pattern of degradation observed for heroin was the same for morphine but with relatively higher degradation in primary sludge. As one of the major human metabolites of cocaine, its biodegradation studies in aquatic environment become important to understand the final fate of heroin. In the current study, its sorption potential (K_d< 2.5) indicated biodegradation as predominant removal process compare to sorption to solids.

Also, morphine is one of the metabolites of heroin; it was selected primarily to monitor its biodegradability and its final fate. Therefore, the result of a relative higher degradation of morphine within a biological secondary aerated sludge compare to primary sludge was observed from our batch studies with 85 – 100% removal for morphine.

Though many of the biological wastewater units have different characteristics, yet most compounds tend to exhibit general tendencies to accumulate to solids and sediments. But the removal rate of morphine appears to be related to degradation processes and less of sorption. Gradual removal rate of morphine in both primary and secondary sewage with the decline in the concentration of morphine may be due to bio-degradation mechanism.

In this current work, another human metabolite of heroin studied in both primary and secondary treatment sludge was 6-monoacetylmorphine (6-MAM). The idea was to observe the 6-MAM trend of degradation to know its final fate. Unlike the four compounds studied earlier, 6-ACM showed similar degradation in the primary sludge with corresponding low sorption potential (K_d< 9) and removal efficiency of between 98 – 100 % in PS, but removal rates were relatively slower after 2h of exposure in SAF-1 (19 – 86 %) from the result shown. In real time, after 2h treatment there are possibilities of most compounds in aqueous phase to pass on to the next treatment tank due to the average 2 HRT for RAF Molesworth. However,

the observed variability in degradation pattern may likely make the removal of 6-MAM faster in primary sludge than in SAF-1. The heroin has over 96% removal in both sludges, but, diazepam showed more removal in primary sludge.

Removal of drugs during primary sewage treatment

Figure 1 further demonstrates the degradation as a removal mechanism for all drugs at different rates with decline in various compounds concentrations distributed between aqueous and solid phases.

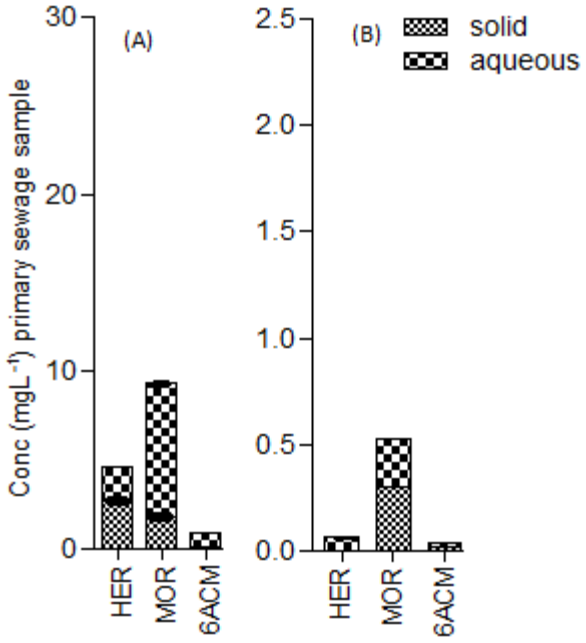


Figure 1:Degradation/partitioning in primary sludge at (A) 15 min and (B) 3h at 19± 0.5ºC.

In Figure 2, it can also be seen that all drug concentrations falls rapidly within the first hour of exposure to sewage with significant removals within the time of contact but slows down as biodegradation advances.

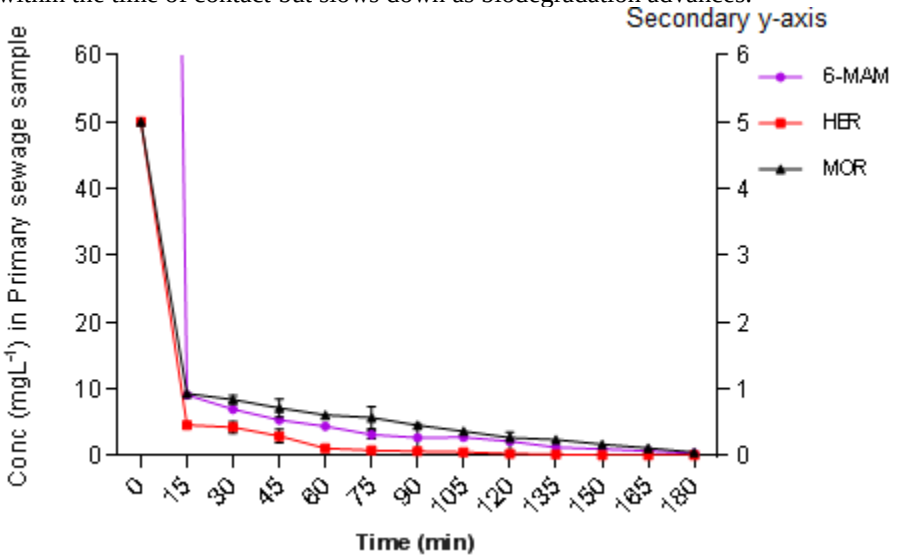


Figure 2: Distribution of drugs in aqueous and solid phases in primary sewage sludge at 19± 0.5ºC.

The concentration of compounds decreases with concurrent accumulation of metabolites such as morphine and 6-monoacetylmorphine for heroin which were in turn being further biodegraded. A second experiment to evaluate the significance of adsorption or degradation on retention time and its effects on removal rates was carried out. The results in Figure 3 below shows the removal rates of different compounds due to their different association with primary sewage solids (suspended solids concentration of 77387 mg L^{-1}) and different degradation rates. The two mechanisms were significant in the removal of compounds in the primary sedimentation unit over the range of retention times with more than 80% removal achieved within the first hour of contact.

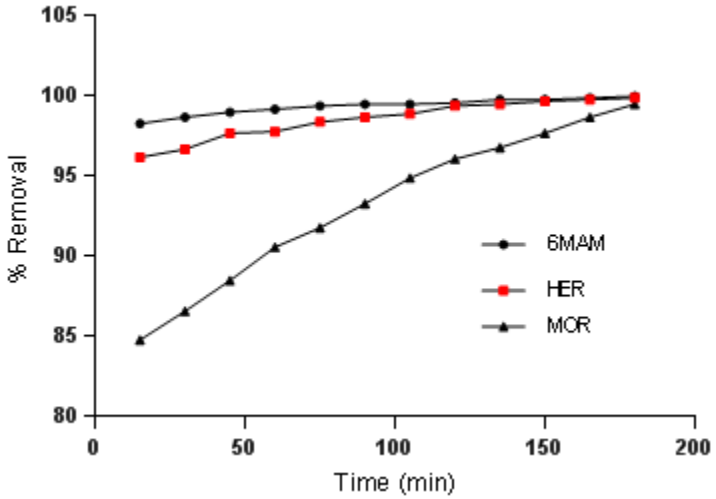


Figure 3:Removal rates against retention times during primary treatment processes.

Removal of drugs during secondary sewage treatment

All six compounds exhibited significant but different removal rates over 3h retention time and the results are presented in Figure 4.

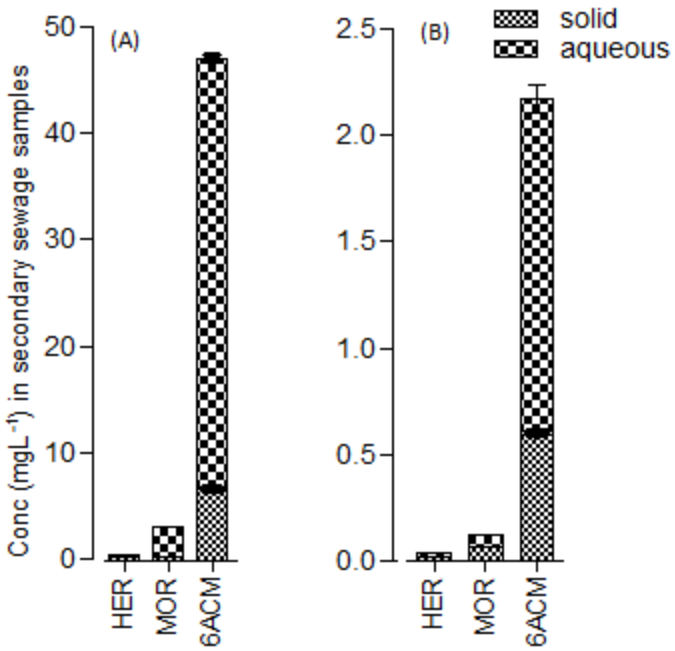


Figure 4: Degradation/partitioning in SAF-1 sludge at time (A) 15 min and (B) 3h at 19± 0.5ºC.

The illustration of combined concentrations of drugs in aqueous and solid phases in the same secondary sewage sample at 19± 0.5ºC is shown in Figure 5. Most compounds expectedly showed greater degradation in biological secondary sewage compared to the pattern observed in primary sludge in Figure 5.

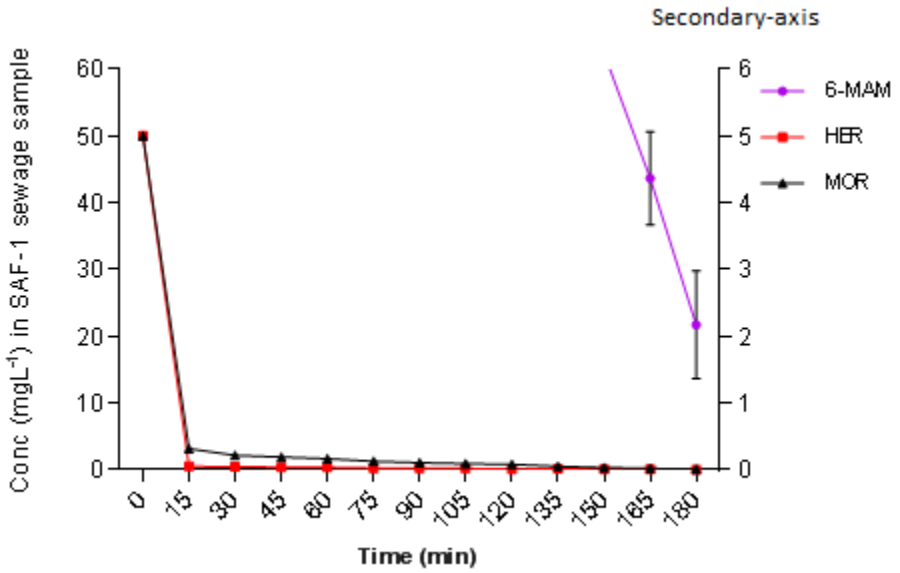


Figure 5.Distribution of drugs in aqueous and solid phases in secondary sludge (SAF-1) at 19± 0.5ºC.

In Figure 6, the effect of retention time on the removal of compounds during the secondary sewage processes can be seen with 6-monacetylmorphine showing average removal rate in the first hour of contact. Since others exhibited maximum removals at the same period of exposure, it was found that the removal of compounds at 19± 0.5ºC was favourable being the normal operational temperature of most STWs.

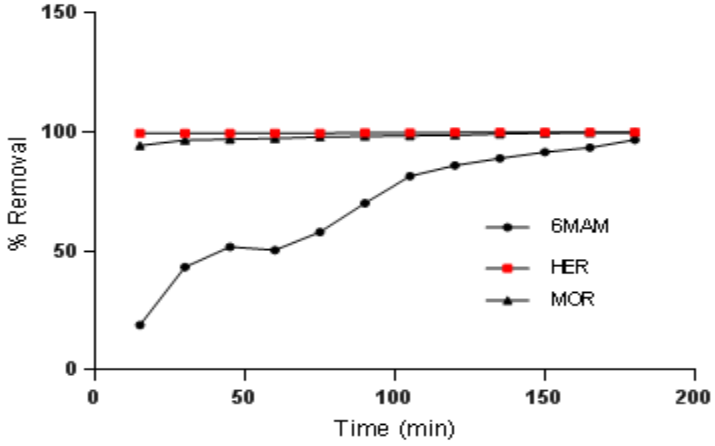


Figure 6: Removal rates against retention times during secondary treatment.

Comparison of Kd values to LogK_{ow} data

The octanol-water partition coefficient (LogK_{ow})is a laboratory-measured property of a substance that are used extensively in environmental chemistry as it provides a thermodynamic measure of the tendency of the substance to prefer a non-aqueous or oily phase (i.e. its hydrophilic/lipophilic balance) while the water-solid partition coefficient (Kd) measure the tendency of the substance to sorption. In this work, the water-solid partition coefficient (Kd) measured for the selected illicit drugs and abused pharmaceuticals in the current work were generally higher compare with literature Log Kow data range of 0.9 – 2.9 in Table 2 as against 1.2 – 69.9 in Table 3 for the drugs. Again, calculating of Kd changes at the timed interval of 15 minutes for 3h could introduce uncertainties as the values would be higher with higher recoveries from the sludge types. However, Table 3 below generally show the relatively higher Kd values in secondary sludge compare to primary sludge with diazepam showing greater values in both sludge types.

Evaluation of biotic versus abiotic degradation

Further batch tests to evaluate biotic and abiotic degradation were carried out with a 250 mL of unfiltered primary sludge samples of the same suspended solids concentration (77387 mgL^{-1}) measured in a flask, refrigerated at 4 ± 0.5ºC for 30 min to inhibit biological activity before the sample was spiked with drugs. Both biologically active and inactive samples were taken at 15 min for 3h. Results show the cocaine faster degradation process at biotic

Table 2: Names andthe octanol-water partition coefficient (Log Kow) data of compounds.

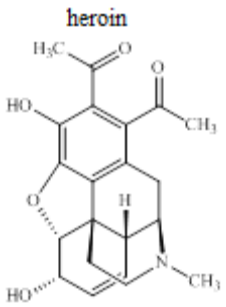
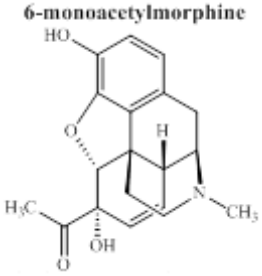
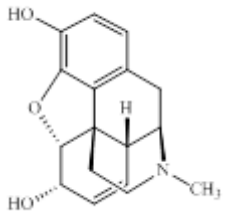
heroin  Log Kow: 1.7	6-monoacetylmorphine  Log Kow:1.6	morphine  Log Kow: 0.9

Table 3: Water-solid partition coefficients (Kd) data of compounds in both PS and SAF.

	Primary sludge (PS)			Secondary sludge (SAF)		
Time(min)	HER	6MAM	MOR	HER	6MAM	MOR
15	18.2	1.6	3.1	9.7	2.3	3.3
30	20.4	1.3	3.9	26.1	2.7	4.2
45	20.8	1.2	3.7	19.4	2.5	4.0
60	0.0	1.2	3.3	26.9	2.6	3.6
75	0.0	2.5	5.1	16.1	1.8	5.6
90	0.0	1.9	6.6	19.8	2.5	7.2
105	0.0	3.3	6.2	18.7	5.2	7.4
120	0.0	3.0	6.4	12.0	6.3	7.9
135	0.0	2.2	5.0	18.7	5.4	5.5
150	0.0	3.1	7.4	24.4	7.0	8.1
165	0.0	5.1	6.7	12.8	5.3	7.3
180	0.0	7.1	4.6	15.1	5.2	5.1

temperature of 19 ± 0.5ºC and a relatively slowly abiotic process at 4± 0.5ºC were observed. The low temperature inhibited the biological process as gradual transformation of initial compound concentration to degradation products at the low temperature have demonstrated biodegradation process and chemical hydrolysis as two major removal mechanism, as there is no loss through volatilisation. Since gradual decline in the levels of cocaine were observed in spite of microbial inhibition, therefore it was correct to assume that bio-degradation was part of the removal processes and not only chemical degradation and reported in the performance differences of both activated sludge and trickling filters experiment (Kasprzyk-Hordern, 2007).

Figure 7 further demonstrates how microbial inactivity has slowed down metabolic processes with obvious relative slower changes in concentrations observed indicating the degradation of compounds were both biological and chemical with an increase degradation products and greater partitioning in solid phases.

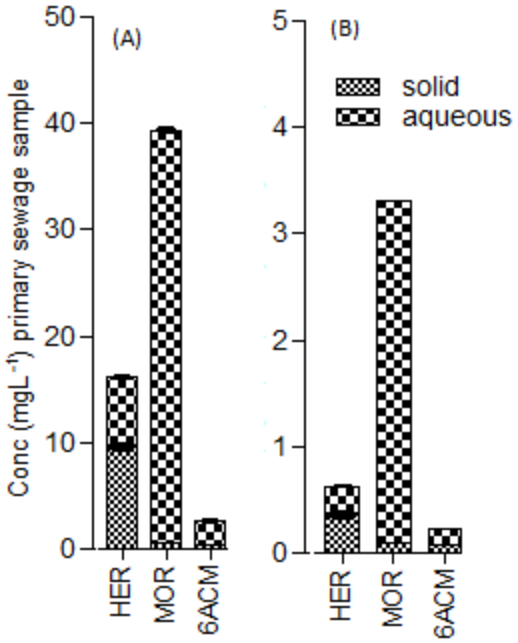


Figure 7: Degradation in primary sludge at abiotic conditions (4± 0.5ºC) at (A) 15 min and (B) 3h.
Figure 8 further confirmed the degradations were temperature independent as chemical hydrolysis did occur for all compounds at low temperature

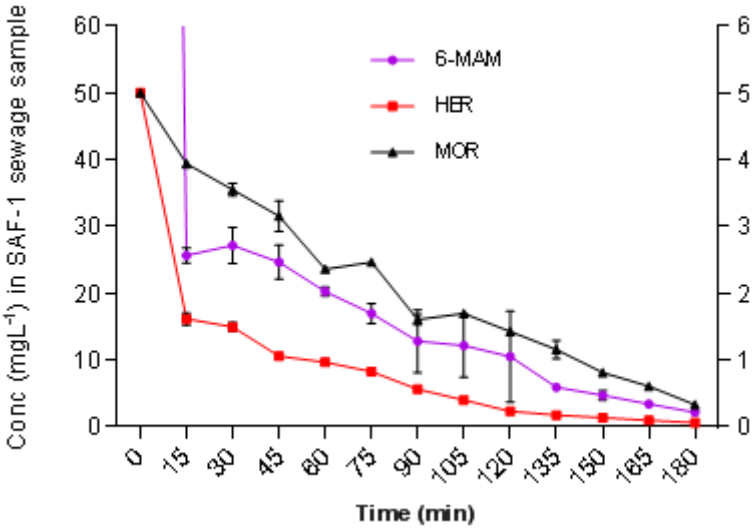


Figure 8: Plot showing combined concentrations of compounds in aqueous and solid phases in abiotic conditions (4± 0.5ºC).

Inhibition of the biological activities in the samples was expected at 4 ± 0.5ºC to slow the metabolic processes. Observed changes in the concentration indicating that the degradation was chemical with possible biological processes may be involved. No changes in the concentrations would have been observed if degradation were only biological, but that was not the case here as metabolic processes though were slowed down compared to degradation at 19± 0.5ºC. The changes suggest chemical degradation of compounds indicating that the degradation was both biological and chemical. The temperature change affects the rate of removal of compounds with the K_d values of morphine showing greater sorption at 19± 0.5ºC while 6 monoacetylmorphine were better sorped at 4± 0.5ºC.

Evaluation of suspended solids on the removal of compounds

High removals of organic compounds during primary treatment have largely depended on water-solid partition coefficient (K_d) values which normally determine the degree of partitioning of compounds between aqueous and solid phases.

In the current work, the effect of suspended solids on the removal of compounds was done by evaluating the levels of compounds adsorbed onto the solids in primary sludge at 19±0.5ºC.

The results in Table 4 indicate adsorption as one of the removal mechanisms with significant removal of heroin in both primary and secondary sewage samples, compared to morphine and 6-monoacetylmorphine removals in secondary sludge. Heroin and morphine exhibited negligible associations with the suspended solids and therefore have minimal removals in both primary and secondary sludge samples.

Table 4: Adsorption of compounds onto sludge of different suspended solids concentration (%) in 3h.

	Suspended solids (mg L^{-1})			
Compounds	77386.5 (PS)	70793.5 (SAF-1)	8465.0 (MSAF)	3563.5 (HS)
Heroin	0.0	0.03	0.01	0.38
Morphine	0.59	0.12	0.31	0.02
6-monoacetylmorphine	0.03	1.19	0.02	0.0

Further comparison of the effects of adsorption on the removal of compounds at abiotic (4±0.5ºC) and biotic (19±0.5ºC) temperatures exhibited similar adsorption pattern (Fig. 9). However, heroin, showed greater adsorption at chilling temperature whereas morphine and diazepam exhibited better adsorption at biotic temperature. The sorption by organic compounds has therefore be reported with log K_{ow}< 2.5 (low sorption potential), log K_{ow}> 2.5 and < 4.0 (medium sorption potential) and log K_{ow}> 4.0 (high sorption potential) for chemicals that partition to organic phases to estimate a clear relationship with the degree of partitioning of contaminants during treatment (Rogers, 1996).

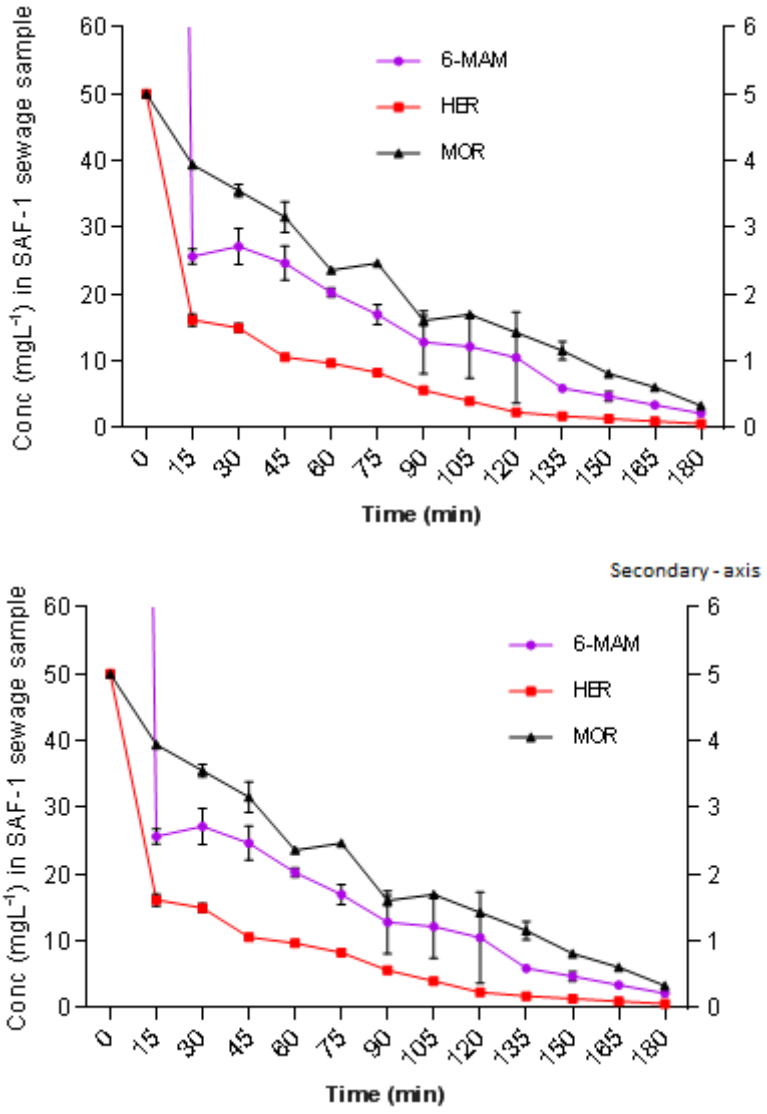


Figure 9: Removal of compounds by adsorption in primary sludge at (A) 4±0.5ºC (B) 19±0.5ºC.

The solid-water partition coefficients (K_d) in the current study were in the range for morphine (0.2 – 1.3), 6-monoacetylmorphine (0.1 – 0.5) and heroin (0.7 -1.7). The association of drugs with biological solids may have exhibited adsorption as an important removal mechanism during primary and secondary wastewater treatment while other drugs have no significant adsorption. Also, removal efficiencies above 75 % in primary sludge and biological secondary sludge for all the compounds were observed. The K_d values of compounds studied in this work showed positive correlation with their removal efficiencies as reported for ten quinolone and fluoroquinolone antibiotics in sludge samples(Ai, 2012).

Conclusions

In the current work, the main conclusions for the novel work are three representative compounds of opiate drugs (heroin, 6 monoacetyl morphine, and morphine) that exhibited comparable removals when in contact with both primary and biological secondary treatment sludge during the batch studies of 3h exposure time. Observed rapid removals were exhibited in the first few minutes of contact with both primary and secondary sewage samples with increase in the degradation products as compounds exposed to microbial and chemical hydrolysis but the rate slows down as availability of nutrient source reduces.

Degradation batch studies of heroin, morphine and 6-monoacetylmorphine on sludge samples at two different temperatures showed consistent duplicates results with the degradation of compounds at 19 ± 0.5° C relatively greater but still occurred slowly at 4 ± 0.5° C, demonstrating that degradation was both biotic and abiotic but the degradation of compounds at 19 ± 0.5° C was faster than at 4 ± 0.5° C, by between 5 and 10%. Both biological and chemical degradations affects the removal of compounds in different rates at 4 ± 0.5 °C, the degradation/partitioning is therefore temperature dependent.

Compounds removal by biodegradation, chemical degradation and sorption were the dominant removal processes (volatilization is unlikely) with removal rates of heroin (97.9%), morphine (99.7%) and 6 monoacetylmorphine (93.3%) having corresponding partitioning coefficients (K_d) ranged from 1.8 – 26.9Kg $L^{-1}$for the same 8 HRT. Heroin has the highest sorption removal in both primary and secondary sludge treatments and its exhibited tendencies of accumulating in sediments with identical K_d values in all sludge types could possibly provide empirical relationship between drug removal and HRT.

Optimal experimental strategy was developed by incorporating good temperature process variables with knowledge of individual's compound degradation and possible transport occurring in the STWs to achieve complete removals as demonstrated in the batch studies.The data derived from the batch studies is aimed to achieve the best removal conditions to reduce the problems of chemical pollution due to persistence or non-degradation of these classes of drugs in the environment for the first time, a novel aspect of the work.

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